ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

SYNTHESIS AND CHARACTERIZATION OF NANOCOMPOSITE RESINS

M.Sc. THESIS

Gözde ÖZKARAMAN

Department of Polymer Science and Technology

Polymer Science and Technology Programme

JANUARY 2012

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Thesis Advisor: Prof. Dr. Nilgün KIZILCAN

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<u>İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ</u>

NANOKOMPOZİT REÇİNE SENTEZİ VE KARAKTERİZASYONU

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To my family,

viii

FOREWORD

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January 2012

Gözde ÖZKARAMAN Chemist

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ABBREVIATIONS

DMA	: Dynamic Mechanical Analyzer
DSC	: Differential Scanning Calorimetry
F	: Formaldehyde
FTIR-ATR	: Fourier Transform Infrared Spectroscopy
MMT	: Montmorillonite clay
Р	: Phenol
PDMS	: Hydroxyl Chain Ended Polydimethyl Siloxane
PDMS-LC-PFR	: PDMS Modified Resol/Clay Nanocomposite Resin
PDMS-PFR	: PDMS Modified Phenol Formaldehyde (Resol) Resin
PFR	: Phenol Formaldehyde (Resol) Resin
PUFPCR	: Phenol Urea Formaldehyde/Pomace Composite Resin
PUFR	: Phenol Urea Formaldehyde Resin
SEM	: Scanning Electron Microscopy
$T_{\rm g}$: Glass Transition Temperature
TGA	: Thermogravimetric Analyzer
U	: Urea
UFR	: Urea Formaldehyde Resin

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SYNTHESIS AND CHARACTERIZATION OF NANOCOMPOSITE RESINS

SUMMARY

This study can be categorized into two parts. The first part aims to synthesis new hydroxyl chain ended polydimethyl siloxane (PDMS) modified layered clay resol type phenol formaldehyde nanocomposite resins (PDMS-LC-PFR) by in-situ preparation method, which can be used for thermal insulation materials, coatings, molding compunds, foundry materials, wood product industry and aerospace components due to their high strength, structural integrity, thermal stability, heat and solvent resistance. In this study, nanocomposites resol resins were synthesized by direct addition of clay (montmorillonite: whose cation-exchange capacity is 80 meq / 100 g sodium, average particle sizes are smaller than 10 μ m, density is 2,6 g cm⁻³) into synthesis of phenol formaldehyde resins media, in the presence of base catalyst. Through the synthesis PDMS have also been added in the media to improve the surface of the material. With this method PDMS added polymeric nanocomposite material would be synthesized in one step. The influence of the clay content on mechanical and thermal properites of nanocomposite resin materials were investigated. For that reason with adding different amounts of clays (0,5 wt%, 1 wt%, 3 wt%, 5 wt%) nanocomposite resin samples were synthesized. Mechanical, thermal, spectroscopic and microscopic properties of the nanocomposite resins have been researched and determined. The characterizations of the nanocomposite samples were performed by Fourier Transform Infrared Spectroscopoy (FTIR-ATR), Differential Scanning Calorimetry (DSC), Thermogravimetric Analyzer (TGA), Dynamic Mechanical Analyzer (DMA) and Scanning Electron Microscopy (SEM). In FTIR-ATR measurements, with the characteristic peaks of neat phenol formaldehyde resin (PFR), Si – O – Si bond vibraiton peaks of PDMS and C – H stretching peaks of clay were obtained for nanocomposite resin samples. The effect of the clay amount on the thermal properties of materials were investigated by DSC and TGA. Glass transition temperatures (T_g) of noncured nanocomposite resin samples and maximum cure temperatures of cured nanocomposite resin samples were determined with DSC. In TGA analysis, resin samples heated at linear heating rate of 10°C. Degradation was carried out in a static air atmosphere to the maximum temperature of 900°C. The weight loss (wt%) of the resins were calculated with TGA. YoungS modulus values of the resins were calculated by DMA measurements. Distribution of clay particles in polymeric resol resin matrix and morphology of resin samples were determined with SEM measurements.

The second part of this study aims to obtain produciton of polymer wood composite material from pomace for to eliminate the existing disadvantages of wood materials and to reduce the damage to the environment with the production of these wood materials. In this part, firstly urea formaldehyde resin (UFR) and resole type neat phenol formaldehyde resin (PFR) were used as binder resin matrix. With use of PFR in the resin matrix was aimed to decrease the water absoption capacity of the materials. Secondly to invesitgate the influence of clay particles on the mechanical properties of the materials, PDMS modified layered clay resol nanocomposite resin

(PDMS-LC-PFR3) were used instead of PFR with UFR in resin matrix. Effect of the pomace amount and the resin matrix content on the mechanical properties of the materials were determined by 3-point bending measurements. Also morphology of the composite materials were determined with SEM measurements.

NANOKOMPOZİT REÇİNE SENTEZİ VE KARAKTERİZASYONU

ÖZET

Bu çalışma iki bölümden oluşmaktadır. Birinci bölümde, yüksek mukavemetleri, yapısal bütünlükleri, termal kararlılıkları, ısı ve çözücü dirençleri sebebiyle; termal yalıtım, kaplama, döküm, ahşap ürün endüstri malzemesi ve uzay ve havacılık malzemesi olarak kullanılabilecek yeni; hidroksil zincir sonlu polidimetil siloksan (PDMS) ile modifiye edilmiş, kil katmanlı resol tipi fenol formaldehit nanokompozit reçinelerinin (PDMS-LC-PFR) in-situ hazırlama yöntemiyle sentezi amaçlanmıştır. Nanokompozit resol reçineleri, kilin fenol formaldehit reçinelerinin baz katalizörü bulunan sentez ortamına direkt eklenmesiyle sentezlenmiştir. Malzemenin yüzeyini geliştirmek için, sentez aracılığıyla PDMS de ortama eklenmiştir. Bu yöntemle PDMS eklenmiş polimerik nanokompozit reçine malzemelerin mekanik ve termal özellikleri üzerine etkisi incelenmiştir. Bu amaçla değişik miktarlarda kil ilavesiyle (0,5%, 1%, 3%, 5%) nanokompozit reçine örnekleri sentezlenmiştir. Nanokompozit reçinelerin mekanik, termal, spektroskopik ve mikroskopik özellikleri araştırılmış ve belirlenmiştir.

Nanokompozit örneklerin karakterizasyonu FTIR-ATR spektrometre, diferansiyel taramalı kalorimetre (DSC), termogravimetrik analiz cihazı (TGA), dinamik mekanik analiz cihazı (DMA) ve taramalı elektron mikroskobu (SEM) ile yapılmıştır. FTIR-ATR ölçümlerinde, öncelikle resol tipi saf fenol formaldehit reçinesinin (PFR) karakteristik pikleri ile PDMS ile modifive edilmis resol tipi fenol formaldehit reçinesinin (PDMS-PFR) karakteristik pikleri karşılaştırılmıştır. Bu ölçümlerin sonucuna gore PDMS ile modifiye edilmis resol tipi fenol formaldehit recinesi icin karakteristik resol reçine piklerinin yanında, 1020 cm⁻¹'de PDMS'e ait Si – O – Si bağı titresimi pikleri elde edilmiştir. Daha sonra değişik miktarlarda kil ilavesiyle elde edilen PDMS ile modifiye edilmiş nanokompozit reçine örneklerinin FTIR-ATR spektrumları incelenmis ve bu örnekler icin karakteristik resol recine pikleri ve PDMS'e ait Si – O – Si bağı titreşim piklerinin yanında, 2800 – 2900 cm⁻¹ civarında kilin alkil amonyum katyonlarına ait C – H bağı esneme pikleri elde edilmiştir. Buna göre bu çalışmada yapılan FTIR-ATR ölçümlerine gore PDMS ve kilin nanokompozit reçine örneklerinin yapısına katıldığı söylenebilmektedir. Kil miktarının malzemenin termal özellikleri üzerine etkisi DSC ve TGA ile belirlenmiştir. Öncelikle nanokompozit reçine örneklerinin camsı geçiş sıcaklıkları (T_g) ve maksimum kür sıcaklıkları DSC ile belirlenmiştir. Bu ölçüm sonuçlarına gore en yüksek camsı geçiş sıcaklığı (Tg) ve maksimum kür sıcaklığı değerleri 3% oranında kil içeren nanokompozit reçine örneği için elde edilmiştir. Nanokompozit reçine örneklerinin termal bozunma davranışları termogravimetrik analiz (TGA) ile belirlenmiştir. TGA analizinde, nanokompozit reçine örnekleri 10°C doğrusal ısıtma hızı ile ile ısıtılmış ve bozulma sabit hava atmosferinde 900°C maksimum sıcaklıkta gerçekleştirilmiştir. Nanokompozit recine örneklerinin kütle kaybı (%) termogravimetrik analiz (TGA) ölcümleri ile hesaplanmıştır. Bu ölcümlerin sonucunda 900°C maksimum sıcaklıkta en düşük oranda kütle kaybı, 3% oranında kil iceren nanokompozit reçine örneği icin elde edilmiştir. Ayrıca 3% ve 5% oranında kil iceren nanokompozit recine örneklerinin termal bozunmalarının saf resol tipi fenol formaldehit recinesinden yaklasık olarak 50°C daha yüksek sıcaklıkta başladığı gözlemlenmiştir. Bu sebeple belli oranlarda kil ilavesiyle elde edilen nanokompozit reçine örneklerinin termal kararlılıklarının resol tipi saf fenol formaldehit recinesinden vüksek olduğu gözlemlenmistir. Nanokompzoit recine örneklerinin mekanik özellikleri DMA ölçümleri ile belirlenmiştir ve bu amaçla örneklerin YoungS modülüs değerleri hesaplanmıştır. Örnekler için 3% oranına kadar artan kil miktarı ile modulus değerlerinin arttığı, 5% oranında kil içeren örnek için ise az miktarda azaldığı gözlemlenmiştir. Kil yüzdesine bağlı olarak bu durum camsı geçiş sıcaklıkları için de elde edilmiş olup, bunun sonucu olarak 5% oranında kil miktarının bu çalışma için termal ve mekanik olarak optimum değerin üzerinde olduğu tespit edilmiştir. Kil parçacıklarının polimerik resol reçinesi matrisindeki dağılımı ve reçine örneklerinin morfolojisi taramalı electron mikroskobu (SEM) ölcümleri ile belirlenmistir. Bu ölcümlerin sonucuna gore: 0,5%, 1%, 3% oranında kil içeren nanokompozit reçine örnekleri için homojen bir kil dağılımı gözlemlenmistir. Bu sonucların elde edilmesinde, PDMS'in nanopartiküllerin yüksek yüzey enerjisini düşürme görevi görmesinin etkili olduğu tespit edilmiştir. 5% oranında kil içeren örneğin ölçüm sonuçlarında kil parçacıklarının topaklanmaya başladığı gözlenmiştir. Bu sebeple 5% oranında kil ilavesinin bu çalışma için morfolojik olarak da optimum değerin üzerinde olduğu tespit edilmiştir. Sonuç olarak bu çalışmaya göre 3% oranında kil içeren PDMS ile modifiye edilmiş, resol tipi fenol formaldehit nanokompozit recine örneği; termal, mekanik ve morfolojik olarak en iyi özelliklere sahiptir.

Ahşap mobilya ve yapı malzemeleri üretiminde ağaçların kesilerek kullanılması uzun yıllardır günümüze kadar süregelen ve ekosistemin temel taşlarından olan ormanların yok olmasına sebep olan bir uygulamadır. Bu şekilde üretilen ahşap malzemelerin vanma, sudan etkilenme ve böceklenme gibi dezavantajları olduğu bilinmektedir. Bu calışmanın ikinci bölümünde, Balıkesir'deki bir zeytinyağı fabrikasından temin edilen atık durumundaki yağsız pirina (zeytinin işlenmesi sonucu kalan katı ürün) kullanılarak polimer ahsap kompozit malzeme üretimi yapılmıştır. Böylece hem ahşap malzemelerin var olan dezavantajlarının ortadan kaldırılması ve bu ahşap malzemelerin üretimi ile çevreye verilen zararın en aza indirilmesi, hem de atık durumundaki pirinanın ekonomiye geri kazandırılması hedeflenmiştir. Bu amaçla bu bölümde, öncelikle üre formaldehit reçinesi (UFR) ve resol tip saf fenol formaldehit reçinesi (PFR) 50% - 50% oranlarında eklenerek, bağlayıcı reçine matrisi olarak kullanılmıştır. Sabit recine matrisi oranına sahip örneklere, 20%'den 65%'ye kadar farklı miktarlarda dolgu maddesi (pirina) ilave edilerek farklı polimer ahsap kompozit malzemeler hazırlanmış ve bu kompozit malzeme örneklerine üç noktadan eğilme testi uygulanarak, en yüksek eğilme direncini gösteren optimum dolgu maddesi değeri tespit edilmeye çalışılmıştır. Bu çalışma için, 65% oranında pirina ilavesinin optimum değerin üstünde olduğu ve bu oranda dolgu maddesi iceren malzemenin kurutma aşamasında ufalanmaya başladığı gözlemlenmiştir. Ayrıca bu çalışmada, 20% oranında pirina içeren polimer ahşap kompozit malzeme örneğinin en yüksek modülüs değerine sahip olduğu belirlenmiştir. Daha sonra kil parçacıklarının varlığının polimer ahşap kompozit malzemenin mekanik özellikleri üzerindeki etkisini araştırmak için, reçine matrisinde üre formaldehit reçinesi ile birlikte resol tipi saf fenol formaldehit reçinesi (PFR) yerine, bu çalışmanın birinci bölümünde sentezlenen nanokompozit reçineler içerisinde en iyi malzeme

özelliklerine sahip olduğu tespit edilen, 3% oranında kil içeren PDMS ile modifiye edilmiş resol tipi nanokompozit recine (PDMS-LC-PFR3) kullanılmıştır. Bu recine matrisi için de; sabit reçine matrisi oranında farklı miktarlarda pirina ilavesiyle farklı polimer ahşap kompozit malzemeler hazırlanmıştır. Bu örneklere uygulanan üç noktadan eğme testi sonuçlarına göre; saf resol tipi fenol formaldehit reçinesi yerine PDMS ile modifiye edilmiş resol tipi nanokompozit reçine kullanıldığında malzemelerin modülüs değerlerinde bir miktar artıs gözlenmis ve avnı kilsiz örneklerde olduğu gibi 20% oranında dolgu maddesi ilavesi ile hazırlanan polimer ahşap kompozit malzemenin en yüksek modülüs değerine sahip olduğu belirlenmiştir. Optimum dolgu maddesi miktarının belirlenmesinden sonra, reçine matrisinin oranı değiştirilerek, sabit pirina miktarı ve reçine matrisinde farklı miktarlarda üre formaldehit ve resol tipi fenol formaldehit reçineleri içeren örnekler hazırlanmıştır. Kullanılan farklı reçine miktarlarının, polimer ahşap kompozit malzeme örneklerinin modülüs değeriyle birlikte su absorpsiyon kapasitesi özellikleri üzerine etkisi incelenmiştir. Cünkü bağlayıcı olarak fenol-formaldehit recinesi kullanımı ile malzemenin su absorpsiyonunun en aza indirilmesi hedeflenmiştir. Buna göre, bağlayıcı reçine matrisi içerisinde resol tipi fenol formaldehit recine miktarı arttıkca; malzemelerin modülüs değerinin arttığı ve absorpladıkları su miktarının azaldığı gözlemlenmistir. Ayrıca yanma geciktirici etkisi olduğu bilinen alçı taşının malzemenin modülüs değeri üzerine etkisini gözlemlemek için kütlece 20% oranında dolgu maddesi (pirina) ile birlikte 10% oranında alçı taşı içeren bir örnek hazırlanmış ve bu örneğin özellikleri 30% oranında pirina içeren örnekle karşılaştırılmıştır. Son olarak dolgu maddesi olarak kullanılan pirinanın bağlayıcı reçine matrisi içerisinde homojen olarak dağılıp dağılmadığını anlamak icin, farklı miktarda pirina içeren polimer ahşap kompozit malzeme örneklerinden ince film örnekleri hazırlanmış ve bu örneklere taramalı elektron mikroskop (SEM) ölcümleri uvgulanarak morfolojileri belirlenmistir. Bu analizlerin sonuçlarına göre dolgu maddelerinin bağlayıcı reçine matrisi içerisinde homojen olarak dağıldığı gözlemlenmiştir.

1. INTRODUCTION

Nanocomposites are a special class of materials originating from suitable combinations of two or more such nanoparticles or nanosized objects in some suitable technique, resulting in materials having unique physical properties and wide application potential in diverse areas. Novel properties of nanocomposites can be derived from the successful combination of the characteristics of parent constituents into a single material. Materials scientists very often handle such nanocomposites, which are an effective combination of two or more inorganic nanoparticles. To exploit the full potential of the technological applications of the nanomaterials, it is very impoartant to endow them with good processability which has ultimately guided scientists toward using conventional polymers as one component of the nanocomposites, resulting in a special class of hybrid materials termed "polymeric nanocomposites". These materials are also intimate combinations (up to almost molecular level) of one or more inorganic nanoparticles with a polymer so that unique properties of the former can be taken together with the existing qualities of the latter. Mant investigations regarding the development of the incorporation techniques of the nanoparticles into the polymeric matrices have been published. In most of the cases such combinations require blending or mixing of the components, taking the polymer in solution or in melt form [1].

Conventional polymer composites are filled with a high load of 20- 40% w in order to improve their properties, but also resulting in a weight increase. On the other hand, nanocomposites need much lower amounts of filler to reach remarkable improvements in their behavior. For instance, the load of a clay nanocomposite oscillates between 5 to 10% wt with barely noticeable weight increase [2,3]. In order to use clay as a nanofiller, different authors as Shina Ray and Vaia [4,5] advised that the surface of the MMT must be organically modified to reduce surface energy of the clay sheets helping to develop stronger interactions between the phyllosilicate and the non-polar polymer matrix. As an alternative or as a complement to the clay organic modification (MMT-O) a modified polymer matrix may be used to improve the clay dispersion in the matrix. These materials are commercially known as coupling agents. Polymer-layered clay nanocomposites preparation methods achieve nanometer-scale incorporation of the layered silicate [e.g. MMT clay, or synthetic layered silicates] in the polymer matrix by addition of a modified silicate either to a polymerization reaction (*in situ* method) [6-11], to a solvent-swollen polymer (solution blending) [12], or to a polymer melt (melt blending) [13-15]. Additionally, a method has been developed to prepare nanocomposites by polymerizing layered silicate precursors in the presence of a polymer [16]. Polymer layered silicate nanocomposites based on montmorillonite (MMT) clay have attracted a great deal of attention because of the enhanced properties in mechanical, thermal, barrier, and clarity properties without a significant increase in density, which is not possible with conventional fillers. These enhanced properties are presumably a result of the nanometer size, large aspect ratio, and large surface area of the silicate layers [17].

A composite is a structural material that consists of two or more combined constituents that are combined at a macroscopic level. Onu constituent is called the reinforcing phase and the one in which it is embedded is called the matrix. The most common advanced composites are polymer matrix composites (PMCs) consisting of a polymer (e.g., epoxy, polyester, urethane) reinforced by thin diameter fibers, metals, ceramics and so on. The reason why they are the most common composites include their low cost, high strength, and simple manufacturing principles [18]. They are designed and manufactured for various applications including automotive components, sporting goods, and aerospace parts. The matrix material used in polymer-based composites can either be thermoset (epoxies, phenolics) or thermoplastic resins (low density polyethylene, high density polyethylene, polypropylene, nylon, acrylics). The filler or reinforcing agent can be choosen according to the desired properties.

2. THEORETICAL PART

2.1 Nanocomposites

A nanocomposite is as a multiphase solid material where one of the phases has one, two or three dimensions of less than 100 nanometers(nm), or structures having nanoscale repeat distances between the different phases that make up the material [19].

Nanocomposites are found in nature, for example in the structure of the abalone shell and bone. The use of nanoparticle-rich materials long predates the understanding of the physical and chemical nature of these materials. Jose-Yacaman *et al.* [20] investigated the origin of the depth of colour and the resistance to acids and bio-corrosion of Maya blue paint, attributing it to a nanoparticle mechanism. From the mid 1950s nanoscale organo-clays have been used to control flow of polymer solutions (e.g. as paint viscosifiers) or the constitution of gels (e.g. as a thickening substance in cosmetics, keeping the preparations in homogeneous form). By the 1970s polymer/clay composites were the topic of textbooks [21], although the term "nanocomposites" was not in common use.

In mechanical terms, nanocomposites differ from conventional composite materials due to the exceptionally high surface to volume ratio of the reinforcing phase and/or its exceptionally high aspect ratio. The reinforcing material can be made up of particles (e.g. minerals), sheets (e.g. exfoliated clay stacks) or fibres (e.g. carbon nanotubes or electrospun fibres). The area of the interface between the matrix and reinforcement phase(s) is typically an order of magnitude greater than for conventional composite materials. The matrix material properties are significantly affected in the vicinity of the reinforcement. Ajayan et al.[19] note that with polymer nanocomposites, properties related to local chemistry, degree of thermoset cure, polymer chain mobility, polymer chain conformation, degree of polymer chain ordering or crystallinity can all vary significantly and continuously from the interface with the reinforcement into the bulk of the matrix.

2.1.1 Clay (Montmorillonite)

The montmorillonite (MMT) is the kind of clay the most widely used in industry as well as the bentonite and the saponite clays. The size of the clay is a determinant factor of the clay physical-chemical properties. In the montmorillonite case, it presents a very small particle size (less than 2 mm) and a high aspect ratio (between 10 and 1000). Such characteristics added to its high cationic interchange capacity (about 60 and 200 meq / 100g, the highest value in clays), and its specific area (between 60 and 300 m²/ g), make the MMT a good candidate for nanofiller [22].

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 [22-24]. Layered clay-based polymer nanocomposites have become an area of active interest due to the possible technological applications as well as scientific issues concerning them.

2.1.2 Preparation methods of polymer-clay nanocomposites

The preparation of a nanocomposite can be achieved through three methods [25-28]:

Intercalation of polymer or pre-polymer from solution, also known as the exfoliation absorption method: it involves the swelling of the clay in a solvent (such as water, toluene, or chloroform) where the polymer or pre-polymer is soluble. On account of the separation of the clay sheets into the solvent, polymer chains stick onto the gallery and therefore a permanent clay exfoliation takes place. Finally, the solvent is removed and the polymer layered silicate (PLS) structure remains. Despite the usefulness of this method in the production of thin films, it can only be used with certain polymers. For instance, Greenland et al have used PVA [29], Jeon et al used HDPE [30], and Kawasumi et al [31]experimented with liquid crystal. Moreover, it has a high environmental cost related to the solvent removal.

In-situ intercalative polymerization: after swelling the clay in a solvent where the monomer is soluble, polymerization process is initiated by heat or radiation. Therefore, polymer chains are formed into the clay stacks reaching a reinforced PLS structure. The N6/MMT produced by Toyota is the most representative example of

clay nanomaterial obtained by this method, which has been thoroughly described by Usuky et al [28].

• Melting Intercalation method: this technique involves a mechanical action used to mix the clay with the polymer in molten state in order to obtain either an intercalated or an exfoliated structure. The melting intercalation method does not require any solvent, thus open the possibility to make clay nanocomposites with any polymers that could not be processed by the previously mentioned methods. Nowadays, such method has become standard for the preparation of nanocomposites.

Different preparation methods and experimental conditions generate distinct types of nanocomposite morphology, with several levels of interaction between the components and phases present in the system.

2.1.3 Morphology of nanocomposites

In nanocomposites three main different morphological states can be identified [25,26]:

a) Immiscible: this state is characterized by the non-mixture of the clay into the matrix. Two distinct phases, with equivalent associations to those found in a microcomposite, can be seen. Figure 2.1 a) illustrates such situation in an immiscible novalac-based cianate ester nanocomposite obtained by Gilman et al [32] by mixing ester resin at high-shear with montmorillonite clay and coupling agent at 150°C.

b) Intercalated: this morphology corresponds to the first step in the separation of the clay stacks towards their segregation into individual clay sheets. In fact, clay presents a finite expansion of its layers allowing some polymer chains to penetrate into the gallery, it results in a well ordered multilayer structure constituted by alternated clay and polymer layers. Figure 2.1 b) is an example obtained by Vaia et al. [33] by using melt state processing in a polystyrene montmorillonite system.

c) Exfoliated: the last step to attain a full separation of the clay stacks in a random but homogeneous distribution at nano and microscopic scale in the polymer matrix is called exfoliation. Extensive polymer chain penetration occurs into the gallery: each clay layer is surrounded by polymer chains permitting high superficial interactions improving material the behavior. To illustrate, Figure 2.1 c) corresponds to a fully exfoliated clay polystyrene nanocomposite obtained by Doh et al. [34] using the insitu polymerization method.



Figure 2.1 : Morphological states in nanocomposites.

Finally, two intermediary states can be seen: the immiscible-intercalate and the intercalate-exfoliated which correspond respectively to the transition state between immiscible and intercalate and between intercalate and exfoliate configurations. Their characteristics are a result of the mixing of the two predominant morphological states from which they are derived. Figure 2.1 d) and Figure 2.1 e) exemplify intercalate-exfoliate arrangement for a clay high density polyethylene obtained by Swain et al. [35] and for a clay polystyrene nanocomposites by Zhu et al. [36], respectively. Such type of morphology is often obtained in of the nanocomposite prepared by using the melt state intercalation method.

2.1.4 Nanocomposite resole resins

Industrial resins are generally low molcular weight solid materials and they can be processed easily they are often mixed with cellulose nitrate and alkyd resins for surface coating applications. Resins are mainly used in surface coatings, varnishes, inks, and textile and paper industries[37].

Nanocomposites produced by organic polymers and inorganic clay minerals containing silicate layers such as montmorillonite (MMT) have attracted great interest because of unexpected mechanical, thermal, barrier and clarity property improvements without an important increase in density, which is not possible with conventional fillers [38–45]. For the preparation of polymer layered silicate composites commonly used layered silicates that belong to general family of 2:1 phyllosilicates. Montmorillonite, hectorite, and saponite are most commonly used layered silicates miscible with the polymer matrices, one must transform the normally hydrophilic silicate surface to an organophilic one, making the intercalation of many engineering polymers possible. This can be done by ion exchange reactions with cationic surfactant including primary, secondary, tertiary, and quaternary alkyl ammonium or alkyl phosphonium cations [46].

Polymer/layered silicate (P/LS) nanocomposites generally show off improvements in properties of polymeric materials even at very low volume fraction loading (1-5%) of layered silicates, in response to the high volume fraction loading (*50%) in the traditional advanced composites [47].

Nanocomposites are materials that comprise dispersion of nanometer size particles in a (polymer/ceramic/metal) matrix. The polymers containing layered silicate clay minerals as reinforcing agent can be classified as speared (intercalated) or dispersed (exfoliated) depending on dispersing of clay in the matrix[48-50]. Hybrid organic-inorganic substances, which are composed of nanometer-sized particles, dispersed in a polymer matrix known as polymer/clay nanocomposites. Clays exhibit plastic behavior when they are heated, and they remain as a hard material at elevated temperatures. The distribution of the inorganic materials in polymer matrix is a very important issue for preparation of a desired nanocomposite. If the exfoliation cannot be achieved properly, inorganic material forms clusters in the polymer matrix and this limits the improvement of the properties[51].

Phenolic resins have been widely used due to their excellent ablative properties, structural entirety, thermal stability, and solvent resistance that make them proper for thermal insulation materials, wood products industry, coatings, molding compounds, foundry, and composite materials[52–56].

The addition of layered silicates to the phenolic resins could increase their thermal resistance and mechanical properties. In the most studies of the thermoset polymers, a significant amount of research has been performed on nanocomposites with epoxy resins. In those studies, the epoxy polymerization reaction [57-59], thermal and mechanical properties [60-62], and the addition of different clay modifiers [63-65] were analyzed. However, phenolic resin/clay nanocomposites have not been studied as much as epoxy resins due to the three-dimensional (3D) network structure of the phenolics, subsisting even before crosslinked. This network is a result of polyfunctionality of phenol i.e., having more than one reactive site for aromatic substitution reaction and excess of formaldehyde. Their structure makes it more difficult to intercalate the layered silicate galleries than with linear polymers.

Byun et al. [66] had the first study about producing nanocomposites from resole type phenolic resin layered silicate nanocomposites using various layered silicates by melt intercalation. They have concluded that exfoliation was expected to be more difficult with resol type phenolic resins than novolac type phenolic resin, due to the 3D structure of resol resins that even they have before to curing. This 3D structure is due to the polyfunctionality of phenol and the excess formaldehyde available during the production of the resins, as the structure tends to become 3D and bulky when there are more than one reaction sites. These structural peculiarities may cause resins to be too bulky to synthesize a nanocomposite, especially compared to other thermosetting resins such as widely studied epoxy or even novalac type phenolic resins, which are rather linear and easier to intercalate. These can be concluded by referring to illustration below (Figure 2.2) [67].



Figure 2.2: (a) Resole type phenolic resin; (b) Novalac type phenolic resin [67].

L. B. Manfredi et al. [68] studied the influence of the nanoreinforcement in the curing process and in the final properties of the cured resin. Kaynak and Tasan investigated the effects of several produciton parameters on the structure of resole type phenolic resin/layered silicate nanocomposites. They examined the effects of temperature, mixing method, resin type, cure method, clay amount, and clay source by assessing the morphology of the final products via XRD, SEM, TEM analyses and mechanical tests [69]. M. Lopez et al. [70] studied about curing characteristics of resole/layered silicate nanocomposites and they investigated the effects of clay content in a resole resin on curing process by DSC and FT-IR.

2.2 Composites

The term composite could mean almost anything if taken at face value, since all materials are composed of dissimilar subunits if examined at close enough detail. But in modern materials engineering, the term usually refers to a "matrix" material that is reinforced with fibers. For instance, the term "FRP" (for Fiber Reinforced Plastic) usually indicates a thermosetting polyester matrix containing glass fibers, and this particular composite has the lion's share of today's commercial market [71].

Contemporary composites results from research and innovation from past few decades have progressed from glass fiber for automobile bodies to particulate composites for aerospace and a range other applications. Ironically, despite the growing familiarity with composite materials and ever-increasing range of applications, the term defines a clear definition. Loose terms like "materials composed of two or more distinctly identifiable constituents" are used to describe natural composites like timber, organic materials, like tissue surrounding the skeletal system, soil aggregates, minerals and rock [72].

Many composites used today are at the leading edge of materials technology, with performance and costs appropriate to ultrademanding applications such as spacecraft. But heterogeneous materials combining the best aspects of dissimilar constituents have been used by nature for millions of years [71].

Fibers or particles embedded in matrix of another material would be the best example of modern-day composite materials, which are mostly structural [72]. In matrix-

based structural composites, the matrix serves two paramount purposes viz., binding the reinforcement phases in place and deforming to distribute the stresses among the constituent reinforcement materials under an applied force [72].

The demands on matrices are many. They may need to temperature variations, be conductors or resistors of electricity, have moisture sensitivity etc. This may offer weight advantages, ease of handling and other merits which may also become applicable depending on the purpose for which matrices are chosen [72].

Solids that accommodate stress to incorporate other constituents provide strong bonds for the reinforcing phase are potential matrix materials. A few inorganic materials, polymers and metals have found applications as matrix materials in the designing of structural composites, with commendable success. These materials remain elastic till failure occurs and show decreased failure strain, when loaded in tension and compression [72].

2.2.1 Polymeric composite matrix materials

Polymers make ideal materials as they can be processed easily, possess lightweight, and desirable mechanical properties. It follows, therefore, that high temperature resins are extensively used in aeronautical applications.

Two main kinds of polymers are thermosets and thermoplastics. Thermosets have qualities such as a well-bonded three-dimensional molecular structure after curing. They decompose instead of melting on hardening. Merely changing the basic composition of the resin is enough to alter the conditions suitably for curing and determine its other characteristics. They can be retained in a partially cured condition too over prolonged periods of time, rendering Thermosets very flexible. Thus, they are most suited as matrix bases for advanced conditions fiber reinforced composites. Thermosets find wide ranging applications in the chopped fiber composites form particularly when a premixed or moulding compound with fibers of specific quality and aspect ratio happens to be starting material as in epoxy, polymer and phenolic polyamide resins [72].
2.3 Resins

According to DIN 55947, resin is the general term used technically for solid, hard to soft, organic, noncrystalline products having a broader or narrower molecular mass distribution. They normally have a melting or softening range, are brittle in the solid state, and then usually show conchoidal (shell-like) fracture. They have a tendency to flow at room temperature ("cold flow"). Resins are in general raw materials, for example for binders, curable moulding compositions, adhesives and coatings.

Another definition of a resin is somewhat different and more concise: "A solid, semisolid or liquid substance of nonuniform and often high molecular weight, which in the solid state usually possesses a softening or melting range and exhibits conchoidal fracture. Note: In the broader sense, this expression is used to denote any polymer which forms the basis of a thermoplastic. Following agreement, bitumen, grades of pitch, gums and waxes are excluded" [73].

Resins may be of vegetable origin or of animal origin (natural resins) and synthetic origin (synthetic resins). [74]. A natural resin is a "glassy amorphous substance produced either in the metabolism of tree growth, e.g. copal, or by insects, e.g. lac.[75]. A synthetic resin belongs to a group of chemically produced substances that resemble and share some of the properties of natural resins. The term is generally understood to mean a member of the heterogeneous group of compounds produced from simpler compounds by condensation and/or polymerization. Note: Chemically modified natural polymers, such as cellulose derivatives, are not considered to be synthetic resins [75]. The resins can be colorless or can be colored. The synthetic resins, originally viewed as substitutes for certain natural resins, have a large place of their own in industry and commerce. Phenol-formaldehyde, phenol-urea, and phenol-melamine resins are some of the most important synthetic resins and are important commercially. Any unplasticized organic polymer is considered a resin, thus nearly any one of the common plastics may be viewed as a synthetic resin [76].

2.3.1 Thermoset resins

Common thermosetting resins include [77] :

- Polyester Resin
- Vinyl Ester Resin

- Epoxy Resin
- Phenolic Resin
- Urethane

The most common thermosetting resin used today is polyester resin, followed by vinyl ester and epoxy. Thermosetting resins are popular because uncured, at room temperature, they are in a liquid state. This allows for convenient impregnation of reinforcing fibers such as fiberglass, carbon fiber, or Kevlar.

2.3.1.1 Properties and Benefits of Thermoset Resins

As mentioned, a room temperature liquid resin is easy to work with. Laminators can easily remove all air during manufacturing, and it also allows the ability to rapidly manufacture products using a vacuum or positive pressure pump. Beyond ease of manufacturing, thermosetting resins can exhibit excellent properties at a low raw material cost.

Properties of thermoset resins include:

- Excellent resistance to solvents and corrosives
- Resistance to heat and high temperature
- Fatigue strength
- Tailored elasticity
- Excellent adhesion
- Excellent finishing (polishing, painting, etc.)

In a thermoset resin, the raw uncured resin molecules are crossed linked through a catalytic chemical reaction. Through this chemical reaction, most often exothermic, the resin creates extremely strong bonds to one another, and the resin changes state from a liquid to a solid.

A thermosetting resin, once catalyzed, it can not be reversed or reformed. Meaning, once a thermoset composite is formed, it cannot be remolded or reshaped. Because of this, the recycling of thermoset composites is extremely difficult. The thermoset resin itself is not recyclable, however, there are a few new companies who have

successfully removed the resin through pyrolization and are able to reclaim the reinforcing fiber [77].

2.3.2 Phenolic resins

Phenolic resins, also called phenolic plastics or phenoplasts, were among the first synthetic resins composed by deliberate synthesis and a re therefore among the earliest synthetic binders of any kind. Consequently, it is hardly surprising that the reaction mechanisms in the synthesis of these resins and their reactions with other substances have been the subject of particularly intense study [78].

2.3.2.1 Types of phenolic resins

Phenolic resins are of two main types. The resins resemble either the phenolic alcohols or the dihydroxydiphenylalkanes in basic structure. If they are prepared with an excess of formaldehyde and an alkaline catalyst they will resemble the phenol alcohols and have methylol side or end groups. Such resins are often referred to as resoles. They are capable of being cured by the application of heat and acids, cure resulting through condensation of the methylol groups. By cooling the resin the reactions may be conveniently stopped, or at least effectively retarded, anywhere between the addition of the formaldehyde and the final curing process. To resume reaction the temperature is raised or an acidic catalyst is added. Since there is no sharp break in these reactions such resins have been termed the One-Stage resins. The majority of the One-Stage resins employ formaldehyde as the aldehyde, although certain other aldehydes may be used [79]. Formaldehyde is preferred because of its high reactivity and freedom from side reactions.

On the other hand, if the phenolic resin is prepared with an acidic catalyst and less than a mole of formaldehyde per mole of phenol the resin will resemble a dihydroxydiphenylmethane in structure, e.g. the chains are phenol ended. These resins, commonly referred as novalacs, are permanently soluble and fusible and cure only upon the addition of a curing agent. As the preparation of the novalac resin represents one process and the addition of the curing agent represents a seperate and distinct process, resins based on a novalac resin and a curing agent are referred to as Two-Stage resins. An outline of the two processes is given in Figure 2.3 [80].



Figure 2.3: Phenolic resin processes [80].

'Phenolics' are prepared by condensing phenols with formaldehyde. Phenol is reactive at the 2, 4 and 6 positions and will condense with formaldehyde ultimately forming a densely crosslinked network that was the basis of the early plastic 'Bakelite', developed by Leo Baekland in 1907. In the coatings industry it is more usual to employ 4-substituted phenols so that linear materials are produced. Other aldehydes can form polymers with phenols, but are less reactive than formaldehyde and are rarely used. When formaldehyde is in excess, short chains terminated with methylol groups known as 'resoles' (Figure 2.4 : a) are formed. If the reaction is carried out in an alcohol the resole hydroxyl groups are alkylated. An excess of phenol provides 'novolacs' (Figure 2.4 : b) with reactive aromatic sites at the chain ends. Branches can be introduced by judicious incorporation of unsubstituted phenol. In both cases a certain amount of ether bridging also takes place [81].

Novolacs will condense with further formaldehyde or resoles, but otherwise are inert except with respect to their phenolic groups which canbe used to cure epoxy polymers or converted to epoxy groups. The methylolgroups on resoles, whether alkylated or not, are reactive with polyols on stoving under basic, acidic or neutral conditions, though acidic catalysis is most effective. The reaction proceeds by addition to a quinomethide intermediate (Figure 2.5). Addition of a further resole group to the quinomethide can occur either directly to form an ether bridge, or by a Diels–Alder reaction between two quinomethides to form a spiro-linkage. The overall effect is self-condensation [81].





Figure 2.4 : a) Resole and b) Novalac.



Figure 2.5 : The reaction of methylolgroups on resoles by addition to aquinomethide intermediate [81].

Resoles are sometimes cured and processed with alkyd resins, when addition of the olefinic sites to the o-quinomethide intermediate can yield chroman ring structures (Figure 2.6) [81].



Figure 2.6 : Chroman ring structure.

Oxidation of phenolic residues produces highly conjugated groupings of intense red or yellow colour (Figure 2.7). The dark colour inevitably associated with phenolic polymers prevents their widespread use in coatings. However, they are valued in can linings for their great chemical inertness, and are often used in conjunction with epoxies. They are also used as adhesion promotors in, for example, epoxy–amine aerospace primers [81].



Figure 2.7 : Production of highly conjugated groupingd by oxidation of phenolic residues.

Resoles

The initial phenol-aldehyde condensation products obtained with alkaline catalysts were named "resoles" by Lebach; [82-84] they correspond to the soluble and fusible A stage resins as defined by Baekeland [85-87]. Chemically, resoles are a complex mixture of mono and polynuclear phenolic bodies possessing reactive methylol groups, the polynuclear compounds being derived from the simpler mononuclear phenol alcohols [88-91]. The exact nature of the linakges in the more complex resole

molecules and their mode of formation are among the most interesting aspects of the chemistry of the phenolic resins.[92]

Reese, in a detailed study of the condensation of o- and p- methylolphenol, 2,4- and 2,6- dimethylolphenol, and trimethylolphenol, later found that none of the compounds formed dibenzyl ether derivatives under alkaline conditions [93]. Lilley [94] has examined the possibility of ether formation as compared to methylene bridge formation on the basis of purely theoretical considerations. He concluded that dibenzyl ethers can only be formed within certain limited and critical pH ranges. These ranges do not coincide with common technological practice fort he preparation of resoles.

A far more important means than ether linkages for tying phenol alcohols together is by methylene bridges. Many of the early workers were aware of the importance of this reaction [95-97]. It has been confirmed by many workers, that phenol alcohols such as the monoalcohols of 2,4- and 2,6-xylenol from dihydroxydiphenylmethanes and eliminate formaldehyde on heating with alkalies [90, 98, 99, 100].

Some of the effects of reaction conditions on resin properties may be illustrated by use of phenol and formaldehyde at a single ratio, e.g. 1:1.3, with NaOH as a catalyst. At low temperature and a high concentration of catalyst a product consisting almost entirely of mononuclear phenol alcahols results. The product will be infinitely soluble in water. With less caustic and a short time reflux temperature a resole which will tolerate dilution with several volumes of water is stil possible although it may no longer have infinite water dilutability. However, with low catalyst concentration and particularly after an extended period of reaction at reflux temperature a resole will be obtained which will be composed mainly of polynuclear bodies, soluble only in sotrong solvents such as acetone. If the condensation is carried too far, solubility in all solvents will be lost. [92]

Bettleheim and Nihlberg [101] recognize six distinct steps in resin manufacture: (1) warming-up time; (2) ripening, the time at condensation temperature before the resin starts to precipitate; (3) post ripening, the time the resin is held at condensation temperature after resin seperates from the aqueous phase; (4) distillaton; (5) concentration, the period the resin is held under vacuum and heated to advance to the desired viscosity; (6) cooling. Bettleheim and Nihlberg strongly emphasize that such

properties as viscosity and density alone are not true criteria of the status of a resin or of the behavior to be expected of the resin. The type of resin obtained depends on the way each of the six steps of the manufacture are handled. If each step in the process is made to follow a set Schedule, then, and then only, do the viscosity, refractive index, etc., have any meaning so far as over-all properties of a resin are concerned.

Resoles generally contain appreciable quantities of unreacted phenol. This is particularly true for resins prepared with less than 1.5 moles of formaldehyde perm ole phenol. The quantity of unreacted phenol in commercial One-Stage resins may be as high as 20% according to Lewin and Robitschek [102]. Smith, Rugg, and Bowman [103] found between 2 and 15% phenol in the resins they examined. The conditions of reaction, at a constant phenol-to-formaldehyde ratio, also have a large effect on this figure, low reaction temperature and strong alkaline catalysts tending to increase the amount of unreacted phenol [92]. Vanscheidt [104] has measured the phenol content of phenol-formaldehyde reaction mixtures as a funciton of time of reaction, formaldehyde consumption, and catalyst at several phenol-to-formaldehyde ratios.

Water is extremely difficult to remove from One-Stage resins [105]. This means that most commercial resins, even in the solid form, will contain water. In addition, further quantities of water are eliminated during cure.[92]

Such phenol-based resole resins cross-link on heating and are used in adhesive and plastics applications. However, they are not suitable for coatings applications, primarily because their cross-link density is higher than appropriate for any coating. Furthemore, the package stability of the resins is limited. Resole phenolics useful in coatings applications are made from monosubstituted phenols with phenol. The use of substituted phenols reduces the potential cross-link density. There are two broad categories of such resins: (1) those that are soluble in alcohol and other low molcular weight oxygenated solvents, commonly called alcohol-soluble, heat-reactive phenolics; and (2) those that are soluble in vegetable oils and are called oil-soluble, heat-reactive phenolics [106].

Alcohol-soluble,heat-reactive resole resins are prepared by reacting phenol, o- or pcresol, and formaldehyde in the presence of a base catalyst at less than 60°C while removing water under vacuum. The catalyst neutralized, alcohol is added, and the salt resulting from catalyst neutralization is removed by filtration. Potential crosslink density is controlled by the ratio of formaldehyde to phenols and by reaction time [106].



Figure 2.8 : Idealized structure of resole type phenolic resin (from p-cresol) [106].

Such resole phenolic resins are used in interior can coatings and tank linings. They require baking using an acid catalyst in order to cure in short times. To enhance flexibility and adhesion, they are commonly blended with low molecular weight poly(vinyl butyral) as a plasticizer. The films are resistant to swelling by oils such as encountered in canned fish and are completely resistant to hydrolysis. These resins and other heat-reactive phenolics discolor during baking, which restricts tehir usage to applications for which development of a yellow-brown color is permissible. These resins are also blended with epoxy resins in thermosetting coatings for applications such as primers and can coatings. The absence of hydrolyzable bonds and generally excellent adhesion properties are their chief advantages [106].

Oil-soluble, heat-reactive phenolics are preapared by reacting a para substituted phenol, (e.g., p-phenylphenol, p-t-butylphenol, or p-nonylphenol) with somewhat less then 2 moles of formaldehyde per mole of substituted phenol. The resulting resole phenolics are cast from the reactor after nuetralization of the catalyst. The resulting resole phenolics are solid, linear resins with terminal methylol groups. The most common use for such resins is to make varnishes with linseed oil and/or tung oil. However, since varnishes have, in large measure, been replaced by other vehicles, the consumption of these resins has declined markedly [106].

Novolacs

Novalac resins were named by Baekeland [87, 107], who saw a superficial similarity in their properties to those of the lac resins. Most of the commercial novolac resins are made by the condensation of phenol with formaldehyde, although other aldehydes, such as furfural and acrolein, have had limited use [108-110]. Novolac resins are phenolended chain polymers in which the phenolic nuclei are joined by methylene bridges located *ortho* and *para* to the phenolic hydroxyl groups. The resins are almost invariably prepared with acidic catalysts, although non-catalyzed or even base-catalyzed reactions are occasionally employed [92].

Numerous reports on the elemental analysis of novolac resins may be found in the literature [111]. The analytical data agree well with the calculated values for products, assuming a polynuclear methylene structure, provided that the calculations are mad efor products of known molecular weight. That the phenolic hydroxyl groups are intact has been shown by analysis for hydroxyl content, the preparation of acetate, and benzoate esters, benzyl ethers, and phenyl isocyanate reaction products [112]. Analytical data on these derivatives also agree with calculated values assuming a methylene bridge structure for the novalac resin.

The presence of the phenolic hyroxyl group is also indicated by the alkali solubility of the resins. If the resin is of high molecular weight, its solubility in aqueous caustic may be very low. The resin form sodium salts, but the salts of the higher polymers are practically insoluble caustic solution[113]. However, essentially all novolac resins are soluble in alcoholic potassium hydroxide solution [92].

When heated in an inert atmosphere below their point of decomposition, novolac resins remain permanently soluble and fusible. If heated in contact with air, a skin of reddish brown resin will form which is both insoluble and infusible. The formation of the insoluble and infusible skin is undoubtedly due to oxidative changes and not to the presence of methylol groups. It has been shown, for example, that dihydroxydiphenyls may be formed by the treatment of certain phenols with peroxides[114]. Similar reactions may be responsible for the crosslinking of novolac resins on exposure to air, although such a coupling reaction has not been proved conclusively for phenolic resins. Heating in the presence of air may also bring about degradative changes which will decrease the molecular weight of the higher-

viscosity novolac resins. Such reactions have been reported to occur even in the solid state and at temperatures as low as 70 °C [115]. Bender [116] thinks that some linkages are much less stable than other linkages, particularly in the higher-viscosity novolac resins.

Methylol groups were not detected in a commercial novolac resin by Martin [117]. Later by means of chromatographic techniques which are much more sensitive than methods of the abover workers, phenol alcohols were found in small amounts of novolac resins, especially during the early stages of their preparation [118]. However, these findings do not alter the over-all Picture of a novolac resin, since the phenol alcohols were minor constituents present in insufficient quantity to make the resins self-curing.

Several workers have studied the decomposition of phenolic resins. Herzog [119] found that phenol could be recovered by digesting various phenolic resins with caustic. Allen, Meharg, and Schmidt [120] also used caustic but carried out the reaction in an autoclave at 300°C. They found that the decomposition products always contained more of the methyl-substituted phenols than the phenol from which it was made. The methyl substituents appeared to be derived from the combined formaldehyde since the higher phenols were obtained in greater quantity from the more advanced resins as well as from resins prepared with a higher ratio of formaldehyde to phenol.

Waterman and Veldman [121] studied the decomposition of resins under hydrogen pressure, using molybdenum as catalyst. Megson [96] studied the purely thermal decompositon of novolac resins by heating purified resins in a flask up to 450°C, after removing volatile products under a vacuum.

The conventional resins, prepared with acidic catalystsi appear to be essentially linear. This appears to be true even when the resin is prepared from a trifunctional phenol where branching is at least theoretically quite possible [92]. On the other hand, novolac resins prepared by the condensation of resoles with excess phenol are highly branched. These novolac resins show pronounced differences in viscosity when compared to novolac resins prepared in a more conventional manner by direct reaction of phenols with formaldehyde under acidic conditions. A model of a highly branched novolac resin was prepared by Vanscheidt by condensing tetramethyloldiphenylolmethane with an excess of phenol. This product, which was called an "isonovolac", showed approximately twice the viscosity of the conventional novolac resins [92].

Sulfiric acid is often favored as acidic catalyst to prepare novolac resins, because of price, lack of volatility, and ease in handling. Oxalic acid is one of the best catalysts fort he production of light-colored resins, although phosphoric acid also gives beter than average color. Acids soluble in the resin layer, such as p-toluenesulfonic acid, give beter formaldehyde and phenol utilization than water-soluble catalysts.[92]. Surface-active agents promote the reaction of the higher alkyl phenols that have low solubility in formalin[122]. High concentrations of acids are to be avoided so that the reaction does not become so vigorous as to be difficult to control. Too much acid may also cause excessive bodying of the resin.[92].

Novolac resins have occasionally been prepared without the benefit of an added catalyst[123]. Because of the low reactivity of phenols with formaldehyde in the absence of catalysts high temperatures are required. The early resins of this type were prepared in autoclaves. More recently tube reactors have been used. This permits beter control of reactions at the high temperatures required when a catalyst is not employed.[92]

Novolac phenolics of interest for coating are made with acid catalyst and o- or psubstituted phenols. Molecular weight is controlled by the molar ratio of phenol and formaldehyde, which is always greater than 1. In contrast to resole phenolics, the terminal phenol groups are not metholylated, as shown in the idealized structure [106].



Figure 2.9 : Novalac type phenolic resin [106].

Three types of novolac resins are used in coatings:

1. Alcohol-soluble nonheat-reactive low molecular weight phenolics are derived from o- or p-cresol. An important use for these resin is in the preparation of novalac epoxy resins by reaction with epichlorohydrin.

2. Oil-soluble nonheat-reactive phenolic resins are made using o low ratio of formaldehyde, an ac,d catalyst, and a subtituted phenol. They are used together with drying oils, particularly tung oil or tung-linseed oil mixtures, to make varnishes. Such varnishes are still used to a small extent as marine spar varnish, for which their reputation for durability maintains their position in the do-it-yourself marine yatch market. The durability of phenolic varnishes may well result, at least in part, from the antioxidant activity of the phenolic groups.

3. Rosin-modified phenolic resins are the principal type of modified phenolics still in use. Their use in coatings is limited to low cost varnishes. The largest volume use is in printing inks. For inks, the phenolic resin prepared in the presence of rosin esters and/or zinc or calcium salts of rosin. The structures of the reaction products, which are high melting hydrocarbon-soluble resins, are not completely known. An important example of their use is in publication gravure inks such as those used in mail-order catalogs and some magazine and paperback book applications [106].

2.3.2.2 Polymerization mechanisms of phenolic resins

The mechanism of polymerization involves aromatic electrophilic substitution, followed by condensation reactions that lead to crosslinking. Phenol is by far the most common substrate, but occasionally other similar compounds such as cresols, resorcinol, or bisphenol A are used. Formaldehyde is provided as as aqueous solution ("formalin") or as a presursor, hexamethylene tetraamine (HMT), which decomposes to formaldehyde and ammonia under the reaction conditions [124].

Base catalysis

The reaction begins when phenol is deprotonated by the base catalyst. The negative charge is accomodated by resonance forms with the charge on two ortho positions and the para position of the ring. These three structures cause phenol to be trifunctional.



The phenoxide then attacks formaldehyde via the ortho or para positions:



Of course, the reaction can occur again at the remaining activated positions. The result is a mixture of all of the possible "methylol" compounds, mono-, di-, and tri-substituted.



Further reactions produce methylene or ether bridges at any of the possible positions. At early stages of the reaction, highly branched, oligomeric compounds form that are still soluble. Later on, the mixture is heated strongly to complete the reaction.



The result is a highly crosslinked, irregular structure.



Figure 2.10 : Polymerizaton mechanism of PFR with base catalyst [124].

Acid catalysis

A series of analogous reactions occur under acidic conditions. First, methylol derivatives are formed.



Later, acid-catalyzed condensation reactions build methylene or ether bridges.





Figure 2.11 : Polymerization mechanism of PFR with acid catalyst [124].

The ratio of methylene to ether bridges is different, depending on whether acid or base is used, but the final crosslinked product is pretty much the same.

Side reactions

Numerous side reactions occur at the same time as the chemistry above. The precise course of the reaction is difficult to follow because of the insolubility of the product. The final polymer is inevitably highly colored, usually black. It is believed that quinone methide compounds such as the one shown Figure 2.12 (for a base-catalyzed example) are responsible for the ultimate formation of colored species.



Figure 2.12 : Side reactions for a base-catalyzed example [124].

2.3.2.3 Crosslinking and the phenol/formaldehyde ratio of phenolic resins

When the molar ratio of formaldehyde : phenol reaches one, in theory every phenol is linked together via methylene bridges, generating one single molecule, and the system is entirely crosslinked. This is why bakelites (F:P <1) don't harden without the addition of a crosslinking agent, and why resins with the formula F:P >1 will.

Being thermosets, hydroxymethyl phenols will crosslink on heating to around 120 °C to form methylene and methyl ether bridges. At this point the resin is a 3-dimensional network, which is typical of polymerised phenolic resins. The high crosslinking gives this type of phenolic resin its hardness, good thermal stability, and chemical imperviousness [125].

2.3.2.4 Applications of phenolic resins

Phenolic resins are found in myriad industrial products. Phenolic laminates are made material by impregnating one or more layers of а base such as paper, fiberglass or cotton with phenolic resin and laminating the resin-saturated base material under heat and pressure. The resin fully polymerizes (cures) during this process. The base material choice depends on the intended application of the finished product. Paper phenolics are used in manufacturing electrical components such as punch-through boards and household laminates. Glass phenolics are particularly well suited for use in the high speedbearing market. Phenolic micro-balloons are used for density control. Snooker balls as well as balls from many table-based ball games are also made from Phenol formaldehyde resin [125].

2.3.2.5 Trade names of phenolic resins

Trade names of phenolic resins were giving according to the literature [125].

- 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.

2.3.3 Urea formaldehyde (UF) resins

Urea formaldehyde (UF) is a type of thermosetting resin that finds applications in coatings, adhesives, laminating, and molding compositions [126]. Urea/formaldehyde glue resins are the most important type of urea/formaldehyde resins. Monographs on the chemistry of urea/formaldehyde resins include those by Dunky, Meyer and Pizzi, Dijk [127-130].

The industrial production of urea/formaldehyde glue resins fort he wood-working industry started in 1931. Environmental concerns demanded a change of the formulation of urea/formaldehyde resins to decrease the molar ratio of formaldehyde to urea to avoid formaldehyde emissions.

2.3.3.1 History of UF resin

The reaction of urea with formaldehyde was first noted in 1884, with commercial interest in the polymers commercing at about 1918 with a patent issued to Hanns John (1891-1942) [131-133]. However, ,n 1896 Carl Goldschmidt described precipitates formed when aqueous solutions of ures and formaldehyde were reacted under acidic conditions [134]. It is believed that the primary precipitate formed by Goldschmidt and empirically identified as $C_5H_{10}O_3N_4$ was, in fact, a cyclically structured condensation product [135].

2.3.3.2 Synthesis of UF resin

Polymerization

The synthesis of a urea/formaldehyde (UF) resin proceeds via the methylolation of urea and condesation of the methylol groups. The reaction can be conducted in an aqueous medium because of the good solubility of both urea and formaldehyde. The basic reactions are shown in Figure 2.13. The methylolation of urea is done in alkaline or slightly acidic solution in a two-fold excess of formaldehyde. Following methylolation, further condensation into methylene urea oligomers occurs, with a degree of oligomerization of 4 to 8. Because of the functionality of the nitrogen, branched products can be formed. Ether bridges also may be formed. These ether bridges can be rearranged into methylene bridges, expelling formaldehyde. Dimethylol urea is not a stable compound. In the presence of another formaldehyde reactive compound, dimethylol urea will donate its two formaldehyde groups to the more stable phenol, ammonia, melamine, etc. This leaves raw urea in the resin which reduces the durability significantly[136].



Figure 2.13 : Basic Reactions of Urea and Formaldehyde [137].

Manufacture of UF resins

The production of UF resins is usually achieved in three stages [129].

- 1. Methylolation: urea reacts with aqueous formaldehyde under alkaline conditions at temperatures up to 100° C.
- 2. Condensation: the condensation of methylols in slightly acidic medium yields oligomers with different molar mass and various functionalities. The condensation is then stopped by adding alkaline substances.
- 3. Post treatment: evaporation of excess water and formaldehyde, or addition of secondary urea to decrease the ratio of formaldehyde to urea.

The multistage process is useful to fulfill the requirements of retaining the reactivity and the strength of the cured resin under the condition of minimal emission of formaldehyde during service.

2.3.3.3 Applications and uses of UF resins

Glue resins

The main application of UF resins is in the adhesive industry. UF glues are used in pressed wood products such as particle board, and plywood as laminating resins. Because of the potential for formaldehyde release, UF resins have been modified for indoor applications. Formaldehyde is a potent primary irritant.

Binders

Typical binders used to bind glass fiber mats include UF resins, phenolic resins, melamine resins, bone glue, polyvinyl alcohols, and latices. These binder materials are impregnated directly into the fibrous mat and set or cured by heating to obtain the desired integrity in glass fibers. The most widely used glass mat binder is urea/formaldehyde, because it is relatively inexpensive [138].

Foundry sands

In the manufacturing of low nitrogen-containing foundry sands, the hexamine crosslinker is replaced partly with another agent that does not contain nitrogen. Nitrogen, when present in coated foundry sand can gice rise to nitrogen defects during steel casting. It is preferable to have as low of nitrogen content as possible. Usually this other crosslinking agent is thermosetting resol phenol/formaldehyde

resin. During the manufacturing of low nitrogen-containing sands, a novalak resin added, followed by the resol resin and then the hexamine[136].

2.4 Phenol-Urea-Formaldehyde (PUF) Systems

He and Yan investigated the effects of formulation variables of co-condensed alkaline phenol-urea-formaldehyde (PUF) resol resins on thermal curing properties using Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Analysis (DMA). They were able to demonstrate a strong pH reactivity dependency and the presence of multiple reactions during cure [139]. He and Yan also investigated the effects of formulation var, ables of co-condensed alkaline phenol-urea-formaldehyde (PUF) resol resins on their structure, composition, and thermal curing properties. They used liquid ¹³C-NMR to yield information regarding reaction mechanism, composition, and structure of the uncured PUF resol. Solid state ¹³C-NMR was conducted to characterize the network structure of the curing or cured PUF resin. They found that urea co-condensed with methylolphenols almost exclusively in the para position to form methylene-bridged structures, while no ortho ureamethylolphenols formed, suggesting that the effect was due to the higher reactivity of the para methylolphenols. Further, the ureas formed ether bridges with other methylol ureas but not with methylolphenols and were absent above pH = 13. They concluded that pH influences the structure and composition of the liquid resin, with the ratios of para to ortho methylolphenols and para-para to ortho-para bridges decreasing with increasing pH. Urea methylene ether bridges were not present in the cured state [140].

3. EXPERIMENTAL PART

3.1 Materials

Phenol (P, C₆H₆O), Formaldehyde (F, CH₂O, 37%), Sodium hyroxide (NaOH), Hydroxyl chain ended polydimethyl siloxane (PDMS, Mw: 950±80), Sulfiric acid (H₂SO₄) and Urea (U) were purchased from Riedel-de Haen, LAB-SCAN, Riedel-de Haen, GOLDSCHMIDT, MERCK and CARLO ERBA REGANTI, respectively. All chemicals were used without further purification.

3.2 Synthesis of Phenol Formaldehyde (Resol) Resin (PFR)

Formaldehyde solution (37%) and phenol were put into a three-necked round bottomed flask. As a catalyst NaOH solution (20%) was prepared and added to the flask to increase the pH value of mixture.



Figure 3.1 : Monomers used in synthesis of PFR.

The P/F ratio of reaction was 1/2, therefore P amount was 9,4 g (0,1 mole) and F amount was 16,5 mL (6 g – 0,2 mole). The mixture was stirred with a mechanical stirrer for 4 h at 65°C. During the reaction pH value of the system was controlled and it was fixed at 10. After 4 h, colourless sample solution started to become brownish and transferred in a two-necked round bottomed flask, then mixture was stirred with a magnetic stirrer for more 4 h at 70°C. During the reaction viscosity of the mixture was increased and at the end of the reaction, like a gel, a very viscous resin was obtained. Polymerizatin mechanism of PFR was shown in Figure 3.2.



Figure 3.2 : Polymerization mechanism of PFR [141].



Figure 3.3 : Experimental setup for synthesis of PFR.

Experimental setup of the polymerization was showed in Figure 3.3. The polymer product was dried under vacuum for 2 hours at 65°C. Then sample was put in a drying oven and was dried for more 1 hour at 100°C. By the effect of heating solid and reddish resin sample was obtained.

3.3 Synthesis of PDMS Modified Resol Resin (PDMS-PFR)

Formaldehyde solution (37%) and PDMS solution were put into a three-necked round bottomed flask and then phenol was added the mixture. The structure of PDMS was shown in figure Z. As a catalyst NaOH solution (20 wt%) was added to the flask to increase the pH value of mixture. For the reaction including P:F ratio of 1:2, P amount was 9,4 g and F amount was 16,5 mL (6 g) and also PDMS amount was 2 wt%.



Figure 3.4: Hydroxyl chain ended polydimethylsiloxane (PDMS).

The mixture was stirred with a mechanical stirrer for 4 hours at 60°C. During the reaction pH value of the system was controlled and it was fixed at 10. After 4 hours, colourless sample solution started to become brownish and transferred in a three-necked round bottomed flask, then mixture was stirred with a magnetic stirrer for more 4 hours at 70°C. The obtained polymer was dried under vacuum for 2 hours at 65°C. Then sample was put in a drying oven and was dried for more 1 hour at 100°C.

3.4 Synthesis of PDMS Modified Layered Clay Resol Nanocomposite Resin (PDMS-LC-PFR) Samples

PDMS-LC-PFR was synthesized in four different initial feed clay contents by weight (0,5 wt%, 1 wt%, 3 wt%, 5 wt%). Constant ratio of monomers of 1:2 and constant amount of PDMS of 2 wt% was applied at each polymerizations. Unmodified montmorillonite clay was used to prepare resol/clay nanocomposite resins and the

amount of the clays were 0,047g for 0,5 wt% sample, were 0,094g for 1 wt% sample, were 0,282g for 3 wt% sample and were 0,47g for 5 wt% sample. Both PDMS-LC-PFR nanocomposite samples (PDMS-LC-PFR1, PDMS-LC-PFR2, PDMS-LC-PFR3, PDMS-LC-PFR4) synthesized by the same way and by the same experimental setup with PFR and PDMS-PFR.

		1	
Sample Name	Clay Content (wt %)	P:F molar ratio	PDMS (wt %)
PFR	0	1:2	0
PDMS-PFR	0	1:2	2
PDMS-LC-PFR1	0,5	1:2	2
PDMS-LC-PFR2	1	1:2	2
PDMS-LC-PFR3	3	1:2	2
PDMS-LC-PFR4	5	1:2	2

Table 3.1 : Contents of resin samples.

3.5 Preparation of Thin Films From PFR, PDMS-PFR and PDMS-LC-PFR

The same procedure was applied to synthesize fim samples; stirring of mixtures carried on until a viscous solution was obtained following as it was seen in Figure 3.5, the solvent casting of the viscous solution as film on 5 x 5 cm² glass substrate area at about 1 mm height. Homogeneous viscous film was dried under vacuum at 70°C. After vacuum film samples were dried at 100°C in a drying oven for 1 hour.

3.6 Synthesis of Phenol-Urea-Formaldehyde/Pomace Composite Resin (PUFPCR) Samples

PFR mixtures were prepared as it was said before in 3.2 (synthesis of PFR). Formaldehyde solution (37%) and phenol were put into a round bottomed flask. As a catalyst NaOH solution (20%) was prepared and added to the flask to increase the pH value of mixture. The P:F ratio of reaction was 1:2, the mixture was stirred with a magnetic stirrer for 4 hours at 65°C. During the reaction pH value of the system was controlled and it was fixed at 10. After 4 hours, colourless sample solution became brownish.



Figure 3.5 : Preparation of thin films.



Figure 3.6 : Thin film sample of PDMS-CL-PFR3.

To synthesize urea formaldehyde resin, aqueous formaldehyde solution (37%) and a few drops concentrated H_2SO_4 were put into a round bottomed flask and were started to mix at 45°C. Then solid urea was added to the flask, the mixture was stirred with a magnetic stirrer for 2 hours at 60°C. The U:F ratio of reaction was 2:5, and reaction was involved condensation between the nucleophilic nitrogen of urea with the electrophilic carbonyl carbon of formaldehyde. At the end of the reaction, white and glue UFR prepolymer was obtained.



Figure 3.7 : The chemical structure of Urea monomer.



Figure 3.8 : Repeating unit of UFR.

PFR and UFR mixtures were put into a one-necked round bottomed flask with the content of 50 wt% PFR-50 wt% UFR and were stirred with a magnetic stirrer for 2 hours at 65°C, therefore phenol-urea-formaldehyde resin (PUFR) system was obtained. Then different amounts of pomace were added to PUFR mixtures to obtain PUFPCR systems (PUFPCR1, PUFPCR2, PUFPCR3, PUFPCR4). Then mixtures were stirred for more 2 hours at 65°C to disperse the pomace homogeneously. When reaction was completed PUFPCR samples were left for drying at the room temperature for 3 days. Then samples were molded in conformity with ISO 178 standard for mechanical (3-point bending) measurements and dried under vacuum at 90°C for 1 hour then at 100°C for 20 hours. Also to determine the effect of the PFR-UFR resin matrix content on the material properties of the specimens, containing same amount of pomace (5 g) with different PFR-UFR resin matrix content PUFPCR samples were shown in Table 3.2.

Sample	UFR content (wt%) ^a	PFR content (wt%) ^a	Amount of pomace (wt%) ^b
PUFR	50	50	-
PUFPCR1	50	50	20
PUFPCR2	50	50	30
PUFPCR3	50	50	50
PUFPCR4	50	50	65
PUFPCR5	25	75	20
PUFPCR6	75	25	20

Table 3.2 : Contents of PUFPCR samples prepared with PFR and UFR.

^a According to the total resin matrix.

^b According to the total weight of material.

Containing different amount of bagasse PUFPCR samples were prepared in addition PFR and UFR, with PDMS-LC-PFR3 and UFR to understand the effect of the clay particles on the material properties of the specimens.Contents of samples were given in Table 3.3.

Sample	UFR content (wt%) ^a	PDMS-LC-PFR3 content (wt%) ^a	Amount of pomace (wt%) ^b
3%-PUFR	50	50	-
3%-PUFPCR1	50	50	20
3%-PUFPCR2	50	50	30
3%-PUFPCR3	50	50	50

Table 3.3 : Contents of PUFPCR samples prepared with PDMS-LC-PFR3 and UFR.

^a According to the total resin matrix.

^b According to the total weight of material.

3.7 Characterization of Solid State PFR, PDMS-PFR, PDMS-LC-PFR Samples and PUFPCR Samples

The structures of the specimens were characterized by means of Fourier Transform Infrared (FTIR-ATR) spectroscopy. FTIR analysis of samples were carried out with FTIR-ATR reflectance spectrophotometer (Perkin Elmer, Spectrum One, with a Universal ATR attachment with a diamond and ZnSe crystal).

Differential Scanning Calorimeter (DSC) measurements were performed with DSC TA Q10 V9.9 Build 303, with 1 cycle and a heating rate of 10°C/min. Thermogravimetric analysis (TGA) were made by Perkin Elmer Pyris 1 TGA with a heating rate of 10°C/min.

Dynamic Mechanical Analysis measurements of PDMS-LC-PFR nanocomposite resin samples (PDMS-LC-PFR1, PDMS-LC-PFR2, PDMS-LC-PFR3, PDMS-LC-PFR4) were operated with DMA Q800 V7.5 Build 127 with a heating rate of 3 °C/min to 400 °C and with a forcing rate of 2N/min to18N.



Figure 3.9 : FTIR-ATR spectrometer.



Figure 3.10 : DSC TA instrument Q10.



Figure 3.11 : Dynamic Mechanical Analyzer.

To determine the water absoption capacity, composite resin specimen was waited for 24 h in a beaker that filled with water. Then, samples were dried for 1 h at 100 °C, aftee that, weight increase of specimen was measured. Mechanical properties of the composite resin (PUFPCR) samples were determined with the 3-point bending test with 60 mm span distance and 5 mm/min crosshead speed conditions. Instron 2810 series 3 point bend/flexure fixture was used for 3-point bending tests of samples.

Obtaining samples were also characterized as morphological by Scanning Electron Microscope (two diffrent SEM devices are used, firstly ESEM XL30 ESEM-FEG Philips and lastly, Carl Zeiss EVO MA 10) and the samples for the SEM measurement are prepared by coating of gold.

4. RESULT AND DISCUSSION

4.1 Nanocomposite Resin Samples Characterization

4.1.1 FTIR-ATR spectrophotometric analysis

The FTIR-ATR spectra of phenol and formaldehyde solution were presented in Figure 4.1 and collected in Table 4.1 and Table 4.2. The characteristic absorbances of phenol and formaldehyde solution were shown on the Table 4.1 and Table 4.2 were done on the basis of relevant literature[142]. In Figure 4.1 FTIR spectrum of resole type phenol-formaldehyde resin (PFR) is also represented.

In this study the characteristic peaks of the phenol were observed at 1593, 1497, 1222, 1167, 999 and 745 cm⁻¹ instead of the literature data of peaks (Table 4.1) at 1605, 1510, 1240, 1180, 990, and 747 cm⁻¹ were diminished with increasing reaction time, while the absorbance band of hydroxymethyl and methylene groups increased. According to the literature [143] the characteristic peaks of phenol, that they were observed at 1594, 1498, 1224, 1170, 999.7, and 748.8 cm⁻¹. The peak at 1368 cm⁻¹ which corresponded to the phenol O-H in plane bend was also detected for phenol-formaldehyde resin. The width of the band at 1368 cm⁻¹ indicates it is due to an O-H rather than C-H or C-C bond.

The formaldehyde aqueous solution was added into the reactor at the beginning of the process, therefore the characteristic peaks of methylene glycol C-O, O-H, and C-H bends at 1108, 1023, and 992 cm⁻¹ were observed in the first spectrum, respectively. After the reactor content heated to preferred temperature a sharp decrease of phenol and formaldehyde peaks was observed as a result of the reaction. At the beginning the characteristic peak of the formaldehyde at 911 cm⁻¹ decreased with increasing reaction time and afterwards slightly increased due to the conversion of methylene ether bridges into methylene bridges with the loss of formaldehyde and water. The absorbances for other characteristic groups were less observable because they overlapped with other absorbances of the product [143].

In this study, the characteristic peaks of methylene glycol C-O, O-H, and C-H bends at 1105, 1022, and 989 cm⁻¹ were observed in the first spectrum, respectively (Figure 4.1, Table 4.2).



Figure 4.1 : FTIR spectra at the wavelengths in the range of interest for a) phenol, b) formaldehyde solution and c) resole type phenol-formaldehyde resin (PFR).

The FTIR spectra of the PFR, PDMS-PFR, PDMS-LC-PFR1, PDMS-LC-PFR2, PDMS-LC_PFR3 and PDMS-LC-PFR4 were presented in Figure 4.2, Figure 4.4, Figure 4.5, Figure 4.6, Figure 4.7, and Figure 4.8, respectively. FT-IR spectra were recorded in the absorbance mode. The characteristic peaks of the resole type phenolic resin (PFR) are assigned in Table 4.3, using the literature [144, 145]. These signals were helpful in identifying the components of the condensation reaction of phenol and formaldehyde.

The FTIR spectra of the PFR, PDMS-PFR, PDMS-LC-PFR1, PDMS-LC-PFR2, PDMS-LC_PFR3 and PDMS-LC-PFR4 were presented in Figure 4.2, Figure 4.4, Figure 4.5, Figure 4.6, Figure 4.7, and Figure 4.8, respectively.

Phenol			
Literature data of	iterature data of Observed Functional group		
wavenumber, cm ⁻¹	wavenumber, cm ⁻¹		
3400	3215	OH stretch	
1605	1593	C = C aromatic ring	
1510	1497	C = C aromatic ring	
1485	1472	C = C aromatic ring	
1380	1368	OH in-plane bend	
1240	1222	C-C-O asymmetric stretch	
1180	1167	CH aromatic, in-plane	
1160	1152	C-O stretch	
1060	1070	Single bond C-O stretching vibrations	
		of –C-OH group	
1020	1023	-C-OH	
990	999	-C-H	
880	887	-C-H	
800	809	Asymmetric stretch of phenolic C-C-	
747	745	ОН	
680	687	CH aromatic, out-of-plane	
		Ring bend	

Table 4.1 : Functional groups and their literature and observed wavelength values for phenol.

Table 4.2 : Functional groups and their literature and observed wavelength values for formaldehyde.

Formaldehyde				
Literature data of	Observed	Functional group		
wavenumber, cm ⁻¹	wavenumber, cm ⁻¹			
3400	3338	OH stretch		
2822	2976	OH stretch, general		
2724	2914	OH bend overtone		
1722	1642	C = O stretch (overlapped		
		with OH scissors of water)		
1390	1446	C-H bend		
/	1105	-C-OH		
/	1022	-C-OH		
/	989	C-H		
/	910	С-Н		

FT-IR spectra were recorded in the absorbance mode. The characteristic peaks of the resole type phenolic resin (PFR) are assigned in Table 4.3, using the literature [144, 145]. These signals were helpful in identifying the components of the condensation reaction of phenol and formaldehyde.

According to the previous study[143]; it was observed that peaks occurred at 3389 cm⁻¹ and 1610 cm⁻¹. These peaks were attributed to – OH groups and C = C band vibrations of the product aromatic ring. In the phenol-formaldehyde resin spectrum additional characteristic signals of methylene bridge C – H bend at 1478 cm⁻¹ and methylene-ether bridge C – O – C bend at 1116 cm⁻¹ were present. In this study, the characteristic peaks of PFR were observed at 3271 cm⁻¹, 1595 cm⁻¹, 1456 cm⁻¹ and 1117 cm⁻¹ corresponded to the – OH groups, C = C aromatic ring vibrations, methylene bridge C – H bends and methylene ether bridge C – O – C bend 1151 cm⁻¹ corresponded to the C – C – O asymmetric stretch and C – O stretch respectively, while the peaks at 887, 825 and 753 cm⁻¹ belonged to the C-H out of plane vibrations (Figure 4.2).



Figure 4.2 : FTIR spectrum of PFR.
PFR				
Literature data of wavenumber, cm ⁻¹	Observed wavenumber, cm ⁻¹	Functional group		
3400	3271	-OH		
2925	2920	in phase stretching vibration of		
		-CH ₂ - alkane		
2850	2880	out of phase stretching vibration		
		of –CH ₂ - alkane		
1610	1595	C = C aromatc ring		
1517		C = C aromatc ring		
1504		C = C aromatc ring		
1480	1474	C-H aliphatic		
1450	1456	C = C benzene ring obscured by		
		-CH ₂ - methylene bridge		
1390	1369	OH in plane		
1237	1236	asymmetric stretch of phenolic C-		
		C-OH		
1153	1151	C-O stretch		
1100	1117	asymmetric stretching vibration of		
		C-O-C aliphatic ether (methylene		
		ether bridge)		
1000	988	aliphatic hydroxyl		
885	887	CH out-of-plane, isolated H		
835	825	CH out-of-plane, para-substituted		
760	753	CH out – of – plane, ortho-		
		substituted		
694	691	adjacent 5H		

Table 4.3 : Functional groups and observed wavenumbers for resol type phenol-formaldehyde resin (PFR) and their literature values.

To synthesize PDMS-PFR and PDMS modified layered clay resole type phenol formaldehyde nanocomposite resins (PDMS-LC-PFR1, PDMS-LC-PFR2, PDMS-LC-PFR3, PDMS-LC-PFR4); PDMS and unmodified montmorillonite clay were added the reaction mixture. Therefore, the charactersitic peaks at around 1110 - 1000 cm⁻¹ corresponded to Si – O – Si stretchings of PDMS and clay, and at near 2900 cm⁻¹ belonged to C – H stretching bonds of alkylammonium cations of clay [146] were obatined, respectively in the FTIR spectra of these samples.

The FTIR spectrum of MMT clay was presented in Figure 4.3 and collected in Table 4.4. The characteristic absorbances of MMT clay were shown on the Table 4.4 were done on the basis of relevant literature [147, 148].

The characteristic peaks of MMT clay were observed at 3389, 2928, 1446 and 1032 cm⁻¹. These peaks were corresponded to the –OH stretching vibrations of H₂O present in the smectite, C – H stretching bonds of alkylammonium cations, δ_{as} (C – H) bending vibration of both CH₃ groups and Si – O – Si stretching respectively.



Figure 4.3: FTIR spectrum of MMT clay.

Table 4.4 : Tentative assignments and observed wavenumber values of absorption maxima in FTIR spectra of montmorillonites.

Literature data of	Observed wavenumber, cm ⁻¹	Functional Groups
wavenumber, cm ⁻¹		
3433	3389	H – O – H hydrogen bonded water
3020 - 2800	2928	C-H stretching bonds of alkylammonium cations
1487	1446	$\delta_{as} \ (C - H)$ bending vibration of both CH_3 groups
1040	1032	Si – O – Si stretching
778	774	Si–O deformation perpendicular to the optical axis
671	693	Si–O deformation parallel to the optical axis

The FTIR spectrum PDMS-PFR was presented in Figure 4.4 and the characteristic peaks of PDMS-PFR were observed at 3307, 1610, 1457 and 1020 cm⁻¹. These peaks were attributed to the –OH groups, the C = C aromatic ring vibrations, methylene bridge C – H bends and Si – O – Si bond vibrations respectively. Also the absorbances at 1153 and 1115 cm⁻¹ assigned to the C – O stretch and methylene ether bridge peak respectively, while the peaks at 888, 827 and 757 cm⁻¹ belonged to the C – H out of plane vibrations.



Figure 4.4 : FTIR spectrum of PDMS-PFR.

The FTIR spectrum of PDMS-LC-PFR1 was shown in Figure 4.5 and the characteristic peaks of PDMS-LC-PFR1 were observed at 3271, 2908, 1455 and 1027 cm⁻¹ due to the –OH, C – H stretching bonds of clay, methylene bridges and Si – O – Si bond vibrations respectively. The absorbances at the 1610 cm⁻¹ corresponded to the C = C aromatic ring vibrations. The peaks at 1151 and 1119 cm⁻¹ assigned to the C-O stretch and methylene ether bridge peak respectively, while the peaks at 887, 824 and 756 cm⁻¹ belonged to the C-H out of plane vibrations.



Figure 4.5: FTIR spectrum of PDMS-LC-PFR1.

The FTIR spectrum of PDMS-LC-PFR2 was shown in Figure 4.6 and the characteristic peaks of PDMS-LC-PFR2 were observed at 3271, 2904, 1460 and 1006 cm⁻¹ due to the –OH, C – H stretching bonds of clay, methylene bridges and Si-O-Si bond vibrations respectively. The peaks at 1611, 1151 and 1116 cm⁻¹ assigned to the C = C aromatic ring vibrations, C - O stretch and methylene ether bridge peak respectively, while the peaks at 886 and 790 cm⁻¹ belonged to the C-H out of plane vibrations.



Figure 4.6 : FTIR spectrum of PDMS-LC-PFR2.

The FTIR spectrum of PDMS-LC-PFR3 was presented in Figure 4.7 and the characteristic peaks of PDMS-LC-PFR3 were observed at 3191, 2942, 1456 and 1018 cm⁻¹ due to the –OH, C – H stretching bonds of clay, methylene bridges and Si-O-Si bond vibrations respectively. The peaks at 1612, 1151 and 1116 cm⁻¹ assigned to the C = C aromatic ring vibrations, C - O stretch and methylene ether bridge peak respectively, while the peaks at 895, 865, 822 and 755 cm⁻¹ belonged to the C-H out of plane vibrations.



Figure 4.7 : FTIR spectrum of PDMS-LC-PFR3.

The FTIR spectrum of PDMS-LC-PFR4 was shown in Figure 4.8 and the characteristic peaks of PDMS-CL-PFR4 were observed at 3271, 2910, 1456 and 1017 cm⁻¹ due to the –OH, C – H stretching bonds of clay, methylene bridges and Si-O-Si bond vibrations respectively. The peaks at 1595, 1151 and 1111 cm⁻¹ corresponded to the C = C aromatic ring vibrations, C - O stretch and methylene ether bridge peak respectively, while the peaks at 883, 825 and 753 cm⁻¹ belonged to the C-H out of plane vibrations.



Figure 4.8 : FTIR spectrum of PDMS-LC-PFR4.

The observed characteristic peaks of the PFR, PDMS-PFR, PDMS-CL-PFR1, PDMS-CL-PFR2, PDMS-CL-PFR3 and PDMS-CL-PFR4 resin samples were corresponded in Table 4.5 and FTIR spectra of all these resins were outlined in Figure 4.9. As shown in Table 4.5 characteristic Si - O - Si bond vibraiton peaks were obtained for samples except PFR by presence of PDMS and characteristic C - H stretching peaks of clay were observed for clay containing nanocomposite resin samples (PDMS-LC-PFR1, PDMS-LC-PFR2, PDMS-LC-PFR3, PDMS-LC-PFR4) by adding of clay. Therefore FTIR spectra of resin samples revealed that PDMS and clay had effectively participated in polymerizations. As it was seen in Figure 4.9 C - H stretching peaks of clay slightly were increased with increasing clay content until 3 wt%, then decreased for the sample with 5 wt% clay content from 0.5 wt% to 5 wt%.



Figure 4.9 : FTIR spectra of resin samples (*a* : PDMS-CL-PFR1, *b* : PDMS-CL-PFR2, *c* : PDMS-CL-PFR3, *d* : PDMS-CL-PFR4).

	Literature	ce Observed wavenumbers, cm ⁻¹					
Characteristic peak	wavenumbers, cm ⁻¹	PFR	PDMS- PFR	PDMS- CL- PFR1	PDMS- CL- PFR2	PDMS- CL- PFR3	PDMS- CL- PFR4
C = C aromatic ring	1610-1504	1595	1615	1610	1611	1612	1595
-OH	3400	3271	3307	3271	3271	3191	3271
Methylene bridge	1450	1456	1457	1455	1460	1456	1456
Methylene ether bridge	1100	1117	1115	1119	1116	1116	1111
C - H stretch (clay)	3020-2800	-	-	2908	2904	2942	2910
Si - O - Si (PDMS)	1110-1000	-	1020	1027	1006	1018	1017
-OH in plane bend	1390	1369	1370	1362	1363	1365	1369

Table 4.5 : Characteristic peaks for resin samples.

4.1.2 Differential scanning calorimetry measurements (DSC)

Differential Scanning Calorimeter (DSC) measurements of PFR, PDMS-PFR, PDMS-LC-PFR1, PDMS-LC-PFR2, PDMS-LC-PFR3 and PDMS-LC-PFR4 were operated with 1 cycle. The cycle was heated from 30°C to 200°C with 10 °C/min heating rate. According to the literature [149] T_g value of the commercial PFR was given as 147,28 °C. In this study T_g values of the PFR, PDMS-PFR, PDMS-LC-PFR1, PDMS-LC-PFR2, PDMS-LC-PFR3 and PDMS-LC-PFR4 were determined as 109,10 °C (Figure 4.10), 116,20 °C, 121,95 °C, 124,10 °C, 128,73 °C and 122,78°C, respectively.



Figure 4.10 : DSC thermogram of PFR.

As it was seen in Figure 4.11, it is realized that from the results of DSC measurements, T_g values of the PDMS modified and layered clay samples are higher than PFR. Also T_g values of clay containing samples slightly change with the increasing clay content (wt %), that increased until 3 wt% clay contents and then decreased for the sample with the 5 wt% clay content.

Produced resin samples were partially cured by heating at 100 °C for more 1 hour. The curing reaction involves condensation reactions of hydroxymethyl groups that were previously formed through reaction of phenol with an excess of formaldehyde in the presence of an alkaline catalyst to form methylene bridges of the resols[150].



Figure 4.11 : Variation of T_g (°C) for various resole clay reinforced nanocomposites with different filler content.



Figure 4.12 : DSC thermograms for cured PDMS-PFR, PDMS-LC-PFR2, PDMS-LC-PFR3 and PDMS-LC-PFR4 samples.

According to the [151] upon cure, the exothermic reaction was taken placed in the range of 120 °C 190 °C and the exothermic maximum cure temperature peak was found in between 165 °C and 170 °C. The shape and the maximum of the exothermic curves depended on the given cure temperature and time. To remove H₂O and volatile components, the uncured resin needed a heat-treatment at 100 °C for 60 min at least prior to cure or molding. In this study, exothermic peaks were observed in between 165 °C and 195 °C for the curing reactions (Figure 4.12).

The main application of DSC for cured phenolic resins is the determination of maximum cure temperatures and onset of cure temperatures. Maximum cure temperatures and onset of cure temperatures of PFR, PDMS-PFR (Figure 4.13), PDMS-LC-PFR2, PDMS-LC-PFR3 and PDMS-LC-PFR4 were determined properly with the literature [152].



Figure 4.13 : Determination of the maximum cure temperature and onset of cure temperature for cured PDMS-PFR from DSC plot.

According to the [153] maximum cure temperature or upper use temperature of the adhesive may dictate the maximum environmental exposure temperature of the component. There are several cure temperature ranges:

- Room temperature to 225 °F (107,22 °C). Generally for paste adhesives for noncritical structures.
- 225-285 °F (107,22-140,56 °C). For nonaircraft critical structures. Cannot be used for aircraft generally, because moisture absorption may lower HDT (heat deflection temperature) below environmental operating temperature.
- 350 °F (176,67 °C) and above aircraft structural bonding. Higher are temperature may mean more strain discontinuity between adhesive and both mating surfaces (residual stresses in bond).

As shown in Table 4.6, clay containing resin samples PDMS-LC-PFR2, PDMS-LC-PFR3 and PDMS-LC-PFR4 had maximum cure temperatures above 350 °F (176,67 °C) and could be used for aircraft applications.

Sample	Maximum Cure Temperature (°C)	Onset of Cure Temperature (°C)
PFR	168,42	167,02
PDMS-PFR	170,79	163,47
PDMS-LC-PFR2	188,68	185,64
PDMS-LC-PFR3	194,65	176,18
PDMS-LC-PFR4	187,62	186,05

Table 4.6 : Maximum Cure Temperature and Onset of Cure Temperature values for samples.

4.1.3 Thermogravimetric measurements (TGA)

Thermal decomposition behaviors of neat resol; PFR and clay-filled nanocomposite resins; PDMS-LC-PFR1, PDMS-LC-PFR3 and PDMS-LC-PFR4 were determined with TGA measurements. In order to prepare TGA samples, neat resol resin and the clay-filled nanocomposite resol resins were partially cured at 100°C for 1 h. A 5mg powder sample of the cured resin was subjected to TGA analysis, and heated at linear heating rate of 10°C. Degradation was carried out in a static air atmosphere to the maximum temperature of 900°C. The weight loss (wt%) of the resins were calculated, the weight loss (%) rates were shown as a function of temperature in Figure 4.14 and Table 4.7.

According to the [154] different stages of degradation could be obtained in the TGA thermogram: the first stage (until 350 °C) and the second stage (350-700 °C). In the first stage, the release of formaldehyde because of the break of ether bridges, and the presence of phenol and water, and in the second stage the oxidation of the network were observed. In this study first stage was obtained until 300 °C and second stage was observed in the temperature range 300-900 °C. In the second stage of thermal decompositon, all the clay containing nanocomposite resins were displayed higher thermal resistance than the PFR. As shown in Figure 4.14 and Table 4.7, the weight loss rates of common resol resins were higher than that of PDMS-LC-PFR. Also, weight loss (%) rates of the clay-filled nanocomposite samples were decreased with the increasing clay content . PDMS-LC-PFR3 and PDMS-LC-PFR4 were seemed slightly more thermally stable because their thermal degredations started at higher temperatures than PFR and PDMS-LC-PFR1.



Figure 4.14 : TGA thermograms of a) PFR, b) PDMS-LC-PFR1, c) PDMS-LC-PFR3, d) PDMS-LC-PFR4.

Sample	Residue at 500 °C (weight %) ^a	Residue at 900°C (weight %) ^a
PFR	66,785	51,447
PDMS-LC-PFR1	67,354	51,995
PDMS-LC-PFR3	69,777	54,475
PDMS-LC-PFR4	71,818	56,033

Table 4.7 : TGA results for resins.

^a Detected by TGA.

4.1.4 Dynamic mechanical analysis measurements (DMA)

4.1.4.1 YoungS modulus measurements

YoungS modulus values of the PDMS-LC-PFR1, PDMS-LC-PFR2, PDMS-LC-PFR3 and PDMS-LC-PFR4 thin film specimens were obtained with DMA measurements from Stress-Strain curves. The slope of the stress-strain curve gives us the YoungS modulus of the sample. When the slope of curve is steep, sample has a high modulus and it resists deformation. If the slope of curve is gentle, then the sample has a low modulus, which means it is easily deformed. As it was seen from Figure 4.15; slopes of the stress-strain curves were reasonably steep, which means that it was needed a lot of force to deform the samples. Therefore, YoungS modulus values of the samples were relatively high, which were detected as 2712MPa for PDMS-LC-PFR1, 3625MPa for PDMS-LC-PFR2, 3946MPa for PDMS-LC-PFR3, and 3403MPa for PDMS-LC-PFR4.

Moreover when a specimen has a steep slope like the samples in this study, that means there were not much area under the stress-strain curves of the samples, thus they had low impact toughness properties and so that they were strong, but were not tough. That was resulted in; the samples could be resisted a lot of stress but they could not be deformed very much and resisted elongation before breaking, in other words they were brittle. As shown in the Figure 4.15, elasticity properties of the samples were generally similar, but PDMS-LC-PFR2 had a higher elongation than PDMS-LC-PFR1, PDMS-LC-PFR3 and PDMS-LC-PFR4.

Specimen with the highest clay content (5 wt%) could have lower crosslink density than having lower clay content (0,5 wt%, 1 wt%, 3 wt%) specimens. Because

increasing clay content was caused a bad dispersion of clay particles in the polymer matrix (see Figure 4.26) and that could be induced the forming hindrance between chains for crosslinking of polymers. Decreasing of crosslink density was resulted in decraesing of YoungS modulus value of the sample. As it was seen in Figure 4.16 YoungS modulus values of the samples were slightly increased with increasing clay content until 3 wt%, then it was decreased for the sample with 5 wt% clay content (PDMS-LC-PFR4), that it had the clay content above optimum values. PDMS-LC-PFR3 sample had the highest YoungS modulus value among the samples.



Figure 4.15 : Stress-Strain graphs of the PDMS modified layered clay resole type phenol formaldehyde nanocomposite resin specimens.



Figure 4.16 : Variation of YoungS modulus (MPa) for various layered clay resole nanocomposites with different filler content.

4.1.4.2 Thermal measurements

Glass transition temperature values of the PDMS-LC-PFR1, PDMS-LC-PFR2, PDMS-LC-PFR3 and PDMS-LC-PFR4 thin film samples were determined according to 3 different parameter (storage modulus, loss modulus, tan delta) by dynamic mechanical analysis method.



Figure 4.17 : *T*_g graph of PDMS-LC-PFR1.



Figure 4.18 : *T*_g graph of PDMS-LC-PFR2.







Figure 4.20 : T_g graph of PDMS-LC-PFR4.

It was observed from the graphs that the tan delta parameter was given the nearest results with DSC measurements for T_g values of the specimens. PDMS-LC-PFR3 sample had the highest T_g value among the all samples. This result is in agreement with observed T_g results from DSC measurements of the specimens. According to the DMA measurements, PDMS-LC-PFR3 has better thermal and mechanical properties than other samples.

	<i>T</i> g (°C)				
Sample	Storage Modulus	Loss Modulus	Tan Delta	DSC	
PDMS-LC-PFR1	50,63	90,10	104	121,95	
PDMS-LC-PFR2	53,54	92,63	105,95	124,10	
PDMS-LC-PFR3	57,86	94,80	130,37	128,73	
PDMS-LC-PFR4	55,65	107,46	125,61	122,78	

Table 4.8 : Observed Tg values of samples from DMA and DSC measurements.

4.1.5 Scanning electron microscope measurements (SEM)

SEM analysis were done to understand the distribution of clay particles in polymeric resol resin matrix and to have an idea about the degree of intercalation and/or exfoliation of the clay layers. SEM images of the PFR, PDMS-PFR, PDMS-CL-PFR1, PDMS-CL-PFR2, PDMS-CL-PFR3 and PDMS-CL-PFR4 were taken from the their thin film samples.

SEM images of PFR were shown in Figure 4.21 with magnification of x2000 and x10000 respectively. As it was seen in SEM images of PFR, void-free and clear phenolic resin structures were obtained by the heat thin films of PFR. To provide such a structure, reaction time was kept long enough for the slow water vapor release to be completed and sample was waited under vacuum before heat curing in the oven.

SEM images of PDMS-PFR were shown in Figure 4.22 with magnification of x2000 and x10000 respectively. As it was seen in Figure 4.22 formation of micro and macrovoids were observed in the SEM images of PDMS-PFR, because during the

polymerization reaction of PDMS-PFR by-product water molecules was released; and the water vapor bubbles getting trapped in the PDMS-PFR during heat curing. Unlike PFR, keeping long enough of the reaction time and waiting under vacuum conditions before heat curing in oven, was not beneficial to solve this problem for PDMS-PFR. Also the tendency of PDMS molecules to move to the surface due to the difference in surface tension induced the forming of voids and that is why the SEM images of PDMS-PFR was not clear such as the SEM images of the PFR.



Figure 4.21 : SEM images of PFR (a; x2000, b; x10000).



Figure 4.22 : SEM images of the PDMS-PFR (a; 2000x, b; 10000x).

With SEM images of PDMS-LC-PFR samples were shown in Figure 4.23 and Figure 4.24 with magnification of x5000 were indicated of PDMS-LC-PFR1 and PDMS-LC-PFR2, and in Figure 4.25 and Figure 4.26 with magnification of x10000 were indicated of PDMS-LC-PFR3 and PDMS-LC-PFR4, respectively.



Figure 4.23 : SEM image of PDMS-LC-PFR1.



Figure 4.24 : SEM image of PDMS-LC-PFR2.

Dispersing of clay particles was not a certain problem for samples having clay contents of 0,5 wt%, 1 wt% and 3 wt%. But as it was seen in Figure 4.26., in the PDMS modified resole type phenolic resin with clay content of 5 wt% (PDMS-LC-

PFR4), clay particles were dispersed less homogeneously than PDMS-LC-PFR1, PDMS-LC-PFR2 and PDMS-LC-PFR3.



Figure 4.25 : SEM image of PDMS-LC-PFR3.



Figure 4.26 : SEM images of PDMS-LC-PFR4.

High surface energy of nanoparticles force them to agglomerate and to form clay tactoids. Therefore resol type phenolic resins with clay content higher than 1,5 wt% had the problem to disperse clay particles homogeneously. Dispersion can be

improved by using techniques like high shear mixing and ultrasonification [69]. PDMS was added in the media to improve the surface of the material and to decrease the surface energy of the nanoparticles. As a result of that the resins with the clay content of 3 wt%, 1 wt% and 0,5 wt% had a good dispersion of clay particles, and had good material properties. Higher amount of clays need for higher rates of mixing, to intercalate the polymer into the clay layers and homogeneously distribute these layers in the polymer matrix [69]. However, the amount of bubbles trapped and the space was occurred in the resin sample was increased with the higher rates of mixing, and the formation of the material weakening clay tactoids was resulted in the decreasing of the mechanical properties of the PDMS-LC-PFR4 resin (see Figure 4.16). Also, SEM images of PDMS-LC-PFR samples were not as clear as the SEM images of the PFR due to the presence of the PDMS.

4.1.6 Effect of the reaction time

PDMS-LC-PFR4 sample were synthesized with 4 different reaction time (2h, 4h, 6h, 8h). FTIR analysis were done for all reaction times and spectrums were compared to understand the effect of the reaction time on the polymerization of the nanocomposite resins.

As it was seen in Figure 4.27 charactersitc absorbance peaks of the PDMS-LC-PFR4 were shown differences to be incident to the various reaction times. According to the FTIR spectrum for the 2 hours reaction (see Figure 4.27 : a) characteristic –OH groups, aromatic ring C = C bond and methylene bridge peaks were not observed due to the polymerization was not completed. Also C - H stretching peak of clay and C - H out-of-plane peaks of the sample with 2 hours reaction time are more intensive and sharper than the peaks of other samples with higher reaction times.

With the increasing reaction time absorbance intensity of the –OH groups peaks was decreased from 4 hours to 8 hours. The intensity of the –OH peaks for the 4 hours reaction is higher than 6 hours and 8 hours reactions because of the presence of the methylol –OH peaks with the phenolic –OH peaks for 4 hours reaction. Methylol groups were formed at the beginning of the polymerization by the reaction of the phenol and formaldehyde. With the increasing reaction time amount of branching of PDMS-LC-PFR4 was increased and amount of the methylol groups. Therefore with the increasing reaction time characteristic methylol groups. Therefore

CL-PFR4 were increased. Also as it was shown in Figure 4.27, as the reaction was continued aromatic ring C = C peaks were decreased and C - O - C methylene ether bridge peaks were increased.



Figure 4.27 : FTIR spectrum of the resins with the clay content 5 wt% (PDMS-LC-PFR4) and with the different reaction times (a) 2 h, b) 4 h, c) 6 h, d) 8 h).

As shown in Figure 4.28 and Figure 4.29, SEM images of the same sample with different reaction times were shown noticeable differences. SEM image of 2 hours reaction was looked like clay particles more than a nanocomposite resin. For 2 hours reaction size of clay tactoids are so greater and dispersion of the clays worse than for 8 hours reaction. As it was explained before in the SEM analysis part, in this study 5 wt% clay content was above the limit and high clay content was needed to higher mixing rate and longer reaction time. Therefore, 2 hours were not enough to complete the polymerization.



Figure 4.28 : SEM image of the PDMS-LC-PFR4 for 2 hours reaction time.



Figure 4.29 : SEM image of the PDMS-LC-PFR4 for 8 hours reaction time.

4.2 Composite Resin Samples Characterization

4.2.1 FTIR-ATR spectrophotometric analysis

The FTIR spectrum of noncured UFR was shown in Figure 4.30 and characteristic peaks of sample were collected in Table 4.9. The –NH stretching of the bonded –NH group was observed in the 3500-3100 cm⁻¹ region at near 3340 cm⁻¹, a broad bond with a high noise level was seen in this region indicating less of the amino structure is present. When prepolymers gived a stronger, more distinct band at 3340 cm⁻¹, that would indicated the amount of bonded NH is higher compared to the free NH₂ [155].

In this study at 3306 cm⁻¹ a broad bond with high noise level was obtained in this region. Amount of formaldehyde was higher than urea therefore, amount of free NH_2 was lower compared to bonded NH.

According to the previous study [155], in disubstituted urea compunds, such as methylene diurea (1635 cm⁻¹), 1,3-dimethylurea (1640 cm⁻¹), and in derivatives with linear ether linkages DMMU (1674 cm⁻¹) a strong absorption band was appeared. In case of the disubstituted urea derivatives, where there were no free $-NH_2$ groups, the contribution of the NH mode of free NH₂ was minimal. Thus, only a singlet was seen. In this study a distinct single absorption band was appeared at 1634 cm⁻¹, was indicating a high conversion of the NH₂ group. This peak was mainly due to the C = O stretch of amide I. A weak shoulder band was seen at 1547 cm⁻¹. This was characteristic of the NH deformation mode (amide II) secondary, noncyclic amides and this indicated that NH absorption mode of the secondary amide II was present [155]. As it was seen in Figure 4.30, the other characteristic peaks of UFR were observed at 1383, 1271 and 1017 cm⁻¹, that were indicated the CH mode in CH₂, amide III bond for secondary amide and C – O stretch in methylol, respectively.



Figure 4.30 : FTIR spectrum of UFR.

Literature data of	Observed	Functional groups
wavenumber (cm ⁻¹)	wavenumber (cm ⁻¹)	
3340	3306	-NH stretching of the bonded -NH
		group and –OH group
1660 - 1630	1634	Amide I mainly $C = O, C - N, N - H$
		deformation
1600 - 1550	1547	Amide II (C – N and NH deformation)
1400 - 1390	1383	CH mode in CH ₂
1265-1260	1271	Amide III bond for secondary amide
1005-1000	1017	C – O stretch in methylol

Table 4.9 : Absorption bands in UFR.

4.2.2 3-point bending test meausurements

Determination of the mechanical properties for composite resin samples were done with the 3-point bending tests. Firstly, effect of the pomace content on the flexural modulus value were investigated for the constant polymeric resin matrix rate, that was 50 %wt PFR - 50 %wt UFR (see Table 3.2). Then PDMS-LC-PFR3 was used instead of PFR in the resin matrix, with the rate of 50 %wt PDMS-LC-PFR3 - 50 %wt UFR, to observe the change in the flexural modulus values with clay effect.

As shown in Figure 4.31, pomace-free product (PUFR) looked like the ceramic and, had hard and bright surface. When the mixed pomace ratio was increased surface hardness and surface brightness of the materials were decreased and wood like material was obtained for PUFPCR1, PUFPCR2 and PUFPCR4. These results are in agreement with the literature [156].

As shown in Figure 4.32 and Table 4.10, Flexural modulus values of the samples were decreased with the increasing pomace content for both PUFPCR and 3%-PUFPCR systems. These results are in agreement with the literature [157, 158]. 3-point bending test could not be applied for PUFPCR4 sample. Because it was come

to pieces with heating before test. Also presence of PDMS-LC-PFR3 instead of PFR in the polymeric resin matrix, was induced the slightly increase of the modulus values of the composite samples (see Figure 4.32 and Table 4.10).



Figure 4.31 : Molded composite resin samples for 3-point bending test; a)PUFR, b)PUFPCR1, c)PUFPCR2, d)PUFPCR4.



Figure 4.32 : Flexural modulus values for samples with constant PFR-UFR and PDMS-LC-PFR3 matrix rates and various pomace contents.

Resin matrix	Pomace content	Flexural modulus values (MPa)			
content (wt%) ^a	(wt%) ^a	PUFPCR systems	3%PUFPCR		
			systems		
100	-	2322	2464		
80	20	2234	2337		
70	30	1944	2080		
50	50	1535	1684		
35	65	-	-		

Table 4.10 : Flexural modulus values for samples with constant PFR-UFR and PDMS-LC-PFR3 matrix rates and various pomace contents.

^a According to the total weight of material.

Then, effect of the resin matrix rate on the mechanical properties were investigated. To observe this effect, PUFPCR5 and PUFPCR6 samples were synthesized with constant pomace amounts and different polymeric resin matrix contents. It was obtained that from the 3-point bending test results, when PFR content was increased and UFR content was decreased in the resin matrix, flexural modulus value of material was increased (see Figure 4.33 and Table 4.11).



Figure 4.33 : Flexural modulus values for samples with constant pomace content and different resin matrix rate.

Sample	PFR content (wt%) ^a	UFR content (wt%) ^a	Pomace content (wt%) ^b	Flexural modulus (MPa)
PUFPCR5 PUFPCR1	75 50	25 50	20 20	2395 2234
PUFPCR6	25	75	20	2087

Table 4.11 : Flexural modulus for samples with constant pomace content and different resin matrix rate.

^a According to the total resin matrix. ^b According to the total weight of material.

Volatile ash was used as flame retardant in several studies [156, 157, 159]. Effect of the volatile ash content on the bending strength was investigated and the highest bending strength value was determined for sample with 10 (wt%) volatile ash content, according to the total weight of material [157]. In this study gypsum (CaSO4.2H2O) was used instead of volatile ash. In order to determine effect of the gypsum on the flexural modulus value of the material, PUFPCR7 was synthesized with 30 wt% filler content (20 wt% pomace - 10 wt% gypsum) and its flexural modulus value was compared with PUFPCR2 which have same amount of filler (30 wt% pomace). Flexural modulus value for PUFPCR7 was obtained higher than PUFPCR2 (see Table 4.12).

Sample	PFR	UFR	Pomace	Gypsum	Flexural
	content	content	content	content	modulus
	(wt%) ^a	(wt%) ^a	(wt%) ^b	(wt%) ^b	(MPa)
PUFPCR2	50	50	30	-	1944
PUFPCR7	50	50	20	10	2138

Table 4.12 : Flexural modulus values (MPa) for PUFPCR2 and PUFPCR7 samples.

^a According to the total resin matrix.

^b According to the total weight of material.

4.2.3 Water absorption capacity measurements

Water absorption capacity measurements were done for samples having resin matrix with different PFR and UFR contents and having same amount of pomace. Effect of the PFR content of the resin matrix on the water absorption capacity property of materials was illustrated in Figure 4.34. Also absorved water amounts of specimens were given in the Table 4.13. According to the results of measurements, it was observed that water absorption capacity of specimens were decreased with increasing PFR (wt%) content of resin matrix. These results are in agreement with the literature [157, 158, 160, 161].



Figure 4.34 : Effect of the PFR content (wt%) of the resin matrix on the water absorption capacity property of materials.

Table 4.13 : Absorbed water	amounts of specimens	prepared with	different resin
matrix contents.			

Sample	PFR content (wt%) ^a	Pomace content (wt%) ^b	Amount of absorbed water (g)	Amount of absorbed water (wt%)
PUFPCR5	75	20	0,019	0,187
PUFPCR1	50	20	0,0435	0,377
PUFPCR6	25	20	0,1116	1,095

^a According to the total resin matrix.

^b According to the total weight of material.

4.2.4 SEM analysis of PUFR and PUFPCR systems

SEM analysis were done to understand distribution of pomace particles in polymeric PUFR matrix and to see the obtaining morphological differences with the adding of different amount of pomaces to samples. SEM images of PUFR, PUFPCR1 and PUFPCR2 were shown in Figure 4.35 with magnification of x1000. It was assigned that pomace particles were dispersed in matrix homogeneously and morphology of the samples changed with increasing pomace content.



Figure 4.35 : SEM images for a) PUFR, b) PUFPCR1, c) PUFPCR2 samples.

5. CONCLUSION

In the first part of this research, PDMS modified layered clay resol nanocomposites resins were synthesized. FTIR-ATR spectroscopy results of nanocomposites clearly indicated the clay particles and PDMS molecules were attached the polymeric resin matrix. DSC analysis showed that the T_g and maximum cure temperature values of neat resol resin was increased by adding PDMS and clay to obtain nanocomposite resins. T_g values of noncured nanocomposite resins and maximum cure temperatures of cured nanocomposite resins were slightly increased with incressing clay content until 3 wt%, then decreased for resin sample with 5 wt% clay content. Furthermore, PDMS-LC-PFR2, PDMS-LC-PFR3 and PDMS-LC-PFR4 nanocomposite resins had maximum cure temperatures above 350 °F (176,67 °C) and could be used for aircraft applications. Thermal decomposition behaviors of neat resol; PFR and clay-filled nanocomposite resins were determined with TGA measurements. The weight loss (wt%) rate of neat resol resin was higher than that of nanocomposite resins. Also, the increasing clay content was induced the decrease in weight loss (wt%) rates of nanocomposite resins. DMA analysis assigned that PDMS-LC-PFR3 had the highest YoungS modulus value and elasticity properties of the samples were generally similar, but PDMS-LC-PFR2 had a higher elongation than other nanocomposite resins. Also, determined T_g values for resins by DMA were supported DSC results. PDMS was added in the media to improve the surface of the material and to decrease the surface energy of the nanoparticles. Thus, SEM measurements showed that the nanocomposite resins with the clay content of 3 wt%, 1 wt% and 0,5 wt% had a good dispersion of clay particles, and had good material properties. However, in the PDMS-LC-PFR4, clay particles were dispersed less homogeneously than PDMS-LC-PFR1, PDMS-LC-PFR2 and PDMS-LC-PFR3. Finally effect of the reaciton time was investigated. FTIR-ATR measurements assigned that, with the increasing reaction time intensity of the characteristic -OH groups peaks were decreased and methylene bridge peaks were increased from 4 hours to 8 hours. For the 2 hours reaction characteristic -OH groups, aromatic ring C = C bond and methylene bridge

peaks were not observed due to the polymerization was not completed. SEM image of PDMS-LC-PFR4 for 2 hours reaction was looked like clay particles more than a nanocomposite resin. For 2 hours reaction size of clay tactoids are so greater and dispersion of the clays worse than for 8 hours reaction. In conclusion, clay particles were successfully dispersed in resol resin matrix and nanocomposites resins having better thermal and mechanical properties were obtained which can be used for thermal insulation materials, coatings, molding compunds and aerospace components.

In the second part of this study, polymer wood composite material from pomace was produced. Firstly UFR and neat resol resin (PFR) were used as binder resin matrix. With the increasing PFR content in the resin matrix, the water absoption capacity of the materials were decreased. Secondly, PDMS modified layered clay resol nanocomposite resin (PDMS-LC-PFR3) were used instead of PFR with UFR in resin matrix to investigate the influence of the presence of clay particles on the mechanical properties of the materials. 3-point bending test results showed that with the use of PDMS-LC-PFR3 flexural modulus values of the composite materials were slightly increased. Also, influence of the pomace amount, resin matrix content and adding gypsum with pomace, on the mechanical properties of the materials were determined by 3-point bending measurements. Flexural modulus values of the samples were decreased with the increasing pomace content for both PUFPCR and 3%-PUFPCR systems. when PFR content was increased and UFR content was decreased in the resin matrix, flexural modulus value of material was increased. Furthermore, obtained flexural modulus value for sample containing gypsum with pomace (30 wt%), was higher than that of sample which have just pomace (30 wt%). Finally morphology of the composite materials were determined by SEM measurements. In conclusion, pomace was succesfully dispersed in polymeric resin matrix and polymer wood composite materials were produced. Therefore, existing disadvantages of wood materials can be eliminated and the damage to the environment with the production of wood materials can be reduced.

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