NEW THERMOSETTING RESINS FROM CASHEW NUTSHELL LIQUID (CNSL) WITH FIRE RETARDANT PROPERTIES

by

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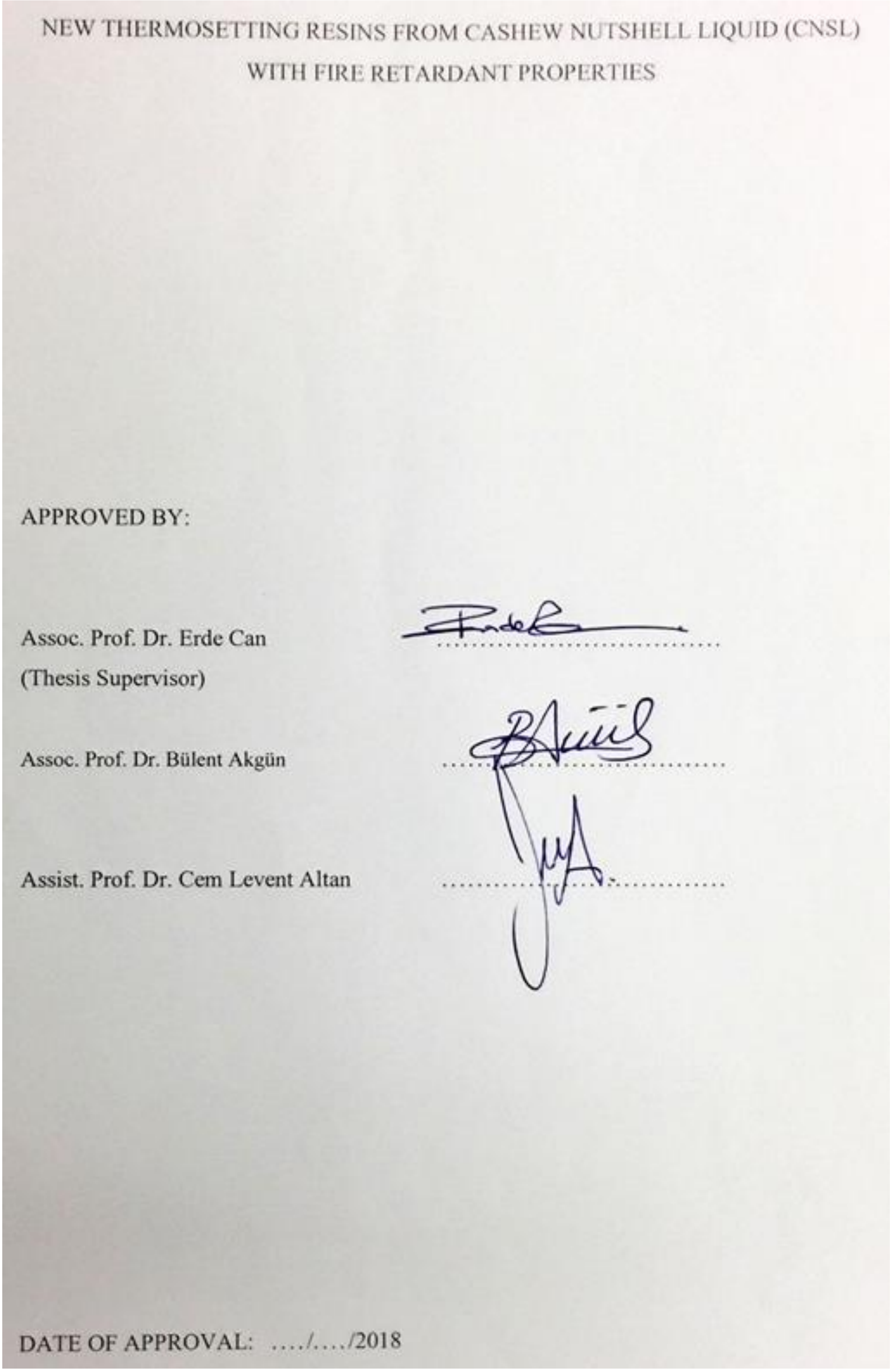

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WITH FIRE RETARDANT PROPERTIES

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ABSTRACT

NEW THERMOSETTING RESINS FROM CASHEW NUTSHELL LIQUID (CNSL) WITH FIRE RETARDANT PROPERTIES

Acquisition of an immense bulk of polymeric materials is currently from fossil fuels. As prevised in numerous studies, fossil resources seem not to be sufficient for use, in the near future. At this point, use of biomass that represents an abundant carbon-neutral renewable resource for the production of new polymers, offers both economic and environmental benefits. The starting material that is used in this study to prepare new thermosetting polymers with fire retardant properties, is based on Cardanol which is the major component of thermally treated Cashew nutshell liquid (CNSL) and is a phenol derivative with a principal meta substituent of a C15 hydrocarbon chain with zero to three double bonds. In this study, an epoxy CNSL resin, NC 514, derived from cardanol, was fully or partially methacrylated with methacrylic acid. Following the methacrylation reactions, the remaining epoxy content was phosphorylated by means of a reaction with phosphoric acid. At this stage the methacrylation and phosphorylation degrees of the epoxies of the NC514 resin were varied. The methacrylated (NC514VE) and phosphorylated resins (NC514VE-PA) were then mixed with styrene diluent in changing amounts and thermally cured. The structures of all the synthesized monomers were characterized via spectroscopic methods. The viscosities of the styrenated resins were determined, cure behavior of the resins was analyzed via DSC, thermomechanical properties were evaluated via DMA, and degradation profiles were characterized via TGA. DMA scans showed that the Tg values of the cured resins were within the range of 60˚C to 80˚C. TGA experiments showed that the char residue at temperatures above 700˚C increased with the introduction of phosphate groups to the NC514VE structure as expected. The deflagration times recorded for experiments in which each sample was exposed to a candle flame under similar conditions increased with increasing phosphate content of the resins demonstrating the fire retardancy effect of the phosphate groups introduced to the structure.

ÖZET

KAJU KABUĞU SIVISI (KKS) BAZLI YANMA GECİKTİRİCİ ÖZELLİĞE SAHİP YENİ TERMOSET REÇİNELER

Polimerik malzemeler çoğunlukla fosil yakıt bazlı kaynaklardan üretilmektedir. Ancak, birçok araştırmaya göre fosil yakıt kaynakları yakın gelecekte kullanılmak için yeterli değildir. Bu noktada, yeni polimer üretimi için yenilenebilir, bol miktarda karbon-nötr kaynak olarak biyokütle kaynaklarının kullanımı ekonomik ve çevresel faydalar sağlamaktadır. Bu çalışmada, yanma geciktirici özellikli termoset polimerler hazırlamak üzere kullanılan malzeme ısıl işlem görmüş kaju fıstığı kabuğu sıvısı (KKS)'nın temel bileşeni olan kardanol bazlıdır. Kardanol 15 karbon uzunluğunda, sıfır ila üç çift bağ içeren bir yan zincire sahip fenol türevidir. Bu çalışmada, piyasada ticari olarak bulunan kardanol bazlı bir epoksi KKS reçinesi, NC514, tamamen ya da kısmi olarak metakrilik asit ile metakrile edilmiştir. Metakrilasyon reaksiyonu ardından kalan epoksi grupları fosforik asit ile reaksiyon sonucu fosfat gruplarına dönüştürülmüştür. Bu aşamada, NC514 reçinesinin epoksilerinin metakrilasyon ve fosforilasyon dereceleri, değiştirilmiştir. Elde edilmiş olan metakrile edilmiş (NC514VE) ve fosfatlanmış (NC514VE-PA) reçineler farklı oranlarda stiren ile karıştırılıp termal küre tabii tutulmuştur. Sentezlenmiş tüm monomerlerin yapısı spektroskopik tekniklerle karakterize edilmiştir. Sıvı reçine karışımlarının viskoziteleri belirlenmiş, kür davranışları Diferansiyel Taramalı Kalorimetre (DSC) ile analiz edilmiş, kür edilmiş reçinelerin termomekanik özellikleri Dinamik Mekanik Analiz (DMA) metodu ile değerlendirilmiş ve bozunuma profilleri Termal Gravimetrik Analiz (TGA) ile karakterize edilmiştir. DMA taramaları sonucu kür edilmiş reçineler için Tan delta maksimum değerinden elde edilen Tg değerleri 60℃ ile 80℃ arasında bulunmuştur. TGA deneyleri 700˚C üstündeki kül kalıntısı miktarının NC514VE yapısına fosfat gruplarının eklenmesi ile beklendiği üzere arttığını göstermiştir. Her bir örneğin benzer koşullar altında mum alevine maruz bırakılarak, tutuşma sürelerinin kaydedildiği deneylerde, yapıya dahil edilen fosfat gruplarının yanma geciktirici özelliğini kanıtlayacak şekilde test edilen reçinelerin fosfat miktarı arttıkça, tutuşma süreleri de doğru orantılı olarak artmıştır.

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LIST OF SYMBOLS/ABBREVIATIONS

cP	Centi Poise
E'	Storage modulus
E''	Loss modulus
F	Methacrylate functionality
MPa	Mega Pascal
Tg	Glass transition temperature
Tm	Melting temperature
ν	Crosslink density

ΔH	Enthalpy of transition
δ	Tangent of the phase angle

ABS	Acrylonitrilebutadiene-styrene
BPA	Bisphenol A Epoxy
CNSL	Cashew Nutshell Liquid
DABCO	1,4-diazabicyclo [2.2.2] octane
DGEBA	Diglycidyl Ether of Bisphenol A
DGEBF	Diglycidyl Ethers of Bisphenol-F
EEW	Epoxy equivalent weight
FREP	Flame retardant epoxy resin
HDPE	High density polyethylene
LDPE	Low density polyethylene
LOI	Limiting Oxygen Index
NC514	Cardanol based di-functional epoxy resin
NC514VE	Fully or partially methacrylated epoxy CNSL resin(NC514)
NC514VE-PA	Methacrylated and phosphorylated epoxy CNSL resin (NC514)
NMR	Nuclear Magnetic Resonance
STY	Styrene
UPE	Unsaturated polyester resins
VE	Vinyl ester

1. INTRODUCTION

Providing fire retardant characteristic in industrial base products is one of the most popular topics for researches done and going on nowadays. There are a considerable number of studies held recently which are focusing on developing fire retardant feature in large amount of polymeric products of variant types. The crucial role chemistry plays in this environment makes the ground for this particular thesis study, as well. The idea of replacing petroleum -the most common but definitely finite- resources with plant based –especially renewable- ones for making polymers is essentially preferred in both economic and environmental terms. As being one of the renewable plantal resources, Cashew Nutshell Liquid which is a mixture of phenol derivatives has a big potential as to be such a replacement. Under the light of this primer information; the main objective of this research project is to obtain new thermosetting polymers with potential fire retardant properties from Cashew Nutshell Liquid (CNSL). For this purpose, a commercially available epoxy resin derived from cardanol which is the major component of thermally treated CNSL and is a phenol derivative with a principal meta substituent of a C15 hydrocarbon chain possessing zero to three double bonds will be methacrylated and phosphorylated and will be cured with styrene to prepare novel thermosetting resins. Thus, the below steps will be followed throughout this study to prepare and characterize these cardanol based new polymers.

Primarily, a commercially available Bisphenol-A type epoxy cardanol resin (NC 514) that is obtained from cashew nutshell liquid will be completely methacrylated or partially methacrylated to different degrees to produce the corresponding vinyl ester resins (NC 514VE). Then, these partially methacrylated epoxy resins will be subjected to phosphorylation reactions to convert the remaining epoxies to phosphate esters, aiming to obtain materials with fire retardant properties as a result. Following all, at the end of these processes, NC514VE and NC514VE-PA resins will be diluted with styrene to form a liquid molding resin. The next step to take will be curing of these liquid molding resins in the presence of a suitable radical initiator. Acid number titration and spectroscopic techniques like FT-IR and ^{1}H-NMR spectroscopy will be utilized to characterize the methacrylated and phosphorylated products. Viscosities of the styrenated resins will be determined to see if the synthesized resins are suitable to be used for molding operations or not (the check for ability of being processed). Differential scanning calorimetry (DSC) will be used both to see the effect of phosphorylation on the cure behavior and to examine if the subject resins were fully cured or not. Next, thermal gravimetric analysis (TGA) will be utilized to characterize the thermal stability and thermal degradation profiles of the methacrylated and phosphorylated epoxy resins. In addition, dynamic mechanical analysis (DMA) will be employed to evaluate the thermo-mechanical properties of the cured vinyl ester resins. Fracture surface morphology of all cured samples will also be examined by means of Scanning Electron Microscopy. (SEM). Finally a simple fire retardancy test will be applied to the cured resins, where the samples are exposed to a candle flame under the same conditions and the deflagration times are recorded for each sample.

Before going in depth to the above mentioned experimental case study, the second chapter of this thesis initiates the analysis primarily by focusing on basic information about polymer science, bio-based thermosetting resins and fire retardant polymers as the theoretical background. Following this, in chapter three, chemicals which are used in this project are remarked together with explanations on various characterization methods utilized for this particular study. In chapter four, experimental procedures for the preparation and characterization of the polymers are described. The results obtained from the experimental work and measurements and discussions regarding these results are presented in the following chapter; chapter five. As final to all, at chapter six, conclusions based on the results of the above mentioned experimental study on these novel cardanol based resins and future work that may follow this project are acquainted.

2. THEORETICAL BACKGROUND

2.1. POLYMERS

The word *polymer* is joined form of Greek prefix of poly - meaning “many” and the second component word *meres* –meaning “parts”. This simple word derived from “Many parts” gained a depth, in chemistry science, where composition of numerous *repeating units* with identical structures, constitute a long-chain molecule that is a polymer. There are some basic polymers found in nature, like sugar based starch, cellulose, DNA; or polypeptides like enzymes and proteins to which silk is one of a good example. On the other hand, by means of synthetic combinations, a vast amount of polymer types like nylon, polyethylene, polyesters -the most common of all- synthetic plastics are produced. However, naturally available polymers can also be a part of synthetic production chain, like one of the most important example (Hevea) rubber – the natural form-, named as polyisoprene when it is formed synthetically.

Elastomers are polymers, with high ability to prolong when provided conditions completely enveloping. Very well-known elastomers can be classified as natural and synthetic where natural rubber is among first class, as it can be understood by its name, where nitrile and butyl rubber are inside the second class. Some polymers have possibility to be fabricated in form of long fibers which makes them suitable to be utilized in textile industry, such that synthetic fibers of nylon and polyester materials. These are being used so common because of being productive alternatives to natural fibers. Which means, they help to reduce excessive use of naturally occurring fibers like cotton, wool, and silk.

At this point, it must be stated that the word *polymer*, do not come up common in commercial terminology, instead it is *plastics to refer for describing* materials other than elastomers and fibers that are derived from synthetic polymers. Moreover, particular properties of plastics can be improved by means of various additives and fillers to the composition of typical commercial plastic resin with two or more polymers. By this way, the end product becomes able to be processed easier, or gains thermal /environmental stability, or even some of them improve in mechanical properties [1].

2.1.1. Introduction to Polymers

Following the basic definitions given in previous part, this study looks deep in introducing polymers, beginning with a chronological summary of polymer science.

As it can be traced back to mid-nineteenth century, the initiation of polymer science is considered in studies of Charles Goodyear by 1830s. The vulcanization process developed by him, was aiming to improve elasticity and strength of rubber for to be used in tire production, and it was merely transformation of natural rubber's sticky latex into a useful elastomer.

In the meanwhile, in year 1847, German-Swiss chemist Christian F. Schönbein made a study focused on reacting cellulose with nitric acid and came up with cellulose nitrate. By 1860s, this discovery has cleared the way to the use of celluloid, that is commencement for thermoplastics production by man. Later, by 1907, Leo Hendrik Baekeland, who has been called "the father of plastics industry" produced Bakelite that is *the phenol−formaldehyde resin*. The invention of, unsaturated-polyester resin, Gylptal followed all these studies. Gylptal was developed as a protective coating material resin, by General Electric Company, in year 1912.

During 1930s, in the United States, researchers from one of the first chemistry companies, DuPont, developed synthetic rubber, Teflon and even nylon amongst a variety of new polymers. by the end of this decade, within year 1938, another chemistry company, Dow Chemical Canada ULC, in Canada pioneered production of polystyrene in commercial scale, while just one year later in 1939, scientists at ICI in England, innovated polyethylene (low-density). The next decade has been dominated by especially synthetic rubber, where because of World War II researches focused on developing new polymeric materials, to overcome source and supply shortage in naturally occurring materials such as Hevea rubber. The studies on polymers have been accelerated by 1950s so much that, independent scientists German Chemist Karl Ziegler and his Italian colleague Giulio Natta made a groundbreaking study where they formulated group of stereospecific transition-metal accelerators.

This particular study made it possible –tough common- polypropylene to be involved in commerce as one of the leading materials in plastic trade market. Following these developments, there emerged a variety of polymers those were high-performance engineering plastics, during 1960s and 1970s. These materials were able to compete favorably with traditional perception of metals, which used to be preferred for durability and strength in automotive and aerospace industry. High-performance engineering plastic polymers competing with metals include high-temperature rigid-chain polymers like poly (p-phenylene oxide) and carbonate involved thermoplastics like polycarbonate, as well as polyimides and aromatic polyamides -such as Kevlar-, and polysulfones of sulfone group, etc. In the near past, the industry of plastics is enriched by special types of polymers like those with conductive abilities, photoconducting characteristic, and liquid-crystalline property, and are being vastly used with different applications in respective fields.

Presently in almost all fields of life, polymeric materials get hold of a very common series of functions that their making has a major share amongst all types of worldwide base material production industries [1].

2.1.2. Classification of Polymers

This section of the study describes classification of polymers with respect to first, molecular configuration; second, types of initiation-occurrence; third types of thermal reaction by polymers and last but not least important, polymer formation structure.

2.1.2.1. Homopolymers and Copolymers

A polymer is made up of monomers, which can be described as repeating subunits linked in form of chains or rings to end up with this large molecule. A polymer might be containing all monomers identical to each other , and is called a homopolymer. While the synthesis of a polymer consists of two or more un-identical monomers this forms a copolymer.

Since copolymer is formed from two different types of monomers and these monomers join in various fashions to form a polymer, creation of a copolymer can be described as a useful process.

To exemplify this statement; while there are two identical monomers with eligible properties they may produce a homopolymer, while combining two different monomers results in a copolymer with variety of properties. As can be derived from the variety process itself possess, the copolymer created here shall behold properties depending on both the specification of monomers and their configuration. There are four types of arrangement for polymer parts, which are namely alternating, random, block and graft [2].

So, as stated above, differentiation in typology of a polymer is defined via ways of formation of the bond between one type of monomer and the other type of monomer.

As in case of an alternating copolymer that it occurs when there are two monomers distributed in an alternating mode (e.g., where two monomers labelled A and B, if the copolymer has an alignment like ...ABABABABAB..., this is called alternating copolymer). In another case, variant monomer blocks are formed by way of each monomer joining with similar monomers such as ...AAAAABBBBBAAAA... and this time they are members of a classification called block copolymers. Sometimes, it is also possible monomers to be randomly coming together as ...AAABABBBAABBAAAB..., and then samples of this type of arrangement is called as random copolymers. Additional to all above, there are branched copolymers which is the most common types of copolymers are named as “graft”, and inside the structure of these side chains are separate from the main chain [3].

Above mentioned copolymer typology can also be described in different words referring to specifications and properties of their molecular order as;

- alternating copolymers being a combination of strictly alternating but repeating units
- block copolymers consisting of two or more segments of pure homo-sequences,
- random copolymers having an arbitrary hetero-sequence,
- Graft copolymers those have one repeating unit at polymeric side chains and that is grafted to another repeating unit string, when considered within all typologies of copolymers listed here.

The different types of copolymer arrangements are depicted in Figure 2.1.

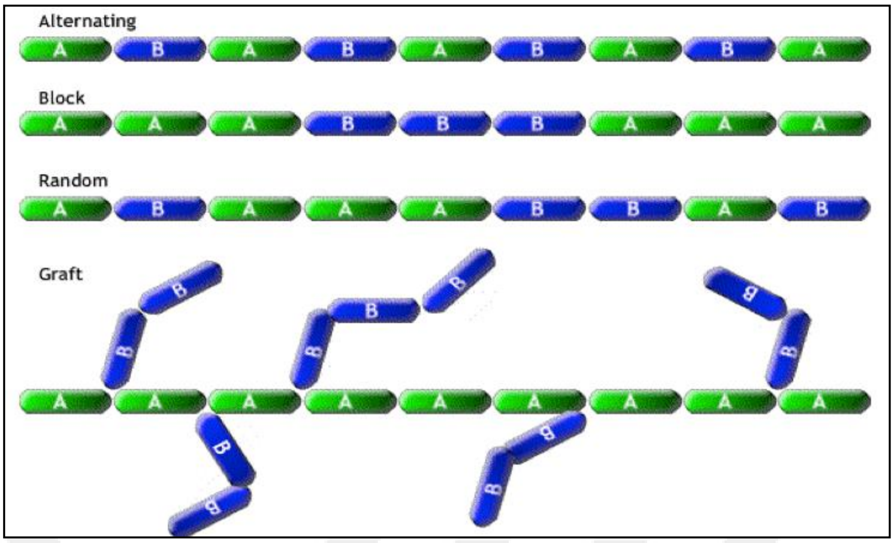


Figure 2.1. Types of Copolymer Arrangements [5].

Meshing characteristics of often-complementary homo-polymers into a single block copolymer strand is not comparable to the mere blending of homo-polymers and opens the access to novel properties not found in either homo-polymer, often arising from the possibility of micro segregation of segments or chirality and solubility transfers [4].

2.1.2.2. Classification of Polymers According to their Source

Polymers can be classified based on their source of availability:

i. Natural polymers
ii. Semi-synthetic polymers
iii. Synthetic polymers

2.1.2.2.1. Natural Polymers

This type of polymers are very essential for life, and as it is understood clearly from the name, they exist in nature, occur in both plants and animals. To exemplify more directly, like proteins which constitute a vast amount in the animal body; like nucleic acids which make up the basic unit of all living cells and viruses controlling heredity at molecular level; and like cellulose that is used in production of food, clothing and shelter.

To be more specific about examples to natural polymers; protein, silk, starch, cellulose, natural rubber and wool can be listed as some very well-known ones.

2.1.2.2.2. Semi Synthetic Polymers

As it can be derived from the title, these are basically a synthesis originating from the natural polymers derived by chemical modifications. Some examples can be listed of semi-synthetic polymers are, cellulose diacetate, vulcanized rubber, and gun cotton. As stated in the introduction of this thesis study, semi-synthetic polymers are produced because of their possibility in being vastly used in daily life. To go in depth the examples listed before; cellulose diacetate, that is formed by natural cellulose on acetylation with acetic anhydride in the presence of sulphuric acid, is used in making materials like films, glasses and threads etc. Vulcanized rubber, as stated before was synthesized aiming to make tires; the cellulose nitrate, namely Gun cotton, is used in making explosives.

2.1.2.2.3. Synthetic Polymers

These are vastly used in several industries, as stated at the very beginning. Following the natural polymers' use , completely man-made synthetic polymers have come to use. The most common examples those can be stated generally are plastics like polyethylene, PVC and a vast more examples such as Teflon and Dacron and synthetic rubbers, polystyrene, fibers (eg. Kevlar), elastomers (rubber and silicones) [6].

2.1.2.3. Classification of Polymers Based on Thermal Response

Polymers may have two different thermal responses, and basically can be classified as thermoset or thermoplastic.

2.1.2.3.1. Thermoplastic polymers

Polymers having linear or branched chain structure with intermolecular forces between polymer chains are classified as thermoplastics. They can be softened on heating and hardened on cooling to room temperature. Thus they are feasible to be recycled multiple times. Example of thermoplastic polymers are polyolefins, polystyrene, nylons, linear polyesters, polyethers, poly (vinyl chloride),etc.[7].

2.1.2.3.2. Thermoset polymers

Polymers in which polymer chains are connected at several positions via covalent bonds, and posses an exceptionally cross-linked polymer structure are classified as thermosets. They have consequential high quality in resisting to various impacts like high tension, excessive load or changing temperature. The structure of thermosetting materials are of exceedingly cross-linked and created by synthetic bonds amongst. This structure is straight forwardly responsible for high mechanical and physical quality, that is aimed to be present in these polymers in contrast to thermoplastic or elastomer type of materials. On the other hand, this exceptionally cross-linked structure ends up in poor flexibility or modest elongation of thermoset polymers.

There are two basic features of thermosetting polymers, to be singled out here. One of these characteristics is “the gel point” of a thermosetting material that refers to a point in curing process. The encountering of the gel point is irreversible, such that, the material stops flowing at this very point and it cannot be molded or processed anymore. This is the result of material’s state change, that is from an irreversible way-viscous liquid state to a solid one.
The other aspect of thermosetting materials is a negative one that makes them impossible to be recycled. This is again a change in state, that once they are crosslinked or cured, they change from liquid state to a solid one and it becomes impossible to go back to a liquid phase.

Consequently, thermosetting polymers do not melt or deform by applying low or high temperature, not even before passing from a gaseous state to a liquid one.

Thermosetting polymers have below the following properties:

- They cannot be melt
- They are insoluble.
- In general, they react to certain solvents with swelling

- Their resistivity to longitudinal movements is high

Below are listed some thermosetting polymer based plastic materials and their uses;

- Epoxy resins - insulation material production, or nonconductive bases, like sealant solvents and circuit boards etc.
- Phenolic resins - rockets, insulation, varnish, printing technology and etc.
- Unsaturated polyester resins – fiberglass reinforced plastics production, corrosion prevention, etc . [8].

2.1.2.4. Classification of Polymers According to their Structure

The structural alterations of polymers are named as linear, branched and cross-linked. Classification of polymers with reference to changes in structure is going to be evaluated under these three main titles.

2.1.2.4.1. Linear Polymers

When single chains formed by repeating units of polymers are joined together end to end, they form a linear polymer. This arrangement makes linear polymers to be composed of flexible long chains. A pile of spaghetti can be thought of if it is to visualize linear polymers, as schematically depicted in Figure 2.2, where each repeating unit is represented by a circle. In case of linear polymer formation, there exists an extensive van der Waals and hydrogen bonding between the chains. Some examples to this type of polymers are nylon, polyethylene, polystyrene, poly (vinyl chloride), fluorocarbons and poly (methyl methacrylate) [9].

2.1.2.4.2. Branched Polymers

When the architecture of polymers have branches along the polymer chain with irregular intervals, they are called branched polymers. Because of the branched structure, these polymer molecules have difficulty for regularly bundling, and as a result a less dense –penetrable- and less crystalline polymer is created. Intermolecular forces do not work expeditiously because the branches often prevent necessary proximity of chains to achieve so. At this point, it should be stated that the amount and type of branching have effects on degradation of physical properties like viscosity and elasticity [10].

During the synthesis of the polymer, there occur some side reactions which may result in branches that make up the main-chain molecule. As stated above, with respect to amounts of side branches formation chain packing efficiency is reduced. To state clearly; where there is increase in branching, polymer density is lowered with respect to this phenomenon.

Additional to all these features of branched polymers, there are cases with linear structures becoming branched [9]. For example, PE which is a relatively simple polymer, has two common forms (high and low-density) each with unique properties. High density polyethylene (HDPE), as hidden in the name, is initiating from the PE, the linear polymer with more impenetrable structure of branches, whereas low-density polyethylene (LDPE) is composed of branches with short chain. Hence, the property comes from the length of the polymer chains, where individual chains will begin to curl and try to fold back onto one another. For low-density polyethylene example, the longer the chain length becomes, the more curling a chain will undergo, and decrease its ability to be packed together. It should be pointed out here that packing ability and density of polymer chains is relative to the ability of rigidity consequently to obtain a more rigid and durable polymer, packing shall be more impenetrable [11].

2.1.2.4.3. Cross-Linked Polymers

This type of polymers are characterized by covalent bonding between the linear chains constituent in which are joining to each other at diverse positions. Cross-linked polymers' positioning is represented in Figure.2.2. The process of crosslinking is achieved either during synthesis or at the end of an irreversible chemical reaction. Often, concatenating atoms or molecules' ability for making covalent bonds to subject chains is the key to accomplish this crosslinking. By great majority, in chemistry, the process of rubber elastic materials being synthesized to have cross-linked structure is called vulcanization [11]. The vulcanization mentioned is not always fully synthetic as in crosslinking process but may also be a derivation from natural rubber, by way of marking – synthesizing- short chains of sulfur atoms those link the polymer chains inherent in it. The crosslinking in vulcanization process is a result of raising temperature of liquid rubber with sulfur, where the reactions occur in rubber molecules Rubber molecules refer to polymers or macromolecules made up of the monomer: isoprene. The amount of this reaction shall be controlled properly to obtain an increase in the strength and the elasticity of rubber about ten times more, otherwise the result may be ending up with a brittle and inelastic substance.

Here it shall be mentioned the elastomers as the elastic polymers of which cross-linking is limited. In this case, viscosity (the resistance to flow) of polymers are lessened because of diverse positioning of covalent bonding in linear chains and result in these elastomers.

When it is referred to the flow of a polymer, chains have to be moving unrestricted next to one another where this possibility is no longer in picture due to cross-linking. Therefore, when there constitutes more amount of cross-links inside a polymer structure, the result is a more rigid one. That is to say, when crosslinking becomes too high, it cannot stretch to a good deal, moreover it might even turn into a brittle one.

As mentioned and explained above, the structure of a polymer’s either main chains or side chains makes the bases for classification of it as cross-linked such that to what extent these chains on the polymer backbone link covalently to neighboring chains of polymer. However this is not always easy to determine because stronger intermolecular forces may mimic cross-linking. In this case, polymer chains may have a geometry similar to cross linked combination or may sometimes contain chemical groups which increase the intermolecular forces between chains. While these are not cross-linking, they do mimic the effect on physical properties of polymer such as elasticity and viscosity, just like the way cross-linking does. In order to distinguish between these categories, he easy way is to study the response of polymer while various solvents are applied on it. Cross-linked polymers are usually insoluble in solvents as a result of strong covalent bonds tying polymer chains together and making the polymer resistant. On the other hand, polymers those are mimicking elastomers, usually dissolved in one or more solvents because when the bond between polymer chains is not covalent, links are easily broken [12]. Figure 2.2 depicts the three different conformations of the polymers, those are namely; linear, branched and cross-linked.

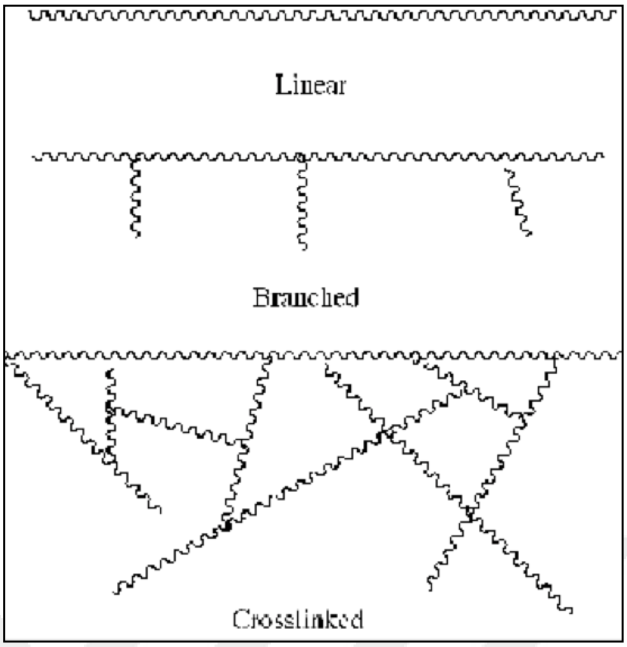


Figure 2.2. Three different conformations in which polymer chains may be set up within a polymeric material [12].

2.1.2.5. Classification of Polymers According to Ways of Synthesis

At this part of this particular thesis study, classification of polymers in terms of polymerization reaction mechanisms, namely step growth and chain-growth polymerizations, will be explained.

2.1.2.5.1. Step Growth Polymerization

Referring to the name of it, in this type of polymerization, there are several steps to obtain the ultimate long chain polymer. During all these steps, a slow build up in molecular weight of the polymer chain is observed, and by the time polymer forms there is only one reaction process. In order to form linear polymer with high molecular weight, at least one bifunctional monomer or equal molar amounts of two different bifunctional monomers are required. Case by case reactions of these functional monomer groups make the polymerization reaction to occur [13].

Within this process monomers join to each other to obtain dimers:

$$M_1+M_1 \rightarrow M_2 \quad (2.1)$$

Dimers and trimers can similarly join within themselves or with each other and may obtain higher oligomers:

$$M_1+M_2 \rightarrow M_3 \quad (2.2)$$

$$M_2+M_2 \rightarrow M_4 \quad (2.3)$$

$$M_2+M_3 \rightarrow M_5 \quad (2.4)$$

$$M_3+M_3 \rightarrow M_6 \quad (2.5)$$

Similar to this step-growth mechanism exemplified above, high molecular weight polymer is obtained only toward the end of the polymerization. Some basic kind of polymers those are conveyed by this sort of polymerization include; polyamides (nylons), polyesters, polyurethanes, polycarbonates, phenolic resins, and so forth [14].

For each monomer molecule there is an average amount of reactive functional groups gathering, and this is called the functionality of a monomer; which determines types of products formed in a condensation reaction. Such that, low-molecular-weight products are obtained from mono-functional monomers; bi-functional monomers, on the other hand end up with linear polymers, while branched or cross-linked (3D) polymers are outcome of monomers with more than two functional groups per molecule, those are namely poly-functional ones [15].It shall be noted that step-growth polymerization differs from chain-growth polymerization, another type of reaction that has initiation, propagation, and termination steps distinct and not applicable to this type. This differentiation of chain-growth polymerization will be explained in the following section.

2.1.2.5.2. Chain-Growth Polymerization

Chain growth polymerization can shortly be stated as randomly mechanized polymerizations of distinctive free-radical reactions. To explain, as a start, the radicals are formed with an *initiation* starting the chain reaction, then, development of products via *propagation* follows, lastly a *termination*, drawing the end line for the free-radical chain reactions happens. In these type of polymerizations, each initiation is followed by a series of rapid repetitive phases, which are propagations, and thousands of monomers are added to the process as a result of these chain reactions. Vinyl monomers' polymerization process is an example of what has been described in above sentences, and this occurs by scarifying double bonds, -C=C →C- C-. As stated before, initiation, propagation and termination are the three steps of a free radical chain growth polymerization, and these are shown in Figure 2.3. To go in depth when the subject is an initiation reaction, the rate-determining step is the constitution of initiating radicals. As it is shown in Figure 2.3, formation of them may result in segmentations of compounds such as peroxides, or from other sources. Initiation requires high activation energy, because when compared to other steps in a chain growth polymerization process, it is a slow step. At this point, it must be stated that, constitution of free radicals may be resulting from several reactions however, initiating radicals, because of them being slow, have to be brisk to get into a reaction with the vinyl unions. For vinyl monomers, chemical attraction range of some radicals and the reckoned energy necessitated in localizing an electron at the -carbon of the subject monomer is linearly correlated [16].

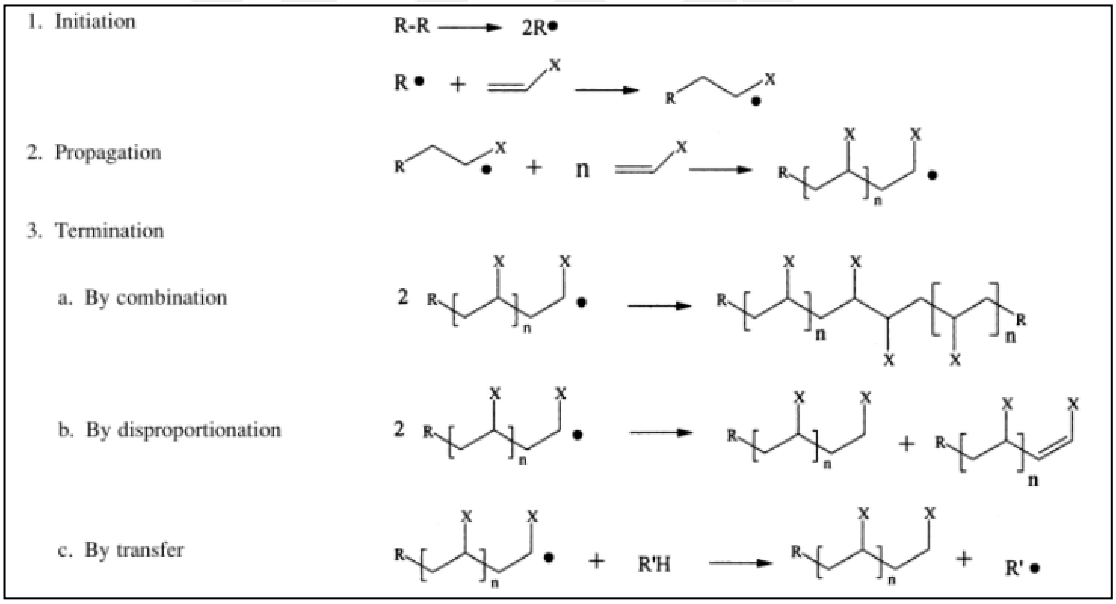


Figure 2.3. Illustration of a free radical chain growth polymerization [16].

2.2. SOLID STATE PROPERTIES OF POLYMERS

Polymers have alternate chain compliances, those can be obtained in various phases, which are amorphous state and crystalline state.

2.2.1. The Amorphous and Crystalline State

2.2.1.1. Amorphous Solids

If the chains in a polymer sample have no regular order then the polymer is in an amorphous state. In some particular cases, polymer material is composed of long chains which are stable and do not allow polymer to flow, as it is depicted graphically in Figure 2.4. This structure may be considered analogously as a bowl of spaghetti, inside which it is not easy to pick one piece and disperse from others with the help of a fork. When there are these type of polymer compositions, if only chains are short, it will be easy to remove one strand from others. Basically, polymer chain motions are affected by chain entanglements. Hence, detection of entanglement can only be achieved in case of polymer dynamics to get slow-down and consequently several viscoelastic properties may become visible.

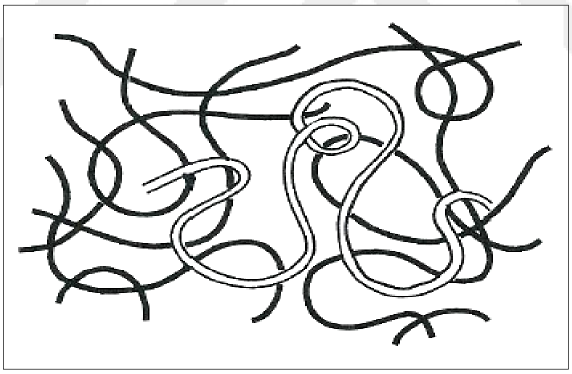


Figure 2.4. Representation of a polymer chain intertwined in a network of entangled chains [17].

In addition to these, chain entanglements have a crucial impact on properties like melt viscosity, stress relaxation, creep and craze formation.

2.2.1.2. Crystalline Solids

The basic units of crystalline polymer morphology include crystalline lamellae which can be described as occurring in distinct layers- that consist arrays of folded chains as depicted in Figure 2.5. When figure 2.5 is examined, it is possible to see that reentry of each chain in the folded structure can either be adjacent or nonadjacent. A chain participating in adjacent reentry can form a tight loop (see Figure 2.5 B) or a loose one (see Figure 2.5C), where the thickness of a typical crystallite may only be between 10 to 20 nm. Under favorable conditions, some polymers cooled from the melt can organize into these regular crystalline structures. Such crystalline polymers are not as much perfectly organized as crystals of low molecular weight polymers those are crystallized from a solution.

As the melt gets cooled, lower-energy conformations are favored and chains become free to get organized into a lamellar structure. In structures of polymers such as polyethylene, syndiotactic vinyl polymers, poly vinyl alcohol and nylons, lower energy conformation can be observed as extended chain type or in a planar zigzag conformation [17].

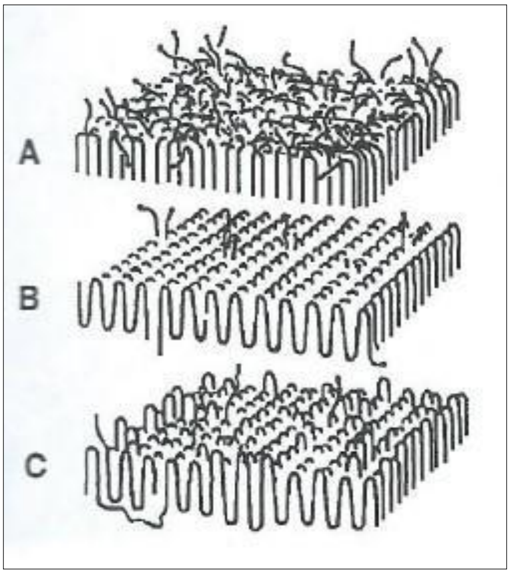


Figure 2.5. Polymer crystalline lamellae structure, Nonadjacent reentry (a), Regular adjacent reentry (b), Irregular adjacent reentry (c) [17].

2.2.2. Glass Transition Temperature (Tg)

Determination of uses of a certain polymer is usually done through its one of the most crucial property; glass transition temperature, in abbreviation; Tg. In order to make it more explanatory some key points regarding the glass transition property of polymers are mentioned below:

The critical temperature of an amorphous material, at which behavioral definition of the subject material changes from being 'brittle' to 'elastic' is this above mentioned crucial property of that material, the glass transition temperature (Tg). In this context, the brittleness will be referred to as being 'glassy' which pertains relatively easy to get broken, while, the elasticity will be referred to as 'rubbery' which pertains elastic and flexible. Non-crystalline solids are the only materials which are either glass or rubber in definition, have the property of Tg. ‘Glassy’ materials have short range atomic or molecular order, and they have Tg below the temperature limit where any rearrangement in their atoms or molecules is possible to take place. ‘Rubbery’ ones, on the other side, are amorphous materials, atoms or molecules of whom are still able to pass through rearrangement. These 'amorphous materials' are also called as non-crystalline solids. Because the arrangement of atoms or molecules constituting amorphous materials do not have a regular periodic pattern, that repeats in space, independent from its being organic polymers, glasses, or even metals, glassy and rubbery behaviors for all amorphous solids are differentiated by their Tg as being the critical temperature.

A material at a temperature below its Tg, is basically frozen, so it is not possible to observe molecular motion at large-scale. On the opposite, when a material is at a temperature above its Tg, it is possible to observe molecular motion. The repeat unit of it, like a single mer in a polymer, is the determinant, such that the scale of it allows the polymer to become 'rubbery' or maybe ‘soft’ in accordance [18].

In relation to alteration in glass transition temperature of any polymer, some physical properties of it pass through a drastic change, that is why Tg is the most important mechanical property for all polymers. In fact, it has to be measured first, while making a synthesis of a new polymer. Essential mechanical properties, impacted under Tg alterations are:

- volume (the 3D space occupied)
- hardness (resistance to pressure)
- modulus (Young’s module)
- percent elongation-to-break [19].

In addition, also for epoxies for example, glass transition temperature (Tg) is a crucial property because Tg of a polymer being the temperature region where there takes place the transformation from glassy state of material into a rubbery one. Unlike thermoplastic materials, epoxies are thermosetting ones, which, when undergoes a curing process a chemical cross-linking occurs, so the end result of this curing process is not recyclable, that it does not have the ability of reflowing or melting when exposed to heat, but instead a phase change at elevated temperatures occurs, where only a slight softening takes place.

As exemplified above, the glass transition temperature (Tg), refers to the temperature range between the “glassy” state of a thermosetting polymer and a “rubbery” one. This relationship showing alteration from a hard, rigid state to more pliable and compliant one is shown in Figure 2.6. In a reaction, degree of cure, chemical structure of the epoxy resin, or hardener type are some factors determining the eventual Tg value. Because in reality, Tg, rather than being a separate transition of thermodynamic type, it is only a range in temperature that is significant to observe the ascendant movements of polymer chains over it. Here it has to be mentioned that there is a basic relationship between modulus and Tg of thermosetting polymers such as epoxies, which can be stated as that the elevation in Tg value, results in increase in denseness of cross-linking together with the modulus values increasing. That is why, the storage modulus value decreases in when an epoxy has reached to values above its Tg.

A high Tg along with a high storage modulus, results in high stiffness of material which in most cases equates to a low percent elongation, and poor energy dissipation under stress at ambient temperatures. Tough it is apparent that, the modulus below the Tg has a particularly linear and surely inverse relation to temperature [20].

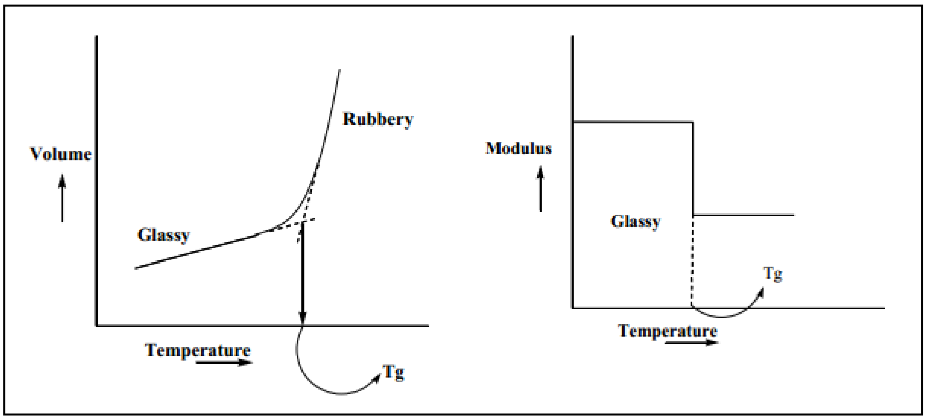


Figure 2.6. The observation of Tg in volume vs. temperature and modulus vs temperature graphs [20].

2.2.3. Melting Temperature (Tm)

When the polymer crystal is heated to the melting temperature, there happens a transformation in state as from solid to viscous liquid. In molecular base, this phenomenon refers to transformation from the ordered structure of a solid material's aligned molecular chains, into a highly random structure defining a liquid state. Melting temperature, that is in abbreviation; T_m [20], has a very narrow range for any material, so usually referred to as single temperature. When the coherent regions of a crystalline polymer melt, this very little range of temperatures is described as the melting temperature (Tm) of the polymer similar to small molecules [21].

Melting process of polymers have particular features those are not noticed in melting of ceramics and/or metals. Polymer's molecular structures and lamellar crystalline morphology creates this particularity in results of polymer melting. When melting temperature is studied, annealing – or tempering- shall be raised up as an important feature to state. Annealing elevates the melting temperature by reducing the gaps or other imperfections inside polymer structure and makes crystallite thickness increased. In this case, this increase in lamellar thickness of a polymer is possible to be stimulated just below melting temperature [20].

In addition, attaining a polymer's melting temperature causes the structure of it to fall apart, such that the crystals begin to dissipate, previous arrangements of chains do not stay in order and become freely moving. This impact of melting on polymer structure makes the data about melting point of a polymer as one of the basic information in determination of possibilities in polymer's use. Melting temperature depends mostly on the type of polymer but at the same time on its crystal forms, and also on additives like plasticizers [22].Crystallization is essential for many high-performance polymers because it greatly increases the strength of the material [21].

2.3. THERMOSETTING LIQUID MOLDING RESINS

2.3.1. Epoxy Resins

As a result of the reaction of epi-chlorohydrin and bisphenol A, epoxy resins or plastics are constituted. Epoxy resins (either monomers or oligomers) are found in form of powder, or in other cases they can be thick liquids with white or yellow color. The examples to some typical epoxy resins can be listed as EponR and EpikoteR, phenol novolac resins, diglycidyl ether of bisphenol A (DGEBA),cycloaliphatic epoxy resins, diglycidyl ethers of bisphenol-F (DGEBF) , brominated resins, epoxide type olefins, and etc. [23].

The reaction depicting typical formation of epoxy resins is shown in Figure 2.7

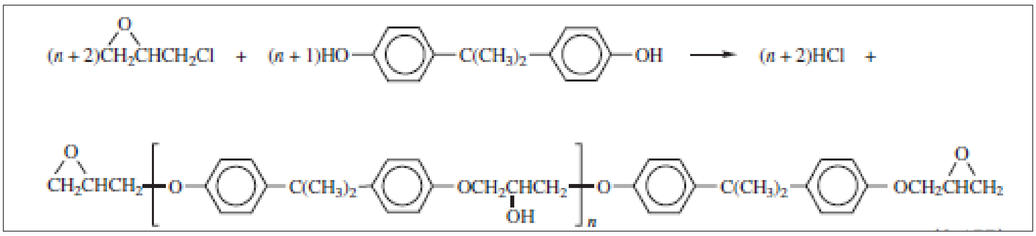


Figure 2.7. Formation of the epoxy resin reaction scheme [23].

The sodium salt of bisphenol A participates in the reaction occurring for epoxy resin formation, while within a temperature range between 50˚C to 95˚C polymerization is completed with putting sodium hydroxide equivalent in reaction media. It is important that hydrolysis of epichlorohydrin, epichlorohydrin reaction to hydroxyl groups of polymer or impurities, taking place in parallel have to be controlled together with stoichiometric ratio of the reactants, in order to bring forth a pre-polymer that has two epoxide end groups.

Monomers with two or more epoxide groups are formed when there is the reaction between epichlorohydrin and compounds of hydroxy, carboxy, and amino, in variant ratios. These monomers are then used in the reaction with bisphenol A. At this point epoxidized diolefins are also employed.

As stated above, a variety of co-reactants either through the epoxide or hydroxyl groups are involved in epoxy resins' curing. Polyamines are the most common of these, with an addition of amine, that is definitely ring-opening (Figure 2.8). In this process primary amines are utilized together with secondary ones where it shall be stressed out that there is a difference in their ability to react in ratio to the order given as primary and secondary. Yet, again in the order given, primary and secondary amine groups can be bi and mono functional, hence in the curing each nitrogen– hydrogen bond becomes reactive. Diethylene triamine (f =5), triethylene tetramine (f =6), 4, 4'diaminodiphenylmethane (f = 4), and polyaminoamides (e.g., diethylene triamine and a dimerized or trimerized fatty acid based diamine) are utilized as agents of crosslinking epoxy resins.

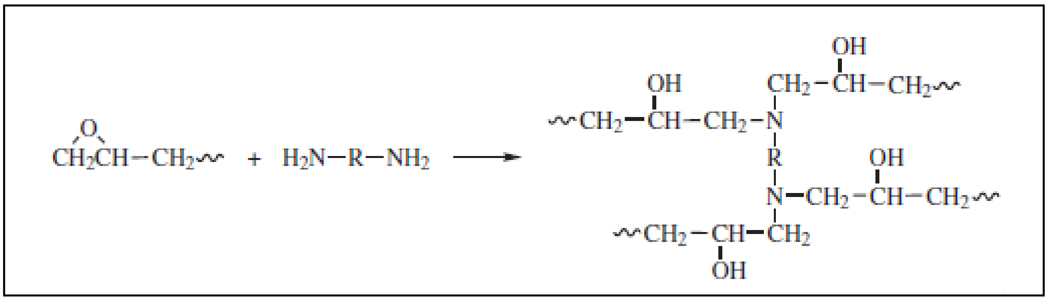


Figure 2.8. Examples to polyamine curing reactions [24].

Additional to above, some other compounds being used in epoxy resins' curing process by means of the epoxide groups are listed here; polythiols, dicyandiamide (cyanoguanidine), diisocyanates, and phenolic prepolymers. Tertiary amines and imidazole derivatives might be required by some of these agents, in order to speed up the curing process. Hydroxyl groups of the repeat unit are involved in crosslinking of epoxy plastics to obtain prepolymers with low epoxide group contents. While acid anhydrides such as nadic methyl, tetrahydrophthalic, and chloroendic anhydrides are used in particular cases, phthalic anhydride is the most common curing agent for this process.

Components in most of epoxy formulations may be of reinforcing type of materials, and stiffener reactants, or fillers and thinning agents of diluents. As it can be derived from the names, roles of these components can be differentiated regarding their behavior in reaction such that, toughening (or providing various degrees of flexibility) agents, are taking place in crosslinking reaction where in the case of diluents (thinning agents), there are passive and active behavior during a reaction. As an example, to reinforcing materials, 1,3-butadiene-acrylonitrile copolymers with carboxyl end groups, polyesters with light-molecular-weight or aliphatic diepoxides where the example for second type of agents, mono- and diepoxides the reactive ones or di-n-butyl phthalate as nonreactive. In the end, epoxy resins may become highly resistant to chemical actions and corrosive impacts, tough and pliant, good in terms of mechanical and electrical conduct and also gain extraordinary bonding ability. The consequence is a great variety of products with many different features at different curing temperatures.

This elaboration in epoxy resin is provided through additives, and curing agents and correctly selected monomers, by means of which end results are finding diverse and excessive place in several markets of daily use [24].

2.3.2. Vinyl Ester Resins (VE)

As a result of their ability to react quickly and easily, vinyl ester resins are vastly used, even more than epoxy resins briefly explained above. This type of resin is again an epoxy-based, thermosetting one, which goes under a curing thorough free-radical initiation of polymerization. This mechanism of curing is looking like that of conventional unsaturated polyester resins.

The end product of vinyl esters, following the cure, are not similar in characteristics to one another tough, because of the variant reactants, those constitute each and every vinyl ester. At this point, there is typology commonly followed in chemistry by referring to the most varied of these resins. Before mentioned vinyl ester is obtained by a reaction between a Bisphenol-A (BPA) epoxy and methacrylic acid. In this reaction a free-radical acts as initiator, and following terminal carbon-carbon double bonds cross-linking, polymerization occurs consequentially. As to note it, this structure makes the behavior of epoxy similar to a polyester. The fact that, difference between acceleration of epoxy reactions, which are usually slow, and polyester free-radical reactions which are relatively faster is what makes this crucial. In addition to that, subject structure is styrene soluble; where styrene takes part in free-radical reactions. Resin solution obtained can easily be worked in processes of stiffened plastic, because vinyl ester resins obtained as a result of solutions of styrene are less viscous. Epoxy resins, on the other hand, are highly viscous, thus processing methods necessitated are effortful and expensive. As explained above, vinyl esters are faster and easier to work with, because of their abilities like quick curing and being versatile. Moreover, in creation of vinyl esters most eligible features of epoxy resins are possible to be contained.

To exemplify, features like fatigue resistance of BPA vinyl esters, tensile enduringness, and lengthening ability, can be considered considerably similar to aromatic amine-cured epoxies with superior quality, in terms of their abilities and are way greater than a regular orth phthalic resin [25].

Since vinyl ester is obtained by unsaturated monocarboxylic acid esterified with epoxy resin, this reaction produces a resin which may then be dethawed 35 - 45 percent of its weight in a reactive solvent, such as styrene, and it becomes an alternative to polyester and epoxy materials within matrix or composite materials. In this case, strengths, specific features, and bulk toll of the product arbitrate between polyester and epoxy. When it is compared with one feature like resin viscosity values, vinyl ester is low in counts (approx 200 cP), where the same value for polyester (approx 500cP) and epoxy (approx 900cP). Because of the chemical resistance they provide, in some industries, these are preferable, like in case of pipe manufacturing, relative parts of chemical plants and particular storage tanks [26].

2.3.3. Unsaturated Polyester Resins (UPE)

Nowadays, science and technology people are putting a lot of attention at the field of thermosets used as composite matrices considering their structure-property relationships. Among all the these, different types of unsaturated polyesters, briefly UP thermosetting resins are important, because they are being base for fiber-reinforced plastics [1]. These matrix composites are in used in field of technology for a couple of decades some of which can be exemplified as naval construction, offshore applications, waterlines, and of course building construction. The reasons UPs are so favored can be primarily being an economical thermoset material with its excellent process ability and good crosslinking trend, additional to its ability to gain mechanical properties when cured. Natural fiber reinforced polymers are mainly used in automotive and construction industries. Their specific features like low weight, low density and even low cost, are the main reasons, where in addition they may have high particular properties and availability as being produced from renewable resources [27].

As stated above, electrical, aircraft industry, automotive, as well as component production for appliances are involved in the extensive field thermoset polyesters are being used. Properties like being less in cost and allowing to be more flexible in design, they are preferable to substitute with conventional materials. Additional points of promotion for these resins to be expressed here are their ability to protect thermal and dimensional features, being nonconductive, having very high mechanical properties, being strongly resistant to chemicals and having low density. The hint to explanation of having these abilities is in their structure. There takes place crosslinking with –usually- a reactive diluent such as styrene (STY) or some other monomer, by way of which unsaturated polyesters with insolubility and infusible property is obtained. The capability of resin and styrene to be mixed is dependent to the resin composition, where in general, about 30-40% of the mass of commercial resins contain styrene [28].

2.4. BIOBASED THERMOSETTING RESINS

There is a high demand and an increased attention to materials, resources or energy that is renewable in both industrial and academic areas. Environmental sustainability is the initiator phenomenon behind this interest and concerns as well. Nowadays, non-renewable resources are dominating the market for polymers, and this makes up approximately 7% of all oil and gas used worldwide. As a very common concern shared by many researchers and scientist, fossil oils getting less and less in resource, environmental concerns, dramatic fluctuations in the price of oil, gave birth to an urgent act, causing to focus on alternatives, where as a part of this concern developments in plastics industry makes use of renewable resources in production of polymeric material crucial. Some examples to highly preferred raw materials with renewable resource are vegetable oils, cellulose - polysaccharides - (also starch), wood and proteins. These are biomass-derived materials from which a variety of chemicals are possible to be prepared. For instance, bio-oils and syngas (mainly CO and H_2) are obtained by the pyrolysis of wood and agricultural wastes. Bio-oil can be elaborated into a product that becomes fuel for means of transportation, while syngas interchanges with methanol, where both are valuable and utilized in chemical industry [29].

Epoxies, unsaturated polyesters, vinyl ester resins, polyurethanes, and formaldehydes are some examples to thermosetting polymers, those are commonly utilized in many industries, as mentioned in previous parts of this study. Among the different types of these most commonly used polymers, estimated global market of polyol and polyurethane have come to USD 22.6 billion and USD 66.4 billion respectively by 2018. Given this reality, still the fastest expanding regional market for polyurethanes consumption and production is thought to be Asia Pacific.

Despite this wide use, the negative aspects of conventional thermosetting polymers lead to researches for alternatives, where bio-based polymers came into stage. For example, thermosetting polymers are unable to be recycled – such that they are not able to recover from changes in shape after their reaction is complete. Diglycidyl Ether of Bisphenol A (DGEBA), one of the most traded epoxy resin, is synthesized from the condensation reaction of bisphenol A and epichlorohydrin in which bisphenol is endocrine disruptor so it is problematic in terms of health, while in manufacture of baby bottles and by products or printer by products some countries do not allow its usage. Following these, in recent years, researches have focalized to find feasible and preferable solutions and formula to utilize resource materials inexhaustible and as a part of this general picture, developments contributing towards sustainability in polymer industry are achieved. Consequent to mentioned concentration alternative resources, bio-based thermosetting resins from natural oils has been under focus. There are some examples those can be listed, like itaconic acid, cardanol, sugars, wood/lignin, tannins, lactic acid etc, in order to see bio-based polymers as a crucial actor dominating the renewable resource market, in the green chemical industry, the efficiency of using alternative resources shall be paid considerable attention to make good out of chemical transformations as well as to get to benefits of bio-based materials, as a part of these studies [30].

2.4.1. Plant Oil Based Thermosetting Materials

When the subject is plant oil, it is very well known that this classification of resource is one of the most important class of renewable ones, as a result of them being at hand when needed additional to their numerous uses.

Recently, polymers based on plant oil, has been established and produced in a great variety. The process takes place via polymerization methods of free radical, olefin metathesis, cationic, and condensation. Consequently, resulting polymers were variable in terms of thermophysical and mechanical properties, which are from soft and elastic rubbers to stiff and inflexible plastics. Come after is an assurance of them becoming eligible alternatives to petroleum-based plastics.

Additional to above, vegetable oils represent more to being the renewable option amongst chemicals and polymers. This is resulting from them being ready to be used, built in biodegradability and small amount of toxicity. Vegetable oil is a commonly used covering material, like paints or coatings, which has been used for over centuries because as being unsaturated, exposition of it to oxygen in air, results in oligomerization or polymerization. As one of these common uses, biodiesel, one of the bio renewable fuels have been effectuated from vegetable oils. This alternative engine fuel is obtained by means of techniques of like catalytic cracking, pyrolysis, and transesterification. Carbon –carbon bonds inside the fatty acid chains make it practical to use unmodified vegetable oils in preparation of bio renewable polymers by using methods of cationic or thermal polymerization. This chemical advantage made the basis to the developments in vegetable oil-based polymeric systems, throughout the last ten years. In the end, modified vegetable oils with acrylic double bonds undergo free radical polymerization, while exhibiting high reactivity, and they become able to spare thermosets with good thermal and mechanical features [29].

Triacylglycerols, are obtained by esterification of glycerol with three fatty acids. For each type of plant oil fatty acids ratio to the total weight of triglycerides is 95% and their content is the particular characteristic of the subject oil. They are main molecules those constitute plant oils (triglycerides, shown in Figure 2.9). Being highly functionalized molecules, Triglycerides take part in the synthesis of cross-linked polymers. This can be achieved in two seminal approaches.

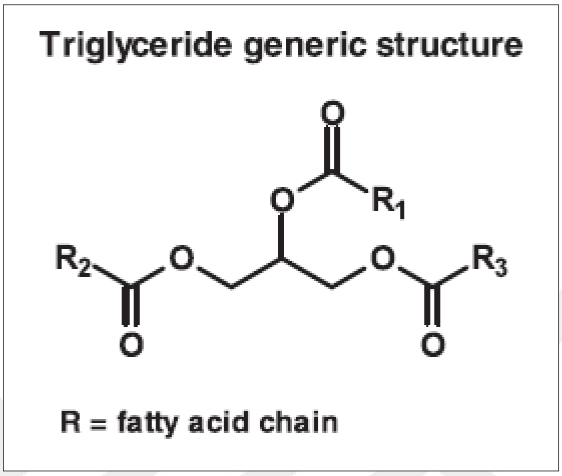


Figure 2.9. General triglyceride structure [31].

In triglycerides there exists functional groups those occurring naturally, and first approach in using triglycerides in polymer synthesis, uses the advantage of this inherent groups, which are internal double bonds, alcohols, or epoxides, where various methods put in action for polymerization of these. The second approach widens the possible synthetic results. In this approach, the aim is the hydrolysis of triglycerides, which in the end, provides glycerol and a mixture of fatty acids. Since the natural triglycerides (which usually only contain double bonds) has a disadvantage as being low in reactivity, this second approach introduces easily polymerizable functional groups, in order to solve it, so depending on chemical modifications done before polymerization, the synthesis is realized [31].

There are two types of resins, preferred in devising of polymer matrix composites used in military and commercial industries. Namely, vinyl ester (VE) and unsaturated polyester (UPE) resins became favorable, because of their low cost and light weight. Containing reactive diluents in high concentrations is typical for these resins, such as styrene, which make it possible for these resins to be molded via some techniques like, some inexpensive liquid molding techniques and resin transfer molding. Fatty acid-based monomers are used in liquid molding resins, and the studies and enhancements on this subject are crucial for a number of reasons. Being derived from plant oils, fatty acids have one of the most desirable features as a resource, which is being renewable. Additionally, they are low in cost and low in volatility. Fatty acid based monomers became possible to supersede some or all of the styrene that takes part in liquid thermosetting resins with these features. In the end use of fatty acids in liquid molding resins has multiple advantageous results, beginning with reduction in VOC emissions, because of which there comes lowering risks in health and environmental areas, while similarly contributing to sustainability at global scale [32].

2.4.2. Cashew Nut Shell Liquid (CNSL) and Cardanol Based Thermosetting Resins

Cashew nut shell liquid (CNSL) is one of the vegetable oils with a wide variety of uses in extended areas, some mentioned previously in this study. There are some similar plant based oils, like soybean, rapeseed, tung, linseed, castor oil and etc. This study is focusing on Cashew nut shell liquid, shortly CNSL. The oil extracted from cashew nut has a unique property that is making it particular, this liquid is containing a phenolic moiety with an unsaturated 15-carbon side chain. Causing CNSL to become a nonedible oil that does not result in excessive coercing in renewable chemical feed stock, as other types of edible oils' utilization as chemical raw material in resin production do.

CNSL is copiously available, all over the world. In many applications this agricultural by-product can potentially replace phenol with equivalent or better results. It is an appealing alternative to utilize CNSL as the initial material for industrial polymer products, in extensive amounts because of its low cost coming next to extravagant availability (450 000 metric tons per year),and being a natural chemical reactant together with other attributes. CNSL has various possibilities of uses like, an initiator in synthesis of polymer or resin like products; a series of value added monomers have it as predecessor; or polymers have it as supplementary.

As it can be derived from its name, there is "Cashew Nut Shell Liquid" (CNSL) inside the shell of cashew nut and is referred to in here. Cashew industry, mainly working on Cashew nut, is producing CNSL, which is harvested from the cashew tree, Anacardium, occidentale-L. Origins of this particular plant is Brazil yet it is available in many other parts of the world, in excessive amounts.

Countries, and regions like Kenya, Tanzania, Mozambique, and some tropical regions of Africa, together with areas like South-East Asia and Far-East Asia, and mainly in countries like India, and Bangladesh Cashew has two major utilization in industry, like while cashew is the product dominant in process in some of these areas, in some others unprocessed cashew nuts are imported.

CNSL that is contained in this special nut is a member of phenolic lipids family, in another words, long-chain hydrocarbon phenols and they are present peculiarly in Anacardiaceae three and its plantar families. As shown in Figure 2.10, below, cashew nut has a shell with honeycomb structure, inside which this greenish-yellow syrupy liquid, CNSL, come to pass.

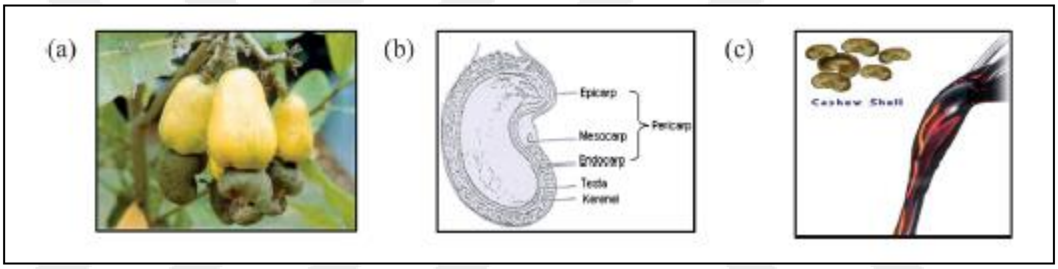


Figure 2.10. (a) Cashew fruit, (b) cross-section of cashew nut, and (c) cashew nut shell liquid [33].

Four main parts comprised by naturally occurring CNSL are: anacardic acid, cardanol, cardol, and 2-methyl cardol. The chemical structures of these compounds are depicted in Figure 2.11. These segments of CNSL are monohydric or dihydric phenols or phenolic acids which all have a hydrocarbon side-chain at the meta-position.

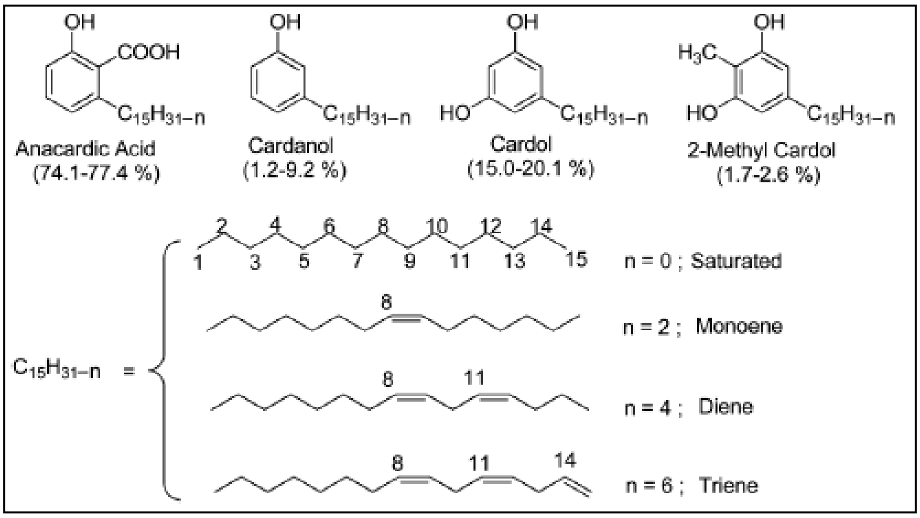


Figure 2.11 Components of CNSL [33].

Commercial-grade CNSL is roasted, which causes decarboxylation to take place in parallel to this process, therefore any anacardic acid is hardly present inside CNSL, since it is converted to cardanol.

As seen in (Figure 2.11), the alternating side chain unsaturation components, found in CNSL are a composition of four, in order of amount, monoene (48–49%), triene (29–30%), diene (l6–17%) and saturated (5–8%). There are some studies executed regarding composition of CNSL, which has both natural and technical type. Researches mainly used chromatographic techniques to do so. One of these researches are accomplished by, Tyman and co-workers, who have reported that when studied in decisive amounts, there is similarity in both natural and technical CNSL regarding the existence of oligomeric and polymeric materials. The results are; phenolic composition of the cardanol in natural CNSL %1.2 and in technical % 62.86; phenolic composition of the cardol in natural CNSL % 11.31 and in technical CNSL %11.25.; phenolic composition of the 2-Methyl cardol in natural CNSL % 2.04 and in technical CNSL %2.08; phenolic composition of the anacardic acid in natural CNSL %64.93 and technical CNSL is not detected. There are some corporate structures leading in CNSL industry.

The worldwide groundbreaker in utilization of this particular liquid is Cardolite Corporation since they develop methodologies, work in manufacture field, and moreover they advance products using natural and renewable cashew nut shell liquid technology.

Following them, other companies can be listed starts from one North America’s leading suppliers, Palmer International, than in India, several companies like Satya Cashew Chemicals (P) Ltd., Sanoor Cashew and Adarsh Industrial Chemicals, Akshar Cashew Industries, etc. whose main focus is supply and manufacturing of CNSL and its base products [33].

Being under attention by several researchers cardanol is analyzed in terms of various polymers and useful products those are possible to be obtained from it, and results have been presented in a number of reviews. There are four groups of cardanol based polymers, namely cardanol based phenolic resins, vinyl ester resins, epoxy resins, and their acrylates (or methacrylate). The studies on cardanol depict several consequences with relation to these four groups of polymers.

In some of these studies, emphasis is on the use of CNSL and cardanol in phenol formaldehyde condensation polymers and the chemical process and cardanol is classified as a base for Novalac or Resoles type phenolic resins. Cardanol based epoxies are focus to another group of studies, where cardanol epoxidized added to Bisphenol A type epoxy resins through its phenol hydroxyls and cardanol-based epoxidized Novalac resins. The consequence was considerably improved ability of elongation-at-break and by means of a polyamine hardener the energy absorption rate at break upon curing becomes elevated [34].Cardanol based epoxies, yielded transparent polymeric films with a high gloss surface within 3h as a result of another study, in which they have been enzymatically synthesized from the polycardanols epoxidized through the unsaturation sites of the alkyl chains and they are cured with amine hardener, phenalkamine thermally at 150 ˚C [35]. In addition to all above, in a recent study, the researchers introduced a new curing system that was developed by varying proportions of these cardanol based monomers in the copolymer mixture and they synthesized a bio-based thermoset resin system from cardanol, where this resin system consisted of benzoxazine and epoxy pre-polymers. As a result, for electronic packaging materials, there emerged the possibility of improvement in the ability to be processed and being flexible which used to be owned by conventional epoxy and thermoset polymer matrices of benzoxazine because, bio-based liquid monomers have acted as good competitors to do so [36].

Another study on generation of vinyl ester resins from cardanol is done by using quantitative data through employment of empirical statistical techniques in multiple regression analysis, and resulted in the experimental data proving the successful application of the model under optimum process conditions. In this study, the prediction for maximum extent of conversion was 95.3%. Here a reaction between the cardanol-based epoxidized novalac with methacrylic acid at a molar ratio 1:0.9, at 89.96˚C for 5h in the presence of the catalyst (triphenylphosphine) at a concentration of 1.49% of total weight of CNE and MA took place [37].

In a study by E.Can et.al, cardanol based resins were methacrylated in order to obtain bio-based VE resins. They used two commercially available resins in this very study. The process was initiated by methacrylation of NC 514; a diepoxy cardanol based resin with approximately two epoxies per molecule and LITE 2513HP a cardanol based monomer with approximately one epoxy per molecule in their idealized structures, as depicted in Figure 2.12 and 2.13. Later, methacrylated NC-514 resin (NC514VE) was used as the cross-linker unit while the mono-functional methacrylated LITE monomer (LITEVE) was used as the reactive diluent in both the conventional DGEBA vinyl ester resin (DGEBAVE) and in NC514VE resin at variant concentrations (10, 20, 30, 40, 50 wt% based on total weight). Resin formulations of NC514VE using styrene as the reactive diluent were also prepared. The above mentioned study of E. Can stated that they produced "both a vinyl ester resin in view of an alternate di-functional cardanol based epoxy and the utilization of a cardanol based methacrylate monomer for the first time, as the reactive diluent in a traditional DGEBA vinyl ester resin and in the cardanol based vinyl ester resin framework: NC 514VE shaping a totally bio-based VE resin." [38]. This subject study of E. Can et.al inspired this thesis study, on its basic idea and initiative.

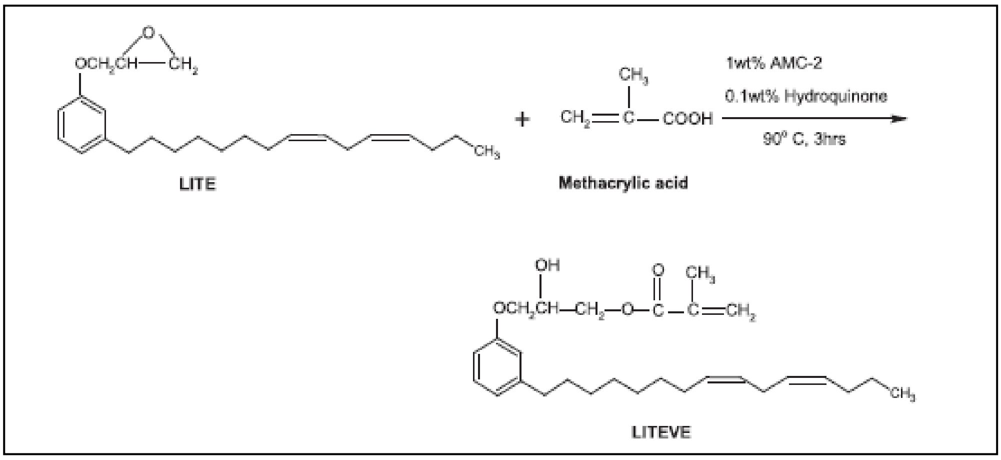


Figure 2.12. Methacrylation of LITE resin, the scheme of reaction [38].

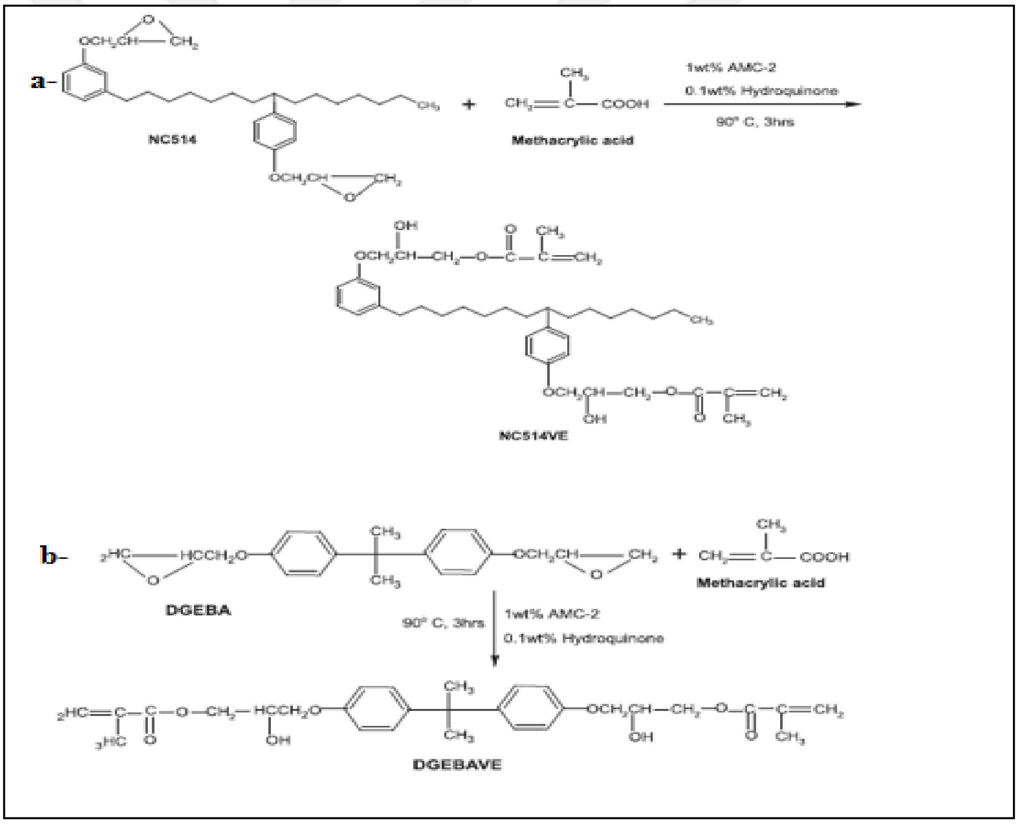


Figure 2.13. Methacrylation of (a) NC514 and (b) DGEBA resin, the scheme of reactions [38].

2.5. FIRE RETARDANT POLYMERS

Sophisticated and complex materials take place in daily lives of people, as a result of developments in science and technology. As a part of this phenomenon, polymeric materials took their considerable place within this picture. On the other hand, their inability in fire resistance makes a parallel ascendance in development and use of fire or flame retardants adjacent incorporated into polymeric products to limit their flammability. To illustrate, with statistics checked in the UK, the number of deaths in relation to fire was 508, by 2004, and it was 593 a year before, while it was 1 096 deaths, with the highest number recorded back in 1979. Which shows, the decrease in number of fire-related deaths throughout 1980s and 1990s. There were various reasons behind descending numbers where the impact of the growing use of flame retardants cannot be ignored.

There was expectation of increase in global demand for flame retardants by 4.8%, which means 2.2 million metric tons per year, by the year 2009. Additional to all, there were legal constraints getting more and more rigid in terms of preventing fire hazards.

Definition of flammability behavior in polymers shall be done on several parameters. The solid degradation rate of them together with heat release rate made up the phenomenal burning rates is the primary one to mention; there is also ignition characteristics which refer to properties like critical heat flux for ignition, delay time and also ignition temperature; rates of spreading out is another parameter to be mentioned, and it refers of pyrolysis, burn-out, characteristic of flame and smolder; the smoke production and product distribution in particular, toxic species emissions shall be accounted as well as other possible parameters [39].

2.5.1. Properties of Fire Retardant Polymers

For thermoset resins in general, Table 2.3 depicts the flame retardation rates of them ranked from more resistant to less, as;

Phenolic > Epoxy > Polyester & vinyl ester

Table 2.1. Ranking of the properties of Epoxy, Poly ester, Vinyl Ester and Phenolic resins

Property	**Ranking**
Mechanical property	Epoxy>polyester and vinyl ester>phenolic
Process ability	Polyester &vinyl ester>epoxy>phenolic
Cost-effectiveness	Polyester &vinyl ester>phenolic>epoxy
Flammability	Polyester &vinyl ester>Epoxy>phenolic

As stated in previous section, if there is not a precaution taken, it is practically inevitable that thermosetting resins utilized in any field will experience fire situations, since they are crucial, common group of materials with a wide range of uses.

In general, polymers react against flames depending on their molecular structure. Polymers with relatively long flexible (aliphatic) linkages are tending to combust more than the aromatic groupings. To state in other words, polymers with aliphatic backbones are not as advantageous as polymers with aromatic and heterocyclic groups in their chains, in being less combustible. The combustion depends upon the aggregation of thermal degradation in the polymer following the ignition of it. At this point, the amount of char that is promoted by the particular system is the crucial thing to focus and char formation is a required property of a thermoset. Because char has two nominal duties, while normally acting as a diffusion barrier against the flame moving from polymer to the fuel flux, it acts as a physical barrier between the flame’s heat flux and the surface of subject thermoset. The governing of char production is dependent upon polymer’s compound structure. cross-linked polymer containing aromatic fragments, which put together by short and flexible bonds those have a tendency in aromatization during thermal decomposition ends up with char formations. Many polymers tend to cross-link at the very beginning of thermal decomposition, but at the end, char formation does not necessarily take place because of this. Hence, through stages of cross-linking, aromatization, fusion of aromatics, and graphitization, charring of polymer keeps on until this chemical structure of the polymer allows [40].

The reduction of fire risk, defined as the probability of blocking the occurrence of fire, delaying the combustion and reducing possible fire hazard, has become a compulsory requirement to be taken into consideration in many applications of polymer materials. This most challenging task is promoting the use of a number of the fire retardants which are instrumental in the exceptional expansion of polymer materials within modern technologies, because of their characteristics of low fire risk and high versatility.

As in all areas, recent firefighting strategies are being developed aiming employment of fire retardant materials complying with the sustainability concept. In the meanwhile, reduction of the aftermaths of fire on people and their properties, namely fire hazard, has become as important as reduction of the probability of the occurrence of a fire, namely fire risk [41].

The first thing in firefighting strategy is to prevent or delay ignition of fire, then to control or bound spreading of flames and thus lessening the possible harms and injuries. In line with this strategy, there are various choices of applications, depending on type of material or type of uses to the material and its relation with fire. Such that, some materials has embedded flame retardants while some others have as a treatment applied on (e.g., textiles, plastics).

When it comes to retardants, some types of them work effectively as by themselves; while others work in increment of fire protective abilities of flame retardants, which make them “synergists”.

The elements flame retardants consist of may react differently to fire, that is to say, depending on their chemical makeup, they interact at different stages of the fire cycle. Hence, flame retardants have to match to each type of material they are conjoined or related to. And it shall be stated clearly that, having a variant composition of retardants is necessary because physical nature and chemical composition of materials those supposed to be fire-resistant are changing a lot, so their behavior at the condition of heat increases (fire), which shall be considered as changing as well.

As stressed out above, several times, being the critical layer of fire protection, flame retardants do play a life-matter role in decreasing fire related risks. Having stated generally before, there are four major areas where flame retardants are predominantly used: building and construction materials, furnishings, electronics - electrical devices, and transportation [42].

2.5.2. Methods of Introducing Fire Retardant Features to Polymers

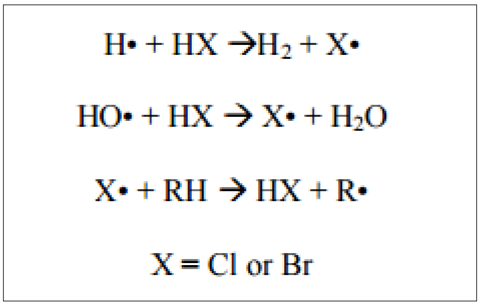
Two things are determinant for the design engineer while choosing a plastic material with fire retardant ability, for any application, one is the properties described in technical specifications and the other is feasibility of the subject product in terms of price/performance ratio. Considering that there are a vast amount of flame retardant compounds available in the market, being able to distinguish the behavior of materials and their fire resistance ability becomes crucial, even regarding chemical structure of all [43].

Fire retardants do usually consist of bromine, phosphorus, nitrogen and chlorine. In addition to these there is the use of inorganic compounds as their own, or sometimes as part of a flame retardant system in conjunction with the ingredients of nitrogen, bromine, or phosphorus. Another crucial note to state here is that, replacement can be difficult because areas of application are often specific for fire retardants, and consequently they are not quickly replaced or substituted [42].

There are two distinct classes of flame retardant polymers, inherently flame retardant polymers and additives. Additives make up the majority of the flame retardant market due to lower costs for processing. As briefly mentioned before, the secondary refers to an amount of diverse organic and/or inorganic compounds, put in commercial polymers, in presence of a synergist. In order to transform a polymer’s flammability such as ABS (acrylonitrilebutadiene-styrene) or polystyrene, and make it a flame retardant one, as said above a synergist is used in these compounds, to step-up polymer’s flame retardant ability, while applying lower loadings.

Being the most effective flame retardant additive, halogenated ones act quickly as a radical trap and delay flames efficiently in this way. In more detail, it can be explained with halogen radicals behavior.

They, in particular chlorine and bromine, catalytically stop the fire by capping the high energy free radicals HO· and H· in the vapor phase, by this way, combustion cycle stops and the flame gets extinguished. The related reactions are shown in Figure 2.14 [44].



$$H\bullet + HX \rightarrow H_2 + X\bullet$$

$$HO\bullet + HX \rightarrow X\bullet + H_2O$$

$$X\bullet + RH \rightarrow HX + R\bullet$$

$$X = Cl \text{ or } Br$$

Figure 2.14. Reactions of halogen radicals [44].

Additive fire retardants, without halogen can be found with a series of chemicals compositions with polymers included, and they can be listed as below:

Phosphorus based ones are covering a wide range of phosphorus compounds with different oxidation states, such as red phosphorus, organic and inorganic phosphates, and phosphonates.

Another type that is Nitrogen based ones can be exemplified as melamine polyphosphate, melon, melamine cyanurate, and melem. These are typically melamine and melamine derivatives and are often utilized together with phosphorus based flame retardants.

Inorganic flame retardants are making up of a category made up of metal hydroxides like magnesium hydroxide and aluminum hydroxide, mainly, where like zinc borate, other types are used rarely.

Intumescent flame retardants are exemplified with a scheme for a better comprehension of their principle, (see mechanism in Figure.2.15), here a typical example for halogen-free flame retardants can be observed. The basic principle of intumescent system, depends on full separation of combustible material from source of heat and fire via an insulating foam which molds over the surface. These intumescent fire retardant mechanisms are vastly preferred when there is the need to decrease the flammability of thermoplastic polymers such as polyesters and epoxy resins, polyurethane, polyethylene, and polypropylene [45].

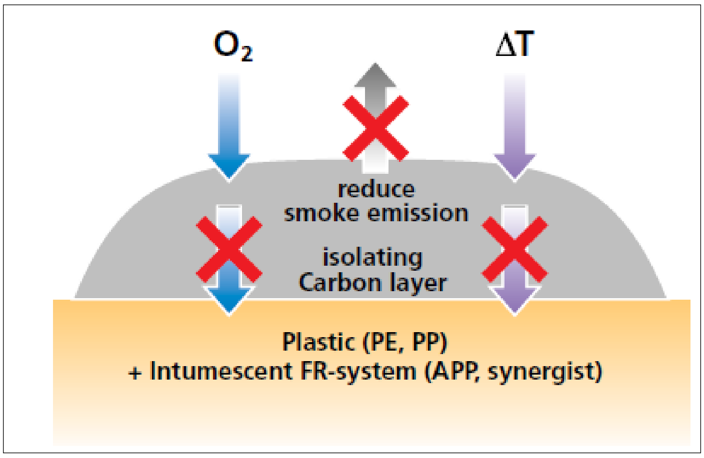


Figure 2.15. Intumescent FRS mechanism against flammability [45].

2.5.3. Phosphorous Based Flame Retardants

This popular option of phosphorous based flame retardants are highly studied in recent researches, and become popular against halogen-containing flame retardants when considered their dominance over and vast use in market.

Even though fire retardants containing halogen, particularly those based on bromine, have played and continue to play in the subject field of firefighting, issues like ecological protection and end-of-life, halogen-free solutions are started to be analyzed with growing interest, and the predominance of these studies on non-halogen flame retardants, with or without patent, focuses on phosphorus-based products [46].

Most of the commercial and industrial common choice of flame retardants already in use are either inorganic compounds or halogen-based organic compounds. While, apart from being ‘organic’ halogen based organic compounds are not ecology-friendly since, where they are utilized, in case of combustion, there arise corrosive gases in addition to toxic smoke.

In order to overcome this problem, in polymer science, there is this trend toward becoming halogen-free in production of flame retardants. Following these trends, among halogen-free products, those that have phosphorus as a component give positive results in flame retardant abilities for epoxy resins. Moreover, toxic gas and smoke extraction during interaction with fire is lessened by use of phosphorus based polymers, which make them favorable when compared to halogen-containing retardants under same conditions [47].

The powerful result in being fire retardant is obtained by creation of a non- flammable layer of char over the outer layer of polymers during combustion when it is checked for phosphorus-containing compounds way of acting. Hence, promising results in the field of flame-retardant systems are reported for epoxy resins modified by phosphorus-containing compounds, due to their high efficiency in performance. [48].

The use of phosphorus-containing compounds in obtaining flame retardant property have two ways of reaction; those are either polymer conflating or by reacting onto polymers. Researchers strongly believe in these compounds abilities to become efficient on both gas state of flame and solid state of heated material, as by becoming liquid. The effect of phosphorus containing compounds in gas state of flame is thought to be extinguishing the flammable particles of H and OH by means of which the power of flame is lessened in this gas state. The other effect results from the esterification of polyphosphoric acid which occurs in the solid phase by means of thermal decomposition in functional groups containing phosphorus. At this stage, polyphosphoric acid causes dehydration of the polymer and then a protective carbonaceous layer that is shielding the underlying polymer from attack by oxygen and radiant heat is formed. This heat-resistant property can be effective even at higher temperatures.

With epoxy polymers, a conventional way to increase their flame resistance is to use flame-resistant curatives, like phosphorus-containing bismaleimide, hydroxyphenyl phosphate, and phosphorylated diamines. Furthermore, the introduction of phosphorus containing functional groups into the backbones of epoxy such as imide-epoxy resin, aryl phosphonate epoxy ether ended up in achieving excellent flame retardant abilities [49].

Following results of studies previously held on the subject, in C. Jiao’s research, synthesis of a flame retardant epoxy resin (FREP) used as a reactive-type flame retardant from bisphenol A epoxy resin (BAEP) and phosphoric acid was reported. The related reactions are show in the Figure 2.16.

As a result, C. Jiao obtained an epoxy resin modified with phosphoric acid that behaves inflammable for a considerably good period of time, in case of fire. Since it was possible to modify bisphenol A epoxy resin by utilizing phosphoric acid, phosphoric acid treatment of epoxy resins was found to be a convenient way to introduce phosphorous component into the epoxy resin structure [47].

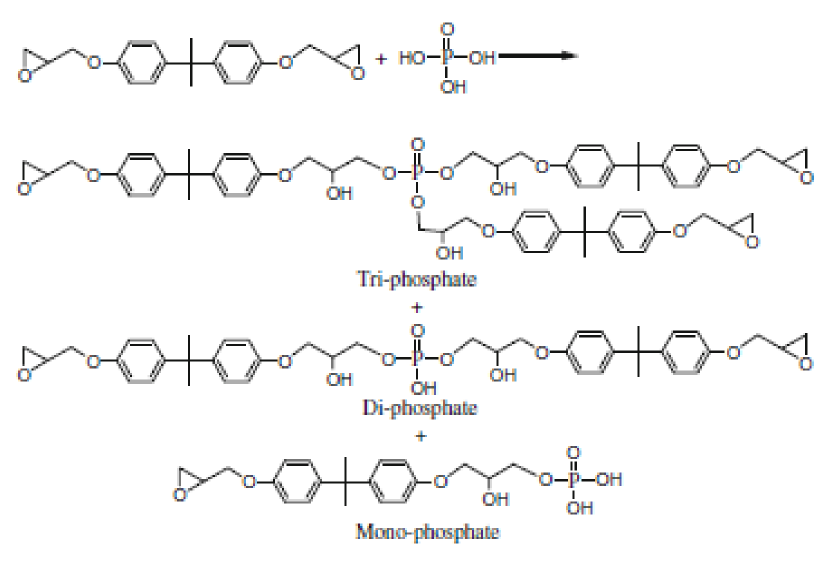


Figure 2.16. Synthesis routes of flame retardant epoxy resin [47].

2.6. AIM OF THE STUDY

In the light of the literature work presented in this chapter, the main objective of this study is to obtain cardanol based vinyl ester resins with fire retardant properties through modification of a commercially available cardanol based epoxy resin with both methacrylic acid and phosphoric acid. Thus for this purpose, first a commercially available Bisphenol-A type epoxy cardanol resin (NC 514) which is obtained from cashew nutshell liquid will be both completely methacrylated or partially methacrylated to different degrees to produce the corresponding vinyl ester resins (NC 514VE). These partially methacrylated epoxy resins will then be reacted with phosphoric acid to convert the remaining epoxies to phosphate esters. The resulting NC514VE and NC514VE-PA resins will be diluted with changing amounts of styrene to form a liquid molding resin. These resins with different formulations will then be cured in the presence of a radical initiator via radical polymerization, applying a thermal cure cycle. The methacrylated and phosphorylated products will be characterized via acid number titration and spectroscopic techniques like FT-IR and ^{1}H-NMR spectroscopy. The liquid resin properties and cured resin properties will be determined and the effect of phosphoric acid modification as well as the effect of phosphate and styrene content on various properties will be evaluated. As a result, we will obtain novel vinyl ester resins based on a renewable resource; cardanol with different degrees of phosphate content possessing potential fire retardant properties.

3. MATERIALS AND METHODS

In this chapter, the following sections focus on the materials, mostly the vast amount of chemicals used for synthesis and cure of cardanol based vinyl esters resins together with explanation of methodology for characterization of the subject resins.

3.1. MATERIALS

Table 3.1. shows the structures and properties of all the commercial epoxy resins and the chemicals used for the synthesis of the vinyl ester resins and their cross-linked polymers.

Table 3.1. Epoxy resins and the chemicals used for the synthesis of the vinyl ester resins and their cross-linked polymers.

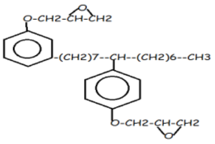
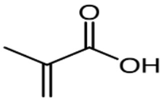
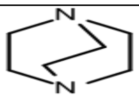
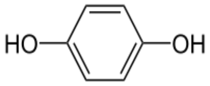
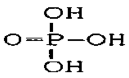
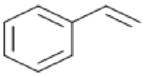
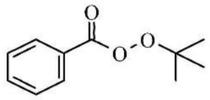
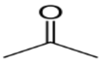
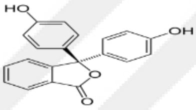
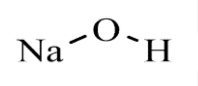
Name	**Formula**	**Structure**	**Supplier**	**Purity (%)**
NC 514(Epoxy Resin)	$C_{33}H_{52}O_4$		Cardolite	99.9
Methacrylic Acid	$C_4H_6O_2$		Sigma-Aldrich	99.9
DABCO	$N_2(C_2H_4)_3$		Sigma-Aldrich	99.9
Hydroquinone	$C_6H_6O_2$		Sigma-Aldrich	>99
Phosphoric Acid	H_3PO_4		Sigma-Aldrich	>99
Styrene	C_8H_8		Sigma-Aldrich	99.9
Tert-Butyl peroxybenzoate	$C_6H_5CO_2OC(CH_3)_3$		Fluka	>95

Table 3.2. shows the chemicals used for the epoxy equivalent weight titration and acid number titration.

Table 3.2. Chemicals used for the titration procedure

Name	**Formula**	**Structure**	**Supplier**	**Purity (%)**
Acetone	C_3H_6O		Sigma-Aldrich	99.5
Phenolphthalein	$C_{20}H_{14}O_4$		Sigma-Aldrich	>99
Sodium Hydroxide	NaOH		Sigma-Aldrich	99.9
Ethanol	C_2H_6O		Sigma-Aldrich	100

3.2. METHODS

There are eight methods used at different stages of production and characterization of the vinyl ester resins and these will be briefly explained under this section, in order to put the base of experimental study and the idea theses put into action.

3.2.1. Attenuated Total Reflection (ATR)

The first method of measurement that will be discussed is the widely known Attenuated total reflection (ATR) which is a tool for measuring via reflecting the periodic vibration of waves which is effectively resulting when used in close association with Infrared Spectrometry.

The way that ATR assembly works, is by inspection of how internally reflected Infrared (IR) beam at the time of pass through some changes when it is in contact with the subject sample. In this application, an IR beam with a certain angle is channelized on to a visually impenetrable crystal, high in refractive index. Thus, an evanescent wave is created by the internal reflectance, and this wave extends beyond the surface of the crystal into the sample positioned in an immediate proximity to the crystal. Typical for evanescent wave, the consequential strength come from the closeness to sample, which is the basic idea behind ATR method of inspection.

Attenuation of evanescent waves is observed when the sample absorbs energy, at particular areas of IR spectrum. Following this, the path followed by the attenuated beam is like; it returns to the crystal, soon afterwards it departs from reverse end of the crystal and finally is headed to the IR spectrometer detector. As a result, the detector records the attenuated IR beam as an interferogram signal, by means of which an IR spectrum can be brought on. This working principle is shown in the Figure 3.1.

What makes ATR as the ideal technique of measurement to be used on strongly absorbing or thick samples lies in the results of alternative measuring technique of transmission which often produces intense peaks on these type of samples. Optically dense samples are worked through ATR better, because as stated before, the basis to measurement is proximity; the closer the sample, the higher the strength of evanescent waves.

These waves descend in an exponential rate to the space between the surface of the ATR crystal and sample, and in almost all cases this makes measuring with ATR unresponsive to thickness of subject sample.

Other good choices of samples to be measured better in this technique of ATR are, a multi-layered solid's surface layer, samples of homogeneous solids, or the coating on a solid. Even a diamond as being an ATR crystal can be used to analyze hard-solid structure with irregular shapes. Hence, for ATR method use, solids that can be powdered can be called as ideal solids. Some examples to these are, laminates, paints, plastics, rubbers, coatings, and natural powders.

In addition to all above, ATR is often the preferred in analysis of liquids because of its feasibility. To use this method in liquid analysis is so easy that, a single drop of liquid is necessitated to be placed on the crystal. Types of liquids in analysis of which ATR can be used are viscous liquids, coatings, free-flowing aqueous solutions, and some biological materials [50].

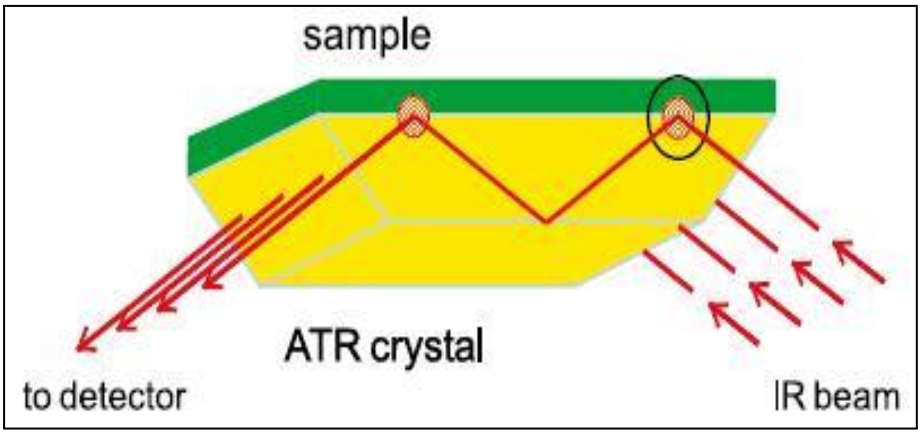


Figure 3.1. ATR working principle [50].

3.2.2. Proton Nuclear Magnetic Resonance (^{1}H-NMR) Spectroscopy

The second method is able to identify the carbon-hydrogen organization inside an organic compound, this method is named as NMR or nuclear magnetic resonance spectroscopy. By this particular method, it is possible to determine a compound's unique structure. Using this method together with other instrumental methods like infrared and mass spectrometry, allows scientist to characterize the entire structure of a molecule.

As comprehensible from the name, nuclear magnetic resonance spectroscopy method works via manipulating magnetic attributes of center of an atom. Being a molecule charged by whirling atomic nucleus generates a consequent magnetic field. The nuclear movements are impulsive and randomly oriented when there is no manipulating magnetic field affecting from outside, on the opposite conditions, hence, with an external magnetic field, subject nuclei either align with or line against external magnet's field [51].

A typical CW-spectrometer, a nuclear magnetic resonant, may serve as to exemplify this method and some of its original aspects. This is the simplest procedure, while in actual procedure the ways to obtain spectrum is divergent. The typical continuous wave (CW) is shown in Figure 3.2. Before starting, there must be the tuning of NMR spectrometer to a particular nucleus. In this case, it is the proton. Beginning with choosing a magnet powerful enough, a solution of the sample in a uniform 5 mm glass tube located between the poles is spun to average any magnetic field variations and tube imperfections in parallel. Veracious energy of radio frequency radiation is transmitted from an aerial coil into the sample (colored red). Sample tube is covered by a receiver coil, and radiation of absorbed RF energy is monitored by means of dedicated electronic devices and a computer. While doing so, magnetic field manipulated as variant or swept totally over a small range, and consequently an NMR interval can be found. On the other hand, as an alternative technique, that is considered equally effective; the frequency of the RF radiation can be altered while providing a stable (firm) external field.

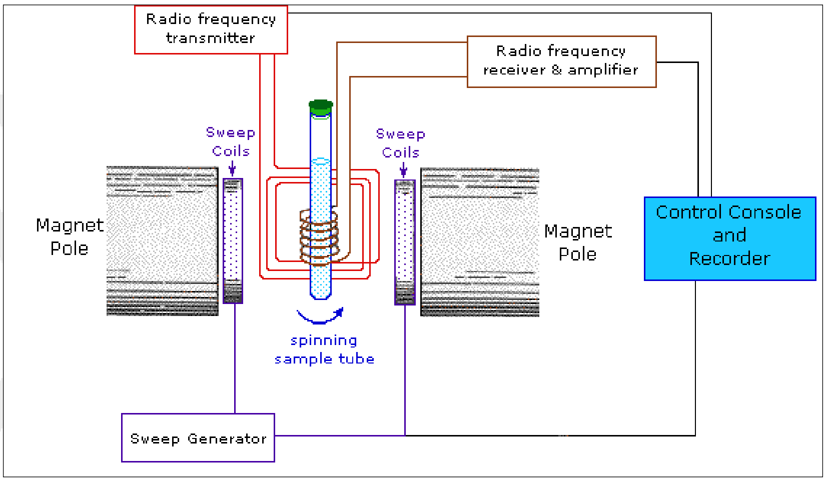


Figure 3.2. ^{1}H-NMR Device [51].

Figure 3.3. summarizes how proton chemical shifts are assigned to different functional groups. With reference to the given scheme, because of hydrogen linkages altering in different sample concentrations, the ranges specified for OH and NH protons (colored orange) are wider than those for most CH protons, and because these ranges are not exact other spectroscopic methods such as FT-IR spectroscopy may be necessary for a full structural characterization [52].

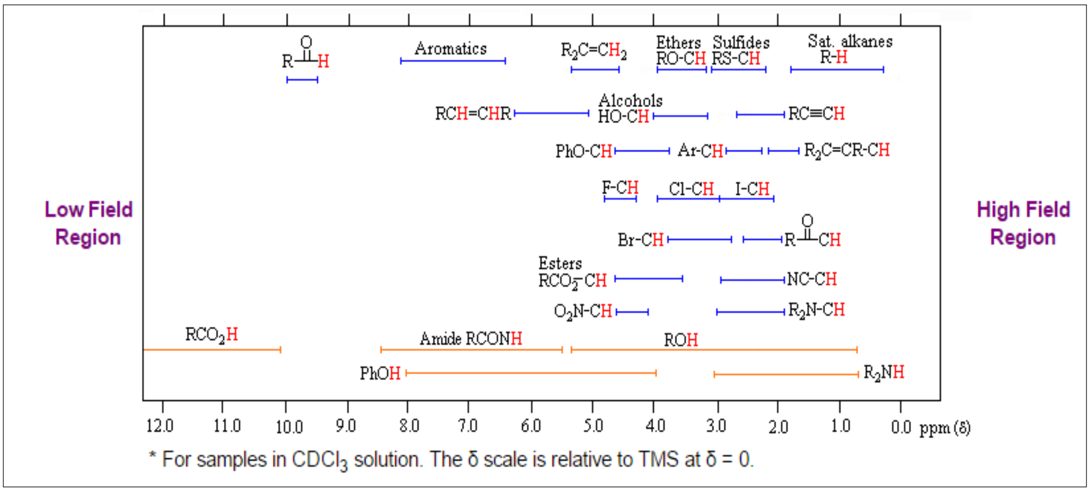


Figure 3.3. Ranges of proton chemical shifts [52].

3.2.3. Rheometer

Rheometer is the basic instrument used in rheology study that deals with flow of complex liquids in both simple and complex flow geometries. In practice, most of these subjects to study are complex flows. But, fluids’ behavior in a complex flow has highly complex dynamics and kinematics, which makes it unlikely to measure behavior of fluids in these flows, in a general and decimally precise manner.

To overcome this problem, it is a requisite to study fluid behavior in simple flows primarily, because in simple flows, the fluids’ response can be studied accurately, and flow dynamics can be well established before getting elevated in ’scale of complexity’. As explained, rheometer is the method of measuring the flow of complex liquids in simple geometries, aiming to understand the flow behavior in complex flows. As the study focuses on flow of fluid, rheometer has various substances with complex microstructure, those can be subject to study with several properties of theirs, where the target property for these subjects fluids to be studied is viscosity [53]. A typical rheometer with its basic components is shown in Figure 3.4.

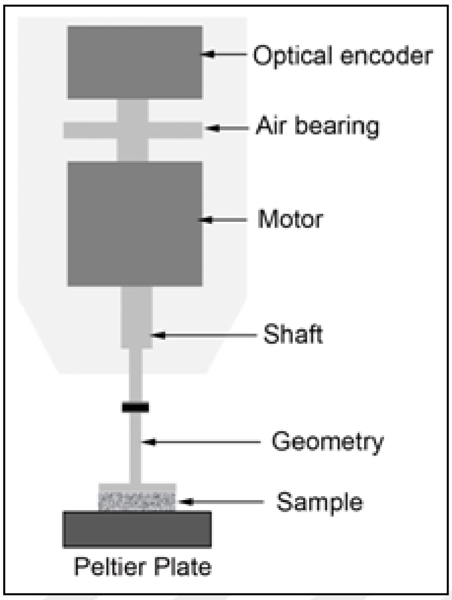


Figure 3.4. A device of rheometer [53].

3.2.3.1. Measurement of Viscosity:

When rheometer is used to measure viscosity rates, shear viscosity is the basic rheometric measurement possible. The end result of the measurement gives if the liquid is a Newtonian one, in case that as a part of shear stress or shear rate measured viscosity is uniform and viscoelastic effects are absent, then however, the viscosity, for the kind of liquids those are involved in this study, decreases as the shear stress/shear rate increases since it is uniform at low stresses/shear rates [53].

3.2.4. Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis, is a method applied by putting periodically vibrating stress either of tension, compression, or torsion, on the sample, where the resulting deformation is measured as oscillator. This method –in abbreviation “DMA”, is the one employed to classify the mechanical properties of bulk polymer specimens. Energy storing ability of a polymer, elastically is represented by E’, which is storage modulus. On the other hand, polymer’s ability for dissipation of energy in form of heat is represented by lost modulus, E”. DMA test gives the opportunity of understanding abilities of polymers by means of a complex modulus of material that consists of E’ and E’’ modulus. It is revealed via phase analysis of DMA mechanics, that the storage and loss modulus are compactly related to loss factor that is the tangent of the phase angle, δ, which makes deformation hang back the stress [54]. The formula for tan δ is as below;

$$\text{loss factor} = \tan\delta = \frac{E''}{E'} \qquad (3.1)$$

3.2.4.1. Instrumentation of DMA

Considering the efficiency of DMA method, one of the basic choices to be done is to decide the focus of control. Here there is the option of choosing between two ways to apply deforming load onto sample as either strain (displacement) or stress (force) control, as depicted in Figure 3.5 a and b. The working mechanism of strain-controlled analyzers, either for DMA or for simple static testing, works like first by moving the probe to a set distance and then using a force balanced transducer or load cell in order to measure the stress. As well, DMA analyzers are featured in a way to apply the stress or strain in two different ways, those are twisted or direct applications. As depicted in Figure 3.5c and 3.5d, force can be applied direct or force can be applied in a twisting motion where sample is tested in torsion. Latter type of instrument can be called as rheometers with dynamic analog of constant shear spinning disk. The advantages of this torsion test, is their ability to obtain a short time response when used in low viscosity materials, together with another ability of them easy to perform stress relaxation experiments.

Another common advantage to state here is the possibility of measuring normal forces, when they are arranged in torsion. On the opposite, there is this major disadvantage that their transducers may wander randomly at long times or with low signals [55].

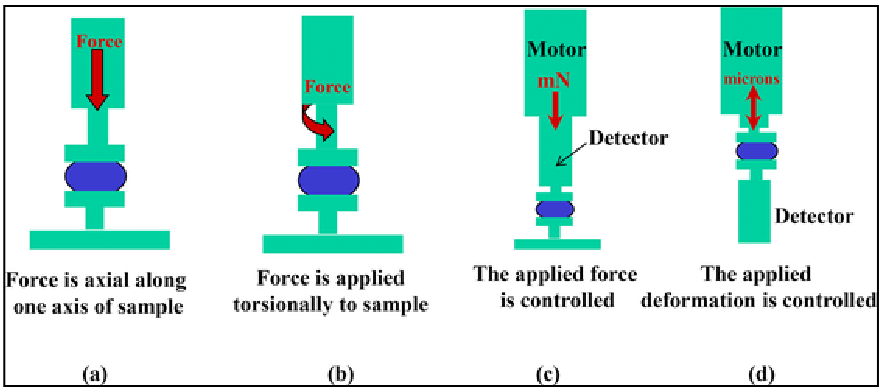


Figure 3.5. Instrument types for the DMA [55].

3.2.4.2. Applications of DMA

DMA method is used in evaluating polymer composition or measuring glass transition temperature of them. The use of dynamic mechanical analysis method in measuring Tg of polymers is described in this section.

Beginning with Figure 3.6, showing curves of amorphous thermoplastics undergone typical alteration. The explanation is lying in the behavior of macromolecular segments which cannot change shape, especially through rotation about C–C bonds, and as a result the molecular entanglements act as rigid crosslinks. So, it can be seen that at low temperatures, the molecules remain stiff as a result of losing their capability of moving that they become unable to resonate with or against oscillatory loads. On the other hand, as the temperature gets elevated, the reaction of molecular segments are opposite to previous situation, such that they gain the ability to be mobile promptly, which make them easily resonating with the load. While staying steady and firmly in place is the great possibility, the entanglements may occasionally slip and become disentangled no independent from the value of temperature, thermosets and elastomers have additional chemical crosslinks those have kept. Here it shall be noted that while curing, for every 1000 atoms of a weakly crosslinked rubber, there is one crosslink where the ratio is one crosslink for 20 atoms in case of brittle thermosets.

The temperature alteration has the impact of the definition of materials state, as interpreted from above descriptions that is to say, in case of temperatures less in degree; the material is in glass state or energy elastic state while in high –or elevated- temperature the material is in rubber or entropy elastic state. By definition glass transition refers to any differentiation or exchange between brittle state and the rubber-elastic one.

Where mechanical deformation coincides with timescale of molecular motion, each oscillation turns into internal friction at limits, and there remains no room for any elastic deformation. Consequent to this time-temperature superposition, the dissipated energy as heat, namely the loss modulus, reaches a top possible level.

The typical change of storage, loss and complex modulus as well as the loss factor with respect to temperature for an amorphous polymer is depicted in Figure 3.6. In the glass transition region of the graph in Figure 3.6, it can be observed that, the temperature of the loss factor is at its peak ends up higher than the temperature corresponding to maximum loss modulus. To go in depth, by the period of heating, the storage modulus falls to a level of one-thousandth to one ten-thousandth of its original value, and consequent to this fall, the initial rise in the loss factor, as being the ratio of the loss modulus to the storage modulus, is suppressed by the drop in storage modulus [56].

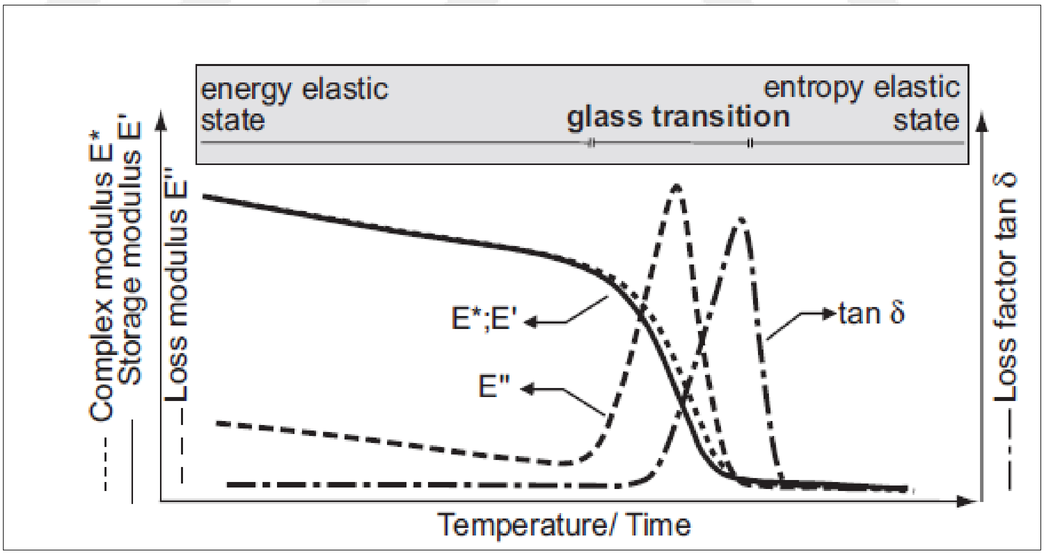


Figure 3.6. Typical graph of the DMA curves for an amorphous polymer [56].

3.2.4.3. Types of Measurements and Single/Dual Cantilever Clamps in DMA

As mentioned before in DMA methodologies, the deformation control test and force controlled tests are the two basic types of DMA approximation. The first type measures the stress by applying a sinusoidal deformation to the sample, and second measures the distortion by applying a dynamic sinusoidal stress on it. There are two types of analyzers instrumented in accomplishment of dynamic load in either free vibration or forced one.

These devices are;
i- Torsion type,
ii- Bending, tension, compression, shear type.

As it can be described generally, in the second type of analyzing method, the sample is clamped at both ends and either flexed in the middle (dual cantilever) or at one end (single cantilever). Cantilever bending is a commonly preferred mode for evaluating thermoplastics and highly dulled materials like elastomers, where dual cantilever mode is ideal for identifying the cure of thermosets keeping their conditions. Single/dual cantilever clamp is demonstrated in Figure 3.7 [57].

Figure 3.7. The Single/Dual cantilever clamp [57].

3.2.5. Differential Scanning Calorimetry (DSC)

As hidden in its name, this method of Differential Scanning Calorimetry uses thermo-analysis as to measure temperature's function, by comparing the amounts of heat required to increase the temperature of a sample and the heat required to increase the temperature of the reference maintaining both at almost the same temperature. For a typical DSC study, the temperature program is generally designed to obtain a linear increase in sample holder temperature aligned to increase as a function of time. One of the key point to be mentioned here is the importance of defining precisely the heat capacity of reference sample over the range of temperatures to be monitored and recorded [58].

As shown schematically in Figure 3.8, the sample is placed inside a suitable pan that is located onto a constantan disc that sits on a platform in the DSC cell, with a chromel wafer just underneath. The sample's temperature is measured by a chromel-alumel thermocouple under the constantan disc. A symmetrical platform has been created for the empty reference pan where there are its own underlying chromel wafer and chromel-alumel thermocouple. This allows comparing the difference between temperatures across the sample and the reference in order to measure heat flow [59].

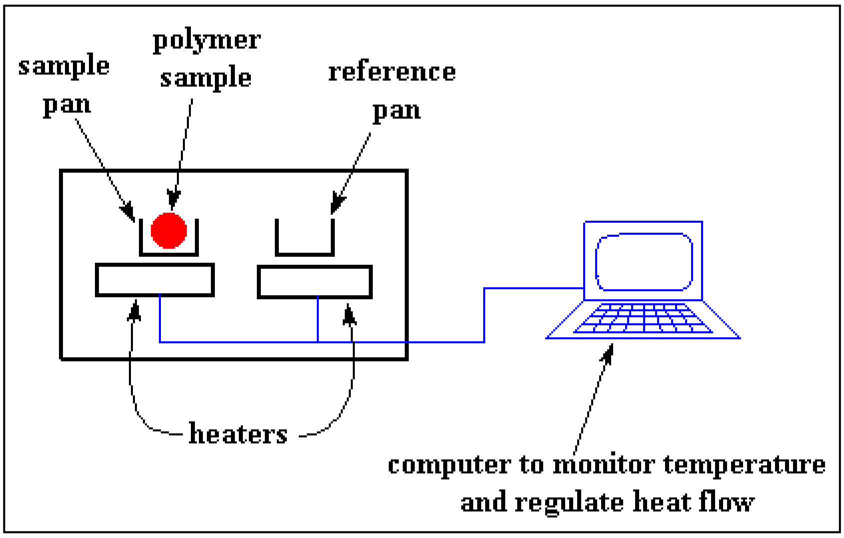


Figure 3.8. Components of the DSC instrument [59].

Detection of phase transitions: DSC method makes it possible to detect transitions in heat capacity or energy alterations, in a manner of great sensitivity. This ability makes main application of DSC in studying phase transitions, such as glass transitions, melting, or exothermic decompositions. A Typical DSC thermogram of a semi crystalline polymer, showing the phases in relation to heat flow while temperature changes is shown in Figure 3.9.

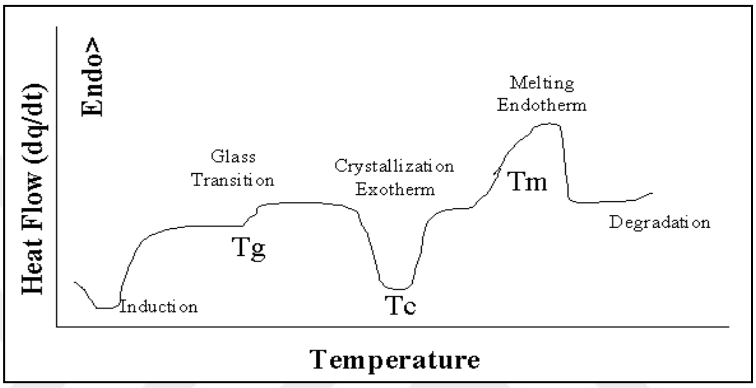


Figure 3.9. Typical DSC thermogram for a semi-crystalline polymer [58].

The basic principle underlying Differential Scanning Calorimetry technique is based upon the balance between sample and reference temperatures, such that, in case the sample undergoes any of the above mentioned phase transitions, in order to preserve both sample and reference at the same temperature, heat will more or less need to flow rather to sample than the reference. Type of reaction, such that being exothermic or endothermic is the determinant factor to state if the amount of heat flow to sample will be less or more. To exemplify this; let us consider a solid sample melting into a liquid state, where it means the process will require more heat flowing to the sample so that its temperature increases at the same rate as that of reference. This occurs due to heat absorption by the sample since it undergoes an endothermic phase transition that is to say from solid to liquid. On the opposite, in case a sample undergoes an exothermic process to have aligned temperatures of sample and reference the same inside the reaction the required heat is less. The result of a DSC experiment, as in Figure 3.10, is a curve of heat flux versus temperature or versus time.

When the peak corresponding to a given transition is integrated, the calculation of enthalpies of transition can be done by using this curve. Following equation shows the enthalpy of transition:

$$\Delta H = KA \tag{3.2}$$

In the above equation; *K* represents calorimetric constant, and *A* refers to the area below the curve where as it can be derived ΔH stands for transition enthalpy. The calorimetric constant will vary from instrument to instrument and can be determined by analyzing a well-characterized sample with known enthalpies of transition.

Consequently, by using DSC method, the difference value of heat flow between the sample and reference, measured by means of differential scanning calorimeters gives the opportunity to observe amount of heat absorbed or released during above mentioned transitions. Additionally, DSC may also be used to observe changes as glass transition, which are more elusive. With its ability in evaluating sample purity and uses in polymer curing studies, DSC method has a wide use in industrial settings as a quality control instrument [58].

3.2.6. Thermogravimetric Analysis (TGA)

This method of thermogravimetric analysis is based on the observation of sample's mass over time, under a temperature alteration. The process is applied by a laboratory tool named, Thermogravimetric Analyzer (TGA) which is utilized for material classification done via this method. This technique of characterizing materials has variety of uses in environmental, food, pharmaceutical, and petrochemical industries [60].

As stated above, in Thermogravimetric Analysis (TGA) the mass of the material is measured, in terms of its amount and rate of alteration in regard to temperature and time in a controlled atmosphere. By way of this analysis, the subject material may decompose and alter in weight; increase or decrease, or materials may oxidize or dehydrate which helps to classify them. Hence, the primary use regarding these measurements can be said as to determine a material's composition and to be able to anticipate their endurance in relation to thermal changes, at temperatures up to 1200°C [61].

TGA method, requires a sample pan that is maintained by a precision balance system, and this pan is located on a furnace where it is heated or cooled during experiments done. Through this method of measurement, the objective of experiment is to observe the mass of the sample. A sample purge gas controls the sample environment, this gas may be inert or reactive, and is flowing over the sample and exhausted afterwards. Other components included to the experimenting instrument are the microbalance, the furnace, the programmer controller, and a computer or data acquisition system. Typical arrangements of the components for TGA are shown in Figure 3.10.

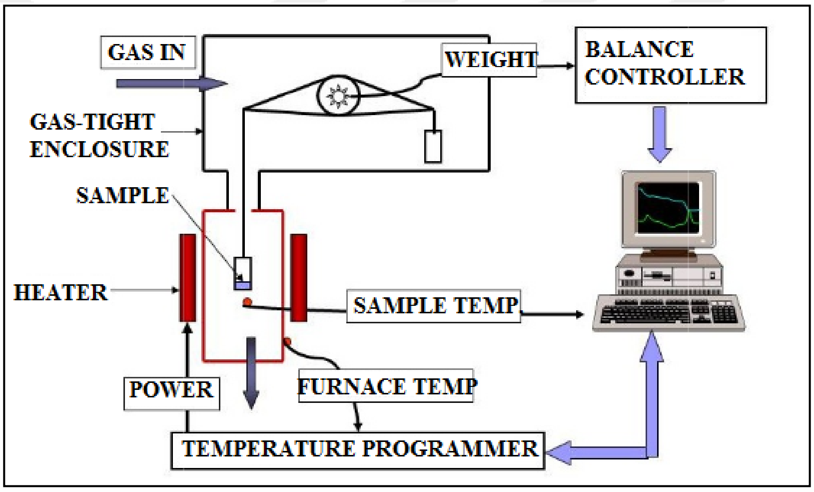


Figure 3.10. Typical arrangements of components of TGA [61].

Thermogravimetric Applications: There are several results those can be derived by using thermal gravimetric analysis, in relation to the basic measurement of mass, temperature and time. One application of TGA may take place in a decomposition reaction, to determine temperature and mass alterations with a quantitative composition analysis, so that water content of the subject material can be detected. Another possible analysis, this method can be applied to is to measure evaporation discharge rates of liquid mixtures. Additionally, by means of TGA method, reactions between air and oxygen or other reactive gases can be measured. As well, there is another use for it, in finding Curie temperatures belonging to magnetic transitions, where the measurement of the particular temperature of sample under the force put to use by a closely positioned magnet gives opposite results when heated or cooled down, as disappearing with the first while reappearing with the latter. Moreover to all, TGA has another supportive use in identifying plastics and organic materials where by way of calculating temperature differences during either bond cutting process of subject material under conditions of inert atmosphere, or oxidation process in air [62].

3.2.7. Scanning Electron Microscopy (SEM)

The scanning electron microscopy (SEM) is referring to a method which uses electron beams to cause interaction with atoms of the sample at various depths. Information like chemical composition, texture, external morphology, position of materials making up the sample and crystalline structure are revealed about the sample to do so, a variety of signals are generated at the very surface of solid specimens and the microscope uses a focused beam of high-energy electrons. By means of signals derived from electron-sample interactions, information about sample is collected. In general, a selected area is picked and collection of data is performed over that part of sample's surface. A 2-dimensional image displaying spatial variations according to above mentioned properties of physical structure of the sample is generated. These images cover areas ranging from approximately 1 cm to 5 microns in width by using conventional SEM techniques in scanning mode. The magnification ability of microscope allows a range from 20X to approximately 30,000X, with a spatial resolution of 50 to 100 nm.

Analyzing selected points located on the sample by using SEM is particularly feasible and preferred in qualitative or semi-quantitative determination of chemical compositions, crystalline structure, and crystal orientations.

Considerable amount of kinetic energy possessed by accelerated electrons in an SEM is dissipated into variant signals produced as a result of electron-sample interactions when the incident electrons decelerated upon the surface of solid sample. There are electrons, photons, light and heat included in these signals; such as , secondary electrons (that produce SEM images), backscattered electrons (BSE), diffracted backscattered electrons (EBSD that are used to determine crystal structures and orientations of minerals), photons (characteristic X-rays those are used in elemental analysis and continuum X-rays), visible light (cathodoluminescence–CL), and heat. The act of imaging samples is provided via secondary electrons and backscattered electrons, at this point secondary electrons are mostly eligible for showing morphology and topography of the surface while backscattered electrons are eligible for depicting contrasts in composition of multiphase samples (i.e. for rapid phase discrimination). There occurs an X-ray generation by means of inelastic collisions between incident electrons and electrons in discrete orbitals (shells) of atoms.

As the excited electrons return to lower energy states, they yield X-rays with a fixed wavelength which is related to difference in energy levels of electrons in different shells for a given element. In this way, in a mineral, for each element that is "excited" by the electron beam, characteristic X-rays are produced. Since SEM analysis is considered to be "non-destructive”, and X-rays generated by way of electron interactions mentioned above do not lead to volume loss for the sample, a repeating analysis on the same material becomes possible. Depending on requirements to be verified together with sample’s nature, sample preparation can both be at minimal scale or elaborate levels in case of applying SEM analysis. To explain, preparation of least possible includes procurement of a sample fitting into the SEM chamber together with some adjustment to avoid electrically insulating samples to be charged. In most cases these type of samples have a thin coating of conducting material, commonly carbon, some metal or alloy or gold, to provide prevention from electric current passing. The choice of material for conductive coatings is not random tough, it depends on the type of data aimed to be obtained, where for example, elemental analysis is a priority carbon is the eligible choice for coating or if the objective is to have a high resolution electron imaging, metal coatings are chosen as the most effective.

Apart from all, there is possibility of examining an electrically insulating sample without a conductive coating if an instrument capable of "low vacuum" operation is used to do so [63]. The basic construction of a scanning electron microscope is depicted in Figure 3.11.

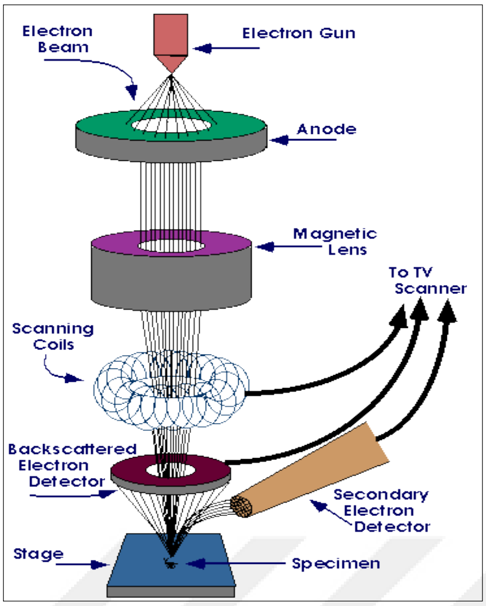


Figure 3.11. Basic construction of a SEM [63].

3.2.8. Fire Retardancy Test

As mentioned in previous chapter, when discussing the fire retardant polymer types there are several industries and commercial products for which being fire retardant is crucial. In this wide range of daily use, from construction products and cables, to textiles and even furniture, testing for fire resistance, flammability, and flame spread can be considered as a must, before any installation or use of these products come into picture [64].

There is a very widely used method of detection for setting the degrees of relative flammability to a polymeric material, and that is called Limiting Oxygen Index Testing (LOI) [65].

This Index (LOI) stands for the ratio of oxygen concentration percentage in a sample polymer, where a small specimen can be thought as a candle, since it will burn downwards in the same manner. Most probably fire retardancy test referring to LOI data is the very popular amongst all other standard ones.

The test aims to check flammability of a tiny sample, by using a small pilot flame in order to determine the minimum oxygen concentration required only to sustain combustion of the sample. In this setting, there is an apparatus holding this small specimen of material. It is clamped vertically in a tube with a controlled atmosphere conditions where the relative concentration of oxygen and nitrogen are possible to be altered. The below formula refers to the consequence of above mentioned setting, where n refers to LOI values;

$$n=\frac{100\times O_2}{O_2+N_2}\% \tag{3.3}$$

The results are put in numerical scale that is simplifying to make comparison between materials. The test has features making it eligible in market, such that being repeatable in multiple times, possibility to be confirming quality checks, and ability of indicating flammability degree of a material. Steady burning conditions can be replicated on a small scale making LOI device one of the few test apparatus of its kind, because when compared to real fire situation where materials with high LOI index values, greater than 21, pass through flaming combustion at oxygen concentrations below 5%, being essentially a small flame test, the high index becomes a sign of a hardly set to fire and almost inflammable material [66].

A Limiting Oxygen Index (LOI) device is shown in Figure 3.12.

Figure 3.12. Limiting Oxygen Index (LOI) Device [66].

4. EXPERIMENTAL STUDY

In this section, experimental procedure to the case study of subject thesis study and devices used all the way through are explained in detail.

4.1. EPOXY EQUIVALENT WEIGHT TITRATION

Epoxide content is commonly expressed as the epoxide equivalent weight (EEW). The EEW is defined as the weight in grams of an epoxy resin containing one mole equivalent of epoxide (g/mol). Therefore, the commercial epoxide NC514 was titrated as per ASTM D1652-11e1 standard test method to determine its respective EEW value. First, 0.4-0.6 grams of epoxy containing resin was added into 10-15 mL methylene chloride (DCM) and it was dissolved in DCM then 10 mL tetraethylamoniumbromide (TAB) and seven drops of crystal violet indicator were added to the same flask, stirred well and titrated against 0.1 N perchloric acid solution to an end point transition from sharp blue to green. After that, the amount of perchloric acid solution used for the titration was recorded and used for further analysis.

Once the amount of perchloric acid used was determined, the epoxy equivalent weight of the resins were calculated using the following equations (4.1) and (4.2) ;

$$E=4.3\times V\times N/W \tag{4.1}$$

$$Eeew=43\times 100/E \tag{4.2}$$

In the above equations, V represents the volume of perchloric acid solution used, N is the normality of perchloric acid solution, W represents weight of the resin titrated, and E_{eew} represents the epoxy equivalent weight. The epoxy equivalent weight of NC514 resin was determined as 399.5 g/mol. Consequently, the calculated molecular weight of epoxy residue was used to determine the amount of methacrylic acid, which shall be used for the methacrylation reaction.

4.2. METHACRYLATION AND PHOSPHORYLATION OF EPOXY CNSL RESIN (NC514VE-PA)

The main objective of this research project is to obtain new fire retardant thermosetting materials from Cashew Nutshell Liquid (CNSL) which is a renewable resource. For this purpose, commercially available CNSL resin, NC514 with approximately two epoxies per molecule was completely or partially methacrylated. The methacrylation reaction was performed to obtain 100%, 90%, 80% and 70% of epoxy groups of the NC514 resin to be methacrylated. Before the reactions, the weight of methacrylic acid was determined using the epoxy equivalent weight of the resin and with mole calculations for fully or partially methacrylated products. Firstly, the number of moles of epoxies of NC514 resin was calculated by dividing its weight (specified amount) to its epoxy equivalent weight (399.5 g/mol) which was determined from epoxy equivalent weight titration. Secondly, by using the mole number of epoxies of NC514, mole of methacrylic acid and its weight was calculated. Then, methacrylation reaction was carried out in the presence of 1wt% DABCO catalyst and 0.1wt% hydroquinone radical inhibitor for 6 hours at 90^{o}C. After the methacrylation reaction, partially methacrylated resin (NC514VE) was reacted with phosphoric acid with different mole ratios %10, %20 and %30 to phosphorylate the remaining epoxy groups. Following the fourth step partially methacrylated epoxy resin is weighted and its mole value is calculated by using the related epoxy equivalent weight value. The next step, this mole value has been taken and mole of phosphoric acid is calculated again due to the percentage of free epoxy. As the last step, phosphoric acid weight and required volume is found. The designations of the resins prepared and their phosphoric acid content can be seen in Table 4.1. For the phosphorylation reaction, partially methacrylated resin (NC514VE) was completely dissolved in pure acetone then calculated amount of phosphoric acid was added into the mixture drop by drop. This phosphorylation reaction was performed in an ice bath for 3 hours at 0^{o}C temperature. After the reaction, acetone was removed by using a rotary evaporator. The methacrylated and phosphorylated Epoxy CNSL Resin NC514 (NC514VE-PA) was obtained as a yellowish viscous liquid.

Table 4.1. NC514VE and NC514VE-PA samples with different methacrylic acid and phosphoric acid content

Polymer	Mole percentage of epoxies of NC514 phosphorylated
NC514VE	0
NC514VE-10PA	10
NC514VE-20PA	20
NC514VE-30PA	30

Schematic representations of methacrylation and phosphorylation reactions of epoxy CNSL resin (NC514)   are shown in Figure 4.1.

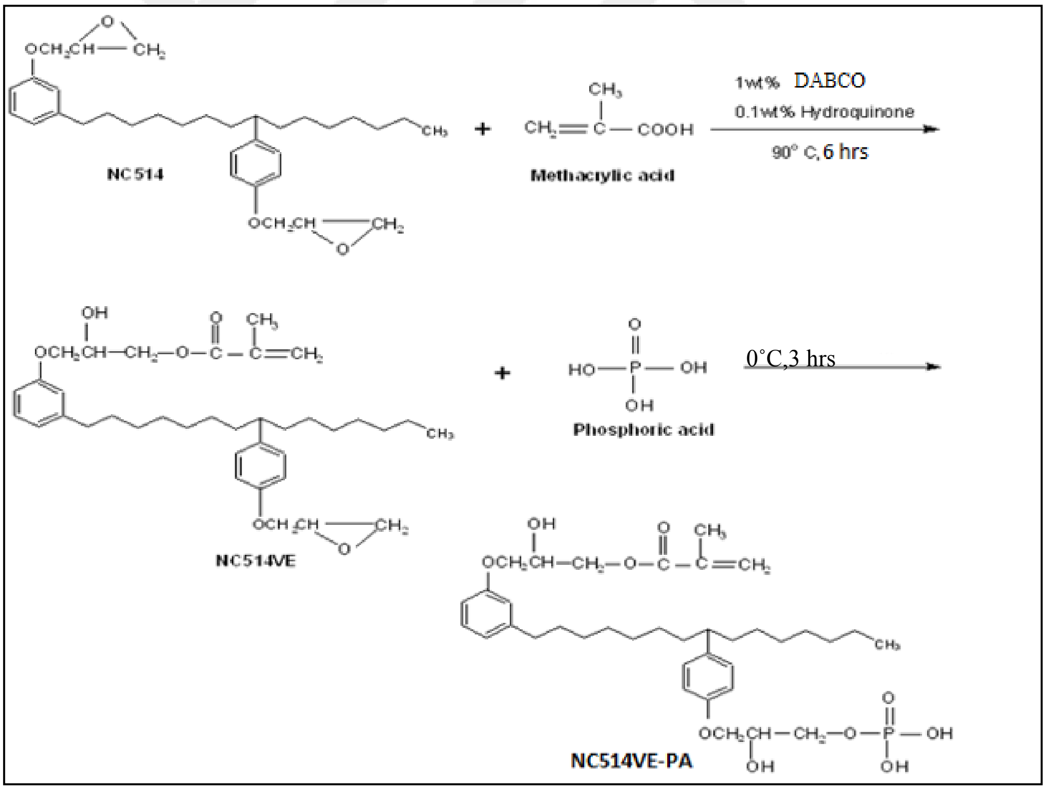


Figure 4.1. Methacrylation and phosphorylation reactions of epoxy CNSL resin (NC514).

Final part of the experiment has been the curing process. Before the curing process, modified resins were diluted with styrene. Thus, styrene was added individually as the reactive diluent to the di-functional vinyl ester resin of NC514VE and NC514VE-PA at reactive diluent compositions of 30, 40 and 50wt%. At this point, %1 tert-butyl peroxy benzoate initiator was added into the mixture and a thermal cure cycle was applied. These modified resins were analyzed with different methods. Prior to all, methacrylated and phosphorylated samples were characterized using ^{1}H-NMR and ATR spectroscopic methods and acid number was determined. Resin viscosity was measured with a rheometer. Then, curing procedure which is explained at the following part, was applied to all modified resins (NC514VE and NC514VE-PA).

Afterwards, cured resins were examined; for their cure characteristics and thermal transitions via DSC, for their thermal stability via TGA, and for their thermo-mechanical properties by using DMA methods.

4.3. ACID NUMBER TITRATION

Acid number titration was used to measure the amount of unreacted (free) acid in the reaction mixture during the methacrylation of the epoxy resin. Approximately 1g of the resin was taken from the vinyl ester (VE) reaction mixture, and it was dissolved in 5 ml acetone. Then, three drops phenolphthalein were added to the mixture as indicator for determining the neutralization point. After that, the mixture was titrated with 0.5N sodium hydroxide (NaOH) until the solution turned to slightly pink in color, for 30s. To calculate acid number of the vinyl ester (VE) the formula below is used;

$$\text{Acid number}=\frac{V_{NaOH}\times N_{NaOH}\times MW_{NaOH}}{m_{resin}} \tag{4.3}$$

Where V is the volume in milliliters of NaOH solution used, N is the normality of the NaOH solution, and m is the VE mass in grams. Acid number value was determined by using equation (4.3). If the acid number was too high, methacrylation reaction would have been allowed to continue until the acid number were below 10.

4.4. ATTENUATED TOTAL REFLECTION (ATR) SPECTROSCOPIC ANALYSIS

In this study, ATR spectroscopy was used to follow the methacrylation and phosphorylation reactions of the epoxy resin NC514. For this purpose, IS50 FT-IR instrument which is shown in Figure 4.2 was used to analyze the chemical structures of the NC514VE and NC514VE-10,20,30 PA resins. Resins placed in transparent sample cells were scanned in the 4000-400 cm^{-1} wavelength region. Before each sample analysis, a background scan was taken from air. Resin samples were put on the IR beam path and data was collected immediately. OMNIC software was used in analysis of the data. This ATR technique is especially useful for liquid samples since no sample preparation procedure is necessary.

Figure 4.2. IS50 FT-IR Device

4.5. PROTON NUCLEAR MAGNETIC RESONANCE (^{1}H-NMR) SPECTROSCOPIC ANALYSIS

Proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy measurements were implemented to detect the final structures of the vinyl esters of NC514VE, NC514VE (%10 mol PA), NC514VE (%20 mol PA), NC514VE (%30 mol PA). Approximately 0.1g of vinyl ester resin dissolved in 1ml $CDCl_3$ was placed into the NMR tube. A Varian Unity

Inova NMR spectrometer with a magnetic field strength of 400 MHz was used in the analysis. A spectral window of 2000 Hz, and a pulse width of 90^o were used, and the digital resolution was 0.427 Hz/pt. All samples were analyzed at 298 K(25˚C).

4.6. VISCOSITY MEASUREMENTS

The viscosity of NC514VE, NC514VE (%10 mol PA), NC514VE (%20 mol PA) and NC514VE (%30 mol PA) resins with various styrene content (30/40/50 STY) was measured by using a Brookfield DV-II +Pro model viscometer, at a sheer rate of 19 s^{-1}(20 RPM) at 25 ˚C. The viscometer used in the measurements is shown in Figure 4.3.

Figure 4.3. Brookfield viscometer device

4.7. CURING PROCESS OF THE RESINS

The methacrylated and phosphorylated NC-514 resins, NC514VE and NC514VE-PA were first mixed with changing amounts of styrene comonomer and stirred for ten minutes. The identification of the styrenated resins and their compositions are listed in Table 4.2. The radical initiator tert-butyl peroxy benzoate (T.B.P.B) (1wt%) was added into the mixture and the mixture was stirred for an additional five minutes more. Following this step, just before the transfer to silicon mold, samples prepared were subjected to nitrogen purge for a while.

Samples with different styrene diluent ratios (30/40/40 STY) were then transferred into a silicon mold which is shown in Figure 4.4. The molded resin was finally placed in an oven and subjected to a high temperature curing process for, in order of writing, 3 hours at 60˚C, 1 hour at 90˚C, 3 hours at 130˚C and finally 2 hours at 160˚C.

Table 4.2. NC514VE/STY and NC514VE-PA/STY samples prepared with different styrene (diluent) concentrations

NC514VE/STY	**Weight percentage of styrene (%)**	**NC515VE-PA/STY**	**Weight percentage of styrene (%)**
70/30	30	70/30	30
60/40	40	60/40	40
50/50	50	50/50	50

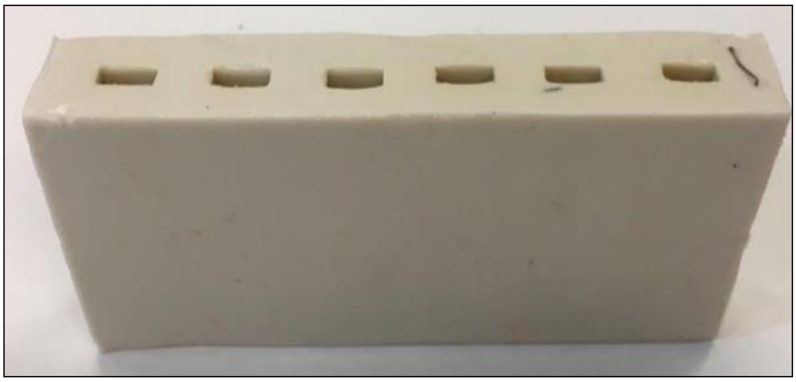


Figure 4.4. Silicon mold used for curing the resins.

At the end of the curing process, samples were taken from the silicon mold and polished to obtain completely uniform and smooth ones. All the silicon molds used had standard rectangular sizes of 25x10x3mm which are suitable for single cantilever measurement method of dynamic mechanical analysis (DMA).

4.8. DIFFERENTIAL SCANNING CALORIMETRY (DSC) MEASUREMENTS

A SETARAM Instruments DSC 131 was used to investigate curing temperatures of the prepared resins as well as to examine the thermal transitions of fully cured resins. Roughly 8-10 mg sample was weighed and placed into the sample pan; the empty reference pan was also prepared next to it. These two samples were located into the furnace of DSC instrument where continuous flow of nitrogen gas was fed to keep the environment inert. The neat resins and fully cured resins were heated from 25^{o}C to 250^{o}C with 5^{o}C/min heating rate. At this stage of the process, heat flow versus temperature plots were constructed and analyzed.

4.9. DYNAMIC MECHANICAL ANALYSIS (DMA) MEASUREMENTS

In this study, thermo-mechanical features of all cured resins with various compositions were investigated via Dynamic Mechanical Analysis (DMA). Samples cured in rectangular silicon molds were obtained as uniform rectangular bars with approximate dimensions of 25 mm x 10mm x 3mm (Figure 4.5.).

These samples were tested in a single frequency mode (1Hz) using a single cantilever clamp with a temperature ramp from -120 to 150^{o}C at a heating rate of 5 ^{o}C /min on a TAQ 800 Dynamic Mechanical Analyzer (TA Instruments LLC). Samples were cooled by feeding the furnace of the DMA continuously with liquid nitrogen, during the cooling process.

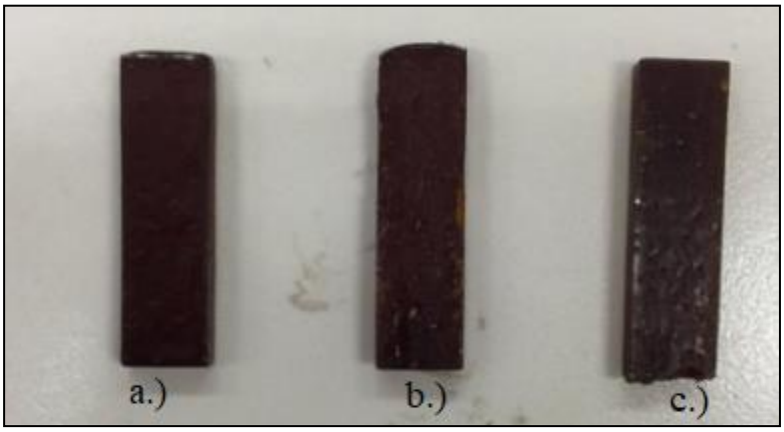


Figure 4.5. a) NC514VE/STY ,b) NC514VE-10PA/STY and c) NC514VE-20PA/STY samples used for DMA

By means of TA instruments Universal Analysis software use, storage modulus (MPa), loss modulus (MPa) vs. temperature plots were obtained ,as measurements are being processed. The glass transition value of the sample deemed to be the temperature that gave a peak value observed in the loss modulus curve. The theory of rubber elasticity was used to reckon the cross-link density (*v*), which is the average number of cross-links for every volume unit.

This calculation was achieved by use of modulus in the rubbery plateau region (*E)* as it can be seen in reference equation (Eq. 4.4):

$$E = 3vRT \tag{4.4}$$

where *R* is referring to the ideal value for gas constant, while *T* is standing for the absolute temperature [67].

4.10. THERMAL GRAVIMETRIC ANALYSIS (TGA) MEASUREMENTS

A PERKIN ELMER Instrument Pyris 1 TGA was used to detect the degradation profiles of NC514VE/STY and NC514VE-PA/STY resins which were fully cured. Before each measurement, balance of TGA instrument was calibrated with an empty sample pan to get accurate results. Roughly, 8-10mg resin was transferred into a platinum sample pan of

TGA where it was introduced into the furnace of the device with an auto sampler. In the sampler, continuous nitrogen gas was supplied to keep the environment inert.

A temperature ramp from 30^oC to 800^oC with 10^oC/min increments was applied to samples to obtain percentage mass degradation versus temperature plot of the sample during the experiment.

4.11. SCANNING ELECTRON MICROSCOPY (SEM) ANALYSIS

In this work, a ZEISS EVO 40M Instrument was used to investigate the morphology of fractured surfaces of the cured vinyl ester resin samples: NC514VE, NC514VE-PA with %30,40% ,%50 styrene. Before the SEM analysis, all samples were coated with Gold for approximately 45 seconds. Thicknesses of the Gold coating was approximately 15 nm.

4.12. FIRE RETARDANCY TEST

The Limiting Oxygen Index Test (LOI) which is the most commonly used method for determining the flammability of polymeric materials could not be carried out in this study because of economic restrictions to the project. However, to see the effect of the phosphorylation modification on the flammability of the NC514VE resin, a simple test was performed in our laboratory. In this test, the samples were exposed to a candle flame under the same conditions and the deflagration time for each resin was recorded.

5. RESULTS AND DISCUSSION

5.1. SYNTHESIS OF VINYL AND PHOSPHATE ESTERS OF THE CNSL RESIN (NC514VE AND NC514VE-PA)

The required methacrylic acid amount for the methacrylation reactions of the NC514 resin was calculated using the epoxy equivalent weight value of the NC514 resin (399.5 g/mol), determined by using the ASTM D1652-11e1 standard test method. This number was utilized as molecular weight of the epoxy residue to determine the amount of methacrylic acid to methacrylate the desired mole percentage of the epoxy groups.

Thus for this purpose to provide methacrylation of the CNSL resin ,NC514 was reacted with methacrylic, in an epoxy to methacrylic acid molar ratio of 1:1,1:0.9,1:0,8,1:0,7 in the presence of 1wt% DABCO catalyst and 0.1wt% hydroquinone radical inhibitor, for a duration of 6 hours at 90^{o}C. As the reaction between the epoxy groups and methacrylic acid took place, a decrease in the acid number of the reaction mixture has been monitored. Therefore, the acid number titration was carried out every hour during the reaction and the amount of free (unreacted) acid in the reaction mixture was followed. Anything below the acid number value of 10 was accepted as complete reaction [68]. The acid numbers determined during the methacrylation reactions are shown in Table 5.1. So, at the end of the reaction time, the methacrylated NC514 resin; NC514VE was obtained.

In the next step, partially methacrylated resin (NC514VE) was reacted with phosphoric acid with different mole ratios of %10, %20 and %30 of the epoxy content. Phosphorylation reaction was performed in an ice bath medium for 3 hours at 0^{o}C. The obtained resins were further characterized for their chemical structure and physical properties.

Table 5.1. Acid number values determined by titration during the methacrylation reactions

Methacrylated Epoxy Resin	Acid Numbers Determined During the Reaction					
	1 hour	2 hour	3 hour	4 hour	5 hour	6 hour
NC514VE(%100MA)	80	43	30	18	13	9
NC514VE(%90MA)	60	42	30	20	15	8
NC514VE(%80MA)	60	42	30	20	15	8
NC514VE(%70MA)	45	30	23	16	12	9

5.2. FT-IR SPECTROSCOPIC ANALYSIS OF VINYL AND PHOSPHATE ESTERS OF THE CNSL RESINS (NC514VE AND NC514VE-PA)

The methacrylation and phosphorylation reactions of NC514 resins were monitored using FT-IR Spectroscopy. Figure 5.1 shows the FT-IR spectra of the one hundred percent methacrylated (%100) and the partially methacrylated and phosphorylated epoxy resins, NC514VE and NC514VE-30PA respectively.

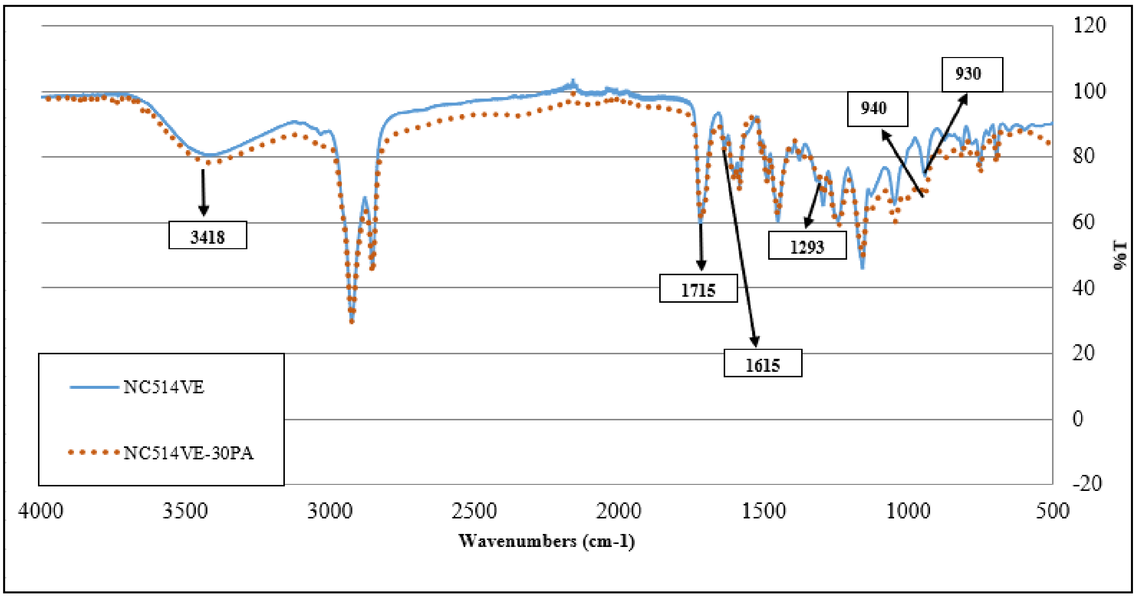


Figure 5.1. FT-IR spectra of NC514VE(%100MA) and NC514VE%30PA resins.

The spectrum of NC514VE resin exhibited the characteristic peaks associated with its functional groups: the peak at 930 cm^{-1} was related to the out of plane bending vibrations of the methacrylate vinyl groups, the peak at 1715 cm^{-1} showed methacrylate ester carbonyl and the peak at 1615 cm^{-1} showed the methacrylate vinyl group ; C=C stretching vibrations. These peak values are references to the findings of E.Kınacı's study [38] which indicates that the synthesis of the NC514VE was successfully achieved in alignment with his results.

When the FT-IR spectrum of the NC514VE-30PA was compared to that of NC514VE majority of the peaks matched. However, NC514VE-30PA exhibited some unique peaks, such as the peak at 940 cm^{-1} that represents the stretching vibrations of the P-O-C group. In addition, the peak at 1293 cm^{-1} corresponds to a stretching vibration of the P=O bond. The broad peak at around 3418 cm^{-1} represents a stretching vibration of C-OH bond present in both structures. These values matched the related FT-IR data in literature. Other samples with different degrees of phosphorylation, NC514VE-10PA and NC514VE-20PA, exhibited similar characteristic peaks as NC514VE-30PA and therefore are not shown in Figure 5.1. Hence, according to literature data, the phosphorylation reaction of the NC514VE resins were achieved successfully [47].

5.3. ^{1}H-NMR SPECTROSCOPIC ANALYSIS OF VINYL AND PHOSPHATE ESTERS OF THE CNSL RESINS (NC514VE AND NC514VE-PA)

The ^{1}H-NMR spectra of NC514VE and NC514VE-PA resins are shown in the Figure 5.2 and 5.3 respectively. The chemical structures of the resins and the corresponding peak assignments for the different types of protons are also depicted in these figures.

In Figure 5.2, in addition to the peaks associated with the NC514 backbone structure, NC514VE structure has methacrylate end groups and this groups gave those two separate peaks at 5.60 ppm and 6.20 ppm that refer to two methylene protons of the ($CH_2=C(CH_3)$) group and the peak at 2.00 ppm that relates to the methyl protons (CH_3-) of the methacrylate functional group. The tertiary –CH- proton (-CH(OH)-) of the (phenyl-OCH_2-CH-(OH)-CH_2O-(C=O)-) part and (-OCH_2-) protons gave multiple peaks in the 4.00-4.60 ppm region. These values are in accordance with E.Kınacı et.al's work[38].

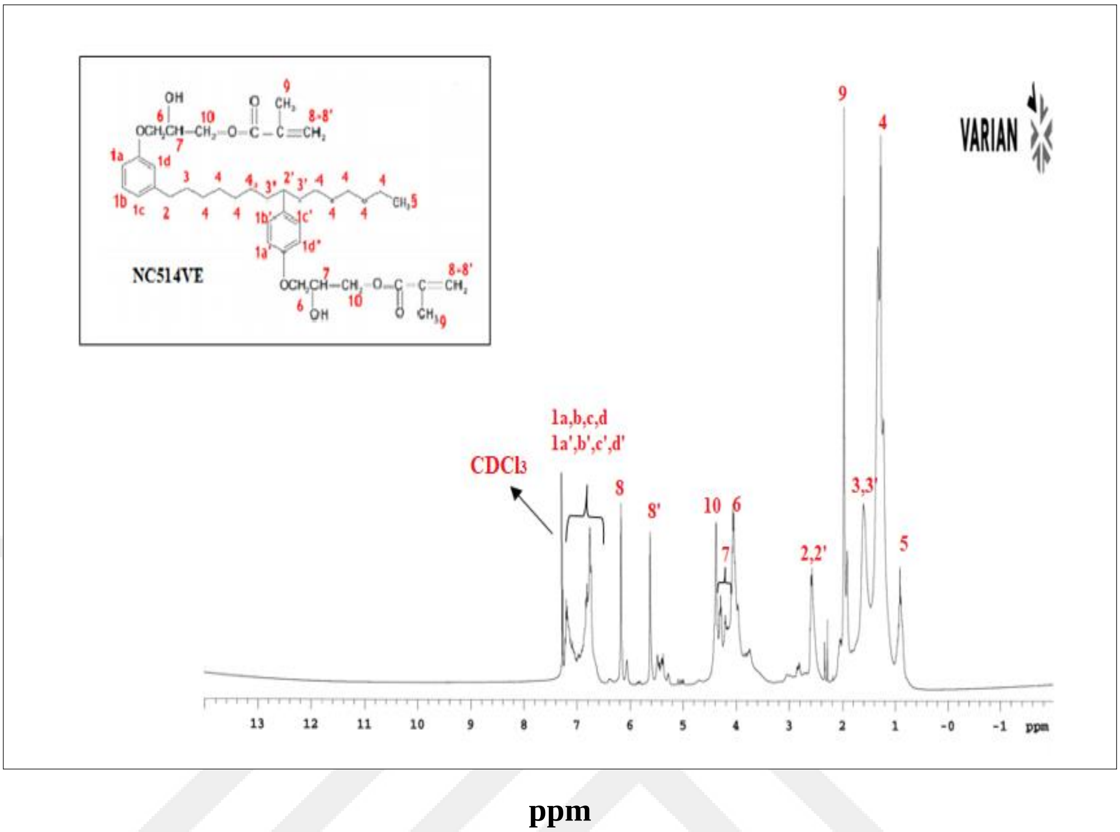


Figure 5.2. ^{1}H NMR spectrum of the NC514VE resin

As can be seen in Figure 5.3, NC514VE%20PA has a similar structure to that of NC514VE%100MA with the exception of the attached phosphate group. Therefore, similar peaks as those observed for NC514VE%100MA are also present in this spectrum. The major difference is that the phosphate ester of the epoxy group gave new peaks at 4.40 ppm and 2.30ppm associated with the proton of CH-O-P group (10) and the P-O-H protons (11) respectively. These findings are also in accordance with literature data [69]. In addition, the NC514VE%10PA and %30 PA resins gave similar ^{1}H NMR spectra as that of the NC514VE%20PA resin.

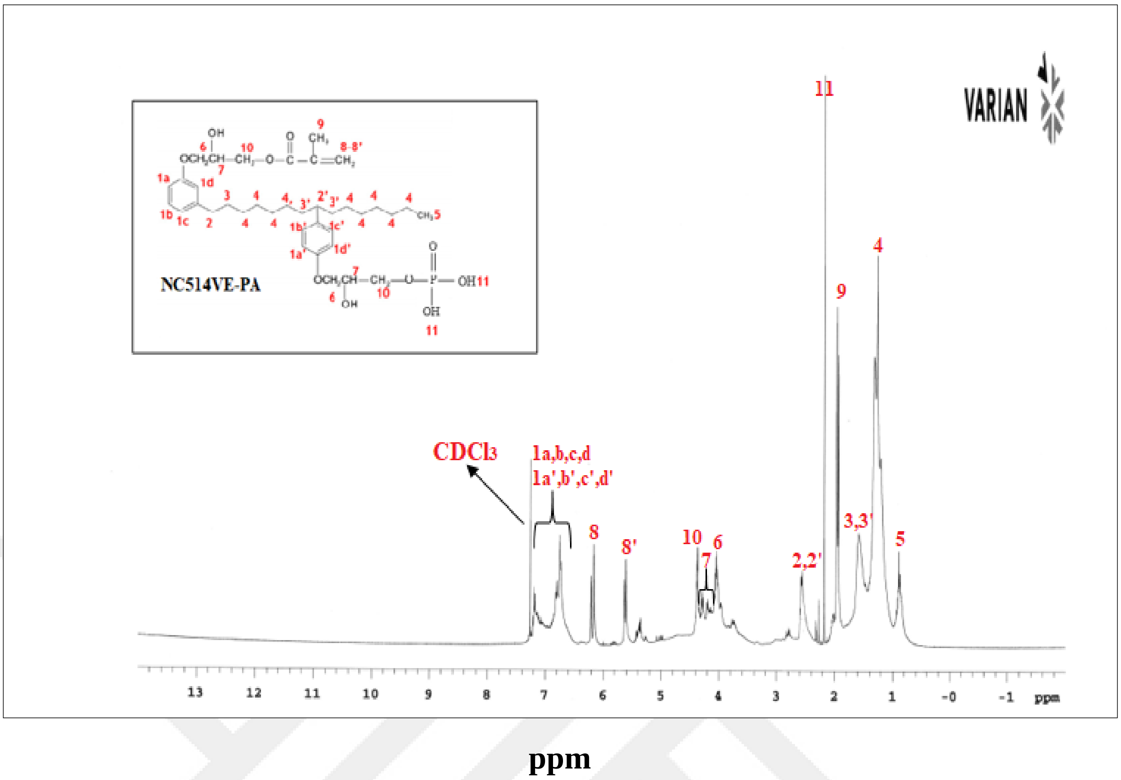


Figure 5.3. ^{1}H NMR spectrum of the NC514VE-20PAresin

The average number of methacrylate functionality of the NC514VE and NC51VE-PA units were calculated using ^{1}H NMR data, by the following equation (Eq.5.1):

$$F = \frac{(I_8+I_{8'})}{(I_5)} \times \frac{\text{terminal methyl protons of side chain}}{\text{methylene protons of methacrylate group}} = \frac{(I_8+I_{8'})}{(I_5)} \times \frac{3}{2} \tag{5.1}$$

I_8 and $I_{8'}$ =integration of the peaks of methylene protons of methacrylate end group

I_5=integration of the peaks of terminal methyl protons of the aliphatic side chain

The calculated methacrylate functionalities are shown in the Table 5.2. According to data in this table, as the methacrylic acid used in the methacrylation reaction decreased the corresponding methacrylate functionality also decreased as expected. The methacrylate functionality of the NC514VE(100%MA) resin was found as 1.48. The epoxy functionality of the NC514 resin was approximately 1.55 (as calculated from the epoxy equivalent weight value).

There are oligomeric species and low molecular weight derivatives in NC514 as reported by Jaillet F. et al [70] which explains an epoxy functionality lower than 2 for NC514. Thus 95.5% of epoxy groups of NC514 were converted to methacrylate for the NC514VE100%MA resin, and 78.7%, 69.1% and 65.8% of epoxy groups were converted to methacrylate's for the NC514VE90%MA10%PA, 80%MA20%PA and 70%MA30%PA resins respectively. Although the methacrylate functionality of the phosphate esterified resins approached 1, as the phosphate ester hydroxyls (2 hydroxyls for each phosphate group) also condense at the high temperature cure cycle, the real functionality of the methacrylate and phosphate ester of the NC514 resins was higher than 1 and these molecules can act as crosslinker units when polymerized with styrene.

Table 5.2. Methacrylate functionality of the synthesized resins

Resin	**Methacrylate Functionality (F)**
NC514VE %100MA	1.48
NC514VE90%MA10%PA	1.22
NC514VE80%MA20%PA	1.07
NC514VE70%MA30%PA	1.02

5.4. VISCOSITY OF STYRENATED NC514VE AND NC514VE-PA RESINS

The viscosities of NC514VE/STY and NC514VE-PA/STY resins were measured at 20 rpm at 25^0 C. These values are shown in Table 5.3. In this table it is clearly visible that while the styrene content increases, viscosity of the resins decreases as styrene is a low viscosity(0.7cP) reactive diluent in the system. In addition, when the phosphoric acid content increases, viscosity of the samples also increases. This result is also expected as phosphate ester groups with free hydroxyls can make intermolecular hydrogen bonds increasing the viscosity of the system.

Table 5.3. Viscosities of the NC154VE/STY and NC514VE-PA/STY resins measured at 20 rpm at 25^0 C

Resin	**(%30STY)** **η(cP)**	**(%40)STY** **η(cP)**	**(%50)STY** **η(cP)**
NC514VE(100%MA)	650	250	120
NC514VE90%MA10%PA	1068	480	380
NC514VE80%MA20%PA	1100	1040	810
NC514VE70%MA30%PA	**18050**	**2400**	1078

The viscosity of a liquid molding resin must be below 2000 cP to provide processability at room temperature. Here the increase of styrene content significantly decreased the viscosity of the NC514VE-PA resins. The viscosities of the NC514VE-PA/STY resins with 10 and 20 mol% PA were all below 2000 cP which is the upper limit for most liquid molding operations. The viscosities of the NC514VE-30PA/%30STY and %40STY resins were higher than 2000 cP. These samples are not suitable to be used in molding operations at room temperature, and additionally, samples with phosphate functionality can not be heated to reduce the viscosity since these phosphorylated resins undergo gelation when heated which is believed to occur due to intermolecular reactions through phosphate groups. Thus, when only viscosity data is considered, with the exception of the NC514VE-30PA/%30STY and %40STY resins, all other NC514VE/STY and NC514VE-PA/STY compositions listed in Table 5.3 are appropriate for liquid molding operations at room temperature.

5.5. DIFFERENTIAL SCANNING CALORIMETRIC (DSC) ANALYSIS OF THE NC514VE AND NC514VE-PA RESINS

In this part, first differential scanning calorimetric (DSC) analysis of cure reaction of NC514VE and NC514VE-PA resins are discussed. Then, in the preceding part, differential scanning calorimetric (DSC) analysis of the cured resins is presented.

5.5.1. Differential Scanning Calorimetric (DSC) Analysis of Cure Reaction of NC514VE and NC514VE-PA

The curing behaviors of the NC514VE/STY(70/30) and NC514VE-10,20,30PA/STY(70/30) resins were analyzed by means of DSC. Figure 5.4 shows the dynamic DSC scans of the NC514VE/STY(70/30) and NC514VE-10,20,30PA/STY(70/30) resins in the presence of the initiator at a heating rate of 10^{o}C/ min from 30^{o}C to 200^{o}C. In addition, the peak temperature which represents the cure temperature (T_P) and the total heat of cure reaction (ΔH) as obtained from the DSC analysis are listed in Table 5.4.

Both figure 5.4 and table 5.4 indicate that the heat of the cure reaction decreases as methacrylate functionality of the resins decreases from 100%MA0%PA resin to 70%MA30% PA resin as expected. In addition, the temperatures of maximum cure also increases with increasing phosphate content of the resins as compared to the NC514VE/STY(70/30) resin. This result can also be attributed to the decreasing methacrylate functionality of the resins with increasing phosphate content and possibly due to the inhibiting effects of phosphate hydroxyls on radical polymerization. In Kınacı et al’s work [38] two peak exotherms were observed for the cure reaction of the NC514VE/STY(70/30) resin and the second peak was attributed to styrene homo-polymerization. However in our study the NC514VE/STY(70/30) and NC514VE-PA/STY(70/30) resins exhibited only one cure exotherm and styrene homo-polymerization was not detected for these samples.

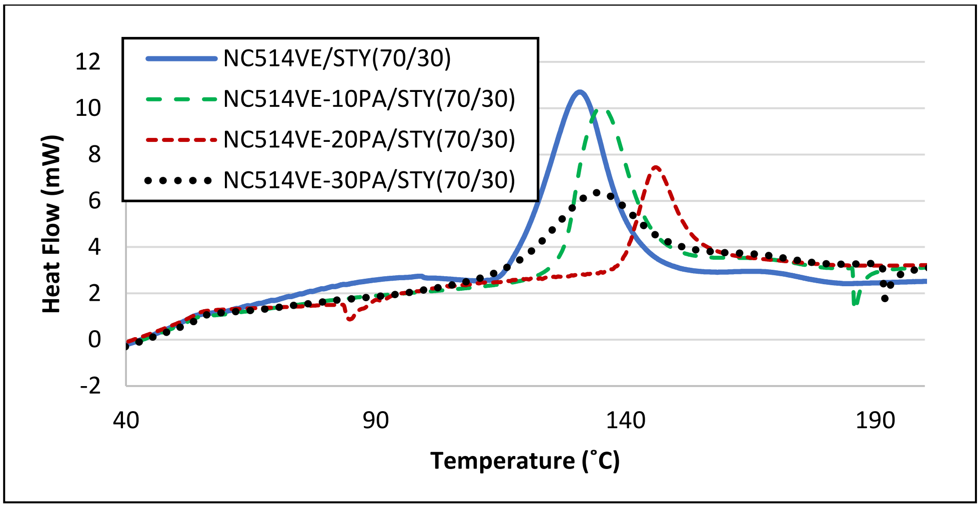


Figure 5.4. DSC analysis of cure reaction of epoxy resins

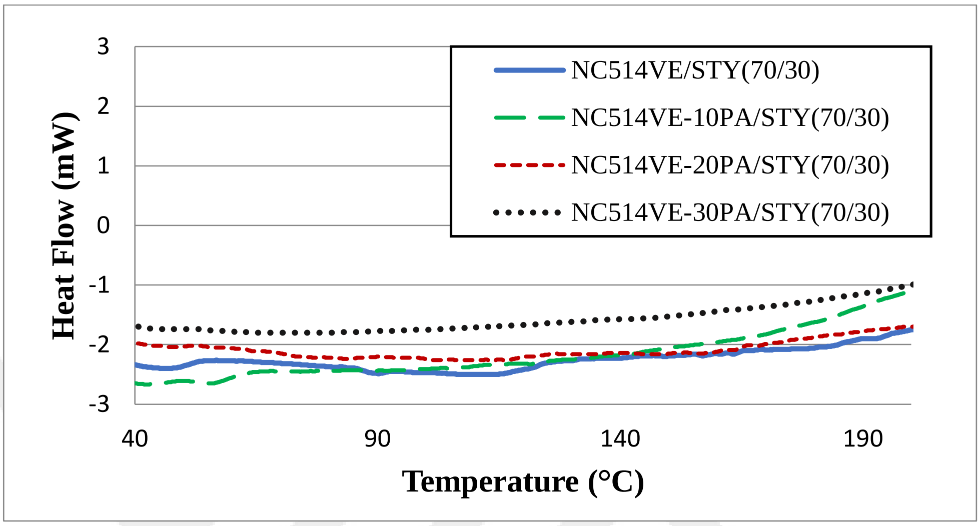
Table 5.4. Results of DSC Analysis of the cure of NC514VE/STY and NC514VE/PA/STY resins

Resin	**Temperatures of the cure maximum (Tpeak)(˚C)**	**Heat of cure reaction (ΔH) (J/g)**
NC514VE(70/30STY)	130.8	184.3
NC514VE-10PA(70/30STY)	135.2	141.3
NC514VE-20PA(70/30STY)	146.1	89.9
NC514VE-30PA(70/30STY)	134.6	85.3

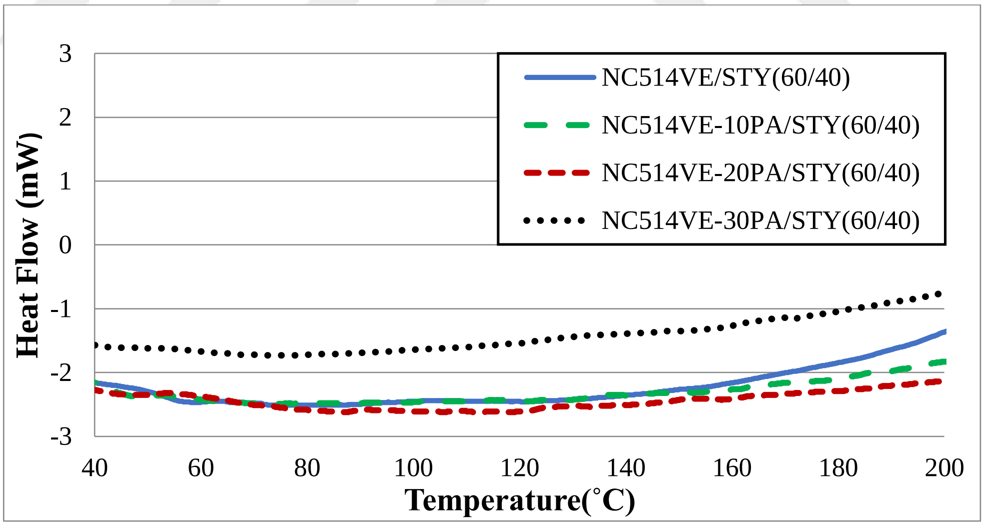
5.5.2. Differential Scanning Calorimetric (DSC) Analysis of Cured NC514VE and NC514VE-PA Resins

In this part, before the DSC analysis, curing process was applied to all methacrylated and phosphorylated resins. So, all resins were diluted in styrene and mixed homogeneously, then %1 T.B.P.B initiator was added into the resin-styrene mixture and cure process was carried out as resins were kept for 3 hours at 60˚C, 1 hour at 90˚C, 3 hours at 130˚C and finally for 2 hours at 160˚C in an oven. DSC scans of the cured samples from 30^{o}C to

200°C at a heating rate of 10°C/ min were performed to examine if the prepared polymer samples were fully cured or not. Thus Figure 5.5 shows the DSC thermograms of the cured NC514VE and NC514VE-PA resins with 30,40 and 50wt% styrene content.



(a)



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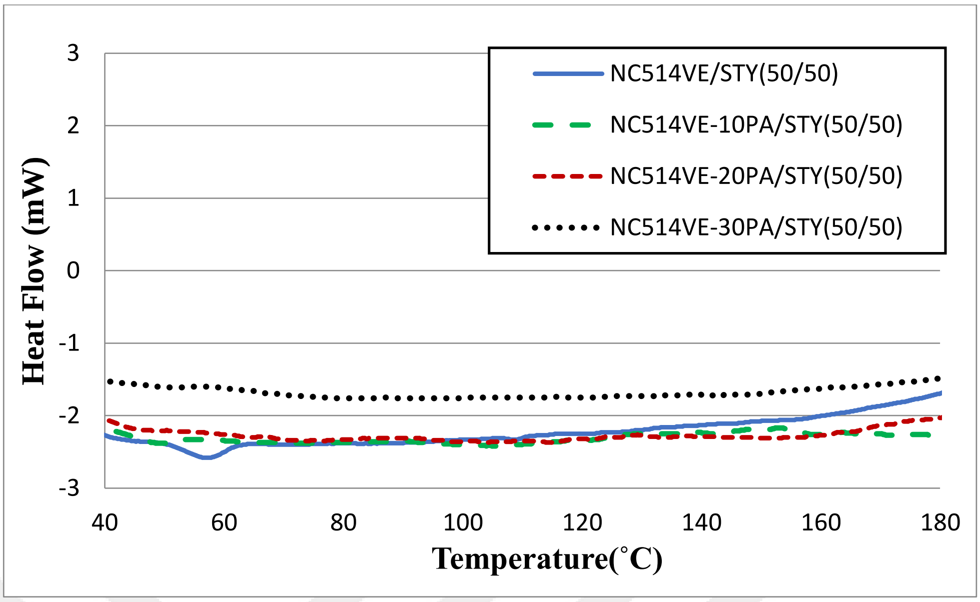


(c)

Figure 5.5. DSC analysis of the cured resins a) comparison of NC514VE/STY-NC514VE-PA/STY(70/30) b) comparison of NC514VE/STY-NC514VE-PA/STY(60/40) c) comparison of NC514VE/STY-NC514VE-PA/STY(50/50)

The DSC thermograms presented in Figure 5.5 display no exothermic peak that stands for a post-cure reaction. Since, for fully cured samples, any kind of transition (primary, secondary transitions etc.) should not have been observed because of their highly cross-linked structure, these samples were totally cured under the applied curing conditions.

5.6. THERMAL GRAVIMETRIC ANALYSIS (TGA) OF THE CURED NC514VE AND NC514VE-PA RESINS

In this section, fully cured resins were examined via Thermal Gravimetric Analysis (TGA). TGA analysis gives information about the degradation profiles and thermal stability. According to literature survey, thermal stability is especially important for the polymeric material that is used as a flame retardant. Figure 5.6. presents the TGA analysis of the cured NC514VE/STY and NC514VE-PA/STY(70/30) resins. As can be seen both NC514VE/STY and NC514VE-PA/STY resins exhibit a one stage degradation profile.

According to Figure 5.6, initial minor weight loss of NC514VE/STY(70/30) resin started at approximately 242˚C and for the NC514VE-10,20,30PA/STY(70/30) samples the initial weight loss started at approximately 210-240˚C. These values were lower than that of NC514VE/STY(70/30) sample.

In decomposition process, NC514VE-10,20,30PA/STY(70/30) resins decomposed faster than NC514VE/STY(70/30) resin due to lower thermal stability of the phosphate groups. The reduction of initial degradation temperature represented the fact that P-O-C is less stable than the usual C-C bond [71]. Next, the major weight loss showing the main degradation of the network started at around 365 ˚C for the NC514VE/STY(70/30) resin and the main degradation temperature shifted to lower temperatures as PA content increased (350 - 325 ˚C). However the phosphorylated resins did not exhibit a significant weight loss and were stable up to this temperature range. Moreover, the decomposition of phosphate groups creates a big advantage for the formation of the compact char residue, which preserves the sample from further decomposition. Therefore, after the decomposition process NC514VE/STY (70/30) sample was nearly fully consumed at 780 ˚C. However, the char residue at 780˚C was about 10-12 wt% for the NC514VE-10,20,30PA (70/30STY) samples which contained phosphate groups.

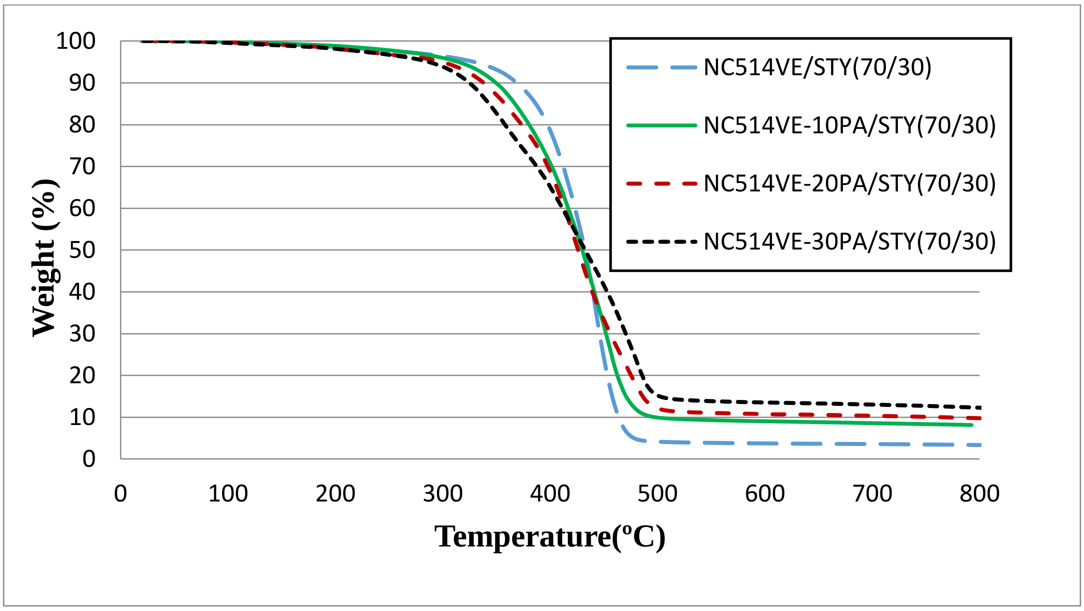


Figure 5.6. TGA analysis of the cured NC514VE/STY and NC514VE-PA/STY(70/30) resins.

Figure 5.7. shows the TGA analysis of the cured NC514VE/STY and NC514VE-PA/STY(60/40) resins. According to Figure 5.7, the initial minor weight loss of the NC514VE/STY(60/40) resin stated at approximately 260˚C and at around 220-245˚C for the NC514VE-10,20,30PA/STY(60/40) samples. Again the phosphorylated resins degraded faster than the completely methacrylated resin NC514VE. The reason was the lower thermal stability of phosphate groups which was mentioned previously. The main weight loss showing the polymer network degradation on the hand stated at around 360 ˚C for the NC514VE/STY (60/40) resin and at around 329-332 ˚C for the NC514VE-PA/STY (60/40) samples. In addition the char residue in the 500-800 ˚C region increased ,with increasing phosphate content of the resins. After the decomposition process, the NC514VE/STY(60/40) sample was fully consumed at 786 ˚C. However, the char residue for the NC514VE-10,20,30PA/STY(60/40) resins were about 12-13 wt% at 786 ˚C.

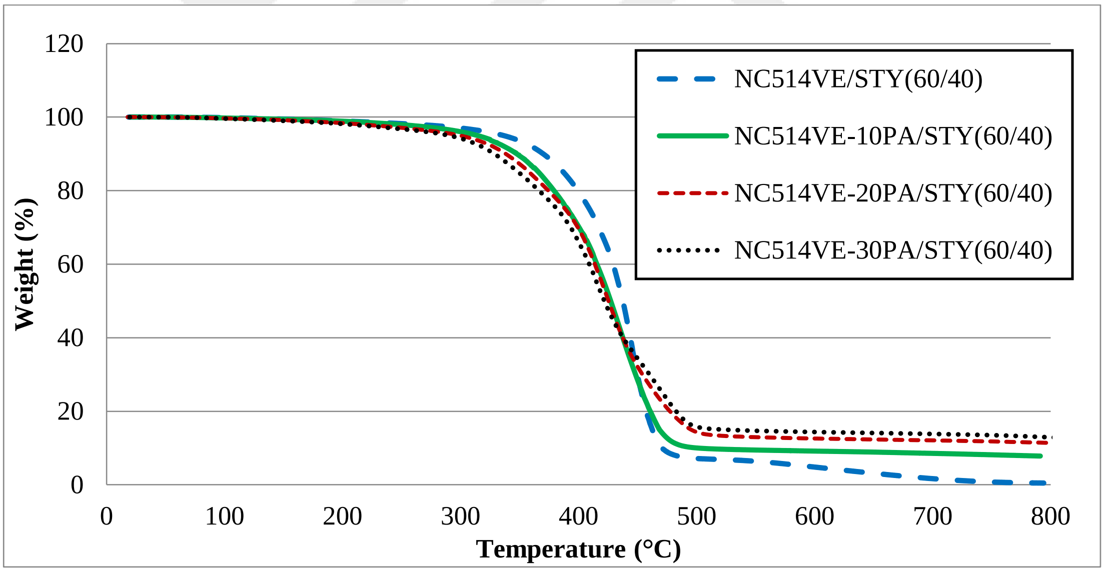


Figure 5.7. TGA analysis of cured NC514VE/STY and NC514VE-PA/STY(60/40) resins

Figure 5.8 shows the TGA analysis of cured NC514VE/STY and NC514VE-PA/STY(50/50) resins. Similar trends were observed for these series of samples. The major network degradation started at around 336 ˚C for the NC514VE/STY(50/50) sample and at around 318 ˚C to 320 ˚C for the NC514VE-PA/STY(50/50) samples. So the phosphorylated resins did not exhibit significant weight loss and were stable up to this temperature region. Finally, after decomposition process the NC514VE/STY(50/50) sample was fully consumed at 778 ˚C. However, the char residue for the NC514VE-10,20,30PA/STY(50/50) samples containing phosphate groups in their structure, was 10-12 wt% at 778 ˚C. Remaining char residue again increased with increasing phosphate content of the resins.

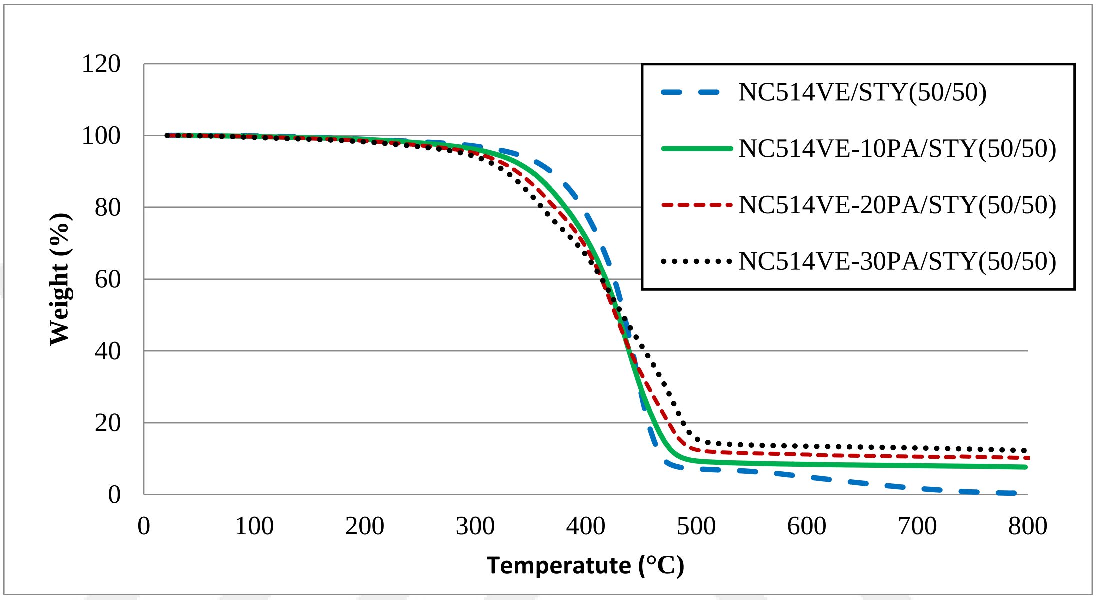


Figure 5.8. TGA analysis of cured NC514VE/STY and NC514VE-PA/STY(50/50) resins.

Figure 5.9 shows the derivative weight percentage vs. temperature plots of the fully cured NC514VE/STY(70/30) and NC514VE-PA/STY(70/30) resins. For the NC514VE/STY(70/30) resin the maximum weight loss occurs at around 440 ˚C that stands for the network degradation. The minor peak in the derivative weight % versus temperature plot at the lower temperature can be related to the degradation of the aliphatic side chains [38] or lower molecular weight impurities present in the resin. For the NC514VE-10PA/STY(70/30) resin there seems to be one temperature where major weight loss occurs related to network degradation at around 450 ˚C .

For the NC514VE-20PA/STY(70/30) resin the temperature where major weight loss occurs due to network degradation is observed at around 425 ˚C . For the NC514VE-30PA/STY(70/30) resin on the other hand, the temperature of major weight loss occurs at around 475 ˚C and there is a minor peak at around 350 ˚C that may designate the degradation of the phosphate groups . At lower phosphate contents this minor peak due to phosphate group degradation seems to be invisible

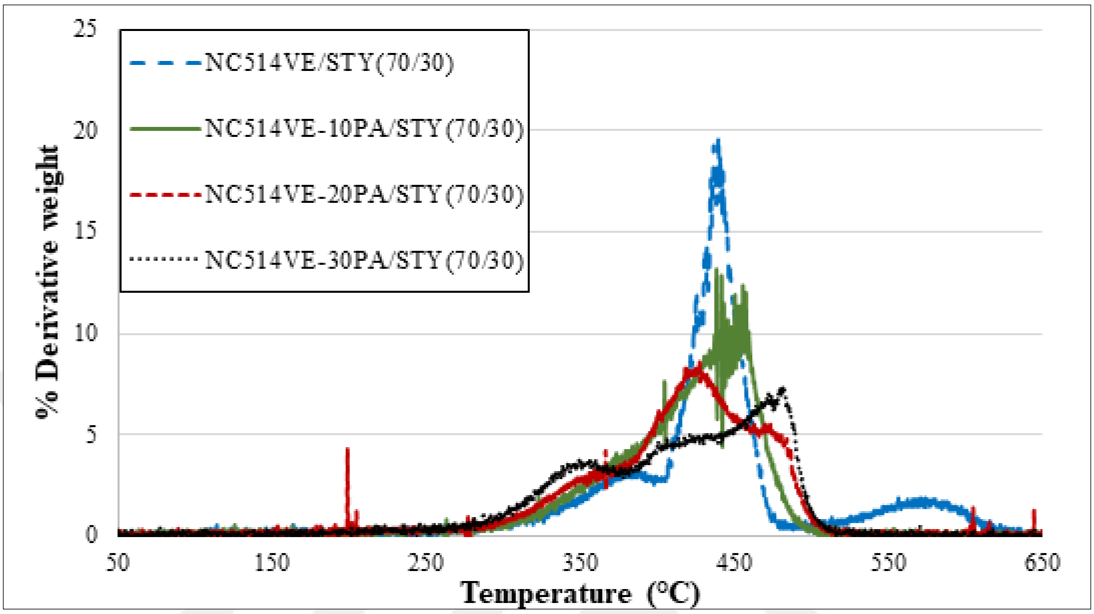


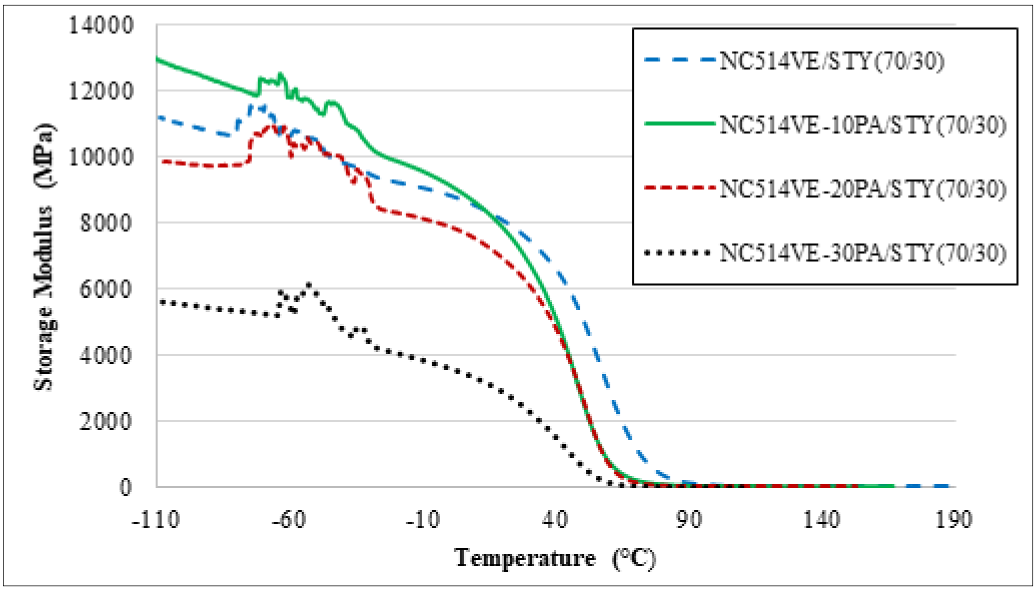
Figure 5.9. Derivative weight percentage vs. temperature plots of the fully cured NC514VE/STY(70/30) and NC514VE-PA/STY(70/30) resins

5.7. DYNAMIC MECHANICAL ANALYSIS (DMA) OF THE CURED NC514VE AND NC514VE-PA RESINS

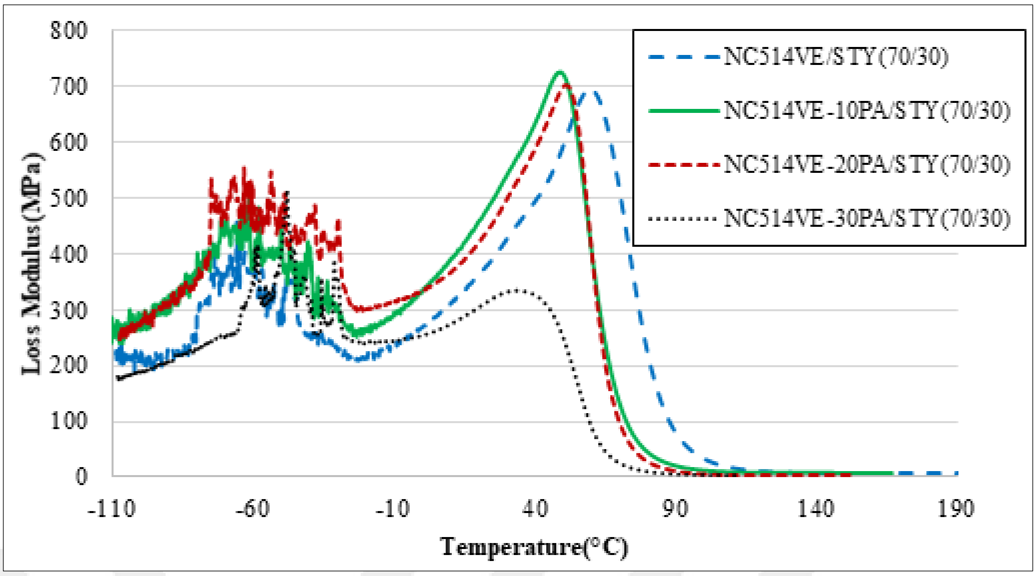
The thermo-mechanical properties of NC514VE and NC514VE-10,20,30 PA resins with different styrene contents were determined by Dynamic Mechanical Analysis (DMA). Storage modulus (E’) and Loss Modulus (E’’) variations with respect to temperature for NC514VE and NC514VE-10,20,30PA resins with 30wt% STY content, NC514VE and NC514VE-10,20,30PA resins with 40wt% STY content and NC514VE and NC514VE-10,20,30PA resins with 50wt% STY contents are shown in Figure.5.10, 5.11 and 5.12 respectively.

In general, phosphorylated samples used in this study have shown variant mechanical property. Such that, while phosphate content has been increased, methacrylate functionality has decreased, which should lead to a decrease in crosslink density of the cured samples. However, condensation reactions must also occur during the high temperature cure cycle through phosphate hydroxyls which should increase the cross-link density. So, these two effects were both considered in explaining the change in storage modulus and Tg of the resins with increasing phosphate content.

An examination of Figure.5.10 indicates that the storage modulus decreases with increasing phosphate content of the resins. According to the figure, the storage modulus values in the glass transition region decreases in the following order NC514VE>NC514VE-10PA> NC514VE-20PA> NC514VE-30PA because, the crosslink density was decreasing with increasing phosphate content. In order to follow the changes in glass transition temperature (Tg) for different compositions, the loss modulus peak temperature was taken as the Tg of the polymer tested [38]. Figure.5.10 shows that the Tg of the resins generally decreases with increasing phosphate content again due to the decrease in cross-link density. Glass transition temperature (Tg) decreases in the following order; NC514VE> NC514VE-20PA> NC514VE-10PA> NC514VE-30PA. In addition, a secondary transition was detected in the loss modulus plots in the -74 to -58˚C region and these secondary peaks represent the motion of amorphous region side chains or branches from the main polymer backbone as noted in Kınacı et.al’s study[38].



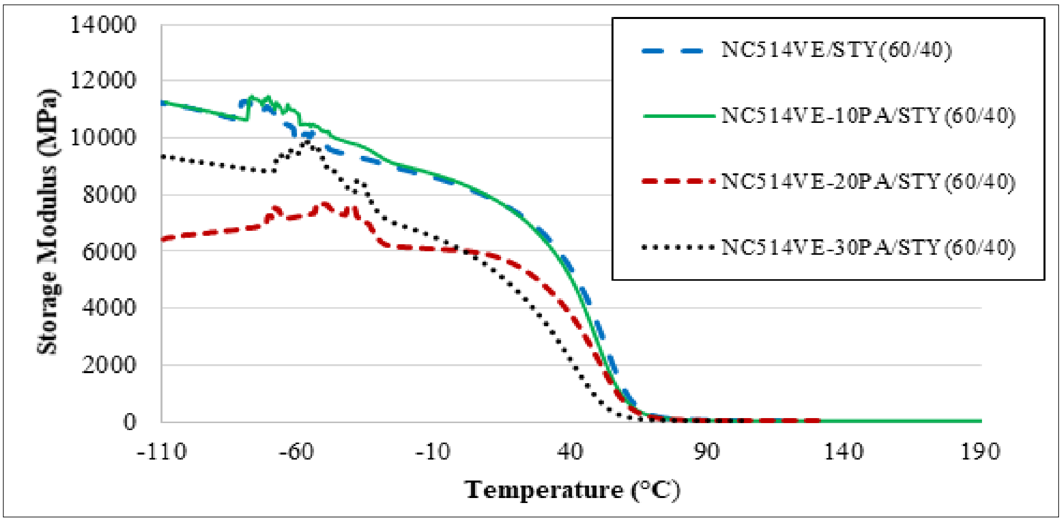
(a)



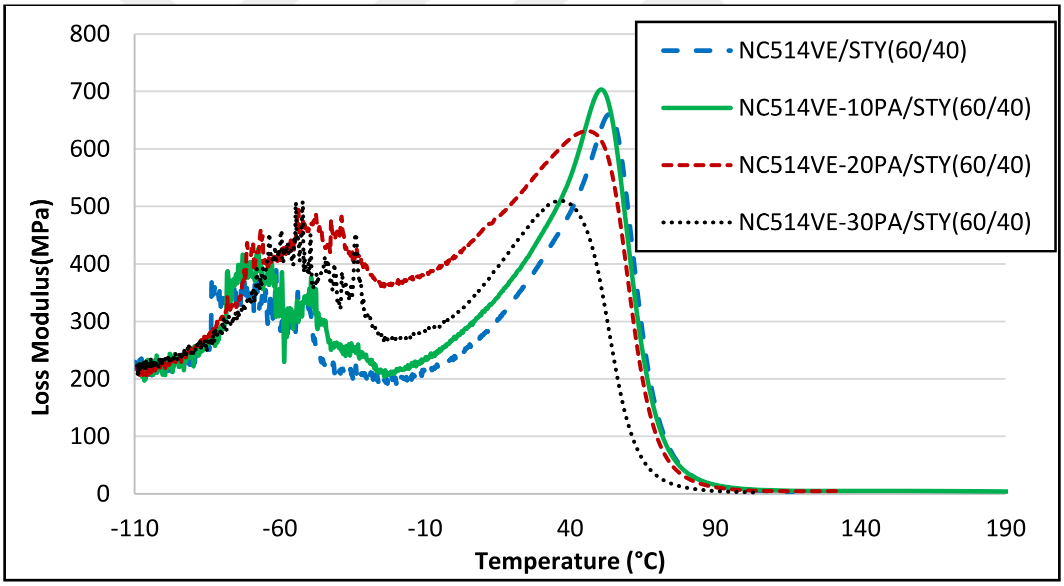
(b)

Figure 5.10. (a)Storage modulus vs. temperature (b)loss modulus vs. temperature plots of NC514VE and NC514VE-10,20,30PA resins with 30wt% STY content.

Figure 5.11 show similar trends for the NC514VE and NC514VE-PA resins with 40wt% styrene content. The storage modulus values in the glass transition region decrease with increasing phosphate content of the resins according to the following order; NC514VE=NC514VE-10PA>NC514VE-20PA>NC514VE-30PA. And also, glass transition temperature (Tg) again decreases with increasing phosphate content of the resins which can again be attributed to the decrease in crosslink density with increasing phosphate content. The secondary transitions related to the motion of the amorphous region side chains or branches from the main polymer backbone were also present in the -78 to -52˚C region.



(a)

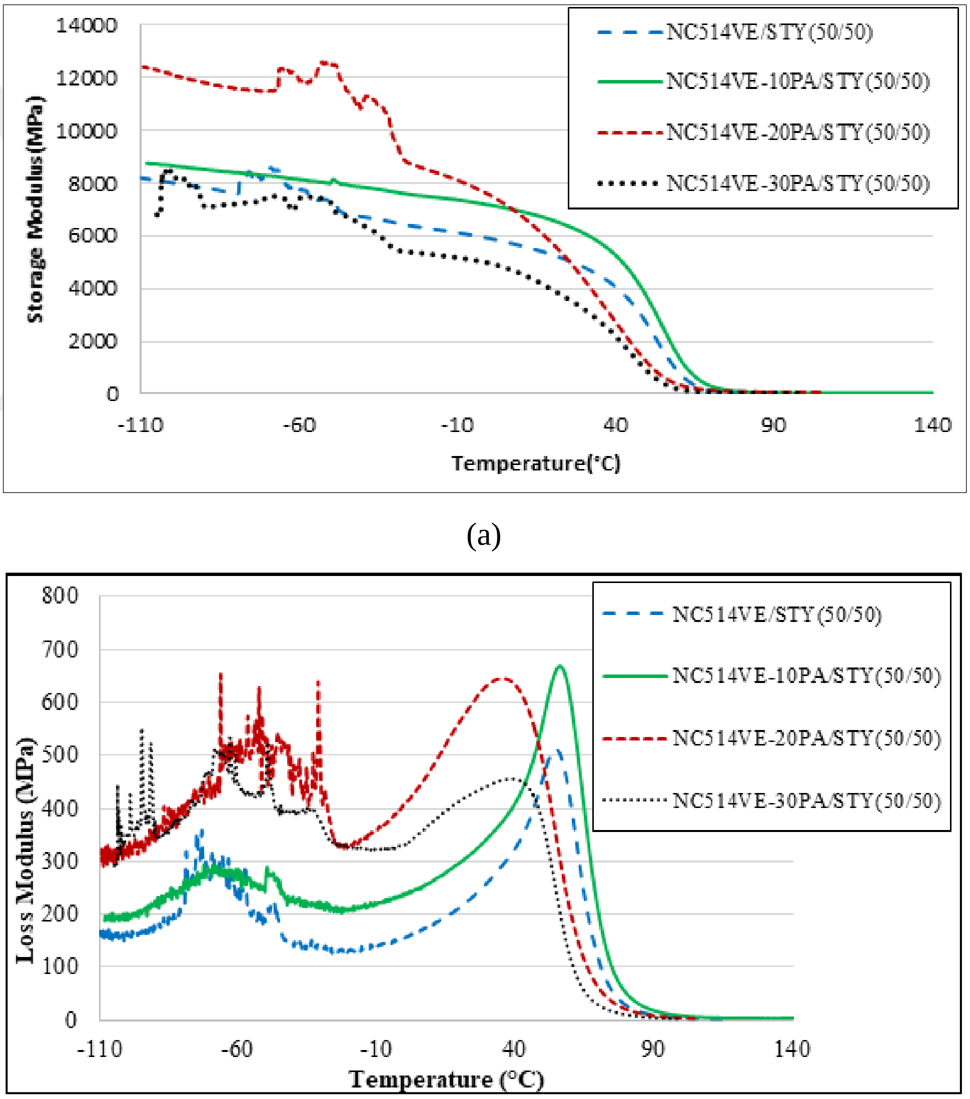


(b)

Figure 5.11. (a)Storage modulus vs. temperature (b)loss modulus vs. temperature plots of NC514VE and NC514VE-10,20,30PA resins with 40wt% STY content.

Finally, in Figure 5.12, at 50wt% styrene content, the storage modulus and Tg of the resins decrease at 20 to 30mol % PA content, however the effect of phosphate groups on these properties are more complicated. The storage modulus values in the glass transition region decreased in the following order; NC514VE-10PA>NC514VE>NC514VE-

20PA>NC514VE-30PA. And this order significantly changed at temperatures below the glass transition region. On the other hand, the glass transition temperature values decreased in the following order; NC514VE= NC514VE-10PA > NC514VE-30PA> NC514VE-20PA. Thus, PA condensation may also have played a role in increasing the cross-link density and therefore increasing the Tg or the storage modulus in some cases. It should also be noted that the secondary transitions linked to the motion of the side chains have been observed in the loss modulus plots in the -69 to -49˚C region, as well.



(a)

(b)

Figure 5.12. (a) Storage modulus vs. temperature (b)loss modulus vs. temperature plots of NC514VE and NC514VE-10,20,30PA resins with 50wt% STY content.

In the second part of the DMA analysis, the crosslink density (*v*) of the cured resins with different compositions were determined using the modulus values in the rubbery plate region and equation 4.4 according to rubber elasticity theory, as described in the Experimental Section. Thus table 5.5 lists the storage modulus values at 100^{o}C in the rubbery plate region for all the polymer compositions studied and the calculated cross-link density values.

An examination of the cross-link density data presented in Table.5.5 shows that the crosslink density decreased with increasing styrene content apart from the NC514VE-30PA resin formulations. This is an expected result since the cross-linker unit NC514VE content of the resins decrease with increasing styrene concentration. Thus for the %100 methacrylated resin the cross-link density decreased in the following order: NC514VE/STY(70/30)>NC514VE/STY(60/40)> NC514VE/STY(50/50) and the same order was observed for the NC514VE%10PA and NC514VE%20PA resin formulations. However for the NC514VE%30PA resins, cross-link density decreased in the following order:NC514VE-30PA/STY(60/40)>NC514VE-30PA/STY(50/50)>NC514VE 30PA/STY(70/30). The viscosity of the NC514VE-30PA/STY(70/30) resin was recorded as **18050 cP** at 25℃ (Table 5.3). The viscosity decreased to 2400cP and 1078cP at 40 and 50wt% styrene content respectively. Thus, at 30wt% styrene content the viscosity was so high that a significant amount of the methacrylate double bonds could not participate in polymerization due to limited mobility of the NC514VE-30PA units and the lowest cross-link density was observed at 30% styrene concentration.

When the effect of phosphate content on the cross-link density is examined, it can be seen that in general as phosphate content increased, the cross-link density decreased due to the decrease in methacrylate functionality of the resins as discussed previously. This order applied especially to resins with 30 wt% styrene content. At 40wt% styrene content NC514VE and NC514VE-10PA resins exhibited similar cross-link density but cross-link density decreased for the –20PA and -30PA resins. For the resin formulations with 50wt% styrene, the cross-link density increased from NC514VE to NC514VE-10PA and then started to decrease at 20-PA and 30-PA formulations. At 50wt% styrene content, both NC514VE-10PA and NC514VE-20PA resins had higher cross-link density than the NC514VE resin. At higher styrene concentrations, cross-linking through condensation of phosphate groups may have played a role in increasing the crosslink density for the phosphorylated resins as compared to 100% methacrylated resin.

Table 5.5. Crosslink-density data for all resin formulations

Polymer	**E’ (100˚C) (MPa)**	***v* (crosslink density) (mol/m^3)**
NC514VE/STY (70-30)	92.059	7812
NC514VE/STY (60-40)	39.079	3316
NC514VE/STY (50-50)	23.833	2022
NC514VE-10PA/STY(70-30)	51.191	4344
NC514VE-10PA/STY(60-40)	39.180	3325
NC514VE-10PA/STY(50-50)	38.457	3263
NC514VE-20PA/STY(70-30)	40.683	3452
NC514VE-20PA/STY(60-40)	35.062	2975
NC514VE-20PA/STY(50-50)	34.826	2955
NC514VE-30PA/STY(70-30)	16.306	1384
NC514VE-30PA/STY(60-40)	20.162	1711
NC514VE-30PA/STY(50-50)	17.963	1524

Table 5.6 lists the storage modulus values at 30˚C and T_g (°C) values as determined from the loss modulus and Tan delta peak temperatures for the NC514VE and the NC514VE-PA resins at changing PA and styrene contents. An examination of the data in the table indicates that, at 30wt% styrene content, both the storage modulus values at 30°C and T_g values decrease as phosphate content of the resins increase. At 40 and 50wt% styrene content on the other hand, at 10mol%PA content, the modulus values increase and at 50wt% styrene content and at again 10mol%PA content the T_g value increases. At higher phosphate contents, both the modulus and T_g generally decrease due to decreasing methacrylate functionality. At 10mol%PA content, at higher styrene concentrations, the condensation of phosphate groups during the high temperature cure may have contributed to higher cross-link density and therefore to higher modulus values. When the effect of styrene concentration is examined, it can be seen that both modulus at 30°C and T_g values

decrease with increasing styrene concentration for the NC514VE resins. For the phosphorylated NC514VE resin formulations the T_g increases slightly with the increase in styrene content. The modulus values on the other hand show different dependencies, it decreases with increasing styrene concentration at 10mol%PA content and it decrease slightly from 30% to 40% styrene and increases from 40 to 50wt% styrene at 20 and 30 mol % PA. Normally a decrease in cross-link density and therefore in modulus and T_g values may be expected with the increase in styrene content as the cross-linker unit is NC514VE in these formulations. However, for the phosphorylated resins at higher PA contents as the viscosity of the phosphorylated resin is too high, the effect of the decrease in viscosity at 50wt% styrene content may lead to more efficient polymerization of NC514VEPA double bonds and act to increase the crosslink density.

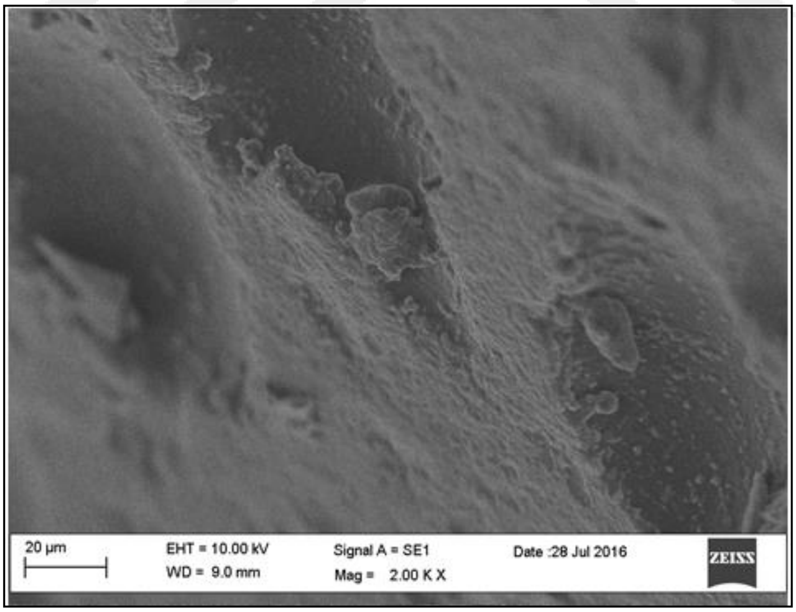
Table 5.6. Storage modulus values at 30˚C and T_g (°C) values as determined from the loss modulus and Tan delta peak temperatures for the NC514VE and the NC514VE-PA resins at changing PA and styrene contents.

POLYMER	**E' (30˚C) (MPa)**	**T_g (˚C) (E'' max.)**	**T_g (˚C) (Tan delta max.)**
NC514VE/STY (70-30)	7177 ± 333	59.8±0.7	79.2±0.3
NC514VE-10PA/STY(70-30)	6591±177	50.2±0.4	68.4±1.1
NC514VE-20PA/STY(70-30)	6382±297	48.6±0.2	66.2±0.0
NC514VE-30PA/STY(70-30)	3765±169	39.5±1.5	59.4±0.3
NC514VE/STY(60-40)	5703±41	54.0±1.5	69.5±1.5
NC514VE-10PA/STY(60-40)	6423±7	50.1±1.6	69.3±1.0
NC514VE-20PA/STY(60-40)	3446±333	47.9±0.1	66.1±0.3
NC514VE-30PA/STY(60-40)	3714±125	40.6±1.7	61.0±0.4
NC514VE/STY(50-50)	5140±326	52.3±3.3	71.3±1.2
NC514VE-10PA/STY(50-50)	6167±81	55.9±0.3	71.2±0.5
NC514VE-20PA/STY(50-50)	4439±112	50.9±4.2	64.9±0.1
NC514VE-30PA/STY(50-50)	4473±72	42.8±1.0	62.5±0.1

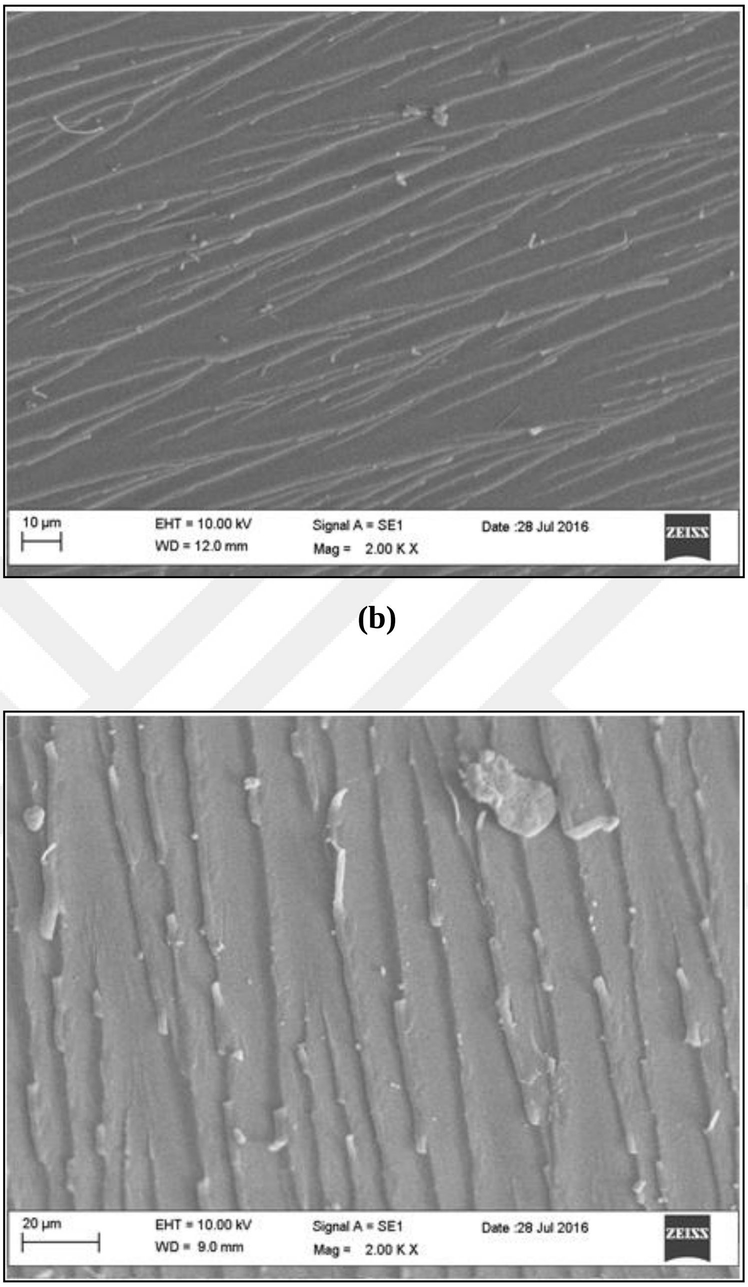
5.8. SCANNING ELECTRON MICROSCOPIC (SEM) ANALYSIS OF THE CURED NC514VE AND NC514VE-PA RESINS

5.8.1. Effect of Styrene Content

The SEM micrographs of the fracture surfaces of NC514VE/STY resins with 30,40 and 50wt% styrene and NC514VE-30PA/STY resins with 30 and 50wt% styrene are presented in Figure 5.13 and 5.14 respectively. The SEM pictures shown in Figure.5.13 present a rougher fracture surface for the NC514VE/STY polymers at 30 wt% styrene content and a more brittle fracture surface at 40 and 50wt% styrene content. In a similar manner, the NC514VE-30PA/STY polymer with 30 wt% styrene present a rougher fracture surface whereas at 50wt % styrene the fracture surface is smooth indicating a brittle fracture. In these resin compositions the more rigid styrene component should contribute to brittleness whereas the plasticizing effect of the long carbon chains in the NC514VE and NC514VE-PA units should contribute to toughness and a more ductile fracture [71 and 38].



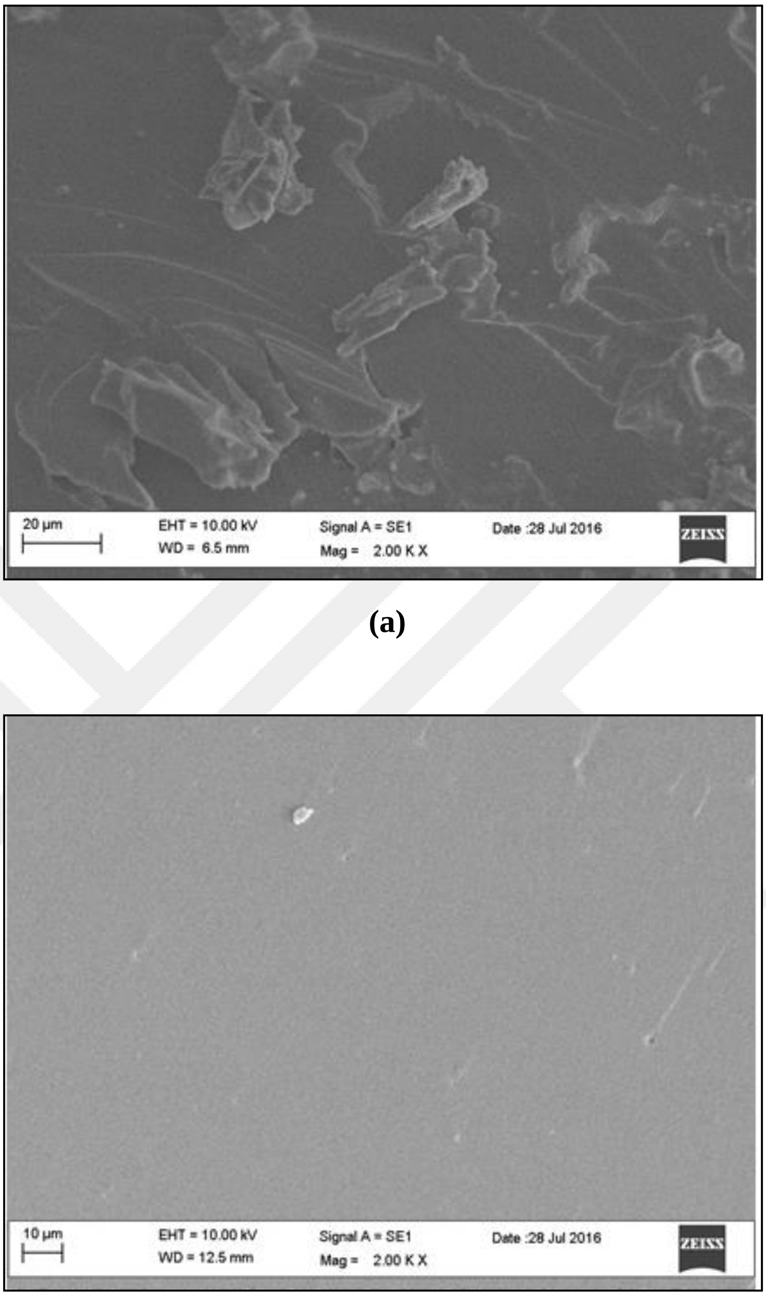
(a)



(b)

(c)

Figure 5.13. SEM micrographs of the fracture surfaces of a) NC514VE/STY(70/30) b) NC514VE/STY(60/40) c) NC514VE/STY(50/50) at 2000X magnification



(a)

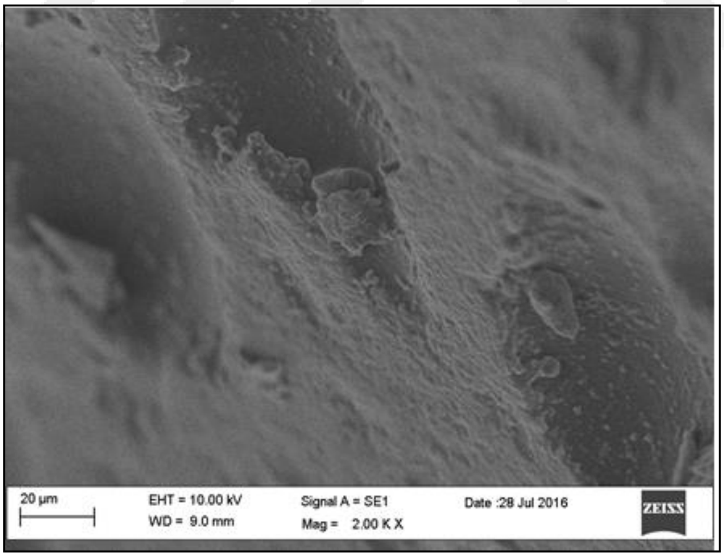
(b)

Figure 5.14. SEM micrographs of the fracture surfaces of a) NC514VE-30PA/STY(70/30) b) NC514VE-30PA/STY(50/50) at 2000X magnification

5.8.2. Effect of Phosphate Content

Figure 5.15 and 5.16 show the SEM micrographs of the fracture surfaces of NC514VE and NC514VE-30PA polymers with 30wt% styrene content and NC514VE and NC514VE-20PA polymers with 50wt% styrene content respectively.

An examination of the SEM pictures presented in these figures indicates a relatively rougher and more ductile fracture surface with the introduction of the phosphate groups instead of methacrylate. This may be attributed to the significant decrease in cross-link density of the NC514VE-30PA resin (1384 mol/m^3) as compared to that of NC51VE resin (7812 mol/m^3) at 30wt% styrene content (Table 5.5). However the cross-link density increased for the NC514VE-20PA resin (2955 mol/m^3) as compared to that of NC514VE resin (2022 mol/m^3) at 50wt% styrene content. Thus, it is suggested that the cross-linking of phosphate groups instead of methacrylate may also contribute to ductility as both polymethyl methacrylate and polystyrene are rigid and brittle polymers [72].



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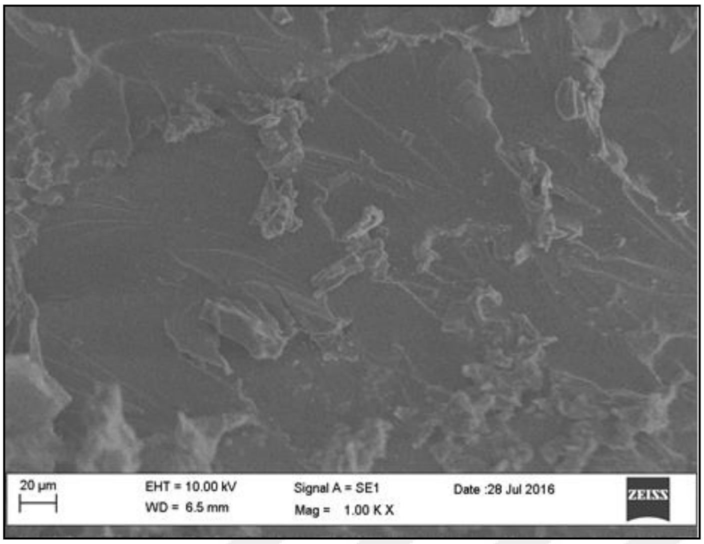
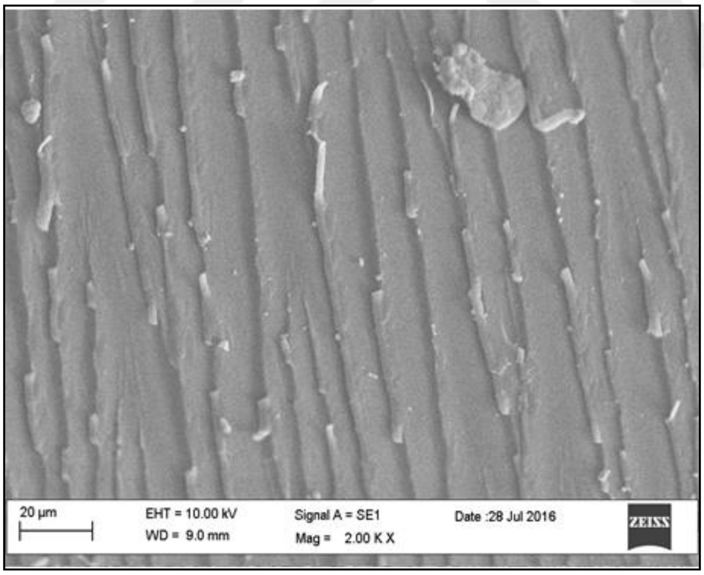
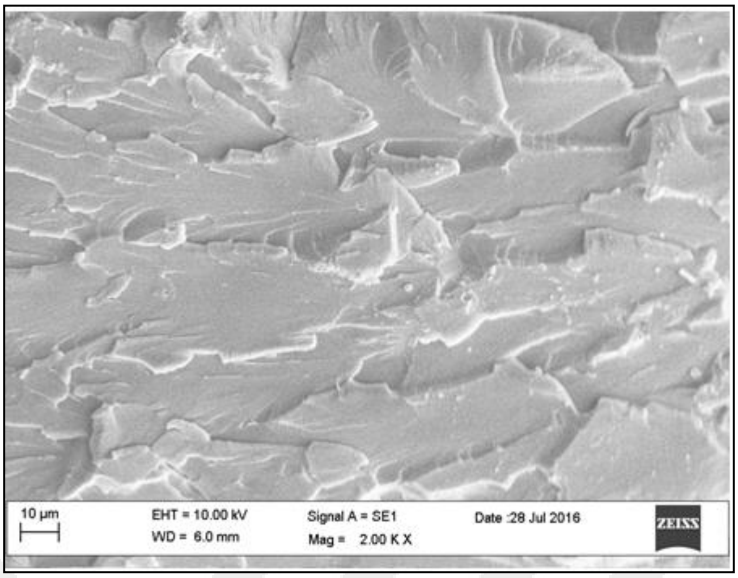


(b)

Figure 5.15. SEM micrographs of the fracture surfaces of a) NC514VE/STY(70/30) at 2000X magnification b) NC514VE-30PA/STY(70/30) at 1000X magnification



(a)



(b)

Figure 5.16. SEM micrographs of the fracture surfaces of a) NC514VE/STY(50/50) b) NC514VE-20PA/STY(50/50) at 2000X magnification

5.8.3. Pore Formation

In addition at higher PA content and at lower styrene contents pores as large as 300 µm to 600 µm were observed as can be seen in the SEM micrograph of the fracture surface of NC514VE-30PA/STY(70/30) resin presented in Figure 5.17. The undesirable pore formation occurred due to the high viscosity of the NC514VE-30PA resin even in the presence of 30wt% styrene reactive diluent (18050cP)(Table 5.3) .

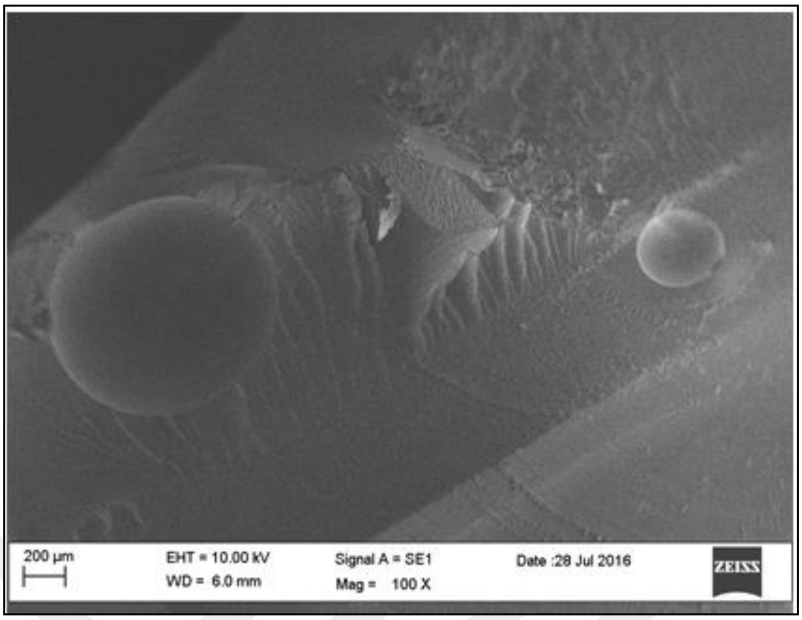


Figure 5.17. SEM micrograph of the fracture surface of NC514VE-30PA/STY(70/30) at 100X magnification

5.9. FLAMMABILITY TEST RESULTS OF THE CURED NC514VE AND NC514VE-PA RESINS

To see the effect of phosphorylation on the flammability of the NC514VE resins, a simple test was performed where the samples were exposed to a candle flame under the same conditions. The deflagration times recorded for each resin are listed in Table 5.7.

The data presented in Table 5.7 shows that the deflagration time increases with increasing phosphate content of the resins. Thus, the addition of phosphate groups to the NC514VE structure clearly had an impact on the sparkling time. There are three types of actions that phosphorus can perform in the solid phase which are to enhance char, to cause intumescence, or to form inorganic glass. Additionally, in the gas phase phosphorus is able to suppress the flame. Chemical structure prone to flame retardant abilities of the phosphorus compounds is efficient in gaining this ability together with reactions that take place during pyrolysis with polymeric material and other additives, there is a supposition about mechanism and efficiency of phosphorous fire retardants as being acting upon as a result of modification on the polymeric compound by means of synergists and adjuvants [73].

Thus by one of these mechanisms, the introduction of phosphate groups to the NC514VE structure is expected to increase fire-retardancy efficiency by providing a protective nonflammable char as the outer layer of the polymer that acts upon during the combustion process[74]. Supporting this fact, the TGA analysis of the resins in various compositions clearly showed an increase in the char residue with increasing phosphate content of the NC514VE-PA resins.

Table 5.7. Deflagration times recorded for the NC514VE and NC514VE-PA resins

Polymer	**Deflagration Time (seconds)**
NC514VE/STY(70/30)	8
NC514VE-20PA/STY(70/30)	10
NC514VE-30PA/STY(70/30)	11
NC514VE-40PA/STY(70/30)	12

6. CONCLUSIONS AND FUTURE WORK

6.1. CONCLUSIONS

The main objective of this research project as explained in the beginning, is to obtain new thermosetting materials with fire retardant properties, from Cashew Nutshell Liquid (CNSL) which is a renewable resource. For this purpose, commercially modified Bisphenol-A type epoxy cardanol resin (NC514) has been subjected to methacrylation reaction to produce the corresponding vinyl ester resin (NC514VE) while modifying thermal and mechanical properties of the epoxy resin. Then, the partially methacrylated epoxy resins have been subjected to different degrees of phosphorylation reaction to produce materials with fire retardant properties (NC514VE-PA).

In the first part of the experiments, vinyl ester of NC514 epoxy resin was synthesized by way of reaction with methacrylic acid with different epoxy: methacrylic acid (MA) mole ratios (%100MA,%90MA,%80MA and %70MA) in the presence of %1wt DABCO catalyst and %0.1wt hydroquinone radical inhibitor for 6 hours at 90˚C. The methacrylation reactions were stopped when the acid no of the reaction mixture reached a value below 10. After the methacrylation reaction, partially methacrylated samples were reacted with phosphoric acid to convert the remaining epoxies to phosphate esters. Thus, different mole ratios of epoxy to phosphoric acid (%10,%20,%30) were employed.. The phosphorylation reactions were performed in an ice bath medium, for 3 hours at 0˚C. The synthesized products were examined with spectroscopic techniques like FT-IR and ^{1}H-NMR spectroscopy to confirm their structures. Before the curing process, synthesized vinyl and phosphate ester resins (NC514VE and NC514VE-10,20,30PA) were mixed with styrene as the reactive diluent at different ratios (30,40,50 %wt). The viscosities of the uncured resins were determined by using a rheometer and curing behaviors of the resins were analyzed with Differential Scanning Calorimetry (DSC).

Next, curing process was applied to all samples. NC514VE and NC514VE-10,20,30PA samples were diluted with styrene at various ratios (30,40,50%wt) and radical initiator %1 T.B.P.B was added into the mixture. Then, these mixtures were transferred to a silicon mold and samples were subjected to a high temperature curing process which has been explained in the experimental study part in detail.

Fully cured resin samples were characterized via Differential Scanning Calorimetry (DSC) for their thermal transitions, via Thermal Gravimetric Analysis (TGA) for their thermal stabilities and via Dynamic Mechanical Analysis (DMA) for their thermo-mechanical properties. In addition, Scanning Electron Microscopy was used to characterize the fracture morphology of all cured resins. In the final part of the studies, the deflagration times of the fully cured samples were determined by exposing the samples to a candle flame under the same conditions.

The FT-IR and ^{1}H-NMR spectroscopic analysis of the methacrylated and phosphorylated samples gave characteristic peaks associated with their functional groups. From ^{1}H-NMR analysis, the methacrylate functionality of the NC514VE(100%MA) resin was found as 1.48 and as the methacrylic acid used in the methacrylation reaction decreased the corresponding methacrylate functionality also decreased as expected. Although the methacrylate functionality of the phosphate esterified resins approached 1 , as the phosphate ester hydroxyls also condense at the high temperature cure cycle, the real functionality of the methacrylate and phosphate ester of the NC514 resins was higher than 1 and these molecules can therefore act as crosslinker units when polymerized with styrene.

The viscosities of the NC514VE and NC14VE-10, 20, 30 PA resins with different styrene weight ratios were determined at room temperature. For all the formulations when the styrene content increased, viscosity of the resins decreased as expected as styrene is the reactive diluent and when the phosphate content increased viscosity of the samples also increased. This result was also expected as phosphate ester groups with free hydroxyls can make intermolecular hydrogen bonds increasing the viscosity.

The viscosities of the NC514VE-PA/STY resins with 10 and 20 mol% PA were all below 2000 cP which is the upper limit for most liquid molding operations. The viscosities of the NC514VE-30PA/%30STY and %40STY resins were on the other hand higher than 2000 cP.

The dynamic DSC scans of the NC514VE/STY(70/30) and NC514VE-10,20,30PA/STY(70/30) resins in the presence of the initiator from 30^{o}C to 200^{o}C showed that the heat of the cure reaction decreased as methacrylate functionality of the resins decreased from 100%MA0%PA resin to 70%MA30% PA resin as expected. In addition, the temperatures of maximum cure also increased with increasing phosphate content of the resins as compared to the NC514VE/STY(70/30) resin. The order of the cure temperature was found as; NC514VE-30PA> NC514VE-20PA> NC514VE-10PA> NC514VE. The DSC thermograms of the cured NC514VE and NC514VE-PA resins with 30,40 and 50wt% styrene content displayed no exothermic peak that stands for a post-cure reaction thus these samples were totally cured under the applied curing conditions.

In the TGA analysis of the cured resins, it was found out that in the decomposition process, NC514VE-10,20,30PA/STY(70/30)resins decomposed faster than NC514VE/STY(70/30) resin due to lower thermal stability of the phosphate groups. The major weight loss showing the main degradation of the network started at around 365 ˚C for the NC514VE/STY(70/30) resin and the main degradation temperature shifted to lower temperatures as PA content increased (350 - 325 ˚C). The decomposition of phosphate groups results in the formation of the compact char residue, which should preserve the sample from further decomposition. Therefore, after the decomposition process NC514VE/STY (70/30) sample was nearly fully consumed at 780 ˚C. However, the char residue at 780˚C was about 10-12 wt% for the NC514VE-10,20,30PA (70/30STY) samples which contained phosphate groups. Similar trends were observed at higher styrene contents (40 and 50wt% styrene).

In this study, dynamic mechanical analysis (DMA) was used to determine the thermo-mechanical properties of the synthesized polymers. The DMA analysis of the resins showed that the storage modulus generally decreased with increasing phosphate content of the resins.

The storage modulus values in the glass transition region decreased in the following order NC514VE>NC514VE-10PA> NC514VE-20PA> NC514VE-30PA at 30wt% styrene content because, the crosslink density was decreasing with increasing phosphate content. The Tg of the resins generally decreased with increasing phosphate content again due to the decrease in cross-link density. Although this order was changed especially for the NC514VE-10PA formulations at higher styrene contents, increasing phosphate content had similar effects on modulus and T_g of the polymers. In addition, a secondary transition was detected in the loss modulus plots in the -74˚C to -58˚C region for the NC514VE/STY(70/30) and NC514VE/STY(70/30)-PA resins and these secondary peaks represented the motion of amorphous region side chains or branches from the main polymer backbone. Similar secondary transitions were also observed at higher styrene contents. The cross-link density data obtained using the rubbery plate modulus values indicated that the crosslink density decreased with increasing styrene content apart from the NC514VE-30PA resin formulations. When the effect of phosphate content on the cross-link density was examined, it was observed that in general as phosphate content increased, the cross-link density decreased due to the decrease in methacrylate functionality of the resins. The storage modulus (E') values at 30ºC for all the NC514VE and NC514VE-PA resin formulations were within the range of 3715 to 7200 MPa, and the T_g values as determined from loss modulus max.(E''max) were changing within 38˚C to 60˚C, and whereas Tg values as determined from tan delta max. were changing within the range of 60˚C to 80˚C.

Scanning Electron Microscopy (SEM) was used to determine the morphology of the fracture surfaces of all the cured resins. According to this analysis, phosphate and styrene content rose up as the important parameters to effect the nature of fracture. While the phosphate content of the resins increased, samples generally exhibited a more ductile fracture. On the other hand, while styrene content was increased, the fracture surfaces indicated a more brittle fracture.

Finally, to see the effect of phosphate modification on the flammability of the NC514VE resin, a simple preliminary test was applied where each sample was exposed to a candle flame under the same conditions. The deflagration times recorded at the end of these experiments increased with increasing phosphate content of the resins demonstrating the fire retardancy effect of the phosphate groups introduced to the structure as expected.

With all the presented results, when all properties of the prepared resins are evaluated the NC514VE-10PA and -20 PA/STY resins at 40 and 50 wt% styrene contents may offer both a significant fire retardancy effect with processable viscosity in liquid state and reasonable mechanical properties in the cured state.

As a conclusion, vinyl ester resins obtained from an epoxy cardanol derived from CNSL; a renewable resource, can easily be modified through a reaction with phosphoric acid and the phosphate esters of the partially methacrylated epoxy cardanol resin exhibited promising properties to be used as a thermosetting resin where fire retardancy is required. In addition, this study offers a new route to introduce fire retardant properties to the vinyl ester resins obtained from epoxy cardanol or other epoxy resins derived from renewable resources.

6.2. FUTURE WORK

One set of tests necessary to complete this study may be to perform fire retardancy tests that determine limiting oxygen index (LOI) for all cured resin formulations to confirm fire retardancy effect of the phosphate modification on the NC514VE structure. A suggestion for a future work of this study may be the partial methacrylation and phosphorylation of the Novalac type cardanol based epoxy resin (NC-547) (Figure.5.18) which has approximately three epoxies per molecule. The resulting NC-547VE and NC-547VE-PA resins are expected to exhibit better mechanical properties and thermal resistance than the NC-514VE and NC-514VE-PA resins due to higher functionality.

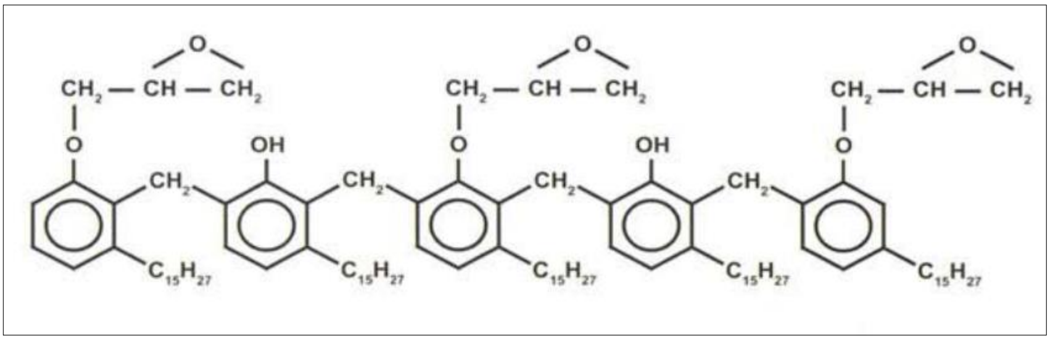


Figure 5.18. Structure of the NC547, novolac resin of Cardolite.

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