SYNTHESIS OF NETWORKS AND INTERPENETRATING NETWORKS OF MALEATED CASTOR OIL AND EPOXY RESINS

by

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SYNTHESIS OF NETWORKS AND INTERENETRATIG NETWORKS OF MALEATED CASTOR OIL AND EPOXY RESINS

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To my mother and father

and

To my sister Sema and her husband

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ABSTRACT

SYNTHESIS OF NETWORKS AND INTERPENETRATING NETWORKS OF MALEATED CASTOR OIL AND EPOXY RESINS

In this study, castor oil is reacted with maleic anhydride to give maleated castor oil (COMA) which can be used as a biobased epoxy curing agent to enhance the problems of brittle structure of epoxy resins and can undergo free radical polymerization with reactive diluents to give interpenetrating networks which increase mechanical properties. The maleation of castor oil is carried out using the known method developed earlier by our research group with small modifications to increase maleation ratio and shorten the reaction time. Then, COMA is reacted with commercial epoxy resins Bisphenol A diglycidal ether (DGEBPA), Novolac epoxy resin, Heloxy 505 epoxy resin- through its carboxylic acid ends to give thermoset polymers. As a third step, the intact double bonds in polymer structure are polymerized free radically with styrene in the presence of an initiator, azobisisobutyronitrile (AIBN) to give a second interpenetrating network. Characterization of the products is done by IR spectroscopy only due to their crosslinked structure. IR spectra of the polymers are also used to decide the optimum ratio of stoichiometry of COMA/epoxy resin. Thermal stabilities of the samples are analyzed with TGA (Thermogravimetric Analysis). Mechanical properties are determined by surface hardness test by Shore A durameter and three point bending test using the home made instrument produced by our lab.

ÖZET

MALEİNİZE EDİLMİŞ HİNT YAĞI VE EPOKSİ REÇİNELER İLE AĞ YAPI VE GEÇİŞİMLİ AĞ YAPI SENTEZİ

Bu çalışmada epoksi reçinenin kırılgan yapısından oluşan problemleri iyileştirmek ve reaktif seyrelticilerle radikal polymerizasyon reaksiyonlarına girerek mekanik özellikleri arttırmak için kullanılabilecek alternatif bir epoksi kürleme maddesi olan maleinize edilmiş hint yağının oluşumu için hint yağı maleik anhidritle reaksiyona sokulmustur. Hint yağının maleinize edilmesi araştırma grubumuzca daha önce tecrübe edilmiş olan methodun maleinizasyon oranını arttırmak ve reaksiyon süresini kısaltmak amacıyla ufak değiştirmeler eklenmiş haliyle yürütülmüştür. Ardından COMA karboksilik asit uçları sayesinde ticari epoksi resinleri olan bisfenol A diglisidil eter, novalak epoksi reçine, Heloksi 505 epoksi reçineleriyle termoset polimerler vermek için reaksiyona girmiştir. Üçüncü aşama olarak, polimerin yapısındaki reaksiyona girmemiş çift bağlar, içerisinde başlatıcı olarak azobisizobütironitril bulunduran stirenle geçişimli ağ oluşturmak için serbest radikal polimerizasyon reaksiyonuna sokulmuştur. Karakterizasyon çalışmaları ürünlerin çapraz bağlantılı yapısından dolayı IR spektroskopisi kullanılarak yapılmıştır. Aynı zamanda polimerlerin IR spektrumları COMA/epoksi reçine stokiometrisindeki en uygun oranı belirlemek için de kullanılmıştır. Ürünlerin termal kararlılıkları TGA ile analiz edilmiştir. Mekanik özellikler, Shore A durometresi ile yüzey sertliği ölçülerek ve laboratuvarımızda hazırlanan cihazla üç noktalı eğme deneyi yapılarak belirlenmiştir.

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LIST OF SYMBOLS

E_f	Flexural Modulus
μ	Flexural Strain
Б	Flexural Stress
N	Newton

LIST OF ACROYNMS/ABBREVIATIONS

COMA	Maleated Castor Oil
DGEBPA	Diglycidal Ether Bisphenol A
ESO	Epoxidized Soybean Oil
IPN	Interpenetrating Polymer Network
IR	Infrared
NMR	Nuclear Magnetic Resonance
MPa	Megapascal
TGA	Thermogravimetric Analysis

1. INTRODUCTION

1.1. Renewable Resources

Dramatic fluctuations of petroleum prices, which are caused by its shortages, force the polymer industry to find alternative renewable resources for polymeric materials. Morever, the threat of global warming and the issue of CO_2emission are other driving forces for searching for enviromentally friendly sources. Plant oils are sensible choices for sustainable development [1]. They have been used for paint formulations since the 19th century; however nowadays their possible areas of use have wideneddue to their renewable nature, low price and ease of availability [2].

The production of common monomers in a ‘green’ way proves that there is a game change in polymer chemistry. Production of green polyethylene in Brazil can be given as an example of this. In addition, the new value added to plant based polymers allows agricultural revitalization in some countries [3]. As a result, the production of major plant oils increased 62 % from 2000 to 2010 [4].

Most of plant oil based polymers undergo biodegradation, they are eco-friendly due to carbon neutrality, which means that the CO_2 generated during natural decomposition is used again in photosynthesis. Figure 1.1 shows the life cycle of plant based polymer. Plant oils usually need modification reactions to enhance their reactivity for polymerization reactions. After the usage of product, it becomes waste and can be a part of biomass again thanks to biodegradation.

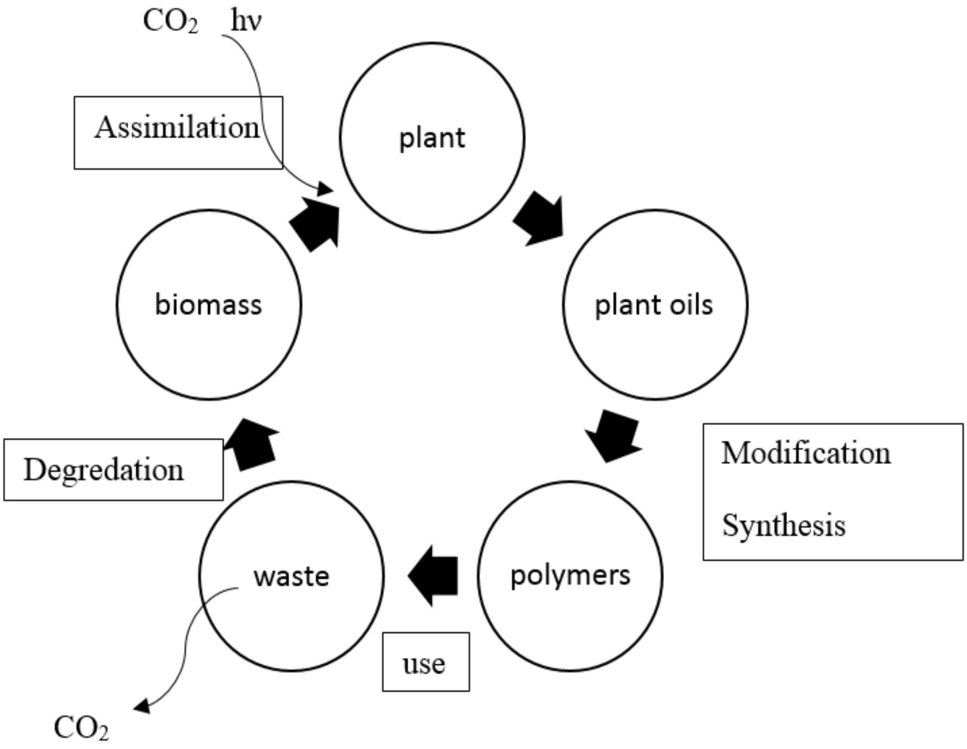


Figure 1.1. The life cycle of polymers based on triglyceride oils[2].

1.2. Plant Oils

1.2.1. Chemical Structure and Properties of Plant Oils

Plant oils, which can be called as triglycerides or triacylglycerols, are the products of esterification reactions of glycerol with three fatty acids. Fatty acids are long alkyl carboxylic acids. Figure 1.2 shows the general structure of triglycerides. Alkyl chains may be completely saturated or may contain one or more double bonds which are in the cis geometry. Additionaly, some natural fatty acids have different functional groups such as; hydroxyl, epoxy, ketone, nitrate etc., which give them distinctive properties. Examples of oils with specific functionalgroups are given in Table 1.1.

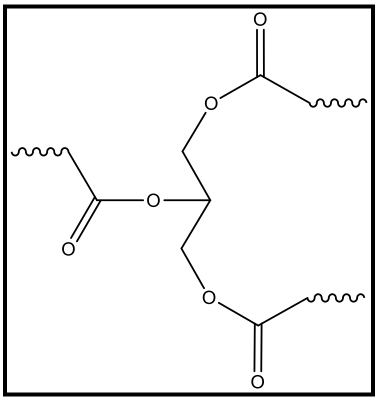


Figure1.2. General structure of triglyceride.

Table 1.1. Fatty acids which have specific functional groups.

Functional group	Oil
Fluoro	Fish oil
Dicarboxylic	Oil of plant cuticles
Isomeric epithio	Canola oil
Nitrate	Oil in human plasma
Hydroxyl	Castor oil
Ketone	Oiticica oil
Epoxy	Vernonia oil

1.2.2. Chemistry of Plant Oils

Ester groups, C=C double bonds, allylic position and the α position of ester groups are the reactive positions of fatty acids. Polymerization of triglycerides can be done directly by thermally or cationiclyusing the C=C double bonds; however, since the reactivity of double bonds in the structure is not sufficient, a polymerizable functional group needs to be attached to triglyceride which facilitates the polymerization reaction [5].

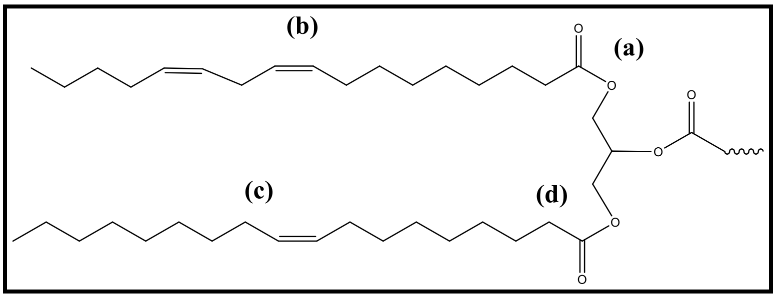


Figure 1.3. Reactive sides of triglyceride.

Synthesis of polymers from plant oils such as polyesters, polyurethanes, polyamides, polyesteramides, acrylic resins, epoxy resins and oxypolymerized oils have been the subject of many studies. Yağcı et al. mentioned the modification of triglycerides and synthesis of polymers in detail in the review ‘Polymers from triglyceride oils’ [2]. Also, Mosiewicki et al. figured clearly the functionalization of the reactive sides of triglycerides to synthesize polmerizable monomers [6].

Characterization of plant oils and plant oil based polymers can be done by using IR. Table 1.2 shows some important absorption band values of functional groups of plant oils.

Table 1.2. Some IR absorption band values for fatty acids [2].

Absorpsion band (cm^{-1})	Functionality
3500	–OH functions corresponding to free glycerol and/or residual moisture
2930-2850	–CH_2– groups (with an additional weakshoulder around 2960cm^{-1} reflecting thepresence of terminal methyl groups)
1745	-COOH groups
1160	C–O–C functions of the ester group
720	–$(CH_2)_n$– sequences of the aliphatic chains of the fatty acids

1.2.3. Application Areas of Plant Oils

Plant oils are used for pharmaceutical industry, cosmetic industry, detergent industry, packaging industry and plastic industry to produce lubricants, surfactants, binders, paint and polymer additives, polymers etc [7]. Also, fatty acids may gain importance for a specific industry with modification reactions. Table 1.3 explains some of the application areas of modified fatty acids.

Due to the difference in chemical structure of fatty acid and distribution of them in triglyceride, each triglyceride has different properties which determine the tendency of application areas. For example, linseed oil, which has reactive unsaturated fatty acids, is used as a paint binder due to the curing reaction of unsaturated bonds with atmospheric oxygen. Morever, castor oil can be a member of interpenetreting polymer networks, because the hydroxyl groups can react with isocyanate and carboxyl groups [2]. Nowadays, investigations of plant oils have aimed to design well defined linear structures, 3D networks and matrices for biocomposites and hybrid materials [4].

Table 1.3. Application Areas of Modified Fatty Acids [8].

Sulfated Fatty Acids	Cosmetics, Detergent
Hydrogenated Fatty Acids	Detergent
Acrylated Fatty Acids	Cosmetics, Pharmaceuticals, Plastic Additives, Bioplastics
Epoxidized Fatty Acids	Additive for PVC, Bioplastics
Alkyd Resins	Paint, Coatings; Baked finishes for automobiles, refrigerators, stoves; Printing ink, Enamels
Acetylated Fatty Acids	Food Packaging, Wax and plastic additive, Food dye solvent, Cosmetics, Foaming Agent

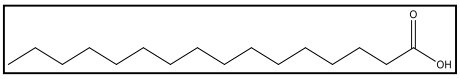
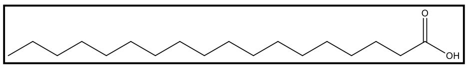
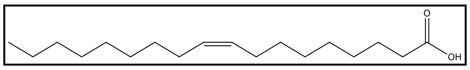
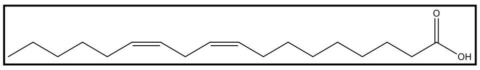
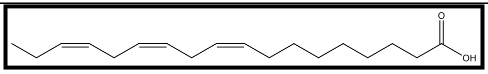
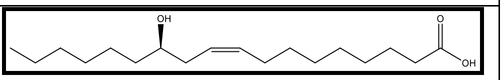
1.3. Castor Oil

1.2.4. Chemical Structure and Properties of Castor Oil

Castor oil is obtained after the extraction of the Ricinus Communis plant seeds. Although the seeds are toxic for humans and animalsdue to their ricin content, the oil can be used for medicinal purposes as laxative. Castor oil is a straw yellow, viscous oil with a characteristic odor. Largest producers of castor oil are India, China and Brazil [9].

Castor oil is a triglyceride composed of different fatty acids like other plant oils. However, the most abundant fatty acid in castor oil is ricinoleic acid. Table 1.4 shows the composition of castor oil.

Table 1.4. Castor Oil Composition [10].

Fatty acid	Molecular formula	Percentage (%)	Chemical Structure
Palmitic	$C_{16}H_{32}O_2$	0.8-1.1	
Steraric	$C_{18}H_{36}O_2$	0.7-1.0	
Oleic	$C_{18}H_{34}O_2$	2.2-3.3	
Linoleic	$C_{18}H_{32}O_2$	4.1-4.7	
Linolenic	$C_{18}H_{30}O_2$	0.5-0.7	
Ricinoleic	$C_{18}H_{34}O_3$	87.7-90.4	

Ricinoleic acid contains an unsaturated double bond anda nonconjugated hydroxyl functional group which give distinctive properties to castor oil. For example,due to hydroxyl group in its structure hydrogen bonding is observed leading to achieve higher viscosity than other plant oils. Additionally, hydroxyl group makes castor oil more polar than most of the plant oils. As a result of being polar, it is soluble in alcohols. Two functional groups give various opportunities to the castor oil for different types of modifications. Table 1.5 shows the possible reactions of these reactive centers.

Table 1.5. Possible reactions of active sides of castor oil [11].

	Nature of Reaction	Added Reactants	Type of Product
Ester linkage	Hydrolysis	Acid, enzyme or Twitchell catalyst	Fatty acids, glycerol
	Alcoholysis	Glycerol,glycols, pentaerythritol	Mono and diglycerides, monoglycols
	Reduction	Na reduction	Alcohols
	Amidation	Alkyl amines, alkanolamines, and other compounds	Amine salts, amides
Double bond	Oxidation, Polymerization	Heat, oxygen, crosslink agent	Polymerized oils
	Hydrogenation	Hydrogen (moderate pressure)	Hydroxystearates
	Epoxidation	Hydrogen peroxide	Epoxidized oils
	Halogenation	Cl_2, Br_2, I_2	Halogenated oils
	Addition reactions	S, maleic acid	Polymerized oils, factice

Table 1.5. Possible reactions of active sides of castor oil [11] (cont).

Hydroxyl group	Dehydration, hydrolysis	Catalyst (plus heat)	Dehydrated castor oil, octadecadicnoic acid
	Caustic fusion	NaOH	Sebacic acid, capryl alcohol
	Prolysis	High temperature	Undecylenic acid, heptaldehyde
	Halogenation	PCl_5, $POCl_3$	Halogenated castor oils
	Alkoxylation	Ethylene or propylene oxide	Alkoxylated castor oils
	Esterification	Acetic-, phosphoric-, maleic-, phthalic anhydrides	Alkyl and alkylaryl esters, phosphate esters
	Urethane	Isocyanates	Urethane polymers
	Sulphation	H_2SO_4	Sulphated castor oil

Castor oil based formulations are used as lubricants, coatings, surfactants, foams and oleochemicals etc. The review article of Hatice Mutlu and Micheal A.R. Meier discusses most possible end products of chemical derivatives [10]. Table 1.6 shows the some application areas of modified castor oil.

Table 1.6. Application areas of modified castor oil.

Oxidized castor oil (blown oil)	Plasticizer in lacquer, artificial leathers, hydraulic fluids adhesives
Hydrogenated castor oil	Cosmetics, hair dressing, ointments, polishes
Sulphated castor oil (Turkey red oil)	Wetting agent for pigments and dyes
Dehydrated castor oil	Used in preparation of alkyd resins; paints, enamels, lacquers and varnishes
Miscellanous medical applications	Formulation of cathartics, formulation of contraceptive creams

The products of castor oil are used commercially. For example, Ultramid, a polyamide 6,10 and is an example of castor oil based product which is introduced to market by the German chemical company, BASF. The product has relatively low density for a polyamide and great dimensional stability due to its low water absorbtion. In addition to these advantages,BASF explained another reason for interest of renewable materials as customer demand [11]. Moreover, Rilsan PA11, which is 100% castor oil based, is produced by Arkema and used in markets such as electronics, sports equipment, furniture and automotive [12].

1.3.2. Maleation of Castor Oil

As mentioned above, generally the double bonds in triglycerides are not active enough to take part in free radical polymerization reaction. Maleation is a method to increase crosslink density of the final polymer thanks to reactive maleate double bonds. As an example, Petrovic et al. copolymerized allyl alcohol ring-opened ESO with maleic anhydride to prepare thermosets by esterification and free radical polymerization. The glass transition temperature and mechanical strengths of the final product were directly affected by the amount of loaded maleic anhydride due to crosslink density [13].

Wang et al. reported the preparation of half ester of castor oil via maleation and copolymerization of this monomer with styrene. As a result of the study the inactivitiy of double bonds problem was solved by the addition of active double bonds, and biodegredable plastic foams with high castor oil content was formed [14].

Moreover, the maleation of castor oil has been experienced in the MS thesis of Şeyma Avcılar a previous member of our research group, using the procedure of US Patent 6,225,485 [15]. As a result of the reaction a biobased carboxylic acid from vegetable oil forms. In Figure 1.4 shows the reaction of maleation of castor oil.

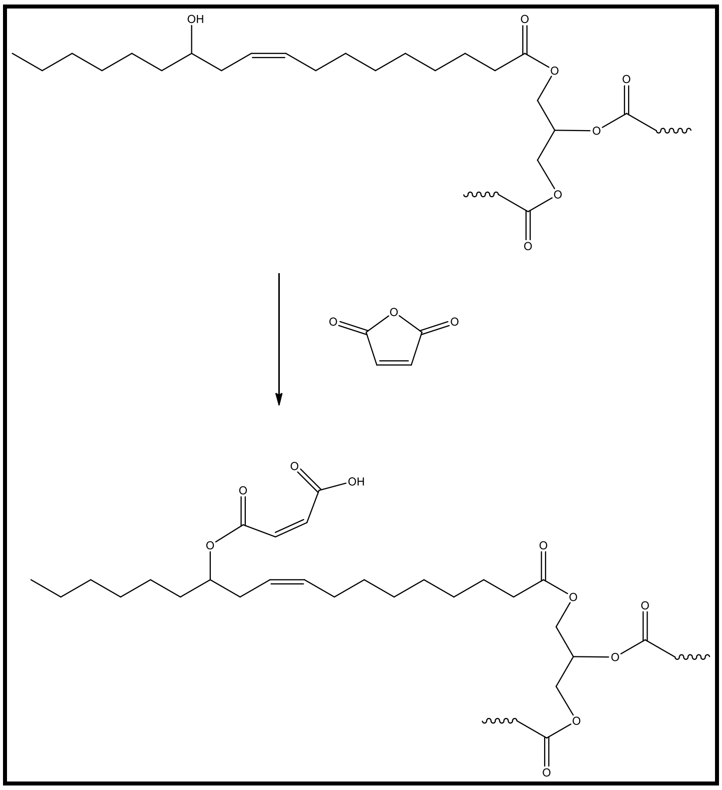


Figure 1.4. Synthesis of Maleated Castor Oil.

1.4. Epoxy resins

1.4.1. Properties of Epoxy Resins

Epoxy resins are short polymers containing epoxide end groups. Epoxides can undergo ring opening reactions with nucleophilic substances. The most common types of epoxy resins are shown in Table 1.7 with their preparation methods.

Table 1.7. Types of epoxy resins.

Epoxy Resins		
Categories	Preparation	Kinds
Glycidyl epoxy resin (Terminal epoxide)	Condensation reaction of appropriate dihydroxyl compound dibasic acid or a diamine and epichlorohydrin	Glycidyl ether glycidyl ester glycidyl amine
Non-glycidyl epoxy resin (Internal epoxide)	Peroxidation of olefinic double bond	Aliphatic epoxy resin Cycloaliphatic epoxy resin

Different ratios of epoxy resins can be combined with curing agents to meet the requirements of the market. Each of the end product has specific physical and mechanical properties according to starting materials.

Excellent chemical resistance, adhesion to various substrates, versatility in crosslinking and good mechanical, thermal and electrical insulating properties distinguish epoxy resins from the other polymers. The usage areas of epoxy resins are structural applications such as tooling, molding, adhesives, laminates and protective coatings and glass fiber and carbon fiber composites. Manufacturing epoxy thermosets is the most advantageous method for industry. Low viscosity of starting materials enables easy molding into complex geometries [16].

Epoxy equivalent weight of an epoxy resin is defined as the amount of resin in grams which contains one mole of an epoxy group. It can be determined by titration, IR and NMR. Epoxy equivalent weight is used to calculate the amount of crosslinking agent to be used in crosslinking.

1.4.2. Epoxy curing agents

Although the epoxy resins have same main functional group, structural differences cause reactivity differences. Therefore, the curing agents of epoxy resins are different. For example, DGEBPA-based resins give the best performance and highest crosslinking degree when they are cured withdiamines by addition mechanism whereas cycloaliphatic epoxies are usually crosslinked with anhydrides. Table 1.8 states the reasons of the best performance of a type of curing agent on a specific type of epoxy resin [17].

Table 1.8. Best curing agent of some epoxy resins types.

Type of epoxy resin	Effecting factor	Reactivity	Curing agent
Diglycidal ether and aliphatic epoxy resins	The linkage between aromatic ring and oxygen has a strong electronwithdrawing effect	Oxirane group highly reactive towards nucleophilic compounds	Amine
Cycloaliphatic epoxy resins	Axial and equatorial protons of cyclohexyl ring against nucleophilic attack [18]	Characteristic low reactivity of oxirane ring. Reactive towards Lewis acids.	Anhydrides

Primary and secondary amines are the largest class of curing agents of epoxy resins (50%) but they are toxic. Adducts of amines are used and non-toxic amine hardeners have been developed to reduce toxicity. The second class is carboxylic acids and anhydrides due to their low price, good flexibility and weatherability (36%). In this study Maleated half ester of Castor oil (COMA) is used as a biobased carboxylic acid type curing agent.

The reaction between carboxylic acid and epoxy resin is shown in Figure 1.5. First, carboxylic acid attacks to epoxy group. It attacks at the less crowded carbon if the medium is basic and attacks to more crowded carbon if the medium is acidic. After that, formed hydroxyl group can react with another carboxylic acid or epoxy group. Due to epoxy resin has at least two functionalities, it is a crosslinking process. Although, this proces occurs at 125 ^{o}C, reaction temperature can be decreased by addition of catalyst. In addition Figure 1.5 indicates the possible starting mechanism of non catalytic reaction [19].

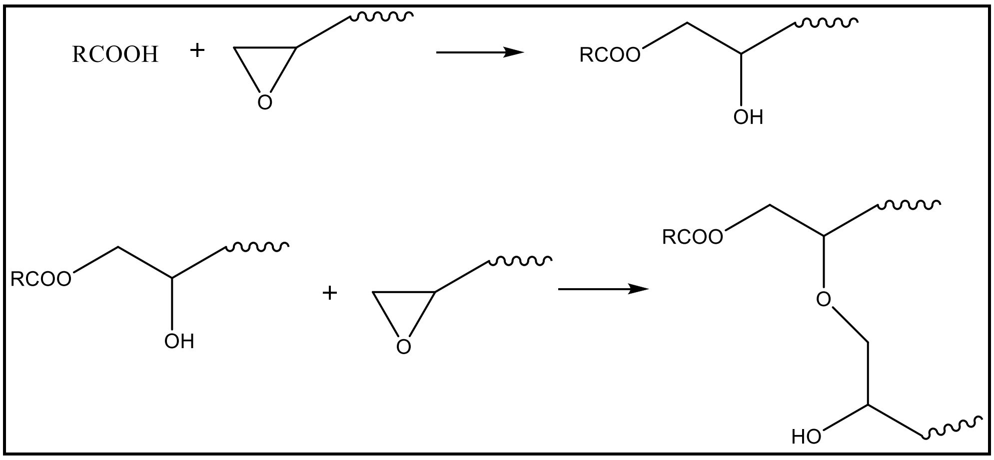


Figure 1.5. The reaction of carboxylic acid and epoxy [19].

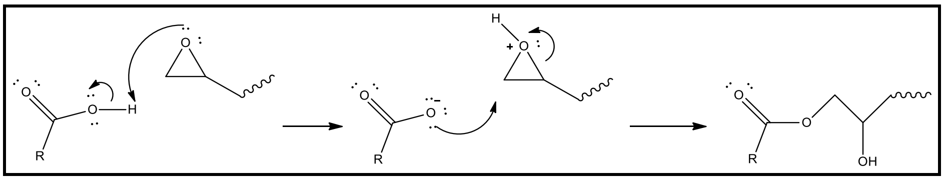


Figure 1.6. The possible mechanisms of the reaction [19].

1.4.3. Most Commonly Used Epoxy Resins

Although epoxy resins can be employed in high performance materials, applications are limited due to their brittleness. Therefore, the epoxy resins should be combined with suitable polymers such as rubbers or elastomers [20]. Plant oil based polymers are also alternative materials for this modification since their long aliphatic chain and low crosslink density make the final product soft. Park et al. reported that the introduction of epoxidized castor oil into the epoxy networks improves the toughness of the epoxy resins, however, the thermal properties decreases [21].

Moreover, the most prefered curing agent for epoxy resins are primary and secondary amines which are harmful. Therefore, using a plant oil based curing agent is useful when considering the toxicity of hardener. Jaillet et al. studied polyacids based unsaturated triglycerides and cured DGEBPA epoxy resin as a model reaction [22].

DGEBPA is the simplest possible epoxy resin. Its molecular weight and properties depend on ‘n’. When the molecular weight increases, the resin gains another reactive group which is hydroxyl. Easy cure, versatility, good chemical and mechanical properties make DGEBPA the most prefered epoxy resin. Novolac epoxy resin is commercially important because high functionality of the resin increases the crosslink density and it causes an improvement in thermal stability and chemical resistance. Heloxy 505 epoxy resin is castor oil based epoxy resin that imparts flexibility, impact resistance and thermal shock resistance.

1.5. Interpenetrating Polymer Networks

Interpenetrating polymer networks (IPNs) are prepared by swelling a crosslinked network with a monomer and then polymerizing this monomer within the network. Such a system is a mixture of two polymer networks that penetrate each other. The two networks cannot be seperated unless chemical bonds are broken.Interpenetrating polymer networks are useful since they combine the properties of both polymer systems used in the network. Such polymer systems can be synthesized sequentially or simultaneously. In sequential IPNs, one network is formed and swollen in another monomer and crosslinker system. The monomer used for simultaneous IPNs, all constituents of both networks are mixed and reacts simultaneously. Figure 1.7 summarizes the definitions clearly. Moreover, if one polymer is crosslinked and the other one is linear or branched, interpenetrating polymer networks are named as semi-interpenetrating polymer networks (SIPN) [23].

IPNs have properties that are considerably different from a simple blend of two networks. The close proximity of one network restricts the motion of polymer chains in the other network and this gives quite unexpected mechanical and thermal properties.

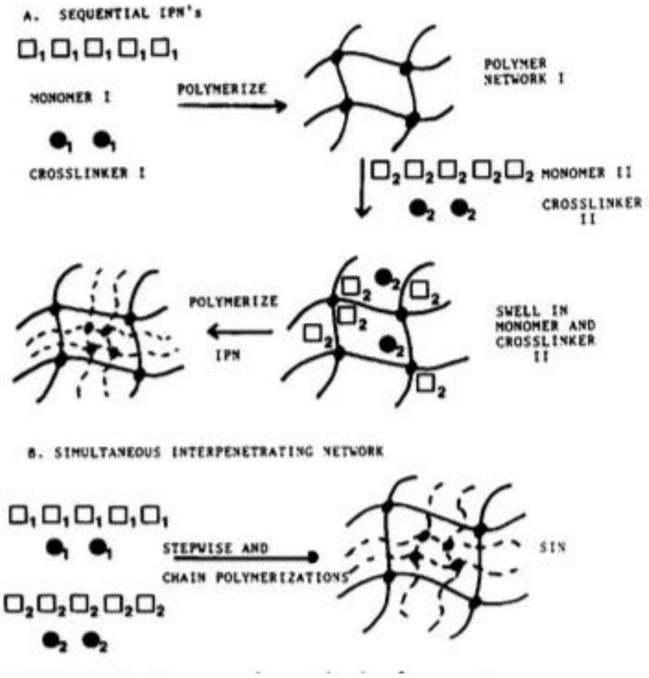


Figure 1.7. Formation of IPNs [23].

Castor oil based polymers are used for interpenetreting polymer networks due to having two funtionalities. First report of castor oil based interpenetrating polymer network is published in 1977by Yenwo et al. The paper discussed the crosslinking of double bonds with sulfur, the reaction of hydroxyl group with diisocyanate, and emulsion polymerization with hydrolyzed castor oil as the soap [24].

Also in our research group interpenetrating networks of castor oil based polymers were synthesized by Şeyma Avcılar. In her thesis, epoxidized soybean oil (ESO) was cured by COMA. To form an interpenetrating network, ESOCOMA reaction was run in styrene and epoxide ring opening polymerization occured simultaneously with the free radical polymerization of double bonds of styrene and unsaturation of COMA [15].

The properties of the network change with the chemistry of polymers. For example, Cunha et al. reported the interpenetrating polymer networks from acrylic monomers, which are polymethyl methacrylate and poly-2-ethoxyethyl methacrylate, and castor oil based polyurethanes. After the formation of acrylic polymer in castor oil based polyurethane, toughness and thermal properties of the formed semi interpenetrating network has incresed. Also, Suthar et al., synthesized interpenetrating polymer networks simultaneously using castor oil based polyesters and acrylic polymers and observed that they are soft and opaque [14].

In this study, COMA-epoxy resin crosslinked polymer system was swollen in a reactive diluent, styrene, which was later free radically polymerized and copolymerized with maleate groups to give an interpenetrating polymer network formed sequentially.

2. RESEARCH OBJECTIVES

In this project, the aim is to synthesize castor oil based interpenetrating polymer networks. To achieve it, castor oil is modified with maleic anhydride from the hydroxyl group to give castor oil maleic anhydride adduct (COMA). As a result of the reaction, castor oil gains a double bond and a carboxylic acid functional group. In the next step, COMA will be reacted with commercial epoxy resins such as Bisphenol-A diglycidyl ether epoxy resin, epoxy novolac resin and Heloxy 505 epoxy resin. In the reaction, carboxyl end of COMA opens the epoxy group and due to multifunctionality of both reactants, the final product is a crosslinked polymer. During the reaction, the unsaturated double bonds are preserved. In the final step, this polymer is swollen in styrene and the double bonds in the polymer are polymerized with styrene to form a sequential interpenetrating polymer network.

In Figure 2.1 the project is summarized clearly. Although the reactansts are multifunctional, the reactions of one functional group are shown for simplicity.

Finally, the chemical, mechanical and thermal properties of products are examined.

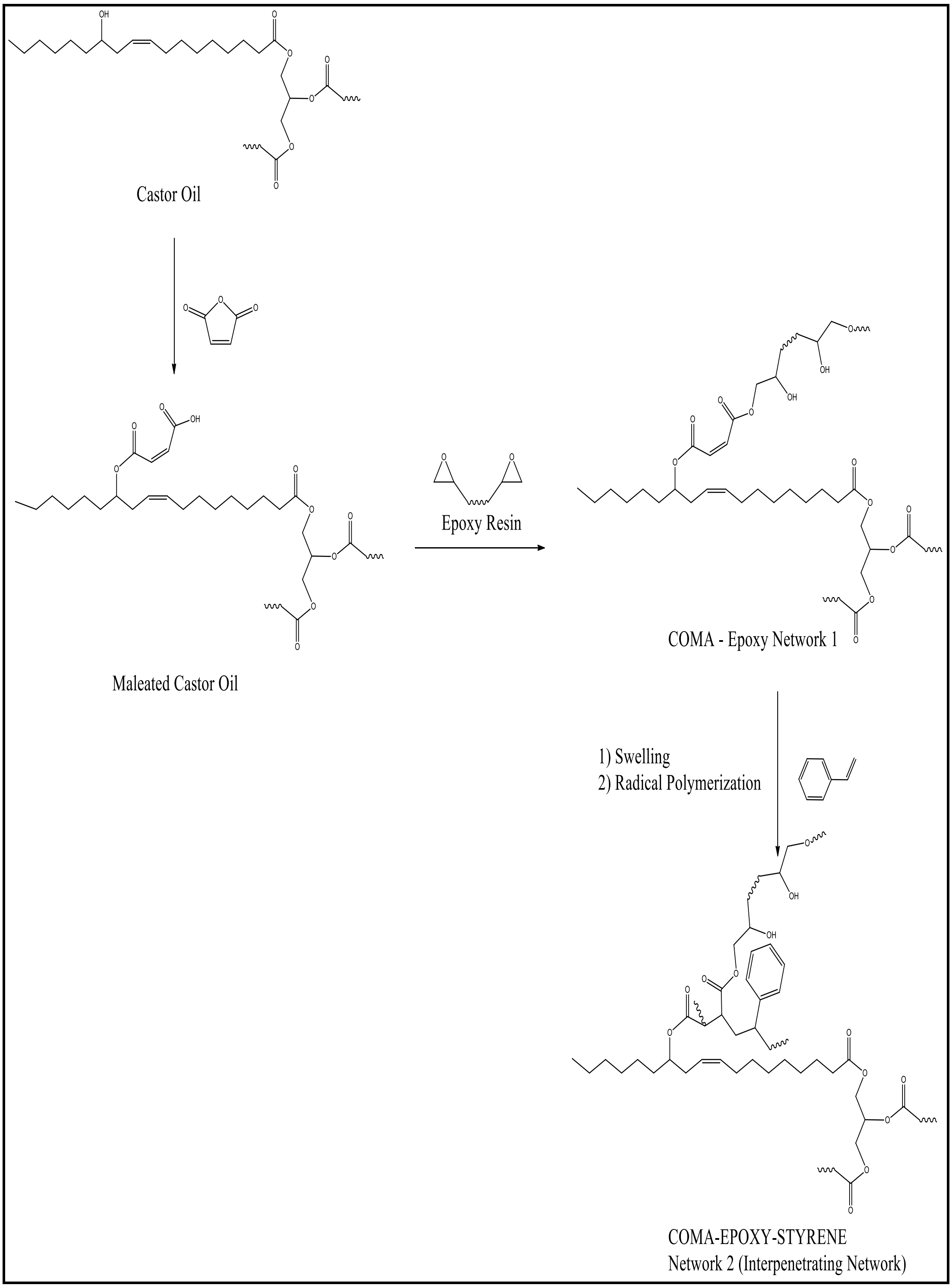


Figure 2.1. Synthesis and polymerization of castor oil based networks.

3. EXPERIMENTAL

3.1. Materials and Apparatus

3.1.1. Materials

Castor oil was obtained from Veskim Kimya, maleic anhydride was supplied by Cam Elyaf A.Ş. and was used after purification. Diglycidal ether bisphenol A epoxy resin and novolac epoxy resin was procured from Cam Elyaf A.Ş. and heloxy 505 epoxy resin was purchased from Momentive. Epoxy equivalent weights of epoxy resins were learned from suppliers, any determination experiments were not done. Toluene and styrene was purchased from Merck (Germany).

3.1.2. Apparatus

The IR analysis were performed on Nicolet 380 FT-IR with Smart Diamond ATR.

The Zwick/Roell Durometer with Shore A was used to determine the surface hardness of polymer samples.

3.2. Synthesis of Maleated Castor Oil (COMA)

COMA was synthesized according to procedure given in the thesis of Şeyma Avcılar with small modifications. There are 2.44 hydroxyl groups in a one triglyceride units and all of them can react with maleic anhydride theoretically. According to this information, the mole ratio of maleic anhydride to castor oil is obtained as 2.5:1 for the reaction. COMA was synthesized in a three-necked round bottom flask which is sealed with a condenser, a rubber septum and a drying tube packed with calcium chloride. 34.24g (36.6 mmol) castor oil and 9 g (91.8 mmol) maleic anhydride were mixed at room temperature under nitrogen for half an hour. After the addition of 40 ml toluene, the mixture was heated to 100^{o}C and stirred at that temperature for 3 days, then at room temperature for 1 day. The reaction was determined by following IR spectrum. Then, toluene was evaporated under vacuum at 100^{o}C and the characterization has been carried out with IR.

IR Spectrum (cm^{-1}): 3007.78 (C=C-H streching), 2925.52, 2854.77 and 1454.40 (C(sp^{3})-H streching), 1723.37 (C=O streching), 1644.44 (-C=C streching), 1414.67, 980.87 (C (=O)-O-H bend), 819.23 (=C-H bend)

Titration with 0.1 M NaOH was used to determine the maleation ratio of COMA thanks to its carboxylic acid functionalities. COMA was dissolved in a ethanol water solution whose ratio is 5:2.

3.3. Synthesis of COMA - Epoxy Resin Polymers

3.3.1. Synthesis of COMA- DGEBPA epoxy resin adduct

The optimum ratio of COMA-DGEBPA was determined as 1:1.2. 4.69 g (3.99 mmol) of COMA and 2.28 g (12 mmol) of DGEBPA epoxy resin are stirred to make the mixture homogeneous. After keeping this mixture at 100^{o}C for half an hour under vacuum, it was transfered to a teflon mold and the mold was heated at 100 ^{o}C during 10 hours under nitrogen. The final product is light yellow, transparent and flexible. Extraction was done with toluene to determine the unreacted amount of starting materials. It is insoluble in any solvent. Therefore, the characterization of the product was done with IR.

IR Spectrum (cm^{-1}): 3496.6 (O-H), 3010.2 (C=C-H streching), 2925.72, 2854.67 and 1454.4 (C(sp^{3})-H streching), 1731.36 (C=O streching), 1644.33 (-C=C streching), 1162.37, 1254.4 (-C(=O=-O streching)

3.3.2. Synthesis of COMA- Heloxy 505 epoxy resin adduct

The optimum ratio of COMA-Heloxy 505 epoxy resin was determined as 1:1. 4.69 g (3.99 mmol) of COMA and 2.28 g (12 mmol) of Heloxy 505 epoxy resin are stirred to make the mixture homogeneous. After keeping this mixture at 100^{o}C for half an hour under vacuum, it was transfered to a teflon mold and the mold was heated at 100 ^{o}C during 10 hours under nitrogen. The final product is light yellow, transparent and flexible. It is insoluble in any solvent. Therefore, the characterization of the product was done with IR.

IR Spectrum (cm^{-1}): 3467.8 (O-H), 3010.2 (C=C-H streching), 2925.72, 2854.67 and 1454.4 (C(sp^3)-H streching), 1735.44 (C=O streching), 1637.4 (-C=C streching), 1160.5, 1091.0 (-C(=O=-O streching).

3.3.3. Synthesis of COMA- Novolac epoxy resin adduct

The optimum ratio of COMA-Novolac epoxy resin was determined as 1:1.3. 4.69 g (3.99 mmol) of COMA and 3.12 g (13 mmol) of Novolac epoxy resin are stirred to make the mixture homogenous at 50 ^{o}C due to the semisolid form of the epoxy resin. After keeping this mixture at 90 ^{o}C for half an hour under vacuum, it was transfered to a teflon mold and the mold was heated at 90 ^{o}C during 6 hours under nitrogen. The final product is white yellow and opaque. The polymer is relatively more rigid than other COMA-epoxy resin adducts. It is insoluble in any solvent. Therefore, the characterization of the product was done with IR.

IR Spectrum (cm^{-1}): 3307.02 (O-H), 3010.2 (C=C-H streching), 2925.72, 2854.67 and 1454.4 (C(sp^3)-H streching), 1724.85 (C=O streching), 1644.49 (-C=C streching), 1157.08, 1102.2 (-C(=O=-O streching).

3.4. Synthesis of Interpenetrating Polymer Networks with COMA Epoxy Resin Adduct

Azobisisobutyronitrile (AIBN) was added in styrene 1 % by weight and the COMA epoxy resin adduct was swollen in styrene until the styrene ratio become 30% of total weight, then it was kept at room temperature for one day to diffuse the styrene everywhere.

After that, swelled first network was kept at 65^{o}C for one day. The characterization of the product carried out with IR.

For COMA-DGEBPA-2-30%S

IR Spectrum (cm^{-1}): 3470.5 (O-H), 3010.2 (C=C-H streching), 2926.7, 2855.12 and 1455.7 (C(sp^3)-H streching), 1727.84 (C=O streching), 1607.86 1509.18, 1644.5 (-C=C streching), 1401.53 (C=C bending) 1162.37, 1254.7 (-C(=O)-O streching),

For COMA-HEL 505-2-30%S

IR Spectrum (cm^{-1}): 3496.6 (O-H), 3010.2 (C=C-H streching), 2925.72, 2854.67 and 1454.4 (C(sp^3)-H streching), 1731.36 (C=O streching), 1644.49 (-C=C streching), 1254.4 (-C(=O=-O streching)

For COMA-NOV-2-30%S

IR Spectrum (cm^{-1}): 3307.02 (O-H), 3010.2 (C=C-H streching), 2925.72, 2854.67 and 1454.4 (C(sp^3)-H streching), 1727.49 (C=O streching), 1610.34 1509.18, 1644.5 (-C=C streching), 1161.85, 1104.95 (-C(=O)-O streching).

4. RESULTS AND DISCUSSON

4.1. Synthesis and Characterization of COMA

4.1.1. Synthesis of COMA

The synthesis of COMA was done according to the described procedure in Şeyma Avcılar's thesis with small modifications. The ratioof castor oil to maleic anhydride was chosen as 1:2.5 because castor oil contains 2.44 hydroxyl groups per triglyceride although in most figures its functionality is shown as 3. In this way, removing of unreacted maleic anhydride step was eliminated. Moreover, a solvent was used toprevent maleic anhydride sublimation and toluene was chosenas a solvent because toluene has the highest boiling point amongthe solvents which dissolve maleic anhydride, castor oil and COMA. The reaction mechanism of COMA is given in Figure 4.1.

Freshly recrystallized maleic anhydride was used for the synthesis because maleic anhydride can convert into maleic acid in moist air. Contamination with maleic acid is a problematic situation for this reaction because hydroxyl groups of castor oil can attack both ends of the maleic acid which leads to a crosslinked structure. Therefore, drying tube should be used in the reaction setup to prevent conversion of maleic anhydride to maleic acid by reacting with water. At high temperatures carboxylic acid ends can give anhydride with another carboxylic acid or an ester with the secondary alcohol on castor oil and water may form. The mentioned side reactions need high temperature, acidic medium and long time. Therefore, when the reaction time shorter is than 4 days, they can be negligible.

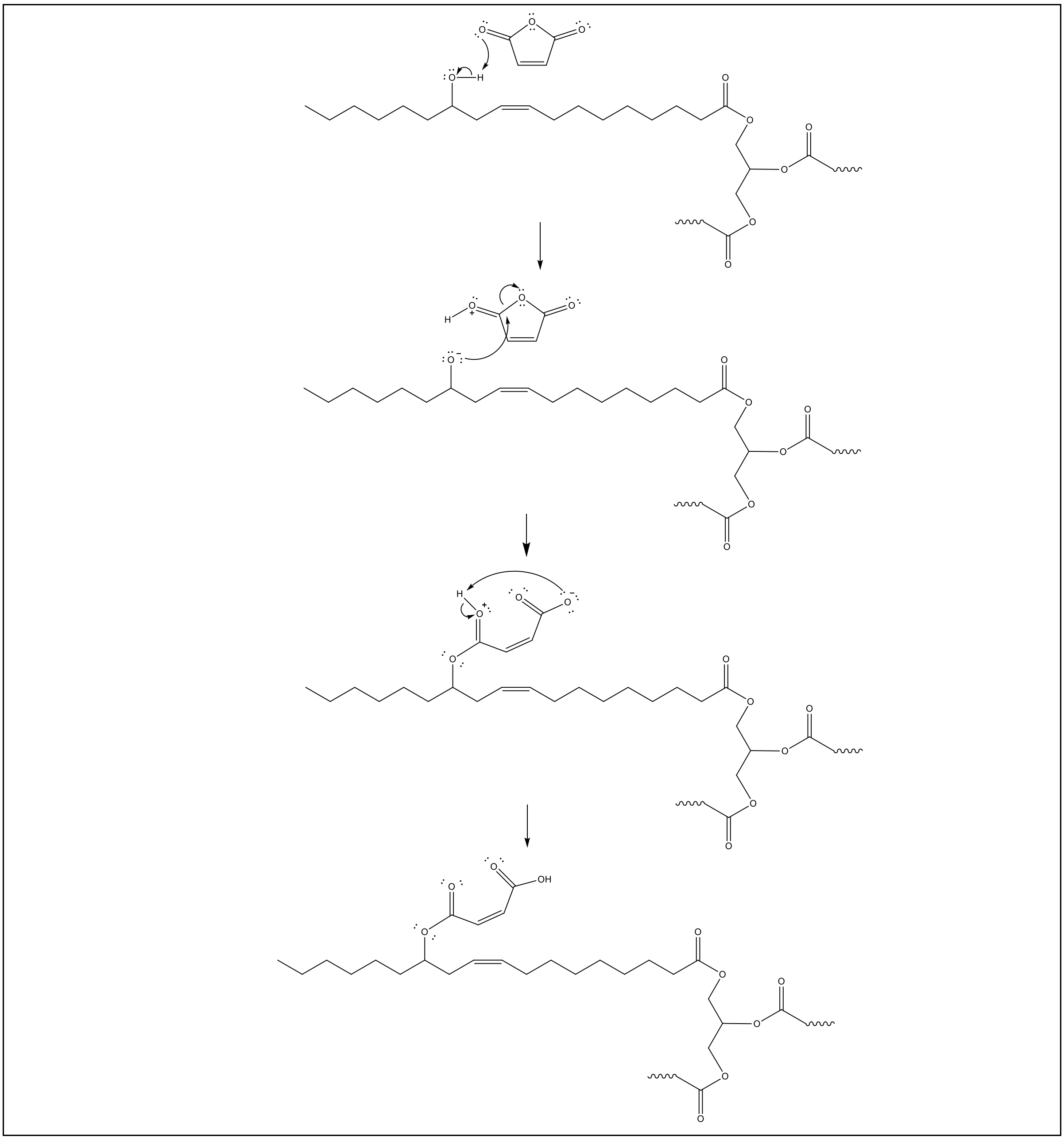


Figure 4.1. Mechanism of castor oil maleic anhydride reaction.

The reaction should be done under nitrogen because double bonds can react with oxygen at high temperatures; however, double bonds should be preserved because they are needed for second network. Also, oxygen can give an ene type reaction with the unsaturation of castor oil and the product is a peroxide type initiator. If COMA synthesis is run at a temperature higher than 75 °C, a peroxide crosslinked product is formed. The possible reaction was shown in Figure 4.2.

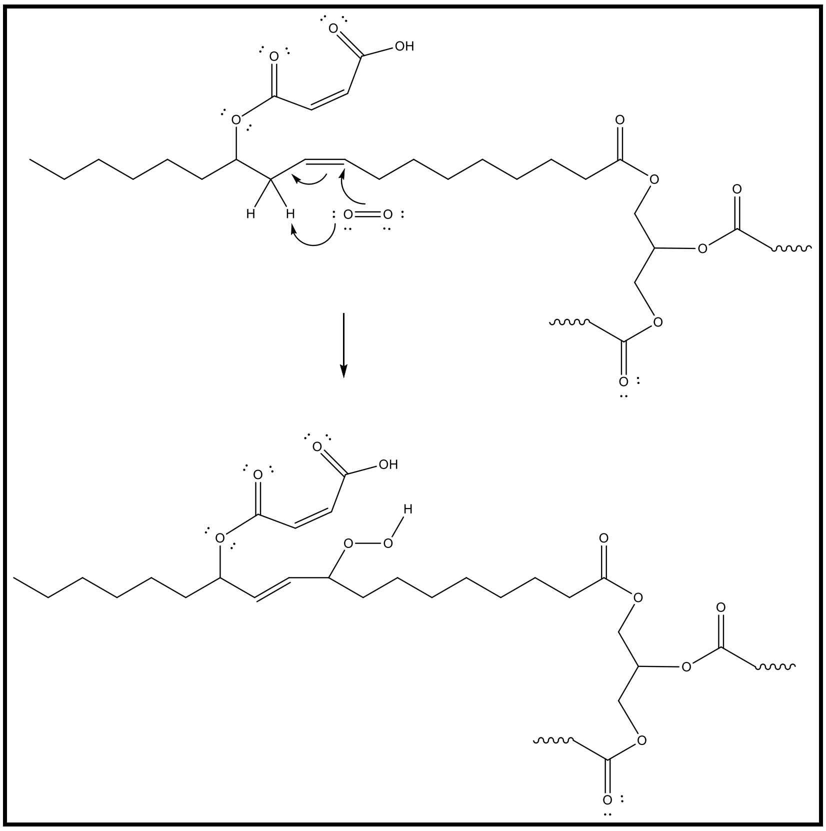


Figure 4.2. Possible side reaction.

4.1.2. Characterization of COMA

The IR spectra of COMA and castor oil are given in Figure 4.3. The peak at 3399 cm^{-1}corresponding to hydroxyl group has disappeared and the broad carboxylic acid peak has formed from 2500 cm^{-1} to 3500 cm^{-1} which indicates the formation of carboxylic ends of the COMA. Also, the new peaks at 1410 $cm^{-1}$and 979 cm^{-1}show the bending motions of -OH in carboxylic acid ends. The carbonyl peak is shifted from 1739 $cm^{-1}$to 1726 cm^{-1}due to the effects of to α-β unsaturation of maleate group and carboxylic acid groups.Also, the broadening of the carbonyl peak is observed because of the overlapping of different carbonyl groupabsorptions by the addition of maleic anhydride.The peaks at 1638 cm^{-1} due to the streching motion of sp^2 hybridized carbons in double bound and 821 cm^{-1} due to bending of vinyl hydrogens show the addition of maleate group. Also, the intensity of 1094 cm^{-1}which corresponds the bending motion of C-O in alcohol has decreased meanwhile the intensity of 1163 cm^{-1} which indicates the streching motion of C-O in ester has increased due to the ester bond formation by the addition of maleic anhydride. The alteration of IR peaks are summarized in Table 4.1.

Table 4.1. IR Peaks Alteration After COMA Reaction.

Peak position (cm^{-1})	Functional Group	Castor Oil	COMA
3399 (broad)	-OH	Present	Absent
1739	C=O	Present	Present, shifted to $1726cm^{-1}$
1638	-C=C-	Absent	Present
1410	-OH in carboxylic end	Absent	Present
1163	C-O in ester	Present	Intensity has increased
1094	C-O in alcohol	Present	Intensity has decreased
821	=C-H	Absent	Present

The maleation ratio of COMA can be calculated by using NMR integration by comparing the vinyl protons on the maleate with the terminal protons of CH_3 at the end of the fatty acid. However, in COMA structure there are also other vinyl protons due to the unsaturation of castor oil and this causes a problem. Therefore, the maleation ratio of COMA was determined by titration. For a titration system water is neccessary, but COMA is not soluble in water because of that ethanol water mixture was chosen as a solvent. The maleation ratio of COMA was determined as 2.25 maleates per triglycerides by titration with NaOH (aq).

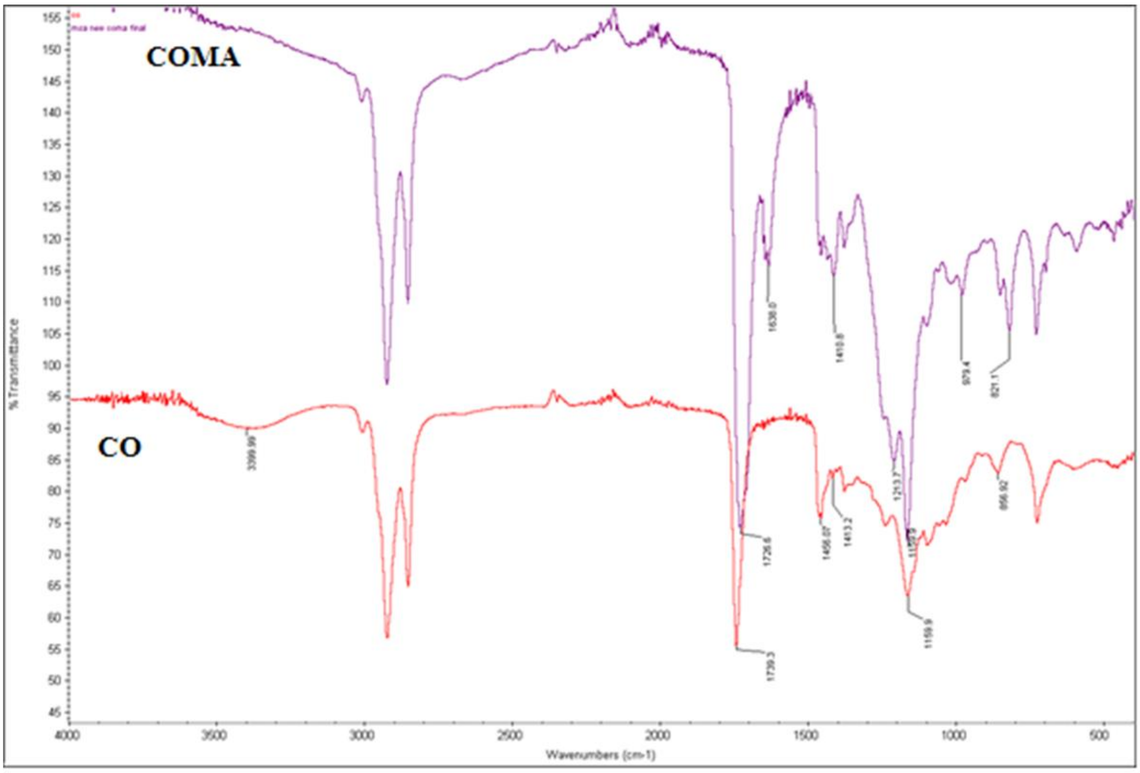


Figure 4.3. IR spectra of Castor Oil and Maleated Castor Oil.

The reaction time was determined by following the maleic anhydride peak at 1780 cm^{-1}. The consumption of maleic anhydride versus time is shown in Figure 4.4. By comparing IR spectra of the COMA reaction after 5 hours, 9 hours and 2 days.

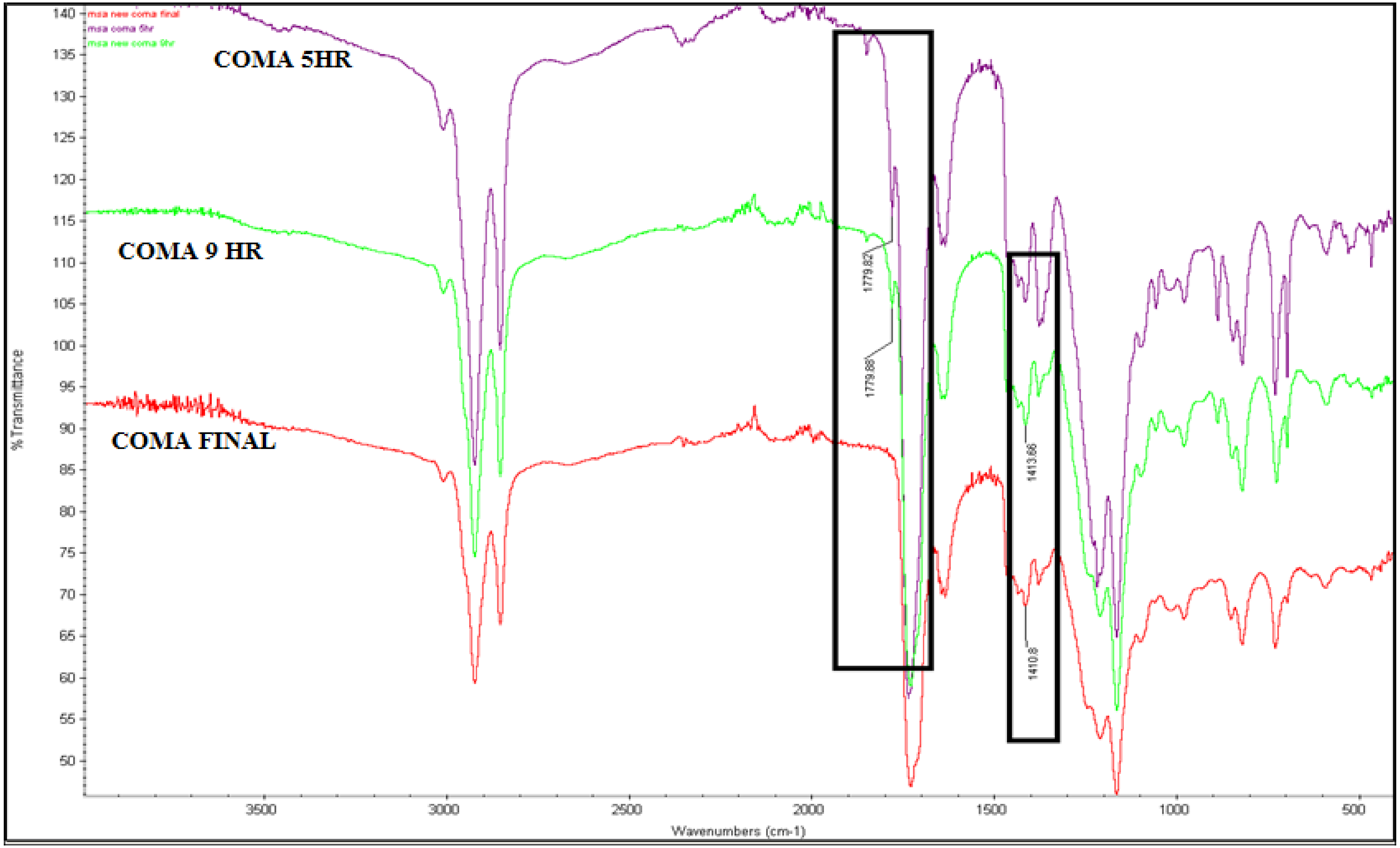


Figure 4.4. Consumption of maleic anhydride.

4.2. Reaction of COMA with Epoxy Resins

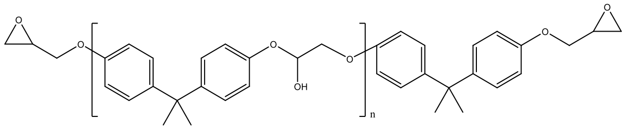
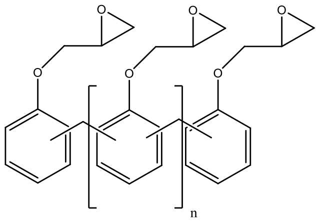
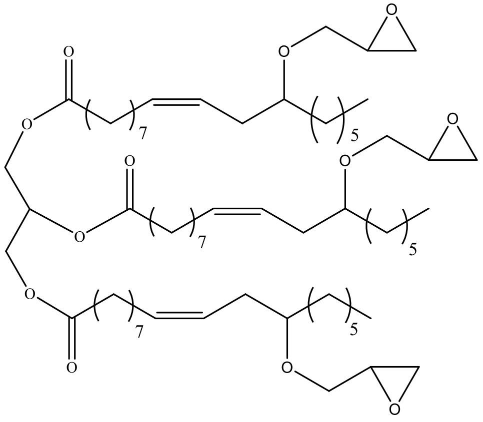
COMA can be used as a vegetable oil based epoxy curing agent thanks to its carboxylic acid ends. The chemical structures and epoxy equivalent weights (E.E.W.) of used epoxy resins are given in Table 4.2 COMA-epoxy resin polymers were synthesized around 100 ^{o}C in a solvent free medium. After the formation of polymer extraction was done with toluene to calculate efficiency and remove unreacted starting materials.

Normally, the addition reaction of carboxylic acids to epoxy group goes at low temperatures with catalysts. However, in this study all epoxy resins have terminal epoxy groups which makes the reaction easier so the formation could be done without catalyst. When the reaction was done by using 4-Dimethylaminopyridine (DMAP) or 1,4-diazobicyclo[2.2.2]octane (DABCO) as catalyst the reaction time, which directly depends on the strucure of epoxy resin, has shortened.

The products of all reactions are thermoset polymers, in other words, they are not soluble in common NMR solvents. Therefore, IR spectroscopy is theonly characterization method of all networks.

For the simplicity the polymer formed by COMA and DGEBPA is defined as COMA-DGEBPA-1, the polymer of COMA and Heloxy 505 epoxy resin is named as COMA-HEL 505-1, and the polymer of COMA and Novolac epoxy resin is called as COMA-NOV-1. Also, in the next parts the reactions are shown by using one functinoality of COMA due to easily follow of the reaction.

Table 4.2. Used epoxy resins.

Epoxy resin	Chemical structure	E.E.W.
DGEBPA		190
Novolac epoxy resin		240
Heloxy 505 epoxy resin		368

4.2.1. Determination of COMA: Epoxy Resin Ratio

The reaction mechanism between the carboxylic acid functionality of COMA and a general terminal epoxy is shown in Figure 4.5. The oxygen of epoxy ringis protonated and this makes the opening of epoxy ring by COMA easier; as a result of the reaction a polyester is formed. Hydroxyl group produced after ring opening may open another epoxy ring, in other words, opened ring of epoxy group acts as a nucleophile for epoxy resin and ring opening polymerization of the epoxy can be observed as a homopolymerization which is shown in Figure 4.6. The relative rates of ring opening polymerization vs. opening of another epoxy group depend on the structures of the epoxy resin and carboxylic compound and cannot be predicted. The stoichiometry must be experimentally optimized.

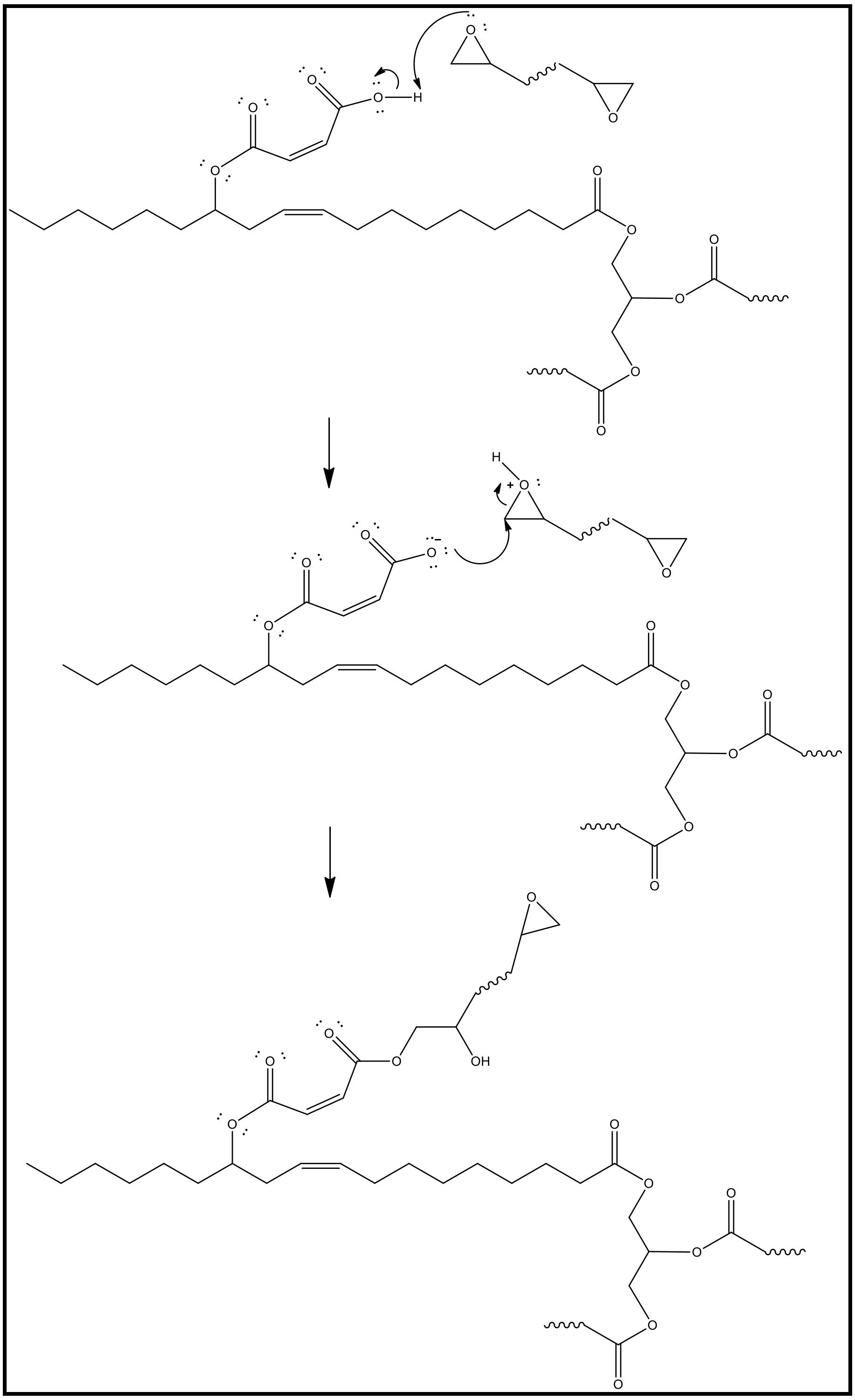


Figure 4.5. Mechanism of COMA terminal epoxy reaction.

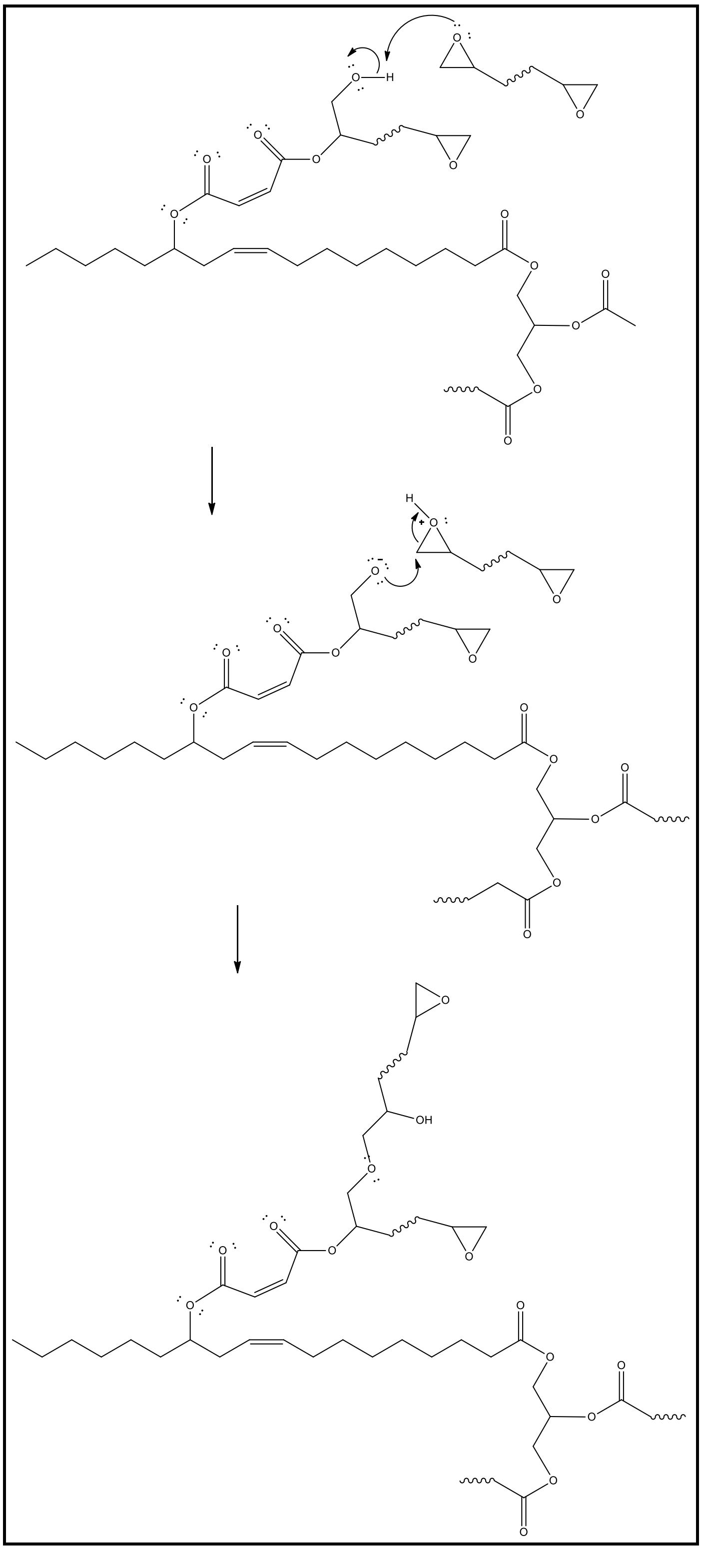


Figure 4.6. Homopolymerization of epoxy resin.

Different mole ratios of COMA and epoxy resins were cured and their IR spectra and surface hardness values were analyzed for the optimization of COMA epoxy resin ratio. The surface hardness results of the polymers having different mole ratios of COMA-DGEBPA are given in Table 4.3.

Table 4.3. Surface Hardness Results for the polymers with different COMA/DGEBPA ratio.

	COMA/DGEBPA ratio				
	1:1.1	1:1.2	1:1.3	1:1.5	1:1.6
Surface Hardness value	52	34,8	40,9	40,8	51,2

Unfortunately, there is not any trend between epoxy ratio and surface hardness. Therefore, the epoxy peak height was compared with a peak height which is intact during the ring opening polymerization. Normally, comparing the peak area is a more reliable way and it is known that the peak height can be used for the very narrow and strong peaks, however, the baseline of the spectrum is not constant although baseline correction have been done, so the peak area measurements are impractical.

The highest consumption of epoxy resin was choosen as the ideal ratio of the COMA/epoxy resin. The optimum mole ratio for COMA-DGEBPA-1 was determined as 1:1.2 according to mole ratio of COMA:DGEBPA. The optimum mole ratio for COMA-HEL 505-1 was determined as 1:1 according to mole ratio of COMA:Heloxy 505 epoxy resin. The optimum mole ratio for COMA-Novolac-1 was determined as 1:1.3 according to mole ratio of COMA:Novolac epoxy resin. The ratios given are the ratios of –COOH groups to epoxy groups.

4.2.2. Characterization of First Networks

4.2.2.1. COMA – Diglycidyl Ether BPA Epoxy Resin Polymer. Thereaction between COMA and diglycidylether Bisphenol A epoxy resin is shown in Figure 4.7, the end product is a yellow, transparent and flexible material which contains 59 % vegetable oil by weight. After the extraction with toluene, the reaction efficiency was calculated as 89.6%. The structure analyzed by IR due to the crosslinked structure of the network. The summary of alteration of the peaks are given in Table 4.4.

The IR spectra of COMA-DGEBPA-1 sample, COMA and DGEBPA are given in Figure 4.8. The peak at 3496 cm^{-1} corresponding to the –OH group has formed in the IR spectrum of COMA-DGEBPA-1 sample, this peak formation indicates the opening of epoxy groups. Also the peak at 980 cm^{-1} which shows the bending motion of –OH in carboxylic acid has disappeared due to the consumption of carboxylic ends during curing reaction. The carbonyl peak is shifted from 1734 cm^{-1} to 1731 cm^{-1} due to the alteration of carbonyl from carboxylic acid to ester. There is not any change in the peak at 1644 cm^{-1} which signifies that double bonds of the COMA are still intact during ring opening of epoxy reaction. The intensity of the epoxy peaks at 916 cm^{-1} and 761 cm^{-1} in IR spectrum of DGEBPA has decreased dramatically in the IR spectrum of final cured product. Also, the new peak at 1245 cm^{-1} indicates the formed C-O bond in COMA-DGEBPA-1 polymer.

Table 4.4. The basic peaks in COMA-DGEBPA-1 Spectrum.

Peak position (cm^{-1})	Functional Group	Epoxy	COMA	COMA-DGEBPA-1
3496	-OH	Absent	Absent	Present
1731	C=O	Absent	Present	Present
1644	C=C	Absent	Present	Present
1608, 1583, 1507	C=C of benzene	Present	Absent	Present
912 & 752	C-O-C (epoxy)	Present	Absent	Intensity has decreased

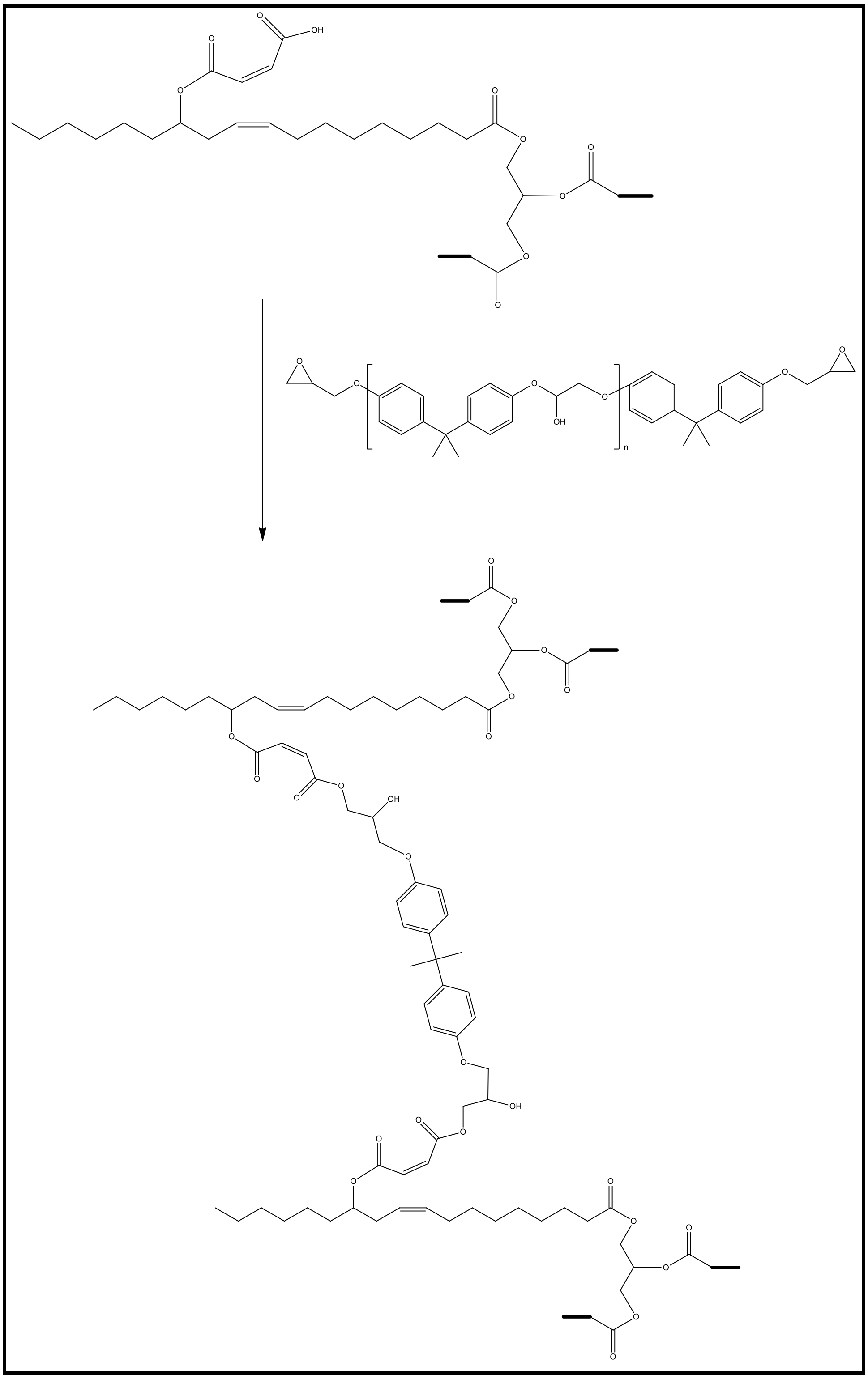


Figure 4.7. Synthesis of COMA-DGEBPA epoxy resin polymer.

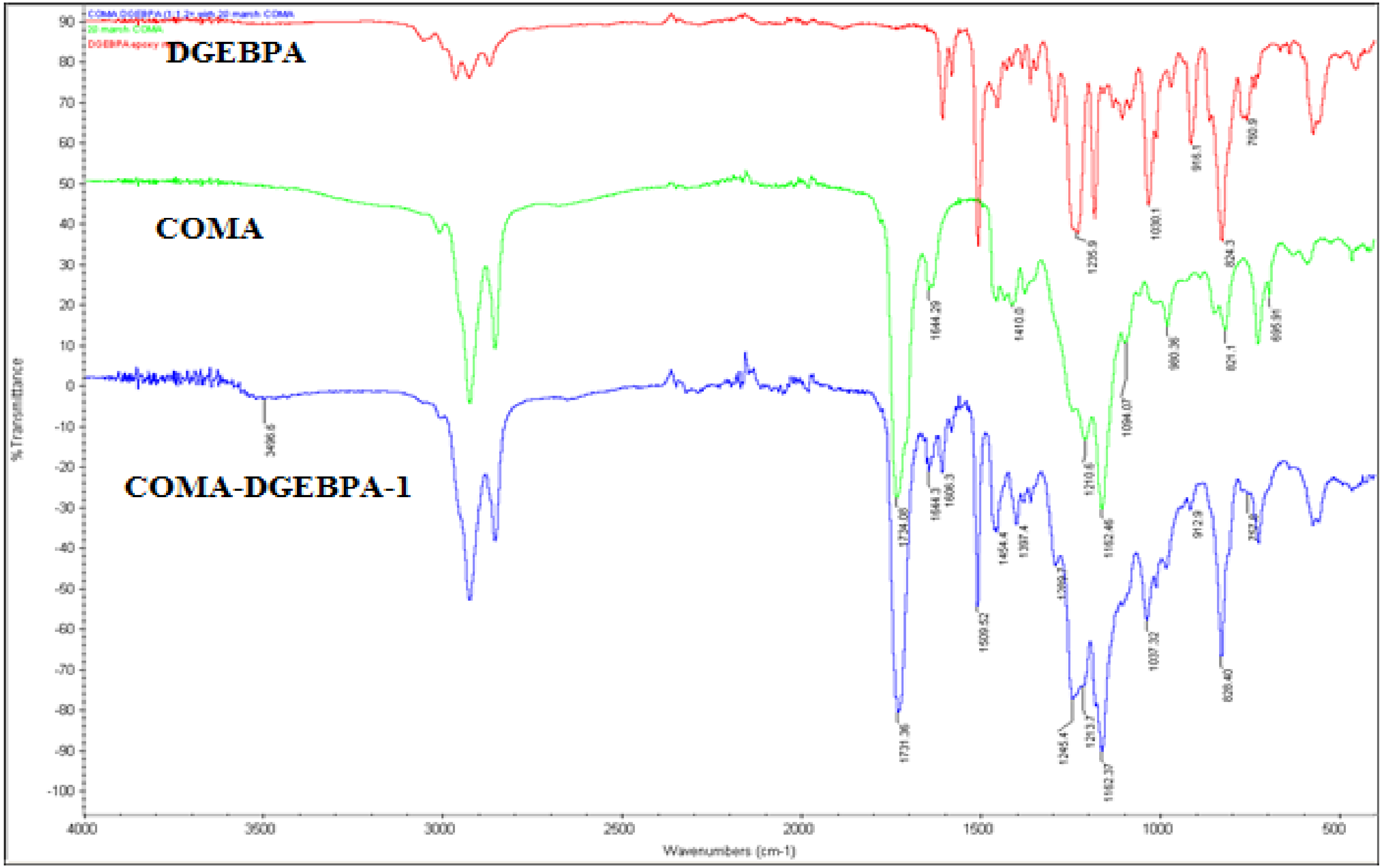


Figure 4.8. IR Spectra of DGEBPA, COMA and COMA-DGEBPA polymer.

4.2.2.2. COMA – Heloxy 505 Epoxy Resin Polymer. The synthesis of COMA-Hel 505-1 resin is shown in Figure 4.9, the polymer product is light yellow, transparent, soft and flexible with 89 % vegetable oil content by weight. Extraction was done with toluene to determine the efficiency and it was calculated as 87.8 %. The characterization of the sample was done by IR spectroscopy because any solvent could not dissolve the sample. The basic peaks in the COMA-HEL 505-1 spectrum and thecomparison of them with COMA and Heloxy 505 spectra are given in Table 4.5.

Figure 4.10 shows the IR spectra of COMA-HEL 505-1, COMA, Heloxy 505 epoxy resin. The broad carboxylic acid peak from 2500 cm^{-1}to 3500cm^{-1} has disappeared and the hydroxyl peak has appeared at 3467 cm^{-1} with respect to the spectrum of COMA-HEL 505-1 with spectrum of COMA. This alteration shows the consumption of carboxylic acid ends by opening epoxy rings because the epoxy peaks at 839 cm^{-1}and 909cm^{-1} has disappeared and the intensity of peak at 751 cm^{-1} has decreased. The carbonyl peak is shifted from 1734 cm^{-1} to 1731 cm^{-1}, the reason of small shift can be explained as addition of carbonyl groups of triglycerides which are very smaller to the carbonyl groups on COMA.

Table 4.5. The peaks in COMA-HEL 505-1 Spectrum.

Peak position (cm^{-1})	Functional Group	Epoxy	COMA	COMA-HEL 505-1
3467	-OH	Present	Absent	Present
1735	C=O	Present	Present	Present
1644	C=C	Absent	Present	Present
839 & 909	C-O-C (epoxy)	Present	Absent	Absent
751	C-O-C (epoxy)	Present	Absent	Intensity has decreased

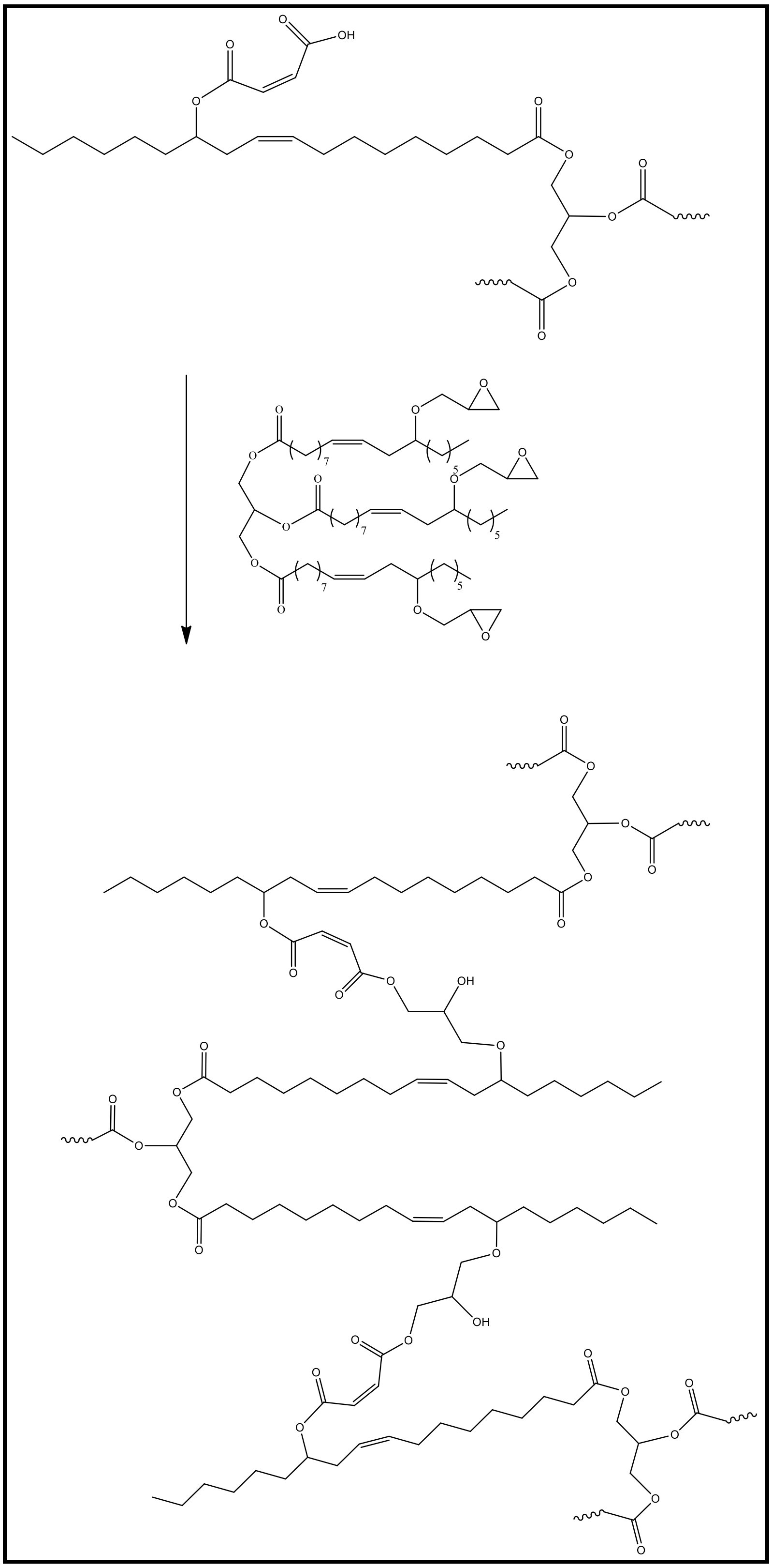


Figure 4.9. Chemical Structure of COMA – Heloxy 505 epoxy resin polymer.

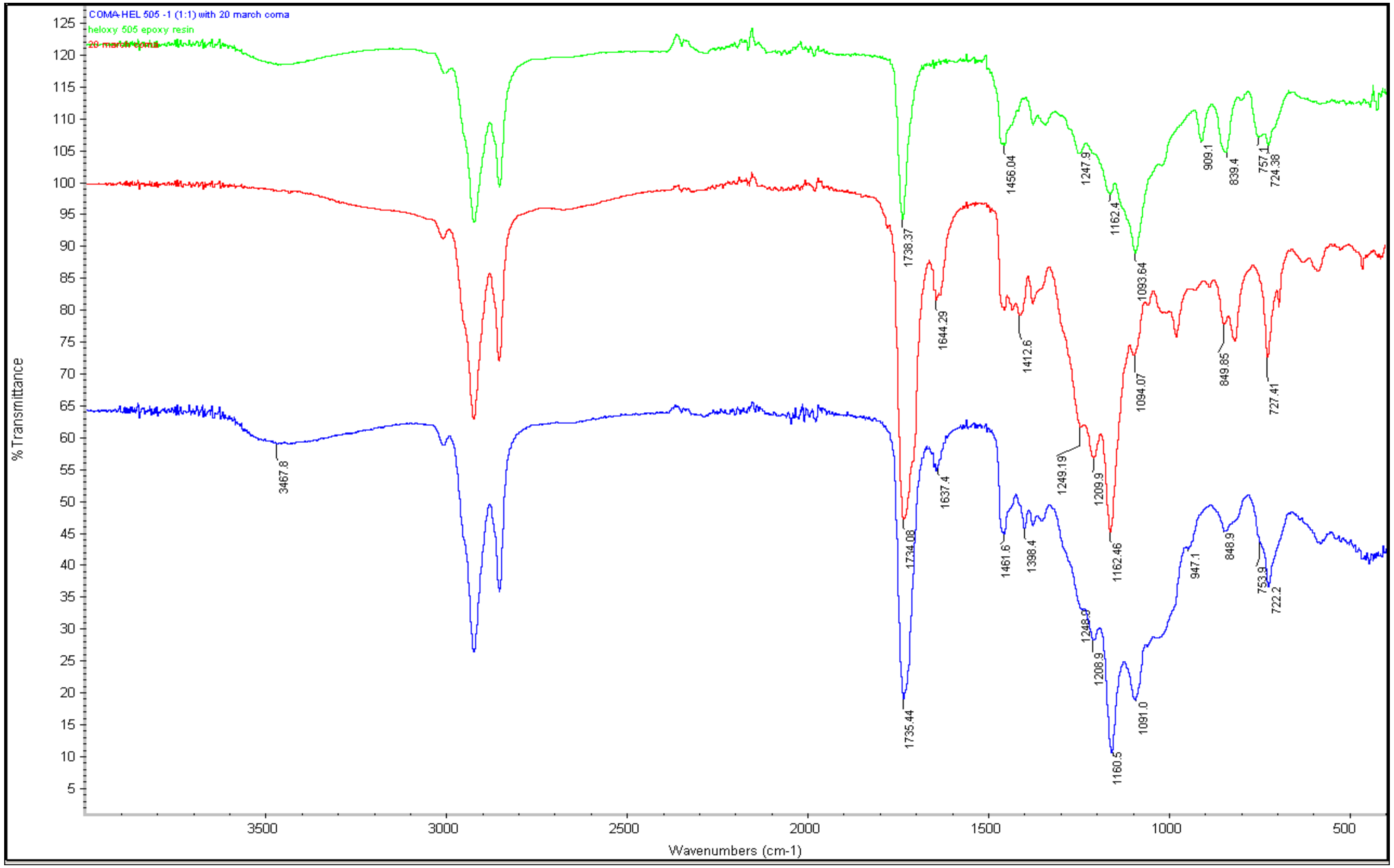


Figure 4.10. IR spectra of COMA-HEL 505-1, COMA and Heloxy 505 epoxy resin.

4.2.2.3. COMA – Novolac Epoxy Resin Polymer. The reaction between COMA and Novolac epoxy resin is shown in Figure 4.11, the product white-yellow and opaque, its vegetable oil content is 55% by weight. Reaction efficiency was calculated as 91.2% as a result of extraction with toluene. The sample was analyzed by IR spectroscopy because product is a thermoset structure. The important peaks of the end product are given in Table 4.6.

The IR spectra of COMA-NOV-1, COMA and Novolac epoxy resin are shown in Figure 4.12. As it is seen there is a low intensity peak at 3479 cm^{-1}corresponding to hydroxyl groups on epoxy resin which means during resin formation all hydroxyl groups is not epoxidized. In spectrum of COMA-Nov-1, the hydroxyl peak at 3307 cm^{-1} has incresed due to the formation of –OH groups as a result of epoxy ring opening by COMA. The carbonyl peak is shiftedfrom 1734 cm^{-1} to 1724 cm^{-1}and got narrowdue to the conversion of carboxylic acid carbonyls to estercarbonyls. There is not any intensity decrease in the peak at 1644 cm^{-1}which indicates that double bonds are still intact. The intensity of the peak at 1235 cm^{-1} corresponding to C-O streching of epoxy ring has decreased in the spectrum of COMA-NOV-1. In addition, the intensity of the epoxy peaks at 909 cm^{-1} , 834 cm^{-1} and 753 cm^{-1} has decreased significantly which proves the opening of epoxy rings. The new peak at 991 cm^{-1} indicates the formed C-O bond of the COMA-NOV-1 sample.

Table 4.6. The peaks in the COMA-NOV-1.

Peak position (cm^{-1})	Functional Group	Epoxy	COMA	COMA-NOV-1
3307	-OH	Present	Absent	Present
1724	C=O	Absent	Present	Present
1644	C=C	Absent	Present	Present
1608, 1504	C=C of benzene	Present	Absent	Present
1235, 909, 834 & 752	C-O-C (epoxy)	Present	Absent	Intensity has decreased

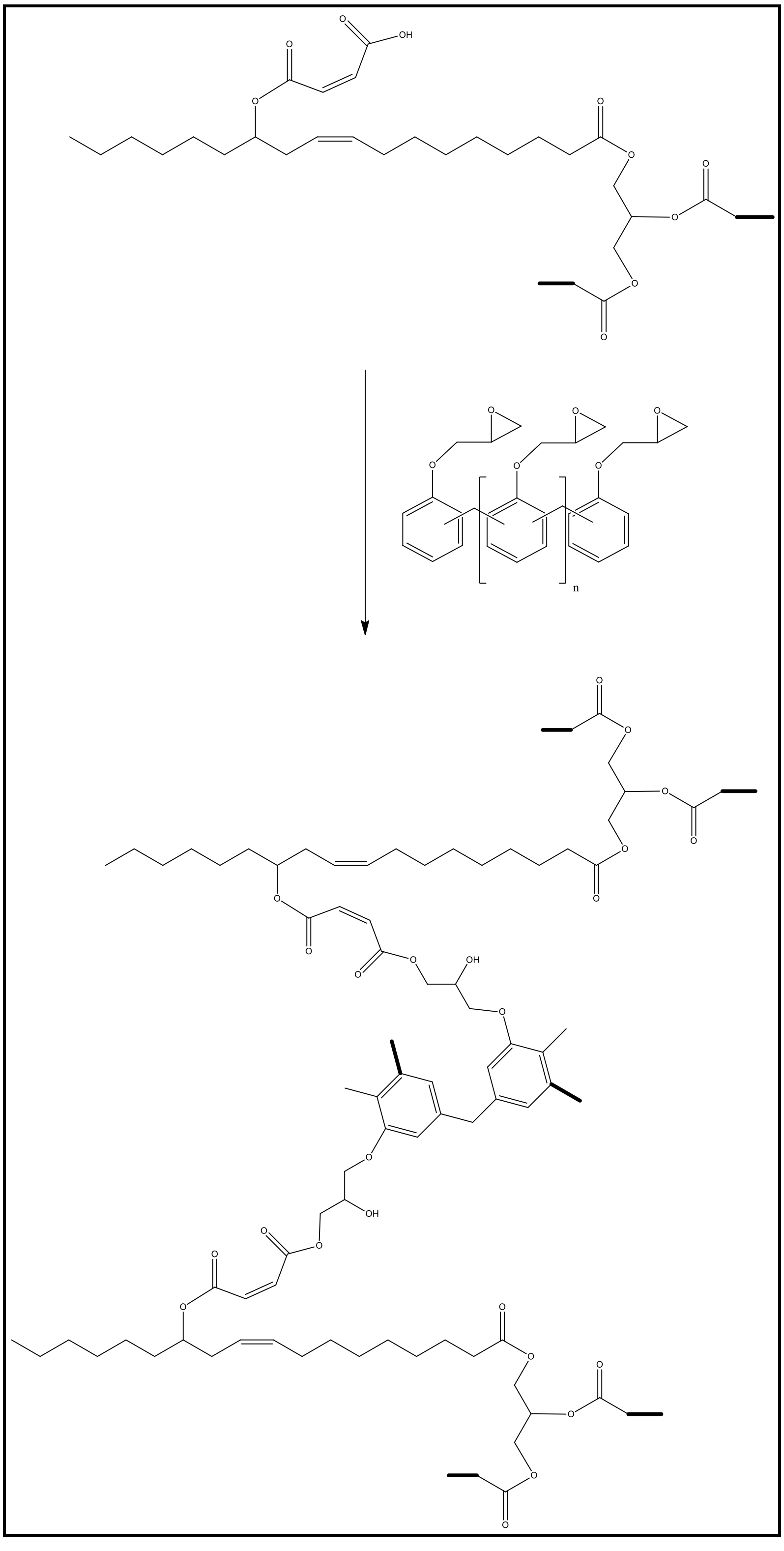


Figure 4.11. The reaction between COMA and Novolac Epoxy resin .

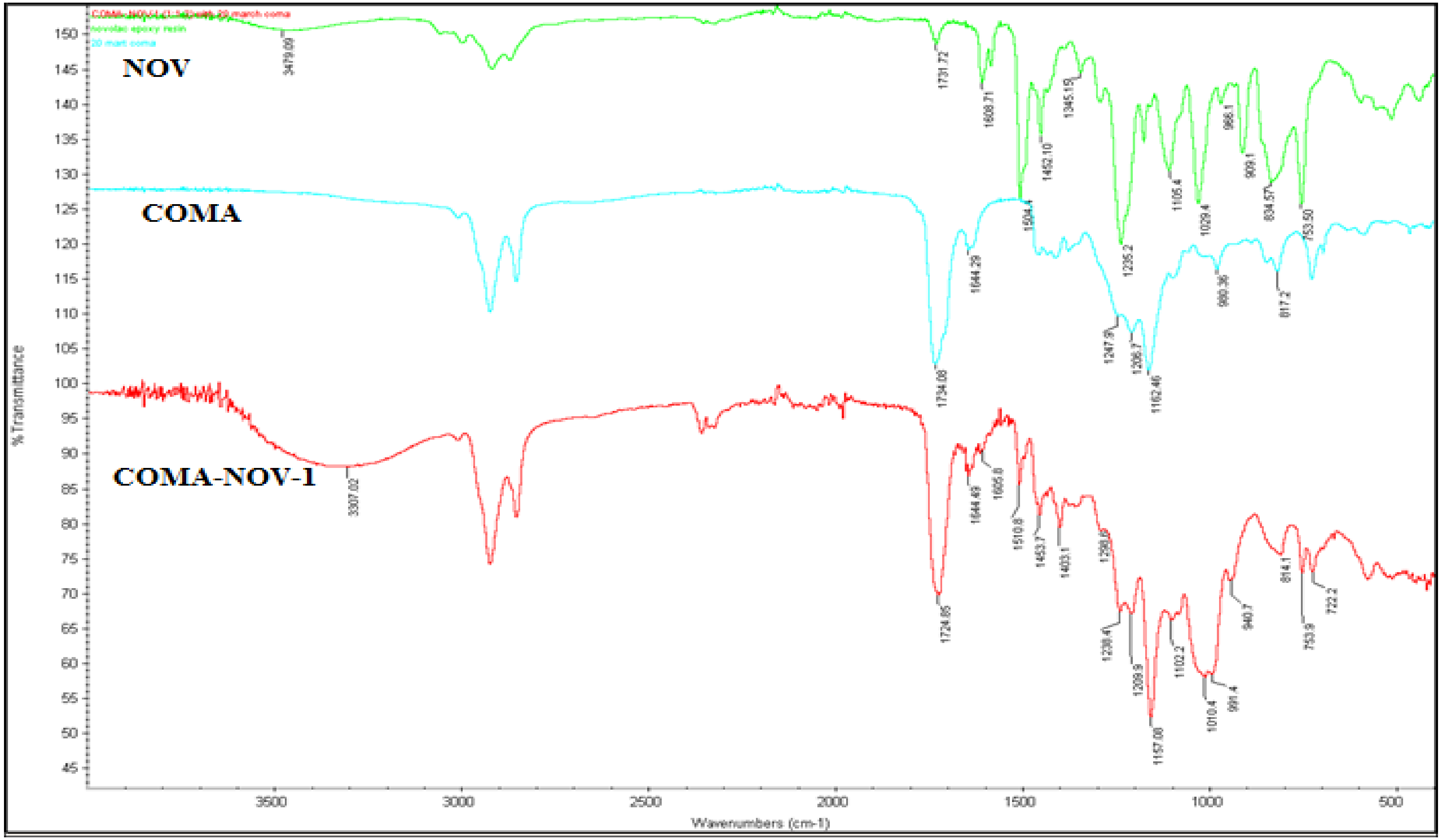


Figure 4.12. The IR spectra of COMA-NOV-1, COMA and Novolac epoxy resin.

4.2.3. Thermogravimetric Analysisof First Networks

4.2.3.1. TGA Analysis of COMA –DGEBPA First Network. Figure 4.13 shows the TGA of COMA – DGEBPA first network sample. Thermally, COMA – DGEBPA polymer is stable up to 303 °C, until that temperature only 5 % of the sample was lost. Then, the polymer undergoes two-stage-decompositionat 303 °C to 396 °C with total weight loss of 25 %. From the literature information the first stage can be the decomposition of labile oxygen containing groups suchas carboxylic and anhydride [25]. Sample decomposes at 396 °C to 472 °C and leaves 9 % wt% solid residue after second stage decomposition. According to litareture, the esters of castor oil decompose at 343 °C and thermal decomposition of castor oil occurs at 340 °C to 460 °C, as a result heptanol and 10 – undecylonic acid form [26]. Moreover, thermal degradation of epoxy resin occurs in this stage, when the DGEBPA was analyzed alone a degradation step was observed between 315 °C and 435 °C .

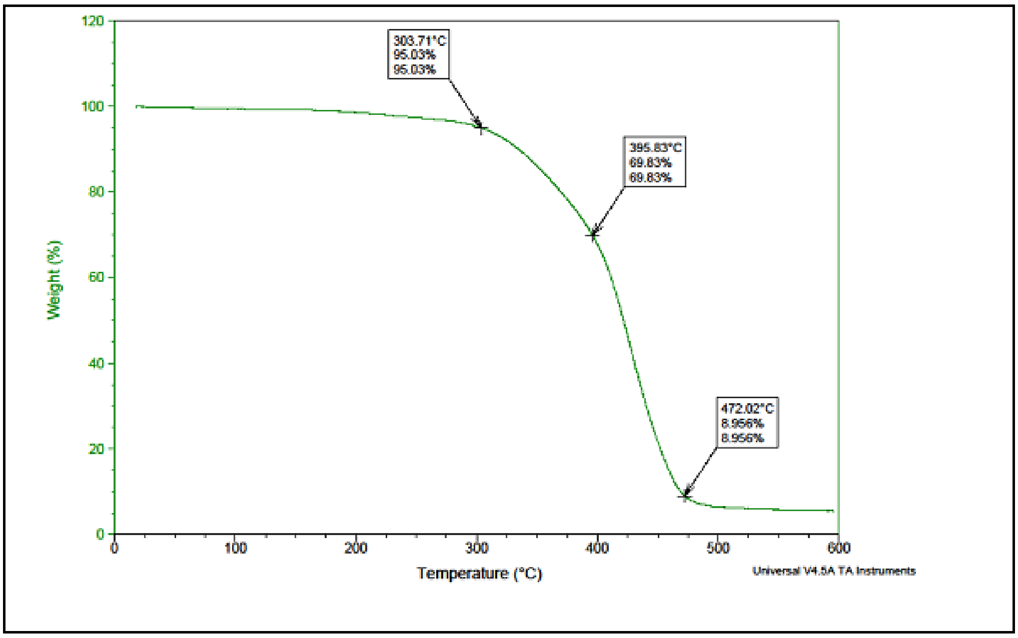


Figure 4.13. TGA of COMA-DGEBPA-1 Sample.

4.2.3.2. TGA of COMA – Novolac Epoxy Resin First Network. Figure 4.14 is the TGA of COMA-Novolac epoxy resin polymer. Decomposition takes place in two steps. Between 273°C and 397 °C, the sample lost 26 % of its total weight. The 57 % weight loss is observed in the second step with 13% of weight solid residue which occurs at 396 °C to 515 °C. Phenolic resins are known for their thermal stability, this is why modern rocket nose cones are made from phenolic composition. Such polymers form a carbon layer which protects the sample againist further decomposition. This behaviour is called as intumisence which can be the reason of high percentage of solid residue.

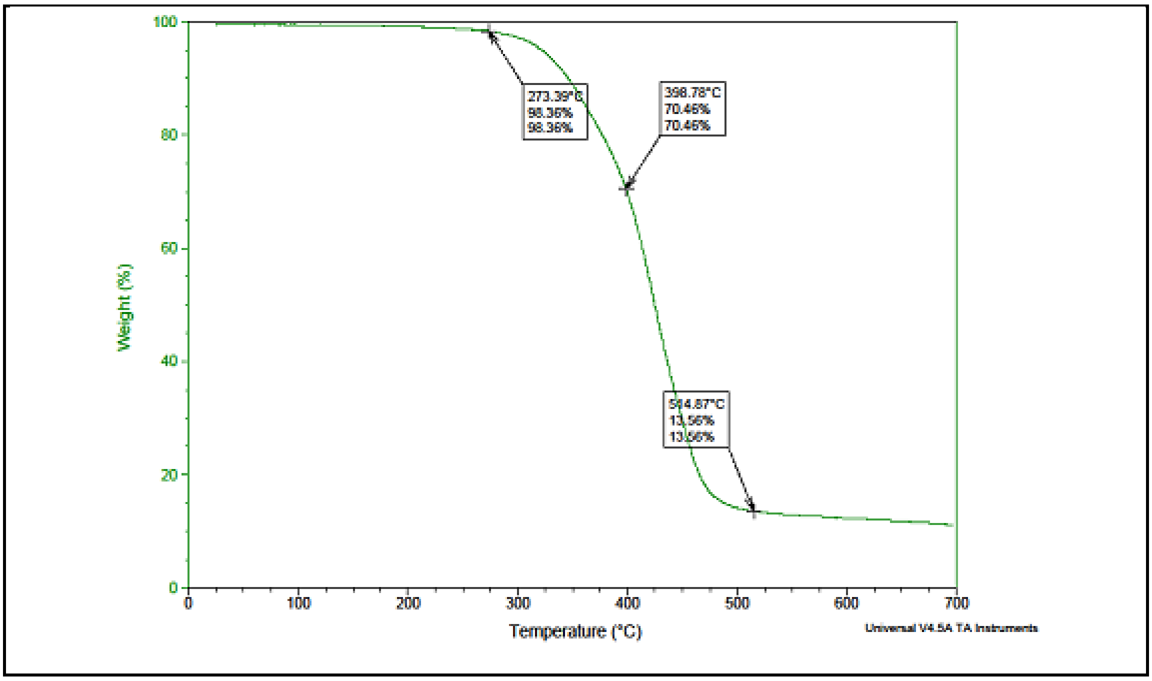


Figure 4.14. Change in weight of COMA – Novolac epoxy resin first network vs temperature.

4.2.3.3. TGA Analysis of COMA-Heloxy 505 Epoxy Resin First Network. TGA thermogram of COMA – Heloxy 505 polymer is given in Figure 4.15. Surface moisture and inherent moisture are emitted until 276 °C. Decomposition of the sample showed a degradation step at 276 °C to 377 °C and another degradation step startsat 377°C and the degradation it finishes at 479 °C with 3 % solid residue.

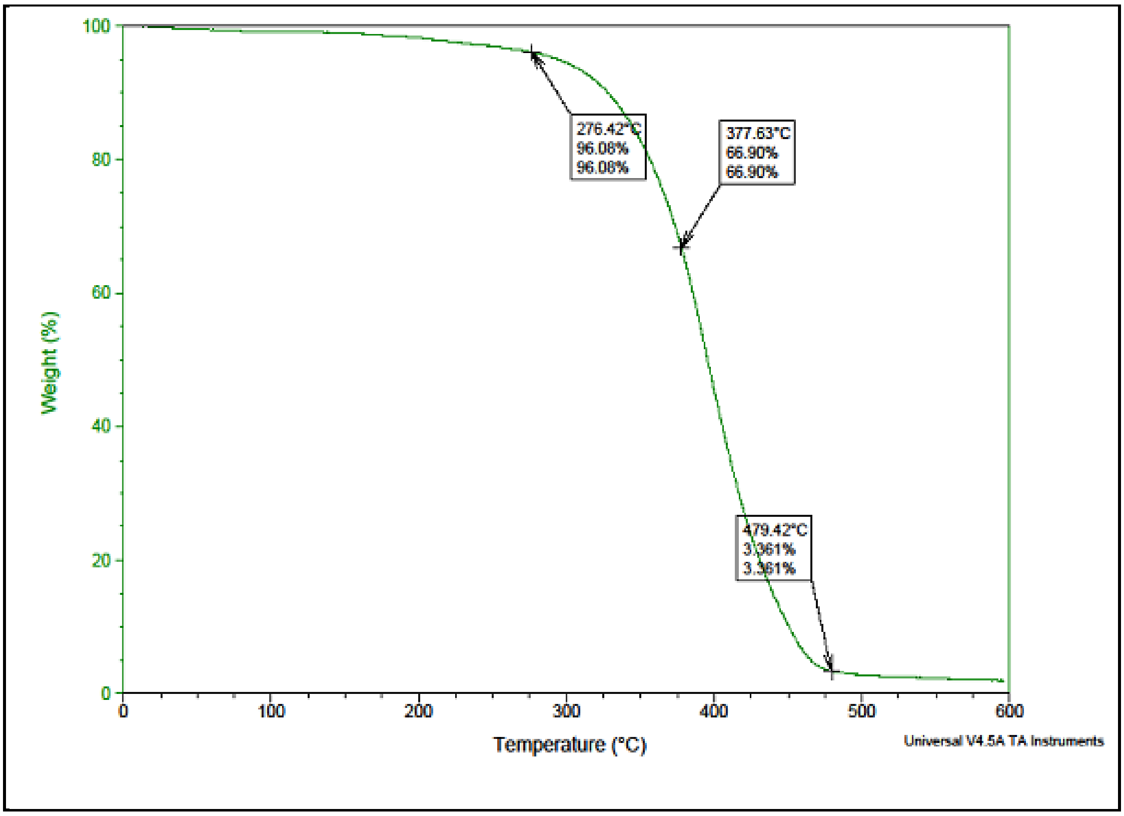


Figure 4.15. TGA of COMA-HEL 505-1 sample.

4.2.4. Mechanical Properties of First Networks

The first samples that synthesized at the beginning of the project contained numerous gas bubbles and they were not suitable for mechanical tests. Later a method was developed where the COMA-epoxy resin reaction started in a large test tube under vacuum until its viscosity reached a reasonable point viscosity and then the product was poured into a teflon mold and reaction continued under nitrogen. Polymer samples that were synthesized by A stage- B stage polymerization method which is necessary to apply in this project to prevent bubble formation , are suitable for surface hardness measurements and three point bending tests.

Surface hardness test is used to determine the relative surface hardness of materials. Surface hardness is not an intrinsic property, results of this test depend on the test method. In this study, surface hardness were measured by Shore A durometer due to the softness of the polymers. Durometer measures the depth in the material caused by a known force and the depth refers to hardness of the material. The results of the first network are shown in Table 4.7.

The differences of surface hardness depend on the differences in structure of epoxy resins. According to measurement results, COMA-Novolac epoxy resin polymer has the highest hardness value for first network due to the presence of aromatic benzene rings and also the high crosslinking density. Moreover, the polymer formed by Heloxy 505 epoxy resin is the weakest product due to having two oil based starting materials. When the epoxy equivalent weights of epoxy resins are compared, it can be clearly predicted that the mesh size and the cavity between polymer chains will be highest for COMA Heloxy 505 epoxy resin polymer which causes low mechanical properties.

Table 4.7. Surface Hardness Results of First Networks.

	Shore A results
COMA-Bisphenol A epoxy resin polymer	14.8
COMA-Novolac epoxy resin polymer	47
COMA-Heloxy 505 epoxy resin polymer	3.5

Flexural testing determines the relation between bending stress and deflection. Three point bending test is a kind of flexural test and flexural properties such as flexural stress, flexural strain and flexural modulus are determined by it. The moduli of the samples were too low to allow three point bending tests to be done on the universal testing equipment available in our laboratories (Devotrans DVT-15). Therefore, a home made test rig was produced in our lab. The schematic of this instrument is shown in Figure 4.16. The instrument uses an electronic balance to measure the stress on the sample and an endless screw to apply the strain. The screw was chosen to provide 1.42 mm of strain every revolution. The distance between supports was chosen as 80mm.

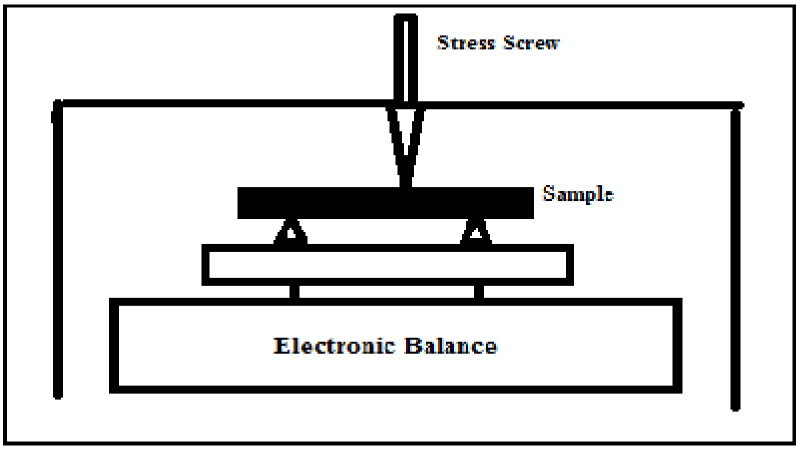


Figure 4.16. Basic representation of the three point bending instrument.

Flexural stress is the resistance to deformation under load. Calculations for flexural stress can be done with any point on the load deflection curve. Flexural strength of the material is the maximum amount of the flexural stress that it can take before breakage. However; breakage point could not be achieved due to flexibility of polymer samples and also restrictions due to the maximum capacity instrument. Therefore, failure was not observed and absolute flexural strengths of the samples could not be calculated.Flexural strain is the fractional change in the length of outer surface of the sample at the middle of its length. Flexural modulus is the ratio of stress to corresponding to strain and it indicates the stiffness of material. Modulud is usually calculated from the slope of the stress-strain curve at 10% strain. The equations of the flexural properties are given in Table 4.8 [27].

Table 4.8. The equations of Flexural Properties.

	Symbol (unit)	Equation [27]
Flexural stress	Б (MPa)	$(3FL)/(2bd^2)$
Flexural strain	μ(mm/mm)	$(6Dd)/L^2$
Flexural modulus	E_f(MPa)	$(L^3m)/(4bd^2)$

Where F is the load at a given point on the load-deflection cure in N, L is the support span in mm, b is the width of beam tested in mm, d is the depth of beam tested, D is the maximum deflection of the center of the beam in mm, m is the slope of load-displacement curve.

Figure 4.17 shows the load vs displacement curves of the first networks of COMA epoxy resin graphs. The slopes were determined from the linear parts of the curves. By using the slope, flexural modulus values for thepolymer networks were calculated and they are shown in Table 4.9.

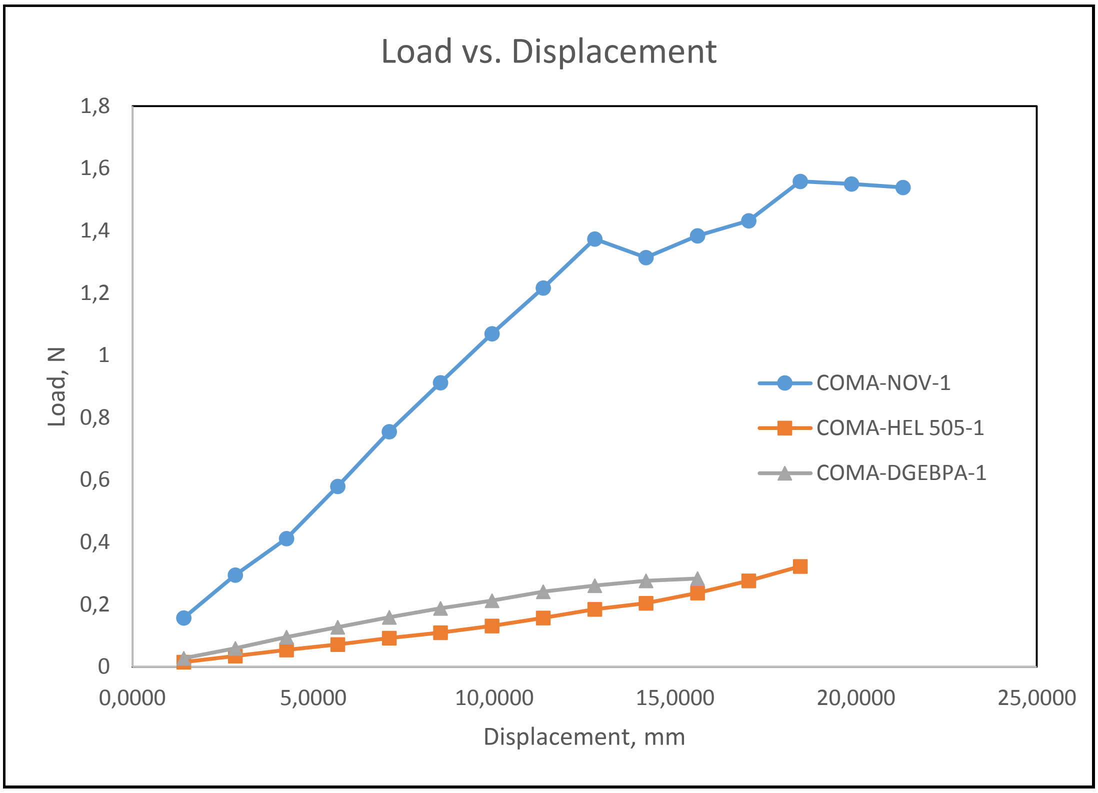


Figure 4.17. Load vs. Displacement curves for First Networks.

Table 4.9. Flexural modulus values of First networks.

	Slope of the F-D curve	Flexural Modulus (MPa)
COMA-DGEBPA-1	0.022	3.83
COMA-HEL 505-1	0.014	2.44
COMA-NOV-1	0.097	33.11

The flexural modulus of COMA-NOV-1 is much more higher than the flexural modulus of other polymers of first networks, which is an unexpected result. When the stress vs. strain graph of the COMA-NOV-1 was drawn, the shape of the curve looks like the shape of brittle materials which shows that there is an immiscibility between monomers and the particle acts like an epoxy resin according to flexural behaviour. Therefore, the flexural test result of COMA-NOV-1 is not reliable.

4.3. Second Networks

There are two types double bonds in first network which are double bonds of castor oil and double bonds of maleate groups. They can be polymerized thermally with styrene to increase the mechanical properties of the network. The reactivity ratio of styrene and maleate is very suitable for random copolymer formation; as a result, a second network has formed.

4.3.1. Synthesis of Second Networks

A crosslinked polymer absorbs some amount of solvent and swells when placed in a suitable solvent. To synthesize the second network, polymers which are formed by COMA and epoxy resins are swollen in several reactive diluents such as styrene, methyl methacrylate or vinyl acetate which were containing benzoyl peroxide (BPO) or azobisisobuttronitrile (AIBN) as an initiator. During the swelling homogeneity of styrene is the biggest problem because the network swells from outside to inside. Swelling the network with the desired amount of solvent and keeping it the polymer sample in that solvent overnight enables the diffusion of absorbed solvent to give a reasonable homogenous sample.

To make a logical comparison between the second networks, reactive diluents used for swelling of each networkand the reactive diluent ratio by weight should be same. Styrene was chosenas a reactive diluent for all networks due to its swelling property and relatively high boiling point. Second networks include 30% styrene by weight. As an initiator AIBN was used because its decomposition temperature is lower than other possible initiators and curing at low temperatures is a neccessity to prevent the evaporation of styrene. Some evaporation of styrene from the sample surface is inevitable and this loss was found to be 10% of added styrene and 3,5 % of total weight of the sample which can be negligible. The general reaction between COMA-epoxy resin and styrene is shown in Figure 4.18.

For simplicity, second network formed by COMA-DGEBPA-1 which is includes 30 % of styrene of total weight is called as COMA-DGEBPA-2-30%S. The second network of COMA-HEL 505-1 is defined as COMA-HEL 505-2-30%S and the second network of COMA-NOV-1 is named as COMA-NOV-2-30%S.

4.3.2. Characterization of Second Networks

As a characterization method, IR spectroscopy is the only analytical instrument that can be used due to the crosslinked structure of network. IR spectra of first and second network of the polymer of COMA-Heloxy 505 epoxy resin are given in Figure 1.19 and the spectra of first and second networks of COMA-DGEBPA polymer are shown in Figure 4.20. As expected, decrease in the intensity of double bond peak at 1644 cm^{-1} is seen clearly in both spectra of second networks which indicates the curing of double bonds in first networks by free radically. There are no more changes in spectrum since the second network formation occurs only with reaction at the unsaturation. Unfortunately, there is not a significant change in the double bond peak in COMA-NOV polymer spectrum, increase in mechanical properties is the evidence of the formation of second network for it.

When the moles of double bonds of styrene and double bonds of polymer are chosen equal, the amount of styrene is not enough to swell the network homogenously. Therefore, an excess of styrene is taken and thismay lead to homopolymerization of styrene.

When the IR spectra of second networks were analyzed it is seen that all maleate double bonds have not consumed, according to literature this fact is expected [28] Although styrene is polymerized slowier than maleate groups, in the end 75% of the maleate reacts whereas all styrene is consumed.

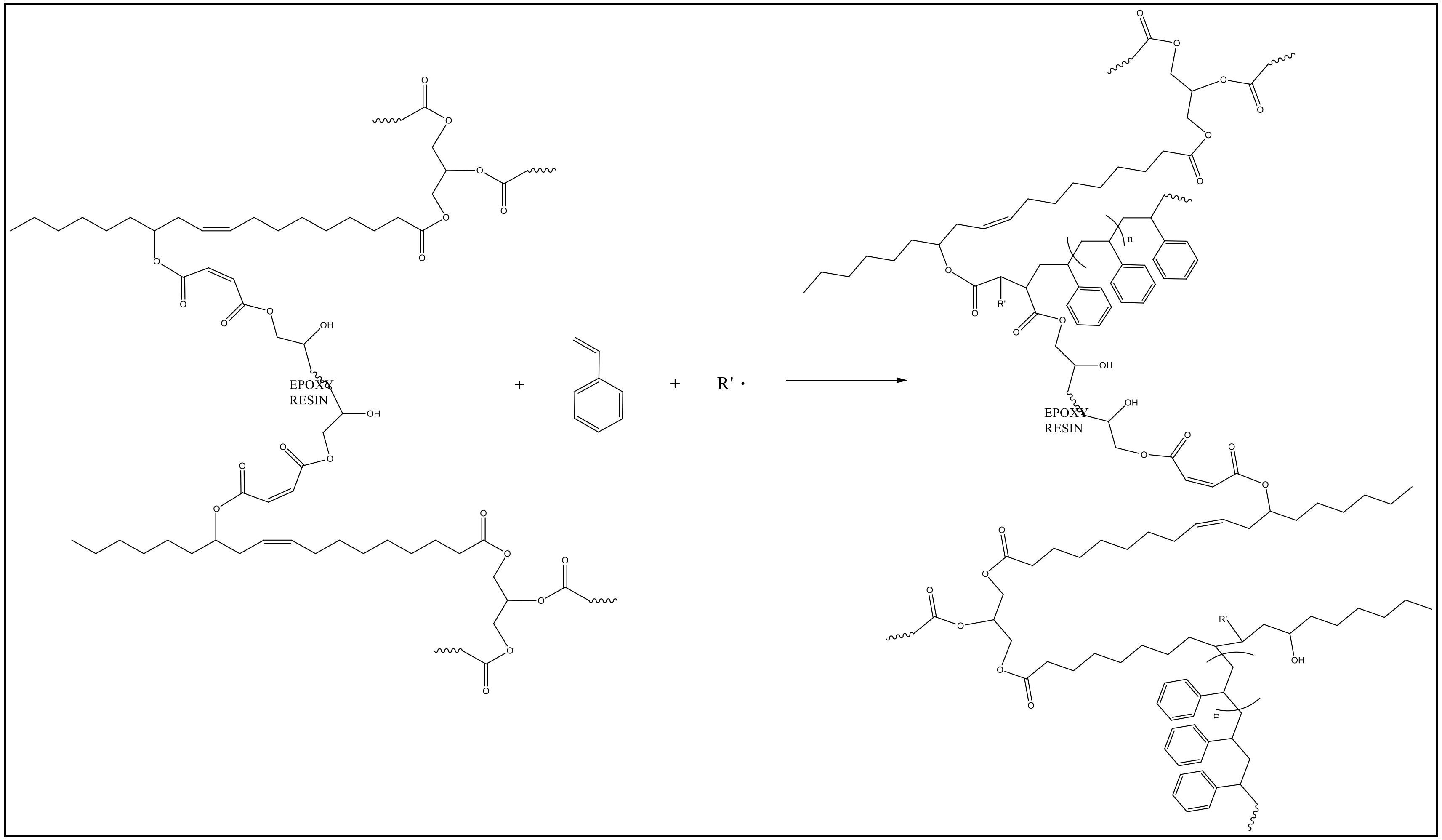


Figure 4.18. General reaction between first network and styrene.

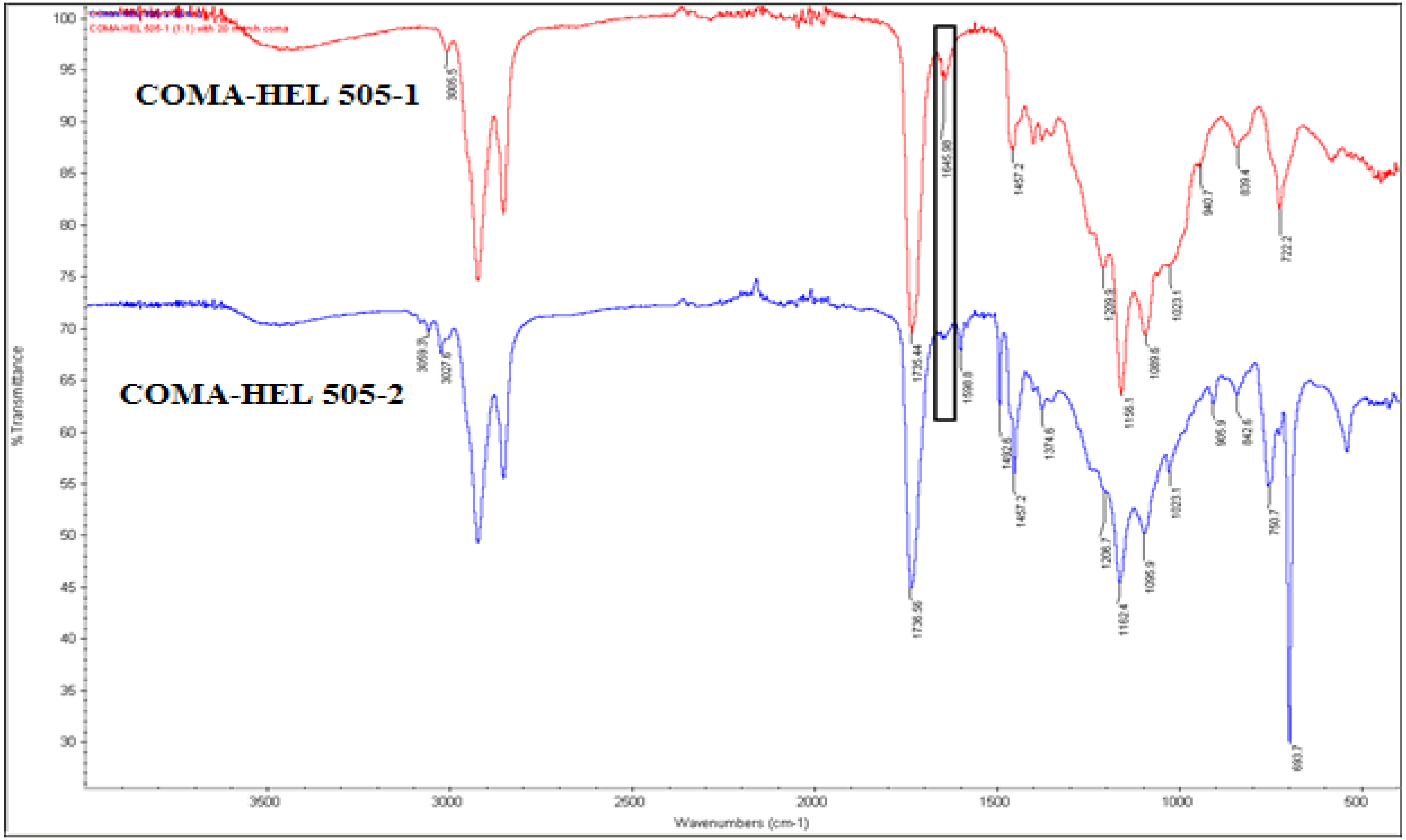


Figure 4.19. IR spectra of COMA-HEL 505-1 and COMA-HEL 505-2-30%S.

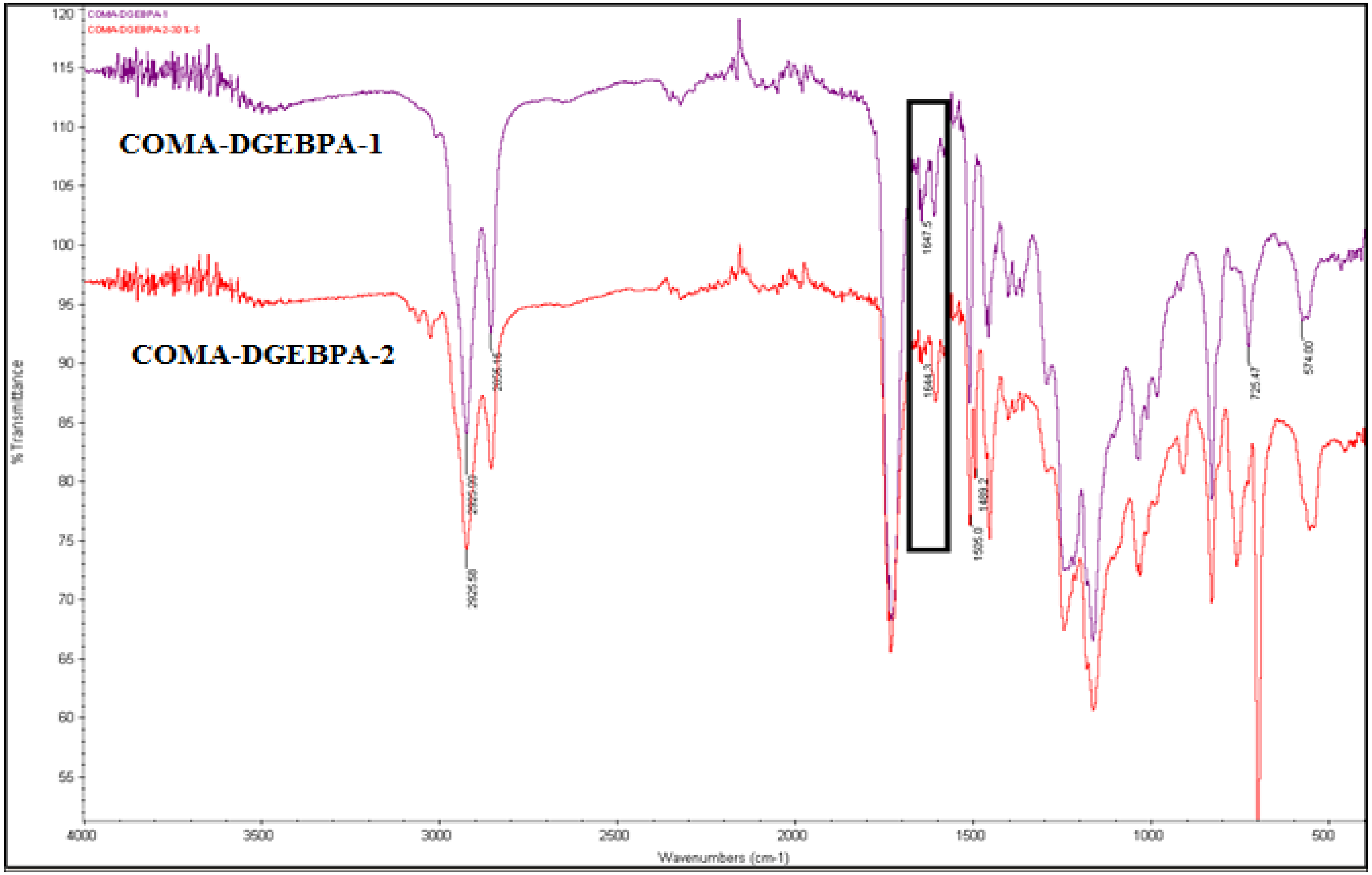


Figure 4.20. The IR Spectra of COMA-DGEBPA-1 and COMA-DGEBPA-2-30%S.

4.3.3. Thermogravimetric Analysis of Second Network

4.3.3.1.TGA of COMA-DGEBPA-2. The second network of COMA-DGEBPA was thermally analyzed and its graph is shown in Figure 4.21. The interpenetrating network was lost 3 % of its weight at 280 °C and it undergoes a degradation at 280°C to 384 °C. During this step 20 % of total weight was lost. After that, the second stage degradation starts at 384°C and it ends at 472 °C with 6 % solid residue. The difference between the first network and second network is the addition of styrene which results the maleate styrene polymer and homopolymer of styrene. According to literature, polystyrene decomposition begins at 270°C and stops at 425 °C [29]. If unreacted styrene exist in the second network, it decomposes around 200 °C; however, it is not expected due to the volatility of styene. Also, the thermogravimetric analysis data for copolymer of styrene and maleic anhydride is observed in the range of 300°C to 450 °C [30].

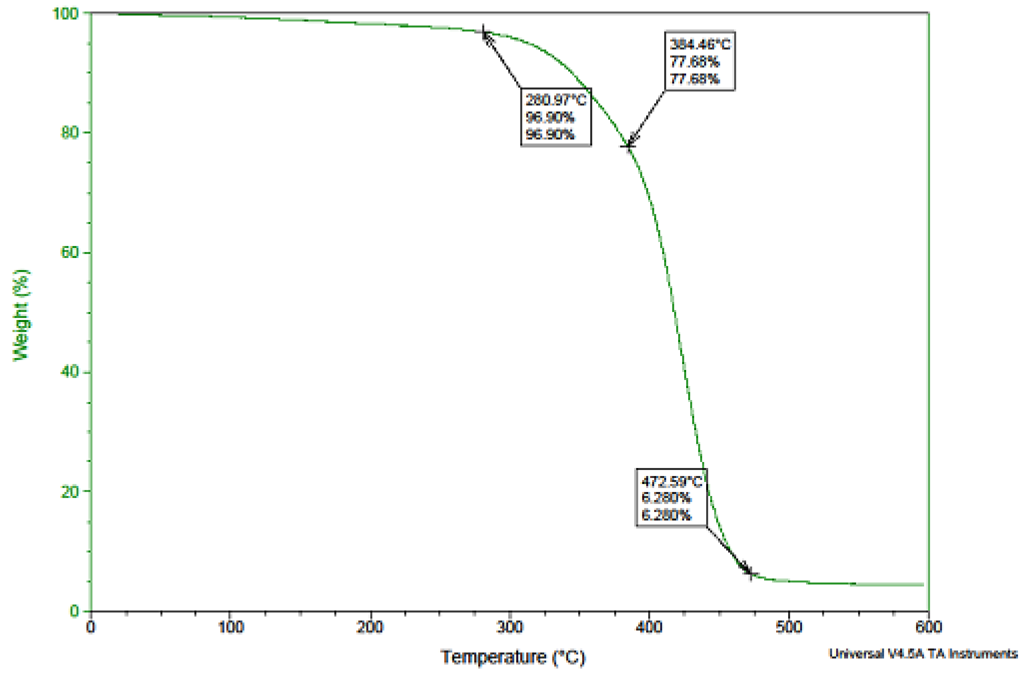


Figure 4.21. TGA of COMA-DGEBPA-2 sample.

<u>4.3.3.2. TGA of COMA-HEL 505-2.</u> The COMA-Hel-2 was stable at 224^{o}C with 4 % weight lost. Then, it undergoes a slow degradation up to 333 ^{o}C, then a second degradation step begins at that temperature and leaves 2.7% wt % solid residue at 490 ^{o}C. Figure 4.22 shows the TGA of COMA-Hel-2.

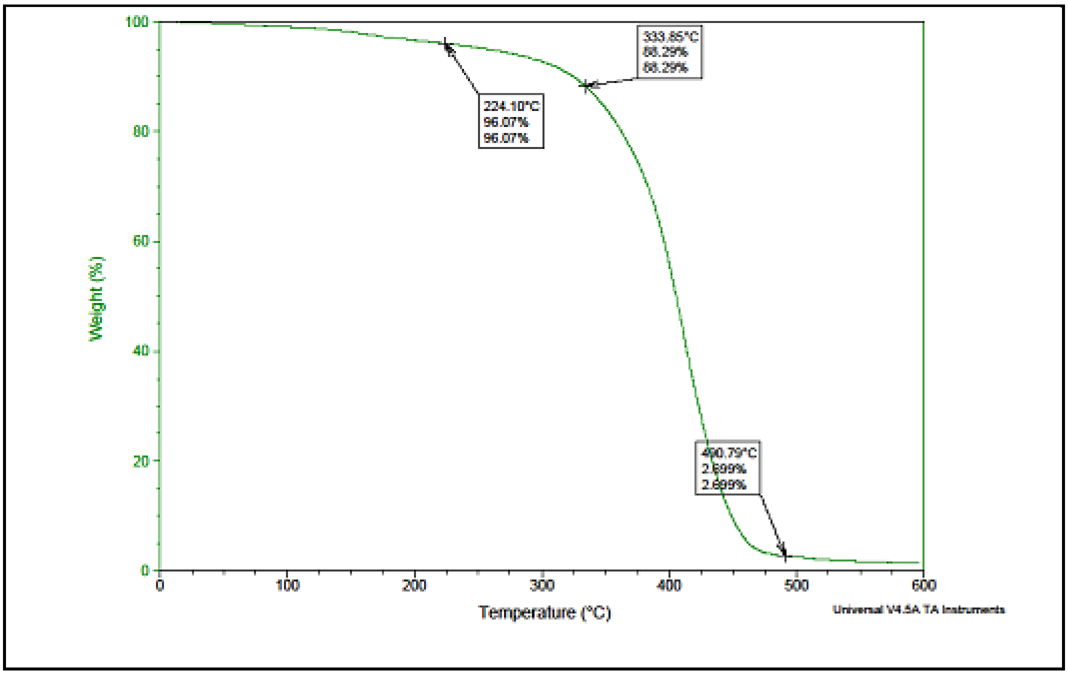


Figure 4.22. TGA of COMA-DGEBPA-2 sample.

<u>4.3.3.3. TGA of COMA-Nov-2.</u> TGA of COMA-Nov-2 is given in Figure 4.23. The sample lost 5.5 % total weight until 308 ^{o}C. As seen in thermogram, there are two degradation steps which starts at 308^{o}C and at 396 ^{o}C. Decomposition ends at 502 ^{o}C leaving 13.15 % weight solid residue.

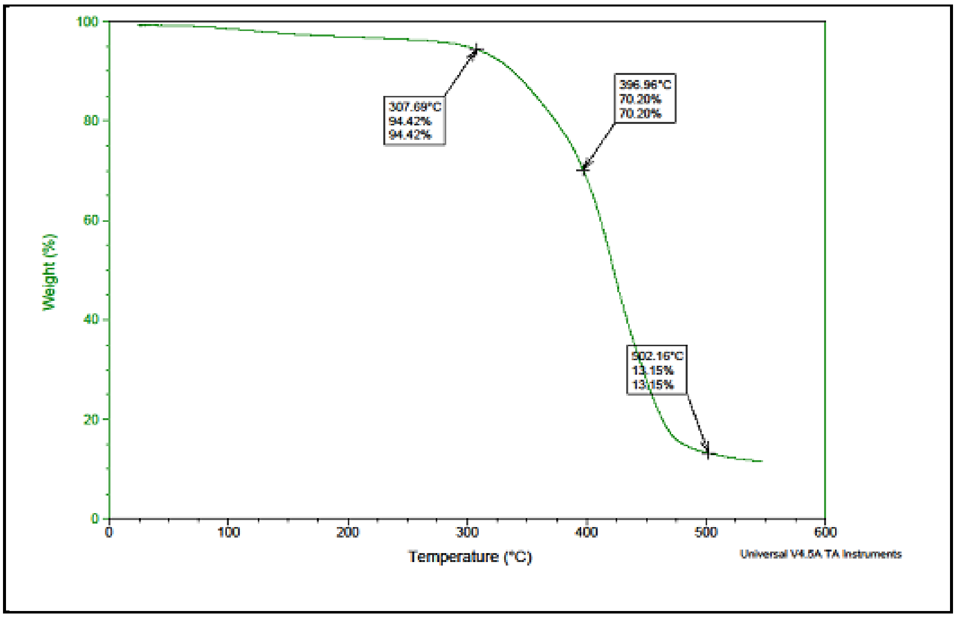


Figure 4.23. TGA of COMA-Nov-2.

In Table 4.10 the temperatures of 5 %, 30 %, 60 % and 90 % weight losses were summarized for the first and second networks of the polymers. As seen, formation of second network does not affect the thermal properties significantly and there is not any trend according to crosslink density.

Table 4.10. The temperature of characteristic weight loses for the samples.

Sample	T of 5 % weigth loss (°C)	T of 30 % weight loss (°C)	T of 60 % weight loss (°C)	T of 90 % weight loss (°C)
COMA-DGEBPA-2	312	398	425	458
COMA-DGEBPA-1	303	394	430	468
COMA-HEL505-2	259	383	414	448
COMA-HEL505-1	294	373	405	449
COMA-NOV-2	295	396	432	>550
COMA-NOV-1	319	398	435	>695

4.3.4. Mechanical Properties of Second Networks

After the formation of interpenetrating network, mechanical properties of the networks have increased as expected. The increase in mechanical properties is the proof of the formation of second network.

The results of surface hardness measurements of second networks by Shore A are given in Table 4.11 with the comparison of first networks. Measurements were done from five different place of the sample and the avarage of results were taken. Different styrene ratios were tested to understand the effect of styrene on surface hardness and it wasobserved that surface hardness increases as styrene concentration increases due to the rigidity of styrene. The highest increase in surface hardness is calculated in COMA-Heloxy 505 epoxy resin polymer. The surface hardness of the final product is ten times higher than the surface hardness of first network. The lowest increase in surface hardness is calculated for COMA-Novolac epoxy resin polymer which becomes nearly two times harder by the formation of the second network with 30 % styrene amount of total weight. The increase in crosslinking density, the addition of rigid styrene to the structure and the effect of interpenetration results in a dramatic increase in surface hardness.

Mixing of two polymers as a blend was tried to understand the effect of interpenetration. To achieve it, first network was swollen in the polystyrene dissolved toluene and after the evaporation of toluene diffused polystyrene stays in the network. However, the final blend splintered because of toluene. Therefore, the solvent was changed to styrene because it was known that styrene does not splinter the network. Unfortunately, dissolved polystyrene could not diffuse completely and after evaporation of styrene a thin film of polstyrene was observed on the sample. Homogenous non-interpenetrating blend of polystyrene with first networks was impossible to produce.

Table 4.11. Summary for the Surface Hardness Result of the Polymers.

		Shore A results	% increase in surface hardness
COMA-DGEBPA polymer	First network	14.8	-
	Second network (30 % styrene by weight)	62.4	422 %
	Second network (20% styrene by weight)	42.2	285 %
COMA – HEL 505 polymer	First network	3.5	-
	Second network (30 % styrene by weight)	40.6	1160 %
	Second netwrok (20% styrene by weight)	37	1057 %
COMA – NOV polymer	First network	47	-
	Second network (30 % styrene by weight)	84.8	180%
	Second network (20% styrene by weight)	52.8	112 %

Three point bending test was done for the second networks and in trials it was observed that the correspoding load for the same length of displacement becomes fifty times higher for second network of COMA-DGEBPA polymer and seven times higher for second network of COMA-HEL 505 polymer relatively their first networks. The load vs. displacement curves are given in Figure 4.24. Using the slope of load displacement curve flexural modulus values for the samples were calculated and they are shown in Table 4.12. According to flexural modulus results, it is understood that formation of second network causes fourty five times increase in stiffness COMA-DGEBPA polymer and twelve times increase in stiffness for COMA-HEL 505 polymer. As expected, the production of interpenetrating network increases the load bearing capacity of the first network dramatically.

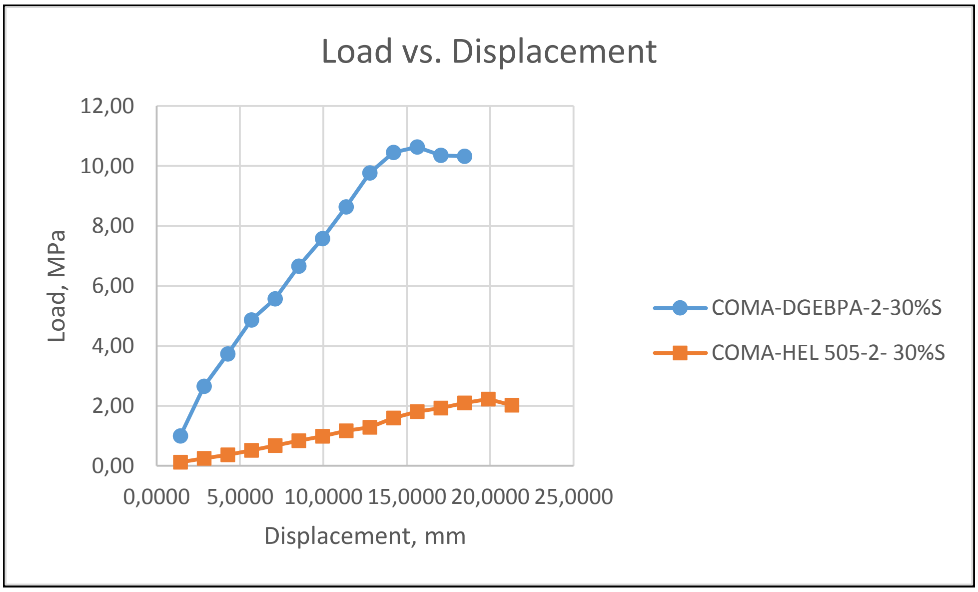


Figure 4.24. Load vs. Displacement Curve of Second Networks.

Table 4.12. Flexural modulus values of Second Networks.

	Slope of the F-D curve	Flexural Modulus (MPa)
COMA-DGEBPA-2-30%S	1.162	189.71
COMA-HEL 505-2-30%S	0.092	29.44

The flexural stress vs. flexural strain curves of first networks of COMA-DGEBPA and COMA-HEL 505 are shown in Figure 4.25. Curves of second networks of the polymers according to same parameters are also shown in Figure 4.26. When the shape of the curve of first network is compared with the shape of second network it is clearly understood that the character of the polymer changed from the elastic to plastic.

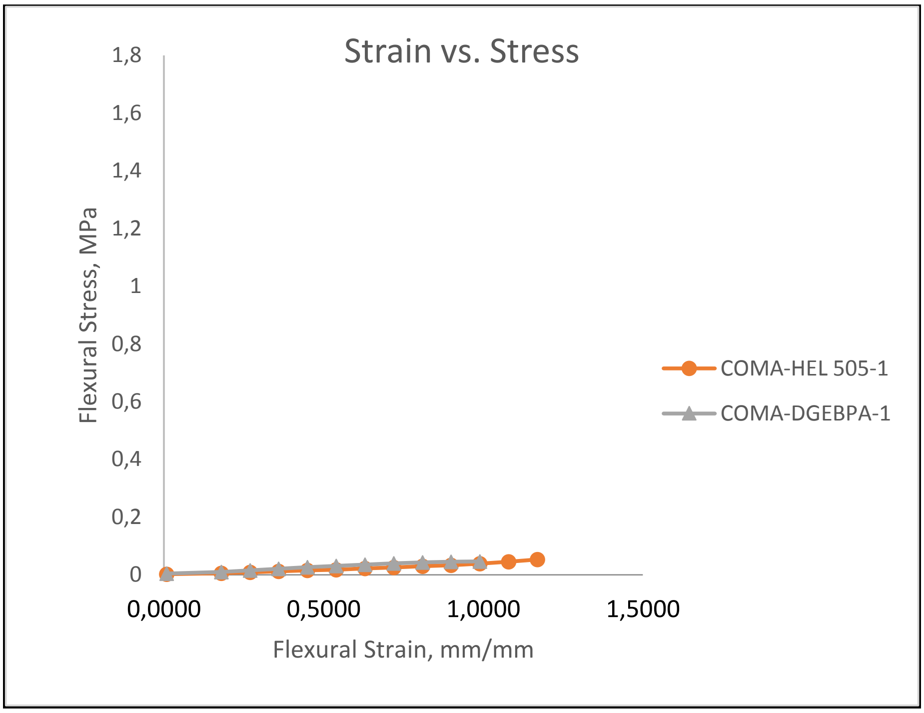


Figure 4.25. Flexural Stress vs. Flexural Strain Curves of First Networks.

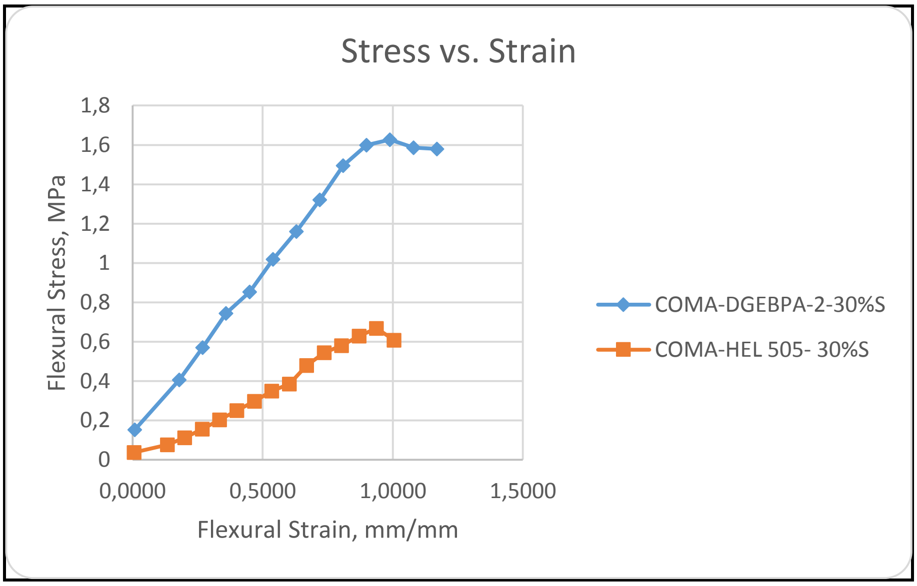


Figure 4.26. Flexural Stress vs. Flexural Strain Curves of Second Networks.

5. CONCLUSION

In this study, castor oil is reacted with maleic anhydride to give maleated half ester of castor oil (COMA) which is then used as an epoxy curing agent to form thermosets with commerical epoxy resins. The used epoxy resins are Bisphenol A Diglycidylether epoxy resin, Novolac epoxy resin and Heloxy 505 epoxy resin. Then, the networks were swollen in a reactive diluent styrene in the presence of AIBN and after swelling the unsaturation on maleate group and castor oil were cured free radically to give a second interpenetrating network.

The characterization of the polymers was done by IR spectroscopy due to crosslinked structure of the polymers. During COMA synthesis consumption of maleic anhydride peak at 1779 cm^{-1}, during the formation of first network consumption of epoxy peaks and during the formation of second network decrease in the intensity of the double bond peak at 1644 cm^{-1} were observed. The thermal analysis was done by TGA and a significant increase in thermal stability is not observed after the formation of second network. Surface hardness test was done by durometer Shore A. The highest values were measured for COMA-NOV networks but the highest increase between first and second network was observed for COMA-HEL 505 polymer due to low crosslinking density of the first network. Three point bending test was done by a home made test rig which was produced by our lab. The flexural modulus of the networks were calculated by the ratio of stress to strain. It was observed that formation of second network increases the stiffness of the polymers.

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