SYNTHESIS AND EFFECTIVENESS OF LOW STYRENE EMISSION AGENTS FOR UNSATURATED POLYESTER

by

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To My Family
and Esra

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ABSTRACT

SYNTHESIS AND EFFECTIVENESS OF LOW STYRENE EMISSION AGENTS FOR UNSATURATED POLYESTER

The aim of this work is to synthesize linear and branched reactive molecules for use as low styrene emission (LSE) additives for unsaturated polyester (UPE). Maleinization reaction of primary alcohols was a specific way to synthesize the linear types of molecules. In this reaction, stearyl alcohol, PEG (2000), isooctyl alcohol, 1,5- pentanediol, PEG (400) mono-oleate and octylphenol ethoxylate were used as the primary alcohol source. Ring opening reaction of epoxidized soybean oil (ESO) with unsaturated acid groups was used to synthesize the branched types of molecules. Monostearoyl maleate, monomethyl maleate and oleic acid adducted epoxidized soybean oil and acrylated epoxidized soybean oil were used as branched types of LSE molecules. The structural analyses of the products were be done with ^{1}H-NMR and IR spectroscopy. To examine industrial usefulness of the additives, styrene emission test and interlaminar adhesion test were be applied to the molecules synthesized according to AS/NZS 4585.1 and AS/NZS 4585.2 test procedures. In the styrene emission test, the amount of styrene evaporation was calculated by weighing the styrene lost from UPE resin mixture containing curing agents and LSE additive (%1 w/w based on polyester resin) during curing. In the interlaminar adhesion test, two ply laminates were prepared with chopped glass mat and UPE resin, curing agents and LSE additive. The force (N) required for delamination was measured as the interlaminar adhesion. For the comparison of LSE additives with blank and commercial additives, the results obtained were reported as a combination in a success factor S defined as; S= Interlaminar adhesion force (N) / Styrene emission (g/m^2). The best three additives were monostearoyl maleate, monomethyl maleate adducted epoxidized soybean oil and peantane bismaleate. The styrene emission results of these additive were orderly 85 g/m^2, 92 g/m^2 and 96 g/m^2. The interlaminar adhesion test results of these additives were orderly 40 N, 37 N and 28 N.

ÖZET

DOYMAMIŞ POLYESTER İÇİN DÜŞÜK STİREN EMİSYON AJANLARININ SENTEZİ VE TESİRLİLİĞİ

Bu çalışmanın amacı, doymamış polyester'de düşük stiren emisyonu (LSE) katkısı olarak kullanılabilecek lineer ve dallı moleküllerin sentezlenmesidir. Birincil alkollerin maleinizasyon reaksiyonu lineer türdeki molekülleri sentezlemek için spesifik bir yoldur. Bu reaksiyonda birincil alkol kaynağı olarak stearil alkol, PEG (2000), izooktil alkol, 1,5 - pentandiol, PEG (400) mono-oleat ve oktilfenol etoksilat kullanılmıştır. Epokside Soya Yağı (ESO)'nın doymamış asit grupları ile halka açılması reaksiyonları dallı molekül türlerini sentezlemek için kullanılmıştır. Monostearil maleat, monometil maleat ve oleik asit'lerin epokside soya yağına adüksiyonu ve akrilatlı eposide soya yağı dallı LSE molekül türleri olarak kullanılmıştır. Ürünlerin yapısal analizleri ^{1}H-NMR ve IR spektroskopisi ile yapılacaktır. Katkı maddelerinin endüstriyel yararlılığını incelemek için, sentezlenen moleküllere AS / NZS 4585,1 ve AS / NZS 4585,2 test prosedürlerine göre stiren emisyon testi ve laminatlar arası yapışma testi uygulanmıştır. Stiren emisyon testinde, stiren buharlaşma miktarı içerisinde kür ajanlar ve LSE katkısı (% 1 polyester reçine ağırlığının) içeren kürleşen doymamış polyester reçine karışımından stiren kaybının tartılmasıyla hesaplanmıştır. Katlar arası yapışma testinde, iki katlı laminatlar keçe cam yünü, UPE reçine, kür ajanları ve LSE katkısı ile hazırlanmıştır. Katlar arası yapışma, delaminasyon için gerekli kuvveti (N) ile ölçüldü. LSE katkıları, katkısız ve ticari katkı maddesi ile karşılaştırmak için, bu elde edilen sonuçların kombinasyonu başarı faktörü "S" şöyle tanımlandı; S= Katlar arası yapışma kuvveti (N) / Stiren emisyonu (g/m^2). En iyi üç katkı maddesi monostearil maleate, epokside soya yağına monometil maleat adüksiyonu ve pentan bismaleat'dır. Bu katkı malzemelerinin stiren emisyon sonuçları sırasıyla 85 g/m^2, 92 g/m^2 and 96 g/m^2'dir. Katlar arası yapışma deneyinin sonuçları sırasıyla 40 N, 37 N and 28 N'dir.

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LIST OF ACRONYMS/ABBREVIATIONS

AESO	Acrylated Epoxidized Soybean Oil
AMC-2	Commercial Catalyst (Cr(III) Carboxylate)
AS/NZS	Australian /New Zealand Standard
cm	Centimeter
EPA	U.S. Environmental Protection Agency
ESO	Epoxidized Soybean Oil
ESO-MMA	Epoxidized Soybean Oil Methyl Maleate
ESO-SMA	Epoxidized Soybean Oil Stearyl Maletate
ESO-OA	Epoxidized Soybean Oil Oleic Acid
FA	Fatty Acid
IR	Infrared
HAP	Hazardous Air Pollutants
NMR	Nuclear Magnetic Resonance
INSERT	Intrinsic Styrene Emission Reduction Technology
Kcal	Kilo Calorie
LSE	Low Styrene Emission
MEKP	Methyl Ethyl Ketone Peroxide
MHz	Mega Hertz
mm	Milimeter
MMMA	Monomethyl Maleate

MOMA	Monooctyl Maleate
MSMA	Monostearyl Maleate
N	Newton
OPE-MA	Octylphenyl Ethoxylate Maleate
OSHA	Occupational Safety and Health Administration
PBMA	Pentane Bis-Maleate
PEG	Polyethylene Glycol
PEG-MA	Polyethylene Glycol Maleate
PEGMO-MA	Polyethylene Glycol Mono Oleate Maleat
PEL	Permissible Exposure Limits
ppm	Part Per Million
RTM	Resin Transfer Molding
STEL	Short Term Exposure Limits
UPE	Unsaturated Polyester
VOC	Volatile Organic Compound
w/w	Weight in Weight

1. INTRODUCTION

1.1. Unsaturated Polyester Resin

Polyester is a category of polymers which contain the repeating ester (–COO-) functional groups in their main chain [1].

Reaction of a hydroxyl compound with a carboxylic acid results in the formation of ester linkages. Polyester also refers to the various polymers in which the backbones are formed by the condensation reaction of diols and dicarboxylic acids. Polyester can be classified as saturated and unsaturated polyester (UPE), depending on whether the backbone contains carbon-carbon double bonds. During the condensation reaction, water is produced as a by-product which must be removed to obtain sufficient molecular weight of 1500-5000 Daltons in the case of commercial UPE (Figure 1.1) [2]. In the production of UPE resin, reactive diluents, usually styrene, is used to reduce the viscosity of the polyester and to act as a crosslinking agent. The UPE resin can be cross-linked from the unsaturated part of backbone with free radical initiators [2, 3].

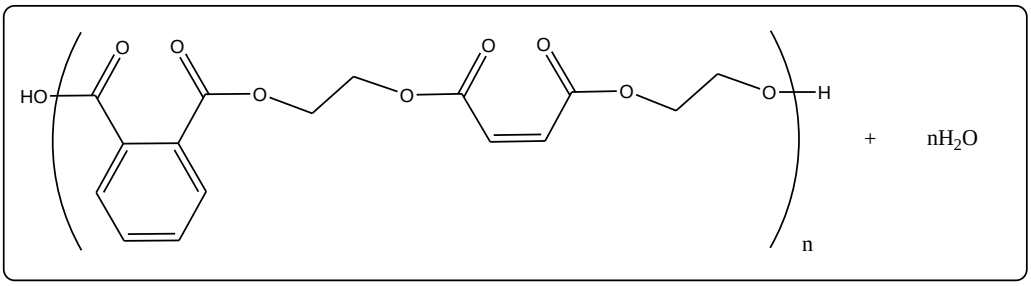


Figure 1.1. General structure of unsaturated polyester [2].

UPE resins gained commercially importance in the last decade when they were reinforced with glass fibers giving high mechanical properties. Today UPE resins are one of the most important matrix resins for composite materials [2]. Composites are made up of matrix and reinforcement. The matrix material which is UPE resin surrounds and

supports the reinforcement materials which are glass, carbon or aramid fibers, by maintaining their relative positions. By the help of reinforcements, the mechanical and physical properties of matrix are enhanced [3].

The UPE resin are used in the marine, automotive, electric and electronic, building, construction, sport, furniture and defense industries. Composite products are processed with UPE resin using different techniques: hand lay-up, spray up lamination, casting, compression molding, pultrusion, resin transfer molding (RTM) vacuum infusion and filament winding [4].

1.1.1. Preparation of Unsaturated Polyester Resin

Linear unsaturated polyesters are prepared by the reacting diols such as ethylene glycol, propylene glycol etc.(Figure 1.2), with a mixture of unsaturated or aromatic diacids and anhydrides, such as maleic, phtalic anhydride or linear diacids (Figure 1.3) in a reactor. Water is removed with downward distillation as by product. UPE is synthesized at 150-200 ˚C to obtain an average molecular weight of 1000-2000. At the end of this reaction, the polymer mixture is cooled to about 90 ˚C and discharged to a blending tank and blended with cold styrene. Stabilizer such as hydroquinone can be added to prevent styrene polymerization during storage. Generally in polyester resins, the styrene content is around 35-40%. The polyester resin produced is cooled to room temperature to a give colorless liquid with 400 cps viscosity [5].

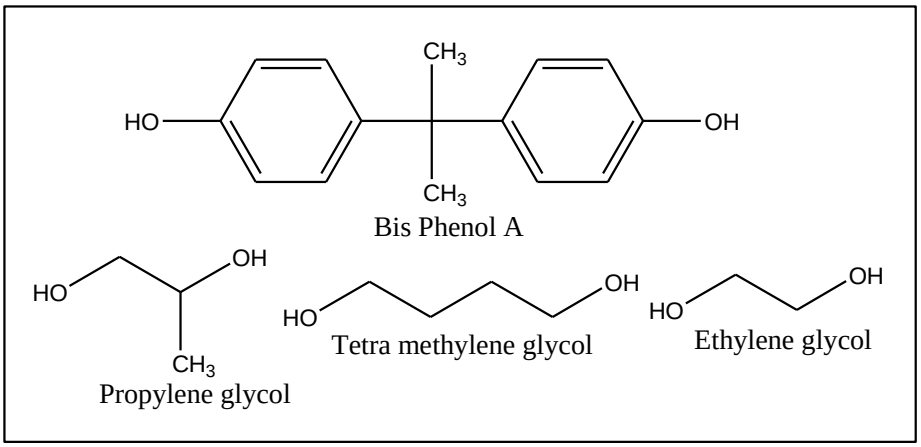


Figure 1.2. Structure of some diols used in polyesterification reaction.

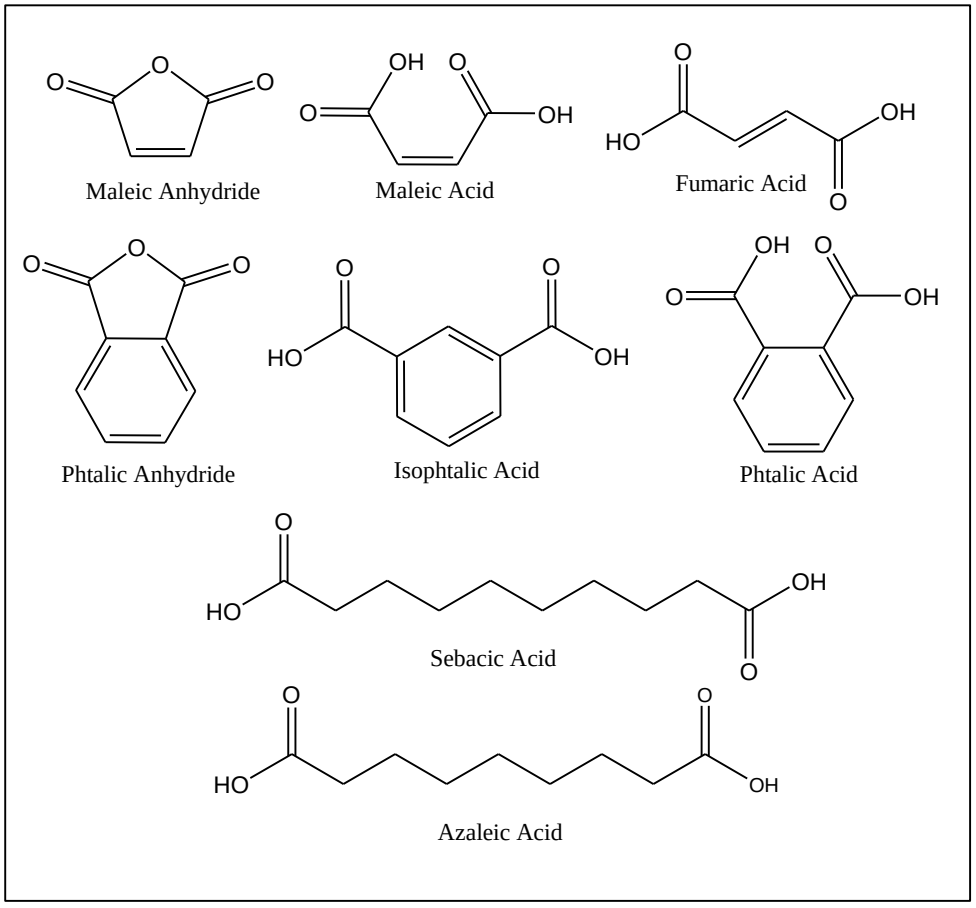


Figure 1.3. Structures of some diacids used in polyesterification reaction.

1.1.2. Cross-Linking

Cross-linking is the process of chemically joining two or more polymer chains by covalent or ionic bonds. In UPE, the maleate double bonds of the linear polyester react with vinyl type reactive diluents upon addition of a radical initiation to form cross-linking. Cross-linking reaction takes place in the mold. At the end of this reaction, molded unsaturated polyester resin gains the rigidity, durability and load bearing properties [6]. The cross linking reaction is exothermic with a ΔH of – 38 kcal per mole of double bonds.

One major advantage of commercial UPE is that the, cross-link density is controllable. To reduce cross-linking density, maleic anhydride content of mixture is reduced. Although, high degree of unsaturation leads to very brittle product due to high cross-link density, low degree of unsaturated polyester has lower mechanical properties [2, 5]. By changing the amount diluents, the cross-link segment length is also adjustable [5].

The cross linked polyesters are called as thermoset materials because these are insoluble and infusible materials. Cured thermo set resin may soften when heated, but do not melt or flow [4, 6].

Peroxide type initiators (Figure1.4), most commonly benzoyl peroxide, are used for cross-linking at 70-150 °C. These thermally decomposable types of initiators are stable at room temperature. However by increasing the temperature to about 70-150 °C, these types of initiators liberate free radicals which initiate the cross linking reaction [7].

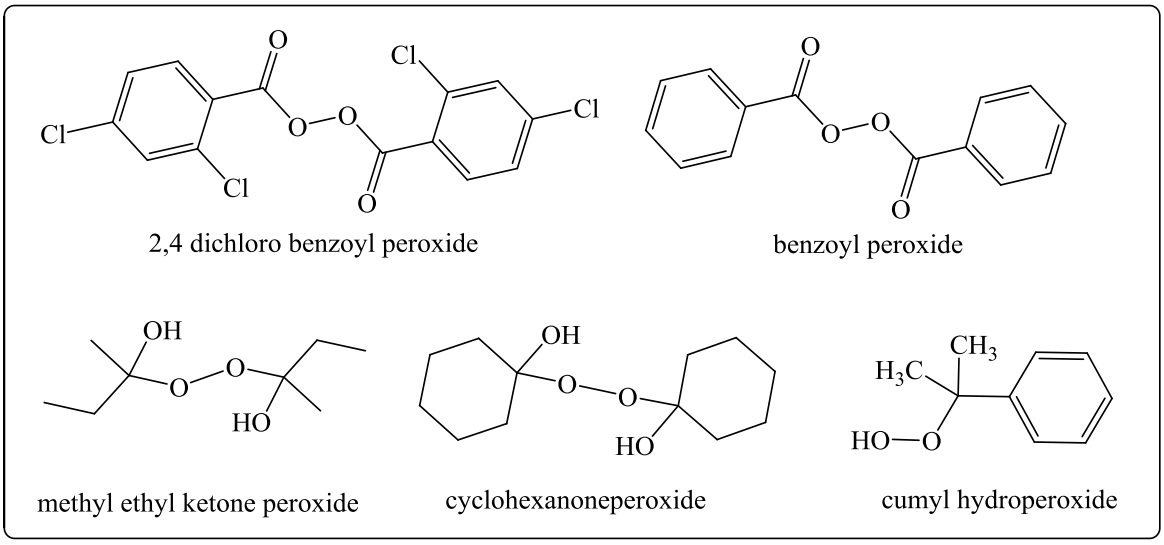


Figure 1.4. Structure of some free radical initiator that are used in polyester cross-linking.

For initiation at room temperature, an accelerator mixture is used with peroxide type initiator. With the help of accelerator, the peroxide rapidly decomposes without any heat. This type of curing system is called cold curing system. When in fact the cross-linking is initiated at room temperature but the exothermic reaction always increases the temperature of the part. Depending on the shape of the part, temperatures up to 150 °C are reached during cure. Most common peroxide type used in cold curing system is methyl ethyl ketone peroxide (MEKP) with metal salts, mostly cobalt naphtenate, as accelerator. The decomposition reaction of hydro peroxide (ROOH) by metal salt is shown in Figure 1.5. This reaction cycle is repeated so that the cobalt salts are needed only in catalytic amounts [3].

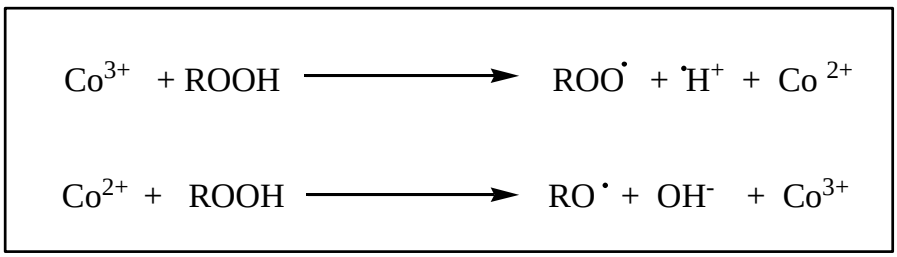


Figure 1.5. Acceleration of the formation of free radicals by cobalt metal [3].

During the crosslink reaction, the resin begins to gel. At that time, the viscosity increases rapidly, the resin becomes elastic and begins to behave as a rubber. The extent of reaction, at which an infinite molecular network starts to form, is called the gel point and the time required for this is called the gel time. The chemical reaction continues beyond the gelation time, and more polyester is linked to form infinite molecular network. Finally each polyester chain is linked to each other at several points, and one gigantic molecule is formed [6]. The cross linking mechanism and cross-linked polyester are shown in Figure 1.6 and Figure 1.7.

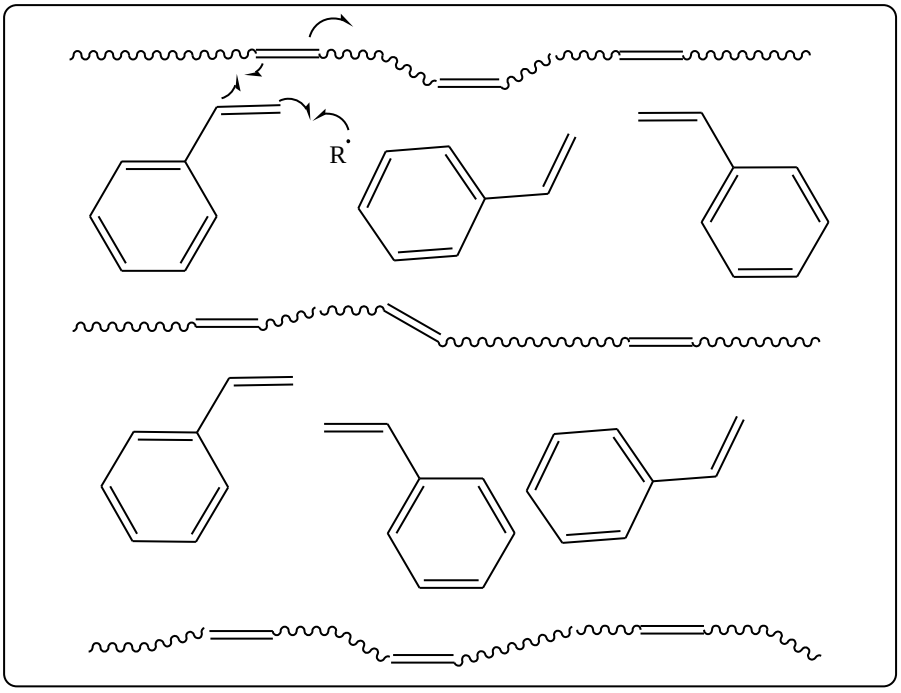


Figure 1.6. Cross-linking mechanism.

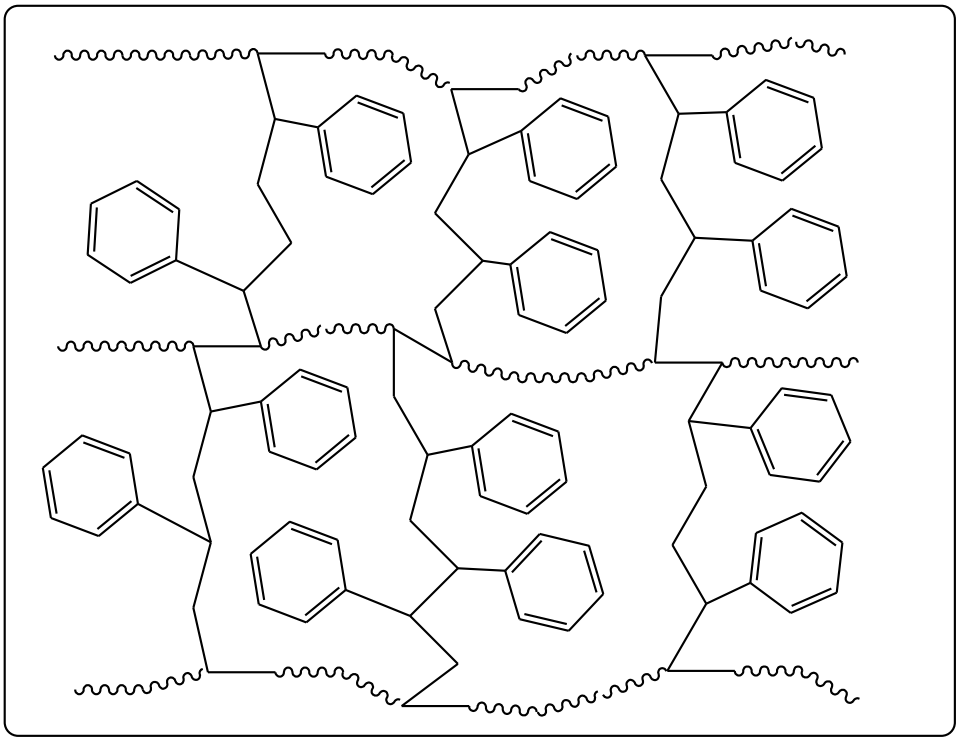
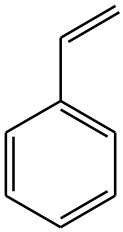


Figure 1.7. Presentation of cross- linked polyester.

1.2. Styrene

Glass fiber reinforced polyester composites are used in the manufacture of boat hulls, automobile parts, structural application, pipes, wind generators etc. Polyester resins are generally prepared with high content of volatile unsaturated organic monomers such as styrene, methyl styrene or methyl acrylate [5]. The existence of the vinyl group allows styrene to polymerize and reactivity ratios of styrene and maleate double bonds are similar. Styrene world production is about 15 million tons annually. With this production rate, it places among the top 50 chemicals worldwide [9]. The most important physical properties are summarized in Table 1.1. A factor to note in this table is the large increase in the vapor pressure as temperature increases. This, we note, is one of the chief disadvantages of styrene as reactive diluents.

Table 1.1. Physical properties of styrene [8, 9].

Property	Value
Chemical Structure	
Molecular Weight	104,15 g mol^{-1}
Boiling point	145,15 ˚C
Freezing point	-30,6 ˚C
Vapour pressure 20 ˚C 25 ˚C 50 ˚C 80 ˚C	0,6 kP 0,87 kP 3,2 kP 12,2 kP
Density	0,906 g mol^{-1}

1.2.1. Emission of Styrene

Most common composite production method using UPE is the “open mold” method. In this method glass fiber mat or textile is wetted with UPE resin in the mold, and then this mixture is cured with initiators. During the curing reaction of UPE with styrene, large amount of styrene is emitted into the work place and atmosphere, as the part heats up during cross linking. This effects, negatively not only the workers but also the environment. Due to the environmental concern of such organic compounds, the U.S. Environmental Protection Agency (EPA) introduced legislation for the reduction in the amount of volatile organic compounds (VOC) by enacting new emission standards through the “National Emission Standards for Hazardous Air Pollutants: Reinforced Plastic Composites Production”. With this standard, styrene, methyl methacrylate, and methylene chloride are regulated as hazardous air pollutants (HAP) [10]. Recently, styrene has been

reported as a carcinogenic chemical in the US by International Agency for Research on Cancer (IARC) [13].

During all stages of composite production, VOC emissions are released into atmosphere (Figure 1.8). Styrene emissions occur during the mixing of catalysts, diluents, and initiators into the production. During the molding stage, 20% of the styrene can be lost because of high surface to volume ratio of most composite parts. During cure, elevated temperatures increase the vapor pressure of styrene and thus increase the rate of VOC emissions. Unfortunately, even after cure during the lifetime of the part, styrene emissions can be substantial [11].

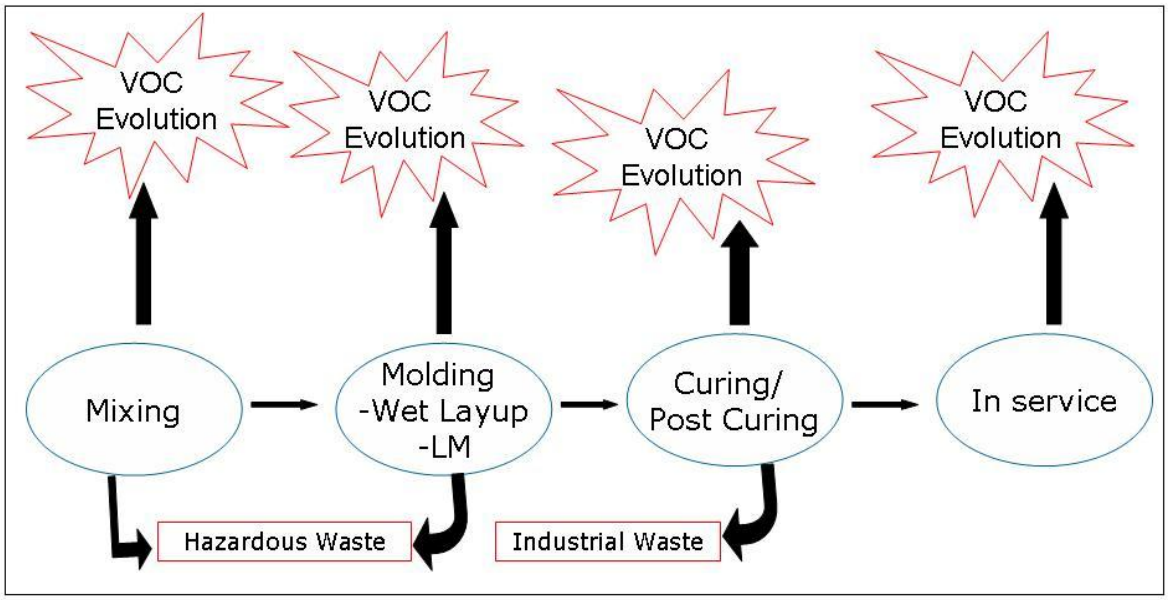


Figure 1.8. Life cycle source of population associated with composite materials processing [11].

1.2.2. Effect of Styrene on Health and Regulations on Styrene Emissions

Styrene is detected in the atmosphere in many places on Earth. Its source is chiefly emissions of the polymer industry, but also vehicle exhaust, cigarette smoke and the other forms of combustion and decomposition of plastic waste are also responsible. Benzaldehyde and peroxides are formed from the reaction of styrene with ozone. All of

these products have irritation affects on the skin, eyes, and the upper respiratory tract. Chronic styrene toxication shows depression, headache, fatigue, weakness symptoms [12]. Also, there is sufficient evidence to show that styrene has carcinogenic affects in humans [13]. Also styrene is seen as active part of photochemical smog [11]. Because of these negative affects in 1989 the U.S. Occupational Safety and Health Administration (OSHA) regulates styrene in the work place. The current OSHA permissible styrene a short-term exposure limit (STEL) is 50 parts per million (ppm) and permissible exposure limit (PEL) (8h time-weighted average) for styrene is 20 ppm. This regulation means that a worker should not be exposed to more than an average of 20 ppm styrene in air during a regular workday, without respiratory protection. The current occupational exposure limits vary between 20 and 100 ppm in different countries and is 100 ppm in Turkey [11, 14]. While styrene emission is important from health and safety point of view, there is also an economic loss as up to 10-12 % of styrene may be lost to the atmosphere during the process. This results in about 5 % loss overall and such a loss of valuable resin is totally unacceptable.

Table 1.2. Occupational Exposure Limit for Styrene in Different Countries [11, 14]

Country/ Organization	**PEL (ppm)**	**STEL (ppm)**
Belgium	50	100
France	50	
Germany	20	
Finland	20	100
Netherlands	100	
Denmark	25	
Sweden	25	75
United Kingdom	100	260
Japan	50	
USA/OSHA	20	50
Turkey	100	

As styrene emission regulation becomes stricter, producers are looking for ways to reduce styrene emission from their process. There are five ways for reducing styrene emission that are available to the composite industry.

1.2.3. Controlled Spray-up Technique

Most of the composite producer commonly use open mold processes which includes spray-up and open contact molding (hand lay-up) in one-sided molds because of their low cost advantages [15]. In the hand lay-up application, fiberglass mat or woven is manually placed in the mold. Workers wet the fiber with brushes and rollers, the resin flows into the fiber, wetting out and compacting the laminate.

In spray-up application, gel coat is applied to the mold by spraying the mixture of catalyzed resin and chopped fiberglass. Spray-up is particularly effective process to produce a wide variety of composite parts. In the controlled spray-up application, styrene evaporation is controllable by the spray fan angle, spraying pressure, spraying distance and diameter of nozzle [16]. Also controlled spray-up technique is very effective for controlling the amount of surface area of wet resin. If it is compared with hand lay-up application, it provides more substantial reduction than hand lay-up application in styrene emissions [17]. Moreover, controlled spray-up application reduces material loss during the process. This may provide significant in reducing overall costs.

1.2.4. Closed Mold Process

Some of composite manufacturer choose to use closed mold process. In this process dry glass fiber is placed in the mold, the mold is closed and the UPE resin is injected into the closed mold. This process is also called Resin Transfer Molding (RTM). By the help of this process, manufacturer have a cleaner, more compliant, more productive manufacturing facility and more pleasant workplace, and then they make better parts more consistently, reduce labor costs, reduce overall costs by making parts faster with fewer mold and control the styrene emission. However the high cost of equipment, especially metal molds, is a great disadvantage for this process [18].

1.2.5. Alternative Reactive Diluents

The other way to reduce VOC emission from unsaturated polyester resin is replacement of some or all of the styrene with another low viscosity, low volatility monomer. Different types of monomers that fulfill the general requirements for free radical reaction can be used instead of styrene. The most promising monomers are para-methyl styrene which has a higher boiling point than styrene [19]. During the rolling phase, solvent evaporation can be reduced to 30 % from a resin containing these solvents [20].

In addition to these monomers, petroleum based monomers and fatty acid (FA)-based monomers, including difunctional, aliphatic, cyclic, and aromatic types were tested not only for discovering possible styrene replacements, but also for understanding the effect of monomer structure on resin composition, cure kinetics, and polymer properties. In these type of monomers, lauryl methacrylate and glycidyl methacrylate modified fatty acids showed good potential for replacing styrene [11].

However, the costs of such monomers are higher than styrene. Because of commercial availability factor, alternative monomer substituted resins have not found any use in the industry.

1.2.6. Using Styrene Suppressant Additive

For many years, paraffin wax has been used as a styrene suppressant. Such additives are known as LSE (Low Styrene Emission) additives. Linear type of paraffin wax is solid and not soluble in UPE resin. First the wax is dissolved in styrene and the solution is added to UPE. Then the resin is applied and polymerization begins. Paraffin wax separates into a different phase and forms a thin layer on the resin surface (Figure 1.9) [22]. In this figure, the styrene barrier film on the top of the resin can be seen. This film acts as an evaporation barrier and reduces styrene emission. Unfortunately in most applications a second or third layer of glass fiber and resin need to be applied over the first. In such situations the wax surface film effects the interlaminar adhesion between the plies negatively. This is not surprising, because there paraffin has no site for making secondary bonding with UPE. This was the first generation LSE solution.

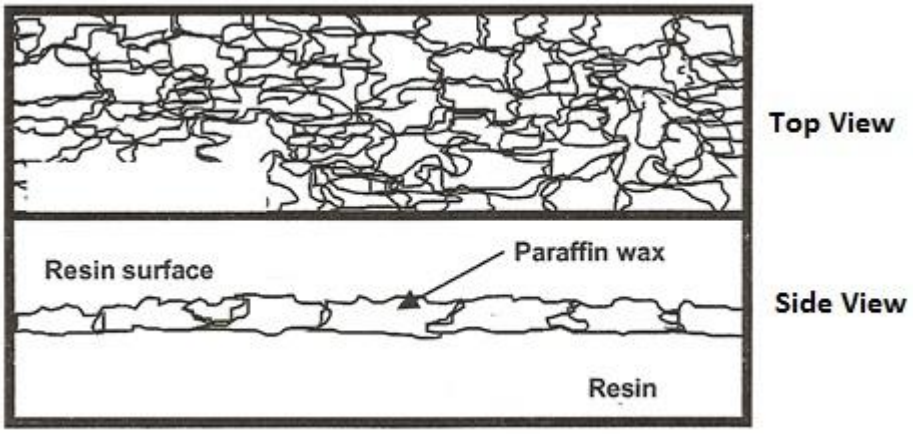


Figure 1.9. Resin surface with paraffin wax [22].

The second generation LSE solution, secondary bonding problem has been solved by mixing paraffin with an adhesion promoter or bonding agents. The adhesion promoters are only partially soluble in polyester resin, and these create adequate surface area for secondary bonding (Figure 1.10) [22]. In this type of LSE additive, paraffin works to reduce styrene emission like the previous surfacing mechanism and adhesion promoter provides a secondary bonding between the laminates.

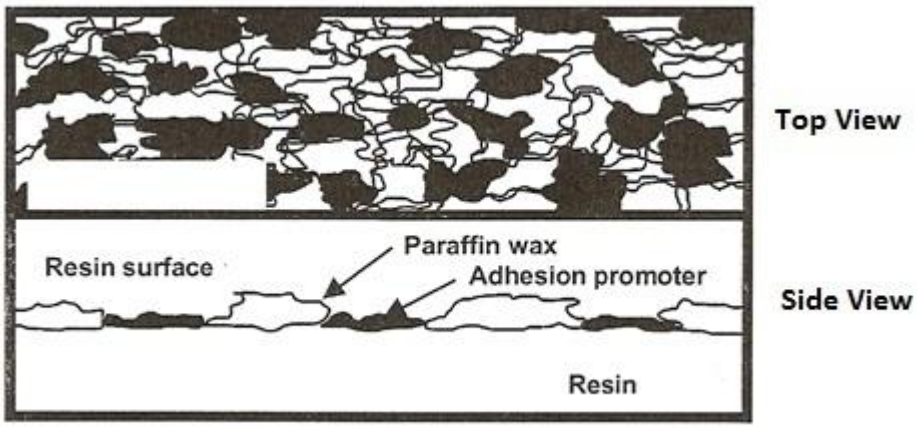


Figure 1.10. Resin surface with adhesion promoter and styrene suppressant part [22].

1.2.7. Using Low Styrene Content

In the standard polyester resin, styrene content is about 35-45 %. During the lamination approximately 7-10 % of the resin is lost because of styrene evaporation. If styrene content could be decreased evaporation would also decrease. However when styrene content is decreased viscosity of the resin increases and processing by vacuum injection or spraying will be impossible. Also the mechanical properties are effected negatively [20]. This problem can be partially solved by changing the polyester backbone.

Styrene content can reduced down to 25%, by reducing the molecular weight of the polyester pre-polymer, and by capping the end groups of the resin with organic molecules which increase the solubility of resin in styrene. As a result less styrene is needed for dissolving the polymer. With this new polymer structure, molecular weight is reduced but the combination of viscosity, mechanical and application properties are acceptable [22]. Such resins are known as INSERT resins in the industry. The acronym stands for Intrinsic Styrene Emission Reduction Technology. Reichold Inc. (USA) is known as a leader in this field.

1.2.8. Delamination in unsaturated polyester laminates

Composite parts that are thicker than 4 mm need to be made by repeated laminations in same mold. Boat manufacturer usually need up to 2 cm thick nulls, which requires up to 5 layers. Delamination is a mode of failure in unsaturated polyester resin laminates, and it can cause separation of layers of the composite structure during use [23]. When the interfacial bonding between the laminate layers are not strong enough, delamination occurs. This is of course a catastrophic failure in a sailing boat or a speed boat.

Interfacial bonding of two layers of unsaturated polyester laminates is very good at normal condition. During the lamination of polyester composites, atmospheric oxygen inhibits the free radical reaction at surface of the first layer. At the end of this reaction the unreacted styrene monomers and polyesters remain at the surface. When the new layer is applied, styrene diffuses into the under-cured lower layer, efficient secondary bondings

between laminates are formed [24, 25]. However, in low styrene emission resin containing film former wax, additives that suppress the styrene emission also prevents oxygen inhibition. Thus dry, cured surfaces are obtained at the lower layer and this prevents the efficient interfacial bonding. Paraffin wax acts as a mold release agents and the two layers can be easily delaminated and any advantage gained by reducing styrene emission is offset by very low interlaminar shear strength. In boats and other transportation applications, delamination which occurs during dynamic use, such as pounding on waves, takes place suddenly and without warning and is one of the main reasons why yachts and speed boats have a short life span. The delamination is the biggest problem of film former LSE additives [25].

1.3. Maleic Anhydride

In the middle of 19 century, maleic anhydride has been freely available from the catalytic oxidation of benzene, industrial chemist have developed a surprisingly wide range of uses for it [26]. Maleic anhydride gains importance in the production of maleinized drying oil, of various copolymers, and of different types of alkyd resin. Today it is a crucial part of unsaturated polyester resin [3]. The structure of maleic anhydride is shown in Figüre1.11.

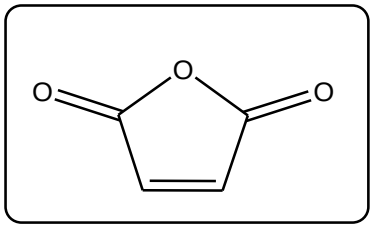


Figure 1.11. Maleic Anhydride.

Anhydride can give esterification reactions with alcohols. The electrophilic character of double bond plays an important role in many reactions of maleic anhydride including, free radical and photolytic reaction and Diels-Alder reactions [27]. This double bond activity separates maleic anhydride from other anhydrides such as phthalic, succinic, etc [28].

1.3.1. Hydrolysis

Maleic anhydride like other anhydrides can be hydrolyzed to the di-acid product. (Figure 1.12)

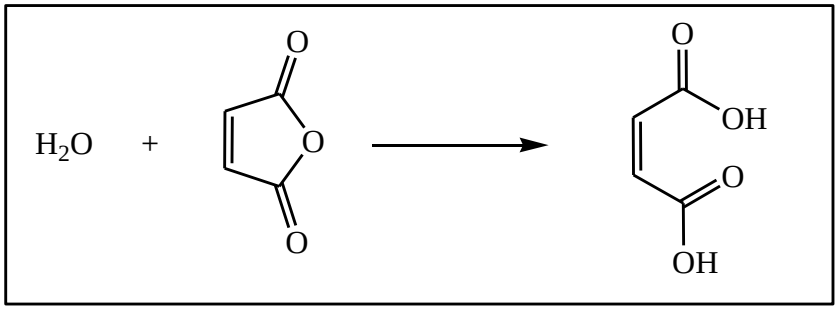


Figure 1.12. Hydrolysis of maleic anhydride.

This hydrolysis reaction is an exothermic reaction. After hydrolysis maleic acid is formed as a cis-(Z) geometry, but if heat is applied, this cis (Z) form of maleic acid is converted to trans (E) form of fumaric acid (Figure 1.13). Maleic anhydride and the two diacid isomers were first prepared in the 1830s [29].

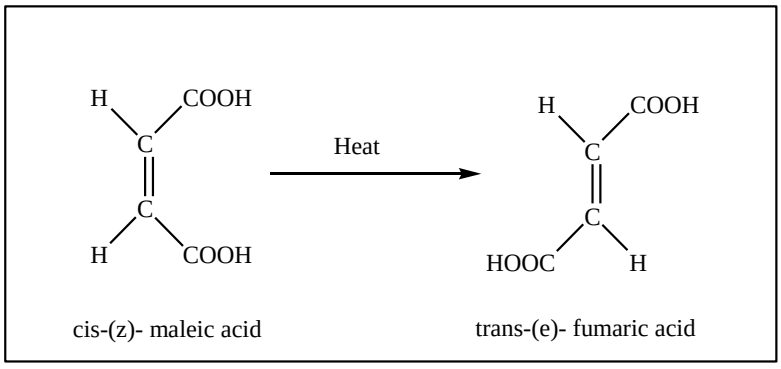


Figure 1.13. The isomerization of the cis-(Z) maleic acid to trans- (E) fumaric acid by heat.

1.3.2. Esterification

Both mono and dialkyl maleates are obtained from the reaction of maleic anhydride with alcohols, alkoxides [28]. These two ester derivatives are shown in Figure 1.14. Mono esterification is an easy reaction that proceeds without a byproduct. This reaction goes at room temperature with most primary alcohols. Diesterification requires temperatures around 180 °C and water must be removed to obtain a good yield.

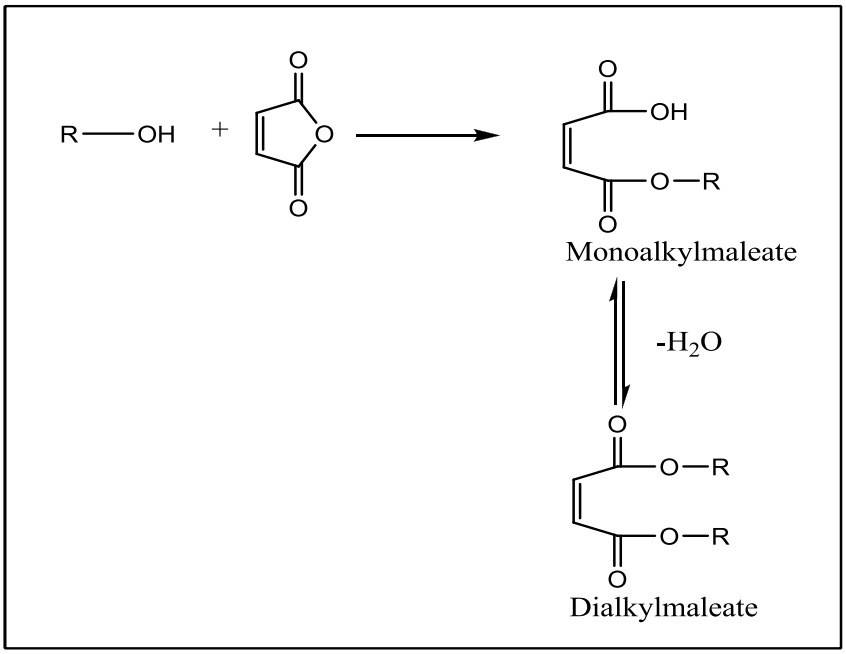


Figure 1.14. Esterification of maleic anhydride with alcohols to form mono and dialkyl maleates.

When maleic anhydride is used in condensation polymers, unsaturated polyester, unsaturation occurs on the backbone of polymers. This reaction is the first step in industrially important polyester resin production [29].

1.3.3. Reactions of the Olefinic Function

In maleic anhydride electrophilic character and reactivity of double bond is very high because of conjugation with carbonyl functions. That is why maleic anhydride

undergoes many reactions through the reactive double bond, such as addition of alcohols, halogen, amine, sulfur compounds and Michael and Diels Alder reactions [28]. Maleate double bond does not homo-polymerize free radically but can be co-polymerized with many other vinyl type of monomers, chief among them being styrene.

1.3 Triglycerides

Plant oils are composed of triglyceride molecules. Triglycerides are neutral lipids, each consisting of three fatty acids saturated or unsaturated and one glycerol that are esterified with each other. The length of the fatty acid chains changes from 14 to 22 carbons. There are also some rare triglycerides containing unusual functionalities such as hydroxyl, epoxies, cyclic groups and furanoid groups.

Figure 1.15 shows the general representation of plant oil molecule. R represents alkyl chain with varying functionalities. Fatty acid distribution changes from plant to plant. Different kinds of triglyceride such as corn oil, hazelnut oil, castor oil, linseed oil contain different values of unsaturation. With the development in genetic engineering, the levels of unsaturation and triglyceride content of plants can be controlled. Genetically modified soy beans provide up to 38 % oil and have become a suitable raw material for the chemical industry.

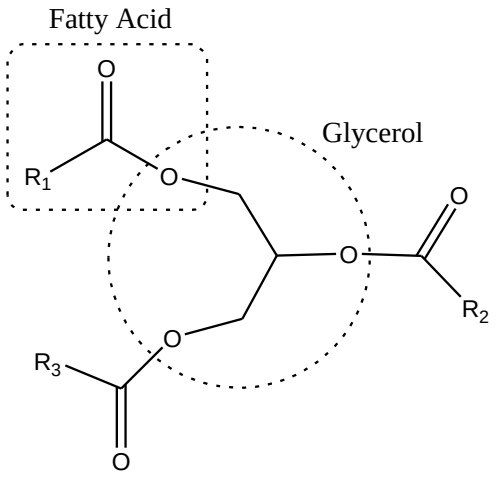


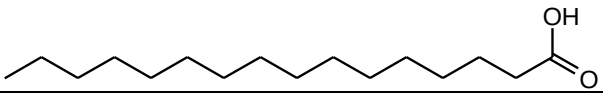
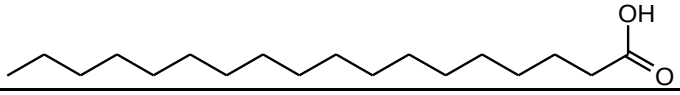
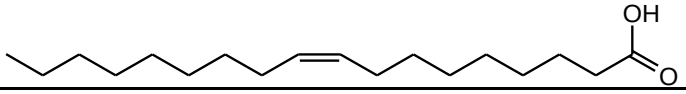
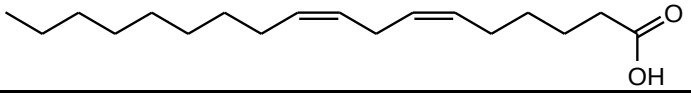
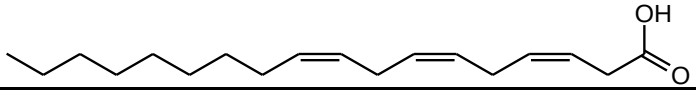
Figure 1.15. General structure of triglyceride.

1.4.1. Soybean Oil

Recently soybean oil has become the most economical, agricultural commodity chemicals because of its chemical composition. Soybean contains the highest protein (40%) and about 20% oil, the second highest content among the all food lagumes. Today among the plant oils, soybean oil is the cheapest one [30].

To produce soybean oil, first soybeans are cracked, adjusted for moisture content, and extracted with hexane solvent. Then the oil is refined for different application it is sometimes hydrogenated. Refined soybean oil contains more than 99 % triglycerides. Like many other oils of plant origin, most fatty acids of triglyceride in soybean oil are unsaturated. The highest percentage of fatty acids in soybean oil is linoleic acid, followed in a decreasing order by oleic, palmitic, linolenic, and stearic acid (Table 1.3). This composition depends on several factors such as genetic modification, environmental factors and quality of soil [31].

Table 1.3. Structure and the compositin of fatty acids in soybean oil [31].

Fatty Acids	**%**	**Structure**
Palmitic Acid	11	
Stearic Acid	4	
Oleic Acid	23	
Linoleic Acid	53	
Linolenic Acid	8	

1.4.2 Reactive Sites of Plant Oil

From an organic chemistry point of view, triglycerides of soybean oil contain four reactive centers. Figure 1.16 shows the all reactive centers and their general reactions. These parts are the ester group (a), alpha methylene group (b), double bond (c), allylic carbon (d). These reactive parts are used as reactive groups to convert the triglycerides into useful monomers. Different materials can be synthesized by the using these reactive parts [32]. In this study epoxidized soybean oil (ESO) was used.

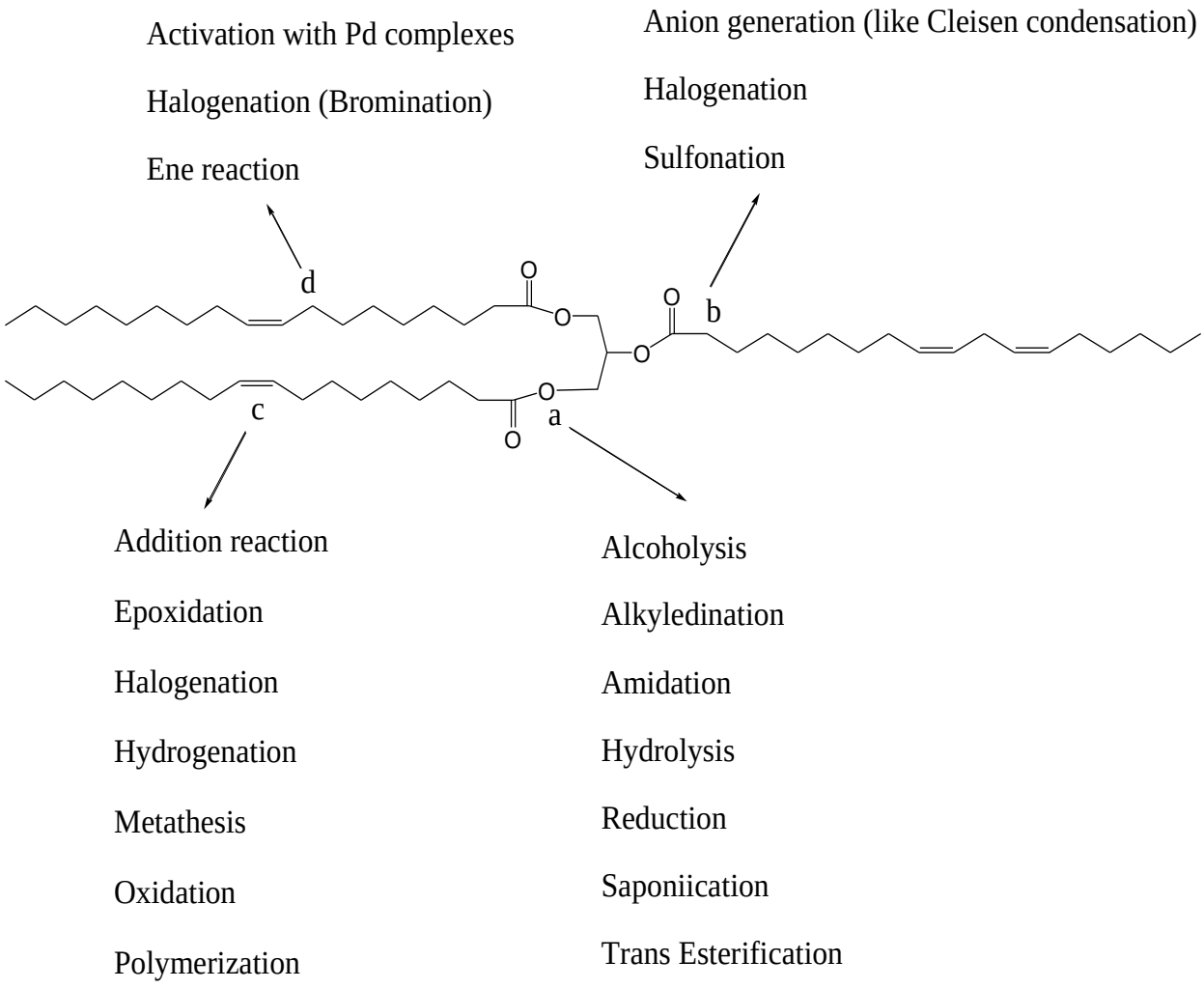


Figure 1.16. Reactive parts of soybean oil triglycerides and their general reactions [32].

1.4.3. Epoxidation of Soybean Oil

Epoxidation is one of the most important reactions at the double bond of unsaturated fatty acids. Most widely used method is the direct single step epoxidation of unsaturated fatty acid compounds with peroxy acids (Figure 1.17). By the acceptance of this method industrially, Epoxidized Soybean Oil (ESO) is mainly used as a safe and non toxic plasticizers for polyvinyl chloride and for similar resins [33]. ESO has gained importance for chemical industry as the starting compound for many triglyceride derivatives.

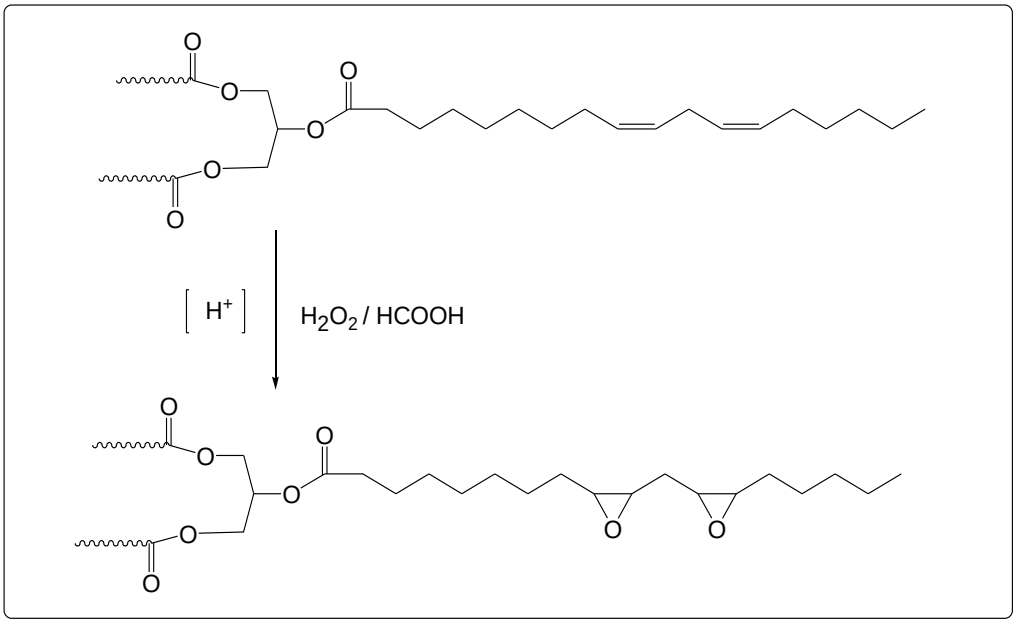


Figure 1.17. Epoxidation of sobean oil with peroxide.

The oxirane rings in the epoxidized triglyceride molecule have considerable ring strain and can be opened by nucleophiles, which lead to large number of products (Table 1.4). Polymerization of ESO with these nucleophiles does not produce any byproduct [34]. This is a very important property especially in liquid molding. Liquid molding resins must polymerize and crosslink without producing any byproducts. When ESO is cured with Epoxy curing agents such as diacides and diamines, no byproduct is formed during the polymerization [32]. In our project we open epoxide groups of ESO with carboxylic acid.

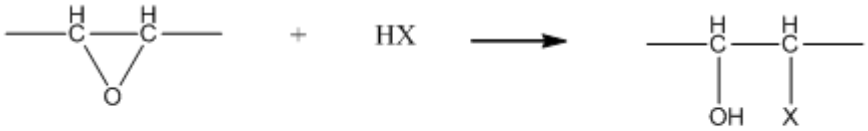


Figure 1.18. Reactions of epoxy group.

Table 1.4. Reactions possible with epoxidized fatty acid [34]

HX	Name of the corresponding structure
H_2	Alcohol
H_2O	Diol
ROH	Alkoxy alcohol
RCOOH	Hydroxy ester
H_2S	Mercapto alcohol
R_2NH	Amino alcohol
HCN	Hydroxynitrile
HCl	Chlorohydrin
$NaHSO_3$	Sodium hydrosulfonate

2. RESEARCH OBJECTIVES

The main aim of this work is to synthesize multi functional reactive monomers (Figure 2.1), which possess the following properties

(i) Partially soluble in unsaturated polyester.

(ii) Act as a barrier to prevent styrene evaporation from unsaturated polyester.

(iii) Has a functional group that can polymerize during cure and thus increase inter laminar adhesion in unsaturated polyester.

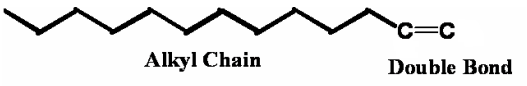


Figure 2.1. Common structure of reactive monomers.

Additives that reduce the styrene emission in unsaturated polyester systems are known and some are commercially available. In these systems the additive molecules come to the surface and form a styrene barrier film due to their partial solubility properties. However such polyester parts suffer from reduced inter laminar adhesion as the additive in the first lay-up, acts as a mold release agents for the second lay-up. Paraffin is such an example. Poor inter laminar adhesion causes delamination in boats and automotive parts made from polyester composites. In this work, new compounds that can both acts as a styrene barrier and that can polymerize and crosslink during the cure cycle will be synthesized. To obtain partial solubility, molecules which contain long alkyl chain groups like a paraffin wax, will be used in the synthesis. The barrier molecules will also have some reactive double bonds that will react with unsaturated polyester during cure. This double bond will work as surface active adhesion promoter group, which increases the inter laminar adhesion (Figure 2.2).

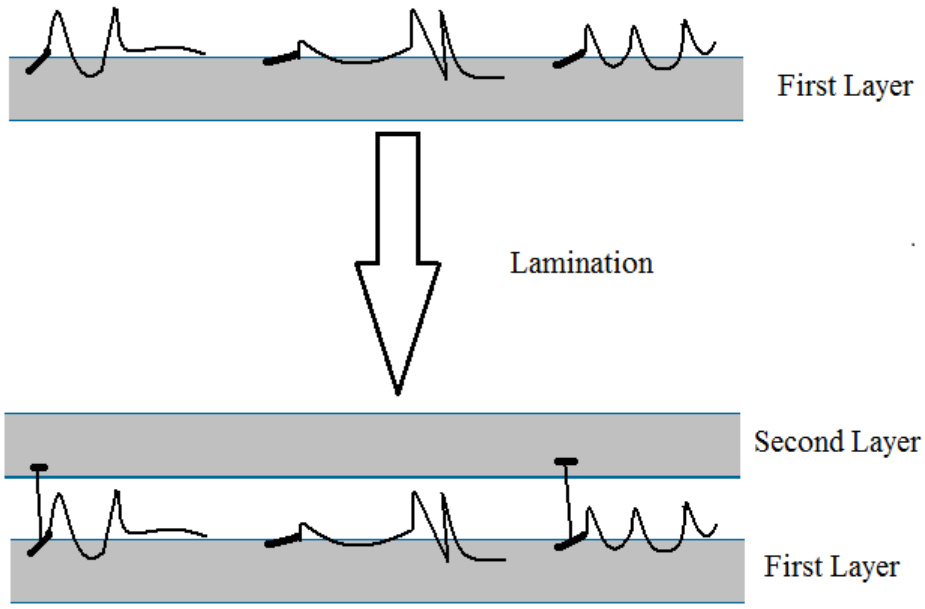


Figure 2.2. Lamination process of unsaturated polyester with additives.

The long alkyl chain of the molecules synthesized will ensure that it comes to the surface to decrease the styrene emission by forming a surface film, during the gelation time of the polyester. Then the unsaturated moiety of the molecules will provide reactivity for cross linking. While some of double bonds react at the first laminate, some of them react with the second laminate, and hopefully give a high inter laminar adhesion. These additives will be synthesized in two groups; linear and branched. Maleate double bonds are used as the reactive double bond to ensure that the reactivity ratio of the barrier molecule matches that of polyester. For the synthesis of linear additives, different types of saturated primary alcohols will be reacted with maleic anhydride. For the synthesis of branched additives, epoxidized soybean oil will be reacted with unsaturated acid groups. These maleinization reactions of alcohol and ring opening reactions of epoxides are summarized in Figure 2.3 and Figure 2.4.

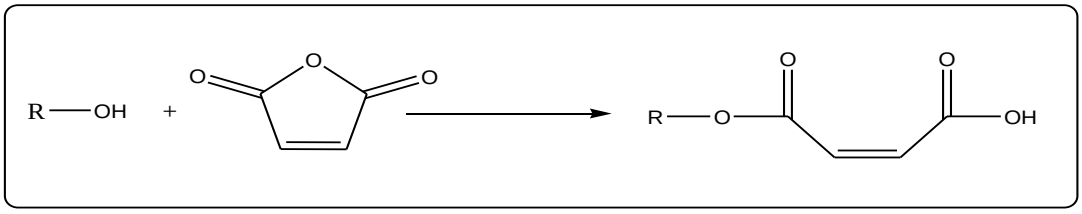


Figure 2.3. Formation Reaction of Maleate Half Ester.

The long alkyl chain, which provides a partial solubility, allows tuning of the barrier properties. These groups determine the styrene suppressant property. In the branched additives, long alkyl chains of soybean oil will be used as styrene the suppressant part and the unsaturation of R groups and soybean oil will be used for secondary bonding.

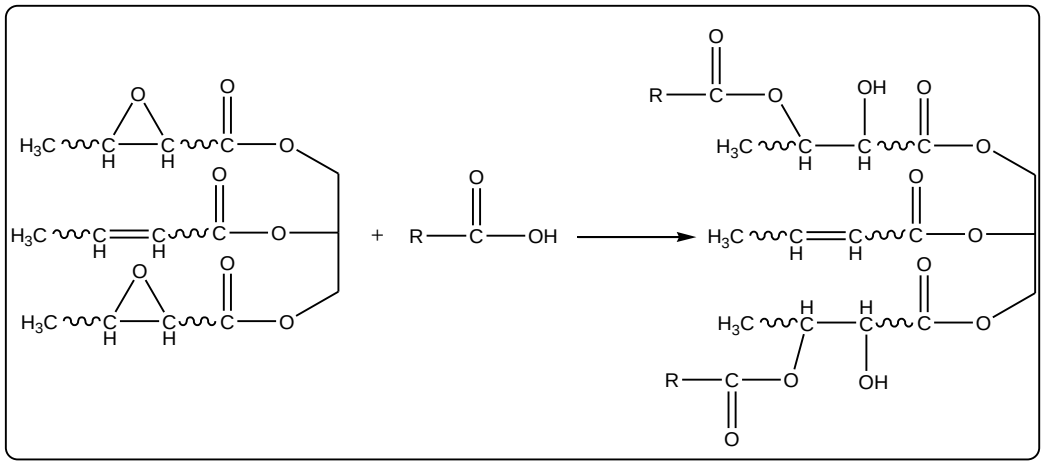


Figure 2.4. Formation of Carboxylic Acid Adducted Epoxidized Soybean Oil.

To improve the reaction yields, different reaction condition will be examined. The structural analysis of the products will be done with 1H-NMR and IR spectroscopy. To examine industrial usefulness of the additives synthesized, styrene volatility test and interlaminar adhesion test will be applied to the molecule synthesized according to AS/NZS 4585.1 and AS/NZS 4585.2 test procedures. With the help of these tests results, the additives synthesized will be evaluated and compared with blank and commercial additives. Barrier molecules that have a promising LSE behavior will then be tested for their ability to provide secondary bonding by doing peel test on two ply laminate.

3. EXPERIMENTAL

3.1. Materials and Apparatus

3.1.1. Materials

Chemicals that are used in this research project are given in Table 3.1.

Table 3.1. Chemicals using in project.

NAME	FORMULA	SUPPLIER
Methanol	CH_3OH	Merck
Epoksidize Soybean Oil	Undefined	Akdeniz Kimya
Stearyl Alcohol	$C_{18}H_{38}O$	Merck
Maleic Anhydride	$C_4H_2O_3$	Undefined
Diethyl Ether	$C_4H_{10}O$	Merck
p-Toluene Sulfonic Acid	$CH_3C_6H_4SO_3H$	Merck
Oleic Acid	$C_{18}H_{34}O_2$	Fluka
Acrylated Soybean Oil	Undefined	Sartomer
Polyethylene Glycol Monooleate	$C_{18}H_{73}O_{19}(C_{18}H_{33}O)$	Undefined
PEG (2000)	$C_{90}H_{182}O_{46}$	Merck
Octyl Phenol Ethoxylate	$C_{14}H_{22}O(C_2H_4O)_{9,5}$	Sigma Aldrich
1-5 Pentanediol	$C_5H_{12}O_2$	Merck
2-Ethyl Hexanol	$C_8H_{18}O$	Merck
Sodium Bicarbonate	$NaHCO_3$	Tecnical
AMC-2 Catalyst	Undefined	Aerojet Chem.
Styrene	$C_6H_5CH_2CH_3$	Undefined
MEKP	$C_8H_{18}O_6$	Undefined
Cobalt Naphtanate	$Co(C_{11}H_7O_2)_2$	Undefined
Deutero Chloroform	CH^2Cl_3	Merck
CE 92 Unsaturated polyester	Undefined	Cam elyaf

3.1.2. Apparatus

The IR analysis was performed on a Nicolet 380 FT-IR with Smart Diamond ATR. Liquid samples were dropped on Smart Diamond ATR window and solid samples were squashed on Smart Diamond ATR window with the screwier of the apparatus.

All the ^{1}H NMR spectra were recorded on a Varian 400-MHz NMR instrument operating at a frequency of 399.986 MHz for proton. The spectra were reported as ppm (δ) with TMS as internal standard.

The secondary bonding effects of synthesized additives was tested with DVT G-21 type of tensile strength machine according to the standard AS/NZS 4585.2 the degree of interlaminar adhesion test.

3.2. Synthesis of Linear Type of Low Styrene Emission Monomers MSMA, MOMA, PBMA, PEG-MA, PEGMO-MA, OPE-MA

3.2.1. Synthesis of Mono Stearyl Maleate (MSMA)

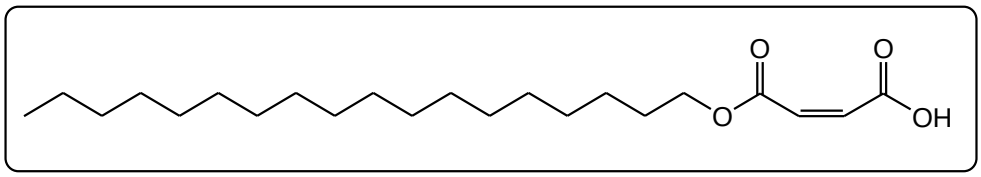


Figure 3.1. Chemical structure of Mono Stearyl Maleate (MSMA).

16.6 g. (0.061 mole) stearyl alcohol and 6.02 g. (0.061 mole) maleic anhydride were placed in a flask with magnetic stirrer. This reaction was performed under nitrogen at 90°C for 5 hour. The reaction product mono stearyl maleate (MSMA) was white solid at RT. The IR data showed the characteristic peaks of both alcohol and maleate.

IR (cm^{-1}): 1720 (s, -(C=O)-O-R), 1646 (s, C=C), 716 (b, =C-H), 1258 (s, C-O-Def), 1215 (s, O-C) 2848(s C-H), 2914 (s,C-H), 2953 (s, O-H), 1358 (b, C-H), 1470 (m, CH2, Def), 3300 (s, O-H), 1422 (m, C-O-H)

3.2.2. Synthesis of Mono Isooctyl Maleate (MOMA)

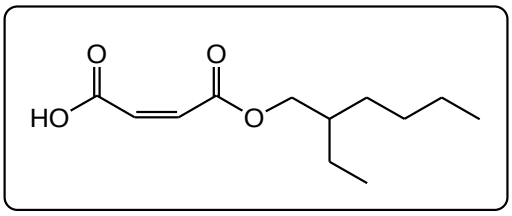


Figure 3.2. Chemical structure of Mono Isooctyl Maleate (MOMA).

6.56 g.(0.066 moles) maleic anhydride was added to 8.70 g. (0.066 moles) 2-ethylhexanol. The solution was stirred for 7 hours at 75 ºC under nitrogen then cooled to room temperature. The reaction product mono isooctyl maleate (MOMA) was transparent liquid at RT.

^{1}H NMR ($CDCl_3$, 400 MHz) ppm: 6,51 (-C<u>H</u>=C), 6,35 (-C=C<u>H</u>-), 4,3 (O-C<u>H2</u>-CH), 2,0 (CH2-C<u>H</u>), 1,0 (CH2-C<u>H3</u>)

IR (cm^{-1}): 1734 (s, -(C=O)-O-R), 1632 (s, C=C), 1213 (s, O-C), 2872 (s, C-H), 2927 (s,C-H), 2957 (s, O-H), 1710 (s, (C=O)-O-H), 1463 (m, CH2, Def), 1413 (m, C-O-H)

3.2.3. Synthesis of Pentane Bis- Maleate (PBMA)

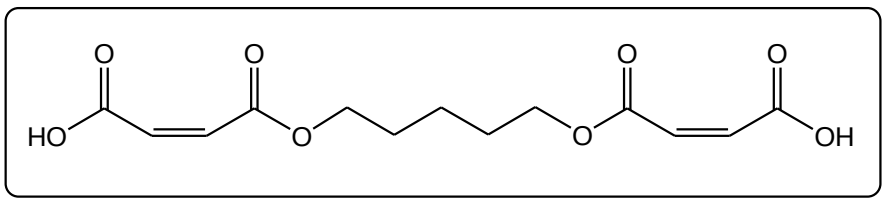


Figure 3.3. Chemical structure of Pentane Bis-Maleate (PBMA).

6.68 g. (0.064 mole) 1,5-pentanediol and 12.60 g. (0.128 moles) maleic anhydride were placed in a flask with magnetic stirrer. This reaction was performed under nitrogen at

60°C for 15 hours then cooled to room temperature. The reaction product pentane bis-maleate (PBMA) was white solid at RT.

^{1}H NMR ($CDCl_3$, 400 MHz) ppm: 6,51 (-CH=C), 6,35 (-C=CH-), 4,2 (O-CH2-CH2), 1,6 (O-CH2-CH2), 1,3 (CH2-CH2-CH2)

IR (cm^{-1}): 1730 (s, -(C=O)-O-R), 1628 (s, C=C), 1205 (s, O-C), 2870 (s, C-H), 2955 (s, O-H), 1710 (s, (C=O)-O-H), 1413 (m, CH2, Def)

3.2.4. Synthesis of Polyethylene Glycol (2000) Bis-Maleate (PEG-MA)

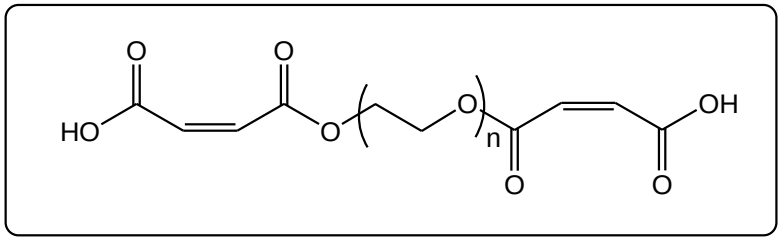


Figure 3.4. Chemical structure of Poly Ethylene Glycol (2000) Bis-maleate (PEG-MA).

3.46 g. (0.0353 moles) maleic anhydride and 35.30 g. (0.0176 moles) polyethylene glycol (Mw:2000 g./mol) were placed in a flask and stirred at 90°C with 0.038 g. (%0.1 w/w) p-Toluene sulfonic acid as catalyst. Reaction was continued for 6 hours under nitrogen and then cooled to room temperature. The product polyethylene glycol bis-maleate was a white wax at room temperature. The IR and 1H-NMR data showed the characteristic peak of both glycol and maleates.

^{1}H NMR ($CDCl_3$, 400 MHz) ppm: 6,51 (-CH=C), 6,35 (-C=CH-), 4,2 ((C=O)O-CH2), 3,54 (O-CH2)

IR (cm^{-1}): 1728 (s, -(C=O)-O-R), 1635 (s, C=C), 1103 (s,C-O-C), 2884 (s, C-H), 1239 (s, O-C), 2945 (s, O-H), 1465 (m, CH2, Def)

3.2.5. Synthesis of PEG (400) Oleate Maleate (PEGO-MA)

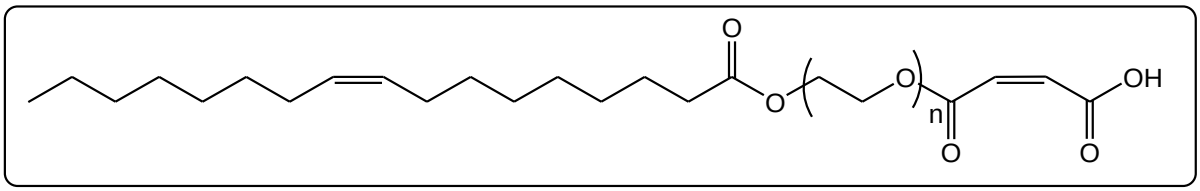


Figure 3.5. Chemical structure of PEG (400) Oleate-Maleate (PEGO-MA).

1.52 g. (0.0156 moles) maleic anhydride and 10.36 g. (0.0156 moles) polyethylene glycol mono oleate (PEG Mw:400 g./mol) were placed in a flask and stirred at 50°C with 0.011 g. (%0.1 w/w) p-Toluene sulfonic acid as catalyst. Reaction was continued for 15 hours under nitrogen and then cooled to room temperature. The product polyethylene glycol oleate- maleate was yellowish liquid at room temperature. The IR and 1H-NMR data showed the characteristic peak of both glycol oleate and maleate.

^{1}H NMR ($CDCl_3$, 400 MHz) ppm: 6,51 (-C<u>H</u>=C), 6,35 (-C=C<u>H</u>-), 4,2 ((C=O)O-C<u>H2</u>), 2,4 (C<u>H2</u>-(C=O)-O), 3,52 (O-C<u>H2</u>)

IR (cm^{-1}): 1730 (s, -(C=O)-O-R), 1639 (s, C=C), 1209 (s, O-C), 2854 (s, C-H), 2922 (s,C-H), 2957, 1455 (m, CH2, Def), 1413 (m, C-O-H), 1097 (s,C-O-C),

3.2.6. Synthesis of Octyl Phenol Ethoxylate Maleate (OPE-MA)

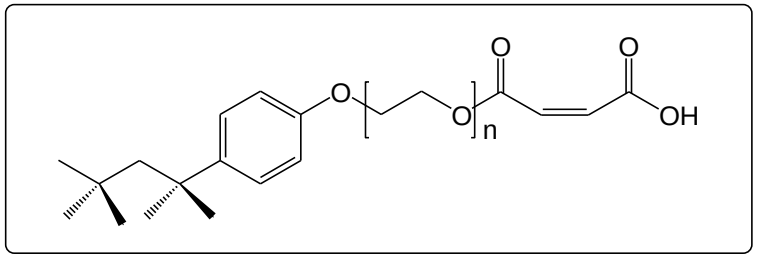


Figure 3.6. Chemical structure of Octyl Phenol Ethoxylate Maleate (OPE-MA).

1.49 g. (0.0153 moles) maleic anhydride and 9.55 g. (0.0153 moles) octyl phenol ethoxylate having a PEG segment of DP: 9.5, were placed in a flask and stirred at 75°C. Reaction was continued for 5 hours under nitrogen and then cooled to room temperature.

The product octyl phenol ethoxylate mono maleate was yellowish liquid at room temperature.

^{1}H NMR ($CDCl_3$, 400 MHz) ppm: 6,51 (-CH=C), 6,35 (-C=CH-), 4,57 ((C=O)O-CH2), 4,2 (Ph-O-CH2)

IR (cm^{-1}): 1727 (s, -(C=O)-O-R), 1640 (s, C=C), 1243 (s, C-O- Def), 2868 (s, C-H), 2949 (s,C-H), 1454 (m, CH2, Def), 1097 (s,C-O-C),

3.3. Synthesis of Branched Type of Low Styrene Emission Monomers ESO-OA, ESO-SMA, ESO-MMA

3.3.1. Synthesis of Epoxidized Soybean Oil- Oleic Acid Adduct (ESO-OA)

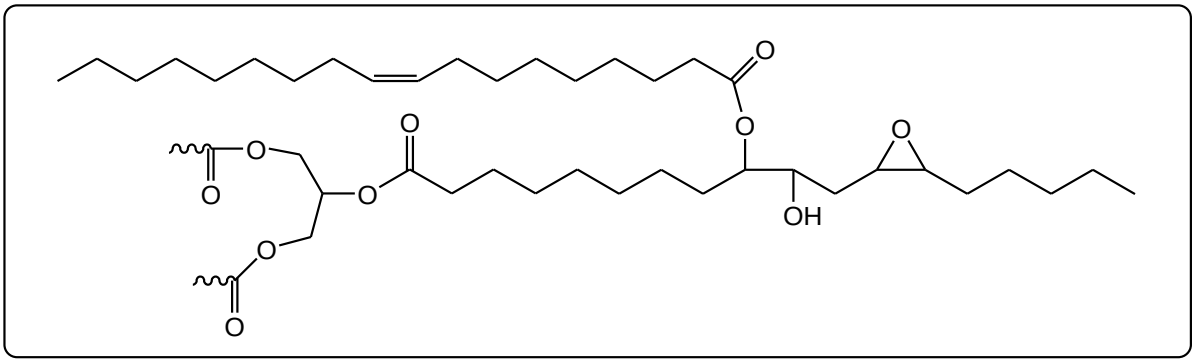


Figure 3.7. Chemical structure of Epoxidized Soybean Oil-Oleic Acid Adduct (ESO-OA).

5.26 g. (0.0186 moles) oleic acid and 5.90 g. (0.0062 moles) soybean oil (assuming an average molecular weight of 950 for ESO) were placed in a flask and stirred at 90°C with 0.01 g. (%0.1 w/w) AMC-2 as catalyst. Reaction was continued for 5 hours then cooled to room temperature. The product was dissolved in diethyl ether and extracted with 10% (aqueous) sodium bicarbonate for the removal of unreacted oleic acid. Aqueous salt solution was added to each mixture to facilitate the phase separation. The ether layer was dried with anhydrous sodium sulfate and evaporated to dryness in vacuum at room temperature.The reaction product epokside soybean oil oleate was greenish viscous liquid at room temperature. Green color is imparted by the tin salts present in AMC-2 catalyst.

^{1}H NMR ($CDCl_3$, 400 MHz) ppm: 0,9 (-CH2-CH3), 1,2 (-CH2-), 2,3 (-CH2-C-O), 3.8 (-(C=O)O-CH2), 4.2 (C-O-CH2),

3.3.2. Synthesis of Epoxidized Soybean Oil- Stearyl Maleate Adduct (ESO-SMA)

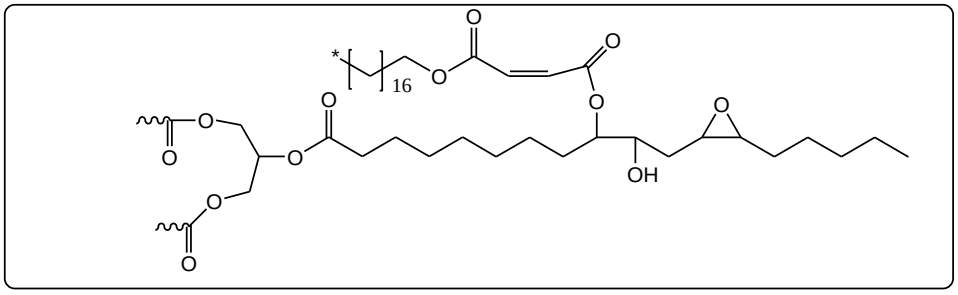


Figure 3.8. Chemical structure of Epoxidized Soybean Oil-Stearyl Maleate adduct (ESO-SMA).

7.80 g. (0.0212 moles) mono stearyl maleate and 6,72 g. (0.0070 moles) epoxidized soybean oil (assuming an average molecular weight of 950 for ESO) were placed in a flask and stirred at 90°C with 0.01 g. (%0.1 w/w) AMC-2 as catalyst. Reaction was continued for 5 hours then cooled to room temperature. The product was dissolved in diethyl ether and extracted with 10% (aqueous) sodium bicarbonate for the removal of unreacted mono stearyl maleate. Aqueous salt solution was added to each mixture to facilitate the phase separation. The ether layer was dried with anhydrous sodium sulfate and evaporated to dryness in vacuum at room temperature. The reaction product of epoxidized soybean oil with stearyl maleate was a greenish wax at room temperature.

^{1}H NMR ($CDCl_3$, 400 MHz) ppm: 0,9 (-CH2-CH3), 1,2 (-CH2-), 2,3 (-CH2-C-O), 3.8 (-(C=O)O-CH2), 4.2 (C-O-CH2), 6.2 (-CH=CH-)

3.3.3. Synthesis of Epoxidized Soybean Oil- Methyl Maleate Adduct (ESO-MMA)

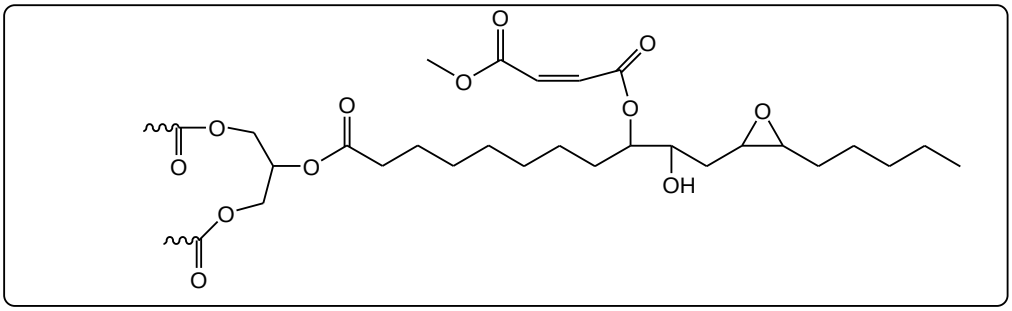


Figure 3.9. Chemical structure of epoxidized soybean oil-methyl maleate adduct (ESO-MMA).

6.56 g.(0.066 moles) maleic anhydride was added to 10 g. (excess) dried methanol. The solution was stirred for 4 hours at room temperature under nitrogen. Unreacted methanol was evaporated in vacuum. The reaction product methy maleate (MMA) was transparent liquid at RT.

IR (cm^{-1}): 1720 (s, -(C=O)-O-R), 1646 (s, C=C), 716 (b, =C-H), 1258 (s, C-O-Def), 1215 (s, O-C) 2848(s C-H), 2953 (s, O-H), 3300 (s, O-H), 1422 (m, C-O-H)

3.46 g. (0.0267 moles) methyl maleate and 8.45 g. (0.0089 moles) epoxidized soybean oil (assuming an average molecular weight of 950 for ESO) were placed in a flask and stirred at 90°C with 0.01 g. (%0.1 w/w) AMC-2 as catalyst. Reaction was continued for 5 hours then cooled to room temperature. The product was dissolved in diethyl ether and extracted with 10% (aqueous) sodium bicarbonate for the removal of unreacted mono methyl maleate. Aqueous salt solution was added to each mixture to facilitate the phase separation. The ether layer was dried with anhydrous sodium sulfate and evaporated to dryness in vacuum at room temperature. The reaction product epoxidized soybean oil with methyl maleate was greenish viscous liquid at room temperature.

^{1}H NMR ($CDCl_3$, 400 MHz) ppm: 0,9 (-CH2-CH3), 1,2 (-CH2-), 2,3 (-CH2-C-O), 3.8 (-(C=O)O-CH3), 4.2 (C-O-CH2), 6.2 (-CH=CH-)

3.4 . Emission Control Test

The styrene emissions of unsaturated polyester resins containing 33-35% styrene were measured with a surface open to the atmosphere using curing agents and LSE additives. LSE additives were dissolved in an equal weight of styrene before addition. Approximately 30 grams of resin were mixed with catalyst (1% MEKP and 0.25% Cobalt Naphtanate (6% cobalt in solution)) and additive mixture (2% w/w) based on polyester resin was added and the mixture was stirred for one minute. Exactly 30 gr. of catalyzed resin additive mixture was then poured into the pre-weighed petri dish (10 cm in diameter). The petri dish was placed in a hood, away from drafts, and kept at room temperature. After 24 hours, the resin was cured, the petri dish was weighed again. The styrene emission can be determined by the difference in weight between cured resin and liquid resin. Evaporation per unit surface area was calculated by dividing the weight of styrene lost to the area of petri dish (78 cm^2).

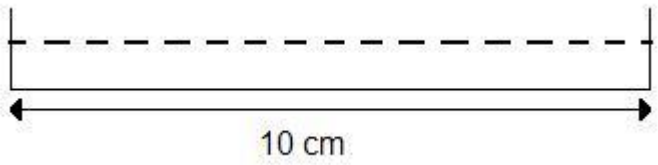


Figure 3.10. Schematic representation of petri dish.

3.5. Interlaminar Adhesion Test

The laminates (Figure 3.12) were prepared with glass mat (400 g/m2), resin (2,5 fold of glass mat weight) curing agents and LSE additive (1% w/w). The first ply laminate was allowed to cure at room temperature for 24 hours. Before the second lamination process, parting film was placed at one end of the laminate and glass laminate with resin was placed on the cured laminate and again allowed to cure for 24 hours. The laminate was cut to dimension of 7 cm x 20 cm and a metal hinge was glued to the upper and the lower laminate. The hinge was free to swing. Thus the force applied to the ends of the laminate during the test was always vertical to the laminate surface regardless of the angle of the laminate. Strain rate of 2 mm/ min was used to make sure that the delamination was quasi equilibrium. A sample graph obtained from the testing machine is shown in Figure 3.11.

The actual delamination force was obtained by interpolating the horizontal region of the trace as this corresponds to the quasi equilibrium delamination force and should in principle be independent of delamination rate. Secondary bonding force in a laminate was determined by double cantilever bean technique for measuring toughness of laminate interface.

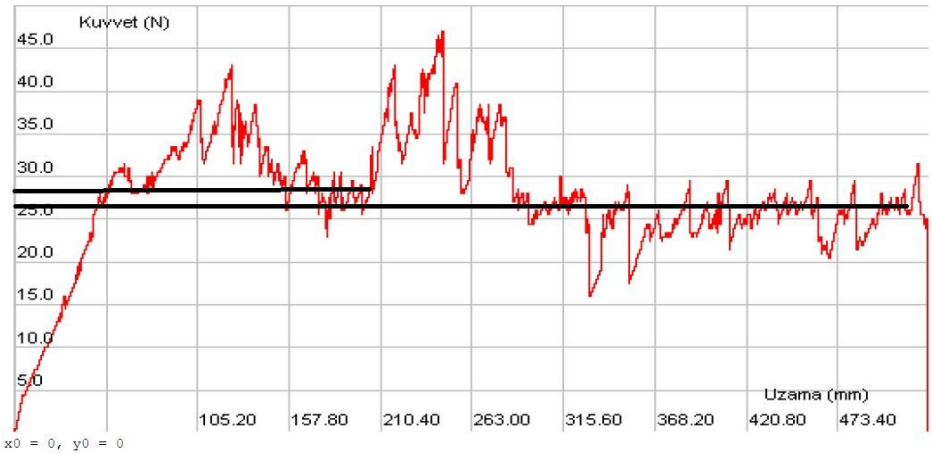


Figure 3.11. Interpolation of interlaminar adhesion test graph.

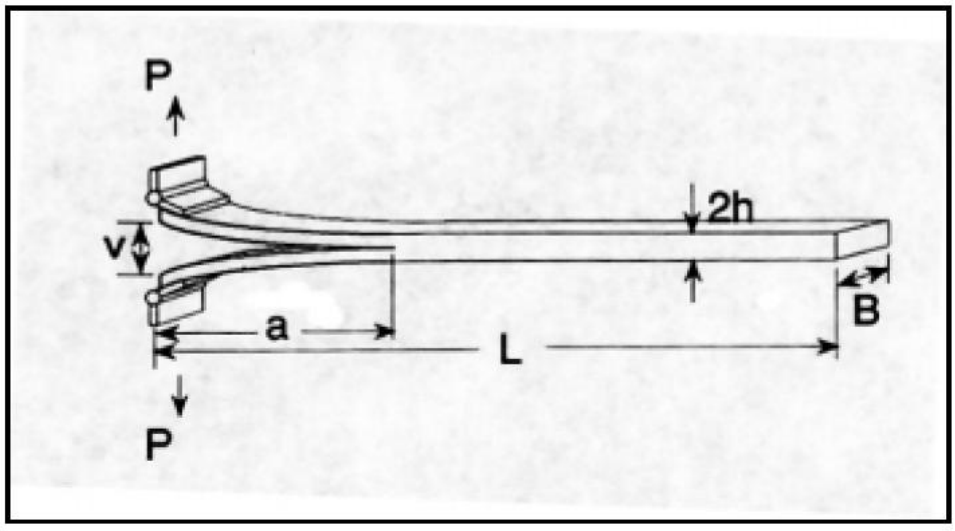


Figure 3.12. Secondary bonding specimen and its dimensions (L: 200 mm, B: 70 mm, a: 40 mm, 2h: 2 mm).

4. RESULTS AND DISCUSSION

4.1. Synthesis and Structure Determination of Maleate Half Ester LSE Additives

No theoretical work exists on the structure of barrier molecules for the prevention of styrene evaporation. However it is clear from early industrial work that, the molecule must be only partially soluble in polyester and must poses a long alkyl chain. The present research aims to incorporate these properties, with a reactive double bond so that after the molecule has performed its duities as a barrier layer, it can be incorporated into the UPE network by covalent bonds. Maleate double bonds seem to be excellent candidate as the same functional group appears in UPE and therefore the reactivity ratios of the UPE chain and the LSE additives are identical. The solubility properties of the LSE additives synthesized in this work are fine tuned by the length and the structure of the non-polar alkyl portion of the molecule and the polar carboxyl terminal groups.

Synthesis of maleate half esters was carried out in the temperature range of 50-100 C with equimolar mixtures of maleic anhydride and alcohol. The reaction proceeds by the addition reaction of anhydride with alcohol and there is no by-product. With primary alcohols the reaction proceeds at lower temperatures and without any catalyst. If higher temperatures are used, condensation reaction may take place and di-maleates may be formed and maleate to fumarate isomerization can take place. This was prevented by the use of low reaction temperatures and long reaction times. Moreover, at the high temperature maleic anhydride sublimed. By increasing the pressure, sublimation of maleic anhydride was minimized. The fumarate formation can be detected with ^{1}H-NMR. The characteristic peaks of fumarate appears as doublet of doublets at 7 ppm which corresponds to trans protons, however the characteristic peaks of maleate appear at 6.3 ppm and 6.5 ppm which corresponds to cis protons. The half ester reactions of maleate can be monitored with FT-IR spectra. In the all FT-IR spectra of half esters, the C=O stretching band of maleic anhydride at 1850 cm^{-1} (low intensity) and 1780 cm^{-1} (medium intensity) decrease and the C=O stretching band of new ester linkages and carboxyl acid at 1720 cm^{-1} and at 1707 cm^{-1} increase in intensity.

Humidity affects the half ester reaction. The maleic anhydride is partially converted to the acid form under moist conditions. Maleic anhydride was converted to maleic acid under water vapor in 4 hours. This conversion was detected with IR spectrum which is shown at Figure 4.1. In this spectrum, it can be observed that the rise of a band at 1707 cm^{-1} and the disappearance of bands at 1856 cm^{-1} and 1780 cm^{-1}. To prevent humidity affects, reactions were carried out under dry conditions [35].

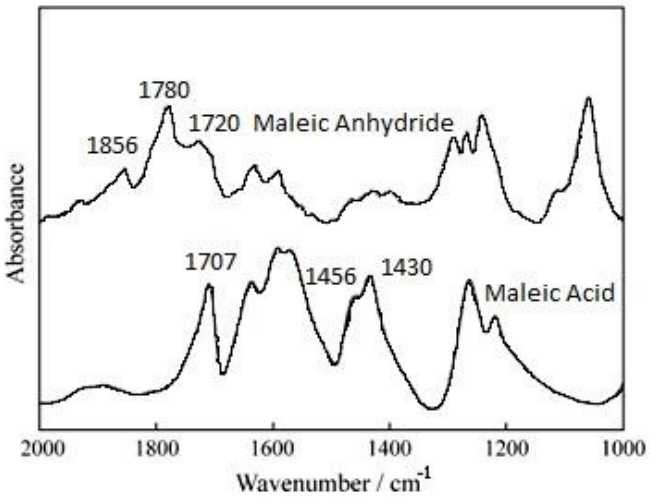


Figure 4.1. IR spectrum of conversion from maleic anhydride to maleic acid under humidity condition.

4.1.1. Methyl Maleate (MMMA)

Esterification of maleic anhydride with methanol is a well known reaction and was carried out at room temperature. Dry methanol was used under dry nitrogen to prevent hydrolysis of maleic anhydride to maleic acids. In order to monitor the progress of reaction, FT-IR of a liquates taken at random intervals (Figure 4.2). The decrease of 1710 cm^{-1}, 1850 cm^{-1} and 1780 cm^{-1} peaks were observed. The appearance of a new peak near the 1707 cm^{-1} (carboxylic acid) proved the methyl maleate half ester product. This product was used as a reactant with epoxidized soybean oil (ESO).

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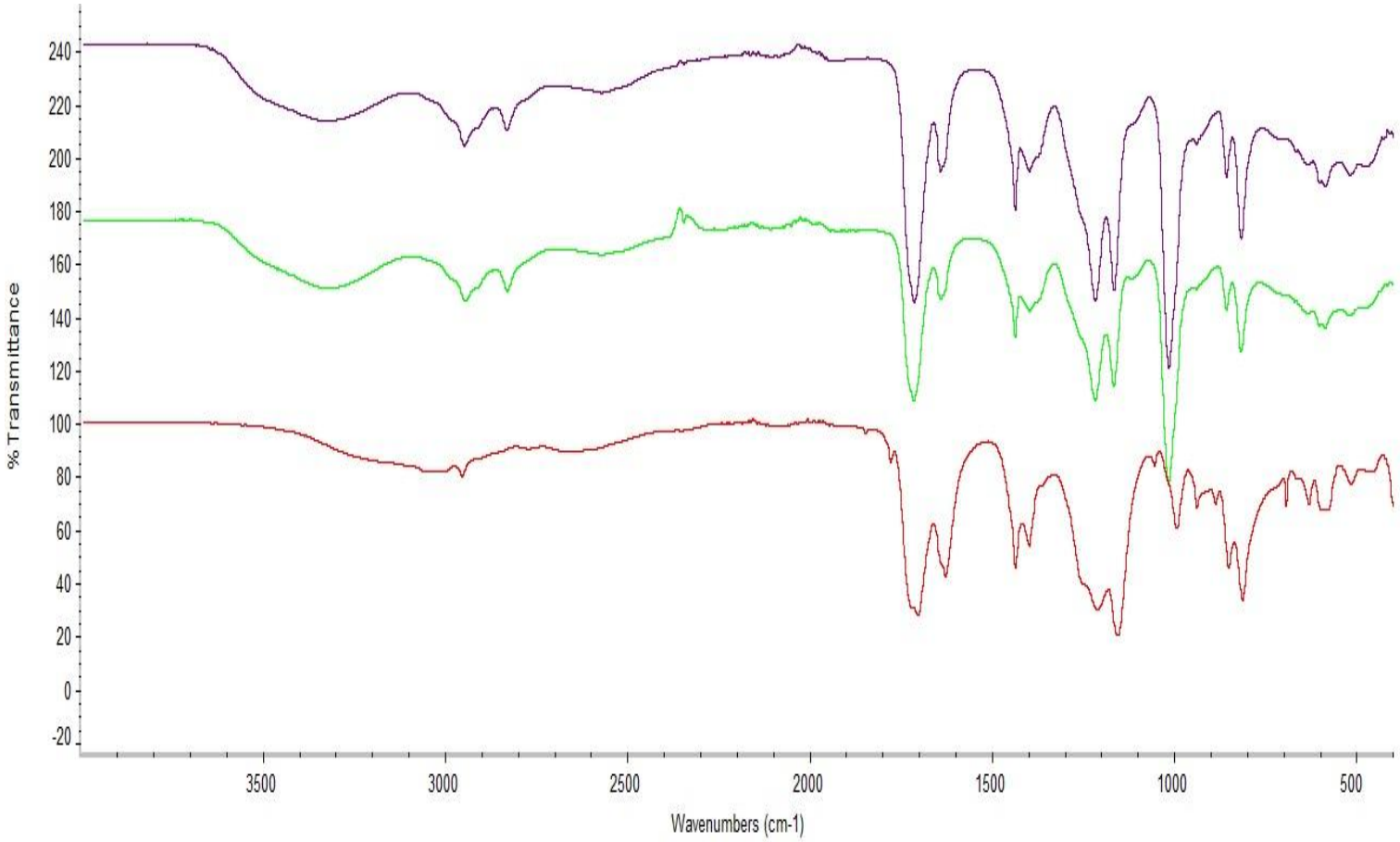

Figure 4.2. FT-IR spectrum of Mono Methyl Maleate (MMMA) at 1 H, 3 H and separated end product.

4.1.2. Mono Stearyl Maleate (MSMA)

In the esterification reaction of maleic anhydride with stearyl alcohol, the best reaction temperature was found to be at 90 °C. Maleic anhydride sublimed at this high temperature; and to decrease its sublimation nitrogen pressure balloons were used. At the end of reaction, small amount of unreacted maleic anhydride was not removed, as it has no detrimental effect on UPE cure reaction. The FT-IR spectrum of MMMA (Figure 4.2) and MSMA (Figure 4.3) exhibits similar features. The decreasing of 1850 cm^{-1} and 1780 cm^{-1} peaks show the consumtion of maleic anhydride, and the increasing of peak at 1720 cm^{-1} shows the formation of new ester at the stearyl maleate half ester product. The peaks around the 3000 cm^{-1} show symmetrical and asymmetrical stretching of –CH2-. In this product, stearyl part of molecule was used as styrene barrier, maleate part of molecule as used as inter laminar adhesion promoter.

4.1.3. Mono Isooctyl Maleate (MOMA)

In order to increase the yield, this reaction carried out at 75 °C. Similar indications were seen at the FT-IR spectrum (Figure 4.4) of this product. In order to calculate the yields of maleic anhydride esterification reaction with isooctyl alcohol, ^{1}H-NMR (Figure 4.5) spectrum of product was analyzed. The ratio of integral value of the peak corresponding to methl protons of octyl alcohol at 0.8 ppm with vinyl protons of maleate at 6.3-6.5 ppm shows 64% yield. Maleic anhydride residue appears at 7.25 ppm. It is known that when paraffin is used as an LSE additive, the branched paraffin works better than the linear ones. This product, containing a branched alkyl chain, was inspired by this fact. Branched alkyl part of molecule was used as styrene barrier, maleate part of molecule as used as adhesion promoter.

4.1.4. Pentane Bis- Maleate (PBMA)

İncreasing the wight percentage of the reactive double bond in the molecule should increase inter laminar adhesion. 1,5-Pentanediol was used for this purpose. At the acylation reactions of 1,5-Pentanediol with maleic anhydride, similar procedure was used. But here as the bis-maleate is the desired compound the stochiometry of the diol to maleic

anhydride was charged to 1:2. This reaction was performed under nitrogen at 60°C for 15 hour then cooled to room temperature. The reaction product pentane bis-maleate (PBMA) was white solid at RT. In the FT-IR spectrum (Figure 4.6), similar conversion peaks are seen at 1850 cm^{-1}, 1780 cm^{-1} and 1720 cm^{-1}. According to 1H-NMR spectrum (Figure 4.7) of pentane bis-maleate, the ratio of integral value of the peak corresponding to middle aliphatic protons of 1-5 Pentanediol at 1.6 ppm and 1.8 ppm with vinyl protons of maleate at 6.3-6.5 ppm gave a 84% yield. In this product, linear alkyl part of molecule was used as styrene barrier, maleate parts of molecule as used as adhesion promoter.

4.1.5. PEG (2000) Bis-Maleate (PEG-MA)

PEG derivatives were used for the synthesizing of LSE additives. At US Patent 5 741 873, PEG diacrylate were synthesized by the Aristech. In US Patent 5 378 743, PEG Bis maleate were synthesized by Dow Chemical. Both of these molecules were claimed to be effective LSE additives. In this research project, PEG (2000) bis-maleate were synthesized to verify the claimed effectiveness of PEG derivatives. This product was synthesized with similar methods. Similar indications were seen at the FT-IR spectrum (Figure 4.8). In order to calculate the yields of maleic anhydride esterification reaction with PEG (2000), 1H-NMR (Figure 4.9) spectrum of product was analyzed. The calculated yield was 64% according to the ratio of integral value of the peak corresponding to –CH2- protons of PEG (O-C$\underline{H}_2$-C$\underline{H}_2$-O) with vinyl protons of maleate. In this product vinyl groups of molecule were used as adhesion promoter and ethoxy groups of molecule were used as styrene barrier.

4.1.6. PEG (400) Mono Oleate Mono-Maleate (PEGMO-MA)

To increase the size of the non-polar group, different types of PEG derivetives were used in this project. PEG (400) mono oleate was the one of them. This molecule has a 18carbon unsaturated group on one end and a maleate on the other end of the PEG residue For the synthesizing PEGMO-MA, same procedure were applied to PEG (400) mono oleate and maleic anhydride at 50 C for 15 h. Para-toluene sulfuric acid was used to increase reaction yield. In the FT-IR spectrum (Figure 4.10) of this product, similar changes were observed. In order to calculate the yields of maleic anhydride esterification

reaction with PEG (400) mono oleate, H-NMR spectrum (Figure 4.11) of product was analyzed. The ratios of integral value of the peak corresponding to methl terminate protons of oleate with vinyl protons of maleate shows 82% yield. Ethoxylate and oleic parts of molecule were used as styrene barrier, maleate part of molecule and the double bonds on the oleate were used as adhesion promoter.

4.1.7. Octyl Phenol Ethoxylate Mono Maleate (OPE-MA)

Octyl phenol ethoxylates are well known emulsifying agents (Triton). They are known to form excellent barriers at the interface of immiscible liquids. To take advantage of this known property octyl phenol ethoxylate was maleated to give a new LSE. For the obtain OPE-MA molecule, similar synthesis method was used and the reaction was carried out at 75 C for 5 h. Similar indications were seen in the FT-IR spectrum (Figure 4.12) of this product. In order to calculate the yields of reaction ^{1}H-NMR (Figure 4.13) spectrum of product was analyzed. According to the the ratio of integral value of the peak corresponding to terminal methl protons of octyl groups with vinyl protons of maleate, yield of reaction was calculated as 86%. Ethoxy parts of molecule was used as styrene barrier, maleate part of molecule as used as adhesion promoter

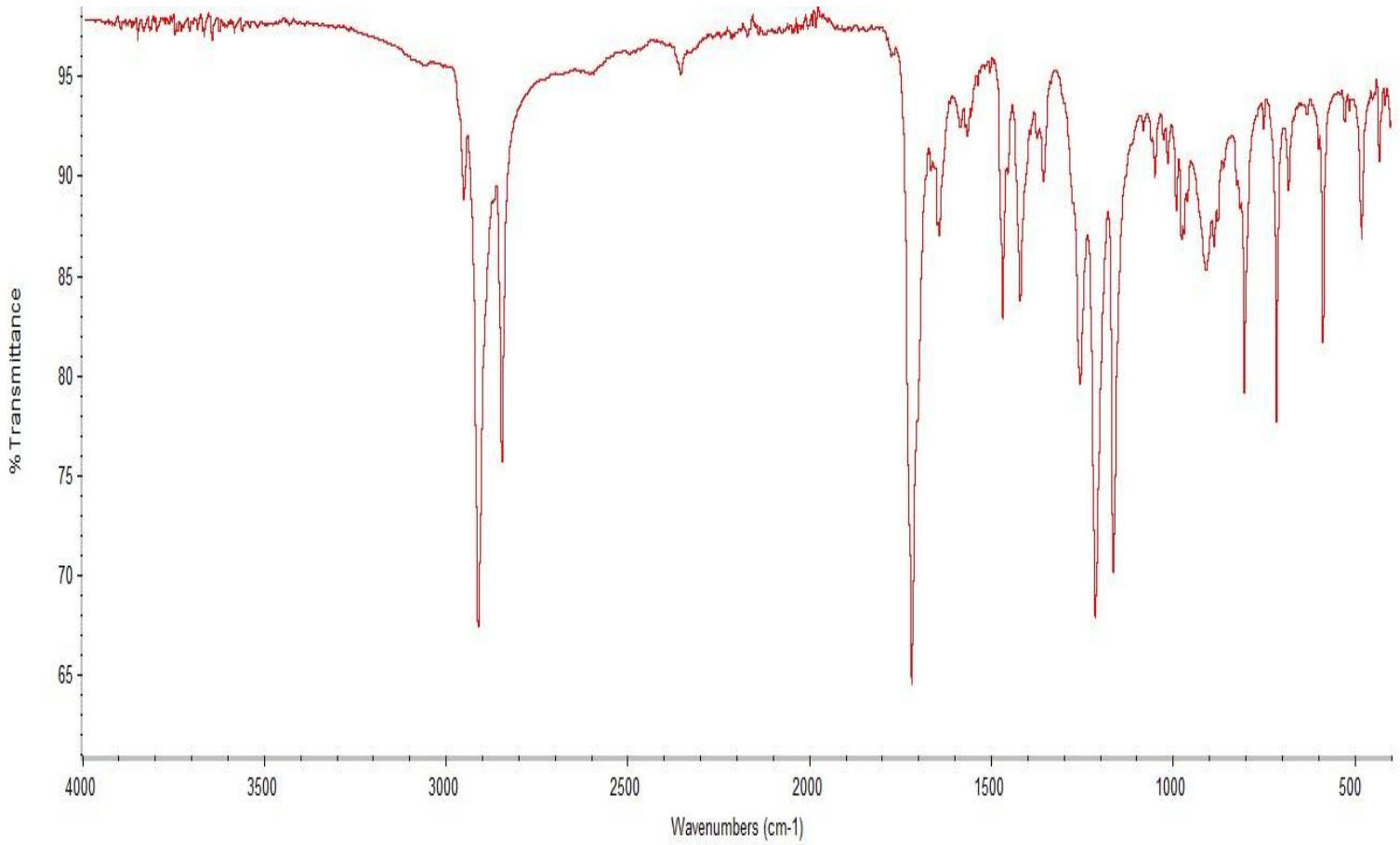

Figure 4.3. FT-IR spectrum of Mono Stearyl Maleate (MSMA).

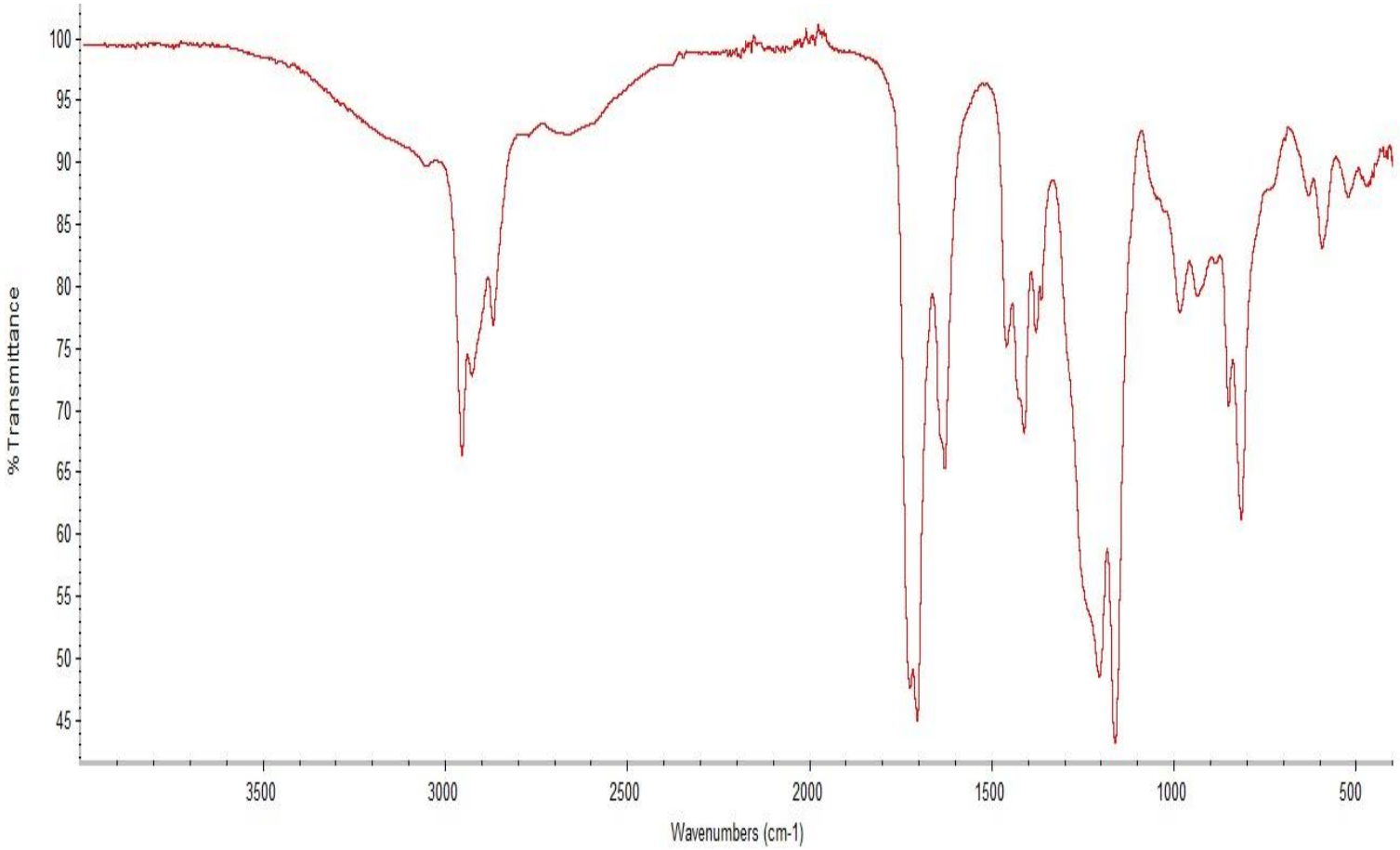

Figure 4.4. FT-IR spectrum of Mono Isooctyl Maleate (MOMA).

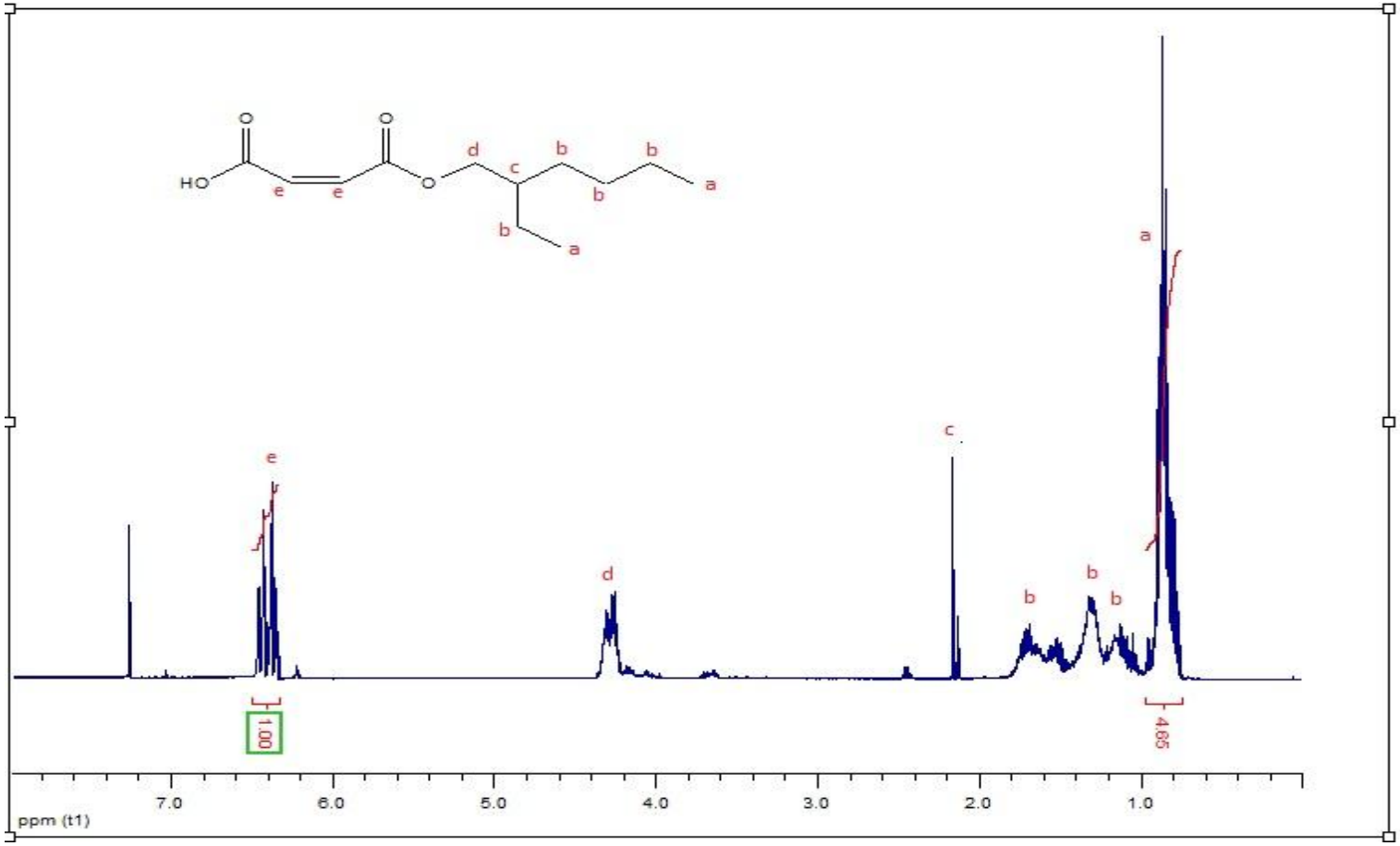

Figure 4.5. ^{1}H-NMR spectrum of Mono Isooctyl Maleate (MOMA).

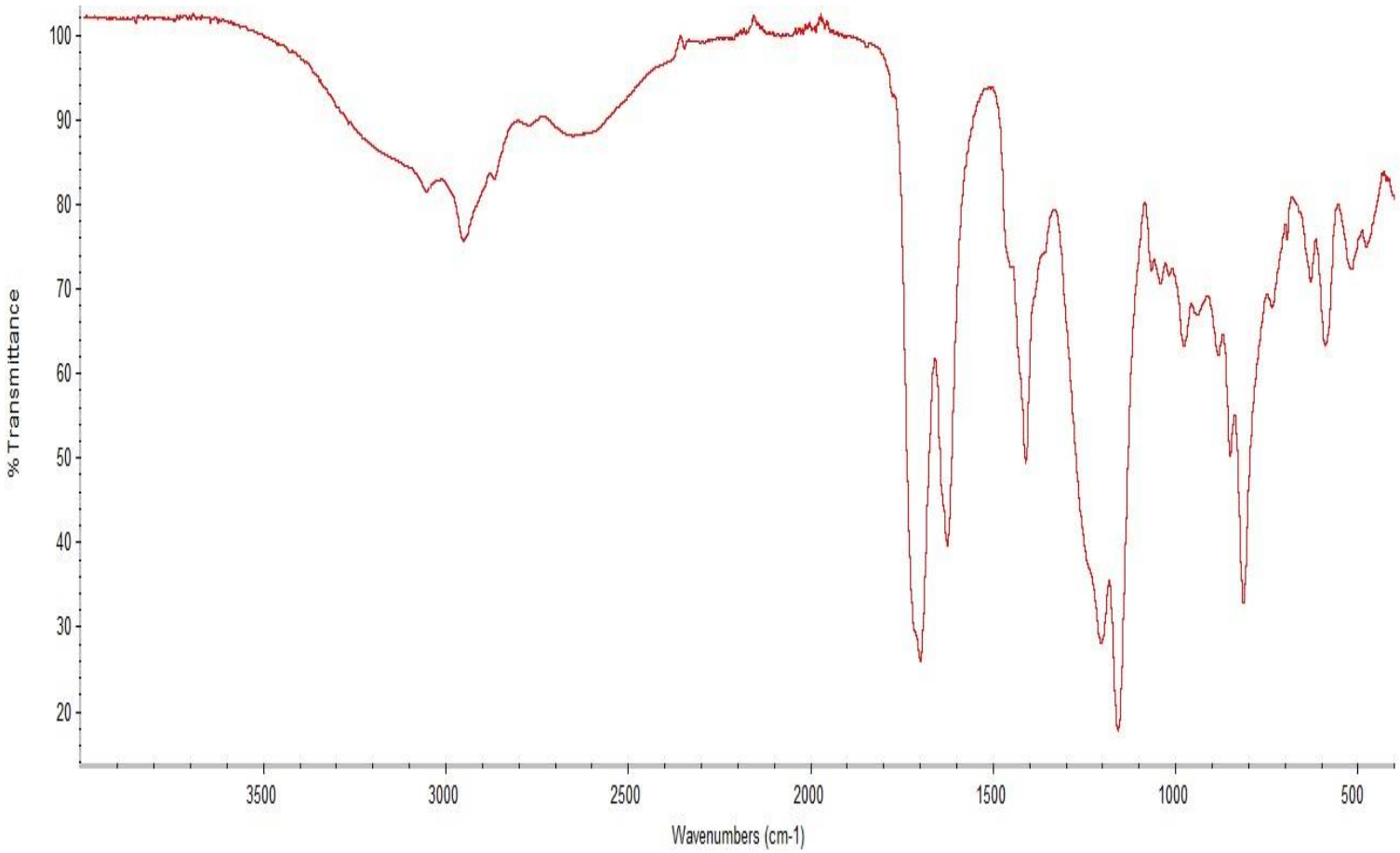

Figure 4.6. FT-IR spectrum of Pentane Bis- Maleate (PBMA).

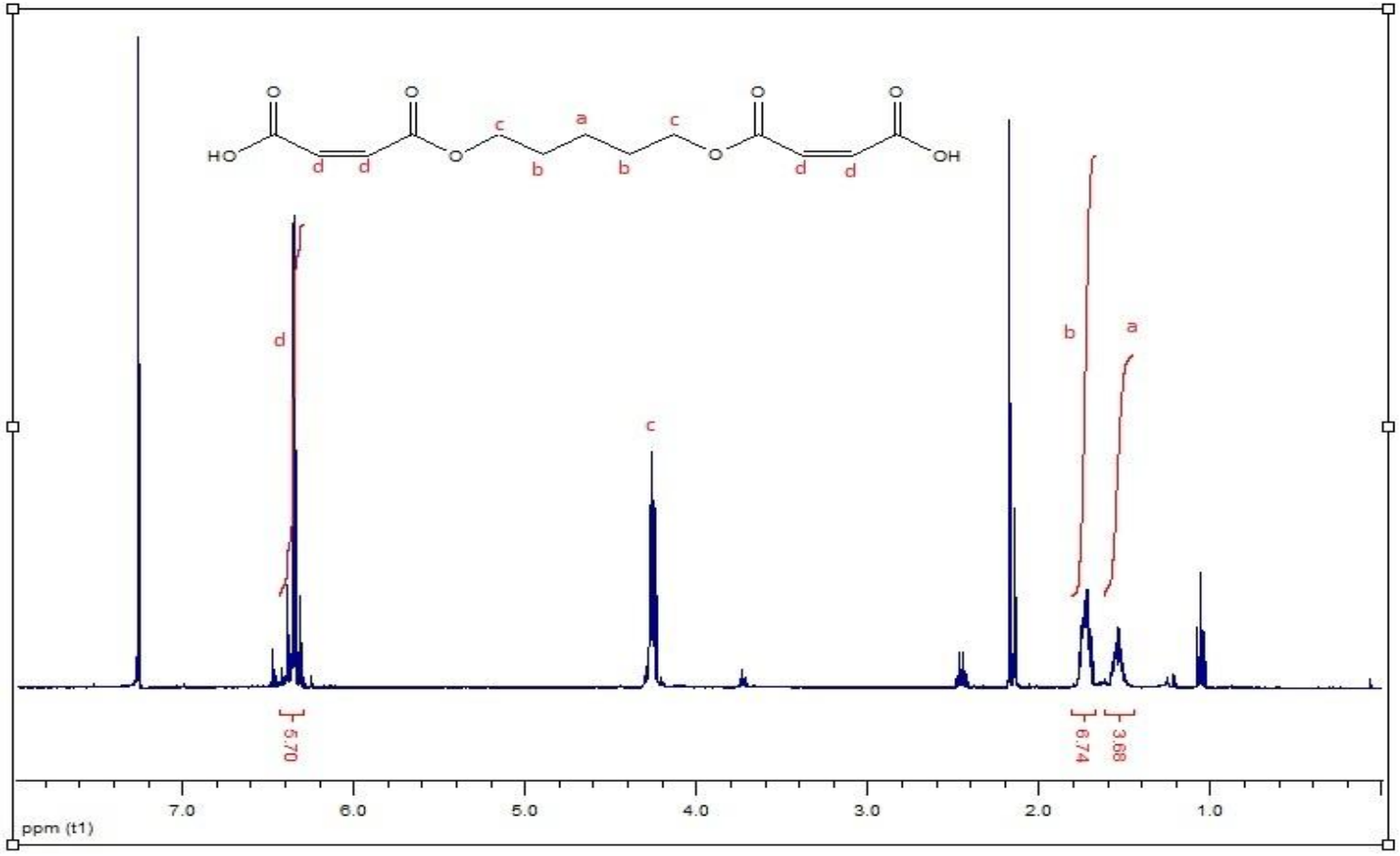

Figure 4.7. ^{1}H-NMR spectrum of Pentane Bis- Maleate (PBMA).

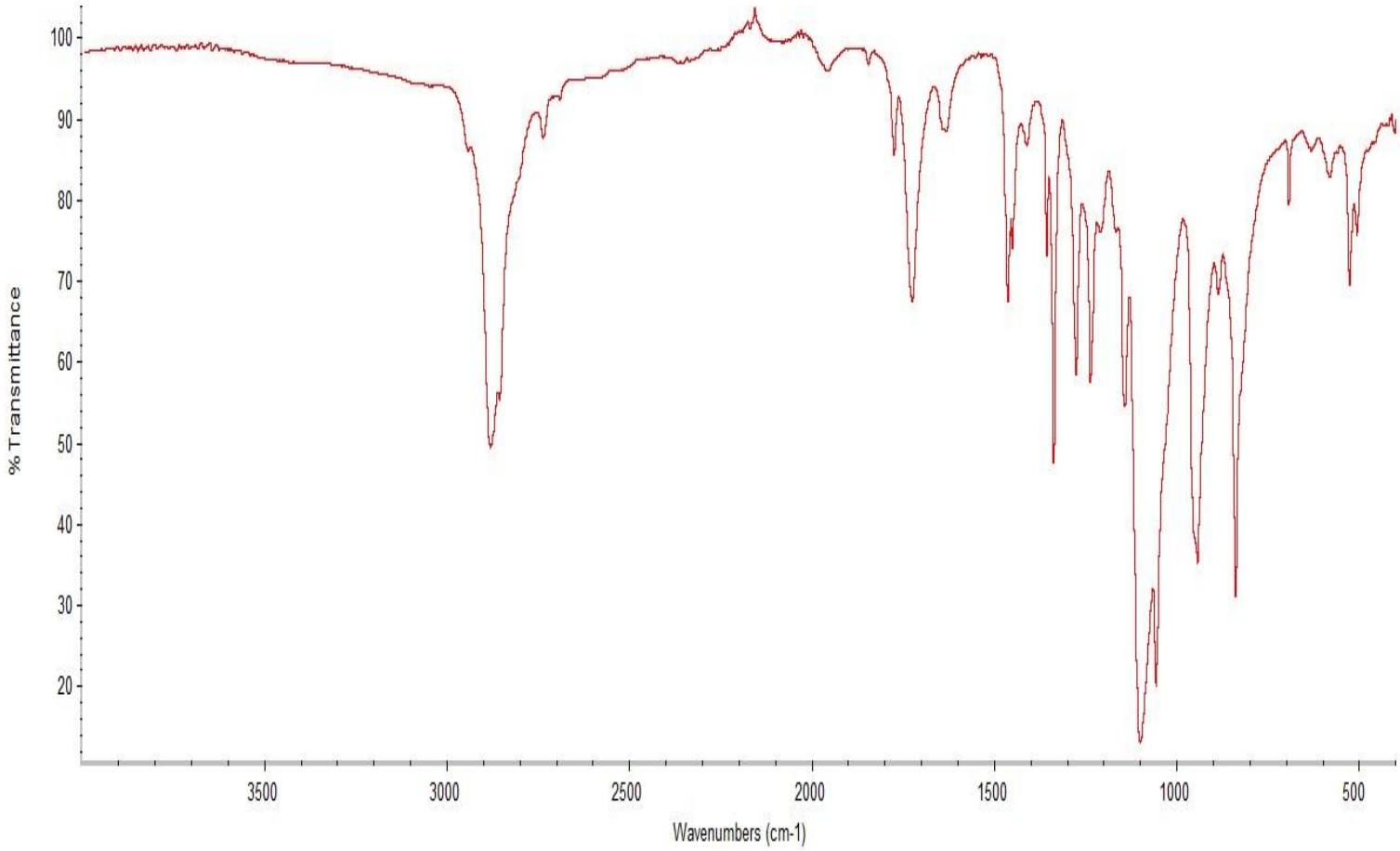

Figure 4.8. FT-IR spectrum of PEG (2000) Bis-Maleate (PEG-MA).

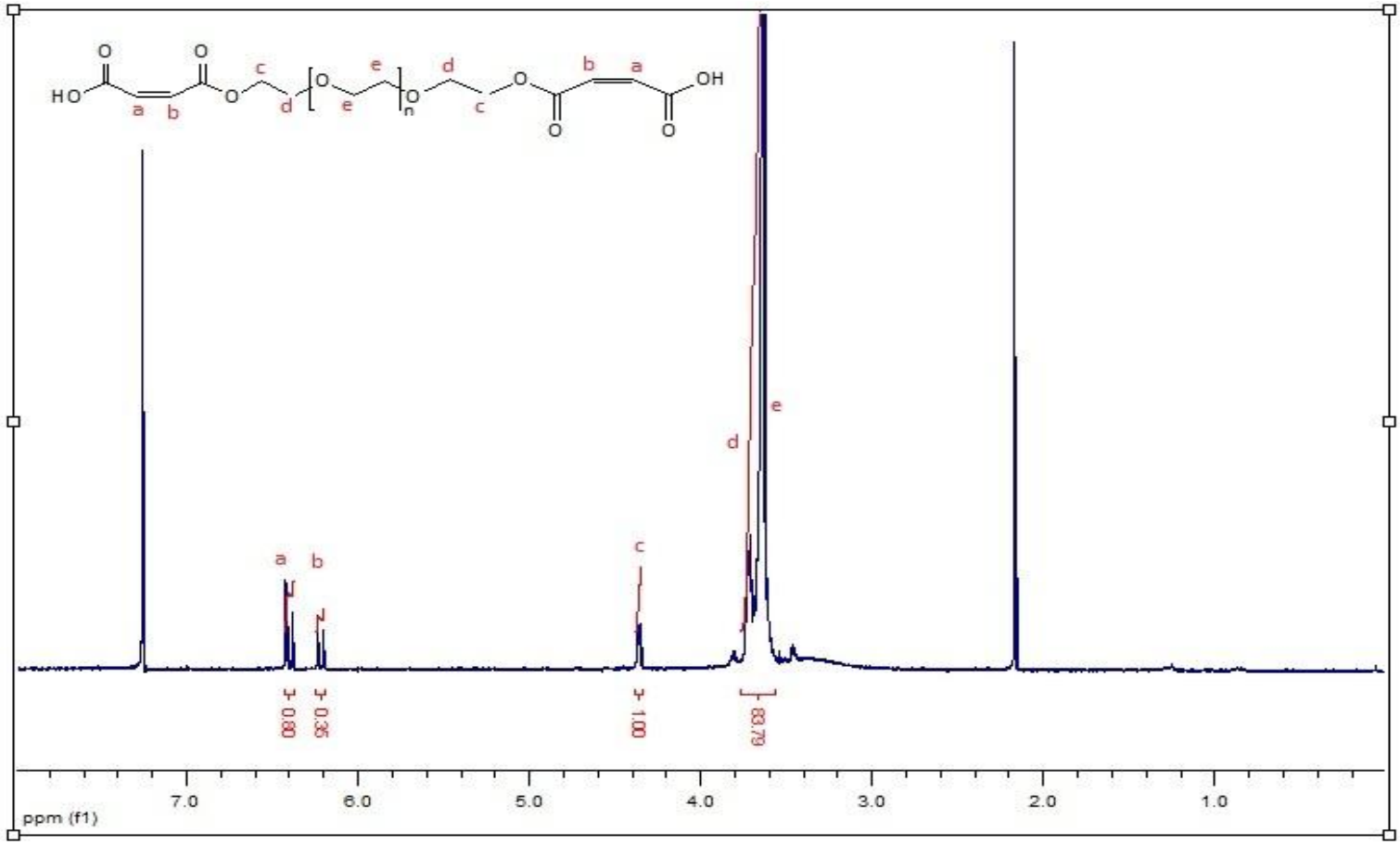

Figure 4.9. ^{1}H-NMR spectrum of PEG (2000) Bis-Maleate (PEG-MA).

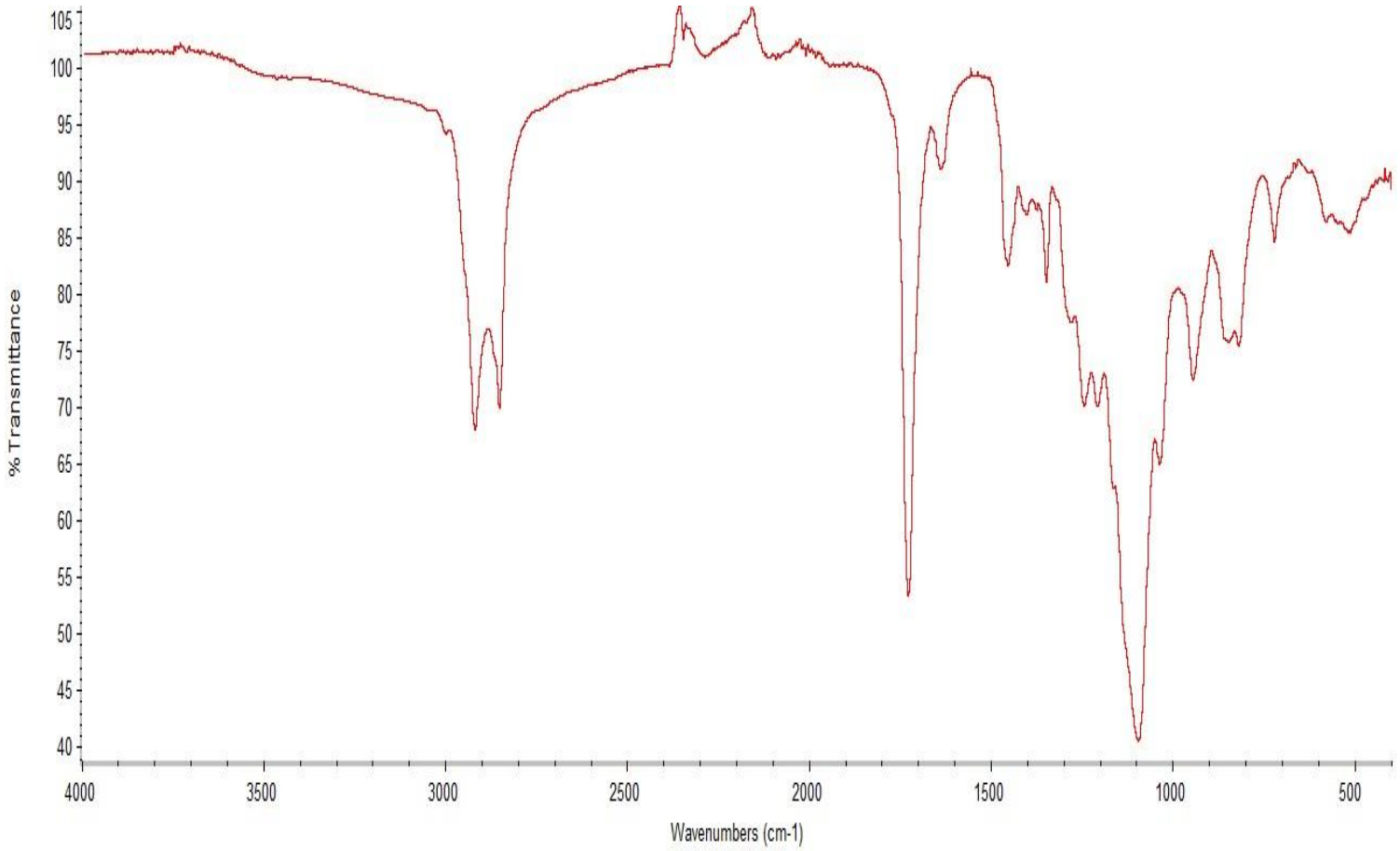

Figure 4.10. FT-IR spectrum of PEG (400) Mono Oleate Mono-Maleate (PEGMO-MA).

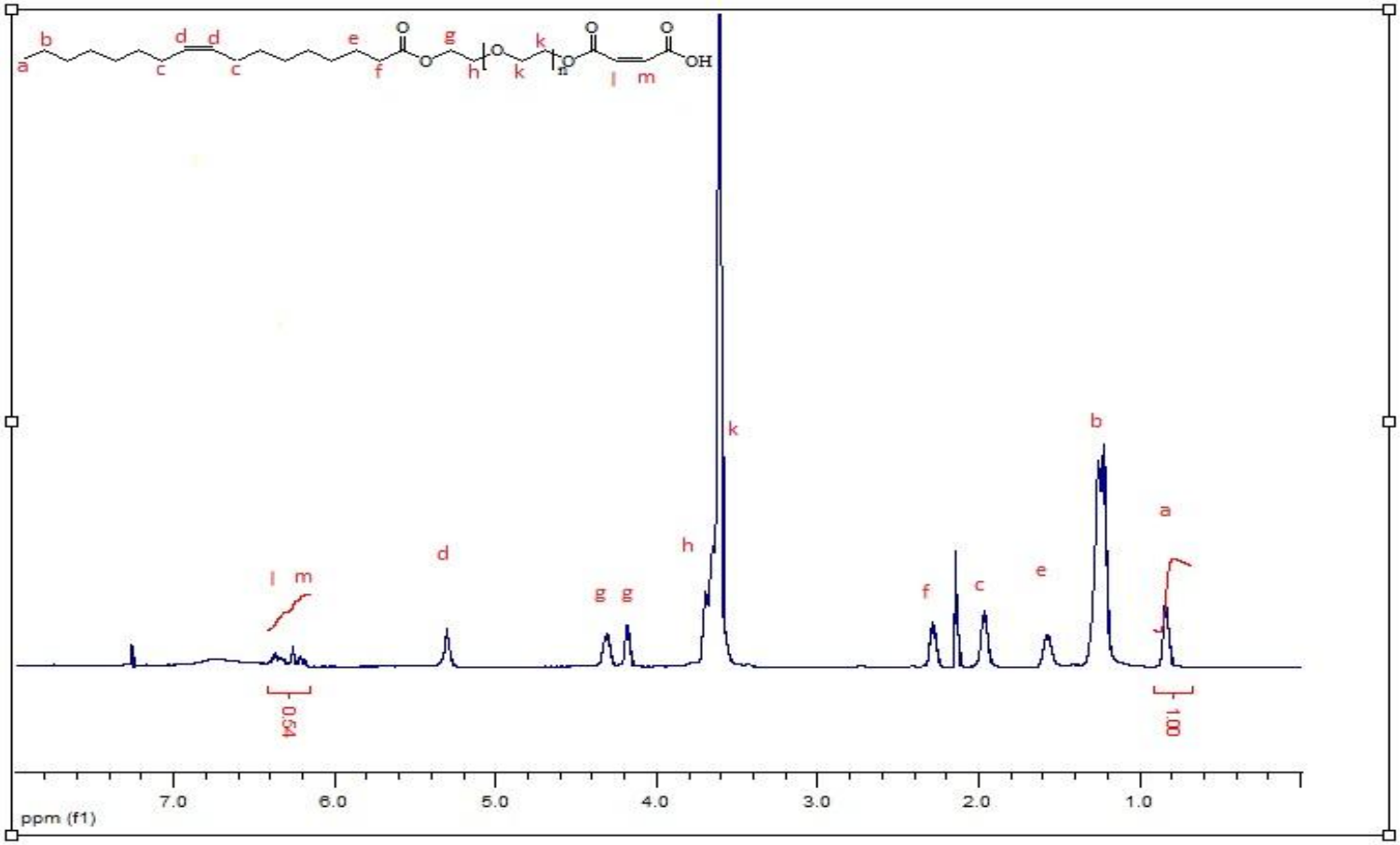

Figure 4.11. ^{1}H-NMR spectrum of PEG (400) Oleate-Maleate (PEGMO-MA.

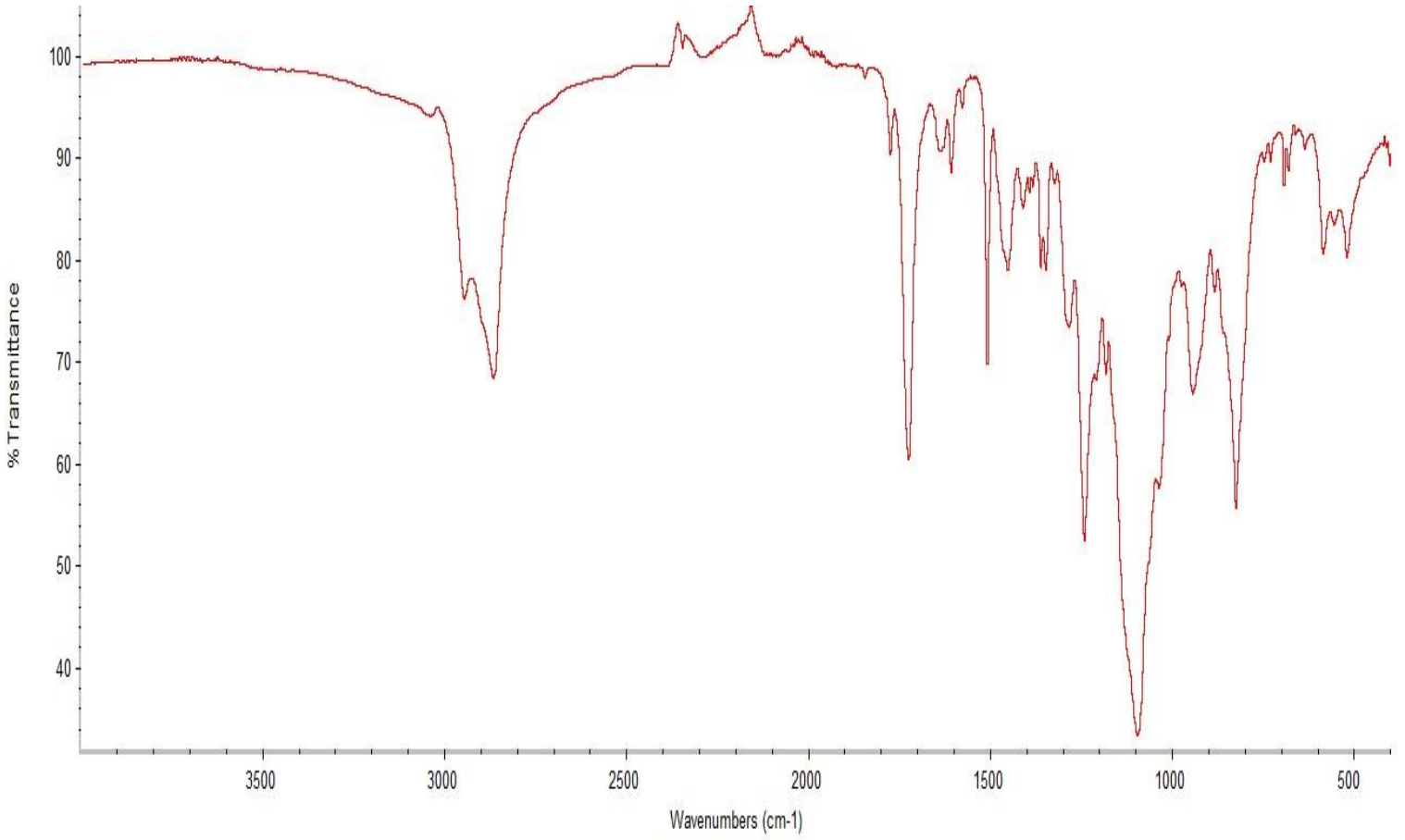

Figure 4.12. FT-IR spectrum of Octyl Phenol Ethoxylate Mono Maleate (OPE-MA).

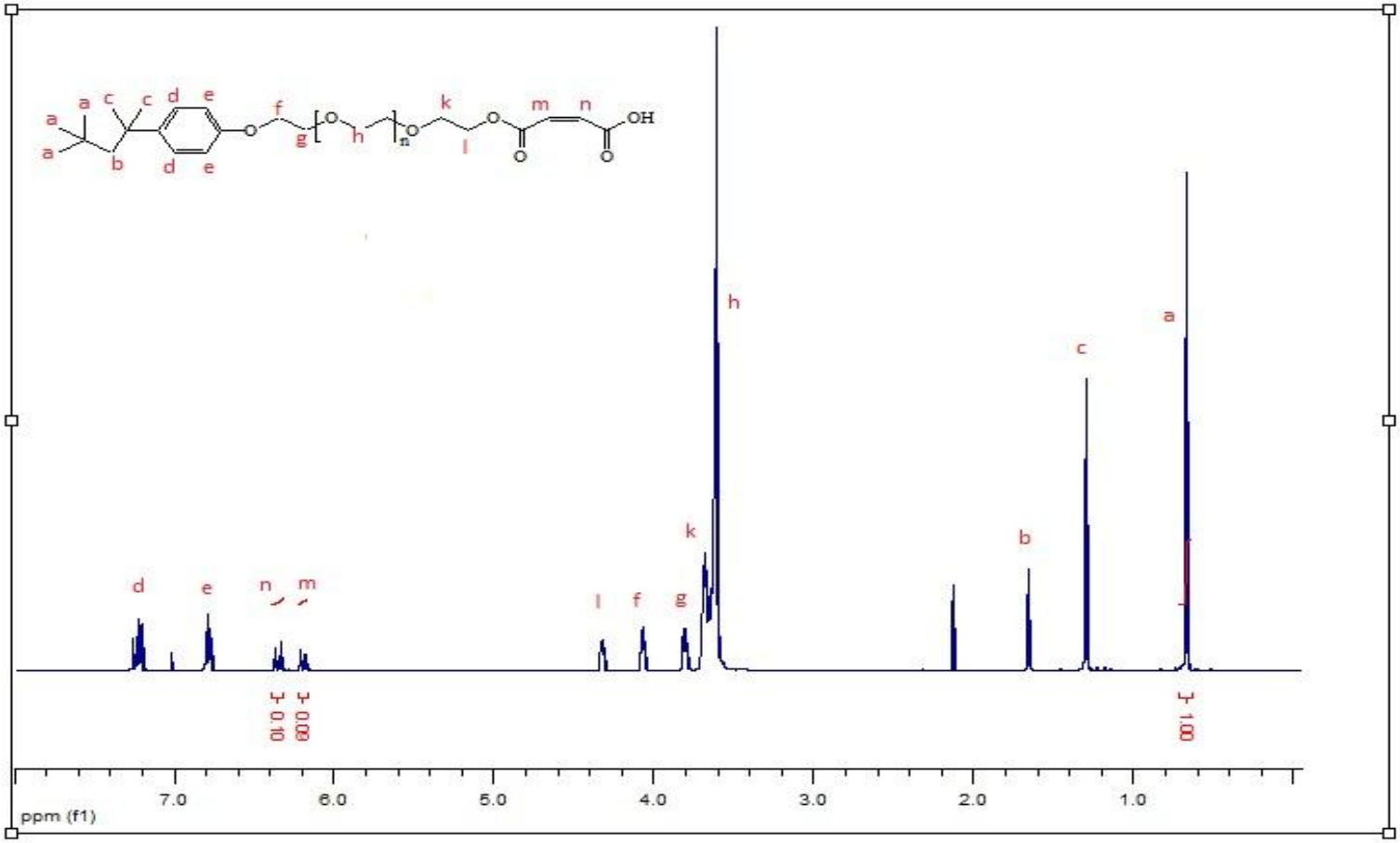

Figure 4.13. [1]H-NMR spectrum of Octyl Phenol Ethoxylate Mono Maleate (OPE-MA).

4.2. Synthesis and Structure Determination Soybean Oil Based LSE Additives

Epoxidized soybean oil (ESO) was obtained from Akdeniz Kimya San. ve Tic. A.Ş. The average functional oxirane ring per triglycerides of epoxidized soybean oil (ESO) used in this work is 4.2. This number was specified by manufacturer as the percent epoxy oxygen and was also determined by epoxy equivalent analysis experimentally. Thus this is the maximum number of functional groups that can be attached to one triglyceride. According to this oxirane number, the average molecular weight of ESO was calculated as 950 g/mol. During the reaction of epoxide groups with carboxylic acids, an intermediate alkoxide ion forms and this can react with another epoxy group (Figure 4.12). This may cause an increase in the molecular weight of ESO by ring opening polymerization. This is an important disadvantage as it results in the consumption of epoxide groups without intrucing carboxylic functional groups. The carboxylic acid reaction with terminal epoxides can be carried out at room temperature, but with internal epoxide groups, which are less reactive, room temperature is not enough. High temperature and catalyst are needed to obtain high yields in this case. The best synthetic method for the reaction of carboxylic functional monomers with ESO was using AMC-2 catalyst at around 90 C for 5 hour. Accelerator AMC-2 is commercial catalyst designed for the specific catalysis of the acid-epoxy reaction. There is no detailed information about the chemical composition, of AMC-2 which is a proprietary product.

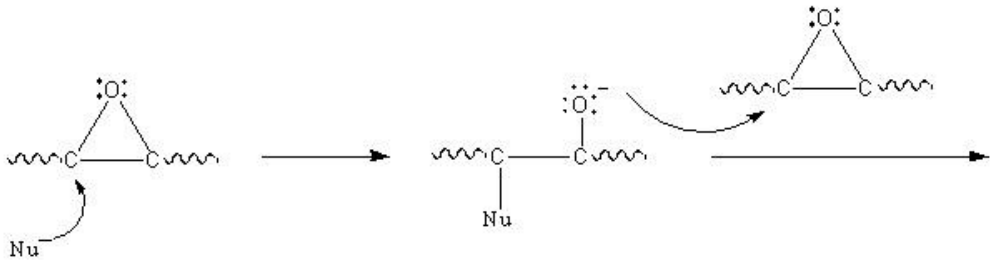

Figure 4.14. Ring opening homopolymerization of epoxide groups.

4.2.1. Epoxidized Soybean Oil- Mono Methyl Maleate (ESO-MMA)

In this reaction, mono methyl maleate (MMMA) was used to introduce unsaturation. The reaction of MMMA with ESO was previously done in our groups [36]. This method was followed, and the product was verified with FT-IR and 1H-NMR spectrums.

The average number of methyl maleate groups per triglycerides was calculated by the ratio of terminal methyl protons peak of fatty acids appearing at 0.8 ppm and vinyl proton peaks of maleate appearing at 6.5 ppm in the ^{1}H-NMR spectrum. According to this ratio, an average number of 2.5 methyl maleate groups per triglyceride were achieved. This represents a 60% conversion to the desired material. In this product, long alkyl chain of ESO was used as styrene barrier, maleate double bonds of molecule as used as adhesion promoter

4.2.2. Epoxidized Soybean Oil- Mono Stearyl Maleate (ESO-SMA)

In this reaction mono stearyl maleate (MSMA) was used to increase unsaturation. For the synthesis, ESO and MSMA were heated in the presence of AMC-2 catalyst at 90 ºC for 5 hour. At the end of reaction, the unreacted MSMA were removed by aqueous sodium bicarbonate solution. In FT-IR spectrum of the product the maleate double bond stretching peaks at 830 cm-1 obscured the epoxy peak at 835 cm-^{1}. So this peak could not used to follow reaction. The appearance of specific secondary alcohol peak at 3524 cm^{-1} was an important indicator for the ring opening epoxide. Conjugated carbon-carbon double bond stretching peak appeared at 1643 cm-1. Also, maleic acid peak at 1720 cm-1 disappeared and new ester peaks at 1728 cm-1 with stearyl ester peak and glycerol ester peak at 1735 cm-1 and 1745 cm-1 appeared. These indications proved the structure of the product. In order to follow this ring opening reaction, 1H-NMR spectrum were used. Maleate double bonds appeared at 6.3 ppm. CH3- protons of fatty acids and stearyl alcohol appeared at 0.8 ppm. According to this peak integration ratio, an average number of 2.8 stearyl maleate groups per triglyceride have been achieved. This represents a 67% conversion to the desired material. In this product, long alkyl chain of ESO and stearyl was used as styrene barrier, maleate double bonds of molecule as used as adhesion promoter. In

both ESO-MMA and ESO-SMA products the final molecule does not contain the polar carboxyl group. Thus barrier properties of these molecule reflects the absence of the carboxyl group.

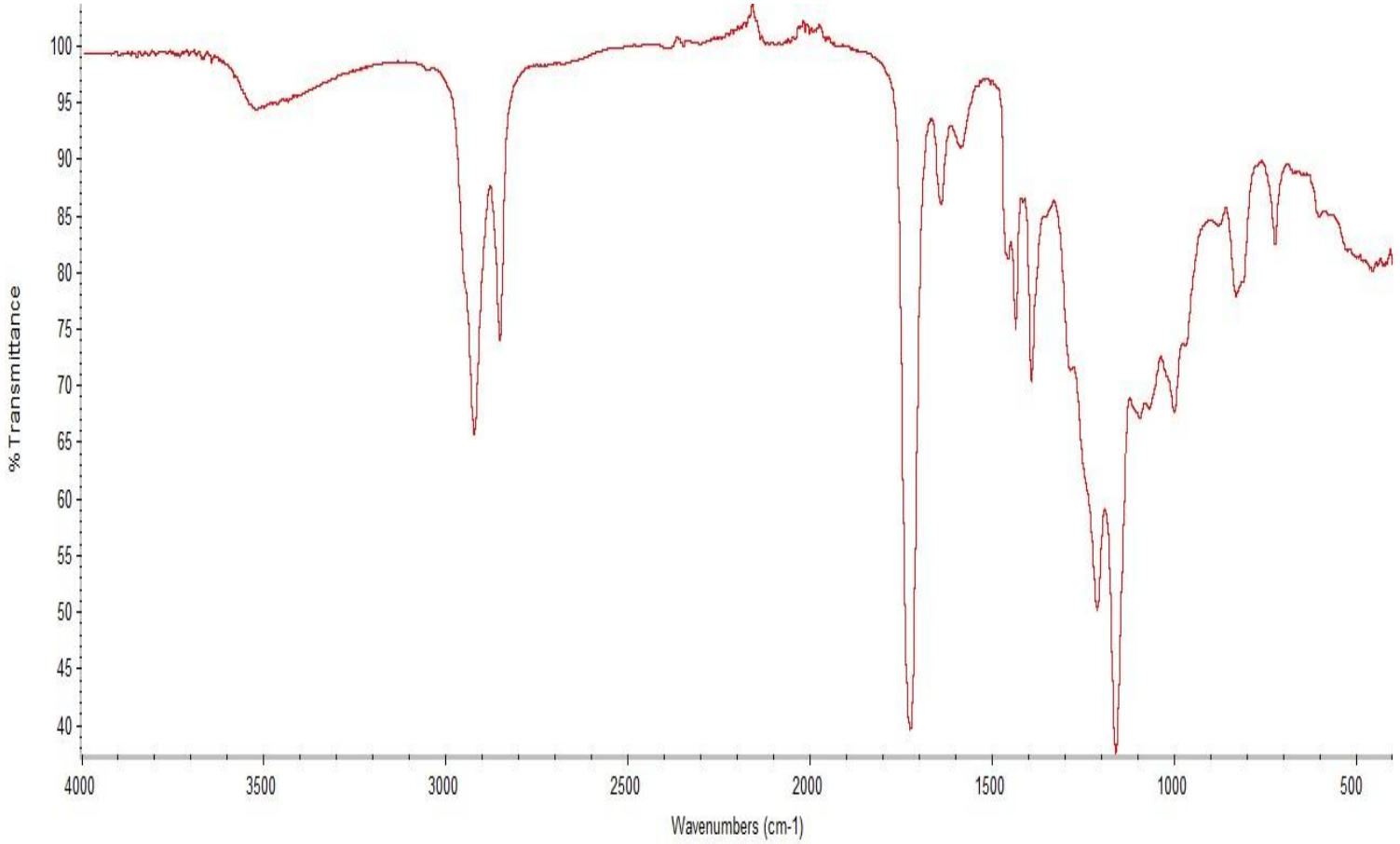

Figure 4.15. FT-IR spectrum of Epoxidized Soybean Oil- Mono Methyl Maleate (ESO-MMA**).**

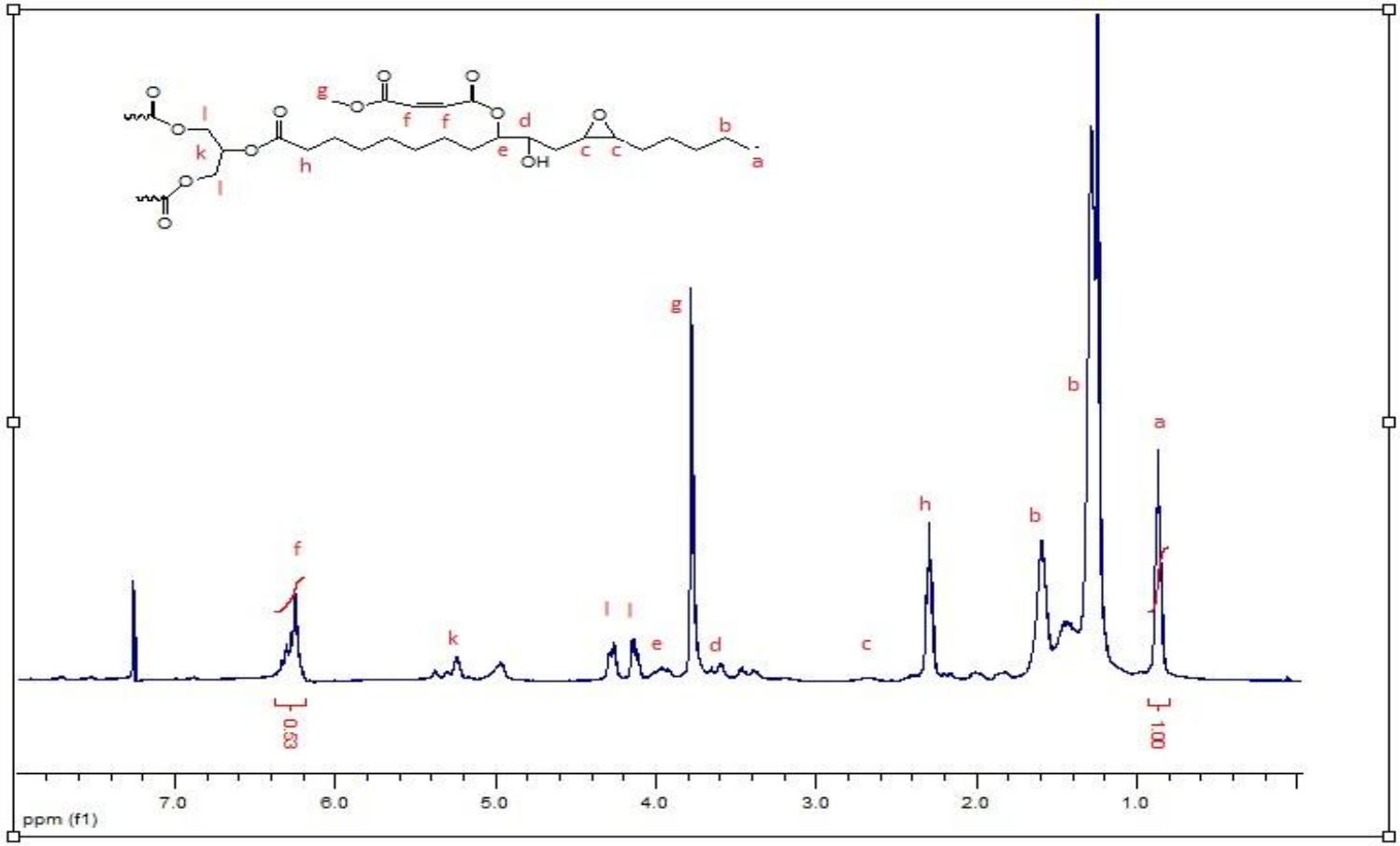

Figure 4.16. ^{1}H-NMR spectrum of Epoxidized Soybean Oil- Mono Methyl Maleate (ESO-MMA).

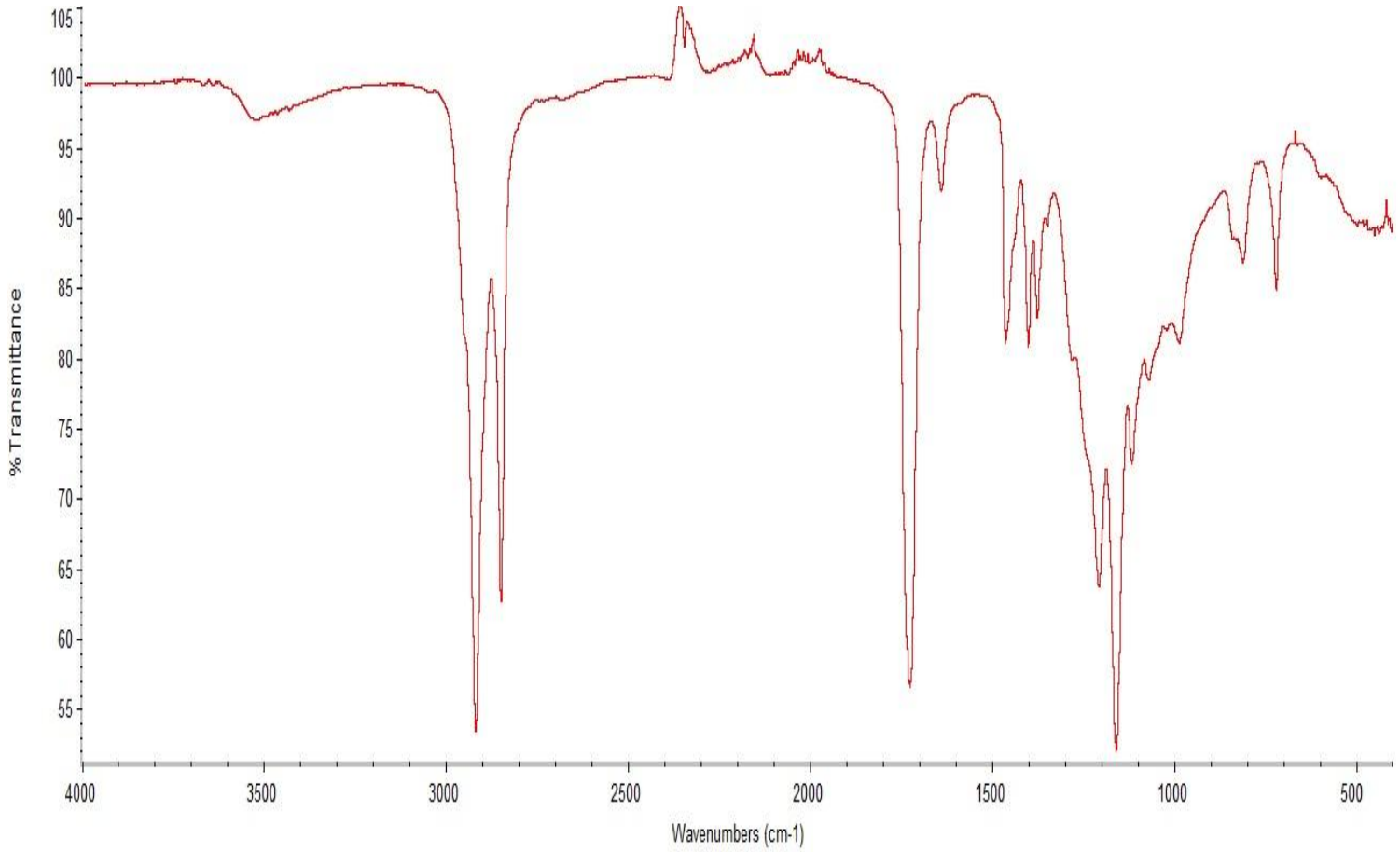

Figure 4.17. FT-IR spectrum of Epoxidized Soybean Oil- Mono Stearyl Maleate (ESO-MMSA).

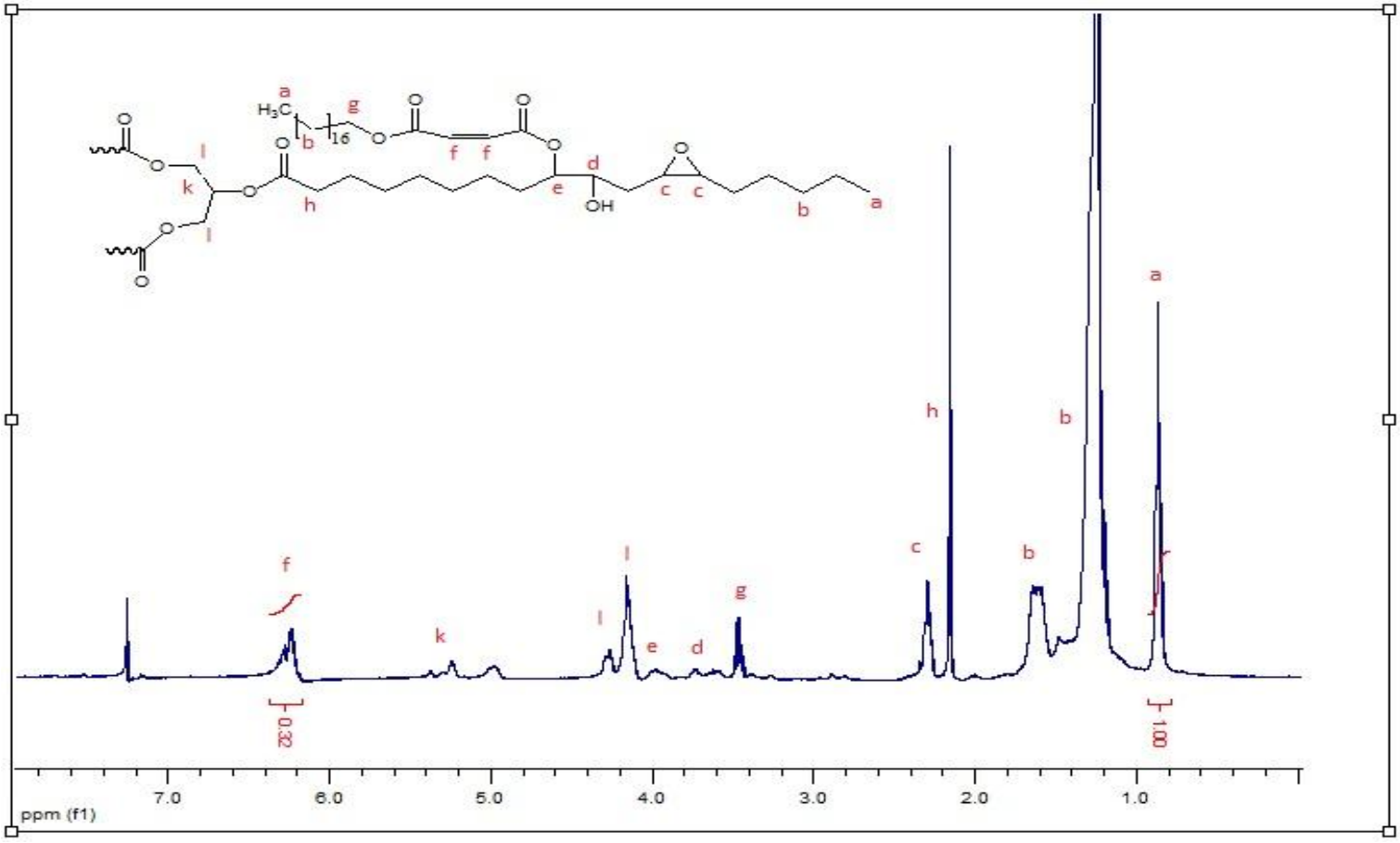

Figure 4.18. ^{1}H-NMR spectrum of Epoxidized Soybean Oil- Mono Stearyl Maleate (ESO-SMA).

4.2.3. Epoxidized Soybean Oil- Oleic Acid (ESO-OA)

A similar procedure was used for the synthesis of epoxidized soybean oil-oleic acid (ESO-OA). The end product was verified with FT-IR and 1H-NMR spectrum. In the FT-IR spectrum epoxy peak at 834 cm-1 disappeared and specific secondary alcohol peak appeared at 3520 cm-1. The new ester peaks were obscured with glycerol ester peaks at 1735 cm-1. These indicators were not enough to follow this reaction. 1H-NMR spectrum was used to calculate reaction yield. Double bonds of oleic acids appeared at 5.4 ppm and CH3- protons of of oleic acids and fatty acids appeared at 0.8 ppm. According to integration ratio of these peaks, an average number of 4 oleic acids groups per triglyceride have been achieved. This represents a 95% conversion to the desired material. In this product, long alkyl chains of ESO and oleic acids were used as styrene barrier, double bonds of oleic acids are used as adhesion promoter.

4.2.4. Acrylated Epoxidized Soybean Oil (AESO)

AESO was obtained from Sartomer Company, Inc. This product was characterized by using 1-H-NMR analysis. At the 1H-NMR spectrum (Figure 4.21) of AESO, methyl protons (CH3-) of the fatty acids appeared at 0.8 ppm, α to the carbonyl peaks (-CH2-CO-) appeared at 2.2 ppm, -CH2 protons of glycerol peaks appeared at 4.0-4.4 ppm and –CH=CH2 protons of acrylate ester appeared at 5.8,6.0 and 6.3 ppm. The functional acrylate groups were calculated with the integral ratio of methyl protons of fatty acids and –CH=CH2 protons of the acrylate ester. According to this ratio, there are on the average 3.4 acrylate functional groups per triglycerides.

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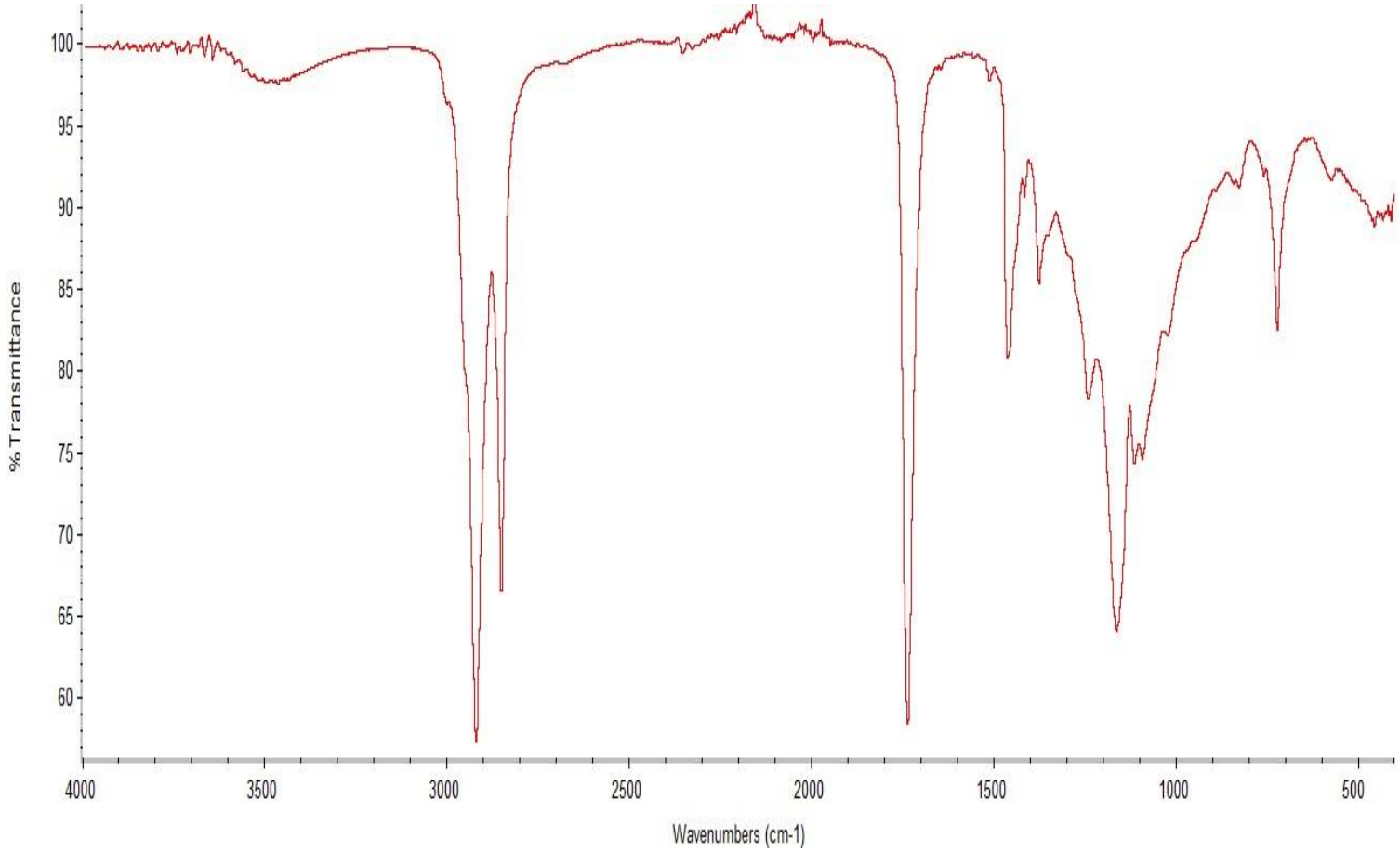

Figure 4.19. FT-IR spectrum of Epoxidized Soybean Oil- Oleic Acid (ESO- OA).

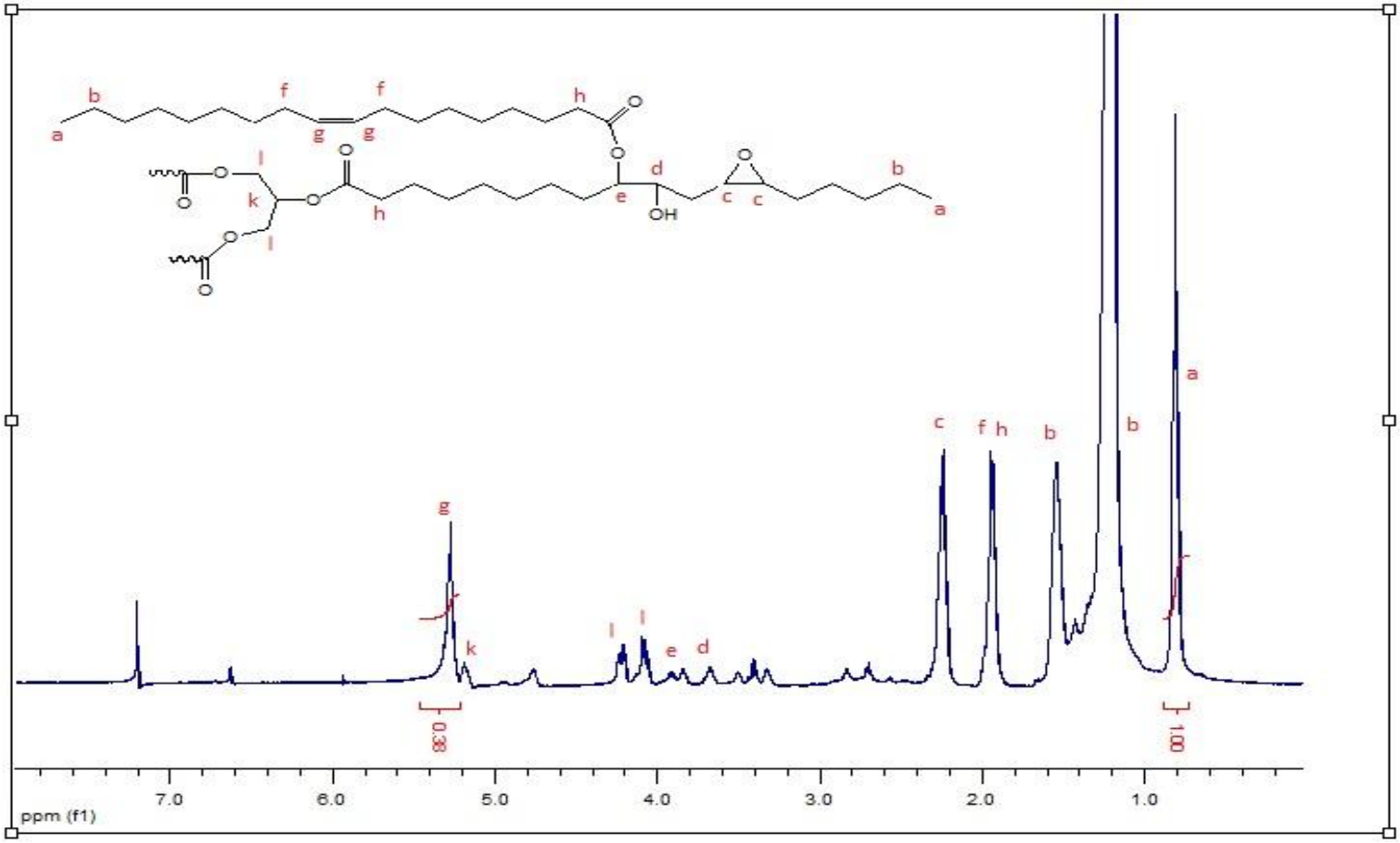

Figure 4.20. ^{1}H-NMR spectrum of Epoxidized Soybean Oil- Oleic Acid (ESO- OA).

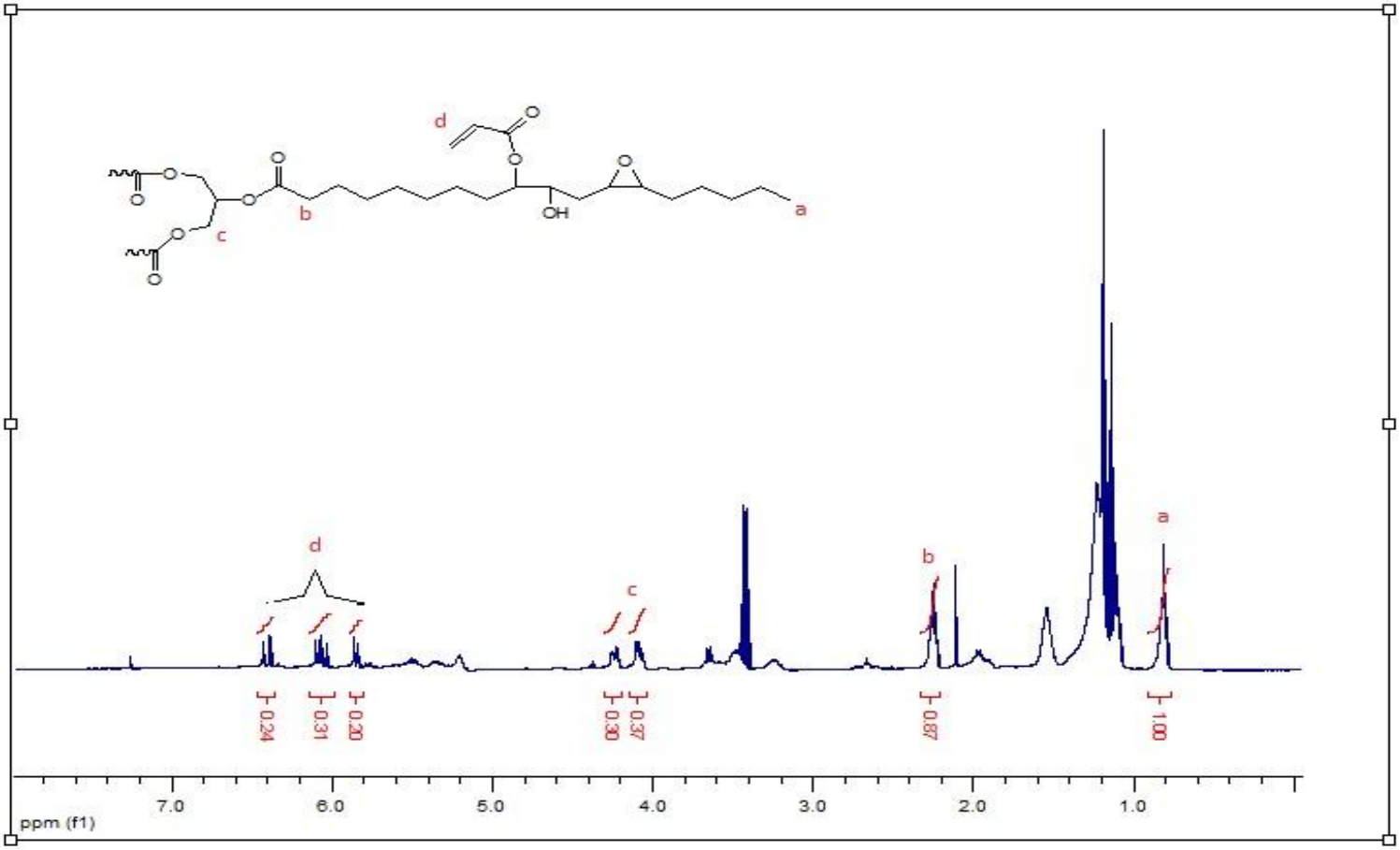

Figure 4.21. ^{1}H-NMR spectrum of Acrylated Epoxidized Soybean Oil (AESO).

4.3. Physical Properties of LSE Additives

Different types of LSE additives were synthesized. They have a saturated long alkyl chain coming to surface to decrease the styrene emission by forming a surface film and saturated moiety providing reactivity for cross-linking between laminates. To examine industrial usefulness of the additives, synthesized styrene emission test and interlaminar adhesion test were applied according to AS/NZS 4585.1 and AS/NZS 4585.2 test procedures. With the help of these tests results, the additives synthesized will be evaluated and compared with blank and commercial additives.

4.3.1. Styrene Emission Test

The styrene emission of each sample was measured by catalyzing 30 grams of the resin and additive, %1 w/w based on polyester, blend with 1 % Methyl Ethyl Ketone (MEK) and 0.25% Cobalt naptanate solution. 30 gr. of catalyzed blend resin was poured into the Petri-dish with a diameter of 10 cm.24 hour after gelation. The petri dish was placed in a hood, away from drafts, and kept at room temperature. Each Petri-dish was reweighed, and the styrene loss in gr./m^2 24 hours after gelations was calculated. The aim of this test is to calculate styrene emission (g/m^2) and compare the synthesized additives with commercial additives and neat UPE resin mixtures. The test results are shown at Figure 4.22.

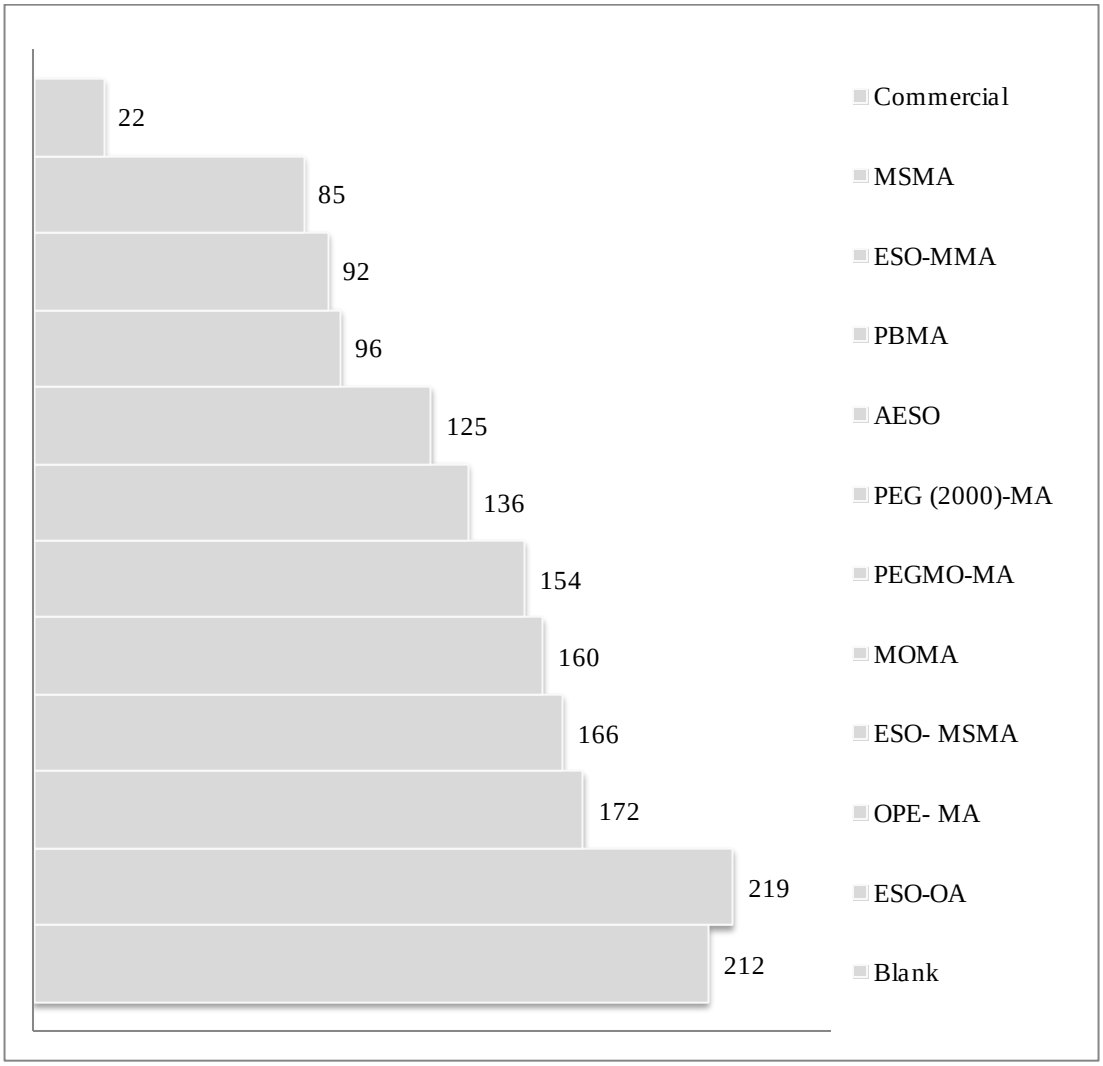

Figure 4.22. Styrene emission test (g/m^2) results.

In this test, it is important to have very accurate dosing of the initiators and accelerator as the rate of the reaction depends on their concentration. The rate of the reaction, which is exothermic by 37 kcal/mole of double bond, determines the temperature reached by the sample and this in turn determines the rate of evaporation of styrene. The air draft over the sample surface also needs to be monitored as styrene evaporation also depends on this factor.

Oxygen is an inhibitor for bulk free radical polymerization. This fact manifests itself as formation of a tacky surface with incomplete polymerization on the final product. The rate of polymerization of a sample in contact with air is also lower. With an LSE additive the surface barrier also presents contact with oxygen and the formation of tacky

surface is not observed and polymerization is faster. Hence there is the dilemma that the LSE additive with better barrier properties also leads to higher temperature during cure. The first effect reduces styrene emission but the second effects increase it.

According to the test results, ESO-OA disrupted the UPE-styrene solubility and produced a styrene layer on the surface. Therefore styrene emission of ESO-OA is higher than the blank. The LSE additive molecules in the present work have different chemical structures, so the styrene emission results cannot be correlated with a relevant chemical structure. There are many patents about additives with PEG derivatives. However the additives synthesized with PEG derivatives did not give good emission results at all. During the application of MOMA, it dissolved in the UPE resin. The alkyl chain of MOMA was not enough to decrease solubility of the product. If it was compared with PBMA, the alkyl chain percentage of MOMA is higher than PBMA. However MOMA contained branched alkyl chain, PBMA contained linear alkyl chain. Thus, the branched structure of MOMA increases solubility. Also the linear alkyl chain effects were shown in the MSMA styrene emission results. MSMA contains stearyl alcohol (C18), the solubility of stearyl alcohol is lower than the 1,5-pentane diol and octyl alcohol in UPE. Because of the alkyl chain linearity, MSMA and PBMA gave better results than the other linear products. In the ESO derivatives, ESO-MMA gave a better result than the others because it has lower molecular weight and lower linearity percentage than the others. ESO-MMA had similar chemical structure with AESO. Polar groups of ESO-MMA were higher than the AESO. This property increases the rate at which the molecules come to the surface. Commercial additive gave the best result. The three best LSE additives synthesized in this work were MSMA, ESO-MMA and PBMA.

4.3.2. Interlaminar Adhesion Test

The laminates prepared were split apart by attaching the two layers to the upper and lower jaws of a tensile testing machine. The force required to split the laminates was then measured in N. The actual delamination force was obtained by interpolating the horizontal region of the trace as this corresponds to the quasi equilibrium delamination force and should in principle be independent of delamination rate. Delaminations of laminate

occurred in a random fashion so the applied force fluctuated. Using too much initiator than recommended and contamination of surface by dust effects the fluctuations.

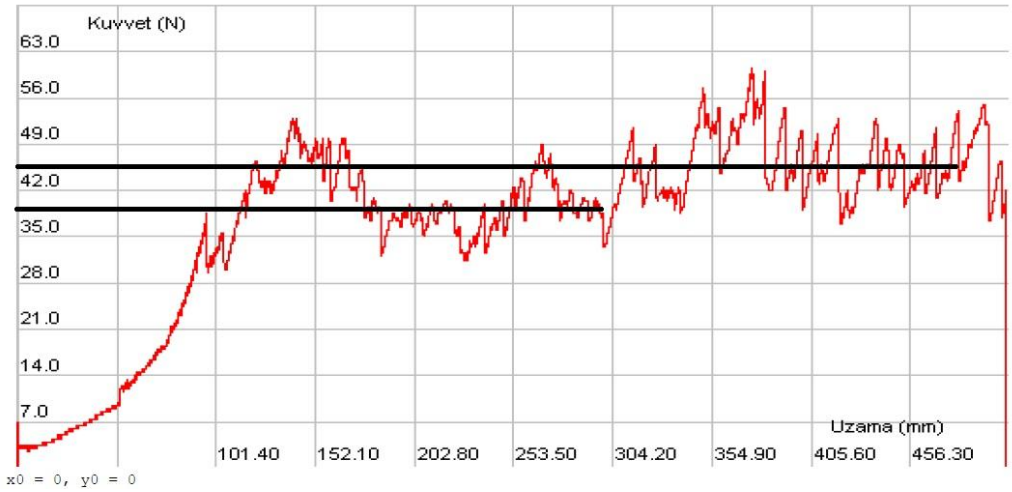

Figure 4.23. Interlaminar adhesion test of blank sample.

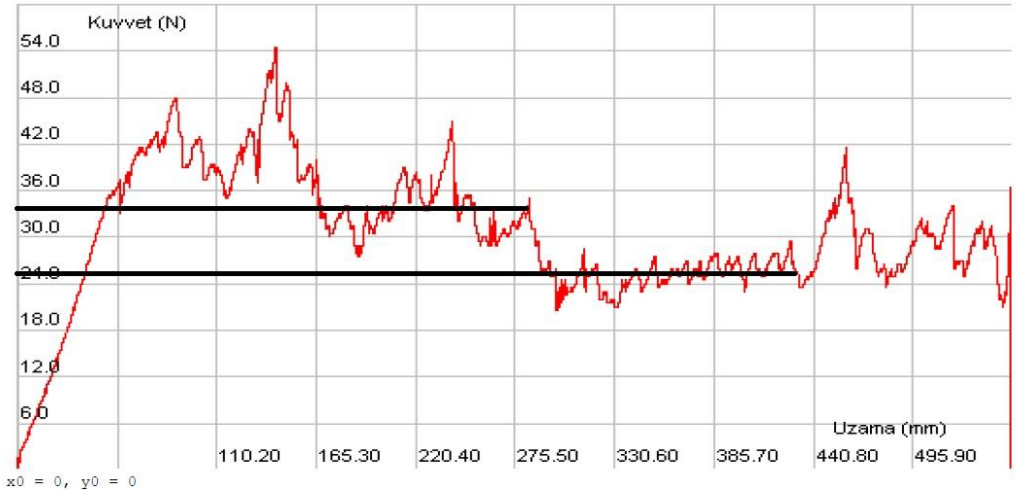

Figure 4.24. Interlaminar adhesion test of PBMA sample.

Figure 4.25. Interlaminar adhesion test of MSMA sample.

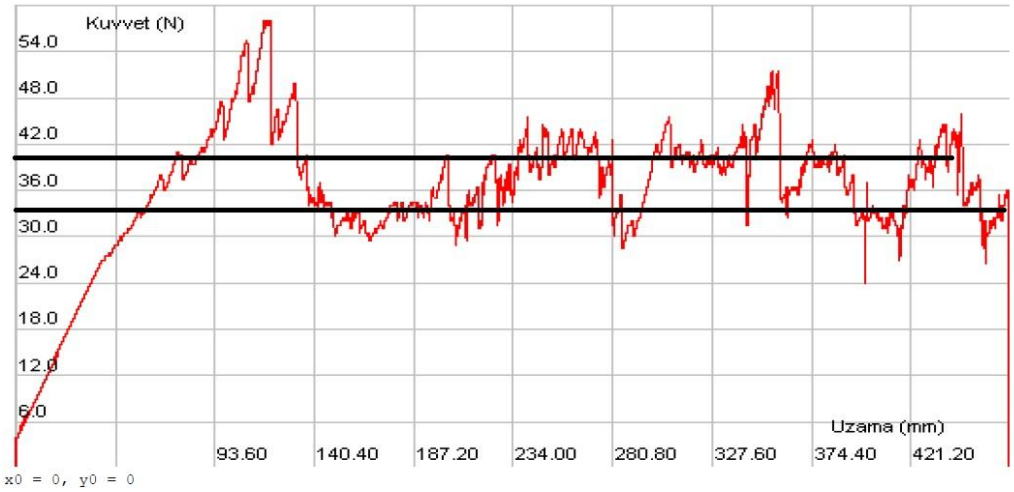

Figure 4.26. Interlaminar adhesion test of ESO-MMA sample.

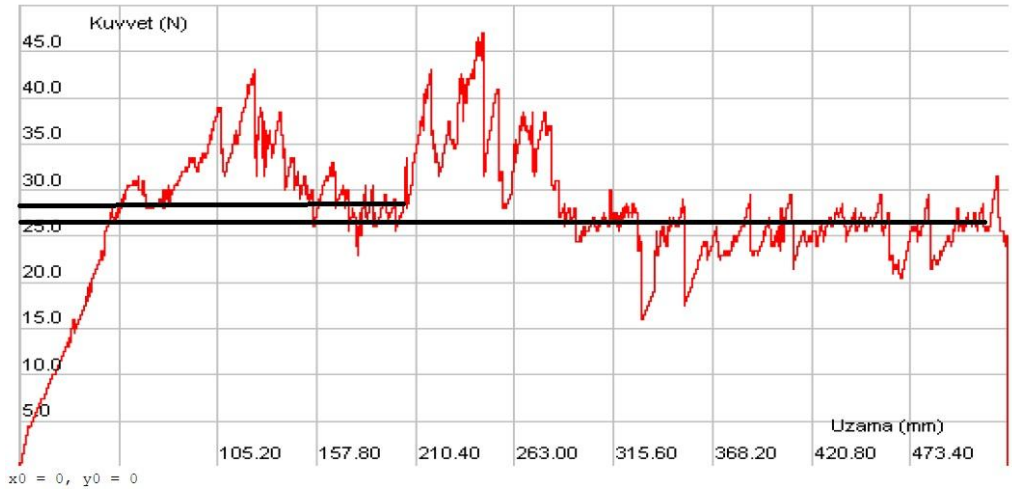

Figure 4.27. Interlaminar adhesion test of commercial sample.

Table 4.1. Total interlaminar adhesion test results (N).

	Interlaminar Adhesion Test Results (N)
Blank	42
MSMA	40
ESO-MMA	37
PBMA	28
Commercial	27

To determine the coherent results, interpolation lines are drawn from the fluctuating maxima and minima points. Averaging these results is shown at Table 4.1. ESO-MMA and MSMA results were close to the blank result. Number of moles of reactive double bonds per unit weight is highest in PBMA. However interlaminar adhesion results did not corralate with the mole fraction of reactive double bonds. Commercial additive gave best styrene emission results but it reduced the interlaminar adhesion seriously. Paraffin wax forms a thin layer on the resin surface. This film reduces the styrene emission, but it reduces the interlaminar adhesion between the plies. The commercial additive results have

big similarities with paraffin wax results. As the commercial additive is a proprietary product, its structure is not known but its behavior is very similar to paraffin wax.

By the application of styrene emission test and interlaminar adhesion test, two independent results were obtained. According to these results, comparison of LSE additives at one point could not be possible. To compare these additives, specific parameter factor S (LSE additive success parameter) was created by us. An increase in interlaminar adhesion force is advantageous, and an increase in styrene emission disadvantageous for additives. By the help of this comment, the function of S was defined as.

$$S = \frac{\text{Interlaminar Adhesion Force (N)}}{\text{g./ m}^2\text{ Styrene Emission}} \qquad (4.1)$$

According to this calculation, commercial sample gave six times better results than blank, three times better results than the best synthesized additive (MSMA). The synthesized MSMA gave 2.5 times better results than the blank.

Table 4.2. S Factors for the LSE additives.

	LSE Additive Success Parameters (N m^2/g.)
Blank	0.20
MSMA	0.47
ESO-MMA	0.40
PBMA	0.29
Commercial	1.22

5. CONCLUSIONS

The low styrene emission (LSE) additives were synthesized by using maleic anhydride and different types of molecules containing alkyl chains. The characterization of these additives was done by 1H-NMR and FT-IR spectroscopy. The additives synthesized were used without any further purification.

Styrene barrier properties and secondary bonding properties of LSE additives were studied with UPE resin and glass fiber mat. Additives were used 1% (w/w) of total UPE resin. These additives were compared with neat UPE resin and commercially available LSE additives.

In these additives, MSMA, ESO-MMA and PBMA gave better styrene emission suppression than the other compounds synthesized. However, commercial additive gave the best result for the emission of styrene. These three additives and commercial additive were tested for the interlaminar adhesion. According to this test results, blank without an additive gives best adhesion results. Among the additives synthesized MSMA and ESO-MMA gave results were very close to the blank results. Commercial additive gave best styrene emission results but it decreased the interlaminar adhesion seriously. MSMA and ESO-MMA decrease the styrene emission to half the value of a blank sample with no appreciable loss in interlaminar adhesion. These two compounds are very good candidates for commercialization both in terms of performance and in terms of ease of synthesis.

As a future project, the mixture of these additives with very small amounts of paraffin should be tested. By the help of paraffin, the emission of styrene can be decreased even further.

REFERENCES

1. *Polyester*, 2011, http://en.wikipedia.org/wiki/Polyester, accessed at February 2011.

2. Gastine, C. F. J., O. Laguna and J. C. Salamone (Ed.), "Unsaturated Polyester Resins (Polyester Composites)", *Polymeric Materials Encyclopedia*, CRC Press, Florida, Vol.11, pp. 8476-8486, 1996.

3. Gündüz, G. and J. C. Salamone (Ed.), "Unsaturated Polyester Resins (Overview)", *Polymeric Materials Encyclopedia*, CRC Press, Florida, Vol:11, pp. 8468-8476, 1996.

4. Strong, A. B., *Fundamentals of Composites Manufacturing: Materials, Methods, and Applications*, SME Publication, Michigan, 2007.

5. Yamashita, H. and Y. Nakano, *Polyester: Properties, Preparation and Applications*, Nova Science Publication., New York, 2008.

6. Sultan, B. A. and J. C. Salamone (Ed.), "Cross linking", *Polymeric Materials Encyclopedia*, CRC Press, Florida, Vol.1, pp. 316-320, 1999.

7. Scheirs, J. and T. E. Long, "Modern Polyesters: Chemistry and Technology of Polyesters and Co-polyesters", Wiley, London, 2003.

8. Chen, S. S. and A. Seidel (Ed.), "Styrene", *Kirk-Othmer Encyclopedia of Chemical Technology*, Wiley, New York, Vol. 23, pp. 325-358, 2006.

9. James, D.H., W. M. Castor, B. Elvers, S. Hawkins and W. Russey (Ed.) "Styrene", *Ullmann's Encyclopedia of Industrial Chemistry*, 5th rev. Ed., VCH Publishers, New York, Vol. A25, pp. 329–344, 1994.

10. "Air Quality Guidelines for Europe", World Health Organization Regional Publication, 2. Ed., Copenhagen, pp. 106-109, 2000.

11. La Scala J. J., E. J. Robinette, G. R. Palmese, J. M. Sands, J. A. Orlicki and M. S. Bratcher, "Successful Initial Development of Styrene Substitutes and Suppressants for Vinyl Ester Resin Formulations", ARL-TR-3023; U.S. Army Research Laboratory: Aberdeen Proving Ground, MD, 2003.

12. *Environmental Health Critaria No.26 Styrene*, 1983, http://www.inchem.org/documents/ehc/ehc/ehc26.htm, accessed at March 2010.

13. "IARC Morphology on the Evaluation of Carcinogenic Risk to Humans", *IARC International Agency for Research on Cancer Some Industrial Chemicals*, 1994, Vol. 60 pp. 233-320.

14. *Material Safety Data Sheet Styrene Monomer*, 2010, http://www.clpchem.com/msds/styrene%20msds.pdf, accessed at March 2010.

15. "Controlled Spraying handbook Composites Open Molding Resin & Gel Coat Application Version 3.2c", *American Composites Manufacturers Association, Arlington*, 2004.

16. Lacovara, R., L. Craigie, T. Corwey, P. Wykowski and G. Webster, "Composites Fabricators Association Open Molding Styrene Emission Test Project. Gel Coat/ Spray up Optimization Study, Final Report" *Composite Fabricators Association*, Mclean, VA, USA, 1996.

17. Kalliokoski, P., R. Niemela, A. Saamanen and P. Pfaffli, "Styrene Emission as Design Paramater for Ventilation in the Reinforced Plastic Industry, Ventilation", *4th International Symposium on Ventilation for Contaminant Control*, Vol.18, pp. 207-210, 1994.

18. *Composite Process*, 2005, http://www.compositesone.com/process.php, accessed at March 2011.

19. Skrifvars, M., *Development of Unsaturated Polyester Resins,* Ph.D. Thesis, University of Helsinki, 1995.

20. Skrifvars, M., M. Johansen, T. Blomqvist and K. Keinanen, "Low Styrene Emission Unsaturated Polyester Resins", *Composites,* No. 3, pp. 42-45, 1992.

21. Skrifvars, M., L. Berglund and M. Ericson, "Microscopy of the Morphology in Low Styrene Emission Glass Fiber/Unsaturated Polyester Laminates", *Journal of Applied Polymer Science,* Vol.71, pp. 1555-1562, 1999.

22. Datso, E., "The Practical Use of Styrene Suppressants and Testing with the CFA's Vapour Suppressant Effectiveness Test Protocol", *Composites Fabrication,* pp. 28-36, 2000.

22. Eren, T., *Synthesis Of New Polymers From Plant Oil Triglycerides*, Ph.D. Thesis, Boğaziçi University, 2004.

23. Cantwell, W. J., J. Morton, "The Impact Resistance of Composite Materials a Review", *Composites*, Vol. 22, No. 5, pp. 347–362, 1991.

24. Perrot, Y., P. Davies, A. Kerboul, C. Baley. "Marine Composites Based on Low Styrene Content Resins. Influence of Lamination Procedure and Peel Plies on Interlaminar Resistance", *Applied Composite Materials*, Vol. 15, No. 2, pp. 87-97, 2008.

25. Skrifvars, M., *Synthetic Modification and Characterization of Unsaturated Polyesters*, M. S. Thesis, University of Helsinki, 2000.

26. Takada, M., H. Uhara, T. Sato, "Process for Catllytic Vapour Phase Oxidation", U. S. Patent 4,203,906, 1978.

27. Eren, T., *Polymerization of Maleic Modified Soybean Oil With Diols and Polyols*, M. Sc. Thesis, Boğaziçi University, 1998.

28. Flett, L. H. and W. H. Gardner, "Maleic Anhydride Derivatives", John Wiley & Sons Publication, New York, 1952.

29. Fethouse, T.R., J. C Burnet, B. Horrel, M. J. Mummey and Y. J. Kuo, *Maleic Anhydride, Maleic Acid, Fumaric Acid*, Kirk Publication, Texas, 2001.

30. Liu, K., "Soybeans Chemistry Thecnology and Utilization", Aspen Publication, New York, 1997.

31. Smith, A.K., S. J. Circle, "Soybeans: Chemistry and Technology", Avi Publication, Colorado, 1972.

32. Çaylı, G., *Functionalization and Polymerization of Plant Oil Triglycerides*, Ph.D. Thesis, Boğaziçi University, 2008.

33. Wypych, J., "Polyvinyl Chloride Stabilization", Elsevier, Amsterdam, 1986.

34. Çolak, S., *Synthesis and Interfacial Properties of Organosilane Derivative of Acrylated Soybean Oil*, M. S. Thesis, Boğaziçi University, 2006.

35. Barra, G. M. O., J. S. Crespo, J. R. Bertolino, V. Soldi, A. T. N. Pires, "Maleic Anhydride Grafting on EPDM: Qualitative and Quantitative Determination", *Journal of Brazilian Chemical Society*, Vol. 10, No.1, pp. 31-34, 1999.

36. Esen, H., S. H. Küsefoğlu and R. Wool, "Photolytic and Free-Radical Polymerization of Monomethyl Maleate Esters of Epoxidized Plant Oil Triglycerides", *Journal of Applied Polymer Science*, Vol. 103, pp. 626-633, 2007.