SYNTHESIS AND POLYMERIZATION OF EPOXIDIZED SOYBEAN OIL - DIAMINO SILANE ADDUCTS

by

Melissa Akdemir

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To My Family

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ABSTRACT

SYNTHESIS AND POLYMERIZATION OF EPOXIDIZED SOYBEAN OIL - DIAMINO SILANE ADDUCTS

In this study, Epoxidized Soybean oil is reacted with a diamino-functional silane, N-2-aminoethyl-3-Aminopropyltrimethoxysilane, through ring opening of the epoxide. This was done in three different stoichiometry where tertiary amine:epoxide ratios were 0.5, 0.7 and 1.0. The adducts were characterized by NMR and IR spectroscopy. Resulting adducts were then moisture cured on a glass surface at room temperature, and were polymerized via self-condensation at room temperature. All the samples were post-cured at 150˚C for 1hour. Cured products, both on glass surface and the self-condensation products were characterized with IR spectroscopy. Mechanical properties of the self-condensation products were analyzed with DMA (Dynamic Mechanical Analysis) and also Tensile strength was measured. Surface hardness tests, swelling tests, adhesion tests and contact angle measurements were done on the treated glass surfaces. As the silane ratio increases, the mechanical strength increases for applications on glass surface and the self-condensation products.

ÖZET

EPOKSİDE SOYA YAĞI / DİAMİNO SİLAN KATILMA ÜRÜNLERİNİN SENTEZİ VE POLİMERLEŞMESİ

Bu çalışmada, Epokside Soya Yağı, epoksi halka açılması yoluyla bir diamino-fonksiyonel silan olan N-2-aminoetil-3-Aminopropiltrimetoksisilanreaksiyona sokuldu. Farklı amin:epoksi oranlarında, 0,5 – 0,7 ve 1,0 olmak üzere, değişik ürünler sentezlendi. Tepkime ürünleri, NMR ve IR ile kimyasal olarak incelendi. Tepkime ürününün cam üzerinde ve kendisi ile, oda sıcaklığında, nem yardımı ile kondensasyonpolimerizasyonu sağlandı. Bütün polimerizasyon ürünleri 150°C'de 1 saat bekletildi. Polimerizasyon sonucu ortaya çıkan ürünler kimyasal olarak IR ile incelendi. Mekanik mukavemetleri DMA (Dinamik Mekanik Analiz) ve çekme germe analizleri ile incelendi. Cam yüzeyine yapılan uygulamalar için temas açısı, adhezyon kuvveti, şişme ve yüzey sertliği testleri uygulandı. Silan oranı arttıkça cam yüzeyde ve kendisi ile oluşmuş olan kondensasyonpolimerizasyonu ürünlerinin mekanik mukavemetlerinin arttığı görüldü.

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LIST OF ACRONYMS/ ABBREVIATIONS

AESO	Acrylated Epoxidized Soybean Oil
DAMO	N-2-aminoethyl-3-Aminopropyltrimethoxysilane
DMA	Dynamic Mechanical Analysis
ESO	Epoxidized Soybean Oil
ESO-DAMO adduct	Reaction product of ESO and DAMO
ESO-DAMO 1	Reaction product of ESO and DAMO (0,5:1) silane:epoxide ratio
ESO-DAMO 2	Reaction product of ESO and DAMO (0,7:1) silane:epoxide ratio
ESO-DAMO 3	Reaction product of ESO and DAMO (1:1) silane:epoxide ratio
IR	Infrared
MPa	Mega Pascal
NMR	Nuclear Magnetic Resonance
Tg	Glass TransitionTemperature

1. INTRODUCTION

1.1. Renewable Resources

Polymer industry has been dependent on non-renewable resources such as petroleum products. Since the beginning of 20th century, there has always been a search for renewable materials. Also, polymers derived are known to be non-biodegradable. This is a huge burden on our planet. To reduce this burden, throughout the world, biodegradability is a desired property. As the need for renewable resources and biodegradable products increase, the possibilities of new polymerization methods for plant and animal based molecules is gaining importance.

1.2. Plant Oils

Plant oils can be extracted from seeds, nuts, and fruits of many different plants. This is achieved either mechanically or by solvent extraction. Plant oils have been a good example in the search of renewable resources. They make good candidates that the industry is becoming more and more aware of. Also the polymerization products of plant oils are usually biodegradable to some extent and by the biodegradation of the discarded product, the resources return to their origin, which is the soil. Plants oils and derivatives have been used as renewable resources for polymerization reactions for some time due to their low toxicity, biodegradability, low price, renewability, and world wide availability. Plant oils can perform as monomers in many polymerization reactions. Although there are many advantages, commercially available renewable polymers still has a very low market share (<%5) due to the high processing and less than desirable physical properties [1]. There are now many examples of plant oil based polymers with excellent mechanical properties, where the long fatty acid chains of plant oils bring desirable flexibility and toughness to some brittle resin systems such as epoxy, urethane and polyester resins [2].

Plants oils can be combined with other monomers to form cross linked polymers. In this research a plant oil derivative, Epoxidized Soybean Oil and an organosilane, namely, N-2-Aminoethyl-3-aminopropyltrimethoxysilane based adduct is prepared and polymerized and characterized.

1.2.1. Chemical Structure of Plant Oils

Plant oils are mainly triglycerides, which have a structure as in Figure 1.1. where R1, R2 and R3 are fatty acid chains. This structure is the product of esterification reaction of glycerol with three fatty acid chains.

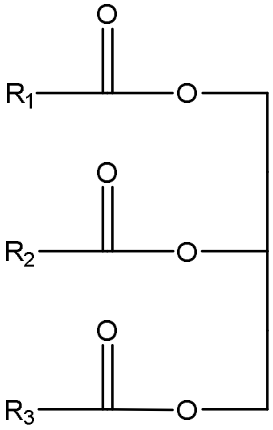


Figure 1.1. Plant oil Structure.

1.2.2. Chemical Composition of Plant Oils

Most common fatty acids have chain lengths that vary from 14 to 22 carbons and contain 0-5 double bonds at different positions along the chain. These double bonds are usually nonconjugated and in cis configuration [3]. Most common fatty acids are given in Table 1.1 and some structure examples are given in Figure 1.2.

Table 1.1. Common fatty acids [3].

Chain Length: Number of Double Bonds	Systematic Name	Trivial Name	Double Bond Position
12:0	Dodecanoic	Lauric	-
14:0	Tetradecanoic	Myristic	-
16:0	Hexadecanoic	Palmitic	-
18:0	Octadecenoic	Stearic	-
18:1	9-Octadecanoic	Oleic	9
18:2	9,12-Octadecadeinoic	Linoleic	9,12
18:3	6,9,12-Octadecatrienoic	γ-linolenic	6,9,12
18:3	9,12,15-Octadecatrienoic	α-linolenic	9,12,15
20:0	Eicosanoic	Arachidic	-
20:1	Eicosaenoic	-	9
20:4	Eicosatetraeonic	Arachidonic	5,8,11,14
20:5	Eicosapentaenoic	EPA	5,8,11,14,17
22:0	Docosanoic	-	-
22:1	Docosenoic	Erucic	13
22:5	Docosapentanoic	DPA	7,10,13,16,19
22:6	Docosahexanoic	DHA	4,7,10,13,16,19

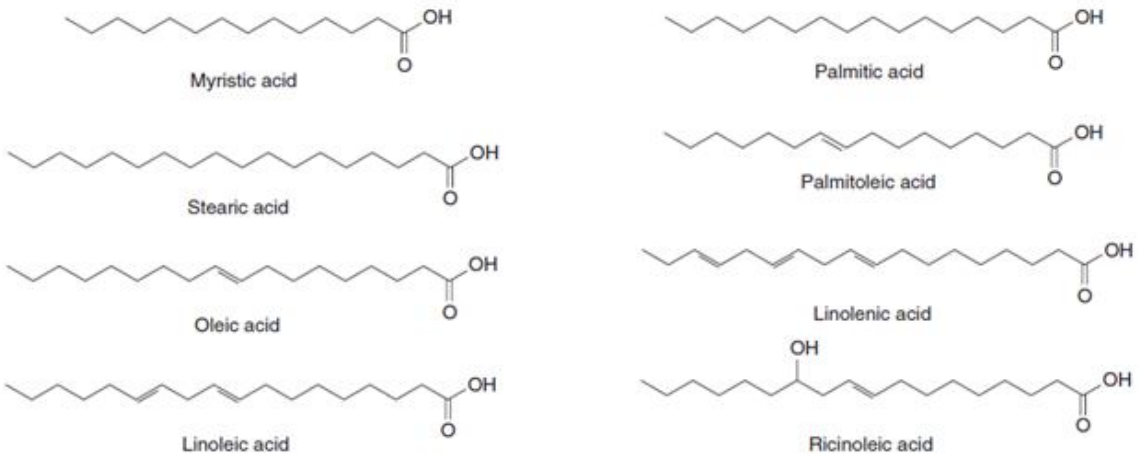


Figure 1.2. Common fatty acid structures [3].

Ratio and type of fatty acids vary greatly among different plant oils. Common plant oils and their contents, also information on average number of double bonds per triglyceride are given in Table 1.2.

Table 1.2. Composition of common plant oils and average number of double bonds per triglyceride [3–5].

Oils	Fatty Acid					Average number of double bonds per triglyceride
	Palmitic	Stearic	Oleic	Linoleic	Linolenic	
Canola	4.1	1.8	60.9	21.0	8.8	3.9
Corn	10.9	2.0	25.4	59.6	1.2	4.5
Cottonseed	21.6	2.6	18.6	54.4	0.7	3.9
Linseed	5.5	3.5	19.1	15.3	56.6	6.6
Olive	13.7	2.5	71.1	10.0	0.6	2.8
Soybean	11.0	4.0	23.4	53.3	7.8	4.6
Tung	-	4.0	8.0	4.0	-	7.5
Fish	-	-	18.20	1.10	0.99	3.6
Castor	1.5	0.5	5.0	4.0	0.5	3.0
Palm	39	5	45	9	-	-
Oiticica	6	4	8	8	-	-
Rapeseed	4	2	56	26	10	-
Refined tall	4	3	46	35	12	-
Sunflower	6	4	42	47	1	-

1.2.3. Uses of Plant Oils

Plant oils are mostly important because they are a consumed as food or animal feed. They provide a concentrated source of energy and act as a carrier for fat soluble components. They are also used for processing food, such as frying, or as additives to add flavor and texture.

Other than their use as foodstuff, they play an important role in non-food applications. Plants oil that are most commonly used are listed in Table 1.3.

Table 1.3. Average annual worldwide plant oil production of 17 commodity oils for 2001-2005 [3].

Oil	Average annual production (million tons)	Main producer
Soybean	26.52	US
Palm	23.53	Malaysia
Rapeseed/canola	15.29	Europe
Sunflower	10.77	Europe
Tallow	8.24	US
Lard	6.75	China
Butterfat	6.26	Europe
Groundnut	5.03	China
Cottonseed	4.49	China
Coconut	3.74	Philippines
Palm kernel	2.95	Malaysia
Olive	2.52	Europe
Corn	2.30	US
Fish	1.13	Peru
Linseed	0.83	Europe
Sesame	0.76	China
Castor	0.56	India
Total	**121.67**	

Detergents, soaps, glycerin and polymers, inks, lubricants, and biodiesel may be derived from fatty acids and their derivatives. There are several oils that are used in the oleochemical industry, while Coconut oil, which mainly consists of saturated fatty acids, is mainly used as a raw material, tallow, crude tall oil, palm kernel, and soybean oils are also widely used.. These oils, their derivatives, or Fatty acids obtained from them are used as the starting material for a wide variety of valuable oleochemical products. A list of several reactions and products obtained from oils and fats are given in Figure 1.3 [6].

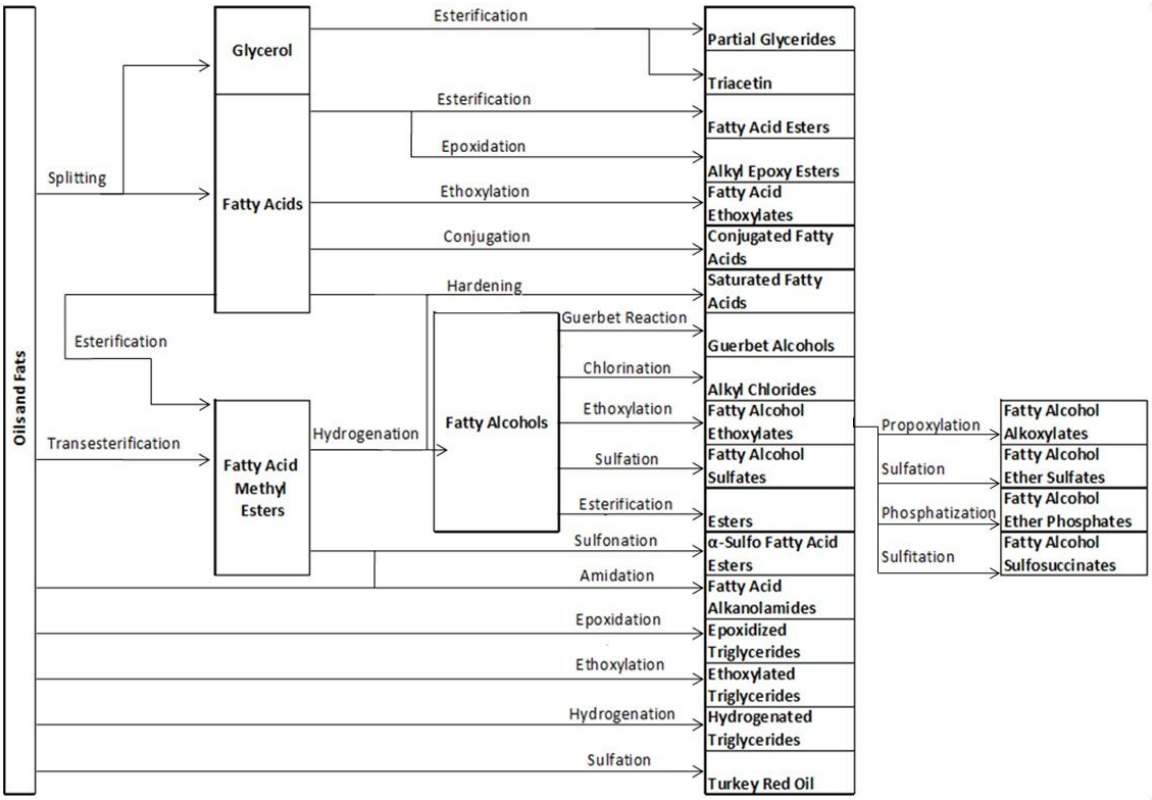


Figure 1.3. Oleochemical raw materials and their derivatives [7].

1.2.4. Polymerization of Plant Oils

To obtain monomers and polymers from plant oils, only a few minor modification reactions are needed. Triglycerides can be polymerized to form cross linked material via two main approaches. First one is using the functional groups on the fatty acid chains and second one is modifying the triglyceride prior to the polymerization to obtain functional groups that are more reactive. This increases possibility of many different reactions, thus widens the use of plant oils in polymerization reactions [8].

There are different functional groups on plant oils, such as carbon-carbon double bonds and epoxy and hydroxyl groups which can be used to form polymers. Double bonds among these functional groups are the main sites for further functionalization.

For polymerization reactions linseed, tung, corn, cottonseed, rapeseed, and soybean are widely used. Among these oils, linseed and the tung oil are called ‘‘drying oils,’’ which is basically polymerization of the oil to form a solid film by air oxidation. This is because they have high unsaturation, therefore have high tendency to react with atmospheric oxygen to form polymeric networks. Soybean oil, sunflower oil, and canola oil are semidrying oils with lower unsaturation and lower reactivity towards oxygen.

Hydroxyl groups also occur naturally in oils such as castor oil, which consists of ricinoleic acid mainly. They can be used to form polymeric materials, such as reaction with isocyanates to form polyurethanes [6].

A summary of reactions of triglycerides to form polymers are given in Figure 1.4. Pathways from a to b, c1, c2, d, i, and j, includes breaking down of triglyceride into monoglycerides. Pathways from a to e, f, g, h and k includes reactions where triglyceride is not converted into monoglycerides, but derivations are formed for further reactions [9].

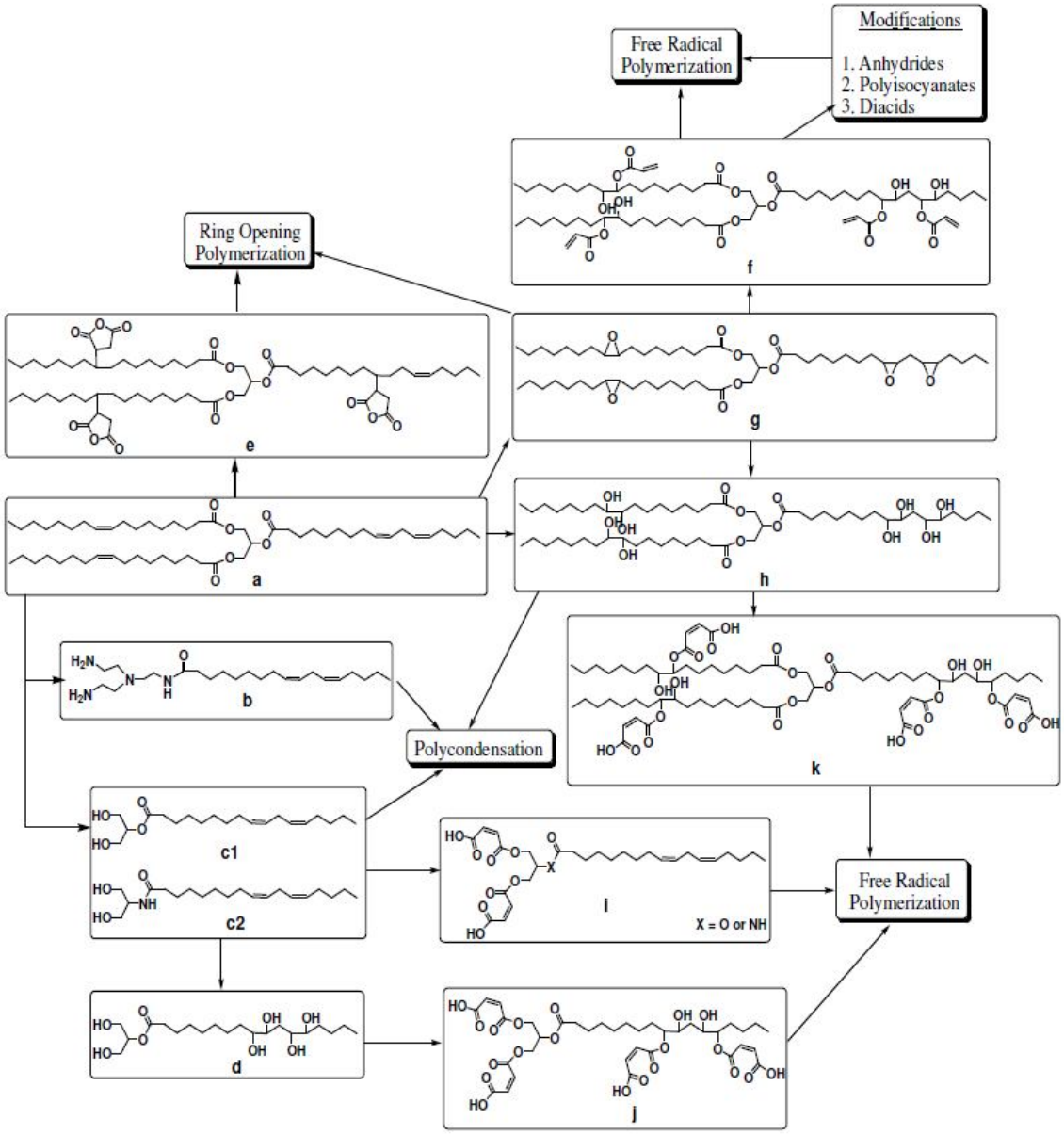


Figure 1.4. Reactions from plant oils.

1.3. Soybean Oil

Soybean oil is extracted from Soybean either mechanically or by solvent extraction. Soybean production was 58% of total vegetable oil crop production in 2003, making soybean the most important oilseed crop. Soybean is richer in protein than other oilseeds, this is the main reason for the preference of soybean to other crops. Its oil content is around 18-22%. In the last 10 years genetically modified soybeans produced by Monsanto Inc. contain up to 38% oil.

In 2001-2002 97% of soybean oil in the United States was used for food, leaving a small share for non-food applications [6]. Soybean oil is used as food as salad oil, but it is usually hydrogenated for use as a margarine stock or frying oil.

1.3.1. Composition of Soybean Oil

Soybean oil has a composition of fatty acids as in Table 1.4. This composition depends on many different factors. Soybean has an average of 4.6 double bonds per triglyceride.

Table 1.4. Average fatty acid composition of soybean oil.

	Palmitic	Stearic	Oleic	Linoleic	Linolenic
Soybean Oil	11	4	23.4	53.3	7.8

1.3.2. Chemical and Physical Properties of Soybean Oil

Soybean oil is liquid at room temperature and typically has physical properties, as given in Table 1.5. Composition of the soybean oil determines the properties.

Table 1.5. Physical properties of soybean oil.

	Viscosity (mPa·s) at 37.8ºC	Specific Gravity at 20ºC	Refractive Index at 20ºC	Melting Point(ºC)
Soybean Oil	28.49	4	23,4	-23 to -20

Soybean oil structure is given in Figure 1.5. where the fatty acids are two linoleic acids and one oleic acid. There are several reactive sites in a triglyceride molecule. The allylic carbons, double bonds, ester groups and carbons alpha to the ester groups are reactive, thus derivatives and other products can be obtained from soybean oil. Many reactions for fats and oils given in Figure 1.4. also applies to soybean oil.

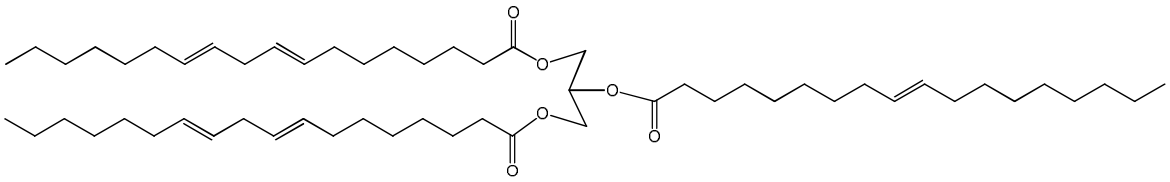


Figure 1.5. Structure of soybean oil.

1.3.3. Epoxidation of Soybean Oil

One of the reactions that soybean can undergo is epoxidation, where all or some of the double bonds are converted to epoxy rings.

Currently there are four known technologies to obtain epoxides from oleophilic types of molecules. First and most common one is epoxidation with percarboxylic acids. This is the Prileschajew reaction, in which the unsaturated oils react with a percarboxylic acid, such as peracetic and performic acid. Peracids are formed from carboxylic acids, in

presence of hydrogen peroxide. Soluble mineral acids such as sulfuric acid catalyses this reaction [10]. This method is currently widely used in the industry. Conversion of double bonds to oxirane rings is shown in Figure 1.6. Second method to produce epoxidized soybean oil is epoxidation with organic and inorganic peroxides, this includes alkaline, nitrile hydrogen peroxide epoxidation and transition metal catalyzed epoxidation [11]. Third method is epoxidation with halohydrins, using hypohalous acids and their salts as reagent. Fourth method is epoxidation with molecular oxygen [12].

Using halohydrins is not desired because of environmental considerations. Using molecular oxygen is a cheap method but yield is very low for epoxidation of molecules other than small molecules such as ethylene or butadiene. Also using molecular oxygen is not desirable because it oxidizes the triglyceride as well, reducing the yield further and producing unwanted impurities. Research for finding better ways to synthesize Epoxidized oleophilic molecules still continues.

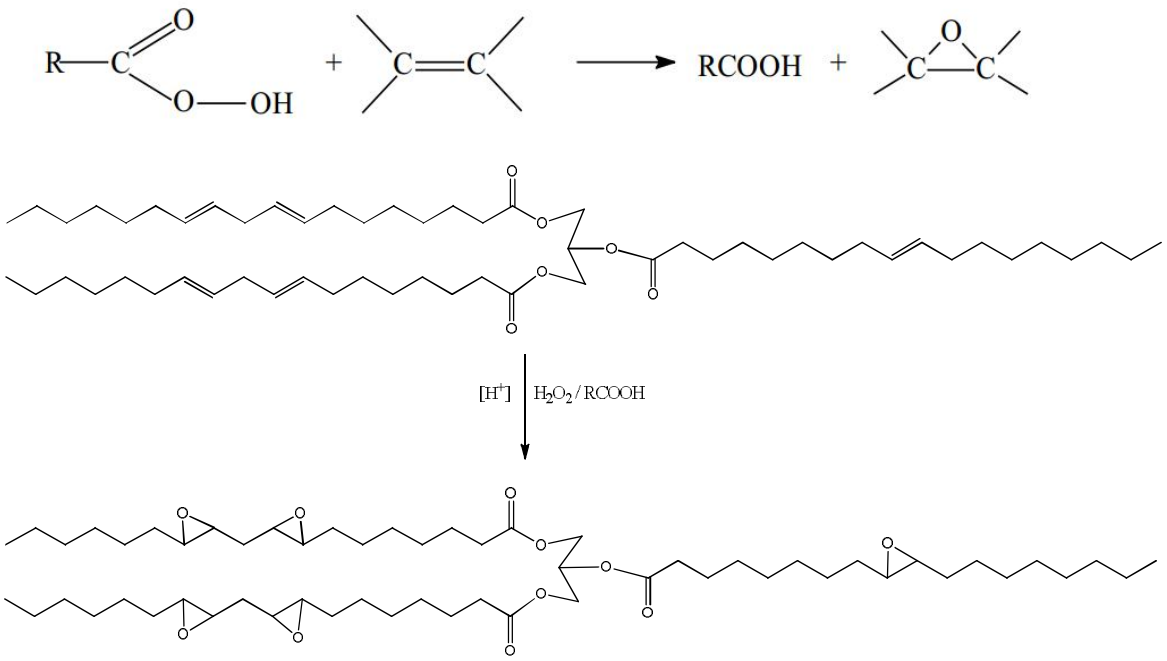


Figure 1.6. Reaction of double bonds to form oxirane rings.

1.3.4. Uses of Epoxidized Soybean Oil and Previous Studies

Epoxides are widely used in polymer industry, it is no surprise that soybean oil is also widely used in its epoxidized form in polymer industry. This extensity of epoxides arises from the reactivity of the oxirane ring, which is strained, due to the 3 membered ring.

Epoxides can react with a large range of nucleophiles. Hydrogen, water, alcohols, carboxylic acids, hydrogen sulfides, amines, hydrogen cyanide, hydrochloric acid, and sodium bisulfite are the compounds an epoxy can react with. Resulting products are alcohols, diols, alkoxyalcohol, hydroxy esters, mercapto alcohols, amino alcohols, hydroxy nitriles, chlorohydrins, and sodium hydroxysulfonates respectively. Reaction can be seen in Figure 1.7.

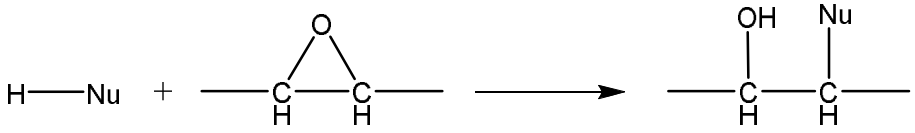


Figure 1.7. Reaction of an epoxide with a nucleophile.

The mechanism for opening of oxirane ring is either S_N1 or S_N2, depending on the nucleophile. Stronger nucleophiles in basic conditions favor S_N2 type of substitution and weaker nucleophiles in acidic conditions favor S_N1 type.

Reaction for epoxides apply for epoxidized soybean oil as well, but there are some cases where the reactions will not occur, because the epoxide is not terminal and sterically hindered in epoxidized soybean oil [13].

Epoxidized soybean oil (ESO) is mostly used as a plasticizer in polyvinyl chloride (PVC) plastics. It is also good as a scavenger for hydrochloric acid, which is liberated from PVC when the PVC undergoes heat treatment [14]. ESO and its derivatives are also used in many applications such as lubricants [15], in polymer industry, in

composites [4], as inks and photoinitiators [16]. ESO is used to form polyols which are important in polyurethane production [17].

One of the most important derivatives of ESO is AESO, acrylated epoxidized soybean oil. ESO is acrylated with acrylic acid where acrylic acid itself and N,N-dimethyl aniline and triethylamine is used as catalyst. Epoxy rings on the ESO molecule can be acrylated partially to the structure given in Figure 1.8. Some epoxy rings are lost to the homopolymerization of the epoxides.

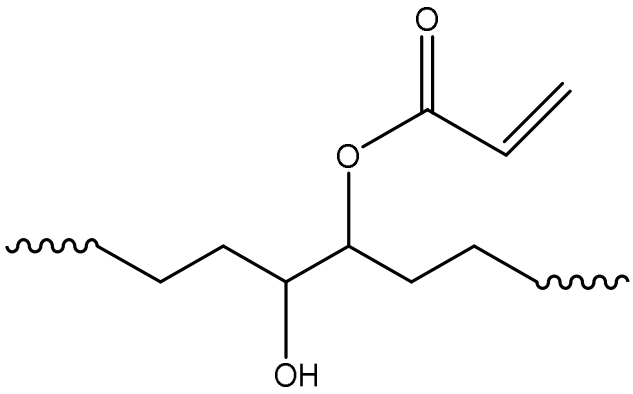


Figure 1.8. Acrylation of epoxy rings.

AESO has been free radically polymerized or co-polymerized in presence of reactive diluents such as styrene, which will give thermoset polymers with similar mechanical properties to commercially available polyester and vinyl ester polymers. Physical properties depend on diluent amount, functionality, so they can be fine-tuned to desired properties [4, 9].

As Reported by Çolak and Küsefoğlu, AESO has been reacted with 3-Aminopropyltriethoxysilane via Michael addition to form a multifunctional monomer which had very high adhesion to glass surface [18]. Resulting silanized-AESO structure is given in Figure 1.9.

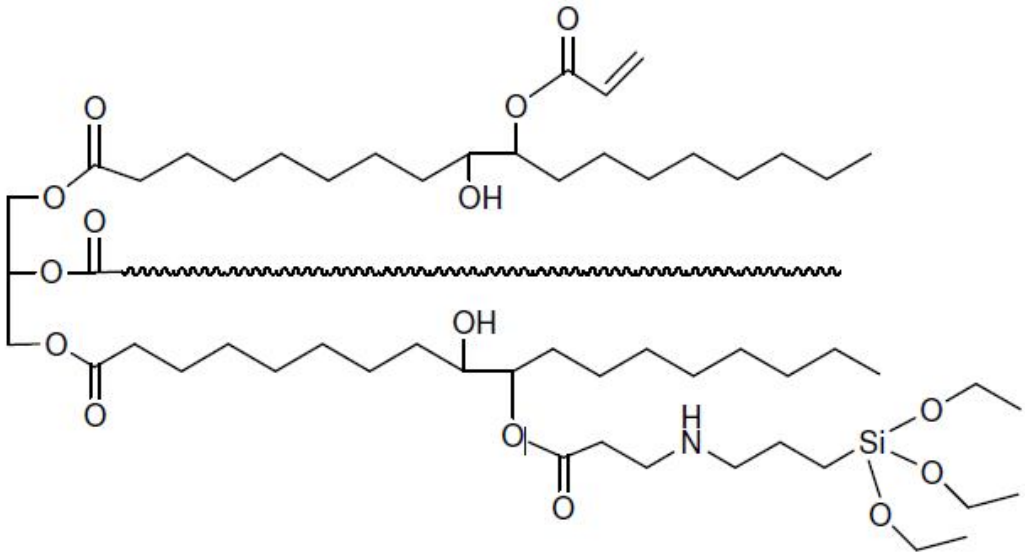


Figure 1.9. Silanized AESO.

1.4. Organofunctional Silanes

Silicone, which consists of a siloxane backbone is valuable for many applications because of its good mechanical and thermal properties, low conductivity and resistance to chemicals and harsh conditions.

Silanes are monomeric silicone, and silane that contains at least one silicone-carbon bond is an organosilane.

The advantages of combining organic functional groups and silanes have been investigated for many years and therefore many organofunctionalsilanes have been developed. These organofunctional silanes are essential today for many applications.

Desired properties of organofunctional silanes come from the very stable Carbon-silicone bond which is also nonpolar. This property enables to combine two very different functional groups in one molecule and organosilanes that consist of two different reactive groups are valued because they can couple two materials with different properties. This

property best presents itself in fiberglass reinforced composites which was discovered around 1940 [19].

1.4.1. Chemical Structure of Organofunctional Silanes

An organofunctional silane generally has a structure as below, where there are alkoxy groups attached to Silicon, which can be hydrolyzed to Si-OH forming a reactive end, and another organofunctional group. A typical trimethoxy silane is given in Figure 1.10.

$X—CH_2\text{-}Si(OR)_{3-n}R'_n$ where n = 0, 1, 2

where R' is usually methoxy, ethoxy…
Where X is usually epoxy, amino, methacryloxy, or sulfide

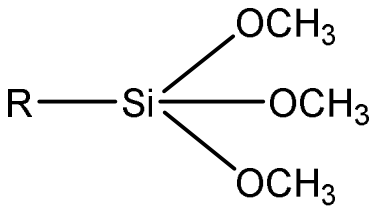
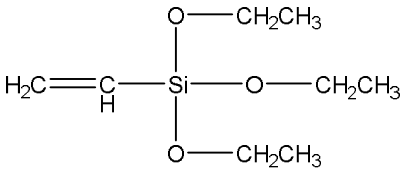
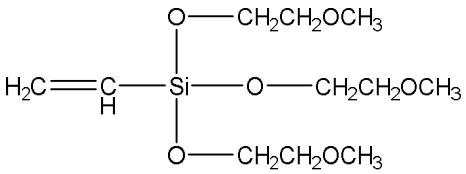


Figure 1.10. A trimethoxy silane.

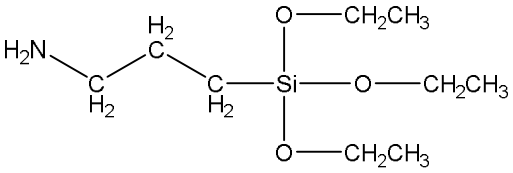
Some examples are given in Figure 1.11.



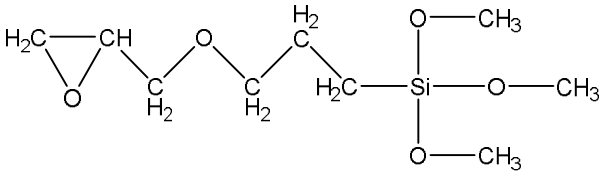
Vinyltriethoxysilane



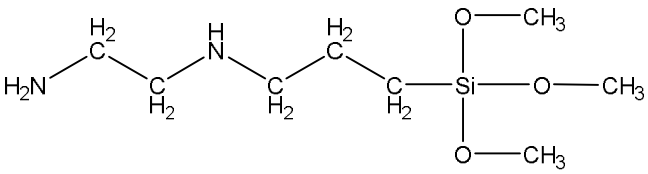
Vinyl-tris(2-methoxyethoxy)silane



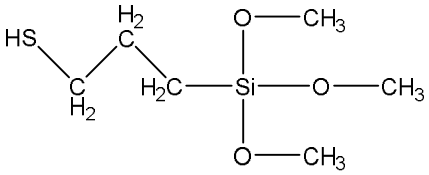
gamma-Aminopropyltriethoxysilane



gamma-Glycidoxypropyltrimethoxysilane



N-beta-(aminoethyl)-gamma-aminopropyltrimethoxysilane



gamma-Mercaptopropyltrimethoxysilane

Figure 1.11. Examples of organofunctional silanes.

1.4.2. Uses of Organofunctional Silanes

Organofunctional silanes are widely used as coupling agents, cross linkers, and surface modifiers. It is important to choose the correct structure for the application. Alkoxy groups in organofunctional silanes are hydrolyzed to silanols very easily with water, even the moisture on the surfaces are enough for this hydrolization. Silanols react with each other and polymerize to form very strong Si-O-Si backbone, or they can condense with hydroxyl groups on glass or metal surfaces, where they show adhesive properties to inorganic surfaces [20].

Organofunctional silanes can be used as cross linkers because they have two functional groups. Also they can be used as surface modifiers for inorganic substances to enhance hydrophobicity when desired.

Organofunctional silanes are used in composites as adhesion promoters. They act as coupling agents, because they enable covalent bonding of two different structures, inorganic, like glass, and organic, like the polymers. Very good mechanical properties such as tensile strength, impact strength, abrasion resistance are observed because of the silanes ability to covalently bind an inorganic surface to an organic polymer.

Reaction of an organofunctional silane with an inorganic surface is summarized in Figure 1.12. An alkoxysilane undergoes four different phases to covalently bond to an inorganic surface.

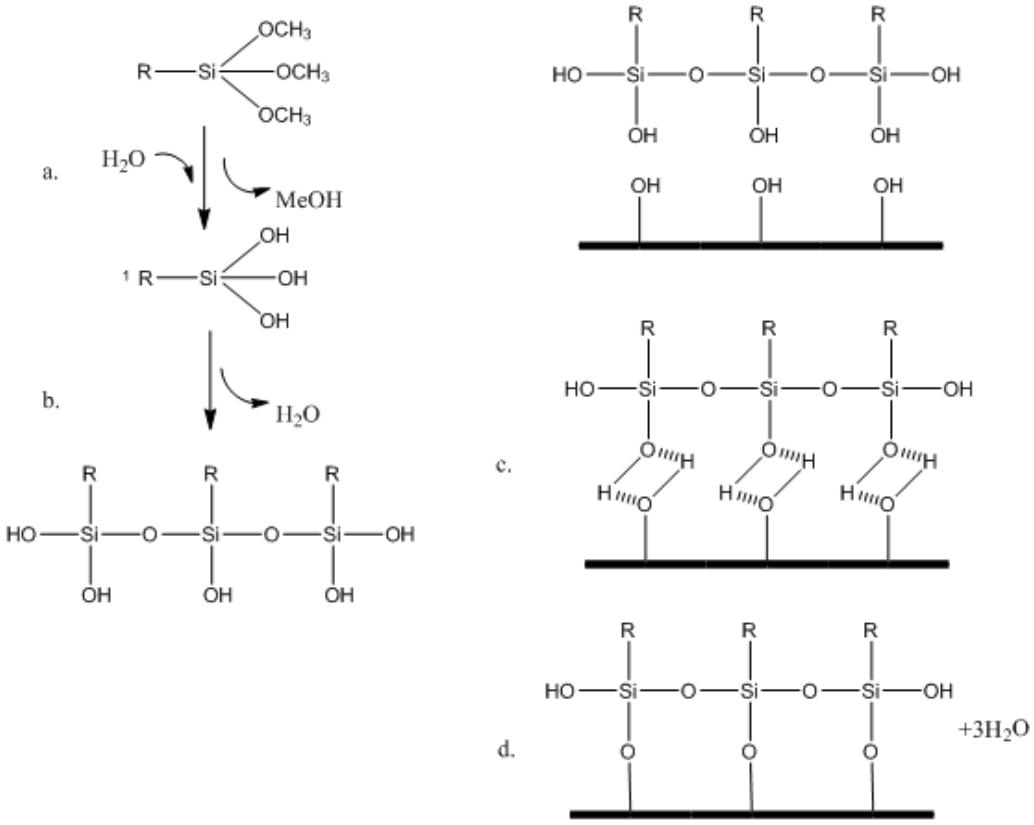


Figure 1.12. Organo-functional silane hydrolysis (a), condensation (b), hydrogen bonding (c) and covalent bonding (d) to an inorganic substrate.

1.4.3. Aminofunctional Silanes

Aminofunctional silanes, just as other silanes, are used as adhesion promoters, coupling agents, and additives for polymeric fibers. They improve chemical bonding of resins to inorganic fillers and reinforcing materials. They are used with epoxies, phenolics, melamines, nylons, PVC, acrylics, polyurethanes, and nitrile rubbers and they can be used as surface pretreatment of fillers and reinforcers.

Aminofunctional silanes have a silane functionality, which is very similar as any organosilane. In addition they have the amine functionality, which enables many reactions such as hydrogenation, alkylation, acylation of the amine group.

All amines react with epoxides by an addition reaction without forming any byproducts which can be seen in Figure 1.13. Amines on aminofunctional silicone can be primary, secondary or tertiary. Primary and secondary amines are widely used for curing epoxy resins. Tertiary amines do not react with epoxides because they lack an active hydrogen, but they are used as catalysts for epoxy curing. Amines react with epoxides with SN2 mechanism. A primary amine will be converted into a secondary amine upon reaction with an epoxide, which is still reactive although reactivity is lower. Reactivity is lower due to steric hindrance. A secondary amine is converted into a tertiary amine, which is no longer reactive for epoxide. A secondary hydroxy groups is also formed on the carbon β to the carbon attached to the amine nitrogen, which is somewhat reactive towards an epoxide ring, when epoxide is present in excess [21].

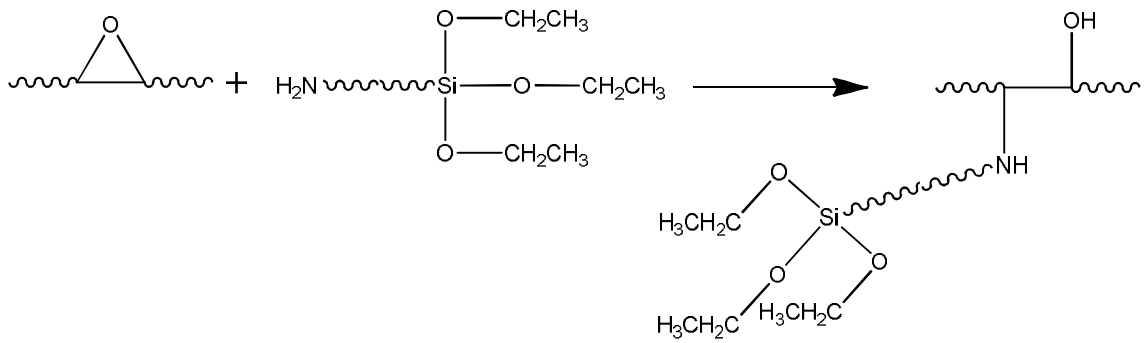


Figure 1.13. Aminofunctional silane reaction with an epoxide.

2. RESEARCH OBJECTIVES

The aim of this work is to synthesize a soybean oil based coupling agent. For this purpose, epoxidized soybean oil (ESO) will be reacted with an aminosilane, N-2-aminoethyl-3-Aminopropyltrimethoxysilane (DAMO).

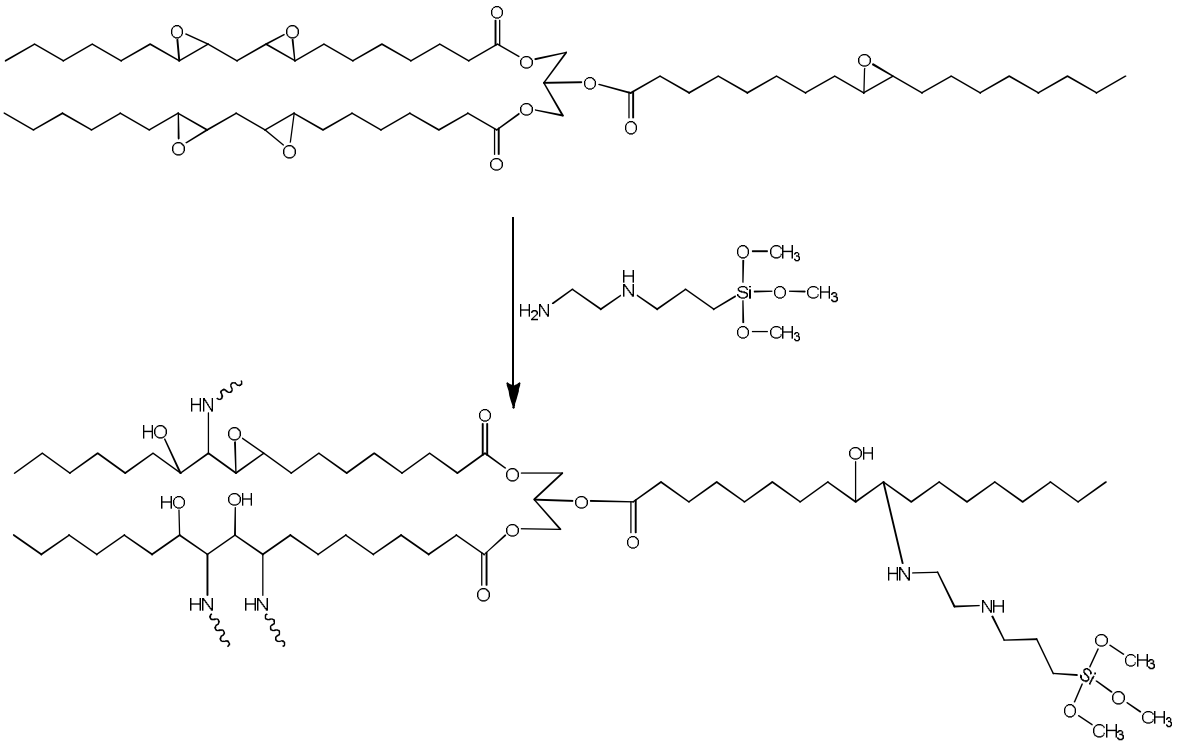


Figure 2.1. Organosilane derived from reaction of ESO and DAMO.

The resulting organosilane in Figure 2.1. will be used in two ways:

(i) It will be hydrolyzed and homopolymerized to give a soybean oil based polymer, as in Figure 2.2.

(ii) It will be hydrolyzed and condensed with a glass surface to give an oleophilic glass surface, as in Figure 2.3.

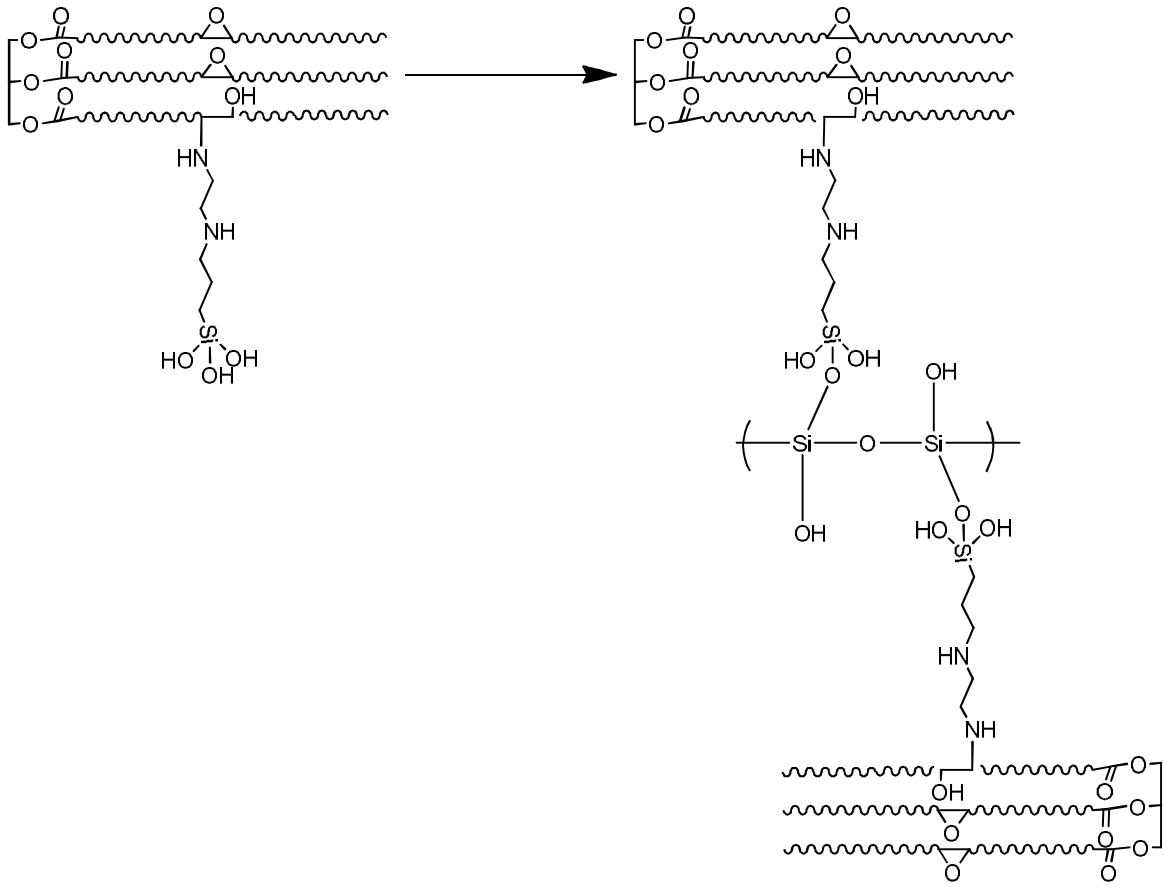


Figure 2.2. Homopolymerization of silanized ESO.

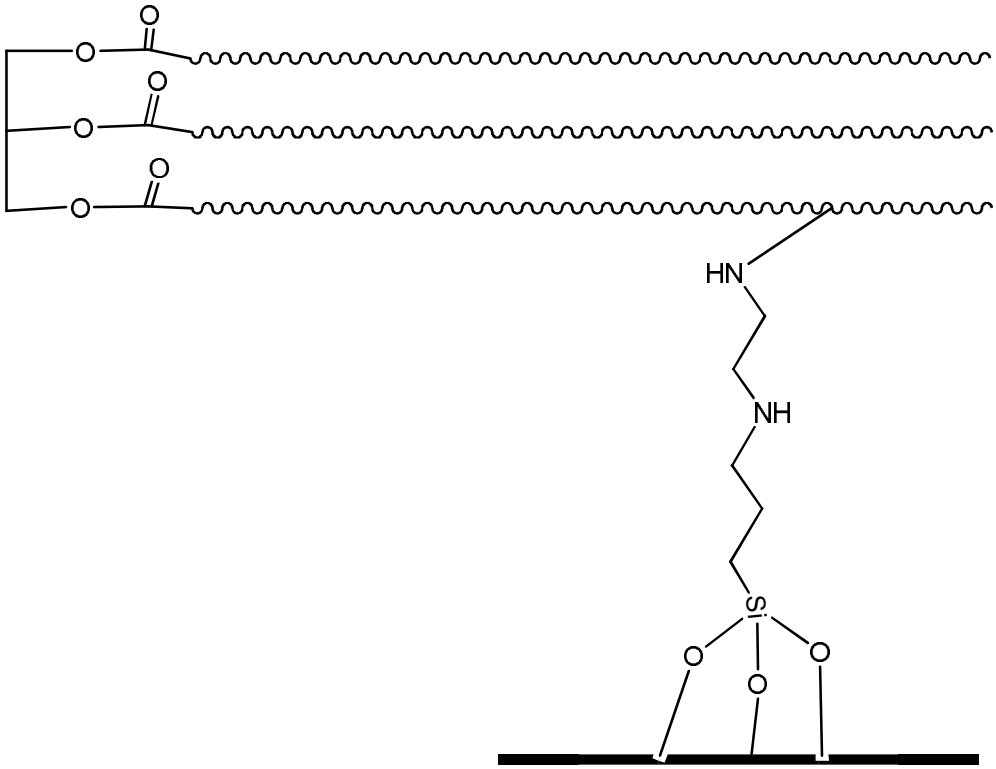


Figure 2.3. Adhesion on a surface for silanized ESO.

The resulting polymer in Figure 2.2. will be chemically characterized by FTIR and ^{1}H NMR. Physically characterized by DMA, and stress-strain tests.

The resulting surface in Figure 2.3. will be characterized by surface hardness, adhesion tests and contact angle measurements.

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3. EXPERIMENTAL

3.1. Materials and Apparatus

3.1.1. Materials

2-Aminoethyl-3-aminopropyltrimethoxysilane (Dynasylan DAMO) was obtained from Evonik Industries AG and used as obtained. Epoxidized soybean oil was obtained from Akdeniz Kimya and used after drying. $CDCl_3$ was obtained from Sigma Aldrich and was used for ^1H NMR analysis. Solvents used for swelling tests, and other chemicals used for tests such as acetone, n-butanol, ethanol, toluene, perchlorethylene, pentane, petroleumether, water, methanol, acetonitrile, dimethylformamide, 2-propanol, chloroform, potassium hydroxide and acetic acid were obtained from Merck. Hexane, and xylene, were obtained from Sigma Aldrich.

Glass used in tests was 2, 4 and 6 mm thick and was produced by Trakya Cam A.Ş. Its surfaces were washed in (25:200:200) of (KOH:2-propanol:water). Glass surface was not thoroughly dried, only wiped off of water droplets, so that moisture on the glass surface would promote film formation on the surface.

3.1.2. Apparatus

The ^1H NMR data were recorded on a Varian 400 MHz NMR instrument operating at a frequency of 399.97 MHz.

Thermo Scientific Nicolet 380 FT-IR with smart diamond ATR was used for IR spectrums obtained from reactants and final products.

Contact angle for polymerization on glass surface was measured by using KSV Instruments CAM 101 instrument. Contact angles were measured by the sessile drop method using water at room temperature.

Surface Hardness of polymerization on glass surface for 3 different stoichiometries were measured by pendulum hardness.

The dynamic mechanical thermal analysis of the polymer samples were performed by using Dynamic Mechanical Analyzer (DMA). DMA measurements were done with TA Instrument Q800. Temperature scans were run from -50˚C to 140 ˚C at a heating rate of 3˚C/min with a frequency of 1 Hz.

The tensile strength for adhesion of two glass surfaces was measured by Devotrans DVT G21.

3.2. Synthesis of ESO-DAMO Adduct

Prior to the reaction, ESO was dried in a vacuum oven at 100ºC for 3 hours and molecular sieve (8Å) were added to absorb residual water. ESO was filtered to remove molecular sieves just before the reaction.

ESO-DAMO adduct was synthesized in a N_2 purged, previously dried flask. A closed system was used to prevent polymerization of the adduct. Reaction mixture consists of ESO and DAMO, and was a homogeneous mixture and was stirred at 650 rpm, at 100ºC for 4.5 hours.

Three different stoichiometric ratios (0.5, 0.7 and 1.0 silane per epoxide ring) were used. Thus, 23.8, 33.33, 47.61 g of silane was reacted with 50g ESO respectively for the three ratios. These are referred to adducts 1, 2 and 3 respectively.

ESO-DAMO adduct formed (0.7 silane per epoxide ring) was analyzed by ^{1}H NMR, to observe reaction of epoxide with the amine group of the silane. This was done before hardening of the adduct. Also IRspectrumof the mixture at the beginning and at the end of the reaction were taken.

3.3. Properties of ESO-DAMO Adduct

ESO-DAMO adduct is a distinct yellow-orange colored viscous liquid at room temperature. It is highly reactive and easily cures at room temperature with ambient moisture, therefore the adduct is stored in a tightly sealed flask. Even in a tightly sealed flask, the adduct cures after about 3-4 weeks, starting from the surface. Due to gelation and hardening of the adduct after some time, adduct was preferably freshly prepared before use. The adduct is miscible with 2-propanoland which is used for diluting purposes, for ease of applying and to reduce hardening.

3.4. Moisture Curing of Polymers

Moisture curing method was used for all three stoichiometries to obtain homopolymers as parts, films, glass surface films from ESO-DAMO adduct that was prepared. This was done at room temperature. Moisture in the air was enough to cure thin films and polymerization on glass surface, but for thick parts, 1% water was added to promote curing. Since water was not soluble in the adduct, it was added after adduct was diluted with 2-propanol. Acetic acid was also added, to adjust pH around 4.0 to promote silane hydrolysisand stability, as per manufacturer's recommendation.

All moisture cured films and parts were carefully post cured after fully hardened at room temperature. Post curing was done at 150˚C for 1 hour. The films hardened in about 2 days at room temperature, thinner films hardened faster. Parts were left at room temperature for about 2-3 weeks for proper hardening thoroughly, because at post cure

conditions, if 2-propanol, water, MeOH, or AcOH was present, bubbles would form in the part, which would result in low mechanical properties.

3.5. Homopolymerization of ESO-DAMO Adduct

3.5.1. Homopolymerization into films

Homopolymerization into films was done by moisture curing of the adduct directly on a Teflon or polypropylene surface. Thinner the film, quicker it hardens and cures. Thin films obtained by this method were between 1.4-2.4 mm of thickness. After 1-2 days of hardening, films were post cured at 150˚C for 1 hour. Tensile strength was measured for three stoichiometries.

3.5.2. Homopolymerization to obtain molded parts

Molded parts were made by carrying out the hydrolysis and condensation in open molds by moisture curing of the mixture as (2-propanol:AcOH:water:adduct) with the ratios (25:8:3:75). A 10 mm deep, 150 mm long, 15 mm wide Teflon mold was used. After hardening for about 1 week at room temperature, parts were taken out of the mold and post cured promote further hardening and evaporation of residual solvent for an additional 1-2 weeks. This was done slowly so that the vapor from evaporation of 2-propanol, AcOH, MeOH or water from condensation would slowly diffuse rather than forming bubbles. Part with higher silane content was harder and also darker in color, where part with higher epoxidized soybean oil content was very flexible and softer.

Post curing at 150ºC for 1hour was done after proper hardening of the part. Post curing hardens the parts significantly. Homopolymerized and post cured parts were also used in swelling tests with solvents: acetone, n-butanol, ethanol, toluene, perchlorethylene, pentane, petroleum ether, water, methanol, acetonitrile, dimethylformamide, 2-propanol, hexane, xylene and chloroform.

Swelling test was done for three different stoichiometries in chloroform. Ratio of volume of the swollen part to initial volume of the part was calculated, using length, assuming swelling is equal for all dimensions.

3.6. Polymerization of ESO-DAMO Adduct on Glass Surface

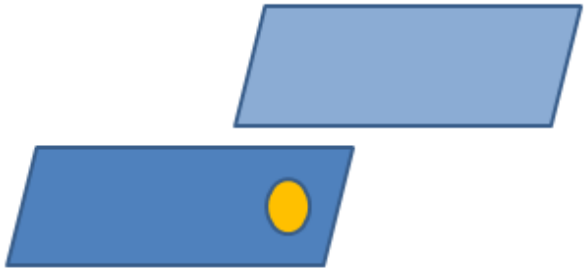
A large drop of adduct was applied on the previously cleaned glass surface 201x 101 mm and was spread over the surface by 201 x75 mm with the help of a glass rod. After hardening of the film on glass surface, post cure was done at 150˚C for 1 hour, thickness of the coating was 50 μm thick. Contact angle and surface hardness was measured for the samples prepared by this method for three different stoichiometries.

Another method for polymerization on glass surface was used for preparing samples for adhesion test to glass surface.

3.7. Procedures for Testing Adhesion to Glass Surface

Homopoymerization of the adduct on glass surface was analyzed for the adhesion of the adduct to the glass surface. Samples were prepared with 6mm glass pieces, where they were joined as seen in Figure 3.1. A small drop of the adduct was applied on one of the glass pieces and the other glass piece was conjoined by tape until curing is complete, Glass plates were overlapped to give a contact area of approximately 5.5-8.5 cm^2 in the samples. Post cure was done at 150˚C for 1 hour.

Devotrans DVT G21 was used to pull the adhered glass surfaces apart with a speed of 2 mm/min.



Two glass surfaces to be adhered with the adduct.

Two glass surfaces after adhesion with the adduct, top and side view.

Figure 3.1. Preparation of lap-shear test samples.

3.8. Procedures for Testing Mechanical Properties

Homopolymers were tested for mechanical properties, by both Dynamic Mechanical Analysis and Static Mechanical Analysis.

Parts were prepared as described in Section 3.5. for Dynamic Mechanical Analysis, highest and lowest silane content (0.5, and 1.0 silane per epoxide ring) samples were tested. Proper formation of parts was very hard to achieve, due to volatile content of the

mixture, bubble formation was observed, and this resulted in substrate failure for mixture 2, where data could not be obtained.

DMA samples were 11-13 mm wide and around 5 mm thick. Length was around 18.5 mm as the instruments set length for samples stabilized from both sides.

Tensile strength of the films were measured by an analytical balance, using an apparatus as given in Figure 3.2 since the films mechanical strengths were below the limits of universal instruments. Films were rectangular and had wooden end tabs glued for support at each end so that the film would not fail at the jaws. Nut on the bolt screw is fixed, and every turn of the bolt screw causes an elongation of 1.1 mm of the film. And force the film could carry could be measured by the analytical balance.

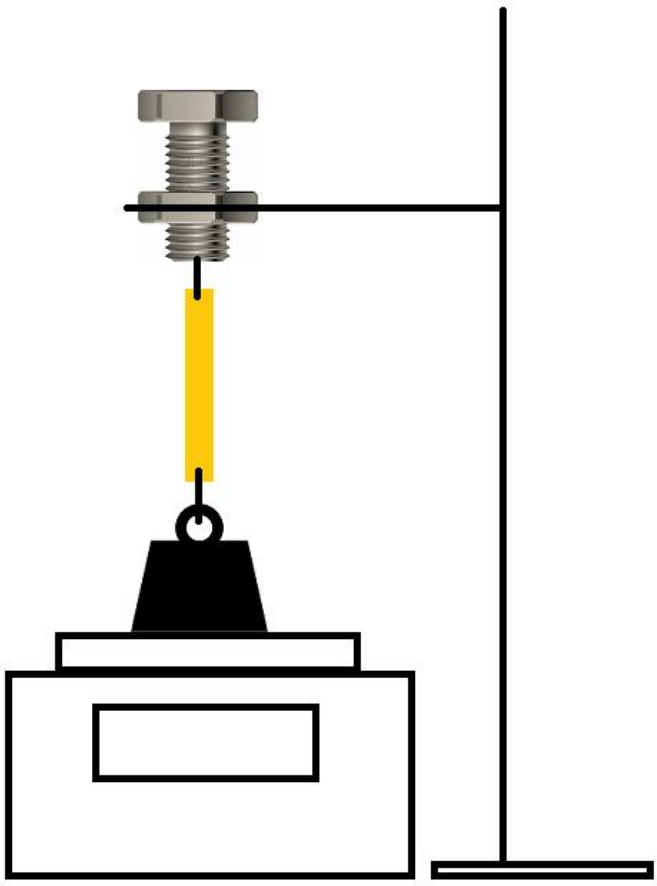


Figure 3.2. System for measuring stress vs. strain for polymer films.

4. RESULTS AND DISCUSSION

4.1. Synthesis of ESO-DAMO Adduct

Epoxy rings can undergo nucleophilic substitution. Terminal epoxy groups, such as those found on commercial epoxy resins, react with primary amines at room temperature. However ESO has internal epoxide groups which require higher temperatures or acidic or basic catalysts to react.

When an epoxy group is opened by an amine, an alkoxide is formed which is capable of opening another epoxide group. This leads to homopolymerization of epoxy groups which consumes epoxy groups without consuming amines. The reaction is shown in Figure 4.1.

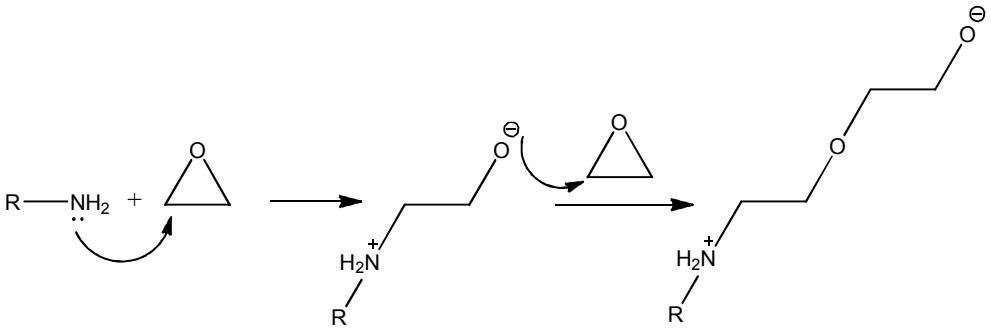


Figure 4.1. Homopolymerization of epoxy groups.

A good estimation of epoxy groups wasted by homo polymerization is 30%. Thus it is a common practice to choose any amine:epoxy stoichiometry of 0.7:1 to allow for the epoxy consumption due to homopolymerization of epoxy groups.

Nucleophile to open the epoxy group used in this study is N-2-aminoethyl-3-aminopropyltrimethoxysilane, which is an organofunctional silane, with an organic

reactive end as well as an inorganic reactive end. Only the terminal amine group is expected to be reactive because secondary amine is highly hindered. Reaction of this aminosilane with epoxidized soybean oil will occur between the epoxide ring on ESO, and the primary amine group on the silane.

A more common amino silane, aminoporopyltriethoxysilane, was first used in our group and surprisingly failed to give any reaction with ESO even at high temperatures and with tertiary amine catalyst. This attempted reaction is shown in Figure 4.2.

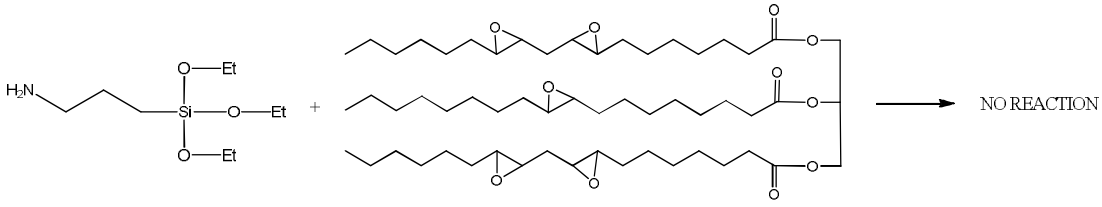


Figure 4.2. Attempted reaction between ESO and Aminopropyltriethoxysilane.

It is believed that aminopropyltriethoxysilane is strongly self-hydrogen bonded which decreases the nucleophilic character of the amino group. This hydrogen bonding can be as in Figure 4.3.

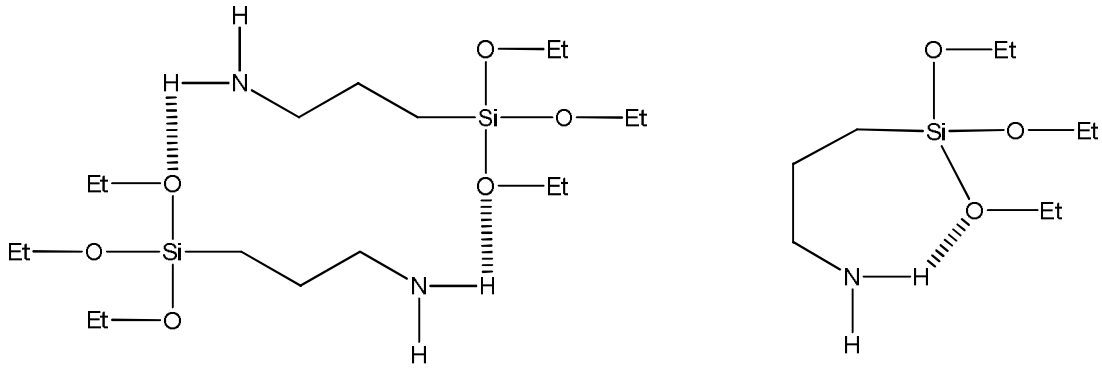


Figure 4.3. Possible self-hydrogen bonding of Aminopropyltriethoxysilane.

In diaminosilane used in this work, the amino group is 2 carbons further away from the silicone atom and this may be the reason why it reacts with internal epoxides with ease. The diamine used reacts only with its primary amine at temperatures below 100ºC, but polymerization products which are believed to be epoxy-2ºamine adducts are observed at higher temperatures.

Epoxy groups consumed by homopolymerization of epoxy groups and the assumption that only the primary amine would react is taken into consideration while calculating molecular stoichiometry.

0,7 ratio of amine:epoxide groups was selected for this study. To observe how the epoxide to silane ratio change effects the mechanical properties, an higher and a lower ratio are used as well. A total of three different stoichiometric ratios, such as 0.5, 0.7 and 1.0 amine:epoxide were used. These were named feed ratios 1, 2 and 3 respectively.

The reaction is carried out by mixing the reactants in three different ratios. The reactants are completely miscible, therefore no additional solvents were used. Since the silane is very reactive in presence of water, all glass apparatus and ESO was previously dried carefully and purged with N_2. Reaction was done under N_2 bed, at 100˚C, under constant stirring at 650 rpm, in a completely closed system for 4.5 hours. Reaction was carried at 100ºC, to maximize reaction between the primary amine with the epoxy ring, while minimizing ESO self polymerization products and the secondary amine epoxy products [15, 22, 23]. 650 rpm was selected because it caused constant stirring well enough without causing bubbles or splashing. Reaction time was selected as 4.5 hours to let the reaction take place fully without risking high cross-linking, which would maximize final product mechanical properties. The desired and undesired reactions are shown in Figure 4.5. In an open system, where water vapor is present, reaction mixture hardens very quickly and the adduct gels in the reaction flask. This is due to untimely hydrolysis and self condensation of the silane groups (See Figure 1.12 a and b).

The reaction mixture in the beginning is very pale yellow. DAMO is colorless and ESO is pale yellow. After the reaction is completed, adduct is a viscous orange liquid. Orange color is presumed to be originating from nitrogen oxides forming in the reaction mixture. In commercial use of aminosilanes, such as in glass fiber manufacture, hindered amine antioxidants are used to prevent N-oxide formation from the aminosilane.

After the reaction is completed, reaction mixture was cooled down in the closed system, and transferred into a sealed, dry container. Sample for ^{1}H NMR was taken and

dissolved in $CDCl_3$. Resulting adduct is miscible with 2-propanol, which was used as a convenient solvent where needed.

The resulting adduct has a structure as in Figure 4.1.and contains methoxy groups which can be converted into silanol groups with catalytic amount of water, either purposefully added or obtained from moisture in the air, which can undergo self condensation reaction, or react with a surface, such as glass, to form a hydrophobic layer due to the long alkyl chains in the ESO. These structures are shown in Figure 4.4.

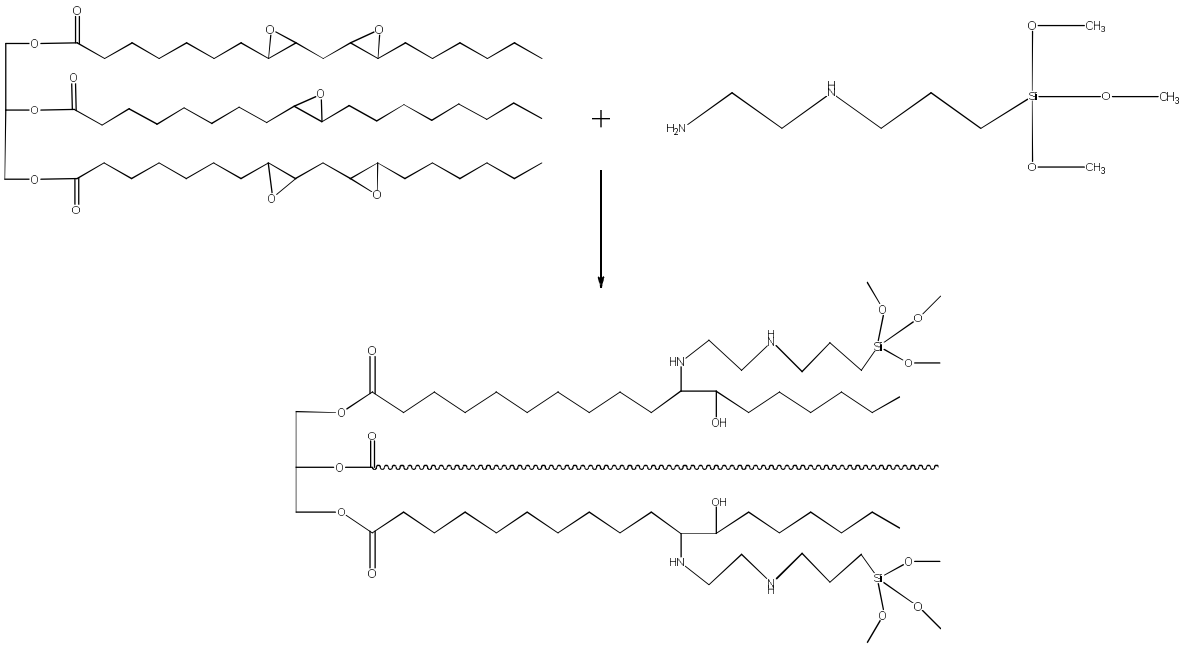


Figure 4.4. ESO-DAMO adduct reaction.

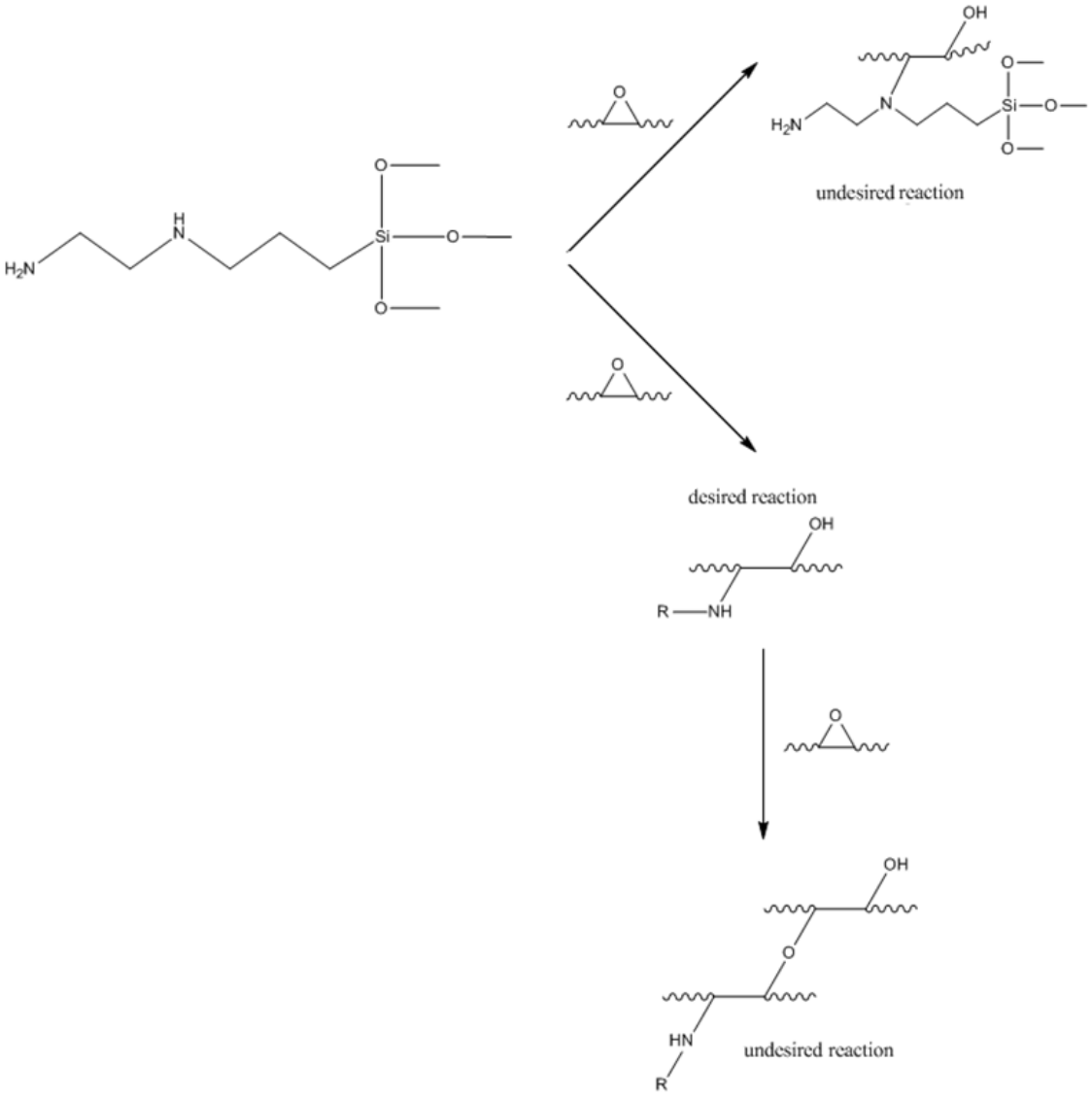


Figure 4.5. Possible amino silane reactions with epoxy group.

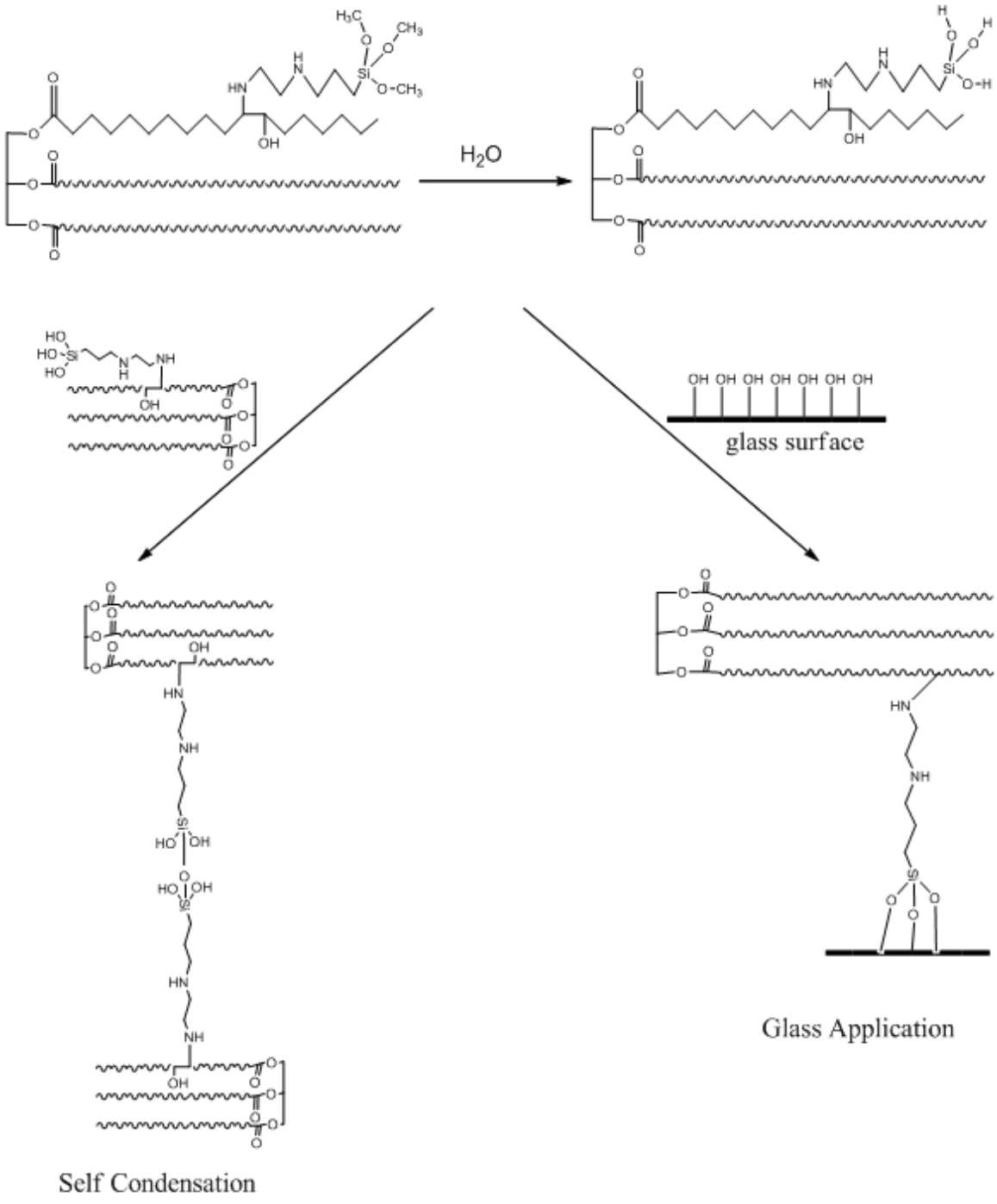


Figure 4.6. ESO-DAMO adduct self condensation and glass application.

4.2. Characterization of ESO-DAMO Adduct

After adduct reaction is complete, unreacted silane, if present, could not be separated from the adduct. With a high boiling point around 260ºC, it was not possible to remove the silane without removing water, which caused condensation of the silane groups and therefore cross linking of the material. Also extraction could not be applied because the adduct was freely soluble in most solvents, and a proper solvent for this application could not be found. Therefore the adduct was used without further purification. IR and ^{1}H NMR spectroscopy was used for characterization of the adduct in an attempt to find the reacted silane content of the adduct.

FTIR spectra were taken for ESO, DAMO, freshly mixed ESO and DAMO, and adduct. Spectra of ESO, DAMO and ESO-DAMO 2 (0.7 silane:epoxide ratio) adduct is seen in 4.7. Disappearance of epoxide rings cannot be concluded from C-O-C stretching peak because as seen in FTIR of ESO, this is a small peak at 825 cm^{-1} and it overlaps with the strong peak for amino silane at around 805-820 cm^{-1}. Another peak for epoxide is around 910-940 cm^{-1} [24] which is also a very small peak and this cannot be observed for the reacted adduct but can be seen in IR spectrum of freshly mixed reactants as in Figure 4.8. After opening of the epoxy ring, peaks corresponding to the hydroxyl groups formed could not be detected significantly.

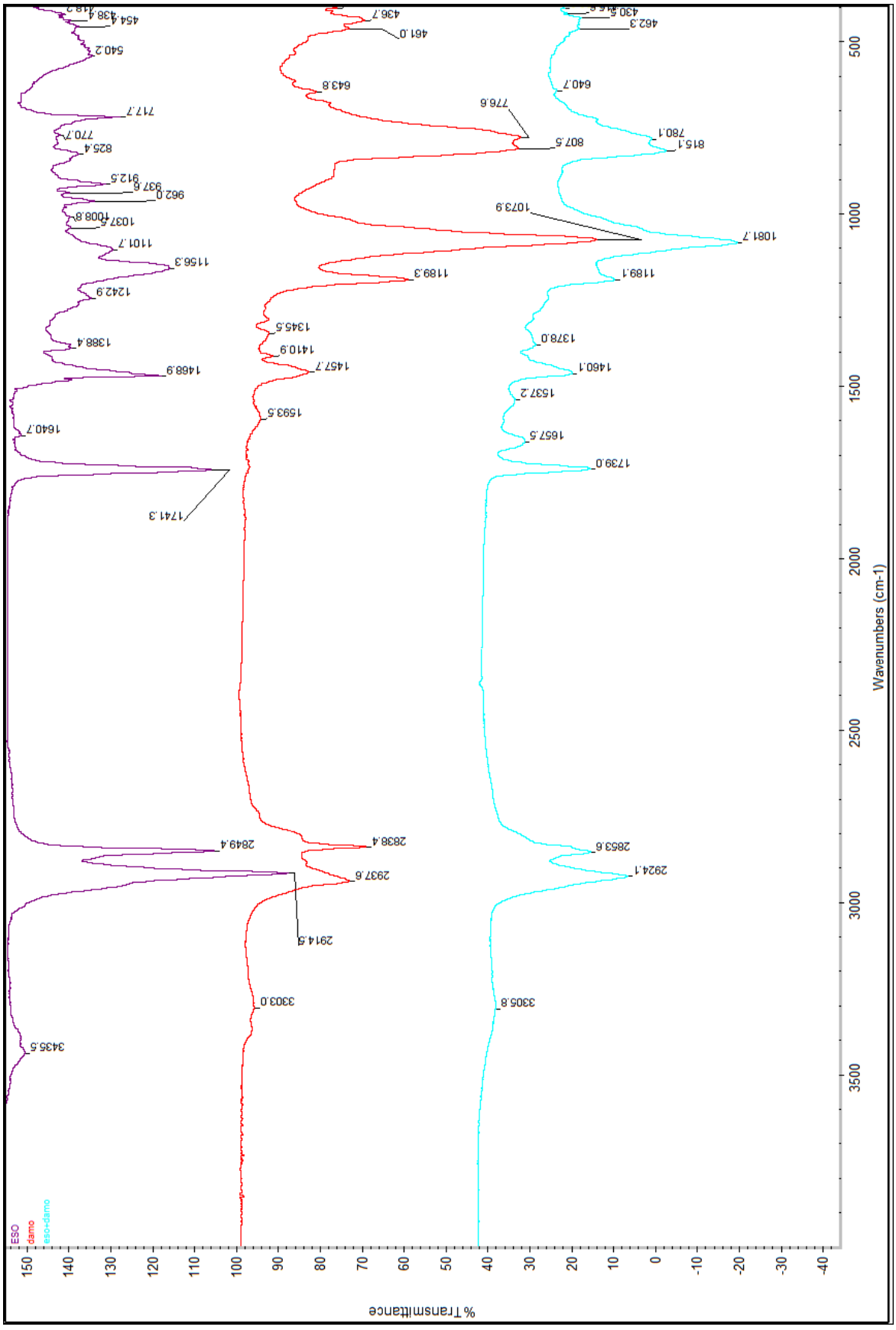


Figure 4.7. FTIR spectra of ESO, DAMO and ESO-DAMO adduct.

IR spectra of freshly mixed ESO and DAMO, and adduct 2 (0.7 silane:epoxide) can be seen in Figure 4.3. Although they are similar, after the reaction, a significant difference is that a new peak is observed at 1658 cm^{-1}. Peak at 1571 cm^{-1} is for primary amine (N-H bending) in the silane, which is converted into a secondary amine as seen at 1537 cm^{-1}.

ESO, DAMO, and also adduct prepared with 0.7 silane/epoxide ratio were analyzed with ^{1}H NMR, which can be seen in Figures 4.9 - 4.11.

Characteristic peaks for ESO (Figure 4.9) are as follows. Peak 1 at 5.25 ppm: CH proton of the glycerol unit, peak 2 at 4.0-4.3 ppm: CH2 protons of the glycerol unit, peak 3 at 3.0 ppm: epoxide protons, peak 4 at 2.2 ppm: protons α to the carbonyl group, peak 5 at 1.6: protons that are α to two epoxides, peak 6 at 1.5: protons that are α to epoxide, peak 7 at 1.2-1.3 ppm: methyl protons of the fatty acid chains, peak 8 at 0.8 ppm: terminal methyl protons of the fatty acid chains.

Table 4.1. NMR peaks for ESO.

peak #	**ppm**	**Assignation**
1	5.3	CH protons of the glycerol unit
2	4.0-4.3	CH_2 protons of the glycerol unit
3	3.0	Protons of the epoxy group
4	2.2	Protons α to the carbonyl groups
5	1.6	Protons α to the epoxy groups
6	1.5	Protons α to the epoxy groups
7	1.2-1.3	Protons of the saturated fatty acid chain
8	0.8	Protons of the terminal methyl groups of the fatty acid chain

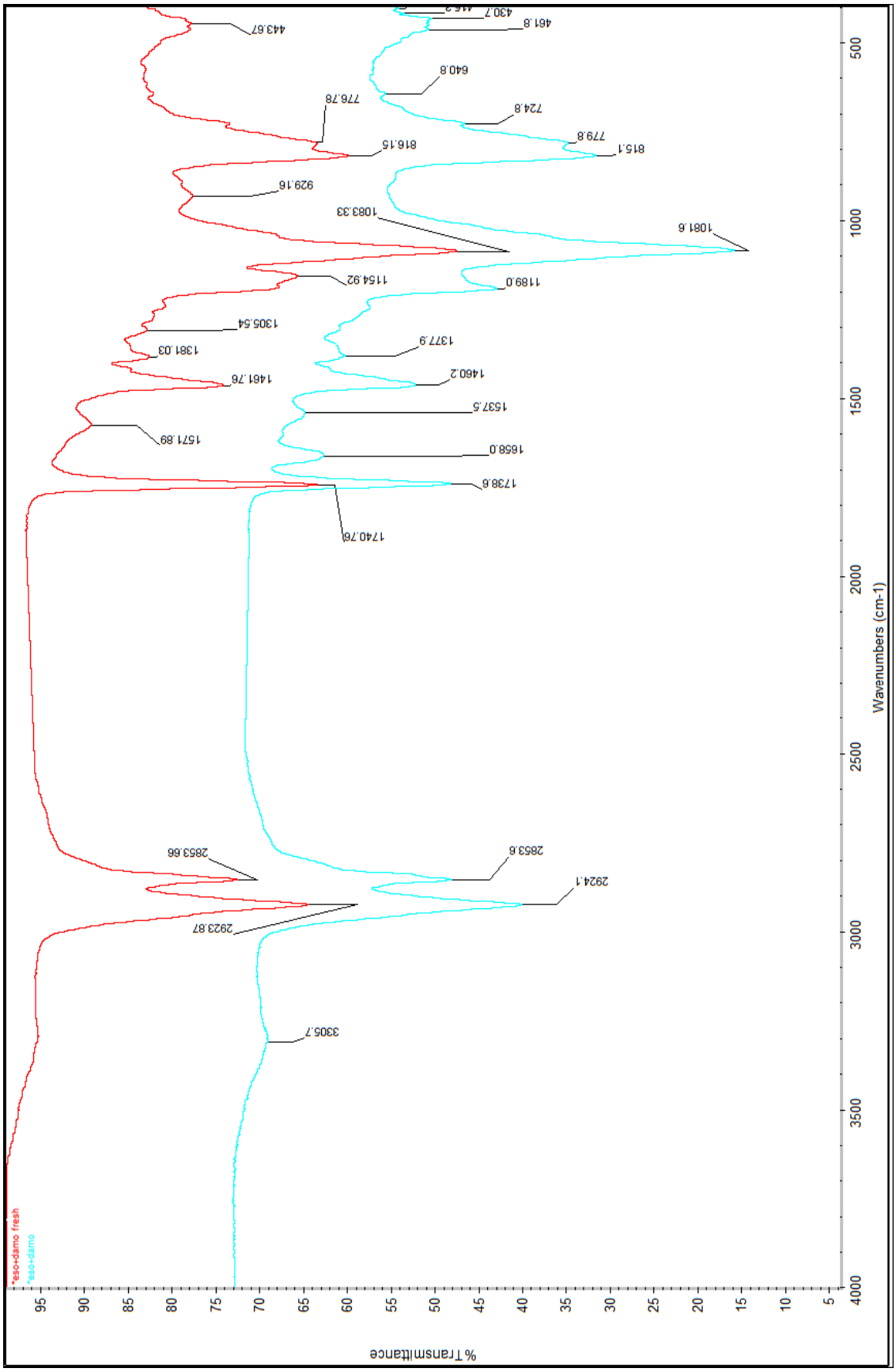


Figure 4.8. FTIR spectra of ESO-DAMO before and after reaction.

Characteristic peaks for DAMO (Figure 4.10) are as follows. Peak 1 at 3 ppm: protons of the methoxy groups, peak 2 at2.0-2.25 ppm: CH2 protons α to amines, peak 3 at1.0 ppm: CH2 proton, peak 4 at 0.6 ppm: protons α to the silane group.

Table 4.2. NMR peaks for DAMO.

peak #	**ppm**	**Assignation**
1	3.0	Protons of the methoxy groups
2	2.0-2.25	CH_2 protons α to the amine groups
3	1.0	CH2 protons
4	0.6	Protons α to the silane group

Characteristic peaks for ESO-DAMO adduct (Figure 4.11) are as follows. Peak 1 at 6.0 ppm : CH proton of the glycerol unit, peak 2 at 4.0-4.3 ppm : CH2 protons of the glycerol unit, peak 3 at 3.6: alcohol protons, peak 4 at 3.5 : reacted DAMO silane methoxy groups, methoxy protons for unreacted DAMO are 3.4 ppm, peak 5 at 3.2 ppm: the protons of CH2 of the alcohol, peak 6 at 2.5-2.7: protons that are α to amine groups, peak 7 at 2.25: protons that are α to carbonyl group, peak 8 at 1.75 : protons that are β to alcohol or amine groups, peak 9 at 1.25-1.5 ppm: methyl protons of the fatty acid chains, peak 10 at 0.8 ppm: terminal methyl protons of the fatty acid chains and peak 11 at 0.6 ppm : protons that are α to the silane group.

Table 4.3. NMR peaks for ESO-DAMO adduct.

peak #	ppm	Assignation
1	6.0	CH protons of the glycerol unit
2	4.0-4.3	CH_2 protons of the glycerol unit
3	3.6	Protons of the alcohol group
4	3.4-3.5	Protons of the methoxy group (unreacted-reacted)
5	3.2	Protons of the CH_2 of the alcohol group
6	2.5-2.7	CH2 protons α to the amine groups
7	2.3	Protons α to the carbonyl groups
8	1.8	Protons β to alcohol or amine groups
9	1.25-1.50	Protons of the saturated fatty acid chain
10	0.8	Protons of the terminal methyl groups of the fatty acid chain
11	0.6	Protons α to the silane group

Since the unreacted DAMO could not be removed by any means, the adduct should still contain ESO:DAMO in the molar ratio 1:3, which was the initial ratio of the reactants. This is calculated using peaks 10&11 corresponding to terminal methyl protons and protons α to the silane group respectively. These peaks are not expected to shift after the reaction takes place, so they can be used for calculation of the ESO and DAMO present in the reaction mixture. Area for peak 10 is 5.97 and for peak 11, it is 3.63. Peaks 10 and 11 correspond to 9 and 2 protons respectively per ESO or DAMO molecule, thus calculations show that 2,74 DAMO per ESO is present in the adduct, whether reacted or not, which is very close to 3.0.

In this study, since unreacted DAMO could not be removed, it was necessary to use NMR characterization to calculate reacted silaneper triglyceride.It is observed that protons of the methoxy groups on the silane group are split into two after the reaction, corresponding to reacted and unreacted DAMO at 3.5 and 3.4 ppm, with areas as 9.09 and 4.11 respectively, which will be used for calculations. Since both of these peaks correspond to 9 protons on the methoxy groups of the silane group, a direct calculation using the peaks are ratios, 0.69, and the DAMO:ESO ratio present in the mixture, 2.74, results in a value of 1.89 DAMO/ESO.

In another calculation method used to calculate reacted silane ratio, terminal methyl group hydrogens, and protons of the reacted DAMO methoxy groups were used for calculations which are at 0.8 ppm and 3.55 ppm respectively (peaks 4&10). Peak at 0.8 and 3.55 ppm both correspond to 9 protons per triglyceride or per silane group. Areas are found to be 9.09 for reacted silane methoxy protons and 5.97 for terminal methyl protons. Only 1.52 DAMO/ESO was calculated to be reacted, although about 3-4 epoxide rings were found to be opened, calculating from peaks 3 and 5 where both correspond to a single proton on the alcohol and the α position of the alcohol. This means that the epoxide ring also undergoes opening by ESO itself, which is expected, as explained in Section 4.1. Synthesis of ESO-DAMO Adduct and as shown in Figure 4.1.

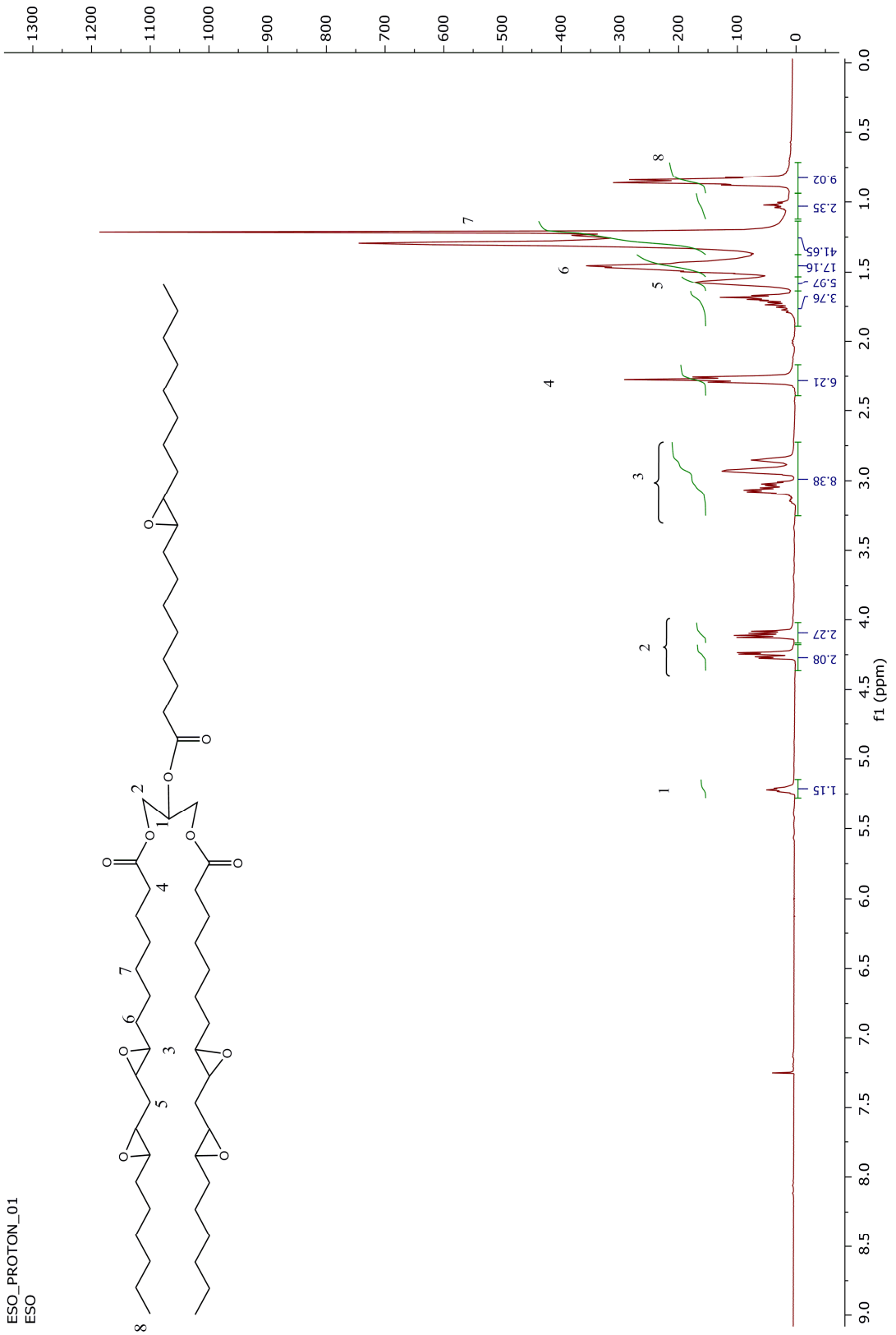


Figure 4.9. ^{1}H NMR spectrum of ESO.

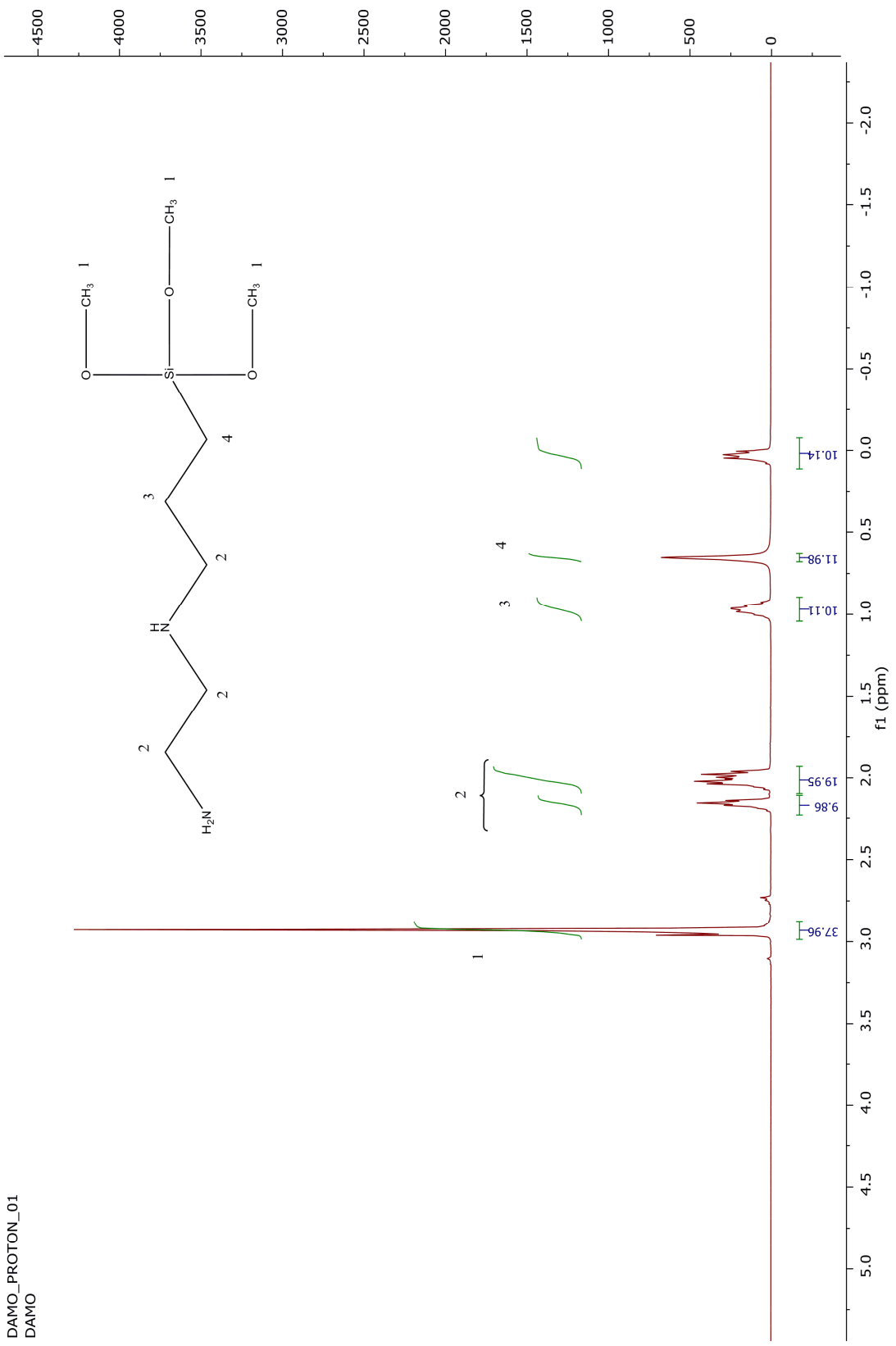


Figure 4.10. ^{1}H NMR spectrum of DAMO.

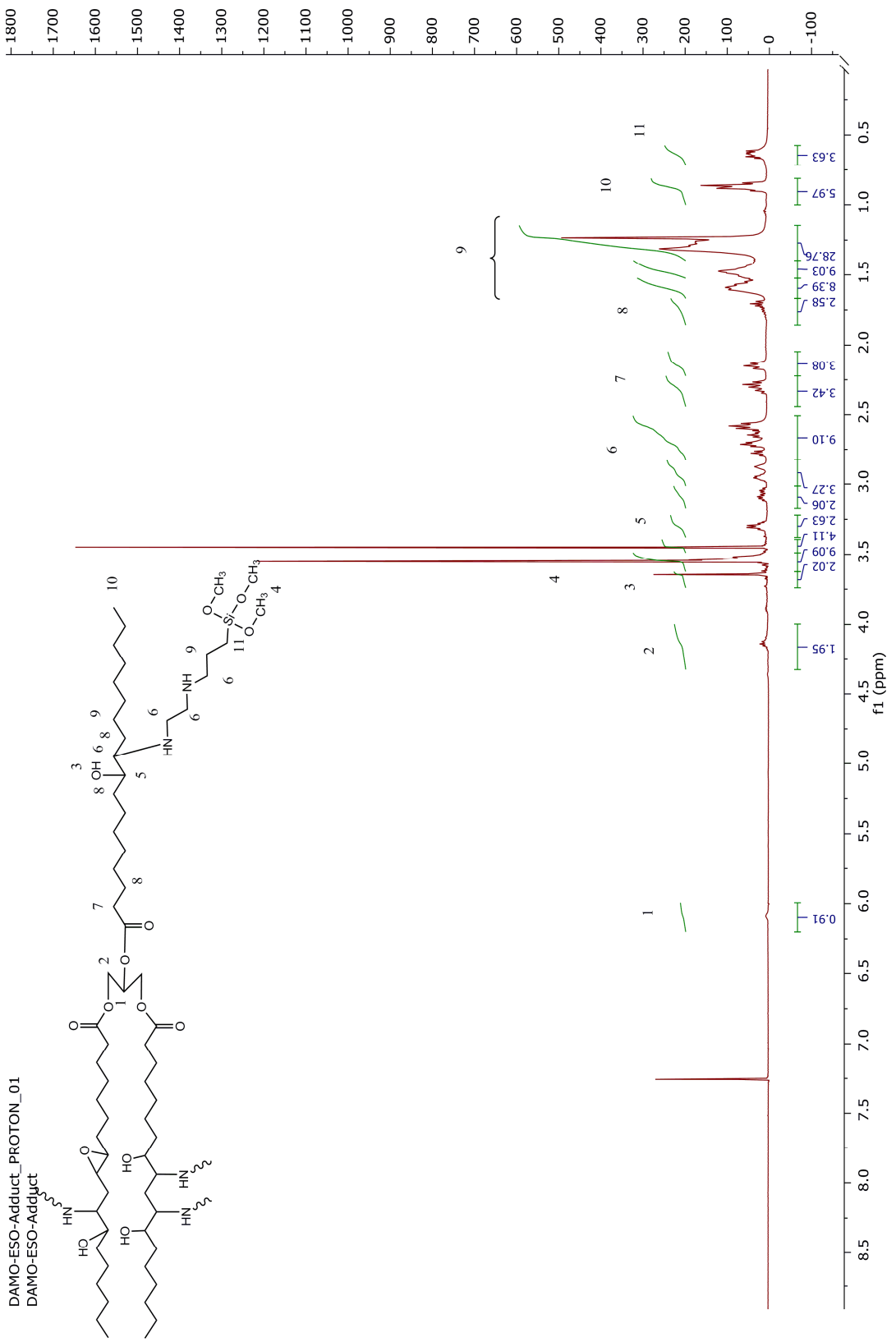


Figure 4.11. ^{1}H NMR spectrum of ESO-DAMO adduct.

4.3. Polymerization of ESO-DAMO Adduct

Inorganic reactive end of N-2-aminoethyl-3-aminopropyltrimethoxysilane, which has methoxy groups, can be easily reacted with catalytic amount of water, even the moisture in the air, and form silanols [25].

Silanols are very reactive and can react easily with hydroxyl groups on materials such as glass, metals, mica. This property makes the reaction product suitable for coupling organic and inorganic compounds with covalent bonds and constituents the most useful property of organosilanes.

The silanols also react with each other to form a cross linked matrix, which causes the adduct to homopolymerize. Small amount of secondary amines can also react with epoxides to add to the cross linking.

Since the organic end of the adduct is essentially a plant oil, it is hydrophobic and oleophilic. The main objective of this study, is to obtain a glass reactive adduct from plant oils, with coupling properties, and adhesion to glass. Treatment of glass and metals with this adduct should provide an oleophilic surface.

As both the adhesion to an inorganic surface and self condensation is caused by silanol groups, mechanical properties of self condensation polymer are improved when the silane content is higher. The cross linking ability is mostly determined by the silane content. In this work, the number of silane groups per triglyceride was found to be 1.5 for ESO-DAMO 2.

Silanol groups condense one at a time and removal of water is necessary to push the reversible reaction to the right as seen in Figure 4.12.

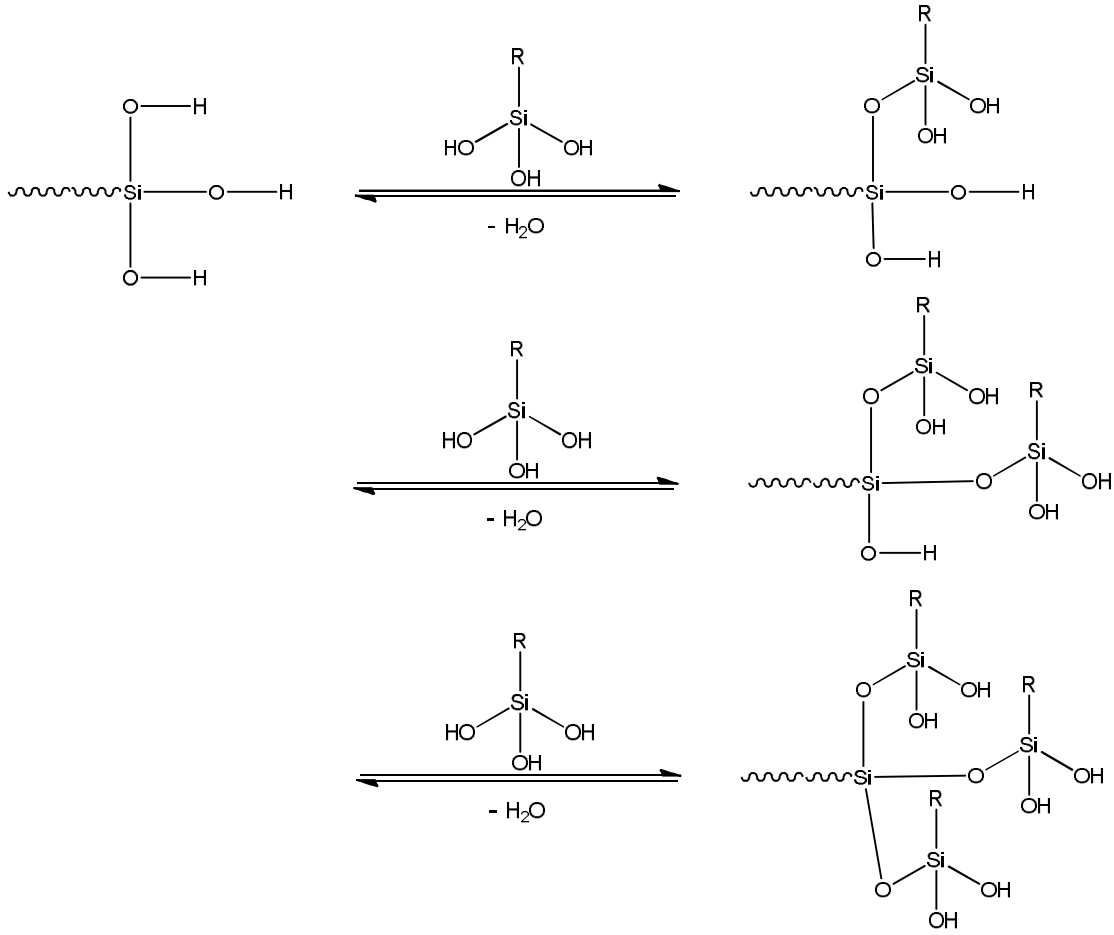


Figure 4.12. Condensation of silanol groups.

Therefore, post curing greatly increases cross-linking. This was observed for highest silane content films. The mechanical properties of molded parts, thin films, and surface coatings all improve upon removal of water by post curing. Material after postcure and material without any postcure were mixed with chloroform under vigorous stirring for 3 hours, and the solvent was then filtered through 0.45µm Nylon syringe filters and solvent was evaporated afterwards, residue amount was 1.1% for post cured film and was around 5.3% for the film that was not post cured. Residue was an oily viscous liquid with IR spectrum indicating that this is mostly silane, and adduct which was not cross linked.

Postcure temperature was chosen as 150ºC to remove water. Higher temperatures would probably be helpful, but discoloration of the adduct prevents the use of higher temperatures.

4.3.1. Homopolymerization of ESO-DAMO Adduct

Homopolymerization reaction was run in a heated open container, and the vapor in equilibrium with the reaction mixture was collected and analyzed by ^{1}H NMR in D_2O. Presence of methanol proves that silane was indeed hydrolyzed to silanol, and increased viscosity and eventual hardening of the adduct proves that polymerization takes place. ^{1}H NMR spectrum of the collected vapor can be seen in Figure 4.13. where peak at 3.36 corresponds to methanol.

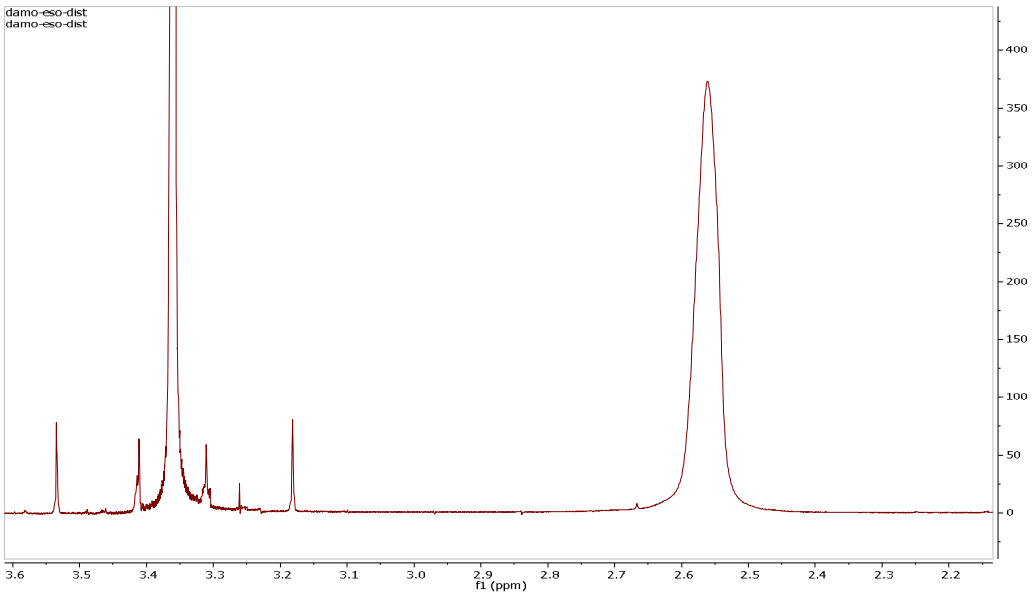


Figure 4.13. ^{1}H NMR spectrum of ESO-DAMO distillate upon polymerization.

Homopolymerized molded parts with different stoichiometric ratios, which were postcured at 150ºC for 1 hour afterwards, were analyzed with FTIR. Polymerization of the adduct causes formation of Si-O-Si bonds, where they can be observed at 1030-1050 cm^{-1}. Samples with higher silane content show a stronger peak at this region. These peaks are not present in the adduct itself. As the silane ratio increases, Si-O-Si band becomes more intense and becomes a larger peak than the ester carbonyl peak at 1740 cm^{-1}. This can be seen in Figure 4.14.

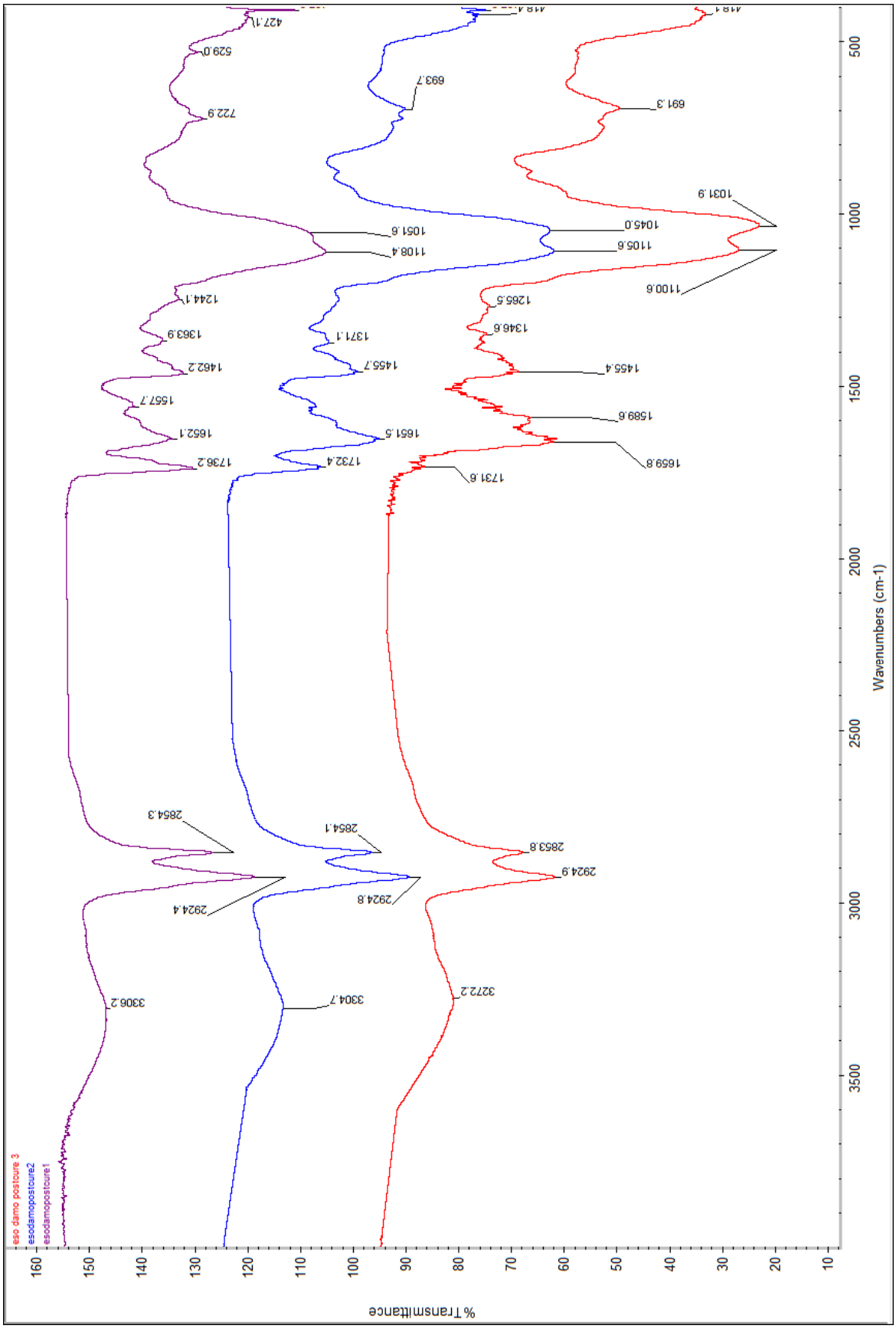


Figure 4.14. FTIR spectra of postcured parts of three different stoichiometric ratios.

4.3.2. Glass surface coating with ESO-DAMO Adduct

After thorough cleaning and removal of water droplets off of 3 mm soda glass, ESO-DAMO adduct was directly applied to the glass surface using a thin film application. The glass was cured at room temperature with ambient moisture, and after hardening, was post cured at 150ºC for 1 hour. This was done for three stoichiometric ratios. FTIR spectrums were taken and shown in Figure 4.15. For silane:epoxide 1:1 as an example, there is no significant difference in the IR of thin films from homopolymers.

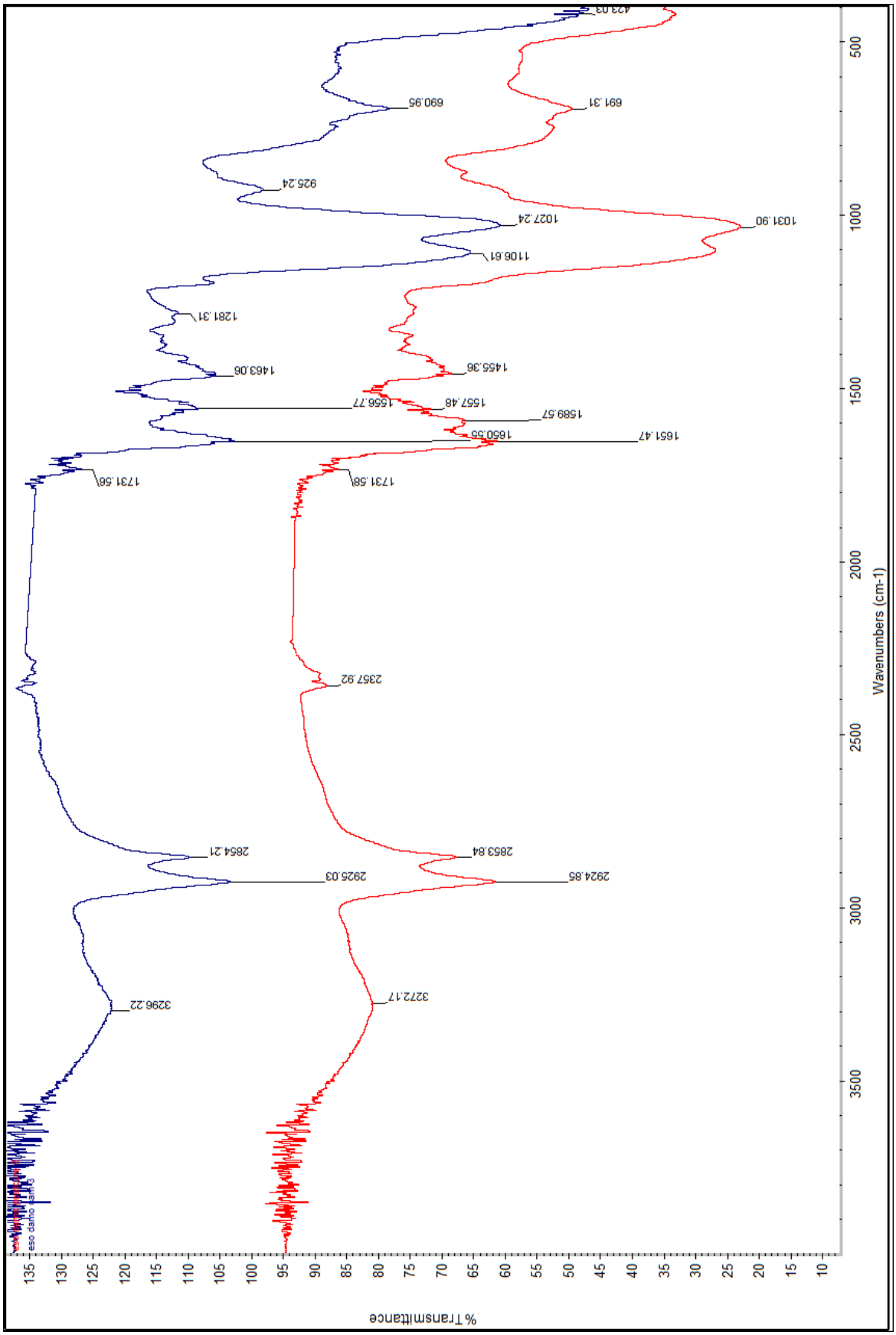


Figure 4.15. FTIR spectra of molded parts and application on glass surface.

4.4. Thermo-Mechanic Properties

4.3.1. Mechanical Properties of Molded Parts

Homopolymerized and post cured films were analyzed for tensile strength. An analytical balance was used as shown in Figure 3.2. and the results for Adduct 1, Adduct 2 and Adduct 3 are shown in Figure 4.16. High silane content (ESO-DAMO 3) was out of measurable limits of the apparatus, no further data could be obtained.

As the modulus of the material was quite low, the test could not be done with a universal testing machine.

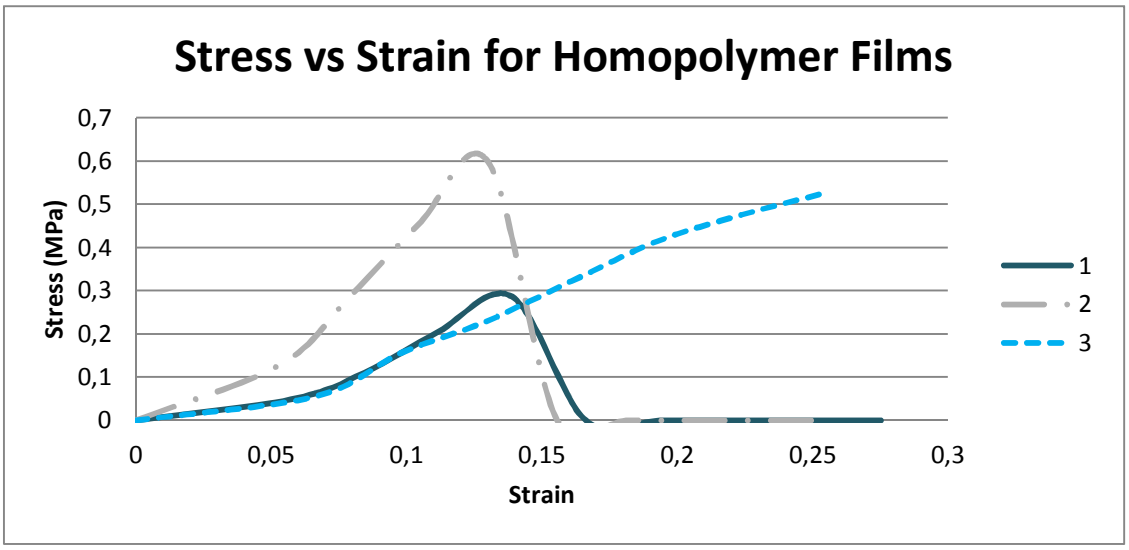


Figure 4.16. Stress vs. Strain graph for homopolymer films.

4.4.2. Dynamic Mechanical Properties of Molded Parts

Dynamic mechanical properties are the mechanical properties of materials as they are deformed under constant oscillation frequency in a range of temperature. With this test, the material can be analyzed for its moduli, elasticity, viscosity, damping behavior, and glass transition temperature.

The stress signal generated provides information such as the degree to which the material behaves as an ideal solid; and the degree to which the material behaves as an ideal fluid. These are elastic stress and the viscous stress respectively.

The ratio of the elastic stress to strain is the storage (elastic) modulus ; the ratio of the viscous stress to strain is the loss (viscous) modulus. In this study, the adduct has reactive silane groups and upon contact with moisture silanol groups are formed. Silanol groups on the adduct are then condensed to form cross-linked parts and these parts are analyzed for dynamic thermo mechanic properties. the tests were done after post cure, because parts that are not post cured are soft and have low fracture toughness. The dynamic mechanical thermal analysis of the polymer samples of the highest and lowest silane content wereperformed,dimensions of the parts were as : 18.56x10.95x4.78 mm for ESO-DAMO 1 and 18.50x12.43x5.27 mm for ESO-DAMO 3.

ESO-DAMO 2 homopolymer could not be analyzed because substrate failed due to imperfections in the part.

DMA measurements were done with TA Instrument Q800. Temperature scans were run from -50˚C to 140˚C at a heating rate of 3 ˚C /min with a frequency of 1 Hz.

Storage modulus for ESO-DAMO 3 is significantly higher than ESO-DAMO 1, i.e. almost 70%, increasing from 803 to 1361 MPa at -50ºC. This is because of a higher silane content, which causes an higher cross-linking, resulted in a more rigid polymer. Higher silane content, therefore higher crosslinking for ESO-DAMO 3 also can be concluded from glass transition temperatures (Tg) which were found to be 9.99 and 17.51ºC for ESO-DAMO 1 and ESO-DAMO 3 respectively. Due to the nature of the adduct, a polymer with

a grainy morphology is expected, this can be observed from DMA Tan δ, so it can be concluded that, cross-linking is not very homogeneous. Traces of Adduct 1 and Adduct 3 can be seen in Figure 4.17.

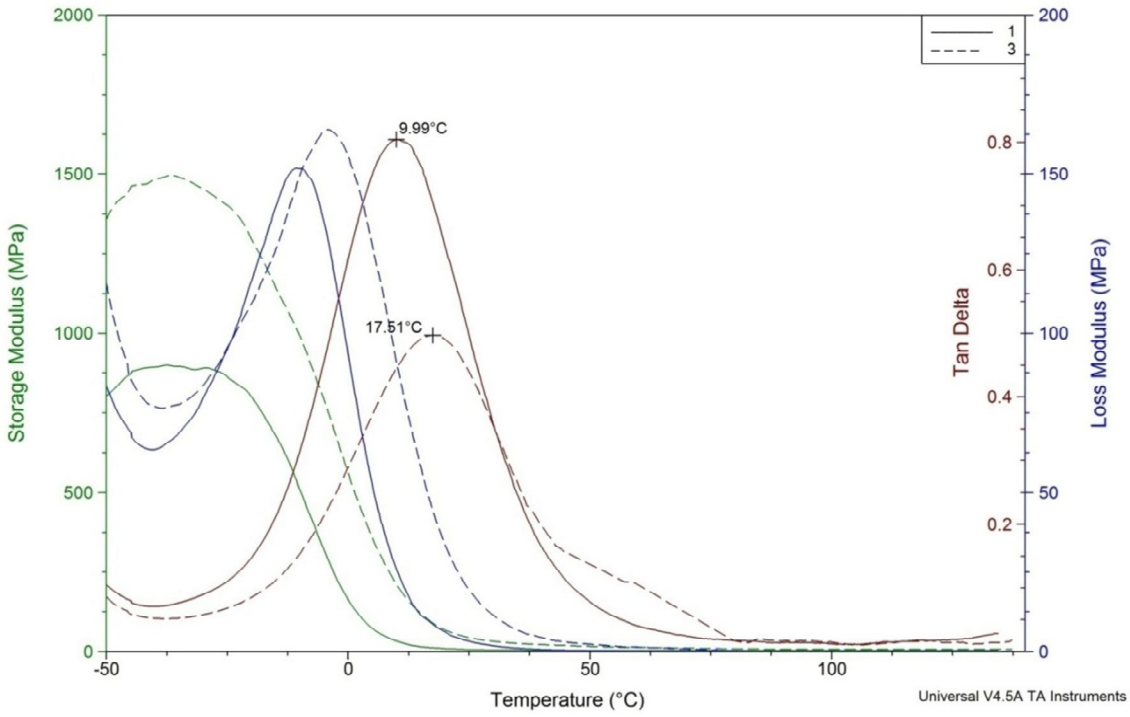


Figure 4.17. DMA traces for parts with highest and lowest silane ratio.

4.5. Use of ESO-DAMO Adduct as Glass Adhesive

Two glass surfaces of dimensions approximately 75x30x6 mm were adhered together using ESO-DAMO adduct. Devotrans DVT G21, universal testing instrument was used to perform a lap shear test on samples with similar lap areas. Adhesion of the two glass surfaces for three different stoichiometric ratios was measured. Results are shown in Figure 4.18. Adhered glass surfaces were pulled apart at a speed of 2mm/min, and separation of glass surfaces was observed. Adhesion area was kept small so that the glass would not break therefore all failures were cohesive failures. The holders for the glass surfaces were made from rubber, there is a deviation in elongation because of this. A blank steel sample of 10mm thickness was measured and the results show a slope of 977.9 N/mm with a R^2 of 0.95. Maximum stresses observed were 1.02, 1.41, 1.44 for three different stoichiometric ratios, increasing with silane content respectively.

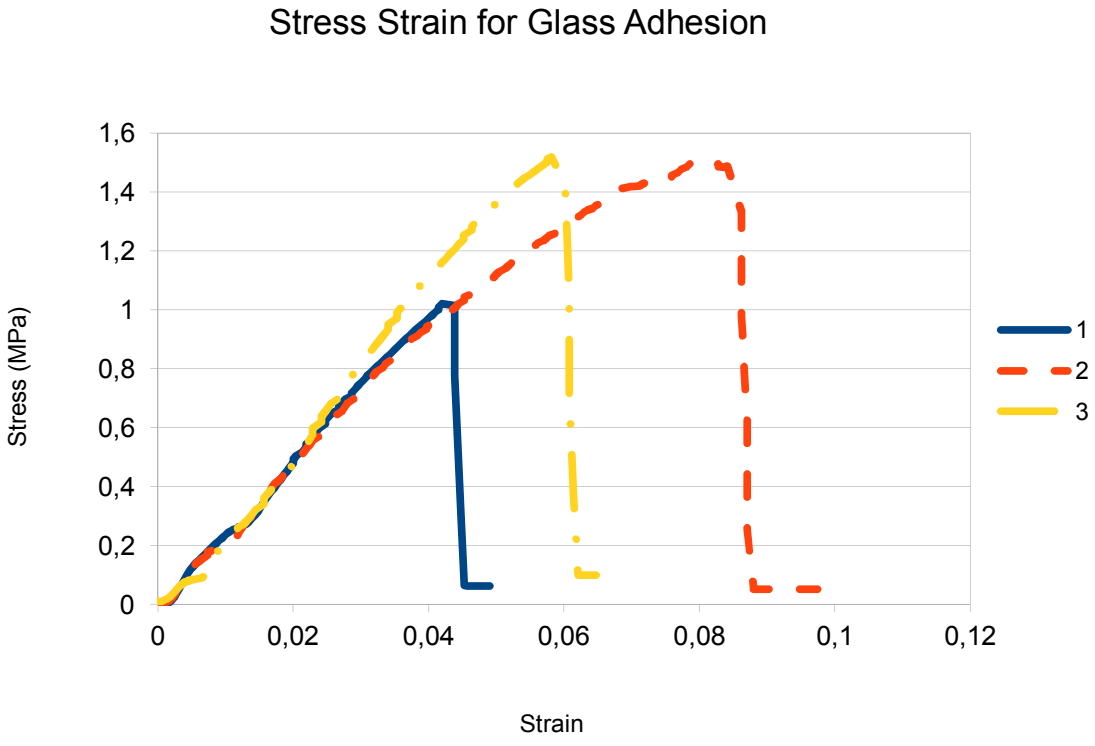


Figure 4.18. Stress vs. Strain graph for glass adhesion.

Examination of the failure surfaces showed that both pieces still had organic residue on them, indicating that cohesive failure has taken place and that adhesive forces were in fact greater than cohesive forces.

4.6. Surface Hardness Tests

Surface Hardness of polymerization on glass surface for 3 different stoichiometries of 50 µm thickness were measured by pendulum hardness. Average from three different readings from each glass surface was taken into account. Results are 40, 43 and 57 kj/m^2 respectively for three different stoichiometric ratios, increasing with silane content which can be seen in Figure 4.19.

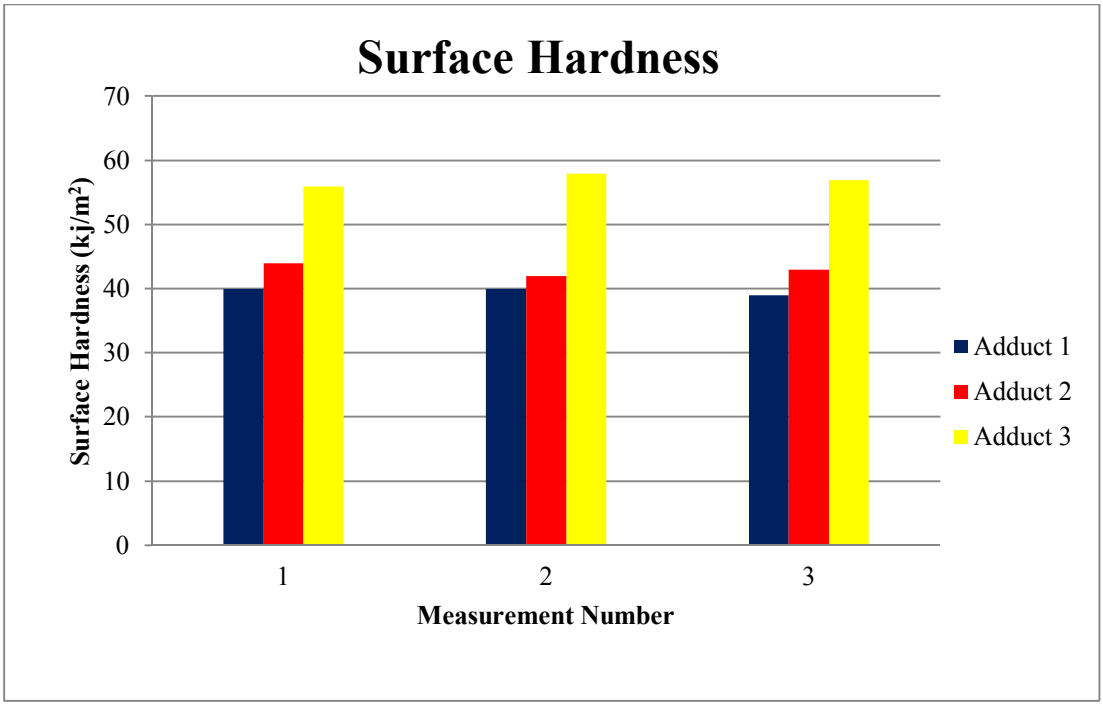


Figure 4.19. Surface hardness graph.

As silane content increases surface hardness increases, which indicates higher silane content causes higher crosslinking, therefore a harder surface.

4.7. Contact Angle Tests

Contact angle of water on glass surface coated with ESO-DAMO adduct were measured by using KSV Instruments CAM 101 instrument. Contact angles were measured by the sessile drop method using water at room temperature. After postcure at 150ºC for 1 hour, thickness of the coating was 50 µm thick. A total of 5 drops were applied to each surface treated with adducts with three different stoichiometries. Average results are found to be 45.6º, 53.0º, and 81,6º respectively for three different stoichiometric ratios, increasing in silane content. Contact angle data from drops of n-octane could not be measured, as the drop of n-octane wetted and dissolved in the sample immediately.

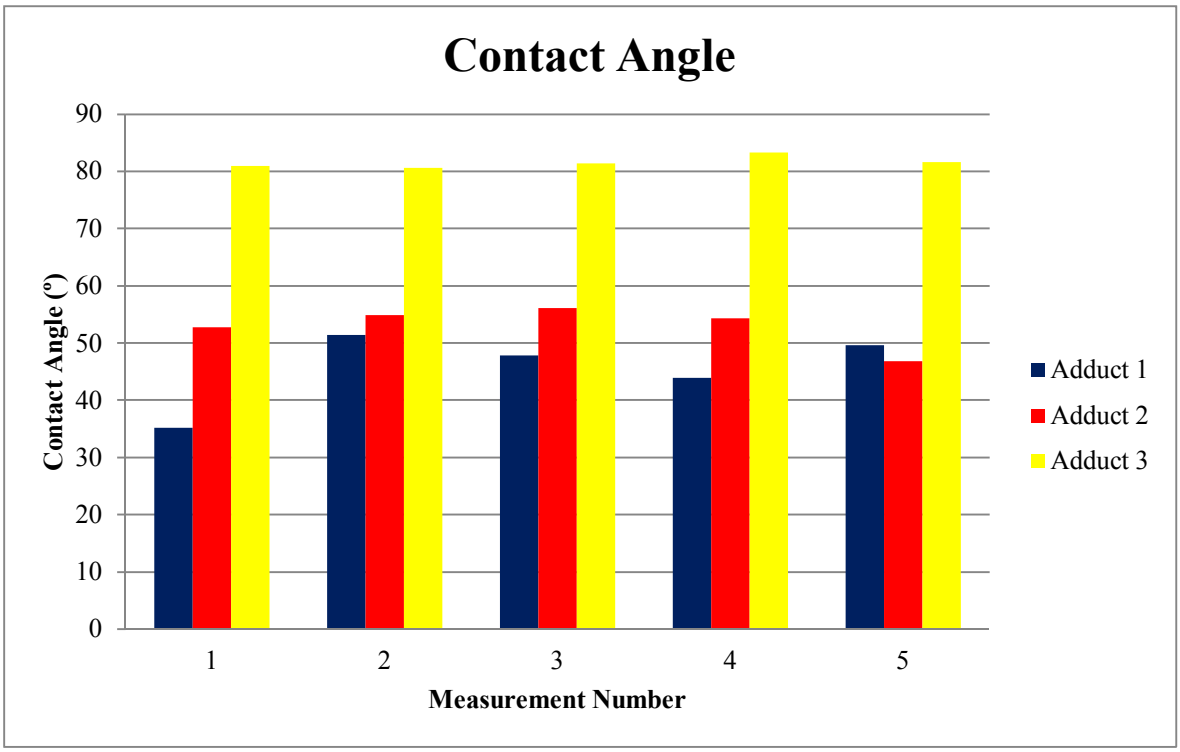


Figure 4.20. Contact angle graph.

Contact angle results show that as silane content increases, hydrophobicity is improved. This is because with higher silane content, adduct is condensed with the glass surface more homogeneously, and cross linking is higher so that the water drop cannot contact the glass surface. This can also be seen in the Figure 4.20., for ESO-DAMO1

precision is very low for contact angle measurement, which suggests an unhomogeneous surface, but for ESO-DAMO 3 results are very close, suggesting an homogeneous coating of the surface.

4.8. Swelling Test

A solvent can diffuse through the cross-linked polymer, and instead of dissolving the polymer, causes swelling. Swelling ratio helps determine the crosslinking density of a polymer. A low swelling ratio should indicate a high cross-link density.

Postcured molded parts for ESO-DAMO 2 were investigated for swelling tests. Although the adduct was freely soluble in a number of solvents, no significant swelling was observed for water, acetone, n-butanol, ethanol, toluene, perchlorethylene, pentane, petroleum ether, water, methanol, acetonitrile, dimethylformamide, 2-propanol, hexane, and xylene. Temperature was increased in order to promote diffusion but there was no significant swelling.

For chloroform, the material would disintegrate upon long exposure. Swelling was not measured with a travelling microscope because although the material grew in size, many cracks formed in the part made from the adduct in presence of water, 2-propanol and acetic acid and material crumbled on the sides and accurate results could not be obtained. However approximate measurements showed that ESO DAMO 3, with highest silane ratio, grew in volume about 24% in 1 hour, 39 % in 2 hours and swelling stopped after this For ESO-DAMO 1 and ESO-DAMO 2 material crumbled in 1 hour so no data could be obtained. For films homopolymerized directly from the adduct, measurements were not taken with a travelling microscope but with calipers. Results are as in Figure 4.21. The film disintegrated in 2hours for ESO-DAMO-1, no visible cracks were observed for ESO-DAMO 2 and ESO-DAMO 3 but material crumbles on the sides by a little amount. Volume approximations were derived from length, assuming the swelling was equal for all dimensions.

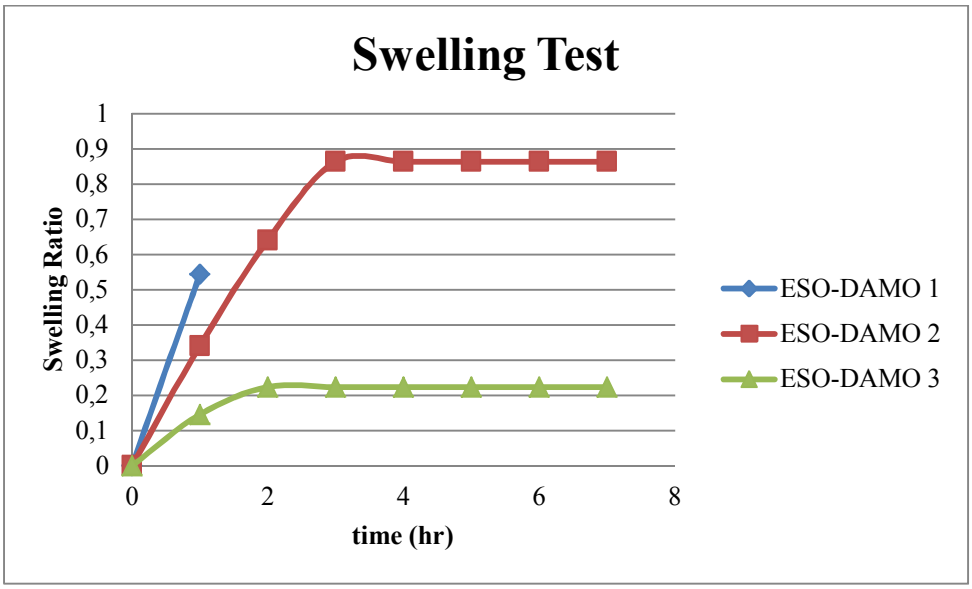


Figure 4.21. Swelling test results.

The non uniform swelling behavior and fragmentation suggests that connectivity is not homogeneous. The sample consists of highly cross linked zones connected to each other by few tie segments. Such polymers show low fracture toughness and tear resistance and are prone to disintegration in good solvents. Figure 4.22. shows a typical molecular architecture that fits above description.

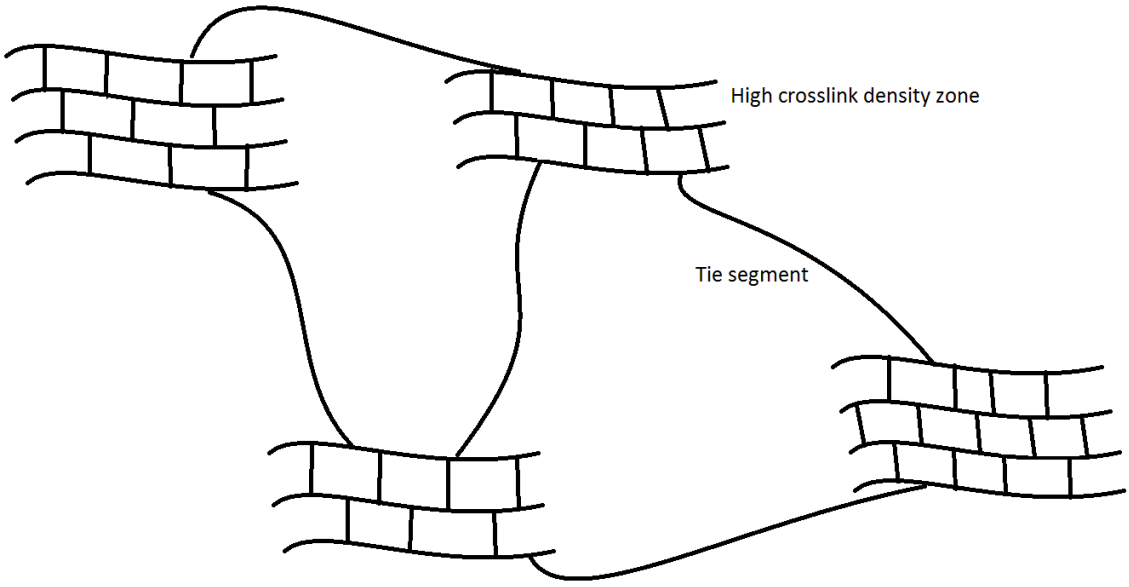


Figure 4.22. Grainy morphology of polymers.

5. CONCLUSIONS

In this study, an adduct, which is basically a monomer with different functionalities was synthesized by reacting epoxidized soybean oil with N-2-aminoethyl-3-Aminopropyltrimethoxysilane. The chemical characterization of this monomer was done with NMR and FTIR spectroscopy.

ESO-DAMO reaction product was homopolymerized at room temperature, with ambient moisture, or with addition of catalytic amount of water into the adduct where the ambient moisture would not diffuse to the depth of the part in case of thick parts, to form films and parts and was also polymerized on glass surface. Dynamic thermal mechanical properties of the parts were analyzed by DMA and stressvs. Strain was measured for the films using an analytical balance. Mechanical properties on glass surface were measured by surface hardness tests and contact angle measurements. Also adhesion properties on glass were observed by lap shear tests. All results show that as the silane ratio in the adduct increase, mechanical and adhesion properties improve, due to higher crosslink density.

The compound synthesized in this study acts as an excellent coupling agent. However it is not good for polymerization into molded parts due to very long curing time to allow diffusion of side products formed during polymerization, such as water and methanol without forming bubbles. This molecule can be used in many composites where the fillers are an inorganic silica based material and the matrix is an organic polymer. Also, this adduct will enable to change surface properties of inorganic materials, where they can be made hydrophobic and oleophilic to be used in different applications. ESO-DAMO adduct can also be used as a glass adhesive, which is very strong and clear, adhering two flat surfaces.

The large triglyceride in the structure of ESO-DAMO provides a flexible and hydrophobic interface so that water ingress into the interface should be minimized.

The fact that ESO-DAMO adduct includes a plant oil based triglyceride, which is a non-petroleum, renewable resource, also makes the adduct and its polymers easily biodegradable [26].

REFERENCES

1. Lligadas, G., J.C., Ronda, M.,Galià, V., Cádiz, "Renewable Polymeric Materials from Vegetable Oils: a Perspective" *Materials Today*, Vol. 16, No. 9, pp. 337–343, 2013.

2. Prashantha, K., K. K. P., Vasant, B.S., Sherigara, S., Prasannakumar, "Interpenetrating Polymer Networks Based on Polyol Modified Castor Oil Polyurethane and Poly(2-hydroxyethylmethacrylate): Synthesis, Chemical, Mechanical and Thermal Properties", *Bulletin of Material Science*, Vol. 24, No. 5, pp. 535–538, 2001.

3. Belgacem, M.N., A.Gandini, *Monomers, Polymers and Composites from Renewable Resources*, Elseiver, Amsterdam, 2008

4. Khot, S.N., J.J., Lascala, E.,Can, S.S., Morye, G.I., Williams, G.R., Palmese, S.H., Kusefoglu, R.P., Wool, "Development and Application of Triglyceride-Based Polymers and Composites", *Journal of Applied Polymer Science*, Vol. 82, No. 3, pp. 703–723, 2001.

5. Güner, F.S., Y.,Yağcı, A.T., Erciyes, "Polymers from Triglyceride Oils", *Progress in Polymer Science*, Vol. 31, No. 7, pp. 633–670, 2006.

6. Shahidi F., *Bailey's Industrial Oil and Fat Products*, John Wiley & Sons, New Jersey, 2005.

7. Brackman, B., J., Knaut, *Oleochemicals*, Henkel KGaA, Dusseldorf ,1984.

8. Montero de Espinosa, L., M. a. R., Meier, Plant oils: "The Perfect Renewable Resource for Polymer Science" *European Polymer Journal,* Vol. 47, No. 5, pp. 837–852, 2011.

9. Khot, S., S., Kusefoglu, G., Palmese, R., Wool, R., Zhao,"High Modulus Polymers and Composites from Plant Oils" 2000. http://www.google.com.tr/patents/US6121398, [Accessed May 2012].

10. Rios, L., P., Weckes, H., Schuster, W., Hoelderich, "Mesoporous and Amorphous Ti–silicas on the Epoxidation of Vegetable Oils". *Journal of Catalysis,* Vol. 232, No. 1, pp. 19–26, 2005.

11. Sharpless, K., S., Woodard, M., Finn, "On the Mechanism of Titanium-tartrate Catalyzed Asymmetric Epoxidation" *Pure and Applied Chemistry,* Vol. 55, No. 11. pp. 1823–1836, 1983.

12. Chadwick, S.S. *Ullmann's Encyclopedia of Industrial Chemistry*, John Wiley and Sons, Inc. Weinheim 1988.

13. Wicks, Z.W. *Organic Coatings: Science and Technology*, John Wiley & Sons, New Jersey, 2007.

14. Hammarling, L., H., Gustavsson, K., Svensson, S., Karlsson, A., Oskarsson, "Migration of Epoxidized Soybean Oil (ESBO) from PVC Gaskets into Baby Food", 2005. www.vwa.nl/txmpub/files/?p_file_id=10406 [Accessed March 2014].

15. Hwang, H. S., S.Z., Erhan,: "Synthetic Lubricant Basestocks from Epoxidized Soybean Oil and Guerbet Alcohols" *Industrial Crops Products,* Vol. 23, No. 3, pp. 311–317, 2006.

16. Luo, A., X., Jiang, J., Yin, "Thioxanthone-Containing Renewable Vegetable Oil as Photoinitiators" *Polymer*, Vol. 53, No. 11, pp. 2183–2189, 2012.

17. Bakhshi, H., H.,Yeganeh, S., Mehdipour-Ataei, M.A.,Shokrgozar, A.,Yari, S.N., Saeedi-Eslami, "Synthesis and Characterization of Antibacterial Polyurethane Coatings from Quaternary Ammonium Salts Functionalized Soybean Oil Based Polyols", *Materials Science and Engineering: C*, Vol. 33, No. 1, pp. 153–164, 2013.

18. Çolak, S., S.H., Küsefoğlu, "Synthesis and Interfacial Properties of Aminosilane Derivative of Acrylated Epoxidized Soybean Oil" *Journal of Applied Polymer Science*, Vol. 104, No. 4, pp. 2244–2253, 2007.

19. Plueddemann, E.P., *Silane Coupling Agents*, Plenum, New York and London, 1991.

20. Marsden, J.G., L.P., Ziemianski, "Organofunctional Silanes Functions, Applications and Advantages", B*ritish Polymer Journal*, Vol. 11, No. 4, pp. 199–205, 1979.

21. Salamone, J.C., *Polymeric Materials Encyclopedia, Twelve Volume Set*, CRC Press, Ann Arbor, 1996.

22. Liu, Z.S., S.Z., Erhan, P.D., Calvert, "Solid Freeform Fabrication of Epoxidized Soybean Oil/Epoxy Composite with bis or Polyalkyleneamine Curing Agents" *Composites Part A: Applied Science and Manufacturing*, Vol. 38, No. 1, pp. 87–93, 2007.

23. Padma, A., R., Rao, "Cure characterization of triglycidyl epoxy/aromatic amine systems". *Journal of Applied Polymer Science*, Vol. 57, No. 4, pp. 401–411, 1995.

24. Banthia, A.K. "A New Method for High Pressure Epoxidation of Unsaturated Compound Using Molybdenumdisulphide as a Catalyst", *Indian Journal of Chemical Technology*, Vol. 6, No. 5, pp. 285–287, 1999.

25. Witucki, G.L. "Back to Basics A Silane Primer : Chemistry and Applications of AIkoxy Silanes", *Journal Of Coatings Technology,* Vol. 65, No. 822, pp. 57-60, 1992.

26. Doğan, E., Küsefoğlu, S. "Synthesis and in-situ Foaming of Biodegradable Malonic Acid ESO Polymers", *Journal of Applied Polymer Science*, Vol. 110, No. 2, pp. 641-1279, 2008.