SYNTHESIS AND INTERFACIAL PROPERTIES OF ORGANOSILANE DERIVATIVE OF ACRYLATED SOYBEAN OIL

by

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B.S., Chemistry, Boğaziçi University, 2004

Submitted to the Institute for Graduate Studies in
Science and Engineering in partial fulfillment of
the requirements for the degree of
Master of Science

Gradute Program in Chemistry
Boğaziçi University
2006

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To My Family

ACKNOWLEDGEMENTS

I would like to acknowledge my most sincere gratitude to my thesis supervisor Prof. Selim H. Küsefoğlu for his endless attention, most valuable encouragement and scientific guidance throughout this study. I greatly appreciate his support and help he has supplied for my further studies. It was an invaluable experience for me to work with him.

I wish to express my appreciation to Prof. Nihan Nugay, for sharing her ideas, most valuable comments during this study, and her careful and constructive review of the final manuscript. I would also thank to Prof. Sabri Altıntaş for reviewing the final manuscript and making helpful comments.

I would like to express special thanks to Gökhan Çaylı, Aylin Ziylan, Sinan Şen, and Ayla Türkekul for their help in obtaining TGA, DSC, DMA and NMR spectra. I would like to express my greatest thanks to all the members of the faculty.

My special thanks go to Gonca Şeber and Zeynep Saraylı, for their friendship and enjoyable company. I also would like to thank to all my friends in the Chemistry Department for their support and friendship.

Finally my deepest thank and love goes to my mother, my father, and my sister, for their continuous moral support, their love, and encouragement throughout these years.

ABSTRACT

SYNTHESIS AND INTERFACIAL PROPERTIES OF ORGANOSILANE DERIVATIVE OF ACRYLATED SOYBEAN OIL

In this study silanized Acrylated Epoxidized Soybean Oil (AESO), a multifunctional monomer was synthesized by reacting Acrylated Epoxidized Soybean Oil with 3-Aminopropyltriethoxysilane via Michael Addition Reaction. The characterization of silanized-AESO was done by NMR spectroscopy. Homopolymer of silanized-AESO was synthesized by using benzoyl peroxide as radical initiator. The silanized-AESO homopolymer was characterized by IR spectroscopy. Improvements in the adhesion upon moisture cure and the effect of prolonged exposure to moisture on interfacial bonding on glass surface of silanized-AESO homopolymer were analyzed according to standard ASTM D 4541 Pull-Off Adhesion Test. After moisture curing process, an approximate of eight fold improvement was observed in the adhesion strength. Prolonged exposure to humidity for 48 hours caused to approximately 15 per cent decrease in the adhesion strength. Silanized-AESO was copolymerized with styrene in 1:1 weight ratio via radical polymerization. 2,2'-azobis(isobutyronitrile) (AIBN) was used as radical initiator. The effect of increased crosslink density upon moisture cure on the mechanical properties of silanized – AESO – styrene copolymer was analyzed by DMA (Dynamic Mechanical Analysis), DSC (Differential Scanning Calorimetry),TGA (Thermal Gravimetric Analysis), swelling, and surface hardness tests. Upon moisture cure 35 per cent improvement was observed in the storage modulus due to the increase in the crosslink density. According to tan δ curves and surface hardness tests, silanized-AESO-styrene copolymer shows heterogeneous morphology in crosslinked areas.

ÖZET

AKRİLATLANMIŞ SOYA YAĞININ ORGANOSİLAN TÜREVİNİN SENTEZİ VE ARAYÜZEY ÖZELLİKLERİ

Bu çalışmada, Akrilatlanmış Epokside Soya Yağı (AESO) ve 3-Aminopropilretoksisilan'un Michael reaksiyonu yolu ile silanlanmış Akrilatlanmış Epokside Soya Yağı sentezlenmiştir. Silanlanmış-AESO'nun karakterizasyonu NMR spektroskopi kullanılarak yapılmıştır. Silanlanmış-AESO serbest radikal başlatıcı benzoil peroksit ile polimerize edilmiştir. Silanlanmış-AESO homopolimeri FTIR spektroskopi kullanarak karakterize edilmiştir. Silanlanmış-AESO homopolimerinin, nem kürü sonrası ve 48 saat yüzde 92 rutubetli ortama maruz kalması sonucunda adezyon kuvvetindeki değişim ASTM 4541 çekme adezyon standart testine göre analiz edilmiştir. Nem kürü sonrası adezyon kuvvetinde ortalama sekiz kat artış gözlemlenmiştir. Rutubetli ortama maruz bırakılan homopolimerin adezyon kuvveti yüzde 15 azalmıştır. Silanlanmış-AESO, stiren ile 1:1 oranında kopolimerize edilmiştir. Radikal başlatıcı olarak 2,2'-azobis (isobutironitril) (AIBN) kullanılmıştır. Nem kürü sonrası çapraz bağlardaki artışın silanlanmış-AESO stiren kopolimeri üzerindeki etkisi dinamik mekanik analiz (DMA), diferansiyel taramalı kalorimetre (DSC),termal gravimetrik analiz (TGA), çözücüde şişme ve yüzey sertliği yöntemleri ile incelenmiştir. Nem kürü sonrası, çapraz bağlardaki artışa bağlı olarak depolama modülünde yaklaşık olarak yüzde 35'lik bir artış gözlenmiştir. Tan δ eğrileri ve yüzey sertliği deneylerinin sonuçlarına göre, silanlanmış-AESO stiren kopolimerinin çapraz bağlarda heterojen morfoloji göstermektedir.

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LIST OF SYMBOLS/ ABBREVIATIONS

AESO	Acrylated Epoxidized Soybean Oil
AIBN	2,2'-azobis (isobutyronitrile)
ASTM	American Society for Testing and Materials
DMA	Dynamic Mechanical Analysis
DSC	Differential Scanning Calorimetry
DVB	Divinyl Benzene
E'	Storage Modulus
E''	Loss Modulus
ESO	Epoxidized Soybean Oil
Hz	Hertz
IR	Infrared
KPa	Kilo Pascal
MA	Maleic Anhydride
MPa	Mega Pascal
NMR	Nuclear Magnetic Resonance
PA	Polyacrylate
PVC	Polyvinylchloride
Tg	Glass Transition Temperature
TGA	Thermal Gravimetric Analysis

1. INTRODUCTION

1.1. Renewable Resources

The prevailing raw material used in synthesis of polymeric materials has been petroleum for the last 50 years. The depletion in the reserves and the increase of the petroleum price has driven the chemical industry to search for new resources. Among different kinds of available resources renewable ones, which have ways of regenerating themselves as they are depleted are mostly preferred by the industry. Due to the wide variety of possibilities for chemical applications and availability all around the world, oils and fats of vegetable and animal origin are preferred by the chemical industry as an alternative.

The application areas of oils and fats in the chemical industry are summarized in the following table [1]:

Table 1.1. Areas of application of oils and fats industry [1]

Fatty acids and derivatives	Plastics, metal soaps, washing and cleaning agents, soaps, cosmetics, alkyd resins, dyestuffs, textile, lather and paper industries, rubbers, lubricants
Methyl esters of fatty acids	Cosmetics, washing and cleaning agents
Glycerol and derivatives	Cosmetics, toothpastes, pharmaceuticals, foodstuffs, lacquers, plastics, synthetic resins, tobacco, explosives, cellulose processing
Fatty alcohol and derivatives	Washing and cleaning agents, cosmetics, textile, lather and paper industries, mineral oil additives
Fatty amine and derivatives	Fabric conditioners, mining, road-making, biocides, textile and fiber industries, mineral oil additives
Drying oils	Lacquers, dyestuffs, varnishes, linoleum
Natural oils derivatives	Soaps

In addition to these application areas, load bearing, high-tech, durable polymers can also be synthesized from natural plant oils.

1.2. Plant Oils

1.2.1. Chemical Structure of Plant Oils

Plant oils are composed of three fatty acid chains joined by a glycerol unit. The fatty acids may be saturated or may contain one, two or three unsaturations. The double bonds are isolated and in the cis geometry. The length of the fatty acid chains vary from 14 to 22 carbons. There are also some rare triglycerides containing unusual functionalities, such as hydroxyls, epoxies, cyclic groups, and furanoid groups.

Figure 1.1. shows the general representation of a triglyceride molecule. R groups represent long alkyl chains with varying functionalities. The functionality of the fatty acid vary depending on the type of plant from which the oil is obtained.

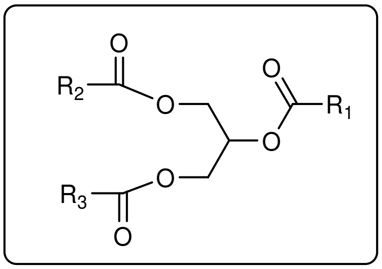


Figure 1.1. General structure of a triglyceride

1.2.2. Composition of Plant Oils

The fatty acid distribution changes from plant to plant. Table 1.2. shows the composition of common oils. The first column of the table shows the ratio of the number of carbons (#C) and number of double bonds (#DB) in the fatty acid.

Table 1.2. Fatty acid percentages in various plant oils [2]

#C: #DB	Corn	Cottonseed	Linseed	Olive	Palm	Soybean
14:0	0.1	0.7	0.0	0.0	1.0	0.1
14:1	0.0	0.0	0.0	0.0	0.0	0.0
16:0	10.9	21.6	5.5	13.7	44.4	11.0
16:1	0.2	0.6	0.0	1.2	0.2	0.1
18:0	2.0	2.6	3.5	2.5	4.1	4.0
18:1	25.4	18.6	19.1	71.1	39.3	23.5
18:2	59.6	54.4	15.3	10.0	10.0	53.2
18:3	1.2	0.7	56.6	0.6	0.4	7.8
20:0	0.4	0.3	0.0	0.9	0.3	0.3
20:1	0.0	0.0	0.0	0.0	0.0	0.0
20:2	0.0	0.0	0.0	0.0	0.0	0.0
22:0	0.1	0.2	0.0	0.0	0.1	0.1
22:1	0.0	0.0	0.0	0.0	0.0	0.0
24:0	0.0	0.0	0.0	0.0	0.0	0.0

As it is seen from the Table 1.2. oils are composed of different types of triglycerides, with different values of unsaturation. But with the recently developed genetic engineering techniques the variation in unsaturation can be controlled in plants such as flax, corn and especially soybean.

1.3. Soybean Oil

1.3.1. Composition of Soybean Oil

Soybean is one of the oldest crops cultivated by humans. It is grown in over 50 countries, but mostly in the USA, China, Brazil and Argentina.

Soybeans can be safely stored at 12% moisture without any noticeable increase in free fatty acids. They have an oil content of 18-22%. But, nowadays, with improvements in genetic engineering, oil content is being increased form 18 to 38%.

Crude soybean oil can be obtained by pressing the bean or by hexane extraction. Soybean oil shows wide variation in composition, but is mainly composed of triglycerides of oleic and linoleic acids [3].

Table 1.3. Structure and composition of fatty acids in soybean oil

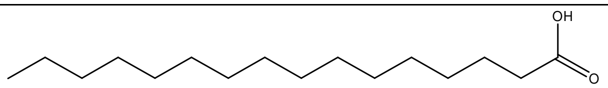
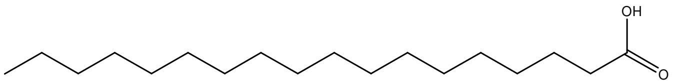
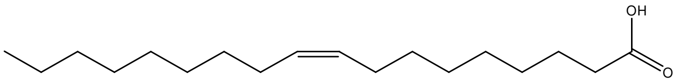
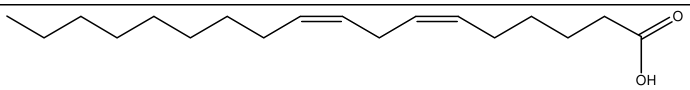
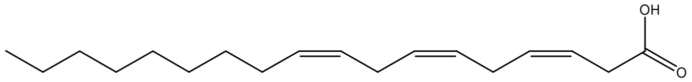
Fatty acid	%	Structure
Palmitic acid	11	
Stearic acid	4	
Oleic acid	23	
Linoleic acid	53	
Linolenic acid	8	

Table 1.3. shows the structure and composition of the fatty acids most abundant in soybean oil. The amount of these fatty acids depends on several factors, such as environmental factors, breeding, and genetic modification.

1.3.2. Chemical Properties of Soybean Oil

The triglyceride molecules of soybean oil contain four different reactive sites. Figure 1.2. shows all active sites, which are capable of doing chemical reactions; (1) allylic carbon, (2) double bond, (3) ester group, and (4) the carbons alpha to the ester group.

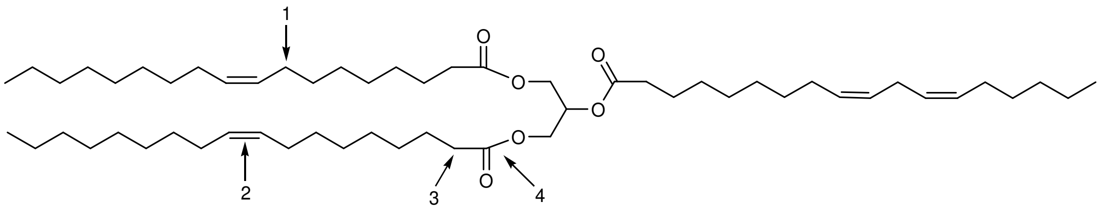


Figure 1.2. Reactive sites of a triglyceride molecule

These reactive sites are used to introduce polymerizable groups on the triglyceride molecules by using the same procedures that have been applied in the synthesis of petroleum based polymers.

Figure 1.3. summarizes some of the chemical routes previously used in introducing polymerizable groups to triglyceride molecule.

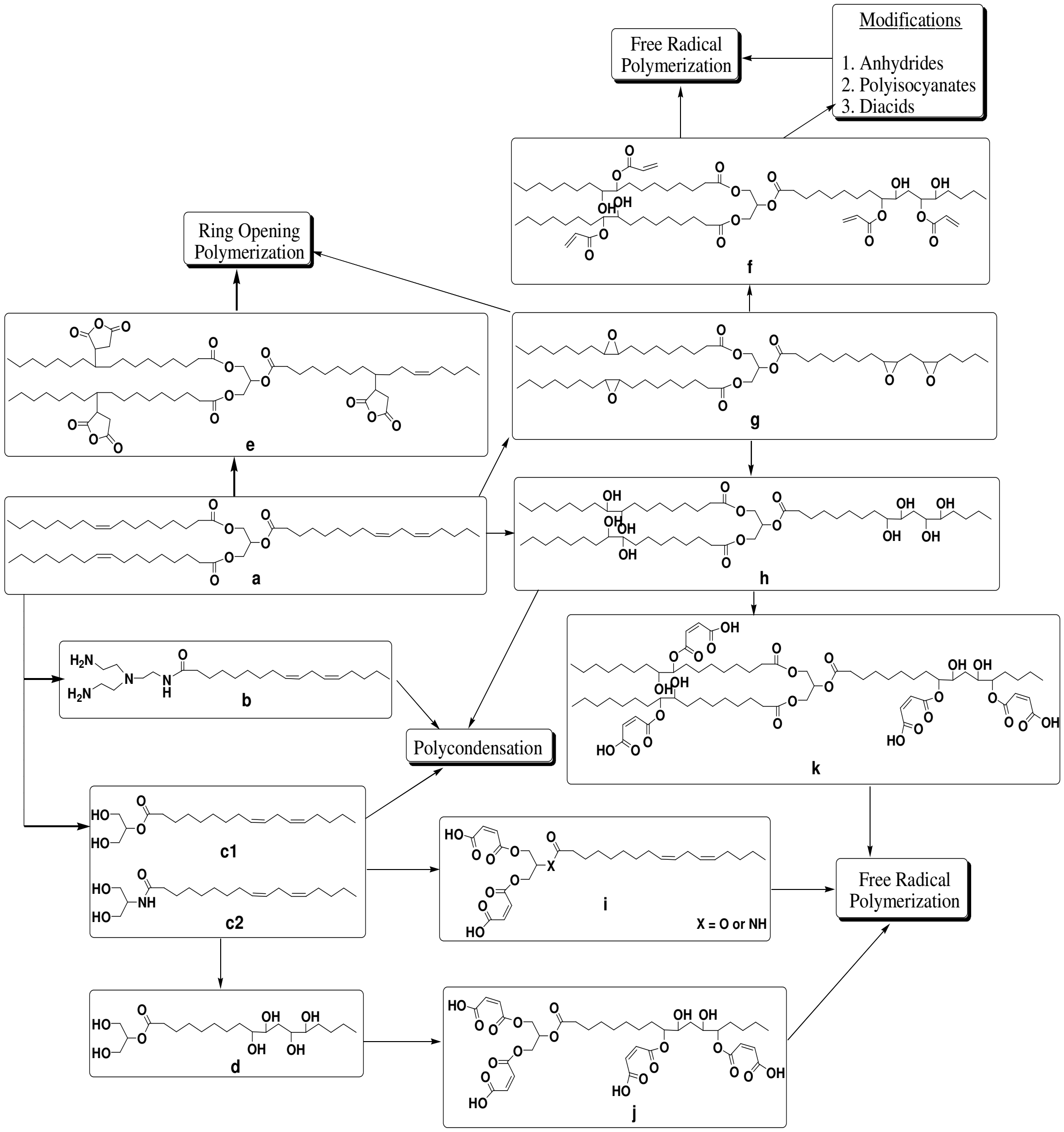


Figure 1.3. Chemical pathways leading to polymers from triglyceride molecules

One of the methods to synthesize polymerizable monomers from triglyceride molecules is the conversion of the triglyceride molecule to monoglycerides through glycerolysis reaction or amidation reaction (a-c) [4]. Monoglycerides containing alcohol functionalities are also able to react with a comonomer, such as a diacid, epoxy or anhydrate. Maleate halfesters can also be attached to monoglycerides (i), which allows them to polymerize by a free-radical route [5].

Functionalization of the unsaturated sites and reduction of triglyceride to monoglycerides can be combined as well. This process can be done by glycerolysis of an unsaturated triglyceride, followed by hydroxylation or glycerolysis of a hydroxy functional triglyceride. The resulting monomer (d) can then be reacted with reactive diluents and cured free-radically.

The functionalization of the double bond with polymerizable groups is the most widely method in synthesis of polymerizable monomers from triglycerides. Attachment of maleates (e), epoxidation of the double bond (g), and introduction of hydroxy functionality (h) are some of the methods of transformations [6].

1.3.3. Epoxidation of Soybean Oil

Epoxidation is one of the most important reactions at the double bond of unsaturated fatty acids. The most widely used method is to react the unsaturated fatty acid compounds with performic acid. Figure 1.4. shows the reaction. This is now the accepted industrial synthesis and the Epoxidized Soybean Oil (ESO) has found uses as a safe and non toxic plasticizer for polyvinyl chloride [7]. In addition to performic acid procedure, epoxidation with aldehydes and molecular oxygen, dioxiranes, H_2O_2/ tungsten heteropolyacids, and H_2O_2/ methyl trioxorhenium have also been used, but none of them has achieved industrial significance [8].

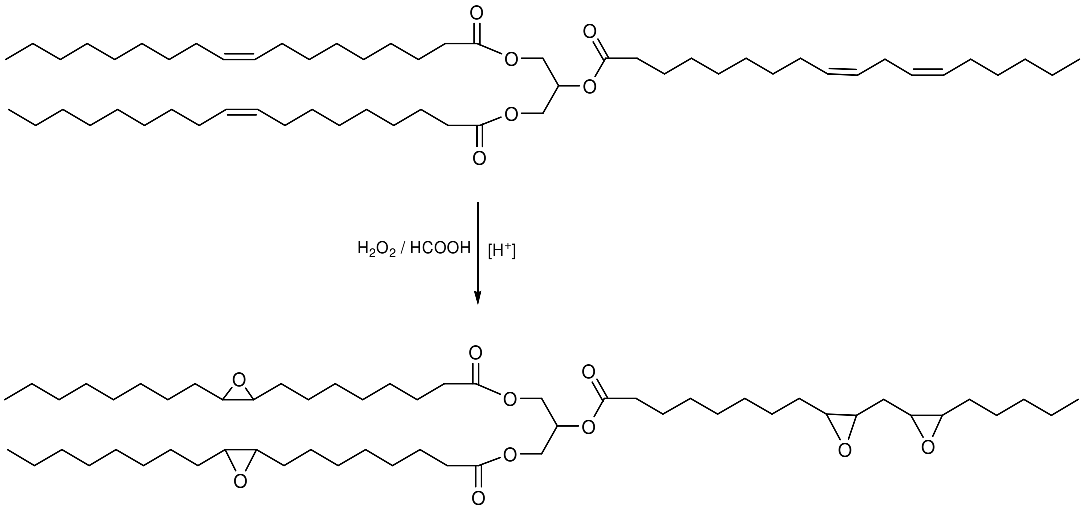
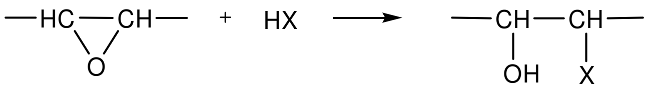


Figure 1.4. Epoxidation of unsaturated triglyceride molecule

The oxirane rings in epoxidized triglyceride molecule can readily react with nucleophilic reagents, which lead to a large number of products. Table 1.4. summarizes some of the products readily obtainable from epoxy groups.

Table 1.4. Reactions possible with epoxidized fatty acid



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 hydroxysulfonate

By hydrolysis of the oxirane ring, polyols, which are suitable for manufacturing polyurethane foams and molding resins with interesting properties can be produced.

Epoxidized soybean oil is mainly used as plasticizer for PVC [7]. By the possibility of photochemically initiated cationic curing new applications have been opened [9].

In a recent study with addition of acrylate functionality, epoxidized soybean oil can be reacted via addition polymerization [10, 11].

1.3.4. Acrylated Epoxidized Soybean Oil (AESO)

The mechanism of the reaction of ESO with acrylic acid is a standard substitution reaction. Although acrylic acid in addition to being a nucleophile also acts as a partial catalyst, additional catalysts are used as well. Commonly used catalysts are tertiary amines such as N,N-dimethyl aniline and triethylamine [10].

The following figure shows the structure of acrylated epoxidized soybean oil.

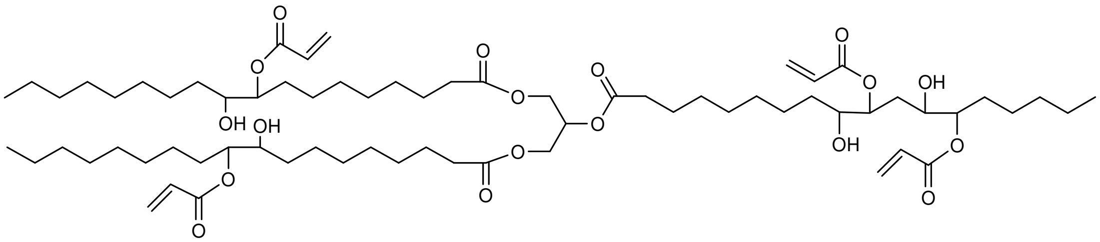


Figure 1.5. Structure of AESO

As reported by S. Küsefoğlu and R. Wool in their US. Patent 6,121,398 (2000) AESO can be free radically polymerized or copolymerized with reactive diluents such as styrene, to give thermoset resins, which will give mechanical properties similar to commercially successful polyester and vinyl ester resins [11]. It has also been reported that polymers with different moduli and glass transition temperatures (Tg) can be produced by varying the amount of reactive diluent. The properties of the polymer can also be controlled by changing the functionality of the molecule.

By the reaction of AESO with chemical species such as diacids, diamines, anhydrides and isocyanates, triglyceride can be oligomerized. After the oligomerization AESO resin can be blended with a reactive diluent and cured as the unmodified AESO resin [10].

Wool and his coworkers studied preparation of composites from renewable sources in which AESO was used as resin. In this study the hydroxyl groups on AESO were reacted with maleic anhydride (MA) to render acid groups on the molecule. Then, the resulting monomer was copolymerized with styrene to form rigid polymers [12].

In another study it has been reported that AESO when emulsion polymerized with methyl methacrylate gives polymers which have application area as pressure sensitive adhesives [13].

It has been reported that acrylate functional monomers are used in production of pressure sensitive adhesives [14].

Larock also reported the direct conversion of soybean oil into useful solid polymers by cationic polymerization with divinylbenzene (DVB) initiated by boron trifluoride diethyl etherate (BF_3:OEt_2) [15].

1.4. Organofunctional Silanes

Organofunctional silanes are capable of reacting with an inorganic material and with an organic material. They form strong bonds in the interface of inorganic and organic materials. They are extremely effective when an organic polymer and an inorganic material are used together

Organofunctional silanes have one end that is capable of binding to an inorganic surface and the other end that is capable of reacting with an organic polymer. The following figure shows the general formula of an alkoxy silane [16].

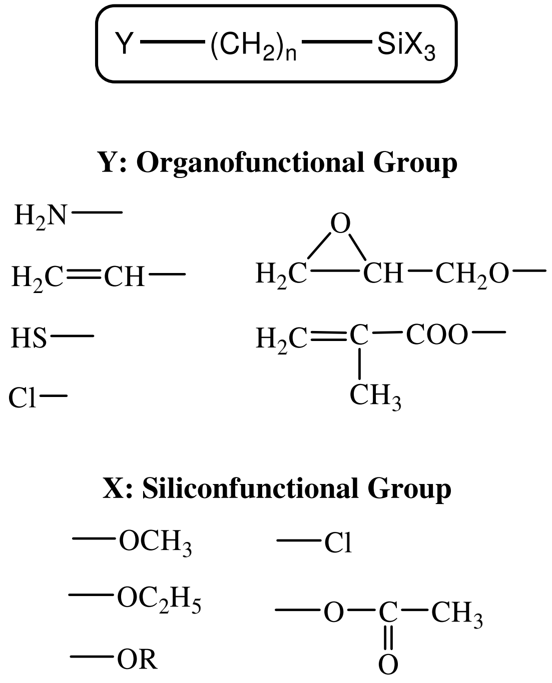


Figure 1.6. General structure of an organofunctional silane

The organofunctional group (Y) is bound to the silicon via a stable unreactive carbon chain. It can be either an alkyl, aromatic, organofunctional or a combination of any of these nonhydrolizable groups. These groups provide the organic compatibility which allows the silane to form covalent bonds with an organic polymer. The adhesion to the polymer is supplied with these organofunctional groups. While the inorganic reactive end of an organofunctional alkoxysilane is always a silanol group, the organic reactive end has to be different for different polymers.

The siliconfunctional group, which is usually an alkoxy (ethoxy or methoxy) group, is directly attached to the silicon. After hydrolysis to the silanol it can react with an inorganic substrate or with other silicon compounds and metal surfaces via condensation to form stable bonds.

1.4.1. Uses of Organofunctional Silanes

Organofunctional silanes are generally used as adhesion promoters/coupling agents, surface modifiers and crosslinking agents [17].

1.4.1.1. Organofunctional Silanes as Adhesion Promoters/Coupling Agents. As adhesion promoters, organofunctional silanes are used between inorganic materials, such as glass, minerals, metals etc. and organic polymers like thermosets, thermoplastics, elastomers etc. Organic polymer – inorganic filler mixtures are called composites. When an organofunctional silane coupling agent is used in composite materials containing an inorganic substrate and an organic polymer, improvement in adhesion and mechanical properties such as tensile strength, impact strength, abrasion resistance is observed. The coupling agents make the two incompatible phases compatible and increase the interfacial adhesion between the two.

Reaction of the silane with the substrate involves four steps. The mechanism is shown in Figure 1.7. The first step is the hydrolysis of the alkoxy groups. Upon hydrolysis reactive silanol groups are formed. After hydrolysis step condensation to form oligomers occurs. Reactive silanol groups, formed after hydrolysis are capable of forming hydrogen bonds and covalent bonds with the hydroxy sites of the substrate. During that step water is eliminated. Figure 1.7. summarizes the process [16].

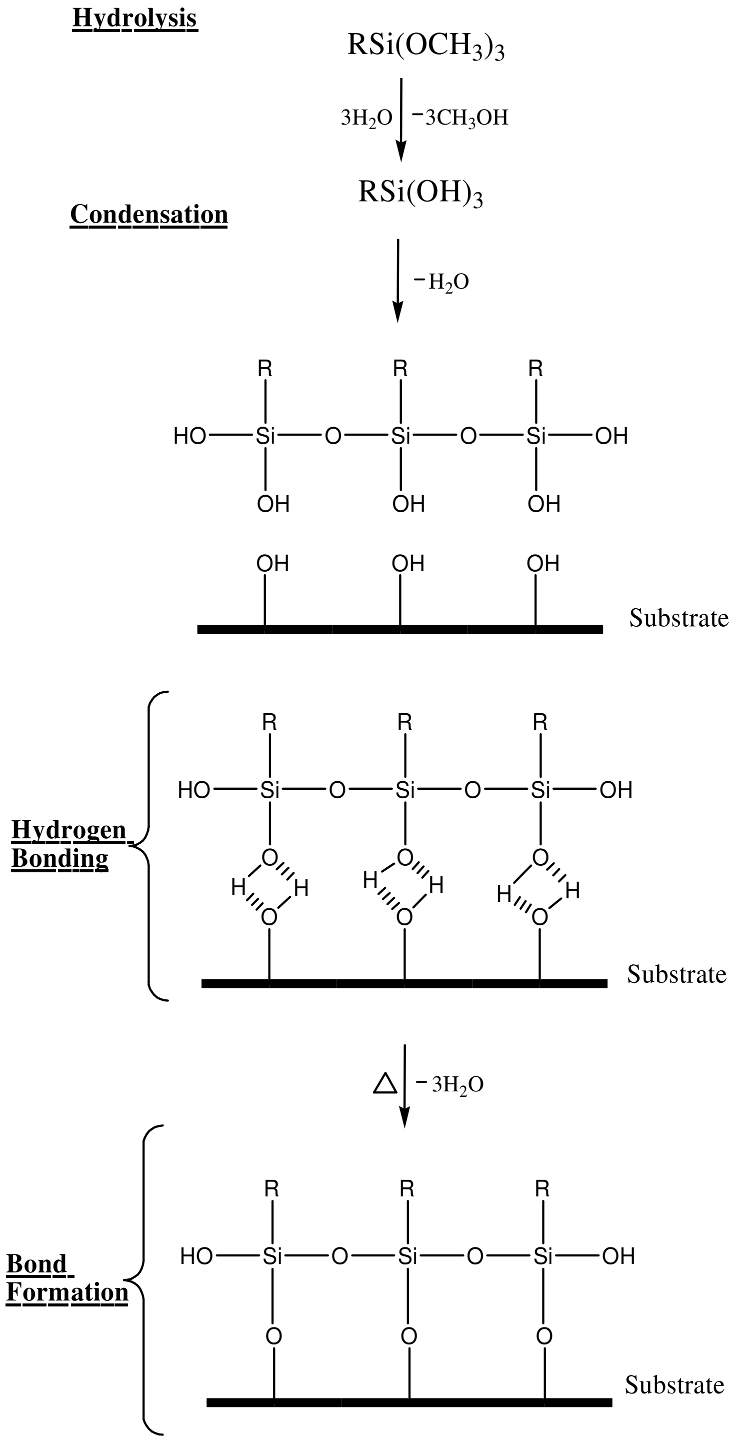


Figure 1.7. Reaction process of alkoxysilanes

1.4.1.2. Organofunctional Silanes as Surface Modifiers. Organofunctional silanes are used to modify surfaces by hydrophobation, give the surface an organophilic character, improve the processing properties, like dispersive behavior or viscosity by supplying compatibility between filler and plastic, improve wetting by the polymer, and improve corrosion or scratch resistance by serving as a protective coating.

1.4.1.3. Organofunctional Silanes as Crosslinking Agents. Moisture cure refers to easy hydrolysis – condensation reactions that take place by the help of moisture in air. By a simple moisture-curing process, organofunctional silanes that are attached to the polymer are able to crosslink the polymer. After moisture-cure hydrolized silanols are able to undergo condensation with other silanols in the medium, thus leading to crosslinks. Such a strategy is used in crosslinking in silicones, polyolefines, and polyacrylates. Figure 1.8. shows the mechanism [18].

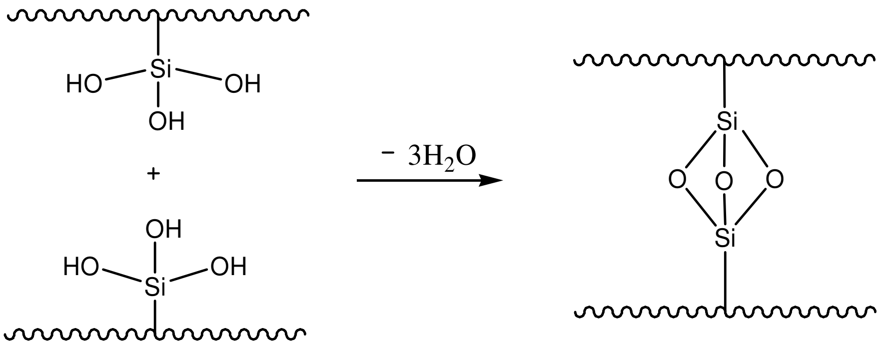


Figure 1.8. Moisture crosslinking of alkoxysilanes

1.4.2. Aminosilanes

Aminosilanes are a type of organofunctional silane, which have amine functionality as the organofunctional group. The general formula is:

$$R_2N\text{—}(CH_2)_n\text{—}Si(OR)_3$$

Amine functionality may be primary, secondary or tertiary. Aminosilanes are generally prepared by the reaction of silicon hydrides or chlorosilanes with ammonia or other amines in the presence of inert solvent [19]. But, they can be also prepared by reacting amines with silylacetilenes over solid base catalysts [20].

The most widely used aminosilane is 3-Aminopropyltriethoxysilane.

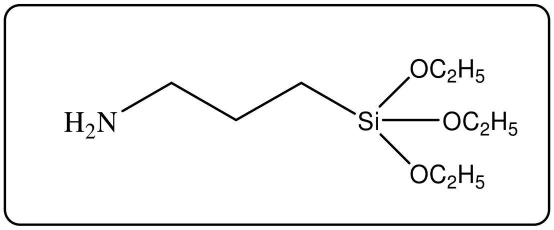


Figure 1.9. Structure of 3-Aminopropyltriethoxysilane

3-Aminopropyltriethoxysilane is a bifunctional compound in which the silicon-functional group can hydrolize in the presence of water to the corresponding reactive silanol and the organophilic amino group can bind to a suitable polymer.

Examples of inorganic substrates are glass, glass fibers, glass wool, mineral wool, quartz, sand, mica, also aluminum hydroxide, kaolin, talc, metal oxides, most metals, etc. Examples of suitable polymers are epoxy resins, polyurethanes, phenolic resins, furan resins, melamin resins, PA, PVC, acrylates and silicone.

1.5. Michael Reaction

Michael reaction is simply the 1,4-addition (or conjugate addition) of nucleophile to α,β-unsaturated carbonyl compounds.

Figure 1.10. summarizes the mechanism of the reaction.

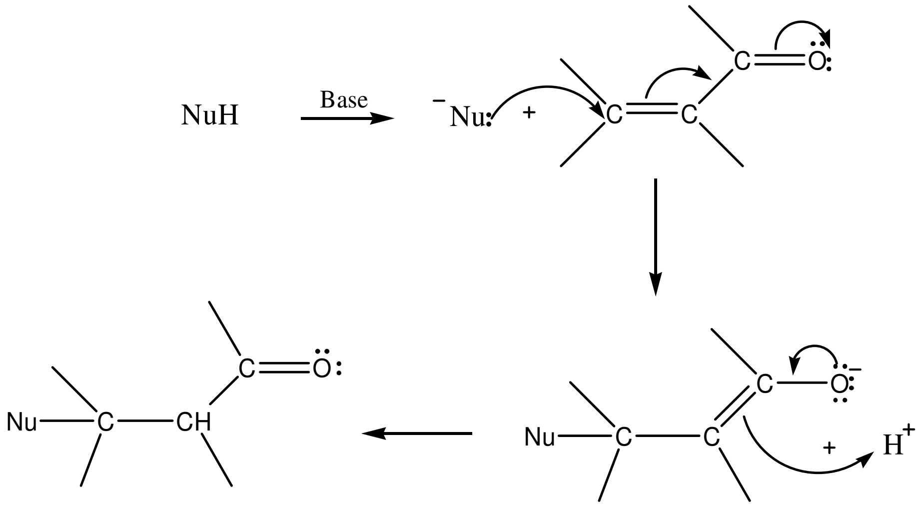


Figure 1.10. Mechanism of the Michael Reaction

The mechanism goes through addition of nucleophile/donor to the α,β-unsaturated carbonyl compound/acceptor to give an intermediate, an enolate. Figure 1.11. shows examples of donors and acceptors.

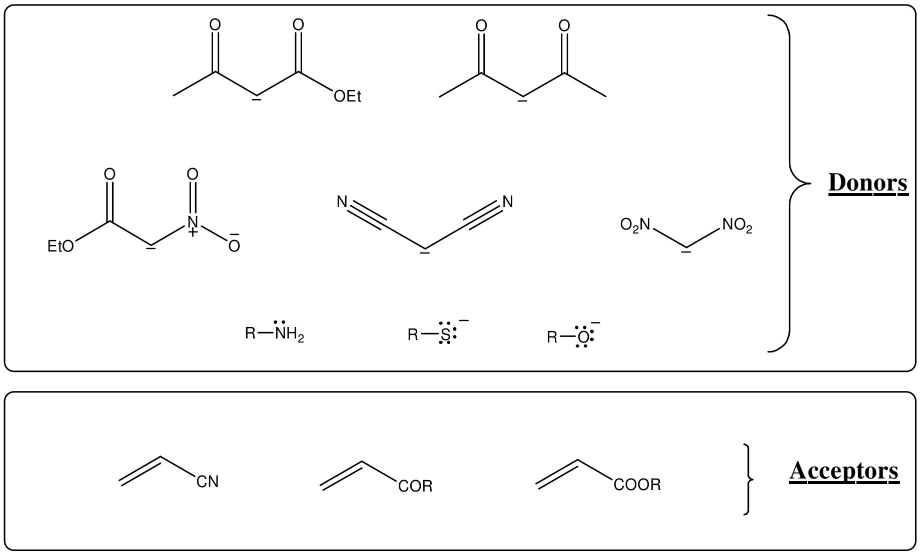


Figure 1.11. Michael Reaction acceptors and donors

The addition of other type of nucleophiles is known as Michael-like addition reactions. Some examples are addition of several primary nitramines to activated unsaturated system giving secondary nitramines [21].

The overall process of the Michael Reaction is the addition of a nucleophilic compound to the carbon-carbon double bond of an α,β-unsaturated carbonyl compound. The particular importance of the reaction in organic synthesis is for the construction of complicated carbon skeletons [22].

2. RESEARCH OBJECTIVES

The aim of this project is to synthesize a multifunctional reactive monomer, which possesses:

a) A free radically polymerizable reactive unsaturation
b) A large alkyl oleophilic group
c) A protected silanol group capable of reacting with inorganic surfaces

The monomer is going to be synthesized by the Michael Reaction of 3-Aminopropyltriethoxysilane on AESO by using less than equivalent amount of the aminosilane, so that some of the acrylate groups will be left intact to provide the polymerization sites.

The chemical structure of the silanized-AESO is shown in Figure 2.1. The silanized-AESO and the mechanism of the reaction are going to be characterized by using ^{1}H NMR spectroscopy.

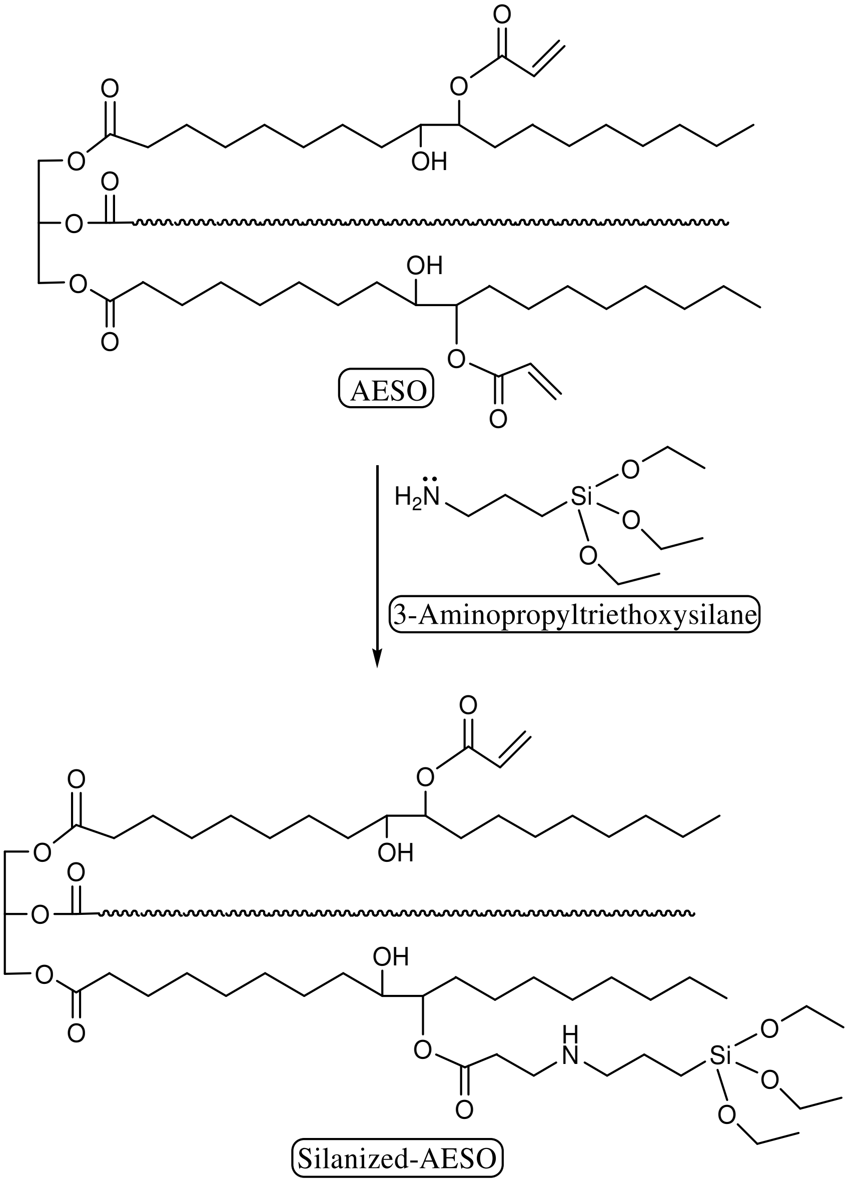


Figure 2.1. Synthesis and structure of silanized-AESO

The silanized-AESO contains acrylate double bonds, which can be radically polymerized and ethoxysilane functional groups, which upon moisture cure can be hydrolyzed. These newly formed hydroxysilanes can react via condensation with each other to increase crosslink density or with an inorganic substrate.

The adhesion properties of the radically polymerized homopolymer on glass before and after moisture cure will be determined according to the ASTM standard pull-off adhesion test (ASTM D 4541-85). The adverse effect of moisture on the adhesion strength is also going to be determined by keeping samples in humid atmosphere. Figure 2.2. shows the adhesion of the radically polymerized homopolymer on glass surface.

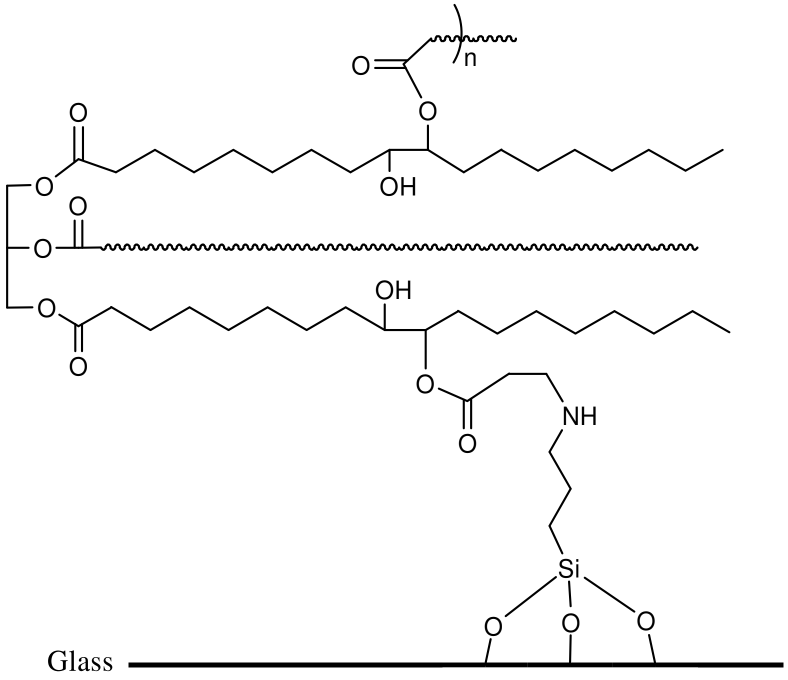


Figure 2.2. Adhesion of silanized-AESO homopolymer on glass surface

The silanized-AESO is going to be copolymerized with styrene via radical polymerization. The radically polymerized silanized-AESO-styrene copolymer will be further moisture cured through the silanol groups and cured to increase crosslink density. Figure 2.3. shows the reaction sequence.

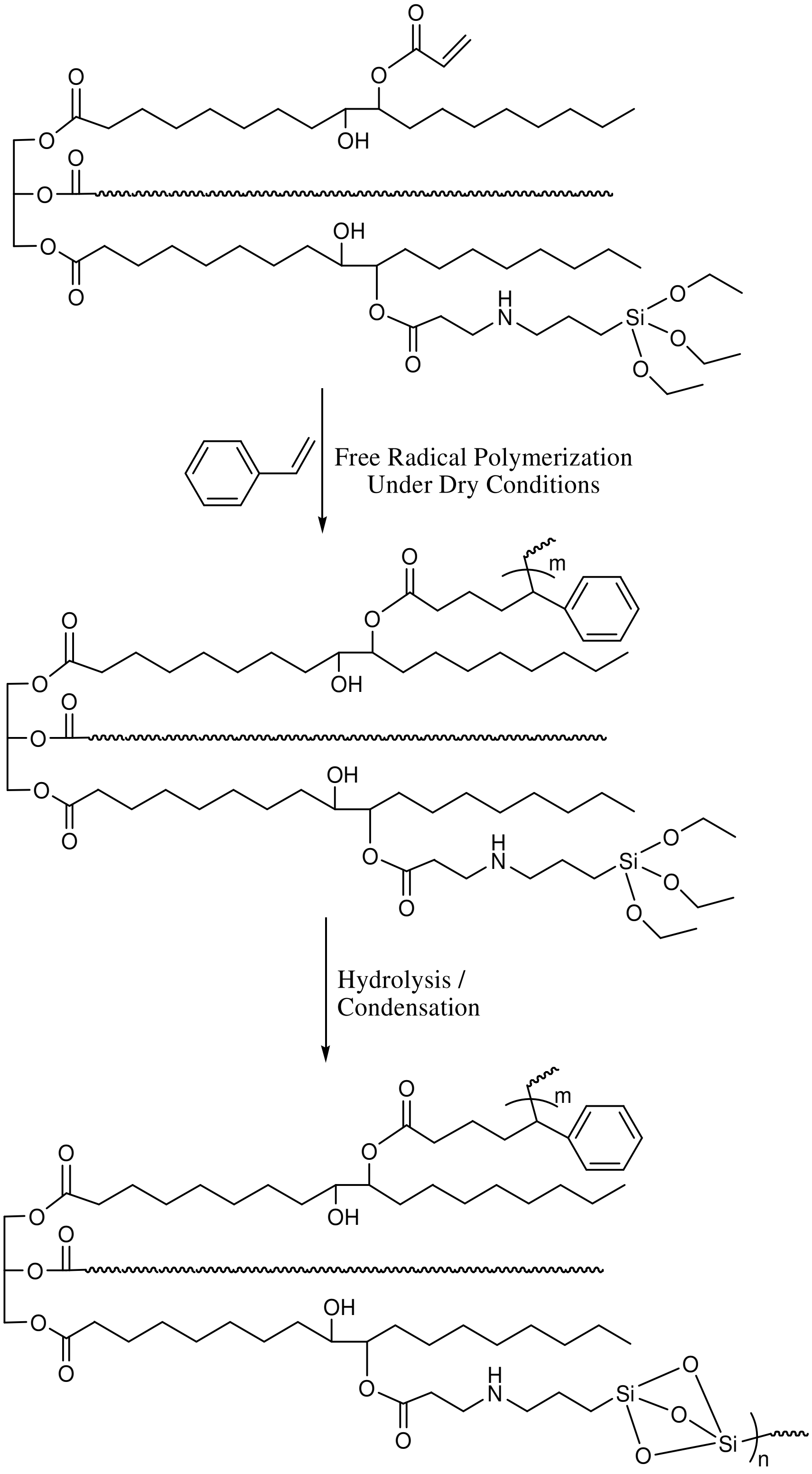


Figure 2.3. Copolymerization with styrene and hydrolysis/condensation of styrene-silanized-AESO copolymer

The improvement in the dynamic mechanical or physical properties upon moisture cure of the corresponding copolymer will be analyzed by DMA; DCS; TGA, swelling and surface hardness.

3. EXPERIMENTAL

3.1. Materials and Apparatus

3.1.1. Materials

Acrylated Soybean Oil was obtained from Sartomer Company, Inc. and was used as obtained. 3-Aminopropyltriethoxysilane was obtained from Cam Elyaf A.Ş. and was used as obtained. Styrene was purchased from Merck and was used as received. $CDCl_3$ obtained from Aldrich was used for ^1H NMR and ^{13}C NMR analysis. The radical initiators benzoyl peroxide and 2,2'-azobis(isobutyronitrile) (AIBN) were obtained from Fisher and Fluka, respectively, and they were recrystallized from methanol prior to use.

3.1.2. Apparatus

The ^1H NMR and ^{13}C NMR spectra were recorded on a Varian 400 MHz NMR instrument operating at a frequency of 399.986 MHz for proton and 100.587 MHz for carbon. The spectra were reported as ppm (δ).

The IR analysis was performed with Genesis FT-IR spectrometer using KBr window.

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 room temperature to 160 ^{o}C at a heating rate of 3 $^{o}C/min$ with a frequency of 1 Hz and strain 0.01 %.

The glass-transition temperature (Tg) for homo and copolymers were analyzed by using differential scanning calorimetry (DSC). DSC measurements were carried out with TA Instrument Q100 at a heating rate of 10 $^{o}C/min$, from 0 ^{o}C to 160 ^{o}C, under nitrogen atmosphere.

The thermal gravimetric analysis of polymer samples was done with TA Instrument Q50. Temperature scans were performed from room temperature to 700 ^{o}C with a heating rate of 10 ^{o}C/min.

The adhesion strength of silanized-AESO styrene homopolymer was tested with DVT G-21 type of tensile strength machine according to the standard ASTM D 4541 Pull-Off Adhesion Test.

The surface hardness of the polymers was analyzed with a Zwick/Roell Durometer according to ASTM D 2240 standard test.

The swelling behavior of silanized-AESO-styrene copolymer was tested in CCl_4 by using a Geartner 7109-46 travelling microscope.

3.2. Synthesis and Polymerization of Silanized-AESO

3.2.1. Silanization of Acrylated Epoxidized Soybean Oil

In a N_2 purged flask to which a drying tube was attached 2.402 g (2.002 mmol) acrylated epoxidized soybean oil and 0.758 g (0.0034 mmol) 3-Aminopropyl triethoxysilane were mixed for 60 minutes. The reaction was followed by IR and NMR scpectroscopy, and loss of vinyl protons was observed in NMR. The product is a viscous liquid.

^{1}**H NMR (CDCl$_3$) δ:** 0.61 (-C$\underline{H_2}$-Si-); 0.87 (-CH$_3$); 1.20 (-CH$_2$-); 1.23 (-Si-O-CH$_2$-C$\underline{H_3}$); 1.605 (-NH-CH$_2$-C$\underline{H_2}$-CH$_2$-Si-); 2.3 (-O(C=O)C$\underline{H_2}$-); 2.6 (-NH-C$\underline{H_2}$-CH$_2$-CH$_2$-Si-); 2.87 (-O(C=O)CH$_2$-C$\underline{H_2}$-NH-); 3.79 (-Si-O-C$\underline{H_2}$-CH$_3$); 3.99 (-CH(OH)-C$\underline{H}$(C=O)CH$_2$); 4.11 (-O-CH$_2$-CH(O-)-C$\underline{H_2}$-O-); 5.24 (-O-CH$_2$-C$\underline{H}$(O-)-CH$_2$-O-); 5.84 (-O(C=O)CH=C$\underline{\text{Ha}}$Hb); 6.11 (-O(C=O)C$\underline{H}$=CHaHb); 6.41 (-O(C=O)CH=CHa$\underline{\text{Hb}}$).

^{13}**C NMR (CDCl$_3$) δ:** 7.68, 8.08 (-$\underline{C}$H$_2$-Si-), 14.07, 14.13, 14.18 (-NH-$\underline{C}$H$_2$-), 18.39, 18.52 (-Si-O-CH$_2$-$\underline{C}$H$_3$), 22.59, 22.69, 22.76, 22.86, 22.96, 23.24, 23.29 (-CH$_2$-$\underline{C}$H$_3$), 24.90, 24.95 (-NH-CH$_2$-$\underline{C}$H$_2$-CH$_2$-Si-), 31.93, 31.98, 31.99 (-$\underline{C}$H$_2$-), 34.06, 34.12, 34.22

(-O(C=O)$\underline{\mathrm{C}}\mathrm{H_2}$-$\mathrm{CH_2}$-$\mathrm{CH_2}$-), 34.83, 34.99 (-O(C=O)$\underline{\mathrm{C}}\mathrm{H_2}$-$\mathrm{CH_2}$-NH-), 44.69, 44.91, 44.99 (-O(C=O)$\mathrm{CH_2}$-$\underline{\mathrm{C}}\mathrm{H_2}$-NH-), 52.18, 52.26, 52.51 (-NH-$\underline{\mathrm{C}}\mathrm{H_2}$-$\mathrm{CH_2}$-$\mathrm{CH_2}$-Si-), 58.31, 58.43, 58.44 (-Si-O-$\underline{\mathrm{C}}\mathrm{H_2}$-$\mathrm{CH_3}$), 62.17(-O-$\underline{\mathrm{C}}\mathrm{H_2}$-CH(O-)-$\mathrm{CH_2}$-O-), 69.04(-O-$\mathrm{CH_2}$-$\underline{\mathrm{C}}$H(O-)-$\mathrm{CH_2}$-O-), 77.06, 77.38, 77.58, 77.70 (-$\underline{\mathrm{CH}}$(OH)CH-O(C=O)-), 80.53, 81.32, 81.42, 81.79, 81.89 (-CH(OH)$\underline{\mathrm{C}}$H-O(C=O)-), 127.81, 128.67(-O(C=O)-$\underline{\mathrm{C}}$H=$\mathrm{CH_2}$), 132.23(-O(C=O)-CH=$\underline{\mathrm{C}}\mathrm{H_2}$), 165.56, 165.72, 165.90, 166.13 (-O($\underline{\mathrm{C}}$=O)-CH=$\mathrm{CH_2}$), 172.19, 172.25, 172.48, 172.64, 172.81, 173.21 (-O($\underline{\mathrm{C}}$=O)$\mathrm{CH_2}$-$\mathrm{CH_2}$-NH-).

IR (Film) υ (cm^{-1}): 3436 (br, O-H), 2929 (s, CH), 2855 (s, CH), 1738 (s, C=O), 1463 (m, $\mathrm{CH_2}$, Def.), 1406 (m, =$\mathrm{CH_2}$, Def.), 1295-1283 (s, C-O- Def.; O-H, Def.), 1192 (m, CO, Def.; C-O-C, Def.), 1103 (s, Si-O, Def.), 1079 (s, C-N, Def.), 809 (m, =$\mathrm{CH_2}$, Def.), 1636 cm^{-1}, 959 cm^{-1}(m, =CH, Def., characteristic for vinyl group conjugated with carbonyl).

3.2.2. Radical Homopolymerization of Silanized-AESO

The radical initiated homopolymerization of silanized-AESO was conducted by using benzoyl peroxide as radical initiator. In a sample procedure, 3.15 g of silanized-AESO was mixed with 0.048 g (1.5 % in weight) benzoyl peroxide. Reagents were mixed for 30 min under N_2 atmosphere. The curing process was done under N_2 atmosphere to prevent any moisture present in the medium. Polymerization was carried out at 70 °C for 12 hours to give a soft, clear, insoluble polymer. Characterization of the homopolymer was done by IR spectroscopy, and the disappearance of the acrylate double bond peak was observed.

IR (Film) υ (cm^{-1}) (Before Moisture Cure): 3452 (br, O-H), 2920 (s, CH), 2853 (s, CH), 1731 (m, C=O), 1456 (m, $\mathrm{CH_2}$, Def.), 1378 (m, =$\mathrm{CH_2}$, Def.), 1294-1251 (s, C-O- Def.; O-H, Def.), 1184 (m, CO, Def.; C-O-C, Def.), 1096 (s, Si-O, Def.), 831 (m, =$\mathrm{CH_2}$, Def.).

IR (Film) υ (cm^{-1}) (After Moisture Cure): 3490 (br, O-H), 2930 (s, CH), 2853 (s, CH), 1746 (s, C=O), 1730 (s, C=O), 1715 (s, C=O), 1453 (m, $\mathrm{CH_2}$, Def.), 1384 (m, =$\mathrm{CH_2}$, Def.), 1253 (b, C-O- Def.; O-H, Def.), 1153 (b, Si-O, Def.), 830 (m, =$\mathrm{CH_2}$, Def.).

3.2.3. Radical Copolymerization of Silanized-AESO with Styrene

Copolymerization of silanized-AESO with styrene was done by using AIBN as radical initiator. In a sample procedure, 2.09 g of silanized-AESO was mixed with 2.13 g styrene in a drying tube attached flask for 10 min. N_2 was purged to the flask. Then, 0.029 g (1.5% in weight)of AIBN was added to the mixture. The mixture was stirred for 15 min. The curing process was done under N_2 atmosphere to prevent any moisture present in the medium at 70 ^oC for 12 hours.

3.3. Moisture Curing of Polymers

Moisture curing process was done after radical polymerization was complete. Polymer samples were prepared as a thin film on glass and were exposed to water vapor for 12 hours to allow enough time needed for hydrolysis of ethoxysilane groups. The curing process was done at 125 ^oC (above boiling point condensation product, water) for 12 hours. After moisture curing process a darkening in the color of the polymer was observed.

3.4. Procedures for Adhesion Tests

3.4.1. Radical Curing Process

For adhesion tests mixture prepared for homopolymerization was applied on a glass surface at a thickness of approximate 80 mμ. The polymerization was done under N_2 atmosphere to prevent any moisture present in the medium at 70 ^oC for 12 hours on the glass surface.

3.4.2. Moisture Curing Process

Moisture cure process was done by keeping the polymer in ambient conditions for 24 hours to allow enough time needed for hydrolysis of ethoxysilane groups, followed by keeping at 125 ^oC for 12 hours.

3.4.3. Adhesion Test

The adhesion properties of the silanized-AESO homopolymer on glass, before and after moisture cure were analyzed according to the ASTM D 4541–85 standard pull–off adhesion test. In the pull-off test a loading fixture, commonly called a dolly or stub, is affixed by an adhesive to a coating. By use of a portable pull-off adhesion tester, a load is increasingly applied to the surface until the dolly is pulled off. The force required to pull the dolly off or the force the dolly withstood, yields the tensile strength in kilo Pascals (KPa).

Prior to any further application surface of the polymer was wiped with acetone soaked wipes to remove any impurities. Then, dollies having same unit surface area were adhered on the surface of the polymer with an epoxy adhesive. After the dollies were attached on the polymer, a cut was made along the circumference of the dolly so that only the area under the dolly would be pulled off during the test.

3.5. Swelling Tests

For the swelling test polymer samples were cut in rectangular pieces of dimensions about 1 x 5 x 10 mm. The tests were carried of 4 different samples for each polymer and the average of the results was taken. The swelling tests were done in CCl_4. The initial values of the sample lengths were recorded. The samples were then put in closed containers, which contained solvent. The increase in the lengths was measured with one hour time interval until solvent uptake ceased.

4. RESULTS AND DISCUSSION

4.1. Characterization and Quantitative Analysis of AESO

AESO was obtained from Sartomer Company, Inc. This company is now producing AESO in pilot plant quantities according to US Patent 6,121,398 (2000). Characterization and quantitative analysis of the functionality of AESO was done by using ^{1}H NMR analysis. Figure 4.1. shows the chemical structure and ^{1}H NMR spectrum of AESO. The characteristic peaks of AESO are peak 1 appearing at 0.8 ppm which corresponds to methyl protons of the fatty acid chains; peak 2 appearing at 2.2 ppm corresponds to protons α to the carbonyl; peak 3 appearing in the 4.0 – 4.4 range, corresponds to $-CH_2$ protons of the glycerol unit; peak 4 appearing at 5.2 ppm, corresponds to $-CH-$ proton of the glycerol unit; and peak 5 appearing at 5.8, 6.0, and 6.3 ppm, corresponds to $-CH=CH_2$ protons of the acrylate esters [10].

In order to calculate the number of functional acrylate groups present in one molecule of AESO, the ratio of integral value of the peak corresponding to methyl protons of the fatty acid chains (peak 1) to the integral value of the peaks corresponding to $-CH=CH_2$ protons of the acrylate esters (peak 5) was calculated. From that ratio it was concluded that there are on the average 3.4 acrylate functional groups per triglyceride.

According to the obtained results, it was also calculated that AESO has an average molecular weight of 1200 g/mol.

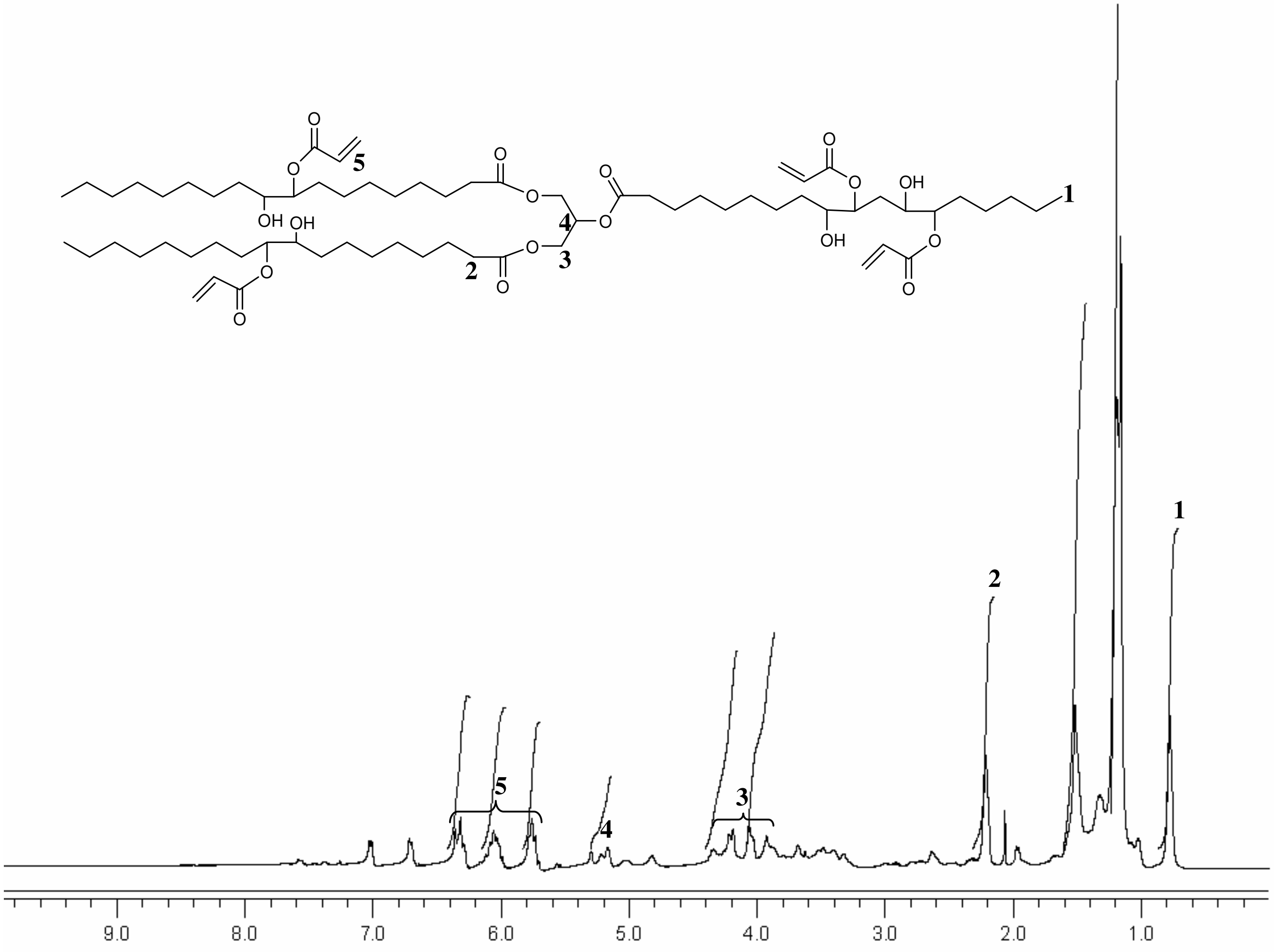


Figure 4.1. ^{1}H NMR spectrum of AESO

4.2. Synthesis and Characterization of Silanized-AESO

Acrylate double bonds of AESO are very susceptible towards nucleophilic attack, which makes them good Michael acceptors. In presence of a good Michael type of nucleophile the addition reaction can easily take place.

Aminosilane is an organofunctional silane which posses both organic reactive and inorganic reactive ends. Ethoxy silane ends of the molecule can be hydrolyzed to silanols which will react with hydroxyl bearing inorganic surfaces such as mica, silicates, glass and metals. The amino end of the molecule is capable of reacting with many organic polymers. Thus the molecule acts as a coupling agent between an organic polymer and an inorganic surface or filler.

The main objective of this project was to synthesize a reactive monomer by reacting AESO with 3-Aminopropyltriethoxysilane via Michael addition reaction. The reaction was carried by mixing the reactants in a certain ratio, so that only a certain fraction of the acrylate groups are reacted and the rest are available for free radical polymerization.

Ethoxy silane groups are known to be very sensitive to moisture. They can be easily hydrolyzed even by the amount of moisture present in the air [16]. Therefore the monomer synthesis was done at room temperature, under dry conditions. Figure 4.2. shows the chemical structure of the silanized-AESO.

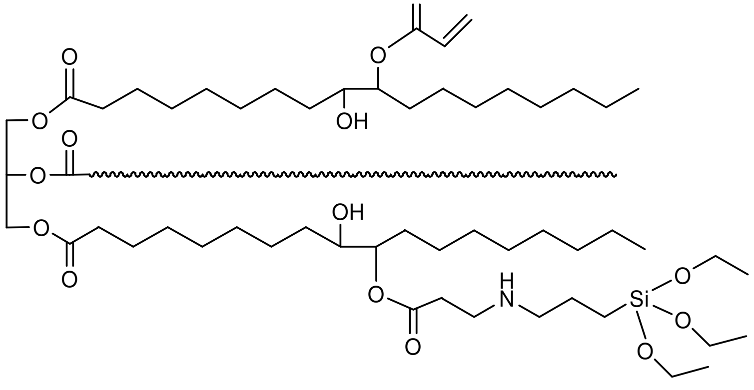


Figure 4.2. Structure of silanized-AESO

The resulting monomer contains three important functional groups. It contains long hydrophobic carbon chains, reactive acrylate double bonds, and hydrolysable ethoxy silane groups. The acrylate double bonds are very reactive and can be easily radically polymerized. The ethoxy silane groups can be easily hydrolyzed to yield hydroxysilane groups. Hydroxysilane groups are capable of self-condensing or reacting with other inorganic substrates containing hydroxyl functional groups and the fatty acid provides a thick and hydrophobic interface.

The characterization of the silanized-AESO was done by NMR and IR spectroscopy techniques. Figure 4.3. and Figure 4.4. show the ^{1}H NMR and the ^{13}C NMR spectra of the silanized-AESO. Figure 4.5. shows the IR spectra of the silanized-AESO.

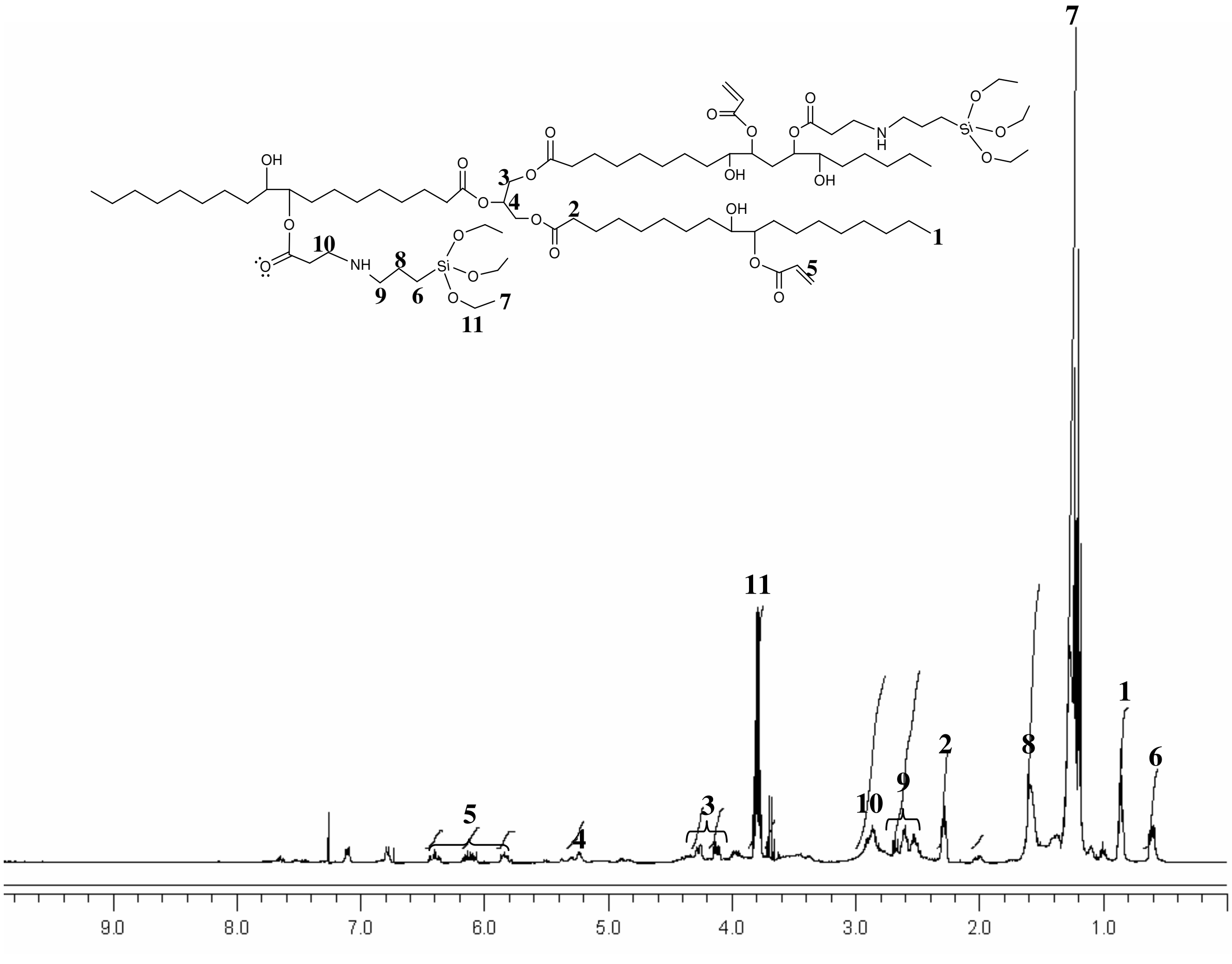


Figure 4.3. ^{1}H NMR spectrum of silanized-AESO

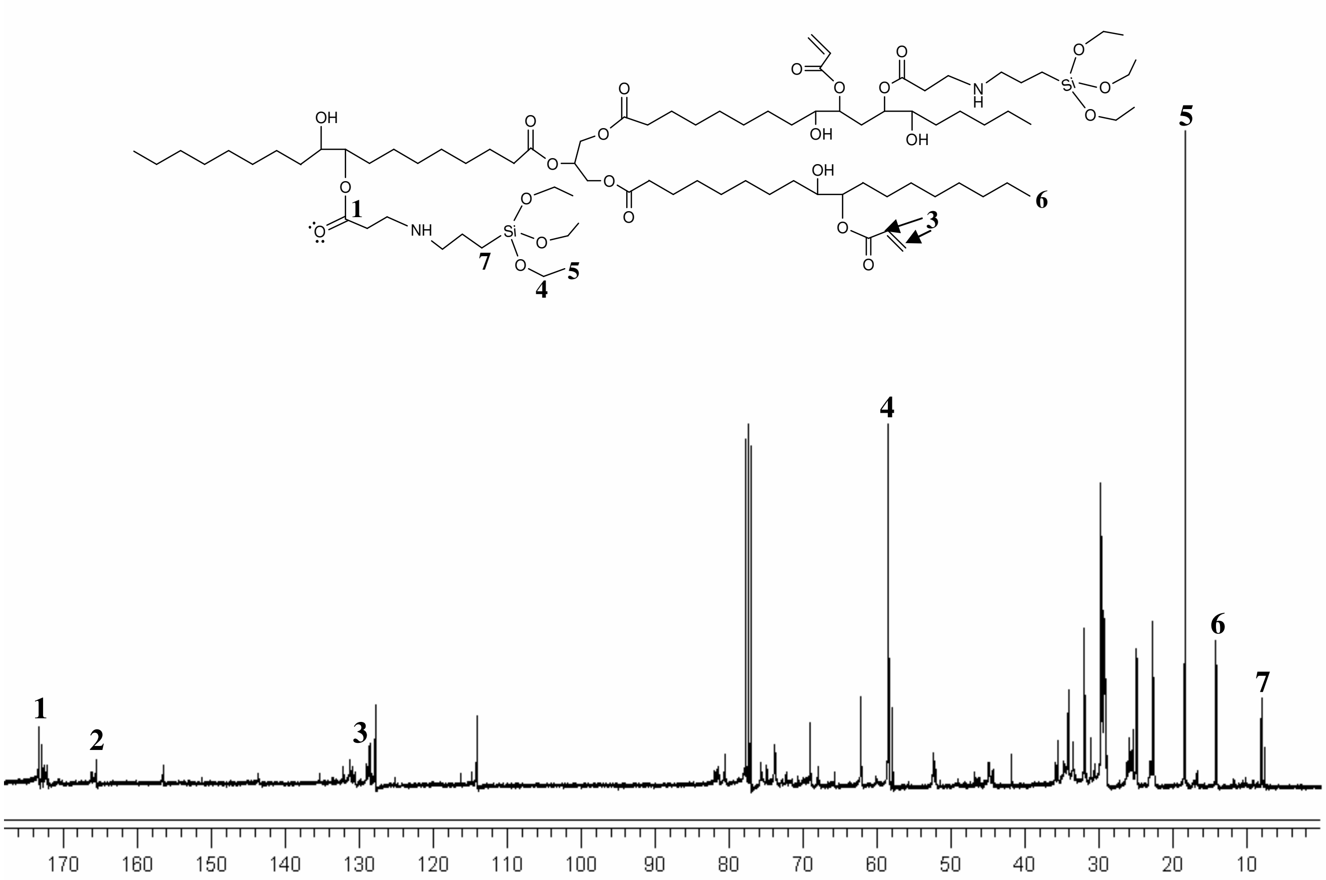


Figure 4.4. ^{13}C NMR spectrum of silanized-AESO

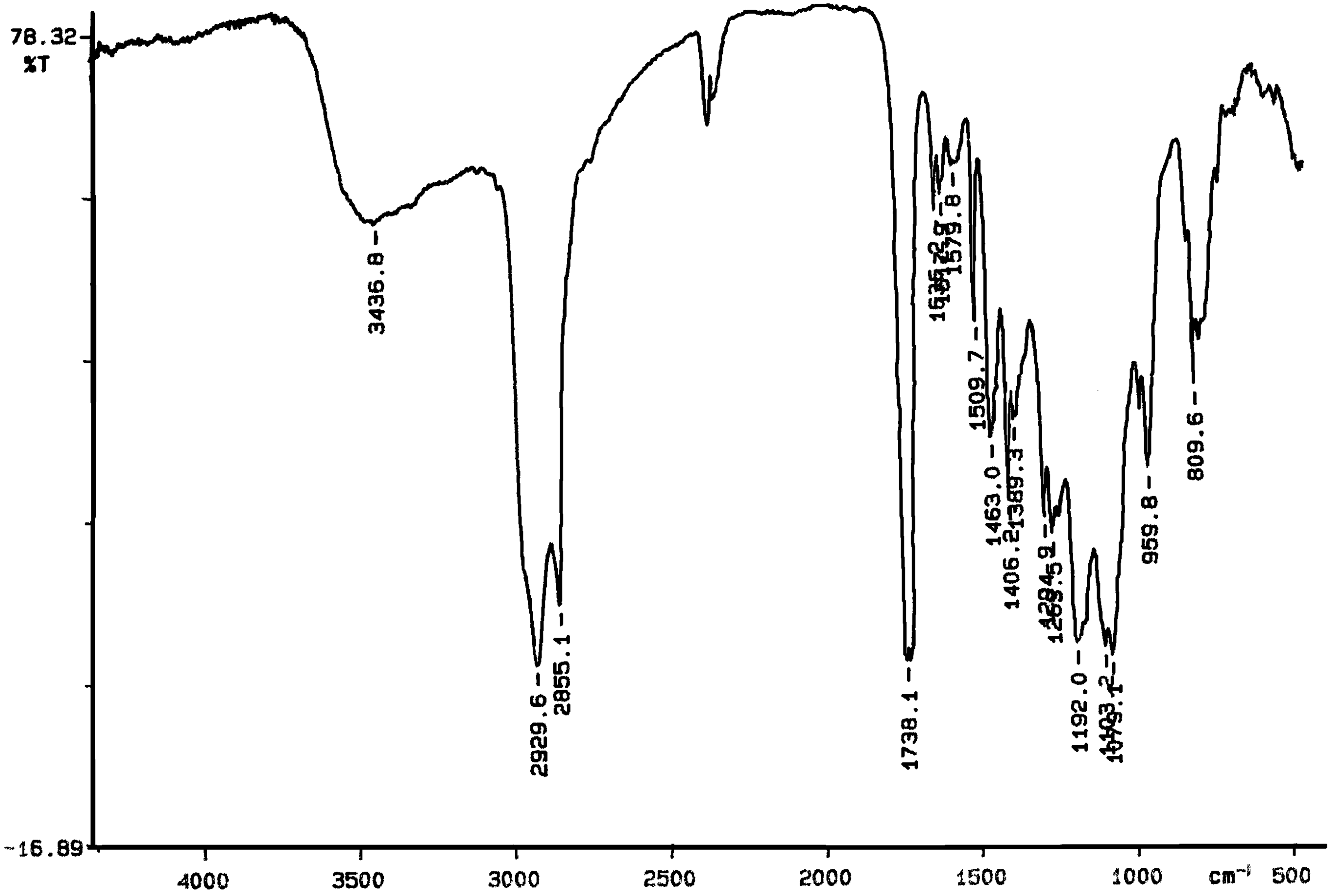


Figure 4.5. IR spectrum of silanized-AESO

^1H NMR of the product shows that there are 1.7 acrylate groups and 1.7 aminosilane groups per triglyceride on the average.

The ^{13}C NMR spectrum shows that carbonyl carbons of the acrylate ester shift to lower field after addition of 3-Aminopropyltriethoxysilane to the double bond.

In the IR spectrum of the silanized-AESO the peaks corresponding to the acrylate $-CH=CH_2$, stretching at 1636 cm^{-1} and bending at 959 cm^{-1}, the carbonyl stretching at 1738 cm^{-1}, and the $-C-Si-O-$ stretching at 1103-1079 cm^{-1} can be clearly observed in Figure 4.5.

The ester functionality of the triglyceride in the presence of an amine can undergo an undesirable amidation reaction. In order to prove that reaction proceeds only trough the Michael Addition, AESO was reacted with 3-Aminopropyltriethoxysilane in 1:1 ratio so that all the double bonds were depleted in the reaction. The reaction was completed in 90 min. Figure 4.6. shows the results and the fully silanated molecule. Spectra A is taken in the beginning of the reaction and Spectra B is taken at the end of the reaction. Complete disappearance of the peaks corresponding to $-CH=CH_2$ protons of the acrylate esters indicated that the reaction proceeded via Michael Addition Reaction.

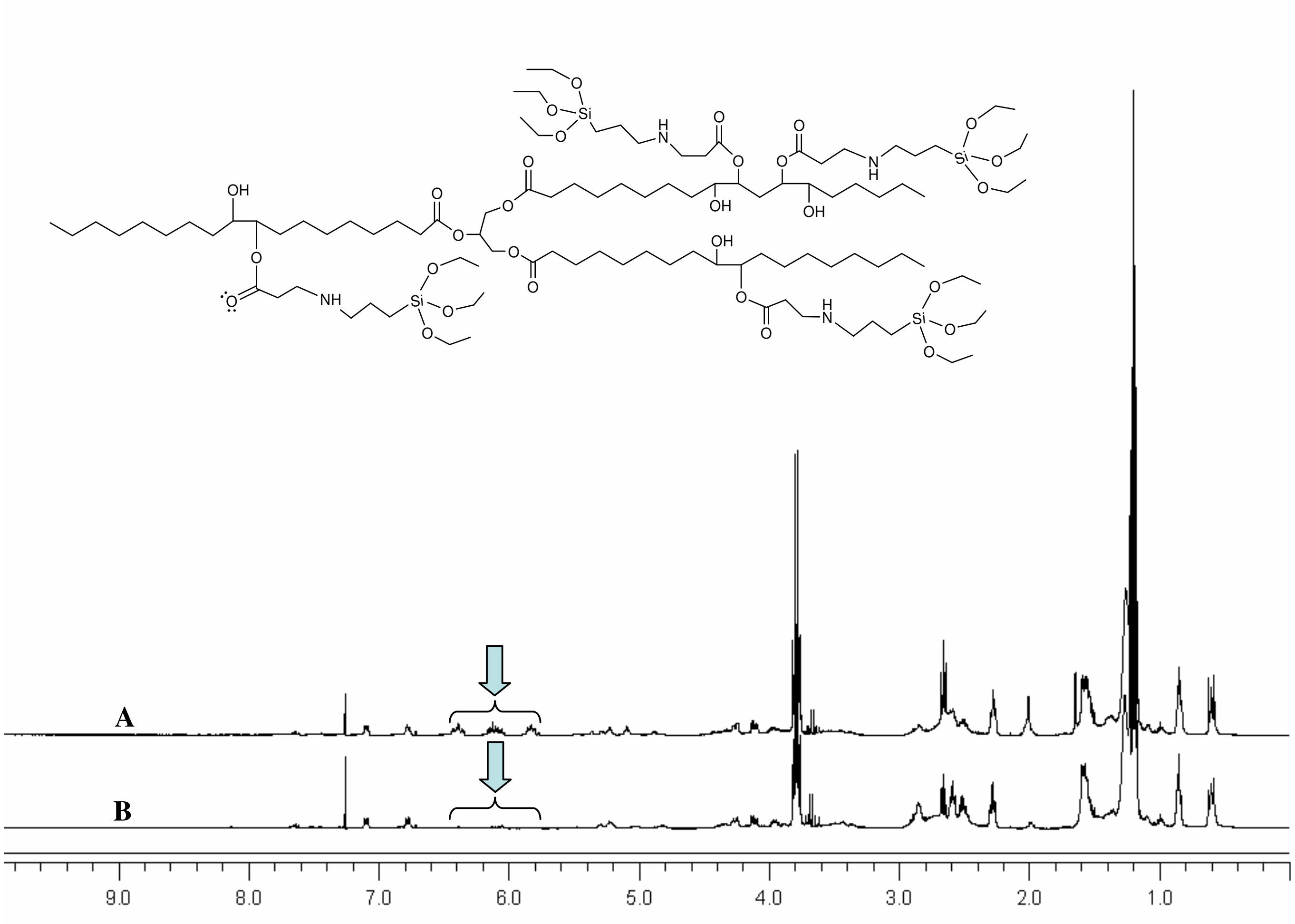


Figure 4.6. Characterization of the Michael reaction; A: beginning of the reaction, B: end of the reaction

4.3. Polymerization of Silanized-AESO and the Adhesion of the Polymer on Glass Surface

Organofunctional alkoxysilanes can be used as adhesion promoters on various surfaces. Upon moisture cure the alkoxysilane groups are hydrolyzed and the resulting silanols can then react with different substrates containing hydroxyl functionality by condensation [17]. Figure 4.7. shows the general mechanism of the moisture curing process.

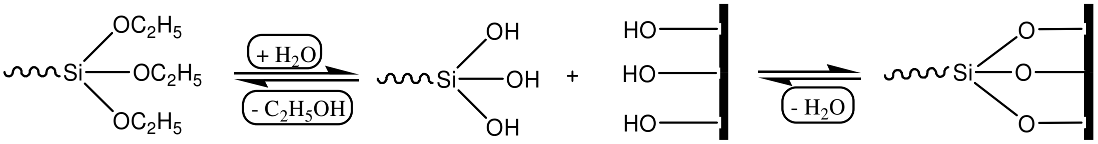


Figure 4.7. Moisture curing process of organofunctional alkoxysilanes

Soucek and his coworkers studied the effect of moisture cure on the adhesion strength of isocyanurate coatings. In this study, aminosilanes functionalized 1,6-hexamethylene diisocyanate was used to formulate a coating. The effect of moisture cure was investigated, and it was reported that moisture curing process dramatically enhances the adhesion and increases the crosslink density [23].

In another study isocyanate-free moisture cure coatings were prepared from epoxidized soybean oil. ESO was used to prepare polyols, which then were used for synthesizing a urethane prepolymer. Prepolymer was then treated with aminosilanes to allow aminosilanes to add to the isocyanate end of the prepolymer. It was concluded that aminosilanes treated samples show better adhesion properties [24].

The improvement in the adhesive properties of the polymer was studied by comparing the adhesion strength of free radically polymerized silanized-AESO before and after moisture cure on a glass surface.

The silanized-AESO was first homopolymerized under absolutely dry conditions to protect ethoxysilane functional groups from hydrolysis. Polymerization was done by mixing the monomer with a radical initiator, benzoyl peroxide, and drawing a thin film of the monomer on a regenerated, dried glass surface. Polymerization was carried under dry conditions for 12 hours on the glass surface and a thin film of polymer of approximately 80 μm thickness was obtained. After radical polymerization was complete, the polymer film was kept in moist air for 24 hours to allow ethoxysilane groups to hydrolyze and after hydrolysis, the polymer was further heated above condensation temperature.

The characterization of the silanized-AESO homopolymer was done by IR spectroscopy. Figure 4.8. and Figure 4.9. show the IR spectra of the silanized-AESO homopolymerized under dry conditions and after moisture curing process, respectively.

The disappearance of the peak corresponding to the acrylate double bonds at 959 cm^{-1} after polymerization can be clearly observed. Afer polymerization the difference in the carbonyl intensities is observed. There are three different carbonyl peaks in both spectra. The wide peak occurring in both spectra in 1000-1200 cm^{-1} region is due to the overlapping of the peaks corresponding to —C—Si—O—, —Si—O—Si—, and —Si—O—C— stretchings.

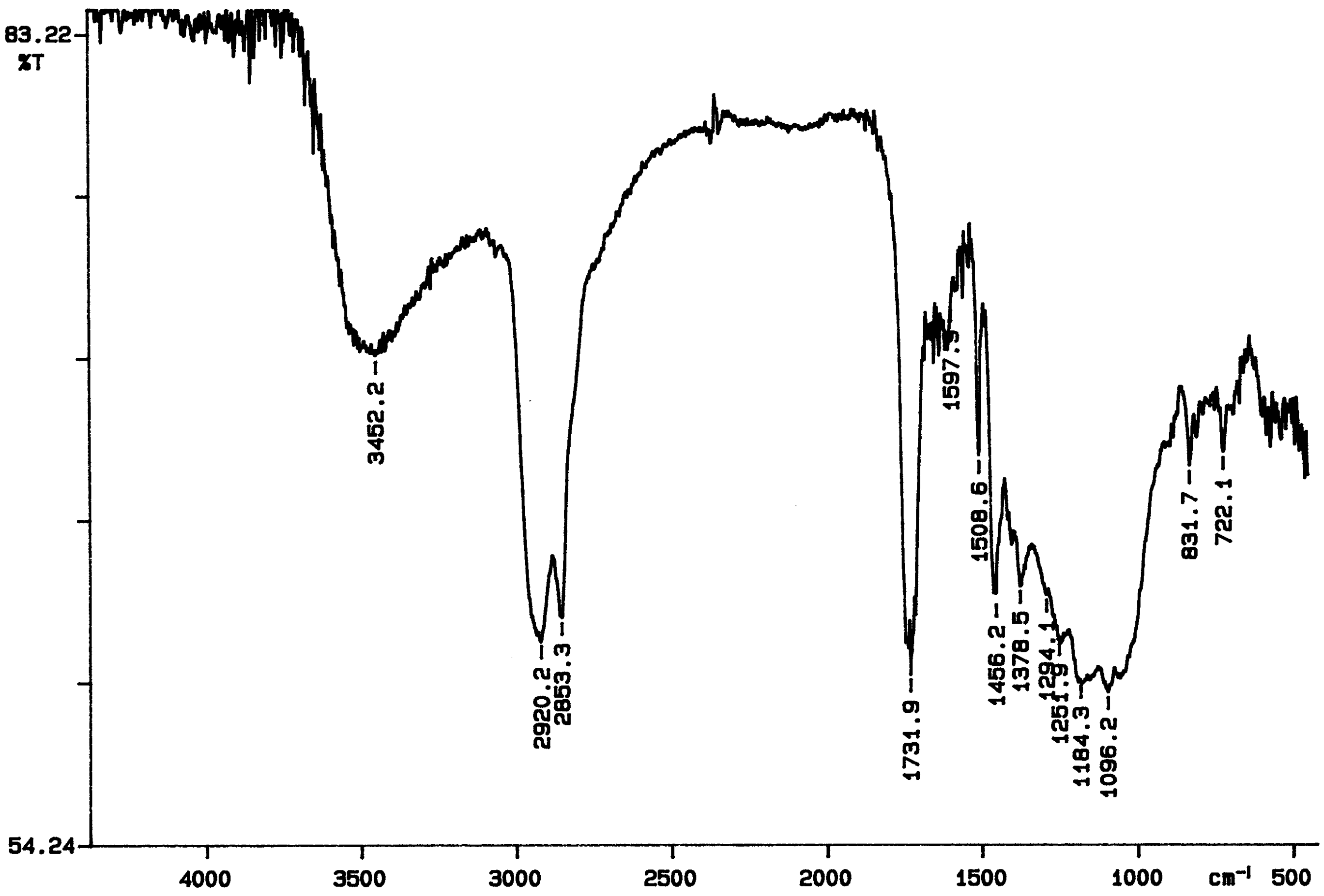


Figure 4.8. IR spectrum of silanized-AESO homopolymer before moisture cure

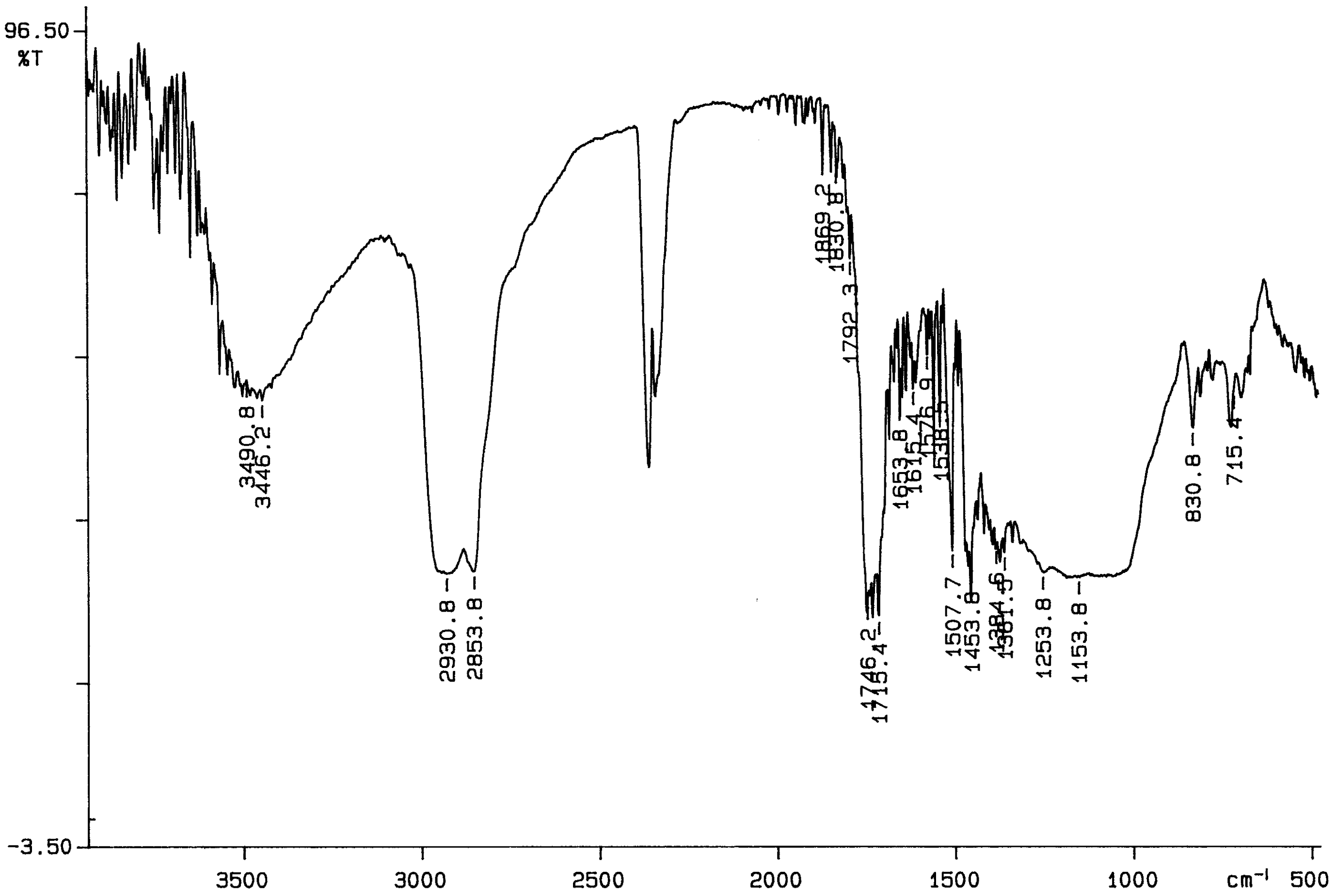


Figure 4.9. IR spectrum of silanized-AESO homopolymer after moisture cure

To study the adhesion, the polymerization process was carried on glass surface. As a result of the condensation process hydroxysilane groups form covalent —Si—O—Si— bonds with the glass surface. Figure 4.10. shows the radically polymerized film after moisture cure and condensation processes has taken place.

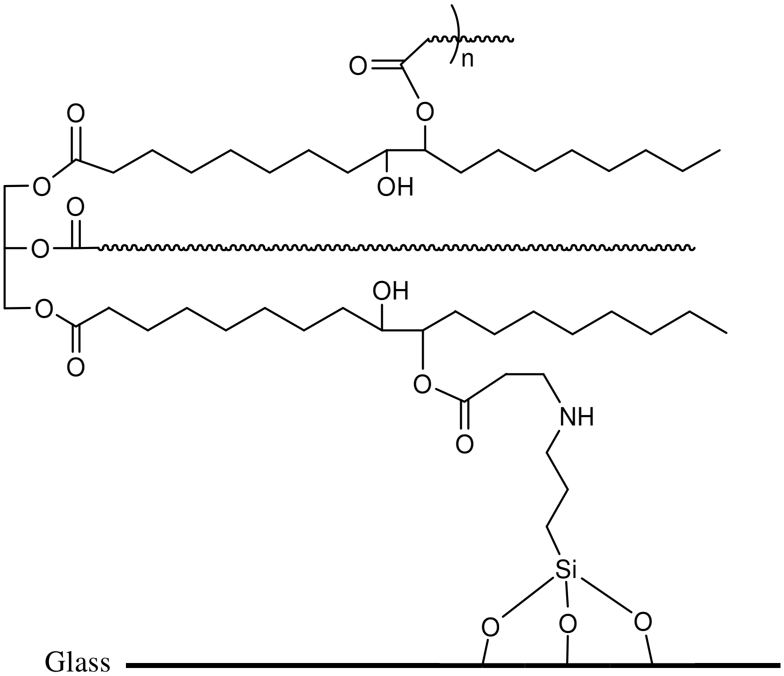


Figure 4.10. Adhesion on glass surface after moisture cure

To study the improvement in the adhesion strength, adhesion strength before and after moisture cure was measured. Before moisture cure the silanol groups are still protected as ethoxy groups. Therefore only weak Van der-Waals type attractions exist at the polymer-glass interface, and the adhesive strength should be low. After moisture cure the ethoxy groups are hydrolyzed and new silyl ether bonds are formed at the interface. These are covalent bonds of about 598 kJ/mol bond strength and the adhesive strength at the interface should be much higher. To observe full benefits of the hydrolysis/condensation steps, the sample has to be heated to a temperature which is high enough to push the silanol-silyl ether equilibrium to the right by allowing ethanol and water to evaporate from the interface.

The adhesion on the glass surface was studied according to the ASTM D 4541-Pull Off Adhesion Test. Figure 4.11. shows a general representation of the instrumentation used for the test.

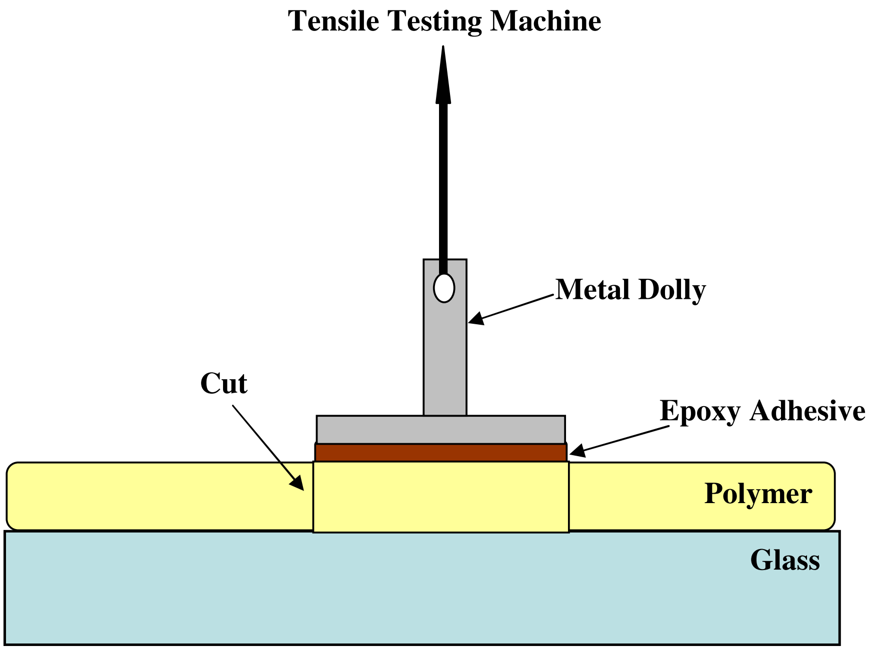


Figure 4.11. Adhesion Pull-Off Testing instrument

To perform the test, a dolly was adhered on the polymer surface by using epoxy adhesive resin. Then it was pulled with a tensile testing machine to measure the force at which adhesive failure of the polymer from the glass surface was observed.

The adhesion before moisture cure was studied on the sample right after radical polymerization process. Then, adhesion strength after moisture cure was measured. The adhesion strength was calculated as force per unit area at which adhesive failure of the polymer from the glass surface was observed. Force is the value obtained from the tensile strength machine and the unit area is surface area of the dolly where it is in contact with the adhesive.

Considerable experimental difficulties were encountered during testing. For the test to yield valid results it is necessary to obtain a clean and complete adhesive failure at the polymer-glass interface. Any other type of failure such as partial adhesive-cohesive failure or failure at the dolly-epoxy adhesive or at the epoxy adhesive-polymer interfaces is not acceptable. Tests where the dolly fails to lift vertically and shears off to one side or test that result in overstressing and breaking of the glass substrate are also not acceptable.

To get valid results at high adhesive strength it was necessary to decrease the polymer-glass interfacial area while keeping the dolly-polymer interfacial area the same, so that adhesive failure at the polymer-glass interface took place exclusively. Figure 4.12. shows this modification.

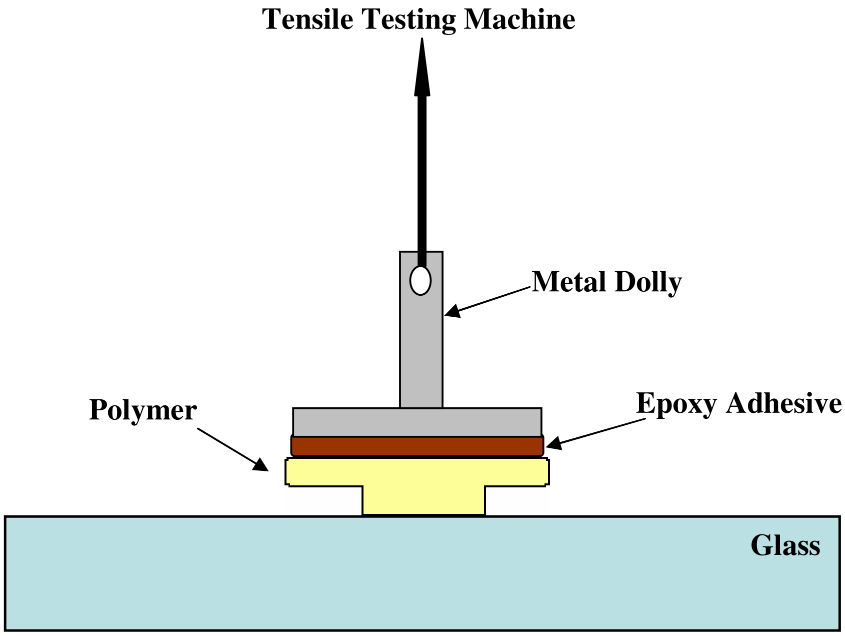


Figure 4.12. Modification done on the adhesion test

Figure 4.13. shows the adhesion strength results before and after moisture cure.

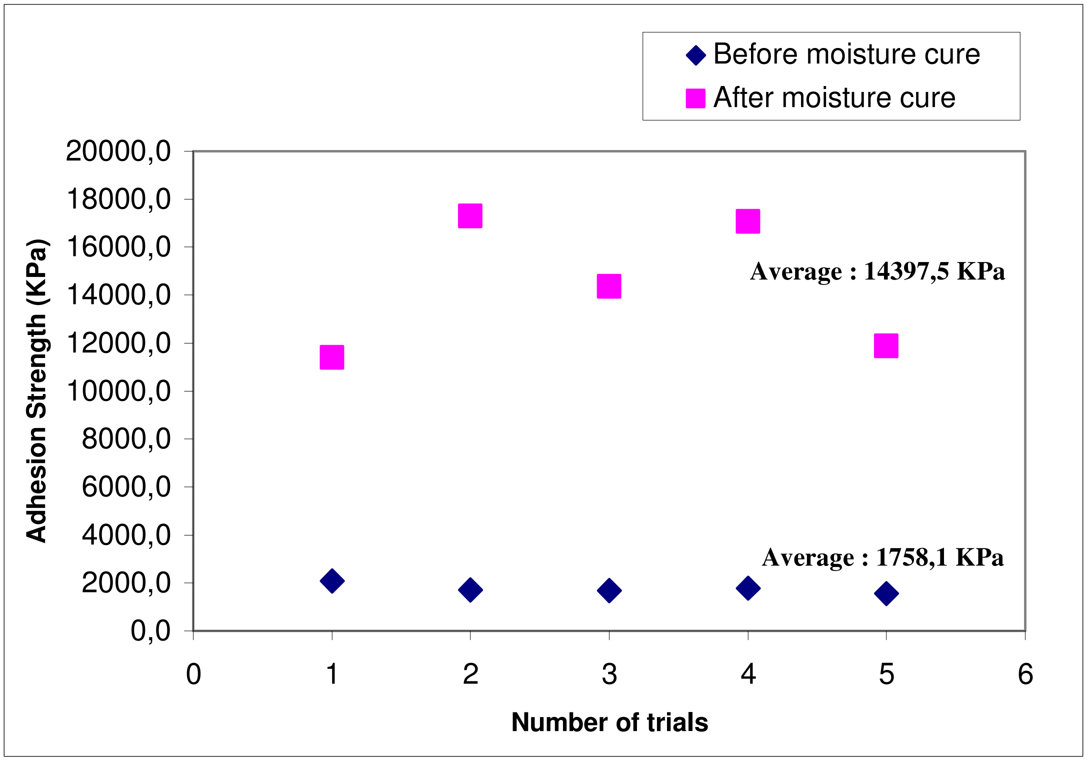


Figure 4.13. Adhesion strength before and after moisture cure

It was observed that upon moisture cure the average adhesion strength of the homopolymer increases from 1758.1 KPa to 14397.5 KPa, a remarkable eight fold increase indicating that with the moisture curing process —Si—O—Si— bond formation took place at the polymer-glass interface.

It is known that the formation of —Si—O—Si— bonds is reversible. With prolonged exposure to moisture or humid air, —Si—O—Si— bonds can hydrolyze back to silanol groups. This reversible bond formation may cause to a decrease in adhesion strength of the polymer with time. This has an important practical importance in the use of silane coupling agents in moist media, such as marine and automotive applications. In general the more hydrophobic the coupling agent is the less susceptible it is to reversal in wet media. Here, the three large alkyl groups on the triglyceride should make silanized-AESO uniquely successful.

The effect of humidity on the adhesion strength of the homopolymer was therefore studied. The moisture cured polymer was kept in a humidity chamber for 48 hours. At room temperature a 92 per cent constant humidity was supplied by keeping the sample within a closed space with a saturated aqueous solution of $Na_2CO_3.10H_2O$ [25]. The following figure shows the decrease in the adhesion upon exposure to humidity.

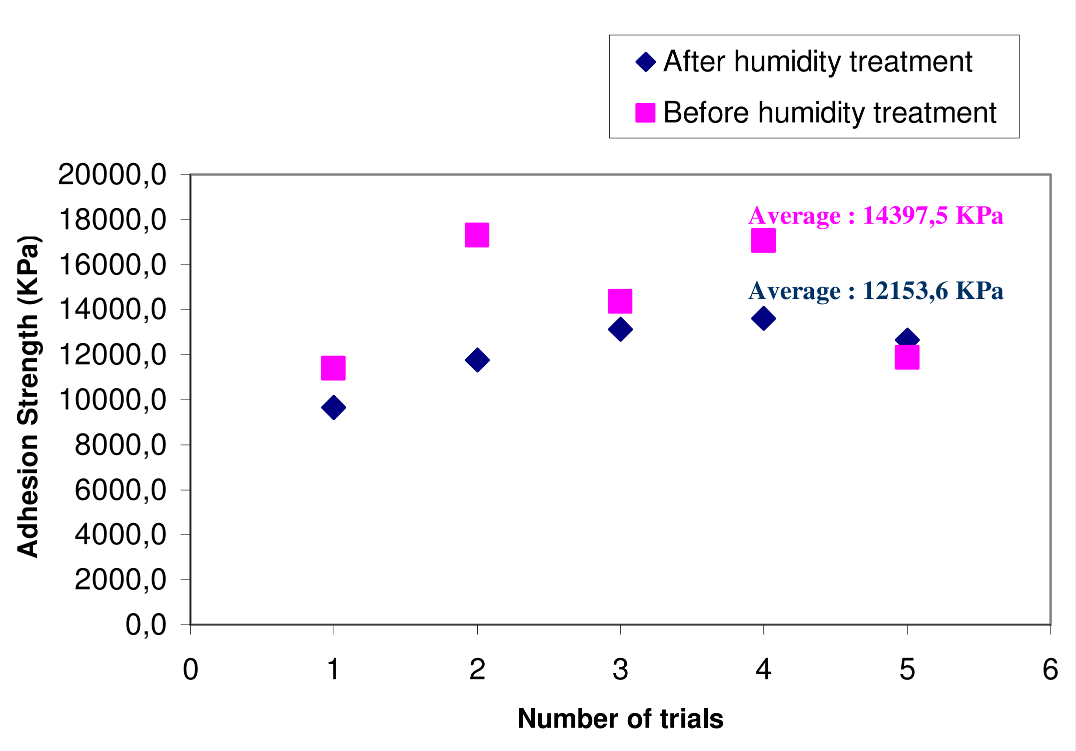


Figure 4.14. Decrease in the adhesion upon exposure to humidity

It was concluded that adhesion strength decreases from 14397.5 KPa to 12153.6 KPa, an average of 15 per cent decrease.

From the results it can be concluded that humidity causes a decrease in the adhesion strength. But the decrease is very small compared to the increased adhesion after moisture cure. The moisture treated interface is still seven fold stronger than the original surface before the activation of the silanol groups. We conclude that the presence of the very hydrophobic triglyceride on the silanized-AESO does in fact protect the interface against water ingress quite successfully.

4.4. Improvement in the Mechanical and Physical Properties of the Copolymer Upon Moisture Cure

Silanized-AESO is capable of free radical polymerization through its acrylate functionality and is also capable of condensation polymerization by the deprotection of its ethoxysilane groups. Under dry conditions and with a free radical initiator only the former mechanism takes place. If the resulting polymer is now moisture cured in the absence of an inorganic surface such as glass, the silanol groups that are produced will self condense and lead to higher connectivity, cross-linking and increased modulus.

Silanized-AESO that is free radically polymerized under dry conditions was very soft and had very low fracture toughness and mechanical testing could not be carried out. To be able to study its mechanical properties the monomer was copolymerized with styrene. Styrene is one of the most widely used reactive diluents used in copolymerization reactions. Also its reactivity ratio is very similar to the reactivity of acrylate double bond towards radical polymerization and true random copolymerization should be observed.

Copolymerization was done by mixing the silanized-AESO and styrene in 1:1 weight ratio. AIBN was used as radical initiator. Polymerization was done under dry conditions to prevent hydrolysis of ethoxysilane groups of the silanized-AESO. As a result a polymer which contains hydrolysable ethoxysilane groups was synthesized. Styrene and silanized-AESO copolymer had a high enough modulus and fracture toughness to allow examination by DMA methods. Figure 4.15. shows the structure of the copolymer obtained after radical polymerization.

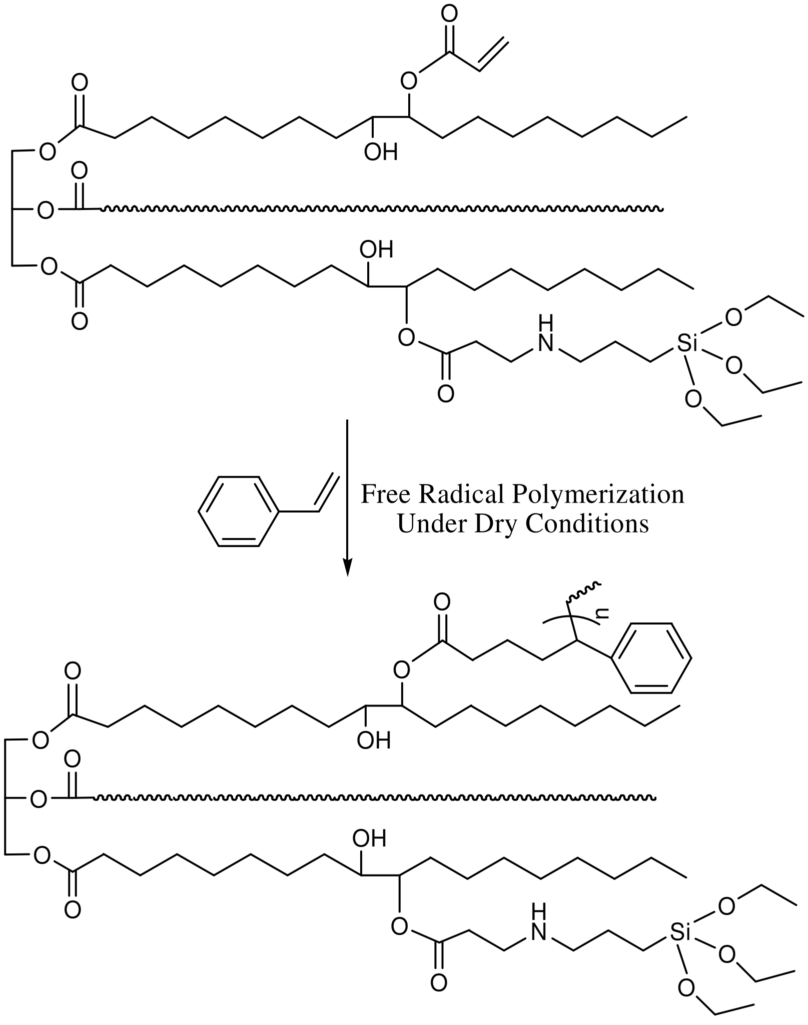


Figure 4.15. Structure of silanized-AESO-styrene (1:1 w/w) copolymer

It is expected that increase in the crosslink density will cause considerable improvement in the mechanical properties of the polymer.

The styrene-silanized-AESO copolymer was then moisture treated to hydrolyze the ethoxysilane groups and then heated to self-condensation of the silanol groups formed. As this experiment was done on the neat copolymer in the absence of an inorganic surface or filler the silanol groups could only self-condense and give a highly crosslinked network.

Figure 4.16. shows the polymer obtained after moisture cure and condensation processes.

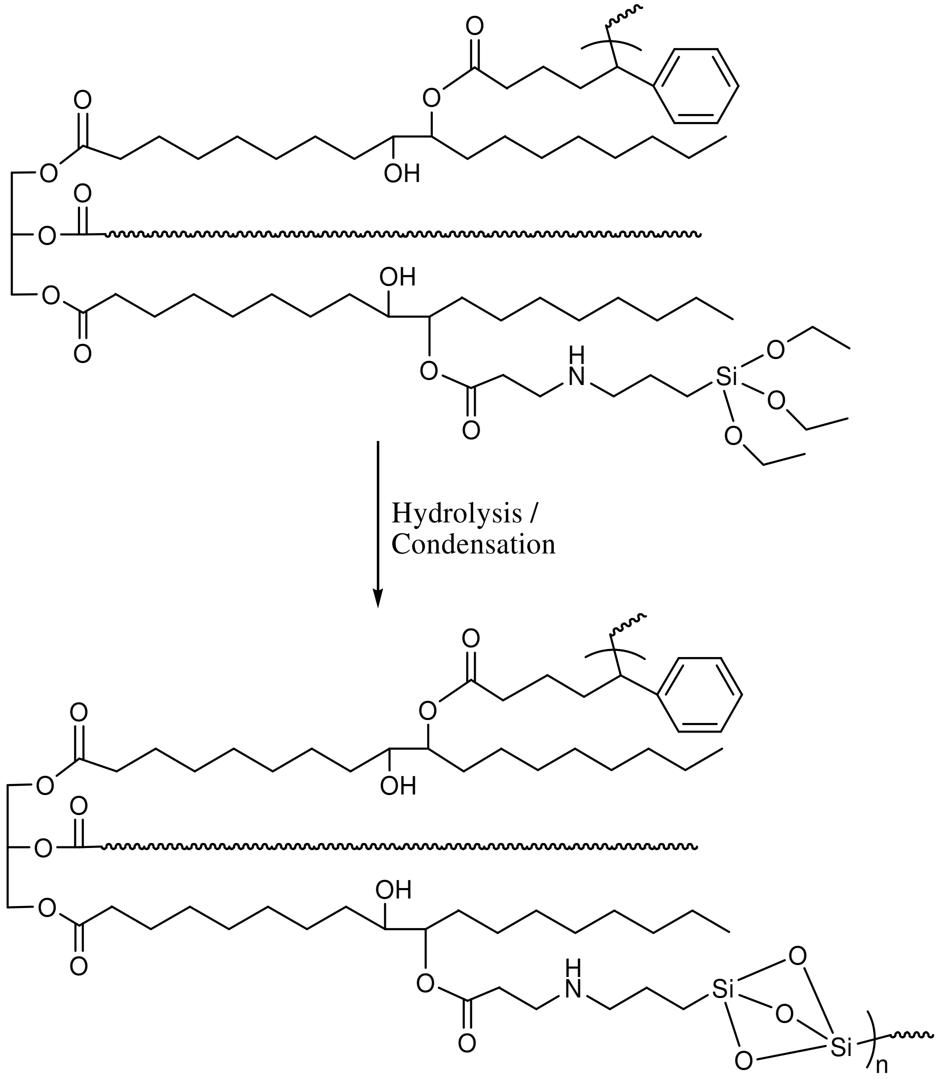


Figure 4.16. Structure of silanized-AESO-styrene (1:1 w/w) copolymer after moisture cure and condensation processes

4.4.1. Improvements in the Mechanical Properties

The improvement in the mechanical properties of the copolymer upon moisture cure was studied with Dynamic Mechanical Analysis (DMA).

Dynamic mechanical properties are the mechanical properties of materials as they are deformed under periodic forces. With DMA test, the material can be characterized in terms of its moduli, elasticity, viscosity, damping behavior, and glass transition temperature, and the changes of these with strain, strain rate, temperature, and oscillatory frequency [26]. In dynamic mechanical test, an oscillating strain (sinusoidal or other waveform) is applied to a sample and the resulting stress developed in the sample is measured. The output signals are analyzed and using established mathematical methods the rheological parameters are computed.

The stress signal generated by a viscoelastic material can be separated into two components: an elastic stress is in phase with the strain, whereas a viscous stress is in phase with the strain rate (90^{o}C out of phase with the strain). The elastic stress measures the degree to which the material behaves as an ideal solid; the viscous stress, the degree to which the material behaves as an ideal fluid. This separation of the stress components vectorially allows the material's dependence on strain amplitude and strain rate to be measured simultaneously.

The elastic and viscous stresses are related to material properties through the ratio of stress to strain, the modulus. The ratio of the elastic stress to strain is the elastic (or storage) modulus E′; the ratio of the viscous stress to strain is the viscous (or loss) modulus E″.

The polymer samples for dynamic mechanical analysis were prepared to dimensions of 25 x 5 x 0.5 mm. Temperature scans were run from room temperature to 160 ^{o}C at a heating rate of 3 ^{o}C/min with a frequency of 1 Hz and strain 0.01 %. Figure 4.17. shows the dependence of the storage modulus E′, loss modulus E″, and the loss factor tan δ for the copolymer after radical polymerization under dry conditions, and Figure 4.18. shows the results after moisture curing and condensation processes are done on the polymer.

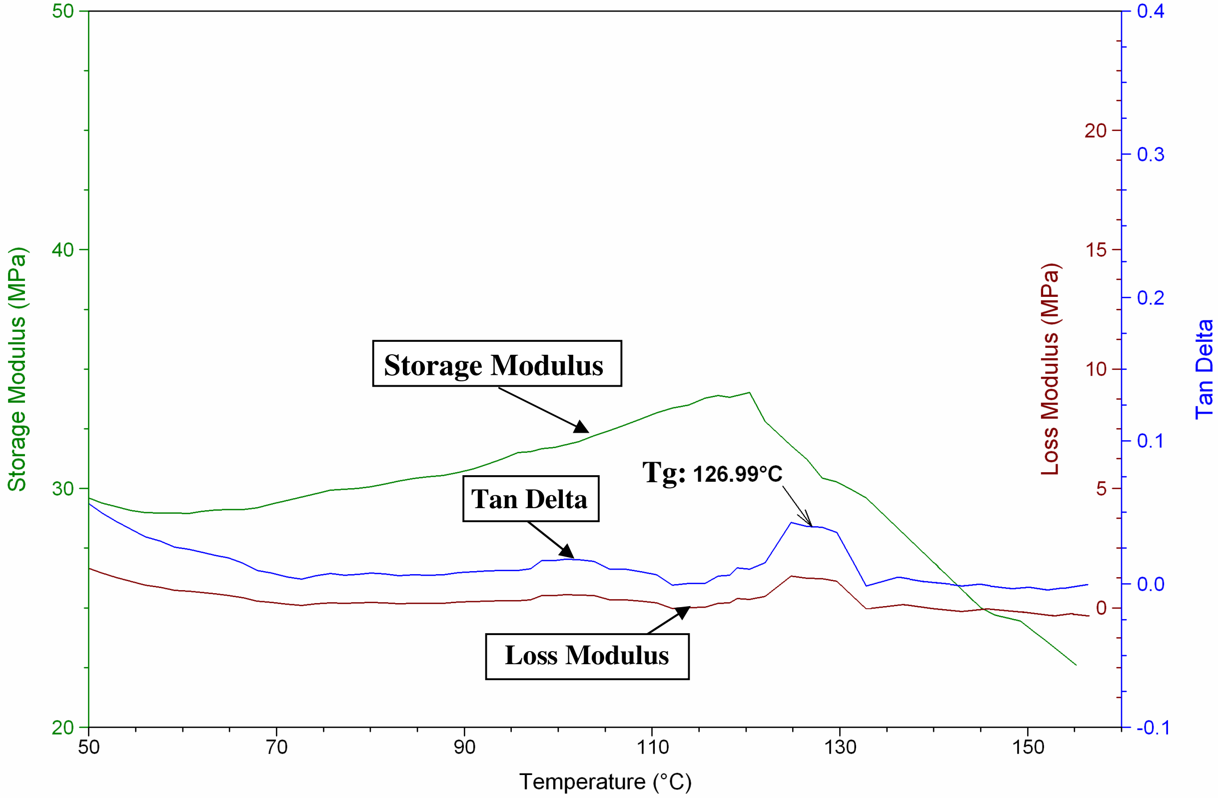


Figure 4.17. DMA traces for silanized-AESO-styrene copolymer before moisture cure

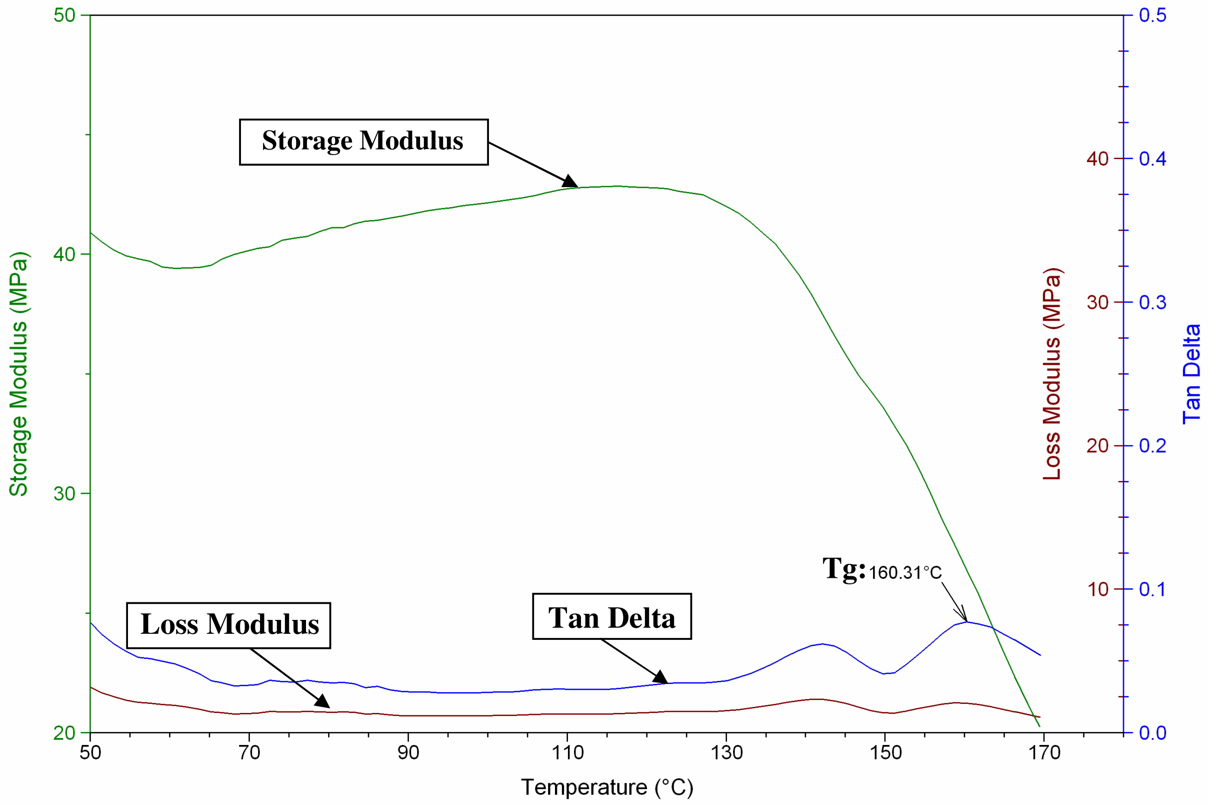


Figure 4.18. DMA traces for silanized-AESO-styrene copolymer after moisture cure

The silanized-AESO-styrene copolymer samples show rubbery behavior in dynamic medium. The effect of self-condensation causing to an increase in the crosslink density was clearly observed with DMA analysis. The free radically polymerized sample showed an average 30 MPa storage modulus. The same sample after moisture curing sample showed nearly a 35 per cent improvement in the storage modulus, from 30 to 43 MPa. The effect improvement in the crosslink density upon moisture cure can also be observed on the glass transition temperatures of the polymer samples. The Tg of the copolymer increases from 125 ^{o}C to 160 ^{o}C. This indicates that a higher temperature is required for the onset of large scale segmental motion in cross-linked polymer.

Tan δ curves of the silanized-AESO-styrene copolymer before and after moisture cure shows two maxima. This indicates an uneven crosslinking density of the polymer morphology. The effect is clearly observed especially after moisture curing process. After hydrolysis step with the self-condensation of silanol end groups some highly crosslinked areas are being formed. These partial highly crosslinked and partial less crosslinked areas with two maxima on Tan δ curve makes polymer morphology heterogeneous. Such behavior known as “grainy morphology” has been observed in other cross-linked polymers such as polyesters before.

4.4.2. Thermal Properties

The effect of moisture curing on the polymer was studied with Differential Scanning Calorimetry (DSC) and Thermal Gravimetric Analysis (TGA) techniques.

Differential scanning calorimetry is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference are measured as a function of temperature. Both the sample and the reference are maintained at very nearly the same temperature throughout the experiment. The basic principle underlying this technique is that, when the sample undergoes a physical transformation such as phase transitions, more (or less) heat will need to flow to it than the reference to maintain both at the same temperature. Whether more or less heat must flow to the sample depends on whether the process is exothermic or endothermic.

With the differential scanning method Tg values of the polymers were determined. Temperature scans were run from 0 ^{o}C to 160 ^{o}C at a heating rate of 10 ^{o}C/min. For each sample two runs were done. But, in the second runs no Tg was observed. This indicates that, silanol condensation is incomplete and it continues during DSC experiment above 100 ^{o}C.

Figure 4.19. and 4.20. show the results obtained for the silanized-AESO homopolymer and the styrene-silanized-AESO copolymer before and after moisture cure.

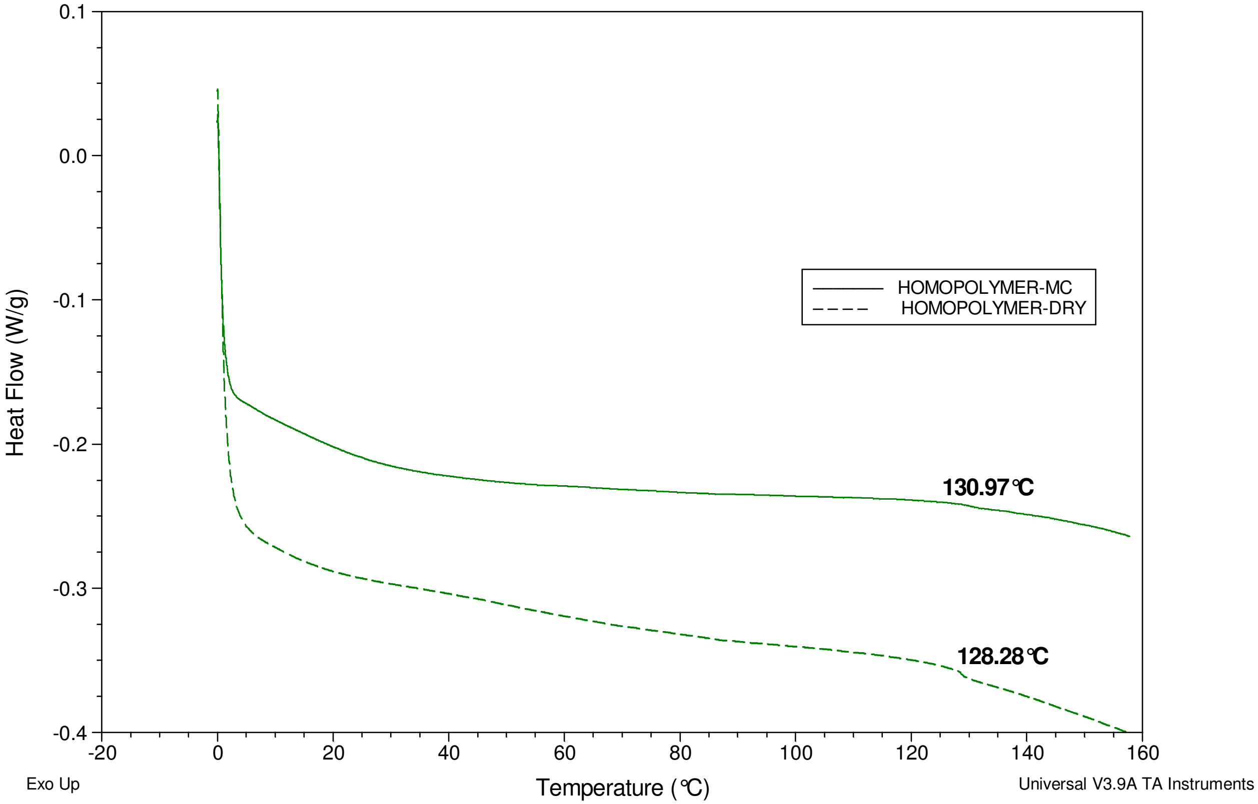


Figure 4.19. DSC traces of silanized-AESO homopolymer before and after moisture cure

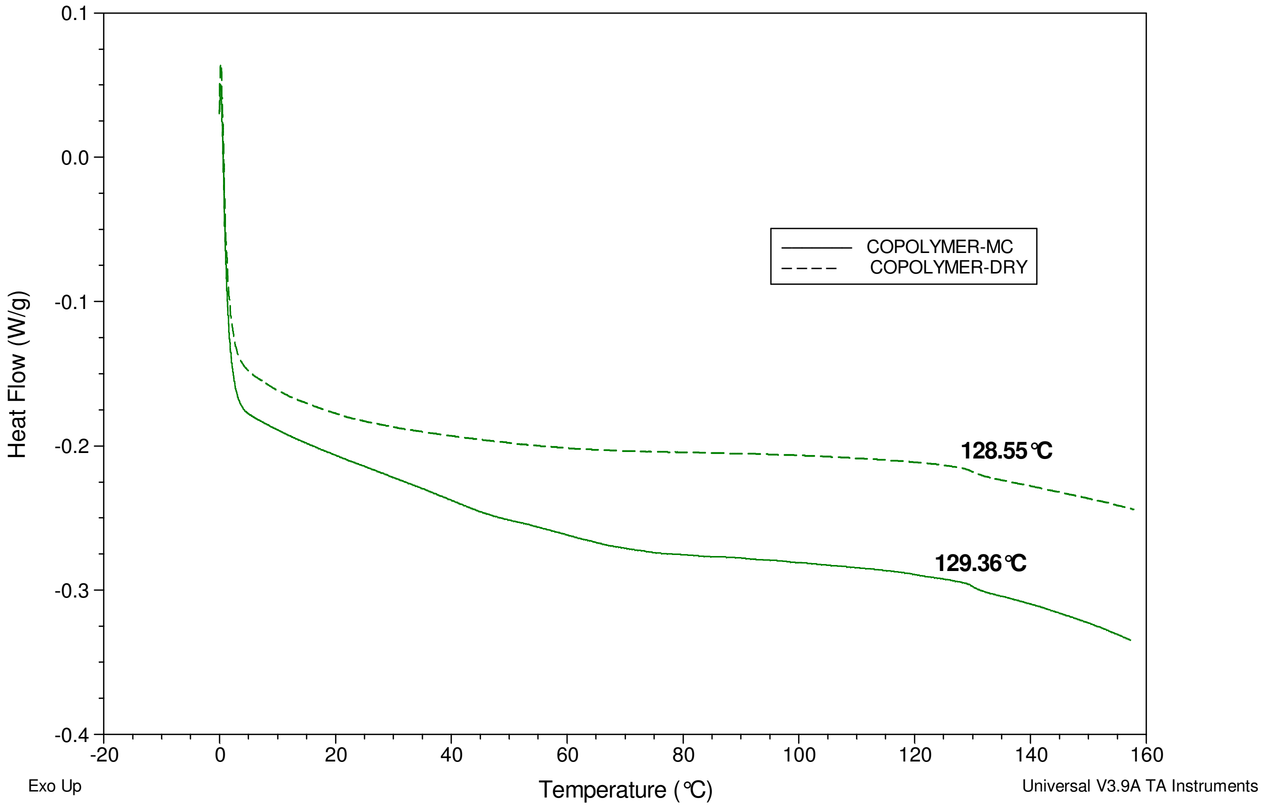


Figure 4.20. DSC traces of silanized-AESO-styrene copolymer before and after moisture cure

In all samples a transition that may or may not be a true glass transition was observed at around 130 ^{o}C. The fact that the second runs did not show this transition leads us to think that these are the endotherms caused by silanol condensation rather that Tg. In any case such similar Tg values for the homopolymer and 1:1 styrene copolymer would be highly unlikely.

With thermal gravimetric analysis the weight changes in materials with regard to temperature are measured. This allows for the effective quantitative analysis of thermal reactions that are accompanied by mass changes, such as evaporation, decomposition, dehydration etc.

TGA analysis was done to the homopolymer and copolymer before and after moisture cure. Figure 4.21. shows the overlayed results for the homopolymer before and after moisture cure and Figure 4.22. shows the overlayed results for the styrene copolymer of the multifunctional monomer before and moisture cure.

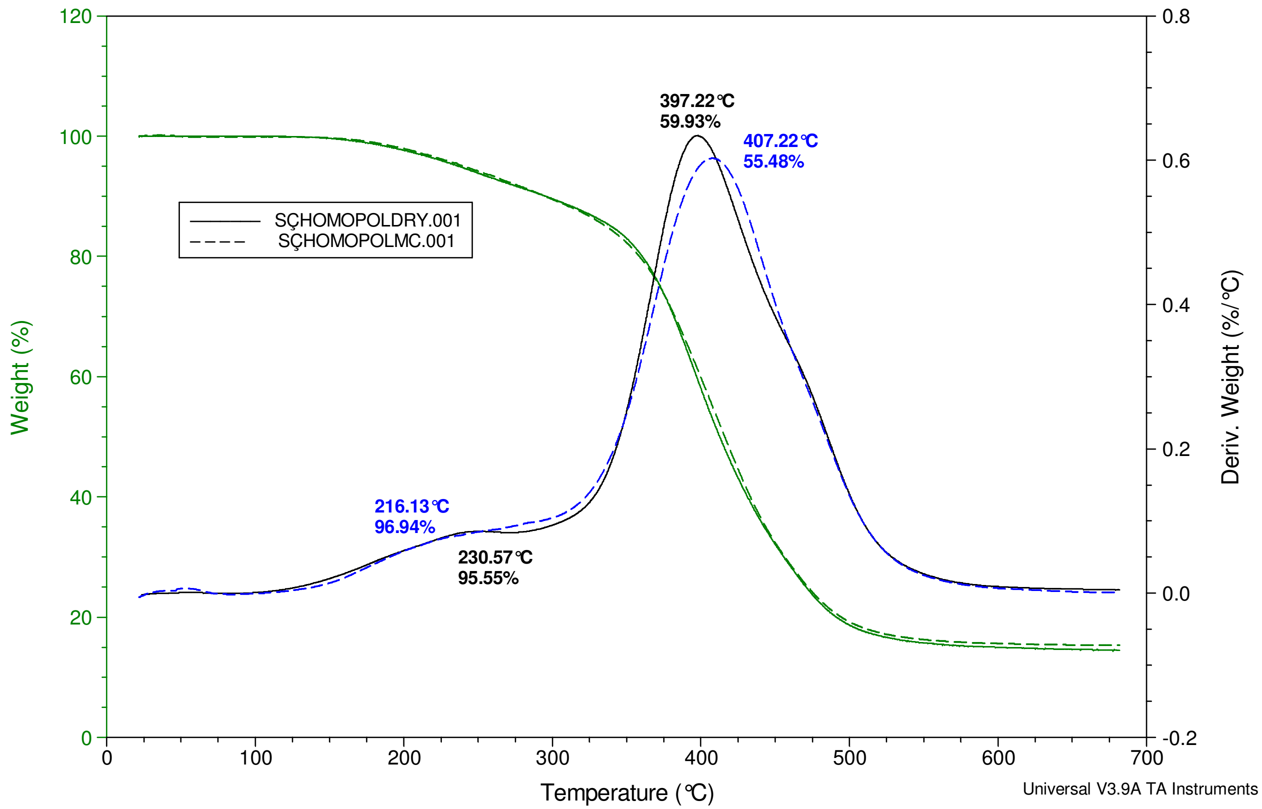


Figure 4.21. TGA traces of silanized-AESO homopolymer before and after moisture cure

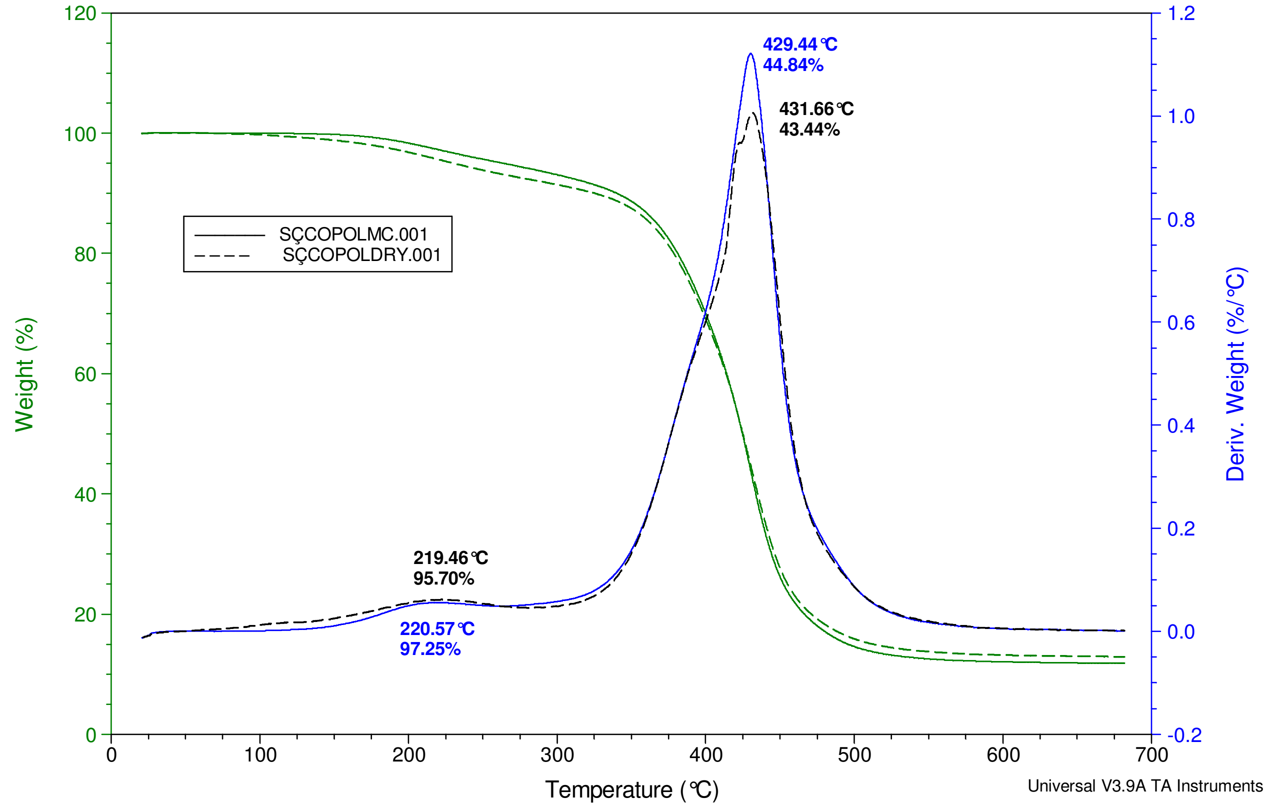


Figure 4.22. TGA traces of silanized-AESO-styrene copolymer before and after moisture cure

The polymer samples were stable up to 200 ^{o}C. Between 200 ^{o}C and 250 ^{o}C an average of 6 per cent weight loss for the silanized-AESO homopolymer and 3 per cent weight loss for the styrene-silanized-AESO copolymer was observed. This can be due to loss of moisture in the samples because of further condensation of unreacted silanol groups. When exposed to elevated temperatures self-condensation may occur with loss of water.

The decomposition was completed at 400 ^{o}C for the silanized-AESO homopolymer and at 430 ^{o}C for the styrene-silanized-AESO copolymer. 10 per cent char remained for both homopolymer and copolymer samples. The onset of weight loss occurs around 430 ^{o}C which is close to the ceiling temperature of most acrylate polymers.

4.4.3. Surface Hardness Tests

The surface hardness of the polymers was measured by using a shore durometer according to the ASTM D-2240 standard.

The shore test uses a hardened indenter, an accurately calibrated spring, a depth indicator, and a flat presser foot. The indenter is mounted in the middle of the presser foot and extends 2.5 mm from the surface of the foot. In the fully extended position the indicator displays zero. When the indenter is depressed flat even with the presser foot's surface, the indicator displays 100.

In use the unit is placed on the sample so that the presser foot is held firmly against the test surface. The spring pushes the indenter into the sample and the detector indicated the depth of the penetration. The deeper the indentation, the softer the material, and the lower the indicator reading.

For the analysis 1 mm thick samples were prepared. The samples were protected from any possible mechanical stress before testing. The samples were tested from 10 different points on the same surface. Figure 4.23. shows the results for the surface hardness of the styrene copolymer before and after moisture cure.

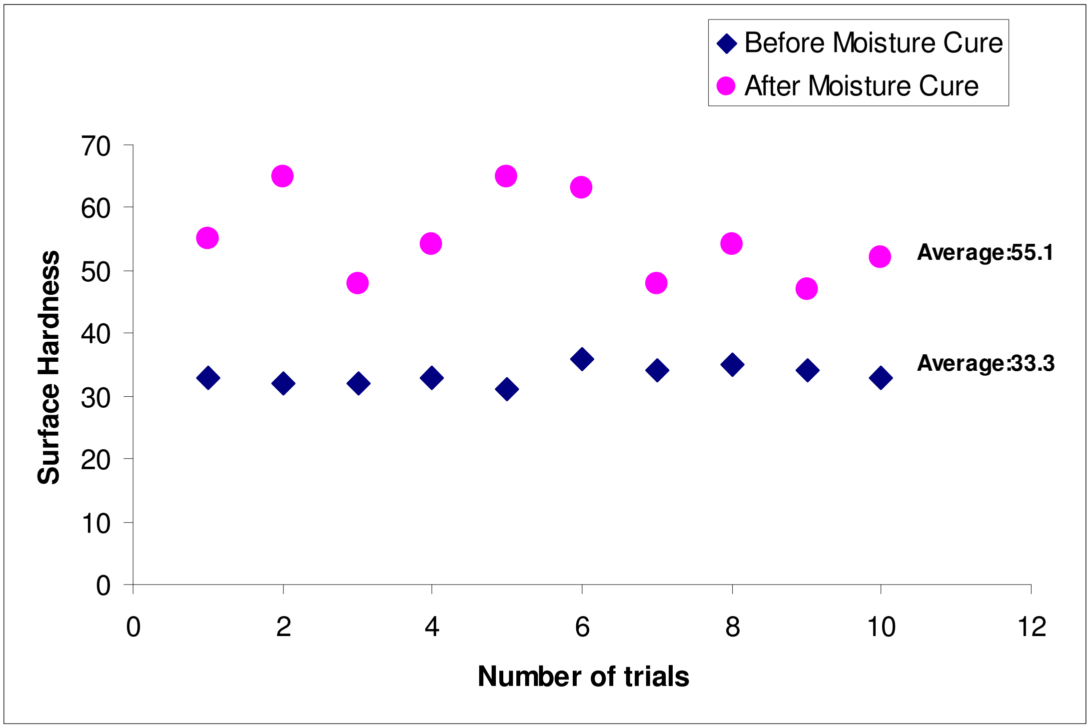


Figure 4.23. Shore test results before and after moisture cure

After moisture curing process an increase from average 33.3 to 55.1 on the polymer surface hardness is observed as expected. The improvement in the surface harness can be attributed to the increase in the crosslink density.

The surface hardness results also show that moisture curing process causes to fluctuations on the hardness of the polymer surface. The reason for this can be uneven crosslink density occurring after self-condensation of the hydroxysilane groups upon moisture cure. In the places where self-condensation process occurs high crosslinked areas are formed, where as the other areas are composed of slightly crosslinked polymer. This is another consequence of the "grainy morphology" that is probably being formed.

4.4.4. Swelling Test

Crosslinked polymers when placed in a good solvent absorb the solvent and swell. The extent of swelling represents a competition between two forces. During mixing the solvent penetrates in the polymer. As the polymer chains in the crosslinked polymer try to elongate, they generate a force in opposition to this deformation. The volumetric swelling reaches a steady state when two forces balance each other.

The swelling behavior of crosslinked polymers is also a good indication for the crosslink density. Higher swelling indicates lower crosslink density.

The swelling behavior of the copolymer in CCl_4 was examined by using a traveling microscope. The samples were put in a closed container and the experiment was continued until the solvent uptake ceased. The swelling ratio (q) was obtained by the following equation:

$$q = V / V_0 = (L / L_0)^3$$

where V_0 and V are the volumes of unswollen and swollen polymer samples, respectively; and L_0 and L are the unswollen and swollen polymer samples, respectively. Figure 4.24. shows the swelling behavior of the samples before and after moisture cure.

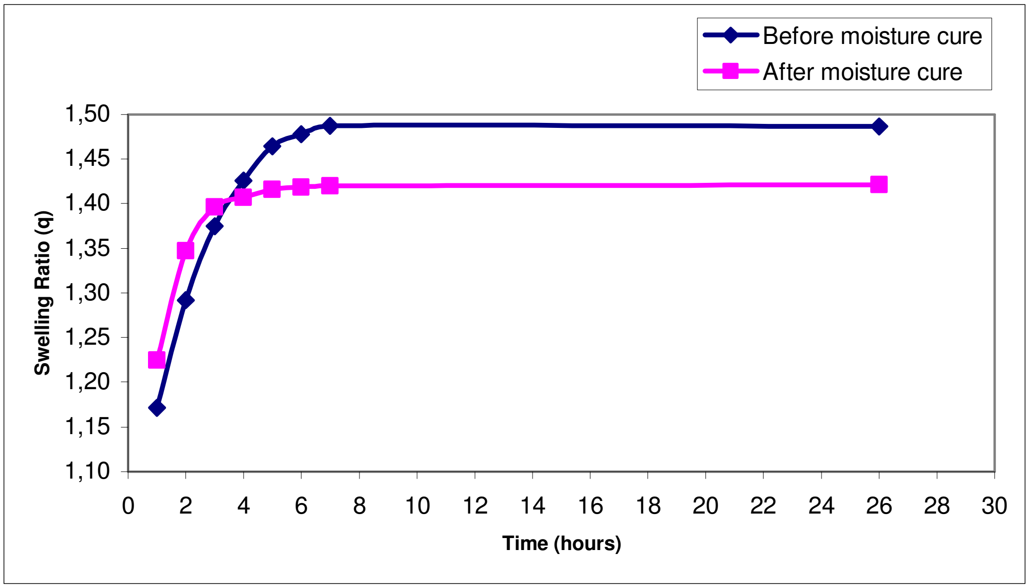


Figure 4.24. Swelling behavior of styrene-silanized-AESO copolymer before and after moisture cure

The free radically polymerized polymer ceases to swell in about 6 hours while the same polymer after moisture cure induced cross-linking ceases to swell in only 3 hours.

In addition to the swelling time, equilibrium swelling ratio (q) of the polymer sample also decreases after moisture curing process, which indicates an increase in the crosslink density.

5. CONCLUSIONS

A multifuncional monomer was synthesized by reacting Acrylated Epoxidized Soybean Oil with 3-Aminopropyltriethoxysilane. The characterization of the silanized-AESO was done by NMR and FTIR spectroscopy. Ethoxysilane groups of the silanized-AESO can easily be hydrolyzed, which makes them very sensitive to moisture. To prevent any possible hydrolysis silanized-AESO was used without any purification for further synthesis.

Adhesive properties of the silanized-AESO homopolymer were studied on glass surface. An eight fold of increase was observed in the adhesion strength of the silanized-AESO homopolymer upon moisture cure. Exposure to 92 per cent humidity for 48 hours caused to a 15 per cent decrease in the adhesion strength of the silanized-AESO homopolymer.

The silanized-AESO monomer was copolymerized with styrene by using 2,2'-azobis(isobutyronitrile) (AIBN) as radical initiator. The mechanical properties of the silanized-AESO-styrene copolymer were studied with DMA, DSC, TGA, swelling and surface hardness tests. A 35 per cent increase was observed in the storage modulus value of silanized-AESO-styrene copolymer after moisture cure treatment. Tan δ curves of polymers indicate that crosslinked areas of the polymer show heterogeneous morphology. The Tg of the copolymers were found to be 130 ^{o}C copolymer before moisture cure and 160 ^{o}C after moisture cure for silanized-AESO-styrene copolymer. In TGA, all samples showed an average of 5 per cent decrease at 230 ^{o}C, indicating loss of water due to condensation of unreacted hydroxysilane groups. Samples were totally decomposed at 430 ^{o}C yielding 10 per cent char. The effect of increasing crosslink density was clearly observed in the swelling test results. After moisture curing process polymer exhibited better solvent resistance property.

As a future project, the composites of silanized-AESO homopolymer can be prepared with different kind of fillers such as, glass fibers, glass wool, mineral wool, quartz, sand, mica etc. The effect of moisture curing process on composite strength can be studied.

Copolymerizaiton of silanized-AESO with styrene was done in 1:1 weight ratio. The effect of changing the amount of styrene in the copolymer composition, on mechanical properties of the copolymer can be studied as another future project. Adhesion of silanized-AESO on metal surfaces should also be studied.

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