# NEW POLYMERS FROM TRIGLYCERIDES AND SILICONES

by

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*To My Family*

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# ABSTRACT

## NEW POLYMERS FROM TRIGLYCERIDES AND SILICONES

In this study Maleinized Soybean Oil (SOMA) was used as a crosslinking agent for two functional polydimethylsiloxanes. In the first example, the silicone used was carbinol silicone. IR of the product proved the formation of a new ester. In the second case, the silicon used had aminopropyl side groups and IR of the product proved the formation of imides. In the case of poymerization between amino silicone and SOMA, Interfacial polymerization technique was used by making thin films of the two monomers and by putting them in intimate contact. This film has two surfaces. One surface is rich in SOMA and the other is rich in amino silicone. Each surface has different surface hardness. The products obtained were characterized by FTIR. For SOMA-carbinol silicone, polymer sample which has lower content of SOMA showed an average 175 MPa storage modulus while sample which has higher content of SOMA showed a storage modulus of 1850 MPa. This shows that increasing SOMA content increases the cross link density of the final product. The effects of compositions SOMA and carbinol silicone monomers were also analyzed by swelling test. The equilibrium swelling ratio (q) of the copolymer sample also decreases from 8.9 to 3.5 upon increasing the SOMA content, which indicates an increase in the crosslink density. Swelling test was also done for SOMA-amino silicone film. The equilibrium swelling ratio (q) value for this film was 12,95 which is a good indication for the formation of cross linking reaction. Surface hardness was measured for both SOMA-carbinol and SOMA-amino silicone polymers. For carbinol silicone, this value was 27 and for the amino silicone this value was 47 respectively. The two surfaces of SOMA-Amino silicone film were characterized by contact angle measurement. Contact angle of the silicone rich surface was $123^0$ while SOMA rich surface was $90^0$ since silicone is more hydrophobic than SOMA. Finally, tensile test were made to analyze mechanic properties of SOMA-amino silicone film. The film was a flexible material and had a maximum tensile strength of 11(MPa).

# ÖZET

## TRİGLİSERİT AND SİLİKONLARDAN OLUŞAN YENİ POLİMERLER

Bu çalışmada, maleinize edilmiş soya yağı (SOMA), iki fonksiyonel polimetildi siloxan için çapraz bağlanma aracı olarak kullanıldı. Birinci örnekte karbinol silikon kullanıldı. Ürünün infrared spektrumu, yeni esterlerin oluşumunu kanıtladı. İkinci durumda kullanılan silicon aminopropil yan gruplarına sahipti ve bu ürünün IR spektrumu, imit oluşumunu kanıtladı. Amino silikon ve SOMA arasındaki polimerleşme reaksiyonunda, arayüzey polimerleşme tekniği kullanılarak, bu iki monomerin ince filimleri yapıldı ve bu çekilen filmlerin birbirleri üzerine koyulmasıyla yakın teması sağlandı. Oluşan film iki değişik yüzeye sahipti. Yüzeylerden birisi SOMA zengin diğeri ise amino silikon zengin yüzeyler idi. Herbir yüzey birbirinden farklı yüzey sertliği değerine sahipti. Elde edilen ürünler FTIR kullanılarak karakterize edildi. Daha düşük SOMA oranına sahip olan SOMA-Karbinol silikon örneği, ortalama 175 MPa storage modül değerine sahipken, daha yüksek SOMA oranına sahip olan örnek 1850 MPa storage modül değerine sahipti. Bu durum, artan SOMA içeriğinin, meydana gelen ürünün çapraz bağlanmasını arttırdığını gösterir. SOMA ve karbinol silicon bileşiminin etkisi ayrıca şişme testi ile analiz edildi. Kopolimer örneklerinin denge şişme oranının (q), artan SOMA oranına bağlı olarak 8.9 değerinden 3.5 değerine düşmesi, çapraz bağlanma oranını arttığının göstergesidir. SOMA-Amino silikon filmi içinde şişme testi yapıldı. Bu film için denge şişme oranı değerinin 12,95 olması, çapraz bağlanma reaksiyonunun meydana geldiğinin iyi bir kanıtıdır. SOMA-Karbinol ve SOMA-aminosilikon polimerleri için yüzey sertliği değerleri ölçüldü. Bu değerler sırasıyla, Karbinol silikonlu olan için 27 amino silikonlu olan için ise 47 dir. SOMA-Amino filminin her iki yüzeyi, temas açısı ölçümü ile karakterize edildi. Silikonun SOMA'ya göre daha hidrofobik olması sebebiyle, silikon zengin olan yüzeyin temas açısı değeri $123^0$ iken, SOMA zengin yüzeyin değeri $90^0$ olarak bulundu. En son olarak, SOMA-amino silikon filminin mekanik mukavemet değerlerini analiz etmek için çekme germe testi yapıldı. Film, elastik ve 11 megapaskal (MPa) maximum çekme mukavemetine sahipti.

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# LIST OF ACROYNMS/ABBREVIATIONS

| | |
|---|---|
| SOMA | Maleinized Soybean Oil |
| DMTA | Dynamic Mechanical Thermal Analysis |
| IR | Infrared |
| Q | Equilibrium swelling ratio |
| NMR | Nuclear Magnetic Resonance |
| PDMS | Poly dimethyl siloxane |
| PET | Poly ethylene teraphthalate |
| PS | Polystyrene |
| PP | Polypropylene |

# 1. INTRODUCTION

## 1.1. New Polymers from Triglycerides and Silicones

Synthesis of polymers from renewable resources such as plant and animal products is attractive due to decreasing reserves and increasing price of petroleum. Social demands of polymers from renewable, agricultural raw materials are also high since they represent a high-tech use for traditional agricultural products. As almost all bacteria excrete lipase enzymes usually biodegradable and cheap polymers are obtained from agricultural raw materials. The very early studies on polymer synthesis using plant oils directly have resulted in low molecular weight and low structural strength-products [1-2]. However recent studies show that the plant oils have the potential to take a major part in thermosetting polymer production. The growing interest and the increase in the research on plant oil based polymers have resulted in the manufacture of many thermosetting polymers exhibiting the required physical and mechanical qualities such as rigidity, strength, high glass transition temperature [3].

Vegetable oils which are known as triglycerides have different fatty acids with varying degrees of unsaturation. It is difficult to polymerize vegetable oils by themselves because they do not have reactive functional groups. It has been described that the reactivity of the soybean oil double bonds is very low and its polymerization is not possible [4-5]. However, the presence of double bonds in the soybean oil makes it possible to add some functional groups through chemical modification. By this method, production of new compounds which are suitable for polymerization is possible. Many chemical pathways for functionalizing triglycerides and fatty acids have been studied. In this work, we examined the reaction of soybean oil and maleic anhydride to synthesize soybean oil maleic anhydride adducts (SOMA) which is capable of polymerization. In the next step, SOMA adduct was used as a crosslinker for functionalized silicones containing hydroxyl and amino groups.

Silicones and vegetable oils are common materials in many personal care formulations, they have interesting properties and good performance in cosmetics industry.

Development of many organic modified silicones led to production of commercial personal care products, mold release agents, antifoam agents, surface modifiers etc. Recently, silicone / plant oil mixtures have been used to produce better personal care products because each class of materials provides unique properties [6].

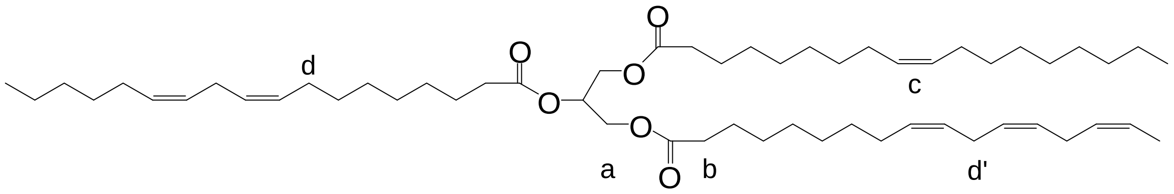
A few successful attempts to make silicone vegetable oil copolymers can be found in the literature. Tania Cristina Dias and Daniel Ferreira (US Patent 20100172856A1) [7] reported the hydrosilation of carbon-carbon double bonds in vegetable oils with organohydrogenpolysiloxane to produce compounds that are silicone/vegetable oil copolymers. An organohydrogenpolysiloxane having at least two silicone bonded hydrogen atoms and vegetable oil containing unsaturated bond were used. They also used hydrosilation catalyst containing platinum to promote reaction between the organohydrogensiloxane and vegetable oil.

In this research, polymers from triglycerides and silicones have been synthesized by using new methods. We discovered a way to polymerize SOMA with two kind of silicones 1- )Carbinol silicone which has OH end groups. 2- )Amino silicone which has amino functional pendant groups. The research goal was to produce new silicone plant oil copolymeric networks and to obtain polymers which have two different hydrophobic segments. While anhydride and alcohol or anhydride and amine reactions are well known in the literature, they have not been used to prepare silicone modified plant oils.

## 1.2. Natural Oils

### 1.2.1. Structure and Properties of Fatty Acid and Triglycerides

Lipids or fats are naturally occurring molecules with molecular weights varying from 750 to 1000. Vegetable oils also known as triglycerides are composed of three fatty acid groups bonded via an ester linkage to a glycerol unit [8]. In nature, lipids have been derived from various sources such as vegetables, animals or marine sources. Lipids have been used as nutrients through the ages and more recently as fuel, lubricant and starting material for synthesis of other chemicals [9]. Such a wide application area could be explained with the unique chemical structure and physical properties which gives rise to many functionalities and variety of chemical reactions. In addition, the properties of the fat may differ due to the combination of different fatty acids that are esterified at the three hydroxyl ends of glycerol. A general structure of triglyceride molecule is shown below [8].



a. Ester groups
b. α to carbonyl group
c. Double bond
d. Allylic hydrogen
d'. Double allylic hydrogen

Figure 1.1. Structure of a Triglyceride Molecule.

Triglycerides are obtained from plant oil such as sunflower oil, corn oil, soybean oil, cotton oil, olive oil. The molecular structure of a typical triglyceride is shown in Figure 1.1. There are several sites suitable for chemical modifications. For example, it has ester groups which are suitable for many reactions such as alcoholysis, alkyledination, amidation, hydrolysis, reduction, saponification and trans esterification. It also has a carbon α to carbonyl. There are acidic hydrogens and this group is suitable for halogenation and sulfonation reactions. It has double bonds. It is well known that all kinds of addition, halogenations, hydrogenation, metathesis, oxidation, epoxidation etc. reactions can be carried out on that double bond. It has allylic hydrogen which is suitable for allylic halogenation and ene reactions. If there is more than one double bond doubly allylic hydrogens are even more reactive. In our study, soybean oil was used as a plant oil to synthesize new polymers [10].

### 1.2.2. Structure and Properties of Soybean Oil

Soybean oil is a mixture of glycerol esters of unsaturated oleic, linoleic and linolenic acids and saturated palmitic and stearic acids and has an average of 4.2 double bonds per triglyceride molecule [11].

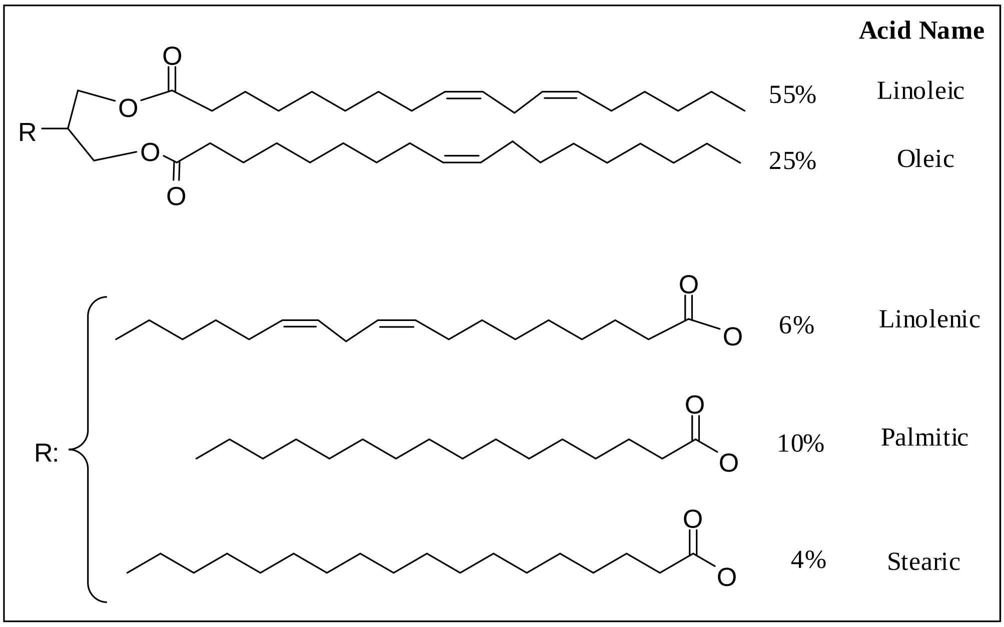


Figure 1.2. Fatty acids in soybean oil.

Table 1.1. The general properties of soybean oil.

| | |
|---|---|
| Iodine Number | 117-140 |
| Saponification Number | 189-195 |
| Viscosity(cP) at 40 °C | 28 |
| Smoke Point | 213 °C |
| Flash Point | 317 °C |
| Fire Point | 342 °C |
| Density(15 °C) | 0.910-0.934 |
| Molecular Weight (g/mole) | 850-870 |

Soybean oil is one of the most preferred renewable feedstock in chemical industry since it is available in large amounts and it has high level of unsaturation, those double bonds are relatively unreactive. Therefore; some functionalization or chemical transformations are needed before Soybean oil can be used as a monomer in polymerization reactions [12-13].

Maleic anhydride can be bonded to soybean oil. Maleinization of Soybean oil has been known for a long time. Reaction between maleic anhydride and soybean oil can be carried out easily with the help of ene reaction pathway.

## 1.3. Ene Reaction

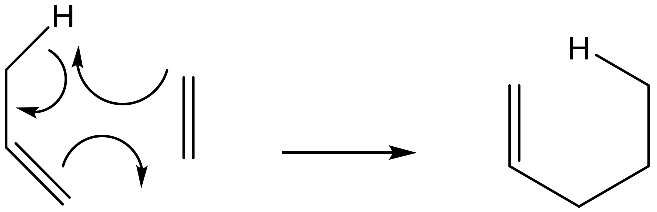


Figure 1.3. Schematic representation of ene reaction.

The ene reaction (also known as the Alder-ene reaction) is a chemical reaction between an alkene having an allylic hydrogen (the ene) and a compound containing a reactive multiple bond (the enophile). With migration of the ene double bond and 1,5 hydrogen shift a new σ-bond can be formed as shown in Figure 1.3. This transformation is a group transfer pericyclic reaction and therefore, usually requires high temperatures. Nonetheless, the reaction is compatible with a wide variety of functional groups that can be added to the ene and enophile moieties [14]. As earlier work done in our group shows [15], maleinization reaction requires at least 200°C and follows an “ene” reaction pathway. Maleic anhydride attacks to the allylic position of the fatty acid as shown in Figure 1.4. Ene pathway does not consume triglyceride unsaturation but shifts the position of double from 3-2 position to 4-3 position. The product is maleic anhydride adduct of soybean oil (SOMA) and contains reactive succinic anhydride groups that are capable of reacting with hydroxyl and amino groups.

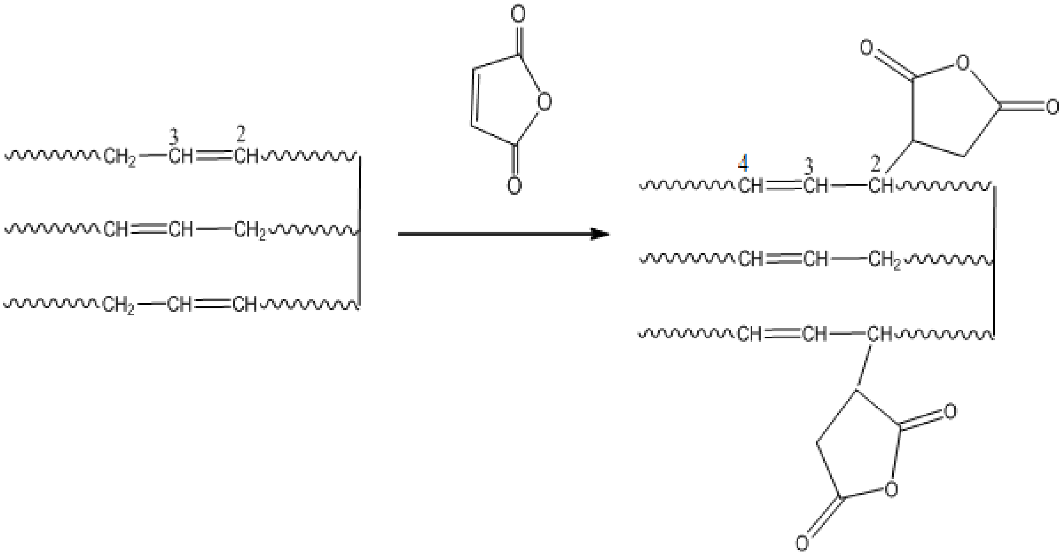


Figure 1.4. Ene reaction product of triglyceride and maleic anhydride.

## 1.4. SILICONES

### 1.4.1. Methods of Silicone Production

There are many types of silicone products, and silicone is used in a wide range of industrial fields including the electronics, transport equipment, chemical, textile, food, cosmetic, and construction industries. The unique properties and the diversity of the structures of silicone polymers make them industrially very useful. Silicone polymers have very different forms including viscous liquids, rubberry solids, and cross linkable resins. Furthermore, when we change the organic groups that are bonded to the silicon, we can also change the properties of silicone polymers [16].

In silicone production, starting material which is dimethyldichlorosilane reacts with water. At the end of this reaction, polydimethylsilicone is obtained as shown in Figure 1.5.

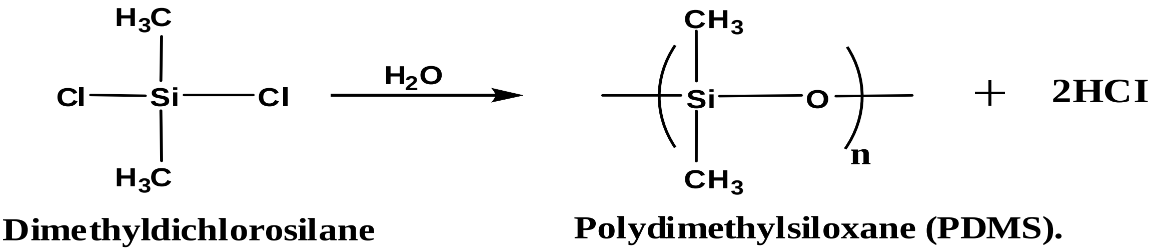


Figure 1.5. Synthesis of silicone polymers.

### 1.4.2. Silicone Fluids

Silicone fluid is a linear polymer including di-functional siloxane units. Silicone fluids have a range of distinguishing properties since they are combination of inorganic siloxane and organic alkyl group characteristics. They have a unique conformation as a polymer. There are two classifications for silicone fluids; unreactive silicone fluids and reactive silicone fluids. The most important one is dimethyl silicone fluid [17].

### 1.4.3. Properties of Silicone Fluids

As for heat resistance, dimethyl silicone fluids exhibit excellent stability up to 175°C. Viscosity change cannot be observed at these temperatures.

There is also another major distinguishing feature which is low surface tension. This feature results from the fact that is silicones are nonpolar polymers with low intermolecular forces. Silicone has excellent release properties, antifoaming properties and water repellency due to low surface tension [18].

Another property is high gas permeability, especially oxygen gas solubility. This is what allows membranes made of silicone rubber to function as gas separation membranes.

Following is a summary of these characteristics:

- Excellent cold resistance, with low glass transition point and pour point

- Viscosity change due to temperature is low, while volume change is high
- Chemically inactive
- High shear resistance
- High compressibility
- Low surface tension
- Excellent water repellency, release properties, and non-adhesiveness
- Antifoaming properties.
- Excellent electrical properties.
- Good gas and steam solubility
- Excellent light transmission and stability
- High flash point, low vapor pressure and excellent flame resistance

### 1.4.4. Applications of silicone fluids

1.4.4.1. Heat transfer liquids. Silicone fluids are used as heating media in many industries because they have good heat resistance and high stability. Silicone fluids are also used as cooling media since they do not solidify even at low temperatures.

1.4.4.2. Hydraulic fluids and lubricants. Silicone fluids are used in automobile fan couplings because of their heat resistance, viscosity-temperature characteristics and shear resistance properties. They are also used in the damper fluids of automotive and air craft instruments due to their high compressibility. Since dimethyl silicone fluids do not have very good lubrication characteristics, they are used as a lubricant in relatively low-loads.

1.4.4.3. Polishing Agents, Water Repellents and Defoaming Agents. Silicone fluids are used in various automotive and household waxes. When we add them to paints and inks, we can make coating films by using their unique properties such as wetting; pigment dispertion and defoaming.They are also used as defoaming agents in waste water treatment and in various industries.

1.4.4.4. Resin additives. When added to thermoplastic, silicone fluids improve lubrication and sliding properties, moldability, release properties and abrasion resistance.

1.4.4.5. Silicones for Cosmetics. The following list shows the characteristics of silicone polymers that are principal reasons they are used in cosmetic applications.

- Highly safe (low irritation)
- Tasteles odorless and colorless (masking is unnecessary)
- Low surface tension, high oxygen permeability (low sense of discomfort)
- High degree of freedom in molecular design (multifunctionality)

# 2. RESEARCH OBJECTIVES

The aim of this project is to use maleinized soybean oil (SOMA) as a cross linker and chain extender for functional silicones. The functional silicones used will be 1-)Carbinol silicone a hydroxyl terminated poly dimethysiloxane and 2 -) Amino silicone a polydimethylsilicone having propyl amino pendant groups. The chemistry is shown in Figure 2.1.

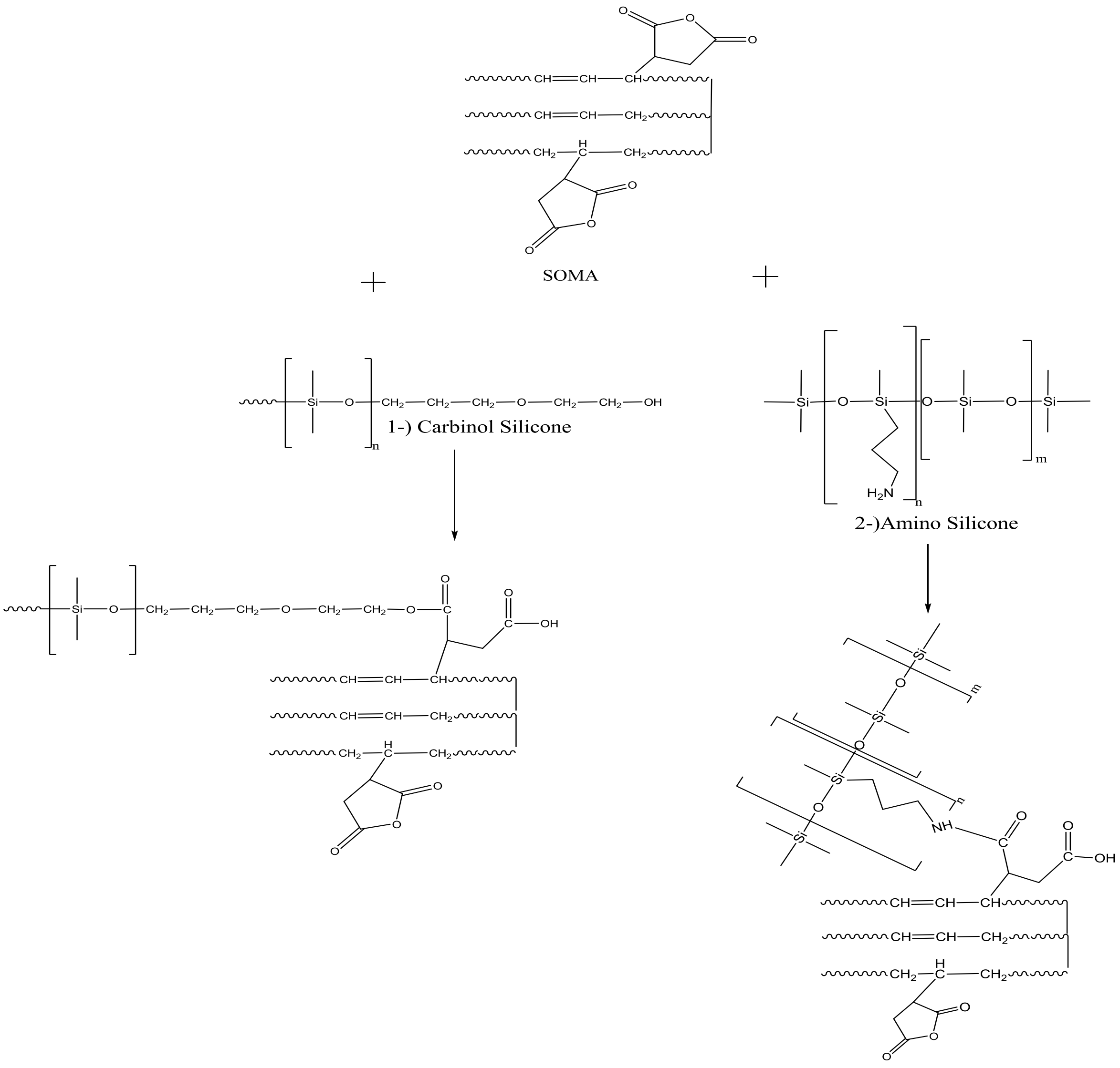


Figure 2.1. Reaction of SOMA with Carbinol silicone and Amino silicone.

In the first case; a reaction between the anhydride and the hydroxyl groups and in the second case a reaction between the anhydride and the amino groups are expected. The products are silicone polymers that are cross linked and chain extended with triglycerides and they contain two segments having different levels of hydrophobicity. The products will be examined by IR spectroscopy, DMTA, mechanical testing, contact angle and swelling for characterization.

# 3. EXPERIMENTAL

## 3.1. Materials and Apparatus

### 3.1.1. Materials

Soybean Oil was purchased from Şifa Kimya, maleic anhydride was supplied by Cam Elyaf A.Ş, carbinol silicone was purchased from Dow Corning and amino silicone was supplied by Sinosi. Toluene was supplied by Merck (Germany), $CDCl_3$ was purchased from Merck (Germany), and used for $^1H$ NMR analysis.

### 3.1.2. Apparatus

The IR analysis was performed on a Nicolet 380 FT-IR with Smart Diamond ATR. All the 1H NMR spectra were recorded on a Varian 400-MHz NMR instrument operating at a frequency of 399.986 MHz for proton. The spectra were reported as ppm (δ) with TMS as internal standard.

DMTA has been used to investigate the dynamic mechanical behavior of the copolymers. The dynamic mechanical thermal analysis of the polymer samples were performed by using TA Instrument Q800 Dynamic Mechanical Analyzer (DMA) in single cantilever mode. Temperature scans were run at a heating rate of 3 ºC/min with a vibration frequency of 1 Hz. Temperature scans were run for polymers containing silicone from -100 ºC to 100 ºC. The average dimensions (t × w × l) of the samples were 2±0.2 x 12±0.2 x 35±0.2 $mm^3$.

The Zwick/RoellDurometer (Ulm, Germany) with Shore A was used to determine the surface hardness of polymer samples; the test was performed according to ASTM D 2240 standard test. The average dimensions (t × w × l) of the samples were.7±0.2 x 12±0.2 x 35±0.2 $mm^3$ and analyses have been done at room temperature (25 ºC). Hardness values range from 0 - for full penetration to 100 - for no penetration. To obtain a reliable analysis data, the samples were tested at least at 5 different points on the same surface.

The swelling behavior of copolymers was tested in $CCI_4$ by using a Geartner 7109-46 travelling microscope. For the swelling test, polymer samples were cut in dimensions about 1×5×10 mm. The tests were carried out of 4 different samples which are SOMA-carbinol and SOMA-amino silicone and the average of the results was taken. The initial values of the sample lengths were recorded and the samples were put in closed container, which contained solvent. The increase in the lengths was measured with one hour time interval until solvent uptake ceased.

Contact angles were measured by the sessile drop method using water at room temperature. Each contact reported was the mean value of four measurements taken at different points on the SOMA-Amino silicone film. The contact angles were measured on both sides of the film and averaged.

Gel Permeation Chromatography (GPS) analyses were done using an Agilent 1100 Series GPS-SEC analysis System with a PL Gel 5µm MIXED-C Column that was calibrated against polystyrene standards.

### 3.2. Maleinization of Soybean Oil

SOMA was synthesized according to the procedure given in literature with some modifications[15].Soybean oil (100 g assuming an average molecular weight 870) was placed in a flask under $N_2$ fitted with a condenser, magnetic stirrer, and thermometer. Maleic anhydride (9 g, 91 mmol) was added into flask. After that, temperature was raised to 180°C.It was kept at 180 for 1 h and the mixture was stirred for 1 h at this temperature. The color of solution changed from yellow to orange during this time. After 1 h, a second portion of maleic anhydride (9 g, 91 mmol) was added to the mixture and the temperature was raised to 200°C. Sublimation of maleic anhydride was prevented by closing the outlet of the condenser with a toy balloon with nitrogen. After 1 hour, the final part of maleic anhydride (9 g, 91 mmol) was mixed in and the temperature was increased to 220–230°C. Solution was stirred one more hour at this temperature. Finally, the mixture was cooled to room temperature. Solution became reddish at the end of this stage and the viscosity increased. Identification was carried out with IR.

IR spectrum: 3006.2 cm$^{-1}$ , 723.9 cm$^{-1}$ (C=C); 2926.1 cm$^{-1}$, 2854.0 cm$^{-1}$ , 1458.0 cm$^{-1}$ (C-H); 1860.8 cm$^{-1}$, 1781.9 cm$^{-1}$, 918.6 cm$^{-1}$ (O=C-O-C=O); 1224.4 cm$^{-1}$, 1161.1 cm$^{-1}$, 1062.8 cm$^{-1}$ (C-C(=O)-O); 1742.4 cm$^{-1}$ (C=O).

### 3.3. Polymerization of SOMA with Carbinol Silicone

In a typical run, SOMA (4.11 g) and Carbinol silicone (4.3 g,) were placed in a test tube and the mixture was continuously stirred at 100°C for 1 hr. After 1 h, this mixture was poured into teflon mold and was placed into oven to continue the reaction. The reaction temperature was kept constant at 120°C for 1 h and then the mixture was cooled to room temperature. The product was a semi rigid rubber at room temperature. After the sample was extracted with toluene, a weight loss of 1% was observed.

The characterization was carried out via IR analysis. The sample is insoluble in organic solvents.

IR Spectrum (cm$^{-1}$): 1861.53 cm$^{-1}$, 1779.76 cm$^{-1}$, 915.03 cm$^{-1}$ (O=C-O-C=O);two anhydride peaks at 1861.53 cm$^{-1}$, and at 1779.76 cm$^{-1}$ from SOMA disappeared during the reaction. 1739.51 cm$^{-1}$ (C=O stretching) ester carbonyl comes from oil remained; 2927.56. cm$^{-1}$, 2847.47 cm$^{-1}$, (C-H stretching ) remained.1257.98 cm$^{-1}$ (Si-C stretching) ;1012.56 cm$^{-1}$ (Si-O-Si stretching) ; 1094 cm$^{-1}$ (Si-O-Si stretching).

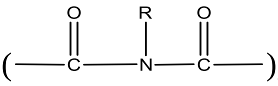
### 3.4. Interfacial Polymerization of Maleinized Soybean Oil with Amino Silicone

SOMA and amino silicone were not soluble in each other, but reacted very fast. Therefore; homogeneous test samples could be prepared only by using interfacial polymerization technique. For polymer synthesis, 2 grams of maleinized soybean oil and 2 g of amino silicone films were prepared on two teflon plates and the two teflon plates were placed face to face. Polymerization takes place at the interface. In the next step, this mixture was placed in an oven and heated to 120°C and kept at this temperature for 2 days. Dark yellow colored thermoset film was obtained at the end of these two days. Unreacted monomers were removed by extraction with toluene in which both starting materials are soluble. After the extraction and solvent evaporation, 1% weight loss was observed.

Characterization was carried out with only IR analysis because SOMA-Amino silicone copolymers are insoluble in organic solvents. Therefore, NMR cannot be obtained from these samples.

FTIR analyses have been performed to characterize the resulting materials.

IR Spectrum (cm$^{-1}$): 1861.53 cm$^{-1}$, 1779.76 cm$^{-1}$, 915.03 cm$^{-1}$ (O=C-O-C=O);two anhydride peaks at 1861.53 cm$^{-1}$, and at 1779.76 cm$^{-1}$ from SOMA disappeared during the reaction.

3006.2 cm$^{-1}$ , 723.9 cm$^{-1}$ (C=C stretching); 2923.74. cm$^{-1}$, 2853.9 cm$^{-1}$ , (C-H bend); 1458.0 cm$^{-1}$ (Si-C stretching) ; 1257.98 cm$^{-1}$ (Si-C stretching) ; 1742.4 cm$^{-1}$ (C=O stretching) ; 1163.70 cm$^{-1}$ ester (C-O-C) ;1707 cm$^{-1}$( $-\overset{\overset{O}{\|}}{C}-\overset{\overset{R}{|}}{N}-\overset{\overset{O}{\|}}{C}-$),1011.94 cm$^{-1}$ (Si-O-Si stretching); 1093.24 (Si-O-Si stretching); 790.97 cm$^{-1}$ (Si-O-Si stretching).

# 4. RESULTS AND DISCUSSION

## 4.1. Synthesis of SOMA

Maleinization of soybean oil has been reported and its synthesis was carried out based on the published work [15]. IR spectrum of the compound is identical to the reported spectrum. Soybean oil maleic anhydride adduct (SOMA) has a reddish brown color and higher viscosity compared to soybean oil.

In the synthesis of SOMA as shown in Figure 4.1, maleic anhydride loss due to sublimation was prevented by a slight over pressure. The NMR spectrum of the adduct shows no peak at 5.5 due to unreacted maleic anhydride. Therefore; it is safe to assume that all the maleic anhydride used is grafted onto the triglyceride. Calculation based on the amount used indicates that SOMA contains, on the average, 4.1 anhydride groups per triglyceride. Thus SOMA has an approximate functionality of 4 and approximate molecular weight of 1110 [15].

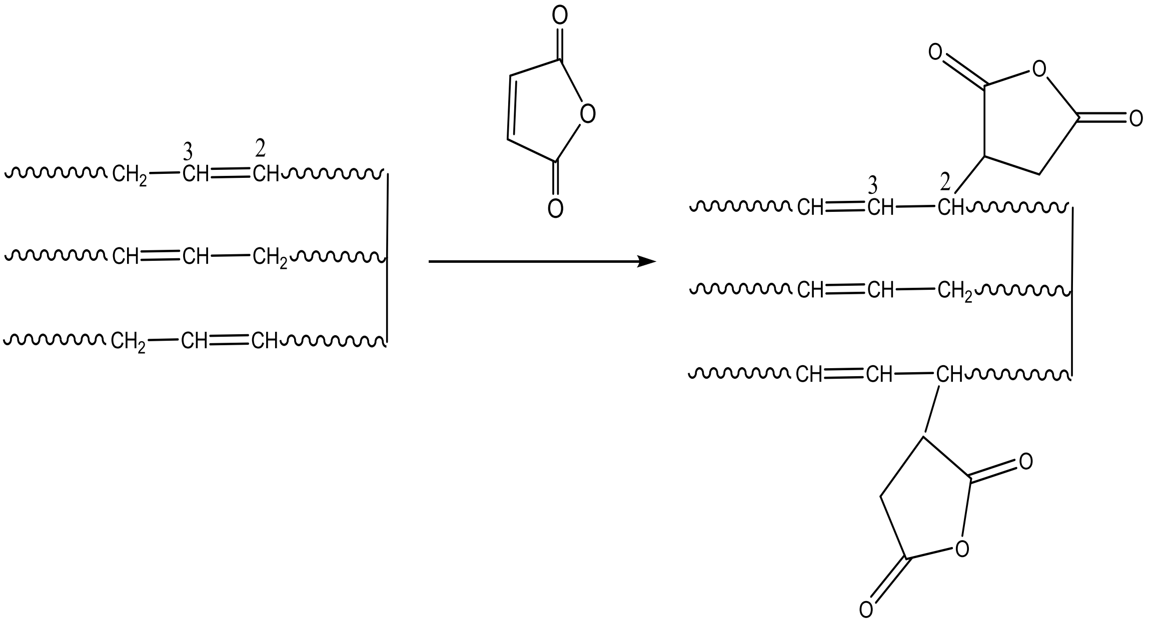


Figure 4.1. Maleinization of Soybean Oil.

IR spectrum of SOMA is shown in Figure 4.2.

IR: 3006 $cm^{-1}$ , 723 $cm^{-1}$ (C=C); 2923 $cm^{-1}$, 2853 $cm^{-1}$ , 1462 $cm^{-1}$ (C-H); 1861 $cm^{-1}$, 1779 $cm^{-1}$, 915 $cm^{-1}$ (O=C-O-C=O); 1221 $cm^{-1}$, 1161 $cm^{-1}$, 1062 $cm^{-1}$ (C-C(=O)-O); 1738 $cm^{-1}$ (C=O).

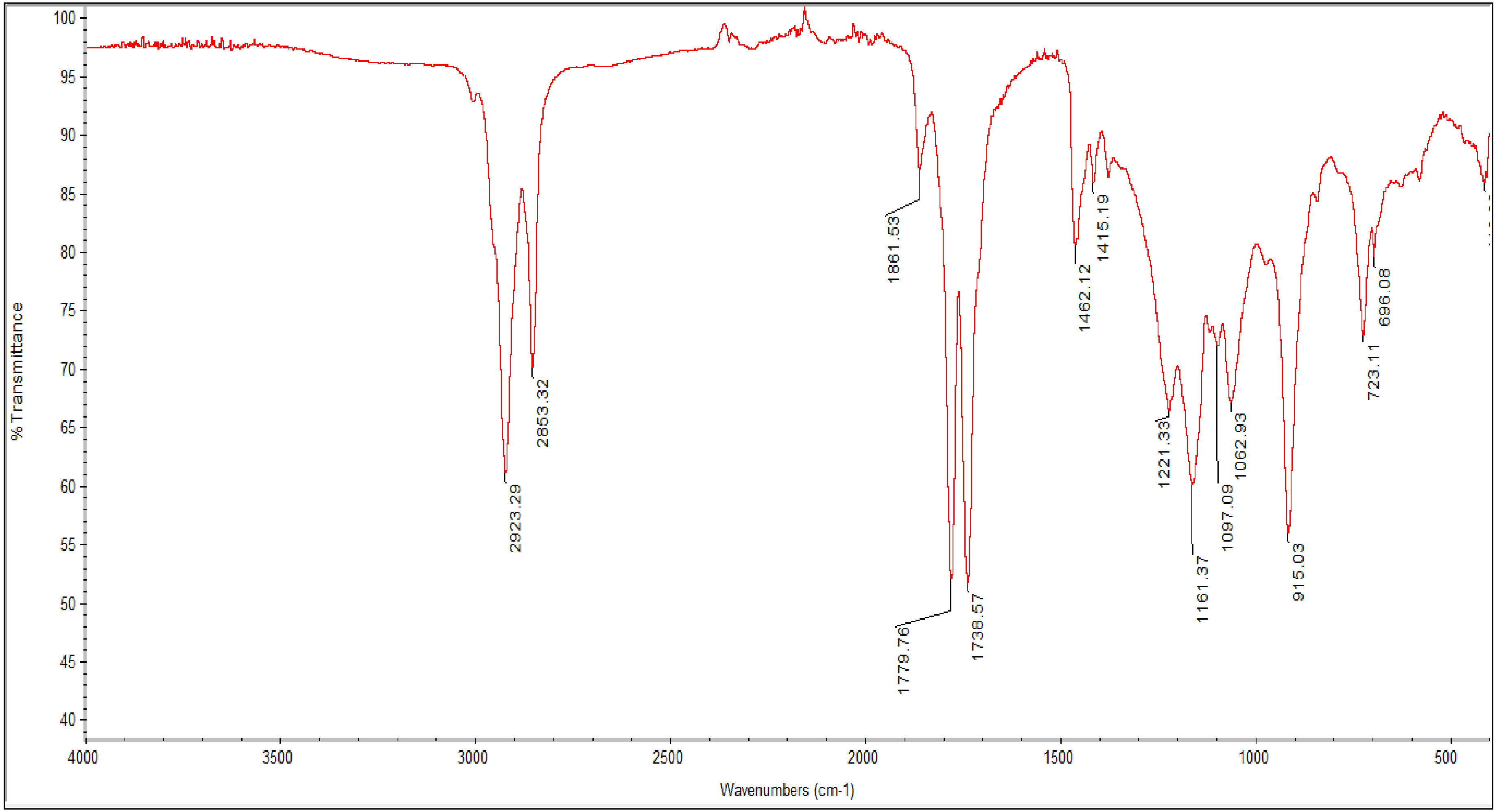


Figure 4.2. IR Spectrum of SOMA.

### 4.2. Synthesisof SOMA- Carbinol Silicone Polymer

Reaction of anhydrides and alcohols are very well known in the literature. Cyclic anhydrides react with primary alcohols at 40-60 $^0$C to give an ester-acid readily. Secondary and tertiary alcohols react slowly and sometimes require basic catalysts. The expected reaction of SOMA with carbinolsilicone is given in Figure 4.3.

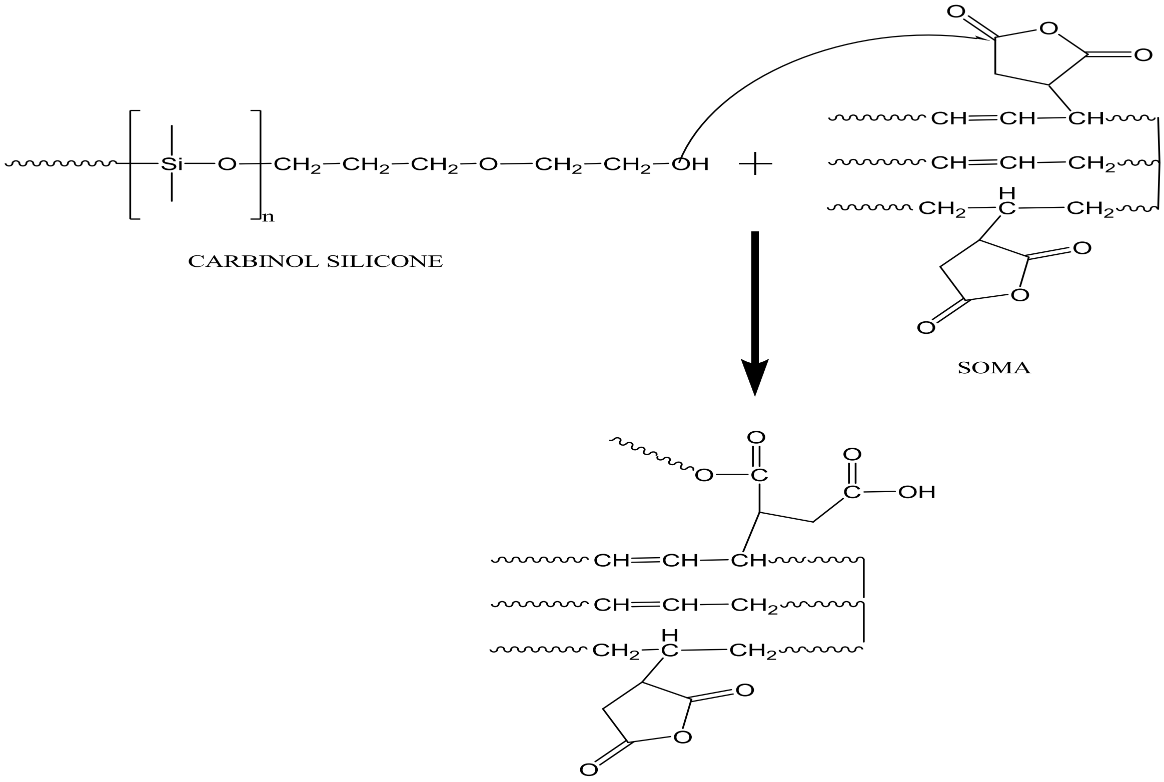


Figure 4.3. Polymerization Reaction of SOMA with Carbinol Silicone.

Different mol ratios of SOMA and carbinol silicone used in this study are shown in Table 4.1. The molecular weight of carbinol silicone is 2600 as determined by using GPC method. Assuming that each chain has two hydroxyl groups, the hydroxyl equivalent of the carbinol silicone is 1300. It should be noted that even Run A has less than stochiometric amount of hydroxyls. This is because in our experience, all of the anhydride groups can not undergo the esterification reaction as diffusion becomes increasingly difficult as the cross link density increases. NMR spectroscopy was not useful in structure determination since all samples became insoluble in NMR solvents at the end of reaction. This suggests that a cross linked structure is formed.

Table 4.1. Different mol ratios used for the reaction of SOMA with Carbinol Silicone.

| Run | A | B | C |
|---|---|---|---|
| SOMA | 1 | 1 | 1 |
| Carbinol silicone | 1.66 | 1 | 0.66 |
| SOMA/Carbinol Silicone | 0.6 | 1 | 1.5 |
| Anhydride/OH | 1.2 | 2.0 | 3.0 |

SOMA and carbinol silicone are miscible. General procedure for reaction of carbinol silicone with SOMA was to mix the two reagents and to heat in a test tubeto 100°C for 1 hr and then transfer the mixture into a mold and continue heating in the mold at 120°C for 1 h. End point of this reaction was determined by observing the disappearance of the anhydride peaks in the IR.

### 4.2.1. Spectral Identification of SOMA-Carbinol Silicone Polymer

The IR spectrum of the reaction product is given in Figure 4.4. After the reaction of SOMA with carbinol, disappearance of anhydride peaks at 1861- 1779 - 915 cm$^{-1}$ and appearance of new Si-O-Si bonds at 1012- 1094cm$^{-1}$ is observed. At the end of the reaction, the peak at 1739 cm$^{-1}$, which is the ester carbonyl peaks of oil remains unchanged. It was not possible to observe the reaction with NMR due to the insolubility of the product in common solvents.

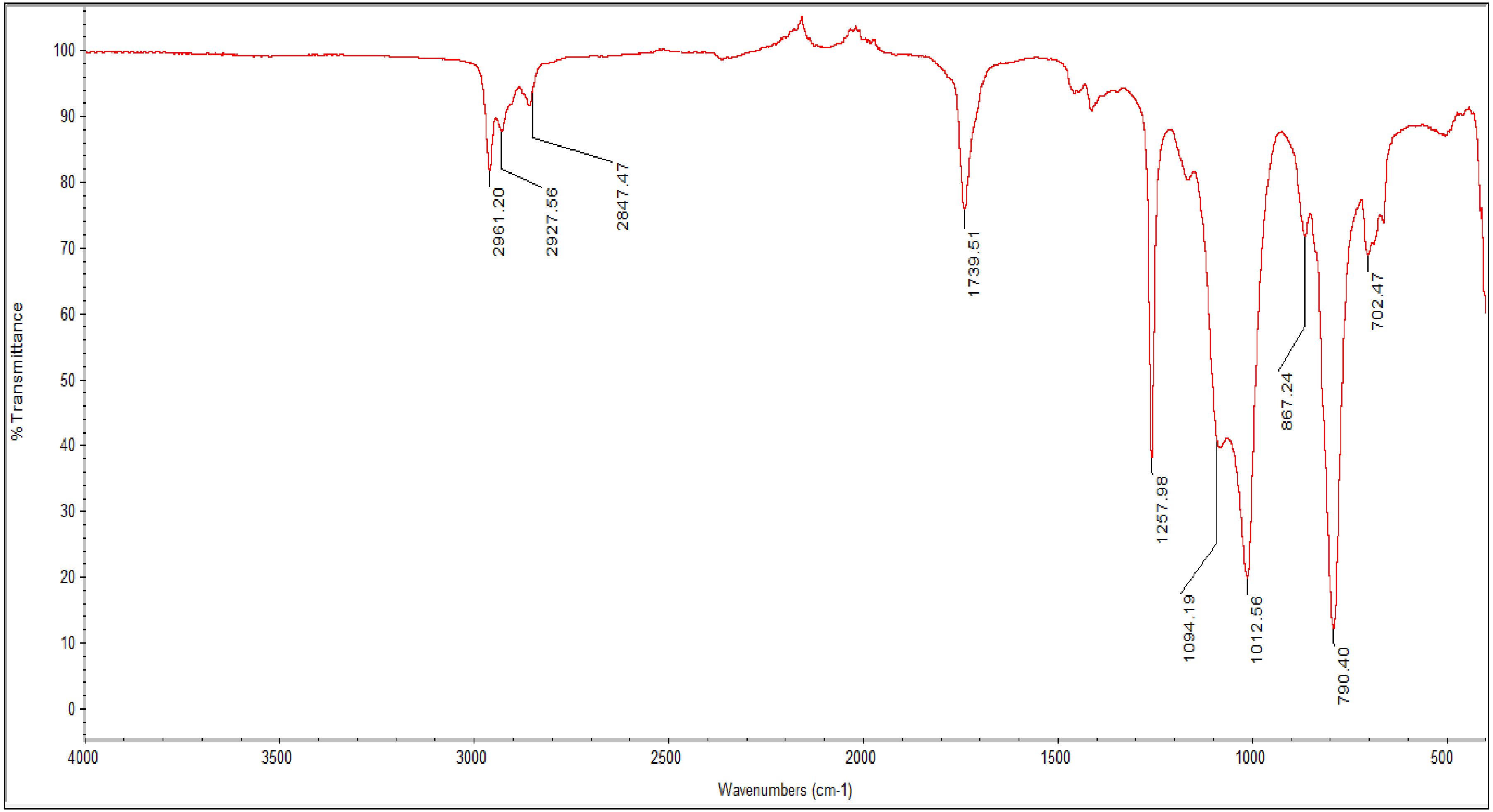


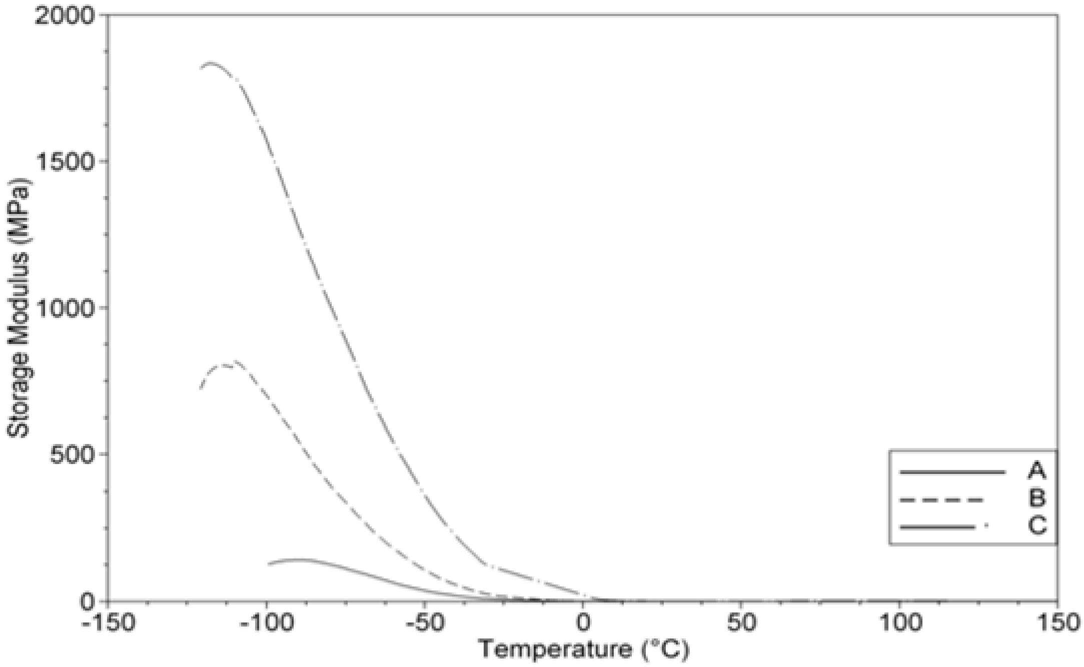
Figure 4.4. IR Spectrum of SOMA-Carbinol Silicone Network.

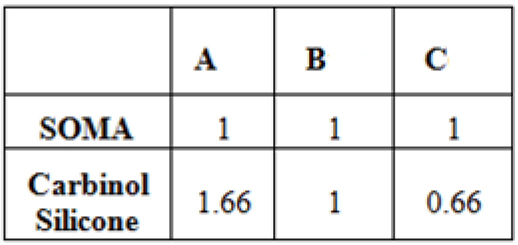
### 4.2.2. Physical Properties of SOMA- CarbinolSilicone Polymer

The physical properties of SOMA-carbinol silicone polymer were analyzed by DMTA, swelling and surface hardness test.

4.2.2.1. Dynamo Mechanical Analysis of SOMA- Carbinol Silicone Polymer. DMTA was used to investigate the dynamic mechanical behavior of the SOMA-carbinol silicone copolymers. Dynamic mechanical properties are the mechanical properties of materials as they are deformed under periodic forces. With the DMTA analysis, the material can be characterized in terms of its modulus, elasticity, viscosity, hysteresis, damping behavior, and glass transition temperature, and the changes of these with strain, strain rate, temperature, and oscillatory frequency of the instrument.

Figure 4.5 shows the storage moduli of samples with different carbinol silicone and SOMA content. Increasing SOMA content increases the cross link density of the final product. At temperatures below -25 °C, the copolymers are in the glassy state and their storage moduli decreases with increasing temperature. SOMA-carbinol silicone copolymer samples show rubbery behavior in dynamic medium. Effect of an increase in the cross link density was clearly observed with DMTA analysis. As the SOMA content of the copolymers increases, the storage modulus increases over the entire temperature range because of the increased cross link density in the copolymers. Polymer sample A which has 1:1.66 mol ratio of SOMA to silicone showed an awarage 175 MPa storage modulus as shown in figure 4.5. The sample B which has 1:1 mol ratio showed nearly a 400 per cent improvement in the storage modulus, from 175 to 900 MPa. Sample C, with 1:0.66 mole ratio of SOMA to silicone showed a storage modulus of 1850 MPa.

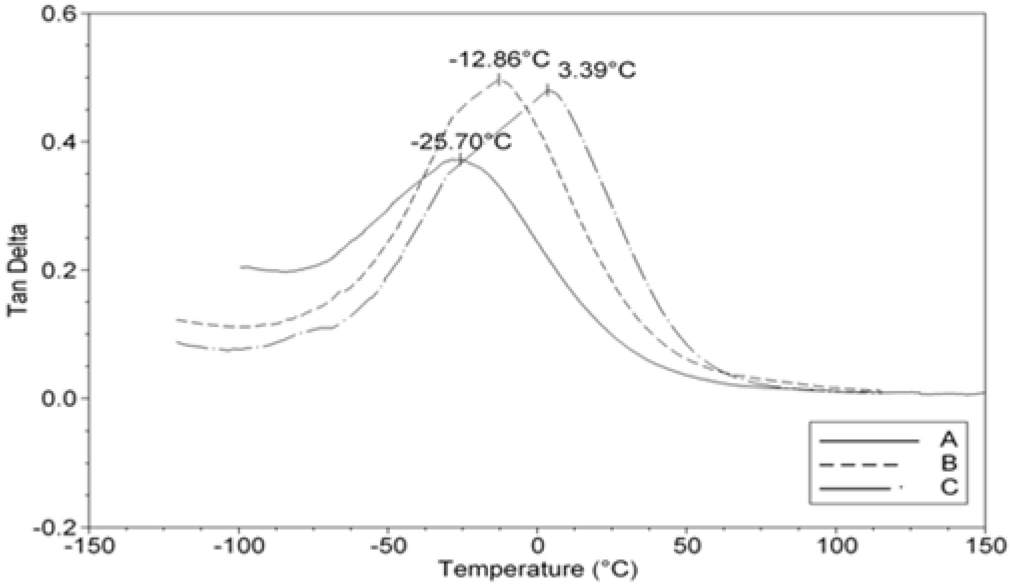




| | A | B | C |
|---|---|---|---|
| **SOMA** | 1 | 1 | 1 |
| **Carbinol Silicone** | 1.66 | 1 | 0.66 |

Figure 4.5. Storage Moduli of SOMA-Carbinol Silicone Copolymers.

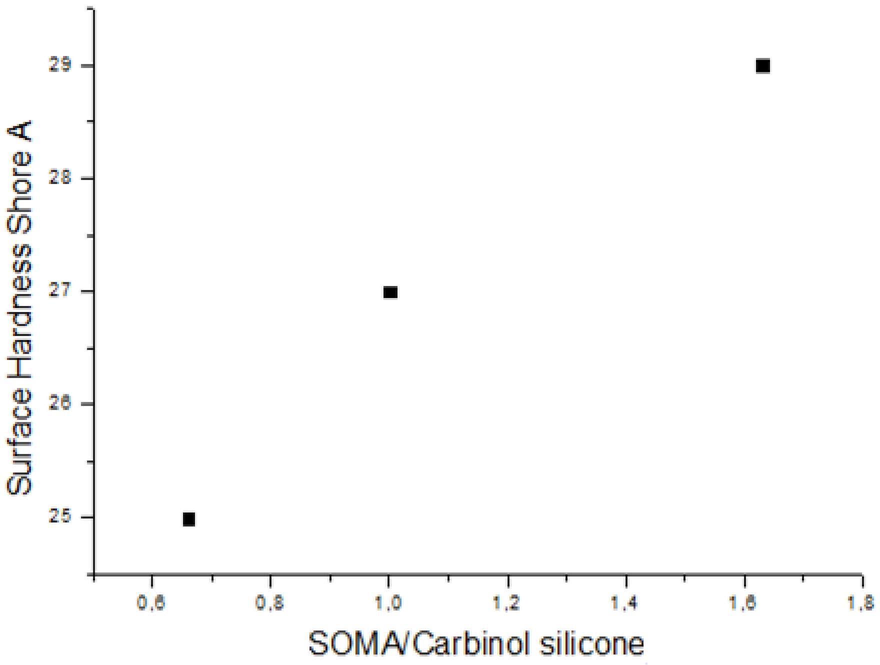
The effect of increased the cross link density can also be observed in the glass transition temperature of the polymer samples. Figure 4.6.shows the tan $\delta$ values of the samples with different carbinol silicone and SOMA content. As the SOMA content of the copolymers increases, the Tg of the copolymer dramatically increases from -25.7 °C to 3.3°C.



| | **A** | **B** | **C** |
|---|---|---|---|
| **SOMA** | 1 | 1 | 1 |
| **Carbinol Silicone** | 1.66 | 1 | 0.66 |

Figure 4.6. Glass Transition Temperature (Tg) of the SOMA-Carbinol Silicone Copolymers.

4.2.2.2. Surface Hardness Tests of SOMA-Carbinol Silicone Polymer. The surface hardness of the polymers was measured by using a shore durometer according to the ASTM D-2240 standard. For the analysis 3 mm thick samples were prepared. The samples were protected from any possible mechanical stress before testing. Hardness values were obtained by averaging 5 individual measurements. The results for surface hardness of the SOMA carbinol silicone copolymer are shown in Figure 4.7.



| | A | B | C |
|---|---|---|---|
| **SOMA** | 1 | 1 | 1 |
| **Carbinol Silicone** | 1.66 | 1 | 0.66 |

Figure 4.7. Surface Hardness of the SOMA- Carbinol Silicone Copolymers.

As the SOMA content of the copolymers increases, surface hardness of copolymer increases from 25 to 29 Shore A units as expected .The improvement in the surface hardness can be attributed to the increase in the cross link density. These results are compatible with DMTA results since sample which has higher content of SOMA show the highest storage modulus values.

4.2.2.3. Swelling test of SOMA-Carbinol Silicone Polymer. When cross linked polymers - are placed in a good solvent they absorb the solvent and swell. The extent of swelling represents a competition between two forces. The solvent penetrates into polymer during mixing. As the polymer chains in the cross linked polymer try to elongate, they create a force in opposition to this deformation. When two forces balance each other, volumetric swelling reaches a steady state.

The swelling behavior of cross linked polymers is also a good indication for crosslink density. Lower swelling indicates higher cross linked 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) can be obtained from the following equation:

$$q= V/Vo = (L/Lo)^3$$

where Vo and V are the volumes and Lo and L are the lengths of unswollen and swollen polymer samples, respectively. Swelling behavior of the samples with increasing mol ratio of SOMA is shown in Figure 4.8.

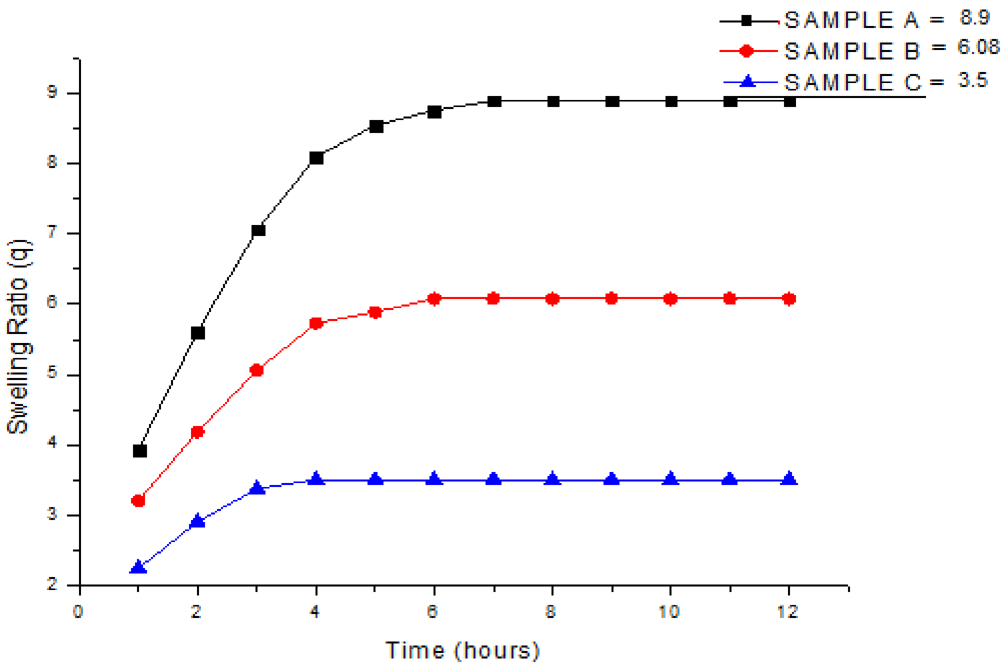


Figure 4.8. Swelling behavior of SOMA- Carbinol Silicone Copolymers with Different Mol Ratios.

As it is seen in Figure 4.8, (q) values increases with time and then reaches a plateu at a certain ratio. This behavior is typical for a cross linked polymer network structure because all structural units in the polymer network are interconnected with chemical bonds, that there is a point beyond which the units cannot be further elongated with the continued uptake of solvent.

Copolymer samples which have lower content of SOMA ceases two swell in about 7 hours while copolymer which has higher content of SOMA stop to swell in only 4 hours.

In addition to the swelling time, equilibrium swelling ratio (q) of the copolymer sample also decreases upon increasing the SOMA content, which indicates an increase in the crosslink density.

### 4.3. Synthesis of SOMA Amino Silicone Polymer

Cyclic anhydrides react readily with primary amines to give amido-acids. These may further condense to imides at elevated temperature as shown in Figure 4.10. and in Figure 4.11.

SOMA and amino silicone are not miscible. After some trials SOMA and amino silicone were found to be both soluble in toluene. When the reaction was run in this solvent, a fast reaction took place but the product which was insoluble in the solvent became jellylike and sticky. The reaction was so fast that the reagents did not have the time to mix homogenely. It was impossible to produce a homogeneous sample by this method. We developed a method for interfacial polymerization by making thin films of the two monomers and by putting them in intimate contact. In addition, such a reaction would be ideal for the reaction injection molding (RIM) type process in which a liquid amino silicone and a liquid multiply maleinized plant oil would be coinjected into a mold and heated to give a thermoset polymer without any byproducts. Polymer formation with amino silicone is shown in Figure 4.9.

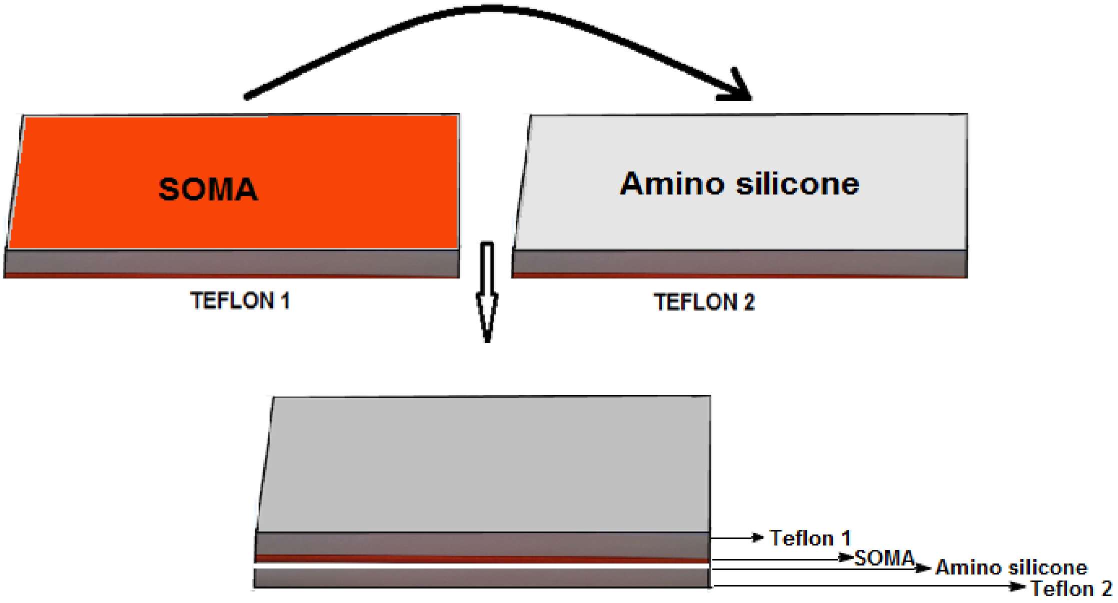


Figure 4.9. Interfacial Polymerization Technique to Synthesis SOMA-Aminosilicone Polymer.

Reaction between SOMA and amino silicone is very fast even at room temperature but to increase diffusion a higher temperature was used. Therefore, the reaction time was increased to obtain a film which is suitable for mechanical tests. In addition, when we increased reaction time and temperature, a thicker film was obtained. Before the mechanical test, unreacted monomers on the film were removed by extraction with toluene in which both starting materials are soluble. It should be noted that SOMA/amino silicone stochiometric ratio is not important because the final product is formed at the interface, where only limited amounts of SOMA and amino silicone can react. In such a situation, the feed ratio is governed by diffusion.

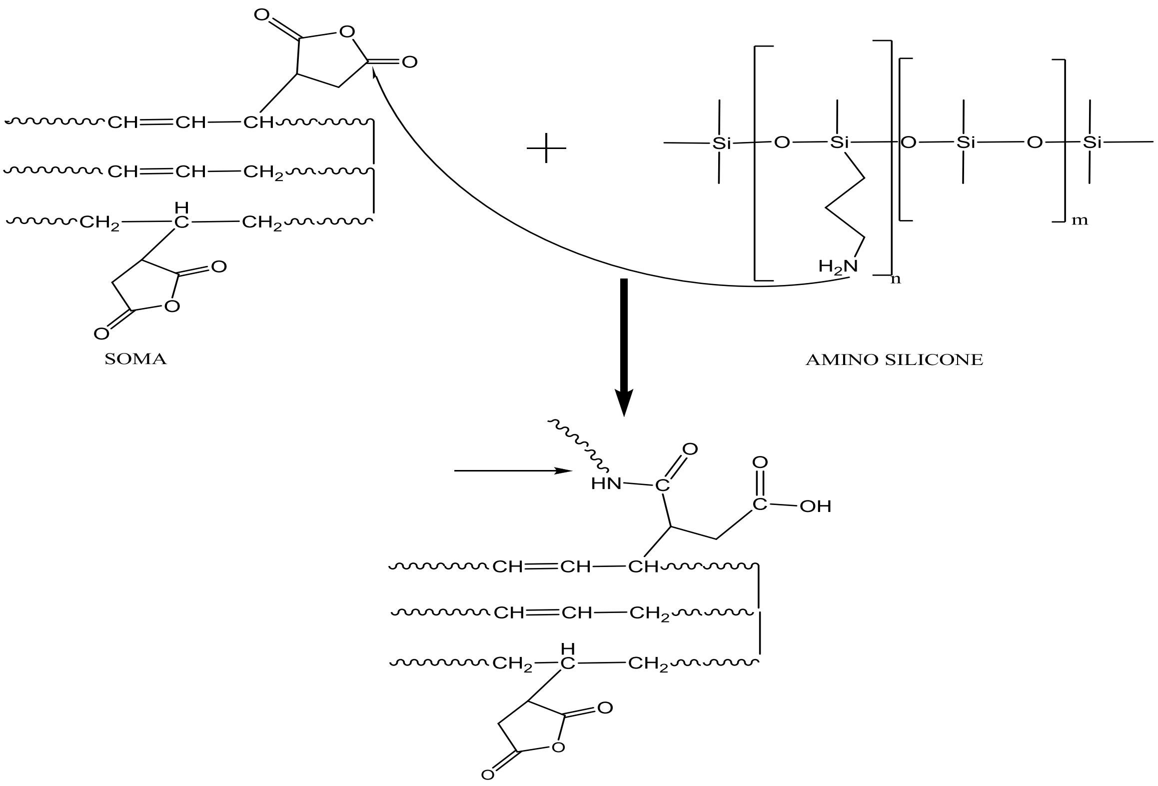


Figure 4.10. Polymerization of SOMA with Amino Silicone.

In the first step of reaction, amino silicone which has amino functional pendant groups attacks the anhydride groups on SOMA and then ring will open to form an amido-acid.

If the initial adduct is heated, a number of interesting reactions can place:

- Imide can be formed as shown in Figure 4.11. In this step, amide which is created in first reaction attacks to carboxylic acid and one mol of water will be removed during this reaction to give an imide.

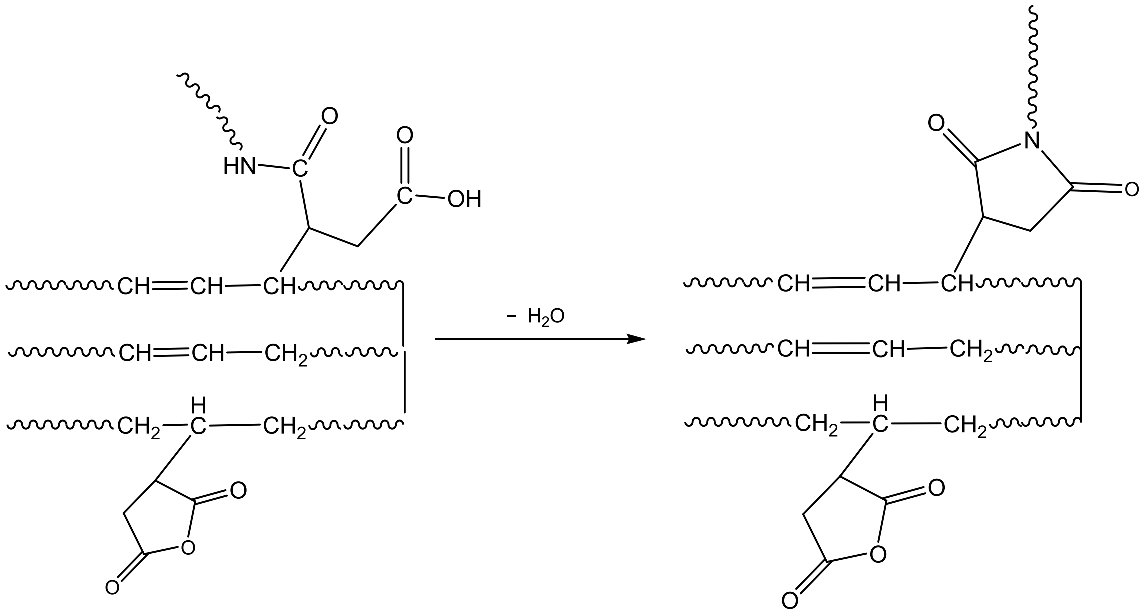


Figure 4.11. Imide Formation.

- Salt can be formed. In this step, amine functional group on another chain is protonated with carboxylic acid and salt formation takes place shown in Figure 4.12.
- Bis- amide can be formed by the dehydration of the salt to give bis amide shown in Figure 4.12.

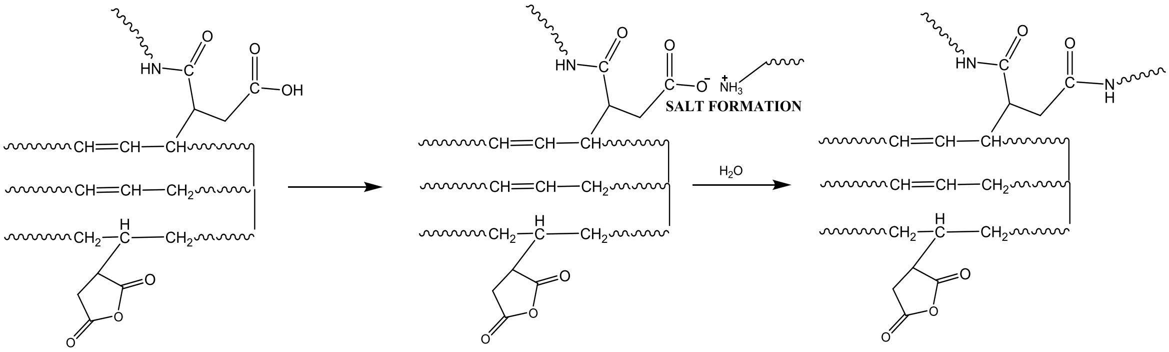


Figure 4.12. Salt Formation and Bis-Amide Formation.

### 4.3.1. Spectral Identification of SOMA Amino Silicone Polymer

The IR spectrum of the reaction product is given in Figure 4.13. After the reaction of SOMA with amino silicone, anhydride peaks at 1861 cm$^{-1}$, 1779 cm$^{-1}$,and 915 cm$^{-1}$ disappeared and a new Si-O-Si bonds are formed at 1011- 1093- 790 cm$^{-1}$ during the reaction. At the end of the reaction, the peak at 1739 cm$^{-1}$ which is the ester carbonyl peaks of oil remains unchanged. Although IR was the only way for chemical identification, the peak at 1707 cm$^{-1}$ is correlated and compared with the imide peaks in the literature and determined as an imide peak. Thus we conclude that at the reaction temperature used, the amido acid closes to a cyclic imid preferentially. It was not possible to observe the reaction with NMR due to the insolubility of the product in common solvents.

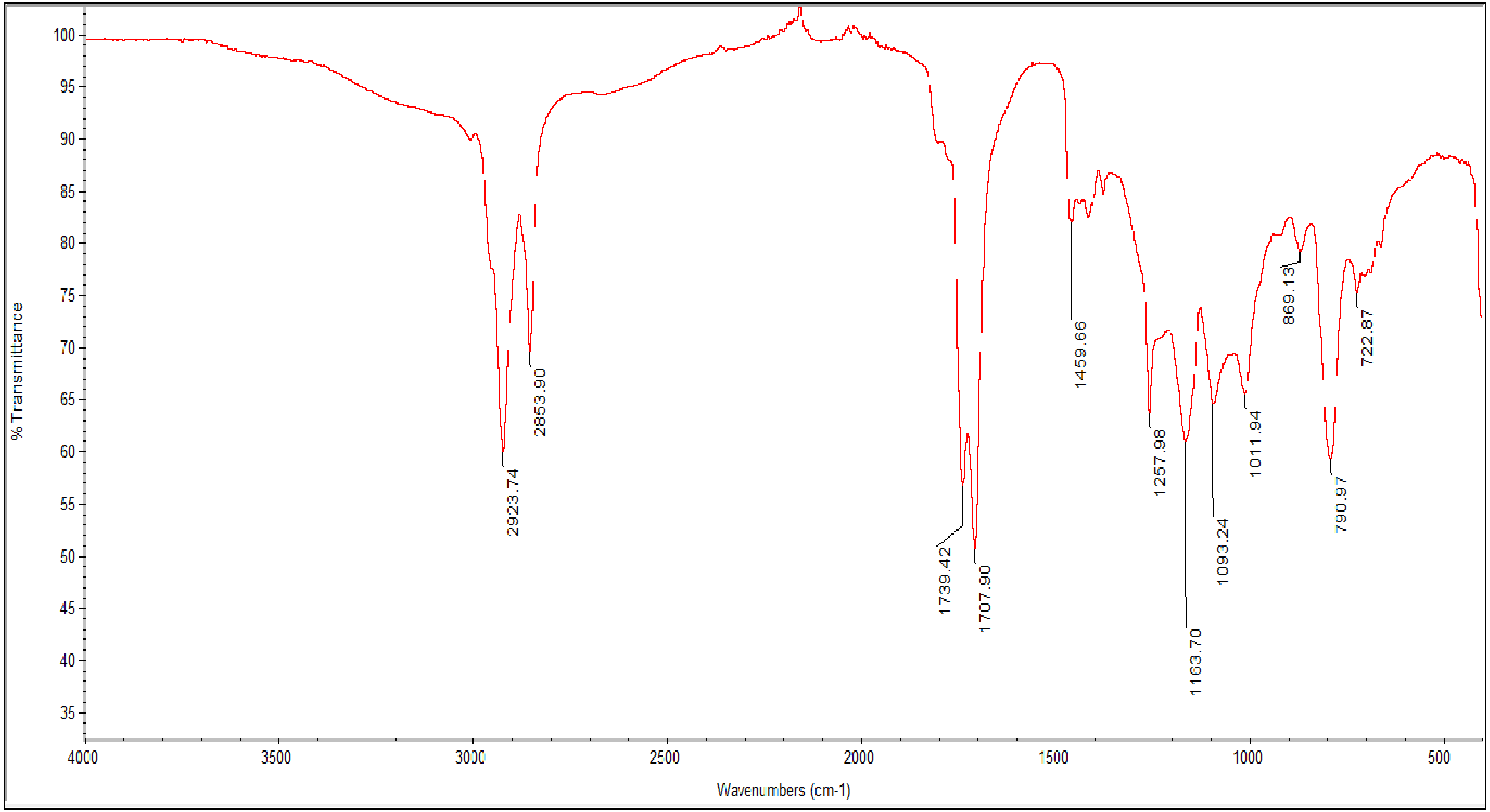


Figure 4.13. IR Spectrum of SOMA-Amino Silicone Network.

### 4.3.2. Physical properties of SOMA Amino Silicone Polymer

The mechanical properties of polymer were be analyzed by swelling, surface hardness and tensile test.

4.3.2.1. Surface Hardness test of SOMA Amino Silicone Polymer. The surface hardness of the polymers was measured by using a shore durometer according to the ASTM D-2240 standard. For the analysis 3 mm thick film sample were prepared. Before hardness test, the sample was protected from any possible mechanical stress and unreacted monomers on the film were removed by extraction with. It should be noted that test sample could be prepared only by using interfacial polymerization technique since SOMA and amino silicone were not soluble in each other. SOMA/amino silicone stochiometric ratio is not controllable because only limited amounts of SOMA and amino silicone can react at the interface. Therefore; only one film sample was prepared. This film has two surfaces. One surface is rich in SOMA and the other is rich in amino silicone. The two surface of the film are characterized by surface hardness measurement.

The film was tested from 5 different points for two different surfaces of it. Hardness value for the surface which has higher amount of silicone was 37. Hardness value for the surface which has higher amount of SOMA was 47. This difference in mechanic property is proven in IR spectroscopy as shown in Figure 4.16.

4.3.2.2. Swelling Test of SOMA Amino Silicone Polymer. The swelling behavior of the SOMA-aminosilicone copolymer in $CCI_4$ 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. As can be seen, in Figure 4.14. (q) values increases with time and then reaches a plateau at a certain ratio. This behavior is typical for a cross linked polymer network structure because all structural units in the polymer network are interconnected with chemical bonds, that there is a point beyond which the units cannot be further elongated with the continued uptake of solvent. This point is called equilibilirum swelling ratio and its value for SOMA-amino silicone
copolymer was 12,95 which is also a good indication for the formation of cross linking reaction.

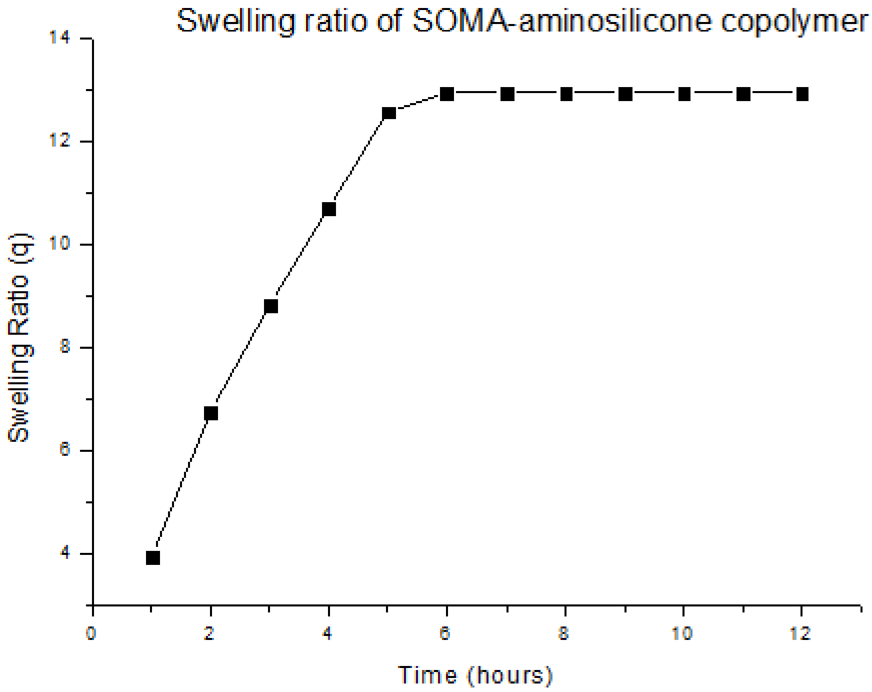


Figure 4.14. The swelling behavior of the SOMA-Aminosilicone Copolymer.

4.3.2.3. Contact Angle Measurement of SOMA Amino Silicone Polymer. Wetting is the ability of a liquid to remain contact with a solid surface due to the intermolecular interactions between the two. The extent of wetting is determined by a force balance between adhesive and cohesive forces. Adhesive forces cause a liquid droplet to spread over the solid the while the cohesive forces cause the liquid to assume a spherical shape and avoid the solid surface. Wettability is measured by contact angle.

When a liquid droplet is placed on a solid substrate, because there are three phases in contact (liquid- solid-air), there will be three surface tensions that have to be considered. Young formulized this phenomenon with a simple mechanical balance, named Young’s equation [19].

$$\cos \theta = (\gamma_s - \gamma_{sl}) / \gamma_{lv}$$

where θ is the contact angle of liquid with solid, and sv, sl, lv are the surface tensions at the interphase of solid vopor, solid liquid,and liquid vopor, respectively (Figure 4.15.). The unit of surface tension is mJ.m-$^2$ or N.m-$^1$.

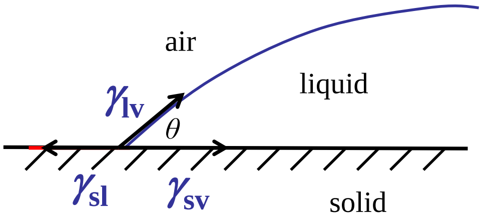


Figure 4.15. Surface Tensions at the Interphase of Solid Vopor, Solid Liquid, and Liquid Vopor.

A contact angle less than 90 (low contact angle) indicates that wetting of the surface is very favorable. Conversely, contact angles greater than 90 (high contact angle) indicates that wetting of the surface is unfavorable. If the liquid is water, a wettable surface is named hydrophilic, while a non-wettable surface is hydrophobic.

Measuring the contact angles of water on a surface provides information about the hydrophilicity and hydrophobicity. Contact angle measurement was done by using the Sessile Drop method. A certain volume of water was placed on film samples with a syringe as a droplet. The shape of the droplet was recorded through a camera and the acquired images were analyzed by the image analyzed software.

SOMA-amino silicone polymer film has two surfaces. One surface is rich in SOMA and the other is rich in amino silicone. The two surface of the film are characterized by contact angle measurement.

It can be noted that the contact angle of the silicone rich surface was 123$^0$ while SOMA rich surface was 90$^0$. Contact angle of the silicone rich surface was larger than the SOMA rich surface. This difference between the two surfaces is not surprising since silicone is more hydrophobic than SOMA. These results are compatible with surface hardness test results and IR results because the SOMA rich surface shows a higher surface hardness.

4.3.2.4. Tensile Test of SOMA Amino Silicone Polymer. SOMA- amino silicone copolymer was not a rigidsolid. It was rubbery. Tensile test were made and the Force-Elongation values are given in Table 4.2.SOMA- amino silicone copolymer is compared with polypropylene, polystyrene and polyethylene teraphthalate (PET) and polybutadiene [20]. The copolymer was softer than polypropylene and polystyrene PET and polybutadiene. Elongation at break of the SOMA was smaller than polypropylene and PET but higher than polystyrene. This behavior is similar with rubbery materials like polybutadiene.

The SOMA-amino silicone product was a flexible material and had a maximum tensile strength of 11(MPa). The tensile strength of SOMA- amino silicone copolymer was smaller than other polymers such as polypropylene polystyrene and PET (Table 4.2.). Silicone polymers are known to have high elongation at break and low tensile strength.

Table 4.2. Force-Elongation values.

| **Polymer Type** | **Tensile Strength (MPa)** | **Elongation (%)** | **Tensile Modulus (GPa)** |
|---|---|---|---|
| **Polypropylene (PP)** | 40 | 23 | 1.9 |
| **Polystyrene (PS)** | 40 | 7 | 3 |
| **Polyethylene Terephthalate (PET)** | 55 | 125 | 2.7 |
| **SOMA-amino silicone copolymer** | 11 | 30 | 1.2 |

There is a need to prove that SOMA-amino silicone film has two different surfaces. Therefore; IR spectrum of the film of the two surfaces was taken. As shown in (Figure

4.16.), the peak at 1738.15 cm$^{-1}$, which corresponds to the ester carbonyl peaks of the triglyceride, is larger in one side. This is the SOMA rich surface. However Side 1 is surface which has contain higher amount of silicone because the typical silicone peaks at 786 –1008- 1257 cm$^{-1}$ have a higher intensity.

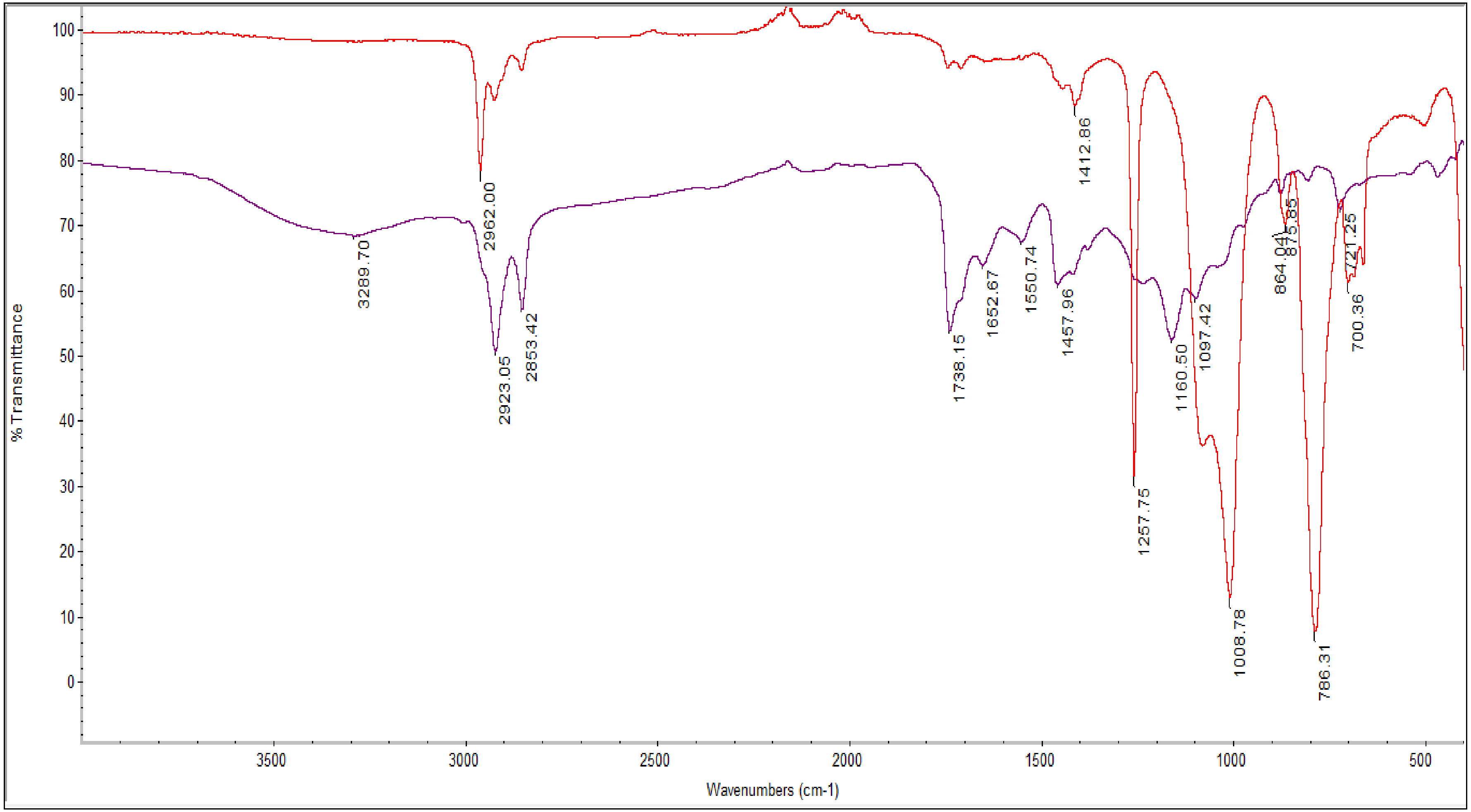


Figure 4.16. IR Spectrum of SOMA-Amino Silicone film for two sides.

# 5. CONCLUSION

In this study, the ene reaction between soybean oil and maleic anhydride was used to produce a soybean oil maleic anhydride adduct (SOMA). And then, novel thermosetting copolymers were prepared by reaction of SOMA with amino silicone and carbinol silicone. Reaction between SOMA and amino silicone was very fast even at room temperature and the reaction was difficult to run due to immiscibility of the monomer. To obtain homogeneous film, interfacial polymerization technique was used. At the end of this reaction a thin film was obtained. IR spectroscopy showed that SOMA-Amino silicone polymer film has two different surfaces. One rich in SOMA and the other rich in amino silicone. Each surface has different surface hardness. IR spectrum also showed that theamido acid closes to a cyclic imid preferentially. Such a reaction would be ideal for the reaction injection molding (RIM) type process in which a liquid amino silicone and a liquid multiply maleinized plant oil would be coinjected into a mold and heated to give a thermoset polymer without any byproducts.

In contrast to amino silicone, SOMA-Carbinol silicone reaction was an easy reaction. We obtained three different polymers with different mol ratios. The final products are silicone polymers that are cross linked with triglycerides and they contain two segments having different levels of hydrophobicity.

The insolubility of both polymers are attributed to the crosslinking because of the presence of triglycerides with multiple maleates and because of the functional silicones used. NMR spectroscopy was not very useful since the samples became insoluble in NMR solvents very early in the reaction. Therefore; IR spectroscopy was the only way for chemical identification.

Connectivity and crosslink density increases by increasing the percent weight of the SOMA in the reaction mixture. Dynamic mechanical analysis of the SOMA-Amino silicone polymers indicates that the cross-linking density and the glass transition temperature increase as SOMA amount increases.

Swelling test for SOMA-Carbinol silicone polymers indicate that equilibrium swelling ratio (q) of the copolymer sample decreases upon increasing the SOMA content. This indicates an increase in the crosslink density.

Surface hardness value for SOMA-Carbinol silicone polymers increases when the SOMA content of the copolymers increases. The improvement in the surface hardness can be also attributed to the increase in the cross link density. It can be concluded that all results are compatible with each other.

As future work, there are many kinds of silicones having different functional groups, their polymers with multifunctional plant oil can be synthesized. These reactions can be extended and can be applied to other functional silicones. These new polymers may have applications such as adhesives, film formers and textile auxilaries.

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