CROSSLINKING OF UNSATURATED POLYESTER BY CONJUGATED SOYBEAN OIL VIA DIELS ALDER REACTION

by

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B.S., Chemistry, Boğaziçi University, 2014

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

Graduate Program in Chemistry
Boğaziçi University
2016

To my family…

ACKNOWLEDGEMENTS

I would like to express my sincerest gratitudes for Prof. Selim Küsefoğlu for his guidance, tolerance and encouragement in our several projects and throughout my education. He is the one who got me to love polymer science and to think creatively, therefore he will always have a special place in my life.

I would like to express special thanks to committee members Inst. Ediz Taylan, Assoc. Prof. Ersin Acar, Prof. Duygu Avcı Semiz and Prof. Nilgün Kızılcan for generously giving their valuable time in reviewing this thesis and for comments and advices on the final manuscripts.

My special thanks go to Ergin, Aykut and Mümtaz for their unique friendship and unforgettable times we spent together since undergraduate years. I would like to thank my dearest chemist friends Ozan, Melek Naz, Aktan, Taner and Tankut for their company and endless support.

Finally, my greatest thanks go to my dear mother, father and my brother for their labors in my growth, continuous support and love through my whole life. My special thanks go to my twin brother Erinç who has always been there for me whenever I needed support since were born and lastly to Simge for being patient and supportive since we met.

ABSTRACT

CROSSLINKING OF UNSATURATED POLYESTER BY CONJUGATED SOYBEAN OIL VIA DIELS ALDER REACTION

In this study, unsaturated polyester (UPE) is crosslinked with conjugated soybean oil (CSO) with using the Diels Alder reaction and to prepare a one component UPE which can be cured in the mold simply by heating. The goal is to use a nontoxic and non-volatile reactive diluent for curing of UPE. Crosslinking reaction occurred between conjugated diene part of the CSO and the maleate double bonds of the UPE via the Diels Alder reaction. Because it was hard to predict the correct stoichiometry of the reaction, it was determined experimentally. The reaction conditions (reaction time and temperature) were determined by using CSO as a diene. The best reaction efficiency and high crosslinking density was obtained only by using trans,trans conjugated soybean oil (t-CSO). Without using any solvent or catalyst. t-CSO was obtained by the elaidinization of CSO. The effects of conjugation and conjugated double bond geometry were investigated by comparing natural soybean oil, CSO and t-CSO as a diene in the crosslinking reaction. Characterizations of products were done by FTIR and NMR spectroscopy and mechanical properties of UPE:t-CSO crosslinked products with different weight ratios of components were analyzed by surface hardness, compression and swelling tests. Mechanical tests showed that, with higher amount of UPE, relative crosslink density, surface hardness and compressive strength of products were increased. Cured UPE samples containing up to 50% renewable, plant oil based t-CSO were produced.

ÖZET

DOYMAMIŞ POLİESTERİN KONJUGE SOYA YAĞI KULLANARAK DİELS-ALDER REAKSİYONUYLA ÇAPRAZ BAĞLANMASI

Bu çalışmada doymamış poliester (UPE) konjuge soya yağı (CSO) ile Diels Alder reaksiyonu kulanılarak çapraz bağlanmıştır. Amaç, toksik ve uçucu olmayan bir reaktif seyreltici kullanmak ve sadece ısıtılarak kalıp içinde kürleşebilen tek parça UPE hazırlamaktır. Çapraz bağlanma reaksiyonu konjuge soya yağının konjuge dien sistemi ve doymamış poliesterin maleat çift bağları arasında Diels Alder reaksiyonu ile gerçekleşmiştir. Reaksiyonun doğru stokiyometrisini hesaplamak imkansız olduğu için bu oran deneyler sonucu bulunmuştur. Reaksiyon koşulları (reaksiyon süresi ve sıcaklığı) ise konjuge soya yağını dien olarak kullanarak bulunmuştur. En yüksek reaksiyon verimliliği ve tek parça termoset ürün hiçbir çözücü yada katalizör kullanmadan yalnızca trans,trans konjuge soya yağı (t-CSO) kullanılarak elde edilmiştir. Trans,trans konjuge soya yağı, konjuge soya yağının eladinizasyonu ile elde edilmiştir. Konjugasyon ve konjuge çift bağı geometrisinin çapraz bağlanma reaksiyonuna etkisi, doğal soya yağı, konjuge soya yağı ve trans,trans konjuge soya yağını dien olarak kıyaslayarak incelenmiştir. Ürünlerin karakterizasyonu FTIR ve NMR spektroskopiyle ve farklı bileşen ağırlık oranıyla elde edilmiş UPE:t-CSO çapraz bağlı ürünlerinin mekanik özellikleri yüzey sertliği, basma-kırılma ve çözücüde şişme testleriyle incelenmiştir. Mekanik testler doymamış poliester miktarı arttırıldığında, ürünlerin çapraz bağlanma yoğunluğu, yüzey sertliği ve sıkıştırma mukavemeti arttırılmıştır. Bu metodla % 50 oranında yenilenebilir bir kaynak olan soya yağı içeren termoset UPE parçaları elde edilebilmiştir.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF SYMBOLS

q	Equilibrium swelling ratio
L	Length
V	Volume
ω	position of the double bond in fatty acids

LIST OF ACRONYMS/ABBREVIATIONS

AESO	Acrylated-Epoxidized soybean oil
ASTM	American Society for Testing and Materials
CLA	Conjugated linoleic acid
CSO	Conjugated soybean oil
ESO	Epoxidized soybean oil
FTIR	Fourier Transform Infrared Spectroscopy
NMR	Nuclear Magnetic Resonance
ppm	Parts per million
SO	Soybean oil (Natural)
SOMA	Maleinized soybean oil
t-CSO	Trans,trans conjugated soybean oil
THF	Tetrahydrofuran
UPE	Unsaturated polyester

1. INTRODUCTION

1.1. Unsaturated Polyester Resin

Polyesters are defined as a type of polymers which contain repeating ester (-COO-) functional group in their main chain. [1] Ester linkage formation is a result of the reaction between a hydroxyl compound with a carboxylic acid. Polyesters are simply formed by the condensation reaction of dicarboxylic acids (or anhydrides) and diols. They can be thermoplastics or thermosets based on their chemical structure. Polyesters can be classified as saturated and unsaturated polyester (UPE), depending on the unsaturation (double bond) on their backbone. For the unsaturated polyester formation, unsaturated dicarboxylic acid (or anhydride) is used in the polycondensation reaction together with the rest of the monomers used in the saturated polyester making. The stoichiometry is such that total moles of carboxylic acids equals to the moles of hydroxide groups and a typical UPE (Figure 1.1) is made from phthalic acid, maleic acid and propylene glycol.

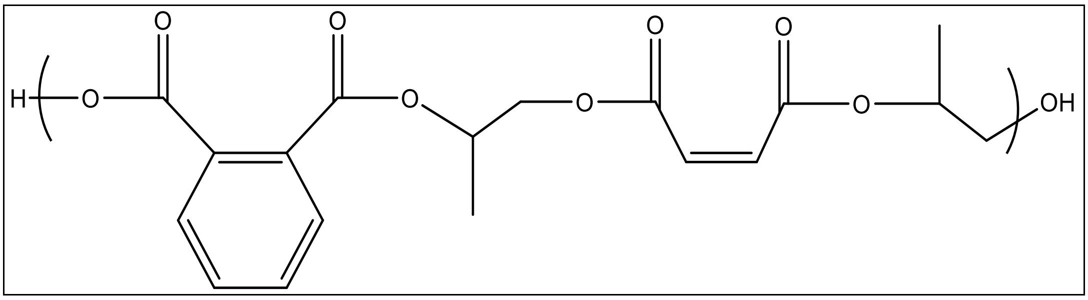


Figure 1.1. General structure of unsaturated polyester

After producing unsaturated polyester, it is blended with the styrene before being sent to the end-user and this mixture it is called UPE resin. The aim of using styrene (called “reactive diluent”) is to reduce the viscosity of the mixture and to act as a crosslinking agent when curing is started. In common UPE resins, the styrene content is around 38 to 45 weight %. [2] With the help of a free radical initiator, crosslinking can be achieved through the double bonds on the unsaturated component (maleate) on the polyester chain and styrene double bond.

Since 1930s various types of unsaturated polyesters have been produced, by changing the molar ratio and type of diol, diacid, unsaturated component and crosslinking agent. Furthermore, end groups of the polyester chain can be change by adding another desired monomer at the last stages of the polymerization.

UPE resins are widely used in marine, sports, automotive, military and construction applications. The most common way of using UPE resins are composites. Composites consist of 2 parts; a polymeric matrix and a reinforcing fiber. One of the most widespread materials that is used as matrix is UPE resin. It is mostly used with glass fibers, however carbon and aramid fibers are also have an important place in the composite industry.

1.1.1. Raw Materials

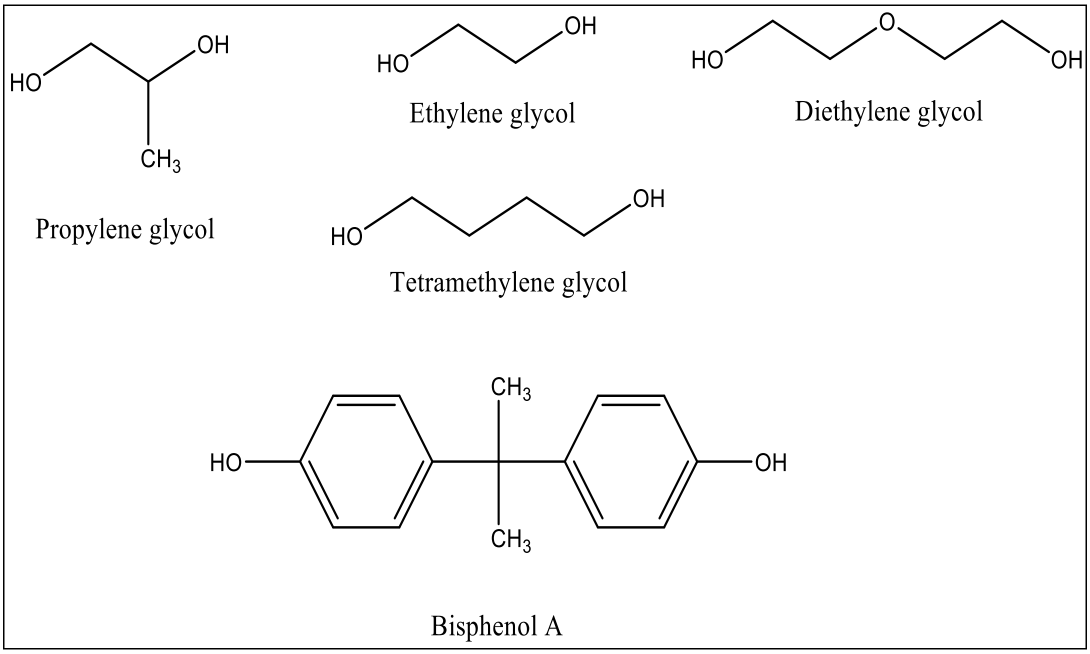


Figure 1.2. Structures of some diols used in polyester production

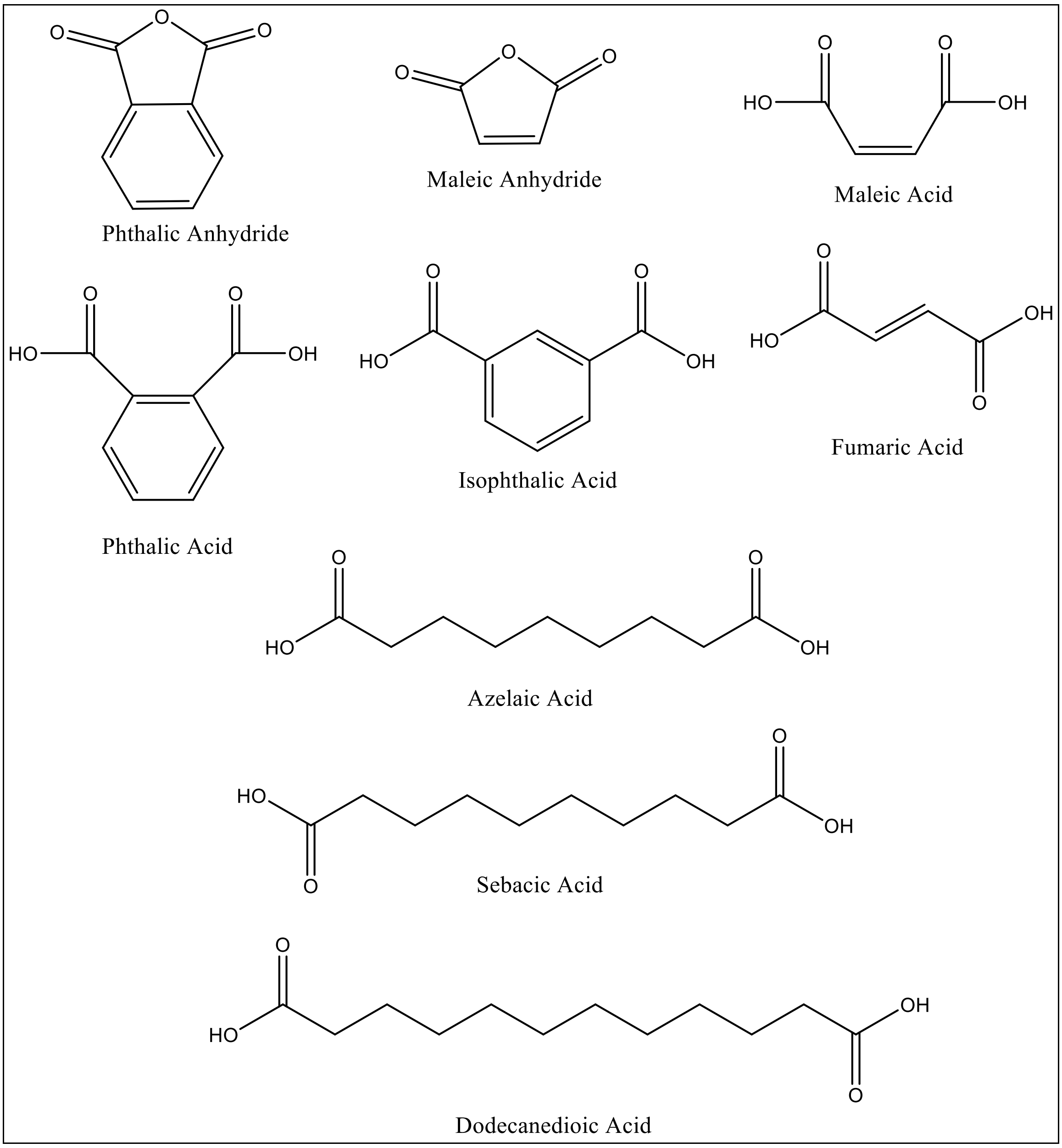


Figure 1.3. Structures of some diacids used in polyester production

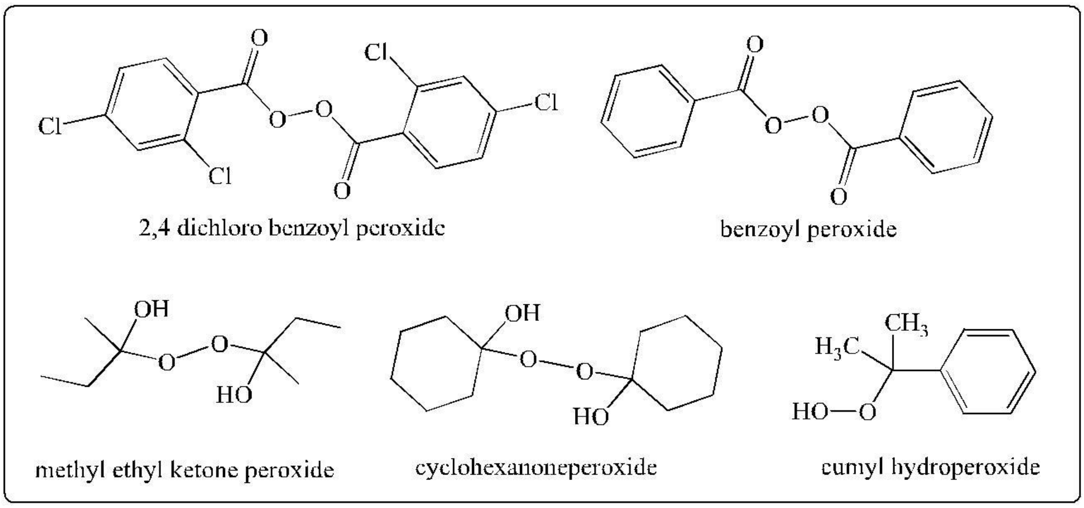
1.1.2. Preparation of Unsaturated Polyester

In the linear unsaturated polyester preparation process, a diol such as propylene glycol, ethylene glycol etc. or mixture of them is heated with a mixture of saturated and unsaturated dicarboxylic acid (or anhydride) in a reactor. Because of the esterification reaction, water is produced and needs to be removed by downward distillation during the reaction.

This condensation reaction takes place at around 150-200 ^{o}C for 6-16 hours. The heating process is continued until the average molecular weight reaches to 1000-2000. The progress of the reaction is followed by acid number titrations and also by viscosity measurements. After the desired molecular weight is obtained, the polymer is cooled to about 90 ^{o}C and moved into a blending tank which has cold styrene in it. The blend is cooled to room temperature and this colorless liquid is called “UPE resin”, which is ready to be sent to end-users [3].

1.1.3. Cross-Linking

Crosslinking reaction in UPE occurs between the unsaturated component of the main chain and vinyl-type monomer used as the reactive diluent with the help of a radical initiator. The initiator is mixed with the resin and the mixture is poured into a mold. The crosslinking takes places in the mold and the liquid resin is transformed into a rigid, load bearing thermoset. The mold is opened and the finished part is obtained.



2,4 dichloro benzoyl peroxide

benzoyl peroxide

methyl ethyl ketone peroxide

cyclohexanoneperoxide

cumyl hydroperoxide

Figure 1.4. Some free radical initiator which are used in crosslinking of UPE

When the initiator is decomposed, it creates a radical so that it can start the crosslinking reaction. For this purpose two kinds of initiators are used; the one which is effective at elevated temperatures and the one which is reactive at room temperature with the help of accelerator (activator).

In the UPE industry, it is very easy to control the properties of the final product. For example, in order to produce highly crosslinked product higher amount of unsaturated monomer can be used in the polyester chain. Crosslink segment length can be modified with the amount of reactive diluent used. At the end of the crosslinking mechanism, this cured polyester is called a thermoset polymer which cannot be melted or dissolved in any kind of solvent, and has excellent mechanical properties. Crosslinking mechanism is shown in the Figure 1.5.

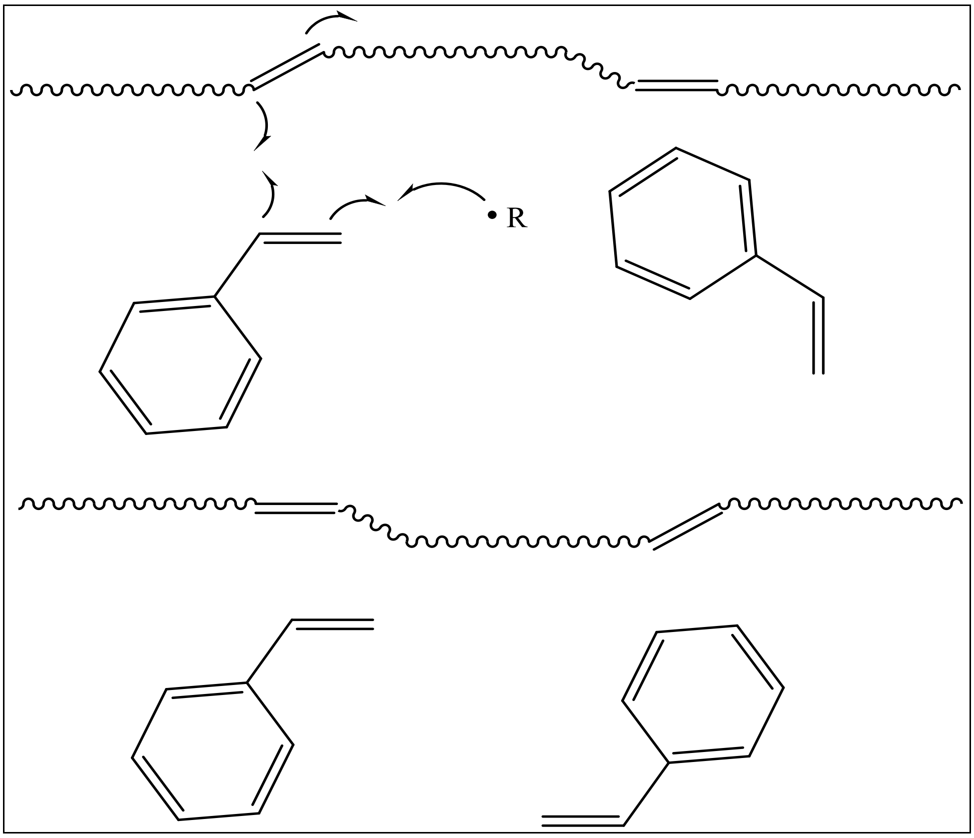


Figure 1.5. Cross-linking mechanism of UPE

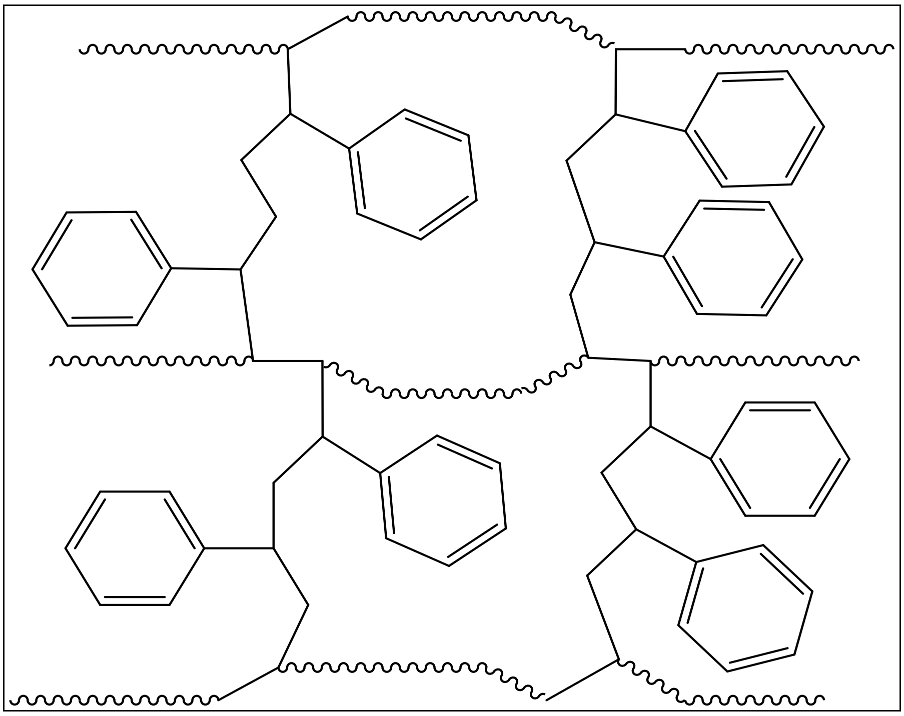


Figure 1.6. Presentation of Cross-linked UPE

The most common reactive diluents used in UPE industry are styrene, methyl styrene and methyl acrylate. Because of the high production rate of styrene (5 million tons annually), styrene places among the top 50 chemicals worldwide [4]. However, toxicity of the styrene is a huge problem especially in composite industry. At the curing reaction of UPE with styrene in an open mold, about 5% of styrene is emitted into the air, because the part heats up during crosslinking.

Up to early 1960s, occupational styrene emission was 200 ppm, however after developing working conditions and new methods, it dropped to 20-100 ppm in Europe and 50 ppm in the US [5]. Because of the emission standards through the “National Emission Standards for Hazardous Air Pollutants: Reinforced Plastic Composite Production” styrene, methyl methacrylate and methylene chloride are regulated as hazardous air pollutants by the U.S. Environmental Protection Agency (EPA) [6]. That’s why industry has to reduce the amount of these chemicals.

In order to overcome this problem, several alternative reactive diluents have been tried. The most promising one is para-methyl styrene because of its higher boiling point. On the other hand, many other petroleum based and also fatty acid based monomers have being investigated for many years [7].

Another method to reduce styrene emission in composite industry is closed mold process. In this technique, dry glass fiber is placed in the mold and UPE is injected after closing the mold. Thanks to this way, it becomes easier to control styrene emission, however high cost of equipment is a disadvantage for this method. Also using low styrene content or using additives to lower styrene emission are other solutions for this problem [8].

1.2. Plant Oils

1.2.1. Physical and Chemical Properties of Plant Oils

Plant oils have been used as a food source since antiquity, however because of their exceptional chemical and physical properties they have been also used as lubricants, fuels and starting materials for many chemicals. They are non-polar and water insoluble triglycerides, which are mostly unsaturated. Esterification reaction of three fatty acids with glycerol produces a triglyceride.

Plant oil triglycerides are excellent renewable raw materials for chemical synthesis. In the last 15 years numerous papers and patents have appeared where these natural materials are used in polymer synthesis. Several papers were published by our group especially by using soybean oil [9-13].

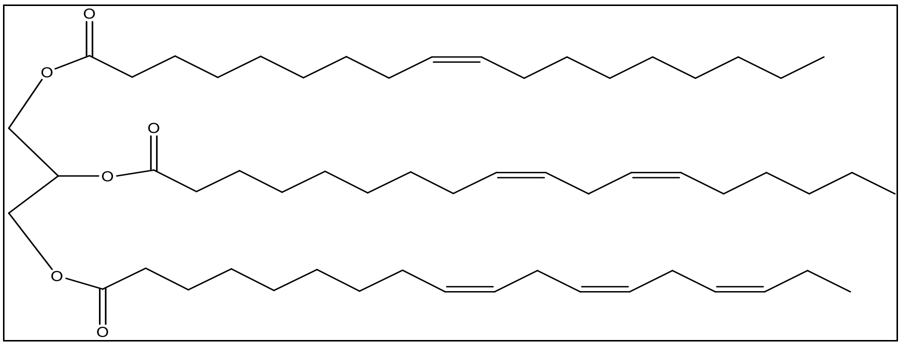


Figure 1.7. General Structure of Vegetable Oils

In nature, the double bonds in fatty acid chains are in the cis geometry which makes them liquid at room temperature. These fatty acid chains can contain 14-22 carbon atoms and have 0 to 6 double bonds along the chain which can be conjugated or unconjugated form. The most abundant double bond positions are 9, 12 and 15th carbons and they are mostly in cis non-conjugated geometry. In order to identify the double bond position in a fatty acid, ω letter is used and for example ω-9 means the double bond is placed between 9th and 10th carbon atoms away from methyl carbon. A typical vegetable oil is composed of around 6 different kinds of fatty acids. Table 1.1 shows the average fatty acid distribution of various vegetable oils.

Table 1.1. Fatty Acid Composition of Various Vegetable Oils

Vegetable Oil	**Fatty Acid %**						
	Palmitic Acid	Stearic Acid	Oleic Acid	Linoleic Acid	Linolenic Acid	Ricinoleic Acid	Other
Castor Oil	1.5	0.5	5	4	0.5	87.5	-
Soybean Oil	11	4	26	52	7	-	-
Linseed Oil	5	4	22	17	52	-	-
Sunflower Oil	6	4	42	47	1	-	-
Palm Oil	39	5	45	9	-	-	2
Rappeseed Oil	4	2	56	26	10	-	2

1.3. Soybean Oil

1.3.1. Chemical Structure and Properties of Soybean Oil

Like most of the vegetable oils, the primary usage of soybean oil is also as a food source. On the other hand, it is also highly used in chemical industry such as in soaps, plastics, coatings, lubricants, biofuel production and many other materials.

After fats and oils were become popular in chemical industry as a renewable feedstock, soybean oil played an important role because of its low cost, high level of unsaturation and its high production. With the advent of genetically modified soybean, seeds that bear up to 30 % oil are now available. The general composition of fatty acids in soybean oil is showed in the Table 1.2.

Table 1.2. Fatty Acid Composition of Soybean Oil [14]

	Name	Structural Formula	Weight Percentage
Saturated	Stearic Acid	$CH_3(CH_2)_{16}COOH$	4
	Palmitic Acid	$CH_3(CH_2)_{14}COOH$	11
Unsaturated	Oleic Acid	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	26
	Linoleic acid	$CH_3(CH_2CH=CH)_2(CH_2)_7COOH$	52
	Linolenic Acid	$CH_3(CH_2CH=CH)_3(CH_2)_7COOH$	7

Soybean oil has an average 4.2 double bonds per a triglyceride molecule. However, although it has double bonds in its structure, they are relatively unreactive therefore some chemical transformations and functionalization must be done in order to be used as a monomer in the polymerization reactions. The most popular ones are epoxidation, maleinization, acrylation, halogenation and conjugation. Because they have relatively high molecular weight and several reactive functional groups, triglycerides can be useful monomers after the double bonds are functionalized. Some functionalized and transformed soybean oil samples are showed in Figure 1.8.

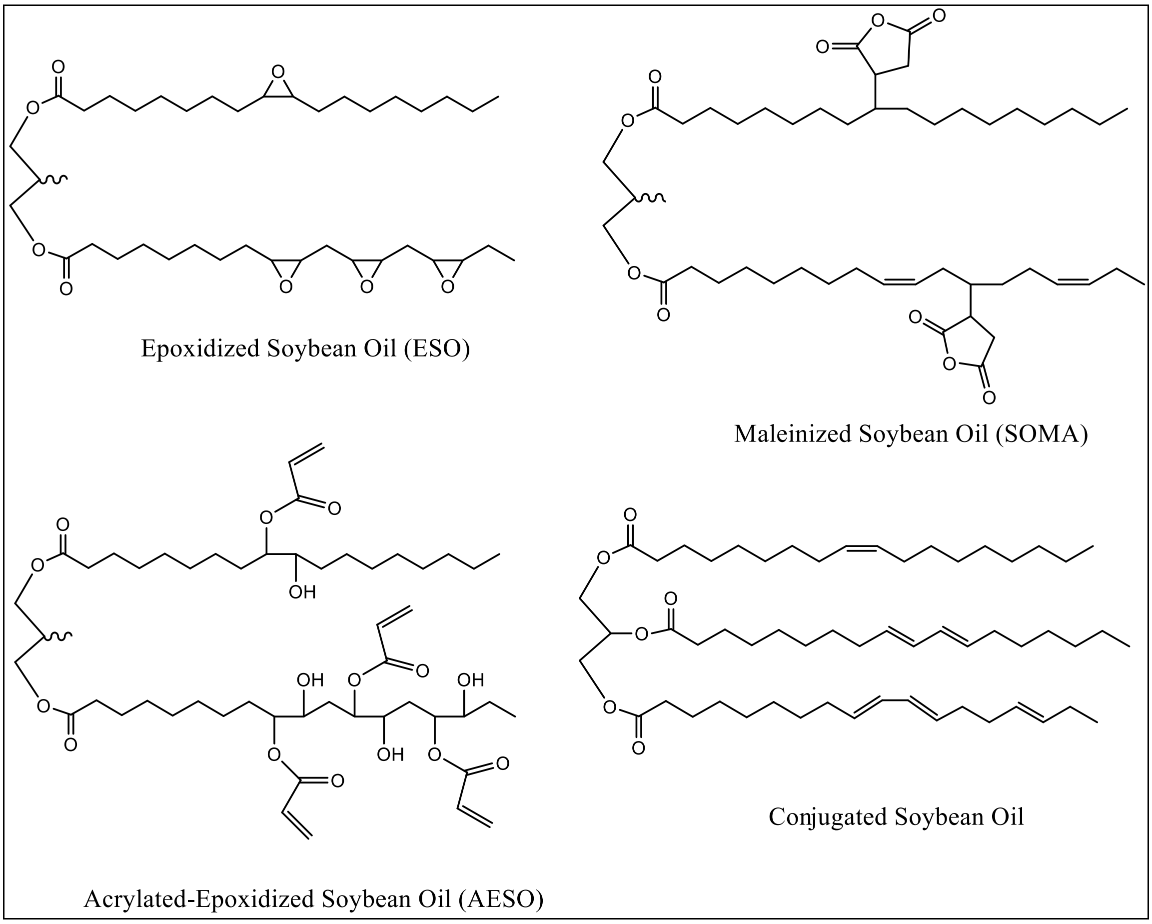


Figure 1.8. Epoxidized Soybean Oil , Maleinized Soybean Oil, Acrylated-Epoxidized Soybean Oil and Conjugated Soybean Oil

1.3.2. Conjugation of Soybean Oil

A conjugated molecule contains an alternating single and multiple bonds system in its structure. Conjugation is a very crucial feature for molecules which can affects their physical properties and also increase their affinity for several reactions like the Diels-Alder reaction. Conjugated vegetable oils are known to produce better “drying” oils. The increased reactivity of conjugated oils with oxygen is responsible for solidification and is the main reason for the suspected carcinogenicity of deep fried foods.

Some of the vegetable oils already have conjugated fatty acids in their compositions like tung oil, bitter gourd oil etc. , however the rest needs high temperature or catalyst in order to be transformed into conjugated structure. In the literature several methods are described for the conjugation of vegetable oils and fatty acids. Homogenous transition metal catalysts, arene carbonyl complexes, alkali, photoisomerization etc. are some of them [15-18].

In bio-based polymer literature, conjugated linoleic acid (CLA) is one of the most popular fatty acids used. CLA is mostly found in dairy products and meat, but also it can be obtained from the conjugation of the unconjugated, natural linoleic acid. After conjugation reaction of linoleic acid, different isomers of CLA are formed, such as trans-8,trans-10 CLA, trans-9,tran-11 CLA, cis-9,trans-11 CLA, trans-10,cis-12 CLA, cis-10 ,trans-12 CLA etc. [19].

1.3.3. Elaidinization of Fatty Acids

Elaidinization is a type of reaction that switches the geometry of a double bond from cis to trans. Name of the reaction is came from the elaidic acid which is the trans isomer of oleic acid [20].

Trans orientation is energetically more favorable, that’s why when a plant oil converted to the trans isomer, it becomes almost impossible to turn back to the cis isomer. Several methods have been described for elaidinization of fatty acids. In the method which J. L. O'Donnell et al. described; iodine is dissolved in pentane-hexane mixture and fatty acid is added into this solution. The solution is placed in direct sunlight for 3 hours and isomerism occurs photolyticly with the light. Then iodine is extracted from the solution and 60-70 % of the cis form is converted to the trans form [21].

1.4. Diel-Alder Reaction

After two German chemists, Otto Diels and Kurt Alder first described this reaction they were awarded the Nobel Prize in 1950 and the reaction was named after them. It is a (4+2) cycloaddition reaction between a conjugated diene and a dienophile and is a very common reaction in organic chemistry. As a result of the reaction between the conjugated diene (a 4 π electron system) and the dienophile (a 2 π electron system), 2 new σ bonds are formed (which is energetically more stable) with the consumption of 2 π bonds [22]. A simple representation of the Diels-Alder Reaction is shown in Figure 1.9.

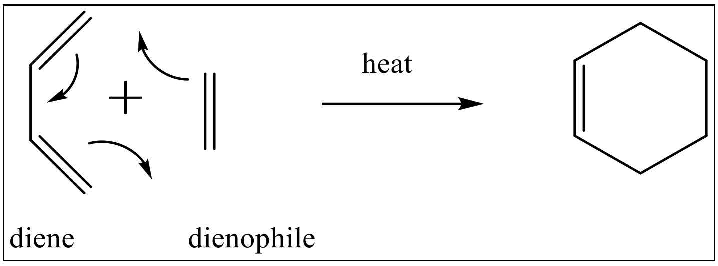


Figure 1.9. Representation of Diels Alder Reaction

In order to enable the best conditions for the Diels-Alder Reaction, the dienophile system should have electron withdrawing groups and the diene system should have electron donating system. Large substituents on the terminal positions of the diene always reduce the rate of the Diels Alder reaction. This is because the substituents prevent the approach of the dienophile within bonding distance. Also various kinds of catalyst like Lewis Catalyst can be used to lower reaction temperature or some chiral catalysts can be used to improve regio- and stereoselectivity. The challenging problem in Diels Alder Reaction is that at higher reaction temperatures Retro Diels-Alder reaction takes place. On the other hand it can be a practical feature for many other purposes as well.

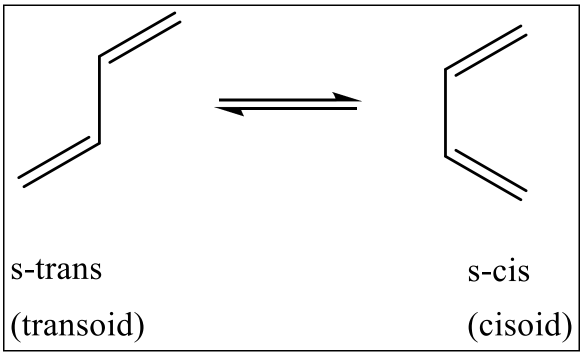


Figure 1.10. s-trans and s-cis Conformation of a Diene

Dienes can be present in two conformations; cisoid and transoid. Cisoid conformation is required to achieve a successful Diels-Alder reaction. Because a six membered ring cannot be obtained with a transoid diene, it is impossible to get a (4+2) cycloaddition reaction. Dienes shown above in the Figure 1.10 are in dynamic equilibrium, however because transoid conformation has lower energy it is more favorable in the medium. When they are used in a Diels Alder reaction, dienophile will consume the cisoid conformation of the diene, therefore equilibrium will be shifted to produce more cisoid conformation [23].

A diene that has substituents in the terminal (1,4) positions can be present in different geometric isomers like trans-trans or cis-cis or cis-trans. Although cisoid conformation is a must for Diels Alder reaction, the most favorable geometric isomer is the trans, trans isomer. The reason is that it has the lowest steric hindrance when it is compared with the rest.

Like in the Figure 1.11, it is impossible for a dienophile to give a Diels Alder reaction with the cis, cis isomer and high temperature is needed for the cis, trans isomer, however for trans, trans isomer mild conditions should be enough to obtain a high yield of product. This difference is more obvious for the diene which have bulky groups or long alkyl chain substituents like unsaturated fatty acids. Several papers were published to discuss the reactivity difference of these isomers in Diels Alder reaction.

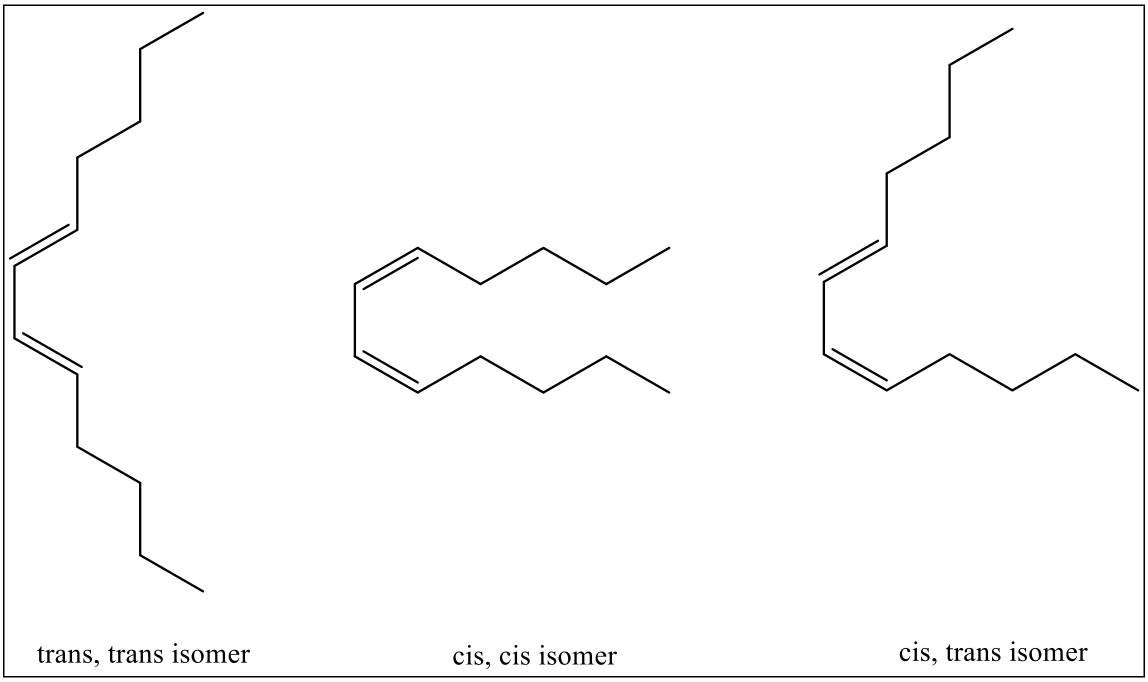


Figure 1.11. Isomers of a Conjugated Diene (cisoid conformation)

In 1951 K. Alder W. Vogt published a paper which shows the reactivity difference of cis, trans conjugated hexadiene from trans, trans hexadiene with maleic anhydride. They discovered that trans, trans isomer reacted easily at 80 ^oC in benzene, however the cis, trans isomer needed 150 ^oC and 15 hours [24].

Also a paper by D. H. Wheeler mentioned the same situation by using different compounds. He used two different isomers of eleostearic acid; α eleostearic acid (cis-9, trans-11, trans-13) and β eleostrearic acid (trans-9, trans-11, trans-13). Diels Alder reaction with maleic anhydride took place for 3.5 hours for β eleostrearic acid, however for the α eleostrearic acid it took 11 hours [25].

1.4.1. Diels-Alder Reaction in Polymer and Macromolecular Chemistry

Diels-Alder Reaction is an irreplaceable reaction in polymer synthesis. In plant oil chemistry, it is also a very feasible reaction if there is a conjugation in the fatty acid chain. This conjugated fatty acid can be used as a dienophile in the reaction, however conjugated fatty acid has to be in trans,trans geometry in order to achieve a successful Diels-Alder reaction [21]. For example fatty acids in soybean oil are mostly in cis,cis geometry and not conjugated, so they must first transformed to conjugated and then to trans-trans conjugated.

Metzger et al. reported a paper about Diels Alder addition of maleic anhydride with conjugated triene fatty acid methyl esters (methyl calendulate and methyl α-eleostearate). Trienes have three conjugated double bonds which have trans,trans,cis conformation. They discovered that the only product obtained is the one from the trans double bonds of the fatty acid [26].

Another paper related to plant oils and Diels Alder reaction is the work of Chengguo Liu et al. Tung oil was used as a toughening agent for dicyclopentadiene-terminated unsaturated polyester resins. Because tung oil already has conjugated trans-trans structure, there is no need for further transformation for Diels-Alder reaction. By adding tung oil into the modified polyester resin dropwise at 200 ^{o}C, product was achieved in order to be used in further steps [27].

2. RESEARCH OBJECTIVES

The aim of the project is to crosslink unsaturated polyester with conjugated soybean oil via Diels Alder reaction. Plant oil triglycerides are triesters of glycerol and unsaturated fatty acids. In the natural oil, as obtained from the seed, the polyunsaturated fatty acids are non conjugated and predominantly in the cis geometry. As such they are not suitable as dienes in a Diels Alder synthesis. However if the triglycerides can be converted to conjugated trans dienes then they would be suitable to react with the maleate double bonds of unsaturated polyesters and this would lead to crosslinked, thermoset polyesters.

Normally unsaturated polyesters are crosslinked with styrene and a free radical initiator. The toxicity and volatility of styrene and the requirement of adding an initiator and accelerator by the part manufacturer has always been a problem in unsaturated polyesters. If the strategy proposed here works, a one component, premixed mixture of unsaturated polyester and a conjugated plant oil would be a valuable material for producing glass fiber composites. The mixture would contain no volatile or toxic ingredients, no initiator and accelerator would be need to be added by the user, and only heating in the mold would produce a thermoset polymer. This polymer would also contain reasonable amounts of renewable plant based raw material which decreases the use of petroleum based raw materials.

Predicted crosslinking mechanism will be a Diels Alder reaction as shown in Figure 2.1. Diene will be the conjugated diene part of the plant oil and the dienophile will be the maleate part of the UPE. Furthermore, reaction efficiency will be increased by transforming conjugated double bonds of CSO to trans-trans geometry which will decrease steric hindrance and provide better yields.

Chemical characterization of crosslinked products will be done by FTIR spectroscopy and the mechanical properties will be determined by surface hardness, solvent swelling and compression strength measurements.

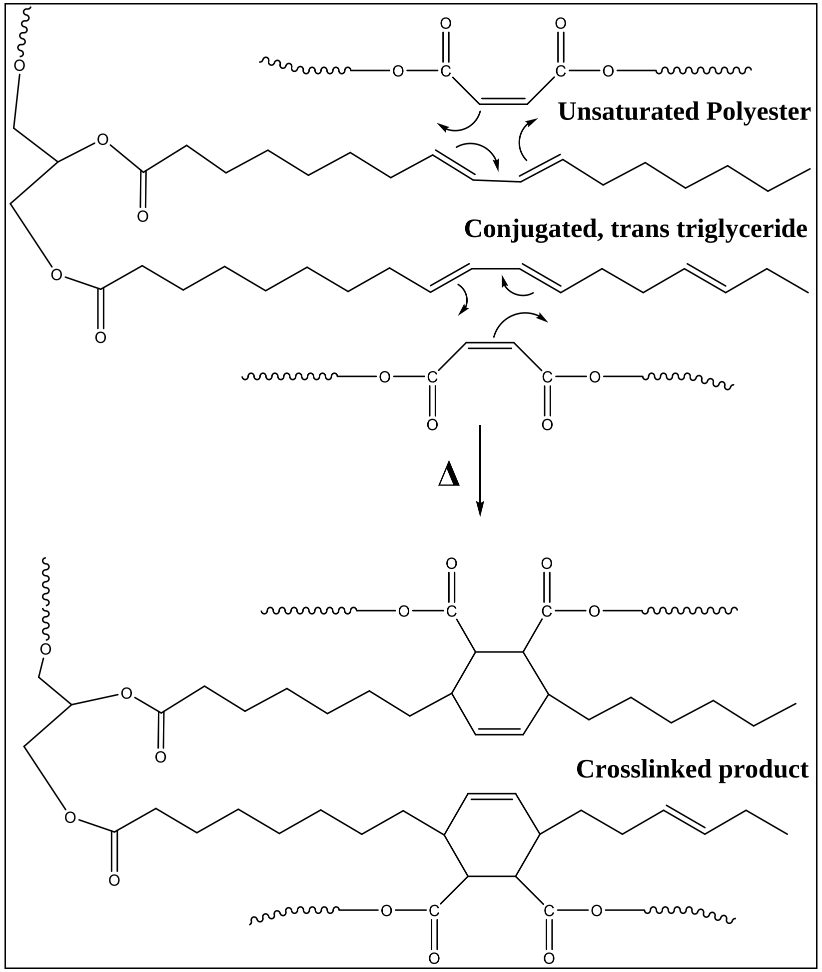


Figure 2.1. Predicted crosslinking mechanism of UPE with CSO

3. EXPERIMENTAL

3.1. Materials and Apparatus

3.1.1. Materials

Unsaturated Polyester Resin (CE 92) was obtained from Poliya (Turkey). Conjugated soybean oil was obtained from ADM (Chicago, Illinois, USA). Chloroform, n-hexane and Acetone were purchased from Merck (Darmstadt, Germany). Iodine was obtained from BDH Chemicals (England).

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 and the spectra were reported as a ppm (δ).

Bareiss Shore D durometer was used for surface hardness test according to ASTM D2240 standard.

3.2. Elaidinization of Conjugated Soybean Oil

0.01 gram of Iodine was dissolved in 10 ml of petroleum ether. When all iodine was dissolve and color turned to dark purple, 10 gram of conjugated soybean was added into this mixture. Mixture was stirred well and transferred into a large test tube. The test tube was placed 30-40 cm in front of to a metal halide lamp. Position of the test tube should be vertical to the incident light. Aluminum foil was used for the background in order to increase light reflection. After 8 hours color turned to dark brown and the mixture was transferred to a separatory funnel. 0.01 gram of sodium thiosulfate was dissolved in water and added into the funnel in order to wash the mixture for 3 times. After extraction, color became lighter brown and petroleum ether was evaporated. A stream colored viscous oil was obtained.

FTIR and ^{1}H NMR were used for characterization and results are given at Section 4.

3.3. Crosslinking of UPE with SO, CSO and trans,trans CSO

1 gram of unsaturated polyester was mixed with 1 gram of soybean oil in a test tube. Then the mixture was purged with nitrogen gas for 3-5 minutes to remove oxygen and residual moisture. Top of the tube was sealed with aluminum foil and paraffin film. Sample was stirred for 3 hours at 180 ^{o}C. UPE dissolved slowly in 30 minutes to give a cloudy yellow solution. After 3 hours, stirrer was removed from the tube and the solution was heated without stirring for an additional 15 hours. At the end, yellowish white solid was obtained. Hexane was added into the tube to dissolve unreacted SO and the solid was extracted at the end. Then finally the solid was washed with acetone to remove unreacted UPE and dried at room temperature. The yield was 7.5%.

For CSO, the procedure was almost same, however the product had pale yellow color and the yield was higher (15-63%). Several weight ratios of UPE:CSO were reacted.

The reaction was run with t,t-CSO and a one piece thermoset sample was obtained. Hexane extraction was done but there was no need for acetone extraction. The yield was 93-97%.FTIR characterization details are given at Section 4.

3.4. Surface Hardness Test

Shore Hardness Tests were done according to ASTM D 2240 standard test. Polymer sample should have at least 6 mm thickness. 10 data points were obtained from the same surfaces of different samples and average of 10 points gave hardness value of each sample. Working principle of the instrument is a 2.5 mm extended indentor is pushed by spring into the sample surface and depth of the penetration is obtained by the detector scale (0-100). 0 means full penetration and 100 means no penetration, which explains why the lower the scale, the softer the material.

3.5. Compression Test

Compression Tests were applied according to ASTM D 695 standard test. Sample sizes were 22 mm x 11 mm (height was twice the diameter). The cross-sectional area of the surface was 0.95 cm^2. For every reaction condition, 5 samples were tested and the results were averaged. The data was presented as a Force/Displacement plot.

3.6. Swelling Test

Crosslinked polymers are not soluble in solvents but they can absorb solvent and this is called swelling behavior. To test this behavior, swelling test was done by using hexane as a solvent. Firstly, initial weight of the polymers were recorded and then samples were placed in a closed container which contained 25 ml of hexane. For every one hour interval weight increase was recorded until swelling reaches equilibrium. The data was presented as a weight gain/time plot.

4. RESULTS AND DISCUSSION

4.1. Characterization and Analysis of Soybean Oil (SO) and Conjugated Soybean Oil (CSO)

Characterizations of soybean oil and conjugated soybean oil were done with ^{1}H NMR and FTIR spectroscopy. FTIR and ^{1}H NMR interpretations of SO and CSO are given in Table 4.1 and Table 4.2 respectively.

Soybean oil is a natural product. Although the approximate content of doubly and triply unsaturated fatty acids is known, the amount of conjugated dienes is essentially unknown. The natural oil, when obtained from the soybean by cold pressing contains only non-conjugated and cis double bonds. During storage heat, light, oxygen, presence of transition metal contaminants, or acids gradually produces conjugation and some trans double bonds.

It was clear at the outset that natural edible soy oil would not yield a crosslinked product with UPE. Heating soy oil by itself under nitrogen did not give a polymeric product. To be useful as a diene, one must maximize the conjugation and trans geometry of the polyunsaturated fatty acids.

“Conjugated” plant oils are commercially available and they used in varnish manufacture. A commercial sample of conjugated soy oil was obtained from Archer-Daniels Midland. How “conjugated” this sample really will essentially determine the yield of crosslinking and this had to be determined by analysis.

^{1}H NMR was used for this purpose. In order to calculate percentage conversion of unconjugated C=C bonds to conjugated bonds, glycerol backbone peaks ($-C\mathbf{H}_2OCOR$) at 4.12 to 4.31 ppm were taken as standards because even in conjugation reaction they do not change. And by calculating the difference between the integrals of the 2.75-2.78 ppm proton peaks ($CH=CHC\mathbf{H}_2CH=CH$) for SO and CSO, dividing by the integrals of same peaks of SO and multiplying by 100[28]. % of conjugation was calculated as 16 for the CSO we used.

Table 4.1. FTIR interpretation of SO and CSO

	Position of the Peak (cm^{-1})	
Assignment	SO	CSO
=C-H stretch	3008	3009
$-CH_2$ stretch	2922 and 2853	2923 and 2853
-C=O stretch	1743	1742
-C=C- stretch	1653	1653
C-O stretch	1159	1159
C=C-H bending vibration of trans,trans conjugated	Absent	992
C=C-H bending vibration of trans nonconjugated (isolated)	Absent	967
C=C-H bending vibration of cis,trans conjugated	Absent	942

Table 4.2. ^1H NMR interpretation of SO

Chemical Shift (ppm)	Assignment
0.90-0.84	$-C\mathbf{H}_3$
0.99-0.95	$-CH=CHCH_2C\mathbf{H}_3$
1.39-1.20	$-C\mathbf{H}_2-$
1.64-1.55	$-OOCCH_2C\mathbf{H}_2-$
2.11-1.98	$-HC=CHC\mathbf{H}_2$

2.33-2.28	$\text{-OOCC}\mathbf{H}_2\text{-}$
2.78-2.75	$\text{CH=CHC}\mathbf{H}_2\text{CH=CH}$
4.31-4.12	$\text{-C}\mathbf{H}_2\text{OCOR}$ (glycerol)
5.28-5.25	$\text{-C}\mathbf{H}\text{OCOR}$ (glycerol)
5.39-5.31	$\text{C}\mathbf{H}\text{=C}\mathbf{H}$

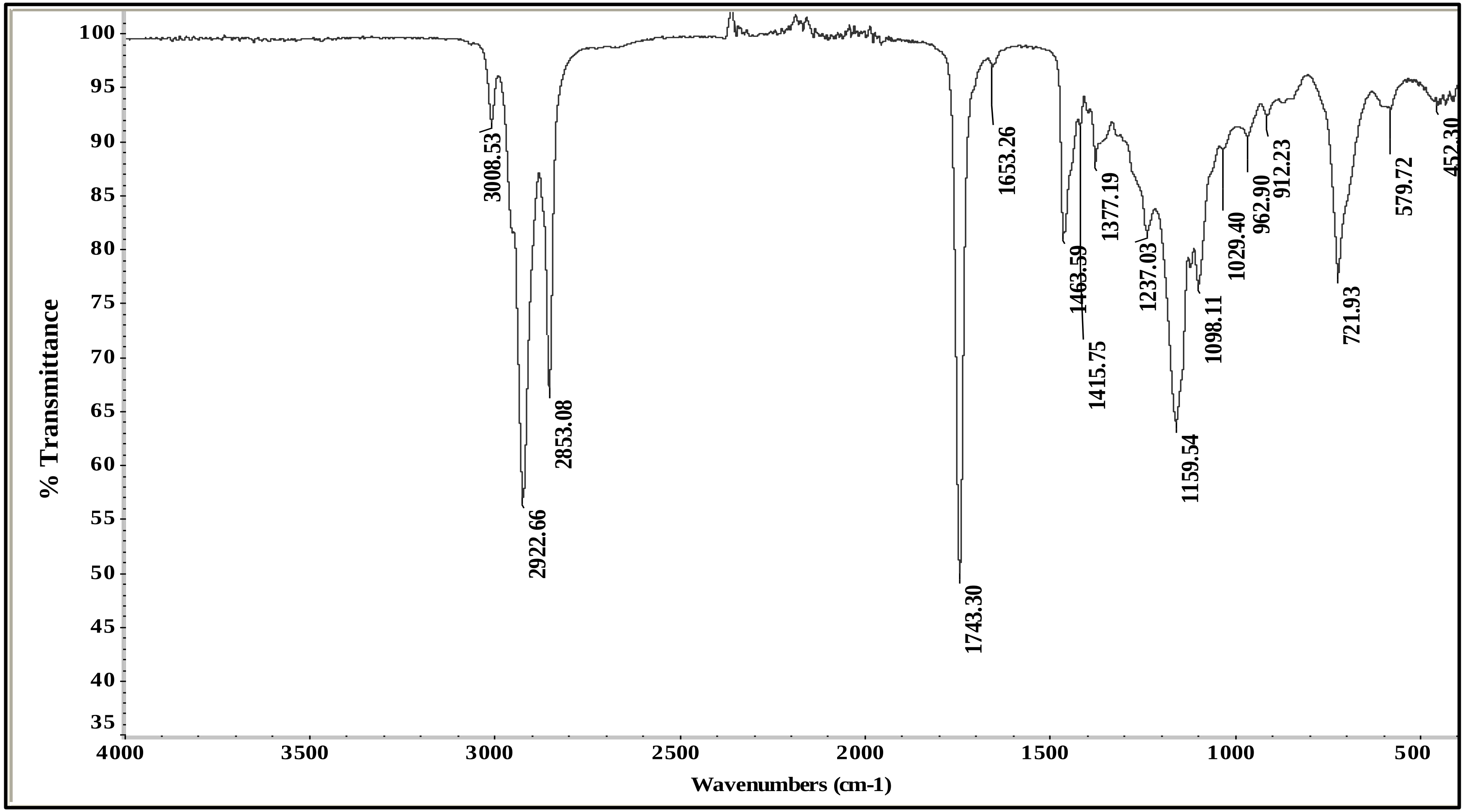


Figure 4.1. FTIR spectrum of soybean oil

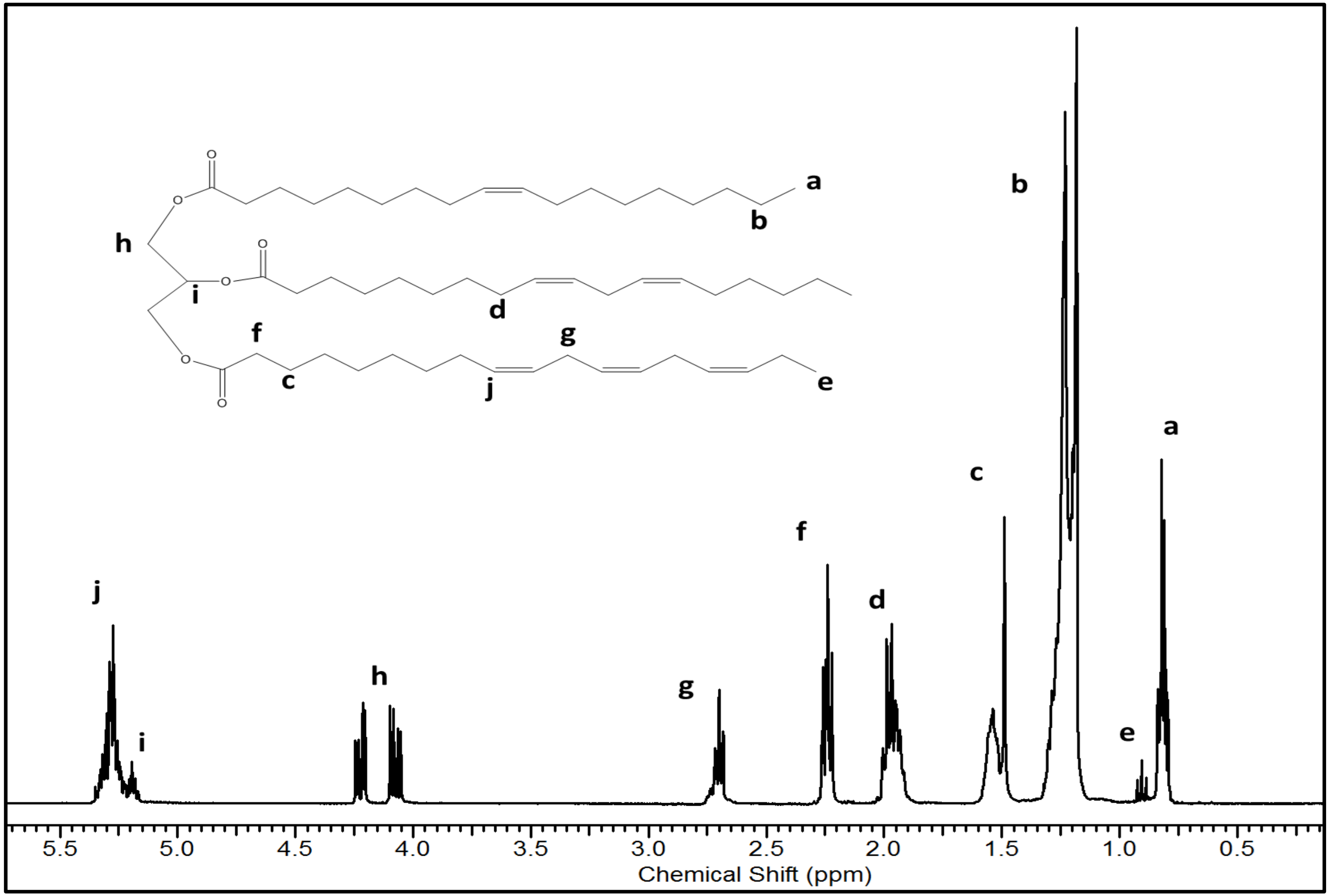


Figure 4.2. ^{1}H NMR of soybean oil

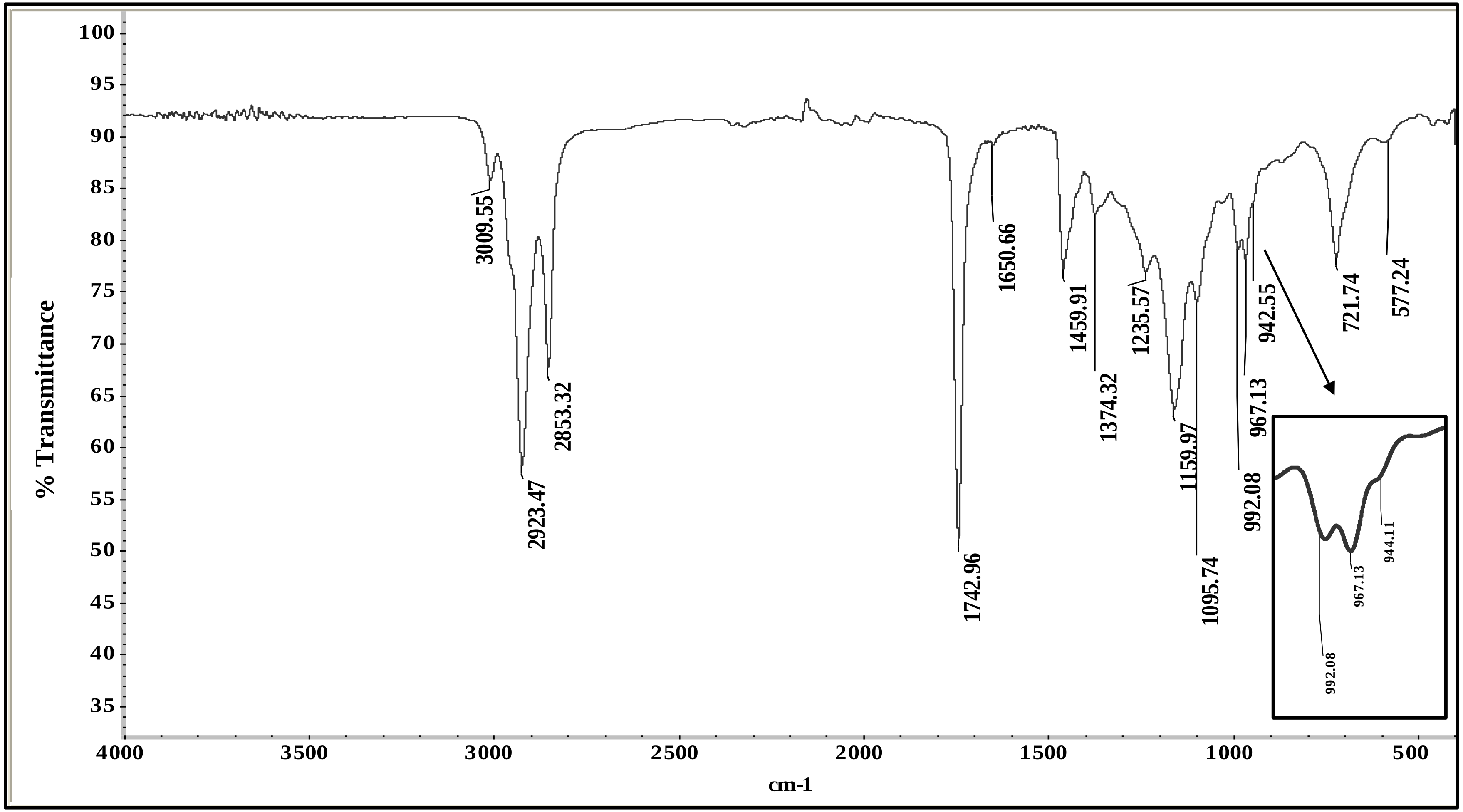


Figure 4.3. FTIR spectrum of conjugated soybean oil

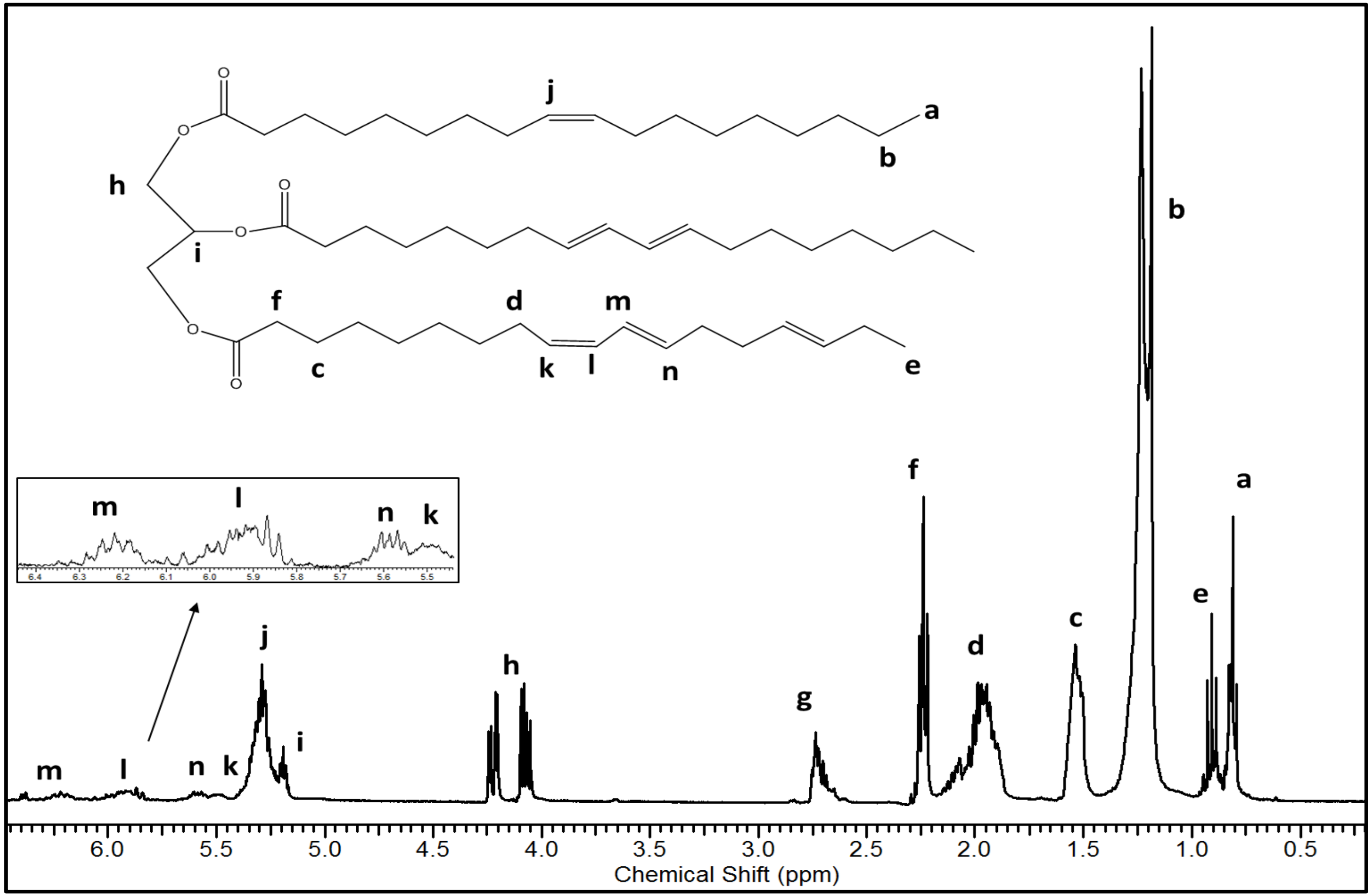


Figure 4.4. ^{1}H NMR of conjugated soybean oil

4.2. Characterization of trans, trans CSO (t-CSO)

Elaidinization of CSO was done by using the method described by J. L. O'Donnell et al. [21]. The method was changed and a metal halide lamp was used instead of sunlight. The aim was to transform the conjugated double bonds into the trans, trans geometry. Transformed soybean oil was characterized by using ^{1}H NMR and FTIR spectroscopy. Easiest way to observe the change was FTIR analysis. There are 2 important peaks on the FTIR data which correspond to the bending vibration of trans-trans conjugated diene's (987 cm^{-1}) and the bending vibration of cis-trans conjugated diene's peak (944 cm^{-1}). After the elaidinization process, intensity of 987 cm^{-1} increased and the intensity of 944 cm^{-1} peak decreased as expected. Yield given in the literature was 60 % but the starting material was the free acids. As we used the triglyceride instead of the acid, the yield in our case would be different. Interpretation of the FTIR peaks are listed in the Table 4.3

Table 4.3. Interpretation of FTIR peaks of trans,trans Conjugated Soybean Oil

Position of the Peak (cm^{-1})	Interpretation
3009	=C-H stretch
2923	$-CH_2$ asymmetric stretch
2853	$- CH_2$ symmetric stretch
1742	-C=O (ester) stretch
1653	-C=C- stretch
1159	-C-O stretch
987	C=C-H Bending vibration of trans,trans conjugated
966	C=C-H Bending vibration of trans nonconjugated (isolated)
944	C=C-H Bending vibration of cis,trans conjugated

The starting material used is commercially obtained conjugated soybean oil. Literature [19] suggests that the conjugated fatty acids will not undergo a Diels Alder reaction unless the double bonds are in the trans-trans geometry. Conversion from cis-cis to trans-trans geometry is traditionally called elaidinization. Scheme of the transformation of nonconjugated SO to conjugated trans-trans SO is shown in Figure 4.5.

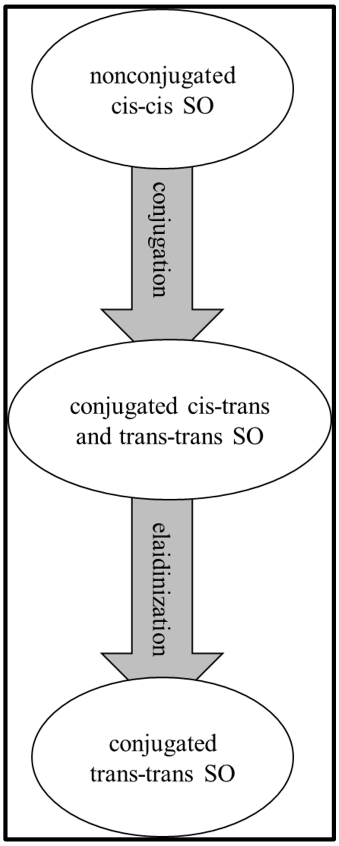


Figure 4.5. Scheme of the transformation of SO to t-CSO

FTIR and ^{1}H NMR spectrums of t-CSO are given in the Figure 4.6 and Figure 4.7 respectively. In Figure 4.8 alteration of FTIR peaks from SO to t-CSO is shown. % of conjugation was calculated with the same method described in previous section. After elaidinization, % of conjugation was also increased to 26%. On the other hand, the % of trans,trans double bond was calculated by sum of trans,trans conjugated peaks at 5.5-6.1 ppm divided by sum of the all conjugated peaks at 5.2-6.1and multiplying by 100 which was found to be 36% . These numbers may seem low, but it has to be remembered that soy oil contains a large amount of oleic acid (26%) which is a mono unsaturated acid and cannot be conjugated.

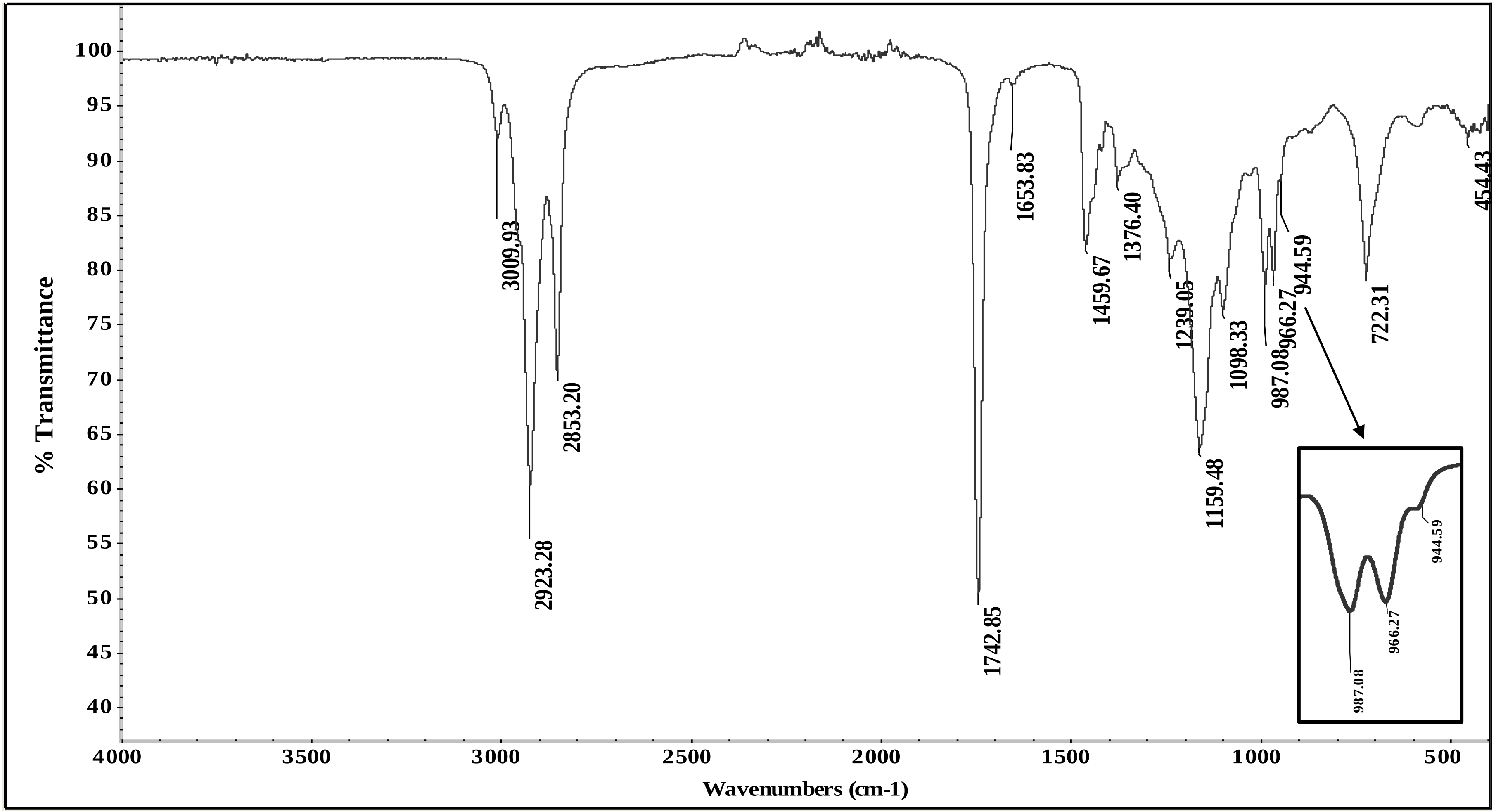


Figure 4.6. FTIR spectrum of trans, trans conjugated soybean oil (t-CSO)

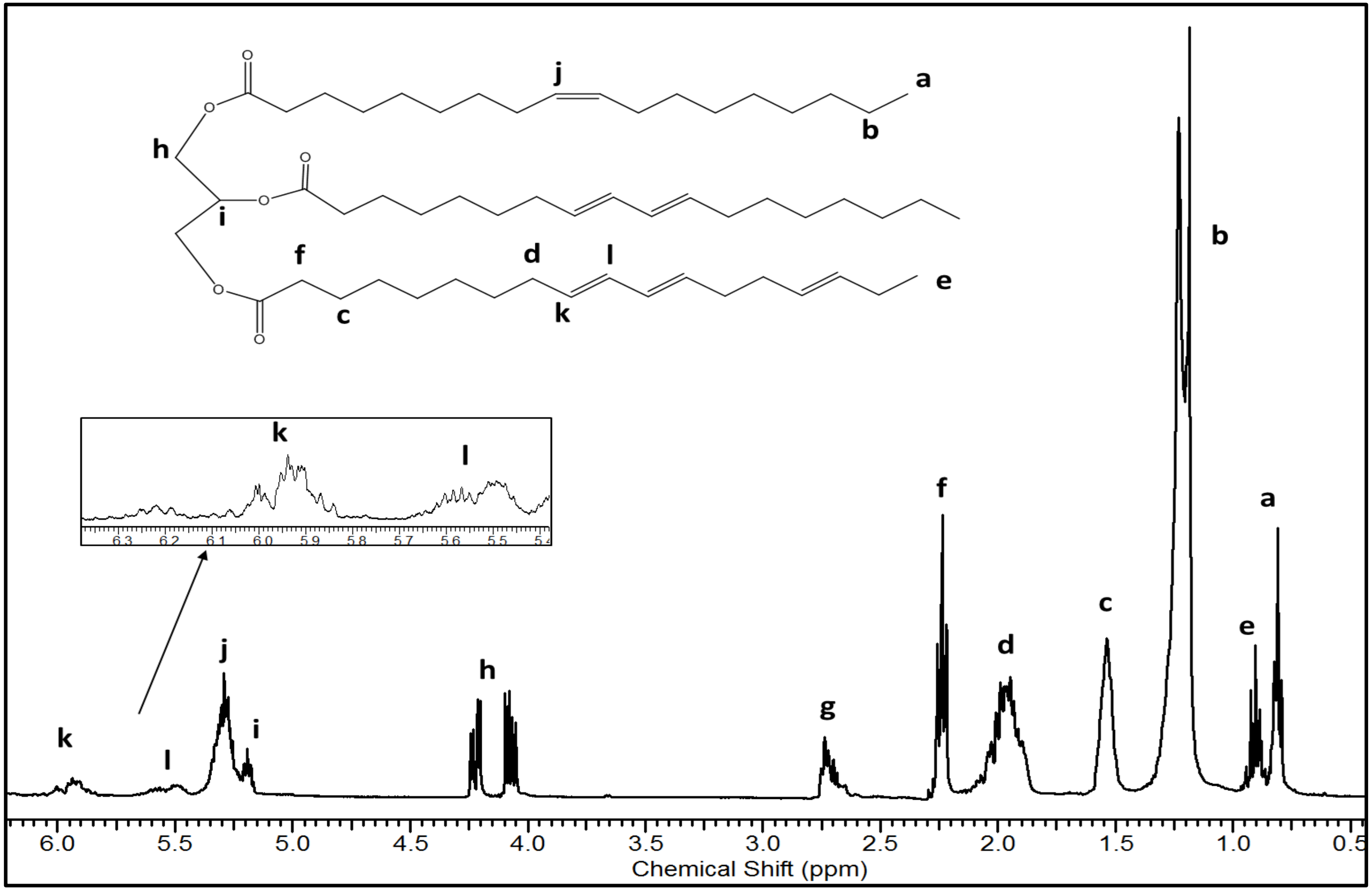


Figure 4.7. ^{1}H NMR spectrum of trans, trans conjugated soybean oil (t-CSO)

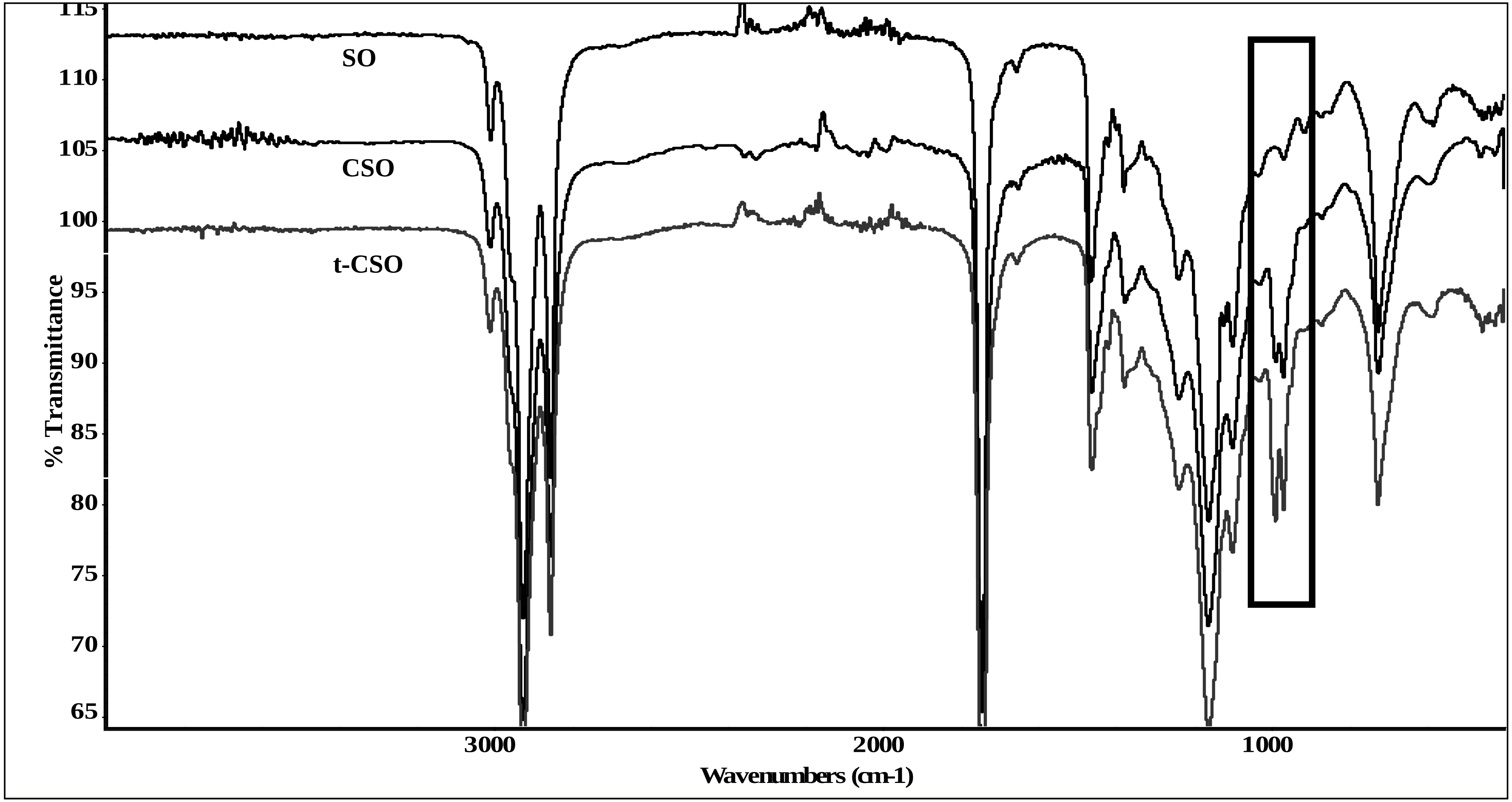


Figure 4.8. FTIR peak changes via conjugation of SO and elaidinization of CSO

4.3. Synthesis and Characterization of crosslinked Diels Alder products of UPE with SO, CSO and t-CSO

Once conjugated and trans soy oil was obtained to the best of our ability, several weight ratios of UPE to plant oil, reaction temperature and reaction time were tested to discover the right conditions for the crosslinking reaction. First of all, closed system was used and nitrogen was purged before the reaction start. Because oxygen itself can act as a dienophile and a conjugated diene is already exists in the medium, oxygen has to be removed from the medium otherwise it will consume conjugated double bonds. And also oxygen can cause a self-polymerization of oil. Secondly, 180 ^{o}C was determined as the reaction temperature after literature survey and several trials. Different reaction times were tested and the best results were obtained in a 24 hour reaction. Also toluene and THF was used as a solvent for this reaction however nothing was gained by using a solvent at the end of the reaction. Because of the lower boiling points of available solvents, reaction couldn’t be run at higher temperatures. Furthermore, from an industrial point of view neither solvents nor the very long reaction times are suitable.

The most challenging part was determining the correct stoichiometry of the reaction. We know the number of moles of maleate in one mole of UPE chain. Commercially obtained UPE has a known molecular weight (≈ 1200) and a known composition. Thus the unsaturation equivalence of UPE can be easily calculated. Soy oil, however, is a natural product. The total unsaturation, as determined by the so called “Iodine number” only gives an average number of double bonds. NMR analysis also gives the average number of conjugation but does not describe the individual triglyceride precisely.

Therefore although we know the average moles of double bonds in soybean oil, it is very hard to say the amount of conjugated double bonds in one mole of CSO. We only know the percentage of conjugation. Besides, just having conjugated double bond is not enough in our reaction; we also need trans-trans conjugated double bonds. After elaidinization of CSO, the majority of conjugated double bonds were transformed to trans-trans geometry, still we do not know the exact amount of trans,trans double bonds in our oil because a mixture of cis-trans and trans-trans exists. Therefore it is almost impossible to determine the amount of trans-trans conjugated double bonds and the correct stoichiometry has to be determined experimentally. If the diene we used was a fatty acid it would be easier to say something about the exact amounts of double bonds. For example if it was a conjugated linoleic acid, we could say that it has 2 double bonds in its structure and it would be easier to convert all the conjugated double bonds in to trans-trans geometry, however we used soybean oil where each molecule contains three fatty acids and a mixture of oleic, linoleic and linolenic acid in its structure which makes it difficult to calculate the actual amount of trans-trans conjugated molecules.

CSO and UPE were also heated alone to make sure that there is no self-polymerization taking place. Because CSO has a conjugated diene part and also an isolated double bond (which can be a dienophile) there is a possibility to obtain a crosslinked polymer via Diels Alder reaction by itself, however after CSO was heated alone for 24 hours at 180 ^{o}C no reaction took place. The sample was still soluble in hexane and FTIR spectrum showed no difference. Probably isolated double bonds cannot act as good dienophiles at this temperature. UPE was heated alone as well and again nothing was changed. It was still soluble in acetone and FTIR spectrum was same as before.

4.3.1. Synthesis of crosslinked UPE-SO polymer

In order to prove that crosslinking reaction occurs from the conjugated diene part of the soybean oil via Diels Alder reaction, a non-conjugated diene which is natural soybean oil was used with UPE. The difference between using a conjugated diene from non-conjugated diene in our reaction was observed. After prolonged heating, mixture was washed with first hexane and then acetone. After extraction a very small amount of yellowish product was obtained. It was insoluble in hexane, acetone and chloroform; therefore it must be a crosslinked polymer. However only 7.5% of soybean oil was consumed in the reaction. Clearly in order to obtain a product via Diels Alder reaction, a conjugated diene must exist. Probably a small amount of conjugation of SO occurred while sample mixture was heated and this material gave a Diels Alder reaction with UPE.

4.3.2. Characterization of crosslinked UPE-SO polymer

This product was obtained at only 7.5% yield. The FTIR spectrum of the UPE-SO product is given in Figure 4.8. Carbonyl peak shifted from only 1715 cm^{-1}to 1716 cm^{-1}. There was a slight intensity increase of the -CH$_2$ peak at 2922 cm^{-1} and 2853 cm^{-1}which is from soybean oil’s long hydrocarbons. Double bond peaks from UPE stayed same at 1646, 978 and 772cm^{-1}. Therefore it was an evidence for a poor crosslinking yield as expected. Conjugated soybean oil must be used in order to obtain a crosslinked polymer via Diels Alder Reaction.

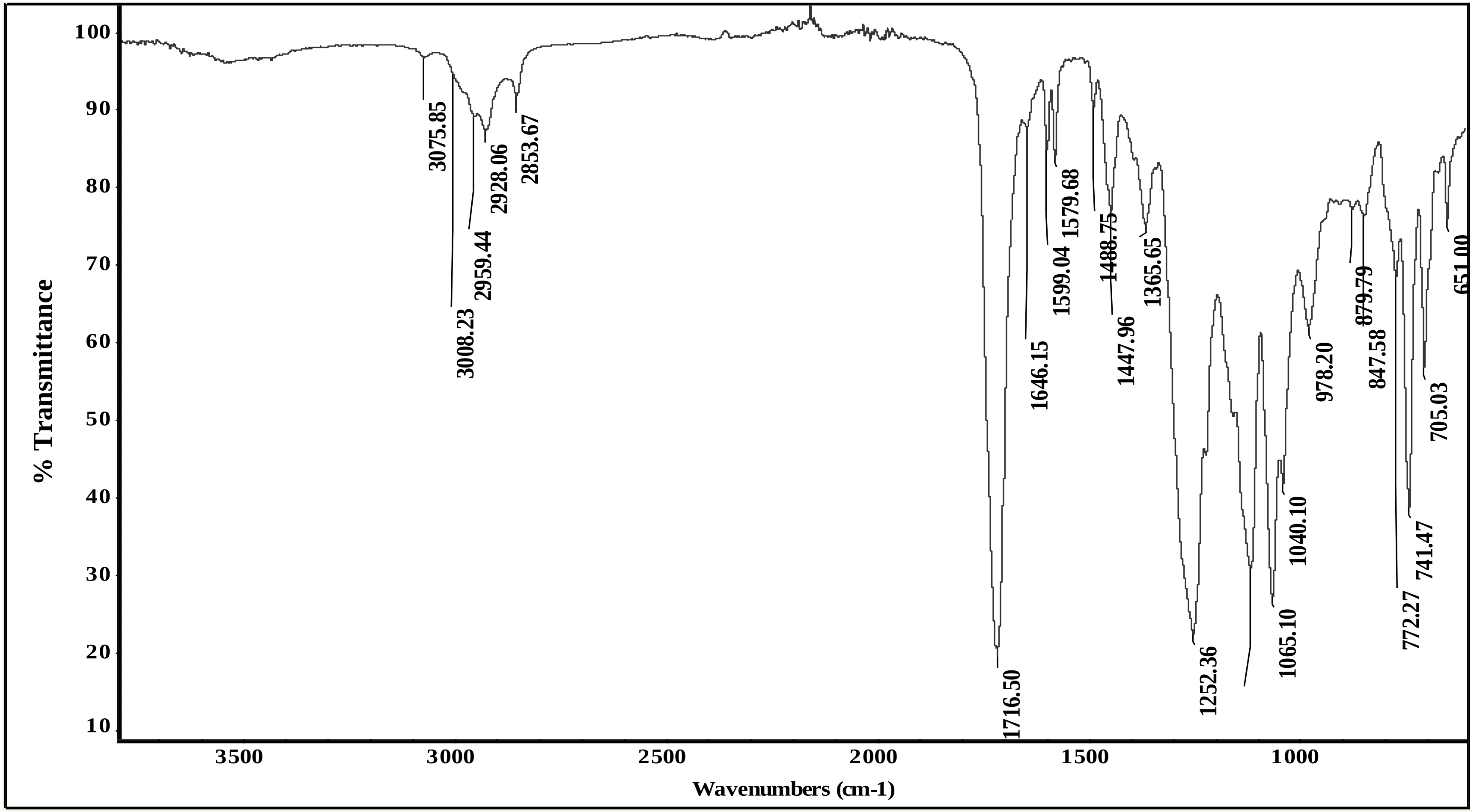


Figure 4.9. FTIR spectrum of UPE-SO crosslinked polymer at 180 ^{o}C for 24 hours

4.3.3. Synthesis of crosslinked UPE-CSO polymer

The same reaction with CSO gave an obvious difference compared to the reaction with SO. First of all, yield was greater. The product was also insoluble in hexane, acetone and chloroform. The predicted crosslinking mechanism of UPE-CSO is shown in Figure 4.10. CSO consumption by weight varied from 15.8 to 63.4% with different weight ratios of UPE:CSO. As we proposed in this study, one triglyceride molecule gives two Diels Alder reactions with two maleate double bonds, therefore if CSO was used in excess amount, UPE double bonds were consumed first and this resulted in mostly CSO grafted UPE with small amount of crosslinked UPE. This CSO grafted UPE dissolved in acetone and the actually crosslinked UPE yield was low. On the other hand if UPE was used in excess amount, it resulted in greater amount of crosslinked product because after maleate groups connected with one fatty acid chain of a CSO triglyceride, they connect with other unreacted chain of the same triglyceride which causes a crosslinked product. As a result, the yield increased and the CSO content in crosslinked polymer became greater.

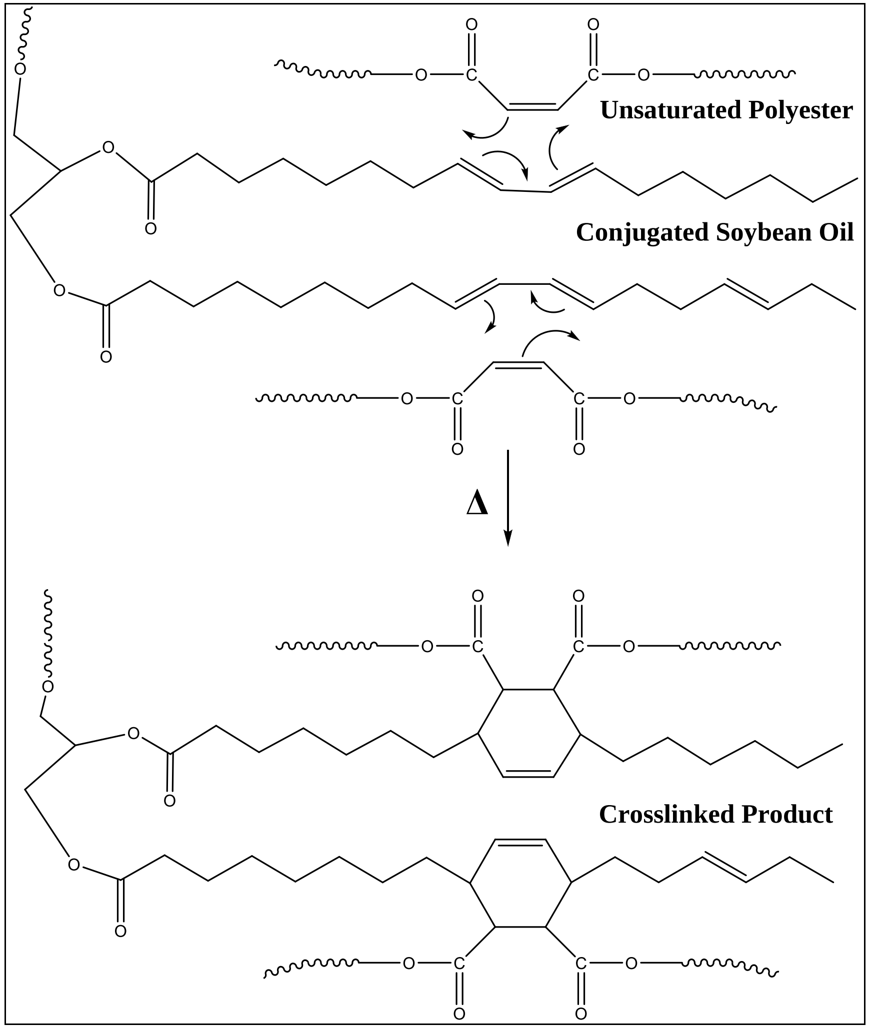


Figure 4.10. Predicted crosslinking mechanism of UPE with CSO

4.3.4. Characterization of crosslinked UPE-CSO polymer

Products characterization was done by FTIR spectroscopy. Some important peaks has to be investigated to observe the changes. FTIR peak changes for the product is given in the Table 4.4.

Table 4.4. FTIR peak changes on UPE-CSO crosslinked polymer

	Position of the Peak (cm^{-1})		
Functional Group	UPE	Conjugated Soybean Oil	UPE+CSO (180 ^{o}C-24 hours)
=C-H	3079	3009	Present
-CH$_2$	2982 and 2879	2923 and 2853	Intensity has increased
-C=O	1715	1742	Shifted to 1724
-C=C-	1645	1653	Intensity has decreased
-C=C- (aromatic)	1599 and 1579	Absent	Present
C=C-H trans, trans (conjugated)	Absent	992	Intensity has decreased
=C-H out of plane vibration	977	Absent	Intensity has decreased
C=C-H trans nonconjugated (isolated)	Absent	967	Present
C=C-H cis, trans (conjugated)	Absent	942	Present
=C-H vibration	772	Absent	776, Intensity has decreased

First proof of crosslinking was the carbonyl peak shift. UPE and CSO have different carbonyl peak position at 1715 cm^{-1} and 1742 cm^{-1} respectively. As expected if crosslinked polymer was obtained from these compounds, the peak’s position must be between them which was 1724 cm^{-1} in this case. Also Diels Alder reaction has to occur from the trans, trans conjugated diene part of the CSO and as a result the peak belonging to trans double bonds at 992 cm^{-1}decreased in the product.

Intensity of =C-H peaks at 977 cm^{-1} and 772 cm^{-1} from UPE decreased, which explains the consumption of double bounds on the UPE chain. A noticeable amount of -CH_2 peaks at 2925 and 2854 increased in the product which belongs to the long alkyl groups of CSO. FTIR spectrum of crosslinked polymer can be seen in Figure 4.11. A comparison of the FTIR spectrum of UPE and crosslinked polymer is given in Figure 4.12.

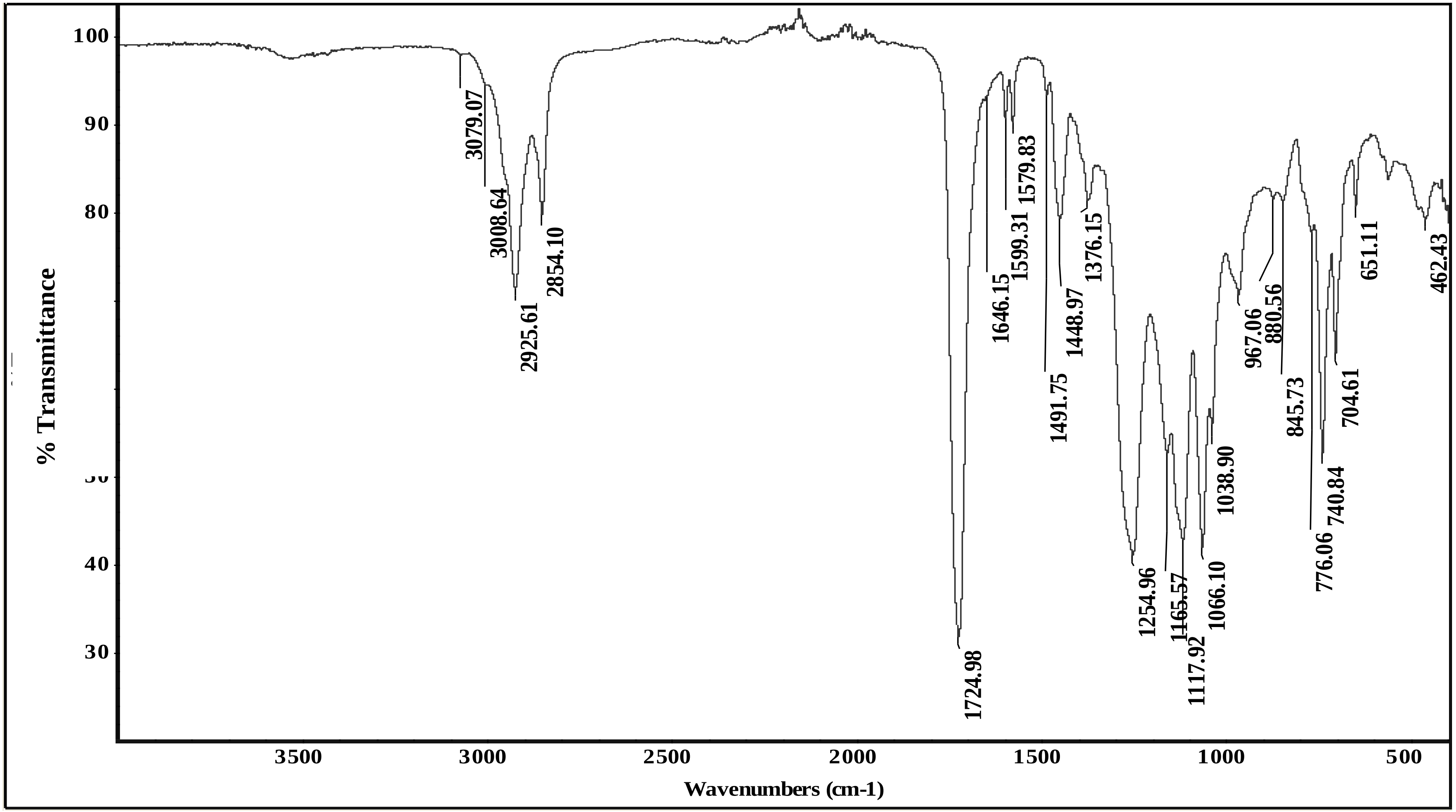


Figure 4.11. FTIR spectrum of crosslinked UPE-CSO polymer at 180 ^{o}C for 24 hours

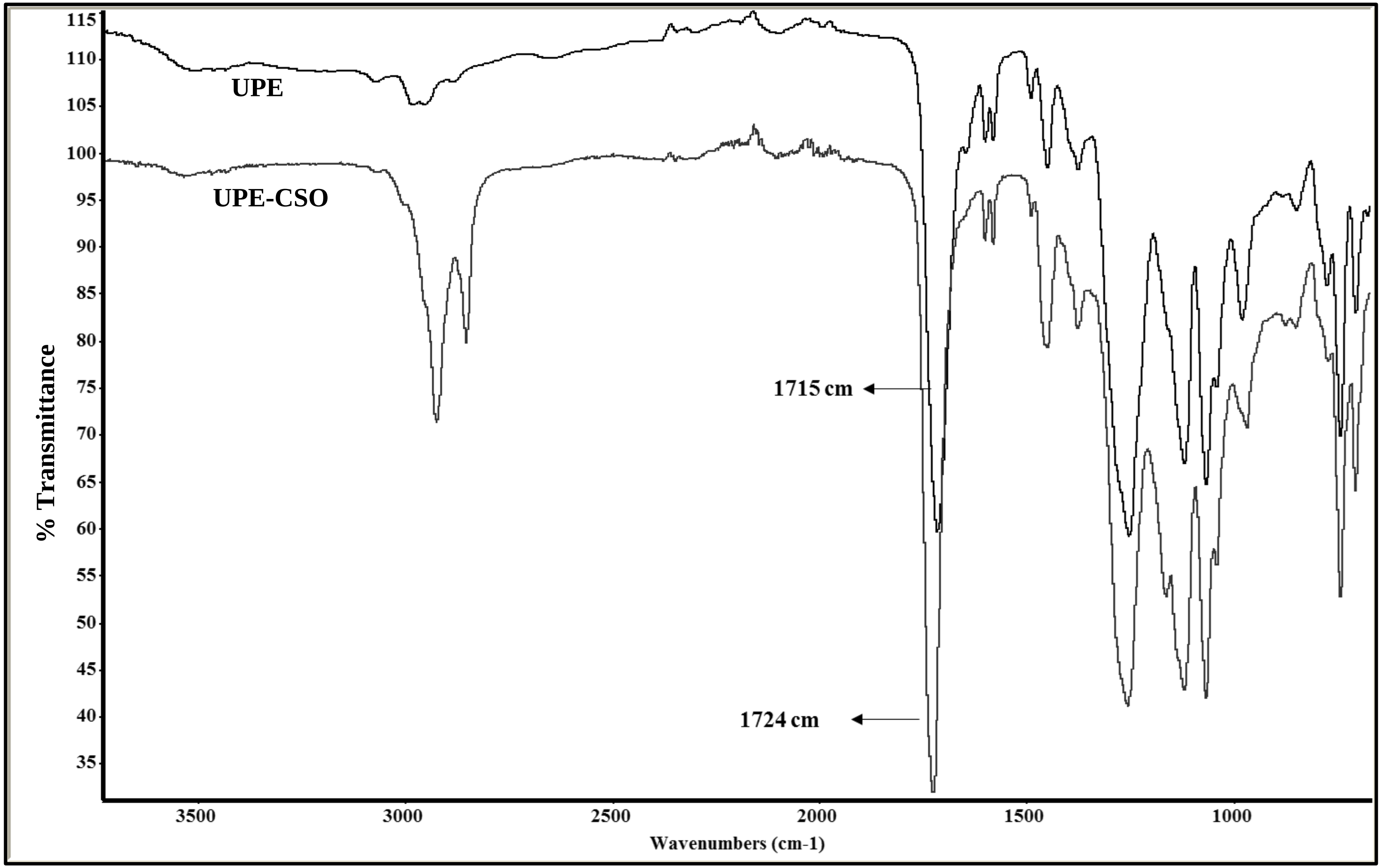


Figure 4.12. FTIR spectrum of crosslinked UPE-CSO polymer vs UPE

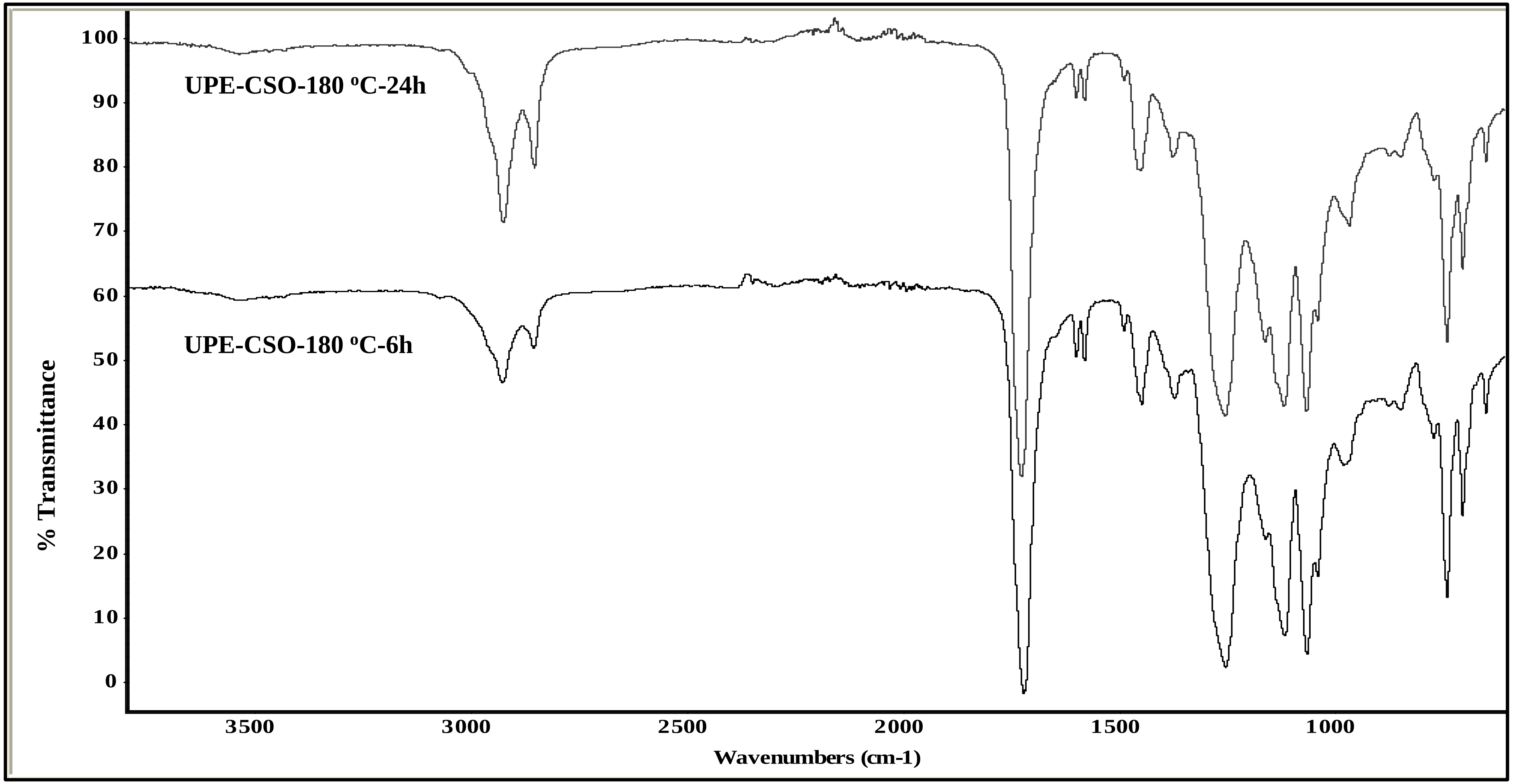


Figure 4.13. FTIR spectrum of crosslinked UPE-CSO polymers at 180 ^{o}C with different reaction time

As shown in the Figure 4.13the effect of reaction time in the crosslinking reaction is noticeable. CSO participation to the product increased when reaction time is longer. Intensity of the peaks which belongs to CSO's aliphatic hydrocarbons (2925 cm^{-1} and 2854 cm^{-1}) were increased and =C-H peak (772 cm^{-1}) from UPE was decreased which is a evidence of higher UPE double bond consumption at longer reaction time. Besides, carbonyl shift was greater for 24 hours reaction time than 6 hours reaction. (1724 cm^{-1} vs 1720 cm^{-1})

Also effect of the reaction temperature was investigated. 150 ^{o}C and 180 ^{o}C was chosen however there was not a large difference in yield between these two temperatures. The difference was investigated by FTIR spectroscopy and shown in Figure 4.14. Carbonyl peak was shifted and double bond consumption of UPE was slightly greater at 180 ^{o}C than 150 ^{o}C.

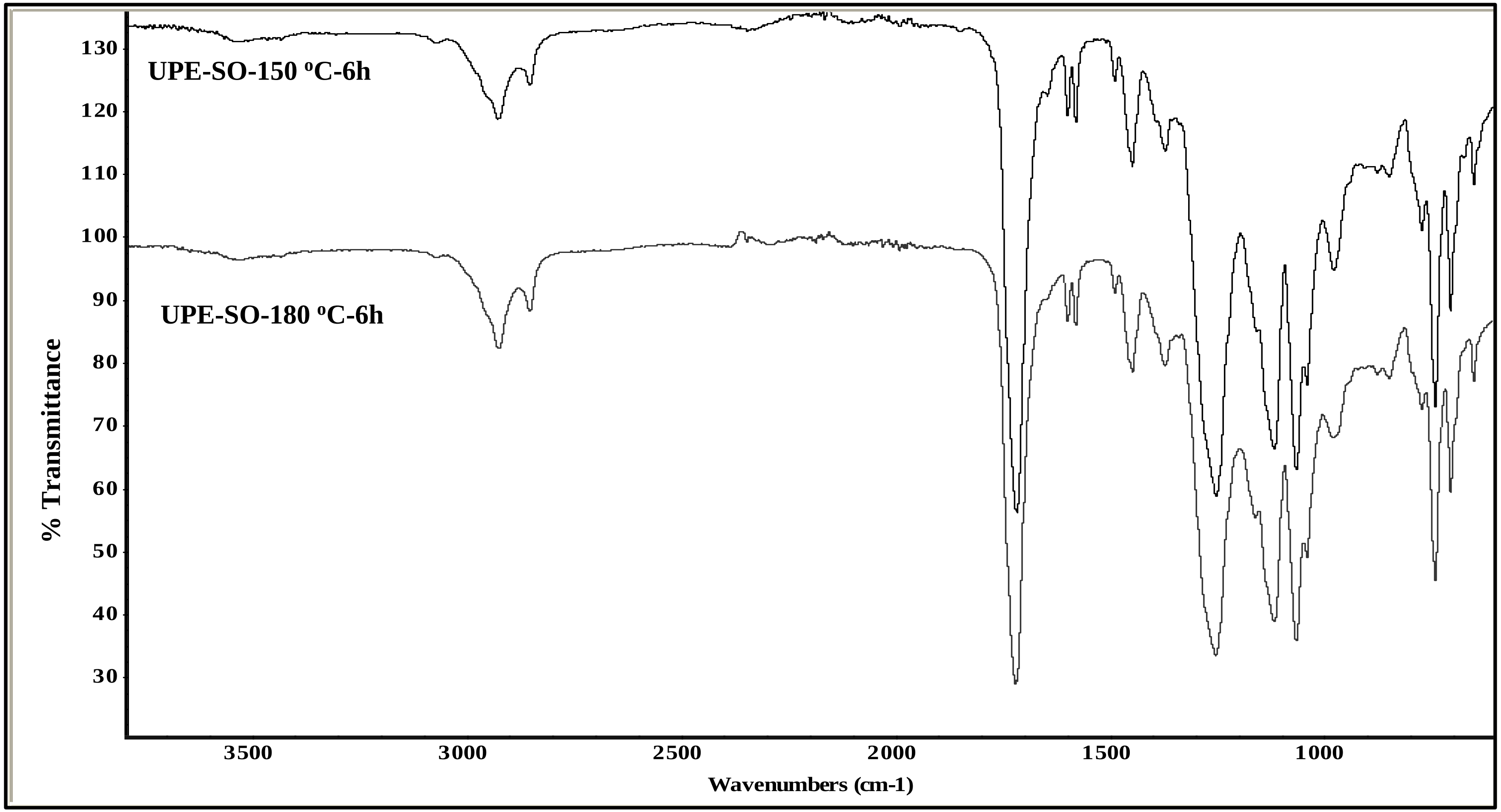


Figure 4.14. FTIR spectrum of crosslinked UPE-SO polymer and UPE-CSO polymer

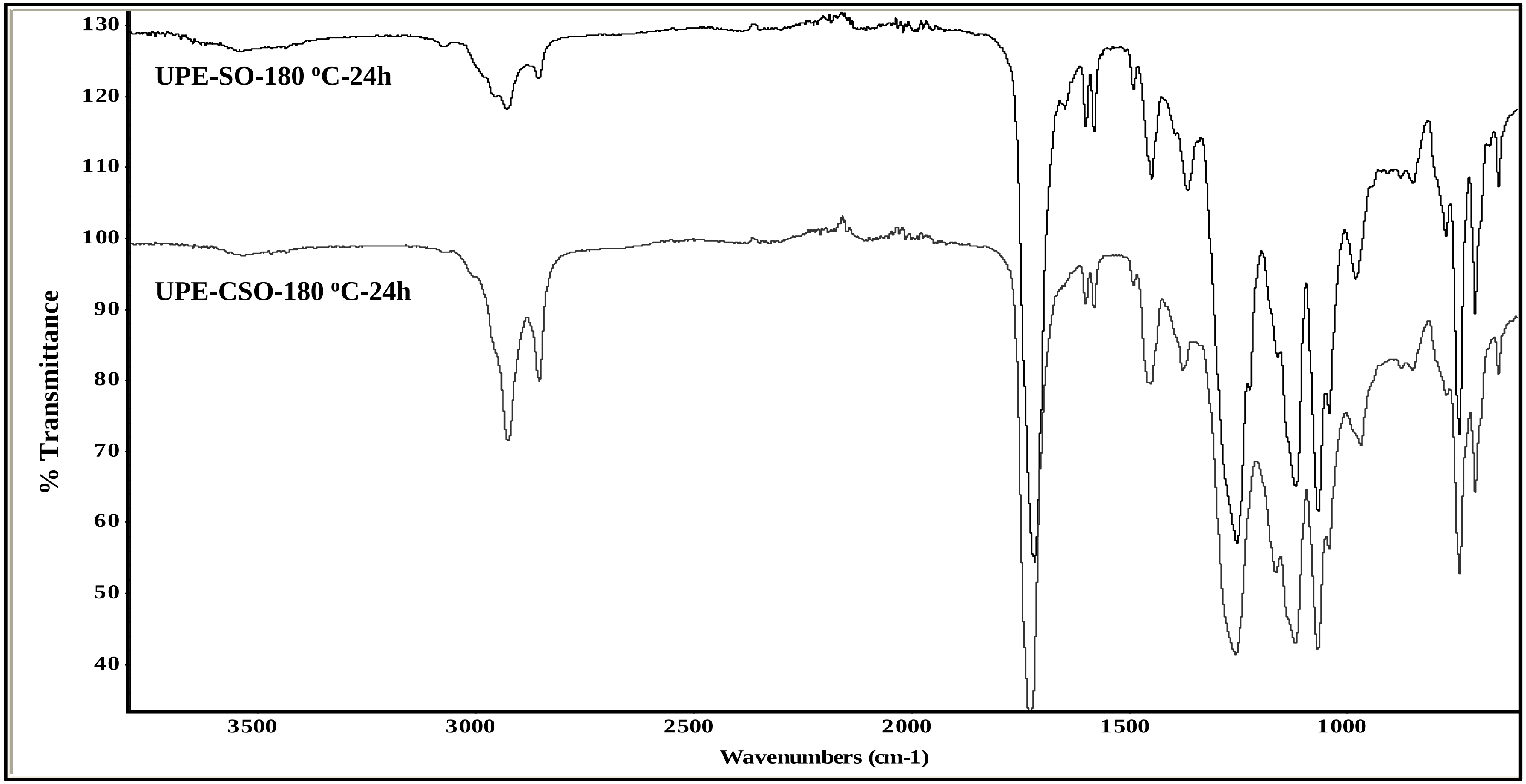


Figure 4.15. FTIR spectrum of crosslinked UPE-SO polymer and UPE-CSO polymer

4.3.5. Synthesis of crosslinked UPE-t-CSO polymer

When large alkyl substituents on the diene are in cis geometry, they interfere with specific geometry of the Diels Alder transition state. In order to increase the yield of the reaction, the conjugated diene was elaidinized to trans-trans geometry. By elaidinization reaction, geometry of the double bonds in CSO were transformed to trans-trans. CSO contains a mixture of cis-trans and trans-trans conjugated double bonds in its structure but the majority is cis-trans, however in order to obtain a better Diels Alder reaction, diene must be in trans-trans geometry. When t-CSO was used, around 95% of diene was consumed. This is a major improvement in yield, as only 63% of the oil was consumed when CSO was used. By this transformation, steric hindrance decreased and dienophile easily approached the diene which increased the amount of crosslinking. The sample obtained by t-CSO was a one piece sample, that had taken mold details and was a strong load bearing material. Finally UPE-t-CSO combination started to act as a genuine liquid molding resin which could be a practical use.

4.3.6. Characterization of crosslinked UPE-t-CSO polymer

While characterizing UPE–t-CSO crosslinked polymer, same peaks were investigated again. Intensity of CH_2 peaks increased noticeably and carbonyl peak shifted to 1726 cm^{-1} which is a proof of better incorporation of oil into the product. Maleate double bond peak which belongs to UPE at 776$cm^{-1}$was decreased as the Diels Alder reaction with conjugated diene consumed it. FTIR spectrum of crosslinked UPE–t-CSO sample is given in Figure 4.16 and a comparison of UPE with the product is presented in Figure 4.17.

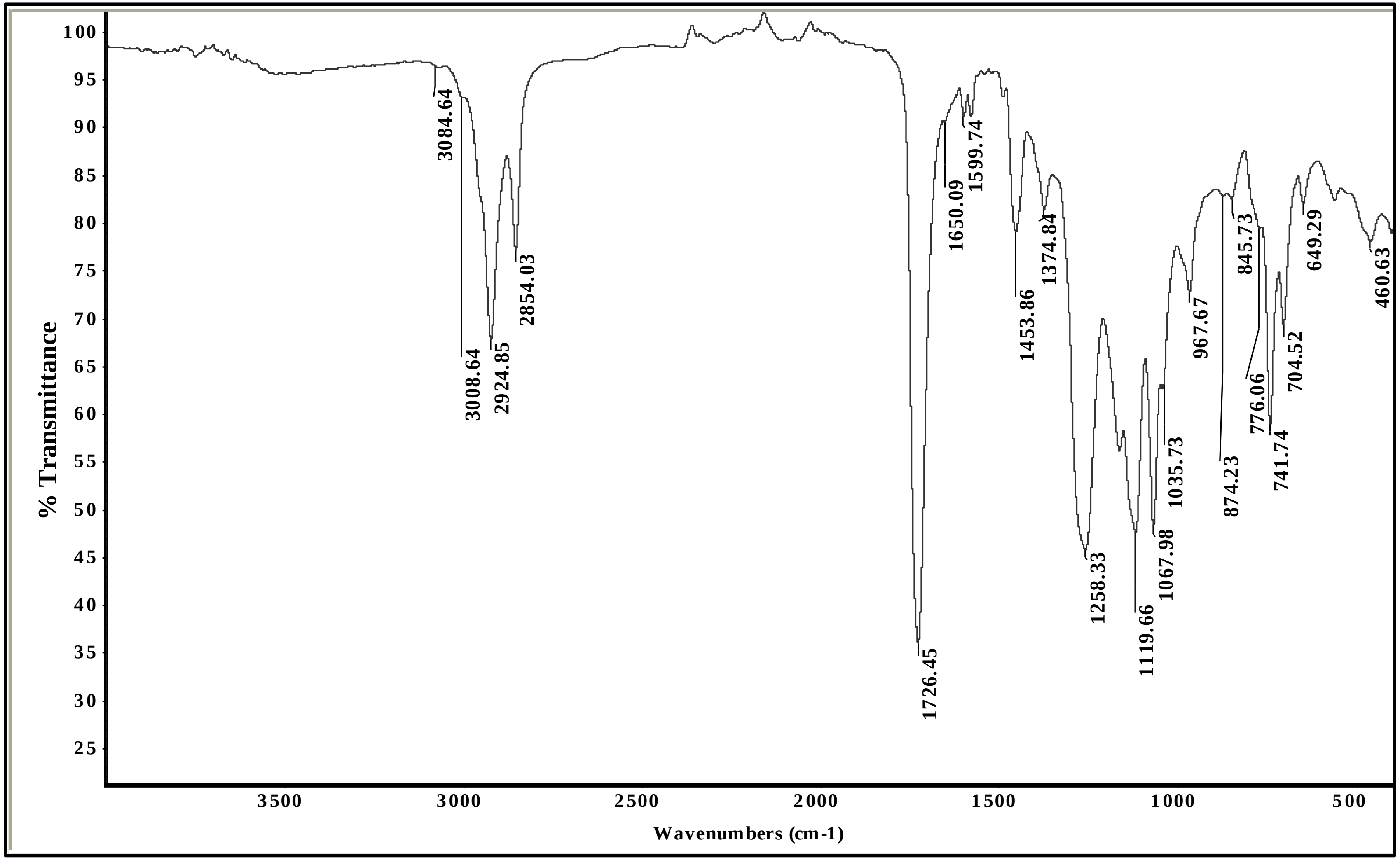


Figure 4.16. FTIR spectrum of crosslinked UPE-t-CSO polymer

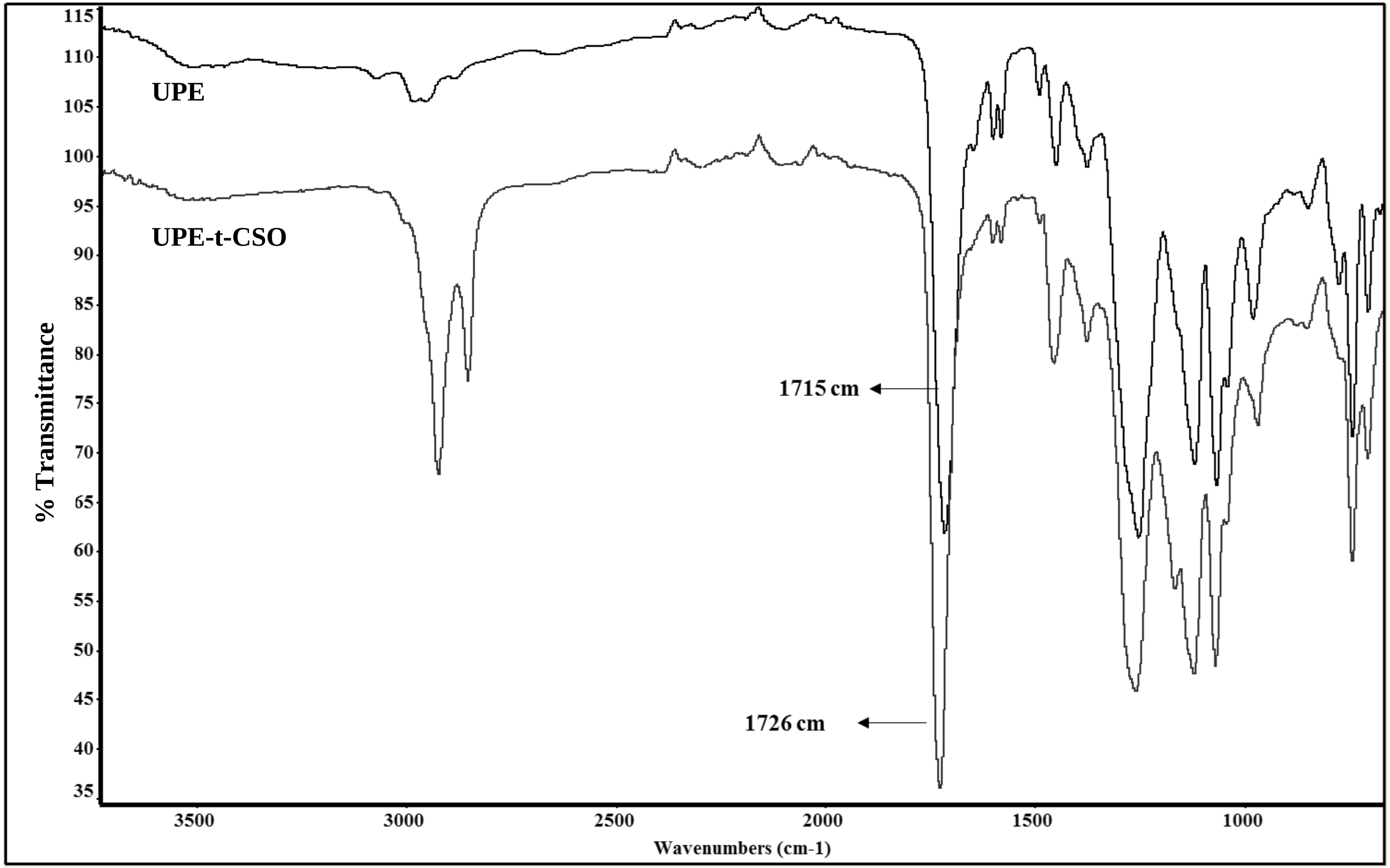


Figure 4.17. FTIR spectrum of crosslinked UPE-t-CSO polymer vs UPE

Several samples were prepared by using different weight ratios of UPE and t-CSO. Except for their mechanical properties all samples give identical FTIR spectra. In the 1:2 weight ratio (UPE-t-CSO) sample, carbonyl shift and maleate double bond consumption on UPE were the greatest because it has higher amount of diene which consumed almost all the dienophile (Figure 4.19). Spectrum of the samples with different UPE-t-CSO weight ratios are shown in Figure 4.18 to Figure 4.20.

Lastly FTIR spectrum comparison between products with different type of diene is shown in Figure 4.21 which was an evidence that best result was obtained by using t-CSO. In all cases 1:1 weight ratio with same conditions was used and the amount of oil consumption is given in the Table 4.5 which explains the success of t-CSO consumption in the crosslinking reaction.

Table 4.5. Oil consumption on each products

Sample (1 g UPE : 1 g oil)	Oil consumption
UPE:SO	0.05 g
UPE:CSO	0.61 g
UPE: t-CSO	0.97 g

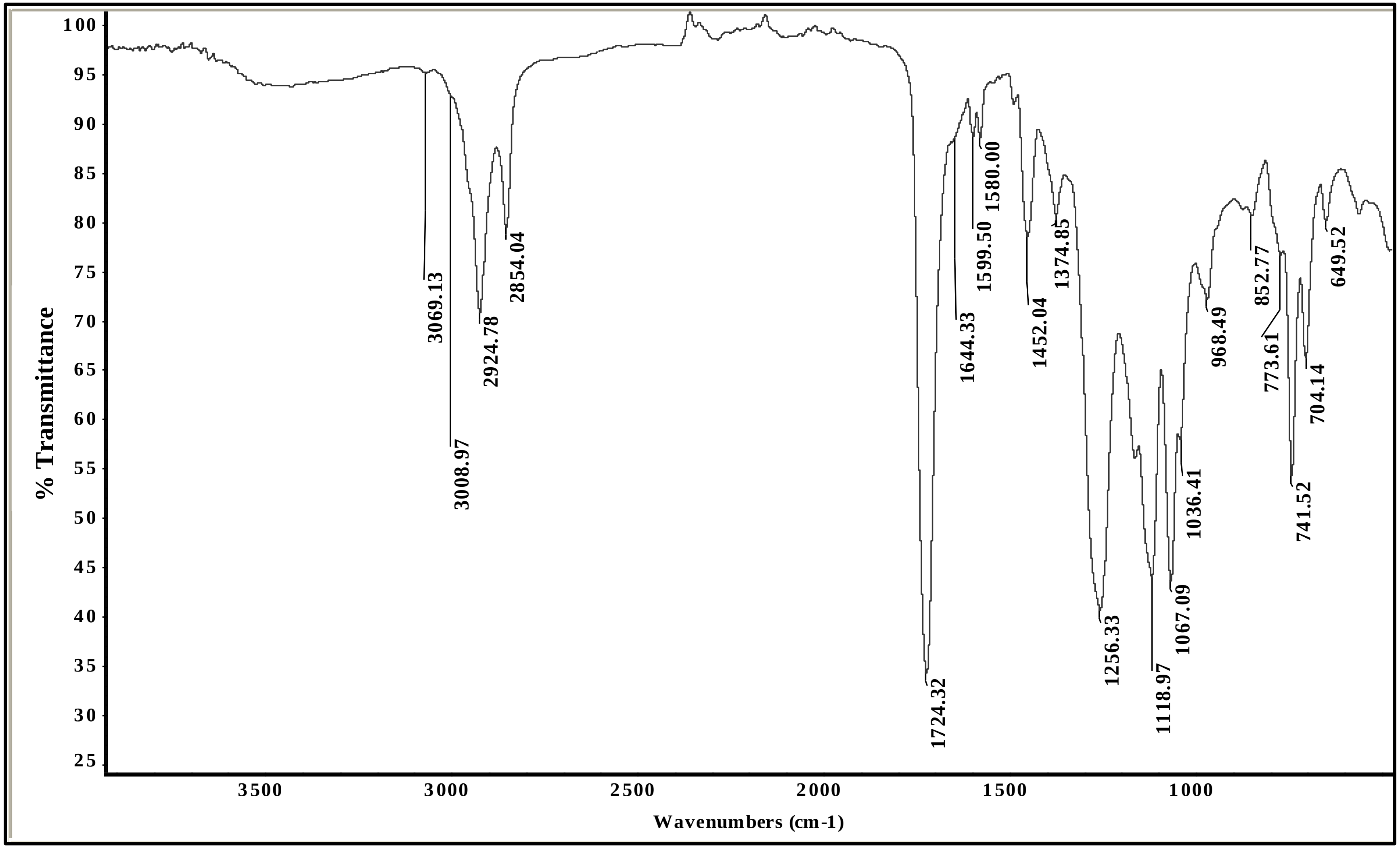


Figure 4.18. FTIR spectrum of crosslinked UPE-t-CSO polymer with 2:1 weight ratio

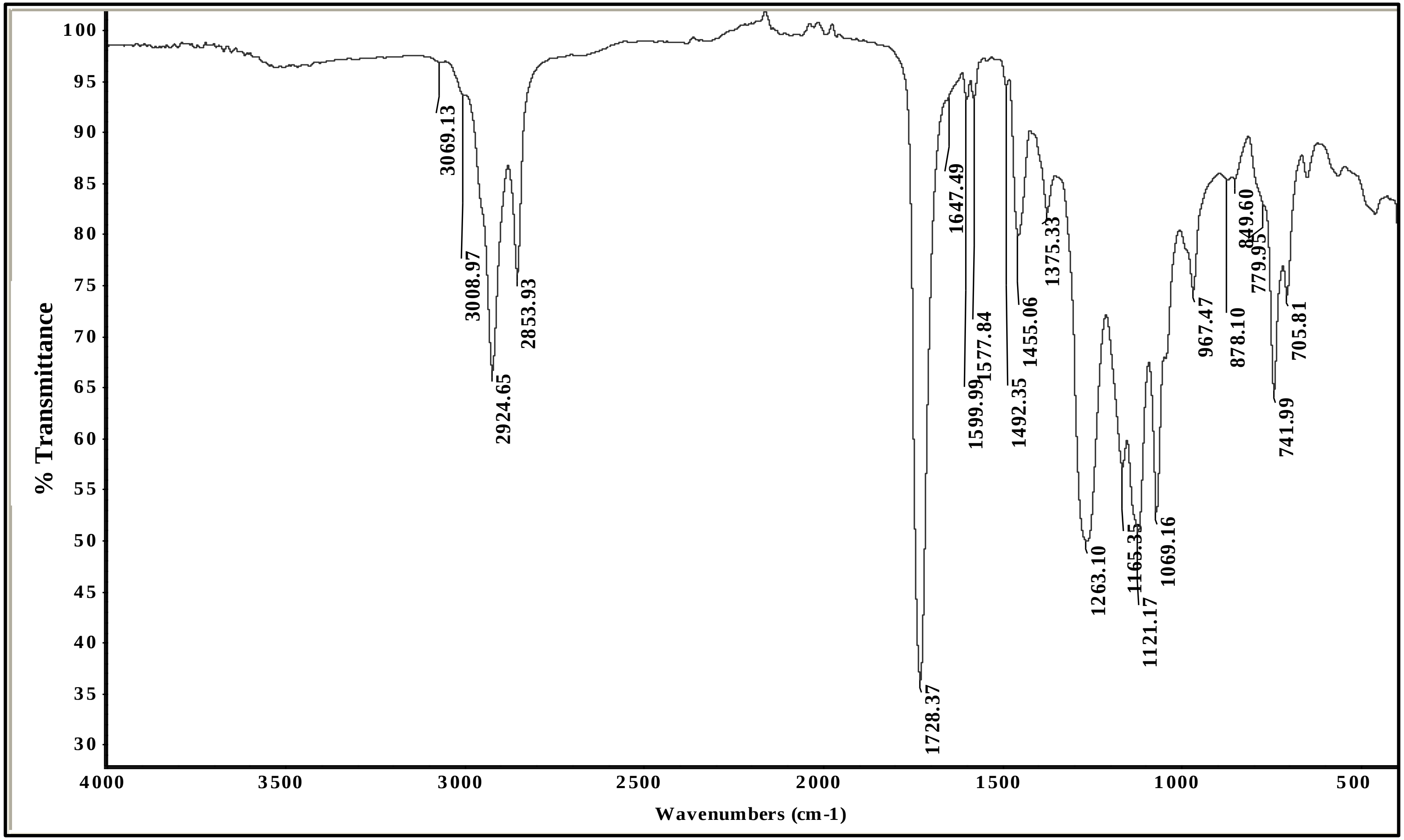


Figure 4.19. FTIR spectrum of crosslinked UPE-t-CSO polymer with 1:2 weight ratio

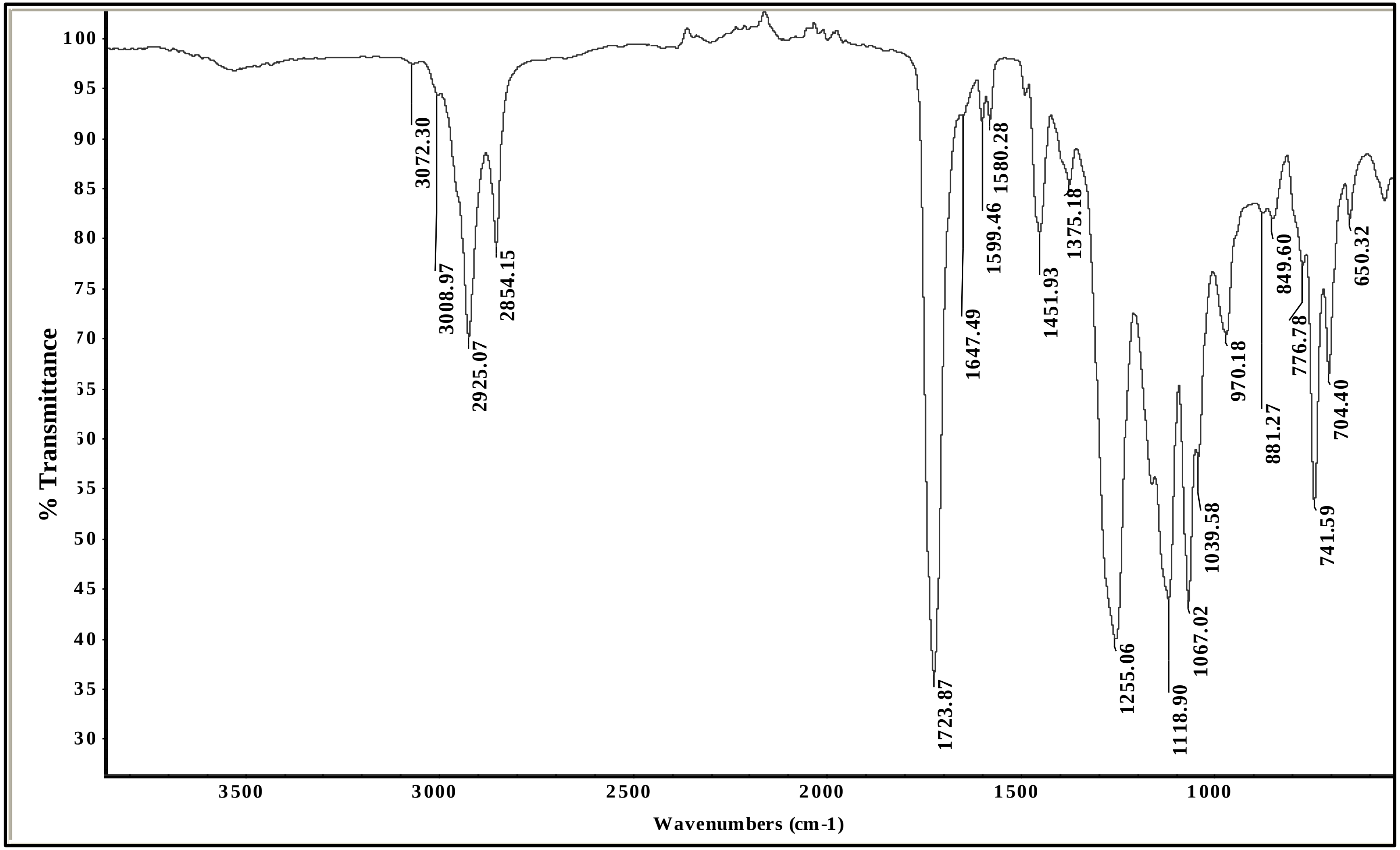


Figure 4.20. FTIR spectrum of crosslinked UPE-t-CSO polymer with 1.5:1 weight ratio

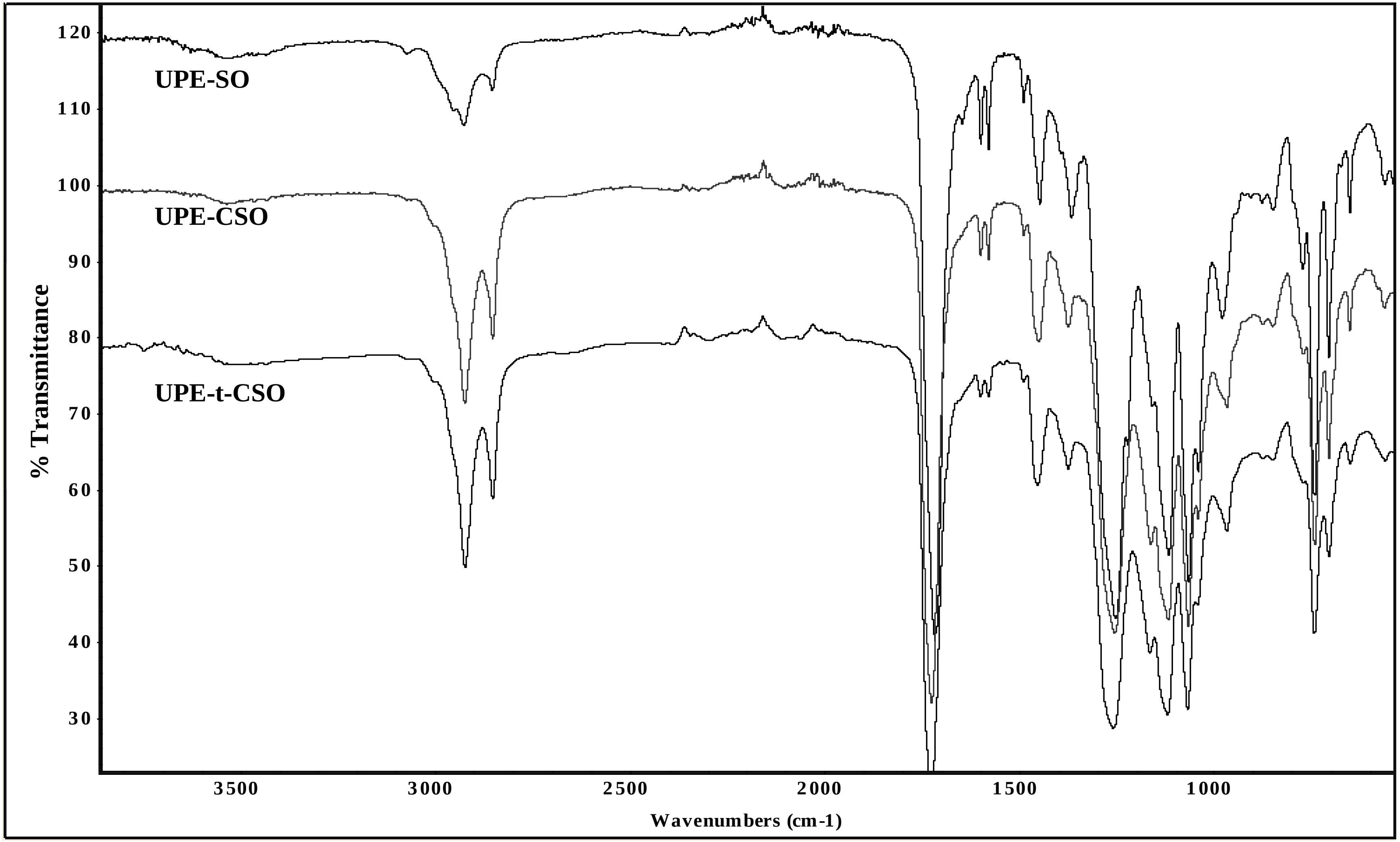


Figure 4.21. FTIR spectrum of UPE-SO, UPE-CSO and UPE-t-CSO crosslinked polymers

4.4. Mechanical Properties of UPE-t-CSO crosslinked polymer

4.4.1. Surface Hardness Test

Surface hardness test is a nondestructive test which measures the relative surface hardness of materials. Test was done according to ASTM D 2240 standard with Shore D durometer. 4 different sample was tested but only 2 of them gave reliable results because the rest were too soft for this apparatus. For every sample 10 data points were collected and the average value is shown in Table 4.4. Results showed that surface hardness proportional to amount of UPE in polymer. Surface hardness of thermoset polymers is a good qualitative measurement of crosslink density. The crosslinking reaction in this work requires that one triglyceride molecule gives two Diels Alder reactions with two maleate double bonds. This is in fact achieved when correct stoichiometry is found. As the t-CSO amount is increased, maleate double bond becomes the limiting reagent and a large number of conjugated diene systems go unreacted. This results in merely grafting of t-CSO onto an UPE chain without leading to a crosslink. The large alkyl groups of the triglyceride also plastify the UPE and a very low surface hardness is observed. Figure 4.22 shows this “excess t-CSO” situation.

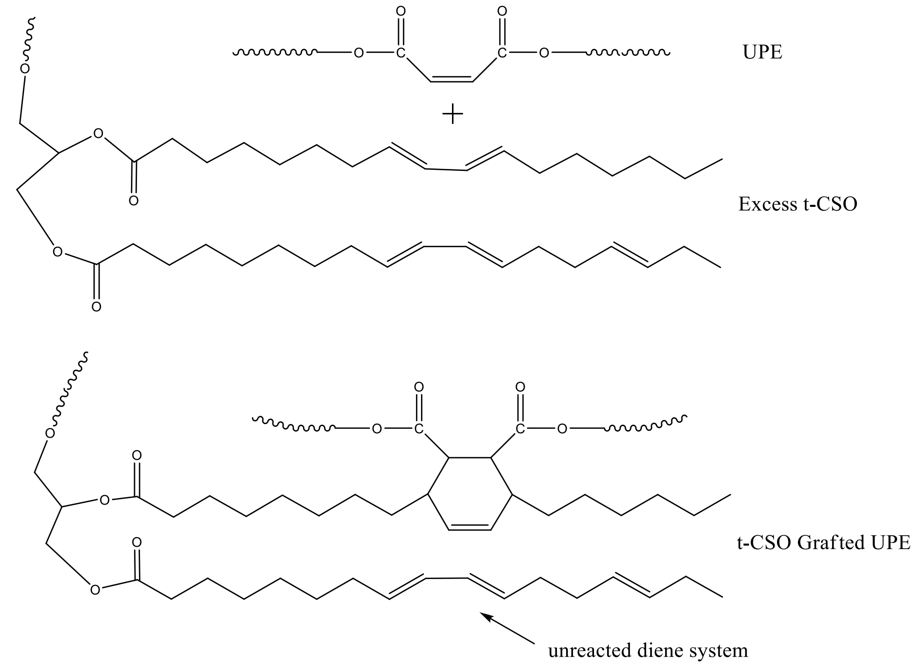


Figure 4.22. Presentation of excess t-CSO situation

Table 4.6. Average Surface Hardness values for each polymer

Test Specimen (UPE:t-CSO weight ratio)	Average Surface Hardness
2:1	51
1.5:1	33
1:1	0-10 (unreliable data)
0.5:1	0-10 (unreliable data)

4.4.2. Compression Test

This test measures the compressive strength of a material. A cylindrical sample is subjected to a compressive force and the decrease in height is measured. The samples obtained in this work had strengths that were too low to be measured by the Devotrans test equipment available to us. A homemade test setup was produced in our lab in which electronic balance measures the stress on sample and an endless screw applies the strain. One whole turn of the screw was 1.42 mm and after every turn, stress was recorded with the data on balance. Cylindrical samples with a radius to height ratio of 1:2 as specified in the ASTM D 695. In order to obtain reliable results, samples should have perfectly parallel surfaces. Again 4 samples with different weight ratio of UPE:t-CSO were tested and results were shown in Figure 4.23.

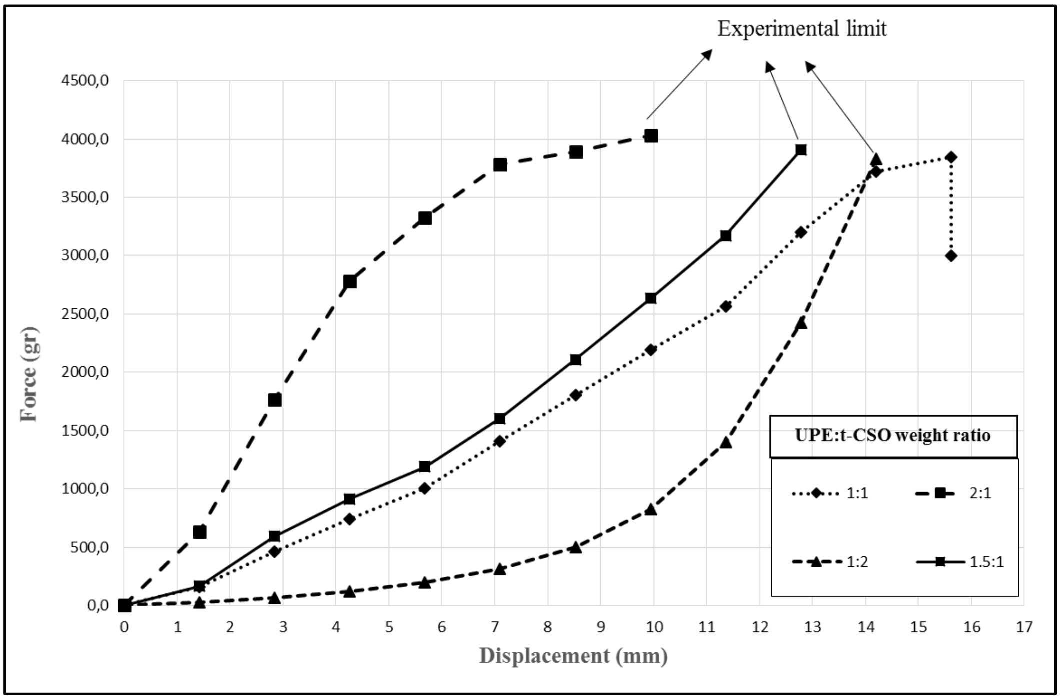


Figure 4.23. Compression test results of UPE-t-CSO samples

As the compression test is run, the sample buckled or ruptured at about 10 mm Strain. This point was taken as the experimental limit of the test and the test was stopped. As shown in Figure 4.23, as UPE amount is increased the sample compressive modulus is increased. For the sample with 1.5:1 weight ratio (UPE:t-CSO) shows a linear stress strain relation which means an elastic behavior and it reaches the experiment limit without cracking, however in the sample with 1:1 weight ratio, plastic deformation occurred at the end of the test. When t-CSO amount is greater than UPE amount as in 1:2 weight ratio sample, it acted as an elastomer and stress increased gradually till it reached the experimental limit.

4.4.3. Swelling Test

Swelling is an important feature for crosslinked polymers and it can be used to compare the relative crosslink density of polymers. Crosslinked polymers do not dissolve in solvents but they absorb varying amounts of solvent which is called swelling. When retractive forces created by crosslinks become equal to solvation forces, swelling reaches equilibrium. Equilibrium swelling ratio can be found by volumetric swelling with using the following equation 4.1, which requires measurement of sample dimensions.

$$q=V/V_o= (L/L_o)^3 \qquad (4.1)$$

A more practical method is to measure the weight gain of a sample immersed in a solvent as a function of time. If needed, this method can be converted to the actual volumetric swelling ratio by using the density of the solvent. For this work weight gain vs time was recorded and the results are shown in Figure 4.24. In this test hexane was used as a solvent and solvent uptake was measured gravimetrically. It is clear that solvent uptake (weight gain) increased as t-CSO amount is increased and after 7 hours all samples reached equilibrium. This results showed that crosslink density is the highest in the 2:1 UPE:t-CSO weight ratio sample which reduced solvent uptake.

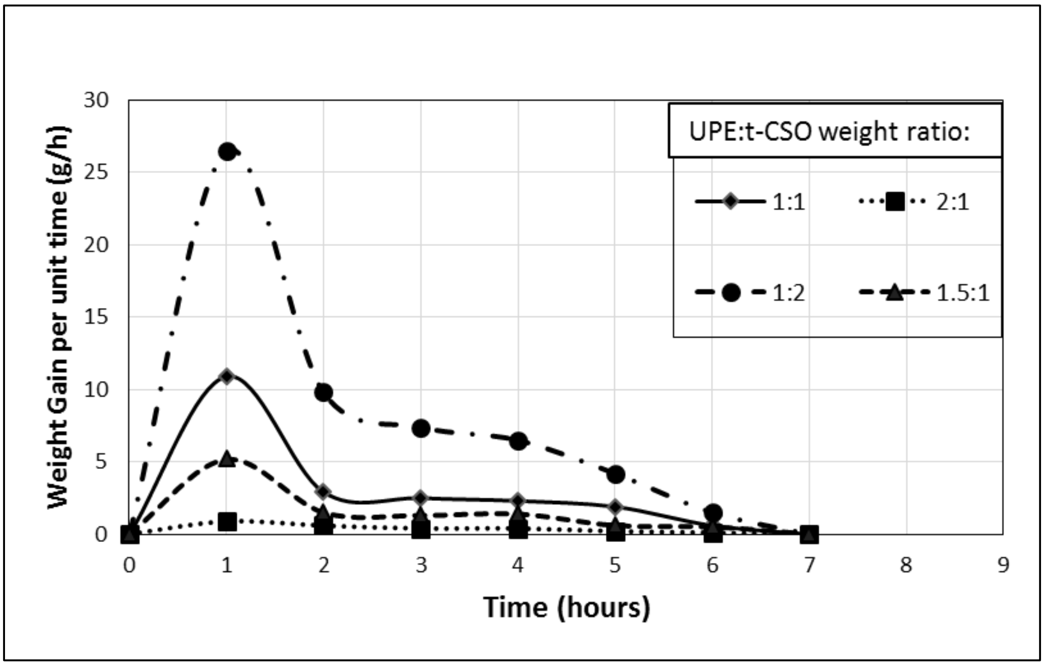


Figure 4.24. Weight gain per unit time vs. Time for UPE-t-CSO samples

5. CONCLUSION

In this work, unsaturated polyester was crosslinked by using conjugated soybean oil via Diels Alder reaction. For efficient crosslinking, the plant oil triglyceride had to be first conjugated and then isomerized to the trans-trans geometry. One piece thermoset polymer was obtained only by using trans-trans conjugated soybean oil which is obtained by elaidinization of conjugated soybean oil. The effect of conjugation and geometry of conjugated double bonds for the reaction efficiency was investigated. The correct stoichiometry of reaction was determined by experimentally. Characterization of the products was done by FTIR spectroscopy. Decrease in the intensity of double bond peaks on both UPE and t-CSO was observed which is an evidence for Diels Alder reaction.

Mechanical properties were tested by surface hardness, compression and swelling tests. As tests showed, increasing UPE amount increased surface hardness and compressive strength. Surface hardness could not be measured when UPE amount is equal or less then CSO amount. Besides, swelling tests proved that as UPE amount increased, relative crosslink density is increased.

The overall goal of this work was to obtain a one part polyester that contains no volatile or toxic reactive diluents and that can be cured by heat only. The relatively high temperatures and long reaction times preclude the use of the present reaction commercially. Unfortunately, cured products do not have mechanical properties comparable to commercial polyesters. However, a crosslinked thermoset polyester containing around 50 weight percentage renewable plant oil based raw material was obtained at the end. As a future project, conjugation of soybean oil can be increased and all the conjugated double bonds can be transformed to trans-trans geometry. In addition to that, a suitable catalyst can be found that will lower the reaction temperature and time.

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