INVESTIGATION OF GENETICALLY MODIFIED SOYBEAN OIL FOR THE SYNTHESIS OF PRESSURE SENSTIVE ADHESIVES

by

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ABSTRACT

Pressure sensitive adhesive are polymer products that are ubiquitous in daily life. They are used in tapes, labels, films, and in many specialty adhesion applications. Demand for adhesives continually increases, and as this happens, it becomes increasingly important to search for a way to move away from petroleum-based starting materials. Such a shift could be performed by moving towards the adoption of vegetable oils for this purpose.

Previous work in the Affordable Composites from Renewable Sources group at the University of Delaware has demonstrated convincing evidence for the possibility of a shift toward the use of vegetable oils and their derivatives in the production of high-performance products in the polymer science and chemical engineering industries. In line with this, a method has been developed for synthesizing monomers for pressure sensitive adhesive synthesis from methyl oleate. A mini-emulsion polymerization process, which reduces surfactant use and improves polymer properties over traditional emulsion polymerization, was developed and was shown to yield pressure sensitive adhesives with properties comparable to petroleum based adhesives, using acrylated methyl oleate as a monomer.

The use of petroleum for the synthesis of pressure sensitive adhesives and other similar lowly cross-linked polymers has been estimated at 14 billion pound per year. If all pressure sensitive adhesives and similar polymers (including elastomers and coatings) were replaced with versions that use this bio-based technology, the fact that they are 70% bio-based would mean that there would be a reduction in petroleum usage of 10 billion pounds per year.

High oleic soybean oil and olive oil were investigated as potential replacements for high purity methyl oleate as a starting product, which is prohibitively expensive. Proton nuclear magnetic resonance was used to determine the average number of double bonds per fatty acid in high-oleic soybean oil (0.9503) and to verify the purity of methyl oleate. The presence of polyunsaturated fatty acids in this oil was also verified.

A new procedure that utilizes gas chromatography for the determination of the fatty acid distribution of oils, developed by MIDI Inc. (Newark, DE), was used to obtain a more comprehensive idea of the fatty acid distributions of high-oleic soybean oil and olive oil. The olive oil results agreed with literature, and the high oleic soybean oil results gave mole percent values for fifteen different fatty acids in the oil, and a very complete characterization, which was in close agreement with literature saturation profiles. It was found that the DuPont high oleic soybean oil consists of 85.53% mono-unsaturated fatty acids, 12.02% saturated fatty acids, and 2.15% poly-unsaturated fatty acids.

A second MIDI procedure, which coupled mass spectrometry with gas chromatography, was used to investigate the partitioning of saturated fatty acids between separate phases that were observed when the fatty acid methyl ester mixture was subjected to refrigeration. The results of this procedure showed that this is a not a viable separation process because the saturated fatty acids did not preferentially migrate to the semi-solid phase to as high a degree as was expected.

Finally, 180˚ peel tests were performed on adhesives synthesized in this research (both from high purity methyl oleate and high oleic soybean oil) as well as commercial adhesives from BASF and Scotch Magic Tape. The adhesives synthesized in this investigation suffered from cohesive failure during the tests, and therefore, their peel energies (24.8 $J/m^2$for HOSO-based and 37.4 J/m^2 for MO-based) were much lower than the BASF Acronal adhesives (2328 J/m^2 for V-210 and 1752 J/m^2 for V-275) and Scotch Magic Tape (330 J/m^2). These properties could be due to the fact the peel speed was reduced to prevent sample failure, and that linear polymers have a limited ability to resist flow under the application of force, as has been shown in previous research with their poor performance in shear time to failure tests. It was found that there was a significant reduction in the peel energy of the PSA synthesized from HOSO. This 33% reduction can be attributed to the presence of impurities (both saturated and poly-unsaturated fatty acid methyl esters). Further testing of this set of adhesives is recommended to get a more comprehensive view of their properties, as well as the effects of saturated and poly-unsaturated fatty acids on polymer properties.

Chapter 1 :

INTRODUCTION

1.1 Background

Pressure-sensitive adhesives (PSAs) are a product in high demand, and exist in a market that is entirely dominated by petroleum-based products. PSAs are used for applications such as Scotch© Tape, labels and Post-it© notes. The purpose of this project is to investigate the use of new starting materials for the production of PSAs. One of the most exciting of possible sources for raw material is genetically modified high-oleic soybean oil (HOSO), which was supplied for this research by the DuPont Company.

It is desirable to work with the goal of reducing the polymer products industry's dependence on non-renewable petroleum, because of its environmental impact, the volatile nature of the industry, and the increases in price that come with the increases in demand for such products. It is with this goal in mind that the Affordable Composites for Renewable Sources (ACRES) was founded at the University of Delaware.

The ACRES group consistently uses vegetable oils (VO) as a starting material for polymer products. Vegetable oils consist of triglycerides, which are glycerides in which

the glycerol has been esterified with three fatty acids. Figure 1.1 shows a typical triglyceride, in which there is a mixture of saturated (having no single bonds), mono-unsaturated (having one single bond), and poly-unsaturated fatty acids.

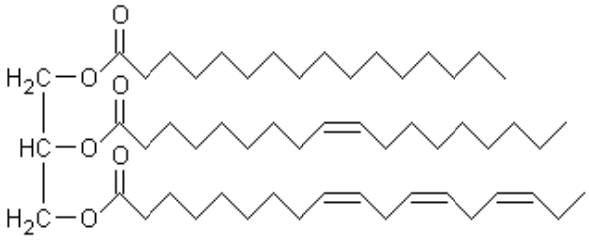


Figure 1.1: Chemical structure of a typical triglyceride

Vegetable oils have very varied saturation profiles. Examples of these profiles for various oils can be seen in Table 1.1 [1, 2]. In this table, SF% stands for the percentage of saturated fatty acids, MF% stands for the percentage of mono-unsaturated fatty acids, and PF% stands for the percentage of poly-unsaturated fatty acids.

Table 1.1: Saturation profiles of vegetable oils (from [1] unless otherwise noted)

	SF%	MF%	PF%
Coconut	85.2	6.6	1.7
Palm	45.3	41.6	8.3
Cottonseed	25.5	21.3	48.1
Wheat germ	18.8	15.9	60.7
Soybean	14.5	23.2	56.5
High-oleic soybean [2]	10	89	1
Olive	14	69.7	11.2
Corn	12.7	24.7	57.8
Sunflower	11.9	20.2	63
Safflower	10.2	12.6	72.1
Rapeseed	5.3	64.3	24.8

Research that has taken place under Dr. Wool in the ACRES group has worked with synthesis of polymers from triglycerides, monoglycerides, and fatty acid methyl esters [2-16].

Acrylated plant oil-based resins (most-commonly soybean oil) have been used to create composites with various natural fibers to enhance mechanical properties of these resins. Some of the natural fibers that have been used are flax, cellulose, pulp, and hemp [14]. Flax has also been used in conjunction with fiberglass to enhance mechanical properties [17]. Lignin, a very difficult to utilize and highly abundant natural resources has also been investigated for novel applications in composite materials using functionalized soybean oil and its derivatives [3, 15].

One more exciting natural fiber for composite production is keratin, which can be derived from chicken feathers through pyrolisis. These chicken feathers are a byproduct of the food industry of the United States and are made at a rate that is on the order of millions of tons per year. These can be used to create composites with very low dielectric constants (due to the air that is held in the fibers). This is an important property for electronics applications, and could lead to the use of such composites in printed circuit boards in household appliances and computers [18].

Previous work has been done within the ACRES group to synthesize PSAs from methyl oleate [2, 4, 5], and the goal of this work is to extend this work to use VO-based starting materials, specifically HOSO. The previous work in the ACRES group with respect to PSAs has been to synthesize the monomers and polymers for adhesives from

methyl oleate [5]. Furthermore, work has been done to shift from conventional macro-emulsion polymerization to mini-emulsion polymerization in order to reduce the quantity of surfactants required and reduce reaction time [4]. The reaction methods for these mini-emulsion-based polymerization processes have been improved beyond their initial development states, and have shown to yield adhesives that have properties comparable to petroleum-based polymers commonly used in PSA applications [5].

The HOSO is in the form of a triglyceride whose fatty acid chains are almost exclusively oleic acid. Olive oil is also a possible candidate for a starting material, because its fatty acids also have a high proportion of oleic acid. This is beneficial because methyl oleate is thought to be a perfect candidate for a starting material for the production of PSAs. Its mono-unsaturation leads to the production of a linear polymer with no cross-linking, which is ideal for PSAs and elastomers [2, 4, 5]. Using this oil, an environmentally friendly PSA can be made, and it can be compared with the fossil oil-based adhesives that are currently available with the goal of their eventual replacement.

Beyond the goal of synthesizing PSA from HOSO, this work is meant to investigate the methods for characterization of fatty acid distributions in triglycerides using ^{1}H-NMR as well as more advanced methods with gas chromatography a mass spectrometry.

1.2 Significance to the Field

The pressure sensitive adhesives synthesized in the process described in this work are about 70 percent bio-based by mass, and with future advancements into bio-based surfactants and co-monomers, this number could approach 100 percent.

The combined market for PSAs and other similar lowly cross-linked polymers in 2005 was around $50 billion, and the market specifically for PSAs was approximately 14 billion pounds per year [3]. The possibility of replacing the petroleum-based monomers with a source that can be grown in the ground would be a great step forward for the reduction of the use of petroleum products in the chemical industry. Even when only 70% bio-based, the use of this technology could reduce the use of petroleum products by 10 billion pounds per year. Furthermore, the production of linear polymers from triglycerides can provide a platform for developing other technologies, including coatings, paints, elastomers, and toughening agents.

This research has the goals of testing unpurified HOSO and olive oil methyl esters for their viability as a raw material for the synthesis of these PSAs. Another main aim is to develop a better understanding of the HOSO itself, including using different methods to determine its fatty acid distribution.

Chapter 2 :

SYNTHESIS AND REACTION CHARACTERIZATION

2.1 Overview

The synthesis of pressure sensitive adhesives (PSAs) from vegetable oil is a four-step process. First, the oil, which is in the form of triglycerides (three fatty acids on the branches of a glycerol molecule, Figure 1.1), is subjected to methanolysis, which yields the fatty acid methyl esters (FAME) and glycerol by-product. Next, the unsaturated sites on the FAME chains are epoxidized and then acrylated. These monomers are then polymerized through miniemulsion polymerization [2, 4, 5]. The optimal fatty acid for this process has one single bond, which leads to linear polymers. This ideal fatty acid is oleic acid.

This first step is the same as the process used for the synthesis of biodiesel from natural oils (such as vegetable and animal oils), and is similar to the Fisher esterification, which is acid-catalyzed, whereas this is base-catalyzed. The use of a basic catalyst reduces the chances of side reactions [2]. This procedure involves the methanolysis of

the triglycerides, which is done by adding the oil to a basic solution of sodium hydroxide in methanol.

The second step of the process is the epoxidation of the unsaturated double bonds on the chains of the methyl esters formed in the first step. This is done by adding a solution of formic acid (FA) and hydrogen peroxide to the FAME. FA and hydrogen peroxide react to form performic acid (PFA), which in turn reacts with the double bond to form the epoxide and regenerate FA.

The third step, the acrylation of the epoxide, is an acid-catalyzed reaction [5]. Acrylic acid protonates the epoxide, then nucleophilically attacks the protonated form of the epoxy. This results in a more stable leaving group than would be formed in the alternative base-catalyzed synthesis reaction [2]. The leaving group is an alcohol instead of the alternative, which is an alkoxide. The product is acrylated epoxidized methyl ester.

The final step in the synthesis of a PSA from vegetable oil is the polymerization of the acrylated methyl ester. This is done with a miniemulsion technique, a favorable method over the traditional emulsion technique, which has slower kinetics and requires much more surfactant. Slow kinetics yield long reaction times, and high concentration of surfactant in the adhesive is known to be a detriment to adhesive qualities [4]. The miniemulsion is formed in the solution through ultrasonication, which forms droplets with a diameter of approximately 400μm [4]. Each droplet in the miniemulsion technique can be considered to be a small batch reaction, as each droplet contains

monomer, initiator, and polymer.

2.2 ^{1}H-NMR Characterization of Extent of Reaction

^{1}H-NMR can be used to characterize the extent of reaction by tracking peaks that appear and disappear as the reactions progress [12, 13]. Each reaction pathway was verified as yielding the correct products, and some troubleshooting was done for a handful of reactions, but reaction extent was not characterized routinely for these reactions, as the reactions are well understood [2, 4, 5]. Figure 2.1 shows the comparative spectra for methyl oleate (MO), epoxidized methyl oleate (EMO), and acrylated epoxidized methyl oleate (AEMO). Peaks are discussed in more depth below.

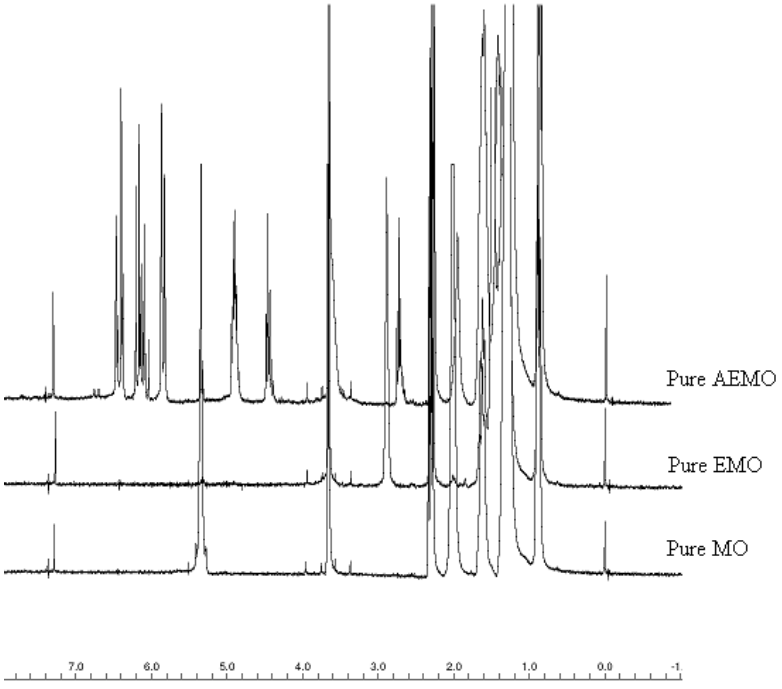
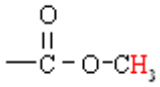
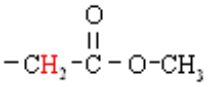
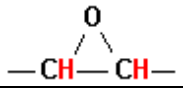
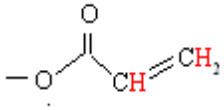


Figure 2.1: ^{1}H-NMR spectra for MO, EMO and AEMO

The characteristic peaks of each of these species can be seen in Table 2.1. The reaction of MO to EMO can be tracked with the disappearance of the peak at 5.27 ppm associated with the double bond, and the appearance of the peak in the range of 2.68-2.7 associated with the epoxide. Reaction to form the acrylated monomer is tracked with the disappearance of the epoxide peak and the appearance of three large peaks in the range of 5.6-6.6 ppm, which are associated with the three protons on the acrylate group [2, 19]. Other peaks that exist in all of the species of interest can also be seen in Table 2.1.

Table 2.1: ^{1}H-NMR Peaks for MO, EMO, and AEMO [2, 19]

Species	Characteristic Proton Type	δ (ppm)
All species		3.7
All species		2.35
All species	-(CH_2)-	1.3-1.4
MO	-CH=CH-	5.27
EMO		2.68-2.7
AEMO		Three peaks in the range of 5.6-6.6

2.3 Step 1: Triglyceride Methanolysis to Biodiesel

The first step of the reaction pathway is the conversion of the vegetable oil (e.g., HOSO) to glycerol and the oil's FAMEs. Figure 2.2 shows the structure of an ideal molecule of HOSO, in which all three of the fatty acids are oleic acid. The molar mass of such a molecule would be 885.432 g/mol. In vegetable oils in general, a typical molecule would have a mixture of different fatty acid chains, which could be of various lengths and be saturated, mono-unsaturated, or poly-unsaturated.

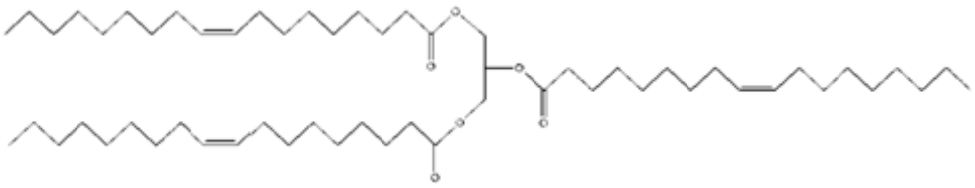


Figure 2.2: Chemical structure of ideal HOSO

The methanolysis of these vegetable oils break the bonds between the long carbon chains and each of the oxygen molecules on the three-carbon glycerol backbone. The resultant fatty acids react with methanol to form the corresponding FAME and glycerol by-product. An example of the FAME is methyl oleate, which has a molar mass of 296.488 g/mol, and is seen in Figure 2.3.

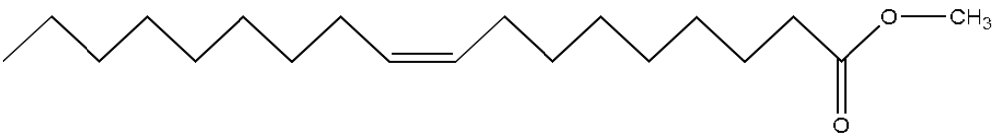


Figure 2.3: Chemical structure of methyl oleate

As mentioned before, glycerol is the byproduct of this reaction. The mixture that is produced has a FAME to glycerol molar ratio of 3:1. The mass ratio of FAME to glycerol is 9.65:1 if all of the fatty acids are oleic acid. The structure of glycerol can be seen below in Figure 2.4.

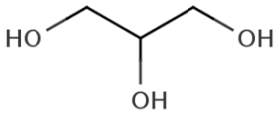


Figure 2.4: Chemical structure of glycerol

This FAME reaction is base catalyzed, taking place in an alkaline solution of sodium hydroxide in methanol. As the reaction takes place and the fatty acids are removed from the glycerol center, phase separation occurs between the denser glycerol, which collects on the bottom of the flask, and the fatty acid methyl esters on the top.

2.3.1 Main Reaction

For this procedure, a typical reactant batch that was used was 100 grams of vegetable oil, 30 grams of methanol (99.9%, Fisher Scientific, Pittsburgh, PA), and 0.92 g of sodium hydroxide (99.6%, Fisher Scientific, Pittsburgh, PA). These amounts, and the resultant typical mole ratios, are shown in Table 2.2. For this table, the molar mass that was used for the oil triglyceride is that of the ideal HOSO, but it could be any VO.

Table 2.2: Typical methanolysis reactants batch

Chemical	Typical mass, grams	Molar mass, g/mol	Mole ratio
Triglyceride (HOSO)	100	885.43	1
Methanol	30	32.04	8.3
NaOH	0.92	39.997	0.20

First, VO was charged to a round-bottom flask (RBF) in an oil bath, which was maintained at a constant temperature of 60°C while being stirred. Attached to the mouth of the vessel was a condenser, which was cooled with circulating cooling water. A diagram of the setup can be seen in Figure 2.5.

While the temperature of the oil mixture was stabilized, NaOH that had been crushed from pellets into powder were added to a beaker containing the methanol and a stir bar. Once the NaOH had fully dissolved into the methanol, the solution was added to the RBF that contained heated oil. The temperature of the mixture was then raised to 70°C and was maintained for 1 hour.

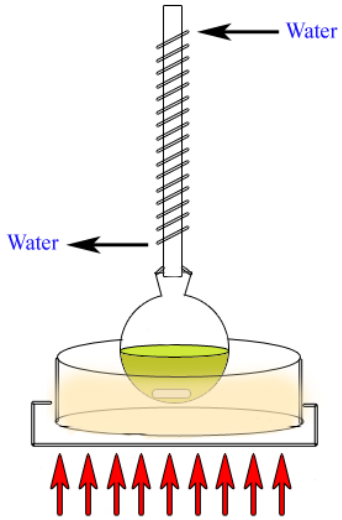


Figure 2.5: Esterification reaction setup

In the very first trial that was performed, which was with a sample of normal soybean oil, the NaOH pellets were not crushed before being added to the methanol and subsequently to the oil, and even after the reaction was allowed to react for an hour at 70°C, the NaOH pellets had not fully dissolved. This led to the conclusion that crushing the pellets was necessary. When dissolving the NaOH in the methanol, care was taken to assure that there was not any considerable evaporation. The mass of the beaker and chemicals was monitored as the dissolution progressed to assure that no appreciable amount of mass was lost.

The completed reaction mixture was removed from the RBF, and added to a 250 ml separation funnel. The glycerol was decanted from the solution for half an hour.

2.3.2 Fatty Acid Methyl Ester Purification

A first washing of the FAME from a typical batch was done with 10.0 ml of a 0.015 N sulfuric acid solution. This was done to react with residual NaOH from the methanolysis procedure and neutralize the solution. The two were either lightly shaken in the separation funnel or mixed with a stirring bar in the reaction vessel, then decanted for 10 minutes. The solution was allowed to sit for about an hour to allow separation of phases, and the acid was decanted off with the separation funnel.

Subsequently, three washes with approximately 10 ml of distilled water or 5 wt% aqueous NaCl (99+%, Acros, New Jersey) solution were performed in the same manner as the acid wash. The NaCl rinses were used for the first one or two rinses, when phase separation took much more time. This is because the NaCl in solution increases the interfacial energy between the aqueous and oil phases compared to pure water, and therefore speeds up the separation process. These were repeated until the pH of the solution (measured with pH paper) was neutral. Phase separation happened for approximately 30 minutes after each of the water rinses.

This reaction step was performed on both olive oil and high oleic soybean oil. The HOSO FAME required much more time to separate from the water phase during these rinses than any other oil, but otherwise behaved similarly.

The fatty acid methyl esters were added to a round bottom flask and were dried in the rotary evaporator for three hours at 60°C in a vacuum to remove any water left over from the rinsing process. The fatty acid phase was weighed. The theoretical yield of the reaction is 1.005 times the initial mass of vegetable oil, again assuming that the oil is ideal HOSO, and that there was no mass lost during the separation process. Batches of various sizes were reacted over the course of the work, and in general, there was a lower yield in smaller batches, as a higher proportion of material is lost from the smaller batches in each decanting step and vessel transfer.

2.3.3 Fatty Acid Methyl Ester ^{1}H-NMR

An example of a ^{1}H-NMR spectra for a product of methanolysis can be seen in Figure 2.6, which is from a sample of HOSO FAME. The characteristic peak associated with the double bond can be seen just above 5.2ppm.

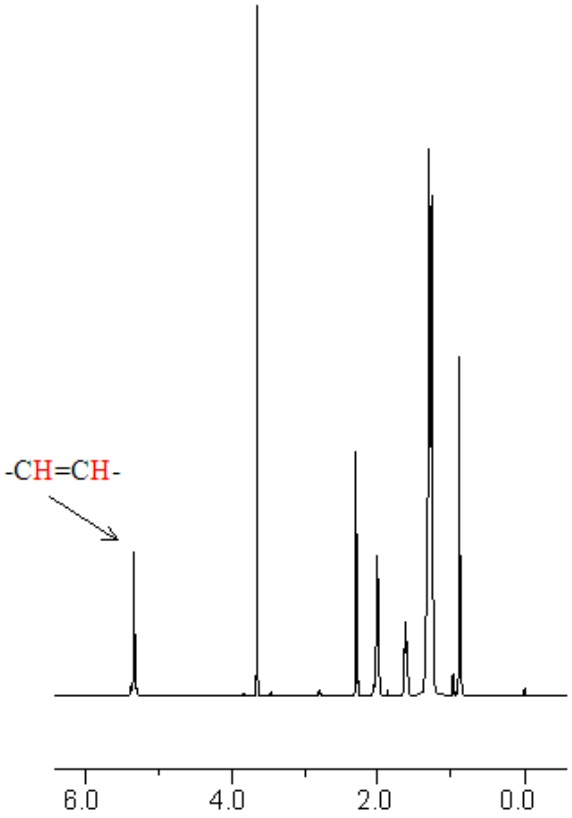


Figure 2.6: High Oleic Soybean Oil Fatty Acid ^{1}H-NMR Specta

2.4 Step 2: Epoxidation of Fatty Acid Methyl Ester

The second step for the synthesis of PSAs from high oleic soybean oil (HOSO) is the epoxidation of the oleic acid methyl esters. Methyl oleate, which was either purchased from Aldrich (with purities of 70% or 99%) or synthesized in the lab from HOSO or olive oil, was used in this process. The procedure described herein reacts the

active double bonds of the methyl oleate with performic acid to form the epoxide, which is called epoxidized methyl oleate (EMO) or epoxidized FAME (EFAME).

The process for synthesizing EFAME from FAME as described by Campanella et. al is best performed at moderate temperatures and low concentrations of formic acid (FA) [7]. Low temperatures are preferred because at high temperatures, selectivity towards ring-opening reactions increases. A less than stoichiometric amount of formic acid can be used because it is not consumed in the reaction, as is clearly shown in the schematic of Figure 2.7.

PFA is generated in the aqueous phase from hydrogen peroxide and FA, then PFA and FA "shuttle" between both phases throughout the course of the reaction. After the PFA is formed in the aqueous phase, it is transferred into the organic phase, where it reacts with the C=C bonds, forming EFAME. The FA is then transported to the aqueous phase, where it reacts with H_2O_2, again forming PFA, which then restarts the reaction loop.

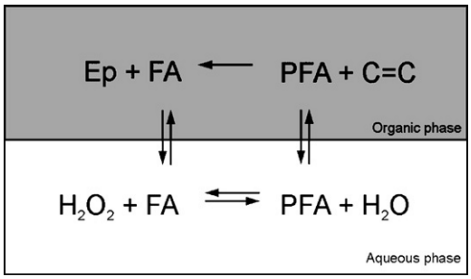


Figure 2.7: Mechanism for epoxidation of double bonds by PFA formed in situ [7].

2.4.1 Main Reaction

A typical batch of reactants for the epoxidation procedure consists of 100 grams of FAME, 10.7 grams of formic acid (98%, Acros Organic, New Jersey), and 58.8 g of hydrogen peroxide (30% aqueous, Fischer, St. Louis). These typical amounts and the resultant molar ratios are shown in Table 2.3.

Table 2.3: Typical epoxidation reactants batch

Chemical	Typical mass, grams	Molar mass, g/mol	Mole ratio
Fatty acid methyl ester	100	92.0936	1
Formic acid	10.7	46.0246	0.7
H_2O_2, 30% (aqueous)	58.8	34.0147	1.5

The FAME and the formic acid are added to the reaction vessel first, and the vessel is hooked up to a condenser and put into a water bath at room temperature (24.3°C). This setup is identical to the setup used for the esterification reaction, shown in Figure 2.5. A stirring bar was added, and the vessel was continuously stirred. The H_2O_2 was then added through the top of the condenser. The sample was allowed to react for six hours.

2.4.2 Epoxidized Fatty Acid Methyl Ester Purification

An ether extraction was performed to remove the acid and peroxide from the EMO. The solution was dissolved in approximately 20 ml of diethyl ether (99.9%,

Fischer Chemical, St. Louis), stirred well with a glass rod, and then added to a 250ml separation funnel. It was then washed with a series of solutions.

First, the oil/ether solution was rinsed three times with 10 ml samples of distilled water to wash away excess acid. Next, the product was rinsed with approximately 10 ml of saturated aqueous sodium bicarbonate solution (5 grams $NaHCO_3$ (100%, Fischer Chemical, Fair Lawn)/100 grams H_2O), which neutralized the solution by eliminating any free acid. As the bicarbonate was added to react with the remaining acid and lightly shaken, the stopcock of the separation funnel was pointed away and into the fume hood and periodically opened to allow generated gasses to be released safely from the funnel. This part of the procedure was repeated until pH paper indicated that it was neutral, showing that the only components remaining in the organic layer was the epoxidized FAME. If the solution was too basic, it would be rinsed again with water; if it was too acidic, it would be rinsed again with the bicarbonate solution.

Next, the sample was rinsed with 10 ml of saturated sodium chloride solution (5 grams NaCl/100 grams H_2O) to remove any residual water from the organic phase. The aqueous layer was removed from the system and discarded.

For each of these extractions, the amounts stated above are approximate. Greater volumes were sometime used to avoid the need to do multiple extractions and to reduce the time need for decanting. In these cases, more time was allowed for phase separation.

The organic layer was moved to a round bottom flask and attached to a rotary evaporator and was evaporated for at least 30 minutes while submerged in a water bath at

80°C to evaporate both the ether and any leftover water from the organic phase.

2.4.3 Epoxidized Fatty Acid Methyl Ester ^{1}H-NMR

An example of a ^{1}H-NMR spectra for an epoxidation product can be seen in Figure 2.8. The peak associated with the double bond just above 5.2ppm has all but disappeared, and the peak associated with the epoxide group at approximately 2.9ppm is clearly seen.

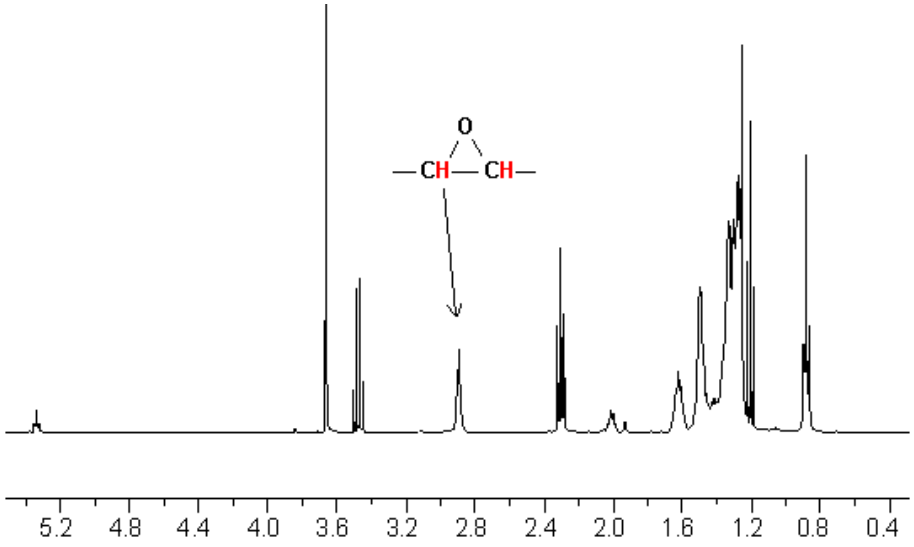


Figure 2.8: Epoxidized High Oleic Soybean Oil Fatty Acid Methyl Ester ^{1}H-NMR Spectra

2.5 Step 3: Epoxidized Fatty Acid Methyl Ester Acrylation

Once the epoxidation of methyl esters is completed in the procedure of the synthesis of PSA, it is necessary to acrylate the epoxide groups to form the monomers for the PSA synthesis reaction. This procedure is done in a round-bottom flask, using acrylic acid as the nucleophile. The product of this reaction step is the methyl ester of fatty acids that have been acrylated where there were double bonds, as can be seen in Figure 2.9.

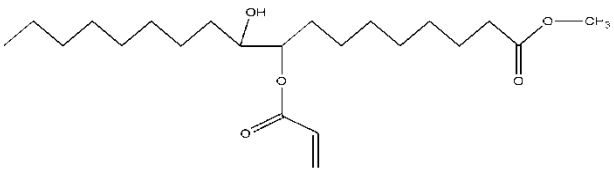


Figure 2.9: Chemical structure of acrylated methyl oleate

2.5.1 Main reaction

A sample of the epoxidized methyl esters was mixed with a stoichiometric amount of acrylic acid. Hydroquinone (HQ) was also used (as a free-radical inhibitor) in the amount of 0.07 wt% of the total reactant's weight. For some initial trials, 1,4-diazobicyclo[2.2.2]octane (DABCO, 98%, Aldrich, St. Louis) was used as a catalyst in amount of 0.01 wt% of the total reactant's weight. A typical batch of reactant that was used for these trials can be seen in Table 2.4.

Table 2.4: Typical acrylation reactants batch (with DABCO)

	Typical mass, grams	Molar mass, g/mol	Mole ratio
EMO	100	312.4819	1
Acrylic acid	30.8	72.0627	1.336968
Hydroquinone	0.104	110.1106	0.002958
DABCO	0.136	112.173	0.003798

DABCO acts by deprotonating the acrylic acid, which then is able to act as a stronger nucleophile to attack the epoxide. This greatly speeds up the rate of the ring-opening reaction. It was used because it is basic enough to deprotonate the acid, but not a strong nucleophile itself because of its sterically hindered structure, which can be seen below in Figure 2.10. Unfortunately, this catalyst does not inhibit the undesirable homo-polymerization of the epoxide. The epoxide groups in the EMO have been found to form ether-links, and this catalyst does not inhibit this side reaction to a high enough extent [4]. DABCO was abandoned after this mistake was realized.

Figure 2.10: 1-4-diazobicyclo[2.2.2]octane structure

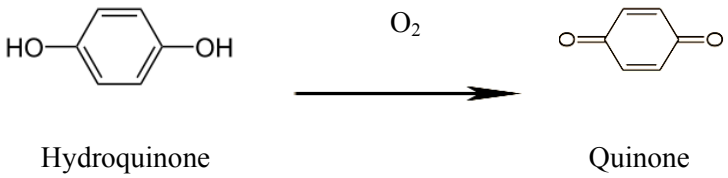
A better catalyst for this reaction is AMC-2 (Aerojet Solid Propulsion Co.) The exact chemical composition of this catalyst is not given by the company, but the MSDS states that the contents are 50% C-7,-9, -11 phthalate esters and 50% trivalent organic chromium complex. The use of this catalyst, like the DABCO, increases the rate of reaction of the acrylation reaction, but has been experimentally verified to greatly reduce

the epoxide homo-polymerization [2]. The same mass of catalyst was used as described above, but the molar ratios that this corresponds to of course can't be calculated since the exact chemical composition (and therefore molar masses) could not be determined.

Table 2.5: Typical acrylation reactants batch (with AMC-2)

	Typical mass, grams	Molar mass, g/mol	Mole ratio
EMO	100	312.4819	1
Acrylic acid	30.8	72.0627	1.34
Hydroquinone	0.104	110.1106	0.0030
AMC-2	0.136	Unknown	Unknown

Hydroquinone is added to the reaction as a stabilizer. When it reacts with oxygen that is present in the air, it forms quinone, which can be seen in Figure 2.11. Quinone retards free-radical polymerization by the delocalization of radicals from monomers [2, 4].



Hydroquinone Quinone

Figure 2.11: Oxidative conversion of hydroquinone to quinine

A mixture of the acrylic acid, hydroquinone and catalyst was prepared in a beaker, and stirred with a magnetic stirrer until all solid had dissolved. The solution was measured before and after the dissolution in order to assure that the acrylic acid had not evaporated to an appreciable extent. This solution was subsequently added to a three-

mouth round bottom flask which was in an oil bath being held at 95°C. The beaker was equipped with a condenser to control the evaporation of acrylic acid. Once the reaction mixture was given time to come to temperature, the epoxidized soybean oil was added to the round bottom flask at a rate of a few grams per minute. The mixture was stirred with a magnetic stir bar and brought up to the reaction temperature of 95°C and reacted for about 11 hours, after which it was allowed to cool to room temperature.

The product of this reaction was not washed of remaining water or excess acid. This is because the quality of the adhesive would not be harmed at all by the presence of either. Acrylic acid acts as a co-monomer in the polymerization step of the reaction, and the water will evaporate as the adhesive dries. Furthermore, the amount of water in the monomer at this point is very smaller compared to what is added during the polymerization step.

2.5.2 Acrylated Fatty Acid Methyl Ester ^{1}H-NMR

An example of an ^{1}H-NMR spectra of an acrylated product can be seen in Figure 2.12, which was synthesized from 99% MO. The peak associated with the epoxide has disappeared, and another just below 2.8 appeared, which is consistent with what is shown in Figure 2.1. Also, the peak associated with the acrylate double bonds in the vicinity of 6ppm have appeared.

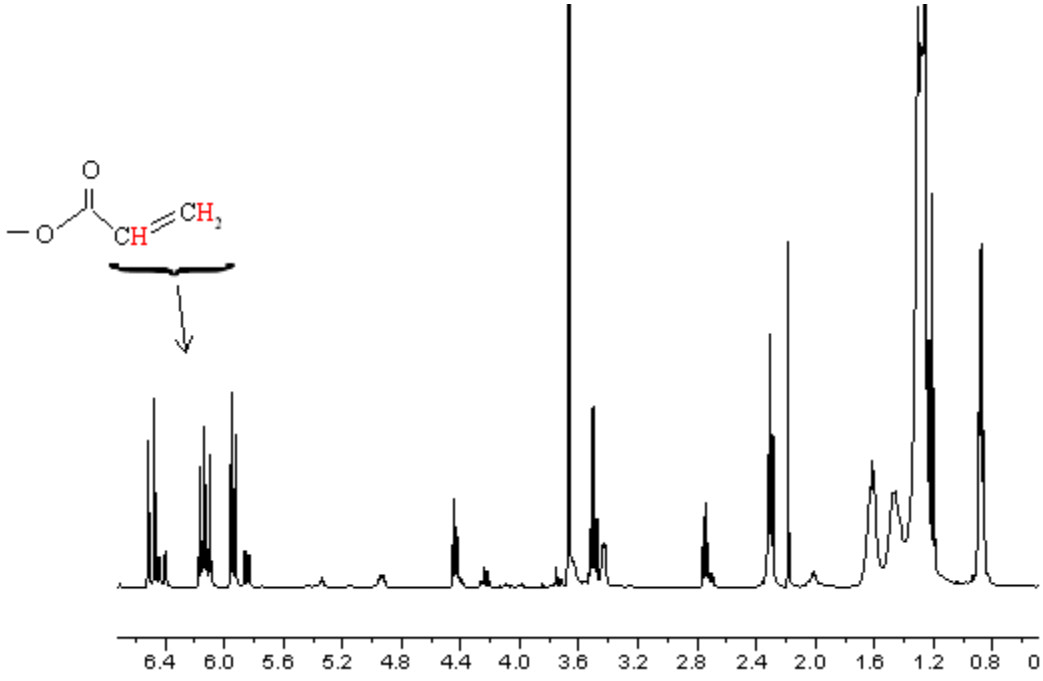


Figure 2.12: Acrylated Epoxide Methyl Oleate (99% MO-based) ^{1}H-NMR Spectra

2.6 Step 4: Mini-emulsion Polymerization

The last step in the procedure for the synthesis of PSAs from HOSO is the miniemulsion polymerization process. The polymerization of the acrylated epoxidized high oleic soybean oil fatty acid methyl esters takes place on the surface of small miniemulsion particles in a solution of water, sodium lauryl sulfate (SLS, a surfactant), Vazo 67 (initiator, azobis(2-aminopropane)dihydrochloride), and methyl methacrylate (MMA), which as a co-monomer in the reaction. This procedure was also done with the AEMO synthesized directly from commercially purchased methyl oleate. PSA was not

synthesized from the FAME from olive oil because it was clear that the fatty acid distribution contained too many saturated and poly-unsaturated fatty acids.

The product for the previous acrylation procedure is not purified for this step. There will necessarily be some unreacted acrylic acid mixed in with the monomer, but this can also as a co-monomer is PSA polymerization reaction, so its presence is not a detriment to downstream processes.

2.6.1 Main Reaction Procedure

The materials used for this procedure are shown below in Table 2.6. The AEMO was first mixed with the initiator and the methyl methacrylate. This was done to make sure that the initiator was completely dissolved before the reaction was begun. The three chemicals were mixed at room temperature in a beaker with a magnetic stirring bar. Next, the water and the SLS were added a separate mixture and stirred together for as much time as was necessary to ensure that the surfactant was fully dissolved, which was usually about 10 minutes.

Table 2.6: Typical mini-emulsion polymerization reactants batch

Chemical	Typical mass, grams	Molar mass, grams/mol	Mole ratio
AEFAME	90	384.54	1
MMA	10	100.11	0.43
SLS	20	288.38	0.30
H2O	400	18.02	945
Initiator (Vazo 67)	0.3	192.14	0.00667

The water/surfactant and monomer/initiator solutions were combined, and of course exhibited phase separation. This solution was then treated with an ultrasonicator for 5 minutes to create a miniemulsion. In the case of the larger HOSO FAME batch, the time was increased to about 10 minutes to assure that the emulsion was formed in all of the organic phase. While the solution was being treated with the ultrasonicator, it was placed in an ice bath in order to keep the solution below 50°C, which kept the initiator from prematurely decomposing [2]. The resulting emulsion, which has organic droplets with diameters of approximately 400μm, was purged with N_2 for 15 minutes, and then added to a three-mouth reaction vessel with a condenser and a nitrogen purge. This setup can be seen in Figure 2.13. The reaction was done in a nitrogen atmosphere because O_2 is a known polymerization inhibitor [20]. The mixture was brought to a reaction temperature of 80°C and reacted for one hour while being continuously stirred.

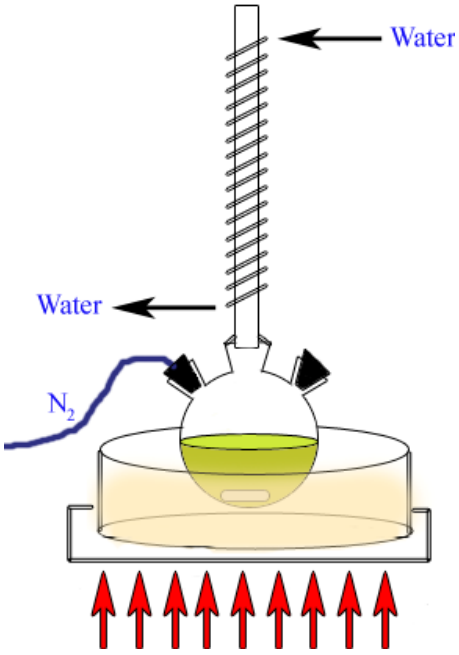


Figure 2.13: Polymerization reaction setup

^{1}H-NMR was attempted as a method of reaction characterization for the PSA reaction, but low solubility of the polymer in the NMR solvent led to poor signal strength (even after a change from D_2O to $CDCl_3$ as the solvent). Again, since the reaction pathways are proven well known [2, 4, 5], testing of the PSA with peel tests was carried out.

Chapter 3 :

METHYL OLEATE AND OIL CHARACTERIZATION

3.1 ^{1}H-NMR Data for Extent of Unsaturation of FAME

Proton nuclear magnetic resonance measurements were used to monitor the reactions done in the PSA synthesis as well as to characterize the saturation of fatty acid methyl esters of HOSO. The samples were prepared by dissolving 60 mg of the sample in 0.6 ml of CDCl3. A Bruker AV400 Spectrometer (Bruker, Germany) was used to analyze the samples. A pulse width of 90˚ was used in all cases. The samples were analyzed at 293 K and 16 scans of each sample were taken. The relaxation delay was varied according to the level of functionality of the vegetable oil [11]. For the vegetable oils, epoxidized VO, fatty acids and methyl esters a relaxation delay of 5 seconds was used. A relaxation delay of 10 seconds was employed for acrylated methyl esters and PSA.

For the analysis of the ^{1}H-NMR spectrums Knothe's [19] and Miyaki's [21] papers were employed. The peaks around 3.6 ppm on the ^{1}H-NMR plots are the methyl protons on the carbon next to the ester linkage (shown as B in Figure 3.1) [19]. This group is normalized to an area of 1. The protons next to any double bonds (A in Fig. 1)

come in at around 5.4 ppm [21]. Multiplying the relative area of this peak by three yields the average number of protons adjacent to double bonds (per fatty acid methyl ester molecule). The average number of double bonds per methyl ester is half of this number.

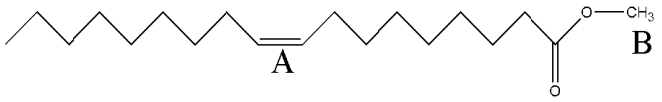


Figure 3.1: Methyl oleate with marked structures for ^{1}H-NMR

3.1.1 99% Methyl Oleate (Aldrich)

It can be seen in Figure 3.2 that this commercially purchased 99% methyl oleate (Aldrich) has an average of 1.977 (0.6591*3) protons adjacent to double bonds, which means an average of 0.989 double bonds per fatty acid. This is consistent with the structure shown in Fig. 1 and with the supposed purity.

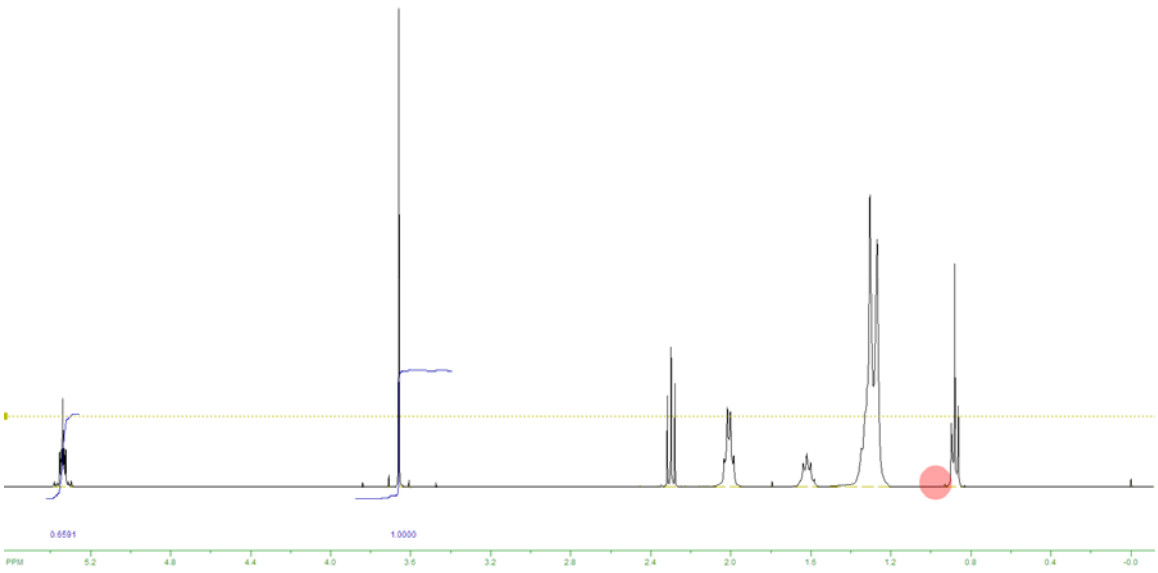


Figure 3.2: ^{1}H-NMR Spectra of 99% Methyl Oleate (Aldrich)

Figure 3.3 shows the important features of the spectrum in higher resolution.

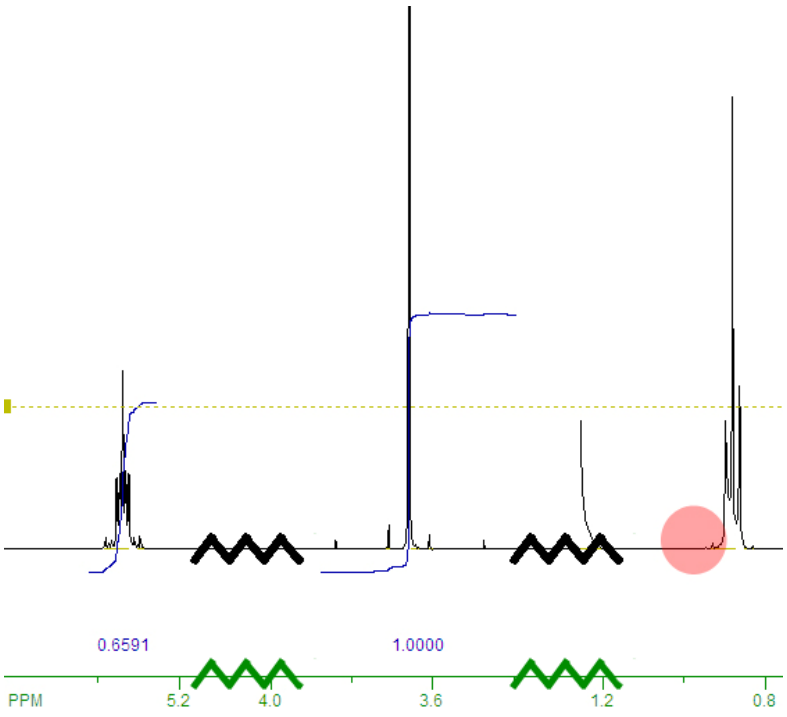


Figure 3.3: Important features ^{1}H-NMR Spectra of 99% Methyl Oleate (Aldrich)

The red circle in Figure 3.2 marks the position in the spectra that is used to determine whether or not there is poly-unsaturation in the fatty acid methyl esters [6]. It can be seen that there is no peak in this position, and therefore there is not a considerable amount of polyunsaturated methyl esters in this sample. It is therefore likely that the impurities in the mixture are saturated fatty acids or other compounds.

3.1.2 70% Methyl Oleate (ACROS Organic)

The ^{1}H-NMR of the 70% technical grade methyl oleate (ACROS Organic) in Figure 3.4 is very similar to that of the 99% MO. It has a little bit of the evidence of the

multi-unsaturated methyl esters, but it is almost negligible. This sample had an average of 2.042 (3*0.6808) protons adjacent to double bonds, which means an average of 1.021 double bonds per fatty acid methyl ester. This is consistent with the presence of the poly-unsaturation. The 30% of impurities in this sample is most likely a mixture of poly-unsaturated and saturated fatty acid methyl esters because the average number of double bonds per molecule is so close to 2.

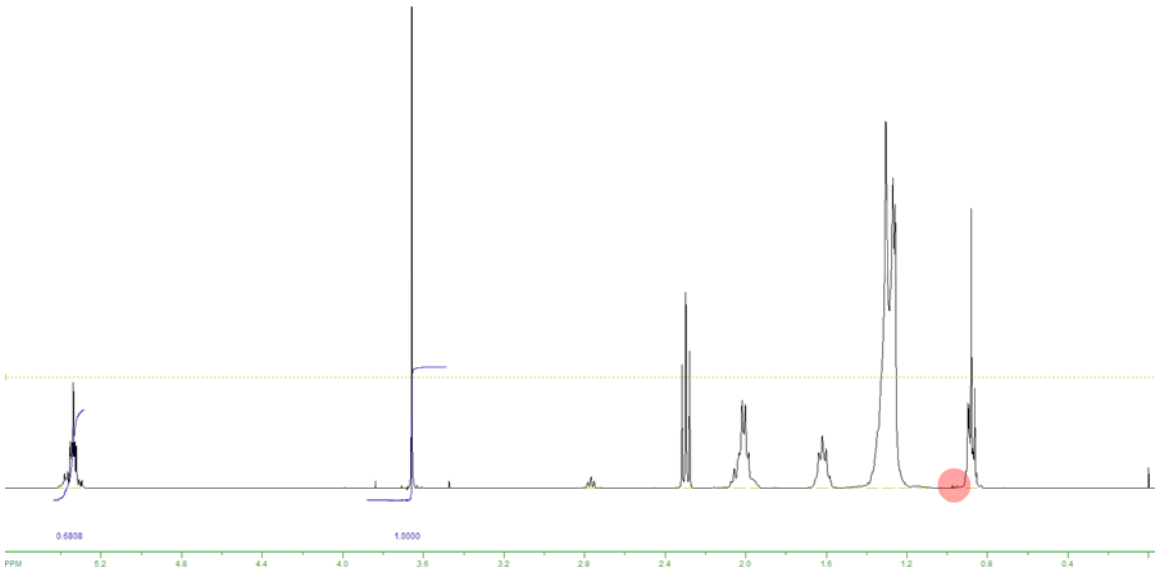


Figure 3.4: ^{1}H-NMR Spectra of 70% Methyl Oleate (ACROS Organic)

Figure 3.5 shows the important features of the spectrum in higher resolution.

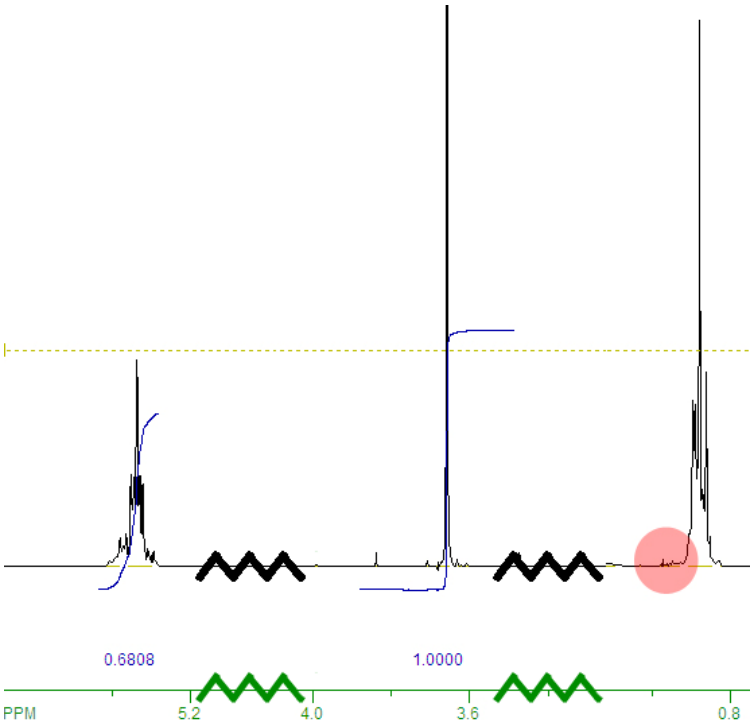


Figure 3.5: Important features of ^{1}H-NMR Spectra of 70% Methyl Oleate (ACROS Organics)

3.1.3 HOSO Biodiesel

Figure 3.6 shows the ^{1}H-NMR spectrum of the HOSO fatty acid methyl esters. It can be observed that it has an average of 1.918 (0.6392*3) protons next to double bonds, so it has average of 0.9503 double bonds per fatty acid. This could be a result of a mixture of unsaturated acids and saturated acids. Evidence to the presence of polyunsaturated fatty acid methyl esters in the mixture is present in the three-point peak shown in the red circle that can be clearly seen in Figure 3.7. These peaks are not present in the NMR of the 99% methyl oleate (Aldrich), and they are known to be associated

with linolenic and linoleic acids [6]. With this, the presence of methyl esters with more than one double bond was confirmed.

The reduced overall average number of double bonds, coupled with the apparent presence of multi-functional fatty acids, suggests the presence of a considerable amount of unsaturated fatty acids. This is consistent with the fact that the oil winterized when cooled.

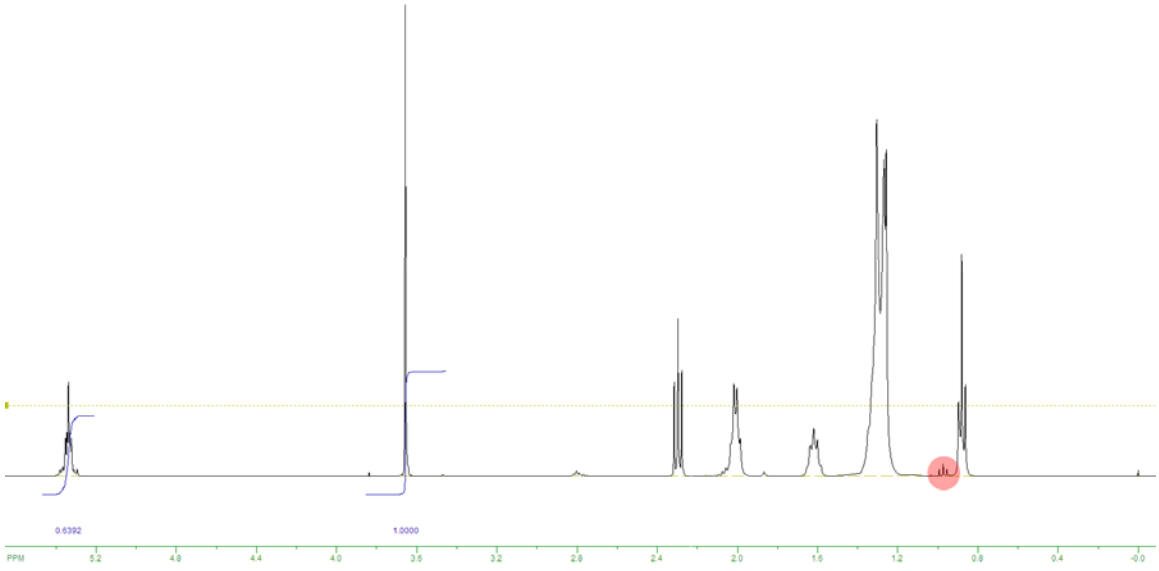


Figure 3.6: ^{1}H NMR Spectra of HOSO FAME

Figure 3.7 shows the important features of the spectrum in higher resolution.

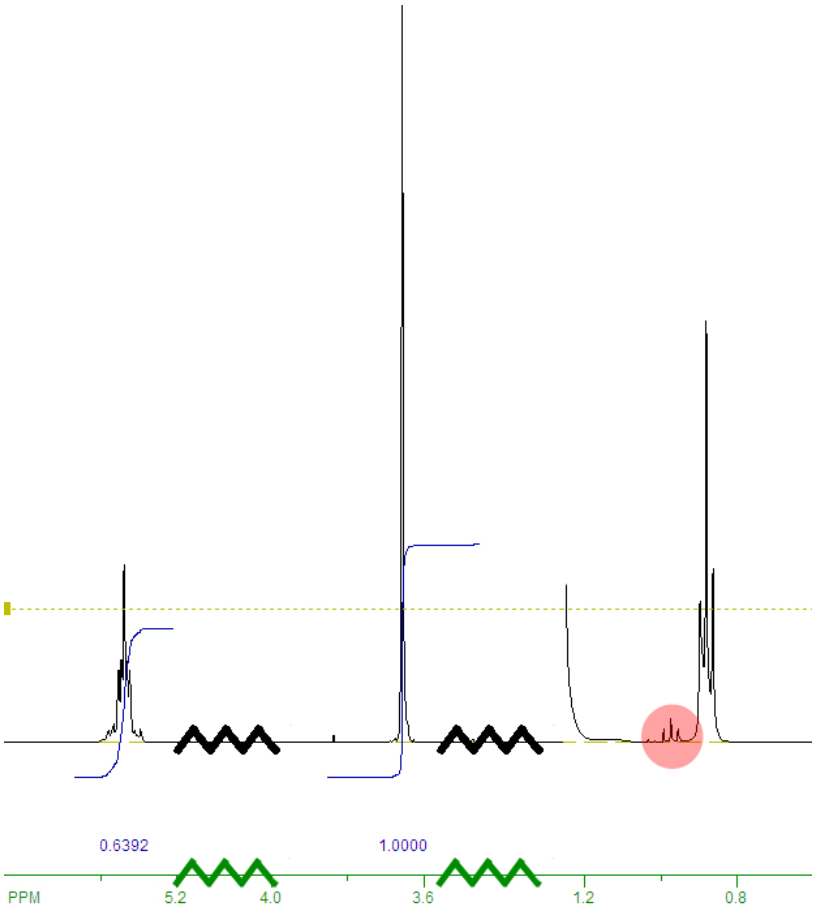


Figure 3.7: Important features of ^{1}H NMR spectra of HOSO FAME

3.2 Gas Chromatography and Mass Spectrometry from MIDI Inc.

Microbial Identification Inc. (MIDI) is a company that specializes in techniques for the identification of bacterial and other microbial life, and is located in Newark, DE. One of their processes involves the identification of these organisms by obtaining a profile of their fatty acid composition. In a reaction very similar to the biodiesel methanolysis reaction that is performed on vegetable oils for the production of PSAs, MIDI reacts the lipid layers found in bacterial cell structures to form the fatty acid methyl esters. These FAME samples are tested with a specialized gas chromatography (GC) setup.

The fatty acid composition profile of the sample is then determined by comparing the spectra from this GC test against a library of fatty acids. The profile of fatty acids is then compared against yet another database, which contains a library of fatty acid profiles of many microbial species. This allows MIDI to determine the identity of an unknown microbe with a simple test that takes just a few minutes.

In the application for this research, the test's characterization of the oils and their fatty acid compositions stops before the comparison with the microbe database, as the raw fatty acid distribution is what is desired.

The ability of the MIDI method to give specific FAME distribution in terms of mole percents of specific fatty acids from oils is incredibly useful to this research. The specific saturation profile, which cannot be obtained from ^{1}H-NMR studies, is found

easily using this testing procedure. This is important to this research because it gives an incredibly clear picture of what the requirements of a separation process would be. In addition to this advantage, there are not highly specialized chemical requirements for this process, whereas expensive deuterated solvents are needed for ^{1}H-NMR. Furthermore, nuclear magnetic resonance machines are much more expensive than gas chromatographs, and therefore would be a more likely investment for continued research.

3.2.1 MIDI Method

The method for testing the fatty acid composition with MIDI Inc. is as follows. First, the oil is put through a series of reactions that has the same result as the triglyceride methanolysis reaction in the PSA synthesis process. The goal of this series of reactions and extractions is to yield a sample of FAME in the solvent that is needed for GC. Figure 3.4 shows an outline of this procedure as given in the MIDI Microbial Identification System Operating Manual [22], which was used with some modifications, due to improvements MIDI has made to their procedure since the handbook had been updated.

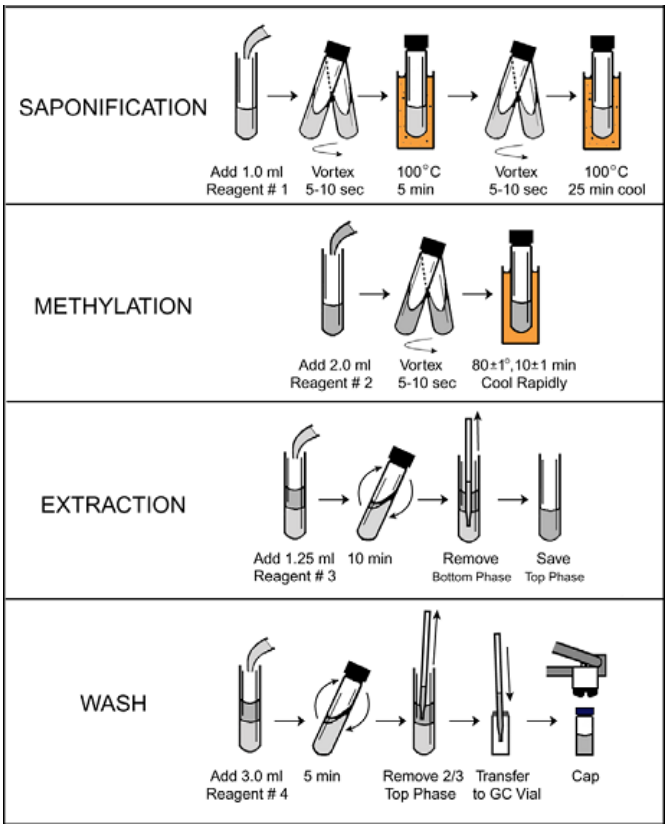


Figure 3.8: MIDI Reaction Procedure [22]

There are a number of reagents that are mentioned in Figure 3.8, and the methods for their preparation are described below in Table 3.1. Reagent 1 is a saponification reagent, which is used when for cell cultures to cleave fatty acids from cell lipids, and acts to remove fatty acids from glycerol and begin the methanolysis of the fatty acids from the triglycerides in the case of VO. Reagent 2 is a methylation reagent, and converts remaining fatty acids to FAME, which increases the volatility of the fatty acids for the GC analysis. Reagent 3 is used to extract the FAME to an organic phase with liquid-liquid extraction. Reagent 4 is a base wash that removes residual fatty acids from the organic extract, which could damage the GC system as well as cause a decrease in the

quality of data that is obtained [22]. All of the reagents were supplied by MIDI for these tests.

Table 3.1: MIDI Procedure Reagents

Name	Content	Preparation
Reagent 1:	- 45 g NaOH (certified ACS) - 150 ml MeOH (HPLC grade) - 150 ml DI distilled water	Combine water and methanol. Add NaOH pellets to the solution while stirring. Stir until the pellets dissolve.
Reagent 2:	- 325 ml 6.00N HCl - 275 ml MeOH (HPLC grade)	Add acid to methanol while stirring.
Reagent 3:	- 200 ml Hexane (HPLC grade) - 200 ml MTBE (HPLC grade)	Add methyl tert-butyl ether to hexane and stir well.
Reagent 4:	- NaOH (certified ACS) - DI distilled water	Add NaOH pellets to water while stirring. Stir until dissolved.

In the slightly modified procedure, there is no heating required between reagents as is shown in Figure 3.8. The reagents are also slightly different. The volumes of the reagents are controlled by calibrated pumps. First 250 µl of Reagent 1 is added to a miniscule sample of VO. The mass of the oil sample was not measured, but was obtained by dipping the point of a plastic stick into a vial of the oil, and scraping the point in the reaction vial. The volume of oil used was on the order of a few microliters. Once Reagent 1 is added, the vial is vortexed for 10 seconds using a vortex shaker (Fisher Genie 2). This base-catalyzed methanolysis is all that is needed to yield the FAME (acid-catalyzed methanolysis with Reagent 2 is not necessary).

250µl of Reagent 3 is added, and the mixture is vortexed for 3 seconds. Finally, 250µl of a mild acid reagent (like Reagent 4, but with a weak acid instead of NaOH) is added.

The last reagent is dyed red to make removal of the organic top layer simple. The organic layer is removed from the vial, and is added to a GC vial, and the sample is put into a GC machine. The Sherlock MIS Software (which assigns fatty acid distribution based off an internal standard, a mixture of fatty acids) can be used conjunction with one of these different hardware configurations: an Agilent 6890 GC, with an automatic liquid sampler, injector controller, and 100-vial tray (see Figure 1-1); an Agilent 6850 GC with a 7683 Automatic Liquid sampler, injector, controller, and 8 or 27-vial turret. In these trials the Agilent 6890 GC was used.

In the case of the testing of FAME synthesized from HOSO, the FAME was subjected to the entire reaction pathway in order to ensure that any triglycerides or fatty acids were removed.

3.2.2 MIDI Analysis of Olive Oil

A typical food-grade olive oil (Mazola Oil) was tested with the MIDI technique to act as a base case for the composition analysis. Table 3.2 shows the results of this analysis. The length of the acid in the second column represents the number of carbons that are present in the fatty acid, and the unsaturation is the number of double bonds. The well-known health benefits of olive oil are based in its low proportion of saturated fatty acids, which is corroborated with the data below. It is clear that this oil would not be a good starting material for a PSA because of its high proportion of poly-unsaturated

linoleic acid, which comes in at a mole percent of 14.15%, as well as its high proportion of saturated fatty acids.

Table 3.2: Olive oil FAME distribution

Name	Length:Unsaturation	C=C	%
Palmitic acid	16:0	-	15.33%
Octadecanoic acid	18:0	-	2.85%
Eicosanoic acid	20:0	-	0.60%
Palmitoleic acid	16:1	ω7c	1.68%
Oleic acid	18:1	ω9c	61.55%
Linoleic acid	18:2	ω6c, ω9c	14.15%
Other	-	-	3.84%
		Sum	100.00%

Table 3.3 shows the overall saturation profile of the olive oil sample, and shows that there is a fair amount of both unsaturated and poly-unsaturated fatty acids in the oil.

Table 3.3: Olive oil saturation profile

Saturated	18.78%
Mono-unsaturated	63.23%
Poly-unsaturated	14.15%
Other	3.84%

As it can be seen clearly in Figure 3.9, the percentage of mono-unsaturated FAME in the olive oil is only slightly above 60%, and there are high proportions of unsaturated and poly-unsaturated fatty acids present, both of which would be a detriment to PSA properties after polymerization, either because of the lack of reactivity of the saturated fatty acids or the cross-linking that would result from the usage of the poly-unsaturated fatty acids.

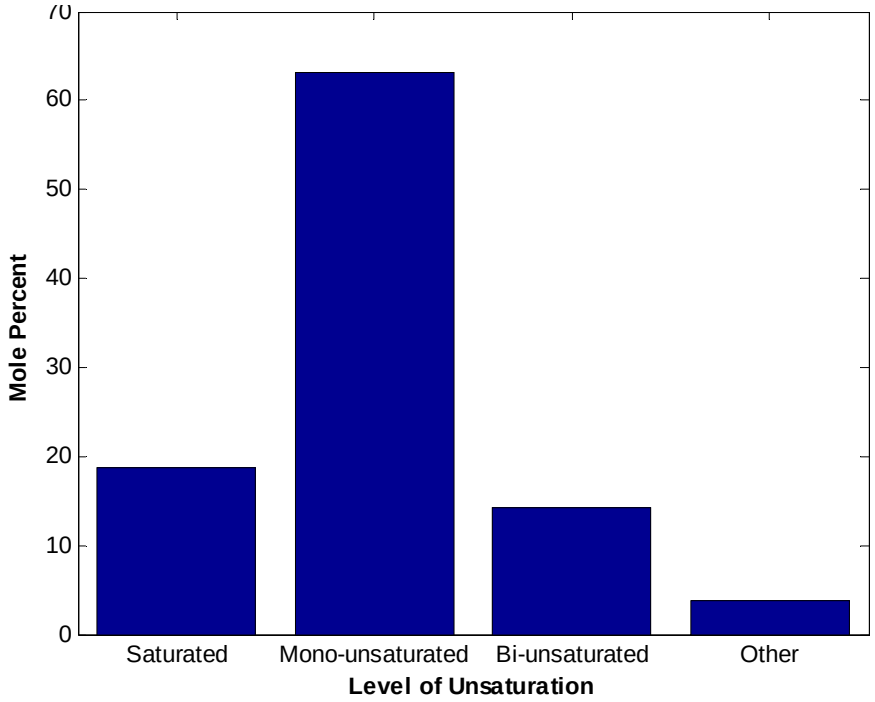


Figure 3.9: Fatty acid methyl ester distribution of olive oil

A notable characteristic of the olive oil FAME is that when it is refrigerated for extended periods (greater than a week), the mixture separates. A semi-solid phase separates from the liquid phase. This semi-solid "lard" phase is believed to contain a higher proportion of the saturated FAME that is undesirable in the PSA synthesis process, because saturated fatty acids winterize more readily than unsaturated fatty acids. The winterization of this lard phase can be used as the basis of a separation process for the production of the raw material for vegetable oil-based polymers, especially if this separation can be used to increase the concentration of mono-unsaturated FAME in the HOSO FAME mixtures.

3.2.3 MIDI Analysis of High Oleic Soybean Oil

The same fatty acid distribution analysis was carried out on the HOSO. It is a much more complex oil than the olive oil investigated above, as it contains many more fatty acids, as can be seen in Table 3.4. This table shows that the percentage of oleic acid in HOSO is 81.6%, which is significantly higher than that of the olive of oil.

Table 3.4: HOSO FAME distribution

Name	Length:Unsaturation	C=C Position	%
Palmitic acid	16:0	-	6.36
Heptadecanoic acid	17:0	-	0.78
Octadecanoic acid	18:0	-	3.87
Eicosanoic acid	20:0	-	0.43
Docosanoic acid	22:0	-	0.42
Tetracosanoic acid	24:0	-	0.16
Palmitoleic acid	16:1	ω7c	0.11
Heptadecenoic acid	17:1	ω8c	1.28
Oleic acid	18:1	ω9c	81.6
Oleic acid	18:1	ω9t	1.44
Oleic acid	18:1	ω5c	0.16
Nonadecenoic acid	19:1	ω11c	0.31
Nonadecenoic acid	19:1	ω8c	0.26
Eicosenoic acid	20:1	ω9c	0.37
Linoleic acid	18:2	ω6c, ω9c	2.15
Other	-	-	0.29

The saturation profile of HOSO, which can be seen in Table 3.5, shows that the distribution of fatty acids in HOSO is much better suited for the production of PSAs. The proportion of both unsaturated and poly-unsaturated is much lower than that of olive oil. Perhaps more important than this is that proportion of unsaturated fatty acids is much

greater than that of poly-unsaturated fatty acids. This is promising because the most viable separation methods are those that would remove the saturated fatty acids; those are winterization, which would precipitate saturated fatty acids out of the mixture, and low-temperature urea-addition crystallization [23].

Table 3.5: HOSO saturation profile

Saturated	12.02%
Mono-unsaturated	85.53%
Poly-unsaturated	2.15%
Other	0.29%

Figure 3.10 shows the same data that is in Table 3.5, and is a clear improvement over what is show in Figure 3.9 with the olive oil saturation profile.

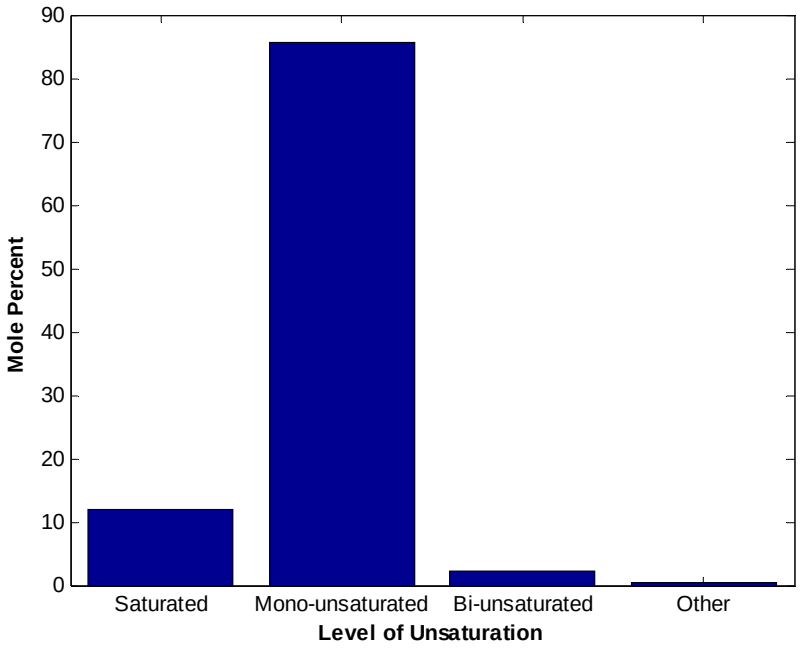


Figure 3.10: MIDI Analysis: High Oleic Soybean Oil

3.2.4 MIDI Analysis of Winterized and Non-Winterized HOSO FAME

Like the olive oil FAME, HOSO FAME experiences significant phase separation when refrigerated at 4˚C. The appearance of the separated phases is different than happens in olive oil, however. In olive oil, the lard phase is white and denser than the liquid phase, and settles to the bottom of its container. The semi-solid phase that was observed in a sample of HOSO FAME that had been refrigerated for seven days was translucent, and formed in the center of the liquid phase in a gel. It was denser than the liquid phase, but did not collect at the bottom of the container as in the olive oil FAME case. The volume fraction of the semi-solid phase was considerably larger in the HOSO sample.

Samples of the liquid and semi-solid phases in the HOSO FAME samples were tested at MIDI Inc. using a method that combined GC and MS. The reaction procedure described in section 3.2.1 was used on these samples, but instead of using the calibrated internal standard to assign the fatty acid distribution, the effluent from the GC was fed to an Agilent Telechnologies 5973 MS Machine, which calculated relative abundances of chemicals, and assigned identifications using the NIST database. The different fatty acid percentages between this method and the method described in section 3.2.3 is attributed to the change in method. The important comparison is not between the methods, but rather the comparison between the fatty acid distributions of the semi-solid and liquid phases present in the HOSO FAME sample.

Table 3.6 shows the fatty acid distribution that was found in the winterized and non-winterized phases of HOSO FAME using this method. It can be seen that there was not a significantly larger proportion of saturated fatty acids in the semi-solid phase. It is possible that the semi-solid phase was not a product of preferential winterization of saturated fatty acids. The temperature of the refrigerator could have been such that it was just above where the entire sample would have entered the semi-solid phase, as evidenced by the lack of considerable partitioning of fatty acids.

Table 3.6: HOSO FAME distribution (liquid vs. semi-solid phases)

Name	Length:Unsaturation	Liquid	Semi-solid
Myristic acid	14:0	0.04%	0.04%
Pentadecanoic acid	15:0	0.04%	0.03%
Palmitic acid	16:0	11.12%	11.35%
Heptadecanoic acid	17:0	1.42%	1.47%
Octadecanoic acid	18:0	6.11%	6.32%
Nonadecanoic acid	19:0	0.04%	0.04%
Eicosanoic acid	20:0	0.48%	0.50%
Docosanoic acid	22:0	0.34%	0.36%
Tetracosanoic acid	24:0	0.06%	0.05%
Palmitoleic acid	16:1	0.13%	0.12%
Heptadecenoic acid	17:1	2.05%	2.12%
Oleic acid	18:1	77.07%	76.42%
Nonadecenoic acid	19:1	0.68%	0.71%
Eicosenoic acid	20:1	0.44%	0.46%

However, as a general weak trend, the saturated fatty acids were present in higher quantities in the semi-solid phase. This is consistent with the idea that the saturated fatty acids should winterize more readily. Figure 3.11 shows this behavior for the three FAMEs in the mixture of the highest concentrations. Palmitic and ocatdecanoic acid

methyl esters are present is higher proportions in the semi-solid phase, while the mono-unsaturated oleic acid is present in higher proportions in the non-winterized phase.

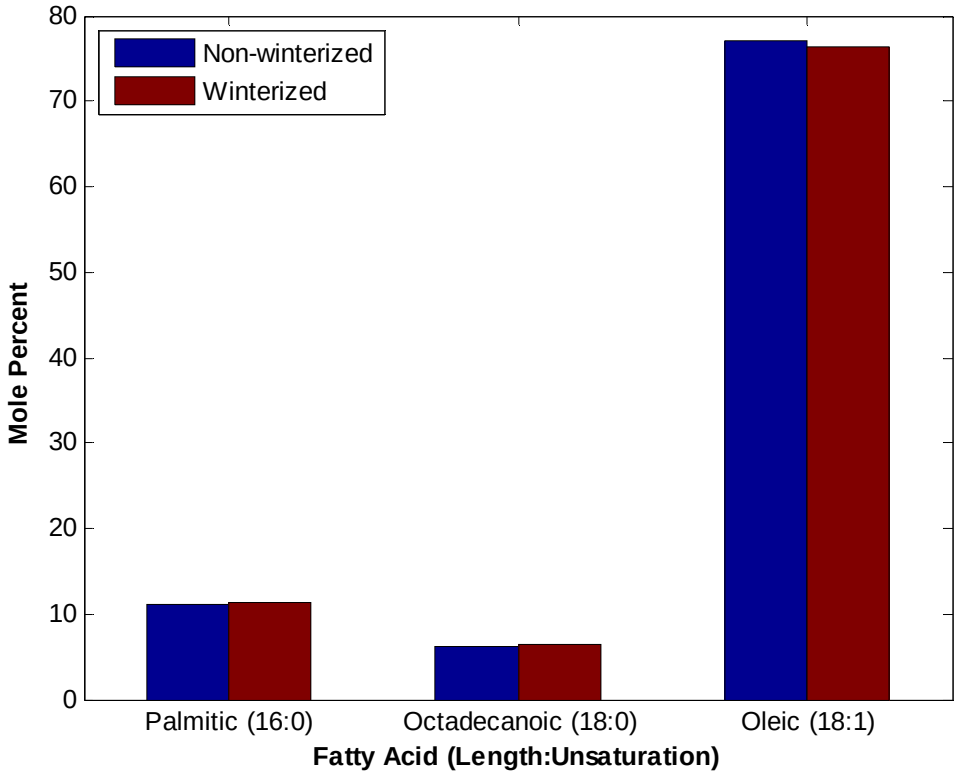


Figure 3.11: Specific fatty acid partitioning in refrigerated HOSO FAME

Of course, the overall effect of this behavior is that the non-winterized phase is slightly enriched with unsaturated fatty acids, and therefore has a make-up that is more desirable as a starting product for PSAs. Unfortunately, the partitioning of the fatty acids between the two phases in this experiment was minimal, as can be seen in Figure 3.12. Furthermore, the increase in concentration of mono-unsaturated oil is not nearly significant enough to justify the yield that would be obtained from performing a

separation of this type at this temperature. There is, however, a chance that the partitioning of mono-unsaturated could be increased if the cooling was performed at a lower temperature, if cooling rate was investigated as a control option for the separation, or if urea-addition crystallization was used as a purification technique [23].

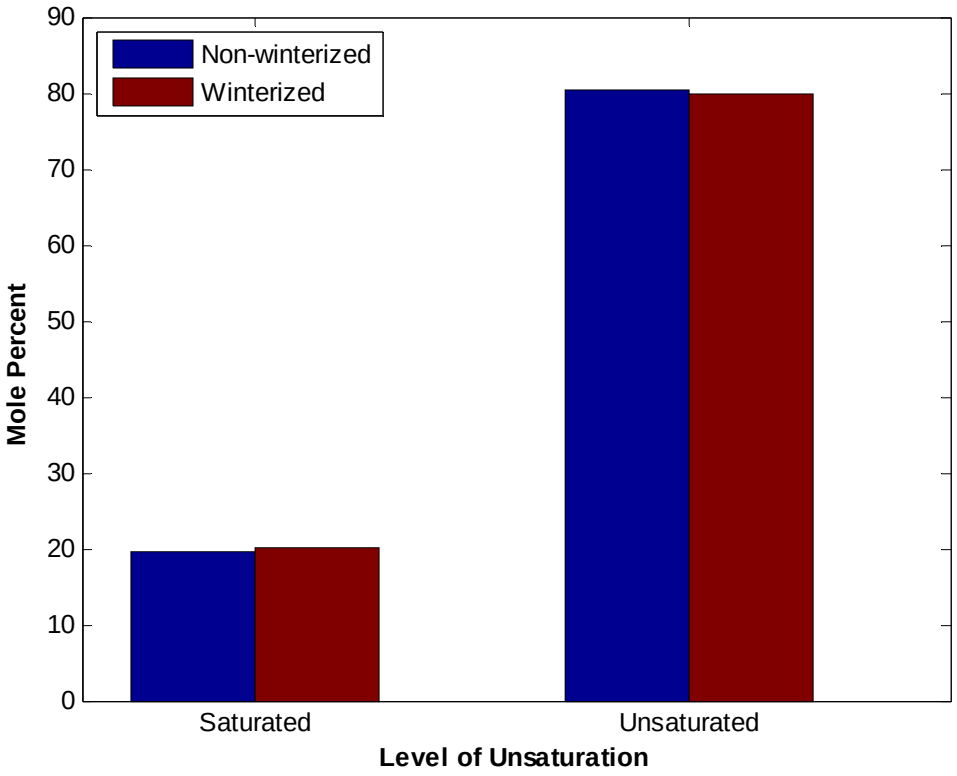


Figure 3.12: Partitioning of saturated and unsaturated FAME between phases in HOSO FAME

Chapter 4 :

PEEL TESTING OF VARIOUS PRESSURE SENSITIVE ADHESIVES

Two of the adhesives that were tested with the procedure below were synthesized using the procedure described herein. They were made from HOSO (DuPont) and methyl oleate (Aldrich, 99%).

The two other adhesives that were employed were commercially produced adhesives, made by BASF for various applications. Theses adhesives serve a similar purpose as the proposed uses of the adhesives that would be made using the procedure described in earlier chapters.

BASF Acronal V-210 is an excellent general-purpose PSA with high cohesion [24]. It is an aqueous acrylate copolymer immersion, and is intended for the production of pressure sensitive adhesives. Adhesives formulated with V-210 develop good adhesion with corrugated paper, and is most useful with applications in permanent paper and film labels, tapes, and construction adhesives [25].

BASF Acronal V-275 is a very high cohesion pressure sensitive adhesive, which is an acrylic/vinyl acetate copolymer emulsion. Its most common applications are laying

PVC floor coverings and carpets with many different backings. Adhesives made from V-275 demonstrate high tack, quick grab, and heat stability [26].

4.1 Peel Testing Background

One of the most important characteristics of adhesives that must be tested is the peel strength, G_{Ic}. It is the amount of energy per unit area that must be used to remove an adhered backing from a substrate. This quality is most commonly determined by performing a 180º peel test, and it can be calculated using:

$$G_{Ic} = \frac{2P}{b}$$

where G_{Ic} is the peel energy (J/m^2), P is the peel force (N), and b is the width of the sample (m).

In this laboratory procedure, the peel energy of the above-noted adhesives was found, when applied to aluminum foil and applied to an aluminum substrate. The test was performed on a Mini-Instron 44 according to ASTM D903 [27], with a variation in the speed of the peel. The speed of the peel that is called for in the ASTM standard is 305mm/min, but it early tests, this led to significant sample failure, as will be discussed below.

The first part of this procedure involves the application of the adhesive to an aluminum foil substrate. An Industry Tech Accu-lab Jr. drawdown machine with a #50 wire size was used to apply a film with a thickness of 0.05 inches (0.127 mm). It was

applied to aluminum foil, which was 0.1 mil (Fischerbrand), 1mil (Shop-Aid Brand), or 2 mil (Shop-Aid Brand). The strips of foil that the adhesive was applied to were 1 inch wide, as specified in ASTM D903 [27]. They were 9 inches long, and the adhesive was applied to approximately four inches on either end. Early trials showed that the both the 0.1 mil and 1 mil foils were too thin to be used with these adhesives, as the tension applied caused rips in the foil very consistently. This consistent failure was caused both by how thin the foil is, as well as the high peel speed that was employed. The speed of the peel was reduced from 305mm/min to 100mm/min to reduce the force, and the thinnest foil was replaced by the 2 mil foil.

Aluminum foil was used to cover the aluminum plates and provide a more uniform surface for adhesion. The plates measured 2.5 inches by 8 inches, and the foil was applied to one side with a quick-drying epoxy. The surface of this foil was thoroughly cleaned with acetone and wiped with a paper towel. A strip of the PSA-coated foil was applied directly to the aluminum-foil coated plate lengthwise, adhering about 4 inches, leaving the rest hanging off. A 2 kg roller was passed over the adhered portion of the foil 4 times (back and forth), moving at a rate of approximately 8 inches/sec to assure uniformly pressed adhesive.

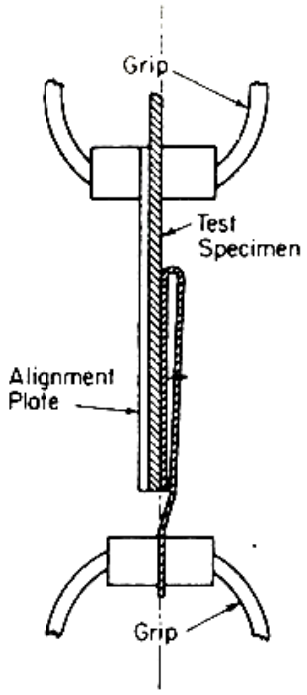


Figure 4.1: 180˚ Peel Test Setup

Once the foil was secured to the plate, this sample was put into the Instron machine. The metal plate was put into the bottom grip, and the tail end of the tape was put in the top grip, in a manner that is like what is shown in Figure 4.1, but inverted. The speed of the crosshead was set to 100 mm/min, as mentioned above. This provided a separation rate of 50 mm/min, and this was uniform throughout all of the tests. The test was done at ambient temperature and humidity (73.4 ± 2°F and 50 ± 2% relative humidity), according to ASTM D-809 [27].

4.2 Peel Testing Results

Figure 4.2 shows the instantaneous peel energies as a function of displacement for the two BASF adhesives. It can be seen that the peel average peel energies appeared to be fairly consistent. Notes were taken during these peel tests, and averages for each test were taken over intervals where there was no evidence of cohesive failure of the adhesive. Two examples of intervals that were removed from the average are the outlier peaks in the first and second trials of V275. For these trials, the average was taken for the time in the trial after the peak.

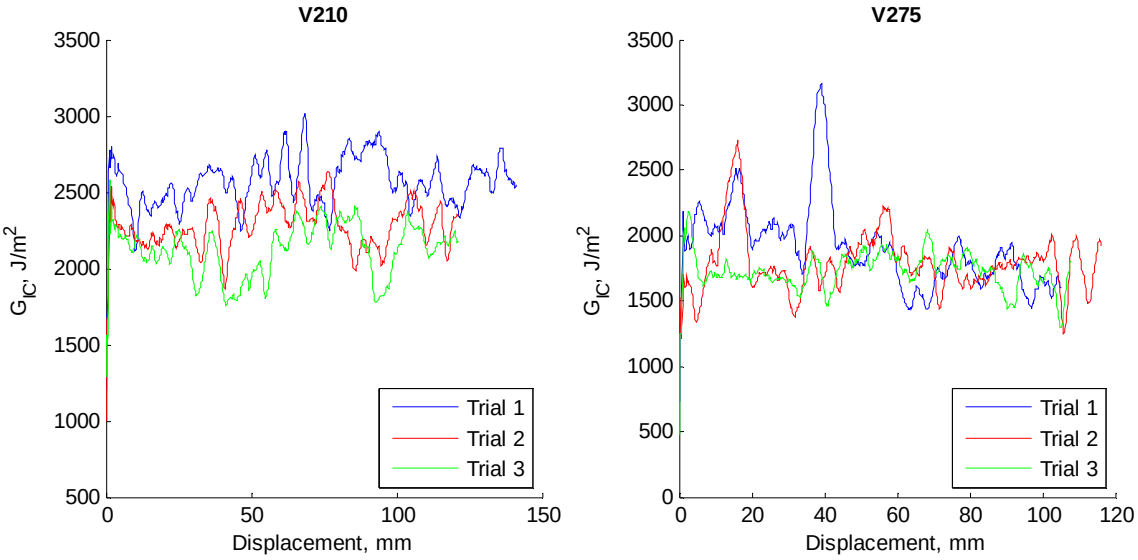


Figure 4.2: Peel energies as a function of sample displacement from peel tests (BASF Acronal PSAs)

Figure 4.3 shows similar data of instantaneous peel energy for the two adhesives that were synthesized with the miniemulsion polymerization process. The two adhesives of interest were synthesized from HOSO (DuPont) and MO (Aldrich, 99%). The first

notable observation is that the HOSO- and methyl oleate-based adhesives had low enough cohesive strength that during the peel tests, the force that was being measured was not the interfacial peel strengths, but the cohesive strengths. The peel energies for these adhesives were not as consistent as they were for the BASF adhesive because the foil was not fully pulled at an angle of 180˚ at the beginning of the test. The low peel energies meant that it took a few seconds of extension before there was a consistent flex of the aluminum foil. The averages for these trials were taken after the samples reached this point of reasonably consistent peel mode. The results of these tests may not be reproducible because of the very varied peel forces that are clearly shown in Figure 4.3 and because of the aforementioned inconsistency of the peel mode.

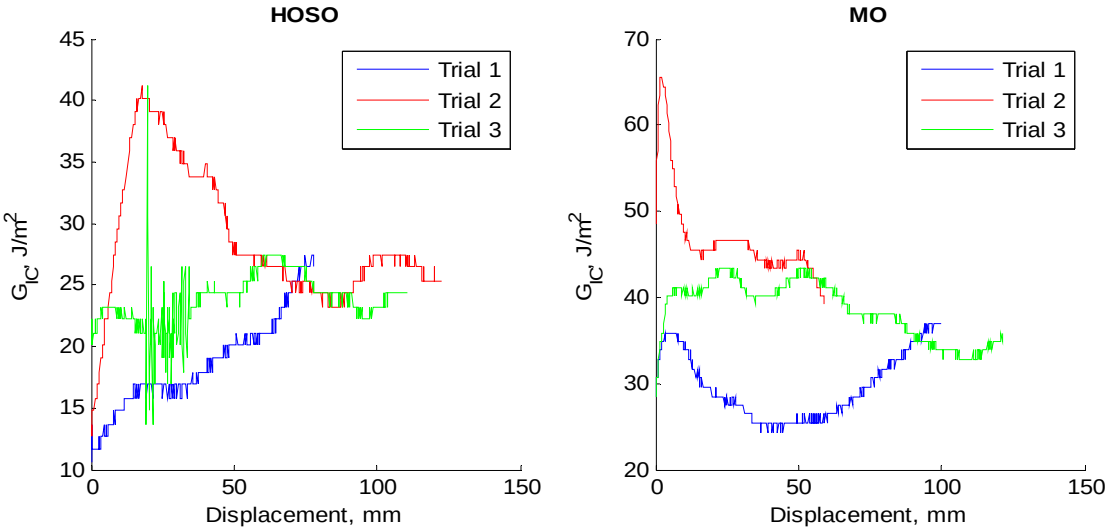


Figure 4.3: Peel energies as a function of sample displacement from peel tests (mini-emulsion synthesis adhesives)

Peel tests were also performed on 3/4" Scotch Magic Tape, which is used as an everyday office supply. The tape, which consists of a thin film of adhesive on a sheet of

plastic, was adhered directly to the aluminum foil (Shop-Aid Brand) in the same manner as the other PSA samples. This tape was the most straightforward to test due to the very flexible nature of the backing material and the moderate peel strength which did not lead to failure in the sample. None of the Scotch Magic Tape samples showed any signs of cohesive failure.

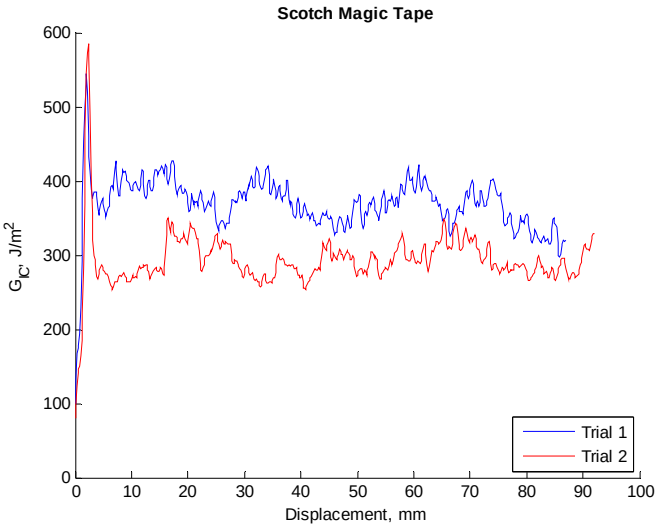


Figure 4.4: Peel energy as a function of displacement from peel test for Scotch Magic Tape

The average of the peel energies for each of the adhesives that were tested and their percent relative standard deviations are shown below in Table 4.1. It can be seen that the BASF adhesives and Scotch Magic Tape exhibit higher peel energies than either of the adhesive synthesized in this investigation. Unfortunately, the cohesive strengths of the adhesives synthesized were not high enough for a direct comparison.

Table 4.1: Peel energy averages and %RSD for various adhesives

Adhesive	G_{IC}, J/m^2	% RSD
V-210	2328.8	10.1%
V-275	1752.5	2.1%
Scotch Tape	369.6	16%
HOSO	24.8	4.5%
MO	37.4	21.2%

Even though they cannot be compared to the BASF PSAs, they can be compared against each other. The MO adhesive demonstrated consistently higher peel energies, and was tackier to the touch. This is consistent with its higher proportion of functional double bonds in the raw material. Furthermore, the presence of greater than 12% saturated fatty acids in the HOSO is, as expected, a detriment to the polymer properties. Their lack of reactivity led to their presence in the final product, and the product PSA does have a slight oily texture, indicative of the presence of these unreacted fatty acid methyl esters. Furthermore, the cross-linking introduced into the polymer by the poly-unsaturated fatty acids could have led to reduced adhesive properties.

The slower rate of peel that was employed in the test could have led to the low peel energies that were seen. Shear time to failure tests performed on these adhesives in previous work have shown very low performance [4], which shows that these polymers have a low shear resistance. This behavior could manifest in a slow peel test as the reduced cohesive strength. Shear time to failure tests, as well as tack testing should be performed on these adhesives to more fully characterize them. Also, PSAs that are synthesized from these starting materials in the future could be synthesized with a co-

monomer that introduces more cross-linking (such as 1,4-butanediol diacrylate) to increase the modulus and decrease the chance of cohesive failure [4].

The same data as Table 4.1 is shown in below in Figure 4.5. The error bars shown in this figure are the standard deviations between the trials.

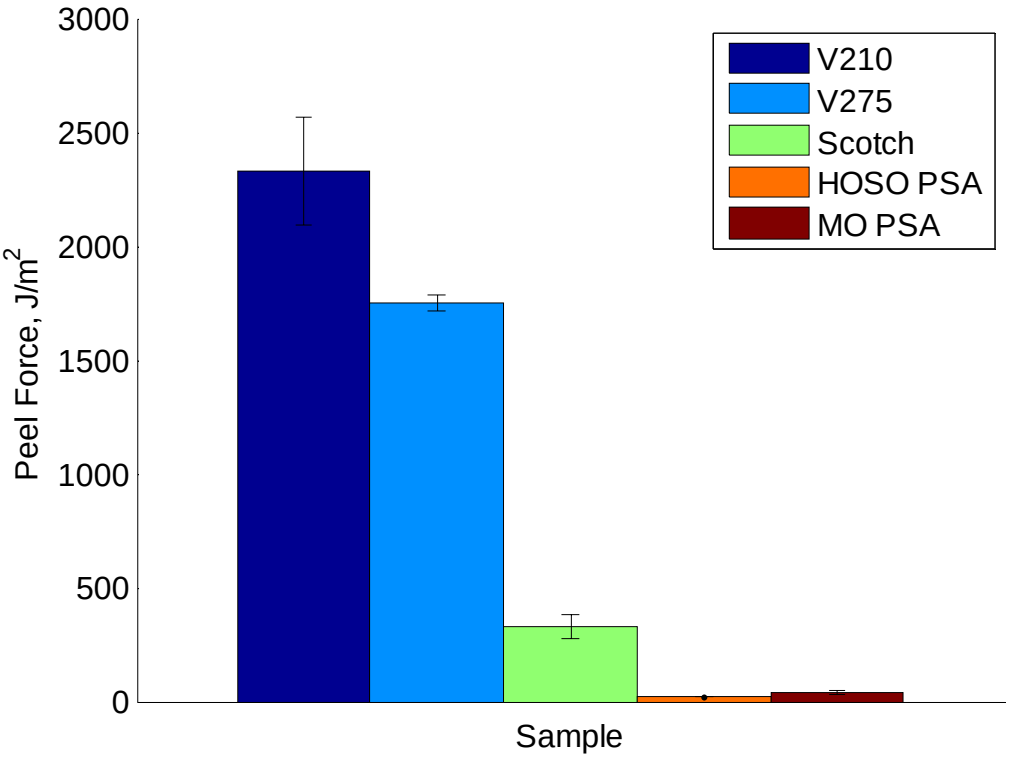


Figure 4.5: Peel energy averages and %RSD for various adhesives

Since comparison with the BASF adhesive yields a plot that is hardly meaningful due to the large range of value of average peel force, a plot was constructed without these values. Figure 4.6 shows this trimmed set of data.

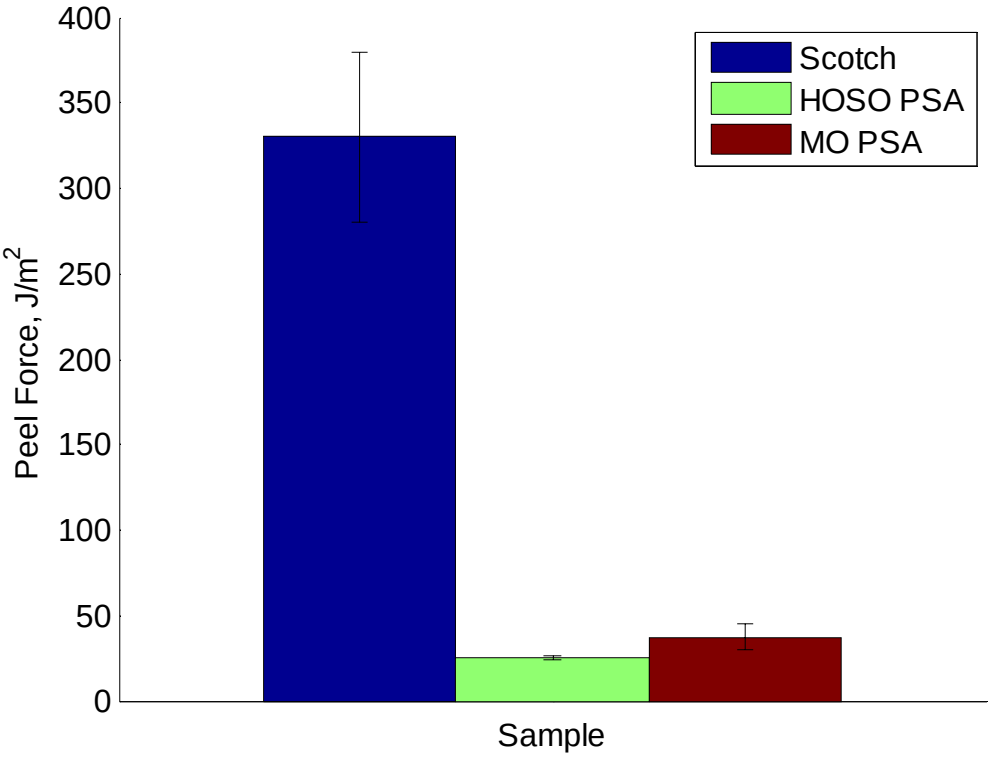


Figure 4.6: Peel energy averages and standard deviation for various adhesives (BASF adhesives excluded)

The most important comparison, however, is the comparison only between the MO- and HOSO-based adhesives. Considerable work has been done in the past to bring the mechanical performance of methyl oleate-based adhesives up to the level of those made from petroleum [2,6,7], but that was not the purpose of this research. The purpose of this work is to simply see whether HOSO could act as a surrogate for high-purity

methyl oleate, and to see how similarly the two behave in PSA synthesis. Figure 4.7 shows the averages and standard deviations for these adhesives, and shows that the HOSO-based has peel energy comparable to that of the MO-based adhesive. However, it is seen that there was a significant reduction in the peel energy of the PSA synthesized from HOSO. This 33% reduction can be attributed to the presence of impurities (both saturated and poly-unsaturated FAME). The improvement of these HOSO-based adhesives will be the goal of future investigations, especially those dealing with purification of FAME.

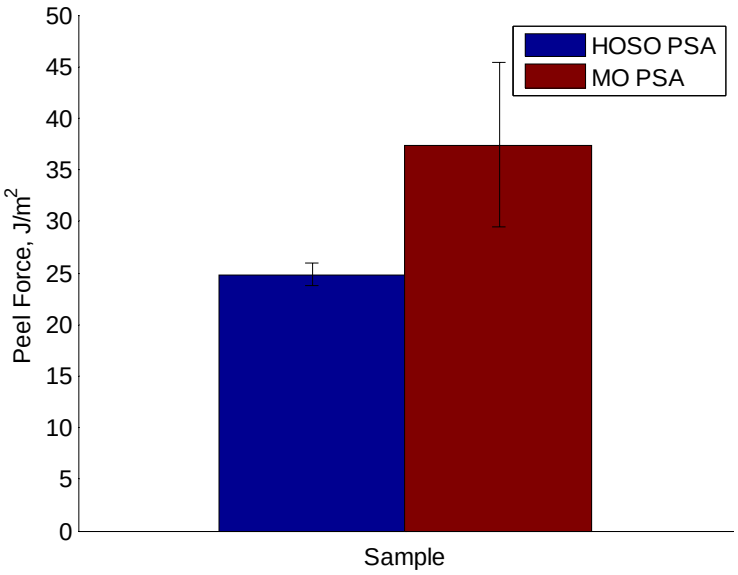


Figure 4.7: Peel energy averages and standard deviations for HOSO- and MO- based adhesives

Chapter 5 :

CONCLUSIONS

5.1 Synthesis and Reaction Characterization

The steps for the synthesis of PSA were performed using various starting materials. Using methods that have been developed and verified in previous work done by the ACRES group, PSA was synthesized from both HOSO and high purity methyl oleate.

It was found that after the methanolysis reaction, the methyl esters of HOSO took considerably longer to separate from aqueous phases, but otherwise acted similarly. After some time was spent using the wrong catalyst (DABCO instead of AMC-2) for the acrylation reaction, acrylated PSA monomer was synthesized from both HOSO and MO, again using previously demonstrated reaction procedures [2, 4, 5].

While reaction extent was not routinely monitored with ^{1}H-NMR for these reactions, each step was verified using this technique.

Syntheses of tacky PSAs were performed, using both 99% MO (Aldrich) and DuPont HOSO as starting materials.

5.2 Methyl Oleate and Oil Characterization

Both ^{1}H-NMR and GC techniques were employed for the characterization of commercially purchased MO, HOSO, and olive oil. The more commonly used ^{1}H-NMR method gives an idea of the average number of double bonds per fatty acid in each sample, and gives an idea of whether or not there exists any poly-unsaturation. It does not, however, give any insight into what specific fatty acids are present in oil, or what fraction of fatty acids are poly-unsaturated [19]. It was determined with this procedure that the HOSO of interest in this research had an average of 0.9503 double bonds per fatty acid, and showed evidence of poly-unsaturation.

The claimed purities of commercially purchased MO were also verified with this method. For example, it was shown that the 99% MO (Aldrich) had an average of 0.989 double bonds per fatty acid and no evidence of poly-unsaturation.

Procedures developed by MIDI Inc. were used to get a better idea of the specific fatty acid compositions in HOSO and olive oil. It was determined that HOSO consists of 85.53% mono-unsaturated fatty acids, 12.02% saturated fatty acids, and the remainder poly-unsaturated fatty acids. The specific fatty acids in this oil were also obtained on a mole fraction basis. Close agreement was also found between this work and previous literature values for olive oil fatty acid saturation profiles.

Furthermore, the possibility of using refrigeration-based phase separation of HOSO was investigated, using a method that involved both GC and MS. It was

determined that the partitioning of saturated fatty acids between the liquid and semi-solid phases observed in refrigerated samples was not enough to justify using it as a viable separation process, and that further work needs to be done to improve separation efficiency.

5.3 Peel Testing of Various Adhesives

180˚ peel tests were performed on the MO- and HOSO-based PSAs as well as commercially produced adhesives from BASF and Scotch Magic Tape. The PSAs synthesized in this research were found to have insufficient cohesive strength to measure the strength of the adhered interface, and therefore the results show that they have very low peel energies. The speed of the peel in these tests was reduced in order to prevent sample failure for the high-peel energy BASF Acronal V210 and V275 adhesives, and this could have enhanced the evident failure in the HOSO- and MO-based adhesives. Adhesives synthesized in previous work showed poor performance in shear time to failure tests, and this poor performance in resisting a slow and consistent force, which is a result of having a linear polymer structure [4], could explain the results seen here. Most importantly, the HOSO-based adhesive was shown to have peel energy on the same order of magnitude of the MO-based adhesive (showing a 33% reduction). This shows that the HOSO-based adhesive is a viable possibility for future work, and that purification work has to be done to bring it up to the same level of the MO-based adhesives.

Measurement of tack area and shear time to failure of all of these adhesives is recommended for future work, and this could be used to get a better idea of the effect of the presence of saturated fatty acids in HOSO on the PSA properties.

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