NOVEL SYNTHETIC ROUTE TO BIOBASED SILYLATED SOYBEAN OIL FOR USE AS COATING MATERIAL

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ABSTRACT

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Bio-based materials synthesized from sustainable and renewable resources are gaining considerable attention in academe and industry. Soybean oil is a bio renewable molecule suitable for conversion to useful materials. It possesses unsaturated (double bond) structure in its molecular chain, and can be modified or reacted with other reactive chemical species to produce value added biobased materials.

Coating materials prepared from the reaction of soybean oil and reactive silanes (vinyl trimethoxy silane and vinyl terminated polydimethylsiloxane) are described in this thesis. The silylation reaction occurs at high temperature and pressure in the presence of peroxide as catalyst. The silane molecule was grafted onto soybean oil backbone and on curing with water gave coating materials with water resistant property. Biobased products containing different molar ratios of soybean oil and silane were synthesized and characterized. The silylated soybean oil was coated on the substances and the coating performances evaluated. These coating materials were evaluated for biodegradability and showed that they were biodegradable under aqueous conditions. Biodegradability of these coating materials was also measured to demonstrate that these materials were biodegradable

These coating materials are recommended as protective coatings for water sensitive substances, such as wood, paper and starch foams.

DEDICATION

This thesis is dedicated to my family in China

ACKNOWLEGEMENTS

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Chapter 1: Introduction and background

1.1 Introduction

Carbon is the major basic element in the world, from which organic materials and some inorganic materials are derived. How to sustain these products in the abuse of petroleum based products and maintain environment status becomes a major issue.

Nowadays, many scientists and engineers are focused on bio-based materials which have almost the same function as petroleum based products but can be fully degraded by the environment itself. Soybean oil is one of these bio-based materials, and this kind of material is widely planted all over the world, thus providing a sustainable source of raw materials as reactants for biocomposites. By using this bio-based material, researchers want to produce new materials which can replace petroleum based products with almost the same function and help to reduce global warming issues. Moreover, soybean oil, which is extracted from soybean seeds, can be easily biodegraded in the environment. [1]

By adding functional groups or reactive groups, soybean oil can be used to synthesize biocomposites in many fields. These biocomposites made from vegetable oil have been used in alkyd resin formulations, especially for coating applications. [2]

1.1.1 Objectives

In this project, oil-based coatings are prepared by reacting unsaturated soybean oil with reactive silane. This reaction occurs at high temperature and high pressure conditions, and finally silane is grafted onto the soybean oil chain to provide coating and curing, and the soybean oil will also provide a water resistant property to this oil product. There are three main objectives in this project that have been studied.

(1) Reaction scheme between soybean oil and reactive silane; this can help us to control the products properties and improve reaction conversion. It can be studied by using different reaction molar ratios, reaction times and reactants.

(2) Performance of different coating systems on coating appearance and water resistant property. There are many methods of paper coating and different additives could be added into the coating material to provide multiple functions. Which is the best to provide adhesion and water resistant property will be our aim in this project.

(3) Biodegradability of this coating material. As has been stated, this project is based on soybean oil, which is a renewable resource and environmentally friendly, and thus "green". Successful completion of this work should lead to a new bio-based and biodegradable coating material with water resistant property and will also help to better understand the mechanism of reaction between soybean oil and reactive silanes.

1.1.2 Organization of this Thesis

The thesis is divided into five main parts. In Chapter 1, the need for new bio-based coating material is addressed. This chapter also includes comprehensive reviews and background information of current problems as well as current research activities in this field.

In Chapter 2, detailed experimental procedures are given including the synthesis of these novel oil-phase coating materials, which can be later applied to different coating systems for paper coating. This chapter also includes detailed structural analyses of the products using FT-IR, NMR, and other chemical methods.

In Chapter 3, different coating systems and coating procedures are described. Water resistant property and biodegradability tests investigated include water vapor transmission test, water contact angle, Cobb test, and biodegradable test.

In Chapter 4, the focus is on alternative reactants to substitute soybean oil or reactive silane to synthesize coating material with water resistant property.

Chapter 5 draws conclusions based on the finished work and suggests future research plans.

1.2 Background

The fact that bio-based coating material is an important and active research topic has attracted many researchers into this field. In order to further understand this topic, in this section, soybean oil, reactive silane, coating system and normal coating procedure are discussed.

1.2.1 Soybean oil

Soybean oil is a widely-used annually renewable vegetable oil. The main structure of soybean oil is triglyceride, and five main triglycerides in soybean oil are consist of saturated and unsaturated long chain fatty acids, which is shown in Figure 1. [1]

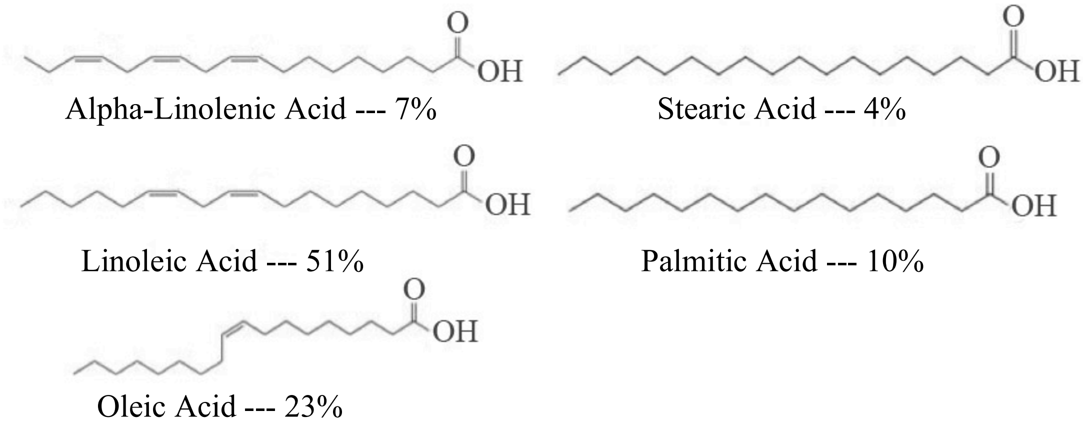

Figure 1 Five Major Fatty Acid Components in Soybean Oil

In the United States, soybean oil is easily obtained and is relatively inexpensive, which makes it a great resource for bio-synthesis. But raw soybean oil is not a good coating material, because it dries very slowly and has poor coating quality. After reacting with other chemicals at the double bonds, the reactive soybean oil can be expected to yield more flexible and better color retention composite coating materials, which meet the requirements of the coating. [3]

1.2.2 Reactive Silanes and Silicones

Both silanes and silicones are silicon-based chemicals, which mean that there is at least one silicon atom in its structure. Silicon atom, which is in the same column of carbon atom in the periodic table, can be attached four other atoms to make molecules that are structurally similar to carbon-based chemicals. [4]

Reactive silanes. Silanes are silicon-based monomers that are similar to alkynes. A basic silane has the following structure:

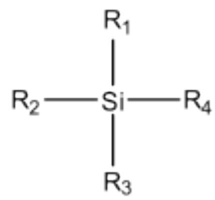

Figure 2 Silane basic chemical formula

in which R_1, R_2, R_3 and R_4 can be substituted by any chemical groups or atoms.

Reactive silanes, especially vinyl silanes (-Si-CH=CH_2) and silicon hydrides (-Si-H), can be reacted with other functional groups to produce useful materials. [5]

Silicones. Silicones are polymers with the repeat unit of silicon and oxygen atoms in the main polymer chain and other chemical elements in its structure. They are man-made compounds with a wide variety of forms, and the most common organic silicone is polydimethylsiloxane (PDMS), as shown in Figure 3. [6]

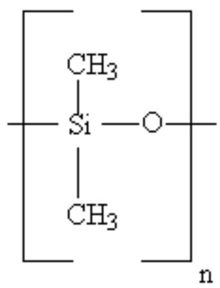

Figure 3 Structure of Polydimethylsiloxane

Unlike most polymers prepared from monomers, PDMS cannot be simply polymerized from a silicone group with a double bond between oxygen and silicon, for in nature, it is common to see the silicon atom attached by a single bond with two oxygen atoms, rather than a double bond to a single atom. To obtain PDMS, people may use dimethyldichlorosilane to react with water as follows: [7]

$$n\ Si(CH_3)_2Cl_2 + n\ H_2O \rightarrow [Si(CH_3)_2O]_n + 2n\ HCl$$

PDMS can be used to prepare water-repellent coating materials which can later be used as waterproofing applications. Zimmermann [8] group recently synthesized a kind of superhydrophobic silicone coatings, which could be applied to many substrates as waterproofing coatings. Moreover, this transparent coating material showed antifouling and self-cleaning potentials as well as long-term stability in the environment.

PDMS with functional end groups may have other useful applications. Vinyl terminated PDMS can form a cross-linked structure during the reaction with a multifunctional cross-linker. [9] If this cross-linked PDMS mixes with garnet, we can prepare materials used in Light Emitting Diodes (LEDs). [10]

1.2.3 Coating

Coating is a protective layer of materials at the surface of a substrate. Coating can help to improve corrosion resistance, wear resistance, wettability and other properties of the surface, so this technique is widely applied in industry.

1.2.3.1 Anticorrosive Coatings

Corrosion is a common problem for all the substrates in modern society, because it affects the appearance of this substrate; and can even cause serious damage of the structure of the substrate, which leads to dramatic consequences. [11]

There are series of stimuli in the environment for corrosion, such as high temperature, CO_2 and acid solution. [12] These environmental elements lead to different types of corrosion, which cannot be overcome by a single layer of coating. Thus, anticorrosive coatings combine several different layers of coating material together to achieve the best overall coating performance. These layers can be organic, inorganic or metallic. Moreover, anticorrosive coatings should also have a good adhesion to the coated substrate to ensure its durability.

Anticorrosive coatings usually consist of three parts, a primer, one or several intermediate coats, and a topcoat. [13] The primer layer will prevent corrosion of the surface and improve adhesion of the coating, and the intermediate layers can provide sufficient thickness of the coating and isolate the invasion of the outside world. In addition to provide gloss and required color, the top layer must have resistance to radiation and different weather conditions.

1.2.3.2 Waterproof Coatings

Waterproof coatings, which have the property of high water repellence, are potential surfaces for antifouling or self-cleaning products. [8] These coated surfaces usually have the water contact angle larger than 150° and low surface energy. Silicone or silane is usually an important component of these coatings.

Li [14] group recently fabricated superhydrophobic cellulose-based materials, and this material can later be applied in textile industry and packaging field. A solution-immersion process enables them to transform the normal hydrophilic group on the cellulose into superhydrophobic ones. Hydrolyzed silane group Si-OH reacted with the –OH group on the molecular chain of cellulose and formed a covalent bond. This reaction condensed the siloxane polymer outside of the cellulose and became a kind of coating with waterproof property.

1.2.4 Coating Procedure

1.2.4.1 Surface Activation

A surface activation step is commonly applied for cleaning or oxidization of substrate surfaces to improve surface energy and facilitate bonding the coatings to the substrate. More importantly, surface activation gives rise to reactive -OH functional groups on the surface, which enhances the subsequent coating or grafting procedure. [15]

1.2.4.2 Coating

Coating the substrate with coating materials. This step can be done by either brushing or spraying required thickness of the coating materials.

1.2.4.3 Curing

During the cure step, the coatings cross-link to form a network of the coating material and the surface becomes hard or tough. Curing conditions can affect the quality of the coatings. Heat or chemical additives can be used to improve the cure.

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Chapter 2: Synthesis silylated soybean oil product and component analysis

2.1 Introduction

Coating is a versatile and useful procedure in industry and daily life, because it can protect the substrate or surface from corrosion or moisture, which will help to prolong the lifetime of coated materials. In this project, the objective is to synthesize new coating materials based on soybean oil and reactive silanes, and this new coating material should enhance water the resistant properties of the coated substrate. Soybean oil can provide water resistant property, but since it is oily and has no functional groups to form a network to cure, this indicates that we need to find a reaction that can graft silanes onto the backbone of soybean oil to help to form the network and to make this coating curable.

A grafting reaction attaches a monomer or monomers onto the backbone of a polymer or another medium to provide or to improve certain properties of this medium. Grafting reactions can be achieved by free radical, anionic, cationic or condensation mechanisms. [1-5] Normally, a grafting reaction system consists of a reactive polymer or medium, an active monomer and low concentration of a homopolymerization inhibitor compound. [6]

Unsaturated soybean oil is one kind of reactive vegetable oil, and the reactivity is from the double bonds. Extensive reactions have been done on this unsaturated bond to synthesize compatibilized blends via high temperature and high pressure reactors. [7] Epoxidized soybean oil is another kind of reactive vegetable oil. Epoxy groups can be polymerized by ring opening reaction to form polymerized epoxidized soybean oil, and these polymers can later be hydrolyzed to hydrogels, which could further find applications in medical or health care areas. [8]

The Parr reactor has been designed for high temperature and high pressure reaction systems. A typical Parr reactor has three parts, which are head, cylinder and controller. A gasket is used to seal the head and the cylinder together. The head part's scheme is shown below. (Figure 4)

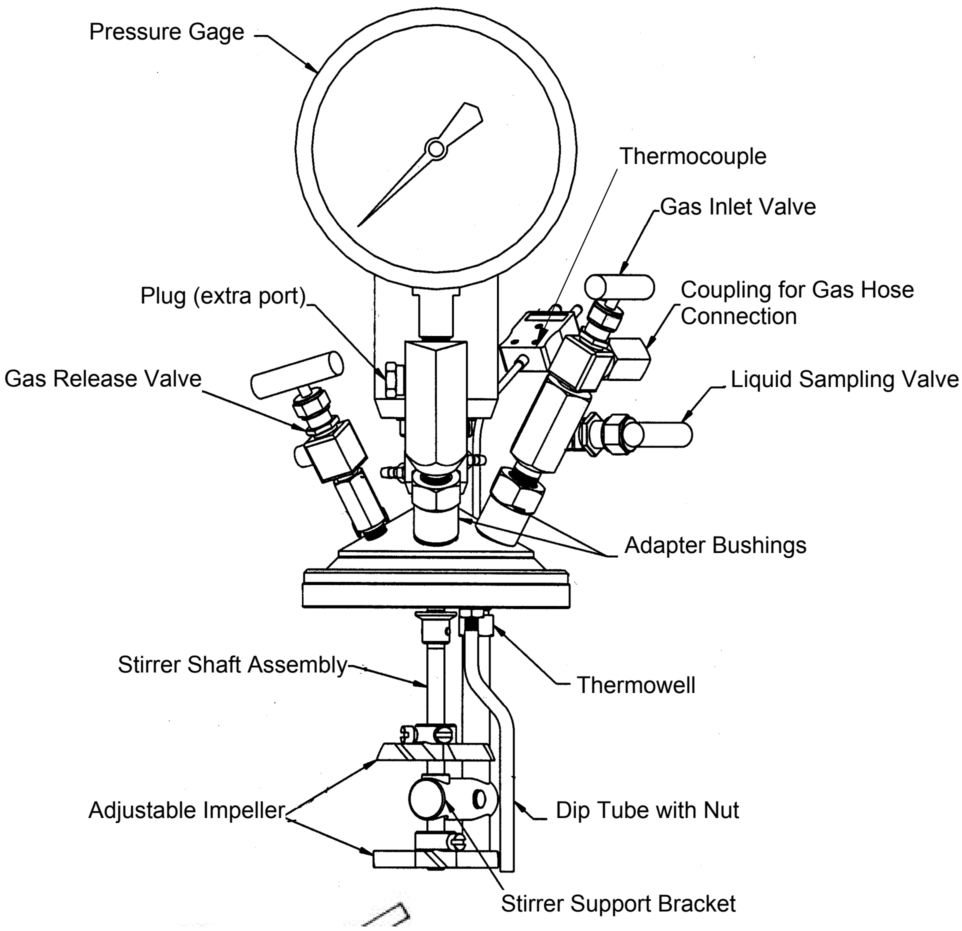

Figure 4 Scheme of the head part of Parr Reactor

A gas inlet valve and gas release valve are often used to purge the reactor or to pressurize the system before reacting. Users can take liquid samples during the reaction from the liquid sampling valve. A thermowell is used to measure the temperature, and a stirrer will enhance the mixture of the reacting liquid. Both the temperature and pressure can be monitored and adjusted by the controller and the pressure gauge. Furthermore, parameters of Parr reactor, such as heating time, the starting pressure and original oxygen concentration in the cylinder, can affect the viscosity of the product.[9] This result enables us to produce consistent viscosity products by using this reactor.

2.2 Experimental

2.2.1 Materials

Unsaturated Soybean oil was obtained from Zeeland Farm Services Inc., Zeeland, MI. 97% Silanes with a purity of vinyltrimethoxy silane (VTMOS) [CAS 2768-02-7], vinyl terminated polydimethylsiloxane (V-PDMS) [CAS 68083-19-2] were obtained from Gelest Inc., Morrisville, PA. Luperox 101 (L101) [CAS 78-63-7] -2,5-Bis (tert-butylperoxy)-2,5-dimethylhexane (90% technical grade) used as the peroxide catalyst was obtained from Sigma Aldrich, St. Louis, MO. All the reagents were used as received without any further purification.

2.2.2 Synthesis of silylated soybean oil

There are approximately five double bonds in 1 mole of soybean oil, so three different molar ratios of reactants were applied to synthesize different silylated soybean oil products. Two reactions were processed with 1:3 and 1:7 molar ratios of soybean oil and VTMOS, the other one had the molar ratio of 1:2:0.5 of soybean oil, VTMOS and V-PDMS.

A calculated weight of soybean oil, VTMOS and V-PDMS were mixed in a closed flask. L101 (1wt% of soybean oil) was added into this mixture as the peroxide initiator. The mixture was then poured into a 2L Parr reactor produced by Parr Instrument Company. An external controller was used to set and control the temperature of the reactor. Reaction temperature was set at 280C. The stirrer was kept at the speed of 200 rpm to mix the reactants and to uniform the heat.

Before the reaction began, nitrogen was purged into the cylinder of the Parr reactor for about 2 minutes to exclude air from the system. A high-rate heating was chosen for the early period of heating stage, and then we switched it to low-rate heating when the temperature reached 180℃. The reaction time started when the temperature reached 280C and maintained for 12 hours.

10 samples were taken via the sampling valve into vials. Three of them were taken during heating period at various time intervals, and the other seven were taken every two hours after the reaction time started. All the samples were sealed and frozen in the refrigerator prior to analysis to prevent unreacted VTMOS escaping from the sample.

2.2.3 Purification of silylated soybean oil products

The final product of this reaction was a mixture of silylated soybean oil, unreacted silane and unreacted oil. To calculate the reacted VTMOS percentage and reaction conversion, distillation was used under reduced pressure to remove unreacted

VTMOS from the oil products. A large three-neck flask was used as the container to hold the entire product. The middle outlet was connected with a vacuum, another outlet was equipped with a thermometer, and the third one is closed with a hollow plug. A magnetic stirrer was used to completely drive out volatile VTMOS. The silylated soybean oil product was purified at 110C with the vacuum about 0.3 Torr for 1 hour, or till there was no further distillate generated. The unreacted VTMOS was trapped in dry ice and acetone traps and weighed.

2.2.4 Iodine value of silylated soybean oil products

The iodine values of silylated soybean oil products were measured according to ASTM D1959. Both the products after purification and pure soybean oil used in this reaction were measured to compare the values before and after reaction. Sample weights were calculated using the conversion obtained earlier and assuming that there was no change of the number of double bonds on the oil.

2.2.5 TGA

Thermo gravimetric analysis was conducted by a TA Instrument Q 2950 high resolution thermogravimetric analyzer. Pure soybean oil, pure VTMOS and 1:3 oil product samples were tested through certain heating profile to separate components' contents in the final product. The heating profile was by starting at the room temperature, and then to heat till 150°C by the heat rate of 20°C per minute. After keeping isothermal stage at 150°C for 20 minutes, ramp up the temperature to 300℃ with the heating rate of 10°C per minute.

2.2.6 FTIR

Infrared spectra were obtained with a PerkinElmer 2000 FTIR spectrometer. Each spectrum was obtained with at least 16 scans to ensure a high signal-to-noise ratio. The wavelength range was between 4000 cm^{-1} to 450 cm^{-1}.

2.2.7 NMR

Both proton NMR and carbon NMR spectra were obtained with a Varian 500 MHz superconducting NMR-Spectrometer operating at 499.738 MHz interfaced with a Sun Microsystems Ultra5 UNIX console. The solvent was $CDCl_3$ with single peak at 7.24ppm in proton NMR and triplet at 77ppm in carbon NMR. Standard acquisition parameters were used for the proton spectra and a recycle delay of 2 seconds was used for the carbon spectra.

2.2.8 Molecular weight measurement

Molecular weight distribution of original reactants and final products was measured by Gel permeation chromatography (GPC). The output of a GPC reflects the residence time of a given polymer chain, which is directly related to the molecular weight of the sample. From a GPC output, the number average molecular weight, weight average molecular weight and polydispersity index were calculated in comparison to standards. The polydispersity index (PDI), which indicates the distribution of individual molecular masses in a batch of polymers, is calculated by the weight average molecular weight divided by the number average molecular weight.

2.3 Results and Disscussion

2.3.1 Mechanism of silylated reaction

The reaction between unsaturated soybean oil and the silane with a vinyl group in the presence of peroxide happens at the double bond and vinyl group. There are three possible reaction pathways for this reaction:

1. An Alder – Ene type reaction, where the double bond on the soybean oil acts as the ene and the silane acts as the enophile. The silane is grafted onto the molecular chain of the oil by forming another adjacent double bond.

2. A Diels – Alder type reaction, where conjugated double bonds in the oil react with the silane to form a ring on the molecular chain of the oil. In this reaction pathway, the soybean oil acts as the diene and the silane acts as the dienophile.

3. Peroxide mediated grafting of the silane onto the fatty acid backbone in the oil.

Since the temperatures involved in the present reaction are fairly high, the most possible reaction pathways might be the Alder – Ene reaction and the grafting reaction. The Diels – Alder reaction could have a strong reversal reaction at these temperatures.

The reaction pathways are illustrated as follows.

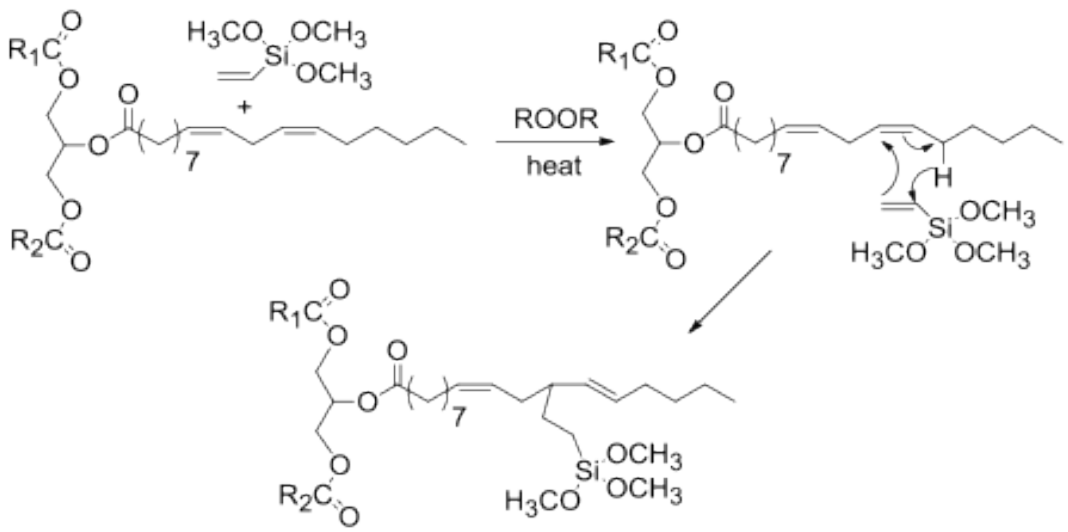

Figure 5 Alder - ENE reaction pathway between VTMOS and soybean oil

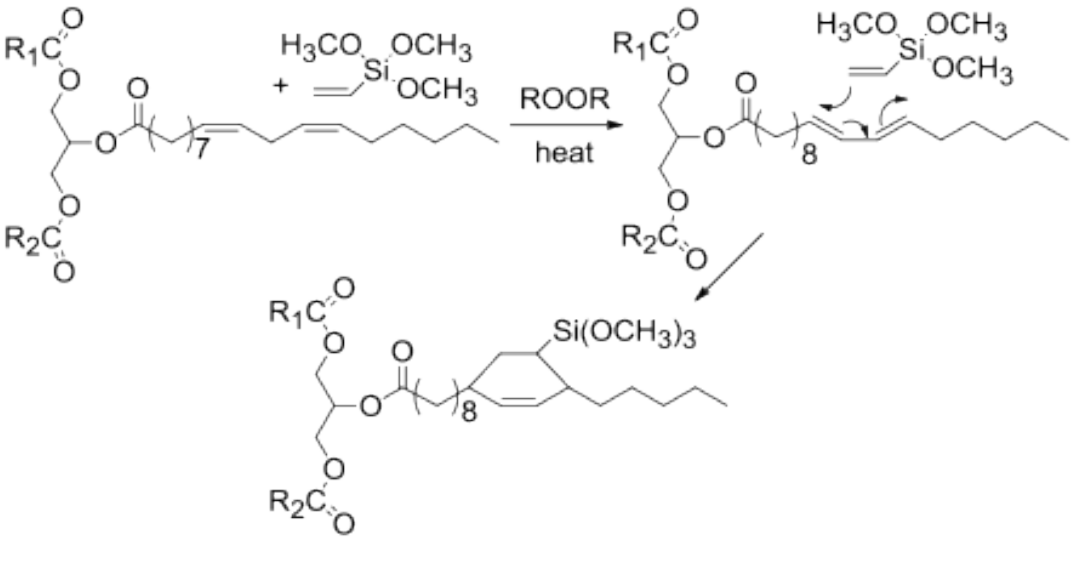

Figure 6 Diels - Alder reaction pathway between VTMOS and soybean oil

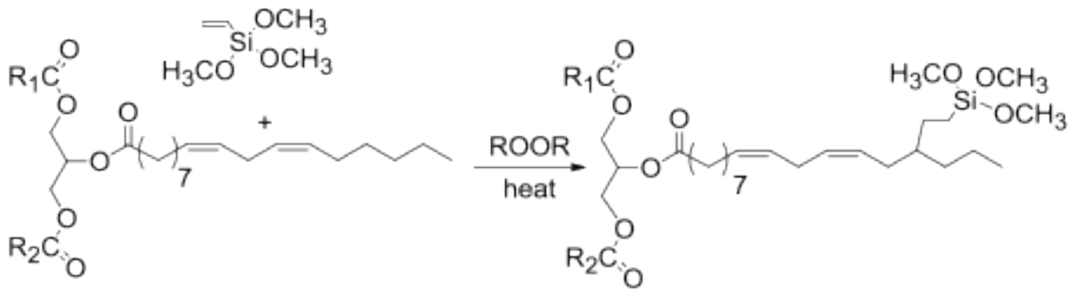

Figure 7 Peroxide mediated grafting pathway between VTMOS and soybean oil

From the above schemes, we can deduce that the Alder – Ene reaction does not affect the number of double bonds on the soybean oil, while the Diels – Alder reaction causes a reduction of one double bond on the vegetable oil chain per grafting. Moreover, Diels – Alder reaction can only happen between conjugated double bonds on soybean oil and vinyl group on silane, and the reaction molar ratio of conjugated double bonds and vinyl group is restricted to 1:1. For peroxide mediated grafting, the number of double bonds on the oil will remain unchanged, which is quite similar to the Alder – Ene reaction.

We can use iodine values to determine which reaction pathway happens between soybean oil and VTMOS, because iodine values will indicate the concentration of double bonds in the products, which could clearly distinguish products from different reaction pathways.

2.3.2 Iodine values of reactants and different reaction products

The iodine values of pure soybean oil, pure VTMOS and products (after removal of unreacted VTMOS) made from different reaction ratios are listed in the

Table 1. Due to the consumption of one double bond on soybean oil chain during the Diels – Alder reaction pathway, the corresponding decrease of iodine value will represent this pathway.

Table 1 Iodine values of original reactants and silylated products

Sample	Content	Sample weight/g	IV	Average IV
1	Pure Soybean Oil	0.17	157.1	154.4
2	Pure Soybean Oil	0.18	151.6	
3	Pure VTMOS	0.24	161.2	160.8
4	Pure VTMOS	0.28	160.3	
5	1:2:1 oil product	0.21	75.5	77.9
6	1:2:1 oil product	0.20	80.3	
7	1:3 oil product	0.23	126.6	127.3
8	1:3 oil product	0.22	128.0	
9	1:7 oil product	0.21	107.7	108.0
10	1:7 oil product	0.21	108.2	
11	Blank	0.00	0.0	

Above data show that the iodine value decreased in the product of soybean oil and VTMOS compared to pure soybean oil. This indicates that a portion of VTMOS did react with soybean oil and graft on the molecular chain of soybean oil, the number of double bonds decreased in the product which caused the change in iodine value. Also, it can be pointed out that most of the products were formed through either the Alder – Ene reaction or the peroxide mediated reaction.

2.3.3 Mass balance and reaction conversion of silylated reaction

From the purification in Chapter 2.2.3, we can calculate the mass balance and grafting percentage of this soybean oil and VTMOS reaction. (Table 2) The weight loss after purification was due to the unreacted VTMOS in this oil product. So the grafting percentage was based on the weight loss.

Table 2 Mass balances and grafting percentages of 1:7, 1:3 and 1:2:1 silylation reactions

Molar ratio of Soybean oil, VTMOS and V-PDMS	Weight before vacuum [g]	Weight after vacuum [g]	Weight loss [g]	Weight of Original VTMOS [g]	Grafting percentage [%]
1:7	866.98	595.35	271.63	481.81	43.62
1:3	1086.03	999.75	86.28	360.39	76.06
1:2:1	937.93	844.49	93.44	177.60	47.39

2.3.4 TGA results of silylated soybean oil products

TGA analysis can be used to confirm the reaction ocurred between soybean oil and VTMOS and V-PDMS, and can be used to determine the conversion of this reaction. Since the boiling point of VTMOS is 123°C, the isotherm stage temperature of TGA test for all these products was set to be 150°C, so that unreacted VTMOS can evaporate sufficiently to give us the correct grafting percentage. Unreacted soybean oil is quite stable under 300°C, thus during the whole TGA test, there should be no weight change due to decomposition of soybean oil.

Gravimetric determination of conversion of silane was calculated by the total amount of silane before reaction divided by the amount of grafted silane after reaction. The amount of grafted silane can be calculated by subtracting the weight loss through

TGA test from the total amount of silane before reaction. 1:3 oil product was applied by this method to calculate the conversion, conversion and later compared with the theoretical expected and the conversion calculated from purification, with excellent agreement.

Pure soybean oil remained unchanged in weight during TGA test. (Figure 8)

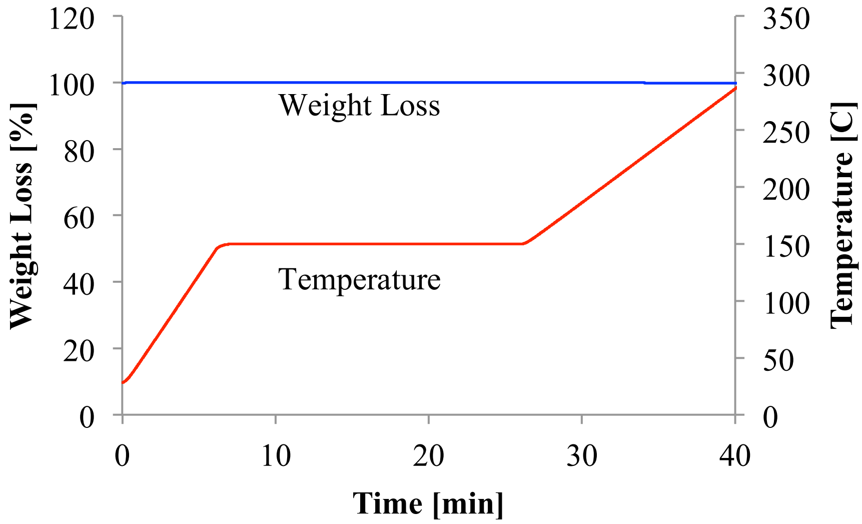

Figure 8 Pure soybean oil TGA weight loss plot

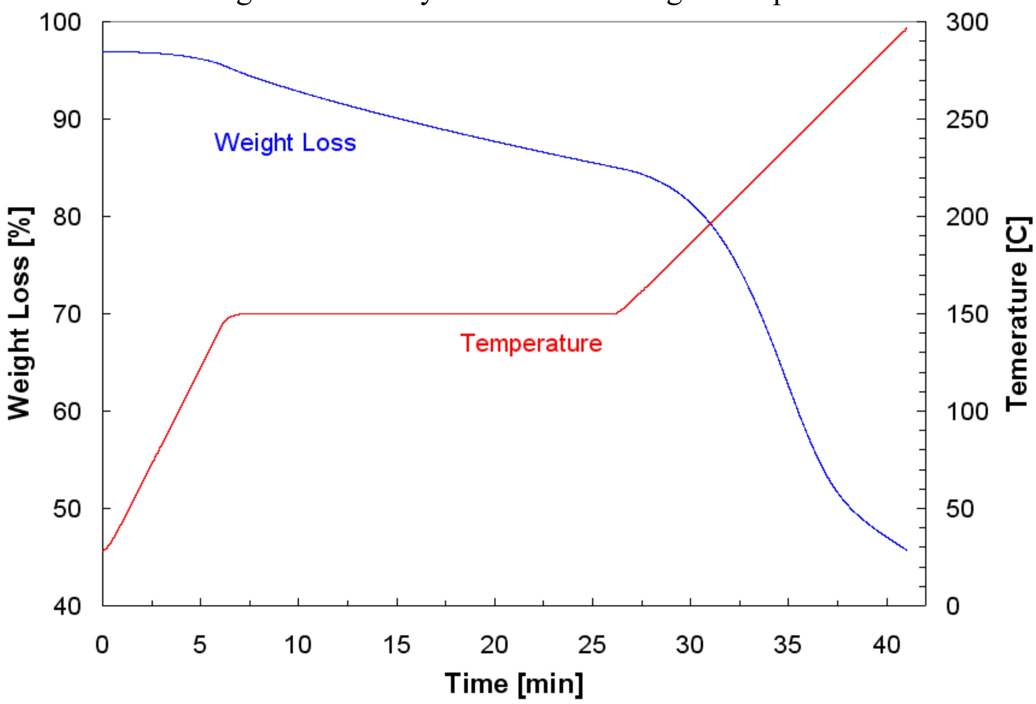

Figure 9 1:3 molar ratio oil product TGA weight loss plot

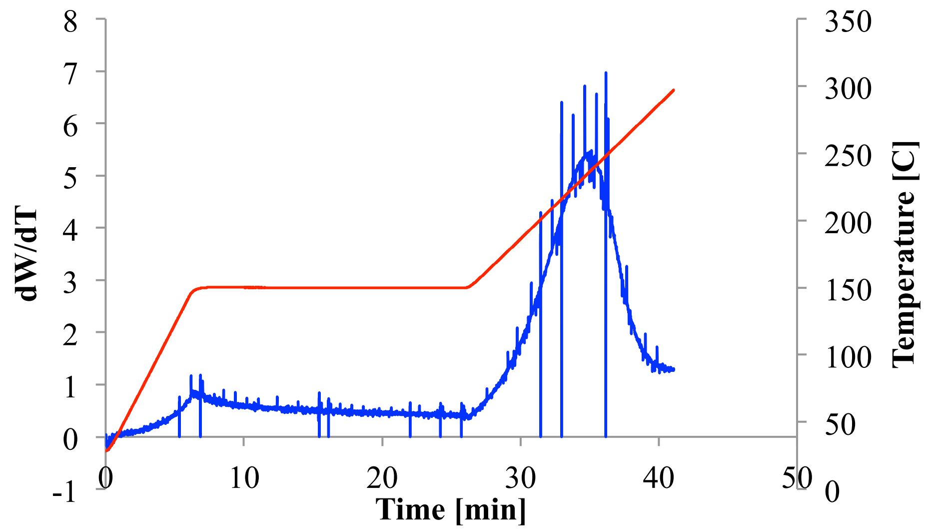

Figure 10 1:3 molar ratio oil product TGA derivative plot

For the 1:3 molar ratio product, the initial weight of testing sample was 15.43mg, and we can calculate that there was 10.22mg of soybean oil and 5.21mg of VTMOS in this mixture before grafting reaction. There were two degradation modes, one was prior to 6.3 min and the other one is after 6.3 min, which can be seen in the derivative plot (Figure 10). Unreacted VTMOS had evaporated even before the isotherm stage, which caused the first degradation. After that, the product itself began to degrade because it has poor temperature stability compared with soybean oil. So the grafted percentage of VTMOS should be calculated at the time of 6.3min and the percentage was 80.32%. Detailed calculations were shown in Table 3.

Table 3 Calculation table of grafting percentage of 1:3 oil product from TGA data

	Soybean Oil	VTMOS	Total weight
MW (1:3 molar ratio)	900	149*3=447	1347
Initial weight before reaction	10.22mg	5.21mg	15.43mg
Final weight after isotherm	10.22mg	4.19mg	14.41mg
Grafted (%)		80.32%	

Compared with 76.06% conversion of grafting calculated by purification, this conversion from TGA is reasonable.

2.3.5 FTIR results of silylated soybean oil products

Oil samples taken during the reaction were examined by FTIR spectrum to confirm the reaction occurred, and to determine the reaction kinetics parameters. The following plot is the FTIR spectrum for 1:3 original reactants (soybean oil and VTMOS blend) and final product after 12 hours reaction. (Figure 11) The red curve is original reactants and the blue curve is final product.

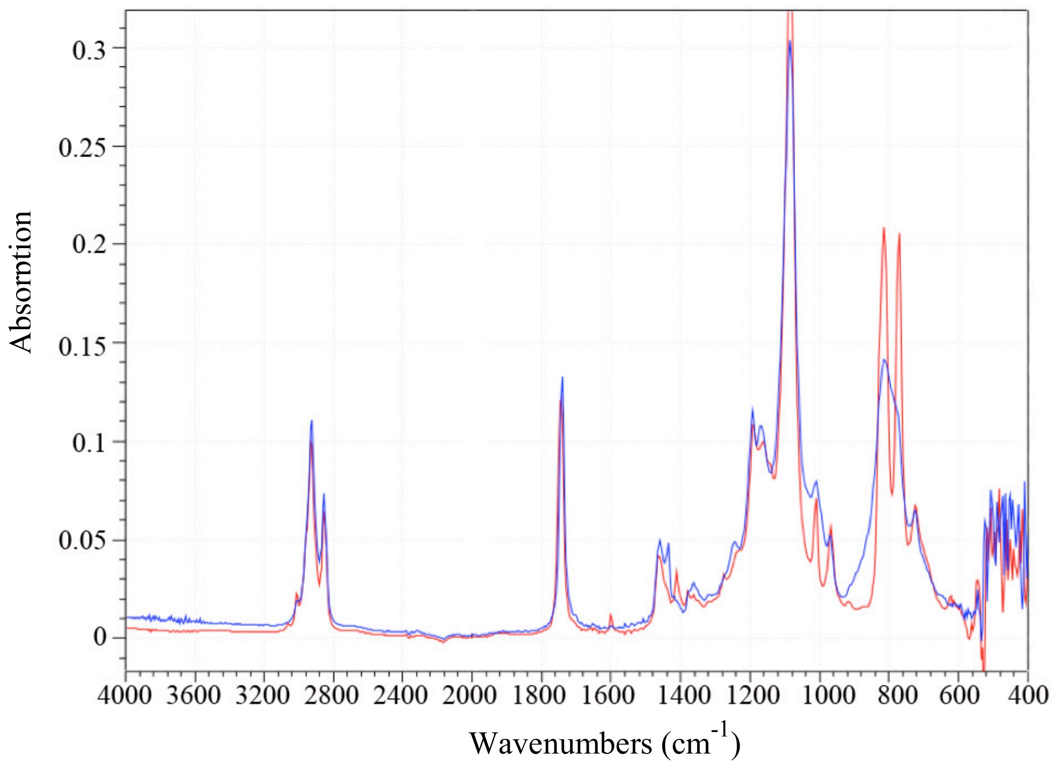

Figure 11 FTIR spectrum for comparison of original reactants (red line) and final oil product (blue line)

The wavenumber range for Si-C bond vibration was 850-650 cm^{-1}, [10] and there was a broad peak around 800 cm^{-1} in the final product while peaks were separated in the original reactants, this could demonstrate that VTMOS was successfully grafted onto soybean oil chain.

Comparing these two samples around the same region, we can see the difference before and after reaction. (Figure 12)

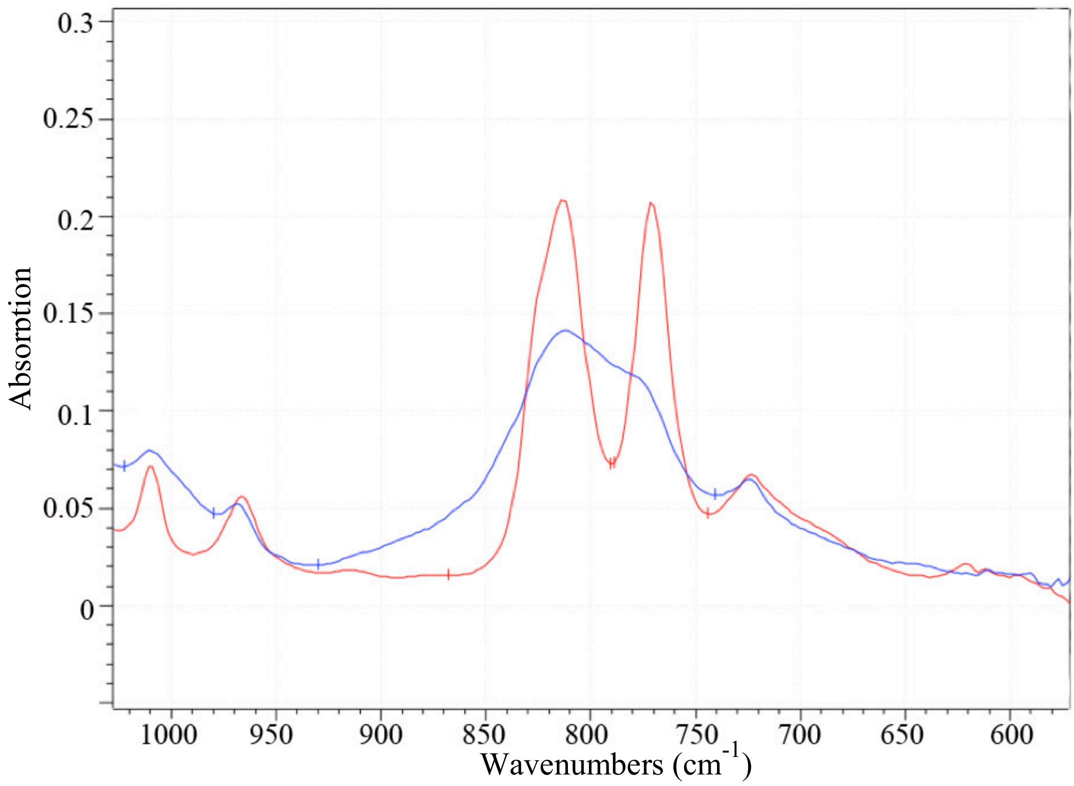

Figure 12 Comparison of FTIR spectrum for original reactants (red line) and final oil product (blue line) around 800 cm^{-1}

The tendency to form this 800 cm^{-1} peak could be monitored by combining the FTIR spectrum of the 9 samples. (Figure 13)

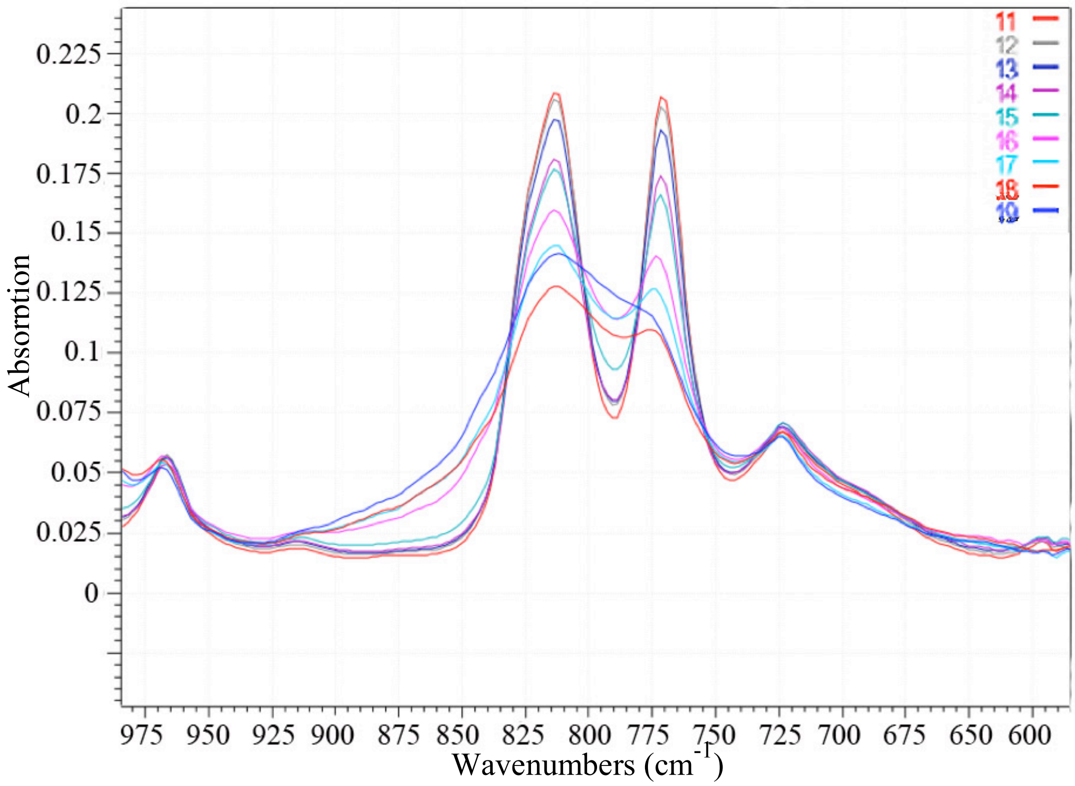

Figure 13 Comparison of FTIR spectrum for all samples taken during reaction

Since the absorption area of each peak is proportional to the content percentage of each bond, by plotting the peak area change vs. reaction time (Figure 14), we could get the kinetic constant and reaction order for this grafting reaction.[11,12]

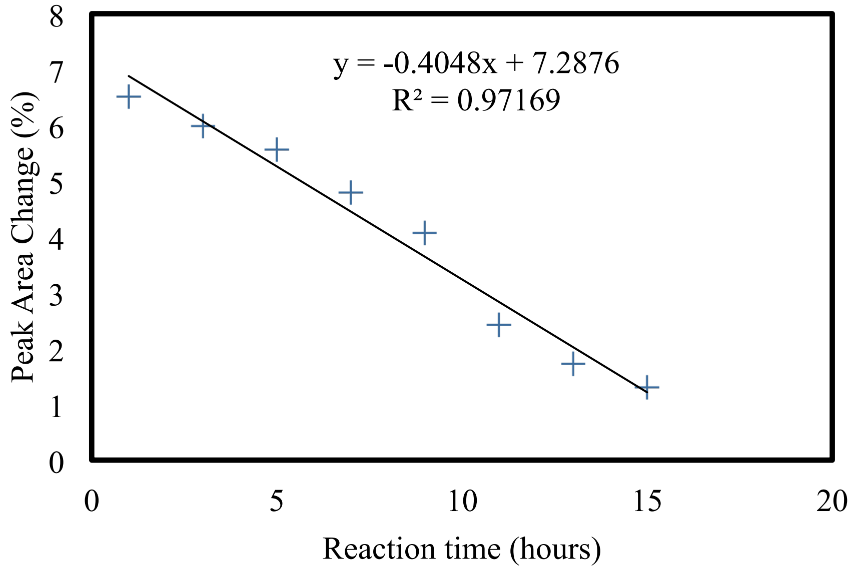

Figure 14 Peak area changes of samples in FTIR v.s. reaction time

so

$$-\frac{dCa}{dt} = -0.404\ Ca + 7.287$$

where Ca is the concentration of original soybean oil in the reaction system.

Compared to the power law model, $-\frac{dCa}{dt} = kCa^{\alpha}$, the order of this reaction is between 0 and 1.

2.3.6 NMR results of silylated soybean oil products

1:3 Oil product was treated under vacuum to remove the unreacted VTMOS and then used as NMR sample. Pure soybean oil was also tested for comparison. (Figure 15) The proton and carbon NMR spectra were provided in Figure 16 and Figure 17. The assignments for the oil have been made from reported literature on fatty acid residues [13-15] and silylated hydrocarbons [16, 17].

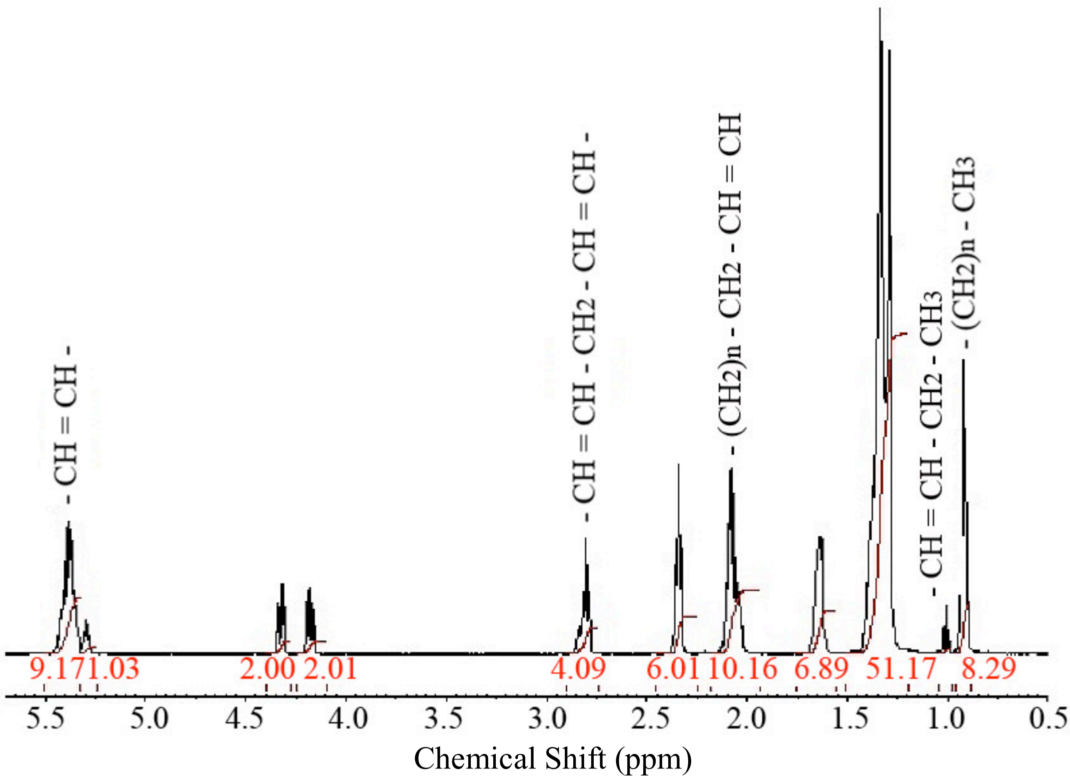

Figure 15 ^{1}H-NMR spectrum of pure soybean oil with peak assignments

Before reaction, there was no significant peak around 3.5 ppm in the proton NMR spectrum of soybean oil, in which area these peaks correspond to the methoxy groups in the structure. After reaction, peaks at 3.55 ppm arise, also the sharp singlet at 3.6 ppm arise, which corresponds to the methoxy group of a methyl ester. This could be the result of small extent of transesterification at the high temperatures used in the reaction. The double bonds in the soybean oil remain unaffected.

The integration in proton NMR of the oil product shows that about 2.5 mole of VTMOS grafted onto soybean oil, which meets the grafted percentage calculations by using TGA and iodine values.

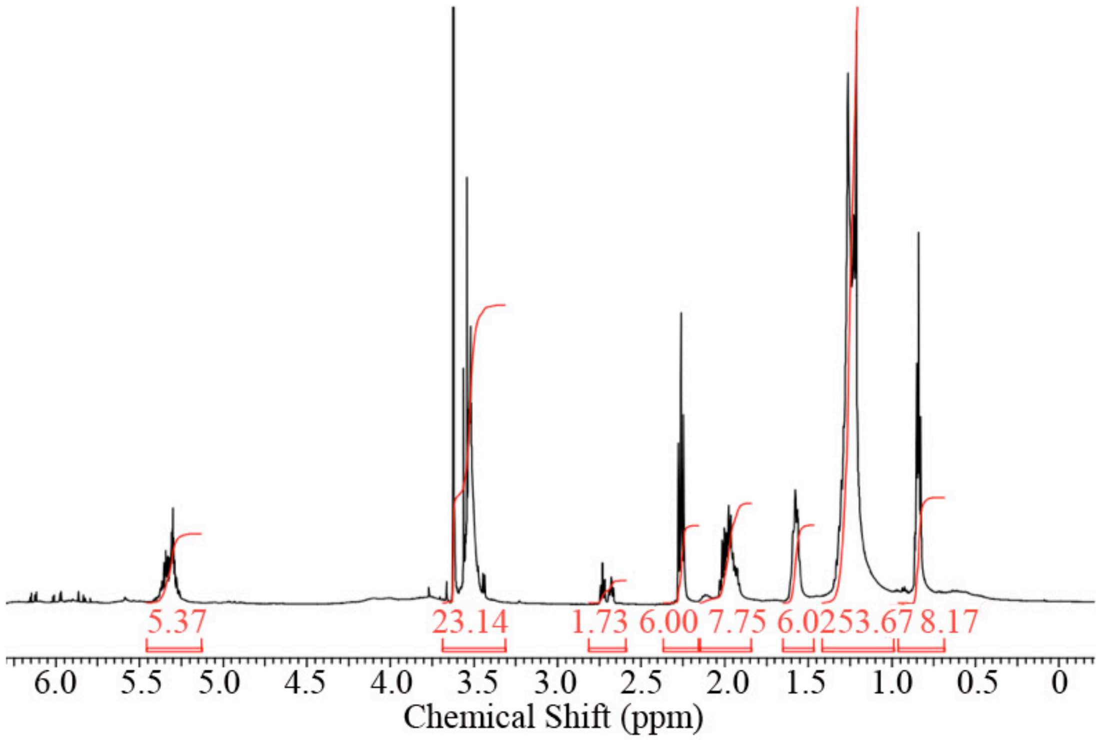

Figure 16 ^{1}H-NMR spectrum of 1:3 oil product with integration

In carbon NMR spectrum of the oil product, Peaks at 50 – 51 ppm are the methoxy peaks of the silane, which indicates that VTMOS has been grafted onto soybean oil chain.

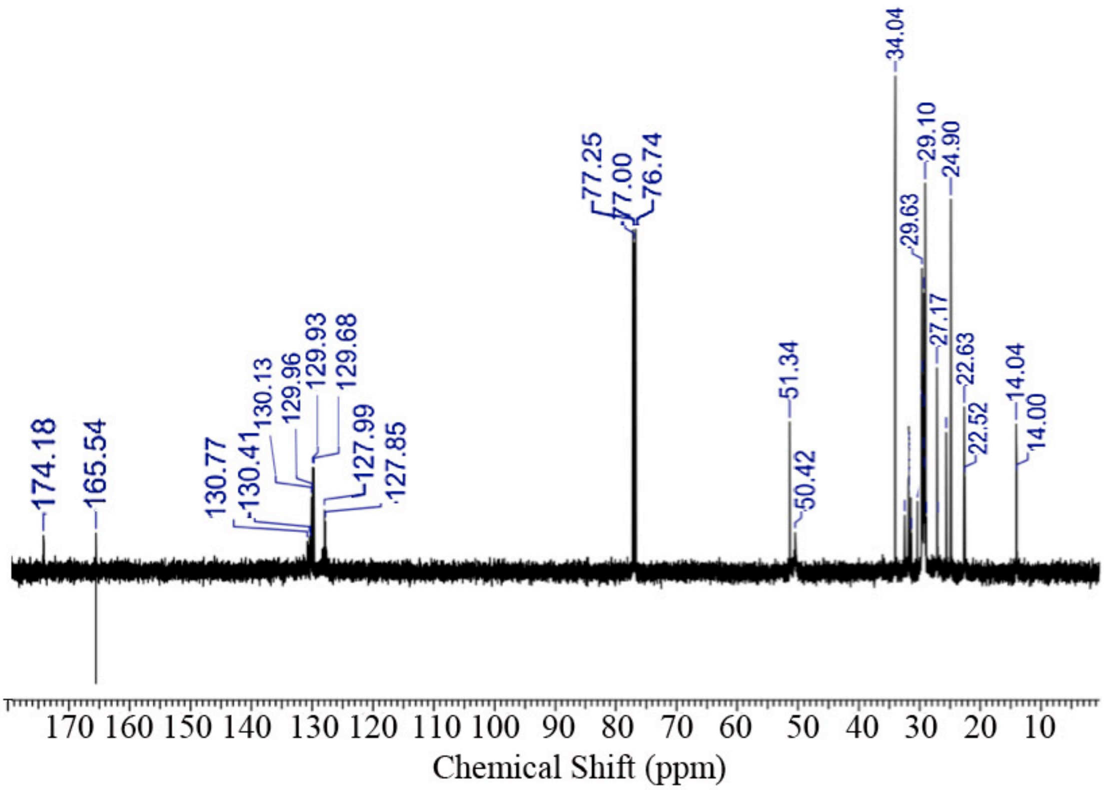

Figure 17 ^{13}C-NMR spectrum of 1:3 oil product

2.3.7 Molecular weight results of silylated soybean oil products

The calculated average molecular weights of 1:3 silylated soybean oil product and pure soybean oil are shown in Table 4.

Table 4 Average molecular weights and PDI of 1:3 oil product and pure soybean oil

Sample	Mn [Da]	Mw [Da]	PDI
Pure soybean oil	735	893	1.21
1:3 oil product	947	6722	7.10

From the data, we can clearly see that after 12 hours reaction, the molecular weight of the oil increased and the PDI broadened. This demonstrates that the VTMOS has grafted onto the soybean oil chain.

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Chapter 3: Coating performance analysis

3.1 Introduction

Vinyltrimethoxy silane (VTMOS) is an organofunctional silane, with the structure $CH_2=CH\text{-}Si(OCH_3)_3$. Hydrolysis (1) and condensation reactions (2,3) can casuse silanes to crosslink and form resins or coatings, and the rates of these reactions depend on temperature, pH and moisture content. [1] The reaction formulas are provided below.

$$CH_2=CH\text{-}Si(OCH_3)_3 + 3H_2O \rightarrow CH_2=CH\text{-}Si(OH)_3 + 3CH_3OH \qquad (1)$$

$$\begin{aligned} &CH_2=CH\text{-}Si(OH)_3 + (OH)_3Si\text{-}CH_2=CH \\ &\rightarrow CH_2=CH\text{-}Si(OH)_2\text{-}O\text{-}(OH)_2Si\text{-}CH_2=CH + H_2O \end{aligned} \qquad (2)$$

$$\begin{aligned} &CH_2=CH\text{-}Si(OH)_3 + (OCH_3)(OH)_2Si\text{-}CH_2=CH \\ &\rightarrow CH_2=CH\text{-}Si(OH)_2\text{-}O\text{-}(OH)_2Si\text{-}CH_2=CH + CH_3OH \end{aligned} \qquad (3)$$

After introduction to the soybean oil chain, VTMOS with methoxy group in its structure will react with moisture in the atmosphere to crosslink and cure the oil product, to form a coating layer on the surface of paper or steel.

The application of silylated soybean oil as a coating material provides be an alternative way to synthesize polymers from bio-based and biodegradable materials. [2] With the advantages of biodegradation and recyclability, coatings made from silylated soybean oil will largely reduce the use of petroleum-based chemicals, providing a more sustainable and environmentally friendly capability.

Moreover, bio-based silylated soybean oil coatings containing fatty acid chain are hydrophobic and have limited liquid water and water vapor barrier properties; it is thus possible to develop further applications incorporating hydrophilic substances such as paper, wood and starch foam to improve the impermeability of these substances. [3]

3.2 Different coating systems of paper coating

The several methods used for paper coating used were; direct oil coating system, a simple emulsion system, an emulsion system with calcium carbonate, and an emulsion system with silica.

Direct oil coating system. Direct oil coating system involves simply applying the oil products obtained from the last synthesis step on paper and curing it to get the coating. However, since the paper readily absorbs the product, it was necessary to increase the viscosity of the oily products to some extent before application to the paper. A certain amount of moisture and cure catalyst (dibutyltin dilaurate, DBTDL) should be added into the oil product to accelerate the crosslinking before application; also some heat could help to increase the viscosity. This step is called the pre-curing step. A typical pre-curing step can be achieved by heating and stirring the oil product for a period of time and mix it with 4 wt % (of oil product) water and 1 wt % (of oil product) of DBTDL catalyst.

Emulsion system. Emulsion system is a mixture of two or more immiscible liquids. [4] It is not like two separate phases, rather it is formed by dispersing liquid droplets with diameter of approximately 1-100 μm into another liquids, to form an emulsion which is stable and uniform under certain conditions. In this project, silylated oil product was dispersed into water by using sonication. First, the oil product was mixed with water (70%) and surfactant (3%) on a weight basis. Then this mixture was stirred well before sonication to ensure that it was exposed to sonication uniformly. Sonication power was kept constant for (5) and the mixture was sonicated for 5 minutes. The pre-curing step was still necessary to increase the viscosity of the coating material to certain extent for application, since the content of water is too high to retain the coating material on the surface of paper before curing. This was done by adding 1 wt% (of oil product) of DBDTL catalyst and heating.

Emulsion with calcium carbonate system. Emulsion with calcium carbonate system was obtained by adding calcium carbonate into the same emulsion made for emulsion system and sonicating for another 5 minutes. Calcium carbonate is widely used in the papermaking industry for whitening and surface effects; also it is a hydrophobic chemical, which could help to improve the water resistant properties. Nano-sized calcium carbonate was used in this system for good dispersibility. The precuring step was the same as the one in emulsion system.

Emulsion with Silica powder system. Emulsion with Silica powder system is 20% solid content emulsion with fine silica powder in it. The emulsion was prepared with 16.7% of oil content and 3.3% of fine silica powder and sonicated for 5 minutes, and this emulsion was pre-cured by the same method as in the emulsion system. Although silica powder is hydrophilic, it has better adhesion to the emulsion coating system than calcium carbonate.

All these pre-cured coating systems were poured onto paper and different wire-wound rods from BYK Instrument Company together with a flat glass board were used to coat the material on the paper by drawing down the rod uniformly and quickly on the paper, thus producing different thicknesses of the coating. The coated paper was cured in an oven for 12 hours at approximately 70°C.

3.3 Coating procedure and curing conditions for paper coating

3.3.1 Pre-curing of oil products

This step is commonly applied for building up the viscosity of oil products to improve surface energy and spread ability on the paper, which enhances the following coating or grafting procedure. [24] 4 wt% (of oil product) of distilled water and 1wt% (of oil product) of DBTDL were added and mixed with the oil product. The mixture was heated at 75°C until the viscosity was almost the same as glycerol. Normally, the heating time was 10 minutes.

3.3.2 Coating

The pre-cured oil product was poured on the beginning edge of paper with adequate amount. The coating apparatus was used to uniformly and quickly draw down the desired coating thickness on the paper.

3.3.3 Curing

The coated paper was left 24 hours at room temperature to absorb moisture from the air for curing, and then placed in the oven at 60°C until fully cured.

3.4 Property Characterization

3.4.1 Water Vapor Transmission Rate Measurement

Water vapor transmission rate is the rate of water vapor which permeates through materials. It is also known as moisture vapor transmission rate (MVTR). The moisture permeability of the substance can be characterized to some extent by measuring WVTR. Since our goal is to synthesize bio-based coating material with water resistant property, low WVTR values for the coating are important.

3.4.1.1 Literature review

At the same time as the "Dow unit" for the permeability coefficient was being created, water vapor barrier was also a topic of interest. The standard method for determination of moisture barrier, commonly termed WVTR or MVTR, was to employ a desiccant to determine, by weight gain, how much moisture got through the barrier and was absorbed by the desiccant. In the experimental setup, the desiccant was on one side of the barrier material (film or package) and the system was exposed to high humidity. As permeation occurred, water vapor passing through the barrier material was absorbed by the desiccant, increasing the weight of the system. It was assumed that the water vapor partial pressure inside the package was constant at 0, so once a steady state transmission rate was reached, the rate was the WVTR of this barrier material. This method is known as "dry cup method". [5]

Nowadays, the more commonly used method to measure WVTR is called "wet cup method". Instead of putting desiccant to maintain 0% reactive humidity (RH), a dish of distilled water is placed on one side of the barrier material to maintain 100%

RH. The driving force of water is the difference between the exterior relative humidity (translated to a partial pressure or concentration) and 100% RH (the internal value). [6]

The units of WVTR is $\frac{g\,mil}{100\,in^2\,day}$. There are two important information in this units. First, the amount of permeation is expressed in terms of mass, rather than in terms of a volume of gas (at STP). It is much less confusing to discuss mass transfer with amounts that are independent of the temperature and pressure at which measurements are made. Second, there is no driving force in the units – no partial pressure difference. Obviously, the amount of water vapor transmission is strongly affected by (in fact is proportional to) the difference in chemical activity (and hence the difference in partial pressure) on the two sides of the material. So, reporting what this is, or calibrating with it, is an essential element. Typically, the users of WVTR report the WVTR value with conditions at which the value was measured. As a result, WVTR values are not compatible even in similar situations and it is necessary to correct for the difference in driving force between the WVTR measurements before comparing these values.

3.4.1.2 Method

This test was done by using the ASTM F1249 as the standard test method, and the equipment for this test was the Mocon Permatran-W from Modern Controls Inc. in the School of Packaging.

The test material was the Kraft paper coated with the silylated soybean oil product, which was made from soybean oil and vinyl trimethylsilane in Chapter 2. Paper with different thicknesses was tested to determine how the thickness of the coating affected transmission rate of the coated paper.

The paper sample was cut to fit the chamber of the test equipment, and humid air was flowed into the chamber to create the designed conditions for this test. Since the paper sample readily absorbed moisture a foil mask method was used to prepare samples. In this method aluminum foil is attached to the test surface of the paper with a certain hole in the centre of the foil to reduce the test area and improve accuracy. In this case, the area of the hole was 3.14 cm^2.

The temperature for this test was set to be 30°C and the humidity of the chamber was about 80% RH. The foil masked side of the paper sample faced the high humidity. There were two chambers, Cell A and Cell B, with the same test conditions for duplication.

The conditioning time for this test was 1 hour, and after that the software collected the data and calculated the transmission rate every half an hour for both cells.

3.4.2 Water contact angle measurement

Water contact angle is the angle measured at the interface of water and solid. It is determined by the interactions of gas, liquid and solid interfaces. Water contact angle can be used to determine whether this surface is hydrophobic or hydrophilic, so it is an important parameter for surface property of a substance.

3.4.2.1 Literature review

Figure 18 is a scheme showing a drop of water over some solid surface.

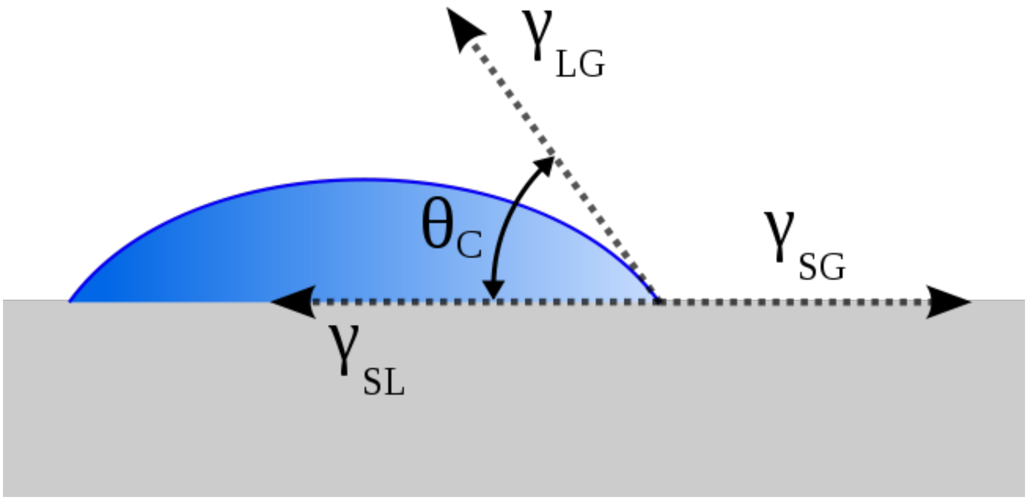

Figure 18 Scheme of the interfacial tensions and water contact angle of a water droplet

The contact angle, θ, is related to interfacial tensions through Young's equation [7]:

$$\Upsilon_{SG} = \Upsilon_{SL} + \Upsilon_{LG} \cos\theta_C \qquad (4)$$

where the subscripts S, G, and L represent the solid phase of the substrate, the gas/vapor phase of the ambient and the liquid phase of the droplet, and θc is the critical contact angle.

When the droplet settles on the solid interface, it instantaneously forms a thermodynamic equilibrium between these three phases. At this equilibrium, the chemical potential in the three phases should be equal, which means the interfacial energies γ of these three phases should be satisfied in the equilibrium equation:

$$0 = \Upsilon_{SG} - \Upsilon_{SL} - \Upsilon_{LG} \cos\theta_C \qquad (5)$$

For hydrophobic materials, θc must be equal or large to 90 degree, and therefore,

$$\Upsilon_{SG} \leq \Upsilon_{SL} + \Upsilon_{LG} \qquad (6)$$

There are several measuring methods to measure water contact angle, and the simplest way is with a goniometer, which allows the user to measure the contact angle visually. A droplet of water is deposited by a syringe pointed vertically down onto the sample surface, and a high resolution camera captures the image, which can then be analyzed either by eye (with a protractor) or using image analysis software.

3.4.2.2 Method

Water contact angle was tested in CMSC lab by using contact angle goniometer. A drop of distilled water was dispersed vertically on the testing coated paper, and an optical subsystem captured the profile of the droplet on the paper. The angle formed between the water/paper interface and the water/vapor interface is the contact angle.

3.4.3 Cobb test

Paper is composed of random fibers; therefore it has a varying degree of porosity. For a paper coating material with water resistant property, it is very important to minimize the ability of fluids, especially water, to penetrate paper.

The Cobb test is used for water absorption rate to determine the paper coating's water resistant property. It measures surface water absorption in 60 seconds, and the procedural standards are explained in TAPPI T 441.[8] The more water absorbed, the larger the Cobb test result the lower the water resistant property of the material.

3.4.3.1 Method

To begin this test the coated paper is first placed on the balance and the weight recorded. 2 milliliters water are added with an eye-dropper. After 2 minutes the excess water is removed by shaking and the paper reweighed. The difference between the initial weight and the final weight is the amount of water that was absorbed through the coating into the paper. To get average results for a coated sheet, 5 different spots for one paper sample need to be tested as duplicate and to determine the uniformity of the coating.

3.4.4 Biodegradability test

Environmental damage by non-biodegradable material is a great concern and is gaining more and more attention. Although recycling could reduce the damage to some extent, it is still restricted to certain plastics or materials. Nowadays, scientists are trying to synthesize materials from renewable, recyclable and degradable resources. [9, 10]

Biodegradable material is a material which can be partially or fully degraded by bacteria or other biological means. Biodegradation can be done either aerobically with oxygen or anaerobically without oxygen. Different environmental conditions, such as soil or aqueous, will also affect the extent of biodegradation.

3.4.4.1 Literature review

As early as 1973, some specific polyesters proved to be biodegradable when disposed in bioactive environments such as soil. Polyesters are water resistant and can be melted and shaped into sheets, bottles, and other products, making certain plastics now available as a biodegradable product. [11]

Later, polyhydroxylalkanoates (PHAs) were produced and used as renewable, biodegradable plastics. Moreover, the physical properties and biodegradability of PHAs can be adjusted by blending with other natural polymers. In the 1980's the company ICI Zeneca commercialized PHAs to be used for the production of shampoo bottles and other cosmetic products. [11]

Nowadays biodegradable technology is highly applied in industry to produce materials for packaging and other disposables. Even plant-based materials, such as starch or soybean oil, are used to process biodegradable materials to minimize waste and toxins. [12]

In nature, different materials have different biodegradation rates. Vegetables and fruits can be fully degraded within 5 days to 1 month. Tree leaves take about 1 year to be fully degraded by bacteria. Plastic bags will take 50 years or even longer to be degraded. It is obviously impossible for scientists to collect biodegradable data for 50 years to know the biodegradability of one material. To make long-term estimates, scientists often use respirometry tests. These tests will collect the amount of CO_2 released from the system to calculate the biodegradability. Since microorganisms digest the sample bit by bit and produce CO_2, the amount of released CO_2 is proportional to the amount of sample digested, which could be an indicator of biodegradation. [13]

3.4.4.2 Method

This test is done by following the ISO/FDIS 14852 “Evaluation of the ultimate aerobic biodegradability of plastic materials in an aqueous medium - Method by analysis of released carbon dioxide”.

The test materials are 1 mil film made by the products of the silylated reactions with molar ratio of 1:2:1, 1:3 and 1:7 of soybean oil and vinyl trimethoxysilane (VTMOS). This film was made by coating the silylated soybean oil products on the Teflon paper and peered off after it was cured. The reference material is cellulose. Both of these two materials are fine powder with the same calculated theoretical amount of carbon dioxide ($ThCO_2$).

The test medium was prepared to be the optimized test medium in this standard. The total volume of the test medium for each sample was 1500 ml. The inoculum for this test was obtained from the sewage water of the water-treatment plant at MSU.

Samples were kept in the incubator room at a constant temperature of 25°C in the dark and were aerated with carbon dioxide free air to maintain aerobic conditions. The flow rate of the air was about 60 ml/min, and a duplicate experiment for each sample flask, control flask and blank flask were made under the same conditions.

The production of carbon dioxide derived from the degradation of the test material was measured, compared to the $ThCO_2$ and recorded as biodegradation percentage. NaOH solution with concentration of 0.2N was made every day to collect the released CO_2 and a standard 0.2N HCl solution was used to titrate the NaOH solution to determine the percentage of biodegradation. The interval of measure was 24 hours.

The activity of the inoculums was checked and measured by the same method for the controlled flask and the blank flask. The process of biodegradation is shown in a curve where carbon dioxide production or biodegradation percentage is plotted as a function of time.

3.5 Results and discussion

3.5.1 Coating performances

Four different coating systems were applied for paper coating on two different paper types provided by Wausau Company. Thus, a total of 10 samples were made for the study of coating performance and property characterization. The information of each sample is shown in Table 5.

The coating procedure and cure conditions were the same for all the samples, and the thickness of coating was 1 mil. Sample 1-4 were made by using 1:3 silylated soybean oil product, and sample 5-8 were made by using 1:2:1 silylated soybean oil product.

The reasons for not using 1:7 silylated oil product for coating application and tests are: 1) purified 1:7 oil product, compared to 1:3 oil product, requires a little more time (2-3 minutes) to cure after added the DBTDL catalyst; 2) the coating from 1:7 oil product was more brittle, because there was more crosslinking between grafted VTMOS and soybean oil due to the excess VTMOS during the reaction; 3) VTMOS is relatively expensive when compared to soybean oil, also the conversion of 1:7 reaction is much lower than that of 1:3 reaction. Hence the 1:3 silylated soybean oil product is less expensive with better performance.

Table 5 Paper coating samples information

Sample #	Paper #	Coating system
1	GN354872	Direct Oil Coating
2	GN353070	Direct Oil Coating
3	GN354872	Emulsion System
4	GN353070	Emulsion System
5	GN354872	Emulsion System with Calcium carbonate
6	GN353070	Emulsion System with Calcium carbonate
7	GN354872	Emulsion System with Silica
8	GN353070	Emulsion System with Silica
9	GN354872	Original paper without coating
10	GN353070	Original paper without coating

For oil product itself, all of these three reactions gave us a uniform stable oily product with pale yellow color, and the viscosity for each product was quite similar to soybean oil.

When applied to coat on the paper or panels, 1:2:1 oil product took much more time in the pre-curing period to build up to required viscosity, and took much more time for curing. This is because 1:2:1 oil product was made from V-PDMS which has long Si-O-Si linkages, when grafted onto soybean oil chain and crosslinked, these linkages have no functional groups to be reacted or crosslinked to be bonded on the coated substance. Normally, the time of curing for this oil product in direct coating system is twice than the time for 1:3 oil product. But this long curing time could provide us more time to apply these materials on paper to coat.

By certain coating procedures, all of the four coating systems were successfully applied on paper to form a uniform and adhesive coating. Emulsion with calcium carbonate system has the lowest adhesion to coated paper, for calcium carbonate particles were not stable in emulsion system, so at the curing step, it precipitated from the emulsion layer to form a layer of powder on the top of coating. For panels, direct oil coating system was the only possible coating system, since other systems contain too much water which affects the spread of coating material on panels.

3.5.2 WVTR results

Both 1:3 and 1:2:1 silylated soybean oil product coating samples were tested at 30°C, 80% RH chamber.

One set of samples were made from 1:3 silylated soybean oil product, and different coating thicknesses of samples were tested. The coating system was direct oil coating system, and the paper was the same which is DOD Kraft paper. The results of WVTR for this set of samples are listed below. (Table 6)

Table 6 WVTR results of coating samples made from 1:3 oil product with different coating thickness

Thickness of the coating (mil)	Cell A	Cell B	Average
2	68.609*	68.423	68.516
1	917.844	474.914	696.379
0.5	1147.835	1163.720	1155.778
0	1439.260	>1600	1439.260

*The unit for the values of WVTR is gmil/(100in^2*day)

Compared with original paper without coating (thickness of coating is 0), silylated soybean oil coating could obviously limit the permeation of water vapor, which to some extent enhanced the water resistant property of the paper.

Along with the increase of coating thickness, the transmission rate dropped significantly. This indicates that the water resistant property of paper is proportional to the coating thickness. When thicker coating is applied to paper, it forms more complicated and intensive crosslinked networks on the surface of the paper. These networks formed by fatty acid chains, which is hydrophobic, will largely narrow the original porosity of the paper and help to prevent the water vapor to permeating the paper.

Another set of samples was made from 1:2:1 silylated soybean oil, and this set of samples was coated using different coating systems. The thickness of the coating was 1 mil for all the samples, and the paper used was Paper# GN354872 from Wausau Company. The results of this set are shown in the following table. (Table 7)

Table 7 WVTR results of coating samples made from 1:2:1 oil product with different coating systems

Coating System	Cell A	Cell B	Average
Direct oil coating system	508.745*	485.190	496.968
Emulsion system	1146.108	1144.105	1145.107
Emulsion with calcium carbonate system	197.619	193.572	195.596
Emulsion with silica system	>1600	>1600	>1600
Original paper	>1600	>1600	>1600

*The unit for the values of WVTR is $gm/(100in^2*day)$

Since the original paper sample is very thin and has large porosity, the test failed because the WVTR result is higher than 1600 gm/(100in^2*day). Emulsion with calcium carbonate system shows the best water resistant property, for calcium carbonate precipitate at the top layer of the coating, and calcium carbonate is super hydrophobic, which results a significant decrease of WVTR. Contrarily, the emulsion with silica system does not improve much in water resistance, for silica on the top layer of coating is hydrophilic, which cannot form a barrier to prevent water vapor going through. The emulsion system does not limit the transmission as much as direct oil coating system, for the concentration of crosslinked fatty acid chain in the emulsion system is much lower than the direct oil coating system. When applied onto paper, the number of fatty acid chains per unit area in emulsion coating is not as large as that in the direct coating system. In the last set of tests, the WVTR results is related to the coating thickness, which is the number of fatty acid chain per unit area, that is why the emulsion system shows less enhancement in water resistant property.

3.5.3 Water contact angle results

1 mil paper coatings with different coating systems were measured the water contact angle, and the results are shown in Table 8.

Water contact angle indicates whether a surface is hydrophobic or hydrophilic, and the cut-off point is 90 degrees. Original paper GN354872 is the paper made without any additives, and original paper GN353070 is the paper with certain hydrophobic modifications.

Table 8 Water contact angle of 1 mil paper coatings with different coating systems

Sample #	Paper #	Molar ratio of silylated soybean oil product	Coating system	Water Contact Angle (Left/Right) [°]
1	GN354872	1:3	Direct Oil Coating	96.3/96.7
2	GN353070	1:3	Direct Oil Coating	104.2/103.0
3	GN354872	1:3	Emulsion System	49.3/47.5
4	GN353070	1:3	Emulsion System	40.0/39.3
5	GN354872	1:2:1	Emulsion System with Calcium Carbonate	105.3/106.5
6	GN353070	1:2:1	Emulsion System with Calcium Carbonate	116.2/114.0
7	GN354872	1:2:1	Emulsion System with Silica	124.3/123.7
8	GN353070	1:2:1	Emulsion System with Silica	121.0/119.8
9	GN354872	-	Original paper without coating	84.7/81.3
10	GN353070	-	Original paper without coating	95.7/93.7

The largest water contact angle shows in the emulsion with silica system. In this system, emulsion provides hydrophobic property to the paper, and silica powder plays the role of smoothing the surface. Surface roughness will affect water contact angle of the surface. Wang et al [14] found out that along with the increase of surface roughness, the advancing contact angle increases and the receding contact angle decreases, which hence increases the hysteresis. When contact angle is smaller than 90 degrees, increasing roughness will decrease the contact angle, and when the contact angle is larger than 90 degrees, increasing roughness will increase the contact angle. In this case, silica reduced surface roughness, thus after coating, paper GN354872 had larger contact angle than paper GN353070. In emulsion with calcium carbonate system, the situation is contrary, since calcium carbonate increased surface roughness of the paper.

Direct oil coating and emulsion with calcium carbonate systems have water contact angles larger than 90 degrees, which could be considered to have good water resistant property. For emulsion with silica system, although the water contact angle was large in this system, compared with WVTR test results, it cannot maintain this hydrophobic property for a long time, which is a severe shortcoming for water resistant coating materials.

3.5.4 Cobb test results

1 mil paper samples that coated with different coating systems were measured the water absorption rate by Cobb test, and the testing samples' information and results are in Table 9. The testing area was 100 cm^2 for each sample, and the absorption lasted for 2 minutes. Since the water absorption is expressed in g/m^2, we can calculate the absorption by using the weight gain.

$$\begin{aligned} water\ absorption &= \frac{average\ weight\ gain\ of\ each\ sample}{100cm^2} \\ &= \frac{average\ weight\ gain\ of\ each\ sample}{100\,cm^2} \times \frac{10000\,cm^2}{1\,m^2} \\ &= 100 \times average\ weight\ gain\ of\ each\ sample\ g\,/\,m^2 \end{aligned} \tag{7}$$

Table 9 Cobb test results of 1 mil paper coatings with different coating systems

Sample #	Paper #	Molar ratio of silylated soybean oil product	Coating system	Average weight gain [g]	Water absorption [g/m^2]
1	GN354872	1:3	Direct Oil Coating	0.009	0.9
2	GN353070	1:3	Direct Oil Coating	0.018	1.8
3	GN354872	1:3	Emulsion System	0.024	2.4
4	GN353070	1:3	Emulsion System	0.109	10.9
5	GN354872	1:2:1	Emulsion System with Calcium carbonate	0.009	0.9
6	GN353070	1:2:1	Emulsion System with Calcium carbonate	0.011	1.1
7	GN354872	1:2:1	Emulsion System with Silica	0.040	4.0
8	GN353070	1:2:1	Emulsion System with Silica	0.041	4.1
9	GN354872	-	Original paper without coating	0.214	21.4
10	GN353070	-	Original paper without coating	0.039	3.9

From this test results, all the coating systems helped to improve at least 81.31% of the water resistant property of the original paper GN354872, for the original paper GN353070, the improvement percentage was 30% by coated with direct oil coating system and emulsion with calcium carbonate systems. There was no significant difference between original paper GN353070 and paper coated with emulsion with silica system, this was because there were already some water resistant additives added into this paper during paper making, which enables this kind of original paper basic water resistant property even without coating. Among these coating systems, the direct coating and the emulsion with calcium carbonate gave the best water resistance for both two kinds of paper, because the former one has sufficient fatty acid chain crosslinked network to prevent water absorption, the later one has calcium carbonate layer on the top of the coating to provide hydrophobic property.

However, the direct coating was very likely to go through the paper to make the paper transparent, and the calcium carbonate had no bonding to the polymer coating layer, which obstructs applications of these two coating systems.

3.5.5 Biodegradability test results

Soybean oil is known as fully biodegradable material, while silanes are very difficult to be degraded due to Si-O bond. The biodegradability of films made with different molar ratios of soybean oil was tested for both VTMOS and V-PDMS by following the ISO/FDIS 14852 standard. The figures below show the biodegradability results of different silylated soybean oil samples.

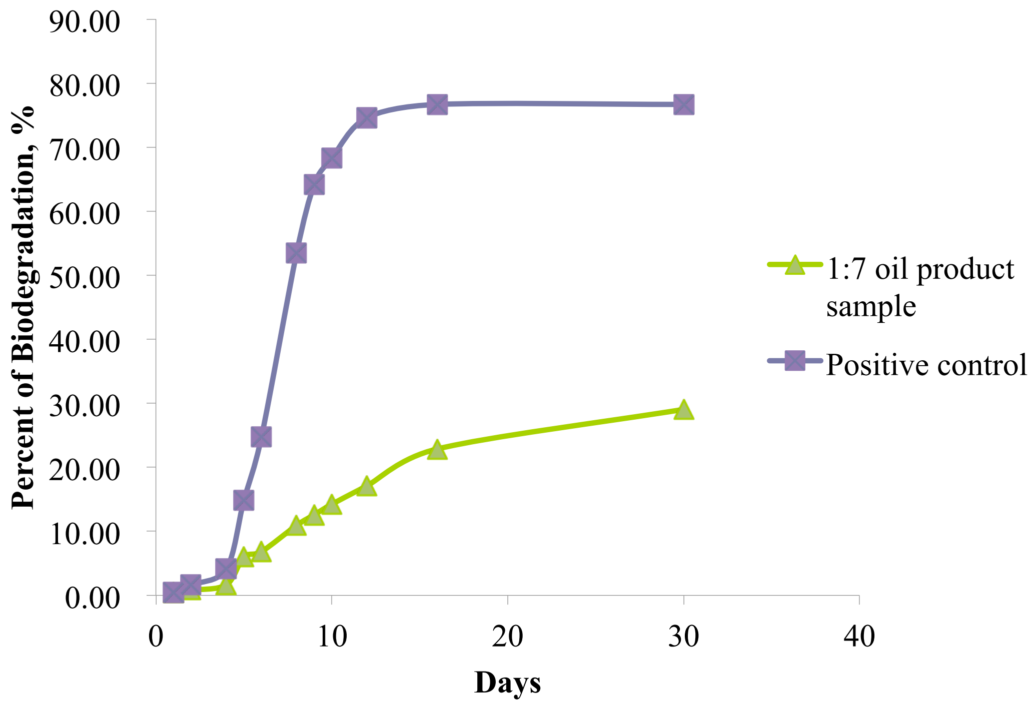

Figure 19 1:7 silylated soybean oil product film biodegradability plot

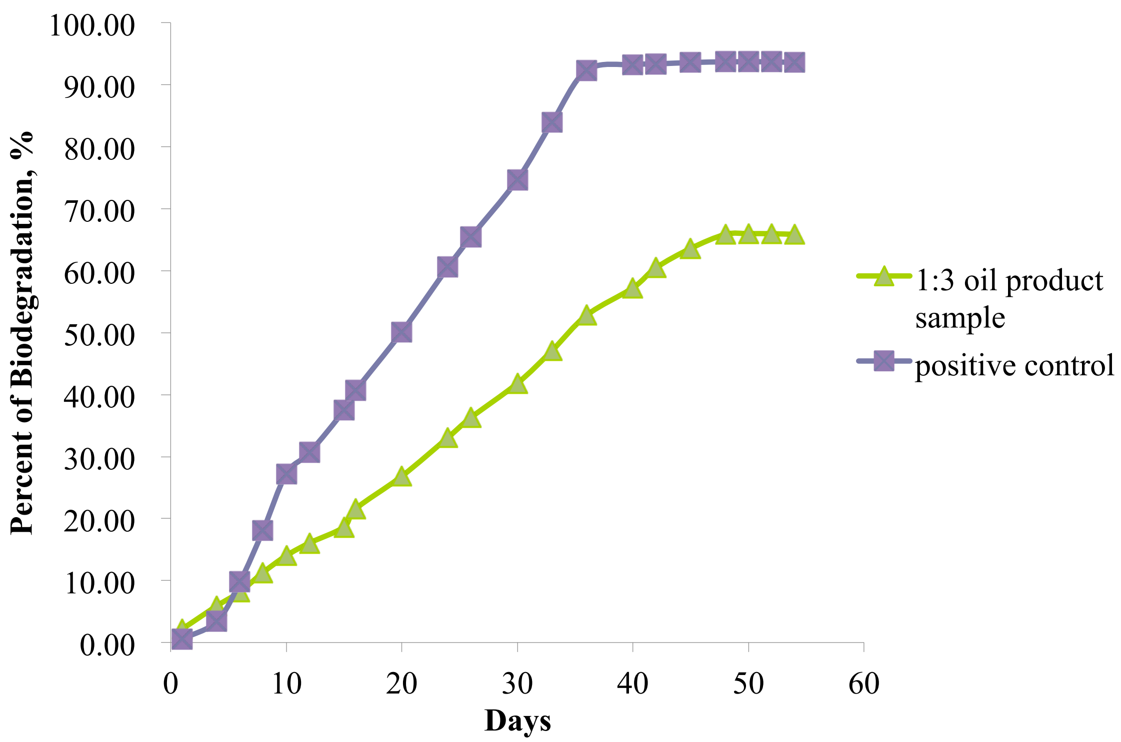

Figure 20 1:3 silylated soybean oil product film biodegradability plot

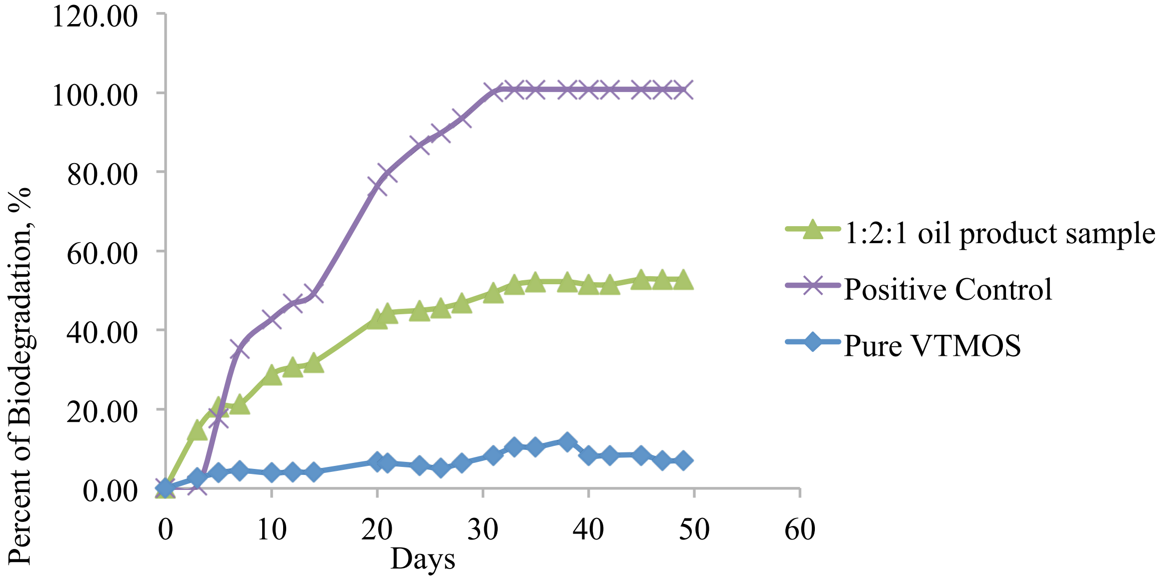

Figure 21 1:2:1 silylated soybean oil product film and pure VTMOS film biodegradability plot

The biodegradation of 1:7 oil product after 30 days was around 29%, compared to 76% biodegradation of the positive control. The biodegradability of 1:3 oil product was 65.85% after 55 days, compared to the biodegradability of 93.58% of cellulose. For 1:2:1 oil product, the biodegradability percent is about 52.86% after 49 days, while the biodegradability of pure VTMOS sample is about 8%, compared to 100% biodegradability of cellulose.

All these three silylated soybean oil can be considered as partially biodegradable materials, which is environmentally friendly and helpful to prevent environmental damage.

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Chapter 4: Alternative reactants to synthesize coating material

Silylated soybean oil coating material has two important parts that enable it to be a water resistant coating material. One is the long fatty acid chain from soybean oil, moreover there are double bonds on this chain which could be reacted with silane or siloxane for later crosslinking or curing of this material. The other part is multiple methoxy groups of the silane, these methoxy groups could hydrolyze to form silanol groups and then dehydrate to crosslink.

Based on this theory, alternative reactants with unsaturated structure and long fatty acid chains could be used to replace the soybean oil to synthesize coating materials, also different kinds of methoxysilane or ethoxysilane could be applied in this reaction.

4.1 Synthesis of methyl oleate and vinyl trimethoxy silane adduct

Methyl oleate is a C18 fatty acid ester with one double bond at C9. It is derived from soy feedstocks and is a primary fatty acid methyl ester in biodiesel fuel. [1]

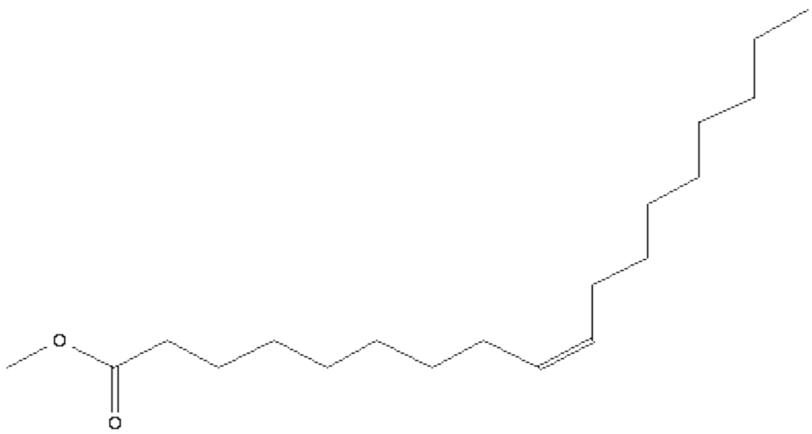

Figure 22 Methyl Oleate molecular structure

Due to the unsaturated structure, methyl oleate can be epoxidized to form methyl epoxy stearate, which plays an important role as an intermediate in the production of a wide series of important industrial products and materials such as lubricants, plasticizers in polymers, pharmaceuticals and biofuel additives. [2, 3] Guidotti et al. [4] synthesized titanium-silica catalysts from titanocene dichloride and mesoporous silica, and then used this catalyst in epoxidation of methyl oleate. Results showed that this catalyst was sustainable and efficient, and high yields of desired methyl epoxystearate were achieved.

Oxidation of methyl oleate is also a hot topic in research and industry. Methyl oleate, the main component in rapeseed biodiesel fuel, has high reactivity, which could make biofuel unstable during the use. Thus, using an oxidation reaction to convert methyl oleate into methyl stearate is of great importance. Bax et al. [5] studied the oxidation of methyl oleate in a fused silica jet-stirred reactor with reaction temperatures from 550 to 1000 K, and pressure of 106KPa. Reaction products were analyzed by gas chromatography coupled with mass spectrometer. This presents a new experimental method for the oxidation of methyl oleate.

With unsaturated structure, methyl oleate has the similar reaction functional group as soybean oil, and we could design the reaction between methyl oleate and silane to yield coating materials.

4.1.1 Experimental

4.1.1.1 Materials

97% purity vinyltrimethoxy silane (VTMOS) [CAS 2768-02-7] was obtained from Gelest Inc., Morrisville, PA. 70% purity of methyl oleate [CAS112-62-9], Luperox 101 (L101) [CAS 78-63-7]-2, 5-Bis (tert-butylperoxy)-2, 5-dimethylhexane (90% technical grade) used as the peroxide catalyst was obtained from Sigma Aldrich, St. Louis, MO. All the reagents were used as received without further purification.

4.1.1.2 Synthesis of methyl oleate and vinyl trimethoxy silane adduct

Methyl oleate was mixed with VTMOS at the molar ratio of 1:5, L101 was added at 1 wt% of methyl oleate as the peroxide initiator. The mixture was then poured into a 2L Parr reactor produced by Parr Instrument Company. An external controller was used to set and control the temperature of the reactor. Reaction temperature was set from 180°C to 260°C with 20°C increments. The stirrer was maintenined at 200 rpm to mix the reactants and to ensure uniform heating.

Prior to the reaction, nitrogen was purged into the cylinder of the Parr reactor for about 2 minutes to eliminate air. A high heating rate was chosen for the early period of heating stage, and then switched to low heating rate when the temperature reached 70% of the final value. The reaction time started when the temperature reached the set point and lasted for 8 hours.

4.1.2 Characterization

The final product of the reaction was a mixture of silylated methyl oleate, unreacted silane, and unreacted oil. To calculate the reacted VTMOS percentage and reaction conversion, gravimetric determination by distillation under reduced pressure was used to remove unreacted VTMOS from the oil products. A large three-neck flask was used as the container to hold the entire product. The middle outlet was connected with a vacuum, another outlet was equipped with a thermometer, and the third closed with a hollow plug. A magnetic stirrer was used to completely drive out volatile VTMOS. The silylated methyl oleate product was purified at 110°C with the vacuum of about 0.3 Torr for 1 hour, or until no further distillate was generated. The unreacted VTMOS was trapped with two dry ice and acetone traps and weighed.

The iodine values of silylated methyl oleate products were measured according to ASTM D1959. Both the products after purification and pure methyl oleate used in this reaction were measured to compare the change before and after reaction. Sample weights were calculated using the conversion obtained earlier and assuming that there was no change in the number of double bonds of the oil.

4.1.3 Results and discussion

4.1.3.1 Gravimetric determination and conversion calculation

From the gravimetric determination, the mass balance and grafting percentage of this methyl oleate and VTMOS reaction can be calculated. The weight loss after distillation was due to the unreacted VTMOS in this oil product. Thus the grafting percentage was based on the weight loss. (Table 10)

Table 10 Mass balances and grafting percentages of 1:5 silylation reaction at different reaction temperature

Reaction Temperature [°C]	Weight before vacuum [g]	Weight after vacuum [g]	Weight loss [g]	Weight of Original VTMOS [g]	Grafting percentage [%]
180	936.54	384.24	552.30	667.03	17.20
200	939.68	409.82	529.86	669.27	20.83
220	937.93	462.83	475.10	668.02	28.88
240	932.59	555.31	377.28	664.22	43.20
260	947.60	685.74	261.86	674.91	61.22

The grafting percentage of VTMOS and the conversion of this reaction increases with the increase of reaction temperature. This indicates that the silylation can be controlled by adjusting reaction temperature.

4.1.3.2 Iodine values

The iodine values of pure methyl oleate, pure VTMOS and products (after distillation of unreacted VTMOS) made from different reaction temperatures are listed in the Table 11.

Compared with soybean oil (IV=154.4 in Chapter 2.3.2), the iodine values of products are not reduced significantly to the pure methyl oleate. This can be explained by the low reactivity of double bond in methyl oleate. Moreover, these iodine values suggest that most of the silylation of methyl oleate occurred through peroxide grafting route.

Table 11 Iodine values of silylated oil products, pure methyl oleate and pure VTMOS

Sample	Content	sample weight/g	IV	Average IV
1	Pure Methyl Oleate	0.36	83.5	85.7
2	Pure Methyl Oleate	0.36	87.8	
3	Pure VTMOS	0.24	161.2	160.8
4	Pure VTMOS	0.28	160.3	
5	180°C reaction product	0.46	70.3	69.1
6	180°C reaction product	0.47	67.8	
7	200°C reaction product	0.54	63.5	63.1
8	200°C reaction product	0.55	62.8	
9	220°C reaction product	0.55	59.3	59.3
10	220°C reaction product	0.55	59.3	
11	240°C reaction product	0.53	51.7	52.1
12	240°C reaction product	0.52	52.5	
13	260°C reaction product	0.52	42.5	44.7
14	260°C reaction product	0.52	46.9	
15	Blank	0.0	0.0	

4.2 Synthesis of epoxidized soybean oil and amino silane adduct

Soybean oil is derived from the second largest crop in the US. [6] The unsaturated fatty acid chain in soybean oil enables soybean oil to be introduced with functional groups to modify its properties. Epoxidized soybean oil is made from modification of soybean oil with epoxy groups. These epoxidized derivatives can be used in various applications as stabilizers and plasticizers in polymers, as additives in lubricants, or as components in plastics. [7, 8] Epoxidized soybean oil can also be converted into polyols to synthesize polyurethane. [9] Liu et al. [10] polymerized epoxidized soybean oil with the presence of BF_3OEt_2 as catalyst. Polymerized epoxidized soybean oil was found to have high crosslinked networks, and the glass transition temperature of this polymer ranged from -16°C to -48°C.

Amino silane is a chemical with the general formula $(X)_3SiY$, where X is an alkoxy ($–OCH_3$ or $–OCH_2CH_3$) or halogen (–Cl) ligand and Y is an organofunctional group (aminopropyl, methacryloxy, glycidoxy, vinyl, etc.). [11] With these two functional groups, amino silane could easily hydrolyze in the presence of moisture, also could be used to make polyurethane. There are mono-, di-, and tri-aminosilanes with different properties and usage. With the ability to hydrolyze and to condense to crosslink, tri-aminosilane was chosen in this reaction to synthesize coating materials.

4.2.1 Experimental

4.2.1.1 Materials

Epoxidized soybean oil DRAPEX 6.8 from Galata Chemicals, Southbury, CT. 3-(aminopropyl)tri-ethoxysilane ($NH_2(CH_2)_3Si(OEt)_3$) [CAS 919-30-2] was obtained from Gelest Inc., Morrisville, PA. All the reagents were used as received without any further purification.

4.2.1.2 Synthesis of epoxidized soybean oil and $NH_2(CH_2)_3Si(OEt)_3$ adduct

The reaction molar ratio was planned to be 1:1 of amino group to epoxy group, since the epoxy value of this epoxidized soybean oil was 7.1, the molar ratio of raw epoxidized soybean oil vs amino silane should be 1:7.1. According to this, 13.75 gram of epoxidized soybean oil was mixed with 215.76 grams of $NH_2(CH_2)_3Si(OEt)_3$ in a dry flask. The reaction between these two reactants was fast and exothermic, thus the reaction conditions were simply to stir the mixture overnight under dry conditions at room temperature. Prior to the reaction, nitrogen gas was purged into the flask to eliminate air in the system.

4.2.1.3 Coating application with silylated epoxidized soybean oil

Pretreatment of the steel panels. 3M™ Scotch-Brite™ Hand Pads and cleaner from NTIC were used to scrub the panels and remove the oxidized surface. The panels were scrubbed four times in each direction for 10 seconds or more to generate rich foam on the panel. This was repeated after 5 minutes. The panel was washed with deionized water, dried with a paper towel, and dried in the oven for 5-10 minutes at 60°C. The panels were then cooled to room temperature.

Prepare the coated oil product. Since the oil was used to coat the panels, it was not necessary to add water. The oil product was mixed with 1 wt% of dibutyltin dilaurate (DBTDL) at room temperature, and stirred for 5 minutes.

Coat the panels. The coating instrument was used to coat the panel and obtain a uniform and rapid draw down. The thickness of the coating was 5 mil.

Coat the PE films. Cut the film to size and use the wired rod to draw oil product on the film to form a uniform coating. The thickness of the coating was 2 mil.

Cure. Leave the coated panel at room temperature to absorb moisture in the air for curing, and then place the panel into oven at 60°C until fully cured.

4.2.2 Charaterization

4.2.2.1 FTIR

Infrared spectra were obtained with a PerkinElmer 2000 FTIR spectrometer. Each spectrum was obtained with at least 16 scans to ensure a high signal-to-noise ratio. The wavelength range was between 4000 cm^{-1} to 450 cm^{-1}.

4.2.2.2 TGA

Thermo gravimetric analysis was conducted by a TA Instrument Q 2950 high resolution thermogravimetric analyzer. Pure epoxidized soybean oil and silylated epoxidized soybean oil product samples were tested through a specific heating profile to separate components' contents in the final product. The heating profile started from room temperature to 220°C with the heating rate of 20°C per minute. After keeping isothermal stage at 220°C for 20 minutes, the temperaturs was ramped up to 500°C with the heating rate of 10°C per minute.

4.2.3 Results and discussion

4.2.3.1 FTIR results of silylated epoxidized soybean oil product

FTIR spectra for the original epoxidized spybean oil and the oil product after reaction with amino silane are shown in Figure 23 and Figure 24.

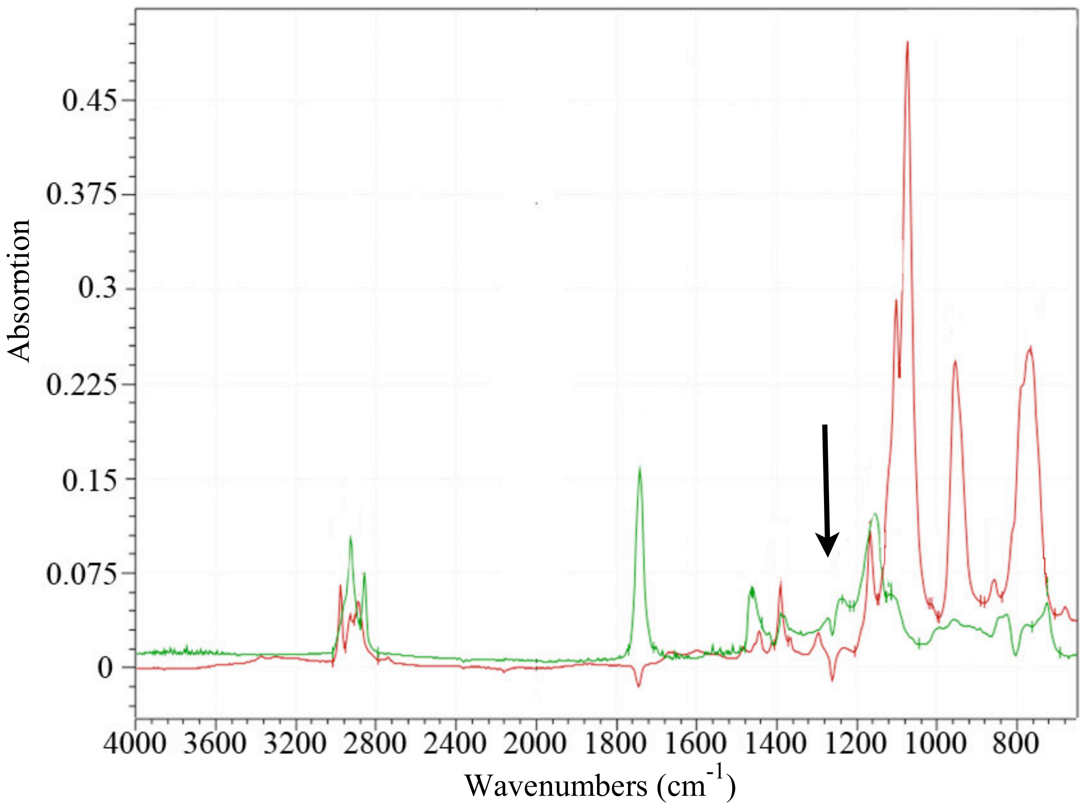

Figure 23 FTIR spectrum of epoxidized soybean oil (green line) and oil product after reaction (red line)

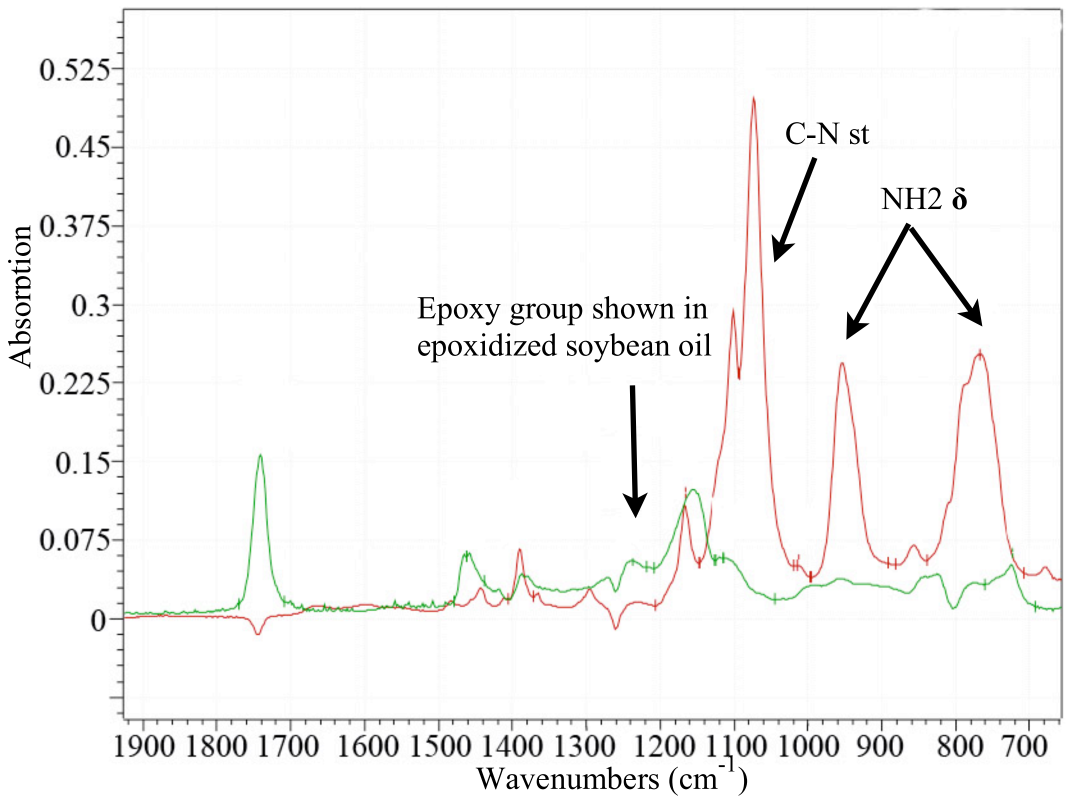

Figure 24 Expanded FTIR spectrum of epoxidized soybean oil (green line) and oil product after reaction (red line)

Before reaction, the peak around 1240 cm^{-1} represents the epoxy group in the oil, while in the product, the peak disappears. The strong peaks around 1100cm^{-1} and peaks around 950cm^{-1} and 760 cm^{-1} arise and represent the C-N stretch and NH_2 group, which means that the amino silane was sucessfully grafted and the reaction occured between epoxidized soybean oil and amino silane.

4.2.3.2 TGA results of silylated epoxidized soybean oil product

Since the boiling point of amino silane is 217°C, the isotherm stage temperature of TGA test for all these products was set to be 220°C, so that unreacted amino silane can evaporate sufficiently to give us correct grafting percentage.

Unreacted epoxidized soybean oil is quite stable under 300°C, thus during the whole TGA test, there should be no weight change due to decomposition of soybean oil before 300°C. (Figure 25)

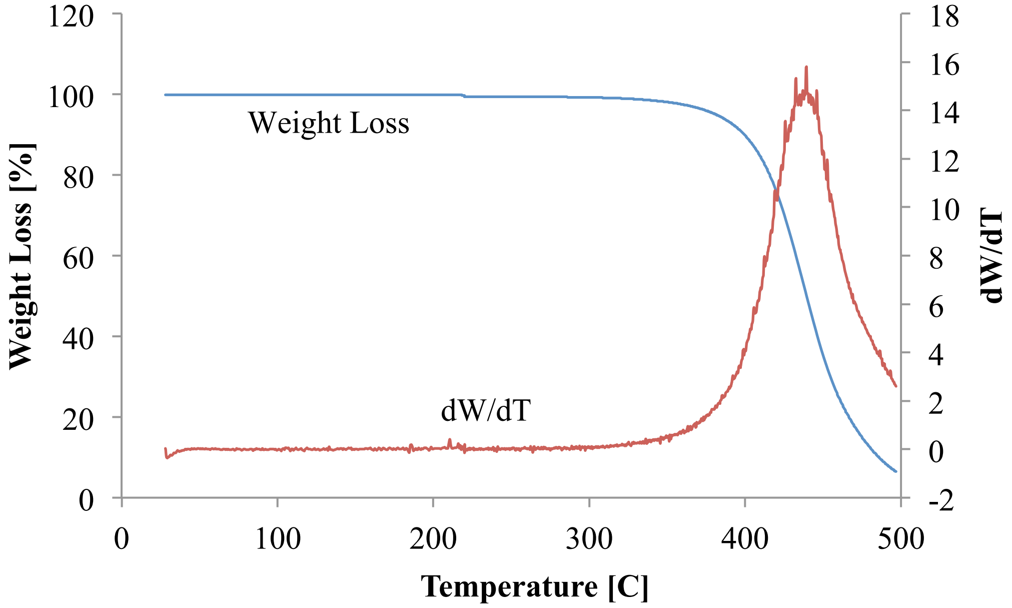

Figure 25 Pure epoxodized soybean oil TGA weight loss and derivative plot

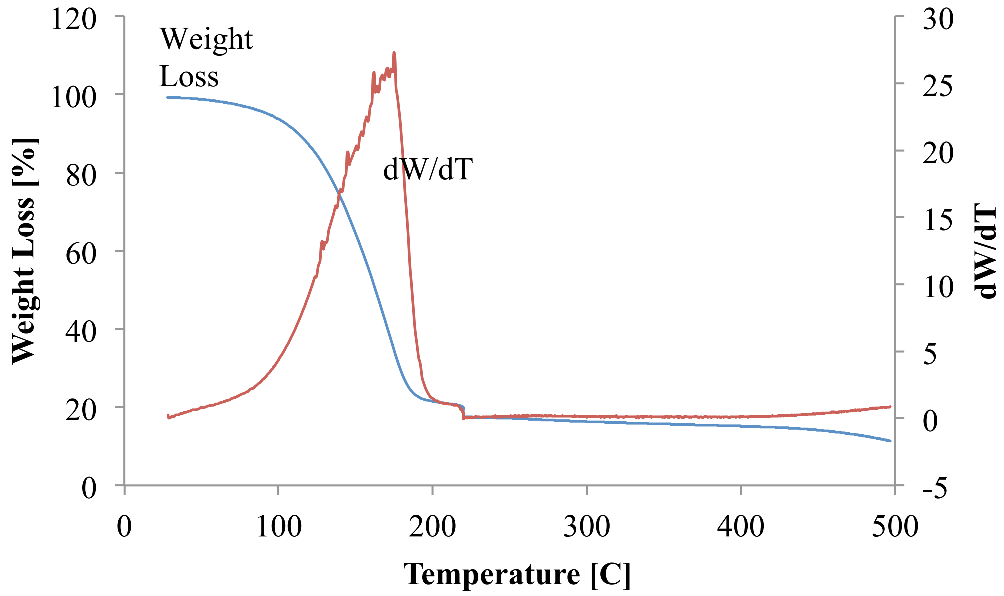

Figure 26 Silylated epoxidized soybean oil product TGA weight loss and derivative plot

The first weight loss period of the product before 220°C was due to the evaporation of amino silane, since pure amino silane almost all decomposed before 220°C in the TGA test. The second weight loss period in the isothermal stage of 220°C might be due to the partial decomposition of the oil product. And the last weight loss period after 400°C was the decomposition of unreacted epoxidized soybean oil. (Figure 26)

To calculate the reaction conversion and grafting percentage, weight loss at 220°C was used as the weight loss due to evaporation of unreacted amino silane.

Table 12 Calculation table of grafting percentage of the reaction between epoxidized soybean oil and amino silane

Original Sample weight [mg]	Original $NH_2(CH_2)_3Si(OEt)_3$ in sample [mg]	Sample weight at 220°C [mg]	Unreacted $NH_2(CH_2)_3Si(OEt)_3$ [mg]
10.9990	10.3400	2.1810	8.8180

so the grafting percentage was (10.3400-8.8180)/10.3400*100%=14.72%

4.2.3.3 Coating performance

When the oil was coated on the panels, it was transparent at the beginning of the coating step, after a while, the oil began to gather in the center area of the coated panel and turned to a milky color. It cured rapidly. The cured panel had a white color in the center area, and was transparent in the margin area, and it firmly adhered to the panels.

Same color change also occurred when applying this coating material on PE films. But the coating on films has better spread performance than on the panels.

It is suspected that the color was due to hydrolysis of unreacted amino silane.

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Chapter 5: Conclusions

5.1 Conclusions

The urgent necessity to develop and improve new synthetic routes to synthesize bio-based coating materials from renewable resources has driven a great amount of research. In the study of this thesis, one kind of bio-based silylated soybean oil coating material was successfully synthesized by reacting soybean oil with silane or siloxane. The synthesized bio-based coating material, silylated soybean oil coating material, can be characterized by FTIR, NMR, and chemical method to analyze the structure and degree of grafting, qualitatively and/or quantitatively. Moreover, the degree of grafting or silylation is controllable by varying reaction conditions.

After applied to paper coating, it is proved to have water resistant property, which depending on the original reactants molar ratios and coating systems during coating steps. This coating material could reduce water vapor transmission rate and increase water contact angle of coated paper, providing hydrophobic properties to paper. Also, this coating material is partially biodegradable, and can thus be specified as environmentally friendly material.

5.2 Recommendations

Further study could be done on the kinetics of curing of this coating material. Since the length of curing time depends on many factors, such as temperature, moisture content and amount of DBTDL catalyst, experiment design could be used to separately study how these factors affect the curing time of this coating material.

More study could be focused on how the catalyst affects reaction kinetics or reaction conversion. Currently, L101 was used as the catalyst for silylation reaction. We can try some other catalyst to optimize the catalyst and the amount of the catalyst.

Further investigation for coating of water sensitive substances could also be conducted for more applications of this coating material.