

DESIGN AND ENGINEERING OF BIO-BASED COATING FOR USE ON PAPER AND
OTHER SUBSTRATES

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ABSTRACT

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An economic infrastructure based on crude oil coupled with dwindling oil reserves has led to extensive research in recent years into bio-based products, minimizing the dependency on petroleum-based products. Soybean oil is a renewable, bio-based material that is readily available domestic crop. Expanding the products they're used for could improve the local economy of rural communities and also enhance the domestic industrial base when used in value-added industrial products. Utilizing the basic unsaturated triglyceride structure of soybean oil and the water-resistant characteristics it demonstrates provides a suitable material for hydrophobic coatings when used in conjunction with siloxane chemistry.

Reacting low-saturated soybean oil and vinyl silanes via a high temperature, high pressure alkyl-substituted reaction results in a silylated soy oil product. When this material is exposed to moisture, a chain of Si-O-Si siloxane bonds are formed between the silylated soy oil creating a viscous liquid suitable for coating on various substrates of which provides enhanced hydrophobic properties. For this project, silylated soy oil was evaluated for use on untreated paper for the production of bio-based, biodegradable, waterproof trash bags. Specifically, a portion of the project involved scale-up trials for consideration as a manufactured product.

Analysis of the synthesized silylated soy product, assessment of the water resistance provided by the silylated soy oil coatings, and the results and estimated economic model from scale-up trials comprise this thesis.

TABLE OF CONTENTS

LIST OF TABLES	vii
LIST OF FIGURES	ix
Chapter 1: Introduction to Project Scope	1
1.1 Thesis Organization	1
1.2 Demand for Bio-Based & Biodegradable Products	2
1.3 Objectives	4
1.4 Background	5
1.4.1 Soy Oil.....	5
1.4.2 Silane and Silicone Chemistry	8
REFERENCES	11
Chapter 2: Synthesis and Analysis of Silylated Soy Oil	13
2.1 Alder-Ene Reaction.....	13
2.2 Reaction Conditions.....	14
2.2.1 Catalysts and Enophiles	14
2.2.2 Reaction Conditions & Reactor Selection.....	15
2.2.3 Reactor Size.....	17
2.2.4 Reactants & Reactant Ratios	18
2.3 Experimental	20
2.3.1 Materials.....	20
2.3.2 Method – Silylated Soy Oil.....	20
2.4 Product Analysis	21
2.4.1 TGA & Graft Percentage.....	22
2.4.2 Viscosity.....	23
2.4.3 Volatile Organic Compound Measurements	24
2.4.4 NMR.....	25
2.5 Results & Discussion – 2 Liter Parr Reactor	25
2.5.1 TGA.....	25
2.5.2 Graft Percentages	28
2.5.3 Viscosity.....	30

2.5.4 Volatile Organic Compound Measurements	32
2.6 Results & Discussion – 5 Gallon Parr Reactor	33
2.6.1 TGA & Graft Percentages	33
2.6.2 Viscosity	37
2.7 Results & Discussion – Varying Silane Reactants and Reactant Ratios	39
2.7.1 Mixture B – 1:1 Molar Ratio Soy Oil:VTMOS	39
2.7.2 Mixture C – 1:3 Molar Ratio Soy Oil:VTEOS	40
2.7.3 Mixture D – 1:1 Molar Ratio Soy Oil:VTEOS	40
REFERENCES	43
Chapter 3: Silylated Soy Oil Coatings	45
3.1 Coating Background & Cure Chemistry	45
3.2 Silicone Coatings & Cure Chemistry	46
3.3 Coating Variables	48
3.3.1 Coating Weight	48
3.3.2 Cure Temperature & Time	48
3.3.3 Catalyst and Moisture Concentrations	49
3.3.4 Paper Types	50
3.3.5 Additional Factors	51
3.3.5.1 Pot Life Time	51
3.3.5.2 Blend (Mixing) Time	52
3.3.5.3 Tack-Free Time	52
3.4 Materials	53
3.5 Product Analysis	54
3.5.1 Cobb Test	54
3.5.2 Water Contact Angle	55
3.6 Experimental	57
3.6.1 Varying Paper Samples with Low Basis Weight	57
3.6.1.1 Method – Varying Paper Samples with Low Basis Weight	57
3.6.1.2 Results & Discussion – Varying Paper Samples with Low Basis Weight	58
3.6.2 – Coat Weight Variations	61
3.6.2.1 Method – Coat Weight Variations	61
3.6.2.2 Results & Discussion – Coat Weight Variations	61
3.6.3 Cure Time & Temperature	63
3.6.3.1 Method – 4hr Cure Time with Cure Temps at 60°C and Room Temp	63

3.6.3.2 Results & Discussion – 4hr Cure Time with Cure Temps at 60°C and Room Temp	64
3.6.4 – Reduced Cure Times at 60°C and Room Temp	66
3.6.4.1 Method – Reduced Cure Times at 60°C and Room Temp	66
3.6.4.2 Results & Discussion – Reduced Cure Times at 60°C and Room Temp	66
3.6.5 – 24hr Cure Time, 60°C vs. 80°C Cure Temp	68
3.6.5.1 Method – 24hr Cure Time, 60°C vs. 80°C Cure Temp	68
3.6.5.2 Results & Discussion – 24hr Cure Time, 60°C vs. 80°C Cure Temp	69
3.6.6 – Varying Paper Samples with High Basis Weight.....	69
3.6.6.1 Method – Varying Paper Samples with High Basis Weight	69
3.6.6.2 Results & Discussion – Varying Paper Samples with High Basis Weight	71
3.7 Optimal Coating Conditions	72
REFERENCES	75
Chapter 4: Scale-Up Trials and Economics.....	76
4.1 Scale-Up Trials	76
4.1.1 Gravure Coating System	77
4.1.2 Line Speed.....	77
4.1.3 Oven Temperature.....	78
4.1.4 Curing Formulation	78
4.1.4.1 Method – Varying Water Concentration for Pre-Coat Mixture	78
4.1.4.2 Results & Discussion – Varying Water Concentration for Pre-Coat Mixture	79
4.2 Scale-Up Trial Results and Discussion.....	81
4.2.1 Grease Resistance of Scale-Up Trial Coatings	82
4.2.1.1 Method – Grease Resistance Measurements of Scale-Up Trial Coatings	82
4.2.1.2 Results & Discussion – Grease Resistance Measurements of Scale-Up Trial Coatings	82
4.3 Scale-Up Trial Economic Evaluation	83
REFERENCES.....	89
Chapter 5: Recommended Future Work.....	90
5.1 Proposed Synthesis Experiments	90
5.1.1 Variation of Reactant Molar Ratios	90
5.1.2 Variation of Reaction Time and Temperature.....	91
5.2 Proposed Coating Experiments.....	92
5.2.1 DBTDL & Water Concentrations	92

5.2.2 Use of Paper GN354872 with High Basis Weight.....	93
5.2.3 Use of Secondary Coating with Silylated Soy Oil.....	94
5.3 Proposed Manufacturing Experiments.....	94
5.3.1 Different Coating System.....	94
REFERENCES.....	98

LIST OF TABLES

Table 2.1	Alder-Ene reactant ratios used in 2 L Parr Reactor for synthesis of silylated soy oil.	21
Table 2.2	TGA results of calibration standards of unreacted low-sat soy oil:VTMOS mixtures	26
Table 2.3	Graft percentages of silylated soy oil products run in 2 L Parr reactor at 280°C for 16 hours. Graft percentages were calculated using Eq. 2.1.	29
Table 2.4	Summary of graft percentage and associated viscosity from Reactions 1-9.	31
Table 2.5	VOC results of convection oven and TGA heating methods. Values indicate weight percent loss for both silylated soy oil and pre-coating mixtures containing 1wt% water and DBTDL.	33
Table 2.6	Graft percentages of silylated soy oil products run in 5 gal. Parr reactor at 250°C, 20 hours calculated using Eq. 2.1.	34
Table 2.7	Summary of graft percentage and associated viscosity from Reactions 10-19.	38
Table 3.1	Comparison of uncoated paper characteristics provided by Wausau Paper Co.	58
Table 3.2	Cobb Values at both two and ten minute intervals of coated and uncoated papers.	60
Table 3.3	Water contact angles of various paper types of both coated and uncoated samples.	60
Table 3.4	Cobb Values of four hour cure time at combinations of 60°C and room temperature.	63
Table 3.5	Coat weights and Cobb Values of samples cured at various time intervals ranging from 15 minutes to 4 hours. Each sample was cured for equal amounts of time at both 20°C (room temp) and 60°C.	68
Table 3.6	Comparison of sample sets cured at 60°C and 80°C for one hour of 24 hour cure time.	69
Table 3.7	Uncoated high basis weight paper characteristics provided by Wausau Paper Co.	70
Table 3.8	Two minute Cobb Values of coated and uncoated high basis weight papers.	71
Table 4.1	Coat weights and Cobb Values of coatings prepared at different mixing times using 0.1wt% water in pre-coating mixture.	80
Table 4.2	Equipment settings and Cobb Values of coatings from first two trials.	81

Table 4.3 Coating and bag production specifications including coating settings from full-scale trials, estimated production volume, bag sizes, and paper requirements..... 83

Table 4.4 Estimated paper costs including purchasing and transportation to coating facilities based off of production demands highlighted in Table 4.3. 84

Table 4.5 Estimated raw material, processing, and production costs associated with the synthesis of silylated soy oil based off of production demands outlined in Table 4.3..... 85

Table 4.6 Estimated raw material costs for curing step during coating process. Quantities were based off of production demands outlined in Table 4.3..... 86

Table 4.7 Estimated coating production costs based off of production demands in Table 4.3.... 86

Table 4.8 Estimated manufacturing, synthesis, and processing costs for production of one million silylated soy oil trash bags..... 87

LIST OF FIGURES

Figure 1.1 The basic chemical structure of a soy oil triglyceride molecule. The R-groups can be any combination of several fatty acid chains.....	6
Figure 1.2 Chemical structure of the five most common fatty acids found in soy oil.....	7
Figure 1.3 Chemical structures of VT MOS and VTEOS used in the synthesis of silylated soy oil.....	9
Figure 2.1 Reaction mechanism of a basic Alder-Ene reaction.....	13
Figure 2.2 Mechanism showing grafted VT MOS onto unsaturated fatty acid chains of soy oil via an Alder-Ene reaction.	14
Figure 2.3 Effects of reaction time and temperature on the reactivity of VT MOS and soy oil [8].	16
Figure 2.4 Relationship between bulk viscosity and graft percentages of silylated soy oil achieved via Alder-Ene reactions carried out in 2 L Parr reactor at 280°C for 16 hours.	19
Figure 2.5 TGA results of low-sat soy oil and VT MOS blanks measuring wt% loss and dwt% as a function of temperature. Dashed lines are VT MOS results and solid lines are soy oil results. 27	
Figure 2.6 TGA calibration curve of unreacted low-sat soy oil:VT MOS mixtures.	28
Figure 2.7 Overlay of TGA plots from Reactions 1-9 using 5°C/min ramp up to 450°C under nitrogen gas.....	30
Figure 2.8 Overlay of TGA plots from Reactions 10-19 using 5°C/min ramp up to 450°C under nitrogen gas.....	35
Figure 2.9 Final product of Reaction 11 from partially cured silylated soy oil. The solid material on the stirrer is fully cured silylated soy oil. A small amount of viscous liquid silylated soy oil was collected, characterized, and analyzed but was not used for further coating tests and applications.	36
Figure 2.10 Viscosity measurements of 5 gal. reactor products with respect to graft percentage.	38
Figure 3.1 Polymer Condensation reaction resulting in a cured silicone polymer with OR representing siloxane substituents (e.g. methoxy or ethoxy groups in VT MOS and VTEOS, respectively) and R substituents representing vinyl groups which graft to the unsaturated double bonds of soy oil during an Alder-Ene reaction.	47

Figure 3.2 Single Roll Euclid Lab Coater used for all coatings made throughout duration of research. Pneumatic pressure gauge allowed for precise coat weights. The design and small size of the coater required the use of minimal coating material. 54

Figure 3.3. Cobb cylinder, blotting paper, and 10-kg roller used for measuring Cobb Values.. 55

Figure 3.4 Surface contact angle represented as θ_c with respect to interfacial energies [8]..... 56

Figure 3.5 Variation in coat weights of silylated soy oil when varying blade pressure on ECS.62

Figure 3.6 Cobb Values when varying the coat weight of silylated soy oil on GN505320 paper.
..... 63

Figure 4.1 Viscosity measurements with respect to mixing time using 1.0wt% and 0.1wt% water for pre-coating mixture formulations..... 79

Chapter 1: Introduction to Project Scope

1.1 Thesis Organization

This thesis is organized into five separate and distinguishable chapters. Each chapter provides further insight into the different segments of the project that were addressed during the course of the research. Finally, the focal points from each chapter are summarized to present the current and future status of the project.

Chapter One discusses the desire for bio-based and biodegradable goods in today's market and the benefits they have over current petroleum-based materials. This chapter also discusses the purpose of the project and provides necessary details and background needed to understand the chemistry and engineering aspects of the project.

Chapter Two describes the process for synthesizing silylated soy oil. The reaction chemistry and settings are introduced including several reaction variables that were examined. The product analysis methods used during the production of silylated soy oil are highlighted along with appropriate interpretations of each experimental result.

Chapter Three describes the paper coating process on a small, lab bench scale. The coating method used is explained and other areas including pot life time, tack-free time, cure time, cure temperature, and mixing time are also described. The results and methods of analysis for each coating variation are presented and summarized.

Chapter Four details the progress made in the large-scale trials that have occurred during this project. This includes common issues experienced during scale-up projects and potential problems specific to this project. Additionally, variables that are not a factor in small scale paper

coating processes such as coating speed, coating method, and drying time and temperature are introduced and discussed.

Chapter Five summarizes the purpose of the project while emphasizing its importance and practical uses. Significant data and results found throughout the course of the research project are organized and presented. Also, the status of the project will be stated as well as potential future work that could further the development of the current product.

1.2 Demand for Bio-Based & Biodegradable Products

In recent years there has been an increasing demand for bio-based products in today's marketplace. Rising oil prices coupled with diminishing oil reserves have resulted in increased investigation of alternatives to fuel and other petroleum-based products. Similarly, regulations on corporations' carbon footprints and disposal methods of petroleum-based plastics have become stricter over the past two decades, resulting in a demand for more eco-friendly products.

The diminishing of the world's oil reserves can be summarized in a simple supply and demand model. Formation of fossil fuels occurs over millions of years and everyday products that are made from these fossil fuels, such as plastic bottles, can take several hundreds of years to decompose in the environment [1]. This replenishment of fossil fuels is a process that cannot be sped up; it is fixed and thus accounts for a fixed available supply.

The use of biobased materials to replace fossil resources offers an intrinsic value proposition and serves to reduce the product carbon footprint. One of the principle values of using biobased materials arises from the use of short, sustainable and in balance biological carbon where the rate and time scales of sequestration into plant biomass as CO₂ is in balance with its use as organic materials. The use of fossil carbon, on the other hand, is sequestered over

millions of years but it is released back into the atmosphere in a much shorter time frame. Consequently the use of fossil resources is unsustainable and leads to a net greenhouse gas accumulation in the atmosphere with all the negative aspects associated with this phenomenon.

World crude oil consumption in 2011 was estimated at over 87 million barrels per day [2]. This results in a worldwide crude oil consumption of more than 30 billion barrels per year. Additionally, crude oil consumption has increased 38% over the last thirty years. Current estimates of the top 17 countries with proven oil reserves indicate a total of 1,234 billion barrels remaining [3]. Therefore assuming crude oil consumption remains at 2011 levels, these reserves will be exhausted in approximately 40 years. This trend of increased consumption of fossil fuels only seems to be growing while the oil supply remains fixed. As a result, the demand for crude oil products will far outweigh the supply in the very near future.

Based on these statistics, replacing petroleum-based products with similar products derived from renewable resources, such as plant-based products, has become a highly researched area. Several new uses are being discovered for the different parts of cash crops, specifically soybean plants including applications in cosmetics, cleaning materials, particle board, adhesives, and pharmaceuticals [4]. Since soybean plants are a major domestic crop, expanding the products they're used for can improve the local economy of rural communities and also enhance the domestic industrial base when used in value-added industrial products. Using a bio-based product, such as soy oil, to replace existing petroleum-based products, while maintaining similar product characteristics and functionality, could help diminish the dependency on fossil fuels. In addition to the fact that soy is readily biodegradable in the environment [5], it provides a renewable resource that could replace petroleum-based products, thus alleviating the supply and demand issues that arise with increased petroleum consumption with limited petroleum reserves.

Using functional groups commonly associated with soy oil as reaction sites, it is possible to synthesize several new biomaterials that replicate common everyday products that are not bio-based. More specifically, several natural oils are excellent coating materials, and when exposed to air, form a tough scratch-free film [6]. The synthesis, chemistry, and characterization of modified soy oil for use as coating material will be discussed in this thesis. Additionally coating applications, coating formulations, as well as product development for bio-based, biodegradable non-plastic bags will also be discussed.

1.3 Objectives

The focus of this research project is to create a bio-based alternative to current petroleum-based plastic bags commonly used for waste disposal. Creating a bio-based and biodegradable coating that could be applied to untreated brown paper used for trash bags was the focus of this project. Using soy oil as the primary ingredient while utilizing commonly practiced silane cure chemistry used in several different areas of coating industries, it is possible to form short siloxane chains by hydrolysis of silicon alkoxy bonds (Si-O-C) upon exposure to atmospheric moisture and the formation of stable siloxane (Si-O-Si) networks [7].

Under high temperature and pressure, the vinyl groups in the silane molecules react with the unsaturated fatty acid chains of soy oil's triglycerides using a peroxide catalyst. The product of this reaction is a modified soy oil grafted with the silane molecule at the site of an unsaturation in the fatty acid chain. Subjecting this product to moisture leads to hydrolysis of alkoxy silanes and subsequent condensation of silanols, creating a crosslinked polymer chain consisting of Si-O-Si bonds. This condensation reaction further increases the molecular weight of the product and creates a viscous liquid suitable for paper coating.

Several variables were considered and investigated throughout this project.

- (1) Determine optimal reaction conditions for producing the desired modified soy oil. Such factors that were examined include variations of the reaction time, temperature, reactant ratios, and type of reactants. The products from each of these variations were characterized and analyzed for their chemical and physical properties.
- (2) Analyze the coating performance of each modified soy oil product. The appropriate conditions that meet the required coating weights, pot life time, tack-free time, mixing time, and cure time were determined. These factors are of critical importance when operating at a large manufacturing scale paper coating facility.
- (3) Define process conditions of industrial standards. The most favorable coating speed, coating thickness, and curing (or drying) temperature were determined in a pilot plant facility. In these trials, the choice of desired paper grade and weight used for making final product was evaluated. The desired result of this project is to have a product that can be mass-manufactured. While each of the mentioned variables affects product performance, it is also important to consider product variations from a fiscal perspective as well.

1.4 Background

Before describing the details of this project, it is essential to first understand the fundamental properties of the materials and instruments that were used throughout the research process.

1.4.1 Soy Oil

Soy oil is extracted from the seed, or the bean, of a soybean plant. Soybeans are comprised of approximately 19% oil with the remainder being proteins, carbohydrates, and

moisture. To isolate the soy oil, the beans are sliced into flakes and immersed in hexane which extracts the oil from the bean. After removing the remaining bean solids, the hexane and soy oil are separated using a distillation or evaporation process.

The basic chemical structure of soy oil is a mixture of triglycerides that are composed of glycerol attached to three fatty acids as shown in Figure 1.1. A fatty acid is a molecule with a carboxylic acid and an aliphatic tail. These aliphatic tails can contain double bonds (unsaturated) or be free of double bonds (saturated). Typically, soy oil contains 4.3-4.6 double bonds on the fatty acid chains per mole depending on the origin of the seed [8]. The fatty acid molecules found in soy oil are linoleic acid [51%], oleic acid [23%], palmitic acid [10%], α -linolenic acid [7%], and stearic acid [4%] (see Figure 1.2). These five fatty acids comprise a total of 95% of the fatty acid chains commonly found in soy oil. For this project, the double bonds of the unsaturated fatty acids were targeted as the reaction sites to achieve the desired silylated soy oil product.

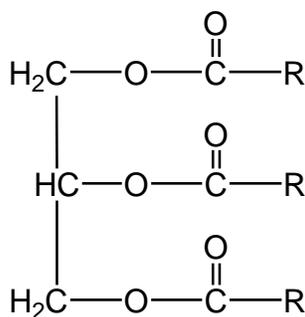
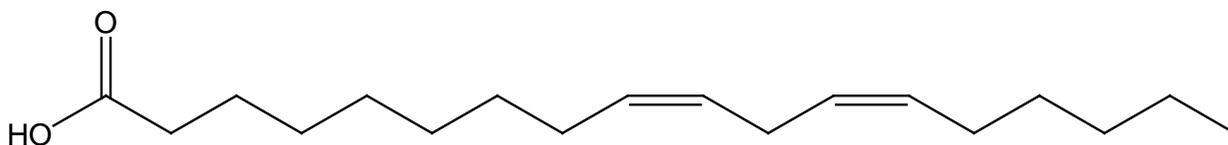
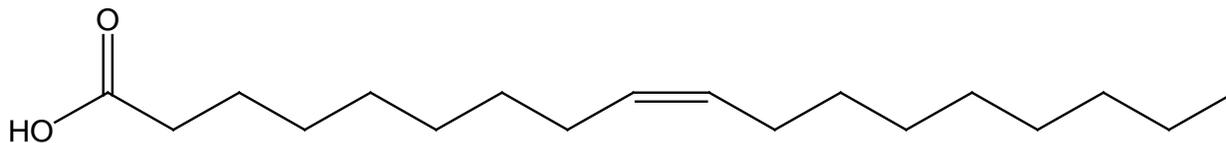


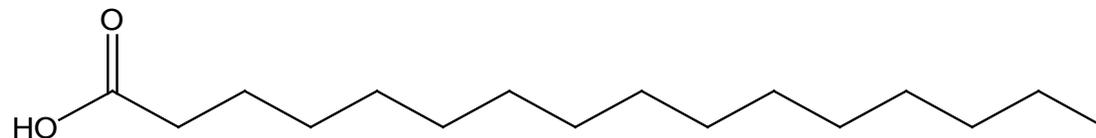
Figure 1.1 The basic chemical structure of a soy oil triglyceride molecule. The R-groups can be any combination of several fatty acid chains.



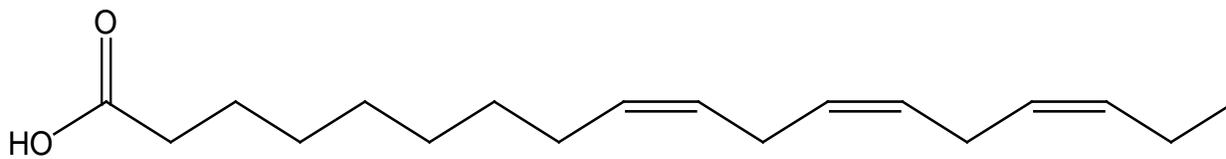
Linoleic Acid (51%)



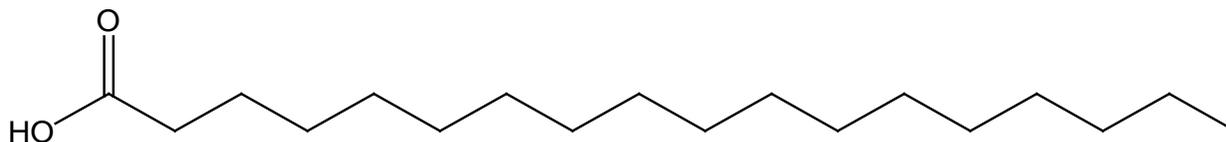
Oleic Acid (23%)



Palmitic Acid (10%)



α -Linolenic Acid (7%)



Stearic Acid (4%)

Figure 1.2 Chemical structure of the five most common fatty acids found in soy oil.

Soy oil is of great interest in this project due to its chemical properties along with its low cost and high availability. For a demonstration of oil's hydrophobic properties, one must simply pour a cup of soy oil into a glass of water resulting in two distinct immiscible layers of water and oil. This observed bilayer is a result of water's polarity. Polarity is an uneven arrangement of charges within a molecule. It is well known that polar molecules are only able to dissolve in polar solvents. Because soy oil is a non-polar molecule it does not dissolve when mixed with water. Therefore soy oil's water-repellent characteristics could, in the right circumstances, be

used in waterproof applications. However, if unmodified soy oil was used directly as a coating it would not demonstrate useful properties due to its low viscosity and inability to crosslink, or form chemical bonds with adjacent soy oil molecules. Using soy oil as a substrate in well established silane chemistry techniques, though, allows its hydrophobic properties to be of much greater use for coating purposes.

1.4.2 Silane and Silicone Chemistry

Silicon is a chemical element that is found in the same column of the periodic table as Carbon and as such, it is a tetravalent metalloid. Due to its four valence electrons, silicon is able to achieve many different chemical bonding formations. Silane, for instance, utilizes silicon's four valence electrons to bond to four hydrogen molecules much like carbon would in a methane molecule.

However, in many ways silicon behaves very differently from carbon. For example, a Si-O bond is longer and more flexible than a C-O bond due to the larger atomic size of silicon compared to carbon. An Si-O bond also has a lower barrier to rotation than a C-O bond. These differences are some of the factors that contribute to the flexible structures and low glass transition temperatures often displayed by several silicone materials [9]. Because of these unique physical properties, silicone materials derived from silicon are often utilized in polymer science. Silicones are organosilicon polymers and are most commonly used in sealant, adhesive, and lubricant chemistry. One unique structure commonly used in silicone chemistry is siloxane which exhibits repeating Si-O-Si bonds that form the backbone of the molecule.

The repeating Si-O-Si backbone has an associated bond energy of ~450 kJ/mol compared to ~360 kJ/mol for a repeating C-O-C bond (ether). Bond energy is the measure of energy required to break a molecule into its separate components. The significance of such a difference

between the two bonds energies is the ability for silicones to better resist hemolytic bond cleavage compared to ether compounds. The larger bond energy of a silicone backbone translates to a more thermally-stable molecule that is more resistant to temperature extremes. Larger bond energy, along with the longer Si-O bonds and lower rotational barrier compared to C-O bonds contribute to lower glass-transition temperatures (temperature at which a material changes from a viscous liquid to a fixed crystalline solid).

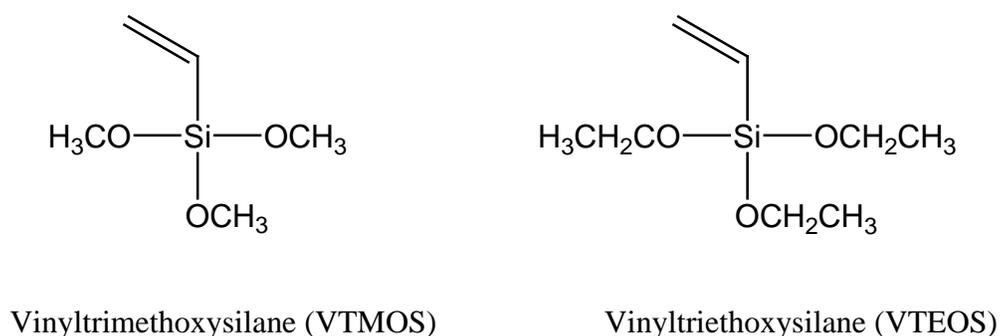


Figure 1.3 Chemical structures of VTMOS and VTEOS used in the synthesis of silylated soy oil.

For the purpose of this project, vinyltrimethoxysilane (VTMOS) and vinyltriethoxysilane (VTEOS) were used in the synthesis of silylated soy oil (Figure 1.3). These compounds were selected for two main reasons. First, these vinyl compounds do not undergo thermal or radical polymerization due to the presence of the silicon atom that stabilizes free radicals. Second, the alkoxy groups attached to the silicon atom are readily hydrolyzed in the presence of moisture and the resulting silanols condense to yield siloxane linkages. This double bond, when reacted with low-saturated soy oil in the presence of a peroxide catalyst at high temperatures, is grafted onto

the fatty acid in the soy oil at the site of the double bonds on the fatty acid chains. This reaction occurs via an Alder-Ene mechanism.

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Chapter 2: Synthesis and Analysis of Silylated Soy Oil

2.1 Alder-Ene Reaction

An Alder-Ene reaction involves an alkene hydrocarbon with an allylic hydrogen and a compound with a multibond (alkene or alkyne) acting as an enophile, a molecule able to donate an extra pair of electrons from its double bond. This reaction results in a substituted alkene with the double bond shifted to the allylic position [1]. This reaction is classified as a pericyclic reaction, a reaction in which the intermediate is a cyclic ring, and can be further described as a rearrangement reaction due to the shift of the double bond on the alkene hydrocarbon (Figure 2.1).

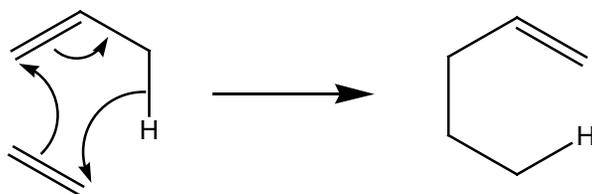


Figure 2.1 Reaction mechanism of a basic Alder-Ene reaction.

Specifically, an Alder-Ene reaction involving unsaturated soy oil and VTMOs allows for VTMOs to act as an enophile and graft onto a double bond of an unsaturated fatty acid chain of soy oil's triglyceride structure (Figure 2.2). Also, because vinyl silanes do not polymerize via free radicals like other organic vinyl monomers (i.e. styrene or acrylates) due to the stabilization of the silicon atom, VTMOs and VTEOS are ideal compounds for reactions carried out at high temperatures. This stabilizing effect inhibits the free radicals formed on the double bond adjacent to the silanes to not result in homopolymers. As a result, this simple addition modification incorporates silicone properties into soy oil that it would otherwise not demonstrate. Incorporating widely used silicone coating technology into a hydrophobic media,

such as soy oil, provides a unique bio-based material than can be readily used in several different water-resistant coating applications.

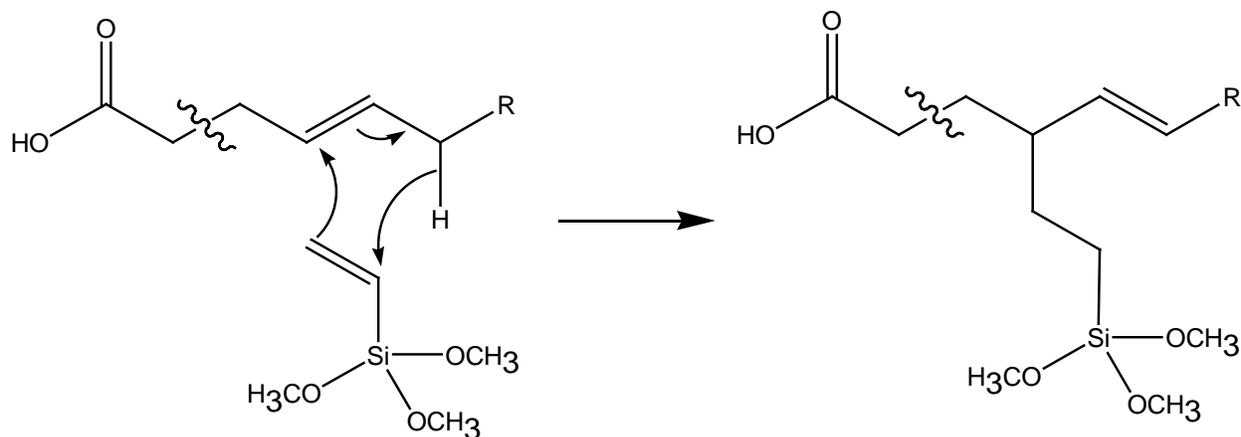


Figure 2.2 Mechanism showing grafted VTMOs onto unsaturated fatty acid chains of soy oil via an Alder-Ene reaction.

2.2 Reaction Conditions

2.2.1 Catalysts and Enophiles

The Alder-Ene reaction has become a widely used application in organic synthesis because of its ability to control the absolute regio- and stereochemistry during the carbon-carbon bond formation [2]. However, due to the reaction's pericyclic group transfer and high activation energies, typically high temperatures and highly activated substrates are required [3]. Often times, Lewis acids are used as catalysts since they are able to form complexes with the electron-deficient enophiles. Selection of the appropriate Lewis acid strongly depends on the enophile being used. For instance, studies have shown that acrylate and propiolate esters require very strong Lewis acids [4-6], whereas reactions with more reactive aldehydes need only a mild Lewis acid, such as iron (III) chloride [7].

Previous work [8-9] involving the synthesis of silylated soy oil used 2,5-Bis(tert-butylperoxy)-2,5-dimethylhexane, Luperox 101 (L101), as a catalyst for the synthesis of silylated

soy oil. This peroxide is often used as a free radical polymerization initiator, but has also been used for the degradation of polypropylene [10]. Other reports of hydrosilylation of fatty acid methyl-esters (FAMES) and triacylglycerols (TAGs) have been reported in the presence of platinum catalysts and radical initiators [8, 11-13]. The most commonly utilized hydrosilanes from these reports are triethoxy- and trichlorosilanes. Of these reports, chlorosilanes in the presence of a mixture of peroxides or platinum-based catalysts are the only reactants that have been successfully used in which non-terminal double bonds were targeted as the reaction site. Achieving a reaction mechanism that can utilize internal double bonds as a reaction site for silane-additions becomes very valuable for the purpose of this project because the most abundant fatty acid chains found in soy oil do not have terminal double bonds. If non-terminal double bonds were not reactive via an Alder-Ene reaction, the yield of the desired silylated soy oil product would be too low to be of any practical use. Only one process has been found claiming to use vinylsilanes and unsaturated naturally-occurring vegetable oils as a method for synthesizing silylated oils onto non-terminal double bonds using a high temperature addition reaction [14].

2.2.2 Reaction Conditions & Reactor Selection

The high temperatures required to overcome the activation energy of an Alder-Ene reaction presents a number of conditions that must be taken into consideration when selecting the appropriate vessel for a reactor. First, it is critical that the reactor be able to maintain an inert atmosphere throughout the entirety of the reaction to prevent any undesired side reactions as a result of curing that may occur from moisture in the air. At a lab bench scale, the most practical setup is a closed batch reactor equipped with inlet and outlet gas valves used for purging the headspace prior to reaction commencement. Second, a closed batch reactor being used at high temperatures will be subject to very high pressures, typically in excess of 100 psi. Pressures this

high remove the possibility of using a glass-lined reactor. Therefore a small stainless steel reactor that can accommodate high pressure/high temperature reactions is best suited for an Alder-Ene reaction.

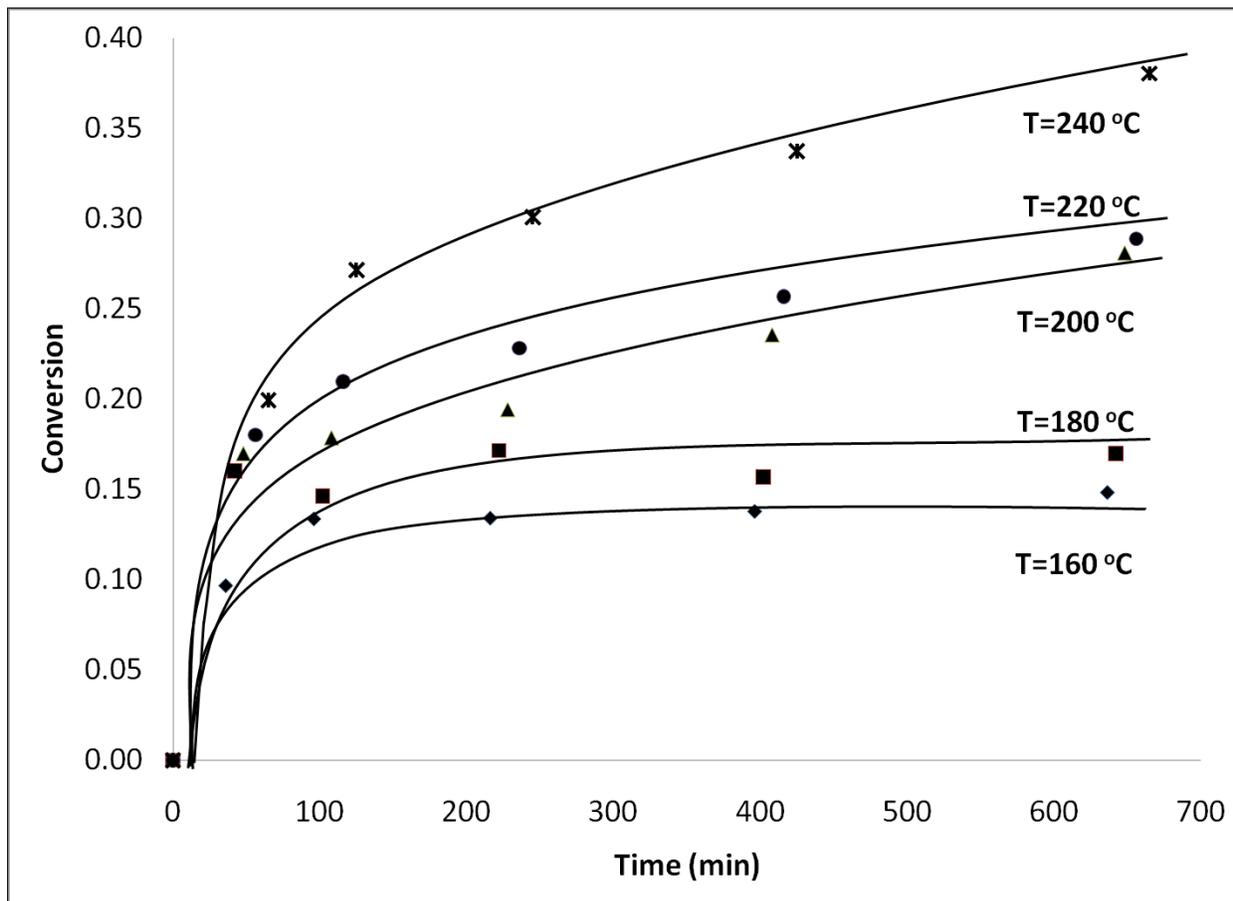


Figure 2.3 Kinetics of reaction time and temperature on reactivity of VTMOs and soy oil [8].

Parr Instrument Company has several models of reactors that cater to the specifications required of a typical Alder-Ene reaction. Initially a 2 L stainless steel Parr reactor was used for synthesizing silylated soy oil for early trials. The reactor was easily able to withstand reaction temperatures of 280°C and pressures between 100-150 psig. Additionally, the reactor was equipped with gas inlet and outlet valves used for purging the headspace of air that may

otherwise result in undesired side reactions. Another useful feature of the selected reactor was the sampling port that allowed samples to be collected in mid-reaction for kinetics data and analysis.

Determining the optimal reaction temperature and time to achieve a silylated soy oil product was investigated in previous studies [8-9]. Initial work showed that the conversion of silane increases as the temperature of the reaction is increased. Likewise, longer reaction times resulted in higher conversion of silanes, though conversion rates slow considerably after the first two hours of the reaction (Figure 2.3)

Further research of this same reaction used a reaction temperature of 280°C to expedite the reaction process. Once at this temperature, a reaction time of 12 hours was used resulting in graft percentages between 75-80% [9]. For this project, a reaction temperature of 280°C was used, however it was found that increasing the reaction time from 12 hours to 16 hours increased the grafting percentage of VTMOs which also resulted in a desired increase in viscosity of the final product.

2.2.3 Reactor Size

The primary goal of this research was to develop a silylated soy oil material suitable for coating at a large industrial-scale output. Because scaling up a process includes incorporating several other unforeseen factors and variables into the coating process, it was necessary to perform test trials at an industrial-scale facility. Coating paper at a larger scale required significantly more coating material which necessitated a larger reactor.

While a 2 L Parr reactor was used for small-scale trials, a 5 gal. Parr reactor of similar design was used for producing silylated soy oil for large-scale test trials. Unlike the 2 L reactor,

the larger reactor exhibited a decreased maximum heat capacity of the heating mantle. Consequently, a reaction temperature of 250°C was used for all reactions performed in the 5 gal. reactor. To adjust for the decreased temperature, the reaction time was extended to achieve similar product properties performed in the 2 L reactor. Ultimately, all reactions carried out in the 5 gal. reactor were run at 250°C for 20 hours.

2.2.4 Reactants & Reactant Ratios

Another factor investigated in previous studies was the reactant ratio of soy oil to VTMOs. Several different molar ratios were evaluated ranging from 1:15 to 1:3 moles of soy oil:moles of VTMOs. The results suggested a more balanced reactant ratio yielded higher graft percentages. This is advantageous for two reasons. Firstly, higher graft percentages result in increased viscosities (Figure 2.4) and therefore provide better properties for surface coatings. Secondly, from a manufacturing perspective, because VTMOs is the cost-determining reactant in this Alder-Ene reaction reducing the amount used per volume of product provides a more economically competitive product.

Two different reaction ratios were investigated and compared for performance properties. A 1:3 molar ratio soy oil:VTMOs (900 g-mol soy oil:445 g-mol VTMOs) was used for paper coating test trials and product development. Reactions were also carried out using a 1:1 molar ratio of soy oil:VTMOs (900 g-mol soy oil:148 g-mol VTMOs) and evaluated with respect to the 1:3 molar reactions.

In addition to varying molar ratios of soy oil and silane used during the Alder-Ene reactions, the selected silane enophile was also varied to determine the impacts on cure and coating properties. Stricter environmental regulations on coating industries have made it highly

desirable to incorporate bio-renewable materials into current technologies [15]. Along with incorporating bio-based, bio-renewable materials into the coating industry, it is also of great

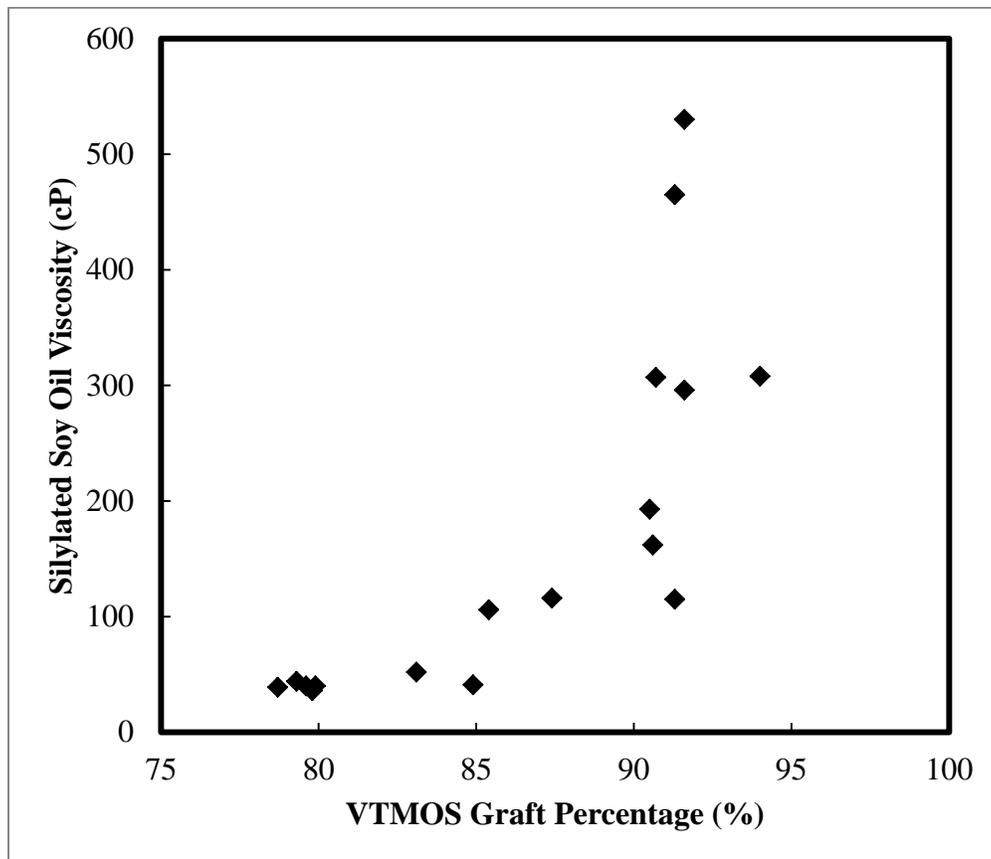


Figure 2.4 Relationship between bulk viscosity and graft percentages of silylated soy oil achieved via Alder-Ene reactions carried out in 2 L Parr reactor at 280°C for 16 hours.

importance to limit the amount of hazardous materials that are used. One area highly regulated is volatile organic compound (VOCs) emissions, commonly associated with coating and paint industries. Section 12 of the Clean Air Act provides a full list of Hazardous Air Pollutants (HAPs) that are regulated in all U.S. manufacturing facilities. Among this list is methanol [16], a byproduct of the proposed curing mechanism in silylated soy oil coatings when using VTMOs as the silane reactant. Ethanol, however, is not on the HAP list. Therefore, using VTEOS as the

silane enophile in the Alder-Ene reaction, thus emitting ethanol instead of methanol during the curing process, provides a way of producing a more environmentally-friendly silylated soy oil. If products from both VTEOS and VTMOs reactions result in similar coating performance properties, the implementation of VTEOS in place of VTMOs in the Alder-Ene reaction would provide a more environmentally friendly product and safer working conditions.

Ultimately, the most desired silylated soy oil would minimize the ratio of soy:silane, thus requiring less amounts of the price-determining silane material. Furthermore, VTEOS would be the preferred silane reactant to VTMOs due to the Clean Air Act's HAP list. However, it is necessary for VTEOS silylated soy oil to demonstrate analogous hydrophobic properties to that of VTMOs silylated soy oil.

2.3 Experimental

2.3.1 Materials

Low-saturated soybean oil was provided by Zeeland Farm Services, Inc., Zeeland, MI. Vinyltrimethoxysilane (VTMOs) [CAS 2768-02-7] and vinyltriethoxysilane (VTEOS) [CAS 78-08-0] were purchased from Gelest, Inc., Morrisville, PA. Luperox 101 (L101) [CAS 78-63-7], 2,5-Bis(tert-butylperoxy)-2,5-dimethylhexane (technical grade, 90%) was purchased from Sigma-Aldrich Co., St. Louis, MO. All reagents were used as received without any additional purification.

2.3.2 Method – Silylated Soy Oil

As mentioned in the “Reactant & Reactant Ratios” section (2.2.4), two molar ratios of soy oil:silane were tested, 1:1 and 1:3 moles. Additionally, both VTMOs and VTEOS were tested as enophiles in the Alder-Ene reaction.

Table 2.1 Alder-Ene reactant ratios used in 2 L Parr Reactor for synthesis of silylated soy oil

Mixture	Soy Oil:Silane (molar ratio)	Silane	Soy Oil (g)	Silane (g)	L101 (g)
A	1:3	VTMOS	900	445	9
B	1:1	VTMOS	900	148	9
C	1:3	VTEOS	900	571	9
D	1:1	VTEOS	900	190	9

For each reaction, adequate amounts of low-sat soy oil and silane were weighed in a 2 L Erlenmeyer flask (Table 2.1). L101 was weighed at 1.0 weight percent of soy oil and added to the Erlenmeyer flask containing the soy oil-silane mixture. The contents of the flask were quickly swirled to ensure a homogeneous mixture and were poured into the Parr reactor. The Parr reactor was closed and, with both the gas inlet and outlet valves open, the reactor was purged for approximately two minutes with nitrogen gas. After purging, both gas valves were immediately closed and contents were mixed at approximately 60 rpm throughout the entirety of the heating, reaction, and cooling process.

The reaction was heated at a high rate until it reached 200°C. Once the reactor reached 200°C, the heating rate was slowed until the final reaction temperature of 280°C was achieved. The reaction time began once the reaction temperature of 280°C was achieved and was allowed to continue for 16 hours. In some cases, intermediate samples were taken via the sampling port both during the heating period and throughout the course of the reaction to evaluate the reaction kinetics. All intermediate samples were collected in small 10 mL scintillation vials and were capped immediately to prevent any unreacted contents from escaping.

2.4 Product Analysis

Several analytical techniques were used to evaluate the results of the reactions, the products that were obtained, and the physical properties of the final products. The following is a

list of each technique used, a brief description what each technique is used for, and how the results are applicable for the analysis of synthesized silylated soy oil.

2.4.1 TGA & Graft Percentage

Thermogravimetric analysis (TGA) is an instrument that measures the change in weight of a sample by varying the temperature in a controlled environment. Increasing the temperature to a point where one of the components of the sample evaporates or thermally degrades results in a weight loss. The temperature and magnitude of weight loss that occurs can provide insight into the composition of the material being tested. For the purpose of this study, TGA was used to determine if a reaction had occurred between low-sat soy oil and the silane compound used in the reaction.

For example, if known quantities of unreacted soy oil and VTMOs were mixed and subjected to TGA using a simple ramp heating method of 10°C/min, it can be expected to see all of the VTMOs completely evaporate by its boiling temperature of 123°C. Likewise, if soy oil and VTMOs undergo an Alder-Ene reaction, it should be expected that only the *unreacted* VTMOs would evaporate by 123°C. If the mass of each reactant used in the reaction is known, the amount of silane that reacts, or grafts, onto the unsaturated double bonds of soy oil can be easily calculated (Eq. 2.1 for VTMOs and Eq. 2.2 for VTEOS). As shown in Figure 2.4, once the graft percentage of the silylated soy oil is known, one can estimate other relevant properties related to its coating potential.

$$\text{(Eq. 2.1) Graft \%} = \frac{\text{wt\%VTMOs} - \text{wt\% loss}_{@123^{\circ}\text{C}}}{\text{wt\%VTMOs}} * 100\%$$

$$\text{(Eq. 2.2) Graft \%} = \frac{\text{wt\%VTEOS} - \text{wt\% loss@160}^\circ\text{C}}{\text{wt\%VTEOS}} * 100\%$$

TGA is also very useful in illustrating the reproducibility of a reaction by comparing the change in weight percentage (wt% loss) with respect to temperature change. Additionally, plotting derivative weight (dwt%) loss with respect to temperature provides another method of further insuring a reaction's reproducibility. This trend highlights the greatest rates of change (inflection points) on the wt% loss curve. Comparing plots using the same temperature profile should provide identical overlaying trends if the same product was achieved during the reaction. Therefore, running multiple products from the same reaction on TGA using the same heating method should result in superimposed wt% and dwt% trend lines if the reaction is reproducible.

2.4.2 Viscosity

The viscosity of a coating material can be a critical factor when considering a scale-up process. The viscosity limits of a coating material can vary dramatically from small bench scale coaters to large industrial scale coating processes. Viscosities that are too low absorb, or bleed, into the coating substrate resulting in a product that doesn't demonstrate the desired coating properties. Alternatively, high viscosities can prove problematic for coating instruments and machinery.

Using a small benchtop coater it's possible to make uniform coatings using extremely viscous liquids. At small scales, factors such as pot life and instrument operation limits are not of any significant concern. Conversely, most large scale coating equipment has very defined viscosity ranges that they're able to operate at. Surpassing these limits could result in equipment malfunction that could shut down an entire plant or coating facility for hours or days at a time. Therefore it is important to determine the lower and upper viscosities of the coating material that

the coating instruments will be subject to during the coating and curing process. Additionally, comparing viscosities amongst products provides another way of verifying the reproducibility of a reaction.

2.4.3 Volatile Organic Compound Measurements

Volatile organic compounds (VOCs) are organic chemicals that exhibit a high vapor pressure at room temperature. The displayed high vapor pressure is a result of a low boiling point which makes these particular substances easier to evaporate into the air. While many VOCs pose little health threat, there are numerous anthropogenic VOCs that are highly regulated under law by the Clean Air Act as Hazardous Air Pollutants (HAPs).

VOC content (ASTM D2369) is measured by weighing 0.2 gram samples into a pre-weighed aluminum dish and placing the samples into a vented oven set to $110^{\circ}\text{C} \pm 5^{\circ}\text{C}$ for one hour. Samples are weighed before and after heating and the weight change is recorded. Using this change in weight, the VOC percentage of silylated soy oil can be found using Eq. 2.3. All materials still present in the sample after heating are considered non-volatile and are deemed “solids”.

The maximum allowable VOC levels vary depending on the organic compound and the product category they're being used for (i.e. contact adhesives, general purpose cleaners, insecticides, etc.). Several products in the coating industry are water or solvent-based resulting in elevated VOC levels. Because soy oil has a very high flash point however (approximately 320°C), and is considered a solid for VOC measurements, silylated soy oil demonstrates much lower VOC levels than other commonly used solvent-based coatings.

$$\text{(Eq. 2.3)} \quad \text{VOC \%} = 100 - \left[\left(\frac{W_2 - W_1}{S_A} \right) * 100 \right]$$

Where: W_2 = weight of dish and sample after heating

W_1 = weight of dish

S_A = weight of sample before heating

2.4.4 NMR

Nuclear magnetic resonance (NMR) is a very common and powerful tool used to determine various physical and chemical properties of an atom or molecule. This analytical technique exploits the magnetic properties given off by all atoms and molecules which, in turn, make it possible to determine the chemical structure of a molecule. While any number of chemicals can be tested using NMR, it is most commonly utilized for organic molecules.

For this project, NMR was used to highlight the discrepancies between the molecular structures of unreacted low-sat soy oil and silylated soy oil. Successfully grafting silane onto unsaturated fatty acid chains results in unique chemical bonding properties that are easily recognizable and detectable in an NMR spectrum. Performing NMR spectroscopy on samples before and after Alder-Ene reactions provides a method of verification as to the extent of the Alder-Ene reaction.

2.5 Results & Discussion – 2 Liter Parr Reactor

2.5.1 TGA

In order to properly evaluate results obtained from TGA it's necessary to run blanks to generate a baseline for all other analyses. Figure 8 shows two overlaid TGA results of pure low-sat soy oil and pure VTMOs. For both tests, a ramp to 150°C at a rate of 10°C/minute was used. As expected, soy oil exhibited no weight loss (solid line in Fig. 2.5) when the temperature

reached 150°C due to its high flashpoint. In contrast, VT MOS experienced a 100% weight loss prior to its boiling point of 123°C (dashed line in Fig. 2.5).

Control samples of unreacted soy oil:VT MOS at different ratios were also evaluated using TGA. Mixtures of unreacted soy oil:VT MOS (25:75, 50:50, and 75:25 respectively) were evaluated using a ramp method up to 450°C at a rate of 5°C/minute. This heating method was chosen to ensure a more precise wt% loss plot. The mixture was heated to 450°C to ensure that weight loss due to low-sat soy oil was also shown. Results from Figure 2.5 suggest that a weight percentage loss at 123°C would be seen totaling the total amount of VT MOS in each respective mixture.

Table 2.2 TGA results of calibration standards of unreacted low-sat soy oil:VT MOS mixtures

wtVT MOS (g)	wt _{soy oil} (g)	wt% VT MOS	wt% _{loss @ 123°C}	Δ wt% _{actual-observed}
0.2505	0.7541	24.94	21.07	3.87
0.5013	0.5020	49.97	44.67	5.30
0.7499	0.2507	74.95	71.06	3.89

The results of the wt% calibration line of 25%, 50%, and 75% VT MOS-containing mixtures are very accurate compared to total weight percentage of VT MOS used in each mixture (Table 2.2). However, none of the mixtures' observed weight percentages account for the total weight percent of VT MOS used in the analyses (Figure 2.6). This is due to the volatility of VT MOS at room temperature. To highlight this effect, an isothermal TGA was run at room temperature with pure VT MOS for a total of 40 seconds (time between loading sample and commencement of TGA analysis). Adding the 40 second wt% loss of VT MOS at room temp to each calibration point resulted in actual wt% losses within 1.0 wt% of the theoretical weight loss percentages.

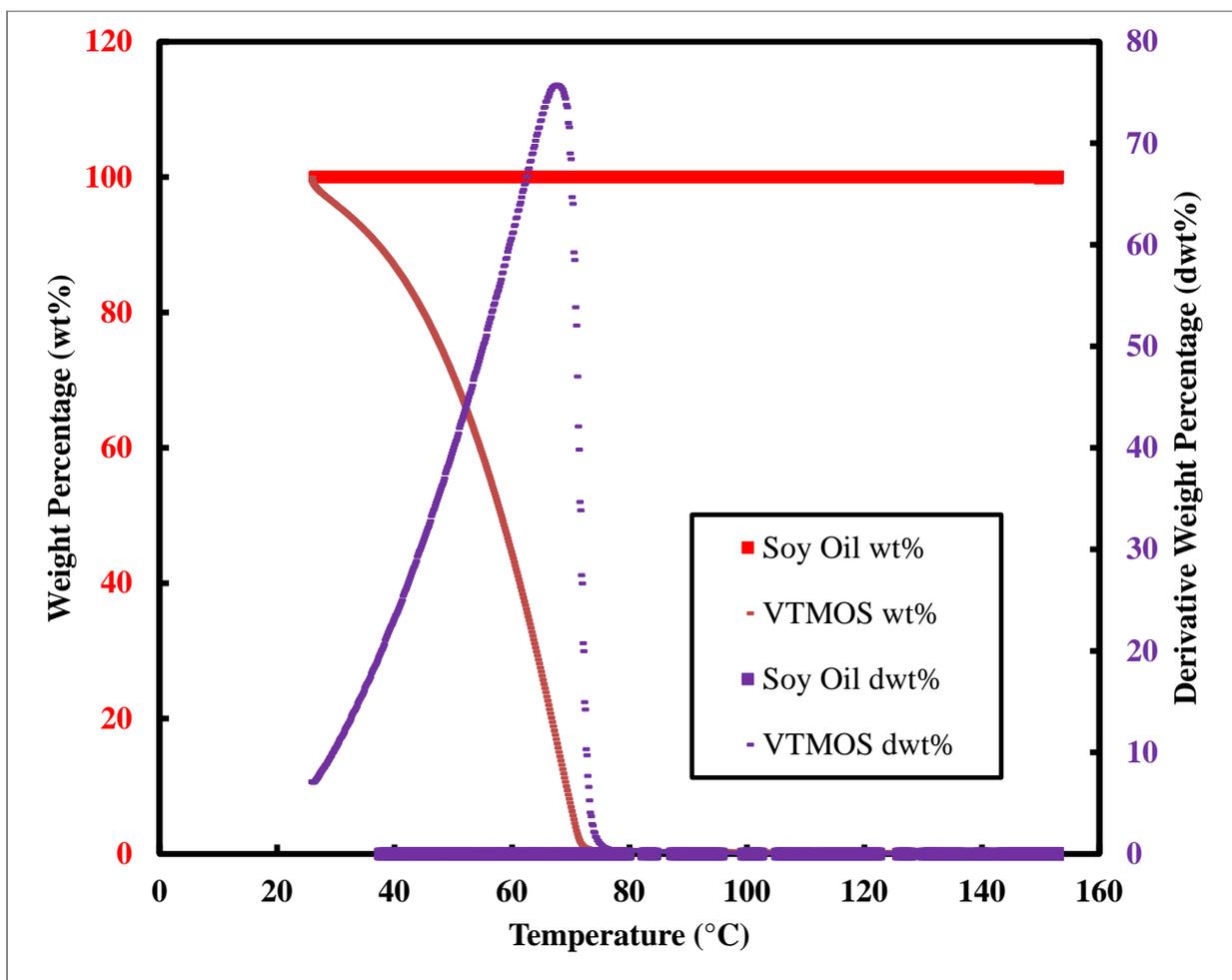


Figure 2.5 TGA results of low-sat soy oil and VTMOs blanks measuring wt% loss and dwt% as a function of temperature. For interpretation of the references to color in this and all other figures, the reader is referred to the electronic version of this thesis.

Ultimately, using a TGA calibration curve and performing an isothermal TGA at room temperature on pure VTMOs provided an accurate, acceptable calibration line. Therefore, it was determined that analysis of silylated soy oil samples could be accurately performed using 5°C/min ramp on TGA. As a result, graft percentages from each Alder-Ene reaction could be accurately calculated using this same method.

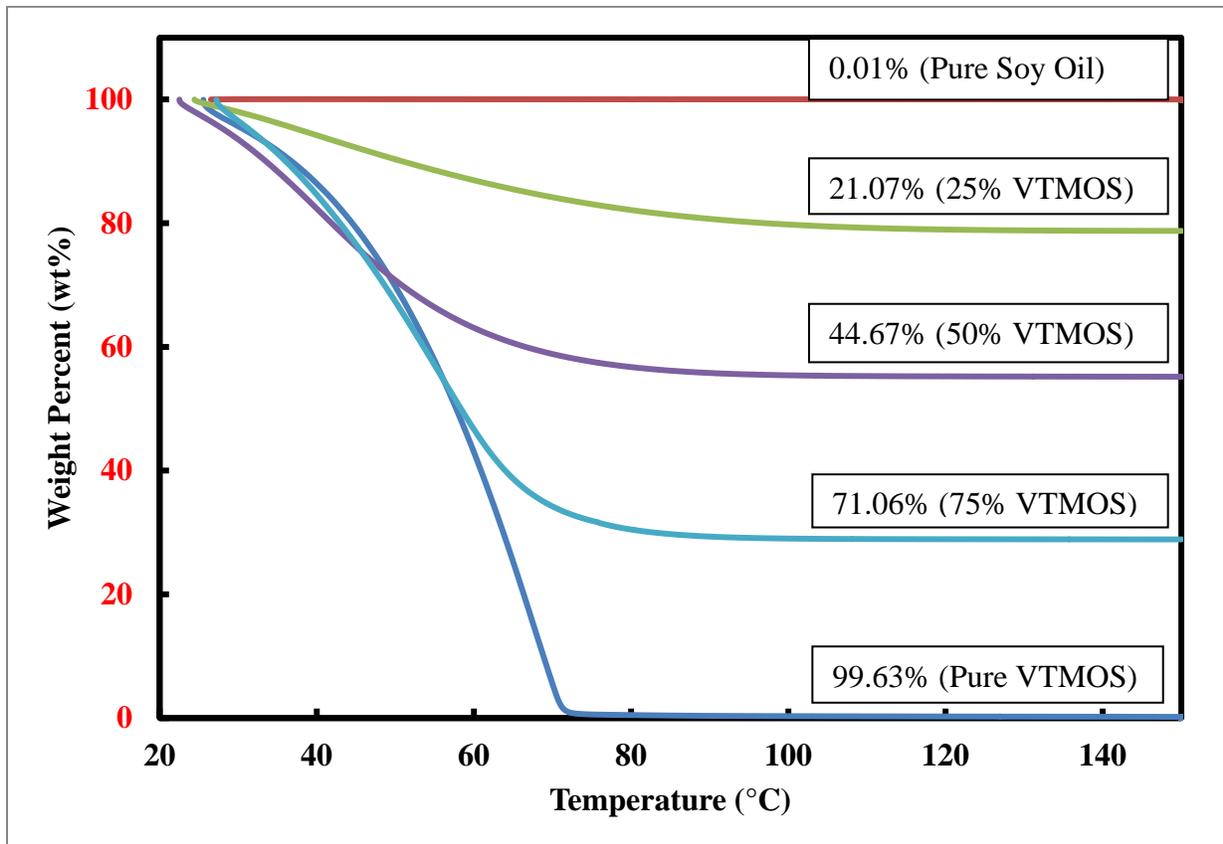


Figure 2.6 TGA calibration curve of unreacted low-sat soy oil:VTMOS mixtures.

2.5.2 Graft Percentages

For initial research, Alder-Ene reactions were performed in a 2 L Parr reactor with a reaction temperature of 280°C and a reaction time of 16 hours. Graft percentages from reaction using Mixture A reactant ratios (Table 2.1) are shown in Figure 2.7 and Table 2.3. Graft percentages were calculated using Eq. 2.1.

For manufacturing purposes, repeatability is of the highest priority. Therefore it's critical to be able to control and accurately predict the silane graft percentage by varying the reaction time or temperature. Similarly, it is important that each silylated soy product fall within predetermined limits for each analytical method used for product evaluation. This ensures that the each reaction product meets certain acceptable criteria thus exemplifying identical properties

from previous reactions. As seen in Table 2.3, the average graft percentage for nine reactions run under the same conditions was found to be $90.3\% \pm 2.5\%$. Because the calculated graft% of reactions 6, 8, and 9 exceeded one standard deviation unit (2.5%) they were not used for any coating studies or evaluation.

Table 2.3 Graft percentages of silylated soy oil products run in 2 L Parr reactor at 280°C for 16 hours. Graft percentages were calculated using Eq. 2.1.

Reaction	wt%VTMOS	wt%loss _{123°C}	graft%
1	33	3.059	90.7
2	33.6	2.827	91.6
3	33.5	3.138	90.6
4	33.5	3.179	90.5
5	33.6	2.809	91.6
6	33.5	2.004	94
7	32.9	2.877	91.3
8	33.3	4.863	85.4
9	32.8	4.143	87.4
Average			90.3
Std. Dev.			2.5

The graft percentage of each reaction also provides insight into the viscosity of the silylated soy product (Fig. 2.4). Higher viscosity silylated soy products result in shorter pot-life times. Pot life time is the time in which a catalyzed thermosetting resin retains sufficiently low viscosity for processing [17]. For initial lab work, pot life is not of major concern because the coating instrument used is not restricted by the viscosity of the coating material. In industrial coating processes however, pot life plays a major factor in determining the feasibility of using a certain coating matrix. A pot life under three hours is generally considered too short for use and implementation at large-scale industrial applications. As a result, achieving precise and consistent silane graft percentages, like shown in Table 2.3, allows for accurate predictions of

pot life during the coating process making the determined graft percentage calculated for each batch incredibly useful.

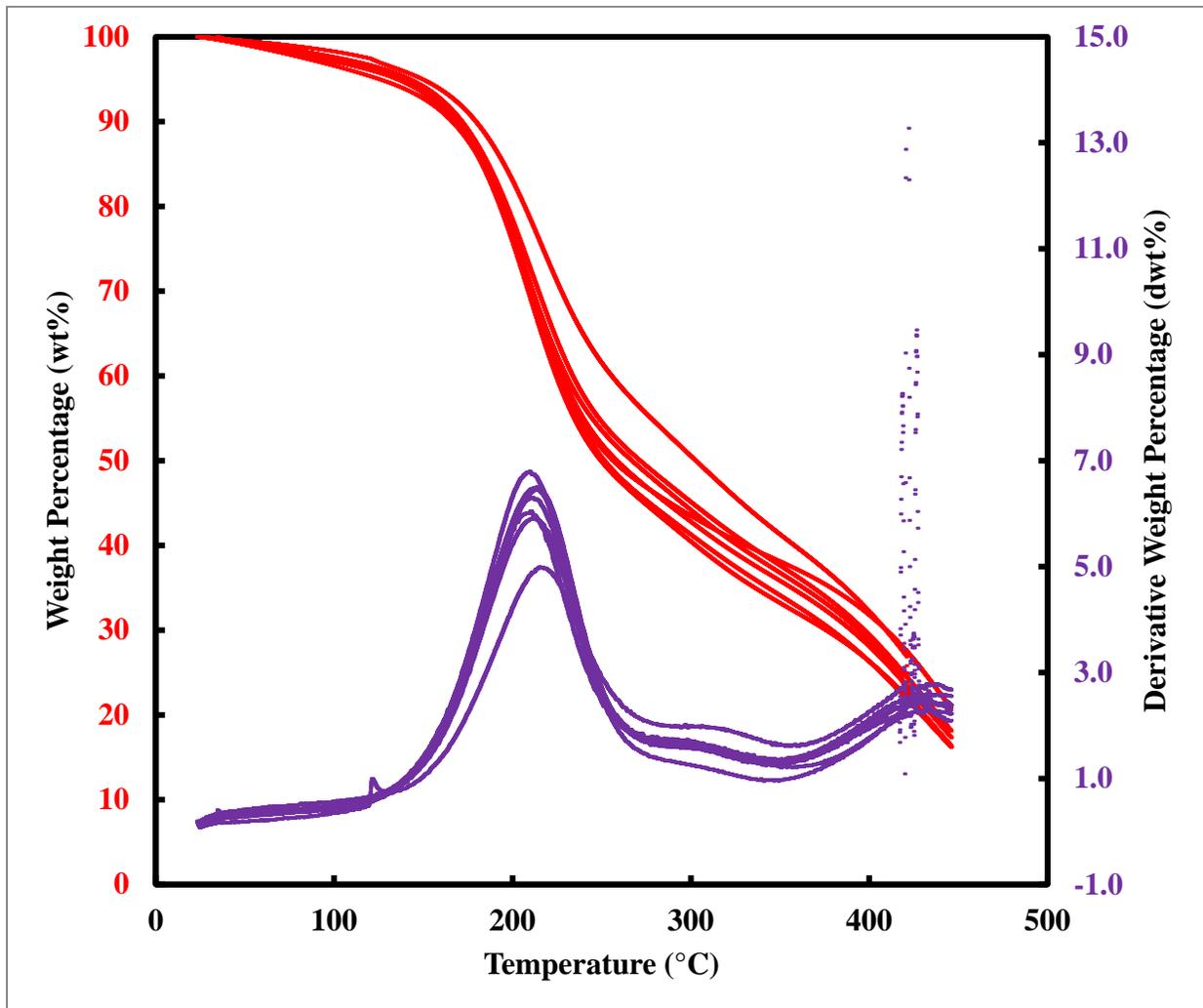


Figure 2.7 Overlay of TGA plots from Reactions 1-9 using 5°C/min ramp up to 450°C under nitrogen gas.

2.5.3 Viscosity

Each product was evaluated for relative viscosity using a Brookfield DV-E viscometer with an LV spindle set at a rate of 30 rpm. Results from Reactions 1-9 are presented in Table 2.4. All viscosities were measured at room temp (22°C) and were taken within 24 hours after removing products from the reactor following reaction completion.

Table 2.4 Summary of graft percentage and associated viscosity from Reactions 1-9.

Reaction	Graft %	Viscosity (cP)
1	90.7	307
2	91.6	296
3	90.6	162
4	90.5	193
5	91.6	530
6	94.0	308
7	91.3	465
8	85.4	106
9	87.4	116
Avg.	90.3	275.9
Std. Dev.	2.5	148.7

While reactions 6, 8, and 9 were not used for coating purposes they did provide valuable insight regarding the relationship between graft percentage and viscosity. Reactions 8 and 9 exhibited slightly lower graft percentages but drastically lower viscosities. Similarly, Reactions 2, 5, 6, and 7 showed graft percentages slightly above average, but had drastically increased viscosities. This data suggests that even slight variations of silane graft percentage will have drastic impacts on the resulting viscosity.

Excluding Reactions 6, 8, and 9 from the viscosity statistical evaluation, the standard deviation becomes 146.1 cP despite reducing the number of data points by 33%. This large standard deviation is most likely due to partial hydrolysis, or crosslinking, of some products (i.e. Reactions 5 and 7) during the reaction. Partially hydrolyzed samples would drastically affect the measured viscosity of silylated soy oil.

2.5.4 Volatile Organic Compound Measurements

VOCs were measured using two separate techniques. The first method was performed in a digitally controlled mechanical convection oven. The second method was done using a TGA heating method. Samples of uncoated, uncured silylated soy oil were tested using both heating methods. All tests were done in triplicate and followed ASTM D2369. For comparison purposes, mixtures of silylated soy oil, water, and dibutyltin dilaurate (DBTDL) were also analyzed to determine the impact gelation may have on VOC levels. Gelation is the process of a polymer cross-linking until which it exhibits no flow when in steady-state. This is another way of describing a polymer's curing behavior and properties [18]. Silylated soy oil, water, and DBTDL mixtures were prepared by adding 1.0 wt% each (based on weight of silylated soy oil) of water and DBTDL. All VOC calculations were performed using Eq. 2.3.

The convection heating method resulted in lower VOCs than the TGA method. This was due to smaller sample weights used in the TGA method. Because TGA is only capable of evaluating sample sizes well below 0.20 g, the sample surface areas using TGA would be higher and therefore easier to evaporate at elevated temperatures. Despite, this difference in sample size between the two heating methods, the results indicate VOCs of approximately 9.5 wt% for pure silylated soy oil and 10.5 wt% for the silylated soy mixture used for coatings. In each heating method, the silylated oil *mixtures* exhibit higher VOCs than pure silylated oil by approximately 1.0 wt%. This is attributable to the addition of water in the mixtures which has a boiling point below the testing temperature (110°C).

Under the Clean Air Act, waterproof coatings have an allowable content limit of 600 grams of VOC per liter of coating material [19]. The average density from all silylated soy products was found to be 0.992 g/mL using a 25 mL specific gravity picometer. Using the

results from Table V, for silylated soy oil *mixtures*, the VOC equates to 99.8 grams of VOC per liter of coating material, well below the regulated 600 gram per liter limit. Similarly, pure silylated soy oil has a VOC content of 88.9 grams per liter of coating. Due to the high solids content as a result of the high soy oil concentration, silylated soy oil coatings demonstrate very low VOC contents. Specifically, the magnitude at which silylated soy oil falls below the allowable VOC limit suggests the coating to be extremely environmentally friendly in regards to air quality.

Table 2.5 VOC results of convection oven and TGA heating methods. Values indicate weight percent loss for both silylated soy oil and pre-coating mixtures containing 1wt% water and DBTDL.

Sample	Convection Oven Heating Method VOC %		TGA Heating Method VOC %	
	Silylated Oil	Silylated Oil with 1 wt% Water & DBTDL	Silylated Oil	Silylated Oil with 1 wt% Water & DBTDL
A	9.06	10.01	10.22	11.05
B	9.12	10.01	9.97	10.68
C	8.70	10.16	10.03	10.83
avg.	8.96	10.06	10.07	10.85
std. dev.	0.23	0.09	0.13	0.19

2.6 Results & Discussion – 5 Gallon Parr Reactor

2.6.1 TGA & Graft Percentages

Large amounts of silylated soy oil were required for manufacturing-scale trials. Consequently, a much larger reactor was needed to achieve the required amount of coating material necessary. Manipulation of a reactor’s dimensions and volume drastically impacts a reaction’s kinetics resulting in variations in heating, cooling, and reaction times. As a result, several reaction conditions were changed between 2 L and 5 gal. reactors in order to meet the hydrophobicity, viscosity, and pot life specifications required of most coating facilities. Additionally, the heating mantle for the 5 gal. Parr reactor was limited to 250°C, further

complicating the heating, cooling, and reaction times needed to provide the desired characteristics of the final product.

Table 2.6 Graft percentages of silylated soy oil products run in 5 gal. Parr reactor at 250°C, 20 hours calculated using Eq. 2.1.

Reaction	wt%_{VTMOS}	wt%_{loss}_{123°C}	Graft %
10	33.1	7.053	78.7
11	33.1	0.842	97.5
12	33.1	6.646	79.9
13	33.1	4.981	84.9
14	32.8	6.619	79.8
15	33.6	5.675	83.1
16	33.3	6.792	79.6
17	33.6	6.959	79.3
18	33.6	6.796	79.8
19	33.6	6.576	80.4
Average			82.3
Std. Dev.			5.7

Ultimately, reactions were carried out for 20 hours to compensate for the reduced reaction temperature and larger reactor volume. Mixture A reactant ratios (Table 2.1) were used for all reactions performed in the 5 gal. Parr reactor. TGA results and graft percentages are shown in Figure 2.8 and Table 2.6, respectively. Graft percentages were calculated using Eq. 2.1.

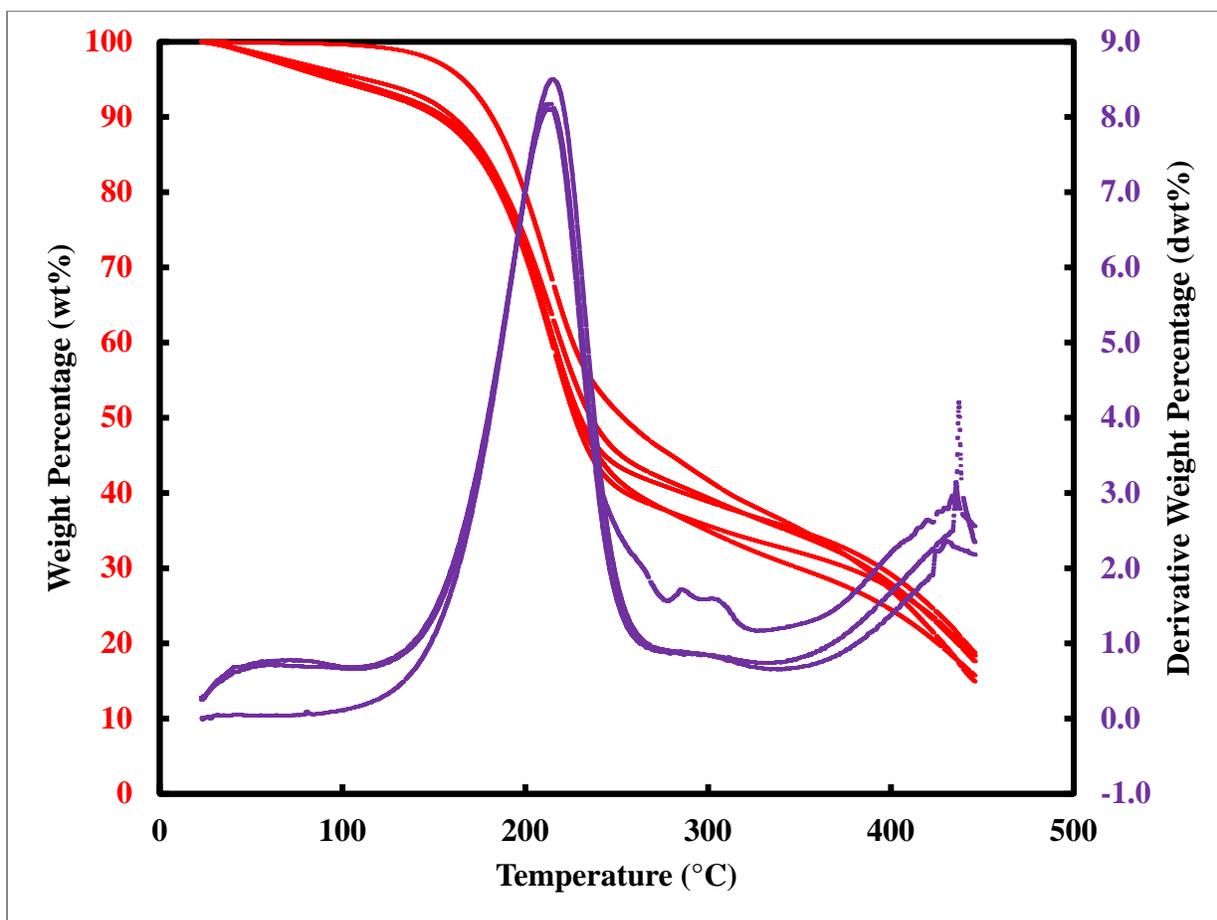


Figure 2.8 Overlay of TGA plots from Reactions 10-19 using 5°C/min ramp up to 450°C under nitrogen gas.

Like the results from Reactions 1-9 carried out in the 2 L Parr reactor, the average graft percentage and standard deviation were found to be $82.3\% \pm 5.7\%$. Reaction 11, however, was subject to partial curing (Figure 2.9) during the reaction causing a gelatinous substance to form within the reactor. The partial curing inside the reactor was most likely due to residual water present in the reactor causing the reacted silane molecules to undergo intermolecular cross-linking. Subsequently this also accounts for its drastically elevated high graft percentage. Like Reactions 6, 8, and 9 from the 2 L reactor, Reaction 11 exceeded one standard deviation unit for

graft percentage and was not used for any coating purposes. Excluding Reaction 11 from the total data resulted in an average graft percentage of $80.6\% \pm 2.0\%$.

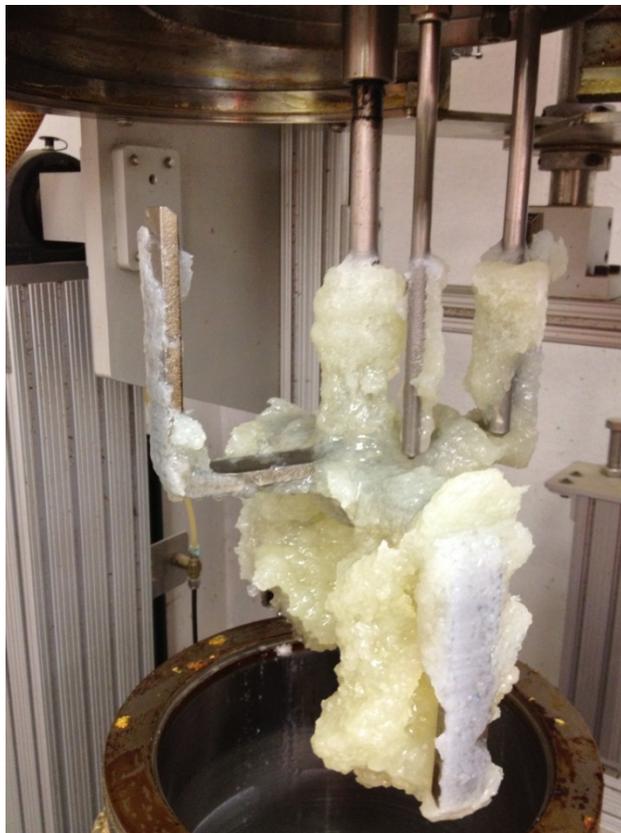


Figure 2.9 Final product of Reaction 11 from partially cured silylated soy oil. The solid material on the stirrer is fully cured silylated soy oil. A small amount of viscous liquid silylated soy oil was collected, characterized, and analyzed but was not used for further coating tests and applications.

Similar to results highlighted in Figure 2.7, the reproducibility of the desired silylated soy oil is shown in the TGA results found in Figure 2.8. The overlapping wt% loss and derivative wt% loss curves indicate products with very comparable thermal degradation properties, thus supporting the reaction's reproducibility in large volume reactors. Establishing reproducibility of the desired product in a larger reactor is a critical component in developing the scale-up process for the synthesis and application of any coating material.

2.6.2 Viscosity

Each product was evaluated for bulk viscosity using a Brookfield DV-E viscometer with an LV spindle set and a rate of 30 rpm. It was important that products from Reactions 10-19 show lower viscosities with less variability to demonstrate pot life times exceeding three hours. Products with lower viscosities require much more time to develop a high viscosity. Because the maximum working viscosity of most industrial coating processes is 800 cP (for gravure coating technique), silylated soy oil with viscosities in 40-80 cP range drastically improve the pot life potential. Therefore, it was desired that Reactions 10-19 demonstrate lower viscosities than Reactions 1-9 while still exhibiting graft percentages large enough to allow the silylated soy oil to completely cure. Table 2.7 summarizes the graft percentages and viscosities of reactions performed in the 5 gal. reactor.

With the exception of Reaction 11, which partially cured, the standard deviation was substantially smaller for reactions performed in the 5 gal. reactor versus those performed in the 2 L reactor. Excluding reactions exceeding one standard deviation, average viscosity was calculated to be $41.2 \text{ cP} \pm 4.5 \text{ cP}$. As a result, the trend between graft percentage and viscosity was much more predictable (Figure 2.10). Plotting the viscosities of Reactions 10-19 with respect to graft percentage of each product provides a very definitive polynomial equation that allows for accurate predictions of viscosity. This plot, in conjunction with pot life experimental data discussed in chapter three, provide an accurate method for estimating pot life of silylated soy oil using only graft percentage and viscosity measurements. This allows for a reliable, yet rudimentary, method for accepting or rejecting a reaction's products for coating use.

Table 2.7 Summary of graft percentage and associated viscosity from Reactions 10-19.

Reaction	Graft %	Viscosity (cP)
10	78.7	39
11	97.5	260
12	79.9	40
13	84.9	41
14	79.8	36
15	83.1	52
16	79.6	40
17	79.3	44
18	79.8	39
19	80.4	40
Avg.	82.3	63.1
Std. Dev.	5.7	69.3

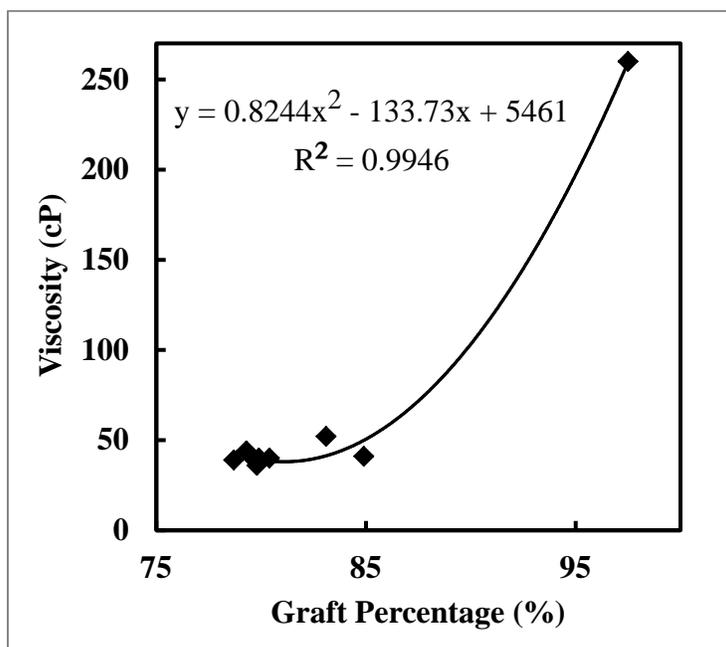


Figure 2.10 Viscosity measurements of 5 gal. reactor products with respect to graft percentage.

2.7 Results & Discussion – Varying Silane Reactants and Reactant Ratios

In an effort to improve coating performance while minimizing production costs, different silane molecules and reaction ratios were investigated. As shown in Table I, Alder-Ene reactions were carried out using four different reactant mixtures. Though Mixture A was the primary focus throughout the entirety of the project; reactions using Mixtures B-D were performed and analyzed for comparison purposes.

2.7.1 Mixture B – 1:1 Molar Ratio Soy Oil:VTMOS

Multiple reactions were performed in a 2L Parr reactor using a 1:1 molar ratio of low-saturated soy oil to VTMOS. Each reaction resulted in a viscous liquid product. The consistencies of the products were similar to that of jelly or jam and with viscosities ranging from 1800-42,000 cP. The increased viscosity seen in the 1:1 molar ratio of soy oil:VTMOS compared to 1:3 molar ratio results from the degree of curing which took place while the large range in viscosity can be attributed to the degree of curing that occurred during the course of the reaction. Similarly, the graft percentages of each reaction exceeded 95%, again, as a result of the curing process.

As may be expected, the physical properties resulting from a 1:1 molar reaction pose several new issues not seen by the products of the 1:3 molar reaction, mostly due to the dramatic viscosity increase. An initial viscosity of 1800 cP already far exceeds the upper viscosity limit of gravure roller coating capabilities. Adding water and DBTDL to promote further crosslinking would only increase the already high viscosity of 1:1 molar silylated soy oil. As a result, an alternative coating process to using a gravure roller would need to be investigated. Additionally, with an increased viscosity comes a decreased pot-life. Because 1:1 molar silylated soy oil has a very high viscosity, its pot-life time is substantially reduced even if using other coating techniques with higher operational viscosity limits. As a result, this particular reaction ratio was

not investigated much beyond initial physical property analysis and preliminary coating evaluations. It is possible that varying the reaction time or temperature may provide a usable silylated soy oil product for coating purposes, however, further investigation would be required to determine if this reactant ratio is feasible and provides a usable product.

2.7.2 Mixture C – 1:3 Molar Ratio Soy Oil:VTEOS

One reaction was performed using VTEOS at a 1:3 molar ratio of soy oil and VTEOS in place of VTMOs. The result of the reaction was very comparable to reactions using Mixture A (VTMOs of the same molar ratio). The graft percentage was calculated to be 75.1% with a viscosity of 62 cP. Additionally, coated samples using VTEOS showed very similar hydrophobic properties to coatings using Mixture A silylated soy oil. For instance, measuring the Cobb Values, a method of quantitatively measuring water resistance, for Mixture C products shows water absorption to be 19.5 grams per square meter (gsm). This value is considered to be quite hydrophobic in the paper industry. These results are discussed in greater detail in Chapter 3: Silylated Soy Oil Coatings. While the majority of research was done using a Mixture A silylated soy oil, it can be safely assumed from the results obtained from TGA, viscosity, and measured Cobb Values that a VTEOS formulation could easily be used in place of a 1:3 molar ratio of soy oil and VTMOs.

2.7.3 Mixture D – 1:1 Molar Ratio Soy Oil:VTEOS

Much like the results seen in Mixture B silylated soy oil, using VTEOS in a 1:1 molar ratio also exhibits a substantial increase in viscosity. Though the viscosity of the Mixture D product has a somewhat lower viscosity at 336 cP with a graft percentage of 81.1%, the elevated viscosity would still prove problematic in most industrial coating settings.

If Mixtures B and D were to be used for coatings, one way to extend their pot life would be to reduce the concentrations of water and DBTDL used during the pre-coating mixing and curing process. Reducing the water and DBTDL concentrations used for the pre-coating mixture may provide extended pot life despite these mixtures exhibiting significantly elevated viscosities. Investigating these variables as well as reaction temperature and time may provide a product similar in physical properties to those seen in Mixtures A and C. Also, Cobb Values, which quantitatively measure water resistance, provide no additional hydrophobic benefit when using Mixtures B and D for coatings.

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Chapter 3: Silylated Soy Oil Coatings

3.1 Coating Background & Cure Chemistry

Coatings are coverings that are applied to a surface, or substrate, that enhances the surface properties of the substrate. They can have several different functionalities including adhesive, wear resistance, corrosion resistance, release properties, and appearance adjustments, as well as several other applications. Much like the numerous coating functionalities, there are many different coating techniques used to apply a coating to a substrate. Coatings can be applied from solutions, emulsions, or directly from the bulk providing the viscosity is sufficient. Additionally, coatings can be synthesized from a multitude of different media such as water, solvents, and acrylics.

Furthermore, the multitude of uses of coatings ranging from protective functions such as anticorrosive paint applied to cars, to decorative properties for things such as camouflaging military equipment or color coding which indicates a container's contents, or even antibacterial coatings used in sterile environments such as hospitals, provide another physical requirement that must be met. Such a broad spectrum of requirements explains why no single coating can simultaneously satisfy every demand. Providing coating materials for the durable protection, decoration, and improvement of objects made of wood, metal, plastic, or paper at reasonable prices can only be met by adopting different formulations using a range of material combinations. Each combination targets a limited field of substrates, a selected application method, and a specific profile of film properties [1].

When the different coating functionalities, application methods, and formulations are considered, there are many ways in which a coating can be produced. Therefore, the quality

achieved during the coating process is not only the function of the material used, but is dependent on the coating material and design, the appropriate applications process, and the substrate that is used. Manipulating any of these variables can drastically impact the performance properties of the final coated product. Thus, it is critical to investigate all aspects of the coating process in order to determine the optimal conditions that result in the desired coated product.

3.2 Silicone Coatings & Cure Chemistry

The incorporation of siloxane molecules into the unsaturated double bonds in soy oil allows the modified soy oil to demonstrate properties that are typical of repeating Si-O-Si bonds associated with siloxane coating chemistry. While several other coating substrates can be used as supplied, silicone polymers must be crosslinked (or cured) to achieve their final properties [2]. This process requires a crosslinking agent which promotes the reaction of a silicone molecule to react with a functional site of an adjacent silicone molecule. When a silicone molecule has more than one functional group, it can react with multiple silicone molecules, thus forming a complex chain or branched network. The most commonly used cure reactions are free-radical, addition, and condensation reactions. Condensation reactions are often used in sealants and waterproofing coatings and were used as the curing mechanism for this project. Crosslinking using a condensation reaction typically uses an organometallic tin catalyst. Specifically, dibutyltin dilaurate (DBTDL) and dibutyltin dioctoate (DBTDO) are commonly used as a catalyst in many condensation curing reactions. In addition to a tin catalyst, the curing process is also dependent on the presence of moisture which allows the silicone molecules to form a crosslinked network. This resulting network is considered to be a cured product (Figure 3.1).

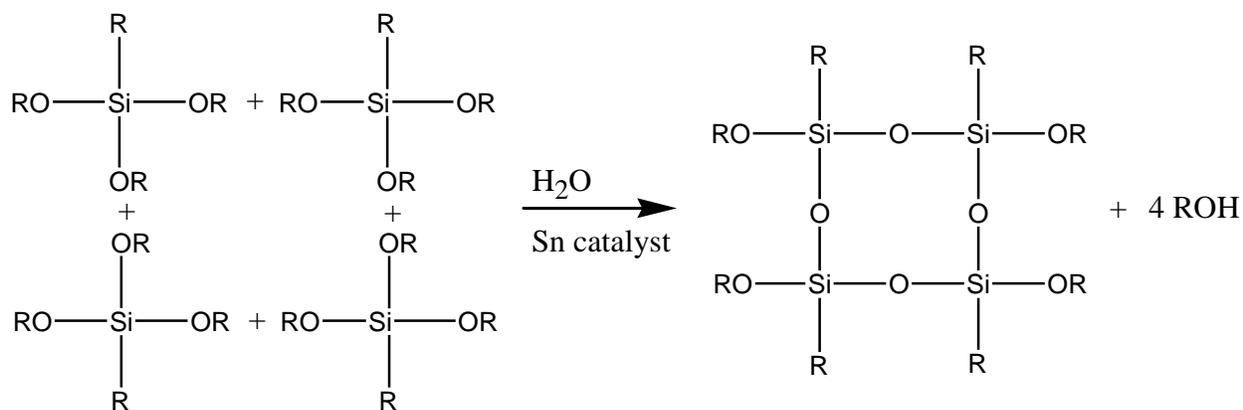


Figure 3.1 Polymer Condensation reaction resulting in a cured silicone polymer with OR representing siloxane substituents (e.g. methoxy or ethoxy groups in VTMOs and VTEOS, respectively) and R substituents representing vinyl groups which graft to the unsaturated double bonds of soy oil during an Alder-Ene reaction.

The cure rate of a condensation reaction is dependent on the amount of catalyst and moisture present and is independent of curing, or drying, temperature. However, because an alcohol is formed during the curing process of silylated soy oil, increased temperatures help remove the undesired alcohol byproducts more rapidly resulting in a shorter tack-free time. Tack-free time is the time required for a coated sample to be dry to the touch once the coating has been applied. Exposing a silylated soy oil coating to increased temperatures can result in a more complete cure with minimal alcohol byproducts. Much like the variety of ways that a coating can be manufactured, adjusting coating variables such as cure temperature, cure time, catalyst and moisture concentrations, paper grade, and coating weight all have impacts on the properties of a coating. In essence, it is necessary to view the final product, not as a series of separate processing steps, but as an integrated system. Furthermore, the functional performance of a silicone coating is affected by the physical properties of the silicone as well as the application process and the performance characteristics required of the final product [3].

3.3 Coating Variables

As mentioned, several variables must be considered when developing a silicone coating that meets certain physical property criteria. Manipulation of coat weights, cure temp, cure time, water content, catalyst concentration, and paper grades were investigated.

3.3.1 Coating Weight

The amount of coating placed on a substrate can substantially affect the desired physical properties. For this project, a high degree of hydrophobicity is desired for a few hours, yet over several weeks, the coating must be biodegradable under aqueous conditions. A coat weight too low wouldn't demonstrate the needed water resistance due to the limited amount of silylated soy oil that can interact with the surface of the paper. Specifically, a low coat weight may not maximize the interactions between the fibers of the paper and the silylated soy coating. This coating-paper interaction depends greatly on the distribution of the fiber bundles in the paper being used.

In contrast, a coat weight too high can result in saturation of the coating material into the paper, thus impacting the strength and hydrophobicity of the coated product. Additionally, using excess silylated soy oil would negatively impact production costs while not providing any additional hydrophobicity beyond a certain point. However, small increases in coat weight can provide improved hydrophobic properties. Therefore, determining a coat weight that is high enough to meet the needed water resistant specifications, yet low enough to be coated on paper without being absorbed while minimizing production costs is critical to product development.

3.3.2 Cure Temperature & Time

Due to the moisture-cured siloxane reaction used in this project, the resulting byproduct of the crosslinking is an alcohol. The presence of alcohol on the surface of the coating has a substantial negative impact on hydrophobicity. Therefore, the alcohol must be removed to

achieve the maximum water resistivity. Heating the finished coatings allows for any residual alcohol on the coating surface to be removed quickly and effectively. However, exposing the paper coatings to temperatures too high may diminish the structural integrity of the coating or paper itself, making it brittle or flaky and rendering it useless.

The time required for the coating to completely cure is varied by the catalyst concentration for silicone condensation reactions. While it is not necessary for a coating to be fully cured in order to demonstrate drastically improved hydrophobicity, the amount of time a coated product is allowed to cure varies its water-resistant properties. Likewise, cure time and tack-free time are directly influenced by the cure temperature that samples are subjected to. A shorter tack-free time would allow a coating facility to operate at a higher coating speed resulting in higher production rates.

While operation and installation costs for a dryer would be expensive, the increase in production volume by significantly reducing cure and tack-free times would drastically improve production costs. Determining the relationship between cure temp, cure time, and hydrophobicity provide insight into the optimal coating conditions that result in the best hydrophobic coating while minimizing energy demands associated with a dryer.

3.3.3 Catalyst and Moisture Concentrations

Two important variables that affect the cure kinetics of a condensation reaction are the concentrations of catalyst and water reacted. As a result, varying the concentrations of the catalyst used in the cure process will have a direct effect on the viscosity and, ultimately, the pot-life of a condensation cure. While viscosity and pot-life are not of primary concern at a small, development-scale volume, they become an increasingly important variable to consider when coating large volumes associated with mass manufacturing. Therefore determining the optimal

formulations of water and catalyst and how they affect cure rate becomes a critical component of the coating development. While it is important to be able to meet predetermined pot-life requirements, it is equally as important to meet the required coating performance criteria. Also, due to the cost of DBTDL, reducing the amount used during the cure process can drastically improve production costs.

3.3.4 Paper Types

There are several variables in paper production that can substantially impact the physical properties, and ultimately, the applications that each paper type is used for. These variables include basis weight (the weight per unit area, commonly expressed in gsm's), fiber source (material used to make the pulp that is developed into paper), fiber orientation (the alignment of the fibers in the paper), filler content (minerals added to the pulp to enhance desired properties), formation (the uniformity of the fibers throughout the paper), and several other factors that contribute to the functionality of the paper [4]. Each of these factors can affect how well a coating interacts with the surface fibers of a paper. This makes the paper selection for this project important when considering the property performance of the final coated product.

For example, a paper with a low degree of formation could negatively impact the water-resistance due to the inconsistent distribution of fiber bundles that interact with the coating. Similarly, low degree of formation can decrease a paper's tensile strength [5]. Because this project is focused on creating coated paper for trash bag production, it is necessary for the product to demonstrate both uniform water-resistance and a high tensile strength. Therefore, using a paper with good construction characteristics should improve the strength and hydrophobicity of the coated product. However, evaluating and considering the several other

variables of paper production that affect a paper's physical properties can also provide a greatly improved coated product.

3.3.5 Additional Factors

When developing a coating such as silylated soy oil, it is essential to view the final product, not as a series of separate steps and components, but as an integrated system. The functional performance of the silicone is affected not only by the physical properties of the silicone, but also by the application process and performance characteristics required of the final product [3]. Therefore factors such as pot life, mixing, and tack-free times must also be considered in development of the silicone coating "system". While the hydrophobicity of the coating and tensile strength of the paper are of utmost importance, it is equally important to demonstrate a long pot life and a short tack-free time. Therefore, improving water resistance is equally as important as reducing a coatings tack-free time. For instance, improving a coating's hydrophobicity while neglecting tack-free time would result in an unusable product at an industrial scale because re-rolling the paper after the coating application would result in the felt side (coated side of the paper) adhering to the wire side (back side of the paper) creating a solid block of paper that couldn't be un-rolled. Similarly, improving tack-free time while neglecting a coating's water resistance would also be undesirable. Consequently, creating a coating system that satisfies both the coating performance and the application process requirements presents the most difficult challenge of this project.

3.3.5.1 Pot Life Time

Pot life time is the length of time from when the curing materials have been mixed to the time where the viscosity increases to the point where the coating material is no longer usable due to extensive curing. When using a gravure roll coater, the upper viscosity limit is approximately 800 cP. For a coating to be considered usable at an industrial scale, the pre-coating mixture must

not exceed the upper viscosity limit for at least three hours. To extend the pot life of the pre-coating mixture, DBTDL and water concentrations can be varied. As a result, the concentrations of DBTDL and water were varied to determine optimal concentrations which would satisfy both coating performance and pot life requirements.

3.3.5.2 Blend (Mixing) Time

Blend time, or mixing time, is closely associated with pot life time. Blend time is the amount of time to achieve a predefined level of homogeneity of a tracer in a mixing vessel. For this project, it is defined as the amount of time between the combination of the curing reactants (silylated soy oil, DBTDL, and water) and the time in which this pre-coating mixture is applied. Varying the blend time impacts the viscosity of the coating mixture which, in effect, impacts how well the coating coats to the paper's surface. As previously mentioned, coating performance varies dramatically with how well the coating interacts with the surface of the paper. Because a certain degree of strength is needed for use as a trash bag, and because a saturated coating diminishes a paper's tensile strength, it is important to have a good surface coating while maintaining a viscosity below 800 cP. Like pot life, blend time is also dependent on viscosity limits while also meeting the desired coating properties.

3.3.5.3 Tack-Free Time

Tack-free time is commonly associated with the cure process and is considered to be the time that has elapsed between mixing and the point of time when the mixture is no longer wet, or tacky, to the touch [6]. It is commonly associated with the cure process itself. Tack-free time is especially critical at larger scales where rolls of paper are used as opposed to single page (8.5"x11") samples. Having a long tack-free time at a large scale would result in the felt side of the coating adhering to the wire side of the roll causing the coated roll of paper to adhere to

itself. More importantly, however, a long tack-free time requires a slow coating rate which increases production costs.

Tack-free time can be varied by adjusting the coat weight and cure temperature. Lower coat weights and higher cure temperatures promote a quicker cure (dry) time whereas heavier coat weights and lower temperatures will exhibit longer tack-free times. While increased coat weights, to a certain point, exhibit improved hydrophobicity, the resulting increase of tack-free time can make the coating system “unbalanced”. Also, while higher cure temperatures provide shorter tack-free times, temperatures too high can result in degradation of the coating itself. Therefore finding a balance between coat weight, cure temp, and tack-free time must be taken into consideration when developing the coating system.

3.4 Materials

Silylated soy oil was used from experiments outlined in Chapter 2. Dibutyltin dilaurate (DBTDL) [CAS 77-58-7] was purchased from Sigma-Aldrich Co., St. Louis, MO and was used as received without any modifications. All papers used for coating purposes were supplied by Wausau Paper, Mosinee, WI.

Coatings were performed using a Euclid Coating Systems Single Roll Lab Coater (ECS). This is a small, pneumatic, bench-top blade-roller coating system that allows the operator to adjust the contact pressure at the blade-roller interface (Figure 3.2). In doing so, a range of coat weights can be achieved.



Figure 3.2 Single Roll Euclid Lab Coater used for all coatings made throughout duration of research. Pneumatic pressure gauge allowed for precise coat weights. The design and small size of the coater required the use of minimal coating material.

3.5 Product Analysis

Coated samples were evaluated for water-resistance using two specific methods that provide insight into the water repellent properties provided by the silylated soy oil coatings. The following section describes each analytical technique used, a brief description of the technique, and how the results were applicable for the silylated soy oil coatings.

3.5.1 Cobb Test

Cobb Testing provides a way of quantitatively measuring the absorption of water (or water resistance) on the surface of paper. A substrate's water absorptiveness is a function of various paper characteristics such as sizing, porosity, and formation, along with several other factors.

Cobb Tests were performed following TAPPI T441 test method by cutting samples into 12.5 cm x 12.5 cm squares. Each sample was weighed and placed on a neoprene mat and

clamped in place by a 100 cm² Cobb Cylinder using a crossbar and tightening knobs (Figure 3.3). One hundred milliliters of water was poured on the sample surface. Timing began at the moment pouring commenced. After one minute and forty-five seconds, the water was poured from the cylinder using care not to drop any water on the portion of the sample outside of the 100 cm² ring. The crossbar was loosened and the sample was placed, with wetted side up, on a sheet of blotting paper. After two minutes, a second blotting paper was placed on top of the sample and was rolled once forward and once back using a 10-kg roller to remove any excess water. No downward force was exerted when using the roller. After rolling, the sample was removed from blotting sheets, folded in half, and reweighed [7]. The total water absorption, or Cobb Value, measured in grams per square meter (gsm) was calculated using Eq. 3.1.

(Eq. 3.1) Cobb Value (gsm) = $\frac{\text{paper mass}_{\text{final}} - \text{paper mass}_{\text{initial}}}{0.01 \text{ m}^2}$

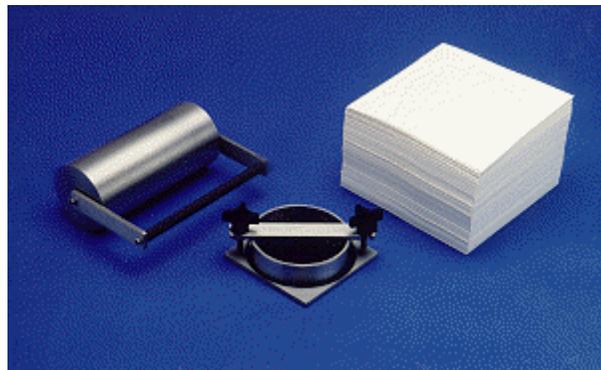


Figure 3.3. Cobb cylinder, blotting paper, and 10-kg roller used for measuring Cobb Values.

3.5.2 Water Contact Angle

Contact angle measures the orientation of a liquid droplet at the liquid-vapor interface when on a solid surface. This observed angle denotes the degree of hydrophobicity but is also

affected by the roughness of the surface and the type of liquid used. The angle made between the liquid and the solid surface can be quantified using Young's Equation. Young's Equation (Eq. 3.2) considers a thermodynamic equilibrium between the liquid droplet (L), the solid surface (S) and the gas, or air, surrounding the droplet (G). Representing each interfacial energy using γ and the equilibrium contact angle as θ_C , the Young's Equation states:

(Eq. 3.2)
$$0 = \gamma_{SG} - \gamma_{SL} - \gamma_{LG} \cos \theta_C$$

The contact angle of a droplet on a solid surface is measured using a sessile drop method (Fig. 3.4). This uses a goniometer, an instrument used to measure angles, and an optical system to measure and record the liquid-solid interface. Typically, water contact angles measuring under 90° are considered hydrophilic, while contact angles above 90° are deemed hydrophobic. While surfaces such as metal normally exhibit contact angles near 0° , or a complete spread of the water droplet on the metal surface, it is common for polymers to behave as hydrophobic surfaces with contact angles over 100° . Surfaces exhibiting low surface energy may even display water contact angles above 120° [8].

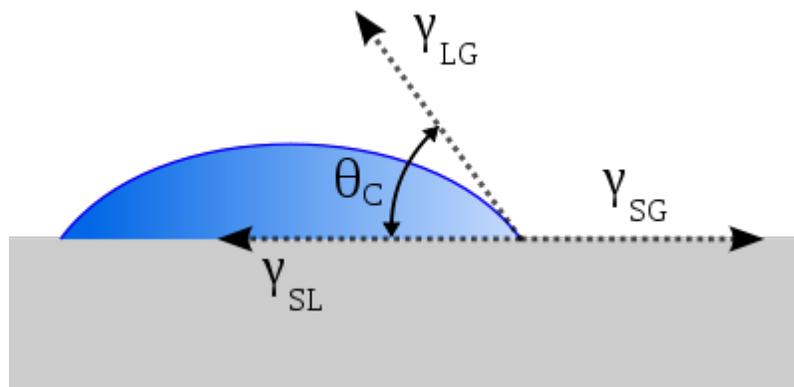


Figure 3.4 Surface contact angle represented as θ_C with respect to interfacial energies [8].

For this project, water contact angles were measured at time intervals of 60, 120, 180, and 300 seconds for both coated and uncoated samples. The angle recorded from both the right and left side of each water droplet was averaged to give the contact angle at each time point. Each paper sample was measured four times at each time interval and the average water contact angle was calculated. Data were summarized for each paper type (coated and uncoated) and time interval.

3.6 Experimental

3.6.1 Varying Paper Samples with Low Basis Weight

3.6.1.1 Method – Varying Paper Samples with Low Basis Weight

Different paper samples (Table 3.1) were tested to evaluate how paper selection would affect the coating performance of silylated soy oil. Each coating was made by mixing 5.0 g of silylated soy oil (Mixture A, Table 1.1), with 4 wt% water (0.2 g), and 1 wt% DBTDL (0.05 g). This was mixed for approximately two minutes on a magnetic stir plate at 1500 rpm. With paper already secured to the ECS roller and blade pressure set at 40 psi, 2-3 mL of mixed coating was spread evenly across the blade-roller interface. The roller was turned one complete revolution and the paper was then removed from the roller. Coat weights were calculated, two minute Cobb Values, ten minute Cobb Values, and water contact angles were measured for each sample. All Cobb Tests were done in triplicate and all data points for water contact angle were done four times. Blank uncoated samples were also tested for Cobb Values and water contact angles.

Table 3.1 Comparison of uncoated paper characteristics provided by Wausau Paper Co.

	Uncoated Paper Characteristics			
	GN553713	GN612899	GN703742	GN354872
Basis Weight (lb./3000ft ²)	55.0	61.0	70.0	35.0
Basis Weight (g/m ²)	89.5	99.3	114.0	57.0
Caliper (mils)	6.0	5.0	6.4	2.9
Cobb Size, 1min (g/m ²)	28	26	35	65
Porosity (sec/100 ml)	17	23	28	35
Tensile CD (lb./in.)	21	29	36	16
Tensile MD (lb./in.)	55	60	58	41
Tensile Ratio	2.6	2.1	1.6	2.6
Tear CD	137	161	107	44
Tear MD	101	136	102	33
Smoothness, Felt	384	133	226	116
Smoothness, Wire	356	133	187	87

3.6.1.2 Results & Discussion – Varying Paper Samples with Low Basis Weight

Uncoated Cobb Values provided by Wausau Paper Co. (Table 3.1) varied dramatically between each paper type. This is likely attributable to the basis weights and porosities of each paper. For instance, GN354872 has a low basis weight and a high porosity, resulting in a high uncoated Cobb Value compared to the other paper types. A higher basis weight is typically a result of a more dense arrangement of fiber bundles in the paper. Therefore the fibers are more compact in the paper, resulting in less fiber surface area that is subjected to water exposure. This contributes to lower Cobb Values. Similarly, a paper's porosity is a result of how quickly water absorbs, or transmits, water through its surface. The lower a paper's porosity, the more water resistant it is.

Two minute Cobb Values show substantial hydrophobicity improvements; GN354872 and GN703742 in particular. While GN354872 demonstrated the worst uncoated Cobb Values, it displayed the lowest two minute Cobb Value and the second lowest ten minute Cobb Value.

This is due to the paper's low-density fiber arrangement. Having a lower fiber content would allow the molecules of the silylated soy oil to better interact with the fiber surface, and thus form a better hydrophobic network across the entirety of the paper; much for the same reason uncoated paper exhibits poor water resistance.

It's also important to consider the difference between the two minute and ten minute Cobb Values. Though all coated samples show acceptable degrees of water resistance for two minutes, none of the ten minute Cobb Values measurements show a high degree of hydrophobicity. Because the trash bags made from the silylated soy oil coatings will likely be exposed to aqueous material in excess of ten minutes, it is critical to demonstrate significantly improved water resistance for time intervals of ten minutes or longer. One potential solution is to use a paper with a higher basis weight. This would result in a lower initial Cobb Value and provide increased hydrophobicity over longer periods of time.

Unexpectedly, results from water contact angle (Table 3.3) did not coincide with the Cobb Values (Table 3.2). Where GN354872 demonstrated the lowest two minute Cobb Values, the coated samples using this paper had the lowest contact angle of the four paper types evaluated, suggesting the worst water-resistance. GN354872 samples did, however, exhibit the largest contact angle improvements between coated and uncoated samples. Though no recordable contact angles were able to be measured for uncoated samples of GN354872 due to complete water absorbance in less than sixty seconds, coated samples maintained a contact angle above 80° for all time intervals. This increase in water contact angle is due to the reduced surface tension, or interface tension, provided by the silylated soy oil coating.

Table 3.2 Cobb Values at both two and ten minute intervals of coated and uncoated papers.

Paper Type	2 Minute Cobb Values (gsm)				10 Minute Cobb Values (gsm)			
	Cobb Value	std. dev.	Blank Cobb Value	std. dev.	Cobb Value	std. dev.	Blank Cobb Value	std. dev.
GN354872	19.1	0.1	62.4	3.0	39.1	8.2	62.5	0.8
GN553713	20.4	0.2	26.2	0.8	36.4	0.3	40.1	2.7
GN612899	24.5	0.2	28.4	0.3	42.3	0.3	43.6	0.6
GN703742	22.2	0.2	91.7	15.3	44.7	0.6	74.6	0.0

Table 3.3 Water contact angles of various paper types of both coated and uncoated samples.

Paper Type	COATED SAMPLE AVERAGES				UNCOATED SAMPLE AVERAGES			
	60s	120s	180s	300s	60s	120s	180s	300s
GN354872	87.4	85.4	83.8	81.3	NA	NA	NA	NA
GN553713	108.4	103.7	102.4	98.2	114.7	111.9	110.8	107.3
GN612899	104.0	101.6	99.6	96.2	122.9	122.2	121.6	119.1
GN703742	107.7	106.4	104.6	102.1	64.4	57.9	46.8	NA

Coated samples of GN703742 also showed significant hydrophobic improvements using contact angle, yet it demonstrated one of the highest Cobb Values; a much better indicator of true water resistance. While the results from the water contact angles were contradictory to the Cobb Test results, the data still provided a useful method of comparing the hydrophobicity improvements between coated and uncoated samples. Ultimately, for trash bag production, Cobb Values provide a better analytical method of evaluating water resistance, while water contact angle can be useful to support the overall improvements seen between the coated and uncoated samples.

In summary, every paper type demonstrated improved water resistance when coated with silylated soy oil. Using Cobb Values and contact angle measurements, paper GN354872 showed the most hydrophobic improvements comparing coated and uncoated samples. Additionally,

GN354872 had the lowest two minute and ten minute Cobb Values. While GN354872 did show several promising hydrophobic improvements, a lower ten minute Cobb Value is essential for the development and implementation of silylated soy oil coatings for trash bag purposes.

3.6.2 – Coat Weight Variations

3.6.2.1 Method – Coat Weight Variations

Silylated soy oil was mixed with 1.0 wt% DBTDL and 4.0 wt% water for approximately two minutes and applied to paper GN505320 using a Euclid Coating System (ECS) at blade pressures between 25-60 psi in 5 psi increments. Each pressure was repeated twice and the coat weight for 8.5” x 11” paper was calculated using Eq. 3.3.

(Eq. 3.3)

$$\text{Coating Weight (gsm)} = \frac{\text{mass}_{\text{post-coating}} - \text{mass}_{\text{pre-coating}}}{0.0603 \text{ m}^2}$$

Cobb Tests were performed on all samples. Results of blade pressure, coat weight, and Cobb Values were evaluated to determine how coat weight affects the water-resistance of the silylated soy oil coatings.

3.6.2.2 Results & Discussion – Coat Weight Variations

Varying blade pressure of the ECS impacts the coat weight of each sample (Figure 3.5). Subjecting each coating to a higher blade pressure removes additional, excess coating material from the surface of the paper providing very low coat weights. However, coatings made with blade pressures between 45-60 psi have little difference in coat weight. This coat weight corresponds to the minimal amount of coating needed to cover the surface of the paper. Therefore, it can be assumed that the minimum amount of silylated soy oil required to make a

surface coating is approximately 3.5 gsm which can be accomplished on the ECS using a blade pressure of 45psi.

While there is a clear trend between blade pressure of the coating system and coat weight, there is much less distinguishable difference between coat weights and Cobb Values. Coatings made using a blade pressure of 25 psi resulted in an average coat weight of 6.0 gsm, whereas coatings made using a blade pressure of 60 psi resulted in an average coat weight of 3.5 gsm. Despite the coat weight being more than 70% higher, coatings made at 25 psi show no statistically significant Cobb Value improvement over coatings made with lower coat weights.

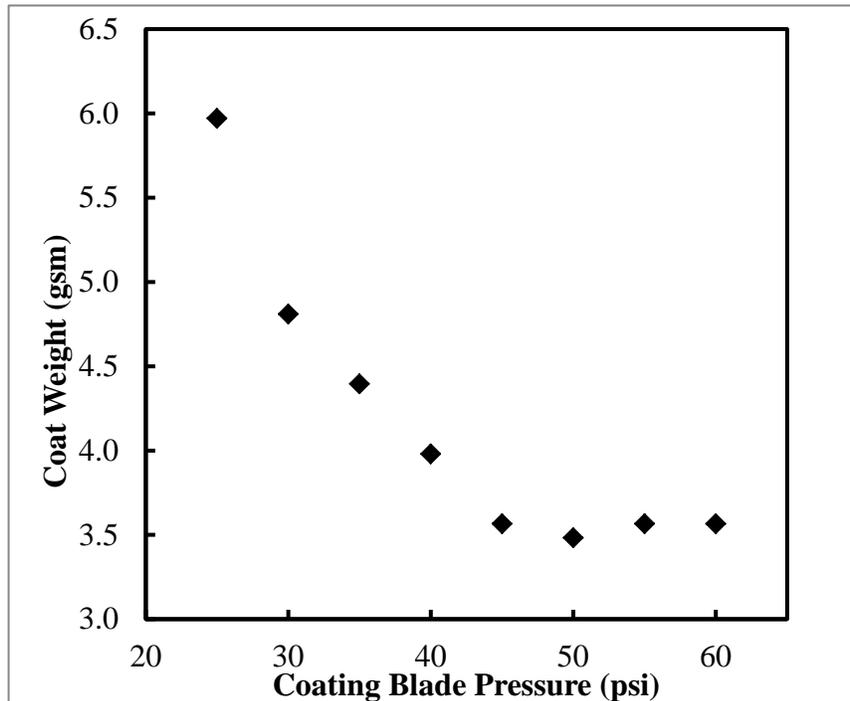


Figure 3.5 Variation in coat weights of silylated soy oil when varying blade pressure on ECS.

Summarizing the data from both Figure 3.5 and Figure 3.6, it is most efficient to operate manufacturing scale coaters that result in a coat weight between 3.0-3.5 gsm. Using a higher coat weight only uses excess coating material while providing limited hydrophobic

improvements. By setting coating equipment to achieve a coat weight near 3.5 gsm, the economics of the coating system is fully optimized while not sacrificing any water resistance performance. This is important when considering any future large-scale silylated soy oil coating operation.

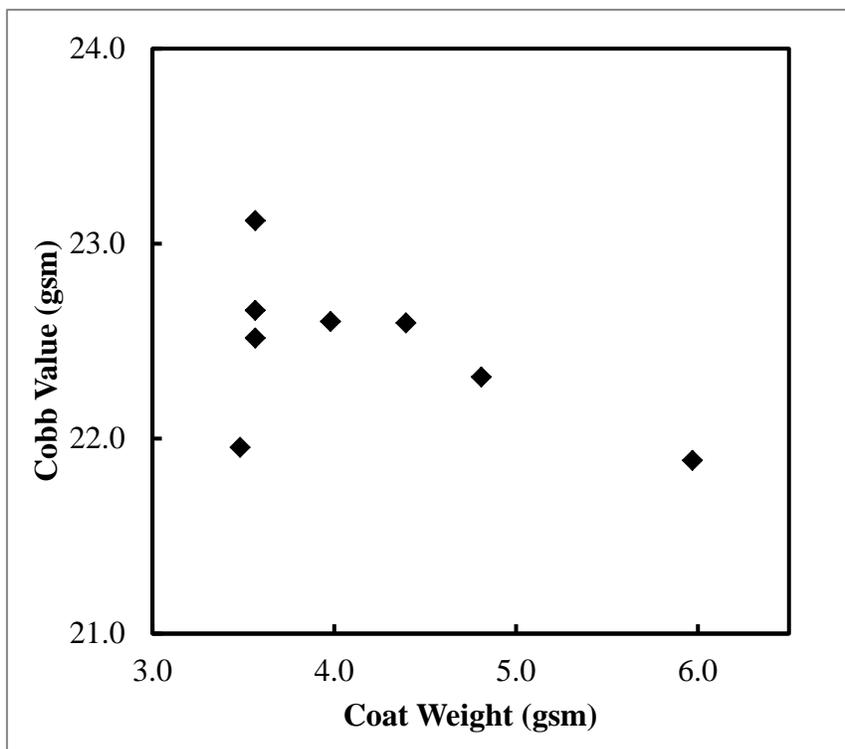


Figure 3.6 Cobb Values when varying the coat weight of silylated soy oil on GN505320 paper.

3.6.3 Cure Time & Temperature

Several experiments were performed to determine the effects of cure time and cure temperature have on the performance of silylated soy oil coatings. The method for each experiment and the results are included in the following sections.

3.6.3.1 Method – 4hr Cure Time with Cure Temps at 60°C and Room Temp

Each coating was made by mixing 5.0 g of silylated soy oil (Mixture A, Table 1.1), with 4 wt% water (0.2 g), and 1 wt% DBTDL (0.05 g). This was mixed for approximately two

minutes on a magnetic stir plate at 1500 rpm. With paper (GN354872) already secured to ECS roller and blade pressure set at 40 psi, 2-3 mL of mixed coating was spread evenly across the blade-roller interface. Roller was turned one complete revolution and paper was removed from the roller.

Each sample was subjected to four hours of total cure time using a combination of 60°C and room temp (approximately 20°C) cure temperatures. Five samples were cured at 60°C for all four hours, five samples were cured for two hours at 60°C and then removed from the oven and allowed to cure at room temp for two hours, and the remaining five samples were cured for four hours at room temp (Table 3.9). Once the pre-determined curing time was complete, samples were tested for two minute Cobb Values. Blank, uncoated samples were also tested.

3.6.3.2 Results & Discussion – 4hr Cure Time with Cure Temps at 60°C and Room Temp

The average coating weight for all samples was 4.1 ± 0.3 gsm; considered a light coat weight by most industry standards. However, even with a low coat weight, the water-resistance improves dramatically as shown in Table 3.4. Silylated soy oil coatings provided water resistant improvements in excess of 160% for samples cured at room temp and 220% for samples cured at 60°C for four hours. Because all coatings had nearly identical coat weights, the 20% Cobb Value improvement between coatings cured at 60°C versus those cured at room temp can be directly attributed to cure temperature.

The improved Cobb Values seen at 60°C cure temps is likely due to the removal of undesired VOCs, specifically methanol, from the coating surface. Subjecting silylated soy oil coatings to temperatures that approach or exceed the boiling point of methanol (65°C) promote the evaporation and removal of this undesired organic byproduct. Therefore when cure times are restricted, Cobb Values improve with increased cure temperatures. Subjecting silylated soy oil

coatings to elevated cure temperatures may also improve the cure kinetics resulting in a more complete cure reaction and, thus, providing a better crosslinked network which would provide an additional explanation for Cobb Value improvement.

Table 3.4 Cobb Values of four hour cure time at combinations of 60°C and room temperature.

SAMPLE	Wt ₀ (g)	Wt _F (g)	Cobb Value (gsm)	Room Temp Cure Time (min)	60°C Cure Time (min)
A1	0.9700	1.1571	18.71	0	240
A2	0.9718	1.1564	18.46	0	240
A3	0.9633	1.1492	18.59	0	240
A4	0.9734	1.1579	18.45	0	240
A5	0.9642	1.1519	18.77	0	240
average			18.6		
std. dev.			0.1		
B1	0.9580	1.1512	19.32	120	120
B2	0.9544	1.1364	18.20	120	120
B3	0.9618	1.1590	19.72	120	120
B4	0.9568	1.1440	18.72	120	120
B5	0.9766	1.1679	19.13	120	120
average			19.0		
std. dev.			0.6		
C1	0.9838	1.2093	22.55	240	0
C2	0.9852	1.1950	20.98	240	0
C3	0.9751	1.2072	23.21	240	0
C4	0.9669	1.1938	22.69	240	0
C5	0.9693	1.2196	25.03	240	0
average			22.9		
std. dev.			1.5		
BL1	0.9297	1.5337	60.40	NA	NA
BL2	0.9336	1.5412	60.76	NA	NA
BL3	0.9083	1.5093	60.10	NA	NA
BL4	0.9153	1.5207	60.54	NA	NA
BL5	0.9002	1.4889	58.87	NA	NA
average			60.1		
std. dev.			0.7		

The difference in Cobb Values between samples cured at room temp and samples cured at 60°C led to additional experiments to investigate cure temperatures above the boiling point of methanol. Variations of cure times at elevated cure temperatures were also examined.

3.6.4 – Reduced Cure Times at 60°C and Room Temp

3.6.4.1 Method – Reduced Cure Times at 60°C and Room Temp

Each coating was made by mixing 5.0 g of silylated soy oil (Mixture A, Table 1.1), with 4 wt% water (0.2 g), and 1 wt% DBTDL (0.05 g). This was mixed for approximately two minutes on a magnetic stir plate at 1500 rpm. With paper (GN354872) already secured to the ECS roller and blade pressure set at 40 psi, 2-3 mL of mixed coating was spread evenly across the blade-roller interface. The roller was turned one complete revolution and the paper was removed from the roller.

Fifteen samples were cured at various time intervals ranging from 15 minutes to 4 hours. Each sample was cured for equal amounts of time at both 20°C (room temp) and 60°C cure temperatures. Each time point was repeated in triplicate. After each cure time was reached, samples were evaluated using two minute Cobb Values. Uncoated blanks were also tested.

3.6.4.2 Results & Discussion – Reduced Cure Times at 60°C and Room Temp

The average coat weight for all samples was 4.0 ± 0.3 gsm (Table 3.5). While the coat weights were very consistent, the Cobb Values varied greatly. Uncoated blanks resulted in Cobb Values in excess of 60 gsm (62.9 ± 1.0 gsm). Samples allowed to cure for a total of four hours showed Cobb Values similar to those in Table 3.7 (19.7 ± 0.9 gsm) which also had a total cure time of four hours. Reducing the total cure time from four hours to two hours resulted in a 1.0 gsm increase in Cobb Value on average. This difference is statistically insignificant, however, due to the standard deviations of both sample sets. As a result, it is not necessary to allow

samples with coat weights near 4.0 gsm to exceed two hours of total cure time in order to reach optimal Cobb Values.

On the contrary, comparing 30 minute total cure times (26.1 ± 0.7 gsm average Cobb Value) to two hour total cure times (20.8 ± 0.5 gsm average Cobb Value) provides significantly different Cobb Values; a 27% improvement. Samples with 10 minute total cure times exhibit comparable Cobb Values (26.4 ± 1.2 gsm average Cobb Values) to those allowed to cure for 30 minutes with equal amounts of oven and room temp cure time. Because there is very little difference in these Cobb Values, it can be deduced that total cure times occurring at 60°C and room temp should fall between 30 minutes and four hours in length.

Samples 13-15 were cured at 60°C for 30 minutes. Comparing the Cobb Values of samples 13-15 with samples 7-9 which have the same cure time but different cure temperatures show a 3.5 gsm decrease in Cobb Value, or a 15% hydrophobicity improvement. Using the data from Table 3.4 and Table 3.5 suggests that silylated soy coatings demonstrate lower Cobb Values when cured at elevated temperatures for 30 and 240 minutes. While shorter cure times demonstrate dramatically improved water resistance compared to uncoated samples, the maximum hydrophobic properties of silylated soy coatings are only achieved at cure temperatures near, or above, the boiling point of methanol for at least 30 minutes. Exceeding cure times of four hours is unnecessary, as subjecting samples to cure intervals longer than this shows no improvement in coating performance.

Table 3.5 Coat weights and Cobb Values of samples cured at various time intervals ranging from 15 minutes to 4 hours. Each sample was cured for equal amounts of time at both 20°C (room temp) and 60°C.

Sample	Coat Weight (gsm)	Cure Condition (°C)	Cure Time (min)	Room Temp Cure Time (min)	Cobb Value (gsm)	Std. Dev.
1	3.48	60	120	120	18.7	
2	3.48	60	120	120	20.0	0.9
3	3.54	60	120	120	20.4	
4	3.81	60	60	60	20.9	
5	3.81	60	60	60	20.3	0.5
6	3.98	60	60	60	21.3	
7	4.15	60	15	15	25.6	
8	4.15	60	15	15	26.9	0.7
9	4.31	60	15	15	25.9	
10	4.31	60	5	5	25.4	
11	4.31	60	5	5	26.0	1.2
12	3.98	60	5	5	27.8	
13	4.31	60	0	30	24.3	
14	4.31	60	0	30	22.4	1.5
15	4.15	60	0	30	21.4	
Blank1	0.00	NA	NA	0	64.1	
Blank2	0.00	NA	NA	0	62.4	1.0
Blank3	0.00	NA	NA	0	62.3	

3.6.5 – 24hr Cure Time, 60°C vs. 80°C Cure Temp

3.6.5.1 Method – 24hr Cure Time, 60°C vs. 80°C Cure Temp

Each coating was made by mixing 5.0 g of silylated soy oil (Mixture A, Table 1.1), with 4 wt% water (0.2 g), and 1 wt% DBTDL (0.05 g). This was mixed for approximately two minutes on a magnetic stir plate at 1500 rpm. With paper (GN354872) already secured to the ECS roller and blade pressure set at 40 psi, 2-3 mL of mixed coating was spread evenly across the blade-roller interface. The roller was turned one complete revolution and the paper was removed from the roller.

Eight samples were subjected to 24 hours of total cure time, with the first hour of cure being at either 60°C or 80°C. After one hour at the designated oven cure temp, samples were removed and the cure process completed at room temp for the remaining 23 hours. At the end of the 24 hour cure period, samples were tested for two minute Cobb Values.

3.6.5.2 Results & Discussion – 24hr Cure Time, 60°C vs. 80°C Cure Temp

The average coating weight was 3.4 ± 0.1 gsm for all coated samples. Similar to the results from the four hour cure time experiment (3.6.3.2), Cobb Values for all samples were greatly improved from uncoated blanks. Samples cured at 60°C for the first hour resulted in an average Cobb Value of 20.9 ± 0.1 gsm, while samples cured at 80°C for the first hour showed an average Cobb Value of 18.6 ± 0.6 gsm (Table 3.6).

Table 3.6 Comparison of sample sets cured at 60°C and 80°C for one hour of 24 hour cure time.

	60°C Samples	80°C Samples
Cobb Average (gsm)	20.9	18.6
Std. Dev. (gsm)	0.1	0.6
Coating Weight Avg. (gsm)	3.57	3.81

While the difference in Cobb Values for samples cured at 60°C versus 80°C is only 1.3 gsm, it equates to a 12% difference. Though increasing the cure temp slightly above the boiling point of methanol does not result in substantial differences in Cobb Value as may be expected, the increased cure temp could provide a shorter tack-free time at an industrial scale.

3.6.6 – Varying Paper Samples with High Basis Weight

3.6.6.1 Method – Varying Paper Samples with High Basis Weight

Most paper trash bags have basis weights ≥ 75 gsm, which is commonly considered a high basis weight. To better assess and simulate the effectiveness and performance properties of

silylated soy oil coatings for use as trash bag coatings, multiple high basis weight papers (Table 3.7) were coated and tested for two minute Cobb Values.

Each coating was made by mixing 5.0 g of silylated soy oil (Mixture A, Table 1.1), with 4 wt% water (0.2 g), and 1 wt% DBTDL (0.05 g). This was mixed for approximately two minutes on a magnetic stir plate at 1500 rpm. With paper already secured to the ECS roller and blade pressure set at 40 psi, 2-3 mL of mixed coating was spread evenly across the blade-roller interface. The roller was turned one complete revolution and the paper was removed from the roller.

Table 3.7 Uncoated high basis weight paper characteristics provided by Wausau Paper Co.

	Uncoated Paper Characteristics		
	GN503832	GN503944	GN505320
Basis Weight (lb./3000ft ²)	50.0	50.0	50.0
Basis Weight (g/m ²)	81.4	81.4	81.4
Caliper (mils)	5.3	6.0	4.0
Cobb Size, 1min (g/m ²)	21	19	21
Porosity (sec/100 ml)	34	14	50
Tensile CD (lb./in.)	26	25	24
Tensile MD (lb./in.)	52	58	56
Tensile Ratio	2.0	2.3	2.3
Tear CD	95	124	88
Tear MD	88	106	69
Smoothness, Felt	375	409	150
Smoothness, Wire	357	397	95

Eight samples were subjected to 24 hours of total cure time, with the first hour of cure being at 80°C. After one hour at oven temp, samples were removed and allowed to finish the cure process at room temp for the remaining 23 hours. At the end of the 24 hour cure period,

samples were tested for two minute Cobb Values. Each different paper type was tested six times. Uncoated blanks for each paper type were also evaluated.

3.6.6.2 Results & Discussion – Varying Paper Samples with High Basis Weight

Each paper type tested had the same basis weight, comparable uncoated Cobb Values, and similar tensile strength properties. The most distinguishable difference between the papers was the porosity of each. Additionally, GN503944 and GN503832 had fluorinated additives in the paper which provide additional water resistance, whereas GN505320 contained no additives. As a result, samples with fluorinated additives show very low two minute Cobb Values for both coated and uncoated samples. Specifically, GN503832 showed excellent hydrophobic properties when coated with Cobb Values below 10 gsm (Table 3.8). However, the tack-free time of GN503832 was considerably longer (> 1 min) even when exposed to 80°C conditions.

Table 3.8 Two minute Cobb Values of coated and uncoated high basis weight papers.

Paper	2 Minute Cobb Values (gsm)			
	Coated Cobb	Std. Dev.	Blank Cobb	Std. Dev.
GN505320	25.5	0.4	43.2	3.2
GN503944	14.9	0.2	13.3	0.4
GN503832	9.6	0.6	25.3	0.4

The environmental impacts of using a paper containing fluorinated additives for use in an environmentally-friendly coating must also be considered. It is well documented that fluorocarbons have negative environmental impacts. While the coated samples of the fluorinated papers demonstrate increased water resistance, the superior property performance these papers exhibit is somewhat negated by the use of fluorocarbons and their inherent environmental impacts.

Comparing the water resistant results of GN505320 and GN354872 (Table 3.8 and Table 3.2, respectively) indicate that both experience significant hydrophobic improvements of coated samples when using two minute Cobb Values to evaluate hydrophobicity. Paper GN354872 has a lower two minute Cobb Value than GN505320 (19.1 versus 25.5 gsm). However, GN354872 has a basis weight too low to be used as a trash bag. One option to consider that was not tested would be to manufacture GN354872 at a higher basis weight (≥ 80 gsm) suitable for use in trash bags. This would provide a higher basis weight that would increase tensile strength while exhibiting lower Cobb Values compared to the other non-additive paper of GN5050320.

3.7 Optimal Coating Conditions

Summarizing the results from the coating experiments (section 3.6), it is clear that cure temperature, cure time, coat weight, and paper grade are very important to the performance properties and production costs of silylated soy oil coatings. Results from sections 3.6.1 and 3.6.6 indicate that a paper's porosity and basis weight have a significant impact on the coating performance of silylated soy oil. Specifically, using a paper with high porosity (>30 s/100mL) and high basis weight (>80 gsm) provides better Cobb Values than papers with low porosity and basis weights. Additionally, the use of a fluorinated paper can significantly improve the water-resistance of a coating, however using such a paper grade can increase costs and has negative environmental impacts.

Similar to paper with high basis weight and porosity, elevated cure temperatures and increased cure times also improve water-resistance of silylated soy oil coatings. Results from Table 3.5 emphasize the significance of how cure time affects the water-resistance properties of silylated soy oil coatings. Furthermore, results summarized in Table 3.4 and Table 3.6 show that increased cure temperatures provide significant improvements in Cobb Values. Therefore,

allowing silylated soy oil coatings to cure for a minimum of four hours at temperatures of 80°C or higher provide the most water resistant product.

Section 3.6.2 investigating the effect of coat weight on measured Cobb Values shows no statistical trend. Because a higher coat weight doesn't result in a more hydrophobic coating, it is most beneficial to operate at the lowest possible coat weight while ensuring that the entirety of the surface is coated. In doing so, coating production is maximized without requiring more coating material, thus reducing the production costs per bag.

Moisture and catalyst concentrations were also mentioned as factors in the rate of cure for silylated soy oil coatings. The effects of varying water and catalyst concentrations also impact the performance properties and pot-life time of silylated soy oil coatings and will be discussed further in Chapters 4 and 5.

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Chapter 4: Scale-Up Trials and Economics

Performing coatings using silylated soy oil in a small lab-scale setting is an essential step in creating a business plan for developing any potential large scale processes. While initial work was performed to provide proof of concept data, the majority of the work in this thesis was generated to provide better operating conditions for mass manufacturing operations of silylated soy oil coatings. For the manufacturing scale-up process two criteria must be met for silylated soy oil to be considered for use in a large-scale coating facility. First, the final product must exhibit a certain degree of water resistance while being synthesized in large volumes. Second, the product must be manufactured in a cost efficient manner.

Previous chapters have shown that silylated soy oil can be synthesized and coated effectively at small scales. However, when considering large-scale production, several economic factors must be considered such as raw material costs, utility costs, equipment costs, operation costs, as well as several other factors. Trials at an industrial scale were performed to determine product performance using significantly larger coating systems and to better evaluate the potential economical model for producing a silylated soy oil coating.

4.1 Scale-Up Trials

To date, two scale-up test trials were been performed at Sierra Coating Technologies, LLC in De Pere, WI. The initial trial was done to determine if similar performance properties were achieved for both small and large-scale coatings. The second trial tested product performance when varying coat weight and line speed. Though several of the same synthesis, analysis, and coating techniques were used at both lab and industrial scales, there were numerous differences between each coating system that were considered.

4.1.1 Gravure Coating System

A gravure coating process has become one of the most popular types of coating techniques used today due to its ability to apply less coating with a high degree of precision [1]. Gravure coatings differ from other commonly used coating techniques in that the coating roller is patterned with a surface engraving, of which both the shape and size of the pattern can be varied to achieve the final coat weight and specifications of the desired coating [2]. These engravings vary in shape and size, thus providing different coat weight parameters. For a given gravure pattern, there is only a small range which the coating thickness can be varied through changing process parameters. Therefore, selecting the correct specification of the gravure pattern at the outset is important [2].

Because a different coating method was used for large-scale trials, it was necessary to determine how gravure coatings would perform with similar coat weights to studies performed using a roller and blade coating apparatus with coat weights ranging from 3.5-6.0 gsm. Additionally, coatings with heavier coat weights were performed to determine if significant increases resulted in improved hydrophobicity.

4.1.2 Line Speed

Line speed is defined as the amount of material coated per time usually expressed in feet per minute (fpm). Coatings made using the ECS were not tested for coating speed because only one sheet of paper was coated at a time. At large scales however, rolls of paper thousands of feet in length are used and coating speeds can be adjusted to vary coating properties and manufacturing time. Most coating facilities provide pricing on a per time basis, thus operating at faster line speeds allows more product to be made in less time, resulting in cheaper coating costs. For both trials, line speed was set at 76 fpm. However, it is important to evaluate Cobb Values with respect to line speed should in future trials to optimize coating production costs.

4.1.3 Oven Temperature

As discussed in sections 3.3.2 and 3.3.5.3, varying the cure or dry temperature can significantly reduce the tack-free time of a coating. At small scales, dry temperatures at room temperature, 60°C, and 80°C were evaluated. However, if line speeds are drastically increased, coatings must exhibit a very short tack-free time. To achieve this, oven temperatures can be increased to promote the removal rate of any undesired alcohol byproducts on the coating surface. For both trials, oven temperatures were set to 125°C. When evaluating line speed in future trials, it may be necessary to increase oven temperatures in an effort to reduce the tack-free time required of coatings made at faster line speeds.

4.1.4 Curing Formulation

Variation of the amount of catalyst and water can affect both pot-life and performance properties of silylated soy oil coatings (section 3.3.3). Experiments done for all small-scale studies used a formulation of 1wt% DBTDL and 4wt% water (weight percentage is in reference to amount of silylated soy oil used). However, this formulation was observed to solidify in less than an hour, rendering it unsuitable for large-scale coatings. Therefore, formulations with reduced water concentrations were studied to determine how this would affect pot life. Water concentrations of 1wt% and 0.1wt% with 1wt% DBTDL were measured for viscosity changes over time.

4.1.4.1 Method – Varying Water Concentration for Pre-Coat Mixture

All pre-coating mixtures were made using 80g of silylated soy oil and 0.8g of DBTDL. Water concentrations of 1wt% and 0.1wt% (0.8g and 0.08g, respectively) were measured for viscosity at various time intervals until measurements exceeded 800 cP. Once each pre-coating mixture was prepared, samples were placed on a magnetic stir plate mixing at approximately 500 rpm. At each measured time interval, stirring was stopped, the sample was manually stirred for

approximately five seconds to assure no surface film had developed and the viscosity was measured using a Brookfield DV-E viscometer with an LV spindle set at a rate of 30 rpm. Each concentration was done in triplicate and the viscosities for each time point were averaged.

4.1.4.2 Results & Discussion – Varying Water Concentration for Pre-Coat Mixture

Viscosities of pre-coating mixtures using 1.0wt% water show steady increases in viscosity. The 800cP upper viscosity limit was reached in 16 minutes (Figure 4.1). Achieving such an elevated viscosity in such a short time makes a 1.0wt% water formulation unusable for large-scale trials. Conversely, pre-coating mixtures using 0.1wt% water maintain significantly lower viscosities for much longer time. In fact, the average viscosity after three hours, the minimum required pot life time for large-scale trials, was well below 300 cP.

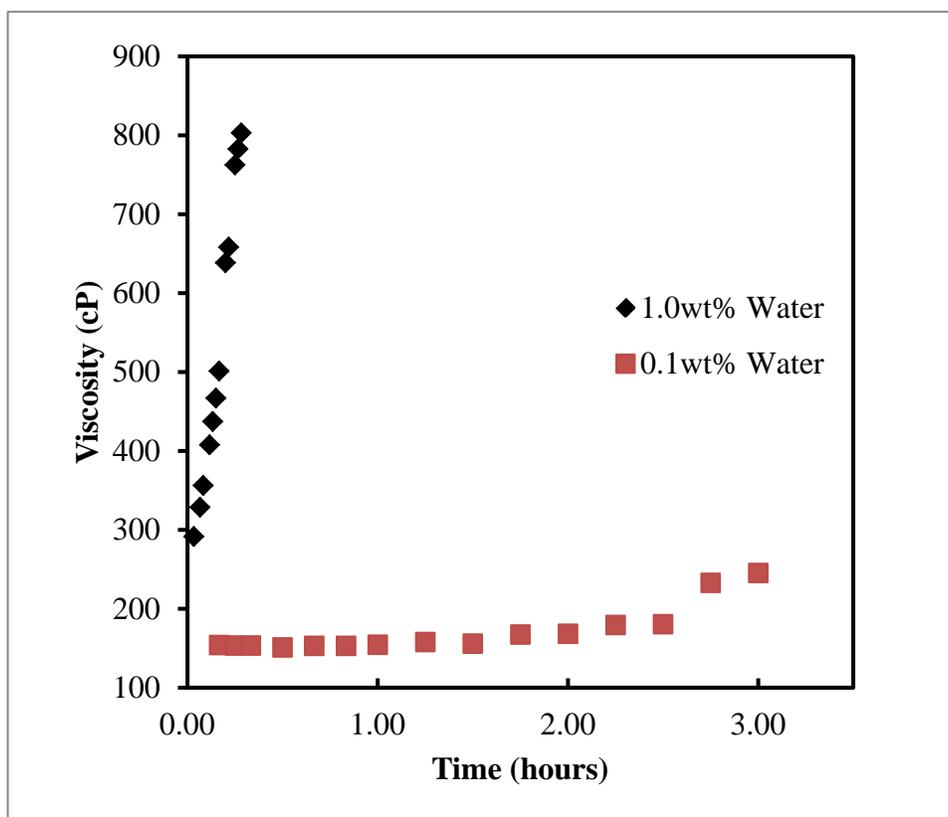


Figure 4.1 Viscosity measurements with respect to mixing time using 1.0wt% and 0.1wt% water for pre-coating mixture formulations.

To demonstrate that the silylated soy oil demonstrated water resistant properties after extended mixing times, coatings were made with the pre-coating mixtures at 0h, 1.5h, and 3h mixing time points. All Coatings were cured for one hour at 80°C and 23 hours at room temperature. After samples were cured, two minute Cobb Values were measured. Results from Cobb Value measurements indicate that increased mixing time using a 0.1wt% water formulation still exhibits improved water resistance (Table 4.1). Similarly, Cobb Values of coatings at various mixing times show no statistically significant difference. Consequently, large-scale coating trials were performed using 1.0wt% DBTDL and 0.1wt% water to ensure a low viscosity. Furthermore, coatings could be made knowing coating performance would not change with respect to mixing time.

Table 4.1 Coat weights and Cobb Values of coatings prepared at different mixing times using 0.1wt% water in pre-coating mixture.

0.1wt% Water using 5/29/12 Silylated Oil					
SAMPLE	Wt ₀ (g)	Wt _F (g)	Cobb Value (gsm)	Mix Time (hrs)	Coat Weight (gsm)
C1	0.9756	1.1469	17.1	0.0	3.48
C2	0.9760	1.1519	17.6	0.0	3.48
D1	0.9654	1.1440	17.9	0.0	3.81
D2	0.9667	1.1457	17.9	0.0	3.81
Average			17.6		3.65
Std. Dev.			0.4		0.19
E1	0.9834	1.1600	17.7	1.5	3.81
E2	0.9648	1.1414	17.7	1.5	3.81
F1	0.9863	1.1621	17.6	1.5	3.81
F2	0.9758	1.1570	18.1	1.5	3.81
Average			17.8		3.81
Std. Dev.			0.2		0.00
G1	0.9811	1.1509	17.0	3.0	3.81
G2	0.9866	1.1583	17.2	3.0	3.81
H1	0.9756	1.1494	17.4	3.0	3.98
H2	0.9691	1.141	17.2	3.0	3.98
Average			17.2		3.90
Std. Dev.			0.2		0.10

4.2 Scale-Up Trial Results and Discussion

The initial scale-up trial was used as a preliminary test to determine if coating silylated soy oil at an industrial level was achievable and also to determine if water resistant properties were comparable to previous studies done at small scale lab experiments. This trial used paper GN354872 (see Table 3.4 for properties). The second scale-up trial investigated how larger coat weights would affect the performance properties of the coatings. The second trial used paper GN505320 (see Table 3.10 for properties). Table 4.2 summarizes the manufacturing settings and two minute Cobb Values of the coatings made at both trials.

Visual inspection of both coat weights from Trial #2 indicated that the coatings exhibited partial saturation into the paper. The partial saturation is likely due to not allowing the pre-coating mixture to develop enough viscosity prior to coating. Much like applying pure soy oil onto a piece of paper would result in saturation, or bleeding, into the substrate, silylated soy oil that hasn't had enough time to develop a pseudo-crosslinked network will also exhibit some saturation. As a result of the partial saturation, the Cobb Values of the coatings from Trial #2 were notably higher.

Table 4.2 Equipment settings and Cobb Values of coatings from first two trials.

	Trial 1	Trial 2 Low Coat Weight	Trial 2 High Coat Weight
Coating Type	Direct Gravure	Direct Gravure	Direct Gravure
Line Speed (fpm)	76	76	76
Oven Temp (°C)	125	125	125
Paper Grade	GN354872	GN505320	GN505320
Coat Weight (gsm)	4.0	4.8	8.0
Cobb Value (gsm)	18.9	23.3	24.0
Cobb Value Std. Dev.	2.1	0.1	0.6

4.2.1 Grease Resistance of Scale-Up Trial Coatings

Grease resistance testing is used to measure the repellency of paper to grease, oil, and waxes. Typically this test is used for products treated with fluorochemical sizing agents which impart both organophobic and hydrophobic characteristics to paper through a reduction in the surface energy of the sheet [3, 4]. The test was developed to allow paper producers to qualitatively measure the application of fluorochemicals into a sheet. By testing reagents with slight variations in “aggressiveness”, the highest numbered solution that remains on the surface of the paper without exhibiting any absorption provides the “kit rating” of the paper. The higher a paper’s rating, the more grease resistance it demonstrates. For trash bag production, it’s important to consider the grease resistance rating due to the contents that it may be exposed to. Grease absorption, like water absorption, can reduce the strength of the paper making it more susceptible to ripping, tearing, or breaking. For this reason, grease resistance was measured for all scale-up trials.

4.2.1.1 Method – Grease Resistance Measurements of Scale-Up Trial Coatings

Grease resistant reagents and analysis were done according to TAPPI T 559. Each coating was repeated five times. The highest reagent number that resulted in no evidence of saturation was considered as “passed. The average grease resistance value was calculated to the nearest 0.5 units.

4.2.1.2 Results & Discussion – Grease Resistance Measurements of Scale-Up Trial Coatings

All coatings from both trials showed no grease resistance (0.0 units). Thus, it may be necessary to use a secondary, outer coating in conjunction with a silylated soy oil base coating in order to achieve the desired water and grease resistance for trash bag production. Alternatively, incorporating fluorochemical additives to the paper source directly could also provide improved grease resistance, eliminating the need for a secondary coating. However, as mention briefly in

section 3.6.6.2, fluorinated additives in paper are associated with negative environmental impacts. Therefore, using a non-fluorinated secondary coating may provide the best option for achieving a high degree of water and grease resistance while having very little negative environmental impacts.

4.3 Scale-Up Trial Economic Evaluation

Economic evaluations were completed for the processes in the production of silylated soy oil coated trash bags including paper, silylated soy synthesis, coating, and bag production costs. Calculations were made assuming one million bags were manufactured each year. Bag dimensions were set at 18"x12"x36" with a coat weight of 7.0 gsm. As a result, 1.5 million square meters of paper are required (Table 4.3). Paper prices were quoted at \$0.15/m² from Wausau Paper resulting in a paper cost of \$220,000. Assuming a transportation cost of \$0.11/kg, and a paper basis weight of 80 gsm, the total paper costs were calculated to be approximately \$240,000 (Table 4.4).

Table 4.3 Coating and bag production specifications including coating settings from full-scale trials, estimated production volume, bag sizes, and paper requirements.

COATING AND BAG SPECIFICATIONS	
coating type	direct gravure
line speed (fpm)	76
oven temp (°C)	125
roll width (in.)	60
# of bags/yr	1000000
bag dimensions	18"x12"x36"
bag size (SA sq. in.)	2376
paper/year (sq. in.)	2376000000
paper/year (sq. ft.)	16500000
paper/year (sq. m.)	1532900
roll length needed (in.)	39600000
roll length needed (ft.)	3300000

Table 4.4 Estimated paper costs including purchasing and transportation to coating facilities based off of production demands highlighted in Table 4.3.

PAPER COSTS	
cost of paper (\$/sq. yd)	\$ 0.12
cost of paper (\$/sq m)	\$ 0.15
total paper cost	\$ 223,803
transportation of coated paper to bag maker (\$/kg)	\$ 0.11
mass of paper (kg)	122632
total transportation cost to bag maker (\$)	\$ 13,518
TOTAL PAPER COSTS	\$ 237,321

Knowing the total paper needed for bag production and assuming a coat weight of 7.0 gsm, the amount of silylated soy oil required per year is almost 11,000 kg. Based off of the mass ratios for a 1:3 molar ratio of soy oil:VTMOS shown in Table 2.1, the required volume of each reactant was calculated. Costs for VTMOS were provided by Gelest, Inc., soybean oil costs were provided by Zealand Farms, and L101 costs were provided by Sigma Aldrich. Raw material costs associated with silylated soy oil synthesis were estimated to be \$120,000 (Table 4.5). Assuming a processing cost of \$1000/100 gallons produced, total synthesis costs were calculated to be \$150,000, with the cost of VTMOS accounting for more than \$75,000. Because VTMOS accounts for half of the synthesis costs, reducing the reactant ratio would greatly reduce material costs. Incorporating the cost of DBTDL needed for curing (Table 4.6), the total raw material costs amount to approximately \$175,000.

Table 4.5 Estimated raw material, processing, and production costs associated with the synthesis of silylated soy oil based off of production demands outlined in Table 4.3.

SILYLATED SOY OIL SYNTHESIS COSTS	
moles soy oil	1
mass soy oil/mole (kg)	0.9
moles silane	3
mass VT MOS/mole (kg)	0.148
mass L101/rxn (kg)	0.009
low sat soy oil price (\$/kg)	\$ 1.81
soy oil wt% of rxn mixture	66.48%
low sat soy oil needed (kg)	7134.0
low sat soy oil cost total (\$)	\$ 12,896
VT MOS price (\$/kg)	22
VT MOS wt% of rxn mixture	32.85%
VT MOS needed (kg)	3524.9
VT MOS cost total (\$)	\$ 77,548
L101 price (\$/kg)	370.58
L101 wt% of rxn mixture	0.66%
L101 needed (kg)	71.3
L101 cost total (\$)	\$ 26,437
Processing @ \$1000/100gal (\$/kg)	\$ 2.90
total processing cost @ \$1000/100gal	\$ 31,153
TOTAL SYNTHESIS COSTS (\$)	\$ 148,035

The coating manufacturing price for this project was estimated based off of settings and results from the trials done at Sierra Coating Technologies. The coating price was quoted at \$0.20/m² resulting in a coating cost over \$300,000 (Table 4.7). Ultimately, coating production was found to be the most costly step in the bag production process. Running the coatings at an increased line speed could reduce coating production costs, however, significantly influencing the overall manufacturing costs. Therefore, evaluating the production limits and coating performance properties at higher line speeds should be investigated.

Table 4.6 Estimated raw material costs for curing step during coating process. Quantities were based off of production demands outlined in Table 4.3.

SILYLATED SOY CURING COSTS	
wt% DBTDL used for curing	1%
mass DBTDL used for curing (kg)	107.3
wt% water used for curing	4%
mass water used for curing (kg)	429.2
DBTDL price (\$/kg) [sigma]	\$ 340.00
DBTDL needed (kg)	107.3
DBTDL cost total (\$)	\$ 36,483.01
TOTAL CURE COSTS (\$)	\$ 36,483.01

Table 4.7 Estimated coating production costs based off of production demands in Table 4.3.

COATING COSTS	
coating price (\$/1000 sq. in.)	\$ 0.13
coating price (\$/sq. m.)	\$ 0.20
coating weight (gsm)	7
coating material needed/yr (g)	10730297
coating material needed/yr (kg)	10730
coating cost/year (\$)	\$ 306,266
transportation of coating to coater (\$/kg)	\$ 0.11
total transportation cost to coater (\$)	\$ 1,183
TOTAL COATING COSTS	\$ 307,449

Costs for bag production were quoted at \$41/1000 bags by Wisconsin Converting Inc. Therefore yearly bag production costs would be \$41,000. Accounting for paper costs, raw material costs, silylated soy oil synthesis, coating costs, and bag production, production of one million bags is estimated to be \$800,000, or \$0.81 per bag (Table 4.8). Though these are estimated costs, reducing the amount of VTMOs used for silylated soy oil synthesis and increasing the coating line speeds could significantly improve the proposed economic model.

Table 4.8 Estimated manufacturing, synthesis, and processing costs for production of one million silylated soy oil trash bags.

RAW MATERIAL & PRODUCTION COSTS	
Paper Costs	\$ 237,320.96
Silylated Soy Synthesis Costs	\$ 148,035.16
Coating Manufacturing Costs	\$ 307,449.06
Curing Costs	\$ 36,483.01
Bag Production	\$ 41,000.00
Total Costs	\$ 770,288.19
Total Costs w/ 5% waste	\$ 808,802.59
COST PER BAG	\$ 0.81

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Chapter 5: Recommended Future Work

Because of the numerous aspects of this project that came into consideration when developing a marketable finished product, many ideas were not fully investigated due to time constraints. While the research highlighted in this thesis provides an outline for synthesizing, coating, and curing silylated soy oil in an effective and efficient manner, there are several small experiments that could be investigated that may provide further insight into enhancing the performance, economics, energy, and time demands in the development of silylated soy coatings. Proposed investigations for synthesis, coating, and scale-up projects have been included, each of which would have a direct impact on the performance, cost, or time required to produce and coat silylated soy oil more efficiently.

5.1 Proposed Synthesis Experiments

5.1.1 Variation of Reactant Molar Ratios

Multiple reactions were done in a 2L Parr Reactor using a 1:1 molar ratio of soy oil and VTMO (900g soy oil and 148g VTMO). Each reaction resulted in a product with a significantly elevated graft percentage and viscosity. As a result of the high viscosities, the products were unable to be used for large scale use due to the constraints of the gravure coating system used for initial trials. If a different coating system was used for large-scale production trials that was capable of handling higher viscosity demands, this 1:1 molar product could be a viable option for drastically reducing raw material costs by cutting VTMO use by 66% compared to the 1:3 molar ratio. Most importantly though, would be to demonstrate similar coating performance properties, as well as reproducibility at a small scale prior to large-scale trials.

Interestingly, the theoretical minimal molar ratio that could result in a complete curing of silylated soy oil is 3:1 molar ratio soy oil:VTMOS (900g soy oil and 49g VTMOS). This is because of the triglyceride structure of soybean oil. Because each soy oil molecule has three fatty acid chains, it is only necessary to graft one vinyl silane molecule to any one of the fatty acid chains in order to achieve a completely crosslinked network. This reactant ratio would provide an 89% reduction in VTMOS required if it fell within viscosity limitations and was shown to provide similar coating properties. Reducing the amount of the cost-determining reactant in the synthesis process would drastically reduce production costs.

5.1.2 Variation of Reaction Time and Temperature

Earlier work investigating the synthesis of silylated soy oil evaluated the affects of varying time and temperature (see Figure 2.3), however this study was done using a 1:7 molar ratio of soy oil:VTMOS [1, 2]. The same principles and kinetics should apply to different reactant ratios though. Therefore, one way to counteract the high viscosities associated with 1:1 molar reactions could be to reduce the reaction temperature or time. This would be beneficial for two reasons. First, it would reduce reaction time allowing more product to be made in a shorter amount of time. Second, a lower temperature would reduce the energy demands required of such a lengthy reaction. Operating at lower temperatures would help minimize processing costs.

Several settings varying the reaction conditions would have to be done to provide sufficient data, though. And because the reaction would still be rather lengthy, this could be quite time consuming since multiple reactions would need to be performed for each reach condition. However, proper evaluation of the affects of reaction time and temperature could greatly improve operational costs for any large-scale production. The major risk of reducing the reaction time and temperature is that the product would have a very low graft percentage.

When used for coatings, this could result in a lower crosslink density which could reduce the water resistance. Ultimately, in order to properly evaluate how reaction temperature and reaction time impact coating performance properties, numerous reactions must be carried out.

5.2 Proposed Coating Experiments

5.2.1 DBTDL & Water Concentrations

As was discussed in section 3.3.3 and 4.1.4, the concentrations of water and catalyst significantly impact the crosslinking rate of silylated soy oil (see Figure 4.1). However, due to the lengthy pot-life time required for scale-up trials, each data point for catalyst and water concentrations took three hours to collect. Additionally, each water and catalyst concentration was repeated a minimum of three times. As a result, thorough analysis of the affects of both DBTDL and water concentrations would take a considerable amount of time.

Analysis of how varying the concentrations of DBTDL and water would be beneficial for several reasons. Being able to accurately predict viscosity as a function of both [DBTDL] and [water] would allow silylated soy oil coatings to be mixed and coated on any coating system, regardless of its viscosity limitations. Having pot-life data with respect to [DBTDL] and [water] would allow manipulations to be made to the pre-coating mixture that would satisfy the viscosity limits and pot-life time for any coating system.

Another benefit of analyzing the affects of [DBTDL] and [water] used in the curing process is how this changes water and grease resistant coating properties. Making coatings with different pre-coating mixture concentrations may result in different Cobb and grease resistance results. Consider the affects of using a high water concentration with a low DBTDL concentration. The high water content would likely increase crosslink density, while a low

DBTDL content would cause the cure process to occur more slowly. While this is theoretical, the potential benefits of varying DBTDL and water concentrations are very intriguing. Likewise, reducing the amount of DBTDL used in the pre-coating mixture would substantially reduce raw materials costs.

5.2.2 Use of Paper GN354872 with High Basis Weight

As shown in section 3.6.1, paper GN354872 provides drastic water resistivity improvements when coated with silylated soy oil. For instance, comparing two minute Cobb Values of both GN354872 and GN505320, the paper used for all large-scale trials, it can be seen that GN354872 experiences a Cobb Value improvement over 220% (62.4 gsm to 19.1 gsm) whereas GN505320 demonstrated a Cobb Value improvement of 70% (43.2 gsm to 25.5 gsm). Though GN354872 provides significantly better hydrophobic improvement than GN505320, due to the low basis weight at which it was manufactured, the paper was not further investigated for implementation as a coated trash bag product. However, if GN354872 was manufactured at a higher basis weight suitable for use in trash bag production, this may provide the desired strength properties needed for trash bags while also providing better hydrophobic properties when compared to GN505320.

Another factor that must be considered is the difference in paper costs between GN354872 and GN505320. If the cost of using GN354872 is significantly higher than GN505320, having slightly improved water resistant trash bags may not be justified from a monetary standpoint. While it's important to make a high quality product, it is equally important to make it economically.

5.2.3 Use of Secondary Coating with Silylated Soy Oil

One issue that has become a concern in the development and testing of silylated soy oil coatings is the lack of grease resistance that it provides. This is of particular concern due to the contents that the coating would likely be subjected to when used for trash bags. A common practice in coating industries, however, is to use different coatings in conjunction with one another, each serving to improve one desired performance property. Therefore, applying several different coatings provides a final product that exhibits all of the desired physical characteristics. Using silylated soy oil with another coating that provides grease barrier properties could help satisfy both the water and grease resistance desired of the final product. Some work has been done by Michelman, Inc. evaluating the coating performance of silylated soy oil when used with other coatings, but a much more in-depth study would be required to determine optimal coating conditions when using two or more coatings in conjunction with one another.

5.3 Proposed Manufacturing Experiments

5.3.1 Different Coating System

All lab-scale coatings have been made using a blade coating system. The benefit of using this simple coating method is little coating material is required, the coating weight can be very easily controlled, and the maintenance and clean-up is quick with the use of a solvent such as acetone or methanol. All full-scale coatings were made using a gravure coating system. This method of coating has become widely used due to the ability to coat very thin layers at high line speeds. The concept of a gravure roll coating system stems from the engravings on the roller itself. A gravure roller traps and retains the coating material in its cells, or grooves. Excess coating material is removed using a primary blade [3]. When the substrate comes into contact with the roller, only the material captured in the grooves of the roller is applied to the surface. Varying the dimensions of the grooves on the gravure roller allows for incredibly accurate ranges

in coat weight. However, due to the nature of silylated soy oil and its quick cure rate, and thus quick viscosity increase in the presence of water and DBTDL, the grooves of a gravure roll can become clogged and filled with gelled silylated soy oil. This results in an inconsistent coat weight throughout the paper roll. Furthermore, it creates downtime in the manufacturing process because the gravure roller has to be cleaned to remove any buildup of cured silylated soy oil in the roller's cells. As a result, the use of a gravure coating system may not be the most ideal coating method for large scale coating production.

As mentioned in Chapters 3 and 4, pot-life also plays a significant role in determining the feasibility of scaling up a coating material. Recent experiments have shown that high viscosity silylated soy oil provides not only a better surface coating, with no leakage into the paper fibers, but also provides better water resistance. Therefore, generating increased viscosities becomes important to the performance of the coatings and also to the future research and development of this project. Gravure coating systems are typically set up so that the coating material is being pumped onto the roller directly. This arrangement forces the silylated soy oil, water, and catalyst to be pre-mixed before being applied to the roller, which accounts for the concern over viscosity and pot-life issues. However, if a blade and roller technique was used at large scale, increased viscosities become much less of a concern. In fact, the use of a blade coating system would allow the necessary amount of water to be added at the blade-roller interface in a continuous process alleviating the concern of increased viscosity and pot-life. While a buildup of cured silylated soy oil may accumulate on the blade itself, this could be quickly and easily removed by simply scraping off the cured, unused excess silylated soy oil. Additionally, implementing large-scale manufacturing using this coating technique would serve to closer replicate any results experienced in lab using the ECS coater.

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