PROCESS AND APPLICATION DEVELOPMENT OF BIOBASED MATERIALS-SILYLATED NATURAL OILS, AND THERMOSETS FROM FUMARIC ACID

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ABSTRACT

PROCESS AND APPLICATION DEVELOPMENT OF BIOBASED MATERIALS-SILYLATED NATURAL OILS, AND THERMOSETS FROM FUMARIC ACID

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This research work focuses on designing biobased products and processes for industrial applications in paper coatings, elastomers for adhesives and sealants, and unsaturated polyester resins (UPR).

A novel method for silylation of internal double bonds of fatty acid chains of triglycerides is presented, where vinyl terminated alkoxysilanes are grafted on the unsaturation of soybean oil through 'ene' reaction mechanism. The process is a very simple one pot synthesis and does not require any solvent which makes it cost effective. This process is applicable to any natural oils with unsaturated fatty acids and it has been demonstrated for other natural oils. The modified soybean oil cures irreversibly to form a cured network just by exposing it to moisture at room temperature. By virtue of this, it opens a variety of applications in the area of coatings and elastomers due to the flexible siloxane (Si-O-Si) linkages in the cured network. Kraft paper, a very commonly used paper in the packaging industry, was coated using silylated LowSat® soybean oil and the moisture resistance of the coated paper was increased by more than 50%. The coating was smooth, uniform with no apparent defects and was cured at room temperature by only utilizing atmospheric moisture. Followed by our success of paper coatings using lab scale roll coaters, the coating process was scaled up and around 50,000 sq.ft. of kraft paper was coated on a commercial gravure roll coaters at Sierra Coatings (De Pere, WI). These coated papers were then converted in to paper bags which was being used on board ships by the US Navy for storing food and other

organic waste, which further can be thrown into sea water where paper and the coating material would completely degrade. Another application developed using this silylated soybean oil is in the area of elastomers, where the flexible nature of siloxane linkages played a major role. Reactive blends were prepared using silylated soybean oil and methoxy terminated urethane containing polysiloxanes at room temperature, which provided flexible network with tunable mechanical properties. The main advantage of blending is that the properties of these blends can be tailored to the requirement simply by changing the composition and it is demonstrated by characterization of several blends. These elastomers are well suited for adhesives and sealants applications and also can be used as an additive for the same applications.

Another industry that relies heavily on petroleum-based materials is the thermosetting resins, more specifically unsaturated polyester resins (UPR). We have developed completely biobased unsaturated polyesters from fermentation derived fumaric acid glycols from renewable sources. Polyesters, polypropylene fumarate (PPF) and poly(ethylene glycol) fumarate (PEGF) were synthesized by a two-step polycondensation process and were characterized. These polyesters were used to prepare UPRs using conventional cross-linking agent via free radical crosslinking mechanism and the cure kinetics was studied isothermally at different curing temperatures. These UPRs showed satisfactory mechanical properties and when used with natural fibers could deliver fully biobased fiber-reinforced composite material.

Dedicated to Prof. Narayan, Dr. Graiver and my family

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KEY TO ABBREVIATIONS

SilSoy	Silylated soybean oil
Polysil-UR	Urethane containing polysiloxanes
PDMS	Polydimethylsiloxanes
UP	Unsaturated polyester
UPR	Unsaturated Polyester resin
VTMS	Vinyltrimethoxysilane
VTES	Vinyltriethoxysilane
DBTDL	Dibutyltin dilaurate
PG	Propylene glycol
PEG	Polyethylene glycol
PPF	Polypropylene fumarate
PEGF	Poly (ethylene glycol) fumarate
FRP	Fiber reinforced plastic
RT	Room temperature
TGA	Thermogravimetric analysis
DSC	Differential scanning calorimetry
ATR-FTIR	Attenuated total reflection- fourier transform infrared spectroscopy
NMR	Nuclear magnetic response
GC	Gas chromatography
SEM	Scanning electron microscopy
TAPPI	Technical association of pulp and paper industry

1. INTRODUCTION

1.1 Background

In recent years, the potential replacement of fossil fuels for the production of relevant monomers by inexpensive and renewable starting material such as lignin, cellulose, starch and vegetable oils is increasingly being explored [1-8] with the aim to develop a more sustainable bio-based economy. Nowadays, most commercially available polymers are derived from non-renewable resources and account worldwide for approximately 7% of all oil and gas used [8, 9]. So, there is still a wide scope and opportunity to switch over to renewable feedstock over depleting petroleum feedstock. In this case, biobased polymers and materials can form the basis for an environmentally responsible, sustainable alternative to current materials that are based exclusively on petroleum feedstocks. Polymers are used in a variety of fields ranging from agriculture to packaging to electronics and are produced in millions of tones every year [10]. Finding alternative biobased resources for these plastics from plant-based biomass offers a value proposition of zero material carbon footprints. Due to increase in demand for the use of biobased products, many industries are adopting to a biobased feedstocks partially or completely. Some examples could be seen from the drinking water bottles, kitchen cutlery, agricultural mulch etc. It should be emphasized that because of the extensive use of plastics in day-to-day life, it also becomes very important to find an environmentally useful and sustainable way to dispose of these materials [2]. In fact, current producers of bio-based polymers estimate that production capacity will reach nearly 12 million tonnes by 2020. With an expected total polymer production of about 400 million tonnes in 2020, the bio-based share should be increased to 3%, meaning that bio-based production capacity will grow faster than overall production [8, 11]. Itaconic acid [12-14], iso-sorbide [14, 15], 2,5-furandicarboxylic acid [16-19], fumaric acid [17], lactide [20-22], caprolactone [23, 24] etc. are some examples of such biobased monomers that are replacing completely or partially their petroleum-based counterparts in the variety of industries like coating, packaging, auto-parts and also ranging from soft elastomeric rubbers to hard and rigid composites. This study focuses on designing some biobased products; chapter 1 deals with a novel silylation reaction of soybean oil. Chapter 2 describes the use of the silylated oil for moisture resistant paper coatings, chapter 3 describes the preparation of elastomers by reactive blending of soybean oil with polysiloxanes and chapter 4 deals with unsaturated polyester resin (UPR) produced from fermentation derived fumaric acid for composite applications.

1.2 Silylated soybean oil

Vegetable oils represent promising route to renewable chemicals and polymers due to their readily availability, inherent biodegradability and low toxicity. Vegetable oils have been considered as monomeric feedstocks for the plastics industry for over 20 years [9, 25-28]. Polymers from vegetable oils have obtained increasing attention as public policy makers and corporations alike have been interested in replacing traditional petrochemical feedstocks due to their environmental and economic impact. In fact, industrial used consumed 15% of all soybean oil from 2110 to 2005 [12, 29]. Vegetable oils have been used in paints and coatings for centuries, because the unsaturated oils can oligomerize or polymerize when exposed to oxygen in air [30-32]. In recent years, bio renewable fuels like biodiesel, which are prepared from vegetable oils by pyrolysis, catalytic cracking and transesterification [4, 33, 34], showed a potential game changer with excellent performance as compared to traditional engine fuel.

Structurally, vegetable oils consist of mainly triglycerides with the basic unit of glycerol attached to three fatty acids as shown in Figure 1.1.

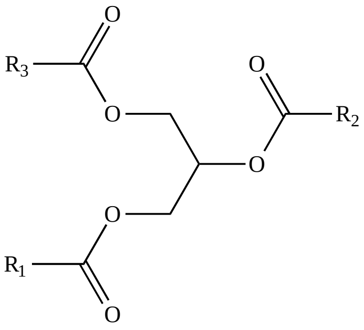


Figure 1.1: General triglyceride structure of vegetable oil where R_1, R_2 and R_3 represent different fatty acid chains.

Table 1.1: Chemical structures and formulas of the important fatty acids (reproduced with permission from Larock et. al. [35])

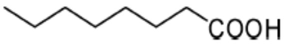
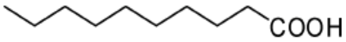
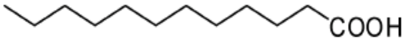
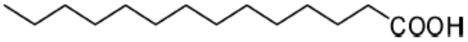
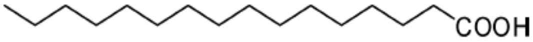
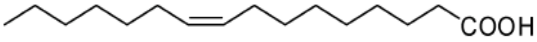
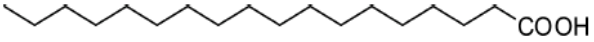
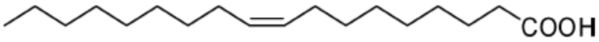
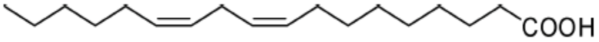
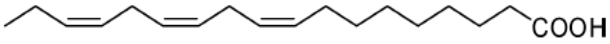
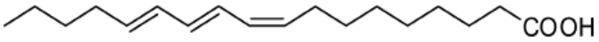
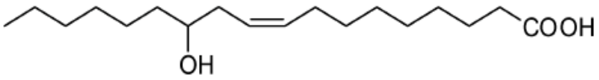
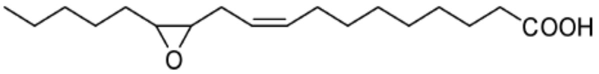
Fatty Acid	Formula	Structure
Caprylic	$C_8H_{16}O_2$	
Capric	$C_{10}H_{20}O_2$	
Lauric	$C_{12}H_{24}O_2$	
Myristic	$C_{14}H_{28}O_2$	
Palmitic	$C_{16}H_{32}O_2$	
Palmitoleic	$C_{16}H_{30}O_2$	
Stearic	$C_{18}H_{36}O_2$	
Oleic	$C_{18}H_{34}O_2$	
Linoleic	$C_{18}H_{32}O_2$	
Linolenic	$C_{18}H_{30}O_2$	
α-Eleostearic	$C_{18}H_{30}O_2$	
Ricinoleic	$C_{18}H_{34}O_3$	
Vernolic	$C_{18}H_{32}O_3$	

Table 1 summarizes the industry's most commonly used fatty acids found in vegetable oils. As can be seen from the table, most of the fatty acids are long straight-chain compounds with an even number of carbons and the double bonds in most of these unsaturated fatty acids possess a cis configuration. However, some fatty acid chains, like those in ricinoleic and vernolic acids, bear functional groups, hydroxyl and epoxy groups respectively [36, 37]. The physical state of vegetable oils depends on both the nature and the distribution of the fatty acids. Most vegetable oils are liquid at room temperature. Generally, higher melting point vegetable oils are obtained with more carbons in the fatty acid chain, a lower number of carbon–carbon double bonds, and an E (trans) configuration and conjugation of the carbon–carbon double bonds. Different vegetable oils contain differing composition of fatty acids depending on the plant and the growing conditions. The chemical and physical properties of the vegetable oils depend heavily on the degree of unsaturation [3, 35].

The unsaturation present in the fatty acids of triglycerides can be modified using different reaction routes like acrylation, epoxidation etc., and the extent of reaction depends on the unsaturation content. Epoxidized soybean oil (ESBO) is reported to be the second largest epoxide following epichlorohydrin [38]. The epoxidation is performed by reaction with percarboxylic acids, hydrogen peroxide, hydroperoxides halohydrins, oxygen and by other methods including chemo-enzymatic methods [38-40]. Another example of chemical modification is the acrylation process which enhances the reactivity of the fatty acids towards further useful modification like the synthesis of acrylated epoxidized soybean oil (AESO) [28, 41, 42]. AESO has been extensively studies in the polymer and composite area and in fact, also commercially available under the brand name Ebecryl 860 from UCB Chemicals Company [43]. For the composite applications, AESO is generally blended with active diluents like styrene in order to cure the material to prepare a thermoset to be used for composites for structural applications [44, 45]. Along with acrylation and epoxidation, these fatty acids were also modified to create conjugated dienes to undergo a free radical polymerization by using rhodium based catalysts. These conjugated vegetable oils were again further copolymerized with monomers like styrene, acrylonitrile etc. to deliver wide range of thermal and mechanical properties compared to petroleum based monomers [26, 46, 47]. Castor oil is also one example of plant oil which is used heavily in the industry for variety of applications like preparation of polymerized oil, halogenated oil, urethane polymers [40, 48, 49]. Castor oil provides excellent reactivity through three major site; ester linkage of glyceride, carbon carbon double bond from unsaturation and pendant hydroxyl group. Vegetable oils were also used for centuries in the paints and coatings areas due to their inherent oxidation ability via carbon-carbon double bonds when exposed to oxygen from air [4]. Linseed oil is the most common example of such kind, which possess high degree of unsaturation (high content of linoleic and oleic fatty acid) and that makes it susceptible to air oxidation and polymerization resulting in cross-linked and tough films upon exposure to the air [50, 51]. For this reason, linseed oil has been used for centuries as a chief ingredient in paints and varnishes. However, the coatings made from this oil are very brittle and also they tend to yellow with age due to the high content of linolenic acid. Also, row drying oils used in the coating formulations are generally processed upstream to lower the viscosity needed for handling using diluents [52]. Soybean oil is another example of vegetable oil mainly consists of linoleic and oleic acid. Soy oil dries three times slower as compared to the linseed oil due to very minimal linolenic content and hence very useful in improving the yellowing characteristics [53]. Much work has been directed in the past few years related to epoxidation of soybean and other vegetable oils by converting some of the double bonds to epoxides [54, 55]. This epoxidized oils were then further reacted with water or alcohols to yield polyols, which could subsequently be reacted with isocyanates or acrylic acid to yield a crosslinked network. In this work, a novel approach of modifying soybean oil with reactive alkoxysilanes, through its vital unsaturation, has been introduced which results in fast cure, low viscosity oil that requires no addition of diluents and its applications have been discussed in further chapters. This is one of the very few attempts of incorporating silicones into natural oils which are otherwise not compatible with each other.

Hydrosilylation is undoubtedly one of the most important routes used to prepare organosilicon compounds. It has been used commercially as the major synthetic route to insert silanes to alkenes via a new Si-C bond. This hydrosilylation reaction where Si-H is inserted to alkenes has been widely investigated and reported in the literature [56-58]. It can be carried out by free radical chain reactions or with catalysts such as platinum and other transition metal catalysts. A wide choice of hydrosilylation catalyst is available and the type of catalyst usually determines the mechanism of this reaction. Unfortunately, the hydrosilylation reaction is most effective with alkenes containing terminal double bonds and unless chlorosilanes are used [59, 60], it normally does not proceed to high yields when the silane is added to alkenes containing double bonds in a non-terminal position as is the case with natural triglyceride oils.

A simple one step synthesis method of grafting vinyl terminated alkoxysilane onto the unsaturated fatty acid triglycerides has been introduced in chapter 2 of this thesis. Unlike previous chemical modifications, silylation of the soy oil using alkoxysilane produces a one-component, low viscosity oil that can be applied as coatings. The curing of silylated soybean oil requires only moisture and essentially can be cured just using atmospheric moisture. Collectively these advantages make it an idea candidate for several industries like paints and coatings etc. The effect of temperature and silane concentration on the yield and the kinetics of the grafting reaction were the subjects of this study. Methyl oleate was also used as a model reactant to better characterize and optimize the silylation grafting reaction. The silylated triglycerides then form a siloxane network by hydrolysis of the inherent hydrolytic instable alkoxysilane followed by condensation of the resulting silanols. Silylation of soybean oil is a new way of incorporating silanes into triglycerides and it is not restricted to soybean oil, any unsaturated fatty acid can be processed in the same way and the degree of silylation or extent of grafting depends on the unsaturation content of fatty acid. Silylation process has been extended to silylate some unsaturated oils (like canola oil, abyssinian oil etc.) and the results are presented in chapter 2 of this thesis.

1.2.1 Paper coating application

This crosslinking ability of silylated soybean oil and the moisture resistant property of the final cured films was utilized for paper coating application. Paper bags are widely used in the packaging industry since the paper is widely recognized as a safe and environmentally-friendly material due to its biodegradability [61-63]. One of the major requirements for papers that are used in the packaging industry is the need to provide a moisture barrier since such barrier plays a critical role in preserving the food quality. Traditionally wax has been used extensively as a coatings material. It provided reasonably good moisture and grease resistance, and although it is still available today, it has been largely replaced by plastic films that provide superior performance. Currently, there is a great interest in the packaging industry in environmentally friendly coating materials that are biodegradable [62]. Such coatings should allow greater use of paper in daily life as food storage as well as for paper bags for waste food collections. Along with the moisture resistance ability, it is also desirable that the coatings will impart smoothness, gloss, brightness, and opacity to the base sheets and provide a resistance to ink film-splitting forces as well as ink holdout and gloss. Furthermore, it is well known that the coating properties and the printability of coated papers do not depend only on the coating itself but are also affected by the base sheets, the coating process, the coat weights and the drying conditions. In other words, many factors affect the properties of coated papers and these factors are usually dependent on each other. Currently, the most common paper coating process is the use of Gravure roll coaters. It allows to accurately manage the coating thickness using blades or a metering bar [64-66] but requires low viscosity liquids and a single component cure system.

In this study, kraft paper was coated with low viscosity silylated soybean oil and the moisture resistance of the coated paper was improved by over 50%. Factors affecting the coating process, the cure reactions to form a barrier network and the properties of the coated papers were studied. This paper coatings process was scaled up and over 50,000 sq.ft. of paper was coated in a coating facility (Sierra Coatings) in Wisconsin in collaboration with Northern Technologies International Corporation (Minneapolis, MN). The results of the characterization of these coated paper and the factors affecting the coating process are also presented and discussed in this chapter. This coated paper was developed to be used as a waste bag on board ships for collection of food and other bio-wastes that can be discharged into the ocean where the paper and the coating would be completely biodegrade.

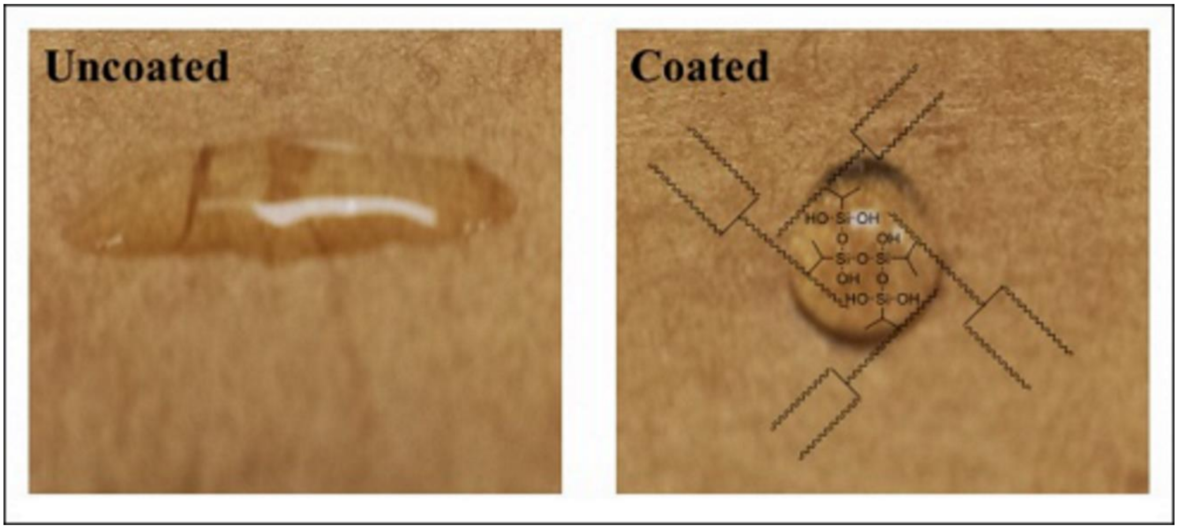


Figure 1.2: Picture representation of moisture resistance of the coated paper using silylated soybean oil

1.2.2 Elastomer application

In the following chapter 4, elastomeric compositions were prepared by reactively blending silylated soybean oil and silicone with tunable physical and mechanical properties. Polymer blending is one of the most effective and economical technique used to reduce material costs as well as developing new materials with different properties than those of each blend component [67]. Using reactive blending technique is also a simpler process than the synthesis of new monomers to produce new polymeric materials. Elastomers play an important role in our daily life. However, most elastomers are derived from petroleum resources. With the increasing emphasis on sustainable development, it is imperative to explore renewable raw material to synthesize biobased elastomers as next-generation rubbers. Renewable natural resources, including lignin, carbohydrates, starch, proteins, and plant oil, have attracted increasing interests because of its low cost, large production, nontoxicity, ready availability [68, 69].

In this study, we have reported on reactive blends derived from methoxysilane terminated linear urethane containing polysiloxane and silylated soybean oil. Polysiloxanes are known for their elastomeric properties owing to the presence of siloxane (Si–O– Si) backbone which is known to yield flexible polymer chain, high bond energy, low Tg, high thermal and oxidation stability, insensitivity to UV light and ozone, waterproof properties, high impact resistance, good electrical insulation, resilience, high oxygen permeability, biocompatibility and low surface energy [70, 71]. Polysiloxanes have been used for the elastomeric compositions with polymers like low density polyethylene etc., but the cure of these blends require free radical initiation and high temperature conditions [72-74]. The present work provides blends of polysiloxanes and silylated soybean oil which could get cured easily, just in the presence of moisture at room temperature. These blends provide optically transparent films without any gross phase separation between constituent phases. These elastomeric films were characterized for their composition to identify reactive sites and, the curing kinetics was studied using thermogravimetric analysis. Mechanical properties of these elastomers were measures and it was shown that these properties can be tailored as per the need of the application simply by changing the composition.

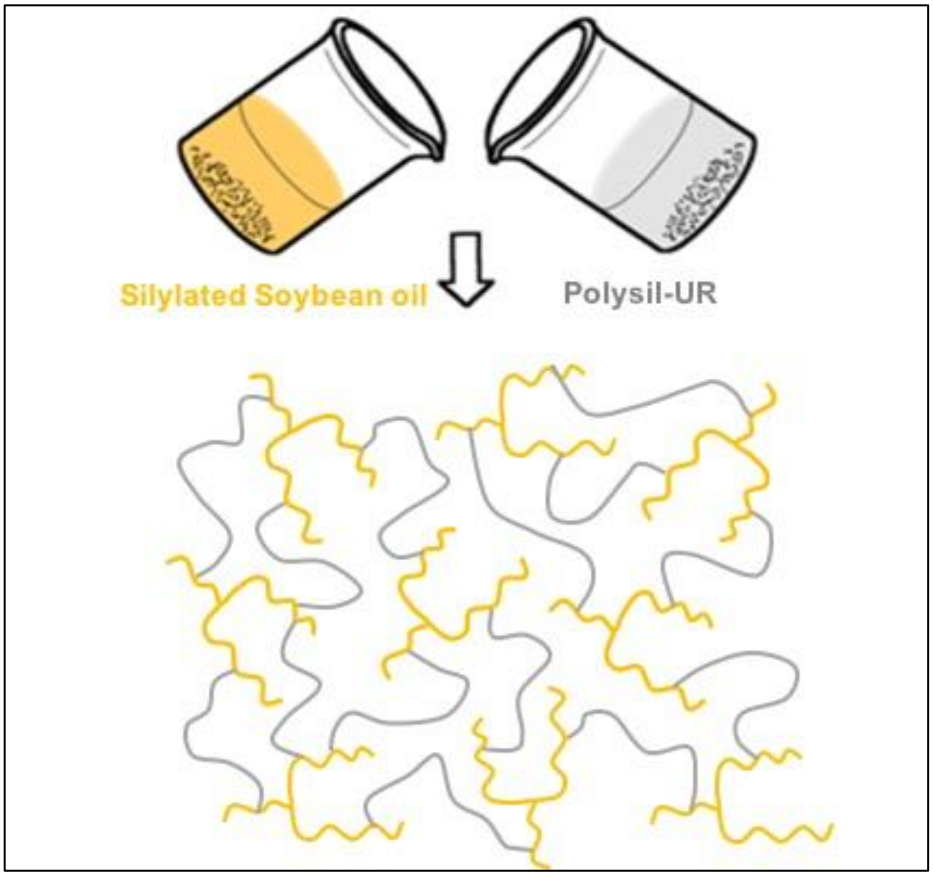


Figure 1.3: Picture representation of reactive blends prepared using silylated soybean oil and methoxy terminated silylated polyurethanes (polysil-UR)

1.3 Unsaturated polyester resin (UPR) from biobased fumaric acid

Another industry that extensively uses the petroleum-based resources is the unsaturated polyester resins (UPR). UPRs are thermosetting resins and are used in variety of applications like body parts for automotive, protective coatings etc. Up to now, large quantities of bio-based thermoplastics, such as poly(lactic acid), polyhydroxyalkanoate and poly(butylene succinate), have been synthesized and commercialized successfully [5, 75-77]. However, compared with the rapid progress on bio-based thermoplastics, much less research has been done on bio-based thermosetting resins [78]. Thermosetting resins, also known as thermosets, are chemical materials in liquid, soft solid or viscous state that can be changed irreversibly into infusible and insoluble polymer networks by curing reactions. Due to their high modulus, high strength and good thermal and chemical resistances, thermosetting resins have been widely used in coatings, adhesives, composites, electronic packaging, etc. [6, 79, 80]. UPRs are generally prepared by blending an unsaturated polyester (UP) with reactive diluent which also acts as a cross-linker, and eventually crosslinked using a suitable free radical initiator. UPs are synthesized using unsaturated dibasic acid and diols by two step polycondensation process. Ethylene glycol (EG) and propylene glycol (PG) are most widely used diols in the production of UP. Phthalic anhydride, Terephthalic acid and Maleic anhydride are among the commonly used acids/anhydrides used in the preparation of UPs. The diol component of these UPs (i.e., propylene glycol and polyethylene glycol) are available from biobased sources [12, 81], but unfortunately the majority of unsaturated acids are still resourced from petroleum sources [8]. Some studies have reported the use of biobased acids like itaconic acid [82], levulinic acid [83] in the preparation of UPs. Although there is still a need to research more such biobased monomers to be used in UPR industry.

In this study, we reacted propylene glycol and polyethylene glycol (which are available 100% bio-based today) with fermentation derived fumaric acid which was kindly provided by Michigan Biotechnology Institute (MBI). Traditionally, fumaric acid was chemically produced from maleic anhydride, which in turn was produced from butane. But due to increasing petroleum prices and high demand for biobased alternatives, the old technology for producing fumaric acid (from 1940) [84] resurfaced and now it is produced via fermentation route on commercial scale [85, 86]. Currently fumaric acid is not preferred in UPR industry because petroleum-based monomers like maleic anhydride are available at lower cost ($1.46-1.63/kg) [87]. However, fumaric acid is a better candidate among all unsaturated carboxylic acid for UP because of its inherent non-toxic behavior. We have prepared UPs based on fumaric acid and it was characterized quantitatively and qualitatively. Further, we prepared resins using cross-linker styrene via traditional crosslinking chemistry and we studied the curing kinetics isothermally at several temperatures. Lastly, with the help of some existing models for the composites property prediction, we predicted the mechanical properties of the final composite using natural fibers as well as some traditional fibers for property comparison.

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2. SILYLATION OF NON-TERMINAL DOUBLE BONDS OF NATURAL OILS

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2.0 Abstract

Silylation of non-terminal double bonds of unsaturated fatty acids with reactive organosilicons was successfully accomplished using the ‘Ene’ reaction route. The ‘Ene’ reaction, which is a subset of the famous Diels Alder reaction, enables grafting of vinyl silanes onto unsaturated organic molecules irrespective of the position of the double bond. This procedure was used to graft vinyltrialkoxysilanes onto unsaturated fatty acids of various triglyceride oils. Methyl oleate and methyl stearate were used as model compounds to investigate this reaction. ^{1}H NMR and TGA were used to characterize the structure of the silylation products and to determine the extent of grafting as a function of reaction conditions. It was found that this grafting reaction follows a second order kinetics. Under extreme conditions a silyl-ester redistribution reaction can also occur where an alkoxy group attached to the silicon atom is exchanged with an alkoxy group of the organic ester. Grafting vinyltrimethoxysilane onto natural oils such as soybean, canola and abyssinian oils leads to a convenient *one-component*, moisture activated cure system of these natural oils.

2.1 Introduction

Hydrosilylation is undoubtedly one of the most important routes used to prepare organosilicon compounds. It has been used commercially as the major synthetic route to insert silanes to alkenes via a new Si-C bond. This hydrosilylation reaction where Si-H is inserted into alkenes has been widely investigated and reported in the literature [1-3]. It can be carried out by free radical chain reactions or with catalysts such as platinum and other transition metal catalysts.

A wide choice of hydrosilylation catalyst is available and the type of catalyst usually determines the mechanism of his reaction. Unfortunately, the hydrosilylation reaction is most effective with alkenes containing terminal double bonds and unless chlorosilanes are used, it normally does not proceed to high yields when the silane is added to alkenes containing double bonds in a non-terminal position.

Carbosilylation is an alternative reaction that can be used to add an organosilane to alkenes. Although it does not provide for a new Si-C bond, it is an efficient and straightforward synthetic method using a 'green' protocol to insert silicones onto organic compounds [4-7]. Similarly, to the hydrosilylation reaction, carbosilylation reactions proceed with no by-product formation (Figure 2.1).

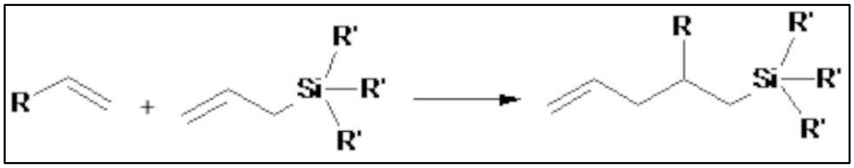

Figure 2.1: Carbosilylation of alkene with allylsilanes

In this reaction, electrophilic activation of a silyl group on the allylsilane is required which can be accomplished with either Lewis acids or Brønsted acids as the catalyst precursors. $AlCl_3$ is commonly used as the Lewis acid catalyst and the reaction proceeds via the formation of a cationic silyl intermediate. The efficiency of this reaction was claimed to approach 100% when allylsilanes are used with terminal alkenes, however, unlike hydrosilylation, internal double bonds (e.g. cyclohexene) can be silylated via this route. The major disadvantage of carbosilylation in comparison to hydrosilylation is the fact that carbosilylation is limited to allylsilanes and cannot be used with vinylsilanes.

Another approach to functionalize alkenes with vinylsilanes is to use transition-metal-catalyzed silylative coupling (also called trans-silylation). These reactions take place in the presence of complexes that contain or generate M–H and M–Si bonds (where M = Ru, Rh, Co, Ir) as shown in Figure 2.2.

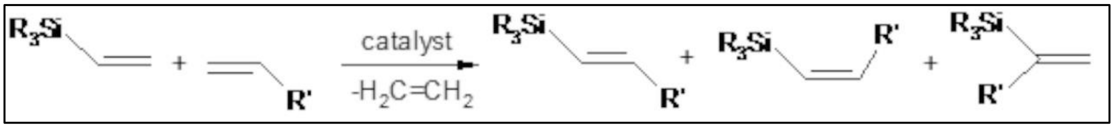

Figure 2.2: Silylative couplings of olefins with vinylsilanes

The mechanism of this reaction involves the insertion of vinylsilane into the M–H bond and β-Si transfer to the metal with elimination of ethylene to generate the M–Si species. This step is then followed by insertion of the alkene and β-H transfer to the metal with elimination of the substituted vinylsilane [8-10]. In a recent comprehensive review, it was concluded that the intermediates of this reaction involve metal complexes involving M-H and M-Si bonds (silicometallics) [11]. Thus, the silylation of alkenes with vinylsilanes generally proceeds via the same types of active intermediates as in hydrosilanes and as such, is more suitable with alkenes containing terminal double bonds than alkenes containing 'internal' double bonds.

The preferred approach to silylate 'internal' double bonds is to employ the 'Ene' reaction which is a subset of the famous Diels-Alder reaction and is defined by Alder [12] as being an "indirect substitutive addition of an olefin containing an allylic hydrogen (the ene) with a compound having a multiple bond (the enophile)" as shown in Figure 2.3.

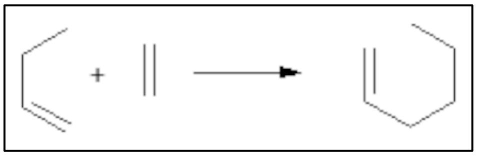

Figure 2.3: The ’Ene’ reaction

The general synthetic and mechanistic aspects of the ‘Ene’ reaction of organic compounds have already been reviewed previously [13-15]. It was shown that ‘Ene’ reactions involving silanes and siloxyl containing olefin substituents could be reacted with compounds having C=C, C=O, C=N and other hetero double bonds as the enophiles. The first such example with a Lewis-acid promoted carbonyl–Ene reaction using vinylsilane as the ene moiety was published in 1990 [16] and most of the explored Ene reactions involved addition of vinylsilanes to carbonyl groups. A recent comprehensive review of ‘Ene’ and Diels–Alder reactions involving vinyl and allylsilanes with emphasis on silyl-substituted 1,3-butadienes building blocks in organic synthesis is available [17]. The general mechanism of this reaction involves a four-electron system, including an alkene π-bond and an allylic C-H σ-bond, that participate in a pericyclic reaction in which the double bond shifts and new C-H and C-C σ-bonds are formed adjacent to the allylic C-H σ-bond. Generally, the allylic system reacts similarly to a diene in a Diels-Alder reaction and, unless catalyzed, requires high temperatures due to the high activation energy requirement needed to cleave the allylic C-H σ-bond. The s-antibonding orbitals of the Si–C bond and the p-bonding orbitals of the C=C bond have a similar energy level which leads to weak hyperconjugation that lowers the overall energy and enhances the reactivity of the silyl substituted olefins. “As a result, the silyl group behaves as an electron-donating group inductively and an electron-withdrawing group in terms of conjugation effect, which makes the reactivity of silyl-substituted olefins different from the simple olefins”. It is important to note that the addition of vinyl silane to olefins via the ‘Ene’ reaction does not depend on the position of the double bond in the olefin and was found to proceed to high yields even with non-terminal double bonds.

The objectives of this work were to silylate soybean oil by grafting trimethoxyvinylsilane onto the unsaturated fatty acid triglycerides and then use the inherent hydrolytic instability of the grafted methoxysilanes to cure the oil by atmospheric moisture. This strategy is based on a process that is relatively simple and free of any hazardous compounds; eliminating all potentially toxic or expensive metal-based catalysts that were traditionally used for silylation of organic compounds. Soybean triglycerides contain 81% unsaturation (23% oleic acid and 58% linoleic and linolenic acids) and these unsaturated fatty acids were used previously to chemically modify the oil by hydroformylation [18], epoxidation [19] and ozonolysis [20, 21]. The coatings based on these cured triglycerides provided good protection of the substrate with excellent UV stability. Silylation of the oil is expected to provide a convenient alternative to produce cured coatings from these readily available biobased oils.

It is interesting to note that highly unsaturated oils (e.g. Linseed oil) have been used for centuries in the paint industry and the best examples are paints derived from alkyd resins that contain, on average, about 50% natural fatty acids. These paints cure upon oxidation of the double bonds in the unsaturated fatty acid residues to yield relatively hard, brittle coatings. Although soy oil contains some unsaturated fatty acids, the type and degree of unsaturation here are not sufficient to cure the oil by a similar oxidation process into a network. Thus, grafting reactive silanes onto the fatty acids provides a simple method to enhance the curing process and provides a novel new moisture-activated cure of common vegetable oils such as soy oil. Unlike previous chemical modifications, silylation of the soy oil using methoxysilane produces a *one-component*, low viscosity oil that can be applied as coatings by conventional brushing, dip-coating or spraying techniques which will cure to a resinous protective coating by simply exposing the oil to atmospheric moisture. The effect of temperature and silane concentration on the yield and the kinetics of the grafting reaction were the subjects of this study. Methyl oleate was also used as a model reactant to better characterize and optimize the silylation grafting reaction.

2.2 Experimental

2.2.1 Materials

LowSat® soybean oil was kindly provided by Zeeland Farm Services, Inc. (MI, USA). Canola oil and Abyssinian oil were purchased from Sigma-Aldrich (MO, USA). The Vinyltrimethoxysilane (VTMS) and Vinyltriethoxysilane (VTES) were purchased from Gelest, Inc. (PA, USA). The catalyst Luperox-101, methyl oleate and methyl stearate were purchased from Sigma-Aldrich (MO, USA). All chemicals were reagent grade and were used without further purification unless noted.

2.2.2 Silylation procedure

In a typical reaction lowSat® soybean oil, VTMS and Luperox-101 catalyst (1 wt. %) were added to a high-pressure stainless steel PARR reactor (PARR Instrument Company, IL. USA). The reactor was purged with nitrogen and the reaction mixture was heated to the desired temperature for a predetermined period of time (Table 2.1) under constant stirring. Samples were taken periodically to monitor the progress of the reaction. The effect of temperature and the initial composition on the yield and the progress of this reaction were further monitored by running the same reaction at different temperatures and with different concentrations of VTMS as indicated in Table 2.1.

Table 2.1: Silylation reaction stoichiometry and the temperature conditions with extent of grafting analysis for samples taken at different time intervals

Sample	Soy oil/VTMS		Temp.	Extent of grafting [%]				
	[gr/gr]	[M/M]	[°C]	2 hrs.	4 hrs.	6 hrs.	10 hrs.	12 hrs.
1	874/296	1/2	225	15.9	26.2	33.7	40.9	42.0
2	874/296	1/2	250	36.5	51.2	64.2	71.4	-
3	874/296	1/2	275	53.2	79.1	80.0	-	-
4	874/444	1/3	225	21.4	-	42.1	47.3	52.0
5	874/444	1/3	250	30.1	33.5	51.7	-	72.4
6	874/592	1/4	225	24.3	40.2	50.1	51.2	-

The silylation reaction was further studied using methyl oleate as a model compound. In this case VTES was used as the silylation reagent instead of VTMS to better identify any possible trans-esterification reactions. The reaction was further examined with a saturated fatty acid (e.g. methyl stearate) to assess the effects of the reaction conditions on any possible side reactions.

2.2.3 Characterization

Thermogravimetric analysis (TGA) from TA instruments (Hi-Res TGA model 2950, New Castle, USA) was used to determine the extent of grafting of the vinylsilane onto the unsaturated fatty acid in the triglyceride oils. The weight loss of a sample was recorded by heating the sample isothermally at 130°C (above the boiling point of the vinylsilane) for 20 minutes to completely remove any unreacted silane. The extent of grafting was then calculated based on the weight loss of the sample related to the free (not grafted) vinylsilane. A control experiment was run under identical conditions using pure oil to ensure that no other volatiles were present in the oil.

The structure of the silylated products was determined by ^{1}H NMR using a 500 MHz NMR spectrometer (Varian Inc., USA, Unity Plus 500MHz). The $CDCl_3$ solvent peak was used as an internal standard. The viscosity of the products was measured at RT using a Brookfield viscometer-LVDV-E model (MA, USA). Spindle 61 was used for the viscosity measurement of silylated oil.

2.3 Results and Discussion

2.3.1 Model compound study

The silylation of vinylsilanes onto the double bonds of triglycerides by the ‘Ene’ reaction was studied initially by grafting VTMS onto methyl oleate (e.g. methyl-octadec-9-enoate) as a model reaction (Figure 2.4). Methyl oleate is a fatty ester of oleic acid, a common fatty acid containing 18 carbons chain and a single double bond at the 9th position. Figure 2.4 shows two possible Ene reaction products, which differs in the attachment of VTMS molecule to methyl oleate.

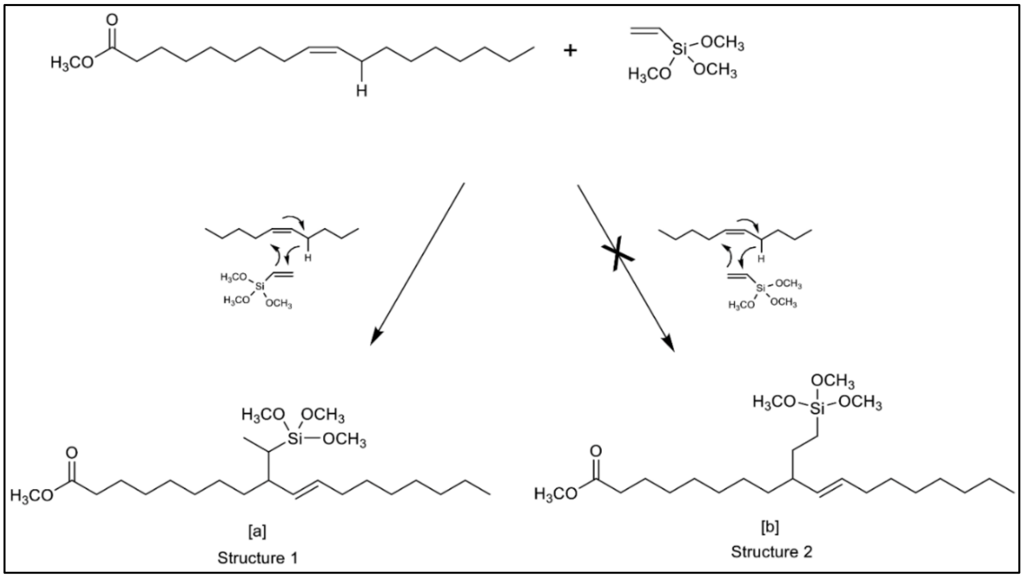

Figure 2.4: Ene mechanism for the silylation reaction of methyl oleate and VTMS

The structure of the silylated product was analyzed by ^{1}H NMR spectra, which is shown in Figure 2.5. In Figure 2.5a the resonance peaks around 6 ppm correspond to the vinyl protons of VTMS and the resonance peaks around 3.5 ppm corresponding to the protons of methoxy groups of VTMS are clearly visible. However, after the silylation reaction (Figure 2.5b) the resonance peaks corresponding to the vinyl protons at 6 ppm disappeared while the resonance peaks related to the silyl methoxy protons are still visible. It should further be noted here that the resonance peaks of the unsaturation protons from the fatty ester around 5.3 ppm are still present in the silylation product indicating that the double bond in methyl oleate was not consumed. Instead, it simply migrated as suggested by the general mechanism of the 'Ene' reaction (Figure 2.3). In Figure 2.5b, there is no peak corresponding to the $–Si\text{-}CH^{*}_2$- (Figure 2.4b) around 0.5ppm, as expected, while a peak corresponding to $–Si\text{-}CH^{*}$- can be seen around the cluster at 1.5 ppm in Figure 2.4a. This leads to the confirmation that the Ene reaction leads to the yield product as shown in Figure 2.4a.

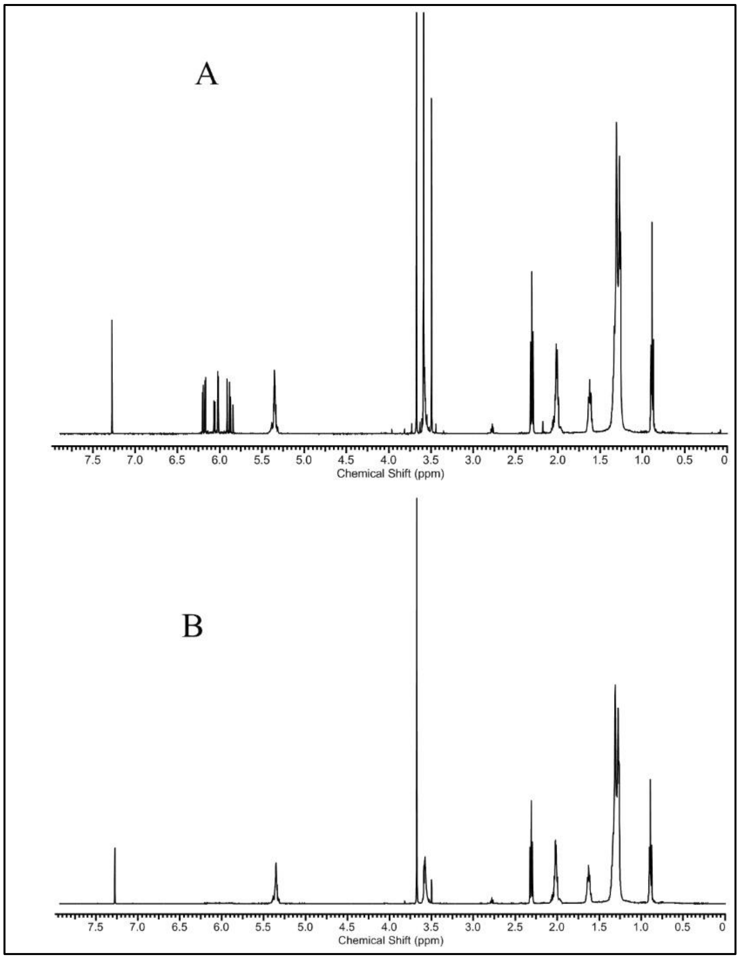

Figure 2.5: The ^{1}H NMR spectra for [a] reaction mixture of methyl oleate before silylation and [b] the silylation reaction product carried out at 225^{0}C

2.3.2 Characterization of the silylated LowSat® soybean oil

LowSat® soybean oil was chosen for the grafting reaction since the lower saturated content ensures that a coating prepared from it will contain no unreacted triglycerides. This soybean oil has an average of 5.1 carbon-carbon double bonds per triglyceride compared with ‘regular’ soybean oil that contains an average of 4.5 carbon-carbon double bonds per triglyceride. The higher unsaturated content (and the lower concentration of saturated fatty acids) provides for higher probability that no triglyceride molecule will contain only unsaturated fatty acids as this will lead to incomplete cure and poor coating.

LowSat® soybean oil contains 75.5 oleic acid (O) having a single double bond, 35% linolenic acid (L3) having 3 double bonds, 15% linoleic acid (L2) having 2 double bonds, 3% saturated palmitic acid (P) and 3% saturated stearic acid (S). Statistical analysis of the oil composition indicates that only 0.022% of the triglycerides contains no unsaturation (Table 2.2). This negligible concentration of triglycerides containing three Stearic acids (SSS), three palmitic acids (PPP) or some combination of these saturated fatty acids (PPS or SSP) ensures that essentially all the triglyceride molecules in the oil can be silylated provided sufficient vinylsilane is used. This conclusion is critical for any coating application where it is important to obtain high gel fraction and a network that contains minimum free 'loose juice' that could migrate to the surface of the coating, change the bulk mechanical properties, or affect the adhesion.

Table 2.2: Statistical analysis of the oil composition LowSat$^{®}$ soybean oil

Triglyceride	**Frequency**	**# double bonds per triglyceride**	**Relative # of double bonds**
PPP	0.000027	0	0
PPS	0.000081	0	0
PPL2	0.000405	2	0.00081
PPL3	0.000095	3	0.00028
PPO	0.002039	1	0.00204
PSL2	0.000810	2	0.00162
PSL3	0.000189	3	0.00057
PSO	0.004077	1	0.00408
PL2L3	0.000945	5	0.00473
PL2O	0.020385	3	0.06116
PL3O	0.004757	4	0.01903
SSS	0.000027	0	0
SSP	0.000081	0	0
SSL2	0.000405	2	0.00081
SSL3	0.000095	3	0.00028
SSO	0.002039	1	0.00204
SL2L3	0.000945	5	0.00473
SL2O	0.020385	3	0.06116
SL3O	0.004757	4	0.01903
L2L2L2	0.003375	6	0.02025
L2L2P	0.002025	4	0.00810
L2L2S	0.002025	4	0.00810
L2L2L3	0.002363	7	0.01654
L2L2O	0.050963	5	0.25481
L2L3O	0.023783	6	0.14270
L3L3L3	0.000043	9	0.00039
L3L3P	0.000110	6	0.00066
L3L3S	0.000110	6	0.00066
L3L3L2	0.000551	8	0.00441
L3L3O	0.002775	7	0.01942
OOO	0.430369	3	1.29111
OOP	0.051302	2	0.10260
OOS	0.051302	2	0.10260
OOL2	0.256511	4	1.02605
OOL3	0.059853	5	0.29926
Total:	1.000000		**3.48**

Based on the model compound study, it was expected that the silylation of soybean oil would follow similar Ene reaction path, although in principle, it can potentially involve any double bonds in the reaction mixture. There the products could be dimerization (or oligomerization) of triglycerides with other triglycerides or several VTMS molecules along with Ene reaction product. However, oligomerization between two (or more) triglycerides requires much higher temperatures and a proper catalyst [22]. Dimerization of two VTMS through the double bonds by the 'Ene reaction' is a possibility but was not observed to any extent when a sample of VTMS was heated with an internal standard and periodically analyzed by GC. This strengthens the occurrence of Ene reaction, which in turn was confirmed by ^{1}H NMR spectra of lowSat® soybean oil (a) and the silylated oil (b) are provided in Figure 2.6 and confirm successful grafting of VTMS onto the oil. Although the spectra are more complicated than those of the model compounds due to the presence of different fatty acids, the presence of the resonance peaks at 3.5 ppm related to the silyl methoxy protons are clearly observed as well as weak resonance peaks from the vinyl protons of VTMS in the 6.0ppm region. These residual peaks at 6.0ppm region could be due to possible condensation and formation of oligomeric vinylsilseqioxane or simply due to incomplete grafting reaction and the presence of unreacted VTMS in the product. However, oligomerization of VTMS to vinylsilseqioxane does not occur under the given reaction conditions, as this condensation reaction requires moisture to be present in the system for the hydrolysis of the methoxy groups. So, the residual peaks appearing at 6ppm indicates the presence of unreacted VTMS.

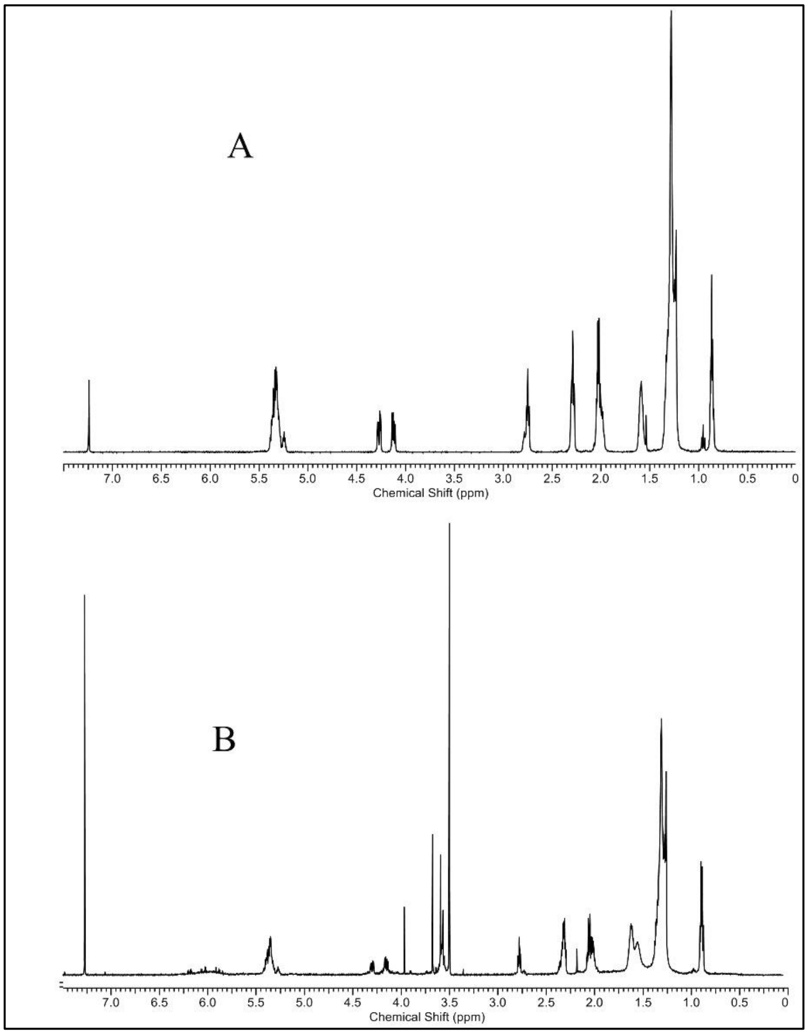

Figure 2.6: NMR spectra for [a] soybean oil and [b] silylated soybean oil after removing excess ungrafted VTMS

The degree of grafting was conveniently derived from isothermal TGA experiments that were set above the boiling point of VTMS. Under these conditions free (un-grafted) VTMS was removed and the grafted VTMS fraction could be determined. A representative TGA weight loss plot as a function of time under isothermal conditions is shown in Figure 2.7.

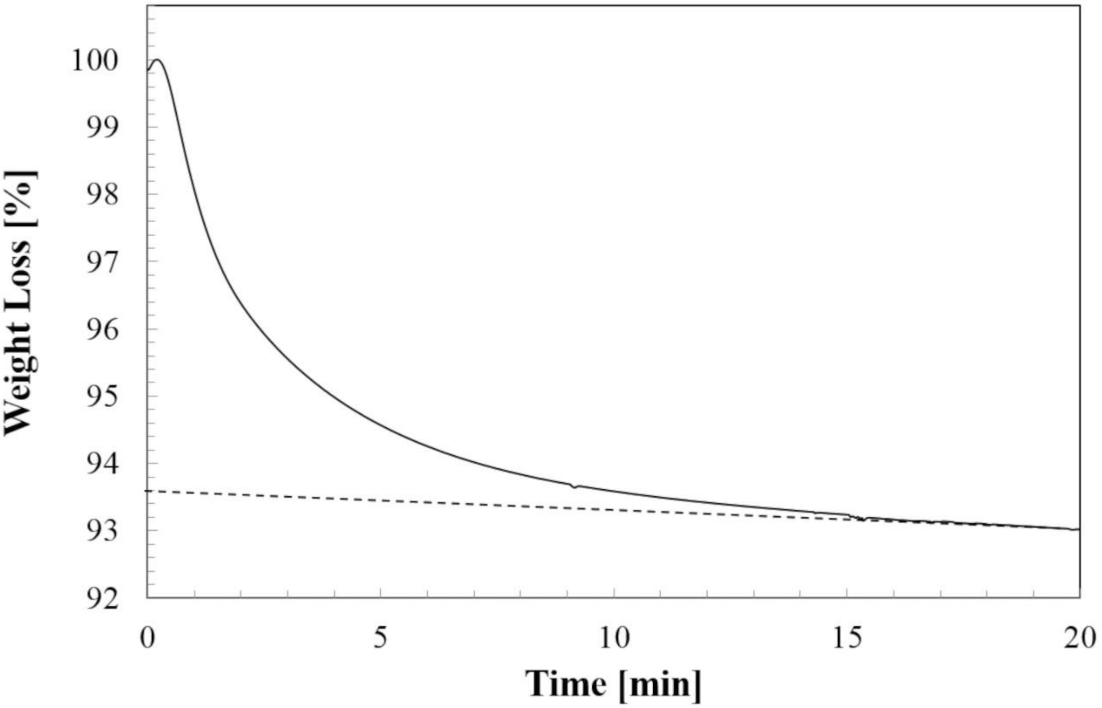

Figure 2.7: Extent of grafting by TGA analysis

The extent of grafting was calculated using Eq. 2.1 by extrapolating the observed weight loss knowing the initial composition of the sample using Equation 1.

$$\%\text{Grafting} = \frac{\%\ \text{VTMS in feed-}\%\text{VTMS loss}}{\%\text{VTMS in feed}} \times 100 \qquad \text{[Eq. 2.1]}$$

2.3.3 Effect of reaction conditions

The effect of reaction temperature and time on the extent of the grafting reaction of VTMS on the lowSat® soybean oil is summarized in Table 2.1 using different molar ratio of the soybean oil to the silane. Thus, a ratio of 1:2 implies that the initial reaction mixture contained 1 mole of soybean oil and 2 moles of VTMS. Since there are multiple double bonds in each triglyceride, this low ratio does not guarantee that each and every triglyceride is silylated, especially if the reaction yield is less than 100%. Since it is desirable that every triglyceride molecule will react to form the crosslink network, higher concentrations of VTMS were also used as indicated in Table 2.1. It is apparent that the extent of silylation is directly proportional to the initial concentration of VTMS in the reaction mixture and the reaction temperature. However, the rate of the reaction is generally slow and requires relatively long reaction times. For example, the extent of the silylation after 2 hours at 225°C increased in proportion to the initial concentration of the silane (entry 1, 4 and 6). The effect of the temperature on the silylation reaction using Soy:VTMS of 1:2 molar ratio is shown in Figure 2.8 and clearly indicates that the extent of grafting is directly proportional to the reaction temperature.

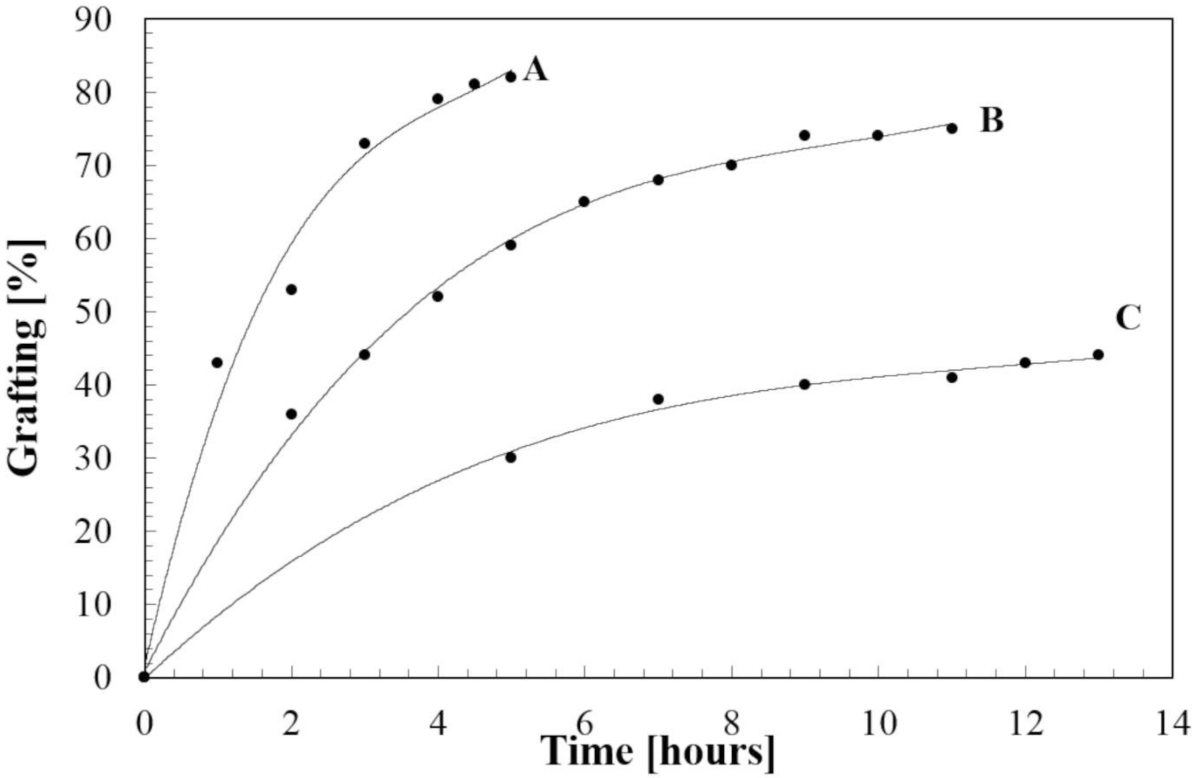

Figure 2.8: Extent of grafting as a function of time with molar ratio 1:2 (soy oil: VTMS) for different temperatures [a] 275^0C, [b] 250^0C, [c] 225^0C

The kinetics of the silylation reaction clearly follows a second order reaction (Figure 2.9). The rate constant (k) of this reaction at different temperatures was calculated from Eq. 2.2 where

C_o is the initial silane concentration and C is the concentration at time t and are 0.0104 L/mol·hr, 0.0403 L/mol·hr and 0.1132 L/mol·hr for 225°C, 250°C and 275°C, respectively.

$$\frac{1}{C} = \frac{1}{C_0} + kt \quad \text{[Eq. 2.2]}$$

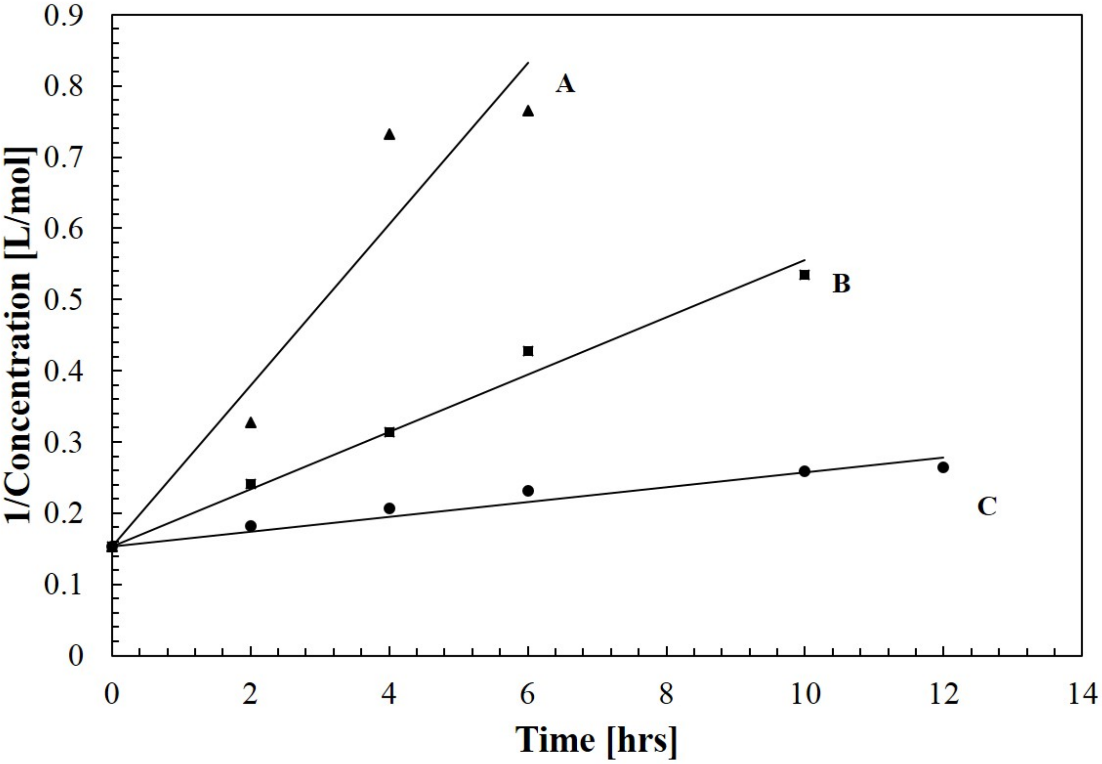

Figure 2.9: Second order kinetics of consumption of VTMS at different temperatures [a] 275ºC, [b] 250ºC, [c] 225ºC

Using these rate constants, it is possible to derive the activation energy of the grafting reaction from the Arrhenius equation (Eq. 2.3) by plotting the rate constants as a function of the reaction temperatures (Figure 2.10).

$$\ln(K) = \ln(A) - \frac{E_a}{RT} \quad \text{[Eq. 2.3]}$$

where Ea is the activation energy, R is the gas constant, T is the temperature and A is a constant.

Using this Eq. 2.3, it was found that the activation energy of this silylation reaction is 240.6 kJ/mole.

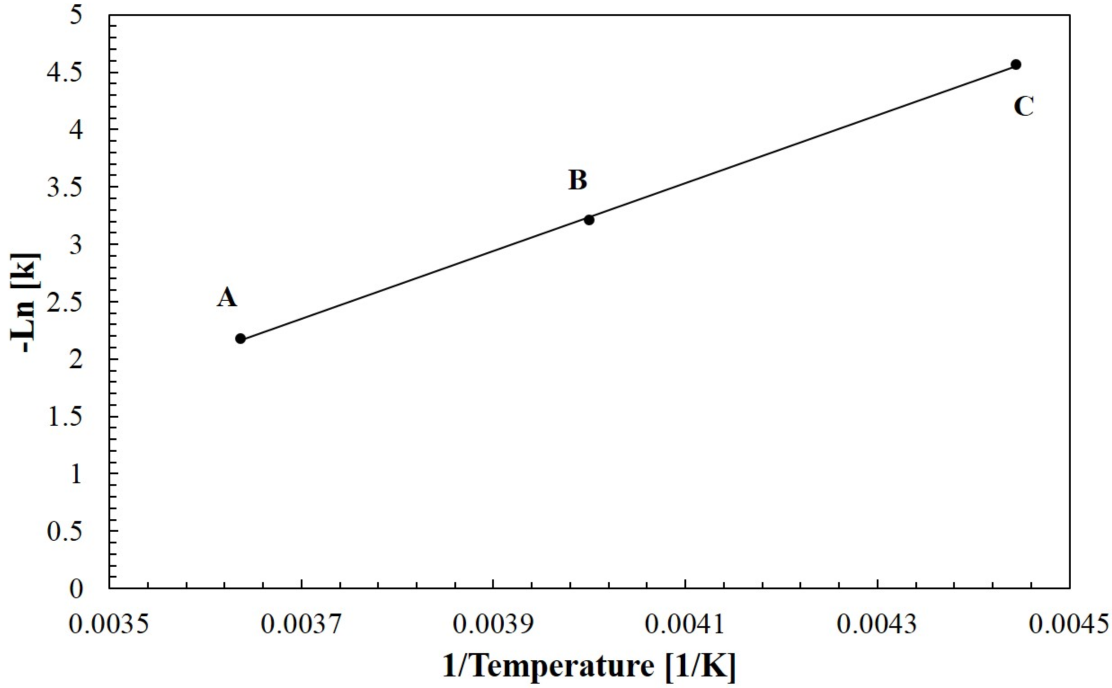

Figure 2.10: Arrhenius plot for the second order kinetics of consumption of VTMS using rate constants for different temperature reactions [a] 275°C, [b] 250°C, [c] 225°C

We noted that when the reaction was allowed to run at high temperatures for a long period of time a siloxy-ester exchange reaction was observed. Under these conditions the methoxy groups of VTMS can potentially react with an ester group of the triglyceride (Figure 2.11) to form new Si-O-C linkages. The formation of methyl esters via this reaction explains the relatively small but apparent weight loss in the TGA spectra (Figure 2.7) in contrast to essentially no weight loss of the soy oil under identical heating conditions. To further investigate this side reaction, the silylation reaction was repeated with vinyltriethoxysilane (VTES) and methyl stearate. This fatty ester contains no unsaturation thus, no silylation via the 'Ene' reaction is possible but the silyl-ester exchange reaction is still possible. VTES was used here instead of VTMS since the ethoxy group can be easily distinguished from the methoxy groups of the fatty methyl ester.

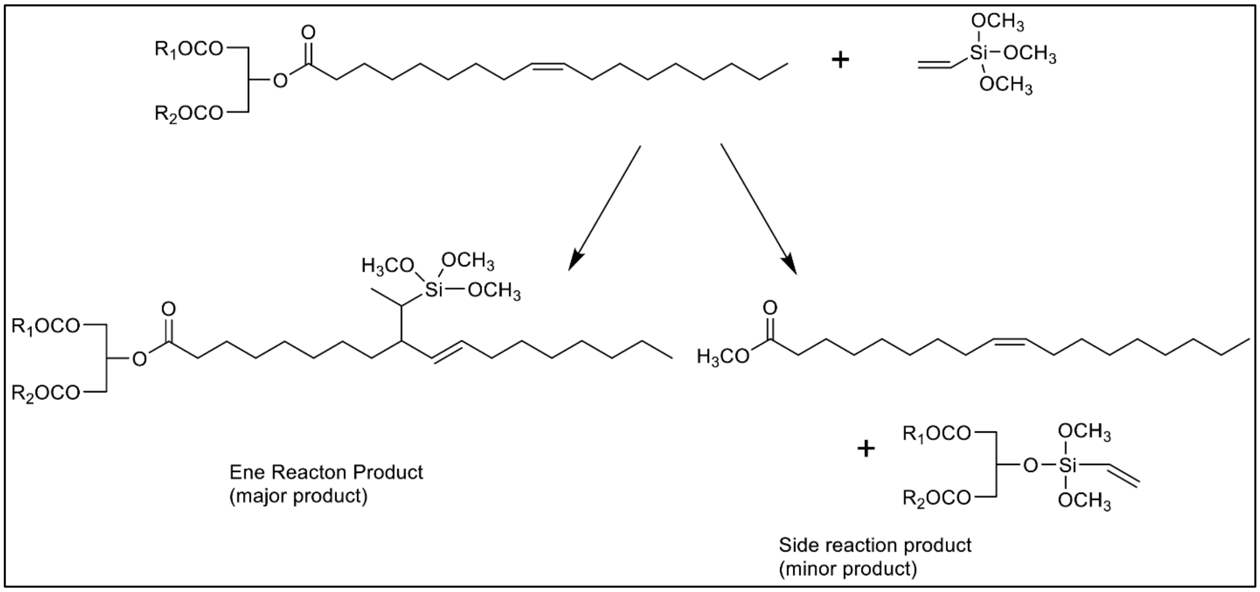

Figure 2.11: Preparation of silylated low-sat soybean oil

The ^{1}H NMR spectrum of the initial reaction mixture and the product mixture after heating for 4 hours at 275°C are shown in Figure 2.12. It is apparent that only the resonance peaks at 3.66 ppm and 3.84 ppm corresponding to the protons of the stearate methoxy ester group and the ethoxy silanes, respectively, are observed initially (Figure 2.12a). However, after long time heating additional resonance peaks at 3.58 ppm and 4.12 ppm corresponding to protons of methoxy silane and ethyl stearate, respectively, are observed (Figure 2.12b).

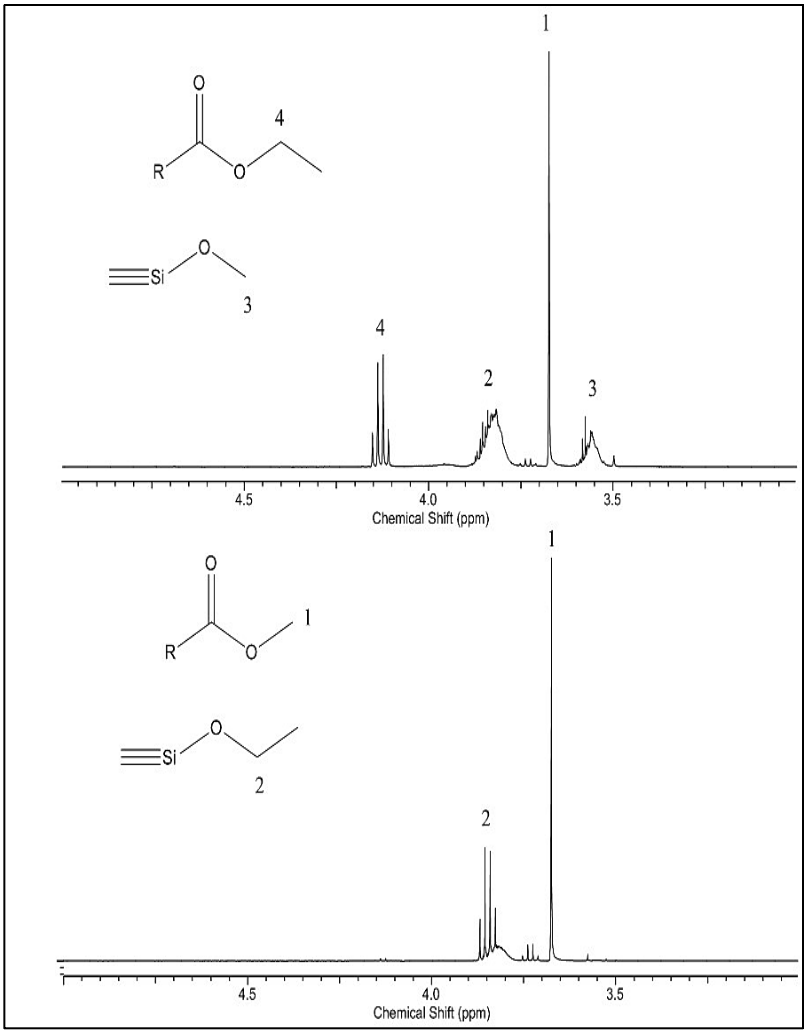

Figure 2.12: ^{1}H-NMR spectra comparison of the reactants and product in the reaction of methyl stearate and VTES carried at 275^{o}C

Redistribution reactions about a silicon atom are well known and were reviewed previously [23]. The redistribution depends on the nature of the ligands and falls into three general classes depending on the ability of a given ligand to participate in the redistribution reaction:

A. Labile ligands: halogen and pseudohalogen, oxy, amino and thio.

B. Semi-labile ligands: hydrogen and silicon.

C. Non-labile ligands: alkyl and aryl.

The labile ligands can be cleaved from silicon by hydrolysis and are most easily redistributed even upon simple mixing. Ligands in class B and C are those that are less susceptible to hydrolytic cleavage and require a catalyst and more severe conditions to initiate redistribution. The redistributions of alkoxy ligands in the absence of a catalyst is generally less facile and slow at temperatures of 150°-200°C but quite rapid in the presence of catalysts such as metal alkoxides or in the presence of aluminum chloride[24].

It should be noted that unlike redistribution reactions about the silicon atom, the observed redistribution reaction here involves a silyl-ester exchange reaction. Furthermore, this redistribution reaction occurred in the absence of water (no hydrolysis) or a catalyst and proceeded, although slowly, by simple heating. It is therefore recommended that similar grafting reactions onto organic esters by the ‘Ene’ reaction should be conducted at low temperatures. However, if elevated temperatures are used, short reaction times are preferred in order to maximize the yield and minimize the extent of the redistribution reaction.

2.3.4 Silylation of different oils

Grafting active silanes by the ‘Ene’ reaction was extended to different natural oils containing unsaturated fatty acids. Canola oil and Abyssinian oil were chosen, as they are biobased oils made from rapeseed and crambe abyssinica seeds respectively. Canola oil contains about 81% unsaturation triglycerides, 63% mono-saturation and 28% poly-unsaturation. Abyssinian oil contains about 55-60% mono saturation and 25-30% poly-unsaturation. The silylation of these oils were carried out using the same conditions used for the silylation of the lowSat® soybean oil. Similar silylated products to the soybean oil were obtained as determined by TGA analyses (Table 2.3).

Table 2.3: Silylation reaction carried out for low-sat soybean oil, canola oil and Abyssinian oil with VTMS at 225^{o}C for different time periods in high pressure reactor (PARR) and its Characterization using thermo-gravimetric (TGA) analysis

Oil	Oil:VTMS [mole ratio]	Reaction Time [hrs.]	Extent of Grafting [%]
lowSat® soybean	1:2	4	53.23
LowSat®	1:4	3	46.25
Canola	1:2	4	43.92
Canola	1:4	3	31.91
Abyssinian	1:2	3	40.36
Abyssinian	1:4	3	32.27

2.3.5 Moisture cure

Silicone moisture activated cure systems are well known and are based on the hydrolytically unstable Si-O-C linkages. Thus, upon exposing oils containing alkoxysilanes to atmospheric water hydrolysis to silanols and subsequent condensation to stable siloxane bonds (Si-O-Si linkages) occur and lead to crosslinked films as shown schematically in Figure 2.13. It is important to note that this cure occurs at room temperature and does not require pre-mixing (e.g. a *one-component* system) or a diluent.

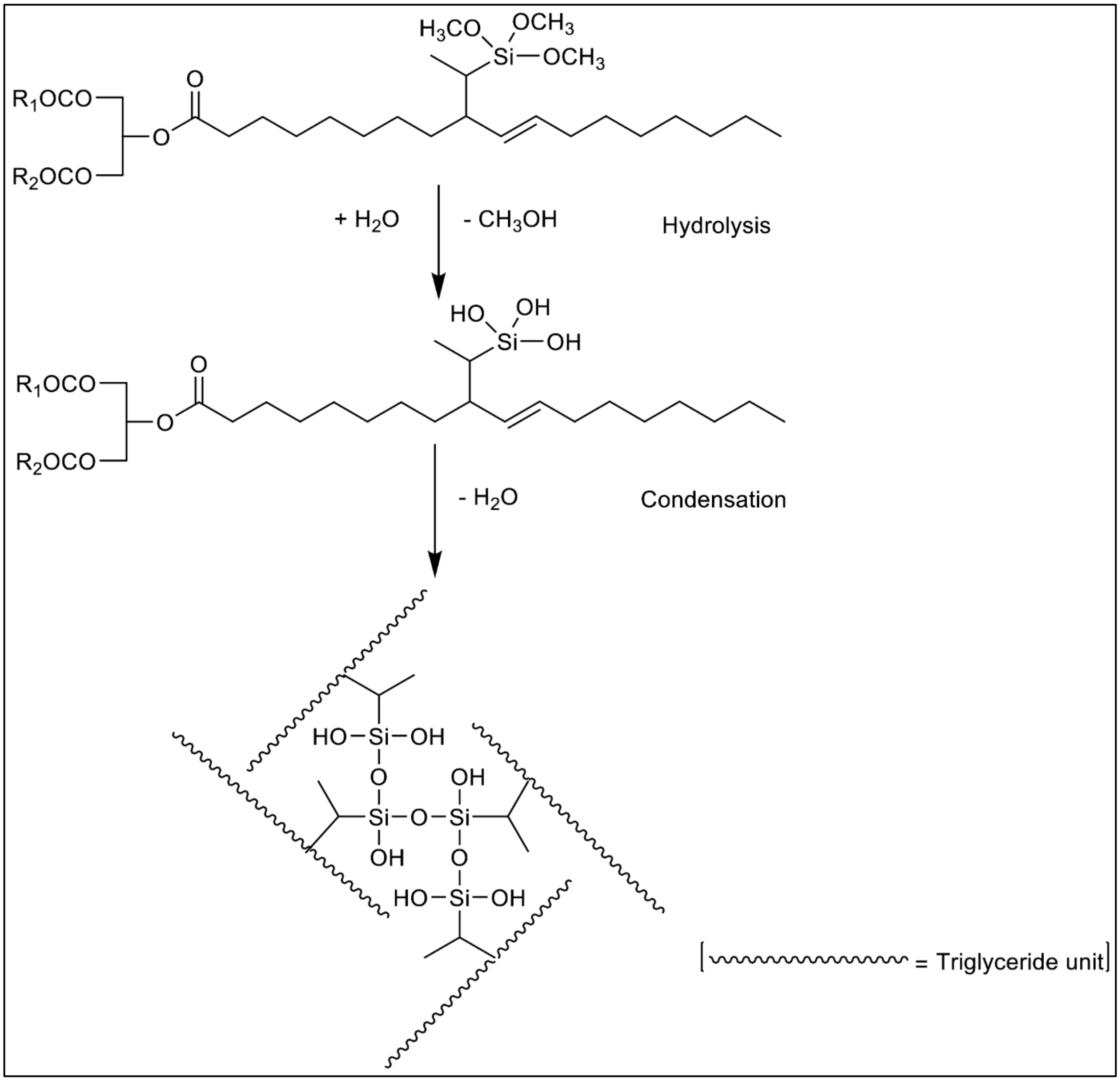

Figure 2.13: The reaction scheme for the cross-linking of silylated product upon addition of moisture

The crosslinking reaction was followed by the change in the viscosity of the oil over time at RT using a Brookfield viscometer. The initial viscosity of the silylated lowSat® soybean oil was 40 cPs identical to the viscosity of the original lowSat® soybean oil indicating that there was no apparent change in the viscosities due to the silylation reaction. Upon adding dibutyltin dilaurate (DBTDL) catalyst and water the viscosity quickly increased in a short period of time to

15,000 cPs (Figure 2.14) and eventually a solid gel coating was obtained. It is expected that coatings made from these silylated triglycerides will have good moisture and UV resistance.

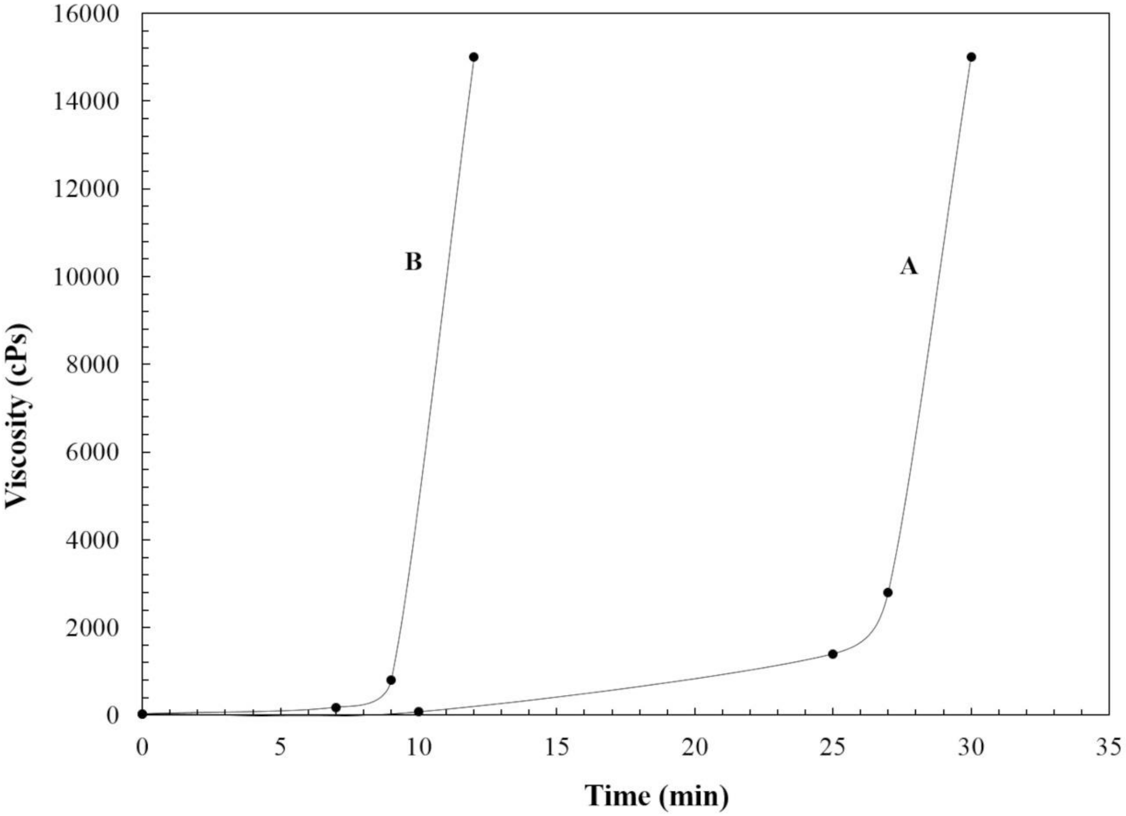

Figure 2.14: Curing analysis of the silylated soybean oil by introducing moisture in the presence of catalyst (DBTDL) at room temperature; [a] 1% w/w catalyst + 4% w/w water; [b] 2% w/w catalyst + 4% w/w water

2.4 Conclusions

Vinylalkoxysilanes were grafted onto unsaturated fatty acids of various natural oil triglycerides by the 'Ene' reaction. The structure of the silylated oils and the effect of reaction conditions were confirmed using methyl stearate as a model compound. The silylation reaction follows a second order kinetics and the yield is directly proportional to the temperature and the reaction time. However, under extreme temperatures and long reaction times, a siloxy-ester exchange reaction was identified whereby an alkoxy group of the silane can undergo a redistribution reaction with a methoxy group from the fatty ester. Successful grafting of reactive silanes, such as vinyltrialkoxysilanes, on to unsaturated fatty acids in vegetable oils yields low viscosity silylated oils that are readily cured by moisture into durable coatings.

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3. MOISTURE RESISTANCE COATINGS OF PACKAGING PAPER FROM BIOBASED SILYLATED SOYBEAN OIL

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3.0 Abstract

The moisture resistance of Kraft paper was greatly improved when it was coated with silylated soybean oil that was cured via silanol condensation. This moisture barrier coating was prepared from LowSat® Soybean oil that was grafted with vinyltrimethoxysilane (VTMS) using a relatively simple process based on the “Ene reaction”. The viscosity of the resulting oil was unaffected by the silylation reaction and remained low (32 cPs). Thus, the paper coating process required no solvent, additional diluent or the need to emulsify the oil which provided a convenient *one-component cure* system. Dibutyltin dilaurate (DBTDL) was found to be an effective condensation catalyst and under optimal conditions complete cure was achieved in a short period of time. The cure rate was a function of the catalyst concentration, available water and the temperature. Initially, Kraft papers were coated with the silylated soybean oil in the lab and this process was followed by a pilot scale-up using a commercial gravure roll coater. Cobb values and water vapor transmission rate indicated the cured coating provided a good barrier coating. Scanning electron microscopy (SEM) images of the coated paper confirmed a uniform coating with good adhesion of the coating material to the paper.

3.1 Introduction

Paper bags are widely used in the packaging industry since the paper is widely recognized as a safe and environmentally-friendly material due to its biodegradability. One of the major requirements for papers that are used in the packaging industry is the need to provide a moisture barrier since such barrier plays a critical role in preserving the food quality. Structurally, a paper consists of a porous cellulose made up of micro-fibrils composed of long-chain crystalline cellulose regions with pockets of amorphous regions. The cellulose structure is inherently hydrophilic due to the multiple hydroxyl groups. In addition, the fiber network is porous, which further limits the moisture barrier of the paper [1]. Consequently, it is well known that water molecules are transported in papers by diffusion of water vapor through the void spaces as well as in a condensed form through fiber cell walls [2]. It follows that papers with high porosity and large pore size, such as Kraft paper, have poor moisture barrier. However, Kraft paper is commonly used in the paper packaging industry because of its low cost of production and thus, it has to be coated with a good moisture barrier material with minimal impact on its cost [3].

Historically, common paper coatings were prepared from wax. Wax is relatively cheap and it provided reasonably good moisture barrier as well as grease resistance properties. Although wax coating is still available today, it has been largely replaced by plastic films like polyolefin [4], polyethylene [5], polyethylene terephthalate (PET), polybutylene terephthalate (PBT) [6], polyvinyl alcohol [7] and fluorocarbons [8, 9] that provide superior performance. However, the use of these synthetic polymers led to the loss of the inherent biodegradability and recyclability of the paper. The desire to prolong shelf-life and enhance food quality whilst reducing packaging waste created an interest in using polymers from renewable resources that can replace synthetic films. Indeed, there is a great interest in the packaging industry in environmentally friendly paper coating materials that are biodegradable [10] and several biopolymers have been investigated as coating for paper packaging. These polymeric materials are based on renewable resources like polysaccharides, lipids, proteins and their combinations [11-13]. However, coatings derived from protein, hydro-colloidal polysaccharide and hydroxypropyl methylcellulose had poor water barrier due to their hydrophilic nature whereby the inherently hydrophobic lipids are preferred. It was noted, however, that although lipid coatings can provide good moisture barrier, they have certain disadvantages including oily surface, brittleness, lack of homogeneity and the presence of pinholes and cracks in the surface of the coating. These studies further revealed that in addition to god and effective coating, the biobased composition needs to be a low viscosity material that is fast drying and can provide a uniformity coating over the porous paper substrate. It is anticipated that successful coatings should allow greater use of Kraft paper in daily life as packaging of fresh food but also as coating for paper bags used for waste food collections.

In addition to advancements in the coating materials, there have been remarkable advancements in the technology of the paper coating process itself ranging from applying and distributing of the coating material using brush like paints in early processes to the use of roll or jet applicators that are used today. The most common choice in modern day paper coating technology is the use the gravure roll coaters which allows to accurately manage the coating thickness using a blades or a metering bar[14, 15]. Indeed, advances in, both, the paper coating materials and the coating process are mainly attributed to the needs and advent of the printing[16] and the packaging[17-19] industries. Most critical factors for the gravure roll coaters are the viscosity of the coating material, the rolling speed and the oven temperature.

Plant oils are readily available, low cost, non-toxic and inherently non-volatile low viscosity oils that are renewable raw materials. The unsaturation present in the fatty acids of these oils have been used in the coatings industry in the past [20]. Natural drying oils have been commercially used for centuries in the paints and coating industries [21-25]. The most common example of such oils is linseed oil that contains a high degree of unsaturation (as it contains high concentrations of linoleic and oleic fatty acids). Upon exposure to oxygen in the air, linseed oil is readily oxidized and cross-linked to a rigid film [26]. Although linseed oil has been used as an ingredient in various industrial paints and coating formulations, coatings derived from linseed oil are very brittle and tend to yellow upon aging. Furthermore, drying oils derived from linseed oil are generally highly viscous and require the use of organic diluents or emulsification in order to lower their viscosity, which further increases the time of cure as the excess solvent needs to be removed from the system. Additionally, this oxidation cure mechanism requires toxic catalysts (e.g., transition metal salts based on cobalt and lead) to accelerate the crosslinking reactions [27-29]. These issues hindered the use of linseed oil and similar highly unsaturated natural oils in the paper coating industries.

Much work has been published on epoxidation of the unsaturated fatty acids where the double bond was converted to reactive epoxides [30-32]. This epoxidized oil could then further be cured with compounds like acrylic acid, isocyanates, etc. Unfortunately, this approach requires multi-steps processes, which in turns increases the cost of the coating materials. Furthermore, curing of these materials is limited by relatively long cure time and high temperatures.

In this work, a low viscosity silylated soybean oil has been used as a paper coating material to provide a moisture barrier coating over Kraft paper. The silylation of soybean oil was accomplished in a single step process [33, 34] resulting in a stable oil when kept in a close container away from atmospheric moisture. Upon exposure to moisture, it quickly cures to yield a good hydrophobic barrier coating. Factors affecting the coating process, the cure reactions to form a barrier network and the properties of the coated papers are described. This non plastic, biobased coating was developed to be used as a waste bag on board ships for collection of food and other bio-wastes that can be discharged into the ocean where the paper and the coating would be completely biodegrade.

3.2 Experimental

3.2.1 Materials

LowSat® soybean oil was kindly provided by Zeeland Farm Services, Inc. (MI, USA). Vinyltrimethoxysilane (VTMS) was purchased from Gelest, Inc. (PA, USA). Luperox-101 and Dibutyltin dilaurate (DBTDL) were purchased from Sigma-Aldrich (MO, USA). Kraft papers with weights of 0.27 kg/m^2 (60 lb/1000 ft^2) and 0.38 kg/m^2 (78 lb/3000 ft^2) were purchased from KapStone Paper and Packaging Corporation (IL, USA). All other chemicals were reagent grade and were used without further purification unless noted.

3.2.2 Silylation of soybean oil

The silylation of LowSat® soybean oil was performed in a 5 gallon high-pressure stainless steel reactor from PARR Instrument Company (IL, USA) as shown schematically in Figure 3.1. In a typical experiment, lowSat® soybean oil (1 mole, 874 grams) and VTMS (3 moles, 444 grams) were premixed with 1 wt. % (87 grams) of Luperox-101 catalyst. Nitrogen gas was purged through the reactor feed port to ensure an inert environment inside the reaction vessel. The silylation reaction was carried out at a constant temperature (250^{o}C) under continuous stirring for 20 hours and the pressure was monitored by a pressure gauge. Since the reaction temperature was higher than the boiling point of VTMS, the pressure continuously decreased as unreacted VTMS was grafted onto the soybean oil. Samples were drawn from the reaction mixture through the sampling port at regular time intervals to determine the extent of the grafting reaction.

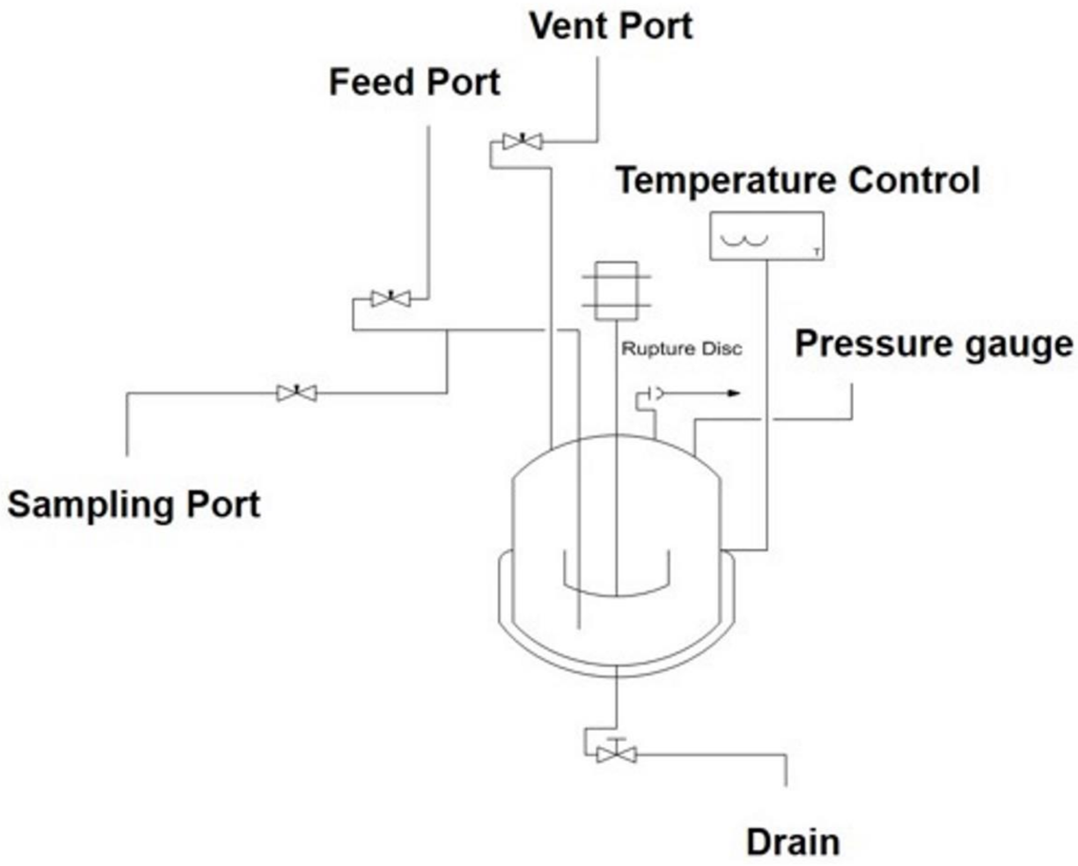

Figure 3.1: Schematic representation of high pressure PARR reactor used for the silylation reaction

The extent of the silylated soybean oil product was measured by Thermogravimetric (TGA) analysis (TA instruments, New Castle, USA; Hi-Res TGA 2950). In a typical experiment, a sample was heated quickly to 130°C (which is above the 123°C boiling point of VTMS) and was held at this temperature for 30 minutes. Under these adiabatic conditions any free (ungrafted) VTMS was removed from the sample and the extent of grafting was calculated from the weight loss using Eq. 3.1.

$$\%\ \text{Grafting} = \frac{\text{wt}\ \%\ \ \text{VTMS in feed} - \text{wt}\ \%\ \text{VTMS ungrafted}}{\text{wt}\ \%\text{VTMS in feed}} \text{X}100 \qquad \text{Eq. 3.1}$$

3.2.3 Network formation

Upon exposing the methoxysilane to moisture, the hydrolytically unstable siloxy bonds (e.g. Si-OCH_3) were hydrolyzed and the resulting silanols (Si-OH) were condensed in the presence of the DBTDL catalyst to form stable siloxane crosslinks (Si-O-Si) as shown in Figure 3.5 [34]. The cure rate of this moisture activated crosslink reactions was studied using different DBTDL catalyst concentrations, temperature and different water content. The cure rate was determined by the change in the viscosity as a function of time using a Brookfield viscometer-LDVE-E model (MA. USA) equipped with Spindle 61. In order to ensure adequate results in these tests, the torque was kept in the range of 10-50%.

3.2.4 Paper coatings

Kraft papers with two different weights (0.27 kg/m^2 and 0.38 kg/m^2) were first coated using a laboratory Roll-Lab Coater (ECS-1211-M1EPDM119) from Euclid Coating Systems (ECS). In a typical experiment, the paper was secured to the ECS roller and the blade pressure was set at 40 psi. Under these conditions the silylated oil was spread evenly across the blade-roller interface to produce an even and complete coverage over the entire surface of the paper. The coated papers were then post-cured in an oven at 80^{o}C for 30 minutes to ensure the crosslink reaction had been completed. The coat weight was calculated by simply subtracting the weight of an uncoated paper of known surface area from the weight of a coated paper.

Large-scale coatings were conducted in a common Gravure coating system. The set up that was used for the gravure roll coatings is illustrated in Figure 3.2. In this process, the paper was thoroughly dried prior to the coating and then rolled over between the two-roll gravure coater from the feed roll. The coating mixture (silylated LowSat® soybean oil, DBTDL catalyst, 3% wt. and water, 3 wt. %) was pumped from the oil bath held at RT and applied to the etched pattern of the rollers by capillary action and then onto the paper as it passed between the nip of the gravure roll and the backup roll. The coated paper was then passed through an oven set at 80^oC to ensure complete cure before it was collected on the receiving roll. The line speed of the paper throughout the coating process was kept constant at 2.7 m/min.

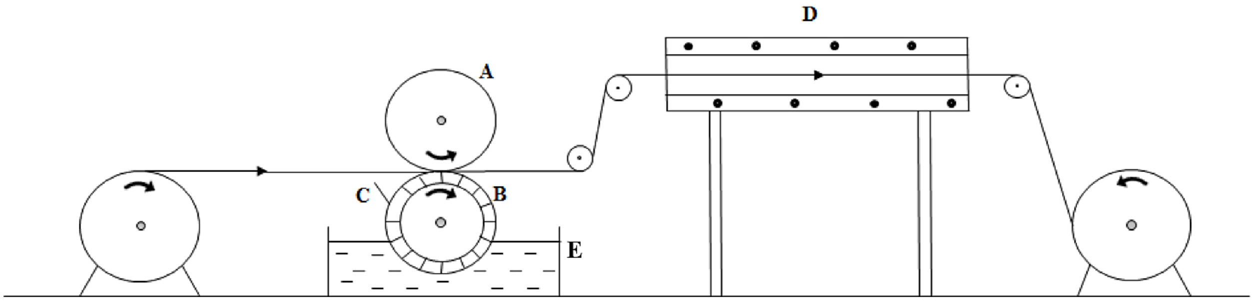

Figure 3.2: Schematic representation of the paper coating process. A: Back-up roll, B: Gravure roll, C: Doctor's blade, D: Oven, E: Silylated soybean oil bath

3.2.5 Characterizations

The Attenuated Total Reflection-Fourier Transform Infrared (ATR-FTIR) spectra were acquired on a Schimadzu IRAffinity-1 spectrometer (Tokyo, Japan) equipped with a single refelction ATR system (PIKE Technologies, MIRacle ATR, Madison, USA). All spectra were acquired between 600 – 4000 cm^{-1} using 32 scans at a resolution of 4 cm^{-1}.

Contact angle measurements were performed using Kruss Contact Angle Equipment (DSA 100, Kruss USA, NC, USA) by placing a drop of 4 μL of water onto the film surface and measuring the contact angle using a static contact angle measurement method. HPLC grade distilled water was used for all measurements. The coated and uncoated paper samples were cut (3cm X 10cm) and glued to a glass slide of the same dimensions. For the uncoated paper samples, the contact angle measurements were somewhat difficult due to water absorption into the paper which caused a continuous decrease in the observed contact angle. For consistency, all measurements were taken within the first 5 seconds where the geometry of the water drop was found to be relatively stable.

Unlike the uncoated paper, the geometry of the water drop on the coated paper was found to be stable for as long as 2 minutes clearly indicating much lower water uptake despite of rough nature of the substrate. The sessile drop method (ASTM D7334) was used to analyze the contact angle.

The water resistance of the coated papers was measured using a 2-minute Cobb test following a standard TAPPI T441 procedure. This test consists of placing a 12.5x12.5 cm square piece of coated paper that was cut randomly from a stack of coated papers on a neoprene mat and clamping it in the Cobb cylinder. Then, 100 mL water was poured over the clamped areas (100 cm^2) and kept in place for 2 minutes. The water was then drained from the paper, any excess water was removed using a 10kg roller and the weight of the paper was measured and compared to the initial dry weight. The Cobb value based on these experiments is defined as the change in the weight (in grams per meter^2) as shown in Eq. 3.2.

$$\text{Cobb value (gsm)} = \frac{\text{final paper weight (g)} - \text{initial paper weight (g)}}{0.01\ \text{m}^2} \qquad \text{Eq. 3.2}$$

The Water Vapor Transmission Rate (WVTR) was determined using a PermtranTM W3/33 analyzer (MOCON, Minneapolis, MN, USA) following ASTM standard F1249-05. For these measurements, pieces of the coated and uncoated Kraft papers were masked on both sides with aluminum foil using an adhesive baking (Mc-Master Carr, Aurora, Ohio, USA) leaving a well-defined test area of 3.14 cm^2. The thicknesses of these paper samples was measured using a micrometer (Dial Thickness gauge 7301, Mitutoyo, Tokyo, Japan) with a 0.001 mm accuracy. The average thickness for the uncoated papers was 0.096 mm and 0.099 mm for the coated papers. For all WVTR measurements, the temperature was maintained at 27±3°C and relative humidity of 37% using humidity probes. Three replicates were carried out for each type of paper.

Scanning electron microscopy (SEM, Japan Electron Optics Laboratories, Japan, JEOL-6400V) was used to study the surface morphology of the coated and compare it with the uncoated papers. Each sample was first coated with gold using a gold sputter coating device to enhance the details. The samples were observed under different magnifications from 20µm to 200µm.

3.3 Results and Discussion

LowSat® soybean oil was chosen for the grafting reaction since the lower saturated content ensures that a coating prepared from it will contain no unreacted triglycerides. Regular soybean oil contains an average of 4.5 double bonds on the fatty acids chains per triglyceride, whereby, LowSat® soybean oil contains an average of 5.1 double bonds per triglyceride. The higher degree of unsaturation ensures that there are essentially no triglycerides that are composed of only saturated fatty acids as these saturated fatty acid triglycerides cannot be silylated. Thus, they will not participate in the network and will remain as free oil in the coating negatively impacting the surface properties of the coating. Specifically, LowSat® soybean oil contains 75.5% oleic acid (a single double bond), 35% linolenic acid (3 double bonds), 15% linoleic acid (2 double bonds), 3% palmitic acid and 3% stearic acid (no double bonds). Statistically, there is a negligible concentration of triglycerides composed of 3 saturated fatty acids [34].

The cure mechanism and network formation in this system follow the typical cure of silanes that have been used extensively in inks, paints and adhesives containing silanes [35-37]. In these systems the crosslink network is obtained when the hydrolytically unstable siloxy groups (Si-O-C) in the alkoxysilanes are hydrolyzed upon exposure to moisture and yield silanols (Si-OH). In the presence of appropriate condensation catalysts these silanols further condense to yield stable siloxane bonds (Si-O-Si). Provided multiple silanols are available, a stable covalent network is formed.

3.3.1 Silylation

Since hydrosilylation is only suitable for silylation of terminal double bonds, the preferred approach to graft a silane onto non-terminal double bonds of the unsaturated fatty acids in the soybean oil is via the 'Ene reaction' (Figure 3.3). The general synthetic and mechanistic aspects of this reaction with respect to olefins have been reviewed elsewhere [38-40] and a feasibility study dealing with grafting of VTMS onto soybean oil is available [34].

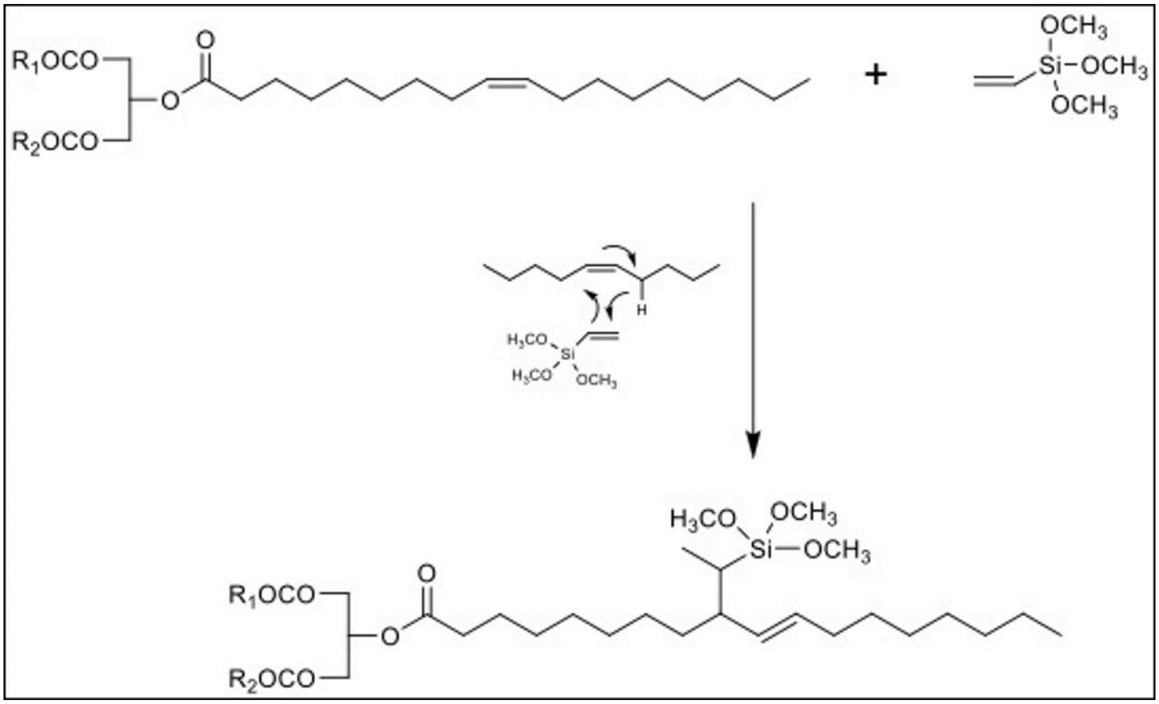

Figure 3.3: Silylation of unsaturated fatty acids of soybean oil

In this system, the 'Ene reaction' proceeds smoothly due to the fact that vinylsilanes do not undergo thermal polymerization like common vinyl monomers such as styrene, acrylates and similar vinyl monomers [41, 42]. Indeed, no apparent oligomerization of the oil was observed under the reaction conditions and the viscosity of the silylated soybean oil remained very low (32 cPs). The low viscosity of the oil was found to be extremely useful as it required no diluent and could be used directly in the coating process.

The yield of the silylation reaction was calculated by Eq. 3.1 from the weight loss in the isothermal TGA analyses. It was observed that the extent of grafting was directly proportional to the reaction time as shown in Figure 3.4 and the kinetics of this reaction was found to follow a second order reaction rate [34]. It is important to point out that there is no need to remove the small fraction of unreacted VTMS from the silylated oil product as these free silanes are miscible in the oil and will be hydrolyzed and condense with the grafted VTMS fraction to be an integral part of the crosslinked network.

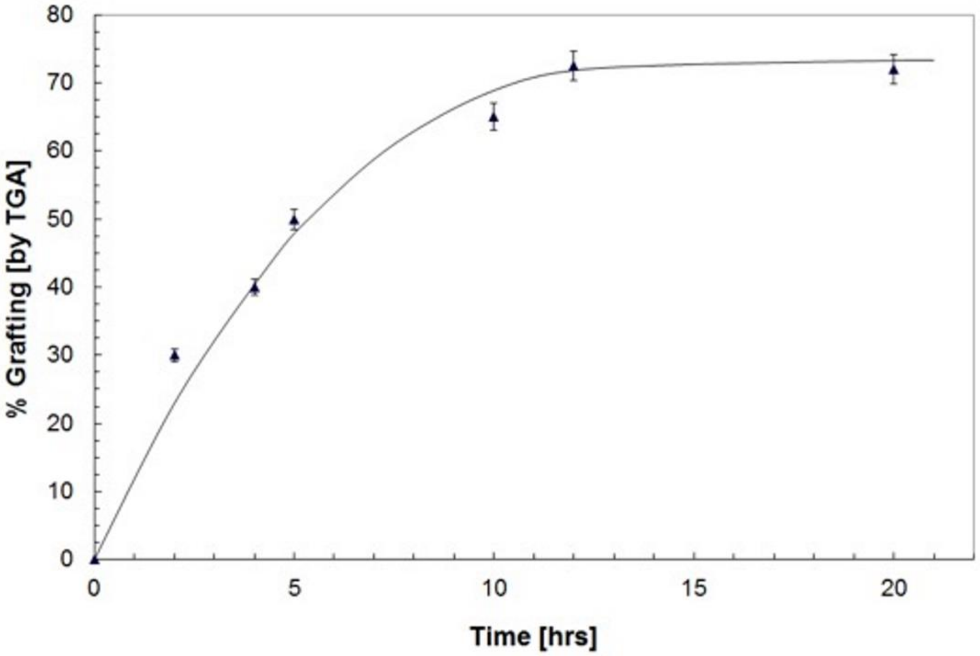

Figure 3.4: Extent of grafting onto LowSat® soybean oil as a function of time at 250^{o}C

No change in the viscosity of the silylated soybean oil was observed (avg. 40 cPs) upon storage in a closed container over a period of 8 months indicating good stability of the oil. However, it should be emphasized, that during storage the silylated soy oil must be kept under an inert atmosphere away from moisture as the presence of moist atmosphere over the oil surface in a close container will lead to a formation of a crusty surface layer in contact with the moist air.

3.3.2 Moisture cure

One-component, moisture activated cure of silicones is well known [35-37, 43] and combines several advantages over other cure systems. The general network formation when the silylated oil is exposed to moisture is shown in Figure 3.5. The methoxy groups on vinylsilanes are easily hydrolyzed initially and, in the presence of a condensation catalyst, condense to form a cured network crosslinked with stable Si-O-Si linkages.

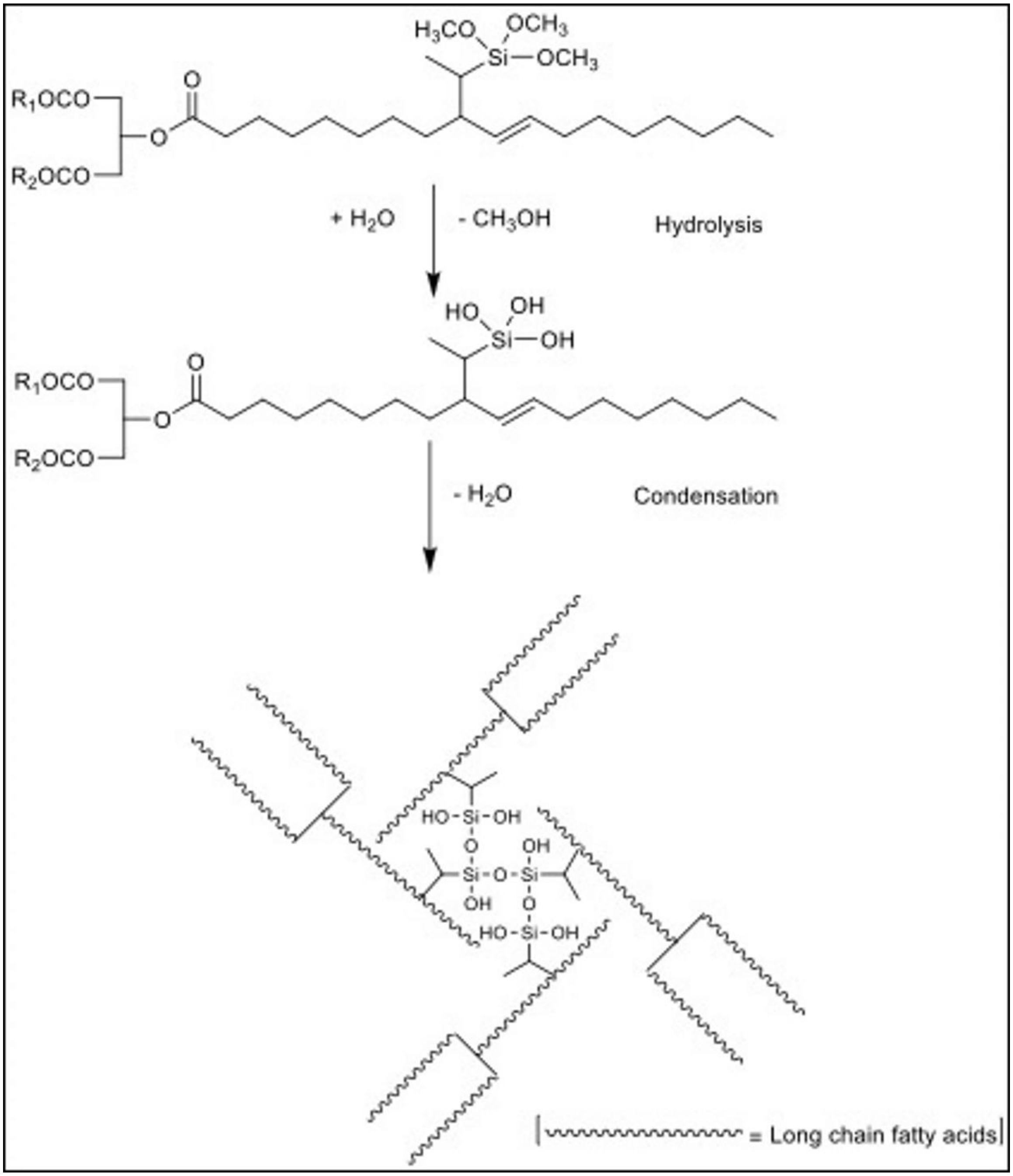

Figure 3.5: Network formation by hydrolysis and condensation of alkoxysilanes to siloxane crosslinks

After applying the oil onto the surface of the paper, the cure process was controlled by adjusting the concentration of the catalyst, the moisture content and the temperature. In this study the catalyst concentration was varied from 1 wt. % to 4 wt. %, along with varying moisture content from 2 wt. % to 4 wt. %. Under these conditions high rates of cure were observed at temperatures above 80°C.The crosslinking reaction was followed by the change in the viscosity of the oil over time (Figure 3.6).

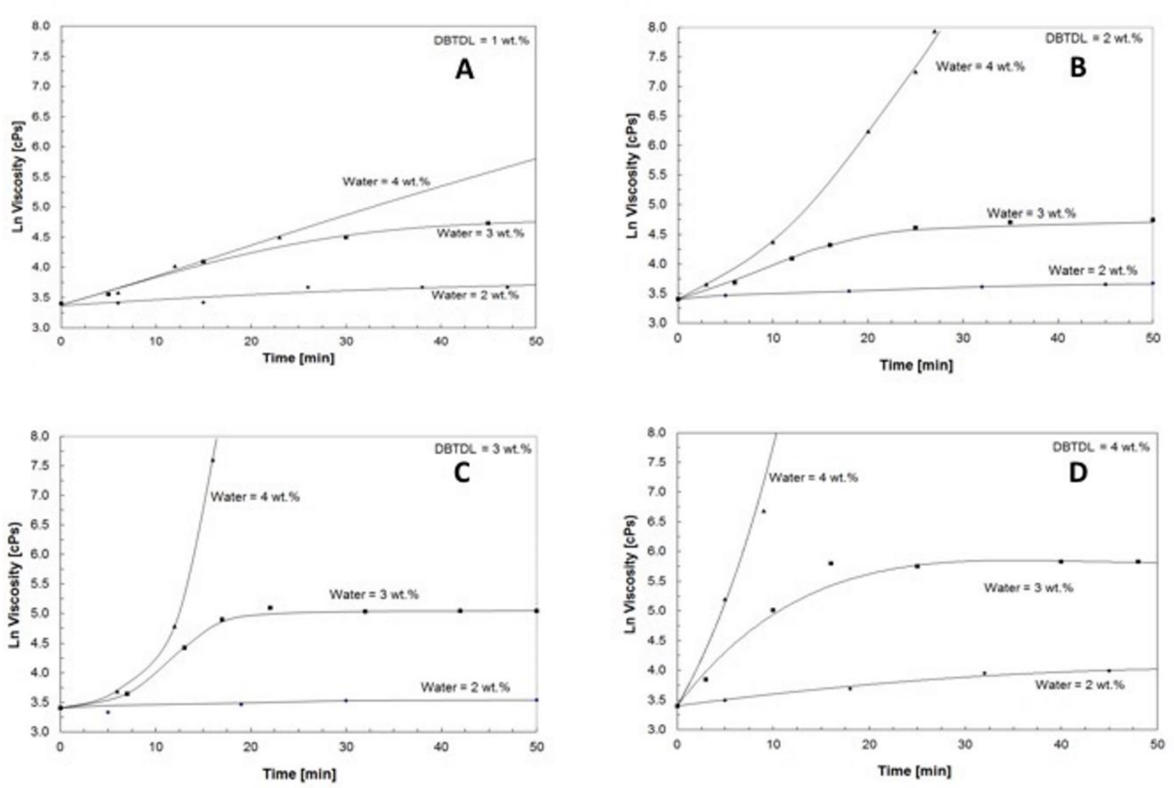

Figure 3.6: Effect of water on the viscosity of silylated LowSat® soybean oil at different concentration of DBTDL catalyst [A= 1wt. %; B= 2wt. %; C= 3wt. %; D= 4wt. %]

It was observed that the rate of cure was directly proportional to the concentration of the catalyst and the water content. Yet, it is important to note that when the water content was less than 3 wt. %, only partial hydrolysis was attained and the initial viscosity of the reaction mixture increased slightly but then remained almost constant over a long period of time. This partial hydrolysis and condensation allowed us to control the initial viscosity of the oil to be sufficiently high so it remained on the surface of the paper with minimum soaking into the interior of the paper yet, it was not too high to interfere with the coating process and the coating equipment.

3.3.3 Paper coatings

The silylated soybean oil was coated on the paper, allowed to cure and the water barrier of the cured coating was examined. Two types of paper (Kraft #60 and Kraft#78) were coated using a Single Roll Laboratory Coater. The silylated oil bath contained 3 wt. % DBTDL and 3 wt. % water. Under these conditions the viscosity of the oil bath increased to 120 cPs and remained constant throughout the coating process. The coatings were cured in a short period of time when the papers were exposed to atmospheric moisture and post cured at 80^{o}C in an oven. Close examination of the cured coated surface indicated that the coatings appeared to be very uniform with good adhesion to the cellulose fibers and with no apparent defects or run-offs.

Successful coatings using the Single Roll Lab Coater allowed us to evaluate the process on a larger scale Gravure coating system as shown schematically in Figure 3.2. The line speed and the oven temperature were adjusted to ensure a uniform coating and a complete cure to prevent the paper to stick on the collecting roll.

ATR FTIR scans of the coated and uncoated surfaces of the paper were run as preliminary tests to identify the success of the coating (Figure 3.7). It is apparent that the spectra of two surfaces appear very similar and is dominated by the broad absorption at 3300 cm^{-1} related to O-H stretching vibration and the strong absorption at 1025 cm^{-1}. Unfortunately, it is not possible to determine if the O-H stretching vibration is related to the hydroxyl groups of the carbohydrates or the silanol groups obtained from the hydrolysis of the methoxy groups of the silane. Similarly, it is not possible to determine if the strong absorption peak at 1025 cm^{-1} is related to C-O stretching vibration of the cellulose fibers in the paper or the siloxane linkages (Si-O-Si) crosslinks. However, by subtracting the uncoated paper spectrum (A) from the coated spectrum (B) one can clearly observe the spectrum of the actual coating material. In Figure 3.7, Spectrum (C) is the result of the subtraction of uncoated paper spectrum (A) from the coated paper spectrum (B). Both, the subtraction spectrum (C) and spectrum (D) of neat cured silylated soy oil, are identical and clearly show the characteristics carbonyl (C=O) stretching vibration of the triglycerides at 1735 cm^{-1} confirming the presence of silylated soy oil coating on the coated substrate.

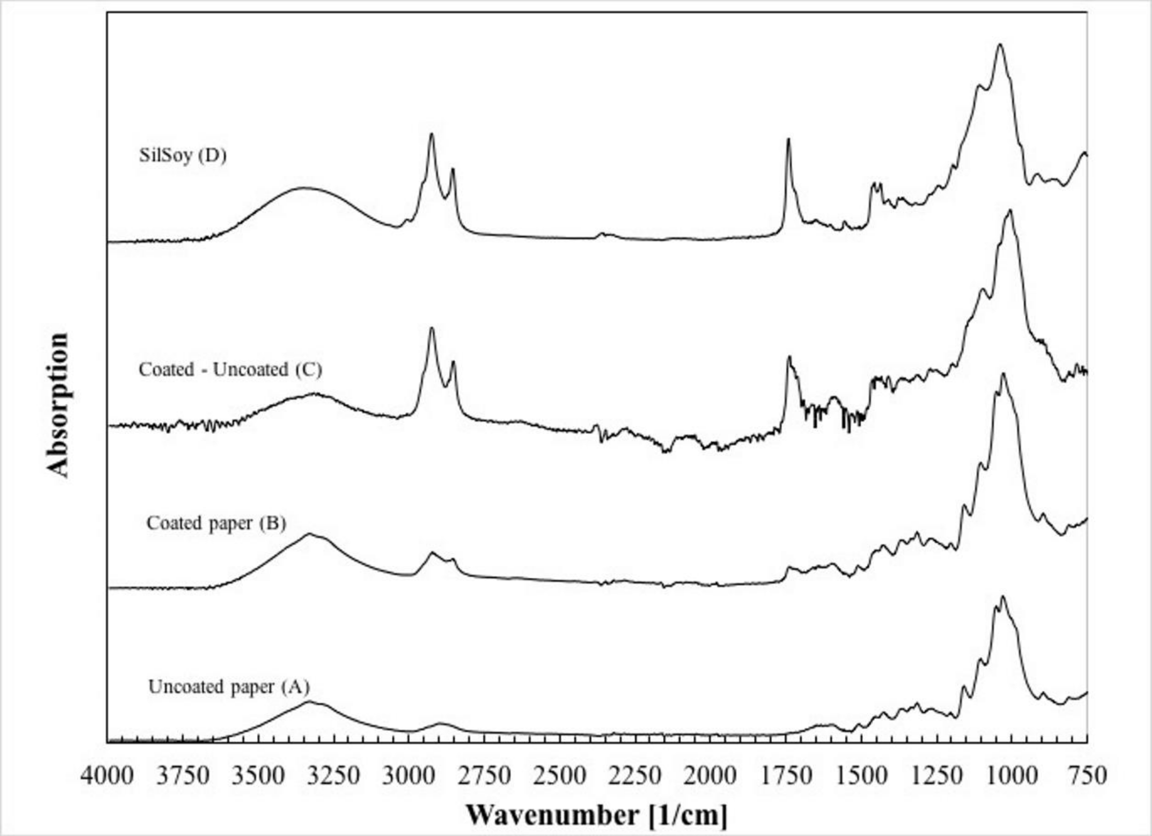

Figure 3.7: ATR-FTIR spectra of coated and uncoated Kraft papers [A]: Uncoated paper, [B]: Coated paper, [C]: Coated – Uncoated, [D]: Silylated soybean oil

Comparing the FTIR spectrum of the silylated oil (Figure 3.8A) to the spectrum of the cured oil (Figure 3.8B) clearly indicates that all the silanols were condensed and the broad absorption peak around 3300 cm^{-1} has disappeared. Furthermore, the characteristic absorption of the methoxy functional groups at 1100 cm^{-1} that arises from the CH_3-O stretching vibration and the Si-O-CH_3 vibration between 750 cm^{-1} and 850 cm^{-1} have also disappeared as these methoxy silanes were reacted to yield the siloxane linkages of the cured product[44].

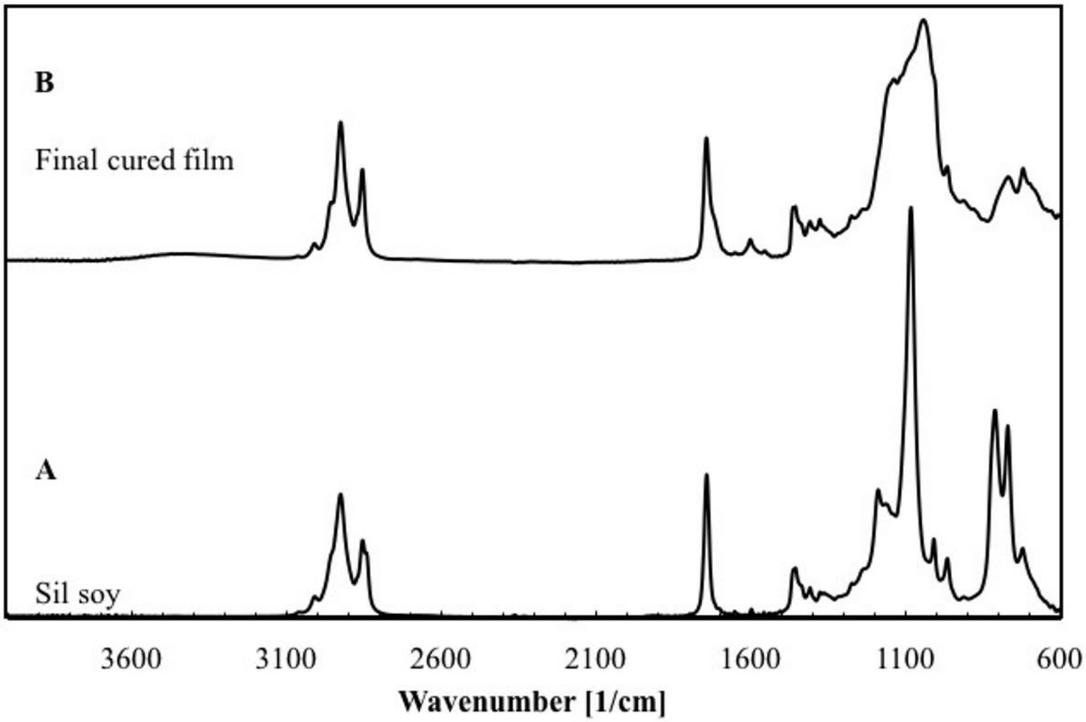

Figure 3.8: FTIR spectra of [A]: Silylated soybean oil and [B]: final cured film

The Cobb values of these coated papers were determined (Table 3.1) and the results clearly demonstrate a significant decrease in the moisture absorption of the coated papers compared with the original, uncoated papers. It is apparent that small but statistically significant differences are observed in the Cobb values between the coatings prepared using the Single Roll Lab Coater and the coatings prepared using Gravure roll coater. We believe that these small differences are simply due to the difference in the operational conditions. The higher coat weight in the papers prepared in the Single-Roll Lab Coater undoubtedly contributed to the higher moisture resistance of the coated paper.

Table 3.1: Cobb values for different papers

	Lab coatings		**Gravure roll coatings**	
	Kraft# 60	Kraft# 78	Kraft# 60	Kraft# 78
Coat weight (g/m^2)	10.45	10.82	10.02	10.11
Cobb value- uncoated (g/m^2)	40.63±0.29	40.78±0.34	40.63±0.28	40.78±0.29
Cobb value-coated (g/m^2)	22.24±0.45	23.47±0.46	25.81±0.52	26.43±0.31
Reduction in Cobb value (%)	45.3	42.4	36.5	35.2

Not surprising is the inverse correlation between the Cobb values and the contact angle of the coating independent of the type of paper used (Figure 3.9). The contact angle of the uncoated Kraft papers is characterized by a typical hydrophilic contact angle of cellulose (75-80°). The relatively large variance in the contact angles here are most likely related to the surface characteristics of the uncoated Kraft papers, namely, the surface smoothness and homogeneity. The contact angles were significantly higher after coating for both papers (greater than 100°) as the silylated oil was embedded in the cellulose fibers and partly filled the paper pores resulting in a more hydrophobic character of these papers.

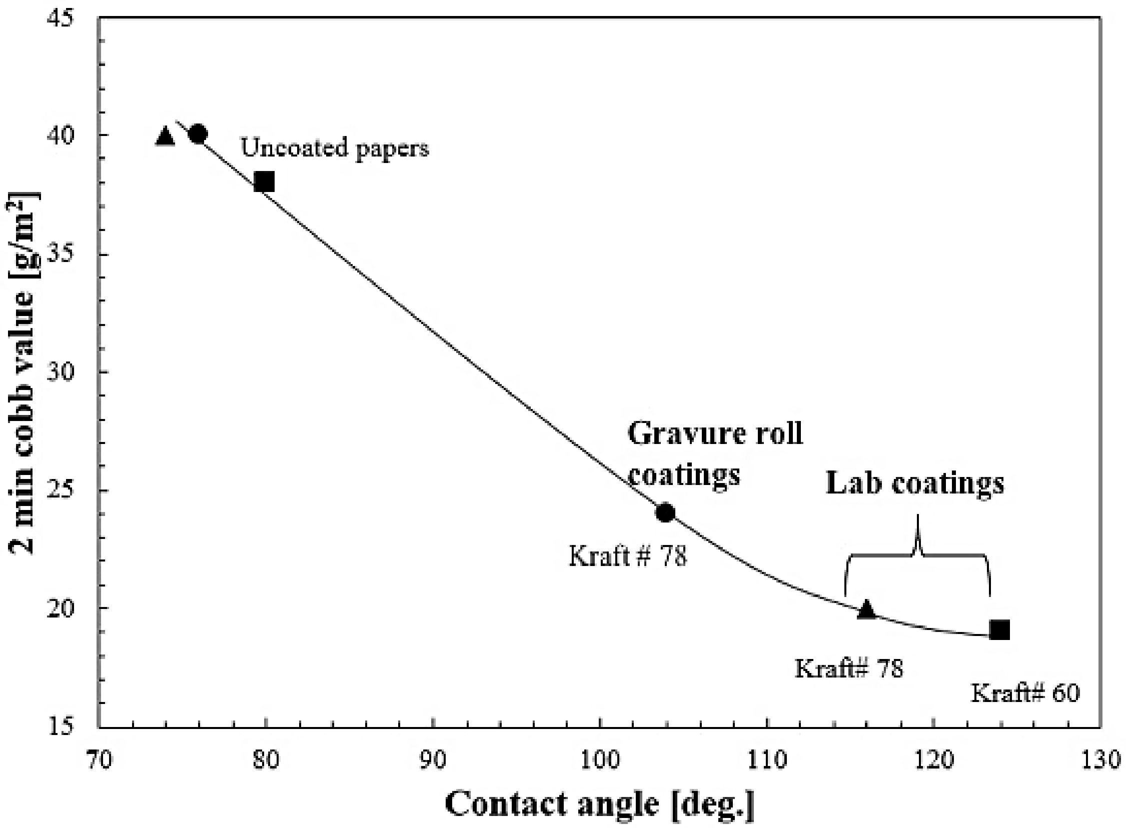

Figure 3.9: The 2 min Cobb values as a function of contact angle for different papers

The WVTR of the silylated soybean oil cured coated papers showed that the coating led to a significant decrease of the paper moisture transfer. The transfer reduction for the Kraft paper #60 was reduced by 47.7% and the WVTR for the Kraft paper #78 was reduced by about 53.1% (Figure 3.10). Undoubtedly, this reduction in moisture transfer is due to the fact that many of the paper pores are filled by the cured oil. Consequently, water molecules can only cross the bulk paper by a lengthy and obstructed path which could explain the decrease of moisture transfer rates. Since the water penetration and absorption into the paper is largely depended on the homogeneity and internal structure of the coating, it is apparent that the silylated oil coatings still have an open structure. However, the improved water repellency here represents an intrinsic barrier property which can further be enhanced by thicker coatings.

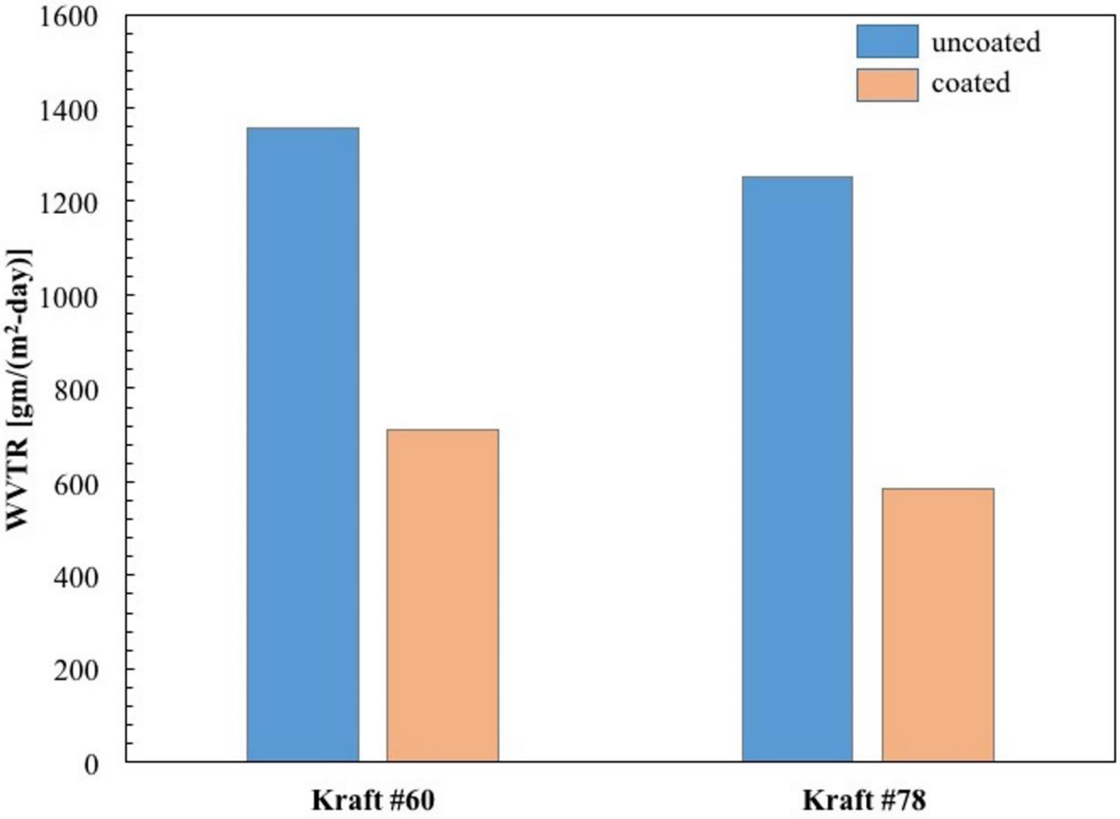

Figure 3.10: Water Vapor Transmission Rate (WVTR) for coated and uncoated papers [Kraft #60 and Kraft#78]

The surface of the papers after coating was examined by SEM and compared to the uncoated surface. It is apparent from the SEM micrographs (Figure 3.11) that the coating appears uniform with no evidence of holes or other imperfection and provided a complete coverage of the individual fibers with no apparent separation of the coating material from the paper fibers. Furthermore, the coating partially penetrated the paper web and wrapped around the individual cellulose fiber bundles.

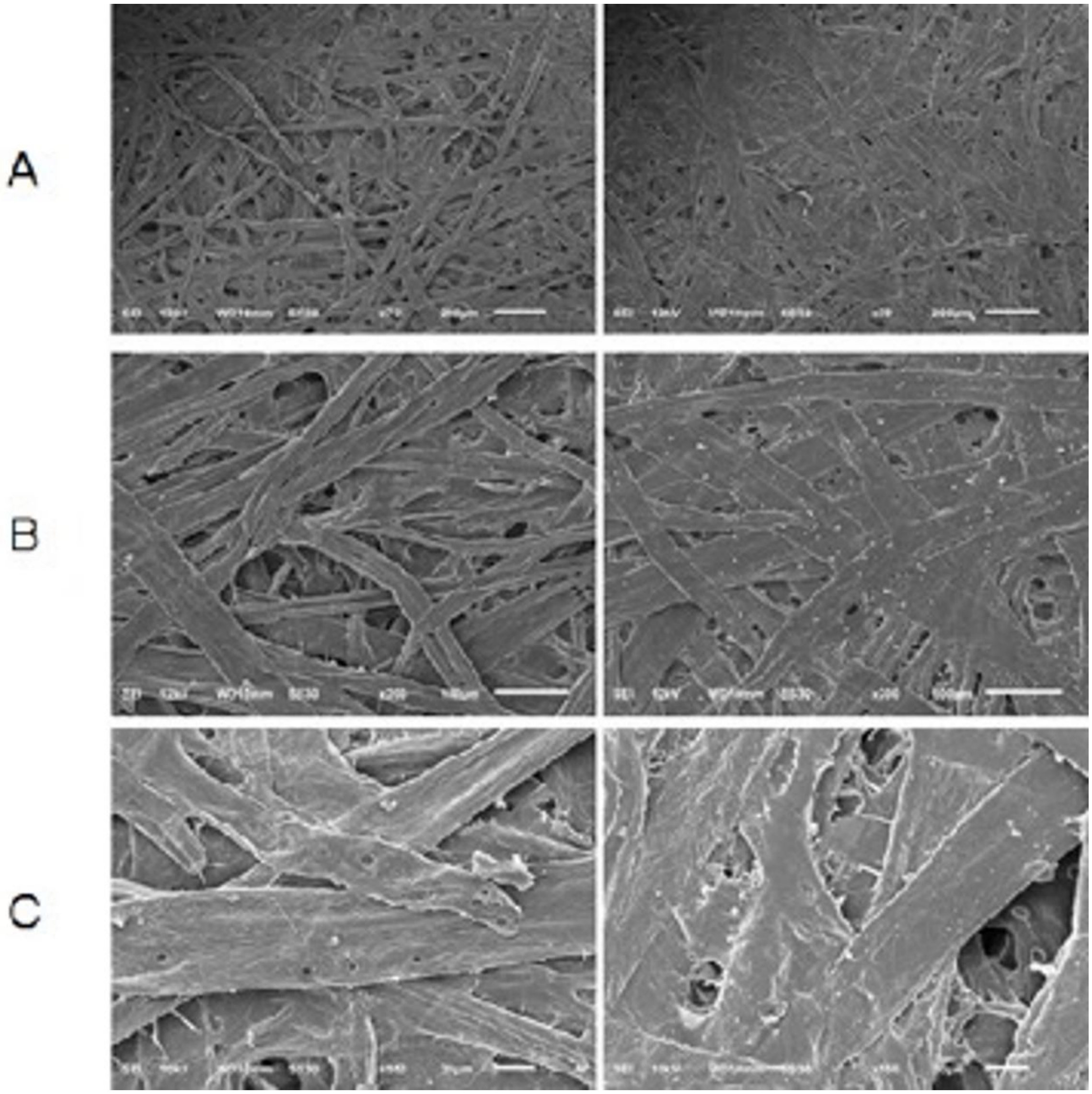

Figure 3.11: SEM of the surface of uncoated paper (left) and coated paper (right) at different magnifications [A]: x70, [B]: x200, [C]: x550

Typical film formation mechanism of aqueous dispersions or polymeric solutions generally consists of evaporation of the water (or the solvent) and consequent deformation of the film. This volume shrinkage can result in local stress concentration and often leads to undesirable cracks in the film coating. However, the relatively low viscosity of the silylated soybean oil allowed it to be used directly in the coating process. Thus, the only change in the volume of the coating material is the small loss of alcohol in the cure process resulting in a smooth crack-free crosslinked coating.

3.4 Conclusions

Moisture activated cure of silylated soybean oil was successfully prepared and used to enhance the moisture barrier of Kraft #60 and Kraft#78 papers. The cure rate of the silylated oil was directly proportional to the concentration of catalyst (DBTDL) and the water content. The coated Kraft papers showed a significant decrease in the Cobb values, indicating that these coating provide a good moisture barrier to the paper. SEM images show a complete coverage of the cellulose fibers of the paper with no apparent defects.

3.5 Acknowledgments

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4. REACTIVE BLENDS DERIVED FROM MODIFIED SOYBEAN OIL AND SILICONE

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4.0 Abstract

Reactive blends prepared from methoxysilane terminated silicone polymers and silylated soybean oil are described and characterized. Although simple mixing of soy and silicones results in gross phase separation, homogeneous polymeric products are obtained by introducing reactive sites. These products can be used as protective coatings, additives to adhesives and new sealants. Exposure of the mixtures to moisture leads to hydrolysis of the methoxysilanes and subsequent condensation of the resulting silanols that yields stable siloxane linkages between the two immiscible phases. FT-IR, TGA and swell-gel analyses indicate effective formation of these siloxane crosslinks. Reactive blends containing less than 20% silylated oil appeared completely transparent but increasing the soy content decreased the optical transparency. SEM micrographs reveal the silicone polymer as the continuous phase with individual spherical silylated soy oil particles distributed in it. The properties of these reactive blends vary from high elongation elastomers to high modulus resins depending on the composition.

4.1 Introduction

Most polymers are immiscible and simple blending usually results in gross phase separation which leads to unstable morphologies and poor mechanical properties. Thus, various compatibilization techniques have been used[1] and the resulting compatibilized blends were found to offer a new set of properties and such homogeneous blends can offer attractive opportunities for developing new materials with useful properties.

Preformed graft or block copolymers have been traditionally used as compatibilizers. Unfortunately, such block or graft copolymers are not viable economically. Alternatively, it is possible to use reactive functional groups compatibilizers “in-situ" during blending to enhance the miscibility of the various blends components and prevent gross phase separation. This strategy is usually cheaper and less time-consuming than the development of new monomers and/or new polymerization routes to achieve desirable polymeric properties. An additional advantage is the possibility to obtain a wide range of material properties simply by changing the blend composition.

Compatibilized blends are characterized by the presence of a finely dispersed phase, good adhesion between the phases, strong resistance to phase coalescence, and properties that are different than the properties of either components [2]. Good adhesion between the phases and proper control of the blend morphology are the key issues required to achieve good properties. Various chemical reactions have been used in the past to prepare reactive blends including amidation, imidation, esterification, aminolysis, ester-ester interchange, amide-ester exchange, ring-opening reactions, concerted ene addition, reactive isocyanates and carbodiimide groups as well as simple substitution between amine and halide or hydroxyl [3, 4]. Although many different reactions are possible, it was noted that the reactants must have sufficiently reactive functional groups and the reaction should be relatively fast, selective and irreversible. In principle, there are two types of reactive blends; when the functional reactive groups are attached to the chain-ends, in-situ block copolymers are produced. Alternatively, if the reactive functional groups are grafted along the polymer chain, branching, crosslinked and interpenetrating polymer networks are obtained. It should be noted that in the latter case crosslinking of the same phase can also occur in addition to crosslinking between phases.

Although there are numerous reactive blends derived from commodity and engineering thermoplastics[1], there are fewer examples in the literature dealing with reactive biobased polymer blends[5]. It was noted that blends of brittle biopolymers with synthetic elastomers yield materials with useful and improved properties. Examples include improvement of the impact resistance of poly(lactic acid) by blending it with polyurethane[6] or natural rubber (NR)[7] and increasing the toughness of polyhydroxyalkanoate blended with poly(lactic acid)[8], or poly(ε-caprolactone)[9].

Blends containing silicone polymers can have distinct advantages due to their siloxane (Si–O–Si) backbone which is known to yield flexible polymer chain, high bond energy, low Tg, high thermal and oxidation stability, insensitivity to UV light and ozone, waterproof properties, high impact resistance, good electrical insulation, resilience, high oxygen permeability, biocompatibility and low surface energy. However, it is this unique, partially inorganic structure and the low intermolecular interaction (when dimethylsiloxane polymers are used) that also make silicone polymers incompatible with most other macromolecules.

Examples of reactive blends containing polydimethylsiloxanes (PDMS) include blends of low density polyethylene (LDPE) and vinyl-containing PDMS which was cured by free radical initiation[10] where the mechanical properties varied with the extent of the crosslinking and the PDMS content. Another example is blends of PDMS with ethylene propylene diene monomer (EPDM) rubber. In this case the compatibility was increased by reactive[11] functional groups grafted onto the two polymers. Thus, the PDMS was grafted with polyacrylamide via a radical polymerization of acrylamide initiated from the PDMS backbone and the EPDM was first sulfonated and then modified with maleic anhydride (MA-g-EPDM). The blends were characterized by high tensile strength, low elongation at break and much better retention of the properties upon ageing as well as better thermal stability than EPDM.

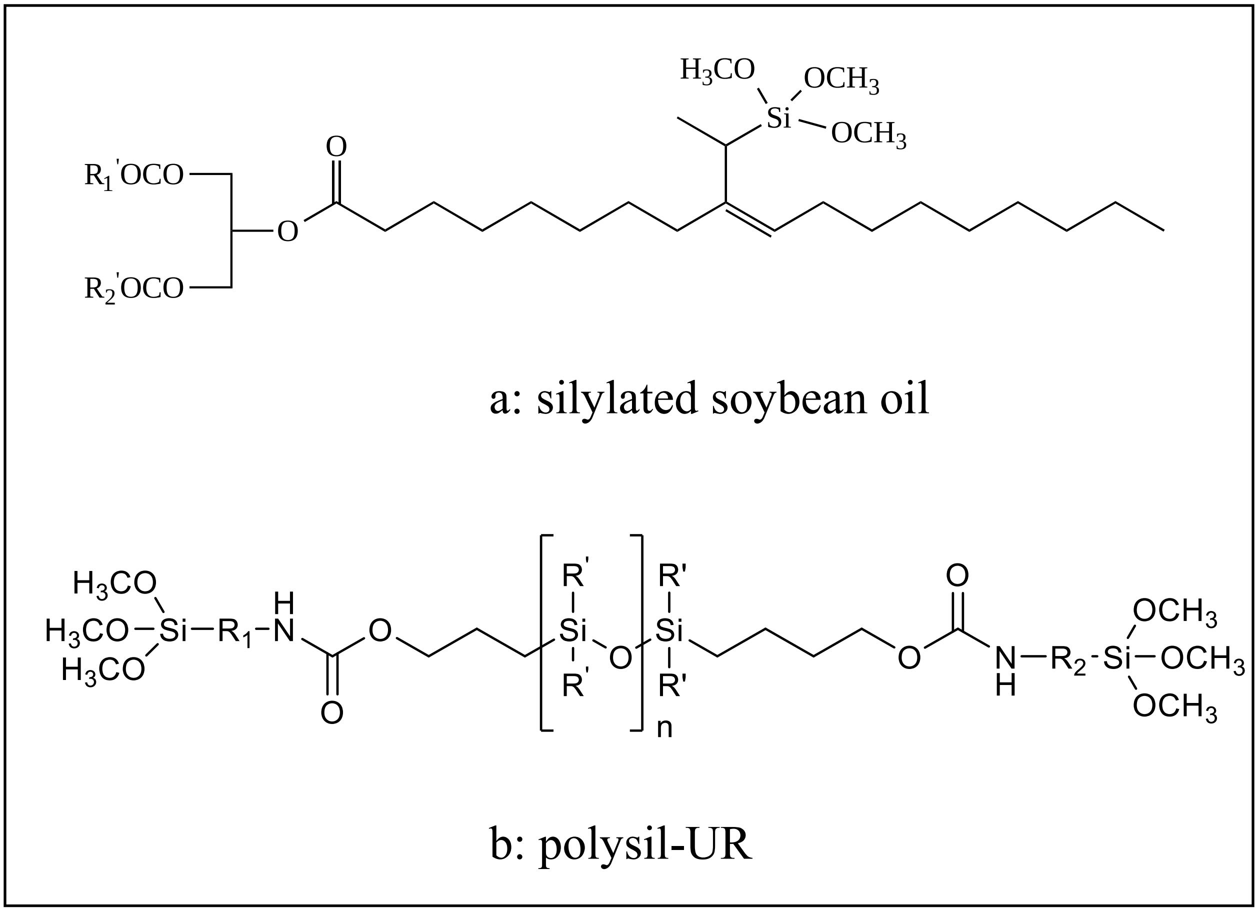
Blends containing vegetable oils have also been investigated and reported in the literature[12]. These oleochemicals are attractive due to their inherent biodegradability, relatively low cost, local availability, desirable environmental and societal acceptability. Here, the triglycerides are initially chemically modified via either epoxidation, metathesis of double bonds, acrylation of epoxies, reaction with maleic anhydride, ozonation or transesterification. Currently, epoxidation of soybean oil is the most common route to introduce reactive groups onto the triglycerides that can then be used in reactive blends[13]. Reactive blends of epoxidized soybean oil (EBSO) with diglycidyl ether of bisphenol-A (DGEBA) using BPH (N-benzylpyrazinium hexafluoroantimonate) as thermally latent initiator were investigated[14] and were found to greatly increase the impact and adhesive strength when 60 wt. % of the EBSO were blended into the epoxy system. Similarly, the mechanical properties and morphology of blends derived from ESO and modified DGEBA that were cured with triethylene tetramine (TETA) hardener were examined[15]. It was found that the blends displayed two distinct Tg values with greatly improved impact. Reactive blends of EBSO and phenolic resin were also investigated and the experimental results showed that the flexural strength and the toughness of the blends that were cured with tertiary amine were superior to other modified phenolic resins.

In this study we wish to report on reactive blends derived from methoxysilane terminated linear urethane containing polysiloxane and silylated soybean oil. Unlike previous reactive blends this series of blends were prepared by silanol condensation reactions that yielded stable siloxane linkages which prevented gross phase separation and resulted in optically clear compositions. The properties of these blends varied from high elongation elastomers to high modulus resins depending on the composition.

4.2 Experimental

4.2.1 Materials

The silylated soybean oil used in this study (Figure 4.1a) was prepared in our lab with the procedure explained in our earlier publication[16]. Briefly, soybean oil, which is composed of triglycerides containing palmitic, stearic, oleic, linoleic and linolenic acids with an average molecular weight of about 900 kg/kmol (1 mole) and vinyltrimethoxysilane (2 moles) were reacted at 250 ^{o}C, in the presence of free radical catalyst. The silylated soybean oil obtained contained about 1 mole of trimethoxysilyl group per triglyceride. The urethane containing polysiloxane (Polysil-UR) is a linear polysiloxane containing urethane linkages and terminal methoxy groups (Figure 4.1b). It is a moderately high molecular weight polysiloxane with a viscosity of 35 Pa-s. Polysil-UR was obtained from Momentive Performance Materials Inc. (Waterford, NY) and contained urethane linkages. Dibutyltin dilaurate (DBTDL) was purchased from Sigma-Aldrich (MO, USA) and was used as a silanol condensation catalyst. All chemicals were reagent grade and were used without further purification unless noted.



a: silylated soybean oil

b: polysil-UR

Figure 4.1: Structure of a: Silylated soybean oil and b: Urethane containing polysiloxane, where $R_1^{'}$, $R_2^{'}$ = long chain fatty acids (mainly steric, palmitic, oleic, linoleic and linolenic), $R^{'}$ = $-CH_3$, and R_1, R_2 = $-(CH_3)_x$

4.2.2 Typical sample preparation

Samples with varying compositions of silylated soybean oil, polysil-UR polymer and DBTDL catalyst were prepared as listed in Table 4.1. All components were mixed together in measuring cups, stirred vigorously for 2-3 minutes and then poured onto a polyethylene petri-dish. The samples were then allowed to crosslink over a period of 24 hours at room temperature before testing. The cure via silanol condensation followed a conventional moisture activated cure where the atmospheric moisture leads to hydrolysis of the methoxy groups and the resulting silanols condense to yield stable siloxane bonds.

Table 4.1: Blend compositions

Sample	**silylated soybean oil [wt%]**	**polysil-UR polymer [wt%]**	**DBTDL catalyst [wt%]**	**Appearance**
A	0	100	5	Clear, Transparent
B	20	80	5	Clear, Transparent
C	40	60	5	Clear, Transparent
D	60	40	5	Clear, Transparent
E	80	20	5	Hazy, Brittle

4.2.3 Optical absorption

The transparency of cast films (average thickness of 1 mm) was measured by a Lambda 25 UV/Visible spectrophotometer from PerkinElmer (Wellesley, MA). Each film was scanned three times for different wavelengths in the region of the visible spectra range (400 to 700 nm).

4.2.4 FT-IR analysis

The Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FT-IR) spectra were acquired on a Shimadzu IRAffinity-1 spectrometer (Tokyo, Japan) equipped with a single reflection ATR system (PIKE Technologies, MIRacle ATR, Madison, USA). All spectra were acquired between 600 – 4000 cm^{-1} using 32 scans at a resolution of 4 cm^{-1}.

4.2.5 TGA analysis

Thermogravimetric analysis (TGA) from TA instruments (Hi-Res TGA model 2950, New Castle, USA) was used to determine the evolution of methanol during the crosslinking reaction as well as to determine the overall volatile content of the mixture. The evolution of methanol was simply recorded by heating the sample isothermally at 70 ^{o}C (above the boiling point of methanol) for 50 minutes. The weight loss data of methanol were used to calculate the relative rate of cure at different compositions. TGA was also used to determine the thermal stability of the samples and in this set of experiments, the samples were heated from 30 °C to 550 °C at 10 °C per minute.

4.2.6 Gel-Swell analysis

Gel-Swell analysis was performed using toluene as a solvent following ASTM 2765 standard procedure as devised for ethylene polymers. Predetermined amounts of solvents were secured in the pouches made from wire mesh (3”x3”). All samples were allowed to equilibrate in the solvent for 5 days. Then, the samples were allowed to dry for 6 hours at room temperature. The gel fraction and swell ratio were determined from the initial weight, swollen weight and the final dried weight of the sample using Eq. 4.1 and Eq. 4.2:

$$Gel\ Content\ [\%] = \frac{W_f}{W_i}\ X\ 100 \qquad \text{Eq. 4.1}$$

$$Swell\ Content\ [\%] = \frac{W_i - W_f}{W_f} X\ 100 \qquad \text{Eq. 4.2}$$

where,

W_f= final weight of film sample after drying (gms)

W_i= initial weight of film samples (gms)

4.2.7 Morphology

Scanning electron microscopy (SEM, Japan Electron Optics Laboratories, Japan, JEOL-6400V) was used to study the surface morphology of films with different compositions. Each sample was stained with 1% w/v OsO_4 solution for 24 hours. These stained samples were observed at different magnifications using back scattered mode and a secondary scattered beam.

4.2.8 Mechanical properties

The mechanical properties were measured at RT using a Universal Testing Machine (United Calibration Corp. and United Testing Systems Inc., USA, SFM-20) according to ASTM D882. The tensile tests were performed at a strain rate of 0.0254 m/min (1 inch/min) and in all cases at least three specimens of each sample were tested and the average value was recorded.

4.3 Results and Discussion

4.3.1 Formation of miscible blends

The solubility parameter of soybean oil was determined by inverse gas chromatography and was found to be 16,152 $J^{1/2}/m^{3/2}$ at 58.7 ^{o}C[17]. This value is lower than computed value using structural group contribution method[18] that was calculated to be 18,212 $J^{1/2}/m^{3/2}$. The difference in these values was explained to be due to the higher cohesional energy density of soybean oil. The solubility parameter of the urethane containing PDMS is not known but is estimated to be close to 14,921 $J^{1/2}/m^{3/2}$, which is the solubility parameter of PDMS[19]. The difference in these solubility parameters is relatively small but sufficient to cause simple blends to be immiscible by direct mixing of soybean oil and the Polysil-UR polymer. Indeed, it was observed that when the blends contain more than 50 wt. % soy, gross phase separation occurs and two distinct phases are observed.

It is well established that preventing phase separation during blend processing of immiscible blends is a function of a complex relationship between the viscosity of the phases, interfacial characteristics, the blend composition and processing parameters. Poor mechanical properties and gross phase separation are usually obtained due to incompatibility and poor interactions between the different phases in the blend. Thus, for our silylated soybean oil – polysil-UR polymer blends, we ensured high degree of interactions by grafting alkoxysilanes onto the unsaturated fatty acids of the triglycerides[16] that are similar to the alkoxy groups on the terminal position of the polysil-UR. Upon hydrolysis the resulting silanols condense to form stable siloxane linkages (Figure 4.2). The network that is formed via these condensation reactions is the result of silanol group condensation on the triglycerides oil with other triglyceride silanols (A-A in Figure 4.2), condensation of terminal silanol groups in the polysil-UR polymer molecules (B-B in Figure 4.2) and silanol condensation between the soy oil phase and the polysil-UR polymer phase (A-B in Figure 4.2). Obviously, the condensation reactions between the soybean oil and the polysil-UR polymer phase, are essential to prevent gross phase separation and stable, uniform morphology. Furthermore, due to the relatively low molecular weight of the soy oil and the high grafting content where vinyltrimethoxysilane is grafted to one fatty acid in each triglyceride, silanol condensation within this phase leads to relatively high crosslink density which leads this phase to act as a reinforcing filler within the high molecular weight polysil-UR polymer matrix. The blends obtained by this method were initially liquids that continuously increased in viscosity due to the silanol condensation and eventually resulted in solid optically transparent films.

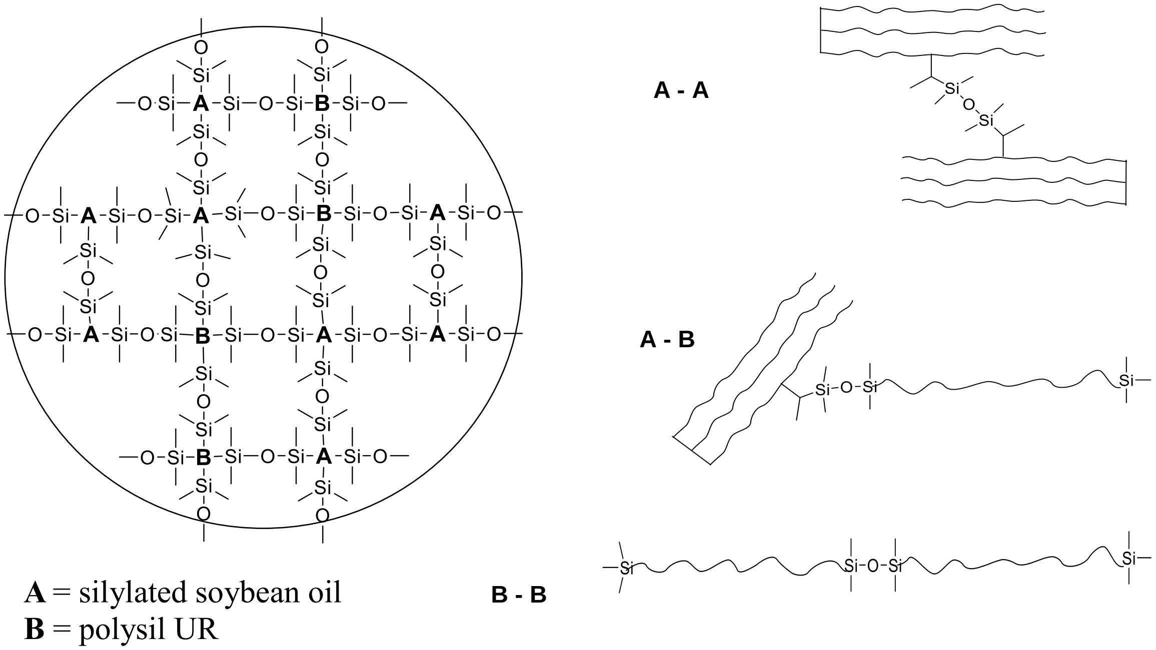


Figure 4.2: Siloxane cross-links in the reactive blends

Due to the relatively close solubility parameters, no solvent was needed during preparation and all blends were prepared by vigorously mixing the two components with the condensation catalyst using a mechanical stirrer, allowing the reaction between the various silanols to proceed and ensure that no gross phase separation takes place during the cure process. The optical transparency of the blends composed of less than 20 wt% silylated soy oil (Figure 4.3B) appeared clear and transparent. However, blends containing higher concentrations of the silylated soy appeared more translucent. However, no gross phase separation was observed in any of the blends and all samples appeared homogeneous to the naked eye.

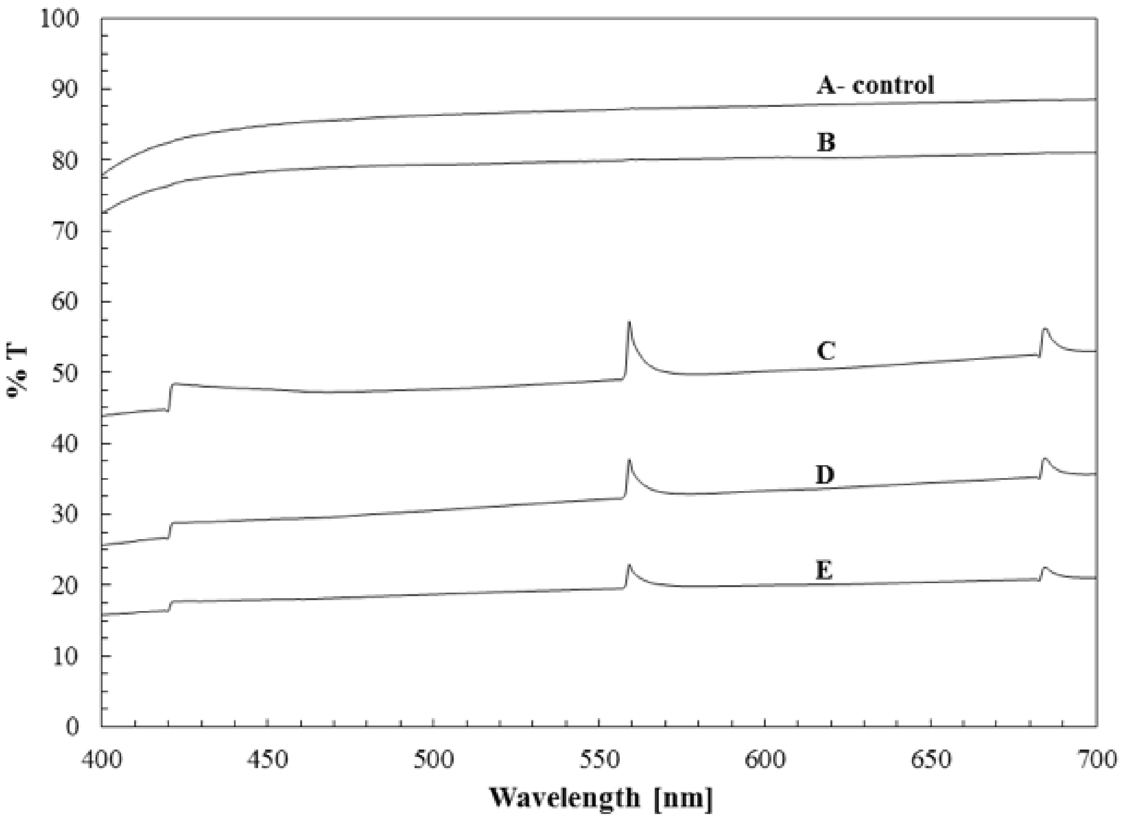


Figure 4.3: Optical transparency as a function of composition

The initial viscosity of the blends is directly proportional to the concentration of the high molecular weight polysil UR in the blend (Figure 4.4). Not surprising, higher viscosity blends prepared with small concentration of unmodified soy oil were slower to phase separate than similar blends prepared with high concentration of unmodified soy oil simply due to the viscosity. However, no gross phase separation was observed when silylated soybean oil was used.

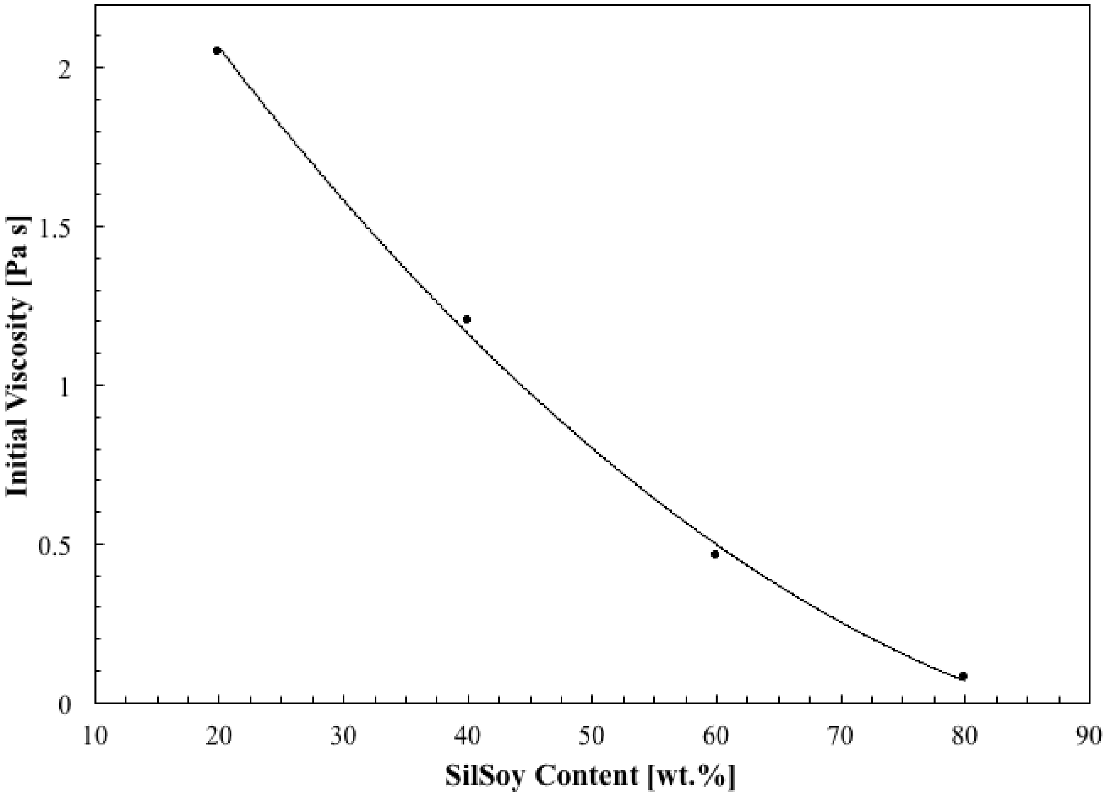


Figure 4.4: initial viscosity as a function of Silylated soy oil content

The silanol condensation and cure can be followed by the increase in the viscosity as a function of time (Figure 4.5). It is apparent that although all the silanols are expected to have the same reactivity, the cure rate is a function of the composition of the blends and appears to be inversely proportional to the concentration of the soy oil, which can be seen from the trend in the initial viscosity. This change in the viscosity as the blends are cured is unexpected since the cure and the change in the viscosity would be more pronounced in the low viscosity blends than the similar high viscosity blends.

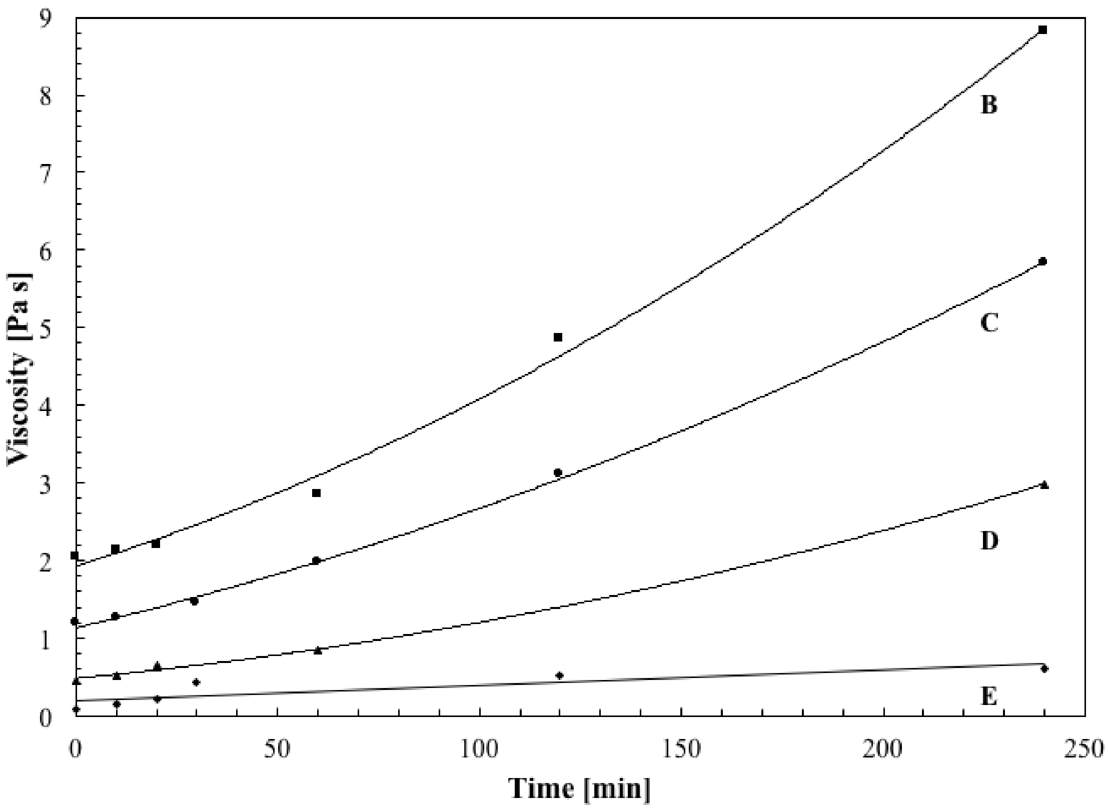


Figure 4.5: Changes in the viscosity as a function of reaction time

To better understand the changes in the viscosity as a function of the cure reactions, TGA was used to follow the evolution of methanol, which is the by-product of the cure reaction. Thus, the weight loss as a function of methanol evolution was recorded adiabatically at 25 ^{o}C (Figures 4.6) and at 80 ^{o}C (Figures 4.7). It is clearly observed from these data that the rate of methanol evolution is much higher at the elevated temperature as expected but the overall rate of the cure reaction is dependent on the blend composition as noted in the viscosity measurements.

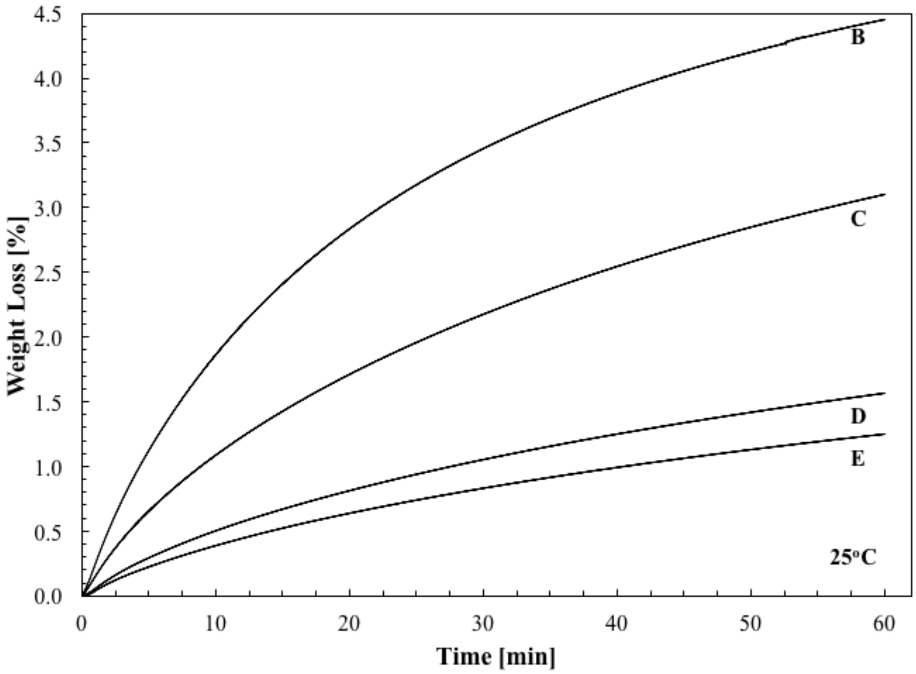


Figure 4.6: Weight loss as a function of methanol evolution at 25^{o}C

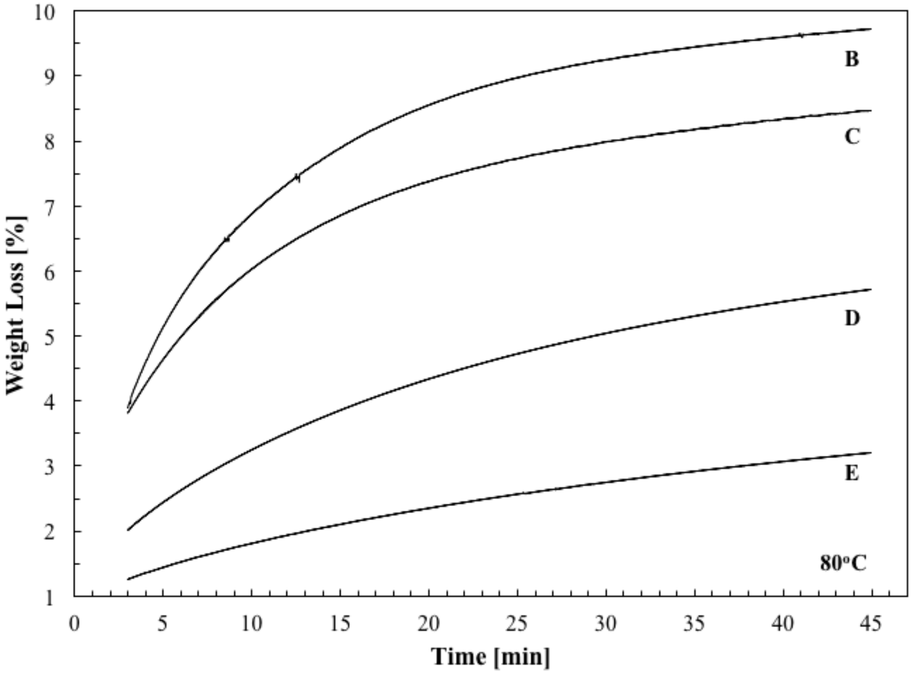


Figure 4.7: Weight loss as a function of methanol evolution at 80^{o}C

There could be different reasons for the unusual dependence of the rate of cure on the composition of the blend; most reasonable explanation is the relatively high permeability of the siloxane matrix to moisture and methanol. Thus, for the cure reaction to propagate, moisture must be diffused into the bulk (leading to hydrolysis of the methoxy groups) and the methanol by-product must be diffused out of the curing samples. It follows that higher concentrations of siloxanes characterized by the relatively high permeability will lead to faster cure rates.

4.3.2 Network characterization

Toluene is a good solvent for both the silylated soybean oil and the polysil-UR polymer. Yet, very high gel fractions were observed in all the blends (Figure 4.8) indicating the formation of a very efficient crosslink network due to siloxane linkages between the two components. It could also indicate high degree of entanglements of the linear polysil-UR polymer within the crosslinked soybean triglycerides as in interpenetrating polymer networks (IPN). Whether a highly crosslinked network was obtained holding the two phases together or a highly entangled IPN structure was formed, only minute fraction of a soluble material could be extracted from these blends. It is apparent from the relatively small but noticeable changes in the gel fraction appeared to be inversely proportional to the silylated soybean oil content in the blend. These small changes are most likely due to incomplete grafting of the alkoxysilane onto the fatty acids in the oil. Obviously, any triglyceride molecule that had not been silylated will not participate in the cure and will be extracted by the toluene.

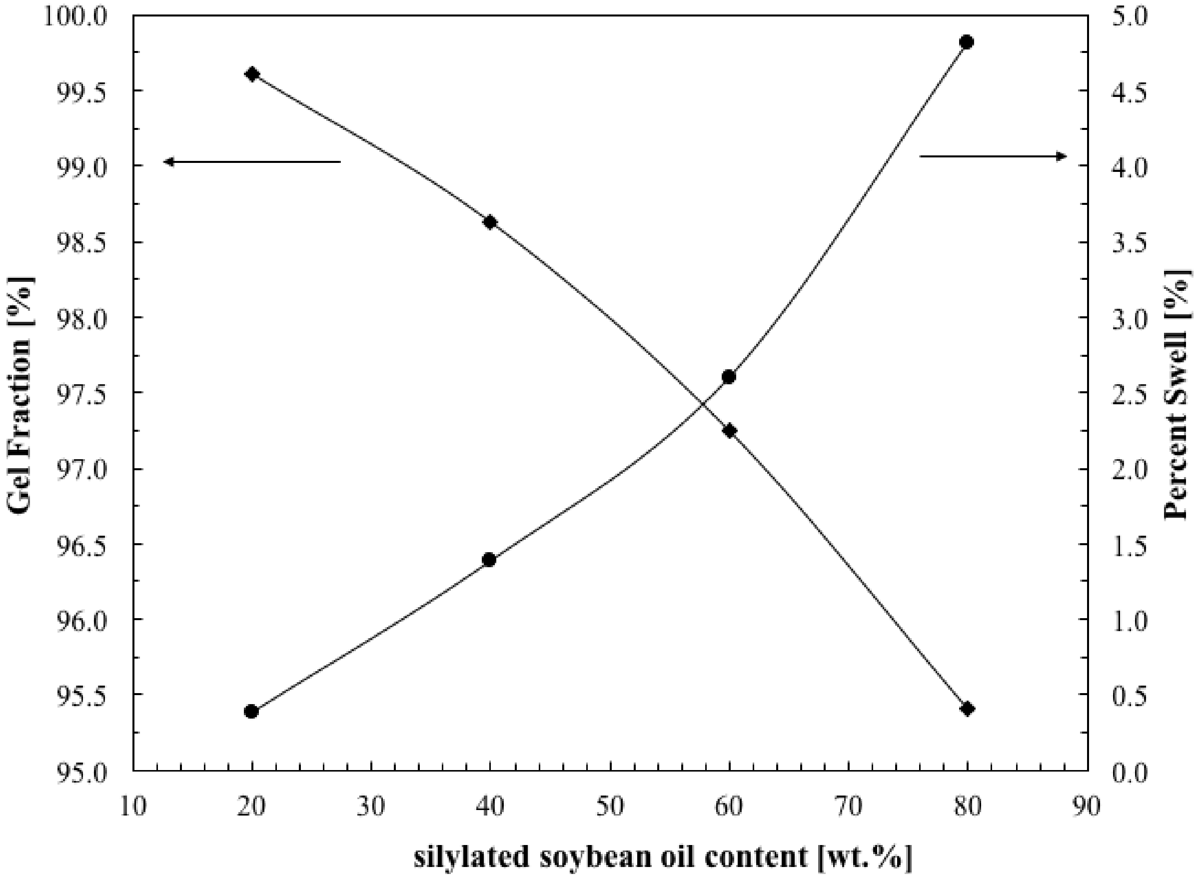


Figure 4.8: Gel Fraction and swell ratio as a function of blend compositions

All blends displayed very limited swelling in toluene (Figure 4.8) indicating very high crosslink density or high degree of entanglements. The swell ratio is inversely proportional to the gel content and is directly proportional to the silylated soybean oil content in the blend.

The composition of the various blends can be conveniently evaluated by FT-IR (Figure 4.9) that clearly display the siloxane content (at 1095 cm^{-1}) and the triglyceride ester functional group content (at 1740 cm^{-1}). These spectra also show a weak and broad peak around 3400 cm^{-1} related to OH adsorption indicating that not all the silanols in the blends had been condensed to siloxanes. As expected the siloxane absorption peak increases linearly with the polysiloxane content whereby the ester peak is directly proportional to the soybean oil content.

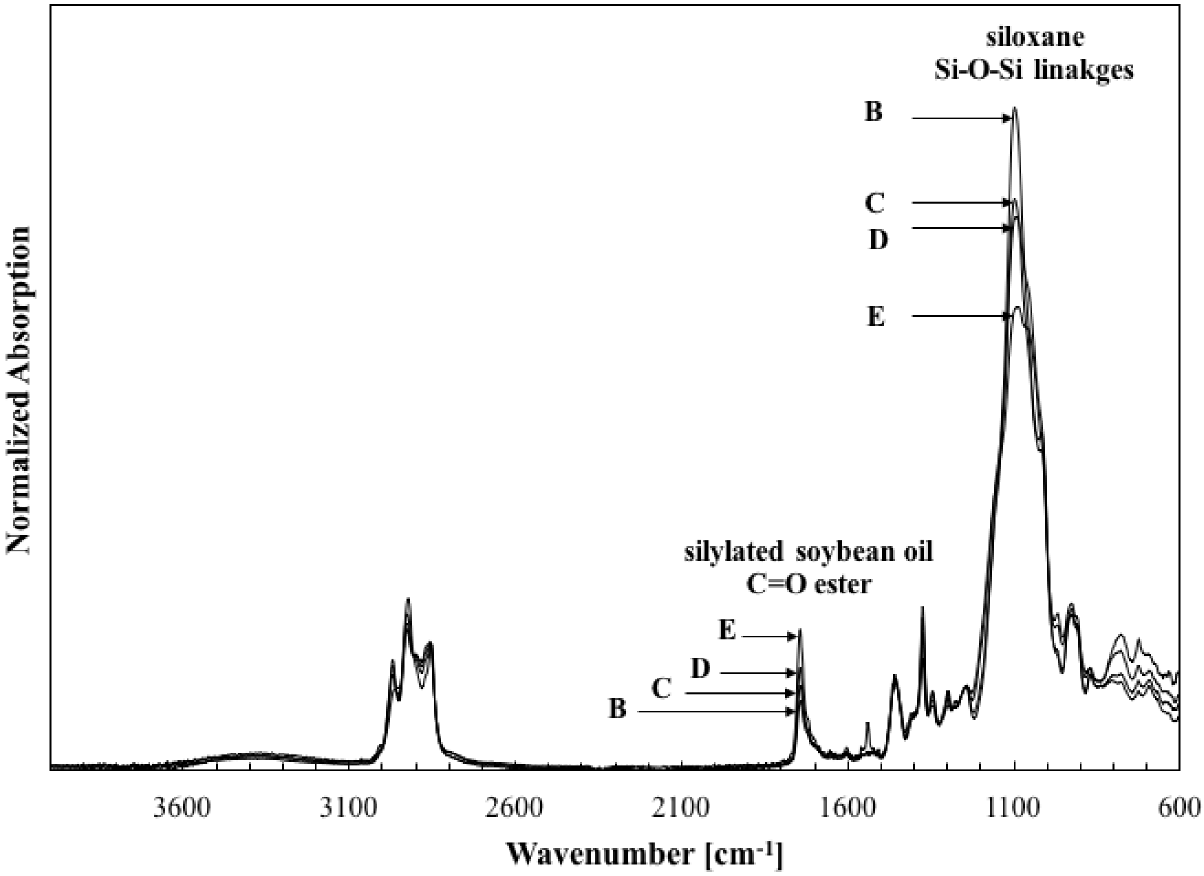


Figure 4.9: FTIR spectra of the Silylated soy and polysil-UR blends

4.3.3 Morphology

The critical factor in these system is the "in situ" formation of crosslinks through silanol condensation to yield siloxane linkages between the two phases. These linkages act as a compatibilizer, increasing the interfacial adhesion that impacts the morphology (and the mechanical properties). In binary systems, the major component generally forms a continuous matrix phase and the minor component appears as a dispersed phase of individual particles. SEM micrographs of fracture surfaces of blends with different compositions are shown in Figure 4.10 and reveal that once the polysil-UR content is greater than 20 wt. % it appears as the continuous phase with individual spherical silylated soy oil particles distributed in it. No apparent aggregation of the dispersed silylated soy phase is observed and no cracks or other interfacial defects are observed between the particles and the matrix indicating a strong interaction between these two phases. With an increase in the silylated soy content, the number of the dispersed particles is increased, yet, no apparent aggregation is observed which would be expected if there was poor miscibility between the two phases in the blend. The average size of the discrete particles slightly increased from 0.53±0.04 µm to 1.86±0.06 µm when the silylated soy content in the blends is increased from 40 % to 60% and no distinct dispersed particles are observed in the blend containing 20 wt. % silylated soy oil. A bicontinuous morphology is observed when the concentration of the silylated soy component is 80% (Figure 4.10E). At this concentration, relatively large area of the stained silylated soy oil components are observed next to the brighter (unstained) areas of the polysil-UR component which contain smaller areas of silylated soy.

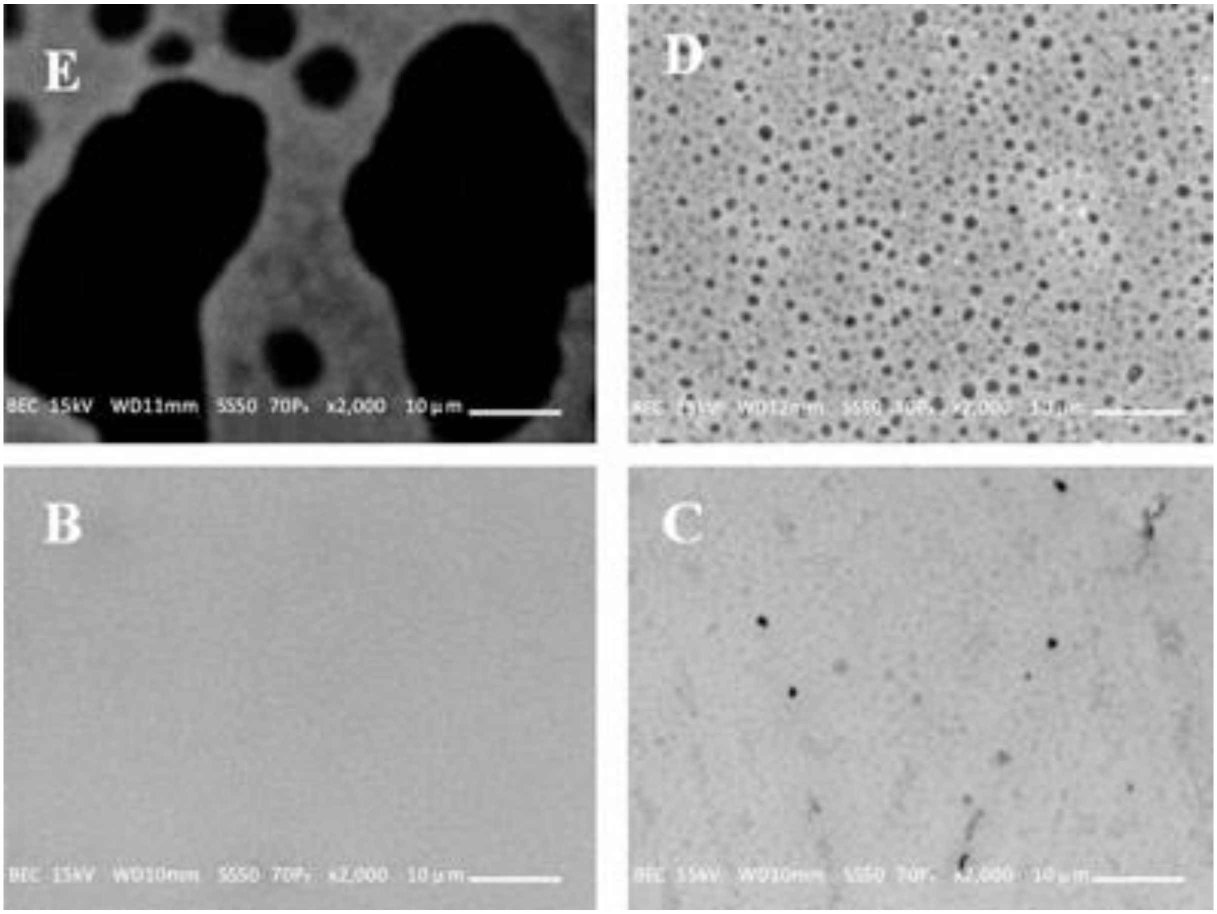


Figure 4.10: SEM images of the silylated soy and polysil-UR blends

4.3.4 Mechanical properties

Typical stress–strain curves of the cured blends are shown in Figure 4.11 and key mechanical parameters are listed in Table 4.2. The stress–strain curves show a gradual transition from a typical low modulus, high elongation polysiloxane to a plastic-like material with higher tensile strength material as the silylated soy content is increased. In the samples with a lowest silylated soy content (samples B), the systems underwent appreciable deformation before failure. As the silylated soy content increased (Sample C and D) appreciably higher initial modulus and lower elongation are observed. In fact, the mechanical properties clearly indicate a very strong reinforcing effect by the simultaneous siloxane curing and silylated soy filling effects. Thus, the Young's modulus is directly proportional to the concentration of silylated soy while the elongation at break decreases at higher silylated soy concentrations. When the concentration of the silylated soy is 80 wt. %, the blends turn to be too brittle as the morphology becomes bicontinuous.

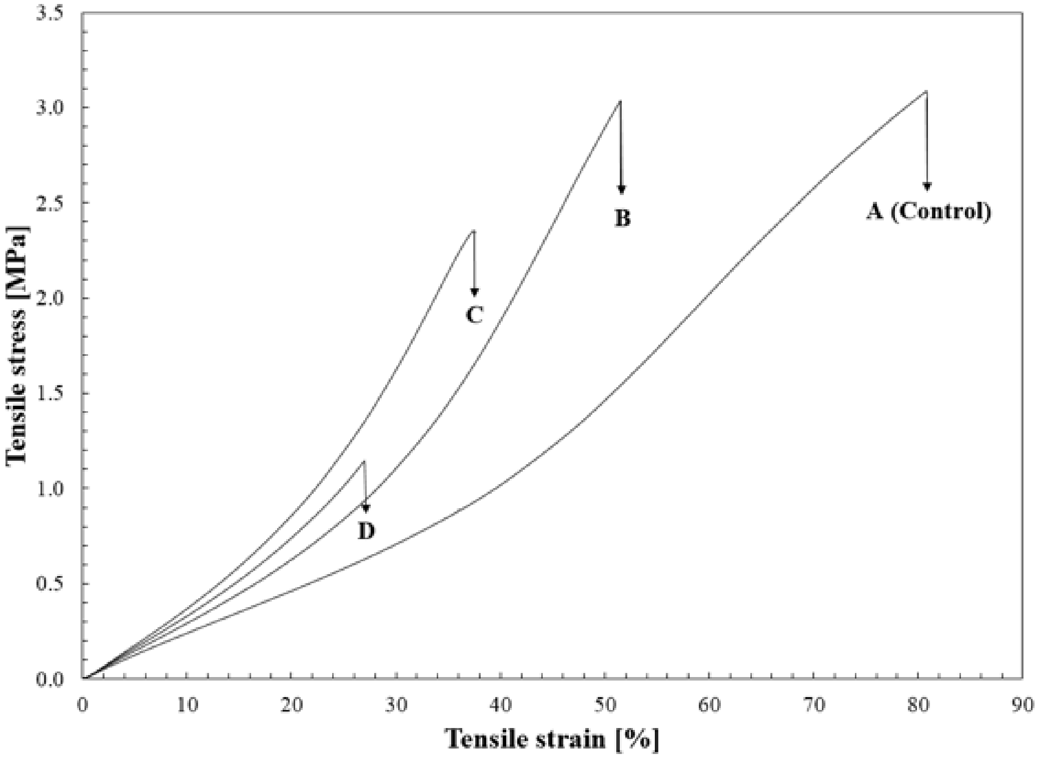


Figure 4.11: Stress-Strain properties the silylated soy and polysil-UR blends

Table 4.2: Mechanical properties at different blends composition*

Sample	silylated soybean oil [wt. %]	polysil-UR [wt. %]	Tensile strength [MPa]	Elongation [%]	Young's Modulus [MPa]	Toughness [MPa]
A	0	100	2.6	80.8	0.0223 ± 0.0011	147.23 ± 5.41
B	20	80	3.0	51.4	0.0261 ± 0.0007	99.13 ± 1.24
C	40	60	2.4	37.5	0.0272 ± 0.0007	53.42 ± 6.75
D	60	40	1.1	27.0	0.0280 ± 0.0006	17.61 ± 2.31
E	80	20	Films are too brittle			

*****Values mentioned for mechanical properties are average values based on 3 different readings.

4.4 Conclusions

Polymer blending is one of the most effective and economical techniques used to reduce material costs as well as developing new materials with different properties than those of each blend component. Using reactive blending technique is also a simpler process than the synthesis of new monomers to produce new polymeric materials. Furthermore, using blends containing biodegradable soybean oil is advantageous from environmental point of view and these new blends can be used in packaging, coating and agriculture applications.

A series of such biobased reactive blends were prepared from silylated soybean oil and methoxy terminated polysiloxanes containing urethane linkages. The crosslinking between these two components was achieved by conventional silanol condensation route using tin-based catalyst at room temperature. The Gel-Swell and FT-IR analyses indicated that the crosslinking density was inversely proportional to the concentration of the silylated soybean oil in the blend. Similarly, the cure rate, measured by the viscosity and the adiabatic TGA experiments, was also found to be inversely proportional to the silylated oil content. The silylated oil phase was found to be well dispersed in the polysil-UR matrix as indicated by the SEM images. The mechanical properties of cast films changed from high elongation rubbery material to high modulus, resin-like materials as the silylated soy content in the blends was increased. Proper blend compositions provide an opportunity to incorporate biobased material in this commercially available elastomer without compromising on tensile strength. It is anticipated that these reactive blends, with properly tailored properties, will find applications in protective coatings, additives to adhesives and new sealants.

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5. BIOBASED UNSATURATED POLYESTER RESIN FROM FERMENTATION DERIVED FUMARIC ACID

5.0 Abstract

Two different unsaturated polyesters were synthesized using biobased fumaric acid and propylene glycol and polyethylene glycol via two step polycondensation route. Unsaturated polyester resins (UPRs) were prepared from these polyesters with satisfactory properties. These UPRs are suitable for thermosetting resin applications like fiber-reinforced composites etc. This environmentally friendly composites can be a substitute for petroleum-based composite materials. The synthesis of polyesters was monitored by acid values and characterized using ATR-FTIR technique. The resin was prepared with 30% w/w loading of traditional cross-linkers and cured at high temperature in the presence of a free radical initiator. The cure of these resins was studied isothermally at different temperatures by understanding the exothermic heat evolved during the curing reaction measure by DSC. These results were used to calculate the degree of cure which was used to develop a cure kinetic model to determine the order of the reaction and rate constant (k) of the cure reaction. The mechanical properties of the final resin were determined and the tensile strength and modulus were found to be 23.68 MPa and 1.03GPa for polypropylene fumarate and, 14.03 MPa and 0.46 GPa for poly(ethylene glycol) fumarate. The mechanical properties of these resins were used to predict the mechanical properties of composite formulated with some natural fibers like jute, hemp and kenaf with known properties, using existing models. These predictions showed satisfactory results for the natural fibers compared to traditional synthetic fibers like carbon, aramid.

5.1 Introduction

Low molecular weight polyesters derived from unsaturated dibasic acids (or anhydrides) dissolved in unsaturated vinyl monomers comprise a family of thermosetting materials generally known as unsaturated polyester resins (UPR). UPRs, because of their excellent mechanical and thermal properties, low cost and thermal stability, are widely used in different industries including construction, transportation includes manufacturing of automobiles, boats and commodities like kitchenware etc. [1-5]. They are processed in the form of fiber reinforced plastics (FRP), sheet-molding compounds (SMC), bulk molding compounds (BMC) etc. UPRs are the most widely used matrix for the composite industry, where in the presence of optimum amount of reinforcing material it delivers excellent tensile and flexural properties. As mentioned earlier, UPR has two major components- unsaturated polyester (UP) and reactive diluents like vinyl monomers (styrene, divinyl benzene etc.) or acrylates etc. The unsaturated polyester (UP) is synthesized via the esterification of diol and dibasic acid or anhydride. Ethylene glycol (EG) and propylene glycol (PG) are most widely used diols in the production of UP. Phthalic anhydride, Terephthalic acid and Maleic anhydride are among the commonly used acids/anhydrides used in the preparation of UPs. Styrene is the most widely used as a reactive diluent part in manufacture of UPR, mainly due to its low cost. Unfortunately, most of the UPRs that are available commercially are derived from petroleum resources and thus, synthesizing UPRs from renewable materials is one of the preferred research topic nowadays.

In recent years, various diacids and diols derived from biobased materials have been studied and used to prepare UPRs. Some of the main examples include itaconic acid, itaconic anhydride and in some studies triglycerides, were reacted directly with styrene and divinyl benzene to prepare the resin [6-9] . Itaconic acid has one carbon-carbon double bond and two carboxylic acids and it is structurally very similar to maleic acid, which is widely used in the UPR manufacturing. Itaconic acid, along with succinic acid, has been reacted with 1,4-butanediol to prepare poly(butylene succinate) prepolymer for UPR[10]. In another study, itaconic acid was used along with D, L-lactic acid to prepare prepolymer by reacting with diols[11]. The cross-linked resins using itaconic acid, with styrene as a cross-linker, exhibited ultimate tensile strength of 10-66 MPa and Young's modulus of 1 GPa[12-14]. Along with this, plant oils have been used as a source of polyester, since these are mainly triglycerides containing different number of carbon-carbon double bonds (source of unsaturation). Some studies showed that these triglycerides have been used directly blended with conventional polyesters and styrene to provide more functionality in the cross-linking mechanism. But since it is very well known that the internal double bonds of triglycerides are not highly reactive, many studies aim to add functionality using acrylates etc. to have an unsaturation available for cross-linking. Acrylated epoxidized soybean oil has been predominantly used in this regards[15, 16]. Also, a mixture of this modified oils with polyesters from other biobased sources like itaconic acid have been studied[13]. They showed good compatibility and the tensile strength, Tg and biobased content of targeted thermoset resin from soybean oil was improved. Overall, there is an increasing interest in developing biobased material to manufacture UPRs with higher biobased content and achieving similar properties.

In this study, we have developed a polyester from fermentation derived fumaric acid[17] by reacting it with ethylene or propylene glycol, which basically provides an opportunity to develop 100% biobased matrix for the developing composites. There are several reasons that make fumaric acid, an ideal choice for synthesizing unsaturated polyester. Unsaturated polyester synthesis is essentially a condensation reaction between diol and diacids/anhydride, and it suffers from side reactions leading to unwanted side products. For instance, it has been reported that "ordelt" reaction is the predominant side reaction in polyester synthesis[18, 19]. It is a reaction of diol with the unsaturation present in the diacids and thus the overall unsaturation content of the UP decreases. Formulations with higher fumaric acid content retained a higher degree of unsaturation, 15% more protection than corresponding maleic acid content[20]. Isomerization of maleate to fumarate during this esterification, is also another important side reaction[21]. Fumarate form is more preferred at high temperatures, at which the esterification reaction is carried out (above 150^{o}C)[22]. It has also been shown that the fumarate polyesters showed reactivity almost 20 times[23, 24] higher than maleate esters, and also that the presence of trans double bonds facilitates cross-linking and has positive influence on the rheological and mechanical properties[25]. Along with this, the overall biobased content was increased since the fumaric acid is 100% biobased fermentation derived product, provided by Michigan Biotechnology Institute (East Lansing, MI).

The second important part of UPRs is the reactive diluent which acts as a cross-linker. Styrene is the most widely used vinyl monomer in the preparation of UPRs. Styrene copolymerizes with the low molecular weight UP through a free radical mechanism over carbon-carbon double bond and, it also polymerizes with itself via same mechanism. This results into high strength cross-linked network upon complete cure. Styrene provides high strength to the final cured resin by virtue of the presence of aromatics, and it is a low-cost material which makes it an attractive candidate for the UPR industry. Effect of styrene concentration in the polyester resin preparation has been widely studied [26-28]. It has been found that the higher styrene concentration produces phase separation which form microstructures while on the other hand the lower concentration doesn’t provide required tensile strength and modulus to the final resin. Also, styrene is considered as “hazardous”, “carcinogenic” and its use in the composites is restricted by the Federal law[29], thus commercially the styrene content in the composite preparation is restricted to ~33% (w/w).

Overall, this study attempts to develop a greener composite by developing bio-based matrix for it. This study focuses on (1) developing unsaturated polyester from biobased fumaric acid and diols (mainly ethylene glycol and propylene glycol), and attempts to (2) predict the mechanical properties of the composites using some natural fibers (e.g., jute, hemp, kenaf etc.). Polyester was synthesized in conventional two-step synthesis process- I) monoester formation and II) polycondensation in the presence of condensation catalyst (titanium butoxide). The product was characterized using acid value (AV), Fourier Transform Infrared Spectroscopy (FTIR), Gel Permeation Chromatography (GPC) for the quantification of yield and molecular weight of UP. The cure kinetics of the styrene-free polyester was studied using Differential Scanning Calorimetry (DSC) and ARES Rheometer. Hydroquinone was used as an inhibitor to protect the unsaturation on UP and to prevent gelling of polyester. It should be noted that the inhibitor needed to be destroyed to have an efficient crosslinking. Styrene generally comes with an inhibitor when ordered from general vendors like Sigma Aldrich. This inhibitor can be destroyed in different ways, one of the faster is by washing it with sodium hydroxide solution and then decanting to separate the free styrene. The cure of resin with styrene was studied using DSC isothermally at different temperatures. The tensile properties of the resin prepared using PPF and PEGF with styrene were reported. And, finally with the help of some of the existing models to predict the composite properties (e.g., Rule of Mixtures, Halpin Tsai etc.), we predicted the final composite modulus (GPa) using some known natural fibers like jute, hemp, kenaf with known mechanical properties.

5.2 Experimental

5.2.1 Materials

Fumaric acid (96.9% purity) was kindly provided by Michigan Biotechnology Institute (MBI) International, MI. Fumaric acid was ground to powder prior to reaction so as to increase the surface area. Propylene glycol, Polyethylene glycol (MW= 200 gms/mole), titanium butoxide, cobalt naphthenate and styrene were purchased from Sigma Aldrich (MO, USA). The stabilizer in the styrene, 4-tert-butylcatechol, was deactivated and removed by simply caustic wash by 0.1% NaOH solution. All other chemicals were reagent grade and were used without further purification unless noted.

5.2.2 Synthesis of polyesters

5.2.2.1 Synthesis of polypropylene fumarate (PPF)

Propylene glycol (200 g, 2.6 mol, 10% molar excess with respect to fumaric acid) was heated in a 2L RB flask to 120^{-}130^{o}C under stirring at which temperature well ground fumaric acid (275 g, 2.4 mol) was added slowly in 10-20 g portions (with stirring to prevent its sticking and charring upon the walls) to the flask. Titanium t-butoxide (6.72 g, ~2%w/w) was then added and the mixture was stirred for 20 min. under a flow of nitrogen to create inert environment. Thereafter the nitrogen flow was stopped and the reaction was heated at 135-140 ^{o}C for 1h. Any water released was continuously collected in a Dean and stark assembly attached to the RB flask. (The first sampling for acidity was done at 1h because the mixture appeared homogeneous at this time). The temperature was then raised to 180 ^{o}C (to keep propylene glycol under reflux to enhance mixing and mass transfer) and was maintained there until the acidity, measured each hour, dropped to around 10 mg KOH /g. The mixture was allowed to cool to 110 ^{o}C at which temperature hydroquinone (inhibitor to protect unsaturation, 1% w/w) was added followed by stabilizer-free styrene (30% w/w). The mixture was allowed to cool further to room temperature and then stored under air-tight conditions.

5.2.2.2 Synthesis of poly (ethylene glycol) fumarate (PEGF)

Poly(ethylene) glycol (PEG -200, 440 g, 2.2 mol, 10% molar excess with respect to fumaric acid) was heated in a 2L RB flask to 120^{-}130^{o}C under stirring at which temperature well ground fumaric acid (232 g, 2 mol) was added slowly in 10-20 g portions (with stirring to prevent its sticking and charring upon the walls) to the flask. Titanium t-butoxide (6.72 g, ~2%w/w) was then added and the mixture was stirred for 20 min. under a flow of nitrogen to create inert environment. Thereafter the nitrogen flow was stopped and the reaction was heated at 135-140 ^{o}C for 1h. Any water released was continuously collected in a dean and stark assembly attached to the RB flask. (The first sampling for acidity was done at 1h because the mixture appeared homogeneous at this time). The temperature was then raised to 190 ^{o}C (to keep PEG under reflux to enhance mixing and mass transfer) and maintained there until the acidity, measured each hour, dropped to around 10 mg KOH /g. The mixture was allowed to cool to 110 ^{o}C at which temperature hydroquinone (inhibitor to protect unsaturation, 1% w/w) was added followed by stabilizer-free styrene (30% w/w). The mixture was allowed to cool further to room temperature and then stored under air-tight conditions.

5.2.3 Characterization of polyesters

5.2.3.1 Acid and Hydroxyl value titrations

The acid value, i.e., the total concentration of the carboxylic groups, was measured by diluting about 1 g of the sample to 50 mL neutralized toluene-methanol mixture (2:1). Then the sample was titrated with 0.1 M KOH in ethanol with phenolphthalein as the indicator, as described in ISO standard[30]. The hydroxyl value was determined by acetylation of the hydroxide groups with acetic anhydride, which was hydrolyzed. The excess acetic acid and the free acid groups in the reaction media were titrated with KOH. The hydroxyl value was determined with the acid value according to the IS0 standard[31].

5.2.3.2 Spectroscopy

The Attenuated Total Reflection-Fourier Transform Infrared (ATR-FTIR) spectra were acquired on a Schimadzu IRAffinity-1 spectrometer (Tokyo, Japan) equipped with a single reflection ATR system (PIKE Technologies, MIRacle ATR, Madison, USA). All spectra were acquired between 600– 4000 cm^{-1} using 32 scans at a resolution of 4 cm^{-1}.

5.2.4 Preparation of polyester resin

The product mixture of PPF-styrene and PEGF-styrene was mixed with 2% (w/w) methyl ethyl ketone peroxide (MEKP) catalyst and 0.5% (w/w) cobalt naphthenate (accelerator), separately. These mixtures were stirred vigorously and degassed to remove any bubbles. After degassing, the material was poured into a silicone mold with dog bone shaped tensile bars geometry. The material was allowed to cure at 60^{o}C for 30 minutes and the thereafter at room temperature. It was found that higher temperatures (than 60^{o}C) caused it to curl (or shrink) because of faster curing rates. This material can also cure at room temperature but takes longer time (more than 6 hours). After complete curing, the dog bone shaped specimens were removed and analyzed for tensile properties.

5.2.5 Cure kinetics measurements

The polyester-styrene mixture (PPF-styrene and PEGF-styrene), polyester (PPF and PEGF) with MEKP and cobalt naphthenate added as a catalyst and initiator respectively, were tested for curing rates at different temperatures using differential scanning calorimetry (DSC). In a typical run, a sample from these respective mixtures (5-10mg) was placed in an aluminum pan and the temperature was rapidly increased to the pre-determined temperature (30^{o}C/min) and it was heated isothermally at that temperature for 30 min. in the furnace of a Q20 Differential Scanning Calorimeter (TA Instruments, DE, USA). The isothermal temperatures were chosen based on a DSC scan over the temperature range of RT to 250^{o}C. For the polyester sample without added styrene, the temperatures chosen for the study were 160°C, 170°C, 175°C and 180°C, and a typical DSC results were shown later in Figure 5.6 and 5.7. Based on the similar DSC scans for both the polyester-styrene mixtures, the temperature chosen were 50°C, 60°C, 80°C and 100°C. The heat flow (mW) was recorded as a function of time (min) for the cure.

5.2.6 Cure kinetics modeling

The main objective of studying the cure kinetics is to correlate the curing reaction rate to the variables involved. The rate of the cure reaction dα/dt is measured by the product of two functions; temperature dependent function k(T) and the cure conversion (α) function-f(α). The temperature dependent function, k(T) is given as the Arrhenius equation-

$$k(T) = A * \exp(\frac{E_a}{RT}) \qquad \text{eq. 5.1}$$

And, the cure conversion function affecting the cure reaction rate is given by the following equation:

$$f(\alpha) = (1 - \alpha)^n \qquad \text{eq. 5.2}$$

The above-mentioned DSC experiments for the cure study provide the information of heat flow (mW) as a function of time at given isothermal temperature. The cure conversion (α) can be deduced from the heat flow at any given time (t). It can be determined using eq. 5.3-

$$\alpha = \frac{\Delta H_t}{\Delta H_{tot}} \qquad \text{eq. 5.3}$$

In eq. 5.3, ΔH_{tot} represents the total enthalpy of the cure reaction, while ΔH_t represents the cumulative heat of exothermic reaction at any given time (t). So, taking the ratio of this quantity provides an accurate way to determine the cure conversion at any given time (t). Overall, the nth order kinetics model as given by eq. 5.4 was utilized to quantify the rate of degree of cure as a function of degree of cure and temperature-

$$\frac{d\alpha}{dt} = k\,(1-\alpha)^n \qquad \text{eq. 5.4}$$

In eq. 5.4, n represents the order of the reaction, α represents the cure conversion as calculated from the enthalpy of the cure reaction and k represents the cure rate constant defined by Arrhenius equation.

5.2.7 Tensile properties

The mechanical properties were measured at RT using a Universal Testing Machine (United Calibration Corp. and United Testing Systems, SFM-20) following ASTM D882. The tensile tests were performed at a strain rate of 0.0254 m/min (1 inch/min) and in all cases at least three specimens of each sample were tested and the average values were recorded.

5.3 Results and Discussion

5.3.1 Synthesis of polyester and characterization

Both the polyesters, Polypropylene fumarate (PPF) and Poly (ethylene glycol) fumarate (PEGF) were synthesized by a two-step process; esterification followed by condensation of fumaric acid with 10% molar excess of propylene glycol (PG) and polyethylene glycol (PEG) respectively, in the presence of condensation catalyst titanium butoxide (2% w/w) as shown in Figure 5.1. In order to prevent the radical crosslinking of C=C present in the fumaric acid, hydroquinone inhibitor (1% w/w) was added to the reaction mixture when the reaction mixture was set to cool down at the end of the reaction at 150°C. Additionally, since polyester turns highly viscous when it cools down to room temperature, styrene monomer was introduced in the reaction mixture while cooling down the reaction temperature at the end of the reaction to obtain the uniform blend of polyester and styrene.

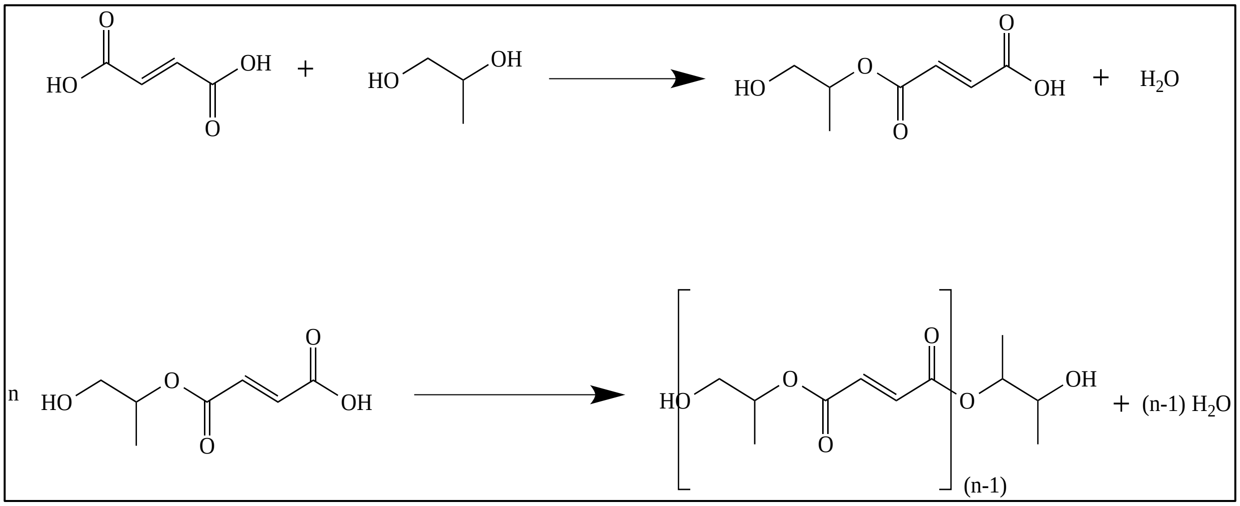

Figure 5.1: Synthesis of polyester PPF: A. Mono-esterification B. Polycondensation

Samples were taken during the reaction at regular intervals to assess the progress of the reaction by measuring acid values. Acid value was an indication of the consumption of fumaric acid during the reaction and helpful in determining the % conversion of the reactants. Acid values were calculated using Equation 5.5.

$$\text{Acid value} = \frac{\#\text{moles of acid} \times 56100}{\text{total amount (in gms)}} \qquad \text{eq. 5.5}$$

The theoretical initial acid value was calculated based on the initial moles of fumaric acid taken for the synthesis of both PPF and PEGF. In case of PPF, the initial acid value was found to be 275 mg of KOH; while for PEGF, the initial acid value was 165 mg of KOH. Acid values of all samples were replicated three times and the obtained average acid value was used to quantify the extent of reaction by calculating % conversion of fumaric acid using Equation 5.6.

$$\%\text{Conversion} = \frac{\text{Initial acid value} - \text{calculated acid value}}{\text{initial acid value}} \qquad \text{eq. 5.6}$$

The extent of reaction and the measured acid values for the preparation of PPF are shown in Figure 5.2, as a function of reaction time. The final acid value achieved was as low as 4.55 mg of KOH, and the conversion of fumaric acid (extent of reaction) of 98.35 %. Figure 5.3 indicates the extent of reaction and measured acid values for the synthesis of PEGF as a function of reaction time. The final acid value achieved was 11.8 mg of KOH, and the conversion of fumaric acid (extent of reaction) of 92.85 %.

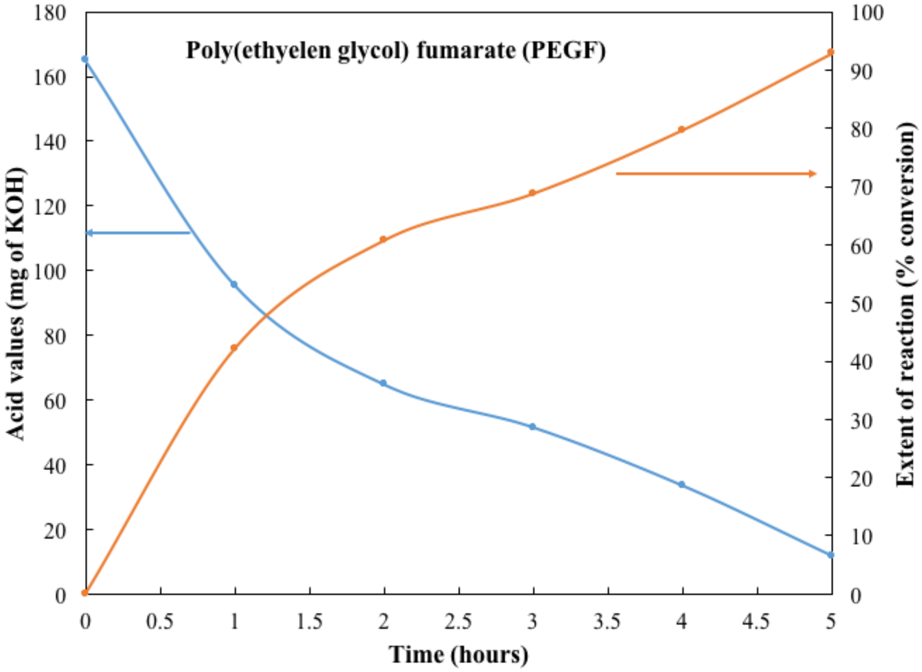

Figure 5.2: Acid values and Extent of reaction for synthesis of PPF

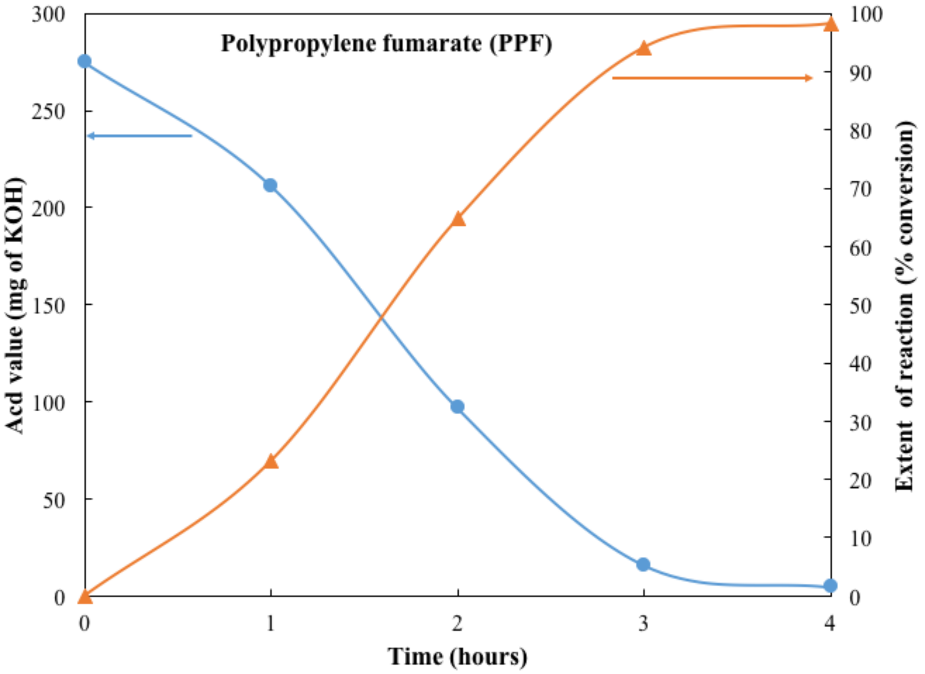

Figure 5.3: Acid values and Extent of reaction for synthesis of PEGF

The hydroxyl values of both the products were also calculated following ISO standard and are mentioned in Table 5.1. There was obvious decrease observed in the measured hydroxyl values. The acid values measured for the final samples were used for determining the molecular weight (Mn) using the Carothers equation. Respective molecular weights for PEF and PEGF are listed in Table 1.

Table 5.1: Characterization of PEF and PEGF

Polyester	Acid values (avg)		Hydroxyl values (avg)		Molecular weight (Mn)
	t=0	t=final	t=0	t=final	
Polypropylene fumarate (PPF)	275±5	4.5±0.92	398±6	16.7±0.7	1136
Poly(ethylene glycol) fumarate (PEGF)	165±5	11.8±1.45	552±9	73±2.1	2168

Fumaric acid was the limiting reagent in the synthesis of both polyesters PEF and PEGF, and thus the respective acid values were used as a basis for determining molecular weights (Mn). Literature suggests that the low molecular weight polyesters synthesized in the preparation of thermosetting polyester resin falls in the range of 800-2000 g/mole. Essentially lower molecular weight is needed to ensure uniform blending with styrene monomer later. Higher the molecular weight of polyester pre-polymer, more difficult will be the compatibility with styrene. In case of PEGF, polyethylene glycol has molecular weight of 200 g/mole, thus consists of around 3 repeating units. Due to this initial high molecular weight of one of the reactant, the final acid value of 11.8 mg of KOH was enough to produce number average molecular weight of 2168 g/mole.

The obtained polyesters PEF and PEGF were characterized using FTIR for the confirmation of the corresponding ester formation. Figure 5.4 shows the FTIR for PG, fumaric acid and the corresponding polyester PPF, magnified in the range of 1500-2000 cm^{-1}. It can be observed that the peak at 1600 cm^{-1} that is corresponding to C=O carbonyl group has shifted to 1715 cm^{-1} in the PPF final and PPF intermediate product. Also, a new peak appears at 1650 cm^{-1}

in both PPF final and PPF intermediate, which is a typical peak for C=O carbonyl group of ester. This observation confirms the formation of esters in the reaction product. PG doesn’t show any peak in this range.

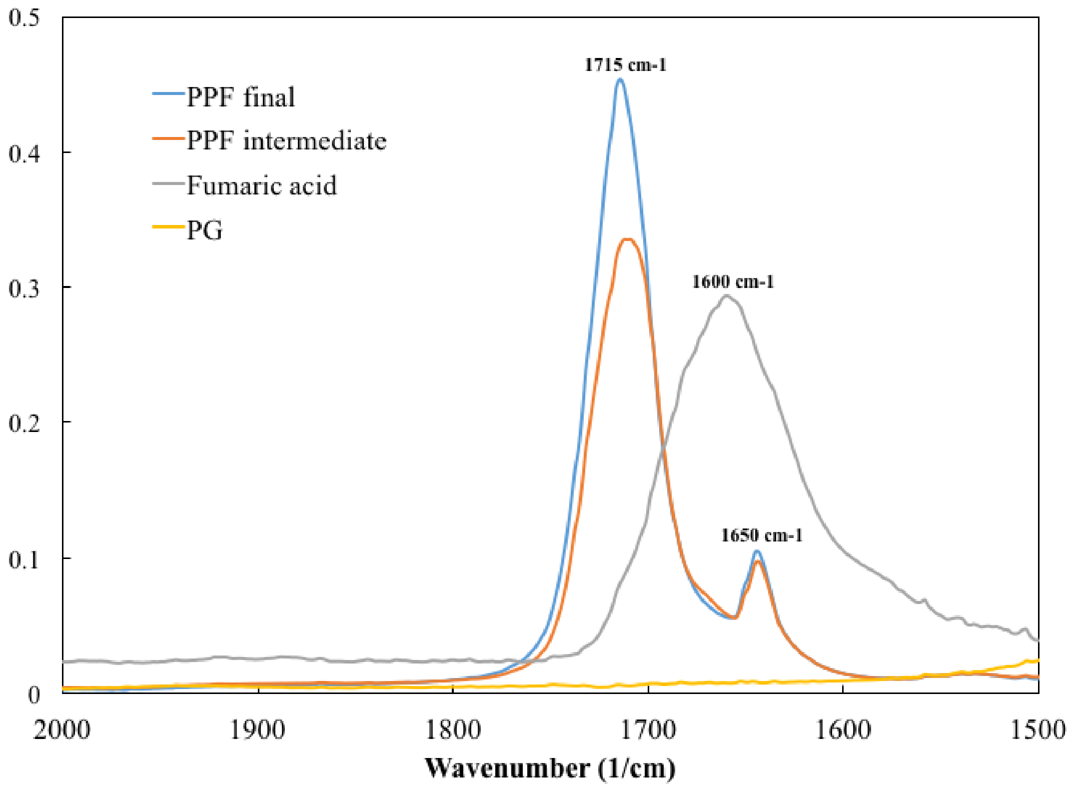

Figure 5.4: FTIR characterization for the polyester PPF (1500-2000 cm^{-1})

Figure 5.5 shows the FTIR peaks corresponding PG, fumaric acid and the polyester PPF, magnified in the range of 3000-3800 cm^{-1}, which is typical range for the hydroxyl groups. PG shows characteristic peak in this region 3000-3600 cm^{-1}. It can be observed that PPF final and PPF intermediate product also shows the corresponding peaks in this region, although the intensity of this peak has reduced, mainly due to the consumption of propylene glycol. Another interesting reason behind the reduced peak intensity might be that not all the oligomers possess hydroxyl group as their end group even though the propylene glycol is used in 10% molar excess. Similar observations were obtained for the polyester PEGF prepared using polyethylene glycol and fumaric acid.

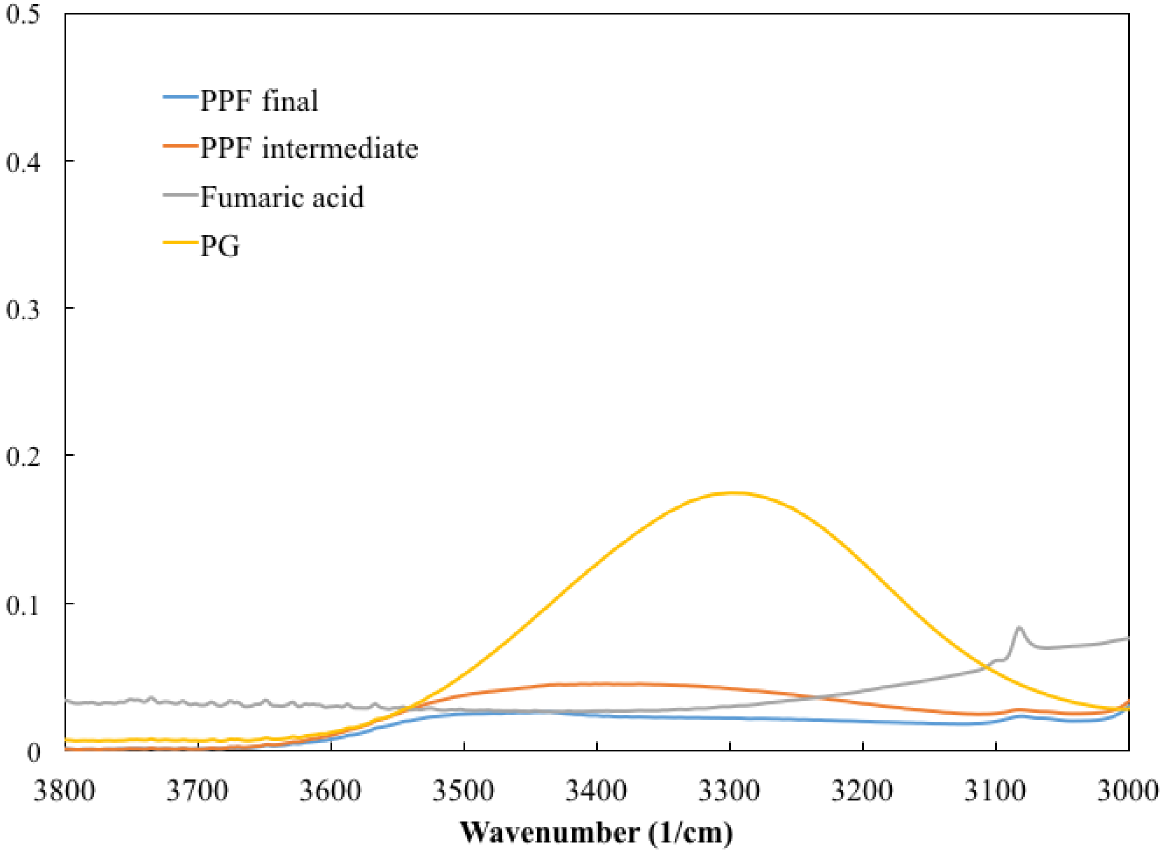

Figure 5.5: FTIR characterization for the polyester PPF (3000-3800 cm^{-1})

5.3.2 Preparation of polyester resin

UPRs have a wide-range of industrial applications, and with the there is an increasing demand for replacement of traditional fossil based UPRs with their "greener" counterparts. To obtain UPR, the synthesized unsaturated polyester is mixed with a cross-linker which will eventually cure it to provide a thermosetting matrix for the composite. Styrene is the most widely used cross-linker in the preparation thermosetting polyester resin, which essentially acts as a reactive diluent. These low molecular weight polyester pre-polymers (UP) are highly viscous (solid, in most cases) at room temperature and thus become incompatible for uniform mixing with styrene monomer. Ideally, the mixing should be done at higher temperature, in the range of 90-110^{o}C. Towards the end of the synthesis process of PEF and PEGF, as mentioned in the experimental section, styrene monomer was added to the reaction mixture when the product was cooling down to the RT after expected % conversion was achieved. This basically ensures uniform mixing of polyester and styrene, and when the mixture reached room temperature the viscosity was 600-800 cPs. This made it easy to handle this material for preparing samples for tensile testing, and also there was no phase separation observed to the naked eye which also confirmed uniform mixing. It is very important to mention that the styrene used was treated prior to mixing to remove the stabilizer. The reagent grade styrene ordered from Sigma Aldrich generally contains 4-tert-butylcatechol as the stabilizer, which was removed by washing with 0.1 % NaOH solution.

Effect of change in styrene concentration in the resin preparation on the resin properties is widely studied. For example, *Felisberti et. al*. [26]styrene concentration was changed between 6% (w/w) to 58% (w/w) in the polyester matrix prepared by the reaction of orthophthalic acid, propylene glycol and diethylene glycol. It suggests that as the styrene concentration was increased beyond 40% (w/w), two phases were observed and concluded as higher styrene concentration of styrene affects the mechanical properties and the morphology of the resin because of this phase separation forming microstructures. While, on the other hand lower concentration (below 20% w/w) doesn’t provide required tensile strength to the thermosetting resin. Based on the literature available, 30-35% (w/w) styrene in the polyester matrix is widely used commercially which provides a good compromise between the mechanical properties and miscibility. So, in the preparation of PEF resin and PEGF resin, 30 % (w/w) styrene was added to the polyester towards the end of the reaction.

5.3.3 Mechanism of cure

The product mixture containing polyester and 30% (w/w) styrene monomer was cured at room temperature and temperatures higher than room temperature, in the presence of radical initiator methyl ethyl ketone peroxide (MEKP) and cobalt naphthenate (CoNap) as an accelerator. This curing reaction is a free radical crosslinking reaction as shown in Figure 5.6, where styrene reacts with itself as well as with the unsaturation present in the polyester backbone.

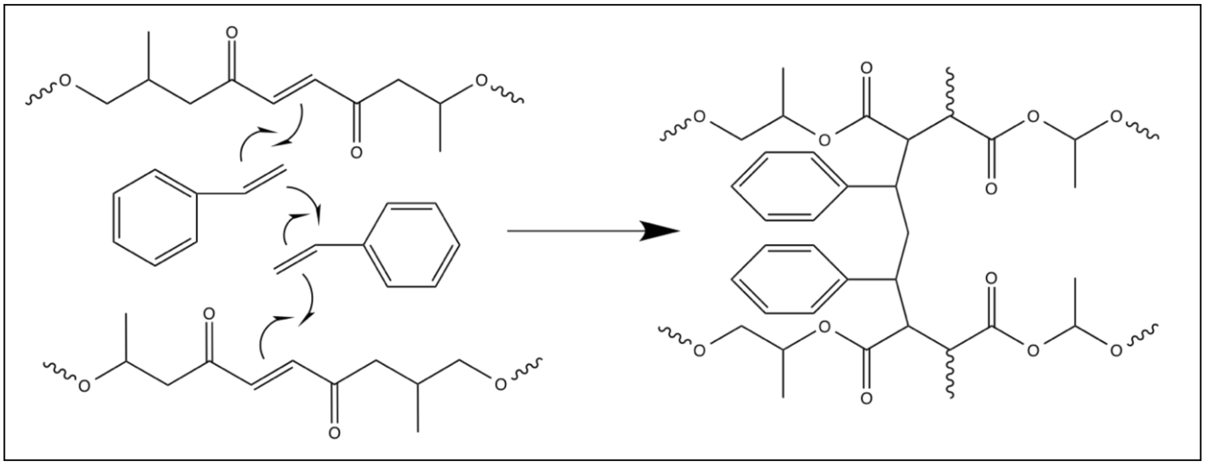

Figure 5.6: General cross linking mechanism in the curing reaction between unsaturated polyester and styrene

5.3.4 Study of cure kinetics

The isothermal temperature to study the cure kinetics effectively, were chosen based on a DSC scan over a temperature range. Figure 5.7 shows a heat evolved during the exothermic curing reaction of PPF (without styrene) as a function of time and it is evident that the onset of curing reaction is around 145^{o}C and the maximum heat flow was observed at the temperature around 185^{o}C. The isothermal temperature were selected in the temperature range of 145^{o}C and 185^{o}C. The reason for selecting temperatures in this region is because below 145^{o}C there is no significant heat flow (the cure reaction is very slow) and beyond 185^{o}C the cure reaction is very fast and it won't provide accurate results for the cure study. Based on such an observation, the temperatures chosen for the study if cure of polyester PPF were 160ºC, 170ºC, 175ºC and 180ºC. Similar DSC scans were performed for PPF resin and PEGF resin mixtures and the temperature chosen for the study were: 50ºC, 60ºC, 80ºC and 100ºC. (Note: The study of cure kinetics presented is only for the case of polyester PPF, and the same method was used to determine the rate constants for the polyester resins).

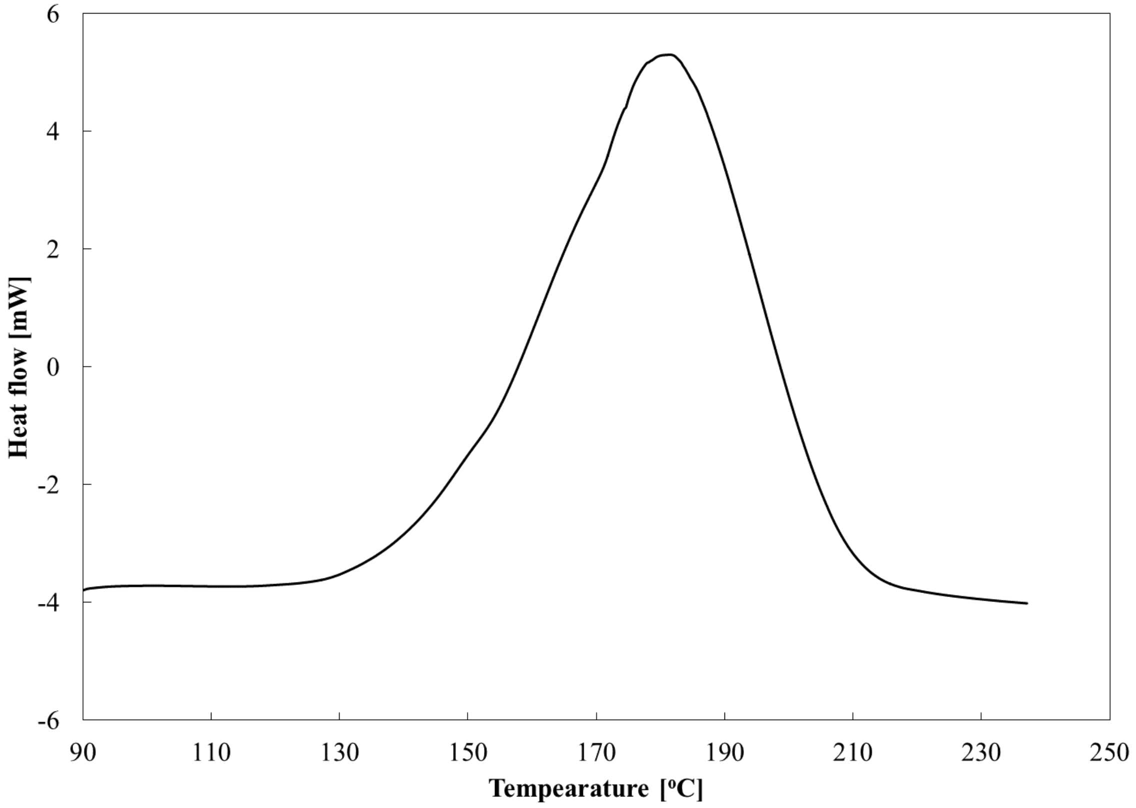

Figure 5.7: Dynamic heat flow curve of PPF curing over a temperature range in differential scanning calorimetry scan

Figure 5.8 shows the heat flow profile for the curing reaction of PPF as a function of time at chosen temperatures for the isothermal study. From Figures 5.7 and 5.8, it can be concluded that the cure rate is a function of both time of cure and temperature for the cure. It can be seen from all individual heat flow profiles in Figure 5.8, the rate of cure is higher at initial stages and it subdued as a function of time. Also, higher the temperature of the cure, higher the degree of cure.

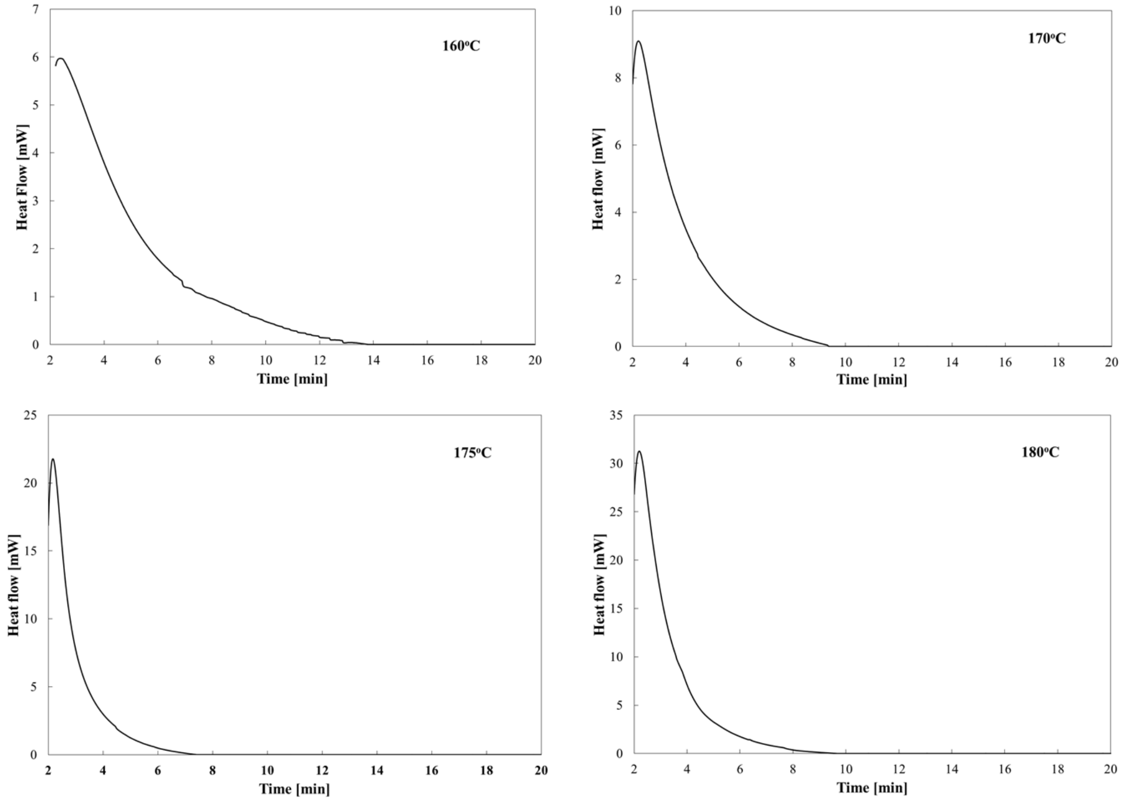

Figure 5.8: Isothermal heat flow profile of PPF curing at 160°C, 170°C, 175°C and 180°C

Based on this degree of cure profile as a function of time from Figure 5.9, the rate of degree of cure (dα/dt) was calculated as a function of time as presented in the eq. 5.3. As indicated in the eq. 5.7, the rate of degree of cure was equated to the rate constant for the cure reaction and the degree of cure (α).

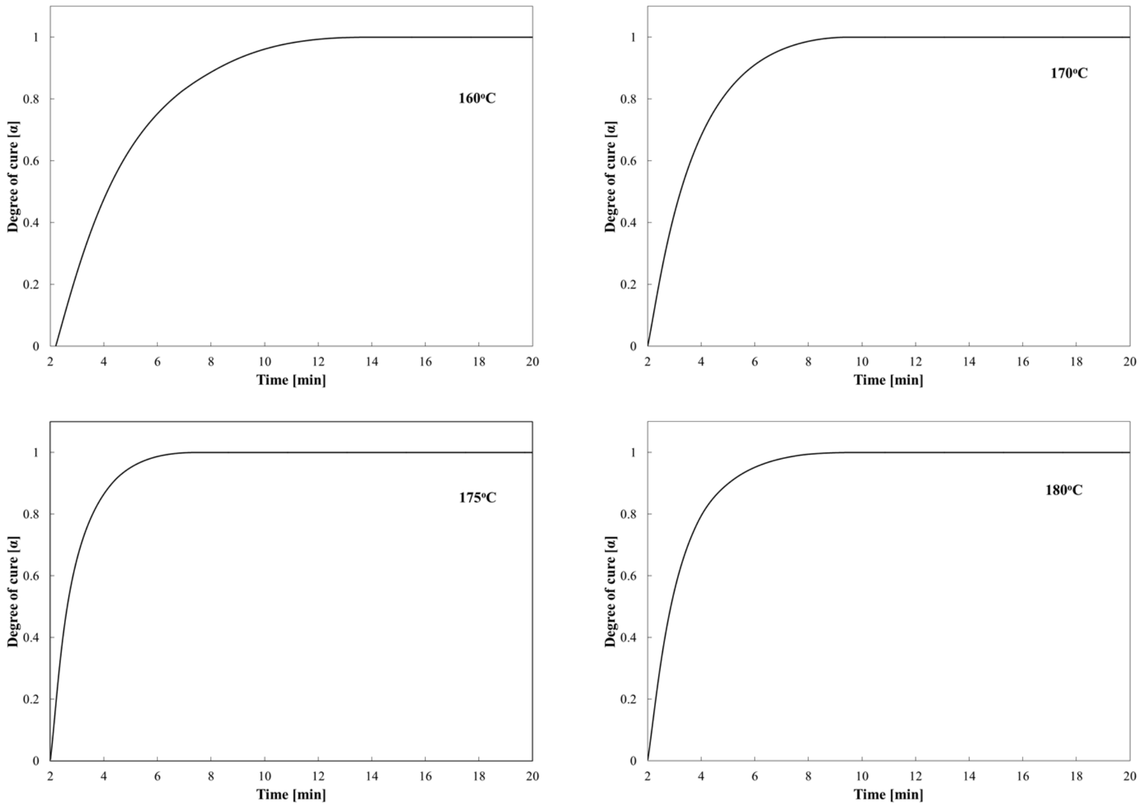

Figure 5.9: Degree of cure of PPF resin curing isothermally 160°C, 170°C, 175°C and 180°C as a function of time

The value for rate constant k(T) and the order of the reaction was determined using following equation derived from the rate of cure-

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln(k) + n\ln(1-\alpha) \qquad \text{eq. 5.7}$$

This empirical rate constant was plotted against (1/T) to determine the goodness of the fit (Figure 5.10) as indicated in the eq. 5.1. Using Arrhenius expression, the frequency factor (A) and the activation energy was found to be: 1.5 x 10^6 min^{-1} and 56.22 kJ/mol respectively.

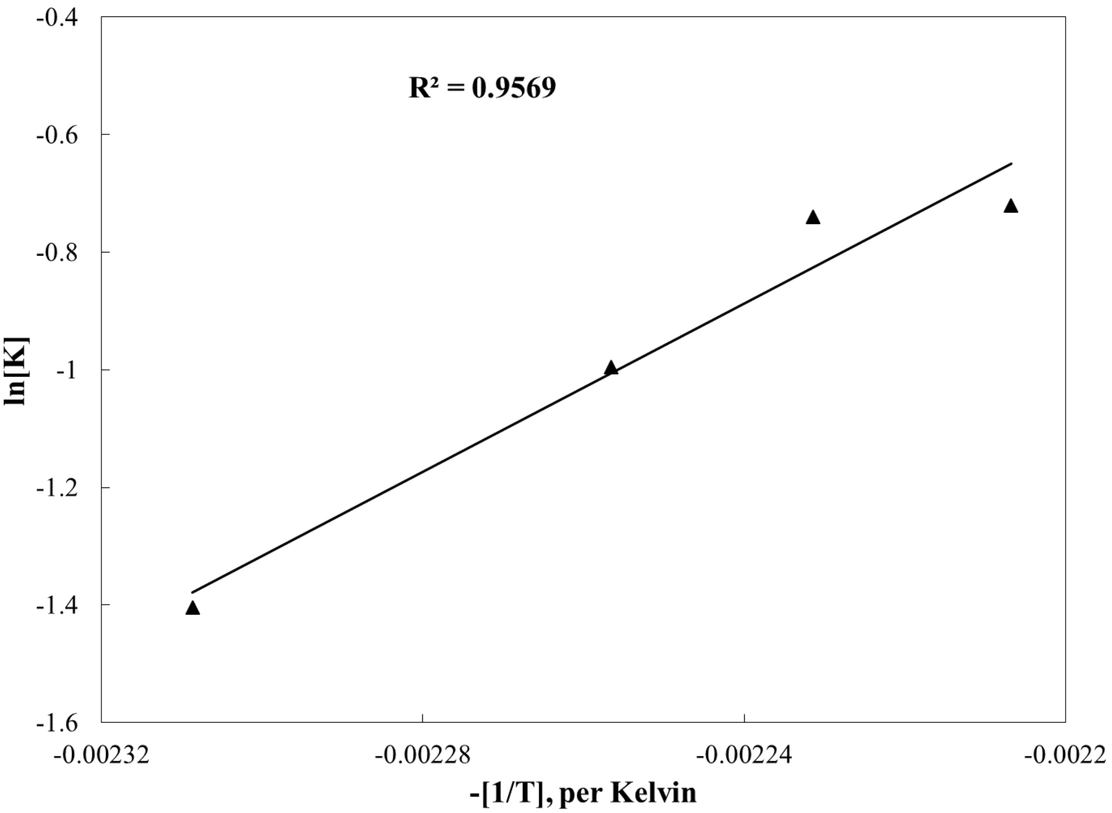

Figure 5.10: Temperature dependence of cure kinetics rate constants (Arrhenius expression)

Table 5.2: Parameter values for nth order kinetic model obtained by fitting to the experimental data

Isothermal temperature [^{o}C]	**Empirical rate constant; K [min^{-1}]**	**Kinetic parameter [n]**	**Goodness of fit [R^{2}]**
160	0.2455	0.6595	0.9819
170	0.3696	0.6481	0.9736
175	0.4770	0.7156	0.9736
180	0.4865	0.7373	0.9737

The rate equation defining the rate of degree of cure as a function of degree of cure and temperature was found to be-

$$\ln(\mathrm{k}) = (-\frac{6762.2}{\mathrm{T}}) + 14.243, \quad \mathrm{R}^2 = 0.9248 \qquad \text{eq. 5.8}$$

$$\frac{\mathrm{d}\alpha}{\mathrm{dt}} = 1.5 \times 10^6 \times \exp(-\frac{6762.2}{\mathrm{T}}) \times (1-\alpha)^{0.69} \qquad \text{eq. 5.9}$$

Similar analysis was performed for the PPF resin and PEGF resin mixtures and the rate constant and the order of cure reaction were determined (Table 5.2). Briefly, the dynamics of this cure was studied using DSC by carrying out this curing reaction isothermally at different temperatures (50^{o}C, 60^{o}C, 80^{o}C and 100^{o}C). This study of cure performed on the resin obtained from the polyester-styrene mixture is very important from the application point of view. For composites this study will be helpful in choosing the appropriate fiber and the temperature for the curing process. Figure 5.11 shows the exotherm observed in DSC, when PPF resin was heated isothermally at different temperatures. It can be clearly seen that the resin cures faster at higher temperature, although there is only a slight difference in time of cure for the temperatures 80^{o}C and 100^{o}C. Also, the maximum peak intensity decreases as the temperature decreases from 100^{o}C to 50^{o}C. Almost similar observation can be seen for the cure exotherm study conducted isothermally at same temperatures for PEGF resin, as shown in Figure 5.12. Although the overall time for the cure for PEGF resin is longer as compared to PPF resin at all temperatures. Again, from Figures 5.10 and Figure 5.12, it is evident that the heat flow rate is a function of temperature and time. With increasing cure temperature, the maximum heat flow rate increases and the time taken for reaction completion decreases.

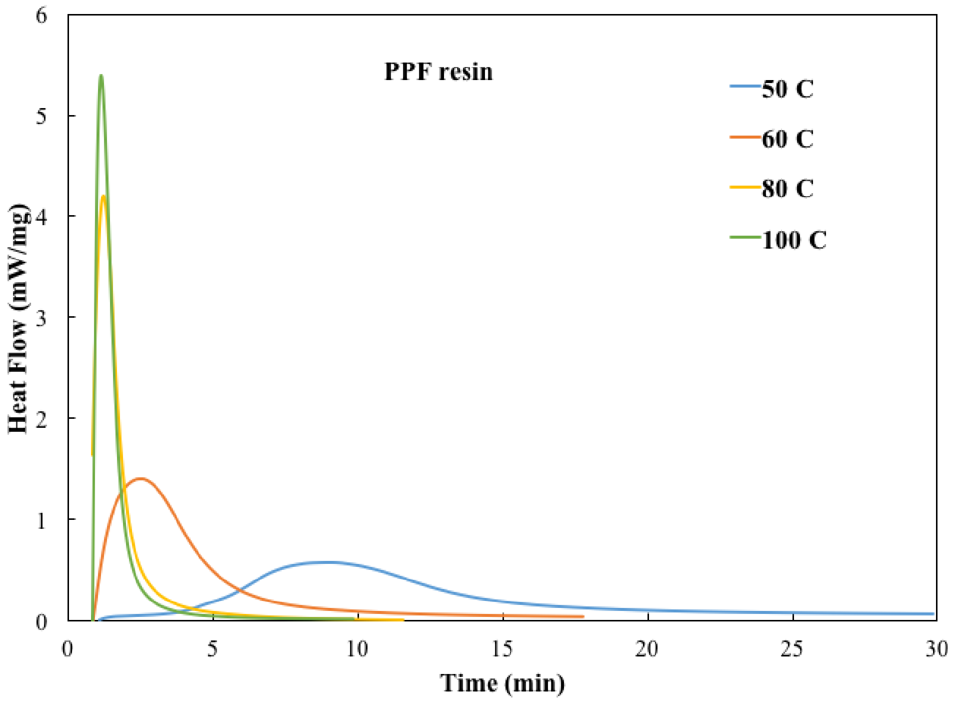

Figure 5.11: DSC curing exotherm for PPF resin, isothermally at different temperatures

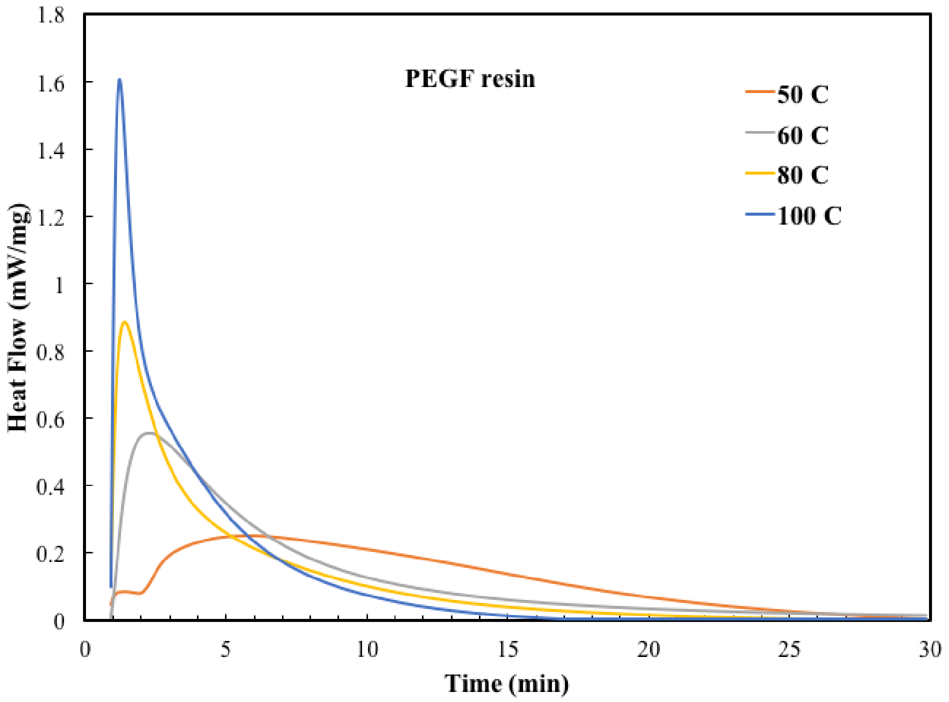

Figure 5.12: DSC curing exotherm for PEGF resin, isothermally at different temperatures

Based on the similar cure kinetic model development for PPF curing, similar calculations were performed for the curing of PPF resin and PEGF resin. The Arrhenius rate constants and the rate of degree of cure as a function of time and temperature was expressed as follows-

For PPF-styrene resin,

$$\ln(\mathrm{k}) = \left(-\frac{5812.8}{\mathrm{T}}\right) + 16.702 \qquad \text{eq. 5.9}$$

$$\frac{\mathrm{d}\alpha}{\mathrm{dt}} = 1.79 \times 10^{7} \times \exp\left(-\frac{5812.8}{\mathrm{T}}\right) \times (1-\alpha)^{0.662} \qquad \text{eq. 5.10}$$

For PEGF-styrene resin,

$$\ln(\mathrm{k}) = \left(-\frac{2690.1}{\mathrm{T}}\right) + 6.5549 \qquad \text{eq. 5.11}$$

$$\frac{\mathrm{d}\alpha}{\mathrm{dt}} = 7.02 \times 10^{2} \times \exp\left(-\frac{2690.1}{\mathrm{T}}\right) \times (1-\alpha)^{0.528} \qquad \text{eq. 5.12}$$

5.3.5 Mechanical properties

Tensile samples of the polyester resins were cured in a silicone molds initially at 80°C for 30 min followed by 3-4 hours curing at RT. Five such samples were prepared for each PEF and PEGF to produce the statistical significant data. Figure 5.13 shows a typical stress-strain curve for PPF and PEGF. Table 2 summarizes the tensile properties of both PPF resin and PEGF resin.

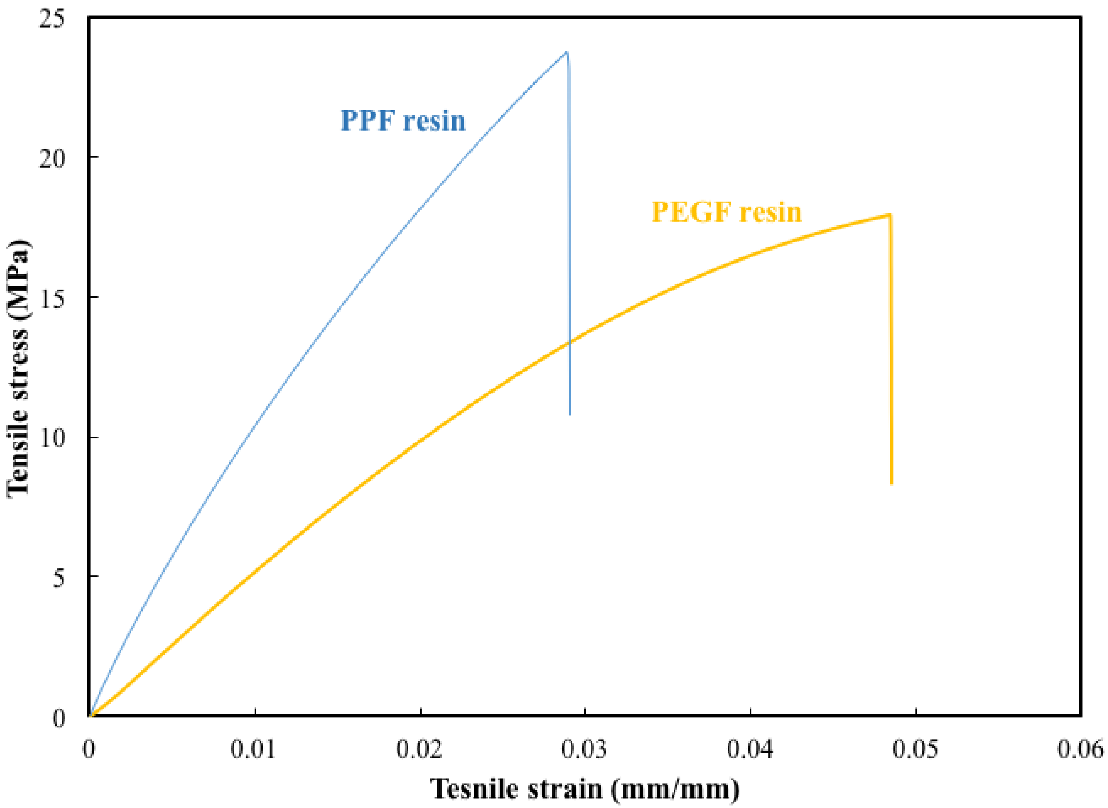

Figure 5.13: Stress-strain curves for PPF resin and PEGF resin

Table 5.3: Mechanical properties of cured resins

Polyester	styrene content (%w/w)	Yield stress (MPa)	Elongation at break (%)	Modulus (GPa)
Polypropylene fumarate (PPF)	30	23.68	3.06	1.03
Poly(ethylene glycol) fumarate (PEGF)	30	14.03	5.31	0.46

It was observed that PPF showed higher yield stress (23.68 MPa) as compared to PEGF (14.03 MPa), although PEGF exhibit more elongation as compared to PPF. This might be attributed to the fact that PEGF was synthesized from PEG which possess higher initial molecular weight (200 g/mole) because of 3 repeating units of ethylene glycol monomer. As a results, the cross-linking density is not as high as compared to PPF where PG is used. Because of this, PEGF showed slightly higher elongation and lower tensile strength. It is also interesting to point out that PEGF resin tensile bars are flexible as compared to PPF resin tensile bars, which can be also attributed to the fact that higher molecular weight linear PEG was used in the preparation of PEGF polyester.

5.3.6 Fiber-reinforced composite application: property predictions

Fiber reinforced plastic composites are widely used since its advent in the early 1900 (with cellulose fiber in phenolics) in diverse fields ranging from sports nets, music instruments to automobile industries[32, 33]. Recently natural fiber-reinforced composites are gaining tremendous importance owing to the increasing environmental consciousness and demands of legislative authorities.

Composites are materials that comprise of load carrying material (known as reinforcement) embedded in a weaker material (known as matrix)[33]. The polymer matrices are broadly classified as thermosetting and thermoplastics which includes- polyurethanes, epoxies, phenolics and unsaturated polyester resins. A polymer matrix is chosen as per the application requirement. For instance, thermosetting matrix [34] provides high strength lot of strength, it doesn’t soften or become moldable when heated (for e.g., epoxies, unsaturated polyester resins). On the other hand, thermoplastics [34]are polymers that require heat to make them processable and on cooling it retains its shape (for e.g., high density polyethylene, low density polyethylene, polylactide and polypropylene etc.). On the reinforcement side of the composites, carbon, glass and aramid fibers are most commonly used fibers in polymer composites[35]. Although, these synthetic polymers provide excellent properties to the composite, they are not biobased and biodegradable and thus, currently lot of attention has been given on developing biobased composites from renewable sources. In that direction, some studies showed better properties of composite where biobased matrix was used with synthetic fibers and also synthetic matrix with biobased fibers [36-40]. Although the mechanical properties provided by biobased composites are not at par with their synthetic counterparts, these recent studies have provided a promising future[40, 41].

Many types of natural fibers have been investigated so far in the manufacture of biobased composites. The most common ones are flax, hemp, straw, wood fiber, kenaf, jute, coconut, banana fiber, pineapple leaf fibers etc[42]. The conventional fibers like carbon, aramid etc., can be produced with a definite range of properties, whereas the characteristic properties of natural fibers vary considerably. This depends on whether the fibers are taken from plant stem or leafs, the quality of plant location, the age of the plant and the preconditioning[43-45]. Also, one of the major advantages with the natural fiber is its cost, which is significantly lower than the conventional synthetic fibers as shown in Table 5.4. It can be clearly seen from the table that these natural fibers could cost as low as 1% of the synthetic fibers like carbon etc.

Table 5.4: Comparison of the price of selective synthetic and natural fibers[46]

Fiber	Cost (US$/kg)
Carbon	200
Glass	30
Sisal	0.36
Jute	0.30
Coir	0.25

In this study, we have chosen four of these fibers namely; jute, hemp, kenaf and cotton to predict the Young's modulus of the final composite material. Table 5.5 shows the mechanical properties of these fibers along with traditional carbon and aramid, which are chosen for the comparison. UPRs, PPF and PEGF, developed in this study were used as the polymer matrices to theoretically develop the composite material. The matrices mechanical properties were previously mentioned in the Table 5.3.

Table 5.5: Physical and mechanical properties of selected synthetic and natural fibers

Fiber	Density [g/cc]	Elongation [%]	Tensile strength [MPa]	Elastic modulus [GPa]	References
Jute	1.3	1.5-1.8	393-773	26.5	[46-48]
Hemp	1.47	2-4	690	70	[47, 48]
Kenaf	1.45	1.6	930	53	[49, 50]
Cotton	1.5-1.6	7-8	400	5.5-12.6	[35]
Aramid	1.4	3.3-3.7	3000-3150	63-67	[47, 51]
Carbon	1.4	1.4-1.8	4000	230-240	[47, 51]

There are different models available in the literature to predict the final composite properties, but for this study we have three basic models:

A. Rule of mixtures (ROM)

B. Inverse Rule of Mixtures (IROM)

C. Halpin Tsai model

The Young's modulus (Y_c) values were predicted using these models. These models briefly describe as follows-

A. Rule of Mixtures (ROM): This is the most commonly used model for predicting the composite properties. The ROM model can be described as-

$$Y_c = (v \times f) + (1 - v) \times f \qquad \text{eq. 5.13}$$

Where,

V= volume fraction of fiber

f= fiber modulus [GPa]

m= matrix modulus [GPa]

B. Inverse Rule of Mixtures (IROM): The IROM model is described as-

$$Y_c = [\left(\frac{v}{f}\right) + \left(\frac{1-v}{f}\right)]^{-1} \qquad \text{eq. 5.14}$$

Where,

V= volume fraction of fiber

f= fiber modulus [GPa]

m= matrix modulus [GPa]

C. Halpin Tsai: The Halpin Tsai model is described as-

$$Y_c = \frac{m\times(1+B\times v)}{1-B\times v} \qquad \text{eq. 5.15}$$

And,

$$B = \frac{\frac{f}{m} - 1}{\frac{f}{m} + 1}$$

Where,

V= volume fraction of fiber

f= fiber modulus [GPa]

m= matrix modulus [GPa]

Figures 5.14 and 5.15 Shows the predicted Young's modulus values using these three different models for different fiber and polymer matrix composites. It can be clearly seen that the results shown by IROM and Halpin-Tsai model are in good agreement as opposed to the results shown by the ROM model. The main reason behind this would be the fact that IROM and Halpin-Tsai models consider the aspect ratio of the fibers in the governing equation, and thus provides better prediction of modulus values. The fiber loading in each case was varied till 50%, but commercially the fiber loading generally doesn’t exceed around 30-35% of the total composite composition. It can be seen that some of the natural fibers like hemp and kenaf showed the modulus similar or higher when compared to aramid fibers. Although, the carbon fibers showed the highest modulus values for any given fiber loading. These observations showed that natural fibers possess potential to deliver similar mechanical properties to the traditional fibers. It should be noted that these values are not the most accurate values, but these values show a trend in the property change as we change the fiber loading.

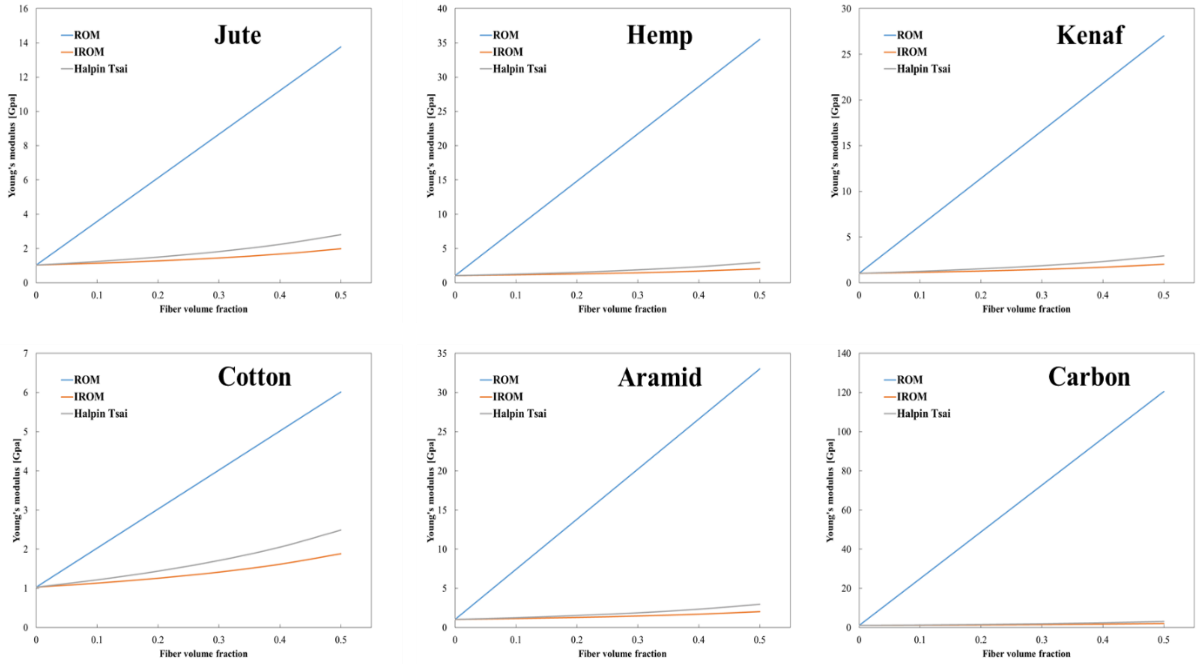

Figure 5.14: Young’s modulus prediction for the composite based on different models using PPF-styrene resin and PEGF-styrene resin and different natural fibers (jute, hemp, kenaf and cotton) and conventional fibers (aramid and carbon)

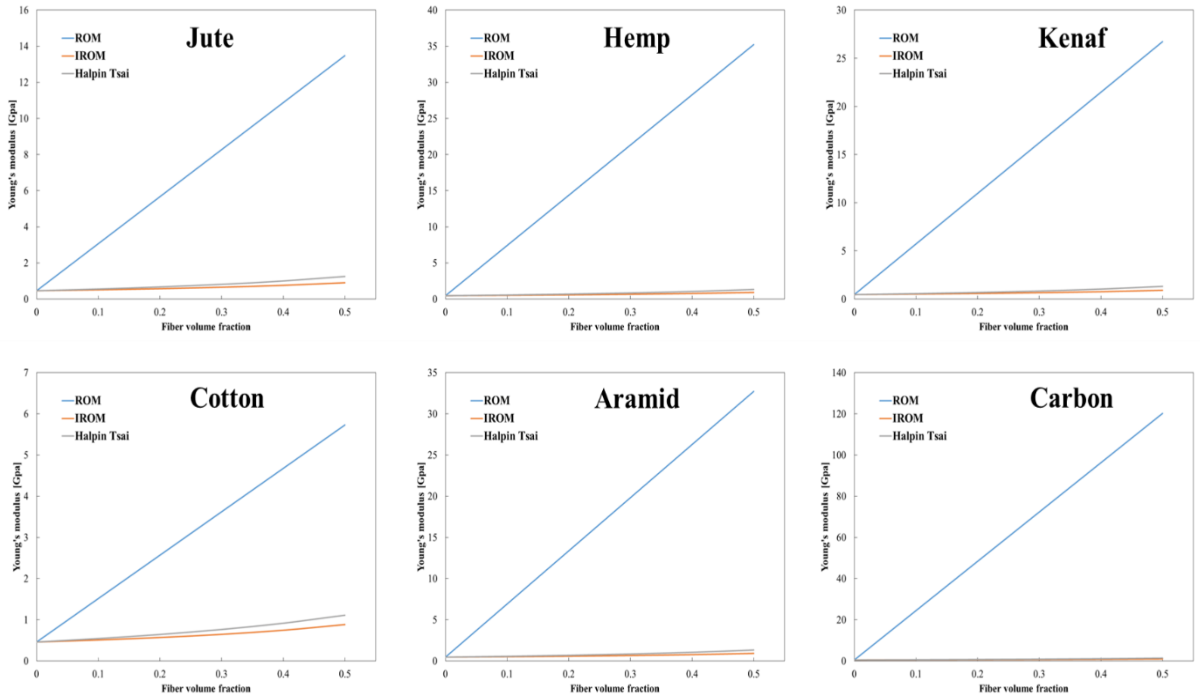

Figure 5.15: Young's modulus prediction for the composite based on different models using PPF-styrene resin and PEGF-styrene resin and different natural fibers (jute, hemp, kenaf and cotton) and conventional fibers (aramid and carbon)

5.4 Conclusions

In this study, biobased thermosetting resins were prepared from unsaturated polyester synthesized using fermentation derived fumaric acid and, propylene glycol and polyethylene glycol which are also available from renewable sources and, their fundamental properties were investigated. Fumaric acid provides an advantage of being 100% biobased and non-toxic feedstock. These thermosetting resins can serve as a potential biobased substitute for petroleum-based matrix for fiber-reinforced composite applications. The mechanical properties of the UPRs were found to be in agreement to the literature. The study of cure kinetics will be helpful in determining the cure conditions for these resins at different cure temperatures, which will be helpful for the composite manufacturing and the fiber selection for the same. Finally, the predicted properties for the fiber-reinforced composites using natural fibers like jute, hemp, kenaf and cotton shows a promising future for biobased thermosetting resin when compared to their petroleum-based counterparts.

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6. SUMMARY AND FUTURE WORK

This thesis focused on developing two biobased products- (a) an organosilicon material using soybean oil and vinyltrimethoxy silanes for paper coatings and elastomer application and, (b) UP based on fermentation derived fumaric acid for thermosetting resin applications. The primary aim of this work is to demonstrate the use of biobased materials for variety of industrial application. With depleting petroleum resources and increasing awareness about sustainable development, it is important to find renewable materials to replace fossil-based materials with commercial viability.

In our work, we have synthesized and characterized silylated soybean and explored its application as a moisture resistant coating material and as an elastomer to be used in adhesives and sealants. In chapter 2, we have presented a novel silylation technique of internal double bonds that cannot be accomplished by conventional hydrosilylation. The grafting of vinyltrimethoxy silane on internal double bonds of the fatty acids of triglycerides by the 'Ene' reaction is a novel approach compared to the traditional method of hydrosilylation, which is limited to terminal double bonds. The process involves a simple one step reaction of vinylsilanes via the 'Ene reaction' mechanism which is particularly useful since these silanes do not undergo thermal polymerization. The silylation reaction is safe, convenient and does not require a solvent. The silylated vegetable oil products can then be cured by moisture via hydrolysis of the methoxy groups followed by silanol condensation to form stable siloxane crosslinks. Different natural oils were silylated with vinyltrimethoxysilane by this route and the products were characterized by ^{1}H NMR and TGA analyses that confirmed the success of the grafting reaction. The kinetics of the silylation reaction was studied and the reaction was found to follow second order kinetics. A potential application as a moisture activated cure for coatings was also presented.

On exposure to moisture, the silylated soybean oil forms a cross-linked network through stable siloxane (Si-O-Si) linkages which provides excellent moisture barrier. This attribute was used for the paper coating application, as described in detail in chapter 3 of this thesis. The most common paper used in paper packaging industry, kraft paper, was coated with silylated soybean oil at room temperature in the lab. The curing kinetics of this coatings on the paper was studied as a function of catalyst concentration, moisture content in order to create the optimum formulation. Followed by our success at lab-scale coatings, we successfully demonstrated a pilot scale up of the paper coating application where we coated over 50,000 sq.ft. of kraft paper on commercial gravure roll coaters at Sierra Coatings (De Pere, WI). These biobased and marine biodegradable coated papers were then used to prepare paper bags by Northern Technologies International Corporation (Minneapolis, MN). These coated papers bags are being used on ships by the US Navy for collection food and other bio-wastes that can be discharged into the ocean where the paper as well as the coatings will completely biodegrade.

In the following chapter 4, we have utilized the inherent flexible nature of Si-O-Si linkages in polysiloxanes to develop elastomeric reactive blends using silylated soybean oil and methoxy terminated silylated polyurethanes (Polysil-UR). These stable homogeneous blends are prepared by introducing grafted alkoxysilanes on the soybean oil and terminal polysiloxanes. Upon exposure to moisture, the hydrolysis and subsequent condensation of the resulting silanols lead to siloxane crosslinks between the two phases that prevent gross phase separation and the formation of a uniform network. The preparation process is simple and consists of mixing these reactive components and casting films. The morphology, mechanical properties and network formation were investigated as a function of the composition. These resulting products provide a synergistic combination of properties that are different from the properties of the individual components or those achieved by copolymerization techniques. Thus, products ranging from high modulus, tensile strength resin-like materials to high elongation elastomers can be obtained. Furthermore, the use of natural oil triglycerides in combination with a linear silicone polymer is new and should be of a broad interest to other researchers who are looking to use biobased materials in combination with traditional polymers. Unlike previous research works in this field that are limited to preparation of reactive blends with castor oil and rely on the presence of hydroxyl groups on the fatty acids, the current work is more general and can utilize any vegetable oil that contains unsaturated fatty acids. To the best of our knowledge, no similar reactive blends containing polysiloxanes and vegetable oils are reported in the literature.

The simple moisture curability through silanol condensation of silylated soybean oil provides an opportunity for exploring different potential applications. For instance, it can be used to coat substrates like wood and metals where its moisture resistance property would be of great importance. Silylated soybean oil offers a great value proposition based on simple synthesis process, ease of processibility due to low viscosity and faster cure rates upon moisture contact. We have established its ability to reactively blend with polysiloxanes, in the similar way it can react on hydrolysis with the most common silicate- tetraethyl orthosilicate (TEOS) as shown in Figure 6.1. The resin that will be produced by this reaction can potentially perform similar to the traditional unsaturated polyester resin.

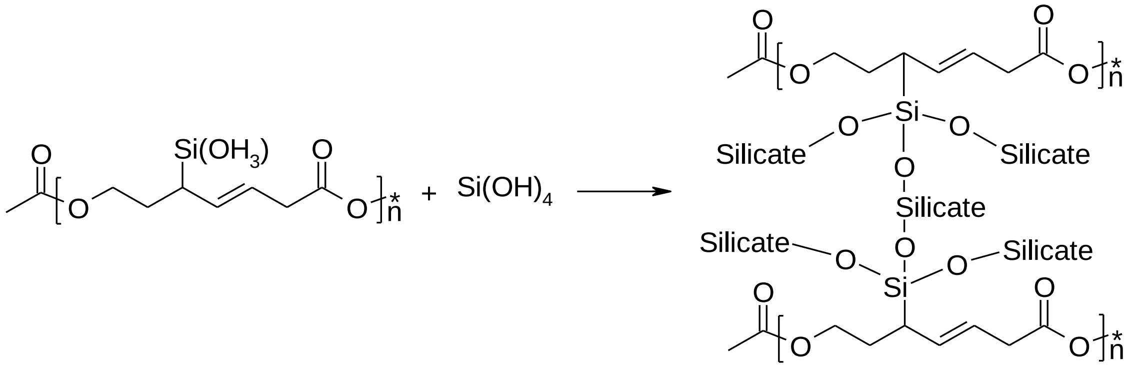

Figure 6.1: Unsaturated polyester-silicate resin

Traditionally in unsaturated polyester resins, styrene is the most commonly used reactive diluent essentially because it is low in cost, can give low viscosity resins at reasonable monomer levels and is copolymerizes in either room temperature or elevated temperature. However, the styrene monomer is volatile and toxic, thus working with it always represents a health issue as the styrene in the air must be kept below 50 to 100 ppm. Furthermore, due to the styrene monomer present in UP, these liquid resins have a flash point below 37.8°C and are therefore classified as flammable liquids, which require a Department of Transportation (DOT) Red Label. In our proposed resin, low cost tetraethyl orthosilicate (TEOS) is used instead of the styrene to reduce the viscosity of the mixture. Since the inorganic silicate is non-flammable and non-toxic, there are no issues with flammability or toxicity. Unlike conventional process where the resin is prepared by free radical polymerization, the low viscosity mixture in our resin is polymerized by condensation polymerization at moderate temperatures (~80°C) to yield a tough, optically transparent resin, based on our preliminary experiments. Another advantage for the polyester-silicate resin would be the inherent low viscosity of silylated oil, which eliminates the use of any reactive diluents like styrene. Furthermore, the bio-based content of UPR is low since styrene is still the most commonly used crosslinking material; styrene is not available from renewable resources and hence only the raw material basis for the polyester backbone can be readily made more sustainable. Therefore, the final “bio-content” of the manufactured ecofriendly product lines are still rather low (8 - 22% for the Envirez product line, 10 - 30% for the EcoTek line, and 12 - 35% for the Envirolite line from Ashland Inc.)[1]. The bio-content of our unsaturated polyester-silicate resins is close to 100%. Finally, UPRs faces an issue of weak interface between the resin and common filler materials like glass beads, glass fibers etc. With the use of silicates, an excellent compatibility with such filler materials is expected. So, we believe that developing such polyester-silicate resins would be attractive route to find replacement for traditional styrene based UPRs for industrial application.

Finally, in the last chapter of this thesis i.e., Chapter 5, a biobased thermosetting resin was prepared using fermentation derived fumaric acid. An unsaturated polyester was prepared via traditional two-step polycondensation route using glycols that are commercially available from renewable sources. This work was driven by an increasing demand for thermosetting resins that can be used for composite applications. UPRs are common type of thermosetting resins and there are several thermosets from renewable resources (for e.g., vegetable oil, iso-sorbide, itaconic acid etc.) are studied so far. Traditionally, phthalic acid/anhydride is widely used as a monomer because of low-cost. However, fumaric acid provides value proposition since it is biobased and non-toxic monomer feedstock for UP production. Thermosetting resins were developed using traditional cross-linking chemistry, the cure kinetics was studied and the mechanical properties of the final cured resin were measured and reported. Further, with the help of existing models, the mechanical properties of the final composite with some natural fibers were predicted. This study demonstrates one potential replacement of the traditional thermosetting resins.

Again, in the production of such thermosetting resins, styrene is heavily used as a cross-linker, and there are many opportunities in developing a material, preferably from renewable resources which can be completely or partially substitute for styrene in developing UPRs (Environmental Protection Agency, Fed Register 68, (2003), 19375–443). Recently, vinyl levulinate, completely biobased vinyl monomers, was used as a replacement for styrene and similar mechanical properties were reported [2-4]. Vinyl monomers developed from fatty acids have been used as a styrene replacement. For example, recently a low viscosity (~1cP) vinyl monomer was prepared by methacrylating fatty acids (made from soybean oil) and used as a reactive diluent to prepare UPR [5-7] in Wool research group at university of Delaware. Likewise, in our preliminary experiments, however we attempted to use fatty acid ally ester developed from plant oils [8] to partially replace styrene in UPR preparation. These allyl esters were prepared by transesterification reaction of triglycerides of soybean oil with ally alcohol at high temperature (90^oC– 100^oC), in the presence potassium hydroxide as a catalyst. Glycerol is the by product in this reaction and provides a way to characterize the extent of the reaction. The triglyceride structure breaks down to individual fatty acids with allyl group at the end of the long chain, which is expected to provide the necessary unsaturation for crosslinking. In the primary results, allyl esters showed a good compatibility with styrene and the UP until styrene concentration of 50%, beyond which styrene started to phase separate. It would be interesting to study the mechanical properties of the final UPR prepared by varying the amounts of styrene and allyl ester.

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