ALKYD-BASED HIGH-SOLID AND HYBRID ORGANIC COATINGS

A Dissertation

Presented to

The Graduate Faculty of The University of Akron

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

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May, 2015
ALKYD-BASED HIGH-SOLID AND HYBRID ORGANIC COATINGS

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ABSTRACT

Alkyds are polyesters derived from oils, dibasic acids and polyols and one of the most commonly used binders for several coating applications such as architectural and wood coatings. Conventional solvent-borne alkyd coatings generally contain 30-60 wt% solvents which contribute to hazardous volatile organic compounds (VOCs) emission. This dissertation focused on the development of high-solid alkyd coating systems with reduced VOC content. This was done by the substitution of organic solvents in coating formulations by using reactive diluents derived from renewable materials. Soybean oil was modified in two steps: 1) conjugation of soybean oil, 2) Diels-Alder addition with 3-(trimethoxysilyl)propyl methacrylate, 2,2,2-trifluoroethyl methacrylate, and triallyl ether acrylate. The structures were characterized using $^1$H NMR, $^{13}$C NMR, $^{13}$C-$^1$H gradient heteronuclear single quantum coherence (gHSQC) NMR spectroscopy and MALDI-TOF mass spectrometry. The $^{13}$C-$^1$H gHSQC NMR spectra confirmed the formation of a cyclohexene ring in all reactions, indicating a Diels-Alder addition.

A long oil soy-alkyd was formulated with three modified soybean oils. Allyl ether-functionalized soybean oil resulted in the highest reduction in the viscosity of the alkyd formulations. The siloxane and allyl ether-functionalized soybean oil enhanced the tensile modulus and crosslink density by 20 % and 70 %, respectively. Coatings with
fluorine-functionalized soybean oil showed enhanced contact angle and solvent resistance, compared to alkyd coatings.

Alkyd-acrylic hybrid coatings are gaining considerable attention due to their ability to combine the beneficial properties of both. Alkyd-acrylic copolymers were synthesized using a combination of step polymerization and reversible addition fragmentation transfer (RAFT) polymerization. FT-IR studies indicated that the autoxidative curing of RAFT polymerized alkyd-acrylic coatings was hindered. A model compound study showed that thiocarbonyl functionality in RAFT agent interferes with autoxidative curing reactions. $^{13}$C NMR spectra confirmed that the thiocarbonyl functionality interferes with autoxidation reaction.

The second half of this dissertation focused on the development of novel alkyd-acrylic copolymers for coating applications using a combination of step polymerization and atom transfer radical polymerization (ATRP). Copolymers were characterized using quantitative $^1$H NMR, $^{13}$C NMR and gradient heteronuclear multiple bond correlation (gHMBC) 2D-NMR spectroscopy. Quantitative $^1$H NMR analysis assisted in the determination of molecular weights and confirmation of protection of unsaturated bonds on fatty acid chains in the alkyd. The performance of autoxidatively cured alkyd-acrylic hybrid coatings was evaluated. Tensile, viscoelastic and general coating properties were investigated to evaluate the coating performance. Alkyd-acrylic copolymer coatings showed improved hardness, glass transition temperature and drying time. General coating properties such as cross-hatch adhesion, MEK resistance, and impact resistance were maintained, except at higher acrylic concentrations.
ACKNOWLEDGEMENTS

It would not have been possible to write this doctoral dissertation without the help and support of the kind people around me, to only some of whom it is possible to give particular mention here.

First, I offer my sincere gratitude to my advisor Dr. Mark D. Soucek, who has supported me throughout my time at the University of Akron with his patience and knowledge while allowing me the room to work in my own way.

I would like to thank Dr. Coleen Pugh for her insightful discussions, and valuable advice. I also would like to thank Dr. Kevin Cavicchi, Dr. Thein Kyu and Dr. Chrys Wesdemiotis for their time and support. I would like to thank the University of Akron Magnetic Resonance Center, Dr. Venkat Dudipala, Stephanie Bilinovich, Chun Gao and Jessi Baughman for their experimental support and valuable discussions. I am thankful for the financial support from the Ohio Soybean Council for soybean oil-based research.

In my daily work I have been blessed with a friendly and cheerful group of colleagues at the Department of Polymer Engineering. I would like to thank them for their support.
I would like to express my heartfelt gratitude to my parents for all of their love and support throughout my life. Finally, I want to thank my better half, Sahil who has supported me throughout this process and has constantly encouraged me when the tasks seemed arduous and insurmountable.
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CHAPTER I

INTRODUCTION

Alkyds are polyesters derived from oils, dibasic acids and polyols.\(^1\) The oils used for synthesizing alkyds generally include soybean, linseed, tung, safflower oil. Alkyds are one of the most commonly used binders for "oil based" coating applications including architectural coatings, wood coatings, etc. Alkyd based coatings can either be crosslinked via autoxidation or by using a crosslinking agent such as isocyanate, melamine-formaldehyde or urea-formaldehyde. Alkyds used in this study are all crosslinked via autoxidation curing process. Alkyd based coatings are mainly known for their low cost, fewer film defects during application, high gloss, being derived from renewable sources like vegetable oils and their ability to undergo autoxidation after application.\(^1\) However, alkyds have some disadvantages such as poor outdoor durability and poor water, acid and alkali resistance. Moreover, they often need organic solvents to achieve appropriate viscosity for their application.

Organic solvents used during application evaporate as volatile organic compounds (VOCs). The deleterious impact of solvent emission on the environment and human health is the main driving force to develop "Low VOC" coatings. Several techniques such as powder coatings, water-borne coatings, radiation curable coatings and high solid coatings have been studied to reduce VOCs. High solid coatings are gaining considerable
attention due to their environmental performance, and economic benefits. The use of reactive diluents is an effective means of achieving high solid alkyd formulations. If the reactive diluent is derived from a renewable source like vegetable oil, it will provide biodegradable properties to the film. Tung oil based reactive diluents were developed by Soucek and coworkers\(^2\) in 2010. However, this approach has limitations such as rapid discoloration and relatively high cost of tung oil. Soybean oil, on the other hand, is a widely available and inexpensive plant based feedstock, making it an attractive choice for use as a reactive diluent.

The first objective (Chapter III) of this work was to synthesize soybean oil based reactive diluents for alkyd coatings. Soybean oil was modified via Diels-Alder reaction in such a way that it provides additional functionalities for crosslinking. Fluorine, allyl ether and siloxane functionalized soybean oils were synthesized. Allyl ether and siloxane functionality participate in the film formation via autoxidation and sol-gel reactions respectively. While fluorine functionality does not participate in the film formation, it is designed as a surface-modifying reactive diluent. 1D and 2D-NMR spectroscopy and mass spectrometry techniques were utilized to confirm the cycloaddition.

Several oil-based reactive diluents have been studied\(^3\),\(^4\). The key technical challenges for developing a reactive diluent is achieving an appropriate viscosity for the application and coating performance comparable to that of conventional coatings. Hence, the subsequent focus of this work (Chapter IV) was on the formulation of modified soybean oils in alkyds and evaluation of coating performance. Allyl ether and siloxane functionalized soybean oil are expected to improve crosslink density of the coatings since
they provide addition sites for crosslinking. Fluorine-functionalized soybean oil is expected to improve surface properties and solvent resistance.

As mentioned earlier, alkyds exhibit poor outdoor durability and poor hydrolytic resistance. Acrylates, on the other hand, have better abrasion resistance, hydrolytic stability, exterior durability and superior mechanical properties. Hence, alkyd-acrylic hybrid coatings offer a combination of both. Several researchers developed alkyd-acrylic copolymers for coating applications. However, these approaches involved reaction of unsaturated bonds on fatty acid chain with acrylics. This resulted in a longer through-dry time and poor autoxidation curing.

Soucek and coworkers developed alkyd-acrylic copolymers by using reversible addition fragmentation chain transfer (RAFT) radical polymerization technique. Alkyd macro RAFT agent was synthesized by attaching RAFT agent telechelically onto the alkyd backbone chain. Then it was used to polymerize different acrylic monomers by a RAFT-mediated process. Maximum acrylic grafting to the alkyd chain was achieved without reacting unsaturated bonds on the fatty acid chains. However, it is assumed that the thiocarbonyl functionality on RAFT polymerized acrylated alkyd inhibits its autoxidative curing. To the best of our knowledge, there are no reports of RAFT agents hindering autooxidation process. Hence, Chapter V focuses on the confirmation of inhibition of autoxidation by thiocarbonyl functionality using FTIR.

With the need for developing alkyd-acrylic copolymers without reacting unsaturated sites on fatty acid chains, a new synthetic pathway that does not hinder the autoxidation is highly desirable. Chapter VI focuses on the synthesis of alkyd-acrylic
copolymers via atom transfer radical polymerization (ATRP) technique. ATRP technique, which is expected to protect unsaturated sites on fatty acid chains, was studied using quantitative $^1$H NMR spectroscopy. Moreover, 2D-NMR spectroscopy was utilized to confirm the acrylic grafting on alkyd backbone chain. Alkyd-acrylic copolymers coatings synthesized via ATRP technique are expected to cure via autoxidation. Hence, Chapter VI also focuses on the formulation and evaluation of alkyd-acrylic copolymer coatings. Coating performance was evaluated by studying tensile properties, viscoelastic properties and general coating properties.
CHAPTER II
BACKGROUND

2.1 Vegetable oils

Vegetable oils are triglycerides, triester of glycerol and fatty acids (Figure 2.1), reacts with oxygen to form solid film. Vegetable oils were used as a binder in most paints in the 19\textsuperscript{th} and early 20\textsuperscript{th} centuries. Oils have also been used for illumination and lubrication purposes.\textsuperscript{8} Although their use as a binder has decreased, they are still an important raw material for other binders such as alkyd, uralkyd, epoxy, polyesteramide.\textsuperscript{1,9,10} Outstanding features like inexpensive, abundant, renewable, biodegradable, non-toxic with their unique chemical structure with unsaturated sites, epoxy, hydroxyl, ester functionalities makes them an attractive feedstock for coatings. Oils used in coatings applications usually have fatty acids with 18 carbon atoms, as listed in Figure 2.2. The letters \textit{c} and \textit{t} denote \textit{cis} and \textit{trans} orientation of double bonds, respectively. The numbers represent the position of the first carbon of the double bond.
Oils are mixtures of triglycerides of various saturated or unsaturated fatty acids. The fatty acid composition of the oil may vary with variation in climate, soil composition, plant strain and other growth conditions. Oils used in coatings and their typical fatty acid composition are listed in Table 2.1. Oils are classified as drying, semi-drying and non-drying oils based on their iodine value. Rheineck et al. defined drying oils as those with iodine value greater than 140; semi-drying oils as those with iodine value 125 to 140; and non-drying oils as those with iodine value less than 125. Non-conjugated oils can also be classified based on their drying indices. The drying index of a non-conjugated oil can be calculated using Equation 2.1. An oil is a drying oil if the drying index is greater than 70. Using Equation 2.1 and the data from Table 2.1, the drying index of soybean oil is 69 and that of linseed oil is 120. Hence, soybean oil is a semi-drying oil and linseed oil is a drying oil.

\[
drying\ index = (\% \ linoleic\ acid) + 2(\% linolenic\ acid)\]  \tag{2.1}

2.1.1 Soybean oil

Soybeans are one of the dominant oilseed produced in the United states, accounting for about 90 percent of oilseed production. Growth of soybean acreage is
favored due to its planting flexibility, high yields from narrow-rowed seeding practices, low production costs. Moreover, soybeans have high protein content (~40%) and good oil content (~20%). Soybean oil is a semi-drying oil and its typical fatty acid composition is given in Table 2.1.

Figure 2.2. Commonly used fatty acids in coatings.
# Table 2.1. Fatty acid composition of oils.

<table>
<thead>
<tr>
<th>Oil</th>
<th>Fatty Acid (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Saturated(^a)</td>
</tr>
<tr>
<td>Soybean</td>
<td>15</td>
</tr>
<tr>
<td>Sunflower</td>
<td>9</td>
</tr>
<tr>
<td>Safflower</td>
<td>11</td>
</tr>
<tr>
<td>Linseed</td>
<td>10</td>
</tr>
<tr>
<td>Castor</td>
<td>3</td>
</tr>
<tr>
<td>Palm</td>
<td>49</td>
</tr>
<tr>
<td>Tung</td>
<td>5</td>
</tr>
<tr>
<td>Maize Oil</td>
<td>13</td>
</tr>
<tr>
<td>Coconut</td>
<td>91(^d)</td>
</tr>
</tbody>
</table>

\(^a\)Saturated fatty acids include stearic (C\(_{18}\)) and palmitic (C\(_{16}\)) acids.

\(^b\)Ricinoleic acid.

\(^c\)α-Eleostearic acid.

\(^d\)Coconut oil also contains C\(_{8}\), C\(_{10}\), C\(_{12}\) and C\(_{14}\) saturated acids.

## 2.2 Autoxidative curing

After oil based coating is applied to a substrate, the films get solidified after curing via autoxidation. The reactions taking place during autoxidative curing are complex. Modern analytical techniques have made it possible to study the exact mechanism of autoxidation. A simplified mechanism of the autoxidation of linoleate moiety leading to a dry film is illustrated in Figure 2.3. The reaction proceeds by a free
radical chain mechanism and can be described in following stages: induction period, initiation, propagation and termination. Induction period exists due to the natural antioxidants such as α- and β- tocopherols, β-carotene.

Initiation reaction involve oxygen attack on the double bond with the formation of a hydroperoxide and a simultaneous rearrangement of the linoleate to conjugated double bonds as shown in Equation 2.15,16 The hydroperoxide further decomposes to either peroxy or alkoxy radical. The activation energy to cleave the O-O bond is ~46 kcal/mol lower than that to cleave the O-H bond.17 Radicals formed in Equation 2.2 can further abstract a hydrogen from linoleate to form an alkyl radical as shown in Equation 2.3. The activation energy required to abstract H in allylic and double allylic positions is ~75 kcal/mol and ~50 kcal/mol respectively.16,18 Propagation reactions involving addition of radicals to double bonds occur in early stages due to the presence of reactive conjugated dienes.19,20 However, unlike most free radical chain processes the carbon, alkoxy and peroxy radicals have very low propensity to add or propagate through the alkenes. The oxygen uptake is very fast and hence propagation via addition of radicals to double bond is not significant.21,22 Termination reactions also involve radical recombination to form C-C, ether and peroxy linkages. Muizebelt et al.23 studied the oxidative crosslinking of unsaturated fatty acids using IR, NMR and pyrolysis/GC/MS and concluded that crosslinking occurs by formation of ether and peroxy bonds. The formation of C-C crosslinks was not significant.23,24

Mallegol et al.21 explained the decrease in the concentration of unsaturation by easy addition of peroxy radicals on the conjugated double bonds, which produces epoxy groups as shown in Figure 2.4. The epoxy formed are unstable and are only intermediates
in saturation reaction.\textsuperscript{22} Radicals can further undergo β-scission to produce volatile and non-volatile low molecular weight oxygenated compounds such as aldehyde, acids, ketone as shown in Figure 2.5.\textsuperscript{25,26,27,28,29,30} Hancock et al.\textsuperscript{31,32} evaluated formation of different by-products during autoxidation. β-Scission reaction occurs when a hydroxyl group is alpha to conjugated double bonds. Russell\textsuperscript{33} proposed and Nakano et al.\textsuperscript{34} studied the termination process for secondary peroxy radicals, which involves formation of a tetraoxide intermediate to produce a ketone, an alcohol and oxygen as shown in Figure 2.6. Different radical species formed during autoxidation can recombine and lead to the formation of a three-dimensional network, which is responsible for the curing of the film.

In this work, allyl ether and conjugated double bond functionalities are also utilized for autoxidative curing. Figures 2-7 and 2-8 show the initiation reaction of allyl ether and conjugated double bonds respectively during autoxidative curing. Termination reactions are similar to those of linoleate system. Muizebelt and coworkers\textsuperscript{46} demonstrated that allyl ether reacts faster during autoxidation than the linoleate fatty acid.
Figure 2.3. Autooxidation process.

Figure 2.4. Epoxide intermediates during autooxidation process.
2.3 Alkyds

Alkyds are one of the most important class of coatings today, albeit not the largest in market volume. Alkyd is a term applied to a group of synthetic resins
best described as fatty acid modified polyester resin. This special class of polyesters is derived from naturally occurring oils, polyols, and dibasic acids. The oils utilized in the alkyd synthesis include soybean, sunflower, tung and linseed oil. The major advantages of alkyds are lower cost, fewer film defects during application and post-application increase in glass transition temperature ($T_g$) via auto-oxidative curing of the fatty acid unsaturation.

Alkyds can be oxidizing or nonoxidizing.\(^1\) Oxidizing alkyds crosslink via autoxidation mechanism similar to drying oils. Nonoxidizing alkyds are used as polymeric plasticizers or as hydroxyfunctional resins, which are cross-linked by melamine–formaldehyde (MF), or urea–formaldehyde (UF) resins or by isocyanate cross-linkers. In this work oxidizing alkyd has been utilized for all studies. Oxidizing alkyds are further classified into three types: short, medium and long oil length alkyds. The oil length of an alkyd is calculated by dividing the amount of “oil” in the final alkyd by the total weight of the weight of all ingredients minus water evolved in reaction, expressed as a percentage (Equation 2.16).

\[
\text{Oil Length} = \frac{\text{weight of oil}}{\text{weight of all ingredients–water evolved}} \times 100 \quad 2.16
\]

Alkyds with oil length greater than 60 are long oil alkyds, those with oil length in the range 40-60 are medium oil alkyds and those with oil length smaller than 40 are short oil alkyds.

Alkyds can be synthesized via the monoglyceride process or the fatty acid process. The monoglyceride process is a two step process as shown in Figure 2.9. The
first step involves formation of monoglyceride from the reaction of oil (triglyceride) and polyol, e.g., glycerol. The monoglyceride formed is then polymerized with dibasic acid e.g. phthalic anhydride(PA) to afford the alkyd resin. Since PA is not soluble in the oil and is soluble in glycerol, transesterification of oil and glycerol is carried out as a separate step before the addition of PA.\(^1\) Although the first step involves monoglyceride formation, the reaction mixture also includes unreacted glycerol, diglyceride and unreacted oil. Fatty acid process on the other hand, is a one step process which involves step polymerization of fatty acid, polyol and dibasic acid as shown in Figure 2.10. Any type of oil can be saponified and fatty acids can be produced. However, cost of separation and purification of fatty acids increases the cost of the alkyd. Fatty acid process provides compositional control of the resin, while monoglyceride process is the more economical process.

\[ \text{Oil} + \text{Glycerol} \xrightarrow{\text{Catalyst} \ \text{heat}} \text{Monoglyceride} \]

\[ \text{Monoglyceride} + \text{Phthalic anhydride} \xrightarrow{-\text{H}_2\text{O}} \text{Alkyd resin} \]

\( R = \text{Fatty acid chain} \)

Figure 2.9. Synthesis of alkyds via monoglyceride process.
2.4 Need for VOC reduction

Alkyd resins are viscous and tacky materials which makes them difficult to handle. Generally, these handling problems are overcome by dissolving the resins in organic solvents, which evaporate during paint drying into the atmosphere as VOC. Alkyds are generally formulated with solvents to obtain an appropriate viscosity for the application. Hence, they are termed as solvent-borne paints. Conventional solvent-borne coatings generally contain 30-60% volatile materials.\(^1\) Toxicity of a solvent and extent of exposure are the two major aspects of studying the toxic risks. Exposures such as ingestion or spillage is dangerous, but appropriate measures are taken to avoid these exposures. Inhalation of solvents is unavoidable during paint drying stage when the solvent evaporates. Hence, during coating formulation, it is important to choose the appropriate solvent to prevent a detrimental impact on the health of the consumer. It is important to read the material safety data sheets (MSDS) and follow appropriate safety measures while using toxic solvents on large basis.

Several researchers\(^{35,36,37}\) studied the concentration and sources of VOCs due to their adverse effect on human health and environment. Solvent-borne coatings being a
major source of VOCs, reduction of VOCs in paints has been an important goal in coatings research in recent years.\textsuperscript{38,39,40,41} The Environmental protection agency (EPA) listed hazardous air pollutants (HAP) on the basis of their toxicity data and set the limit for the usage for paint applications.\textsuperscript{42,43} According to federal standards, VOC content can be no more than 250 g/l and 380 g/l in flat paints and in non-flat, high gloss coatings respectively. The VOC content limit in Pennsylvania, northeastern and mid-Atlantic states limit is much lower at 100 g/l for flat paints and 250 g/l for others. Aromatic solvents such as toluene and xylene dissolve resins better and hence, are used at low levels in coating industries despite being on the HAPs list. Ketones such as methyl ethyl ketone, methyl isobutyl ketone are also used as solvents due to their lower price. Acetone usage has been increased since it is no longer listed as a VOC by the EPA. Due to strict environmental laws, commercial paint manufacturing industries are more focused on low-VOC, EPA-compliant paints. Moreover, being an EPA-compliant paint becomes an attractive driving force for consumers to buy the product.

2.5 Approaches to reduce VOC

Techniques such as powder coatings, water-borne coatings, UV radiation curable coatings, and high-solid coatings have been used to lower the VOCs.\textsuperscript{1,44,45} Several researchers\textsuperscript{44,45,46} in the past decade have been working on high-solid coatings due to their high performance coupled with environmental and economic benefits. High-solid coatings are coating formulations with less than 15 wt% VOCs. Thicker layer of coating can be applied in one go using high-solid coatings which provides better performance and hiding power. Due to reduced number of coating layers, labor cost also reduces. Same equipments and scientific approach as conventional system is applied for high-solid
system, which makes it easier and cheaper to switch to.\textsuperscript{44} The key technological challenges in the development of high solid coatings are being able to achieve appropriate viscosity for application and a curing rate that is not significantly lower than that of conventional coatings.\textsuperscript{47} Moreover, coatings performance should be comparable to that of conventional coatings.

There are different ways to achieve low viscosity with high solid content in alkyd formulations, such as lowering molecular weight, narrowing the molecular weight distribution, increasing oil length and using reactive diluents.\textsuperscript{1} Lowering the molecular weight is an effective way to reduce the viscosity, which can be obtained by lowering the dibasic acid/polyol ratio and by increasing the oil length of the alkyd. Lowering the dibasic acid/polyol ratio forms an alkyd with lower ratio of aromatics to aliphatic which leads to a higher drying time and a lower $T_g$. Narrowing the molecular weight distribution gives a more uniform molecular weight and a lower viscosity. Kangas et al.\textsuperscript{48} prepared a model alkyd with narrower molecular weight distribution and low number average molecular weight than those of conventional alkyds with the same ratio of reactants. Dimerization of model alkyds through reaction of unsaturated bonds on fatty acid chains was reduced since it was polymerized at room temperature. While the model alkyds dried faster, impact resistance was inferior compared to alkyds with broad molecular weight distribution.

One of the most efficient and widely used approaches to obtain high-solid system is to incorporate reactive diluents in the system.\textsuperscript{1,46,3,49,50,51,52,53,54,55,56} A reactive diluent lowers the viscosity of the coating formulation to make it appropriate for the respective coating process and also participate in the film formation by taking part in the curing
Zabel et al.\textsuperscript{46} studied the design of reactive diluents for high-solid alkyds systems in detail. An effective reactive diluent should have low viscosity, low volatility (boiling point >300 °C), good compatibility with the binder, ability to polymerize either by homopolymerization or copolymerization with alkyd under the set cure conditions. The drying rate of the reactive diluent is an important parameter and should be comparable to that of the alkyd binder. A reactive diluent which dries too slowly can retard the overall film drying. On the other hand, a reactive diluent which dries too fast can cause storage problems. Polarity of reactive groups is also a key parameter since it affects pigment stabilization.

The number of reactive sites has been an important parameter for designing a reactive diluent. The reactive diluent may function as a plasticizer if the number of reactive sites is low. If the number of reactive sites is too high, it may be too reactive and negatively affect the shelf life or cause oxidative degradation in the film. The incorporation of reactive diluents in the coating formulation should not change the key properties of the coating either during application, drying or in the final coating performance. To summarize, the key properties of a reactive diluent and coating performance requirements are listed in the Table 2.2. Considering key features of a reactive diluent, reactive diluents derived from renewable sources such as vegetable oils will provide environmental benefits by reducing the VOC content and provide biodegradable properties to the final film.
Table 2.2. Key properties and requirements of a reactive diluent.

<table>
<thead>
<tr>
<th>Reactive diluent properties</th>
<th>Coatings performance requirement</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Low viscosity</td>
<td>• Good in-can storage stability</td>
</tr>
<tr>
<td>• Low volatility</td>
<td>• No influence of drying time</td>
</tr>
<tr>
<td>• Alkyd compatibility</td>
<td>• No toxic degradation products</td>
</tr>
<tr>
<td>• Appropriate number and type of reactive sites</td>
<td>• No influence of coating’s physical and chemical performance</td>
</tr>
<tr>
<td>• Non toxic</td>
<td>• Good through drying (no wrinkling)</td>
</tr>
<tr>
<td>• Low cost (Economic replacement for solvents)</td>
<td></td>
</tr>
<tr>
<td>• Low color</td>
<td></td>
</tr>
</tbody>
</table>

2.6 Reactive Diluent History

In oil-based varnishes, linseed oil has received considerable attention for its use as a reactive diluent since it can adjust the viscosity of the system and also react with the resin via autoxidation. Vegetables oils are attractive candidates for use as a reactive diluents due to their ability to undergo autoxidative curing and low viscosity. Bruson synthesized dicyclopentyl methacrylate and reported that the esters may be used for coating compositions alone or in combination with drying oils and alkyds. DuPont developed acrylic and methacrylic esters of 1,3 cyclic acetals which are suitable for air drying and can be added to the alkyd coating composition. Enomoto et al. studied reactive diluents for alkyd coatings and reported that 1,1-bis(1’-methyl-2’-vinyl-4’,6’-heptadienoxy)ethane was the most suitable reactive diluent amongst the investigated compounds.

In 1994, Cargill® introduced the reactive diluent Dilulin® prepared by modification of linseed oil via DielsAlder reaction of cyclopentadiene at high temperature and pressure to form norbornene groups on the chain. Naturally occurring
epoxidized vegetable oils such as vernonia oil have been studied as reactive diluents.\textsuperscript{54,61} The limited availability and higher cost of vernonia oil limits its use. Muturi et al.\textsuperscript{54} studied and compared the performance of vernonia oil, epoxidized soybean oil, and linseed oil. Partially epoxidized soybean oil and linseed oil have molecular structures similar to vernonia oil and showed similar performance. Chen et al.\textsuperscript{62} synthesized epoxynorbornene linseed oil via Diels–Alder reaction of cyclopentadiene with linseed oil, followed by epoxidation.

DSM disclosed a formulation consisting of an alkyd resin and reactive diluents based on alkyl ester of fatty acids derived from vegetable oils such as tung oil and calendula oil.\textsuperscript{63} Several researchers\textsuperscript{46-54} studied the fatty acid esters derived from vegetable oils as a reactive diluent for different coatings systems such as autoxidative cured alkyds, cationically cured epoxy. However, the additional cost of separation of fatty acids and increased sensitivity to wrinkling during drying of the test paints limits this approach.\textsuperscript{54} Bhabhe et al.\textsuperscript{64} synthesized oil-modified acrylic monomers as a reactive diluent for the alkyd coatings. Biermenn et al.\textsuperscript{55} studied calendula oil which can be used to replace tung oil in coatings application. This study provided a new perspectives to the coating industry because tung oil is expensive and rare. Njuku et al.\textsuperscript{65} reported that cardanol acetate, cardanyl methyl ether and neat cardanol are attractive choices as reactive diluents for alkyds. The main drawbacks of oxidative curing systems are slow drying and residual unsaturation that can lead to autoxidative degradation and yellowing.\textsuperscript{4,54} These drawbacks can be overcome while retaining the advantages of this raw material group by introducing new functional groups that react faster or enable the use of other cross-linking reactions.\textsuperscript{4}
Wutticharoenwong et al. synthesized three different functionalized tung oils which can be used as an reactive diluents for alkyd coatings. Tung oil was functionalized by Diels-Alder reactions with acrylate monomers, including alkoxy silane, triallyl ether and fluorinated alkyl. Functionalized tung oils were formulated with alkyd and coating performance was studied. Alkoxy silane and allyl ether functionalities take part in the film formation via condensation, hydrolysis and antioxidative curing, respectively. Alkoxy silane and allyl ether functionalized tung oil improved the tensile strength, tensile modulus, crosslink density and glass transition temperature of the coatings. While fluorinated alkyl functionality does not take part in film formation, it affects the properties of the final film, including surface energy, thermal stability, hydrophobicity, and solvent resistance. Tung oil dries rapidly but is expensive, and its films discolor rapidly due to the presence of the three conjugated double bonds. These shortcomings were the driving force behind the efforts to synthesize conjugated oils containing esters of fatty acids with two conjugated double bonds, namely conjugated soybean oil. Compared to tung oil, soybean oil is a dominant plant-based feedstock and is a more attractive choice for use as a reactive diluent.

2.7 Diels-Alder reaction

The Diels-Alder reaction is one of the most powerful tools used to construct a carbon-carbon bond in a six membered ring with high stereochemical control. Since 1928 several simple and complex compounds have been synthesized by forming carbon-carbon, carbon-heteroatom and heteroatom-heteroatom bonds making Diels-Alder reaction a versatile synthetic tool. In 1950, Otto Diels and Kurt Alder were awarded the
Nobel Prize in chemistry in recognition of the importance of this reaction to synthetic organic chemistry.

In Diels-Alder reaction, a fragment of four atoms linked together by two conjugated double bonds (a diene) and a fragment containing two atoms linked by a double bond or triple bond (a dienophile) undergo a cycloaddition to afford a six-membered ring. The general scheme of the Diels-Alder reaction is showed in Figure 2.11.

![Figure 2.11. Diels-Alder reaction.](image)

Many diene can exhibit more than one conformations. For example, in 1,3 butadiene \( s\)-cis conformation changes to \( s\)-trans conformation by rotation of the single bond between two double bonds. Possible conformations of 1,3 butadiene are shown in Figure 2.12. Dienes react to form Diels-Alder adduct only in the \( s\)-cis conformation. If the conjugated bonds are rigidly fixed in the \( s\)-trans configuration, the respective diene does not undergo Diels-Alder reaction.

![Figure 2.12. Conformations of 1,3 butadiene.](image)
A simple example of a Diels-Alder reaction is the reaction between butadiene and ethylene to form cyclohexene. Both diene and dienophile show a very low reactivity. Hence, reaction is carried out at high temperature and in presence of excess ethylene. The reactivity of diene and dienophile can be significantly changed by the nature of substituent groups (R,G). A dienophile substituted with electron withdrawing groups (G) and/or a diene substituted with electron donating groups (R) reacts at lower temperature, atmospheric pressure forming cyclohexene derivatives in medium to very high range of conversion. Examples of electron withdrawing groups (G) are CN, CO₂R, SO₂R, NO₂. Examples for electron donating groups (R) are CH₃, OCH₃, N(CH₃)₂. In 1960, Yates et al. reported that a higher reaction rate with a shorter reaction time at room or lower temperature can be achieved using Lewis acid catalysts such as AlCl₃, BF₃, ZnCl₂, SnCl₂.

Cargill reported the synthesis of norbornene functionalized linseed oil via a Diels-Alder reaction with dicyclopentadiene at high temperature and high pressure named as Dilulin. Dilulin can be utilized in coating formulations to reduce VOCs and provide low viscosity. Chen et al. synthesized epoxynorbornene linseed oil via Diels–Alder reaction of cyclopentadiene with linseed oil, followed by epoxidation. High percentage conversion of double bonds was achieved. Soucek et al. reported the modification tung oil via Diels-Alder reaction. Tung oil contains 80% α-eleosteric fatty acid, which is a major source of conjugated double bonds. Acrylate and methacrylates were used as dienophiles since they contain π bond as well as an electron withdrawing group. It was reported that tung oil and acrylate or methacrylate species undergo Diels-Alder reaction under certain reaction conditions.
2.8 Sol-gel chemistry

Sols are dispersions of colloidal particles in a liquid. Colloids are solid particles with a diameter 1-100 nm. A gel is a integrated, rigid 3-D network. Sol-gel process is a process of producing solid materials forming an inorganic network gel through colloidal suspension (sol). Sol-gel chemistry has been studied since mid 1800's. Ebelman\textsuperscript{71} observed that the hydrolysis of tetraethyl orthosilicate (TEOS), under acidic conditions yielded SiO$_2$ in the form of a "glass-like material". The sol-gel process involves formation of colloidal solution (sol) that acts as the precursor for an interconnected network (gel). Metal alkoxides such as alkoxysilanes are generally used as the precursors. Alkoxysilanes undergo simultaneous hydrolysis and polycondensation to form a silica gel by forming an interconnected 3-D network. The hydrolysis and condensation reactions of alkoxysilane are depicted in Figure 2.13.\textsuperscript{72} The properties of the inorganic network are significantly dependant on the pH, catalyst, concentration and temperature of the reaction.

![Diagram of sol-gel reactions](image)

Figure 2.13. Sol-gel reactions.
Sol-gel reactions can occur in both acidic and basic conditions. Under acidic condition, a hydrolysis reaction occurs in two steps according to $S_N^2$ type mechanism.\textsuperscript{72,73} A positive charge develops on the alkoxy silane through the attack of an acid catalyst. Thus, electron density is drawn away from the silicon atom which makes it more susceptible to water. In the rate determining step, oxygen from the water attacks the Si, which has low electron density. This leads to a pentacoordinate transition state in which partial positive charges are developed as shown in Figure 2.14. The rate of the hydrolysis reaction is significantly affected by steric effects due to the alkyd substituents. Later, silanol group undergoes condensation with an alkoxide or another silanol group to form Si-O-Si linkages and the siloxane particles aggregate into a gel as shown in Figure 2.13. Under basic conditions, the hydroxyl anion attached directly to the silicon atom of the alkoxy silane by $S_N^2$ mechanism as shown in Figure 2.15.\textsuperscript{72} The base alkoxide group repels the hydroxyl anion and slows down the reaction. Under basic conditions, hydrolysis reactions of alkoxy silane are much slower that those under acidic conditions.

For most inorganic alkoxides, hydrolysis and condensation reactions can occur without catalyst. However for alkoxy silane, hydrolysis reaction is very slow, requiring the addition of catalyst.\textsuperscript{73} The type of catalyst significantly affects the nature of network. For example, under acidic conditions, networks are more linear-like due to the fast hydrolysis step. Less completely formed networks of siloxane bonds with higher concentration of unreacted silanols are formed under acidic condition. Under basic conditions, a dense crosslinked networks are formed due to the longer time sol particles have to aggregate and arrange themselves in the most thermodynamically stable arrangement. Less concentration of unreacted silanol are left under basic conditions.
Many researchers studied the effect of pH on the rate of hydrolysis and condensation reactions. At pH ~7, the rate of hydrolysis is slow, while condensation reactions occur at a relatively faster rate. The rate of condensation is proportional to the (H\(^+\)) at pH < 2 and (OH\(^-\)) concentration at pH in the range 2-6. Other parameters such as solvent, water content and temperature also play an important role in the final network formation.

Ni et al. developed a moisture cured alkoxy silane-functionalized isocyanurate coating system. Incorporation of alkoxy silane-functionalized improved adhesion, crosslink density, glass transition temperature and impact resistance of the polyurea/siloxane hybrid coatings. Soucek and coworkers reported novel inorganic-organic coatings based on drying oils and alkyds. The organic polymer
network is formed by the autoxidative curing of fatty acid chains in oil or alkyd. The inorganic phase network is formed by the hydrolysis, condensation of the metal alkoxide. Epoxidized soybean oil based inorganic-organic coatings exhibited good flexibility, tensile strength and hardness while adhesion and impact resistance reduced with increasing precursor content.\textsuperscript{88} Titanium (IV) \textit{i}-propoxide, titanium (IV) \textit{di-i}-propoxide bis acetylacetonate, and zirconium \textit{n}-propoxide were used as sol-gel precursors. Coatings with mixed sol-gel precursors showed improved mechanical properties as compared to those with single sol-gel precursors due to an interaction effect.

Sailer et al.\textsuperscript{82} developed linseed and sunflower oil alkyd based ceramer coatings. The linseed oil alkyd based ceramer showed superior performance as compared to the sunflower oil based alkyd ceramer. The ceramer approach improved tensile properties and hardness without giving up the flexibility or impact resistance while adhesion of the coatings were reduced. Teng et al.\textsuperscript{85} developed blown soybean oil based ceramers which showed improved tensile strength, tensile modulus and hardness but decreased impact strength. Tuman et al.\textsuperscript{79} studied the effect of sol-gel precursors on the autoxidation of linseed oil in presence of conventional driers.

2.9 Fluorinated polymers

A fluorinated polymer is defined as a polymer consisting of carbon (C) and Fluorine (F). Fluoropolymers are gaining a lot of attention as coating materials due to their unique properties including outstanding resistance to organic solvents, chemicals, low surface energy and high temperature stability.\textsuperscript{89} Their application as functional coatings are booming due to low coefficient of friction and abrasion, oil and water repellency, antifouling properties and low surface tension. Due to high electronegativity
Fluorine has a poor leaving group ability due to which alkyd fluorides are $10^2$-$10^6$ times less reactive than the corresponding alkyl chlorides in certain solvolysis and displacement reactions. The unique characteristics of fluoropolymers are by virtue of these C-F bond properties. Fluoropolymers exhibit low intermolecular forces due to fluorine's high ionization potential and low polarizability. As a result, the fluorinated species migrate towards the air/film interface to minimize surface energy.

Despite identifying these excellent material properties, application of fluorinated polymers is restricted to small areas such as linings. This is due to the poor processability and difficult handling of fluorinated polymers resulting from their insolvability in solvents, high rigidity and high viscosity even at high temperatures up to 300-400 °C. Therefore, fluorinated polymers have been modified to increase their solubility and combined with several resins to achieve the properties of fluorinated polymers to the final coating.

An example of linear fluoropolymer is poly tetrafluoroethylene (PTFE) or Teflon invented by Du Pont in 1936. PTFE exhibits very desirable properties including low surface tension, high chemical resistance for its use as a coating. However, poor solubility limits its use in coating formulations with other resins. It must be applied as a dispersion of polymer particles, which is sintered at >350 °C to form a film. Due to these harsh application conditions they can be applied to limited substrates.

A hydroxy-functional monomer such as Hydroxyethyl methacrylate (HEMA) copolymerized with vinylidene fluoride (VDF) and cross-linked with a polyisocyanate
gives coatings with superior wet adhesion and corrosion as compared with poly(vinylidene fluoride) PVDF homopolymer. Soucek et al. synthesized fluorine-functionalized tung oil and utilized it as a reactive diluent for alkyd coatings. Fluorine-functionalized tung oil efficiently served as a diluent and contributed to the improved solvent resistance and hydrophobicity. Soucek et al. also developed fluorine-functionalized alkyds and evaluated the coating performance. Compared to basic alkyd coating, fluorine-functionalized alkyds showed improved surface properties.

2.10 Alkyd-acrylics hybrid coatings

Alkyd coatings exhibit fewer film defects during application, are inexpensive and can undergo auto-oxidative curing of the fatty acid unsaturation. However, the durability of alkyd films, especially outdoors, tends to be poorer than that of acrylic, polyester and polyurethane films. When alkyd paints are exposed to UV-radiation, high humidity and thermal fluctuation, the paint shows significant loss of gloss, chalking and degradation. Moreover, alkyds exhibit poor hydrolytic stability. A good solution to improve the outdoor durability of such paints is to modify alkyds with acrylic resin. Acrylated alkyd binders are gaining growing interest since they offer the possibility of combining the ease of application and film forming properties of alkyd with the exterior durability of vinyl and acrylic systems due to their resistance to hydrolysis and UV degradation. Compatibility is ensured when alkyd and acrylic are chemically connected to each other.

The first modification of alkyd was done with styrene (Figure 2.16) and was reported by Armitage and coworkers in the mid-twentieth century. Later, Solomon and coworkers developed a series of acrylated alkyds based on the esterification
reaction of hydroxy, carboxyl functionalities in a prepolymer and alkyd or polyol and dibasic acid. Acrylated alkyds generally have higher glass transition temperature, producing coatings with reduced tack-free time. However, the through dry-time of such coatings is longer due to the decreased degree of unsaturation in the alkyd resulting from the copolymerization with the acrylic compound.\textsuperscript{104}

Figure 2.16. Styrenated alkyd.

Alkyds can also be modified by the polymerization of alkyd resin with a vinyl monomer via free radical mechanism to obtain acrylate-alkyd copolymer. However, the drying time of such coatings is higher due to the decreased unsaturated bonds.\textsuperscript{105} Moreover, paint formulations containing acrylated alkyds require higher amount of organic solvents due to the increased $T_g$ and molecular weight.

Akintayo et al.\textsuperscript{106} modified Albizia Benth alkyds using an acid functional copolymer containing maleic anhydride. Coatings with these resins showed improved
performance. However, beyond certain acrylate content, coating performance was reduced. Saravari et al.\textsuperscript{107} developed acrylate- maleinized alkyd resins which showed heterogenity and poor curing. Then Murillo et al.\textsuperscript{108} developed waterborne acrylated-maleinized alkyd resins which showed better coating performance after employing optimum ratio of hyperbranched alkyd and BMA-MA copolymer.

Schork and coworkers\textsuperscript{109,110,111,112} extensively studied emulsion polymerization of acrylate monomers in the presence of alkyd. They observed low monomer conversion caused by radical delocalization followed by radical transfer to the unsaturated groups in the fatty acids of the alkyd.\textsuperscript{112} They also observed that as the polymerization proceeded, the polyacrylates and alkyd became immiscible and separated into different particles. To overcome these drawbacks, Wang et al.\textsuperscript{109} synthesized relatively stable emulsion of alkyd and acrylic monomer by using mini-emulsion technique, which also diminishes the secondary nucleation significantly\textsuperscript{113} and improves hydrolytic stability of the parent alkyd. Several studies\textsuperscript{110,109,115} have been conducted on mini-emulsions to improve their shelf life and film properties.

Although mini-emulsion polymerization can overcome synthesis limitations, it is still not widely used because of its low solids content and the high shear needed for processing.\textsuperscript{114} For the coatings industry, drying time is a major economic concern because of their impact on energy consumption and high speed productivity requirements. Schork et al.\textsuperscript{110} observed that there are three different polymer chains formed during mini-emulsion: homopolymer of acrylate, ungrafted alkyd and graft copolymer. A potential problem during the synthesis of alkyd/acrylic hybrid latex is that, during mini-emulsion polymerization, the radicals in the mini-emulsion media can react.
with carbon-carbon double bonds of the alkyd. The number of unsaturated groups of the alkyd resin component will then be reduced, and consequently the auto-oxidation during the film formation process and associated network formation and film hardening will be hindered.\textsuperscript{109}

Wang et al.\textsuperscript{115} reacted conventional monoglyceride with carboxyl functional acrylic polymer. This improved the hydrolytic stability of the alkyd and provided better storage stability than conventional water reducible coatings. However, phase separation was observed at a higher glass transition temperature.

Goikoetxea et al.\textsuperscript{116} synthesized alkyd/ acrylic hybrids via synthesis of acrylate functionalized alkyd which is prepared by the reaction of alkyd resin and glycidyl methacrylate (GMA). This way the compatibility between alkyd and acrylic was improved without reducing the number of alkyd unsaturated double bonds. Also, alkyd functionalization ensures a greater amount of grafting between alkyd resin and acrylic copolymer without consuming the unsaturated bonds of the alkyd backbone.\textsuperscript{115} However, the authors did not provide any information about polydispersity index (PDI) to study the extent of control of the reaction. After adding drier to the formulation, hardness of the film increased but phase separation between alkyd and acrylic was observed because of non-uniform cross-linking. Hence, hardness measurements were unreliable.\textsuperscript{115} Another drawback of this approach is that the presence of a polymerization inhibitor in the paint formulations is known to prolong the drying times of the resulting coating films.\textsuperscript{104}

Soucek and coworkers\textsuperscript{117} developed acrylated tung oil alkyd which showed efficient coating performance and drying. Another method was reported which includes
grafting of acrylate groups onto the alkyds via free radical mechanism. Acrylate groups mainly grafted at doubly allylic hydrogens on fatty acid chains. A small percentage of acrylic groups were grafted on to the polyester backbone of the alkyd via hydrogen abstraction of the glycerol. Dziczkowski et al. introduced a new class of acrylated alkyd which is synthesized using RAFT polymerization technique. Alkyd macro RAFT agent was synthesized by attaching RAFT agent telechelically on to the alkyd backbone chain. It was then used to polymerize different acrylic monomers by a RAFT-mediated process as shown in Figure 2.17. This method confirmed the maximum grafting and control over the molecular weight (MW) and PDI and minimum side reactions. However, it is assumed that the trithiocarbonyl functionality on the RAFT polymerized acrylated alkyd inhibits its auto-oxidative curing, which is explained in detail the following sections.

![Diagram of RAFT polymerized acrylated alkyds]

Figure 2.17. RAFT polymerized acrylated alkyds.
2.11 Controlled radical Polymerization (CRP)

Conventional free radical polymerization (RP) is a very important commercial process for preparing high molecular weight polymers because of the following reasons: a) It can be used with a variety of monomers including methacrylates, styrene, vinyl acetate, butadiene and acrylamides; b) it is tolerant to a wide range of functional groups (e.g. OH, NR₂, COOH, CONR₂) and reaction conditions (bulk, solution, emulsion, miniemulsion, suspension); c) it is simple to implement and inexpensive compared to competitive technologies. However, the main limitation of RP is the poor control over some of the key elements of macromolecular structures such as MW, PDI, end functionality, chain architecture, and composition.

An approach to overcome these limitations is controlled radical polymerization (CRP) which is also commonly referred to as living radical polymerization in which the contribution of chain breaking reactions is minimized and the simultaneous growth of all chains can be achieved via nearly instantaneous initiation. Normal bimolecular termination is minimized and lifetime of living polymers is prolonged through the introduction of dormant states for the propagating species. Dormant species of propagating species are formed via either reversible termination or reversible transfer.

The three most commonly used types of CRP are: atom transfer radical polymerization (ATRP), stable free-radical polymerization(SFRP)/nitrooxide mediated polymerization (NMP), reversible addition–fragmentation transfer (RAFT). These three processes have received the most attention because of their versatility in fabricating complex materials with controlled molecular weights, controlled block locations, and narrow molecular weight distributions. Controlled radical polymerization techniques
have good commercial potential because more monomers undergo radical polymerization compared to ionic polymerization. Controlled radical polymerization technique has the ability to control the molecular weight, molecular weight distribution, composition, site specific functionality, architectures and topology of the polymer as shown in Figure 2.18. There are limitation for all types of CRPs. The occurrence of irreversible bimolecular termination of propagating species becomes significant under the following conditions: high monomer conversion, polyfunctional initiators, high initiator concentration, and high targeted molecular weight (about > 100,000). This work includes two CRP: RAFT and ATRP polymerization techniques.

Figure 2.18. Schematic representation of controlled compositions, topologies and functionalities prepared by CRPs.
2.12 Atom transfer radical polymerization (ATRP)

In 1995, Matyjaszewski and coworkers first introduced ATRP technique. ATRP controls chain growth by reversible termination. It was developed by designing a proper catalyst (transition metal compound and ligands), using an initiator with an appropriate structure, and adjusting the polymerization conditions, such that the molecular weights increased linearly with conversion and the polydispersities were typical of a living process.

ATRP is one of the most commonly employed techniques for controlled radical polymerization. It has great potential for the development of new materials due to the ability to control molecular weight and polymer architecture. The general mechanism for ATRP is shown in Figure 2.19. Ligand complexes with the cuprous salt and helps to solubalize it in the organic reaction system. The radicals, i.e., the propagating species ($P_n^\cdot$), are generated through a reversible redox process catalyzed by a transition metal complex (activator, $(M_t^I - Y)/$Ligand, where Y may be another ligand or a counterion) which undergoes a one-electron oxidation with concomitant abstraction of a halogen atom (X), from a dormant species $P_n - X$. Radicals react reversibly with the oxidized metal complexes, $(X - M_t^{I+1} - Y)/$Ligand, the deactivator, to reform the dormant species and the activator. This process occurs with a rate constant of activation $(k_a)$ and deactivation $(k_{da})$ respectively. Polymer chains grow by the addition of the free radicals to monomers in a manner similar to a conventional radical polymerization, with the rate constant of propagation $(k_p)$. Termination reactions $(k_t)$ also occur in ATRP, mainly through radical coupling and disproportionation; however, in a well-controlled ATRP, no more than a few percent of the polymer chains undergo termination. A well controlled
ATRP will have not only a small contribution of the terminated chains, but also a uniform growth of all the chains, which is accomplished through fast initiation and rapid reversible deactivation.

\[
P_n \cdot X + M_l^n Y/Ligand \xrightleftharpoons{k_{act}} k_{deact} P_n^* + X-M_l^{n+1} Y/Ligand
\]

Figure 2.19. Mechanism of ATRP technique.

2.13 RAFT Polymerization

RAFT is among the most successful CRP processes due in large to its applicability to a wide range of monomers. RAFT polymerizations control chain growth through reversible chain transfer. The key feature of the mechanism of RAFT polymerization is a sequence of addition-fragmentation equilibria as shown in Figure 2.20. Initiation and radical-radical termination occurs as in the conventional radical polymerization. Addition of propagating radical (P_n \cdot) to the thiocarbonyl compound (RSC(Z)=S) followed by fragmentation of the intermediate radical gives rise to a polymeric thiocarbonyl compound (P_nS(Z)C=S) and a new radical (R \cdot). Reaction of the radical (R \cdot) with monomer forms a new propagating radical (P_m \cdot). Rapid equilibrium between the active propagating radicals (P_n \cdot) and (P_m \cdot) and the dormant polymeric trithio carbonyl compound provides equal probability for all chains to grow and allows for the production of polymers with narrow polydispersity. Finally, polymer is obtained with most of chains retaining the thiocarbonyl end group.
The presence of sulfur and color, pungent odor in the resulting polymer is most of the time undesirable for final applications. It can be eliminated with further RAFT removal steps.\textsuperscript{129} One of the main advantages of RAFT polymerization is that it can be performed simply adding a chosen quantity of an appropriate RAFT agent to a conventional free-radical polymerization. The same monomers, initiators, solvents and temperatures are used. In this work, it is proposed that acrylated alkyd is synthesized using RAFT and ATRP polymerization technique, in such a way that all the unsaturated bonds on fatty acid chain on alkyd remain unreacted, hence available for auto-oxidative curing.

Figure 2.20. Mechanism of RAFT polymerization.
2.14 2-D NMR spectroscopy

A Belgian scientist Jean Jeener first proposed fundamental concept of two-dimensional NMR which was later executed by Richard Ernst who won the 1991 Nobel prize for Chemistry.\textsuperscript{130} One dimensional NMR shows distinct resonances of different functionalities in a simple molecule. However, for complex molecules, overlapping of resonances sometimes makes it difficult for the interpretation of NMR spectrum. In these cases, 2D-NMR can be utilized to identify the connectivity through both homonuclear and heteronuclear experiments. If nuclei 1 and 2 are of the same element and isotope, the system is referred to as homonuclear. If they are different, it is a heteronuclear spin system.

Correlation spectra plotting $^1\text{H}$ chemical shift vs. $^1\text{H}$ chemical shift are called COSY (for COrelation SpectroscopY), those plotting $^1\text{H}$ chemical shift vs. $^{13}\text{C}$ chemical shift are called HETCOR (for HETero CORrelation Spectra). HECOR has poor sensitivity because the observed nucleus is $^{13}\text{C}$ and has been largely replaced by the reverse detection experiments HMBC and HMQC. Inverse detection experiments record $^1\text{H}$ rather than the heteronucleus spectrum during the detection period. Low abundance of most heteronuclei generally results in proton spectrum overwhelmed with signals with no active heteronuclei, making it overcrowded. Hence, reverse detection experiments have become much more common today.

The 2D HSQC (Heteronuclear Single-Quantum Correlation) experiment was first described by Geoffrey Bodenhausen and D. J. Ruben in 1980. The final spectrum is a 2D heteronuclear chemical shift correlation map between directly-bonded $^1\text{H}$ and X-
heteronuclei (commonly, $^{13}$C and $^{15}$N). HSQC experiment is phase-sensitive. It is widely used because it is based on proton-detection, offering high sensitivity when compared with the conventional carbon-detected 2D HETCOR experiment. The 2D HMQC (Heteronuclear Multiple-Quantum Correlation) experiment is used to correlate proton and carbon signals using one bond couplings. HMBC (Heteronuclear Multiple-Bond Correlation) experiment correlates chemical shifts of two type of nuclei separated from each other with two or three chemical bonds.

2.15 Antioxidant Mechanism Study

An antioxidant can be defined as a compound that significantly delays or hinders the oxidation of an oxidizable substrate, when present at low concentration to those of the substrate. In this work, the substrate is seed oil derived alkyd. Depending on the mechanism to prevent the oxidation, antioxidants can be classified into three categories: enzyme inhibitors, metal chelator and radical scavengers. Radical scavengers type antioxidants will be studied in the work.

An antioxidant (AH) can trap an active free radical via a redox transition involving the donation of a single electron or H atom to a free radical species R as shown in Equation 2.16. A is a antioxidant derived radical.

1) radical trapping stage

\[ R \cdot + AH \rightarrow RH + A \cdot \quad 2.16 \]
2) radical termination stage

A · +X · → nonradical materials

Antioxidant can mainly directly react with the reactive free radicals and destroy them or may hinder oxidation via either of the following\textsuperscript{135}: 1) a process involving the transfer of radical with the formation of "reactive" radical derived from antioxidant 2) a process involving transfer of radical with the formation of a "stable" or "less active" radical derived from antioxidant.

In first case, A is an active radical. It may react with another radical X · and undergo termination which depends on its reduction potential.\textsuperscript{135} X · can be an another radical species or the same species as the A ·. Structural information about these products have contributed to anti-oxidation mechanism studies. For example, vitamin C (AscH\textsuperscript{+}) in the aqueous phase and vitamin E (TOH ) in the liquid phase react with or neutralize hydroxyl, alkoxy or lipid peroxy radicals and form water, alcohol or lipid hydroperoxides, respectively.\textsuperscript{136} Vitamin E itself become a phenyl radical (Figure 2.21a) and vitamin C turns to a very stable radical (Asc\textsuperscript{−}) due to its delocalized structure (Figure 2.21b). Furthermore, vitamin C can also neutralize the radical form of other antioxidants such as vitamin E radical and regenerate the antioxidant (Figure 2.21c).
Figure 2.21. Antioxidative mechanism of a) Vitamin E b) Vitamin C and c) regeneration of vitamin E from vitamin C.

In the second case, A is a stable and less active radical derived from antioxidant. The best example for this case is spin trap, which is a molecule that reacts with an active free radical to form a spin adduct which is more stable than the original free radical and can be detected by electron spin resonance (ESR). For example, a nitrone radical trap phenyl-tert-butyl nitrone (PBN), reacts with a variety of free radicals forming a stable PBN-radical adduct as shown in Figure 2.22.\textsuperscript{135}

Figure 2.22. Radical trapping by phenyl-tert-butyl nitrone (PBN).

Several studies\textsuperscript{137,138,139,140,141} have been done on antioxidant activity of sulfur compounds but mechanism study has received little attention. In mid-twentieth century, Thompson et al.\textsuperscript{140,141} reported several sulfur compounds i.e. β-alkylmercaptoketones as antioxidants.
Okada et al.\textsuperscript{142} reported the first and only study which explains mechanism of prevention of oxidation by a sulfur compound. Okada et al.\textsuperscript{44} studied antioxidant mechanism of allicin (one of the main thiosulfinates in garlic) which does not have active hydroxyl groups and is also an active antioxidant and free-radical scavenger. The radical-scavenging reactions of allicin proceed via a one-step hydrogen atom transfer as shown in Figure 2.23. Combination of the allyl group (–CH\textsubscript{2}CH=CH\textsubscript{2}) and the –S(O)S– group is necessary for the antioxidant action of allicin.

\begin{equation}
\text{MLOO}^- + \text{Allicin} \xrightarrow{k_{\text{inh}}} \text{MLOOH} + \text{Allicin methyl linoleate hydroperoxide}
\end{equation}

Figure 2.23. Radical scavenging reaction of allicin.

Battin et al.\textsuperscript{138} reviewed the antioxidant of several sulfur compounds (Figure 2.24) by studying their ability to scavenge reactive oxygen species and metal-binding. Not all sulfur compounds show similar antioxidant activity, showing the need for a detailed structure-property relation study. A clear mechanism of how ROS scavenging and metal-binding prevent the oxidation is not clear yet. This work is focused on the antioxidant behavior of RAFT agent containing thiocarbonyl functionality.
Figure 2.24. Antioxidants based on sulfur compounds.
CHAPTER III
MODIFIED SOYBEAN OIL AS A REACTIVE DILUENT:
SYNTHESIS AND CHARACTERIZATION

3.1 Introduction

Reduction of solvent emission from paints has been a dominant goal in coatings research in recent years. Conventional solvent-borne coatings normally contain 30-60 wt% volatile materials. The detrimental impact of solvent emission on the environment and human health is the main driving force to develop "environment-friendly" or "greener" coating technologies. Techniques such as powder coatings, water-borne coatings, UV radiation curable coatings and high solid coatings have been used to reduce volatile organic compounds (VOCs). Several investigations in the past decade have focused on high solid coatings due to their environmental effect, performance and economic benefits. High solids coatings are defined as coating formulations containing less than 15 wt% volatile compounds. Several technological challenges arise in the development of high solid coatings, such as difficulty in achieving an appropriate viscosity for application and a curing rate that is not significantly lower than that of conventional coatings. Moreover, films with properties comparable to those of conventional coatings are desired. There are different ways to achieve low viscosity with high solid content in alkyd formulations, such as narrowing the molecular weight
distribution, increasing oil length and using reactive diluents.\textsuperscript{1} The use of reactive diluents is an effective means of achieving high solid alkyd formulation.

A reactive diluent\textsuperscript{49-56} lowers the viscosity of the coating formulation such that the consistency of the formulation is appropriate for the coating process. It serves as a solvent and then participates in the film formation by taking part in the curing process. Low viscosity, low volatility (boiling point $> 300 \, ^\circ\text{C}$), good compatibility with the binder, ability to polymerize either by homo- or co-polymerization with alkyd under the set cure conditions are the key requirements of a good reactive diluent.\textsuperscript{1,46,3} The drying rate of the reactive diluent should be comparable to that of the alkyd. If the reactivity is too low, the reactive diluent can retard the drying rate of the film. The number of reactive sites is also an important parameter. If the number of reactive sites is too low, the reactive diluent will function as a plasticizer instead. If the number of reactive sites is too high, it may be too reactive and adversely affect the shelf life or cause oxidative degradation in the film. Furthermore, if the reactive diluent is derived from renewable sources like vegetable oils, it would provide environmental benefits by reducing the VOC content and provide bio-degradable properties to the final film.

Low viscosity and the ability to undergo auto-oxidative curing makes vegetable oils an attractive choice for use as reactive diluents. In oil-based varnishes, linseed oil is considered the traditional reactive diluent since it can adjust the viscosity of the system and also react with the resin via auto-oxidation. Fatty acid esters derived from vegetable oils have been proposed as reactive diluents for several types of coating systems ranging from oxidative-drying systems to cationically cured epoxy resins.\textsuperscript{46-55} However, the additional cost of separation of fatty acids and increased sensitivity to wrinkling during
drying of the test paints limits this approach. The drawbacks of oxidative-drying systems include slow drying and residual unsaturation that can lead to oxidative degradation and yellowing. These disadvantages can be overcome while retaining the advantages of this raw material group by introducing new functional groups that enable the use of other cross-linking reactions. Faster drying times can be achieved by using radiation curing. Several modified oils such as epoxidized oil, epoxy norbornene oil, and acrylated oil have been developed. Naturally occurring epoxidized vegetable oils such as vernonia oil have been studied as reactive diluents. The limited availability and higher cost of vernonia oil limits its use. Muturi et al. studied the performance of vernonia oil and found it to be comparable to that of epoxidized soybean oil and linseed oil. Cargill® introduced the reactive diluent Dilulin® prepared by modification of linseed oil via Diels-Alder reaction of cyclopentadiene at high temperature and pressure to form norbornene groups on the chain. Chen et al. synthesized epoxynorbornene linseed oil via Diels–Alder reaction of cyclopentadiene with linseed oil, followed by epoxidation.

In previous work, Wutticharoenwong et al. prepared three reactive diluents by functionalizing tung oil with different functional groups by Diels-Alder reactions with acrylate monomers, including alkoxy silane, triallyl ether and fluorinated alkyl. Alkoxy silane and allyl ether functionalities take part in the film formation via condensation and auto-oxidative curing, respectively. These two reactive diluents improved the tensile strength, tensile modulus, crosslink density and glass transition temperature. While fluorinated alkyl functionality does not take part in film formation, it affects the properties of the final film, including surface energy, thermal stability, hydrophobicity,
and solvent resistance. Tung oil dries rapidly but is expensive, and its films discolor rapidly due to the presence of the three conjugated double bonds. ¹ These shortcomings were the driving force behind the efforts to synthesize conjugated oils containing esters of fatty acids with two conjugated double bonds, namely conjugated soybean oil. Compared to tung oil, soybean oil remains a dominant plant-based feedstock and is a more attractive choice for use as a reactive diluent.

In this work, conjugated soybean oil was synthesized via rhodium-mediated isomerization. ¹⁴⁷ Conjugated soybean oil was then modified via a Diels-Alder reaction with different acrylate monomers: methacryloxypropyl trimethoxysilane, 2,2,2-trifluoroethyl methacrylate and triallyl ether acrylate. This is similar to the tung oil modification reported by Wutticharoenwong et al. ² Structures of modified soybean oil were characterized using ¹H NMR and ¹³C NMR spectroscopy, matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) and electrospray ionization (ESI) mass spectrometry, and ¹³C-¹H gradient heteronuclear single quantum coherence (gHSQC) NMR spectroscopy. The diluent efficiency of the modified soybean oil in alkyd was also evaluated.

3.2 Materials

Soybean oil (technical grade) was provided by Cargill™. Rhodium(III) chloride hydrate (RhCl₃·xH₂O) (Rh, 38-40%), 2-propanol (anhydrous, 99.5%), ethanol (anhydrous, ≥99.5%), toluene (ACS reagent, ≥99.5%), cis-cyclooctene, sodium dodecyl sulfate (SDS) (ACS reagent, ≥99.0%), tin (II) chloride dihydrate (SnCl₂·2H₂O) (ACS reagent, ≥98.0%), triphenylphosphine-3-sulfonic acid sodium salt (TPPMS) (technical,
≥90.0%), phenothiazine (purum, ≥98.0%), pentaerythritol allyl ether (technical grade, 70%), acrylic acid (anhydrous, 99%), 3-(trimethoxysilyl)propyl methacrylate, 2,2,2-trifluoroethyl methacrylate, phthalic anhydride (ACS reagent, ≥99%), glycerol, lithium hydroxide monohydrate (ACS reagent, ≥98.0%), p-toluenesulfonic acid (reagent plus, 98.5%), magnesium sulfate (anhydrous, reagent plus, ≥99.5%), neutral silica gel and diethyl ether (anhydrous, ACS reagent, ≥99.0%) were purchased from Sigma Aldrich. All chemicals were used as received.

3.3 Instrumentation

All reactions were performed under a N₂ atmosphere using a Schlenk line unless noted otherwise. All ¹H NMR (500 MHz) and ¹³C NMR (125 MHz) spectra (δ, ppm) were recorded on a Varian NMRS 500 spectrometer in CDCl₃ solvent. All gHSQC NMR experiments were performed using an Agilent Inova 750 MHz spectrometer equipped with a H/C/N 5 mm-PEG triple resonance cryoprobe with Z-gradients. MALDI-TOF mass spectrometry was performed on a Bruker Ultraflex-III TOF mass spectrometer (Bruker Daltonics, Inc., Billerica, MA) equipped with a Nd:Y AG laser (355 nm). All spectra were measured in positive reflection mode. Trans-2-[3-(4-t-butylphenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB, >99%) was used as the matrix as a CHCl₃ solution at a concentration of 20 mg/mL. ESI mass spectrometry experiments were performed using a HCT Ultra II quadrupole ion trap mass spectrometer (Bruker Daltonics, Billerica, MA) equipped with an electrospray ionization source. The FT-IR spectra were recorded on a Nicolet 380 FT-IR spectrometer and analyzed using OMNIC software. Viscosity measurements were accomplished using a Laboratory Brookfield Viscometer (DVII+PRO Digital) at room temperature.
3.4 Synthesis

For each modified soybean oil synthesis, first step involves synthesis of conjugated soybean oil.

3.4.1 Synthesis of Conjugated Soybean Oil

Synthesis of conjugated soybean oil is a two-step process. First step involves precatalyst synthesis.

3.4.1.1 Precatalyst Synthesis

In a 100 mL Schlenk flask, a mixture of 2-propanol (10 mL) and deionized water (2.5 mL) was degassed by three cycles of freeze-pump-thaw, and rhodium (III) chloride hydrate (500 mg, 1.9 mmol) was added. Then cis-cyclooctene (1.5 mL, 11.5 mmol) was added. The solution was stirred for 15 minutes. After standing at room temperature for 5 days, 435 mg (64% yield) of reddish-brown crystals were collected on a filter, washed with ethanol (5 mL), dried under vacuum and stored under nitrogen.

3.4.1.2 Conjugation of Soybean Oil

In a 50 mL Schlenk flask, SDS (7 mg, 0.02 mmol) was dissolved in soybean oil (10 g, 11 mmol). The mixture was degassed and flushed three times with nitrogen, while stirring at room temperature. In a separate 50 mL Schlenk flask, precatalyst (45 mg, 0.063 mmol), TPPMS (87 mg, 0.239 mmol) and tin chloride dihydrate (110 mg, 0.487 mmol) were dissolved in degassed anhydrous ethanol (10 mL). The mixture was flushed with nitrogen and stirred at room temperature. Using a cannula, the mixture containing the soybean oil and SDS was transferred to the flask containing the catalyst solution. The system was stirred at 80 °C for 24 h. The flask was then removed from the oil bath and cooled to room temperature. The oil and catalyst solution separated into two distinct
phases. The oil phase was diluted with diethyl ether (100 mL), washed 3 times with water (100 mL), and dried over anhydrous magnesium sulfate (10 g). After filtration, diethyl ether was removed by rotary evaporation. The oil obtained after extraction was purified by flash chromatography using silica gel (60 g) as the stationary phase and hexane : diethyl ether (80:20) as the eluant to yield 7.8 g of colorless, catalyst-free conjugated soybean oil. The final product was characterized using $^1$H and $^{13}$C NMR spectroscopy and ESI mass spectrometry.

$^1$H NMR: 0.88-0.92 ($m$, 9 H, CH$_3$CH$_2$), 1.24-1.31 ($m$, 64 H, O=C-(CH$_2$)$_2$-CH$_2$-, =CH-CH$_2$-CH$_2$), 1.60-1.65 ($m$, 6 H, -O(O)-C-CH$_2$CH$_2$-), 1.96-2.2 ($m$, 8 H, =CH-CH$_2$-), 2.27-2.35 ($m$, 6 H, O=CH$_2$-), 4.15 ($dd$, 2 H, CHHCHO$_2$C), 4.30 ($dd$, 2 H, CHHCHO$_2$C), 5.27-6.31 ($m$, 7 H, =CHCH=$CH$-, OCH$_2$CH(O)CH$_2$O, =CH, E- =CH-CH=CH-, E- =CH-CH=CH, =CHCH=CH). $^{13}$C NMR: 14.1 (-CH$_3$), 22.7 (CH$_3$-CH$_2$-), 24.9 (-C(O)-CH$_2$-CH$_2$-), 27.6 (=CH-CH$_2$-), 28.7, 28.9, 29.1, 29.3, 29.4, 29.7, 29.8 (=CH$_2$-), 31.5, 31.7, 31.9 (CH$_3$-CH$_2$-CH$_2$-), 34.0, 34.1, 34.4 (-C(O)-CH$_2$-), 60.1, 62.1 (-C(O)-O-CH$_2$), 68.9 (OCH$_2$CH(O)CH$_2$O), 125.7, 128.6, 129.7, 130.0, 130.2, 134.5, 134.7 (=CH=CH-), 172.8, 173.2, 173.8 (=C(O)-O-). IR: $\nu$ = 3009 (=C-H stretch), 1748 (C=O stretch), 1652 (=C=C-stretch), 726 (=C-H bending) cm$^{-1}$. ESI mass spectrometry $m/z$: [M + Na]$^+$, Calculated for C$_{57}$H$_{104}$O$_6$ 907.7833; Found 907.70. The conjugation went to complete conversion based on the complete disappearance of the allylic $^1$H NMR resonance at 2.78 ppm.

3.4.2 Synthesis of Fluorine-Functionalized Soybean Oil

Conjugated soybean oil (1.0 g, 1.1 mmol), 2,2,2-trifluoroethyl methacrylate (0.38 g, 2.3 mmol), and phenothiazine (208 mg, 0.11 mmol) were added into a 50 mL flask
equipped with a reflux condenser and a magnetic stirrer. The reaction mixture was stirred at 150 °C. After 8 h, the reaction mixture was cooled to room temperature. Unreacted 2,2,2-trifluoroethyl methacrylate was removed by rotary evaporation. Product was kept under vacuum overnight at room temperature to obtain 0.938 g of fluorine-functionalized soybean oil. The resulting product was characterized using 1H NMR, 13C NMR and gHSQC 2-D NMR spectroscopies, and MALDI-TOF mass spectrometry.

1H NMR: 0.88-0.92 (m, 9 H, CH3CH2), 1.24-1.31 (m, 68 H, O=C(CH2)2CH2=, =CHCH2CH2, -CCH2CH), 1.19 (s, 3 H, -C(CH3)2), 1.60-1.65 (m, 8 H, -O(O)C-CH2CH2=, -CH-CH=, -CH=CH-CH=, =CH-CH=CH), 2.27-2.35 (m, 6 H, O=C-CH2=), 2.45 (dd, 2 H, CHHCHO2C), 4.30 (dd, 2 H, CHHCHO2C), 4.47 (m, 2 H, -CH2-CF3), 5.26-6.33 (m, 5 H, Z- =CH-CH=CH-, OCH2CH(O)CH2O, =CH, E- =CH-CH=CH-, E- =CH-CH=CH, =CHCH=CH, -C-CH=CH-C-). 13C NMR: 14.1 (CH3), 22.7 (CH3-CH2-), 23.8 (C-CH3), 24.8 (-C(O)-CH2-CH2-), 27.6 (=CH-CH2-), 28.9, 29.1, 29.3, 29.4, 29.5, 29.7, 29.8 (-CH2-), 31.5, 31.7, 31.9 (CH3-CH2-CH2-), 32.9 (-C-CH2-CH-), 34.0, 34.2, 34.4 (-C(O)-CH2-), 39.3 , 42.3 (-CH-), 45.6 (-C-), 60.1, 62.1 (-C(O)-O-CH2-), 65.0 (-CH2-CF3), 68.9 (OCH2CH(O)CH2O), 121.5 (-CF3), 125.6, 125.7, 128.6, 128.7, 129.7, 129.8, 130.1, 130.4, 134.5, 134.7, 134.8 (-CH=CH-), 172.8, 173.2, 173.9 (-C(O)-O-). IR: ν = 3009 (=C-H stretch), 1745 (C=O stretch), 1652 (-C=C-stretch), 1282 (C-F stretch), 726 (=C-H bending) cm⁻¹. MALDI-TOF mass spectrometry m/z: [M + Na]⁺, Calculated for C₆₃H₁₁₁F₃O₈ 1075.8231; Found 1074.998. The conversion to product was approximately 42% based on the ratio of the integration of 1H NMR resonances at 4.47 ppm and 2.32 ppm.
3.4.3 Synthesis of Siloxane-Functionalized Soybean Oil

Conjugated soybean oil (1.0 g, 1.1 mmol), 3-(trimethoxysilyl)propyl methacrylate (0.56 g, 2.3 mmol), and phenothiazine (215 mg, 0.11 mmol) were added into a 50 mL flask equipped with a reflux condenser and a magnetic stirrer. The reaction mixture was stirred at 180 °C. After 8 h, the reaction mixture was cooled to room temperature. The product was kept under vacuum overnight at 40 °C to obtain 0.966 g of siloxane-functionalized soybean oil. The resulting product was characterized using $^1$H NMR, $^{13}$C NMR and gHSQC 2-D NMR spectroscopies, and MALDI-TOF mass spectrometry.

$^1$H NMR (500 MHz, CDCl$_3$) δ 0.68 (t, 2 H, -Si-CH$_2$-), 0.88-0.91 (m, 9 H, CH$_3$CH$_2$), 1.24-1.31 (m, 68 H, O=C-(CH$_2$)$_2$-CH$_2$-, =CH-CH$_2$-CH$_2$), 1.14 (s, 3 H, -C(C=O)-CH$_3$), 1.60-1.65 (m, 8 H, O=C-CH$_2$-CH$_2$-, C-CH$_2$-CH$_2$-), 1.74 (m, 2 H, -CH$_2$-CH$_2$-Si-), 1.95-2.19 (m, 8 H, =CH-CH$_2$-, CH-CH=CH-CH-$^-$), 2.27-2.35 (m, 6 H, O=C-CH$_2$-), 3.58 (s, 9 H, Si-CH$_3$), 4.03 (m, 2 H, -CH$_2$-(CH$_2$)$_2$-Si-$^-$), 4.13 (dd, 2 H, CHHCHO$_2$C), 4.30 (dd, 2 H, CHHCHO$_2$C), 5.26-6.33 (m, 5 H, Z- =CHCH=CH-, OCH$_2$CH(O)CH$_2$O, =CHE- =CH-CH=CH-$^-$, E- =CH-CH=CH, =CHCH=CH, -C-C=CH-C-$^-$). $^{13}$C NMR: 14.1 (-CH$_3$), 22.1 (-C-CH$_3$), 22.5 (-Si-CH$_2$-CH$_2$-), 22.7 (CH$_3$-CH$_2$-), 24.9 (-C(O)-CH$_2$-CH$_2$-), 27.2 (=CH-CH$_2$-), 27.7 (-Si-CH$_2$-), 28.9, 29.1, 29.3, 29.4, 29.5, 29.6, 29.7, 29.8 (-CH$_2$-), 31.9 (CH$_3$-CH$_2$-CH$_2$-), 32.6 (-C-CH$_2$-CH$_2$-), 34.0, 34.2, 34.4 (-C(O)-CH$_2$-), 37.7, 44.0 (-CH-), 45.1 (-C-), 50.5 (-Si-O-CH$_3$), 62.1 (-C(O)-O-CH$_2$-), 68.9 (OCH$_2$CH(O)CH$_2$O), 125.9, 127.9, 128.2, 128.6, 129.7, 129.9, 131.9, 132.0, 134.8 (-CH=CH-), 172.8, 173.2 (-C(O)-O-). IR: ν = 3009 (=C-H stretch), 1745 (C=O stretch), 1652 (-C=C- stretch), 983 (Si-O stretch), 815 (=C-H bending) cm$^{-1}$. MALDI-TOF mass spectrometry m/z: [M + Na]$^+$, Calculated for C$_{67}$H$_{124}$O$_{11}$Si 1155.8913; Found 1155.052.
approximately 57% based on the ratio of the integration of $^1$H NMR resonances at 0.68 ppm and 2.32 ppm.

3.4.4 Synthesis of Allyl Ether-Functionalized Soybean Oil

Synthesis of a triallyl ether acrylate: The triallyl ether acrylate was prepared by esterification of pentaerythritol allyl ether with acrylic acid. A solution of pentaerythritol allyl ether (18 g, 69 mmol), phenothiazine (0.18 g, 0.89 mmol), and $p$-toluenesulfonic acid (132 mg, 0.7 mmol) in toluene (100 mL) was refluxed in a Dean-Stark apparatus. Acrylic acid (10 g, 0.14 mol) was slowly added to the reaction mixture. After 6-7 hrs, the completion of reaction was confirmed by the amount of water (0.7 mL) collected in the Dean-Stark trap. The toluene solution was washed with saturated aqueous sodium carbonate (25 mL), water (25 mL) and dried with anhydrous magnesium sulfate (15 g). After filtration, toluene was removed by rotary evaporation to yield 11.8 g of the triallyl ether acrylate. The resulting product was characterized by $^1$H and $^{13}$C NMR spectroscopy, and ESI mass spectrometry.

$^1$H NMR: 3.42 (s, 6 H, -C-CH$_2$-O-CH$_2$), 3.47 (s, 2 H, -C-CH$_2$-O-C(O)-), 3.92-3.96 (m, 6 H, -O-CH$_2$-CH=), 5.09-6.37 (m, 12 H, -CH=CH$_2$). $^{13}$C NMR: 44.5 (4$^\circ$ C), 63.8 (-C-CH$_2$-O-C(O)), 68.9 (-C-CH$_2$-O), 72.2 (-CH$_2$-CH=), 116.2-134.9 (-CH=CH-), 165.65 (-C(O)-O-). ESI mass spectrometry m/z: [M + Na]$^+$. Calculated for C$_{17}$H$_{26}$O$_5$ 333.178; Found 332.90.

Conjugated soybean oil (1.0 g, 1.1 mmol), the triallyl ether acrylate (0.72 g, 2.3 mmol) were added into a 50 mL flask equipped with a reflux condenser and magnetic stirrer. The reaction mixture was stirred at 120 $^\circ$C. After 8 h, the reaction mixture was
cooled to room temperature. Product was kept under vacuum overnight at 40 °C to obtain 1.11 g of allyl ether-functionalized soybean oil. The resulting product was characterized using $^1$H NMR, $^{13}$C NMR, and gHSQC NMR spectroscopies, and MALDI-TOF mass spectrometry.

$^1$H NMR: 0.88-0.91 ($m$, 9 H, CH$_3$CH$_2$), 1.24-1.39 ($m$, 68 H, O=C-(CH$_2$)$_2$-CH$_2$-), =CH-CH$_2$-CH$_2$), 1.55-1.60-1.65 ($m$, 6 H, O=C-CH$_2$-CH$_2$-), 1.92-2.14 ($m$, 7 H, =CH-CH$_2$-, -O(O)C-CH-CH$_2$-CH$_2$-, -O(O)C-CH-CH$_2$-CH$_2$-, 2.27-2.35 ($m$, 6 H, -O(O)C-CH$_2$-), 2.42 ($m$, 1 H, -O(O)C-CH-CH$_2$-), 2.56 ($m$, 1 H, -O(O)C-CH-CH$_2$-), 3.40-3.48 ($m$, 6 H, -C-CH$_2$-O-), 3.51 ($s$, 2 H, -C-CH$_2$-OC(O)-), 3.94-3.98 ($m$, 6 H, -O-CH$_2$-CH=), 4.13 ($dd$, 2 H, CHHCHO$_2$C), 4.30 ($dd$, 2 H, CHHCHO$_2$C), 5.10-6.38 ($m$, 14 H, Z- =CHCH=CH-, OCH$_2$CHOH, =CH, $E$- =CH-CH=CH-, $E$- =CH-CH=CH, =CHCH=CH, -C-CH=CH-CH-, -O-CH$_2$-CH=CH$_2$). $^{13}$C NMR: 14.0 (-CH$_3$), 22.6 (CH$_3$-CH$_2$-), 24.8 (-C(O)-CH$_2$-CH$_2$-), 27.1, 27.6 (=CH-CH$_2$-), 28.9, 29.1, 29.1, 29.2, 29.4, 29.6, 29.7 (-CH$_2$-), 31.4, 31.7, 31.9 (CH$_3$-CH$_2$-CH$_2$-), 34.0 (-C(O)-CH$_2$-), 34.6 (-C(O)-CH-CH$_2$-CH-, 35.0 (-C(O)-CH-CH-), 44.6 (-C-), 44.9 (-C(O)-CH-), 62.1 (-C(O)-O-CH$_2$-CH-), 68.9 (-C-CH$_2$-O-C(O)), 69.0 (-C-CH$_2$-O-), 70.8 (-CH(O)-), 72.3 (-O-CH$_2$-CH=), 116.2 (-CH=CH$_2$), 125.5, 125.7, 128.6, 130.0, 130.2, 134.7, 134.9, 135.1 (-CH=CH-, =CH=CH$_2$), 172.7, 173.2 (-C(O)-O-). IR: $v =$ 3009 (=C-H stretch), 1745 (C=O stretch), 1652 (-C=C-stretch), 983 (C-O stretch), 724 (=C-H bending) cm$^{-1}$. MALDI-TOF mass spectrometry $m/z$: [M + Na]$^+$, Calculated for C$_{74}$H$_{130}$O$_{11}$ 1217.9613; Found 1217.018. The conversion to product was approximately 36% based on the ratio of the integration of $^1$H NMR resonances at 3.96 ppm and 2.32 ppm.
3.4.5 Synthesis of Soybean oil (Long-Oil) Alkyd Resin

The alkyd resin was prepared via the monoglyceride process. The reaction was conducted in a 500 mL four-neck round bottom flask equipped with a nitrogen inlet, thermometer, reflux condenser, and a mechanical agitator. The transesterification step involved soybean oil (200 g, 0.226 mol) and an excess of glycerol (44.8 g, 0.486 mol). These two materials were sparged with nitrogen gas for 15 min. The mixture was then heated to 120 °C and lithium hydroxide catalyst (67 mg, 1.6 mmol) was introduced into the reactor. The temperature was gradually increased to 240 °C. After approximately 1 h, a 1 mL aliquot was removed, cooled and diluted with ethanol (3 mL). This was repeated until the resulting solution was clear.

The reaction mixture from the previous step was cooled to 100 °C and a Dean-Stark trap filled with xylenes was introduced to the reaction setup. The reactor was charged with phthalic anhydride (72 g, 0.48 mol) and xylenes (5 mL) was used as a reflux solvent. The mixture was slowly heated to 220 °C. After every hour of reaction, a sample was removed, cooled and the acid number was determined. The reaction was stopped once an acid number of <10 was achieved. The acid number was determined by ASTM D4462-98 method using 0.1 N KOH and phenolphthalein indicator. The product was then cooled to room temperature and stored under nitrogen atmosphere. The resulting product was characterized using 1H NMR spectroscopy.

1H NMR: 0.83-0.89 (m, 3 H, CH₃CH₂), 1.24-1.36 (m, 14 H, O=C-(CH₂)₂-CH₂-, =CH-CH₂-CH₂), 1.58-1.60 (m, 2 H, O=C-CH₂-CH₂-), 2.01-2.08 (m, 4 H, =CH-CH₂-), 2.27-2.35 (m, 2 H, O=C-CH₂-), 2.74 (t, 2 H, =CH-CH₂-CH=), 4.15 (dd, 2 H, CHHCHO₂C),
4.25 (dd, 2 H, CHHCHO₂C), 5.31-5.41 (m, 5 H, OCH₂CH(O)CH₂O, =CH), 7.54, 7.73 (m, 4 H, aryl H).

3.5 Viscosity Measurements

Each reactive diluent was formulated with long-oil alkyd resin at three different levels (10, 20 and 30 weight% of total formulation). The total weight of each sample was 15 g. The samples were mixed on a roller mill for 1 h. To measure the viscosity, a spindle SC4-25 (Brookfield Viscometer) was used at a rotating speed of 10 rpm.

3.6 Results

The objective of this study was to develop reactive diluents based on soybean oil to create a cheaper, more accessible feedstock than the previously reported tung oil system.² Soybean oil as a semi-drying oil, reduces the oxidative degradation and yellowing. Siloxane-modified soybean oil was designed in such a way that siloxane functionality undergoes hydrolysis and condensation reactions with moisture. Unsaturated sites on the reactive diluent and alkyd binder undergo auto-oxidative curing. This dual curing will improve the crosslinking density as well as film properties. Due to higher reactivity, allyl ether functionality participates in auto-oxidative curing along with unsaturated sites on the reactive diluent and alkyd. Moreover, allyl ether-functionalized soybean oil can also be used in radiation cured coating systems. As reported by Wutticharoenwong et al.², fluorinated-functionalized soybean oil is designed as a surface-active additive. Although fluorinated alkyl functionality does not take part in film formation, it affects the properties of the final film, including surface energy and solvent resistance. Similar to allyl ether functionalized soybean oil, acrylate functionalized
soybean oil can participate in film formation in both auto-oxidative-cured and radiation-cured systems. The dilution efficiency of the reactive diluents was evaluated by studying the effect of diluent concentration on the viscosity of the soybean oil based alkyd formulation.

Soybean oil is a type of semi-drying oil that contains α-linolenic acid (10%), linoleic acid (51%), oleic acid (23%), stearic acid (4%), and palmitic acid (10%). Soybean oil was conjugated via rhodium-mediated isomerization\textsuperscript{147,148} as depicted in Figure 3.1. Conjugated soybean oil was characterized using \textsuperscript{1}H and \textsuperscript{13}C NMR spectroscopy and ESI mass spectrometry. All of the spectra agree with the results reported by Quirino et al.\textsuperscript{147} Complete disappearance of the resonance corresponding to the double allylic methylene protons on linoleic acid (-CH=CH-CH\textsubscript{2}-CH=CH-) at $\delta \approx 2.78$ ppm indicated that the conjugation of soybean oil reached 100%. Moreover, new resonances in the range of $\delta \approx 5.27$–6.35 ppm indicate that conjugated double bonds (-CH=CH-CH=CH-) are formed.
Figure 3.1. a) Synthesis of precatalyst, and b) conjugation of soybean oil.

3.6.1 Characterization of Fluorine-Functionalized Soybean Oil

The synthesis of the fluorine-functionalized soybean oil is shown in Figure 3.2. The formation of a cyclohexene ring confirms that the conjugated soybean oil reacts with 2,2,2-trifluoroethyl methacrylate by a Diels-Alder cycloaddition. The $^1$H and $^{13}$C NMR spectra of the fluorine-functionalized soybean oil are shown in Figures 3-3 and 3-4, respectively. Figure 3.3 demonstrates that the -CH$_2$-CF$_3$ protons resonate at ~4.47 ppm. The methyl protons connected to the 4° carbon of the cyclohexene ring resonate at ~1.19 ppm. The cyclohexene olefinic protons resonate in the range 5.5-5.6 ppm and overlap the resonances of other olefinic protons in the reactant and/or product. The diastereotopic methylene protons of the cyclohexene ring should resonate in the range ~1.40-1.70 ppm; however, their resonances overlap those of other methylene protons.
Figure 3.2. Synthesis of fluorine-functionalized soybean oil.

Figure 3.3. $^1$H NMR spectrum of fluorine-functionalized soybean oil.
Figure 3.4. $^{13}$C NMR spectrum of fluorine-functionalized soybean oil.

The $^{13}$C NMR resonances at 39.3-45.6 ppm in Figure 3.4 are consistent with a cyclohexene ring formed by a Diels-Alder reaction. The carbon connected to fluorine (CF$_3$) resonates at ~121.5 ppm. The resonances in the range ~125.6-134.8 ppm correspond to the unsaturated carbons, and those at ~172.8-173.9 ppm correspond to the carbonyl carbons. Many of the resonances for the rest of the chemical structure are assigned in the figure; however, the exact connectivity of the structure is not clear due to overlapping resonances.

Figures 3-5 and 3-6 compare the gHSQC spectra of the conjugated soybean oil and the fluorine-functionalized soybean oil. gHSQC NMR spectroscopy identifies directly bonded carbons and protons, and is phase sensitive. In these spectra, the crosspeaks of the methine and methyl groups are red, whereas those of the methylene
groups are blue. Each gHSQC NMR spectrum in all figures is separated into three windows: the first window presents a proton range of 0.8-3.0 ppm and a carbon range of 10-40 ppm; the second window presents a proton range of 3.0-5.6 ppm and a carbon range of 50-90 ppm; and the third window presents a proton range of 5-7.5 ppm and a carbon range of 90-150 ppm. The absence in Figure 3.5 of a $^1$H/$^{13}$C methylene crosspeak at 2.78/25.6 ppm indicates that the soybean oil is completely conjugated. The crosspeaks in window 3 in Figure 3.5 correspond to both conjugated and non-conjugated double bonds. The crosspeaks in Figures 3-5 and 3-6 confirm that the $^1$H and $^{13}$C assignments in the 1D NMR spectra are correct.

Crosspeaks corresponding to the cyclohexene ring are identifiable in Figure 3.6 by comparing window 1 in Figures 3-5 and 3-6. The new $^1$H resonances at 2.03 ppm and 2.47 ppm correlate with the $^{13}$C resonances at 42.6 ppm and 39.5 ppm, respectively (Figure 3.6). These methine crosspeaks correspond to the 3° C-H groups in the cyclohexene ring. New $^1$H resonances corresponding to the diastereotopic methylene protons are observed at 1.45 ppm and 1.65 ppm, and correlate with the $^{13}$C resonances at 32.0 ppm. The CH$_3$ connected to the 4° carbon of the cyclohexene ring is confirmed by a crosspeak between the $^1$H resonance at 1.11 ppm and the $^{13}$C resonance at 24.0 ppm. Furthermore, a -CH$_2$-CF$_3$ crosspeak is observed in Figure 3.6 (window 2) between the $^1$H resonance at 4.41 ppm and the $^{13}$C resonance at 60.6 ppm. In Figure 3.6, window 3, additional crosspeaks are observed between the $^1$H resonances at 5.63 ppm and 5.69 ppm, and the $^{13}$C resonances at 127.9 ppm and 130.4 ppm, respectively. These methine crosspeaks correspond to the new carbon-carbon double bond of the cyclohexene ring.
Figure 3.7 shows the MALDI-TOF mass spectrum of fluorine-functionalized soybean oil. The peak at \( m/z \approx 907 \) corresponds to soybean oil, which could be either the starting oil or the conjugated product. The peaks at \( m/z \approx 1045, 1074 \) and 1243 are consistent with Diels-Alder adducts of conjugated soybean oil with one, one and two \( 2,2,2 \)-trifluoroethyl methacrylates, respectively.
Figure 3.5. gHSQC 2D NMR spectrum of conjugated soybean oil.
Figure 3.6. gHSQC 2D NMR spectrum of fluorine-functionalized soybean oil.
Characterization of Siloxane-Functionalized Soybean Oil

The synthesis of the siloxane-functionalized soybean oil is shown in Figure 3.8. The formation of a cyclohexene ring confirms that the conjugated soybean oil reacts with 3-(trimethoxysilyl)propyl methacrylate by a Diels-Alder cycloaddition. The $^1$H NMR and $^{13}$C NMR spectra of the siloxane-functionalized soybean oil are shown in Figures 3-9 and 3-10, respectively. Figure 3.9 demonstrates that the -Si-OCH$_3$ protons resonate at $\sim$3.58 ppm. The methylene protons -CH$_2$-CH$_2$-CH$_2$-Si-, -CH$_2$-CH$_2$-CH$_2$-Si-, -CH$_2$-CH$_2$-CH$_2$-Si- resonate at $\sim$0.68, 1.74 and 4.03 ppm, respectively. The methyl protons connected to the $4^\circ$ carbon in the cyclohexene ring resonate at $\sim$1.14 ppm. The cyclohexene olefinic protons resonate in the range 5.5-5.6 ppm and overlap the resonances of other olefinic protons in the reactant and/or product. The diastereotopic methylene protons of the
cyclohexene ring should resonate in the range ~1.5-1.7 ppm; however, their resonances overlap those of other methylene protons.

Figure 3.8. Synthesis of siloxane-functionalized soybean oil.

Figure 3.9. $^1$H NMR spectrum of siloxane-functionalized soybean oil.
Figure 3.10. $^{13}$C NMR spectrum of siloxane-functionalized soybean oil.

The $^{13}$C NMR resonances at 37.7-45.1 ppm in Figure 3.10 are consistent with a cyclohexene ring formed by a Diels-Alder reaction. The carbon connected to oxygen (-Si-O-CH$_3$) resonates at ~50.5 ppm. The carbon connected to silicon (-CH$_2$-Si-) resonates at ~14.3 ppm. The resonances in the range ~125.6-134.8 ppm correspond to the unsaturated carbons, and those at ~172.8-173.9 ppm correspond to the carbonyl carbons. Many of the resonances for the rest of the chemical structure are assigned in the figure; however, the exact connectivity of the structure is not clear due to overlapping resonances.

Figures 3-5 and 3-11 compare the gHSQC spectra of the conjugated soybean oil and the siloxane-functionalized soybean oil. Crosspeaks corresponding to the cyclohexene ring are identifiable in Figure 3.11 by comparing window 1 in Figures 3-5 and 3-11. The new $^1$H resonances at 2.09 ppm and 2.53 ppm correlate with the $^{13}$C
resonances at 42.6 ppm and 39.4 ppm, respectively. These methine crosspeaks correspond to the 3° C-H groups in the cyclohexene ring. New ¹H resonances corresponding to the diastereotopic methylene protons are observed at 1.51 ppm and 1.70 ppm, and correlate with the ¹³C resonances at 31.9 ppm. The CH₃ connected to the 4° carbon of the cyclohexene ring is confirmed by a crosspeak between the ¹H resonance at 1.18 ppm and the ¹³C resonance at 24.0 ppm. A -Si-CH₂- and -Si-CH₂-CH₂- crosspeak is observed in Figure 3.11 (window 1) between the ¹H resonances at 0.94 and 1.72 ppm and the ¹³C resonances at 29.4 and 22.1 ppm, respectively. Furthermore, a -CH₂(CH₂)₂-Si- and -Si-O-CH₃ crosspeak is observed in Figure 3.11 (window 2) between the ¹H resonance at 3.96 and 3.55 ppm and the ¹³C resonance at 72.7 and 50.9 ppm, respectively. In Figure 3.11, window 3, additional crosspeaks are observed between the ¹H resonances at 5.69 ppm and 5.75 ppm, and the ¹³C resonances at 127.8 ppm and 130.4 ppm, respectively. These methine crosspeaks correspond to the new carbon-carbon double bond of the cyclohexene ring.

Figure 3.12 shows the MALDI-TOF mass spectrum of siloxane-functionalized soybean oil. The peak at m/z = 907 corresponds to soybean oil, which could be either the starting oil or the conjugated product. The peaks at m/z ≈ 1155 and 1403 are consistent with Diels-Alder adducts of conjugated soybean oil with one and two 3-(trimethoxysilyl)propyl methacrylates, respectively.
Figure 3.11. gHSQC 2D NMR spectrum of siloxane-functionalized soybean oil.
Figure 3.12. MALDI TOF mass spectrum of siloxane-functionalized soybean oil.

3.6.3 Characterization of Allyl Ether-Functionalized Soybean Oil

The synthesis of the allyl ether-functionalized soybean oil is shown in Figure 3.13. The formation of allyl ether acrylate was confirmed by $^1$H and $^{13}$C NMR spectroscopies and ESI mass spectrometry. Similar to previous reactions, the formation of a cyclohexene ring confirms that the conjugated soybean oil reacts with allyl ether acrylate by a Diels-Alder cycloaddition. The $^1$H and $^{13}$C NMR spectra of the allyl ether-functionalized soybean oil are shown in Figures 3-14 and 3-15, respectively.
Figure 3.13. a) Synthesis of triallyl ether acrylate b) Synthesis of triallyl ether functionalized soybean oil.

Figure 3.14. $^1$H NMR spectrum of triallyl ether-functionalized soybean oil.
Figure 3.15. $^{13}$C NMR spectrum of triallyl ether-functionalized soybean oil.

Figure 3.14 demonstrates that the $3^\circ$-CH protons in the cyclohexene ring resonate at ~2.42 and 2.56 ppm. The cyclohexene olefinic protons resonate in the range ~5.5-5.6 ppm and overlap the resonances of other olefinic protons in the reactant and/or product. The diastereotopic methylene protons of the cyclohexene ring should resonate in the range ~1.92-2.20 ppm; however, their resonances overlap those of other methylene protons.

Figure 3.15 demonstrates that the $4^\circ$ carbon from allyl ether and $3^\circ$ carbon from cyclohexene ring resonate at ~43.6-45.3 ppm. The resonances in the range ~66.63-72.15 ppm correspond to $=\text{CH-CH}_2\text{-O}$ and $-\text{O-CH}_2\text{-C-}$ carbons. The resonances in the range
~116.1-135.2 ppm correspond to the unsaturated carbons, and those at ~172.8-173.9 ppm correspond to the carbonyl carbons. Many of the resonances for the rest of the chemical structure are assigned in the figure; however, the exact connectivity of the structure is not clear due to overlapping resonances.

Figures 3-5 and 3-16 compare the gHSQC spectra of the conjugated soybean oil and the allyl ether-functionalized soybean oil. Crosspeaks corresponding to the cyclohexene ring are identifiable in Figure 3.16 by comparing window 1 in Figures 3-5 and 3-16. The new ¹H resonances at 2.02 and 2.37 ppm correlate with the ¹³C resonances at 34.9 and 34.1 ppm, respectively (Figure 3.16). These methine crosspeaks correspond to the 3° C-H groups in the cyclohexene ring. New ¹H resonances corresponding to the diastereotopic methylene protons are observed at 2.2 and 2.26 ppm, and correlate with the ¹³C resonances at 35.1 ppm. A -CH-C(O)O- crosspeak is observed in Figure 3.16 (window 1) between the ¹H resonance at 2.48 ppm and the ¹³C resonance at 35.2 ppm.

Furthermore, a -CH₂-O-CH₂-CH= , -CH₂-O-CH₂-CH= , -C(O)O-CH₂-C- crosspeak is observed in Figure 3.16 (window 2) between the ¹H resonances at 3.89, 3.42, 3.44 ppm and the ¹³C resonances at 72.6, 69.1, 70.3 ppm, respectively. In Figure 3.16, window 3, additional crosspeaks are observed between the ¹H resonances at 5.81 ppm and the ¹³C resonances at 135.3 ppm. These methine crosspeaks correspond to the new carbon-carbon double bond of the cyclohexene ring. The ¹H resonance corresponding to the -O-CH₂-CH=CHₐHₐ diastereotopic protons are observed at 5.18 and 5.07 ppm, and correlate with the ¹³C resonances at 116.9 ppm. A -O-CH₂-CH=CH₂ crosspeak is observed between the ¹H resonance at 6.06 ppm and the ¹³C resonance at 128.5 ppm.
Figure 3.17 shows the MALDI-TOF mass spectrum of allyl ether-functionalized soybean oil. The peak at m/z ≈ 907 corresponds to soybean oil, which could be either the starting oil or the conjugated product. The peak at m/z ≈ 1217 is consistent with a Diels-Alder adduct of conjugated soybean oil with one allyl ether acrylate.
Figure 3.16. gHSQC 2D NMR spectrum of allyl ether-functionalized soybean oil.
3.6.4 Viscosity measurements

The dilution efficiency of a reactive diluent can be evaluated by studying the viscosity of the alkyd formulation at different diluent concentrations. The soybean oil-based reactive diluents are expected to be compatible with the alkyd binder. The viscosities of the formulations were investigated and compared to that of the neat alkyd resin. Figure 3.18 plots the viscosity of the alkyd formulations as a function of concentration of the reactive diluent. The viscosity of the neat soybean oil long oil alkyd is 5600 cP. As expected, all reactive diluents efficiently reduced the viscosity of the alkyd by up to 86%. The overall viscosity of the formulations generally decreased with increasing reactive diluent.

Figure 3.17. MALDI-TOF mass spectrum of triallyl ether-functionalized soybean oil.
Figure 3.18. Viscosity behavior of alkyd formulation at different reactive diluent concentration at a shear rate of 2.2 s$^{-1}$.

3.7 Discussion

In order to prepare reactive diluents from soybean oil, conjugated soybean oil was first synthesized using a recyclable rhodium-based biphasic catalytic system reported previously by Larock and coworkers. Homogeneous and heterogeneous metal catalysts, enzymes and photo-catalysts have also been used to conjugate vegetable oil. Although the rhodium catalyst used here is unlikely to have much commercial relevance due to its prohibitive cost, it is very effective and convenient for academic research; $^1$H NMR analysis indicated that 100% of the unconjugated diene units in soybean oil were converted to conjugated dienes. A few heterogeneous catalytic systems have also proven to be well suited for the conjugation of vegetable oils on an industrial scale.
Reactive diluents for alkyd resins were successfully synthesized by Diels-Alder cycloadditions of different dienophiles with the conjugated soybean oil. MALDI-TOF mass spectra confirmed the expected m/z values of the reactive diluents, and $^1$H and $^{13}$C NMR spectroscopy were used to analyze their chemical structures. However, many portions of the 1D spectra were not well resolved because of a large number of overlapping resonances. This made it difficult to conclusively assign the connectivity between the reactants in the final product. Hence, the $^1$H and $^{13}$C NMR resonances were initially assigned based on previous NMR characterization of conjugated soybean oil$^{147}$ and modified tung oil,$^2$ with the help of Chemdraw NMR predictions, and then confirmed using two-dimensional, $^{13}$C-$^1$H gHSQC NMR spectroscopy.

There are a variety of reaction conditions used to promote Diels-Alder cycloaddition reactions, including high pressure, high temperature$^{70}$ and Lewis acid catalysis.$^{152,153}$ The complexity of scaling-up and commercializing a high pressure system limits the high pressure approach. Lewis-acid catalysis was not appropriate for this study because the conjugated double bonds in the modified soybean oil are unstable based on the reappearance of $^1$H NMR resonances corresponding to doubly allylic methylene protons. The Diels-Alder reactions reported here were therefore promoted using elevated temperature. A control experiment with conjugated soybean oil in the absence of an added dienophile demonstrated that high temperatures (120-150 °C) do not affect its double bonds. The highest temperature reaction was possible with 3-(trimethoxysilyl)propyl methacrylate due to its high boiling point. A lower temperature (120 °C) had to be used with the triallyl ether dienophile due to its higher number of unsaturated sites, which are susceptible to crosslinking and gelation.
Although different temperatures were used, all three Diels-Alder cycloaddition reactions were performed for the same amount of time (8 h). The conversion therefore increased with increasing temperature, with the 3-(trimethoxysilyl)propyl methacrylate reaching the highest conversion (57%), and the triallyl ether acrylate having the lowest conversion (36%), in spite of acrylates being more reactive dienophiles (more electron-deficient) than methacrylates (electron-donating methyl substituent). Similarly, the lower temperature acrylate reaction resulted in only one cycloaddition reaction with the conjugated soybean oil, whereas the higher temperature methacrylate reactions resulted in products with both one and two cycloadditions.

The nature of the catalyst and reaction conditions also dictate the stereochemistry of the 1,3-butadiene segments produced by conjugation, such as that from linoleic acid.\textsuperscript{151} The possible stereoisomers and conformations of the conjugated linoleic acid chain in conjugated soybean oil are shown in Figure 3.19. The diene must be in the s-cis (Figure 3.19: b,d,f) conformation to undergo a Diels-Alder reaction. The rotational barriers of the isomers were estimated from those of 2,4-hexadiene isomers reported by Jensen et al.\textsuperscript{154} The thermodynamic stability of the conformers can be ranked based on the "inside" CH\textsubscript{2}-H or CH\textsubscript{2}-CH\textsubscript{2} or H-H steric repulsion: a,c,e > b > f > d. The diene must be in the s-cis conformation to undergo a Diels-Alder cycloaddition since the end p orbitals are too far apart in the s-trans conformation to overlap with the p orbitals of dienophile. Although the s-trans conformation is of lower energy than the s-cis conformation, this energy difference and the barrier to rotation are not high enough to prevent most dienes from undergoing Diels-Alder reactions. For example, the E,E/s-trans conformation of 2,4-hexadiene is ~2.8 kcal/mol more stable than its E,E/s-cis conformation, and the
rotational barrier between the two conformations (rotation about the single bond between internal C atoms of the diene) is ~6 kcal/mol. Although the equilibrium mixture contains only ~1-2 mol% of the s-cis conformer, the equilibrium is re-established rapidly, and the supply of the needed conformer is therefore continuously and rapidly restored. The rotational barrier from the s-trans conformation to the s-cis conformation contributes to the overall activation barrier for the Diels-Alder reaction. The Diels-Alder conversions reported here for conjugated soybean oil are lower than those of tung oil, which contains a high amount of conjugated dienes with E,E,Z-configuration (~80% α-eleostearic acid). More of the conjugated double bonds of soybean oil may have Z,Z-stereochemistry, which are less able to interconvert from the s-trans conformation to the s-cis conformation due to CH₂-CH₂ steric repulsion (Figure 3.19).

Figure 3.19. Possible stereoisomers and conformations of conjugated soybean oil.
The viscosity of the neat soybean oil reported in this study is in the normal range (4000-6000 cP at 2.2 s\(^{-1}\) shear rate)\(^{44,156}\) of typical soybean oil / long oil alkyds. Wutticharoenwong et al.\(^2\) reported the viscosity of a similar alkyd with a modest amount of solvent xylene (≤10 wt%). The higher diluent effect of modified soybean oil compared to modified tung oil can be attributed to the lower viscosity of unmodified soybean oil than that of tung oil. All of the reactive diluents reduce the viscosity of the neat soybean oil, with the effect being greater with increasing concentration of the diluent. At any given concentration of reactive diluents, the triallyl ether-functionalized soybean oil was more effective at reducing the viscosity than the fluorine-functionalized soybean oil, which was more effective than the siloxane-modified soybean oil. This trend is therefore inversely proportional to the amount of modification of the soybean oil; i.e. the conversion was lowest with the triallyl ether-functionalized soybean oil, which contained no product with two cycloadditions. Furthermore, the lowest diluent effect of the siloxane-functionalized soybean oil can be attributed to the condensation or hydrolysis reaction with ambient moisture (sol-gel reaction), as depicted in Figure 3.20.\(^{72}\)

![Diagram](image)

Figure 3.20. Sol-gel reaction.
Diels-Alder cycloaddition of conjugated soybean oil with different functionalized dienophiles provides a new approach for the modification of soybean oil and its use as a reactive diluent in alkyd formulations. Different functional groups can be selected according to the desired properties of the final film and curing rate. The ability of the functional group to crosslink via other curing methods, such as radiation curing, may be useful in other types of binders, such as epoxies$^{157}$ and unsaturated polyesters$^{158}$. The compatibility between the reactive diluent and the binder can presumably be improved by designing a reactive diluent with a structure and polarity similar to that of the binder. There is a growing requirement for coalescing agents for water-borne coatings that are more environmentally friendly and that meet the stricter controls recently implemented in various countries around the world on volatile organic compounds (VOCs). Modified soybean oil is an attractive choice for a reactive coalescing agent in water-borne systems that can lower the minimum film-formation temperature (MFFT) and that reacts and is incorporated into the cured coating systems.$^{159,160}$

3.8 Conclusions

Conjugated soybean oil was modified via Diels-Alder cycloaddition reactions. Three different dienophiles (trialllyl ether acrylate, 3-(trimethoxysilyl)propyl methacrylate, 2,2,2-trifluoroethyl methacrylate) were reacted with conjugated soybean oil to obtain functionalized soybean oils. The conversion of the cycloaddition reaction was dictated by the temperature of the reaction, with the greater extent of cycloaddition resulting in reactive diluents that had slightly less effect at reducing the viscosity of alkyd formulations than those with lower functionalization. The resulting functionalized soybean oils acted as reactive diluents by reducing the viscosity of the long oil alkyd
formulation by up to 86%. The reduction or substitution of organic solvents in coatings processing by using reactive diluents derived from renewable materials should be an important step in the mitigation of the environmental impact of VOCs.
CHAPTER IV
MODIFIED SOYBEAN OIL AS A REACTIVE DILUENT:
COATING PERFORMANCE

4.1 Introduction

Alkyds have been widely used in the coatings industry for over eight decades.\textsuperscript{161} Alkyds are fatty acid modified polyester that are derived from a naturally occurring oil, polyols and dibasic acids. The oils used to synthesize alkyds include soybean, sunflower, tung and linseed oil.\textsuperscript{1} The major advantages of alkyds are lower cost, fewer film defects, increase in the glass transition temperature ($T_g$) via autoxidative curing of the fatty acid unsaturation.\textsuperscript{1} However, conventional alkyds require the use of organic solvents to attain the required viscosity. Organic solvents can cause environmental problems which led to environmental regulations.\textsuperscript{35,36}

The focus of recent research has been on the improvement of air quality, with particular attention being given to reducing the emission of volatile organic compounds (VOC).\textsuperscript{35,36} The reduction of VOC emissions is of particular significance to the coatings industry. Techniques such as powder coatings, water-borne coatings, UV curable coatings and high solid coatings have been used to reduce volatile organic compounds (VOCs).\textsuperscript{1,44,45} Several investigations in the past decade have focused on high solid coatings due to their environmental effect, performance and economic benefits.\textsuperscript{44,45,46,3}
The use of reactive diluents is one of the most preferred means of achieving high solid alkyd formulation. A reactive diluent lowers the viscosity of the coating formulation so that its consistency is appropriate for the coating process. It serves as a solvent and then participates in the film formation by taking part in the curing process. Low viscosity and compatibility with the binder are one of the qualities required in a reactive diluent. The second is type and amount of functionalized group \( f_n \) to react during film formation.

Several research groups\(^{3,46-55}\) have investigated the use of fatty acid esters derived from vegetable oils as reactive diluents for different types of coating systems ranging from oxidative-drying systems to cationically cured epoxy resins. Bruson\(^{57}\) synthesized dicyclopentyl methacrylate and reported that the esters alone may serve as a vehicle for coating compositions, they can be mixed with drying oils, alkyds. DuPont\(^{58}\) developed acrylic and methacrylic esters of 1,3 cyclic acetals which are suitable for air drying and can be added to the alkyd coating composition. Enomoto et al.\(^{59}\) studied the reactive diluents for alkyd coatings and reported that 1,1-bis( 1'-methyl-2'-vinyl-4’,6’-heptadienoxo)ethane was the most suitable reactive diluent amongst the investigated compounds. Bhabhe et al.\(^{64}\) synthesized oil-modified acrylic monomers as a reactive diluent for the alkyd coatings. Reactive diluents based on acrylate or acryloyl functional oligomers causes storage problems due to the preliminary polymerization.\(^7\) The additional cost of separation of fatty acids and increased sensitivity to wrinkling during drying of the test paints limits the usage of fatty acid as a reactive dileunt.\(^{46}\) Zabal et al.\(^{46}\) studied the key requirements, design aspects and incorporation of reactive diluents in the alkyd coatings.
Soucek and Wutticharoenwong\textsuperscript{2,66} prepared three reactive diluents by functionalizing tung oil with different functional groups by Diels-Alder reactions with acrylate monomers, including alkoxysilane, triallyl ether and fluorinated alkyl. The use of siloxane and allyl ether-functionalized soybean oil improved the tensile strength, tensile modulus, crosslink density and glass transition temperature. Fluorine-functionalized soybean oil provided the surface properties such as surface energy, hydrophobicity and solvent resistance to the coatings. Tung oil dries rapidly but, it discolors rapidly due to the presence of the three conjugated double bonds, and it is expensive. To overcome these drawbacks, conjugated oils containing esters of fatty acids with two conjugated double bonds, such as conjugated soybean oil were synthesized and modified\textsuperscript{24}. Moreover, an abundant and inexpensive supply of soybean in the United States makes modified soybean oil an attractive candidate for reactive diluents.

In this study, the coating performance of alkyd formulated with previously reported three soybean oil based reactive diluents\textsuperscript{162} was investigated and compared to that of tung oil based reactive diluent\textsuperscript{2,66}. Three reactive diluents were synthesized via Diels-Alder reactions with acrylate monomers, alkoxysilane, triallyl ether and fluorinated alkyl side chains and were used as the dienophiles. The reactive diluents were formulated with a long-oil soybean oil alkyd. Tensile, thermomechanical and general coating properties were evaluated as function of concentration of the reactive diluents.
4.2 Materials

Soybean oil (technical grade) was provided by Cargill\textsuperscript{TM}. Rhodium(III) chloride hydrate (RhCl\textsubscript{3}.xH\textsubscript{2}O) (Rh, 38-40%), 2-propanol (anhydrous, 99.5%), ethanol (anhydrous, ≥99.5%), toluene (ACS reagent, ≥99.5%), methyl ethyl ketone (MEK) (ACS reagent, ≥99.0%), cis-cyclooctene, sodium dodecyl sulfate (SDS) (ACS reagent, ≥99.0%), tin (II) chloride dihydrate (SnCl\textsubscript{2}.2H\textsubscript{2}O) (ACS reagent, ≥98.0%), triphenylphosphine-3-sulfonic acid sodium salt (TPPMS) (technical, ≥90.0%), phenothiazine (purum, ≥98.0%), pentaerythritol allyl ether (technical grade, 70%), acrylic acid (anhydrous, 99%), 3-(trimethoxysilyl)propyl methacrylate, 2,2,2-trifluoroethyl methacrylate, phthalic anhydride (ACS reagent, ≥99%), glycerol, lithium hydroxide monohydrate (ACS reagent, ≥98.0%), p-toluenesulfonic acid (reagent plus, 98.5%), magnesium sulfate (anhydrous, reagent plus, ≥99.5%), potassium hydroxide (ACS reagent, ≥85%), potassium hydrogen phthalate (BioXtra, ≥99.95%), phenolphthalein (ACS reagent), neutral silica gel and diethyl ether (anhydrous, ACS reagent, ≥99.0%) were purchased from Sigma Aldrich. Driers used in coating formulations, 5 wt% Cobalt Hydro-Cure II 12 wt% Zirconium Hydro-Cem, and 5wt% Calcium Hydro-Cem were obtained from OMG Group. BYK 333 was obtained from BYK additives. A-36 3003H14 Aluminum panels were obtained from Q-lab. All chemicals were used as received.

4.3 Instrumentation

The viscoelastic properties of the films were evaluated using a Q800 dynamic mechanical thermal analyzer (DMTA). The tensile properties of the films were evaluated using an Instron Universal Tester. The \textsuperscript{29}Si solid NMR experiments were
collected with a Varian narrow bore T3 HXY probe on an Agilent Direct-Drive 500 MHz spectrometer operating at 11.7 T. Samples were packed into 4 mm zirconia ceramic rotors with PTFE bottom spacers, and sealed with PTFE end caps and Vespel drive tips.

4.4 Coating formulation and film preparation

Each reactive diluent was formulated with long-oil alkyd resin at three different concentrations (10, 20 and 30 weight% of total formulation), 2 wt% metal drier package (10 wt% Cobalt Hydro-Cure II 80 wt% Zirconium Hydro-Cem, and 10 wt% Calcium Hydro-Cem) and 0.5 wt% wetting agent BYK 333. Formulation of each mixture are shown in Table 4. Each formulation is named as Soy-x where x is the concentration of conjugated soybean oil, F-x where x is the concentration of fluorine-functionalized soybean oil, Si-x where x is the concentration of siloxane-functionalized soybean oil, AE-x where x is the concentration of allyl ether-functionalized soybean oil. The neat alkyd sample was diluted with 10 wt% MEK solvent to attain an appropriate viscosity for the application. The samples were mixed on a roller mill for 1 h. A film applicator was used to cast films on clean glass panels (6 mils wet film) and on aluminum panels (3 mils wet film). The wet films were cured in the oven at 120 °C for 2 h, followed by a second cure at 160 °C for 3 h. The films were kept at room temperature for 7 days before any tests were performed to ensure a thorough cure was achieved.
Table 4.1. Alkyd formulations with reactive diluents.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Soybean Oil Long Oil Alkyd</th>
<th>Reactive diluent</th>
<th>Drier (2wt%)</th>
<th>Wetting agent (BYK 333) (0.5wt%)</th>
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</thead>
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<td></td>
<td>g</td>
<td>g</td>
<td>g</td>
<td>g</td>
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<td>-</td>
<td>0.2011</td>
<td>0.0523</td>
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<td>0.2008</td>
<td>0.0508</td>
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<tr>
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<tr>
<td>F-10</td>
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<tr>
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<td>3.0149</td>
<td>0.2126</td>
<td>0.0680</td>
</tr>
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</table>

4.5 Coating Tests

The thickness, width and initial length of the films used for tensile testing was 0.05 mm, 13 mm and 10 mm respectively. A crosshead speed of 10 mm/min with a load cell of 100 N was applied to determine elongation-at-break, tensile modulus and tensile strength of each system. Eight samples of each film were tested and the mean tensile data was reported.
The viscoelastic properties of the films were evaluated at a frequency of 1 Hz and a heating rate of 3 °C/min over a range of -50 to 150 °C. The gap distance was set at 4.5 mm for rectangular test specimens of dimensions 15 mm × 10 mm × 0.05 mm. Tan δ shows a maximum at the glass transition temperature (Tg). The crosslink density was determined using Equation 4.1:\textsuperscript{163}

\[ E'_{\text{min}} = 3 \nu_e RT \]  

where \( \nu_e \) is the number of moles of elastically effective chains per cubic meter of the film, \( E'_{\text{min}} \) is the minimum value of the storage modulus at the rubbery plateau at 50 °C above Tg, \( R \) is the gas constant, \( T \) is the absolute temperature. Three samples of each film were tested and the mean values of viscoelastic properties were reported. Free coating films peeled from the glass substrate was used for viscoelastic and tensile tests.

All general coating properties were evaluated according to the corresponding ASTM standard: Pull-off adhesion (D4541), Cross-hatch adhesion (D3359), Impact and reverse impact resistance (D2794), Pencil hardness (D3363), Gloss measurement (D2457), and MEK resistance (D4752), Drying time measurement (D5895). For each formulation, eight specimens of coated aluminum panels were tested for pull-off adhesion, cross-hatch adhesion, impact and reverse impact resistance, pencil hardness, gloss measurement and MEK resistance. Data is reported as the mean with a standard error.

4.6 Results

The main objective of this study was to investigate the coating performance of long-oil alkyds formulated with soybean oil based reactive diluents synthesized in Chapter III\textsuperscript{162} and compare the soybean oil based reactive diluent with the tung oil based
reactive diluents. Figure 4.1 shows the chemical structure of reactive diluents and alkyd. To study the improvement in the coating performance, soybean oil alkyd was chosen as a binder. Long oil alkyd was synthesized via monoglyceride method. A semi-drying oil (soybean oil) was chosen for the monoglyceride to accentuate the role of the reactive diluents. A simplified scheme of autoxidation of soybean oil alkyd is shown in Figure 2.3. A higher number of peroxy and ether linkages are formed, compared to carbon-carbon linkages.

Figure 4.1. Chemical structures of reactive diluents synthesized via Diels-Alder reaction and soybean oil alkyd.

Coatings with alkyd formulated with conjugated soybean oil were evaluated as a control experiment to study the effect of functionalization on the coating performance. Figure 2.7 shows the initiation reaction of autoxidation of conjugated soybean oil. Termination reactions during autoxidation of conjugated system are similar to those of linoleate system. Functionalized soybean oil is expected to improve the coating performance by providing additional sites for crosslinking. Ally ether functionality
provides additional crosslinking via autoxidation as shown in Figure 2.8. Muizebelt et al.\textsuperscript{3} demonstrated that allyl ether reacts faster during autoxidation than the linoleate fatty acid. Siloxane functionality provide additional crosslinking via sol-gel reaction as shown in Figure 2.13.\textsuperscript{72}

Detailed synthesis and characterization of reactive diluents was reported in Chapter III.\textsuperscript{162} Modified soybean oil structures were characterized using \textsuperscript{1}H, \textsuperscript{13}C, \textsuperscript{13}C-\textsuperscript{1}H gHSQC NMR spectroscopy and MALDI-TOF mass spectrometry. The \textsuperscript{13}C-\textsuperscript{1}H gHSQC NMR spectra confirmed the formation of a cyclohexene ring in all reactions, indicating a Diels-Alder addition. The conversions of Diels-Alder addition reactions were 40-60 % in the order: siloxane > fluorine > allyl ether-functionalized soybean oil.

Film properties were evaluated as a function of concentration of reactive diluent in the formulation. To study the effect of functionalization of the soybean oil on the coating performance, evaluation of coatings of alkyd formulated with conjugated soybean oil (non-functionalized soybean oil) was carried out as a control experiment.

4.6.1 Tensile properties

Tensile strength, elongation at break and tensile modulus of coatings are plotted as a function of diluent concentration in Figure 4.2. Incorporation of siloxane and allyl ether-functionalized soybean oil provides additional sites for crosslinking and resulted in improved tensile modulus and tensile strength. Compared to alkyd coatings, coatings with siloxane and allyl ether-functionalized soybean oil showed a 24 % and 16 % improvement in tensile strength, respectively. The tensile modulus of coatings with siloxane and allyl ether-functionalized soybean oil improved by 21 % and 14 %
respectively, compared to alkyd coatings. Although Siloxane-functionalized soybean oil has the highest conversion, its tensile properties were comparable to those of allyl ether-functionalized soybean oil. This can be attributed to the fact that allyl ether crosslinks via the same mechanism as that of alkyd binder leading to a higher average functionality for antioxidative curing. Siloxane functionality, on the other hand, undergoes condensation and hydrolysis reactions, which is different from antioxidative curing.

Tensile properties of coatings with conjugated soybean oil were similar to those of coatings with fluorine-functionalized soybean oil and 60% lower than those of alkyd coatings. Siloxane and allyl ether-functionalized soybean oil, on the other hand, showed better properties compared to those with conjugated soybean oil. This can be attributed to the additional sites for crosslinking provided by siloxane and allyl ether functionality. Percent elongation at break was independent of the type and concentration of the diluent because all reactive diluents are derived from soybean oil and consist of saturated fatty acid chain which contributes to the elongation property.

The value of diluent concentration \( c_d \) most suitable to enhance the tensile strength and tensile modulus can be explained in terms of the balance between the crosslinking provided by alkyd resin and reactive diluent. Below this particular concentration \( c_d \), the rigidity of the polyester backbone and crosslinking of the pendant fatty acid groups mainly contribute to coatings properties. The crosslinking provided by reactive diluent and the minor plasticizing effect from the saturated fatty acid chain in the reactive diluent are balanced by the alkyd's rigidity. Above \( c_d \), the rigidity of the alkyd backbone and crosslinking provided by pendant fatty acid chain are not sufficient to
build-up the film physical properties. Hence, there is only a small window of diluent concentration at which better tensile properties are observed.

![Graphs showing tensile properties as a function of diluent concentration.]

Figure 4.2. Tensile properties as a function of diluent concentration.

4.6.2 Dynamic Mechanical Analysis (DMA)

In Figure 4.3, storage modulus ($E'$) is plotted as a function of temperature. A film with a higher $E'$ value at a particular temperature shows the higher mechanical strength than a corresponding film with lower $E'$ value. Incorporation of conjugated and fluorine-functionalized soybean oil increased the storage modulus in the rubbery plateau by ~50% and ~20% respectively compared to the alkyd coatings. Compared to the alkyd, siloxane and allyl ether-functionalized soybean oil increased the storage modulus
in the rubbaery plateau by more than 100%. This could be attributed to the additional crosslinking provided by siloxane or allyl ether functionality.

Figure 4.3. Storage modulus as a function of temperature.

In Figure 4.4, tan δ is plotted as a function of temperature. The reactive diluents did not affect the width of the tan δ plot, which indicates the relative uniformity in the crosslinked network. The maxima of the tan δ curve corresponds to the glass transition temperature (T_g) above which there is co-operative segmental motion of polymer chains. In Figure 4.4, tan δ peak shifts to the lower temperatures as the concentration of conjugated soybean oil, fluorine and siloxane-functionalized soybean oil increases. T_g is plotted as a function of reactive diluent concentration in Figure 4.5. In case of coatings with fluorine-functionalized soybean oil and conjugated soybean oil, T_g decreased by
~13°C compared to alkyd coatings. This can be explained by the balance between crosslinking and plasticizing effect provided by the diluent. In the presence of the diluent, the polymer chains swell or expand, reducing the thermal energy required to cause chain motion and rotation about bonds. This causes the glass transition to shift to lower temperatures.\textsuperscript{166}

Although siloxane functionality provides additional crosslinking, $T_g$ decreased by ~4°C as the diluent concentration increased. The reduction in $T_g$ may be due to incomplete reaction of siloxane functionality. In order to check the extent of crosslinking of siloxane functionality, $^{29}$Si solid NMR spectra of cured alkyd coating films with siloxane-functionalized soybean oil were studied. Figure 4.6 shows the $^{29}$Si solid NMR spectra of the films with different concentration of siloxane-functionalized soybean oil. In all spectra, a relatively intense resonance at $\delta$ -58.02 ppm indicates the presence of Si sites with two siloxane linkages.\textsuperscript{167} However, a trifunctional alkoxy silane should form three siloxane linkages after crosslinking. The incomplete network formation can be attributed to the low alkoxy silane functionality concentration and difficulty to find other alkoxy silane for the crosslinking.

Increasing the concentration of allyl ether-functionalized soybean oil resulted in additional crosslinking. This led to an increase in the $T_g$ by ~5 °C. In case of allyl ether-functionalized soybean oil, the functionality concentration is not a concern. This is due to the same curing mechanism i.e. autoxidation for both alkyd binder and allyl ether-functionalized soybean oil.
Figure 4.4. Tan δ as a function of temperature.

Figure 4.5. Glass transition temperature as a function of diluent concentration.
In Figure 4.7, crosslink density is plotted as a function of diluent concentration. Siloxane and allyl ether-functionalized soybean oil both improved the cross-link density by 70% due to the additional crosslinking functionality as compared to the alkyd coatings. Incorporation of conjugated soybean oil and fluorine-functionalized soybean oil does not show any effect on the crosslink density at 10% concentration. Above 10% concentration of fluorine-functionality and conjugated soybean oil, coatings showed 50% decrease in the crosslink density, due to the insufficient sites available for the crosslinking.
Figure 4.7. Crosslink density as a function of diluent concentration.

4.6.3 General Coating Properties

A summary of the cured coatings properties is shown in Table 4.2. Cured coatings were evaluated by different coatings tests: cross-hatch adhesion, pencil hardness, impact and reverse impact resistance, gloss, solvent resistance and drying time measurement. Cross-hatch adhesion is independent of type or concentration of reactive diluent. However, pull off adhesion of the coatings is dependent on the type and concentration of modified soybean oil, as shown in Figure 4.8. This discrepancy can be attributed to the cross-hatch adhesion test being insensitive to all but large differences in adhesion. For each type of reactive diluent, the pull-off adhesion was not significantly affected when the concentration of reactive diluent was 10 wt %. At 20 and 30 wt % reactive diluent concentration, the adhesion strength decreased by not more than 40 % due to the reactive
diluent dominated system. Coatings with allyl ether-functionalized oil maintained better pull off adhesion for up to 30 wt % diluent concentration.

As anticipated, pencil hardness improved after incorporation of siloxane and allyl ether-functionalized soybean oil. Incorporation of fluorine-functionalized soybean oil did not affect pencil hardness. Effect of modified soybean oil as a reactive diluent on pencil hardness can be attributed to the ability of siloxane and allyl-ether functionality of taking part in the curing process, while fluorine functionality does not take part. Impact resistance, reverse impact resistance and gloss were not significantly affected after the addition of reactive diluents.

MEK resistance for coatings with fluorine-functionalized soybean oil was better than that with siloxane and allyl ether-functionalized soybean oil. Better MEK resistance is derived from high stability of C-F bond. The diluent efficiency of a reactive diluent was evaluated by studying the viscosity of the alkyd formulation at different diluent concentrations. The reactive diluent effectively reduced the viscosity of the alkyd formulation by 86%. Contact angle is plotted as a function of diluent concentration in Figure 4.9. The contact angle was increased by ~9° after the incorporation of fluorine-functionalized soybean oil. The fluorinated species would migrate toward the air/film interface to minimize the interfacial energy. Incorporation of siloxane-modified soybean oil did not significantly affect the contact angle of coatings.

Alkyds formulated with fluorine and siloxane-functionalized soybean oil showed higher drying time compared to alkyds formulated with conjugated soybean oil. In the formation of fluorine-functionalized soybean oil, conjugated double bonds get consumed.
Moreover, fluorinated alkyl functionality does not undergo autoxidative curing which lead to higher drying time. Despite the highest conversion of siloxane-functionalized soybean oil, coatings showed second lowest drying time. This can be attributed to the fact that siloxane functionality undergoes curing via sol-gel chemistry, not autoxidative curing. Hence, the initial crosslinking achieved by siloxane functionality is not sufficient to build up the film leading to a higher drying time compared to the coatings with conjugated soybean oil. Moreover, $^{29}$Si solid NMR of cured alkyd coatings with siloxane-functionalized soybean oil showed the incomplete reaction of siloxane functionality. Tack-free time for alkyd coatings with allyl ether-functionalized oil were similar to those with conjugated soybean oil. This can be explained by the higher reactivity of allyl ether functionality and conjugated double bond for autoxidation. Alkyd coatings with allyl ether-functionalized soybean oil showed higher dry-hard time than those with conjugated soybean oil. This can be attributed to the higher average functionality provided by the allyl ether-functionalized soybean oil for the autoxidation. Compared to solvent-borne alkyd coatings, all other coatings with modified soybean oil showed higher drying times. This can be attributed to solvent evaporation, which results in faster film formation.
Table 4.2. Coatings properties of alkyd films formulated with reactive diluents.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Pencil Hardness</th>
<th>Cross-Hatch Adhesion</th>
<th>20° Gloss</th>
<th>60° Gloss</th>
<th>Impact Strength</th>
<th>Reverse Impact Strength</th>
<th>MEK Double Rubs</th>
<th>Viscosity</th>
<th>Drying time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>GU</td>
<td>GU</td>
<td>lb/in</td>
<td>lb/in</td>
<td></td>
<td>cP</td>
<td>Tack-free</td>
</tr>
<tr>
<td>GUL</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>time</td>
</tr>
<tr>
<td>Alkyd</td>
<td>2B</td>
<td>5B</td>
<td>124±1</td>
<td>172±4</td>
<td>&gt; 40</td>
<td>&gt; 40</td>
<td>114±8</td>
<td>5614±52</td>
<td>7</td>
</tr>
<tr>
<td>Soy-10</td>
<td>2B</td>
<td>5B</td>
<td>94 ±1</td>
<td>134±1</td>
<td>&gt; 40</td>
<td>&gt; 40</td>
<td>51±4</td>
<td>2207±23</td>
<td>13</td>
</tr>
<tr>
<td>Soy-20</td>
<td>2B</td>
<td>5B</td>
<td>124±1</td>
<td>163±2</td>
<td>&gt; 40</td>
<td>&gt; 40</td>
<td>55±7</td>
<td>1123±41</td>
<td>13</td>
</tr>
<tr>
<td>Soy-30</td>
<td>2B</td>
<td>5B</td>
<td>132±1</td>
<td>166±1</td>
<td>&gt; 40</td>
<td>&gt; 40</td>
<td>50±8</td>
<td>432±64</td>
<td>14</td>
</tr>
<tr>
<td>F-10</td>
<td>2B</td>
<td>5B</td>
<td>120±1</td>
<td>159±1</td>
<td>&gt; 40</td>
<td>&gt; 40</td>
<td>121±11</td>
<td>2415±43</td>
<td>25</td>
</tr>
<tr>
<td>F-20</td>
<td>2B</td>
<td>5B</td>
<td>121±1</td>
<td>163±1</td>
<td>&gt; 40</td>
<td>&gt; 40</td>
<td>128±7</td>
<td>1341±38</td>
<td>25</td>
</tr>
<tr>
<td>F-30</td>
<td>2B</td>
<td>5B</td>
<td>130±1</td>
<td>173±1</td>
<td>&gt; 40</td>
<td>&gt; 40</td>
<td>98±5</td>
<td>691±78</td>
<td>14</td>
</tr>
<tr>
<td>Si-10</td>
<td>B</td>
<td>5B</td>
<td>118±1</td>
<td>159±1</td>
<td>&gt; 40</td>
<td>&gt; 40</td>
<td>89±8</td>
<td>2737±51</td>
<td>12</td>
</tr>
<tr>
<td>Si-20</td>
<td>B</td>
<td>5B</td>
<td>121±1</td>
<td>166±1</td>
<td>&gt; 40</td>
<td>&gt; 40</td>
<td>95±6</td>
<td>1589±23</td>
<td>26</td>
</tr>
<tr>
<td>Si-30</td>
<td>HB</td>
<td>5B</td>
<td>132±1</td>
<td>187±1</td>
<td>&gt; 40</td>
<td>&gt; 40</td>
<td>79±12</td>
<td>989±32</td>
<td>43</td>
</tr>
<tr>
<td>AE-10</td>
<td>HB</td>
<td>5B</td>
<td>117±1</td>
<td>157±1</td>
<td>&gt; 40</td>
<td>&gt; 40</td>
<td>102±9</td>
<td>2209±56</td>
<td>13</td>
</tr>
<tr>
<td>AE-20</td>
<td>HB</td>
<td>5B</td>
<td>125±1</td>
<td>170±1</td>
<td>&gt; 40</td>
<td>&gt; 40</td>
<td>90±5</td>
<td>1103±34</td>
<td>13</td>
</tr>
<tr>
<td>AE-30</td>
<td>F</td>
<td>5B</td>
<td>130±2</td>
<td>185±2</td>
<td>&gt; 40</td>
<td>&gt; 40</td>
<td>82±4</td>
<td>629±24</td>
<td>12</td>
</tr>
</tbody>
</table>

Figure 4.8. Pull off adhesion as a function of diluent concentration.
Figure 4.9. Contact angle as a function of diluent concentration.

4.7 Discussion

The primary goal of this study was to replace the organic solvents used in alkyd based coatings in order to reduce the VOC content. Reducing viscosity without affecting the coating performance is a major challenge for developing a new reactive diluent. Previously reported reactive diluents successfully reduced the viscosity of the formulation. However, coating performance was compromised. The modified soybean oil used in this work efficiently reduced the viscosity of the formulation by 86%.

An overall crosslinked network of alkyd formulated with allyl ether-functionalized soybean oil is depicted in Figure 4.10. Figure 4.10a depicts the autoxidatively crosslinked fatty acid chains in the alkyd. Fluorine-functionalized soybean oil is designed as a surface-active additive. While fluorinated alkyl functionality does not take part in film formation, it affects the properties of the final film, including surface
energy and solvent resistance. energy and solvent resistance. 92,169 Figure 4.10b depicts the autoxidatively crosslinked network of alkyd with unmodified conjugated soybean oil. Allyl ether functionality participates in autoxidative curing with unsaturated sites on the alkyd. The average functionality of formulations with allyl ether-functionalized soybean oil was 5-12% higher than formulations with conjugated soybean oil which leads to a better coating performance. Figure 4.11 depicts a crosslinked network of alkyd formulated with siloxane-functionalized soybean oil cured via autoxidation and sol-gel chemistry. Siloxane functionality that undergoes hydrolysis and condensation reactions with moisture, does not take part in the autoxidation. 64 Unsaturated sites on the unmodified conjugated soybean oil and alkyd binder undergo autoxidative curing. This dual curing of siloxane-functionalized soybean oil improves the crosslink density as well as film properties. Formulations with siloxane and fluorine-functionalized soybean oil have an average functionality for autoxidation comparable to the formulations with conjugated soybean oil. Siloxane-functionalized soybean oil provided an average functionality by 0.85 for curing via sol-gel chemistry. 75
Figure 4.10. Crosslinked network of alkyd with allyl ether-functionalized soybean oil, autoxidative crosslinking of (a) Alkyd-Alkyd (b) Conjugated soybean oil-Alkyd (c) Conjugated soybean oil-Conjugated soybean oil (d) Conjugated soybean oil- Allyl ether functionalized soybean oil (e) Alkyd-Allyl ether-functionalized soybean oil.
There are two curing mechanisms used in the study autoxidation and moisture cure. Unsaturated sites on unmodified conjugated soybean oil undergo autoxidation with alkyd binder system. For alkyd formulated with siloxane-functionalized soybean oil, siloxane functionality undergo moisture cure via condensation and hydrolysis to form inorganic/organic hybrid material. Siloxane functionality does not take part in the autoxidation curing. Improved crosslink density and tensile properties indicated that formation of hybrid organic/inorganic network via sol-gel process and autoxidation. Strong interaction between organic and inorganic phases improves the mechanical properties of the hybrid material.\textsuperscript{169} However, due to the two different curing
mechanisms, average functionality for autoxidation is lower despite having a higher conversion for siloxane-functionalized soybean oil than for allyl ether-functionalized soybean oil. Moreover, $^{29}$Si soilid NMR spectra of alkyd coatings formulated with siloxane-functionalized soybean oil indicated the incomplete curing of siloxane moiety. As a result, the alkyd formulated with siloxane-functionalized soybean oil showed lower $T_g$ compared to those with allyl ether-functionalized soybean oil. Despite having lower conversion, allyl ether-functionalized soybean oil showed lower drying time than that of siloxane-functionalized soybean oil. This can be attributed to the higher average functionality and reactivity of the allyl ether-functionalized soybean oil for autoxidation. Overall, the same curing mechanism i.e. autoxidation for both reactive diluent and alkyd binder is beneficial for the coating performance and drying time.

In this work, coating performance was evaluated as a function of concentration of reactive diluent in the formulation. Coatings with siloxane and allyl ether-modified soybean oil exhibited enhanced pencil hardness, while other general coating properties were not significantly affected. Coatings with fluorine-functionalized soybean oil showed improved hydrophobicity and solvent resistance. Coatings with siloxane and allyl ether-functionalized soybean oil showed improved tensile and viscoelastic properties due to the additional crosslinking. Better performance of the coatings with modified soybean oil as compared to that of conjugated soybean oil confirms the contribution of different functionalities to the coating performance. Better coating performance was observed when reactive diluents concentration is in the range 10-20 wt %, at which most favorable balance between the crosslinking provided by alkyd resin and reactive diluent was attained. In order to achieve the best possible coating performance, optimization of the
concentration and type of diluent can be done using design of experiment. Formulation can be made with the optimized concentration of combination of different reactive diluents.

The study also compared the coating performance of formulations with modified soybean oil to those of modified tung oil reported by Soucek and Wutticharoenwong. The conversions for Diels-Alder reaction were higher for tung oil compared to conjugated soybean oil. The previous chapter reported that the conjugated soybean oil is a less reactive diene as compared to tung oil due to the different reactivity of stereoisomers and conformations. For comparison with tung oil, unreacted conjugated soybean oil was not removed from the product. Coatings performance of alkyd coatings with tung oil based reactive diluents was generally better than those with soybean oil based reactive diluents. Lower conversions of conjugated soybean oil is the first parameter affecting its coatings performance. Secondly, due to the lower conversions, unreacted conjugated oil content is higher as compared to that of tung oil. Unmodified tung oil, being a drying oil (containing 80 % alpha-eleostearic acid), may not harm the drying time or performance of the coatings. Conjugated soybean oil, on the other hand, contains ~ 51 % conjugated linoleic acid, ~ 33 % oleic acid and palmitic acid which may show plasticizing effect on the coating performance at higher concentrations. Unreacted conjugated soybean oil is not as favorable as unreacted tung oil for the better coating performance and drying time. Alkyd coatings formulated with modified tung oil showed faster drying compared to those with modified soybean oil. This can be attributed to the fact that tung oil is a drying oil, while soybean oil is a semi-drying oil.
This work successfully demonstrated that soybean oil can be used to achieve the necessary coating performance, instead of using the more expensive and scarcely available tung oil. Soybeans are the one of the most planted field crop in the United States.\textsuperscript{170} Growth of soybean acreage is favored due to its planting flexibility, high yields from narrow-rowed seeding practices and low production costs. Generally soybeans are planted in May and early June and harvested in late September and October. Tung trees, on the other hand, begin bearing fruit the third year after planting and are usually in commercial production by the fourth or fifth year.\textsuperscript{171} The average life of trees is 30 years. Fruits mature and drop to ground in late September to early November. Late spring cold spells kill spring growth and destroy the fruit for that year.

The ability of allyl ether functionality to crosslink via radiation curing, may be useful in other types of binders, such as thiol functionalized binder\textsuperscript{172}, epoxy\textsuperscript{157} and unsaturated polyester\textsuperscript{158}. There is a growing requirement for coalescing agents for waterborne coatings which are more environmental friendly and meet the stricter environmental regulations implemented on VOCs in various countries around the world. Modified soybean oil is an attractive choice for a reactive coalescing agent in waterborne systems that lower the minimum film-formation temperature and that is incorporated via chemical reaction into the cured coating systems.\textsuperscript{159,160}
4.8 Conclusion

Modified soybean oil significantly reduced the viscosity of the alkyd effectively acting as a diluent. Siloxane and allyl ether-functionalized soybean oil provided additional sites for the crosslinking, which improved pencil hardness, tensile and viscoelastic properties. Although fluorine functionality does not take part in the curing, coatings with fluorine-functionalized soybean oil showed general coating performance comparable to that of alkyd. Coatings with fluorine-functionalized soybean oil showed improved solvent resistance and surface properties. Coatings containing 10-20 wt% of reactive diluents showed maximum coating performance. Although the siloxane functionality provides additional sites for curing, it does not participate in the autoxidation. As a result, coating performance and drying time was compromised. Comparable or better performance than solvent-borne alkyd coatings was achieved via the use of modified soybean oil as a reactive diluent. This demonstrates a viable approach to reduce the VOCs using an inexpensive, abundant and renewable feedstock.
CHAPTER V
AUTOXIDATIVE CURING OF RAFT POLYMERIZED ACRYLATED ALKYDS

5.1 Introduction

Alkyds are one of the most important class of coatings today. A alkyd is a fatty acid modified polyester resin derived from naturally occurring oils, polyols, and dibasic acids. The oils utilized in alkyd synthesis include soybean, sunflower, tung and linseed oil. The major advantages of alkyds are lower cost, fewer film defects during application and post-application increase in glass transition temperature ($T_g$) via auto-oxidative curing of the fatty acid unsaturation. However, the outdoor durability of alkyd films tends to be poorer than that of acrylic, polyester and polyurethane films. Alkyd paints show significant loss of gloss, chalking and degradation when exposed to UV-radiation, high humidity and thermal fluctuation. Moreover, alkyds exhibit poor hydrolytic stability. A good remedy to improve the outdoor durability of such paints is to modify alkyds with acrylic resin. Binders based on alkyd-acrylic copolymers are gaining growing interest because they offer the possibility of combining the ease of application and film forming properties of alkyd with the exterior durability of vinyl and acrylic systems due to their resistance to hydrolysis and UV degradation. Alkyd and acrylic are compatible when chemically connected to each other. Section 2.10 describes the history of alkyd-acrylic copolymer synthesis in detail.
With this need for synthesizing acrylated alkyds, Soucek and coworkers\textsuperscript{7} reported a synthetic pathway for acrylated alkyds via RAFT polymerization. The RAFT agent is attached to the alkyd chain end via esterification reaction named as alkyd macro-RAFT agent. Acrylate blocks were then grafted via RAFT-mediated polymerization as shown in Figure 5.1. This method confirmed maximum grafting and control over the molecular weight (MW) and PDI and minimum side reactions.

RAFT polymerization is one of the most successful controlled radical polymerization processes due in large to its applicability to a wide range of monomers. Exchange reactions in this technique are also very fast, which lead to well controlled systems. The key feature of the mechanism of RAFT polymerization is a sequence of addition-fragmentation equilibria as described in Section 2.13.

RAFT agents with thiocarbonyl functionality are proposed to be antioxidant for alkyd oxidative curing. An antioxidant can be defined as a compound that significantly delays or hinders the oxidation of an oxidizable substrate, when present at low concentration to those of the substrate.\textsuperscript{132} In this work substrate is seed oil derived alkyd.

Figure 5.1. Synthesis of acrylated alkyd via RAFT polymerization.
Depending on the mechanism to prevent the oxidation, antioxidants can be classified into three categories: enzyme inhibitors, metal chelator and radical scavengers. Radical scavengers type antioxidants will be studied in the work.

An antioxidant (AH) can trap an active free radical via a redox transition involving the donation of a single electron or H atom to a free radical species R as shown in Equation 5.1. A is a antioxidant derived radical. \(^{134,135}\)

1) radical trapping stage

\[ R \cdot + AH \rightarrow RH + A \cdot \] \hspace{1cm} 5.1

2) radical termination stage

\[ A \cdot + X \cdot \rightarrow \text{nonradical materials} \] \hspace{1cm} 5.2

Antioxidant can mainly directly react with the reactive free radical and destroy them or it may hinder oxidation via following\(^ {135}\): 1) a process involving the transfer of radical with the formation of "reactive" radical derived from antioxidant, 2) a process involving transfer of radical with the formation of a "stable" or "less active" radical derived from antioxidant.

While several studies have focused on antioxidant activity of sulfur compounds, a comprehensive mechanistic study has not been reported thus far\(^ {137,138,139,140,141,142}\). Generally, antioxidant activity of sulfur-based compounds is explained by the oxidation of sulfur to give a sulfoxide in the initial reaction steps. Sulfoxides are considered to be the most effective antioxidants due to the formation of active radical scavenger sulfenic acid. In the mid-twentieth century, Thompson et al. \(^ {140,141}\) reported sulfur based compounds i.e. \(\beta\)-alkylmercaptoketones as antioxidants. A general structure of a \(\beta\)-alkylmercaptoketone is shown in Figure 5.2. However, the mechanism for antioxidant
behavior was not discussed. Okada et al.\textsuperscript{142} reported the first and only study which explains mechanism of prevention of oxidation by a sulfur compound. Okada et al.\textsuperscript{142} studied antioxidant mechanism of allicin (one of the main thiosulfonates in garlic) which does not have active hydroxyl groups and are also active antioxidants and free-radical scavengers. The radical-scavenging reactions of allicin proceed via a one-step hydrogen atom transfer as shown in Figure 5.3. Combination of the allyl group (–CH\textsubscript{2}CH=CH\textsubscript{2}) and the –S(O)S– group is necessary for the antioxidant action of allicin.

\[
\begin{align*}
\text{R} & \quad \text{S} & \quad \text{C} & \quad \text{C} & \quad \text{C} & \quad \text{R}'
\end{align*}
\]

Figure 5.2. General chemical structure of β-alkylmercaptoketone based antioxidants.

\[
\begin{align*}
\text{MLOO}' & \quad \text{S} & \quad \text{H} & \quad \text{H} & \quad \text{O} & \quad \text{kinh} & \quad \text{MLOOH} & \quad \text{S} & \quad \text{C} & \quad \text{H} & \quad \text{O} & \quad \text{methyl linoleate peroxy radical} & \quad \text{Allicin} & \quad \text{methyl linoleate hydroperoxide} & \quad \text{Allicin}
\end{align*}
\]

Figure 5.3. Radical scavenging reaction of allicin.

Battin et al.\textsuperscript{138} reviewed several antioxidants based on sulfur compounds (Figure 2.24) by studying their ability to scavenge reactive oxygen species (ROS) and metal-binding. The ability of sulfur-based compounds to coordinate metal ions is very crucial in preventing the formation of ROS. A clear chemical mechanism by which sulfur coordination of metal ions prevent the formation of ROS is not clear yet.\textsuperscript{138} In this work
metal driers are not utilized in the model compound study, hence metal-binding mechanism is not studied.

The objective of this work was to study autoxidative curing of RAFT polymerized acrylated alkyds. The synthesized acrylated alkyds and intermediate products were characterized using $^1$H NMR spectroscopy. Autoxidative study was monitored using FT-IR, $^1$H NMR spectroscopy and ESI mass spectrometry. A model compound study was carried out to study the role of RAFT agent autoxidation reaction.

5.2 Materials

Soybean oil (technical grade) was provided by Cargill™. Methyl linoleate ($\geq 99\%$), phthalic anhydride (ACS reagent, $\geq 99\%$), glycerol, lithium hydroxide monohydrate (ACS reagent, $\geq 98.0\%$), 2-Cyano-2-propyl benzodithioate (>97%), 2-(Dodecylthiocarbonothioylthio)-2-methylpropionic acid (98%), 4-Cyano-4-(phenylcarbonothioylthio)pentanoic acid (>97%), Benzoyl peroxide were purchased from Sigma Aldrich. All chemicals were used as received.

5.3 Instrumentation

All $^1$H NMR (500 MHz) and $^{13}$C NMR (125 MHz) spectra ($\delta$, ppm) were recorded on a Varian NMRS 500 spectrometer in CDCl$_3$ solvent. ESI mass spectrometry experiments were performed using a HCT Ultra II quadrupole ion trap mass spectrometer (Bruker Daltonics, Billerica, MA) equipped with an electrospray ionization source. The FT-IR spectra were recorded on a Nicolet 380 FT-IR spectrometer and analyzed using OMNIC software.
5.4 Synthesis

Synthesis of acrylated alkyd included three steps: 1) synthesis of alkyd resin 2) synthesis of alkyd macro RAFT agent 3) synthesis of acrylated alkyd.

5.4.1 Synthesis of Soybean oil Alkyd Resin

The alkyd resin was prepared via the monoglyceride process. The reaction was conducted in a 500 mL four-neck round bottom flask equipped with a nitrogen inlet, thermometer, reflux condenser, and a mechanical agitator. The transesterification step involved soybean oil (200 g, 0.226 mol) and an excess of glycerol (44.8 g, 0.486 mol). These two materials were sparged with nitrogen gas for 15 min. The mixture was then heated to 120 °C and lithium hydroxide catalyst (67 mg, 1.6 mmol) was introduced into the reactor. The temperature was gradually increased to 240 °C. After approximately 1 h, a 1 mL aliquot was removed, cooled and diluted with ethanol (3 mL). This was repeated until the resulting solution was clear.

The reaction mixture from the previous step was cooled to 100 °C and a Dean-Stark trap filled with xylenes was introduced to the reaction setup. The reactor was charged with phthalic anhydride (72 g, 0.48 mol) and xylenes (5 mL) was used as a reflux solvent. The mixture was slowly heated to 220 °C. After every hour of reaction, a sample was removed, cooled and the acid number was determined. The reaction was stopped once an acid number of <10 was achieved. The acid number was determined by ASTM D4462-98 method using 0.1 N KOH and phenolphthalein indicator. The product was then cooled to room temperature and stored under nitrogen atmosphere. The resulting product was characterized using $^1$H NMR spectroscopy.
5.4.2 Synthesis of alkyd macro RAFT agent

A two-neck 500 mL round bottom flask equipped with inert gas inlet, outlet and a magnetic stirrer was used. A solution of long oil soya-alkyd (10.0 g) in chloroform (50 mL) was added to the flask and purged with nitrogen under continuous stirring until a homogenous solution was obtained. The 2-(Dodecylthiocarbonothioylthio)-2-methylpropionic acid (20.6 g, 57 mmol) was then added and mixed until dissolved, followed by the addition of DCC (11.76 g, 57 mmol) and DMAP (3.47 g, 29 mmol). The reaction mixture was left under a constant nitrogen purge and continuous stirring for 24 h. The resulting solution was filtered three times to remove the bi-product, dicyclohexyl urea, followed by evaporation of the solvent.

$^1$H NMR: 0.83-0.89 (m, 3 H, CH$_3$CH$_2$), 1.24-1.36 (m, 14 H, O=C-(CH$_2$)$_2$-CH$_2$-), =CH-CH$_2$-CH$_2$), 1.58-1.60 (m, 2 H, O=C-CH$_2$-CH$_2$-), 2.01-2.08 (m, 4 H, =CH-CH$_2$-), 2.27-2.35 (m, 2 H, O=C-CH$_2$-), 2.74 (t, 2 H, =CH-CH$_2$-CH=), 4.15 (dd, 2 H, CHHCHO$_2$C), 4.25 (dd, 2 H, CHHCHO$_2$C), 5.31-5.41 (m, 5 H, OCH$_2$CH(O)CH$_2$O, =CH), 7.54, 7.73 (m, 4 H, aryl H). IR: $\nu$ = 3009 (=C-H stretch), 1745 (C=O stretch), 1652 (-C=C- stretch), 983 (C-O stretch), 724 (=C-H bending) cm$^{-1}$. 
5.4.3 Synthesis of acrylated alkyd via RAFT polymerization

In a 100 mL one-neck round bottom flask, a solution of alkyd macro-RAFT agent (1 g, 0.32 mmol), AIBN (5 mg, 0.032 mmol) , and MMA (1 g, 0.01 mol) in toluene (5 mL) were added. The reaction mixture was purged with nitrogen for an additional 10 min and then immersed in a pre-heated oil bath at 80°C. Reactions were left in the oil bath for 8 h to ensure high conversions. Reaction mixture was cooled and after removing solvent using rotary evaporator, the product was kept under vacuum overnight at 40°C to yield yellow colored resin. The final products were characterized using $^1$H NMR spectroscopy.

$^1$H NMR: 0.83-0.89 (m, 3 H, CH$_3$CH$_2$), 1.24-1.36 (m, 14 H, O=C-(CH$_2$)$_2$-CH$_2$-, =CH-CH$_2$-CH$_2$), 1.58-1.60 (m, 4 H, O=C-CH$_2$-CH$_2$-, S-CH$_2$), 2.01-2.08 (m, 4 H, =CH-CH$_2$-), 2.27-2.35 (m, 2 H, O=C-CH$_2$-), 2.74 (t, 2 H, =CH-CH$_2$-CH=), 3.57 (s, 3 H, -C(O)O-CH$_3$), 4.15 (dd, 2 H, CHHCHO$_2$C), 4.25 (dd, 2 H, CHHCHO$_2$C), 5.31-5.41 (m, 5 H, OCH$_2$CH(O)CH$_2$O, =CH), 7.54, 7.73 (m, 4 H, aryl H). IR: ν = 3009 (=C-H stretch), 2240 (C≡N stretch), 1745 (C=O stretch), 1652 (-C=C- stretch), 983 (C-O stretch), 724 (=C-H bending) cm$^{-1}$.

5.4.4 Model Compound Study

In a one-neck round bottom flask, methyl linoleate (1 g, 3 mmol), benzoyl peroxide (165 mg, 6.8 × 10$^{-4}$ mol) and RAFT agent (2 mmol) were dissolved in 4 mL THF. The mixture was heated at 70°C for 1 h. Solvent was removed from the reaction mixture using rotary evaporator and final product was characterized using $^1$H, $^{13}$C NMR spectroscopy and FT-IR. Same procedure was repeated for each RAFT agent: 2-Cyano-2-propyl benzodithioate, 2-(Dodecylthiocarbonothioylthio)-2-methylpropionic acid, 4-
Cyano-4-(phenylcarbonothioylthio) pentanoic acid. A control experiment was done without RAFT agent. Final products were characterized using FT-IR, $^1$H NMR and ESI mass spectrometry.

5.5 Film preparation

Acrylated alkyd resin was formulated with 20 wt% MEK, 2 wt% metal drier package (10 wt% Cobalt Hydro-Cure II 80 wt% Zirconium Hydro-Cem, and 10 wt% Calcium Hydro-Cem) and 0.5 wt% wetting agent BYK 333. The samples were mixed on a roller mill for 1 h. A film applicator was used to cast films on clean glass panels (6 mils wet film) and on aluminum panels (3 mils wet film). A normal autoxidative cycle included heating the films in the oven at 120 °C for 2 h, followed by a second cure at 160 °C for 3 h.

5.6 Result and Discussion

The primary goal of this study was to investigate the autoxidative curing of RAFT polymerized acrylated alkyds. Acrylated alkyds were synthesized via RAFT polymerization as reported by Dziczkowski et al. Grafting of acrylate block on alkyd backbone chain was confirmed by using $^1$H NMR spectroscopy. $^1$H NMR spectra of alkyd macro-RAFT agent and acrylated alkyd were in complete agreement with those reported by Dziczkowski et al. Methyl linoleate was chosen as a model compound for alkyd. Autoxidative curing of methyl linoleate in presence of three different RAFT agents were studied.

The acrylated alkyd resin showed lack of film formation after normal autoxidative curing cycle. The physical appearance of the films clearly indicates that the autoxidative
curing was hindered. Figure 5.4 and 5-5 shows the FT-IR spectra of alkyd and RAFT polymerized acrylated alkyd respectively before and after normal autoxidative curing cycle. In FT-IR spectrum of alkyd after normal autoxidative curing cycle (see Figure 5.4), a broad absorption in the range of 3100–3600 cm\(^{-1}\) indicates the formation of hydroperoxides, alcohols and acids.\(^{31,32}\) The absorption centered at 1720 cm\(^{-1}\) corresponding to C=O absorption broadens significantly during the oxidation, implying the formation of carbonyl-containing species, such as aldehydes, ketones and carboxylic acids. Disappearance of absorption at 3010 cm\(^{-1}\) after normal autoxidative curing cycle indicates that C=C bonds reacted during oxidation. All these changes are in agreement with generally accepted oxidation mechanisms.\(^{3}\) In Figure 5.5, =C-H stretch at 3010 cm\(^{-1}\) remained unaffected after normal autoxidative curing cycle. Absence of a broad absorption in the range 3000-3300 cm\(^{-1}\) shows that peroxy linkages are not formed. Hence, FT-IR spectrum clearly indicate the hindrance of autoxidation.

![Image of FT-IR spectra](image)

Figure 5.4. FT-IR spectra of alkyd before and after normal autoxidative curing cycle.
Figure 5.5. FT-IR spectra of RAFT polymerized acrylated alkyd before and after normal autoxidative curing cycle.

Analogous to the antioxidant mechanism proposed by Okada et al.\textsuperscript{142}, antioxidant mechanism of methyl ester of 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid RAFT agent was proposed in Figure 5.6. The radicals formed during the initiation period may possibly be scavenged by the $\alpha$-hydrogen abstraction in 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid.

Figure 5.6. Proposed antioxidant mechanism of methyl ester of 2-(Dodecylthiocarbonothioylthio)-2-methylpropionic acid.

A model compound was studied to confirm the $\alpha$-H abstraction mechanism for inhibition of autoxidative curing. Methyl linoleate (ML) was used as a model compound
for alkyd. Three different RAFT agents were used as shown in Table 5.1. RAFT agents $b$ and $c$ do not have $\alpha$-hydrogen in the structure. Autoxidative curing of ML in the presence of these RAFT agents will be able to assist in proving or disproving $H$ abstraction mechanism. Figure 5.7 shows the FT-IR spectrum for methyl linoleate before and after normal autoxidative curing cycle with and without RAFT agent. Disappearance of =C stretch at 3010 cm$^{-1}$, broadening of C=O stretch at 1700 cm$^{-1}$ and appearance of O-H stretch at 3300 cm$^{-1}$ indicate the occurrence of autoxidative curing. After normal autoxidative curing cycle, =C stretch at 3010 cm$^{-1}$ did not disappear which indicate the hindrance of autoxidative curing. Figure 5.8 shows the ESI mass spectrum of methyl linoleate after normal autoxidative curing cycle it in presence of RAFT agent. A molecular ion peak at $m/z = 317$ correlates to unreacted ML [M+Na]$^+$ after normal autoxidative curing cycle it in the presence of RAFT agent. Signals with no $m/z$ designation are from the background. FT-IR and mass spectrometry analysis confirmed that autoxidation of ML was hindered in presence of all three RAFT agents. Hence, $\alpha$-H abstraction mechanism for the antioxidant activity of RAFT agent is disproved.
Table 5.1. Different RAFT agents and their antioxidant behavior.

<table>
<thead>
<tr>
<th>RAFT agent</th>
<th>Chemical Structure</th>
<th>Antioxidant behavior</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl ester of 2-(Dodecylthiocarbonothioylthio)-2-methylpropionic acid</td>
<td><img src="image" alt="Structure A" /></td>
<td>Positive</td>
</tr>
<tr>
<td>Methyl ester of 4-Cyano-4-(phenylcarbonothioylthio)pentanoic acid</td>
<td><img src="image" alt="Structure B" /></td>
<td>Positive</td>
</tr>
<tr>
<td>2-Cyano-2-propyl benzodithioate</td>
<td><img src="image" alt="Structure C" /></td>
<td>Positive</td>
</tr>
</tbody>
</table>
Figure 5.7. FT-IR spectra of methyl linoleate before and after normal autoxidative curing cycle with and without RAFT agent.

Figure 5.8. ESI mass spectrum of ML after normal autoxidative curing cycle in presence of RAFT agent.
\(^1\)H and \(^{13}\)C NMR spectra of ML after normal autoxidative curing cycle in the presence of 2-Cyano-2-propyl benzodithioate was studied. Figure 5.9 shows the \(^1\)H NMR spectrum of methyl linoleate after normal autoxidative curing cycle it in the presence of 2-Cyano-2-propyl benzodithioate RAFT agent. A resonance at \(\delta\) 2.78 ppm indicates that the double allylic protons remained intact and autoxidative curing did not occur. Figure 5.10 shows the \(^{13}\)C NMR spectrum of methyl linoleate after normal autoxidative curing cycle it in the presence of 2-Cyano-2-propyl benzodithioate RAFT agent. Disappearance of resonance at \(\delta\) 223 ppm which corresponds to C=S carbon indicated the reaction of the bond. Moreover, resonance at \(\delta\) 144 ppm which corresponds to aryl carbon connected to C=S also disappeared. Based on this observation, it is suggested that thiocarbonyl bond C=S mainly interferes with autoxidation reaction by converting to a functionality which acts as an antioxidant. Moreover, a new resonance at \(\delta\) 171.3 ppm appears after the reaction which may be a assigned to a new carbonyl group. A possible reason for new carbonyl group could be radical induced oxidation of RAFT agent as shown in Figure 5.11.\(^{176}\) Resonance at \(\delta\) 120 ppm corresponding to cyano (C≡N) groups also disappeared.
Figure 5.9. $^1$H NMR spectrum of ML after normal autooxidative curing cycle in presence of 2-Cyano-2-propyl benzodithioate raft agent.

Figure 5.10. $^{13}$C NMR spectrum of ML after normal autooxidative curing cycle in presence of 2-Cyano-2-propyl benzodithioate raft agent.
Based on the above results and previous studies, the antioxidant activity of the RAFT agent involves the following effects: (1) Suppression of homolytic decomposition of hydroperoxide which otherwise serves to initiate the reaction as shown in Figure 5.12. Actual antioxidants are sulfones which are formed initially upon absorption of small amount of oxygen. (2) Formation of sulfenic acid on thermal decomposition as shown in Figure 5.12. The sulfenic acids are extremely active radical scavengers particularly due to their weak O-H bond. Koelewijn et al. studied the high reactivity of sulfenic acids towards radicals. It was demonstrated by the formation of isobutyronitrile as the main product obtained from cyanoisopropyl radicals when AIBN was decomposed in the presence of dialkyl sulfoxide. Lynett et al. carried out simulation studies to study the fate of sulfinyl radical that is it may dimerize or react with other peroxy radical to give sulfonate ester of thiosulfonate ester.

Figure 5.11. Oxidation of RAFT agent.
In summary, antioxidant activity of RAFT agents can be explained by the combination of following: 1) suppression of the initiation due to formation of sulfoxides and 2) radical scavenging activity of sulfenic acid intermediate. Bateman et al.\textsuperscript{177} studied the inhibiting effect of several oxygenated products of sulfides on the oxidation of Squalene. Moreover, sulfenic acid is an active intermediate which is responsible for radical quenching. Koelewijn et al.\textsuperscript{174} studied the oxidation rate in presence of different sulfenic acids and proved its strong antioxidant action. Based on the mechanism proposed above, any RAFT agent will show an inhibiting effect on the oxidation of drying oil or alkyd.
5.7 Conclusion

In this work, a new class of sulfur compounds, thiocarbonyl compounds were demonstrated as antioxidants. FT-IR and NMR spectra confirmed the antioxidative curing of RAFT polymerized acrylated alkyd was hindered. Model compound study disproved the \( \alpha \)-H abstraction mechanism for antioxidant activity. NMR spectra suggested the reaction of C=S bond and formation of new carbonyl bond. Antioxidant activity of RAFT agents was explained by the formation of several oxidation products of sulfoxide compounds and sulfenic acid.
6.1 Introduction

Alkyds are one of the most important class of coatings today.\textsuperscript{1} Alkyd is a fatty acid modified polyester resin that is derived from naturally occurring oils, polyols, and dibasic acids. The oils utilized in the alkyd synthesis include soybean, sunflower, tung and linseed oil. The major advantages of alkyds are lower cost, fewer film defects during application and post-application increase in glass transition temperature ($T_g$) via auto-oxidative curing of the fatty acid unsaturation. However, the outdoor durability of alkyd films tends to be poorer than that of acrylic, polyester and polyurethane films.\textsuperscript{1} Alkyd paints show significant loss of gloss, chalking and degradation when exposed to UV-radiation, high humidity, and/or thermal fluctuation. Moreover, alkyds exhibit poor hydrolytic stability. A good remedy to improve the outdoor durability of such paints is to modify alkyds with acrylic resin. Alkyd-acrylic copolymers are the type of binders, which are gaining growing interest which offer the possibility of combining the ease of application and film forming properties of alkyd with the exterior durability of vinyl and acrylic systems due to their resistance to hydrolysis and UV degradation.\textsuperscript{98} Alkyd and acrylic are compatible when chemically connected to each other.

Alkyd was first modified by Armitage and coworkers\textsuperscript{5,99} in the mid-twentieth century. Alkyd-acrylic copolymers were synthesized via free radical polymerization of
alkyd and vinyl monomer. Unsaturated bonds on fatty acid chains participate in the free radical reaction. Solomon and coworkers\textsuperscript{100,101,102,103} developed a series of alkyd-acrylic copolymers based on the esterification reaction of hydroxy, carboxyl functionalities in a prepolymer and alkyd or polyol and dibasic acid. Alkyd-acrylic copolymers generally have higher glass transition temperature, producing coatings with reduced tack-free time. However, the through dry-time of such coatings is longer due to the decreased degree of unsaturation in the alkyd resulting from the copolymerization with the acrylic compound.\textsuperscript{104} Moreover, paint formulation containing alkyd-acrylic copolymers require higher amount of organic solvents due to the increased glass transition temperature ($T_g$) and molecular weight.

Schork and coworkers\textsuperscript{110,111,112,109} extensively studied emulsion polymerization of acrylics in the presence of alkyd. Low monomer conversion was observed due to the radical delocalization followed by radical transfer to the unsaturated groups in the fatty acids of the alkyd.\textsuperscript{112} As the polymerization proceeded, the polyacrylates and alkyd became immiscible and separated into different particles. To overcome these drawbacks Wang et al.\textsuperscript{109} synthesized relatively stable emulsions of alkyd and acrylic monomer by using mini-emulsion technique. Secondary nucleation is significantly diminished and hydrolytic stability of the parent alkyd is improved by the technique.\textsuperscript{113} Although mini-emulsion polymerization can overcome the synthesis limitations, it is still not widely used because of its low solids content and the high shear needed for processing.

Soucek and coworkers\textsuperscript{117} developed acrylated tung oil alkyd which showed efficient coating performance and drying. Another method was reported which includes grafting of acrylate groups onto the alkyds via free radical mechanism.\textsuperscript{6} Acrylate groups
mainly grafted at double allylic hydrogens on fatty acid chains. A small percentage of acrylic groups were grafted into the polyester backbone of the alkyd via hydrogen abstraction of the glycerol. Dziczkowski et al.\textsuperscript{7,119} introduced a new class of acrylated alkyd which is synthesized using RAFT polymerization technique. Alkyd macro RAFT agent was synthesized by attaching RAFT agent telechelically to the alkyd backbone chain. Acrylic monomers were then grafted on alkyd backbone chain by a RAFT-mediated process. This method confirmed maximum grafting and control over the molecular weight (MW) and PDI with minimum side reactions. However, autooxidative curing of the RAFT polymerized acrylated alkyd is inhibited, possibly due to trithiocarbonyl functionality as discussed in previous chapter.

Conventional free radical polymerization (RP) is a very important commercial process for preparing high molecular weight polymers. However, the main limitation of RP is poor control over some of the key elements of macromolecular structures such as MW, PDI, end functionality, chain architecture, and composition.\textsuperscript{125} These limitations can be overcome by using controlled radical polymerization (CRP) which is also commonly referred to as living radical polymerization, in which the contribution of chain breaking reactions is minimized and the apparent simultaneous growth of all chains can be achieved via nearly instantaneous initiation. There are three widely used types of CRP: atom transfer radical polymerization (ATRP), stable free-radical polymerization (SFRP) / nitroxide mediated polymerization (NMP), reversible addition–fragmentation transfer (RAFT).

ATRP is gaining a lot of attention due to it is a potential technique for the development of new materials due to the ability to control molecular weight and polymer
architecture. ATRP controls chain growth by reversible termination. The general mechanism for ATRP is shown in Figure 6.1. Ligand complexes with the cuprous salt and helps to solubalize it in the organic reaction system. The radicals, i.e., the propagating species ($P_n^*$), are generated through a reversible redox process catalyzed by a transition metal complex (activator, ($M_t^n - Y$)/Ligand, where $Y$ may be another ligand or a counterion) which undergoes a one-electron oxidation with concomitant abstraction of a halogen atom ($X$), from a dormant species ($P_n - X$). Radicals react reversibly with the oxidized metal complexes, ($X - M_t^{n+1} - Y$)/Ligand, the deactivator, to reform the dormant species and the activator. This process occurs with a rate constant of activation ($k_a$) and deactivation ($k_{da}$) respectively. Polymer chains grow by the addition of free radicals to monomers in a manner similar to conventional radical polymerization, with the rate constant of propagation ($k_p$). Termination reactions ($k_t$) also occur in ATRP, mainly through radical coupling and disproportionation. However, in well-controlled ATRP, only a few percent polymer chains undergo termination. A well controlled ATRP reaction will have not only a small contribution of the terminated chains, but also a uniform growth of all the chains, which is accomplished through fast initiation and rapid reversible deactivation.

$$P_n^*-X + M_t^n-Y/Ligand \underset{k_{act}}{\xrightarrow{k_{deact}} P_n^* + X-M_t^{n+1}-Y/Ligand}$$

Figure 6.1. Atom transfer radical polymerization mechanism.
In this work, a novel method for the synthesis of alkyd-acrylic copolymers via ATRP is demonstrated. This study shows the grafting of acrylic block on alkyd backbone chain such that the unsaturated bonds remain unreacted and will be available for autoxidative crosslinking. Characterization techniques such as quantitative $^1$H NMR, $^{13}$C NMR and gradient heteronuclear multiple bond correlation (gHSQC) 2D-NMR spectroscopy were utilized to confirm the chemical structures and determine molecular weights.

6.2 Materials

Linseed oil (supreme grade) was provided by Cargill$^TM$. Methyl methacrylate (MMA) (99%), butyl acrylate (BA) (≥99%), toluene (ACS reagent, ≥99.5%), phthalic anhydride (ACS reagent, ≥99%), glycerol (≥99.5%), lithium hydroxide monohydrate (ACS reagent, ≥98.0%), Xylenes (reagent grade), ethanol (ACS reagent, ≥99.5%), magnesium sulfate (anhydrous, reagent plus, ≥99.5%), potassium hydroxide (ACS reagent, ≥85%), potassium hydrogen phthalate (Bioxtra, ≥99.95%), phenolphthalein (ACS reagent), neutral alumina gel (grade), 2-Bromopropionyl bromide (97%), Triethylamine (≥99%), Sodium bicarbonate (ACS reagent, ≥99.7%), Dichloromethane (ACS reagent, ≥99.5%), Copper(I) bromide (98%), $N,N,N',N'',N'''$-Pentamethyldiethylenetriamine (PMDETA) (99%), Inhibitor removers, Tetrahydrofuran (THF) (ACS reagent, ≥99.0%), Acetone were purchased from Sigma Aldrich. MMA and BA were purified by passing through inhibitor remover column and then stored in the refrigerator. All other chemicals were used as received.
6.3 Instrumentation

All $^1$H NMR (500 MHz), $^{13}$C NMR (125 MHz) and two-dimensional $^1$H-$^{13}$C gradient heteronuclear multiple bond correlation (2-D gHMBC) NMR spectra were recorded on a Varian NMRS 500 MHz spectrometer in CDCl$_3$ solvent. The viscoelastic properties of the films were evaluated using a Q800 dynamic mechanical thermal analyzer (DMTA). The tensile properties of the films were evaluated using an Instron Universal Tester.

6.4 Synthesis

Synthesis of alkyd-acrylic copolymer included three steps: 1) Synthesis of alkyd resin 2) synthesis of alkyd macro initiator 3) synthesis of alkyd-acrylic copolymer.

6.4.1 Synthesis of hydroxyl-functional medium oil linseed oil alkyd (MOA)

The alkyd resin was prepared via the monoglyceride process. The reaction was conducted in a 500 mL four-neck round bottom flask equipped with a nitrogen inlet, thermometer, reflux condenser, and a mechanical agitator. The transesterification step involved Linseed oil (150.7 g, 0.172 mol) and an excess of glycerol (46.4 g, 0.504 mol). These two materials were sparged with nitrogen gas for 15 min. The mixture was then heated to 120 °C and lithium hydroxide catalyst (148 mg, 3.5 mmol) was introduced into the reactor. The temperature was gradually increased to 240 °C. After approximately 1 h, a 1 mL aliquot was removed, cooled and diluted with ethanol (3 mL). This was repeated until the resulting solution was clear.

The reaction mixture from the previous step was cooled to 100 °C and a Dean-Stark trap filled with xylenes was introduced to the reaction setup. The reactor was charged with phthalic anhydride (87.12 g, 0.59 mol) and xylenes (5 mL) was used as a
reflux solvent. The mixture was slowly heated to 220 °C. After every hour of reaction, a sample was removed, cooled and the acid number was determined. The reaction was stopped once an acid number of <10 was achieved. The acid number was determined by ASTM D4462-98 method using 0.1 N KOH and phenolphthalein indicator. The product was then cooled to room temperature and stored under nitrogen atmosphere. The resulting product was characterized using $^1$H NMR spectroscopy.

$^1$H NMR: 0.83-0.95 (m, 6 H, CH$_3$CH$_2$), 1.24-1.36 (m, 34 H, O=C-(CH$_2$)$_2$-CH$_2$-, =CH-CH$_2$-CH$_2$), 1.58-1.60 (m, 4 H, O=C-CH$_2$-CH$_2$-), 1.98-2.08 (m, 8 H, =CH-CH$_2$-), 2.27-2.35 (m, 4 H, O=C-CH$_2$-), 2.78 (t, 2 H, =CH-CH$_2$-CH=), 4.07-4.49 (m, 4 H, CHHCHO$_2$C), 5.31-5.41 (m, 7 H, OCH$_2$CH(O)CH$_2$O, =CH), 7.54, 7.73 (m, 4 H, aryl H).

$^{13}$C NMR: 14.1 (-CH$_3$), 22.7 (CH$_3$-CH$_2$-), 24.8 (C(O)-CH$_2$-CH$_2$), 24.8 (-C(O)-CH$_2$-CH$_2$-), 25.6 (=CH-CH$_2$-CH=), 27.2 (-CH$_2$-CH=), 29.1, 29.3, 29.5, 29.6, 29.7, 29.8 (-CH$_2$-), 31.9 (CH$_3$-CH$_2$-CH$_2$-), 34.1 (-C(O)-CH$_2$-), 62.1 (-C(O)-O-CH$_2$-), 65.0 (CO(O)-CH$_2$-CH-), 68.4 (OCH$_2$CH(O)CH$_2$O), 127.1, 128.3, 129.7, 129.9, 130.2 131.9 (-CH=CH-), 173.2, 173.8 (-C(O)-O-).

6.4.2 Synthesis of hydroxyl-functional long oil linseed oil alkyd (LOA)

The alkyd resin was prepared via the monoglyceride process. The reaction was conducted in a 500 mL four-neck round bottom flask equipped with a nitrogen inlet, thermometer, reflux condenser, and a mechanical agitator. The transesterification step involved Linseed oil (125 g, 0.142 mol) and an excess of glycerol (25.7 g, 0.279 mol). These two materials were sparged with nitrogen gas for 15 min. The mixture was then heated to 120 °C and lithium hydroxide catalyst (102 mg, 2.38 mmol) was introduced into the reactor. The temperature was gradually increased to 240 °C. After approximately 1 h,
a 1 mL aliquot was removed, cooled and diluted with ethanol (3 mL). This was repeated until the resulting solution was clear.

The reaction mixture from the previous step was cooled to 100 °C and a Dean-Stark trap filled with xylenes was introduced to the reaction setup. The reactor was charged with phthalic anhydride (57.1 g, 0.39 mol) and xylenes (5 mL) was used as a reflux solvent. The mixture was slowly heated to 220 °C. After every hour of reaction, a sample was removed, cooled and the acid number was determined. The reactor was then charged with glycerol (5.1 g, 55 mmol) once an acid number of ~20 was achieved. The acid number was determined by ASTM D4462-98 method using 0.1 N KOH and phenolphthalein indicator. The reaction was stopped once an acid number of <10 was achieved. The product was then cooled to room temperature and stored under nitrogen atmosphere. The resulting product was characterized using ¹H NMR spectroscopy.

¹H NMR: 0.83-0.95 (m, 6 H, CH₃CH₂), 1.24-1.36 (m, 34 H, O=C-(CH₂)₂-CH₂=), 1.58-1.60 (m, 4 H, O=C-CH₂-CH₂=), 1.98-2.08 (m, 8 H, =CH-CH₂-), 2.27-2.35 (m, 4 H, O=C-CH₂-), 2.78 (t, 2 H, =CH-CH₂=CH-), 4.07-4.49 (m, 4 H, CHHCHO₂C), 5.31-5.41 (m, 7 H, OCH₂CH(O)CH₂O, =CH), 7.54, 7.73 (m, 4 H, aryl H).

¹³C NMR: 14.1 (-CH₃), 22.7 (CH₃-CH₂-), 24.8 (C(O)-CH₂-CH₂-), 24.8 (-C(O)-CH₂-CH₂-), 25.6 (=CH-CH₂=CH=), 27.2 (-CH₂-CH=), 29.1, 29.3, 29.5, 29.6, 29.7, 29.8 (-CH₂-), 31.9 (CH₃-CH₂-CH₂-), 34.1 (-C(O)-CH₂-), 62.1 (-C(O)-O-CH₂-), 65.0 (CO(O)-CH₂-CH-), 68.4 (OCH₂CH(O)CH₂O), 127.1, 128.3, 129.7, 129.9, 130.2 131.9 (-CH=CH-), 173.2, 173.8 (-C(O)-O-).
6.4.3 Synthesis of medium-oil alkyd macro initiator (MOA_AMI)

In a 1000 ml one-neck flask, medium-oil alkyd (41 g) was dissolved in 150 mL dichloromethane. Then TEA (8.1 g, 80 mmol) was added to the flask. The flask was equipped with a magnetic stirrer and kept in an ice bath. The mixture was stirred at a temperature $T < 5\, ^\circ\text{C}$. A solution of 2-Bromopropionyl bromide (8.42 ml, 80 mmol) in 50 mL dichloromethane was added dropwise to the mixture. The reaction was stirred overnight. The reaction mixture was filtered to remove salt produced by the esterification reaction. The resulting solution was washed with a saturated solution of sodium bicarbonate (100 mL) followed by distilled water (100 mL) three times, and dried over magnesium sulfate (25 g). Dichloromethane was removed by rotary evaporator to yield medium-oil alkyd macroinitiator (51.2 g). The final product was characterized using $^1$H, $^{13}$C NMR spectroscopy.

$^1$H NMR: 0.83-0.95 ($m$, 6 H, CH$_3$CH$_2$), 1.24-1.36 ($m$, 34 H, O=C-(CH$_2$)$_2$-CH$_2$-, =CH-CH$_2$-CH$_2$), 1.58-1.60 ($m$, 4 H, O=C-CH$_2$-CH$_2$-), 1.80-1.81 ($d$, 6 H, -CH(Br)-CH$_3$), 1.98-2.08 ($m$, 8 H, =CH-CH$_2$-), 2.27-2.35 ($m$, 4 H, O=C-CH$_2$-), 2.78 ($t$, 2 H, =CH-CH$_2$-CH=), 4.07-4.49 ($m$, 4 H, CHHCHO$_2$C), 5.31-5.41 ($m$, 7 H, OCH$_2$CH(O)CH$_2$O, =CH), 7.54, 7.73 ($m$, 4 H, aryl H). $^{13}$C NMR: 14.1 (-CH$_3$, CH(Br)-CH$_3$), 22.7 (CH$_3$-CH$_2$-), 24.8 (C(O)-CH$_2$-CH$_2$), 24.8 (-C(O)-CH$_2$-CH$_2$-), 25.6 (=CH-CH$_2$-CH=), 27.2 (-CH$_2$-CH=), 29.1, 29.3, 29.5, 29.6, 29.7, 29.8 (-CH$_2$-), 31.9 (CH$_3$-CH$_2$-CH$_2$-), 34.1 (-C(O)-CH$_2$-), 45.8 (CH(Br)-CH$_3$), 62.1 (-C(O)-O-CH$_2$-), 65.0 (CO(O)-CH$_2$-CH-), 68.4 (OCH$_2$CH(O)CH$_2$O), 127.1, 128.3, 129.7, 129.9, 130.2 131.9 (-CH=CH-), 173.2, 173.8 (-C(O)-O-). Molecular weight of alkyd macroinitiator was determined from the ratio of
combined integration of resonances at δ 7.54, 7.73 ppm to the integration of resonance at δ 1.79 ppm.

6.4.4 Synthesis of long-oil alkyd macro initiator (LOA_AMI)

In a 1000 mL one-neck flask, long-oil alkyd (95.1 g) was dissolved in 250 mL dichloromethane. Then TEA (8.6 g, 85 mmol) was added to the flask. The flask was equipped with a magnetic stirrer and kept in an ice bath. The mixture was stirred at a temperature \( T < 5 \, ^\circ \text{C} \). A solution of 2-Bromopropionyl bromide (8.87 ml, 85 mmol) in 50 mL dichloromethane was added dropwise into the mixture. The reaction was stirred overnight. The reaction mixture was filtered to remove salt produced by the esterification reaction. The resulting solution was washed with saturated solution of sodium bicarbonate (300 mL) followed by distilled water (300 mL) three times, and dried over magnesium sulfate (50 g). Dichloromethane was removed by rotary evaporator to yield long-oil alkyd macroinitiator (103.2 g). The final product was characterized using \(^1\text{H}, \, ^{13}\text{C} \) NMR spectroscopy.

\(^1\text{H} \) NMR:  0.83-0.95 \((m, 6 \, \text{H}, \text{CH}_3\text{CH}_2)\), 1.24-1.36 \((m, 34 \, \text{H}, \text{O}=\text{C-(CH}_2\text{)}_2-\text{CH}_2\text{=})\), 1.58-1.60 \((m, 4 \, \text{H}, \text{O}=\text{C-CH}_2-\text{CH}_2\text{=})\), 1.80-1.81 \((d, 6 \, \text{H}, -\text{CH(Br)-CH}_3)\), 1.98-2.08 \((m, 8 \, \text{H}, -\text{CH-CH}_2\text{=})\), 2.27-2.35 \((m, 4 \, \text{H}, \text{O}=\text{C-CH}_2\text{=})\), 2.78 \((t, 2 \, \text{H}, -\text{CH-CH}_2-\text{CH=})\), 4.07-4.49 \((m, 4 \, \text{H}, \text{CHHCHO}_2\text{C})\), 5.31-5.41 \((m, 7 \, \text{H}, \text{OCH}_2\text{CH(O)CH}_2\text{O}, -\text{CH})\), 7.54, 7.73 \((m, 4 \, \text{H}, \text{aryl H})\). \(^{13}\text{C} \) NMR:  14.1 \((-\text{CH}_3, \text{CH(Br)-CH}_3\)) , 22.7 \((\text{CH}_3-\text{CH}_2\text{=})\), 24.8 \((\text{C(O)-CH}_2-\text{CH}_2\text{=})\), 24.8 \((-\text{C(O)-CH}_2-\text{CH}_2\text{=})\), 25.6 \((-\text{CH-CH}_2-\text{CH=})\), 27.2 \((-\text{CH}_2-\text{CH=})\), 29.1, 29.3, 29.5, 29.6, 29.7, 29.8 \((-\text{CH}_2\text{=})\), 31.9 \((\text{CH}_3-\text{CH}_2-\text{CH}_2\text{=})\), 34.1 \((-\text{C(O)-CH}_2\text{=})\), 45.8 \((\text{CH(Br)-CH}_3\)) , 62.1 \((-\text{C(O)-O-CH}_2\text{=})\), 65.0 \((\text{CO(O)-CH}_2-\text{CH-})\), 68.4
(OCH₂CH(O)CH₂O), 127.1, 128.3, 129.7, 129.9, 130.2 131.9 (-CH=CH-), 173.2, 173.8 (-C(O)-O-). Molecular weight of alkyd macroinitiator was determined from the ratio of combined integration of resonances at δ 7.54, 7.73 ppm to the integration of resonance at δ 1.79 ppm.

6.4.5 General Synthesis procedure for alkyd-acrylic copolymers via ATRP

In a 100 mL Schlenk flask, a 50 weight % solution of alkyd macroinitiator, PMDETA, and monomer/s in toluene was degassed by three cycles of freeze-pump-thaw. In a separate 100 mL Schlenk flask, Cu(I)Br was degassed by three cycles of vacuum-nitrogen. Using a cannula, the mixture of initiator, ligand and monomer/s was transferred to the flask containing the Cu(I)Br catalyst. The system was stirred for 15 min at room temperature. Then the reaction mixture was stirred for 24 h at 75 °C under nitrogen. The reaction mixture was cooled and purified by column chromatography using neutral alumina as a stationary phase and THF:Acetone (80:20) as an eluant. After removing solvent using rotary evaporator, the product was kept under vacuum overnight at 40 °C to yield yellow colored resin. The final products were characterized using ¹H, ¹³C NMR spectroscopy.

¹H NMR: 0.83-1.05 (m, 24 H, CH₃CH₂, C-CH₃), 1.24-1.36 (m, 34 H, O=C-(CH₂)₂-CH₂-, =CH-CH₂-CH₂), 1.58-1.60 (m, 12 H, O=C-CH₂-CH₂-, C(O)O-CH₂-(CH₂)₂-), 1.80-1.84 (m, 14 H, -CH-CH₃, -CH₂-C-C(O)-O-), 1.98-2.08 (m, 8 H, =CH-CH₂-), 2.27-2.35 (m, 4 H, O=C-C-CH₂), 2.78 (t, 2 H, =CH-CH₂-CH=), 3.57 (s, 6 H, -C(O)O-CH₃), 3.98 (t, 4 H, -C(O)O-CH₂-(CH₂)₂-CH₃), 4.07-4.49 (m, 4 H, CHHCHO₂C), 5.31-5.41 (m, 7 H, OCH₂CH(O)CH₂O, =CH), 7.54, 7.73 (m, 4 H, aryl H). ¹³C NMR: 14.1 (-CH₃), 22.7
(CH$_3$-CH$_2$-), 24.8 (C(O)-CH$_2$-CH$_2$), 24.8 (-C(O)-CH$_2$-CH$_2$-), 25.6 (=CH-CH$_2$-CH=), 27.2 (-CH$_2$-CH=), 29.1, 29.3, 29.5, 29.6, 29.7, 29.8 (-CH$_2$-), 30.3 (-OC(O)-C-CH$_3$), 31.9 (CH$_3$-CH$_2$-CH$_2$-), 34.1 (-C(O)-CH$_2$-), 35.16 (CH(Br)-CH$_3$), 44.8 (-OC(O)-C-), 51.7 (C(O)O-CH$_3$), 54.42 (-CH$_2$-C-), 62.1 (-C(O)-O-CH$_2$-), 65.0 (CO(O)-CH$_2$-CH$_2$-), 68.8 (OCH$_2$CH(O)CH$_2$O), 127.1, 128.3, 129.7, 129.9, 130.2 131.9 (-CH=CH-, 173.2, 173.8 (-C(O)-O-). Molecular weight of alkyd-acrylic copolymers was determined from the ratio of integration of resonance at δ 3.57, 3.98 ppm to the integration of resonance at δ 1.79 ppm.

6.5 Coating formulation and film preparation

Each resin was formulated with 20 wt% MEK, 2 wt% metal drier package (2.5 wt% Cobalt Hydro-Cure II 95 wt% Zirconium Hydro-Cem, and 2.5 wt% Calcium Hydro-Cem) and 0.5 wt% wetting agent BYK 333. The samples were mixed on a roller mill for 1 h. A film applicator was used to cast films on clean glass panels (6 mils wet film) and on aluminum panels (3 mils wet film). The wet films were cured in the oven at 120 °C for 2 h, followed by a second cure at 160 °C for 3 h. The films were kept at room temperature for 7 days before any tests were performed to ensure a through cure was achieved.

6.6 Coating Tests

The thickness, width and initial length of the films used for tensile testing was 0.05 mm, 13 mm and 10 mm respectively. A crosshead speed of 10 mm/min with a load cell of 100 N was applied to determine elongation-at-break, tensile modulus and tensile strength of each system. Five samples of each film were tested and the mean tensile data was reported.
The viscoelastic properties of the films were evaluated at a frequency of 1 Hz and a heating rate of 3 °C/min over a range of -50 to 150 °C. The gap distance was set at 4.5 mm for rectangular test specimens of dimensions 15 mm × 10 mm × 0.05 mm. Tan δ shows a maximum at the glass transition temperature (T_g). Two samples of each film were tested and the mean values of viscoelastic properties were reported. Free coating films peeled from the glass substrate was used for viscoelastic and tensile tests.

All general coating properties were evaluated according to the corresponding ASTM standard: Cross-hatch adhesion (D3359), Impact and reverse impact resistance (D2794), Pencil hardness (D3363), Gloss measurement (D2457), and MEK resistance (D4752), Drying time measurement (D5895). For each formulation, eight specimens of coated aluminum panels were tested for pull-off adhesion, cross-hatch adhesion, impact and reverse impact resistance, pencil hardness, gloss measurement and MEK resistance. Data is reported as the mean with a standard error.

6.7 Results

In the results section, characterization of alkyd-acrylic copolymers discussed first, followed by their coating performance.

6.7.1 Synthesis and characterization

The primary objective of this work is the synthesis of acrylic blocks grafted onto the alkyd backbone chain without reacting unsaturated bonds on the fatty acid chains. Hydroxyl functional alkyd was synthesized via monoglyceride method as shown in Figure 6.2. Linseed oil was used for the synthesis of alkyds due to its ability to undergo autoxidation efficiently. Excess of glycerol was used to achieve hydroxyl chain ends. A synthetic pathway for alkyd-acrylic copolymer via ATRP is shown in Figure 6.3. For the
synthesis of macroinitiator, 2-Bromopropionyl bromide was reacted with alkyd chain ends. The commonly used MMA and BA monomers were used to synthesize alkyd-acrylic copolymers. 2-Bromopropionyl bromide was chosen since it forms secondary radical which is the same as that formed by BA and leads to efficient polymerization. Due to the higher reactivity of the MMA monomer in radical polymerization, same macroinitiator was used. ATRP technique was used to synthesize alkyd-acrylic copolymers due to its ability to add acrylate blocks on the alkyd backbone chain without chain transferring to unsaturated bonds on fatty acid chains. Moreover, ATRP method allows to grow molecular weight in a controlled manner.

Figure 6.2. Synthesis of Linseed oil alkyd via Monoglyceride method.
Figure 6.3. Synthesis of alkyd-acrylic copolymer via ATRP technique.

$^1$H, $^{13}$C NMR spectra of alkyd confirmed the formation of a polyester backbone chain. Figure 6.4 and 6-5 show the $^1$H and $^{13}$C NMR spectra respectively of alkyd macroinintiator. In Figure 6.4, a new resonance at $\delta$ 1.79 ppm corresponds to methyl protons connected to 3° carbon after the formation of macroinitiator. Molecular weight of alkyd macroinitiators were calculated via end group analysis using quantitative proton NMR spectrum. The unassigned resonance at $\delta$ 3.10 ppm in Figure 6.4 can be attributed to the side product of reaction of free fatty acids in the alkyd and amines. In Figure 6.5, a new resonance at $\delta$ 45.7 ppm corresponds to 3° carbon connected to bromine.
Figure 6.4. $^1$H NMR spectrum of long-oil alkyd macroinitiator.

Figure 6.5. $^{13}$C NMR of long-oil alkyd macroinitiator.
Alkyd-acrylic copolymers with two different alkyd to acrylic ratios were synthesized. Alkyd-acrylic copolymers were characterized using $^1$H NMR, $^{13}$C NMR spectroscopy. The characterization of one alkyd-acrylic copolymer will be discussed in detail in this section. MMA grafted onto the long oil alkyd with Alkyd:MMA weight ratio 2:1 is named as LOA_MMA_2. Figure 6.6 and 6-7 shows the $^1$H and $^{13}$C NMR spectra respectively for LOA_MMA_2. In Figure 6.6, a new resonance at $\delta$ 3.57 ppm corresponds to the methyl protons from MMA repeating unit. The comparison of the integration of the resonance at $\delta$ 2.78 ppm in $^1$H NMR spectra of AMI and LOA_MMA_2 indicates that double allylic protons on fatty acid chain in the alkyd do not interfere with atom transfer radical polymerization (ATRP). Molecular weight of alkyd-acrylic copolymers were calculated via end group analysis of quantitative proton NMR spectra. In Figure 6.7, new resonances in the range $\delta$ 45-55 ppm indicate the polymerization of MMA. Many of the resonances for the rest of the chemical structure are assigned in the figure; however, the exact connectivity of the MMA block to the alkyd backbone chain is not clear due to overlapping resonances.
Figure 6.6. $^1$H NMR spectrum of LOA_MMA_2.

Figure 6.7. $^{13}$C NMR spectrum of LOA_MMA_2.
Figures 6-8, 6-9 and 6-10 compare the gHMBC spectra of the LOA, AMI and LOA_MMA_2, respectively. The gHMBC 2D-NMR spectroscopy identifies the correlations between carbons and protons that are separated by two, three, and, sometimes in conjugated systems, four bonds. 1D and 2D-NMR spectra were assigned based on the previous NMR characterization of poly(meth)acrylates\textsuperscript{179} and NMR database\textsuperscript{131}. gHMBC spectrum of LOA shown in Figure 6.8 was in agreement with 1D proton and carbon NMR. In Figure 6.9, a crosspeak at $\delta_H = 1.78$ and $\delta_C = 44.5$ ppm indicates the correlation of methyl protons to the 3$^\circ$ carbon. A crosspeak at $\delta_H = 1.78$ and $\delta_C = 173.4$ ppm indicates the correlation of methyl protons to the carbonyl carbon.

In Figure 6.10, a crosspeak at $\delta_H = 2.15, 2.4$ and $\delta_C \sim 34.1$ ppm indicates the correlation of nonequivalent methylene protons to the 3$^\circ$ carbon and 4$^\circ$ carbon. A crosspeak at $\delta_H = 1.1$ and $\delta_C \sim 34.1$ ppm indicates the correlation of methyl protons to the 3$^\circ$ carbon. A crosspeak at $\delta_H = 1.92$ and $\delta_C \sim 20.4$ and 44.8 ppm indicates the correlation of methine protons to the 1$^\circ$ carbon and 2$^\circ$ carbon. These correlations indicate the connection of MMA to alkyd backbone chains. Crosspeaks in the range $\delta_H = 0.8-2.1$ and at $\delta_C \sim 44.8, 54.1, 173.3$ ppm indicate the long range correlations of MMA repeating units as assigned in the Figure 7. A crosspeak at $\delta_H = 3.57$ and $\delta_C \sim 176.7$ ppm indicates the correlation of methyl protons to the carbonyl carbon. The remaining correlations were in agreement with those of the starting alkyd.
Figure 6.8. gHMBC 2D-NMR spectrum of long oil alkyd.

Figure 6.9. gHMBC 2D-NMR spectrum of long-oil alkyd macroinitiator.
Figure 6.10. gHMBC 2D-NMR spectrum of LOA_MMA_2.

Table 6.1 lists the different alkyd-acrylic copolymers synthesized with the corresponding alkyd to acrylic ratios. As explained earlier, molecular weights were determined via end group analysis using quantitative $^1$H NMR. $^1$H NMR spectra of other synthesized alkyd-acrylic copolymers are provided in Appendix A. Overall, conversions of acrylic monomers were limited to 70%. This can be explained by the effect of monomer concentration on the polymerization reaction. Due to the presence of macrorinitiator, monomer concentration is not as high as it is in general ATRP polymerization reactions. After a certain monomer conversion, the concentration of monomers in the reaction mixture reduces to such an extent that active radicals have difficulty finding unreacted monomer.
In general, MMA showed higher conversions as compared to BA in ATRP polymerization. This can be attributed to the higher reactivity of MMA monomer than that of BA monomer. With diffusion control of the mobility of the monomer, its reactivity also affects the final conversion of the reaction. Reactions with LOA_AMI showed higher monomer conversion as compared to those with MOA macroinitiator. This can be explained by the number of initiator functionality per alkyd molecule. As mentioned in the experimental section, MOA has a higher number of hydroxyl functionality as compared to LOA. However, for molecular weight calculations it is assumed that each chain has two hydroxyl functionalities. Hence calculated molecular weight of MOA-acrylic copolymers is less than actual molecular weight. The estimated conversions of MOA-acrylic copolymers are low since they are calculated from the corresponding molecular weights which are determined using $^1$H NMR spectra. Integration of resonance of double allylic protons normalized by that of aromatic protons, $A = \frac{[A]_{\text{double allylic } H}}{[A]_{\text{aromatic } H}}$ remains the same after ATRP reaction. This observation indicate that the chain transfer to double allylic protons was too low to be detected by $^1$H NMR spectroscopy and the unsaturated bonds on fatty acid chain in alkyd do not interfere with the radical polymerization significantly.
Table 6.1. Alkyd-acrylic copolymers.

<table>
<thead>
<tr>
<th>Polymer Name</th>
<th>Alkyd: Acrylic weight ratio</th>
<th>Molecular Weight g/mol</th>
<th>Theoretical Molecular Weight g/mol</th>
<th>Conversion %</th>
<th>MMA</th>
<th>BA</th>
</tr>
</thead>
<tbody>
<tr>
<td>LOA_AMI</td>
<td>1:0</td>
<td>1935</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>LOA_MMA_1</td>
<td>1:1</td>
<td>3272</td>
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<td>69</td>
<td>-</td>
<td>0.54</td>
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<tr>
<td>LOA_MMA_2</td>
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<td>2644</td>
<td>2902</td>
<td>73</td>
<td>-</td>
<td>0.54</td>
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<tr>
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<td>3869</td>
<td>-</td>
<td>63</td>
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</tr>
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<td>-</td>
<td>61</td>
<td>0.54</td>
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<tr>
<td>LOA_MMA_BA_1</td>
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<td>3635</td>
<td>3869</td>
<td>-</td>
<td>45</td>
<td>43</td>
</tr>
<tr>
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<td>-</td>
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<td>-</td>
<td>-</td>
<td>-</td>
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<td>3051</td>
<td>62</td>
<td>-</td>
<td>0.43</td>
</tr>
<tr>
<td>MOA_MMA_2</td>
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<td>2288</td>
<td>66</td>
<td>-</td>
<td>0.43</td>
</tr>
<tr>
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<td>3051</td>
<td>-</td>
<td>35</td>
<td>0.43</td>
</tr>
<tr>
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<td>1735</td>
<td>2288</td>
<td>-</td>
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<td>0.43</td>
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<td>2534</td>
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<td>39</td>
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<tr>
<td>MOA_MMA_BA_2</td>
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<td>2215</td>
<td>2288</td>
<td>52</td>
<td>38</td>
<td>0.43</td>
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6.7.2 Coating properties

The second objective of this study was to investigate the coating performance of alkyd-acrylic copolymers. Alkyd and alkyd-acrylic copolymer films were cured via
autoxidative curing. Coating performance was evaluated as a function of alkyd to acrylic ratios. To study the effect of addition of acrylic block onto the alkyd backbone chain on coating performance, non-modified alkyd films were studied as a control experiment.

6.7.2.1 Tensile Properties

Tensile properties of long oil and medium oil alkyd-acrylic copolymer coatings are plotted as a function of alkyd to acrylic ratios in Figure 6.11 and 6-12, respectively. Tensile properties include modulus, tensile stress at break and percent elongation. Tensile testing for LOA and MOA_MMA_1 could not be done due to their highly brittle nature. Overall, grafting of MMA block on alkyd backbone chain improved the modulus by 20 times the modulus of non-modified alkyd. Grafting of BA on alkyd backbone chain, on the other hand, showed 20 and 5 times less modulus than that of LOA and MOA, respectively. Alkyd-MMA coatings showed brittle failure because the elongation at break is low. This can be attributed to the stiffness imparted by the polymethacrylate block in the polymer. BA, on the other hand, decreases the stiffness due to the polyacrylate block as well as n-butyl aliphatic pendant chains. For the same reason, copolymer coatings with BA showed 63% higher elongation at break. LOA-acrylic copolymers showed a higher modulus than MOA-acrylic copolymers. This can be attributed to the fact that, LOA contains higher amount of oil which gives a higher functionality for crosslinking. Due to the higher crosslinking, LOA-acrylic copolymers show higher modulus. For the same reason, MOA-acrylic copolymers showed 40% higher elongation than LOA-acrylic copolymers.
Figure 6.11. Tensile properties of LOA-acrylic copolymer coatings.

Figure 6.12. Tensile properties of MOA-acrylic copolymer coatings.
6.7.2.2 Glass transition temperatures

Glass transition temperature of long oil and medium oil alkyd-acrylic copolymer coatings are plotted as a function of alkyd to acrylic rations in Figure 6.13. DMA testing for LOA and MOA_MMA_1 could not be done due to their highly brittle nature. All copolymers exhibited glass transition temperature between the glass transition temperature of alkyd and acrylic. Glass transition temperatures estimated by the Fox equation\textsuperscript{180} were comparable with those determined by Dynamic Mechanical Analysis (DMA). The occurrence of one glass transition temperature indicates the compatibility of alkyd and acrylic together. This compatibility can be explained by the presence of ester functionality in both and the successful grafting of acrylic block on alkyd backbone chain. Grafting of MMA block on alkyd chain increased the overall glass transition temperature by 30%. Grafting of BA block on alkyd chain, on the other hand, decreased the overall glass transition temperature by 30%.

Figure 6.13. Glass transition temperature of a) LOA-acrylic copolymer b) MOA_acrylic copolymer coatings.
6.7.2.3 General Coating Properties

Table 6.2 lists the general properties of alkyd-acrylic copolymers coatings. Overall, alkyds-MMA copolymers showed higher pencil hardness as compared to the alkyd-BA copolymers coatings. This can be attributed to the improved $T_g$ due to grafting of MMA block on alkyd backbone chain. Cross-hatch adhesion of coatings was maintained after incorporation of any of the acrylic monomer. Due to the improved hardness, alkyd-MMA at 1:1 ratio copolymers showed lower impact resistance as compare to those of non-modified alkyds and alkyd-BA copolymer coatings. Remaining alkyd-acrylic copolymers showed same impact resistance as non-modified alkyd. Except alkyd-BA copolymer, all alkyd-acrylic copolymers showed MEK resistance comparable to that of non-modified alkyd coatings. This can be attributed to the soft coatings formed by alkyd_BA copolymers. Overall, LOA-acrylic copolymers showed faster drying than MOA-acrylic copolymer coatings. This can be attributed to the fact that LOA contains higher amount of oil, due to which reactive sites for autoxidative curing are higher. Alkyd-MMA copolymers showed relatively faster drying than alkyd_BA copolymers. This can be attributed to the higher $T_g$ of MOA-MMA copolymer coatings. Hence, the film hardens faster although chemical crosslinking is not complete.
Table 6.2. General coating properties of alkyd-acrylic copolymers.

<table>
<thead>
<tr>
<th>Copolymer Name</th>
<th>Pencil Hardness</th>
<th>Cross-hatch adhesion</th>
<th>Impact strength lb/in</th>
<th>Reverse Impact Strength lb/in</th>
<th>MEK Resistance GU</th>
<th>Gloss 20°</th>
<th>Gloss 60°</th>
<th>Tack free time h</th>
<th>Dry hard time h</th>
</tr>
</thead>
<tbody>
<tr>
<td>LOA</td>
<td>2B</td>
<td>5B</td>
<td>&gt; 40</td>
<td>&gt; 40</td>
<td>282±6</td>
<td>119±2</td>
<td>158±3</td>
<td>11</td>
<td>21</td>
</tr>
<tr>
<td>LOA_AMI</td>
<td>2B</td>
<td>5B</td>
<td>&gt; 40</td>
<td>&gt; 40</td>
<td>250±5</td>
<td>115±1</td>
<td>136±5</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>LOA_MMA_1</td>
<td>3H</td>
<td>5B</td>
<td>&gt; 40</td>
<td>25</td>
<td>210±8</td>
<td>75±2</td>
<td>124±1</td>
<td>&lt; 0.5</td>
<td>&lt; 0.5</td>
</tr>
<tr>
<td>LOA_MMA_2</td>
<td>2H</td>
<td>5B</td>
<td>&gt; 40</td>
<td>&gt; 40</td>
<td>225±3</td>
<td>101±3</td>
<td>149±4</td>
<td>&lt; 0.5</td>
<td>&lt; 0.5</td>
</tr>
<tr>
<td>LOA_BA_1</td>
<td>&lt; 5B</td>
<td>5B</td>
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6.8 Discussion

The primary goal of this study was to develop alkyd-acrylic copolymer without reaction of unsaturated double bonds on the fatty acid chain in alkyd. Previously reported approaches could not prevent the unsaturated double bonds from taking part in the radical polymerization. As a result, autoxidative crosslinking was compromised. In this study, alkyd-acrylic copolymers were successfully synthesized via ATRP. 1D-NMR and gHMBC 2D-NMR spectra assisted in the confirmation of grafting of acrylic block on alkyd backbone chain. Quantitative proton NMR analysis confirmed that the unsaturated
sites on fatty acid chains were intact. This study proves that double allylic protons do not interfere with ATRP polymerization of acrylic monomer.

Heatley et al.\textsuperscript{181} studied the reactivity of allyl groups in radical polymerization. Conversion of allylic double bonds only becomes significant when conversion of (meth)acrylic double bonds is high. In other words, at a higher ratio of methacrylic to allylic double bonds, higher reactive functionality methacrylic double bonds participate in the reaction. Keul and coworkers\textsuperscript{182} utilized an approach similar to this work for the polymerization of allyl methacrylate. ATRP technique was successfully utilized to polymerize allyl methacrylate without crosslinking.

In this study, to review non-significant interference of unsaturated double bonds in the polymerization (ATRP), possible side reactions during polymerization should be considered. Figure 6.14 lists possible side reactions of the active radical with unsaturated double bonds on fatty acid chain in alkyd. An active radical can abstract double allylic proton from the fatty acid chain in the alkyd to form a double allylic radical. This radical is stabilized by resonance involving carbon double bonds. Resonance structures of the radical are shown as A and B radical. The allylic radicals can either add acrylic monomer via ATRP \((A - M \cdot)\) or \((B - M \cdot)\) or terminate with halogen \((A - X)\) or \((B - X)\).

Quantitative analysis of double allylic protons indicate their participation in ATRP polymerization is not sufficiently significant to detect by integration change. Existence of B radical pathway can be confirmed by occurrence of conjugated double bonds in the proton NMR. Absence of conjugated double bonds in proton NMR and quantitative analysis of double allylic protons confirms that radical B does not form. Radical transfer by double allylic protons is less favored in the beginning of the reaction due to much
higher concentration of monomers in the reaction mixture. Moreover, radicals A or B is not an effective species for reinitiation due to resonance stabilization and the faster activation/deactivation equilibrium. The A-X species formed in this process is not dormant, but is dead. This is because this bond is not sufficiently activated under ATRP condition.

![Diagram](image)

**Figure 6.14.** Possible chain transfer reactions with double allylic protons.

The second goal of the study was to evaluate the coating performance of alkyd-acrylic copolymers and compare it with non-modified alkyd. Alkyd-acrylic copolymer coatings showed improved hardness, glass transition temperature and drying time. General coating properties such as cross-hatch adhesion, MEK resistance, impact resistance were maintained, except at higher acrylic concentrations. At higher concentration of MMA, alkyd-MMA copolymer coatings were brittle. At higher concentration of BA, alkyd-BA copolymer coatings were too soft. Hence, optimization of alkyd to acrylic ratio can be done using design of experiment. This study demonstrates
that a 1:1 ratio of alkyd to MMA or BA is a limit to the coatings. Within this limit, optimization of acrylic content can be done in order to obtain the desired coating performance.

6.9 Conclusions

A synthetic pathway for alkyd-acrylic copolymers via ATRP technique without the interference of unsaturated bonds on fatty acid chain in alkyd was demonstrated. Quantitative proton NMR confirmed the protection of double allylic groups. gHMBC 2D-NMR confirmed the grafting of acrylic block on alkyd backbone chain. Due to the higher reactivity, MMA showed a higher conversion compared to BA. Alkyd-acrylic copolymers coatings were cured via autoxidation and evaluated. Alkyd-acrylic copolymer coatings showed improved hardness, glass transition temperature and drying time.
CHAPTER VII
SUMMARY

The first part of this dissertation focused on the development of high-solid alkyd coating systems to reduce VOCs. The reduction or substitution of organic solvents in coating formulations by using reactive diluents derived from renewable materials is an important step in the mitigation of the environmental impact of VOCs. Conjugated soybean oil was modified via Diels-Alder cycloaddition reactions. Three different dienophiles (triallyl ether acrylate, 3-(trimethoxysilyl)propyl methacrylate, 2,2,2-trifluoroethyl methacrylate) were reacted with conjugated soybean oil to obtain functionalized soybean oils. The conversion of the cycloaddition reaction was dictated by the temperature of the reaction, with the greater extent of cycloaddition resulting in reactive diluents that had slightly less effect at reducing the viscosity of alkyd formulations than those with lower functionalization. The resulting functionalized soybean oils acted as reactive diluents by reducing the viscosity of the long oil alkyd formulation by up to 86%.

Modified soybean oils were formulated with long oil alkyd and coating performance was evaluated. Siloxane and allyl ether-functionalized soybean oil provided additional sites for the crosslinking, which improved pencil hardness, tensile and viscoelastic properties. Although fluorine functionality does not take part in the curing,
coatings with fluorine-functionalized soybean oil showed general coating performance comparable to that of alkyds. Coatings with fluorine-functionalized soybean oil showed improved solvent resistance and surface properties. Coatings containing 10-20 wt% of reactive diluents showed the best coating performance. Although the siloxane functionality provides additional sites for curing, it does not participate in autoxidation. As a result, coating performance and drying time were compromised. Comparable or better performance than solvent-borne alkyd coatings was achieved via the use of modified soybean oil as a reactive diluent. This demonstrates a viable approach to reduce VOCs using an inexpensive, abundant and renewable feedstock.

The second part of this dissertation (Chapter V) was demonstrated a new class of sulfur compounds, thiocarbonyl compounds as antioxidants. FT-IR and NMR spectra confirmed that the autoxidative curing of RAFT polymerized acrylated alkyd was hindered. Model compound study dis proved the α-H abstraction mechanism for antioxidant activity. $^{13}$C NMR spectra indicated the reaction of C=S bond and formation of a new carbonyl bond. Although the exact mechanism remains unclear, antioxidant activity of RAFT agents was explained by the formation of sulfur compounds analogous to β-alkylmercaptoketones.

Chapter VI focused on the development of new alkyd-acrylic copolymers for coating applications. A synthetic pathway for alkyd-acrylic copolymers via ATRP technique without the interference of unsaturated bonds on fatty acid chain in alkyd was demonstrated. Quantitative proton NMR confirmed that acrylate block was added to the alkyd backbone chain with no interference of unsaturated bonds on fatty acid chains. gHMBC 2D-NMR confirmed the grafting of acrylic block on alkyd backbone chain.
MMA showed a higher conversion compared to BA due to its higher reactivity. Alkyd-acrylic hybrid coatings were cured via autoxidation and showed improved hardness, glass transition temperature and drying time. Existence of one glass transition indicates that the formed network was homogeneous. Coatings showed maximum performance at an alkyd to acrylic weight ratio of 2:1. On the other hand, coatings were too soft or too brittle at an alkyd to acrylic weight ratio of 1:1. This study also gives an approximate concentration range for acrylics to display the desired coating performance.

In summary, this study opened new possibilities for high performance coating systems based on renewable, inexpensive and abundantly available feedstock. Soybean oil was successfully modified and utilized as a reactive diluent in alkyd coatings. To obtain the desired performance, a combination of modified soybean oils can be formulated in alkyd coatings. Moreover, this was the first study to report a synthetic pathway for autoxidatively curable alkyd-acrylic copolymers in which unsaturated bonds on the fatty acid chains on the alkyd remain intact during polymerization reaction.
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Figure A.1. $^1$H NMR spectrum of LOA_MMA_1.
Figure A.2. $^1$H NMR spectrum of LOA_BA_1.

Figure A.3. $^1$H NMR spectrum of LOA_BA_2.
Figure A.4. $^1$H NMR spectrum of LOA_MMA_BA_1.

Figure A.5. $^1$H NMR spectrum of LOA_MMA_BA_2.
Figure A.6. $^1$H NMR spectrum of MOA_AMI.

Figure A.7. $^1$H NMR spectrum of MOA_MMA_1.
Figure A.8. $^1$H NMR spectrum of MOA_MMA_2.

Figure A.9. $^1$H NMR spectrum of MOA_BA_1.
Figure A.10. $^1$H NMR spectrum of MOA_BA_2.

Figure A.11. $^1$H NMR spectrum of MOA_MMA_BA_1.
Figure A.12. $^1$H NMR spectrum of MOA_MMA_BA_2.

Figure A.13. Tan $\delta$ of alkyd-acrylic coatings as a function of temperature.