EVALUATION OF TUNG OIL BASED REACTIVE DILUENTS FOR ALKYD
COATING USING EXPERIMENTAL DESIGN

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EVALUATION OF TUNG OIL BASED REACTIVE DILUENTS FOR ALKYD
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ABSTRACT

Tung oil based reactive diluents were prepared via Diels-Alder reactions with four acrylate dienophiles: methacryloxypropyl trimethoxysilane (MAS), 2,2,2-trifluoroethyl methacrylate (TFM), triallyl ether acrylate (TAEA), and glycidyl methacrylate (GMA). The final products were characterized by 1H NMR, 13C NMR, and mass spectroscopy. The conversion of each monomer (acrylate dienophile) was obtained through the 1H NMR integration calculation and GC-MS technique. For the first three tung oil based reactive diluents, a quaternary experimental design was employed to determine the influence of three reactive diluents on the thermal, mechanical properties of the alkyd coating system. The drying time could be altered with the addition of different types and concentrations of reactive diluents. The viscosity of alkyd binder decreased significantly with the incorporation of reactive diluents, indicating that those reactive diluents have the potential to replace organic solvent in alkyd system with modified tung oils.
DEDICATION

To my beloved parents for their exceptional love and support
ACKNOWLEDGEMENTS

I would like to express my sincere appreciation to my advisor, Dr. Mark D. Soucek, for his guidance and support through my research. I would also like to thank my committee members, Dr. Younjin Min and Dr. Avraam I. Isayev for their contributions.

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CHAPTER I

INTRODUCTION

The use of renewable sources in the manufacturing of the coating products has received much attention nowadays because traditional coating system relies on crude oil which is finite and would become scarce soon. Other problems such as waste disposal at the end of a resin’s economic lifetime are also severe. Therefore, bio-based materials such as drying oil have received much attention because they are derived from natural products which have almost infinite supplement and are completely recyclable at the end of their lifetime.

In coating industry, drying oils and alkyd resins are used as binders for paints and coatings for decades. In application, however, drying oil and alkyd-based binders generally show inferior film property as well as application difficulty to other binders derived from crude oil. In addition, the resin is dissolved in 30%-40% of organic solvent like acetone to lower the viscosity for the requirement of paintability. These volatile organic solvents are not only harmful to human health, but also contribute to the environmental problem and depletion of the ozone layer. As strict VOC content rules for coatings have been enacted by government, it is important to reduce the amount of VOC emission from alkyd coating. One solution is the development of waterborne alkyd. They offer very low levels of organic solvent, decreased flammability, and improved safety. For waterborne alkyd, phthalic anhydride can be replaced with different polybasic acid combinations, such as trimellitic anhydride or maleopimaric acid. Another solution is to introduce reactive diluents into the alkyd
binder to replace the traditional organic solvent. The reactive diluent lowers the initial viscosity of the coating during application and becomes part of the polymer matrix after the film drying. A good reactive diluent should also exhibit good compatibility with the binder.

In this thesis, the synthesis and characterization of tung oil based reactive diluents was presented in Chapter III. In Chapter IV, a quaternary experimental design was employed to determine the influence of three reactive diluents on the thermal and mechanical properties of the alkyd coating system. The reactive diluents have shown the potential to replace organic solvent in alkyd system with its good compatibility and viscosity reducing property.
CHAPTER II

LITERATURE REVIEW

2.1 Organic coating

The term “coating” is used to describe materials that after applied to the substrate, will form “dry” film. Coatings are mainly used for one or more of the three reasons: for the protection of the substrate against chemical or atmospheric attack; for the decoration of the substrate or for some other functional purpose. The composition of a typical coating system includes: (1) Binder, which is responsible for adhesion and cohesion; (2) Volatile compound, which is used to reduce the viscosity of coating for paintability; (3) Pigment, which contributes to light scattering properties for coating; (4) Additive; which is added in small amount into the substance to provide special properties. Binder is the major component that is incorporated into the coating formulation thus has the main effect on the properties of coating. For organic coatings, the binder is composed by organic monomer, oligomer or polymer. There are various types of organic coating binders widely used nowadays such as polyester resin, acrylic resin, polyurethane resin, epoxide resin and amino-formaldehyde resin. For traditional coating system, almost all of the volatile components were the organic solvent. They have been determined to be a major contributing factor to form the ground-level ozone which is a public health concern. As numerous state agencies have the regulations to the VOC emission, the reduction of the total amount of organic solvent in coating formulation is the main consideration in coating industry.
The novel coating systems such as high-solid coating, waterborne coating or powder coating are being widely studied.

2.2 Drying oil

Drying oil is the natural oil with a high content of polyunsaturated fatty acids. When exposed to oxygen, the oil will form a tough, solid film completely. The hardening process of drying oil is not about the evaporation of water but a chemical reaction with oxygen. This mechanism is known as autoxidation. Drying oil is prone to autoxidation compared with semi-drying or non-drying oil because of its higher amount of unsaturation. The majority of the drying oils are obtained from the seed of vegetables through heating and pressing. Commonly used drying oils are linseed oil, tung oil, perilla oil, poppy seed oil and walnut oil [1]. Drying oil was used as binders for paints and coatings since prehistoric times and was still one of the major paint binders in the 1940s. After that, the reduction of the drying oil based binder was mainly because other binders such as acrylic resin, epoxy ester which may gave better performance to the coating were invented. For instance, drying oil based alkyd was used as the binder for automobile paint in the 1930s. The advantage of the drying oil based alkyd binder was its nice gloss retention. However, a cleaner spray environment was required for alkyd binder as any dust would stick in the slower drying film surface. Thus, they were replaced by the acrylic lacquers which dry more quickly. However, the usage of renewable sources in the manufacturing of the industrial products still receives much attention nowadays. This trend has been spurred because of the realization that the supply of fossil resources is inherently finite. Moreover, traditional painting systems will cause series of environmental issues, such as volatile organic solvent emissions and recycling or waste disposal problems at the end of a resin’s economic lifetime.
Natural oil is the mixture of triglycerides with different fatty acids distribute among the triglyceride molecules. Fatty acids which are important for coating include stearic acid, palmitic acid, elaidic acid, oleic acid, linoleic acid, linolenic acid, pinolenic acid, ricinoleic acid, and \( \alpha \)-eleostearic acid. Fatty acids can be classified into saturated and unsaturated types. Properties of different oils mainly depend on the fatty acid composition and concentration in the triglyceride molecular. Typical fatty acid compositions of vegetable oils are shown in Table 2-1.

![General chemical structure of triglyceride](image)

Figure 2-1: General chemical structure of triglyceride
Table 2-1: Typical Fatty acid compositions of selected oils\textsuperscript{[1]}

<table>
<thead>
<tr>
<th>Oil</th>
<th>Saturated\textsuperscript{a}</th>
<th>Oleic</th>
<th>Linoleic</th>
<th>Linolenic</th>
<th>Other</th>
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<tr>
<td>Linseed</td>
<td>10</td>
<td>22</td>
<td>16</td>
<td>52</td>
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<tr>
<td>Safflower</td>
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<td>13</td>
<td>75</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Soybean</td>
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<td>51</td>
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<td>Sunflower, MN</td>
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<td>11</td>
<td>51</td>
<td>38</td>
<td>38</td>
<td></td>
</tr>
<tr>
<td>Tung</td>
<td>5</td>
<td>8</td>
<td>43</td>
<td>80\textsuperscript{b}</td>
<td>—</td>
</tr>
<tr>
<td>Tall oil fatty acids\textsuperscript{c}</td>
<td>8</td>
<td>46</td>
<td>41</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>Tall oil fatty acids\textsuperscript{d}</td>
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<td>30</td>
<td>45</td>
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<td>Castor</td>
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<td>Coconut</td>
<td>91</td>
<td>7</td>
<td>2</td>
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\textsuperscript{a}Saturated fatty acids are mainly mixtures of stearic and palmitic acids
\textsuperscript{b}α-Eleostearic acid
\textsuperscript{c}North American origin
\textsuperscript{d}European origin

2.3 Tung oil

Tung oil is a drying oil obtained by pressing the seed of the tung tree, which is originally planted in China and some parts of Japan. Tung oil dries upon exposure to air and forms transparent coating surface. It has been widely used in wood coating, oil paint and printing industry. In China, tung oil is derived mainly from \textit{Aleurites fordii Hemsi} and \textit{Vernicia Montana}\textsuperscript{[2]}. The color of the raw tung oil may vary from clear yellow, yellowish brown to dark red, depending on the species and planting area. The total fatty acid composition is \textasciitilde80\% α-eleostearic acid (triple conjugated diene), 15\% linoleic acid or other unsaturated acids, and 5\% saturated acids. It is considered as a conjugated drying oil as the level of α-eleostearic acid content is extremely high. The viscosity for the tung oil is relatively higher than most other oils. \textit{Eleostearic} acid is a fatty acid, one of two isomers of octadecatrienoic acid: α-eleostearic acid and β-eleostearic acid. In tung oil, the isomer is mainly α-eleostearic acid. With a high level of three conjugated double bonds, tung oil is the fastest polymerizing oil. Except for the rapid drying time, varnish made by tung oil also shows a good water and alkali
resistance compared with other drying oil. However, the problems of yellowing and
discoloration are much severer compared with other drying oils.

Because of its unique chemical structure, tung oil is the excellent choice for the
preparation of new materials. Tung oil can be polymerized by both free radical and
cationic polymerizations. Li \cite{3} introduced cationic copolymerization of tung oil with
the divinylbenzene comonomer using boron trifluoride diethyl etherate as cationic
initiator. The final product was a typical thermal-setting polymer. Tung oil can
undergo thermal polymerization at relatively high temperatures. Copolymer such as
tung oil-styrene-divinylbenzene by thermal polymerization was made and investigated.
The thermal polymerization involves the dimerization of eleostearic acid. The
resulting products ranging from elastomer to plastics can be prepared by varying the
reaction condition \cite{4}. Tung oil based alkyd is generally considered to be one of the
best for the alkyd type formulations. Tung oil based alkyd shows a good water
resistance, fast drying and toughness characteristics. Tung oil is used with soybean or
linseed oil. This is because that the tung oil tends to undergo self-polymerization
when heated up. During the synthesis of the tung oil based alkyd, time and
temperature need to be controlled precisely to avoid the gelation of the material.

2.4 Heat treatment of drying oil

Drying oils can be thermally polymerized by heating under an inert atmosphere
to form bodied oils. The process temperature to heat the oil is generally 300-320 °C
for nonconjugated oils and 225-240 °C for conjugated oils with the exclusion of
oxygen. The drying oils will become polymerized (the molecular structure is changed
while the composition remains), with lower iodine number than the unmodified oils,
drying slowly, yellowing less and form a tough strong film. It is considered that the
conjugated drying oil will dimerize via Diels-Alder reaction between conjugated polyunsaturated polyenes while thermal conjugation precede the Diels-Alder reaction in non-conjugated drying oil. Thermal rearrangement to convert non-conjugated double bond to the conjugated one can also occur \[^5\]. Thermal polymerization of drying oils results in the direct carbon-to-carbon bonds between the polyunsaturated acid groups. The polymerization could be divided as intermolecular and intramolecular. Intramolecular reaction will result in less increase in molecular weight as predicted than intermolecular reaction \[^6\]. Blown oil was produced by passing air through drying oils at temperature ranging from 140 to 150 °C. The reaction is similar to the autoxidative oligomerization. Blown oil shows better performance and is widely used as plasticizer, artificial leathers, etc. Other heat treatment methods such as dehydration of castor oil can yield synthetic conjugated oil, which dries relatively rapidly at room temperature. The process involves the removal of water by interesterification with polyhydric alcohol at 250 °C catalyzed by sulphuric acid \[^7\]. The structural analysis of composition of dehydrated castor oil has been done by George W \[^8\]. The resulting conjugated oil can react with maleic anhydride at moderate temperature via Diels-Alder reaction to form maleated oil. Maleated oil esterified with polyol generally dries at the same rate as bodied oil.

2.5 Autoxidation Mechanism

The drying oil gradually changes from liquid to solid form upon exposure to air. This curing process takes place via autoxidation. In early studies, an understanding of the autoxidative mechanism was fairly limited due to its complexity. But with the development of modern analytical methods, it is possible to understand the mechanism. The autoxidation reaction proceeds by a free-radical chain mechanism and can be described in terms of initiation, propagation and termination.
In the initiation stage, naturally present hydroperoxides decompose to generate free radicals either by thermal hydroperoxide decomposition or by action of the metal drier. Driers are metal soaps of carboxylic acid and act as the catalyst that promote or accelerate the curing or hardening of film. Free radicals are generated from driers via metal hydroperoxide decomposition \[^9\]. Cobalt, calcium and zirconium salts are widely used as drier packages for autoxidation process. Cobalt driers are the most widely used surface driers. They would promote drying process which mainly occurs on the coating surface. Through driers are responsible for drying throughout the entire paint layer. They are active in the cross-linking steps of drying process. Zirconium salt is one of the most widely accepted through drier for many applications. Auxiliary driers act as supporter to accelerate the rate in the autoxidative process and to enhance activity of the surface drier. The appearance and quality of the total film can be improved. Calcium salt is one of the mostly used auxiliary driers to improve the hardness and gloss of the film.

In the propagation step, hydroperoxide is formed. The diallylic methylene hydrogen is abstracted by the high reactive free radicals. The free radicals can react with oxygen to form a conjugated peroxy free radical. The peroxy free radical can also abstract hydrogen from neighboring diallylic methylene groups. The chain reaction is established, resulting in autoxidation. In termination step, the radical-radical combination will end the autoxidative process.

Termination occurs via radical recombination, forming the peroxo, ether and carbon–carbon crosslinks. The procedures of initiation, propagation and termination are shown in Figure 2-2.
2.6 Alkyd resins

Alkyds are prepared from polyol, dibasic acid and fatty acid. They are polyesters, but in the coatings field the term polyester is reserved for “oil-free polyesters”. The term “alkyd” refers to an ester-based polymer with the pendent groups of fatty acid ester on the backbone. The formation of alkyd resins has long been known. In 1847, Berzelius reported a resin from tartaric acid and glycerol, resulting in the first polymeric ester. Van Bemmelnz did the first systematic work. He prepared resins by heating the different type of fatty acids with glycerol. In 1927,
Kienle discovered a new class of alkyd\textsuperscript{[11]}. He reported that the alkyd resin, which was prepared from phthalic anhydride, glycerol, and unsaturated fatty acid, such as linoleic, linolenic, and \textit{eleostearic} acid, showed better properties. The first commercialized alkyds were compounds of glycerol and phthalic acid sold under the name “Glyptal”. Since then, they became the dominant resin in most commercial oil based coatings. Approximately 200,000 tons of alkyd resins are produced each year\textsuperscript{[12]}.  

Alkyd can be classified by different criteria. One classification is to classify alkyds as oxidizing types of alkyds or nonoxidizing ones. Oxidizing alkyds cure through the autoxidation, the same curing mechanism as drying oils. Nonoxidizing alkyds are used as polymeric plasticizers or as hydroxyl-functional resins, which are cross-linked by melamine-formaldehyde resins (MF), urea-formaldehyde (UF) resins or by isocyanate cross-linkers.  

The second classification is based on the oil length of the alkyd. Oil length is the ratio of amount of oil in final alkyd to total weight of all ingredients minus water evolved in reaction. The oil length can be calculated as:

\[
\text{oil length} = \frac{\text{weight of oil}}{\text{weight of all ingredients} - \text{water evolved in reaction}} \times 100
\]

Generally, alkyds with oil lengths greater than 60 are long oil alkyds, the oil length of medium oil alkyds are between 40 to 60, and those with oil lengths less than 40 are short oil alkyds. Another classification is based on unmodified or modified alkyds. Modified alkyds contain monomers other than polyols, polybasic acids, and fatty acids.
Glycerol is the most widely used polyol in the alkyd synthesis because it is present in naturally occurring oils. The other commonly used polyols include pentaerythritol and trimethylolpropane. Phthalic anhydride, isophthalic acid and terephthalic acid are commonly used dibasic acids for alkyd preparation. Phthalic anhydride is the most widely used due to its fastest reaction rate, low melting point and good viscosity of final alkyd product. Xylene is always used as the reflux solvent in alkyd synthesis as it forms azeotrope with water. Thus continuously removal of water during the reaction can be achieved.

There are two methods for the alkyd preparation. One is the monoglyceride process. The other is fatty acid process. In the monoglyceride process, oil is first reacted with polyol via transesterification reaction. The transesterification reaction usually occurs between 230 to 250 °C with a catalyst. Tetraisopropyltitanate, lithium hydroxide, or lithium ricinoleate is usually used as a catalyst. After the monoglyceride is complete, polybasic acid, usually phthalic anhydride is added into the system to start the esterification reaction. Xylene is usually added as the reflux solvent to achieve continuous removal of water. Figure 2-3 is the schematic depiction of the monoglyceride process.
For the fatty acid step, fatty acid is used instead of oil and the reaction only takes one step. The polyol, fatty acid, and dibasic acid are all added to the reactor at the same time and the esterifications of both aliphatic and aromatic acids are carried out simultaneously. Fatty acid procedure can produce higher quality alkyd compared with the monoglyceride one due to its better control of the molecular weight and molecular weight distribution.
2.7 Diels-Alder Reaction

Diels-Alder mechanism is a cycloaddition between a conjugated diene and a dienophile to form a cyclohexane ring with up to four contiguous stereogenic centers. With the intramolecular and transannular variance, the reaction is versatile in developing molecular complexity. Diels-Alder reaction was initially discovered by Professor Otto Diels and his student, Kurt Alder through the reaction between cyclopentadiene and quinone and has been duly exploited since then.

Diels-Alder reaction is the combination of compound of two conjugated double bonds with a single unsaturated center. It has become increasingly clear that the Diels-Alder reaction is $[4\pi+2\pi]$ reaction. Four out of six $\pi$ electrons within cyclic
structure come from conjugated diene while two come from dienophile. The mechanism of the reaction is in controversy. One view claims that the reaction takes place in two steps, with the formation of one single bond between appropriate atoms first, followed by subsequent formation of a second bond. The opposite view claims the simultaneous formation of two single bonds together. The general Diels-Alder reaction is shown in Figure 2-5. For the structure of diene, the group X and Z should confer high reactivity while the group Y in dienophile should be electron withdrawing group \[^{13}\]. In general, higher temperature and pressure will increase the reaction rate and conversion. A useful discovery was that Lewis acids such as AlCl\(_3\) facilitate the reaction, allowing it to occur in mild conditions, often below 0\(^\circ\) C. This is due to the coordination of carbonyl group in dienophile with Lewis acid, which reduced the activation energy of cycloaddition \[^{14}\]. Another attractive feature of Lewis acid catalyst is the enhanced endo diastereoselectivity, which can be used to control the absolute configuration of the product.

![Figure 2-5: Depiction of a Diels-Alder reaction](image)

For vegetable oils, Diels-Alder reaction can occur between double bonds in linseed oil and cyclopentadiene at high temperature and pressure to form norbornene
groups on the fatty acid chain\cite{15}. Soucek\cite{16} developed the norbornene linseed oil with cyclopentadiene at 240 °C and 200 psi with BHT as a free radical retarder to inhibit the homopolymerization of cyclopentadiene and high conversion ratio was reported. Tung oil is unique among other seed oils because it contains approximately 80 % $\alpha$-eleostearic fatty acid, which is triple conjugated diene. Dienophiles such as acrylate monomer which contains electron withdrawing group can be reacted with tung oil via Diels-Alder reaction under certain conditions. Copolymers such as tung oil with 1,6 hexanediol diacrylate or 1,4-butanediol diacrylate via Diels-Alder reaction were synthesized\cite{34}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{synthesis_diagram.png}
\caption{Synthesis of norbornene linseed oil via Diels-Alder reaction}
\end{figure}

2.8 Sol-Gel Chemistry

The sol-gel process is the inorganic polymerization reaction based on molecular precursors, forming inorganic colloid. Sol-gel precursors are members of family consist of organic ligand attached to metal or metalloid atom\cite{17}. Commonly used
ligands are shown in Table 2-2. Organometallic compounds contain direct metal-carbon bonds while alkoxides contain metal-oxygen-carbon linkages. Metal alkoxides are generally used as the precursors because they can react with water readily, providing better reaction control. Sol-gel process between alkoxide and water consists of hydrolysis and condensation. The reaction process is depicted in Figure 2-7.

Table 2-2: Commonly used ligands for Sol-Gel precursor

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Structural Formulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>methyl</td>
<td>( \cdot \text{CH}_3 )</td>
</tr>
<tr>
<td>ethyl</td>
<td>( \cdot \text{CH}_2\text{CH}_3 )</td>
</tr>
<tr>
<td>n-propyl</td>
<td>( \cdot \text{CH}_2\text{CH}_2\text{CH}_3 )</td>
</tr>
<tr>
<td>iso-propyl</td>
<td>( \text{H}_3\text{C(\cdot)}\text{CH}_3 )</td>
</tr>
<tr>
<td>n-butyl</td>
<td>( \cdot \text{CH}_3(\text{CH}_2)_2\text{CH}_3 )</td>
</tr>
<tr>
<td>sec-butyl</td>
<td>( \text{H}_3\text{C(\cdot)}\text{CH}_2\text{CH}_3 )</td>
</tr>
<tr>
<td>iso-butyl</td>
<td>( \cdot \text{CH}_2\text{CH(\cdot)}_2\text{CH}_3 )</td>
</tr>
<tr>
<td>tert-butyl</td>
<td>( \cdot \text{OC(CH}_3\text{)}_3 )</td>
</tr>
<tr>
<td>other</td>
<td>( \cdot \text{OOCCH}_3 )</td>
</tr>
</tbody>
</table>

![Acetylacetonate](image)

![Acetate](image)
In the hydrolysis process, the hydroxyl ion in water is attached to the metal atom. Hydrolysis can go completion depending on the amount of water and catalyst used. The chemical reactivity of metal alkoxides toward hydrolysis depends on the positive charge density of the metal atom, the number of ion coordination bridges, the electronegativity and the pH of aqueous solution. The hydrolyzed molecules can bond together via condensation reaction. The condensation can proceed either by nucleophilic substitution or nucleophilic addition, depending on whether the preferred coordination is satisfied or not. Once the condensation reaction continues, the metal oxo-polymers will form.

Among metal alkoxide, silicon alkoxides such as tetrathoxysilane (TEOS) are widely used. The rate of hydrolysis reaction is influenced by the concentration of acid or based catalyst. Under acidic conditions, hydrolysis reaction occurs according to
$S_N2$ mechanism. The inorganic acids protonate negatively charged alkoxide, producing better leaving alcohol groups once the water molecule attaches to the alkoxide. For basic catalysts, as the nucleophilic hydroxyl group attaches the silicon atom, the resulting deprotonated silanol groups slow down the hydrolysis reaction while enhance condensation rates. Hydrolysis will also be facilitated with homogenizing agents such as THF or acetone. Besides adjusting hydrolysis and condensation rates, catalyst can also adjust the shape of final micelle.

Through the combination of organic phase and inorganic sol-gel precursor, we can derive versatile organic-inorganic hybrid materials. The hybrid products have combined the properties of the inorganic materials and organic polymers. The advantage of sol-gel technique is that the reaction can occur under ambient temperature. Sol-gel hybrid protective coatings have shown excellent chemical
stability and have been applied in coatings for corrosion resistance. T. P. Chou\textsuperscript{[18]} derived corrosion resistance hybrid coatings by copolymerizing TEOS with MPS with a two-step acid catalyst process. Coatings were applied to stainless steel substrates and provided excellent corrosion protection. The coatings act as a physical barrier to separate the anode from cathode. Besides the protective barrier properties, sol-gel binder can form zinc-rich coating which relies more on the cathodic protection of zinc pigment. The volume concentration of the binder, as well as the size and shape of the zinc pigment control the protection ability.

Hybrid networks can also be synthesized by using sol-gel precursor to form inorganic network while incorporate organic groups with different physical properties within it. The precursors of these component have the general formula $R_nSi(OR)_{4-n}$. As the $R$ group is not hydrolysable, it acts as organic modifier, providing hydrogen bonds which act as bridge to incorporate organic nano-composite into continuous inorganic phase\textsuperscript{[19]}. These types of materials are called Ormosils. The combination of inorganic and organic component in this way leads to new area of novel material with a wide range of properties. For example, spiropyran and spirooxazines have the photochromic properties. With the photochromic dye trapped within sol-gel matrix, materials with different photochromism behavior can be formed. Organic-inorganic hybrid materials can also be formed via the copolymerization between organic oligomers and inorganic phase. Covalent bonding between inorganic and organic phases is established. These types of materials are called ceramers\textsuperscript{[20]}.

Most organic-inorganic hybrid coatings combine different sol-gel precursors with organic phase by coupling agent. Soucek\textsuperscript{[21]} and coworkers studied non-volatile TEOS oligomer bonding together with various organic binders, such as HDI isocyanurate crosslinked polyurea. Silane-functionalized isocyanurate mainly
functions as a coupling agent. It provides covalent chemical linkage between organic portion and inorganic portion. The hybrid films showed higher tensile strength and modulus compared to traditional coating. The adhesion to the substrate also increased with the incorporation of inorganic phase.

2.9 Fluorinated Polymers

Fluorine-containing polymers are well known to possess unique properties such as low cohesive and surface energy. The fluorine atom leads to strong polarizability of the C-F bonds, which attributes to its unique properties. They are important in the applications such as antithermal, chemical inert, hydrophobicity, photochemical stability, electrical insulation and lubricant materials. Despite the fact that high-performance polymers such as polyimides have good mechanical properties and thermal stability, they have serious drawbacks such as insolubility with organic solvent, infusibility and poor chemical resistance. With the incorporation of fluorinated substitutions, they can meet wider range of application[22].

Fluorinated polymers are prepared through two distinct routes. Firstly, they can be prepared by polymerization of fluorine containing monomer with other functional monomers. Secondly, fluorinated polymers can be prepared by incorporation of fluorine in or along the backbone of non-fluorinated polymer through chemical modification. For the first method, fluorine atoms can be introduced to the main, terminal or side chain through homopolymerization with other functional monomers to form linear polymers. Fluorinated block copolymers can also be synthesized. Perfluorinated graft block segments are widely used for their better surface modification ability than random copolymers[23]. Polytetrafluoroethylene (PTFE) has excellent exterior durability as well as thermal stability and inertness. TFE copolymer
with functional groups such as hydroxyl group can be crosslinked with isocyanate for application requirement \[^{[24]}\]. Poly-Vinylidene-fluoride copolymers (PVDF) have wide range of applications, such as utilizations among superheated steam systems. They exhibit unusual compatibility with other polymers with strong polar groups. The properties of PVDF copolymers are determined by chemical composition, as well as molecular architecture and molecular weight. In general, emulsion and suspension polymerizations of VDF are widely used because water can absorb large amount of heat generated alone the process of VDF polymerization \[^{[25]}\].

The direct fluorination of macromolecular was discovered in the early 1970s. Several schemes of applying fluorine into macromolecules, such as polydienes, polystyrene, polypropylene were developed. Polydienes contains double bond in the backbone and side chain, it can be modified by fluorine-containing carbenes. The first report of this modification was the reaction between polybutadiene with difluorocarbene generated from (trifluoromethyl) phenylmercury in the presence of NaI. The difluorocarbene was very effective for the modification. More than 99% of the double bonds can be converted. Final product with increased glass transition temperature (T\(_g\)) as well as high decomposition temperature can be achieved through modification \[^{[26]}\].

![Figure 2-10: Modification of polybutadiene by difluorocarbene](image)

For polyaromatic such as polystyrene, hydrogenation of the benzene leads to the direct fluorination to the aromatic ring using F\(_2\). The addition of perfluoroalkyl
radicals was first reported in 1985, with the perfluoroalkyl phenyliodonium trifluoromethanesulphate acts as fluorination agent. Later, fluorine-containing peroxides were used as fluorination monomer. After modification, the final product shows better acidic resistance\textsuperscript{[26]}.

Figure 2-11: Perfluoroalkylation of polystyrene using acyl peroxide
CHAPTER III
SYNTHESIS AND CHARACTERIZATION OF TUNG OIL BASED REACTIVE DILUENTS

3.1 Overview

Four tung oil based reactive diluents were prepared via a Diels-Alder reaction with acrylate dienophiles. The dienophiles were methacryloxypropyl trimethoxysilane (MAS), 2,2,2-trifluoroethyl methacrylate (TFM), triallyl ether acrylate (TAEA), and glycidyl methacrylate (GMA). Phenothiazine was added as the free radical inhibitor to prevent the gelation of final product. The final product was characterized using $^1$H NMR and $^{13}$C NMR to confirm the degree of completion of reaction. Mass spectroscopy was used to determine the molecular weight distribution of the final products. These characterization techniques confirmed the occurrence of Diels-Alder reaction for each tung oil based reactive diluents. The conversion of each monomer (acrylate dienophile) was obtained through the $^1$H NMR integration calculation and GC-MS technique.

3.2 Introduction

To reduce the emission of volatile organic compounds (VOC) and hazardous air pollutants, the coatings industry continues to pursue high performance and efficient products of low VOC-content. The challenge within the coating industry is to maintain the cost and properties while meeting the standard of environmental regulations. Seed oil based coating is one of choice. They are obtained from natural
renewable resources and environmental friendly. Seed oil is the mixture of triglycerides with different fatty acids distributed among the triglyceride molecules. Common types of fatty acids include stearic acid, palmitic acid, elaidic acid, oleic acid, linoleic acid, linolenic acid, pinolenic acid, ricinoleic acid, and \( \alpha \)-eleostearic acid. Seed oils which contain high level of polyunsaturated fatty acid are called drying oil, which means that they can crosslink to form a polymeric film when exposed to air. The process is called the autoxidative curing. The majority of the drying oils are obtained from the seed of vegetables through heating and pressing. Linseed oil, tung oil and walnut oil are the common drying oils used nowadays. They were used as the binders for coatings since prehistoric times and still have applications nowadays.

Tung oil is a drying oil obtained by pressing the seed of the tung tree, which is originally planted in China and some parts of Japan. In China, tung oil is derived mainly from \textit{Aleurites fordii Hemsi} and \textit{Vernicia Montana}. Tung oil is unique among other types of drying oil because it’s conjugated unsaturation structure. It contains 5% saturated acid, 15% linoleic or other unsaturated acid, and 80% \( \alpha \)-eleostearic acid (triple conjugated diene). With a high level of three conjugated double bond, tung oil is the fastest polymerizing oil. Except for the rapid drying time, varnish made by tung oil also shows a good water and alkali resistance compared with other drying oils. It has been widely used in wood coating, oil paints and printing industry.

Diels-Alder reaction is a cycloaddition between a conjugated diene and a dienophile to form a six member ring. The reaction rate and conversion of a Diels-Alder reaction can be improved at higher temperature and pressure, or in the presence of catalyst which lowers the energy of activation. Tung oil can undergo Diels-Alder reaction as a diene because it contains 80% of \( \alpha \)-eleostearic acid. It can be reacted
with acrylate monomers with electron attraction group. In this study, acrylate monomers with different functional group were reacted with tung oil through Diels-Alder reaction. Alkoxysilane can go through sol-gel chemistry and form hybrid inorganic-organic coatings. Fluorinated tung oil can provide low surface energy, and high thermal stability. Triallyl ether can accelerate the drying process of the film and increase the crosslink density by introducing additional number of antioxidative functionality. Epoxy based tung oil can be cured under ultraviolet light.

3.3 Materials

Tung oil, 2,2,2-trifluoroethyl methacrylate (99%), 3-methacyrloxypropyl trimethoxysilane (95%), pentaerythritol allyl ether (70%), acrylic acid (99%), glycidyl methacrylate (97%), p-toluenesulfonic acid (98.5%), phenothiazine (98%), tetrahydrofuran (99.9%), acetonitrile (99.9%) were obtained from Sigma-Aldrich chemical company. All materials were used as received without any purification.

3.4 Instruments and Characterization

$^1$H NMR and $^{13}$C NMR were recorded on a Mercury-500 spectrometer (Varian) in CDCl$_3$ Solvent. The mass spectra were measured through reflection mode. Viscosity measurement was accomplished by laboratory Brookfield viscometer at room temperature. GC-MS was carried using Saturn 2200 Gas APH/MASS Spectrometer. The samples were dissolved in THF or acetonitrile solution. The injector oven temperature was 250 °C. The flame ionization detector was used and the detector oven temperature was 300 °C. Gas flow in the column at 0.9 ml/min whiles the column temperature raised from 50 °C to 280 °C.
3.5 Synthesis of tung oil based reactive diluent

3.5.1 Synthesis of siloxane functionalized tung oil

Tung oil (100g), 3-methacryloxypropyl trimethoxysilane (34g, 0.36 mol), phenothiazine (1.8g) were mixed under nitrogen purge for 15 min in a 250 ml three-neck round bottom flask equipped with mechanical stirrer, nitrogen inlet and condenser. Then the mixture was heated with an oil bath and the temperature slowly increased to 180 °C. After 6 h, the heat was stopped and the product was cooled to room temperature. $^1$H NMR, $^{13}$C NMR and MALDI-TOF MS were used to confirm the formation of desired product.

$^1$H NMR (500 MHz, CDCl3) δ(ppm): 0.62-0.73(-O-Si-CH2-), 0.82-0.95(CH3-CH2-CH2), 1.09(CH3-C-C(O)O-), 1.20-1.40 (-((CH2)2-CH2-C(O)O-, -(CH2)2-CH2-CH=CH-), 1.56-1.67(-CH2-CH2-C(O)O-), 1.69-1.78(-CH2-CH2-Si-O-), 1.93-2.2(-CH2-CH=CH-, -CH=CH-CH(CH=CH)CH2-), 2.28-2.36(-CH2-C(O)O-), 2.71(-CH(CH=CH)CH2-), 3.58(CH3-O-Si-), 4.0-4.09(-Si-(CH2)2-CH2-C(O)O-), 4.13-4.19, 4.27-4.34(-C(O)O-CH2-CH-O-C(O)-), 5.2-5.3(-C(O)O-CH2-CH-O-C(O)-), 5.3-6.4 (-CH=CH-); $^{13}$C NMR(500MHz, CDCl3) δ(ppm): 5.31(-O-Si-CH2), 13.83(-Si-CH2-CH2), 44.02(-CH-C-C(O)O), 45.18(-CH-C-C(O)O), 50.41(-Si-O-CH3), 66.28(-C(O)O-CH2-).

3.5.2 Synthesis of fluorine functionalized tung oil

Tung oil (100g), 2,2,2-trifluoroethyl methacrylate (20.17g, 0.12 mol), phenothiazine (1.8g) were mixed under nitrogen purge for 15 min in a 250 ml three-neck round bottom flask equipped with mechanical stirrer, nitrogen inlet and condenser. Then the mixture was heated with an oil bath and the temperature slowly
increased to 150 °C. After 5 h, the heat was stopped and the product was cooled to room temperature. "H NMR, "C NMR and MALDI-TOF MS were used to confirm the formation of desired product.

"H NMR (500 MHz, CDCl3) δ(ppm): 0.84-0.95(CH3-CH2-CH2), 1.14(CH3-C(O)O-), 1.20-1.46 (-CH2-C(O)-), 1.55-1.67(-CH2-CH2-C(O)O-), 1.90-2.26(-CH=CH-CH=CH-), 2.27-2.37(-CH2-CH2-C(O)O-), 2.77(-CH=CH(=CH)CH2-), 4.12-4.19, 4.26-4.34(-C(O)O-CH2-CH2-C(O)-), 4.41-4.54(--C(O)-CH2-CF3), 5.2-5.3(--C(O)O-CH2-CH2-C(O)-), 5.3-6.4 (-CH=CH-); "C NMR(500MHz, CDCl3) δ(ppm): 43.83(-CH-C-C(O)O), 45.38(-CH-C-C(O)O), 65.12(-CH2-CF3), 122.02(-CH2-CF3), 175.44(--C(CH3)-C(O)O-).

3.5.3 Synthesis of triallyl-ether functionalized tung oil

Triallyl ether functionalized tung oil was synthesized via two-step reaction. In the first step, triallyl ether acrylate was synthesized by esterification reaction. Pentaerythritol allyl ether (53.31g, 0.21mol), phenothiazine (0.53g, 2.67 mol), p-Toluene sulfonic acid (0.40g, 2.10mol), toluene (200ml) were mixed in a 500ml round bottle four neck flask equipped with mechanical stirrer, Dean-Stark trap and nitrogen inlet. The temperature of reaction was maintained at 125 °C. Acrylic acid (30g, 0.42mol) was then slowly added to the mixture. After 7 hour, the amount of water collected in Dean-Stark trap was the confirmation of complete reaction. Then, the product solution was washed with saturated sodium carbonate solution (100ml) and water (300ml) in a separatory funnel to remove the unreacted acrylic acid. Then the product was dried with anhydrous magnesium sulfate (50g). Toluene was removed in vacuo to give the triallyl ether product. The final product was characterized by "H NMR, "C NMR and ESI mass spectrometry.
In the second step, Tung oil (100g), triallyl ether acrylate (37.4g, 0.12 mol) were mixed under nitrogen purge for 15 min in a 250 ml three-neck round bottom flask equipped with mechanical stirrer, nitrogen inlet and condenser. Then the mixture was heated with an oil bath and the temperature slowly increased to 120 °C. After 6 h, the heat was stopped and the product was cooled to room temperature. $^1$H NMR, $^{13}$C NMR and MALDI-TOF MS were used to confirm the formation of desired product.

$^1$H NMR (500 MHz, CDCl3) δ(ppm): 0.84-0.96(CH$_3$-CH$_2$-CH$_2$), 1.22-1.44 (-CH$_2$)$_3$-CH$_2$-C(O)O-, -(CH$_2$)$_2$-CH$_2$-CH=CH-), 1.57-1.68(-CH$_2$-CH$_2$-C(O)O-), 1.96-2.23(-CH=CH=CH-), 2.29-2.38(-CH$_2$-C(O)O-), 2.71(-CH(CH=CH)CH$_2$-), 3.43-3.53(-C(CH$_2$-O-CH$_2$-CH=CH$_2$), 3.75(C(O)O-CH$_2$-C=CH$_2$-O-CH$_2$-CH=CH$_2$), 3.92-3.99(-CH$_2$-O-CH$_2$-CH=CH$_2$), 4.12-4.20, 4.27-4.34(-C(O)O-CH$_2$-CH$_2$-O-C(O)-), 5.3-6.4 (-CH=CH-); $^{13}$C NMR(500MHz, CDCl$_3$) δ(ppm): 44.80(-C(O)O-CH$_2$-C-), 63.93(-C(O)O-CH$_2$-C-), 66.15(CH$_2$=CH-CH$_2$-O-CH$_2$), 72.25(CH$_2$=CH-CH$_2$-O-), 116.64(CH$_2$=CH-CH$_2$), 172.97(-CH-C(O)-O-).

3.5.4 Synthesis of epoxy functionalized tung oil

Tung oil (80g), glycidyl methacrylate (19.47g, 0.14 mol), and phenothiazone (1.6g) were mixed under nitrogen purge for 15 min in a 250 ml three-neck round bottom flask equipped with mechanical stirrer, nitrogen inlet and condenser. Then the mixture was heated with an oil bath and the temperature slowly increased to 150 °C. After 6 h, the heat was stopped and the product was cooled to room temperature. $^1$H NMR, $^{13}$C NMR and ESI-mass spectroscopy were used to confirm the formation of desired product.
\[^1\text{H}\] NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) (ppm): 0.83-0.95(CH\textsubscript{3}-CH\textsubscript{2}-CH\textsubscript{2}), 1.11(CH\textsubscript{3}-C(O)O-), 1.19-1.45 \(-(\text{CH}\textsubscript{2})\textsubscript{5}-\text{CH}\textsubscript{2}-\text{C}(O)O-\), \(-(\text{CH}\textsubscript{2})\textsubscript{2}-\text{CH}\textsubscript{2}-\text{CH}=\text{CH})\), 1.56-1.66(-CH\textsubscript{2}-CH\textsubscript{2}-C(O)O-), 1.96-2.23(\text{CH}2-\text{CH}=\text{CH}-, -\text{CH}=\text{CH}(\text{CH}=\text{CH})\text{CH}2), 2.26-2.37(-CH\textsubscript{2}-C(O)O-), 2.61-2.69, 2.8-2.89(O(CH\textsubscript{2})CH-CH\textsubscript{2}-) 2.71(\text{CH}(\text{CH}=\text{CH})\text{CH}2), 3.24-3.29(O(CH\textsubscript{2})CH-CH\textsubscript{2}-), 4.0-4.05, 4.46-4.52(C(O)O-\text{CH}2-CH(CH\textsubscript{2})O), 4.11-4.20, 4.26-4.32(\text{-C}(O)O-\text{CH}2-CH-O-C(O)-), 5.2-5.3(\text{-C}(O)O-\text{CH}2-\text{CH}-O-C(O)-), 5.3-6.4 (\text{-CH}=\text{CH}-); \[^{13}\text{C}\] NMR (500MHz, CDCl\textsubscript{3}) \(\delta\) (ppm): 44.50(O(CH\textsubscript{2})CH-CH\textsubscript{2}-), 49.22(O(CH\textsubscript{2})CH-CH\textsubscript{2}-), 65.04(O(CH\textsubscript{2})CH-CH\textsubscript{2}-), 135.79(-\text{CH}=\text{CH}-), 173.24(C(CH\textsubscript{3})-C(O)O-).

3.6 Result and Discussion

The ideal reactive diluents for an oxidative drying alkyd system must first act as conventional solvent physically. The low intrinsic viscosity and good compatibility are essential. Besides, they should have reactive sites to crosslink with binders and not act as a plasticizer. The reaction rate of the reactive diluents should also resemble the binder\textsuperscript{[27]}. Tung oil itself is a good source of reactive diluents for alkyd resin because of the chemical compatibility. Several modifications of tung oil have been done to meet the needs of reactive diluents for alkyd resin such as tung oil methyl ester\textsuperscript{[28]}. In this study, Diels-Alder reaction was used to modify tung oil in the preparation of reactive diluents.

3.6.1 Structural Characterization of tung oil

Tung oil was characterized by \[^1\text{H}\] NMR, \[^{13}\text{C}\] NMR, and Mass spectroscopy. Tung oil contains 5% saturated acid, 15% linoleic or other unsaturated acid and 80% \(\alpha\)-eleostearic acid. The ideal structure of tung oil is shown in Figure 3-1. The proton in the triglyceride backbone of tung oil appears at \(\delta\) 4.13-4.19, \(\delta\) 4.28-4.34 and \(\delta\)
5.24–5.3. These resonances will remain constant before and after Diels-Alder reaction. The majority of double bonds in the fatty acid side chain of tung oil are conjugated double bonds from α-eleostearic acid. The corresponding resonance appears in the range of 5.60-6.44. The unconjugated double bond appears at δ 5.3-5.44. The ¹H NMR is shown in Figure 3-2. For the ¹³C NMR, the resonances at δ 65.3 and δ 72.4 correspond to the carbon in the triglyceride backbone. The resonance at δ 127.3-139.7 corresponds to the unsaturated carbon. The resonance at δ 173.1 is the carboxylic group. The ¹³C NMR is shown in Figure 3-3. For the Mass spectrum, the peak at 895m/z indicates the main molecular weight of triglyceride structure of tung oil. The mass spectrum is shown in Figure 3-4.

Figure 3-1: Ideal structure of tung oil

Figure 3-2: ¹H NMR spectra of tung oil
Figure 3-3: $^{13}$C NMR spectra of tung oil

Figure 3-4: ESI mass spectra of tung oil
3.6.2 Characterization of siloxane functionalized tung oil

Tung oil was reacted with 3-methacryloxypropyltrimethoxysilane (MAS) via a Diels-Alder reaction to produce siloxane functionalized tung oil based reactive diluent. 1 mol of tung oil was reacted with 1.2 mol of MAS monomer under 180 °C. The synthetic diagram is in Figure 3-5. The structure of final product was characterized by ^1^H NMR, ^1^H NMR, and MALDI-TOF mass spectrometer. The conversion of monomer was calculated through ^1^H NMR and GC-MS. The ^1^H NMR, ^1^H NMR, and Mass Spectra of the final product are shown in Figure 3-6, 3-7 and 3-8.

![Synthetic diagram of siloxane functionalized tung oil](image)

In the ^1^H NMR of final product, the Diels-Alder reaction between 3-methacryloxypropyltrimethoxysilane (MAS) and tung oil was confirmed by the new resonance appeared at δ 1.09 ppm. This is due to the methyl proton (-CH₃) in the methacrylate monomer attached to the new six member ring generated via Diels-Alder reaction. The resonance of conjugated double bond at δ 5.61-6.49 decreased. The new resonances of final product were assigned in Figure 3-6. Figure 3-7 shows ^1^H NMR of siloxane functionalized tung oil. The new resonance at δ 177.1 is the new
carboxylic carbon from 3- methacryloxypropyltrimethoxysilane monomer attached to
the tung oil backbone. New resonance at δ 42-48 is the carbon from the new six
member ring generated by Diels-Alder reaction. Other resonances of final product
were assigned in Figure 3-7.

MALDI-TOF mass spectrometer was also used to characterize structure of
siloxane-functionalized tung oil. The spectrum of final product is shown in Figure 3-8.
The resonance at 895.9 m/z indicates the presence of unreacted tung oil. The new
peaks at 1144.1 m/z and 1392.3 indicate the mono and di-addition of 3-
methacryloxypropyltrimethoxysilane monomer to Tung oil, which confirmed the
Diels-Alder reaction.

Figure 3-6: $^1$H NMR spectra of siloxane functionalized tung oil
NMR is unique among other spectroscopic methods because the integrated intensity of a signal is proportional to the number of hydrogen atoms that are correspondent with the signal. In this way, by integrating different NMR resonance,
the relative ratio of different hydrogen can be found. The proportion of siloxane functionalized tung oil among the final product can be calculated. For the siloxane-functionalized tung oil, the resonance between δ 1.07-1.1 is correspond to the methyl proton (-CH₃) in the methacrylate monomer attached to the new six member ring generated via Diels-Alder reaction. The resonance between δ 4.25-4.34 is corresponds to the hydrogen from the triglyceride backbone of tung oil which will remain constant before and after Diels-Alder reaction. From the ratio of the resonance areas between these two resonances, the conversion of monomer was calculated and it’s approximately 42%. The corresponding chemical structure of these two resonances and the integration result is shown in Figure 3-9.

Figure 3-9: Resonance integration of siloxane functionalized tung oil

Gas chromatography (GC) is a common type of analytical method to separate and analyze compounds that can be vaporized. Sample contains different chemical components was dissolved in a mobile phase. The components are separated from each other as they travel through stationary phase. Flame Ionization Detector (FID) is
usually used to determine their mass. It provides good sensitivity and precision \(^{[29]}\). To confirm the conversion of monomer calculated from the \(^1\)H NMR, GC was used to detect and calculate the residual amount of monomer in the final product. The calibration curve of 3-methacryloxypropyltrimethoxysilane was obtained. Four calibration samples of 3-methacryloxypropyltrimethoxysilane dissolved in THF solution was prepared. The concentrations of the four samples are 40400 mcg/ml, 4040 mcg/ml, 404 mcg/ml, and 40.4 mcg/ml. The calibration samples were analyzed via GC. Figure 3-10 was the GC spectra of four calibration sample.

![GC spectra of 3-methacryloxypropyltrimethoxysilane monomer](image)

The retention time of 3-methacryloxypropyltrimethoxysilane monomer was around 10.023 minutes. The response area of four calibration sample was collected and the calibration curve was fitted as linear regression trend line using OriginPro 8. Table 3-1 is the corresponding response area of each calibration sample. The linear regression equation is shown in Figure 3-11.
Table 3-1: Response area of 3-methacryloxypropyltrimethoxysilane monomer

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<th>Concentration (mcg/ml)</th>
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</tr>
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<td>404</td>
<td>85755</td>
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<td>8704</td>
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Figure 3-11: Calibration Curve of 3-methacryloxypropyltrimethoxysilane

The value of Adj.R-square is 0.99984, other ANOVA statistics include F-value=18271.9, Prob>F=0.0000547. All the values imply that the linear fit model is significant. Thus this linear fit can be used to calculate the residual amount of monomers in the final product.

To calculate the residual amount of monomer, the final product was dissolved in THF. The concentration of the solution was 42100 mcg/ml. The sample was analyzed by GC for three times. Figure 3-12 is the GC spectra of the product. The response peak of 3-methacryloxypropyltrimethoxysilane was observed and the
average response area was 1448221. The conversion of monomer was calculated via the calibration curve and was approximately 40.1%. This result is close to the conversion calculated by $^1$H NMR which was about 42%.

Table 3-2: Response area of 3-methacryloxypropyltrimethoxysilane in reactive diluent

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</table>

Figure 3-12: GC spectra of siloxane-functionalized tung oil

3.6.3 Characterization of fluorine functionalized tung oil

Tung oil was reacted with 2,2,2-trifluoroethyl methacrylate via Diels-Alder reaction to produce fluorine functionalized tung oil based reactive diluents. 1 mol of tung oil was reacted with 1.2 mol of TFM monomer under 150 °C. The synthetic diagram is in Figure 3-13. The structure of final product was characterized by $^1$H NMR, $^{13}$C NMR, and MALDI-TOF mass spectroscopy. The conversion of monomer
was calculated through \( ^1\text{H} \) NMR. The \( ^1\text{H} \) NMR, \( ^{13}\text{C} \) NMR and Mass Spectra of the final product are shown in Figure 3-14, 3-15 and 3-16.

![Figure 3-13: Synthetic diagram of fluorine functionalized tung oil](image)

In the \( ^1\text{H} \) NMR of final product, the Diels-Alder reaction between 2,2,2-trifluoroethyl methacrylate (TFM) and tung oil was confirmed by the new resonance appeared at \( \delta \) 1.14 ppm. This is due to the methyl proton (-CH\(_3\)) in the methacrylate monomer attached to the new six member ring generated via the Diels-Alder reaction. The resonance of conjugated double bond at \( \delta \) 5.6-6.2 also decreased. Other new resonances of final product were assigned in Figure 3-14. Figure 3-15 shows \( ^{13}\text{C} \) NMR of fluorine functionalized tung oil. The new resonance at \( \delta \) 175.1 is the new carboxylic carbon from 2,2,2-trifluoroethyl methacrylate monomer attached to the tung oil backbone. New resonance at \( \delta \) 42-48 is from carbon in the new six member ring generated by Diels-Alder reaction. Other new resonances of final product were assigned in the figure.
MALDI-TOF mass spectrometer was also used to characterize structure of fluorine-functionalized tung oil. The spectrum of final product is shown in Figure 3-16. The resonance at 895 m/z indicates the presence of unreacted tung oil. The new
peaks at 1063 m/z and 1232 m/z indicate the mono and di-addition of trifluoromethacrylate monomer to Tung oil, which confirmed the Diels-Alder reaction.

Figure 3-16: MALDI-TOF spectra of fluorine functionalized tung oil

The proportion of fluorine functionalized tung oil among the final product can be calculated via $^1$H NMR integration. For the fluorine-functionalized tung oil, the resonance at δ 1.1-1.14 corresponds to the methyl proton (-CH$_3$) in the methacrylate monomer attached to the new six member ring generated via Diels-Alder reaction. The resonance at δ 4.1-4.18 corresponds to the hydrogen from the triglyceride backbone of tung oil which remains constant before and after Diels-Alder reaction. From the ratio of these two resonances, the conversion of monomer was calculated and it’s approximately 31%. The corresponding chemical structure of these two resonances and the integration result is shown in Figure 3-17.
3.6.4 Characterization of triallyl ether functionalized tung oil

Triallyl ether functionalized tung oil was synthesized via two-step reaction. In the first step, triallyl ether acrylate was synthesized by esterification reaction with pentaerythritol allyl ether and acrylic acid. Phenothiazine was added as free-radical inhibitor and p-Toluenesulfonic acid as catalyst. The molar ratio of acrylic acid to pentaerythritol allyl ether was 2:1. The completion of reaction was confirmed by the amount of water collected. Toluene was removed in vacuo to generate the triallyl ether acrylate product. The synthetic route of the first step is shown in Figure 3-18. The final product was characterized by $^1$H NMR and ESI mass spectrometry. The $^1$H NMR spectra is shown in Figure 3-19. In mass spectra, the strong peak of 332.9 m/z corresponds to the molecular weight of triallyl ether acrylate, which confirmed the acquisition of anticipated product.
Figure 3-18: Synthesis of triallyl ether acrylate

Figure 3-19: $^1$H NMR Spectra of triallyl ether acrylate

Figure 3-20: ESI-mass spectra of triallyl ether acrylate
Triallyl ether functionalized tung oil was synthesized from tung oil and triallyl ether acrylate via Diels-Alder reaction. The reaction was conducted at 120 °C for 6h. The synthetic diagram is in Figure 3-21. The structure of final product was characterized by $^1$H NMR, $^{13}$C NMR, and MALDI-TOF mass spectroscopy. The conversion of monomer is calculated through $^1$H NMR and GC/MS. The $^1$H NMR, $^{13}$C NMR and Mass Spectra of the final product are shown in Figure 3-22, 3-23 and 3-24.

![Figure 3-21: Synthetic diagram of triallyl ether functionalized tung oil](image)

The $^1$H NMR Spectra of triallyl ether tung oil is different from those of SFTO and TFO which contain methyl proton (-CH$_3$) in the methacrylate monomer. In $^1$H NMR Spectrum of triallyl ether tung oil, the resonance at δ 1.1 does not exist. In addition, the conjugated double bond at δ 5.5-5.6 is overlapped with the protons from the triallyl ether monomer. The reduction of conjugated double bond can’t be determined through $^1$H NMR. The new resonances of final product were assigned in Figure 3-22. In $^{13}$C NMR of triallyl ether functionalized tung oil. The new resonance
at δ 172.9 is the new carboxylic carbon from triallyl ether monomer attached to the tung oil backbone. Other new resonances of final product were assigned in the Figure.

Figure 3-22: $^1$H NMR spectra of triallyl ether tung oil

Figure 3-23: $^{13}$C NMR spectra of triallyl ether tung oil
MALDI-TOF mass spectroscopy was also used to characterize structure of triallyl ether functionalized tung oil. The spectra of final product are shown in Figure 3-24. The resonance at 895.6 m/z indicates the presence of unreacted tung oil. The new peaks at 1205.9 m/z and 1516.2 indicate the mono and di-addition of triallyl ether acrylate monomer to Tung oil, which confirmed the Diels-Alder reaction.

Figure 3-24: MALDI-TOF spectra of triallyl ether functionalized tung oil

To calculate the conversion of triallyl ether acrylate, the new resonance at δ 3.1 corresponds to the proton (H) originate from acrylate monomer attached to the new six member ring generated via Diels-Alder reaction. The resonance between δ 4.25-4.34 corresponds to the hydrogen from the triglyceride backbone of tung oil which remains constant before and after Diels-Alder reaction. From the ratio of the resonance areas, the conversion of monomer was calculated and it’s approximately
23.4%. The corresponding chemical structure of these two resonances and the integration result is shown in Figure 3-25.

![Figure 3-25: Resonance integration of triallyl ether functionalized tung oil](image1)

GC/MS was used to detect the residual amount of triallyl ether acrylate monomer. The calibration curve of triallyl ether acrylate monomer was obtained through four calibration samples of monomer dissolved in acetonitrile solution. The concentrations of the four samples were 43600 mcg/ml, 4360 mcg/ml, 436 mcg/ml, 43.6 mcg/ml respectively. Figure 3-26 is the GC spectra of triallyl ether acrylate.

![Figure 3-26: GC spectra of triallyl ether acrylate](image2)
The retention time of triallyl ether acrylate monomer was around 12.798 minutes. The response area of four calibration sample was collected and the calibration curve was fitted as linear regression trend line using OriginPro 8. Table 3-3 is the corresponding response area of each calibration sample. The linear regression equation is shown in Figure 3-27.

Table 3-3: Response area of triallyl ether acrylate

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Figure 3-27: Calibration curve of triallyl ether acrylate

The value of Adj.R-square is 0.9997, other ANOVA statistics include F-value=10143.38, Prob>F=0.0000985. All the values imply that the linear fit model is
significant. Thus this linear fit can be used to calculate the residual amount of monomers in the final product.

To calculate the residual amount of monomer, the triallyl ether functionalized tung oil was dissolved in the acetonitrile. The concentration of the solution was 20720mcg/ml. Then the sample was analyzed by GC for three times. The response peak of triallyl ether monomer was observed and the average response area is 431403. Thus the conversion of monomer was calculated via the calibration curve and was approximately 35.9%. This result is close to the conversion calculated by $^1$H NMR which is about 23.4%.

Table 3-4: Response area of triallyl ether acrylate in reactive diluents

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3.6.5 Characterization of epoxy functionalized tung oil

Tung oil was reacted with glycidyl methacrylate (GMA) via Diels-Alder reaction to produce epoxy functionalized tung oil. 1 mol of tung oil was reacted with 1.5 mol of glycidyl methacrylate monomer under 150 °C. The synthetic diagram is in Figure 3-28. The structure of final product was characterized by $^1$H NMR, $^{13}$C NMR, and ESI-mass spectroscopy. The conversion of monomer was calculated through $^1$H NMR and GC-MS. The $^1$H NMR, $^{13}$C NMR and Mass Spectra of the final product are shown in Figure 3-29, 3-30 and 3-31.
Figure 3-28: Synthetic diagram of epoxy functionalized tung oil

The $^1$H NMR and $^{13}$C NMR spectrum of final product is consistent with SFTO and FTO. The new resonance appeared at $\delta$ 1.11 ppm which is due to the methyl proton (-CH$_3$) in the methacrylate monomer attached to the new six member ring generated via Diels-Alder reaction. The resonance of conjugated double bond at $\delta$ 5.6-6.2 decreased. Other new resonances of final product were assigned in Figure 3-29. Figure 3-30 shows $^{13}$C NMR of epoxy functionalized tung oil. The new resonance at $\delta$ 173.2 is the new carboxylic carbon from glycidyl methacrylate monomer attached to the tung oil backbone. Other new resonances of final product were assigned in the figure.
Figure 3-29: $^1$H NMR spectra of epoxy functionalized tung oil

Figure 3-30: $^{13}$C NMR spectra of epoxy functionalized tung oil

ESI mass spectrometer was also used to characterize structure of epoxy-functionalized tung oil. The spectra of final product are shown in Figure 3-31. The
peak at 895 m/z indicates the presence of unreacted tung oil. The new peaks at 1037 m/z and 1170 m/z indicate the mono and di-addition of glycidyl methacrylate monomer to tung oil, which confirmed the Diels-Alder reaction.

Just like SFTO and FTO, the conversion of glycidyl methacrylate was calculated through the ratio of new resonance appeared at δ 1.12 and the resonance at δ 4.25-4.34. The conversion of monomer was calculated and was approximately 26.1%. The corresponding chemical structure of these two resonances and the integration result is shown in Figure 3-32.

Figure 3-31: ESI-spectra of epoxy functionalized tung oil
GC/MS was used to detect the residual amount of glycidyl methacrylate monomer. The calibration curve was obtained through four calibration samples of monomer dissolved in acetonitrile solution. The concentrations of the four samples were 40360 mcg/ml, 4036 mcg/ml, 403.6 mcg/ml, 40.36 mcg/ml respectively. Figure 3-33 was the GC spectra of glycidyl methacrylate.
The retention time of glycidyl methacrylate monomer was around 7.269 minutes. The response area of four calibration sample was collected and the calibration curve was fitted as linear regression trend line using OriginPro 8. Table 3-5 is the corresponding response area of each calibration sample. The linear regression equation is shown in Figure 3-34.

Table 3-5: Response area of glycidyl methacrylate

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The value of Adj.R-square is 0.99892, other ANOVA statistics include F-value=2773.33, Prob>F=0.00036. All the values imply that the linear fit model is
significant. Thus this linear fit can be used to calculate the residual amount of monomers in the final product.

To calculate the residual amount of monomer, the epoxy functionalized tung oil was dissolved in the acetonitrile. The concentration of the solution was 61306 mcg/ml. Then the sample was analyzed by GC for three times. The response peak of glycidyl methacrylate was observed and the average response area was 2022323. Thus the conversion of monomer was calculated via the calibration curve and was approximately 20.3% which was close to the number 26.1 % from $^1$H NMR.

Table 3-6: Response area of glycidyl methacrylate in reactive diluents

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3.7 Conclusion

Four different dienophile: 3-methacryloxypropyl trimethoxysilane (MAS), 2,2,2-trifluoroethyl methacrylate (TFM), triallyl ether acrylate (TAEA), and glycidyl methacrylate (GMA) were used to modify tung oil via Diels-Alder reaction. The reaction created a new way to apply bio-based material on coating system. The conversion of each monomer (acrylate dienophile) was obtained through the $^1$H NMR integration calculation and GC-MS technique. The individual property and the reactivity of acrylate monomer would determine the reaction conditions; therefore affect the conversion of each monomer in final product.
CHAPTER IV

COATING PROPERTY EVALUATION OF TUNG OIL BASED REACTIVE DILUENTS IN ALKYD SYSTEM USING EXPERIMENTAL DESIGN

4.1 Overview

In the last chapter, tung oil based reactive diluents were prepared from tung oil via Diels-Alder reaction with 3-methacryloxypropyl trimethoxysilane (MAS), 2,2,2-trifluoroethyl methacrylate (TOF) and triallyl ether acrylate (TAEA). In this chapter, film properties of the reactive diluents with long oil alkyd system were investigated. A quaternary experimental design was employed to determine the influence of three reactive diluents in the thermal and mechanical properties of alkyd system. Coating properties include impact resistance, pencil hardness, crosshatch adhesion, pull-off adhesion, MEK double rubs and gloss. Dynamic mechanical analysis (DMA) was used to study the viscoelastic behavior of the system including storage modulus, loss modulus, glass transition temperature and crosslink density. The reactive diluents did not have significant effect on the gloss and the impact resistance of the film. Pencil hardness, drying time and solvent resistance were altered by different types and amount of reactive diluents used. The reactive diluents also had the prominent effect on the viscoelastic properties of the alkyd system.

4.2 Introduction

The use of renewable sources in the manufacturing of the coating products receives much attention nowadays. This trend has been spurred because of the
realization that the supply of fossil resources is inherently finite. The traditional painting system would also cause series of environmental issues, such as volatile organic solvent (VOC) emissions and recycling problems at the end of a resin’s economic lifetime. Alkyd resins stand out as major binder due to their excellent chemical resistance, color and gloss retention, film flexibility and exterior durability. Alkyd resins are polyesters derived from naturally occurring oils, which make them much more environmental-friendly compared with traditional binders. However, the viscosity of alkyd resin is relatively high. In traditional alkyd paints, the resin is dissolved in 30%-40% of organic solvent like acetone to lower the viscosity for the requirement of paintability \[30\]. As strict VOC content rules for coatings have been enacted by government, it is important to reduce the amount of VOC emission from alkyd coating. The solutions like high solid alkyd, waterborne alkyd are being widely studied \[31, 32, 33\]. Another way to avoid solvent usage is to replace traditional organic solvent with reactive diluents.

A reactive diluent lowers the initial viscosity of the coating during application and becomes part of the polymer matrix after the film drying. A good reactive diluent should also exhibit good compatibility with the binder. For the alkyd, naturally occurring seed oil should the good choice for their excellent compatibility. They are triglycerides with different types of fatty acid composition. However, it’s hard to using drying oil as the reactive diluents to replace the organic solvent directly because their viscosity is relatively high. As a result, seed-oil based materials are usually being modified before application.

Tung oil is unique among other seed oils because of its high unsaturation and conjugation of \(\text{C}=\text{C}\) double bonds. Tung oil is a drying oil obtained from kernels of nuts of Aleurites fordii Hemsi and Vernicia Montana. It contains 5% saturated acid,
15% linoleic or other unsaturated acid and 80% \( \alpha\)-eleostearic acid (triple conjugated diene). The unique chemical structure makes tung oil the fastest polymerizing oil when drying as long as the excellent choice for the preparation of new material. For example, tung oil tends to dimerize at relatively high temperatures. Copolymer such as tung oil-styrene-divinylbenzene by thermal polymerization was made and investigated. It was also found that tung oil can undergo Diels-Alder with facility. Product such as Tung oil-Diacrylate copolymers was made\(^{[34]}\).

Tung oil based reactive diluents were synthesized via Diels-Alder reaction between tung oil and different acrylate monomers. Siloxane functionalized tung oil can undergo sol-gel chemistry to form organic-inorganic hybrid coating. Sol-gel chemistry is based on the polymerization of metal alkoxides through hydrolysis and condensation to generate the metal oxo-polymers\(^{[35,36]}\). The remaining double bonds in the final product will undergo autoxidation to form the crosslinking matrix while the alkoxysilane generates the inorganic phase. The incorporation of inorganic-organic hybrid system will affect the film properties of final product. Fluorine functionalized tung oil is expected to bring low surface energy, high thermal stability and chemical resistance to the final product. However, it will decrease the crosslink density due to the reduction of crosslinkable sites in tung oil. Triallyl ether functionalized tung oil tends to decrease the drying time and increase the crosslink density of final product because it introduces more crosslinkable allyl group into the system.

The investigation of film properties of alkyd binder with the incorporation of each reactive diluent has been done previously. But each of the reactive diluents was applied to the alkyd system separately. There were no elucidations and quantifications about each diluent. Using design of experiments, it is easier to get relationships to
study the interactions of each reactive diluent via response surface methodology (RSM). RSM deals with multiple responses based on the mathematical fit of empirical models. In this way, linear, quadratic or cubic functions can be used to describe the system\textsuperscript{[37]}. For mixture design, the proportions of each ingredient are major ingredient. Simplex-Centroid Mixture Design (SCMD) was conducted to determine the optimum mixture of tung oil based reactive diluents. For the SCMD approach, the proportions of different variables in the mixture were analyzed to determine their influence on the response and the optimization of the mixture to meet the target of anticipated response can be determined\textsuperscript{[38]}. To determine whether the data fitting function was reliable or not, the application of analysis of variance (ANOVA) was conducted. ANOVA subdivide the variations into two category, the variations due to treatment and variations due to random error and compare them to the generated response.

In this chapter, film properties of the three tung oil based reactive diluents with long oil alkyd system were investigated via a quaternary simplex-centroid experimental design. Viscosities, drying time, viscoelastic properties as well as general film properties were investigated.

4.3 Materials

Linseed oil was obtained from Cargill Inc. Tung oil, 2,2,2-trifluoroethyl methacrylate (99%), 3-methacryloxypropyl trimethoxysilane (95%), pentaerythritol allyl ether (70%), acrylic acid (99%), p-toluenesulfonic acid (98.5%), lithium hydroxide (98%) and phenothiazine (98%) were purchased from Sigma-Aldrich. Driers package used in the formulations, 5 w% cobalt Hydro-Cure, 12w% Zirconium Hydro-Cure and 5 w% Calcium Hydro-Cure were obtained from OMG Group.
Wetting agent, BYK-333 was obtained from ALTANA AG. All the materials were used as received without any purification.

4.4 Synthesis of linseed oil alkyd resin

The monoglyceride process was used to synthesize the alkyd. First, a 500 ml round bottle four-neck flask consisting of a condenser, thermometer, nitrogen inlet and mechanical stirrer was assembled. The flask was charged with linseed oil (100 g) and excess amount of glycerol (22.38g, 0.24 mol). The two materials were stirred under the purge of nitrogen for 15 min. Then temperature of the mixture was gradually heated up to 120 °C and the transesterification catalyst, lithium hydroxide (0.024g) was added into the mixture. The temperature was gradually heated to 240 °C. After approximately one hour, a small aliquot was taken and diluted with three parts ethanol. The transesterification step was considered complete if the resulting solution was clear.

After the transesterification step, the temperature of the mixture was cooled to 100 °C and a Dean-Stark trap filled with p-xylene was added to the reaction set up. The reaction mixture was then added with phthalic anhydride (PA) (35.82g 0.24 mol) and 20 ml of p-xylene. The acid number was determined by titration with 0.1M KOH methanol solution and phenolphthalein indicator according to ASTM D4462-9. The reaction was stopped when the acid number was below 5. The product was then cooled to the room temperature. Figure 4-1 was the reaction path for the linseed oil based alkyd.
4.5 Coating preparation

Three tung oil based reactive diluents, fluorine functionalized tung oil (FTO), siloxane functionalized tung oil (SFTO) and triallyl ether functionalized tung oil (TAETO) were formulated with the model linseed oil alkyd. A quaternary experimental design was employed to elucidate the influence of three reactive diluents on the thermo-mechanical and coating properties of alkyd system. The coating formulations were statistically prepared according to the simplex-centroid mixture. Design constraint was applied, as the proportion of the diluents mixture no more than 30 w% of the total weight in the formulation. TripBlend was used as augment design.
The formulation was shown in Table 4-1. Besides, 2 wt% of metal drier package and 1 wt% wetting agent were added in the formulation. The formulations were combined and sealed in vials and mixed on a roll mill for 3h until homogeneous mixtures with no bubbles were achieved. Films were cast with a thickness of 3 mils on aluminum panel and 6 mils on clean glass panel. The films were cured under ambient conditions for 24 h and baked in the oven at 120 °C for 2 h and then increased the temperature to 160 °C for 3 h. The films were allowed for aging at least 7 days before any test was performed.

Table 4-1: Simplex-Centroid design of formulations

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<td>10</td>
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<td>3.75</td>
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<td>3.75</td>
<td>3.75</td>
<td>88.75</td>
</tr>
</tbody>
</table>

4.6 Instrument and testing protocol

All the experiments were evaluated according to ASTM standard: Drying time was evaluated according to ASTM standard (D 5895-03). The coatings were applied
to the glass panel (1 mil) and Gardco circular Drying Time Recorder was placed on the wet film to record tack-free and dry hard time. The viscoelastic properties of the film were investigated using Q800 Dynamic Mechanical Analysis from TA instruments in Temp Ramp/ Freq Sweep mode with strain frequency of 1 Hz. The temperature range was from -55 °C to 150 °C with the ramp rate of 3 °C/min. Brookfield viscometer (DVII+ PRO Digital) was used to measure the viscosity with the shear rate of 100 s^{-1}. Other tests including pencil hardness, pull-off adhesion, crosshatch adhesion, impact resistance, gloss were all conducted according to the corresponding ASTM standard.

4.7 Result and Discussion

The objective of this study was to determine the interactive effect of tung oil based reactive diluents on model alkyd system. In order to achieve goal, a model linseed-based long-oil alkyd resin was synthesized and the reactive diluents were prepared as described in the previous chapter. The formulations were generated as a quaternary simplex-centroid experimental design performed by Design-Expert 8.0. Tung oil based reactive diluents could be used to replace the traditional organic solvent in the alkyd binder.

It is well known that tung oil is one of the fastest polymerizing oil when drying because of its high concentration of conjugated double bond \(^{[39]}\). It will also provide addition crosslinking sites. Therefore, through the incorporation of tung oil based reactive diluents, general coating properties as well as the viscoelastic properties of the alkyd binder can be changed.
4.7.1 Viscosity measurement

The tung oil based reactive diluents are expected to reduce the viscosity as well as share good chemical compatibility with the alkyd product. The viscosity was measured as a function of different types and weight percent of reactive diluents and compared with alkyd resin. The result is shown in Figure 4-2. The viscosity of linseed alkyd was 1982 cp. All the reactive diluents reduced the viscosity of the alkyd resin. The siloxane functionalized tung oil was the most viscous among three thus showed the lowest viscosity reduction ability. The triallyl ether functionalized tung oil on the other hand, showed the highest viscosity reduction ability. All three tung oil based reactive diluents showed good compatibility with alkyd binder, thus the need of organic solvent can be reduced before application.

Figure 4-2: Viscosity measurement of three reactive diluents with neat alkyd
4.7.2 Drying time measurement

The tung oil based reactive diluents are expected to alter the number of crosslinkable sites. Incorporation of reactive diluents is expected to alter the speed of drying process. In this study, drying time was measured by circular drying recorder under ambient condition (25 °C, RH = of 50 ±5 %). Tack free time and dry hard time were recorded and compared.

Table 4-2: Drying time study experiment

<table>
<thead>
<tr>
<th>Design ID</th>
<th>Tack free time (h)</th>
<th>Dry hard time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>16</td>
<td>&gt;24</td>
</tr>
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<td>&gt;24</td>
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<tr>
<td>3</td>
<td>21</td>
<td>&gt;24</td>
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<tr>
<td>4</td>
<td>3</td>
<td>9</td>
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<tr>
<td>5</td>
<td>5</td>
<td>16</td>
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<tr>
<td>6</td>
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<td>&gt;24</td>
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<td>14</td>
<td>&gt;24</td>
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<td>8</td>
<td>15</td>
<td>&gt;24</td>
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<td>&gt;24</td>
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<td>&gt;24</td>
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<td>&gt;24</td>
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<td>14</td>
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<td>&gt;24</td>
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<td>&gt;24</td>
</tr>
<tr>
<td>18</td>
<td>13</td>
<td>&gt;24</td>
</tr>
</tbody>
</table>

The contour plot in Figure 4-3 was the tack free time results. The incorporation of TAETO would reduce the drying time while the incorporation of SFTO and FTO would significantly increase the time needed for the film to dry. Dry hard time of TAETO with alkyd system was around 9 h compared with 16 h of neat alkyd without the reactive diluents. The reason that TAETO reduced the time needed for drying
could be due to the higher autoxidative functionality provided by allyl ether group \cite{40,41}. The data in Figure 4-3 was obtained from statistical calculation and a linear model relationship between FTO, SFTO, TAETO and neat alkyd was selected. The final mathematical equation in terms of real component for MED double rub is:

\[
\text{Tack free time} = +58.57306 \times \text{FTO} + 49.91634 \times \text{SFTO} - 8.59112 \times \text{TAETO} + 8.12529 \times \text{Alkyd}.
\]

The Model F-value of 30.50 implies the model is significant. There is only 0.01\% chance that a "Model F-Value" this large could occur due to noise. Value of "Prob > F" less than 0.0500 indicates model terms are significant. Other ANOVA statistics of interests include: standard deviation = 2.4, R-squared = 0.8591, mean = 13.79, adj.R-squared = 0.8310, PRESS = 139.22, adeq.precision = 18.301. Adeq.precision measures the signal to noise ratio. A ratio greater than 4 is desirable. The adeq.precision of Figure 4-3 is 18.301, which indicates an adequate signal. This model can be used to navigate the design space.
4.7.3 General coating properties

Coatings were prepared with the incorporation of different types and concentration of reactive diluents with neat alkyd. Metal dries and wetting agent were used as additives into the formulation. The typical coating properties of each formulation were measured and the results were presented in Table 4-3.

In addition to reduce viscosity, the reactive diluents such as siloxane functionalized tung oil and triallyl ether functionalized tung oil would be expected to provide additional crosslinking sites for the network while fluorine functionalized tung oil was expected to decrease the number of crosslinking site \[^{42}\]. Thus the crosslink density of the system is expected to alter with the incorporation of different types and amount of reactive diluents. The general coating properties, such as
hardness, MEK double rub are all related to crosslink density \cite{43,44}. Therefore, these properties are expected to change.

From the test result, several trends can be noted. The impact resistance and crosshatch adhesion were not affected by the incorporation of reactive diluents. It was expected that suitable amount of tung oil based reactive diluents would affect the gloss properties \cite{45}. However, the gloss result seems to be independent to the diluents content. Other properties, such as MEK double rub, pencil hardness as well as pull off adhesion altered with the incorporation of different types and amount of reactive diluents. The results were analyzed by the DOE technique. Through this method, trends of properties can be established. In addition, the target formulation of desired properties can be rapidly determined.
The contour plot in Figure 4-4 was the MEK double rub results. The MEK double rub test showed unexpected results. The incorporation of FTO reduced the solvent resistance while the incorporation of SFTO and TAETO did not significantly alter the solvent resistance compared with the neat alkyd. FTO was expected to exhibit higher solvent resistance than SFTO and TAETO due to the chemical inertness of fluorinated groups $^{[23]}$. The reason that FTO reduced the solvent resistance could be the reduction of crosslink density with the incorporation of FTO. The coating tends to be brittle compared with the neat alkyd. The data in Figure 4-4 was obtained from statistical calculation and a linear model relationship between FTO, SFTO, TAETO and neat alkyd was selected. The final mathematical equation in terms of real component for MED double rub is:

<table>
<thead>
<tr>
<th>Design ID</th>
<th>MEK Double Rubs</th>
<th>Pencil Hardness</th>
<th>Pull-off Adhesion</th>
<th>Crosshatch Adhesion</th>
<th>20° Gloss</th>
<th>60° Gloss</th>
<th>Impact Resistance (lb/in)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>105 ± 4</td>
<td>2B</td>
<td>230</td>
<td>SB</td>
<td>148.6</td>
<td>162.8</td>
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<td>200</td>
<td>SB</td>
<td>144.1</td>
<td>163</td>
<td>&gt;40</td>
</tr>
<tr>
<td>2</td>
<td>120 ± 3</td>
<td>HB</td>
<td>210</td>
<td>SB</td>
<td>158.1</td>
<td>172.8</td>
<td>&gt;40</td>
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<td>HB</td>
<td>300</td>
<td>SB</td>
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<td>176.7</td>
<td>&gt;40</td>
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<tr>
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<td>145 ± 1</td>
<td>HB</td>
<td>280</td>
<td>SB</td>
<td>145.8</td>
<td>159.8</td>
<td>&gt;40</td>
</tr>
<tr>
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<td>85 ± 2</td>
<td>3B</td>
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<td>165.7</td>
<td>&gt;40</td>
</tr>
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<td>79 ± 2</td>
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<td>&gt;40</td>
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<td>125 ± 2</td>
<td>HB</td>
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<td>SB</td>
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<td>161.6</td>
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<td>&gt;40</td>
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<tr>
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<td>SB</td>
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<td>&gt;40</td>
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<tr>
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<td>101 ± 3</td>
<td>HB</td>
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<td>SB</td>
<td>149.5</td>
<td>161.2</td>
<td>&gt;40</td>
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<tr>
<td>18</td>
<td>129 ± 2</td>
<td>B</td>
<td>260</td>
<td>SB</td>
<td>156.5</td>
<td>163.6</td>
<td>&gt;40</td>
</tr>
</tbody>
</table>
MEK Double rub = $-113.33778 \times FTO + 72.03535 \times SFTO + 36.21445 \times TAETO + 143.37863 \times \text{Alkyd}$

The Model F-value of 33.32 implies the model is significant. There is only 0.01% chance that a "Model F-Value" this large could occur due to noise. Value of "Prob > F" less than 0.0500 indicates model terms are significant. Other ANOVA statistics of interests include: standard deviation = 7.67, R-squared = 0.8695, mean = 110.74, adj.R-squared = 0.8695, PRESS = 1325.13, adeq.precision = 21.881. Adeq.precision measures the signal to noise ratio. A ratio greater than 4 is desirable. The adeq precision of Figure 4-4 is 21.881, which indicates an adequate signal. This model can be used to navigate the design space.

In Figure 4-5, the contour plot representative of pull-off adhesion are shown. The pull off adhesion showed the minimum at the corner of FTO and SFTO and the maximum was favored to the side of TAETO. The triallyl ether functionalized tung oil tends to increase the pull-off adhesion compared with the neat alkyd.

The data in Figure 4-5 were obtained from statistical calculation and a quadratic mixture model between FTO, SFTO, TAETO and neat alkyd was selected. The Model F-value of 9.13 implies the model is significant. There is only 0.15% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicates model terms are significant. Other ANOVA statistics of interests include: standard deviation = 12.59, R-squared = 0.9013, mean = 238.42, adj.R-squared = 0.8026, PRESS = 16630.27, adeq.precision = 11.061. Adeq.precision measures the signal to noise ratio. A ratio greater than 4 is desirable. The adeq.precision of Figure 4-5 is 11.061, which indicates an adequate signal. This model can be used to navigate the design space. The final equation in terms of real component is:
Figure 4-4: Contour Plot of MEK double rub and standard error containing 70w% of alkyd in the formulation
Figure 4-5: Contour Plot of Pull-off adhesion and standard error containing 70w% of alkyd in the formulation

The contour plots in Figure 4-6 show the pencil hardness results. Pencil hardness from 8B-B, HB, F, and H-9H were assigned the number from 1-19 according to the hardness of graphite. There was a trend of decreased hardness with
the incorporation of FTO in the range of pencil hardness of 5B. The minimum hardness appeared at the apex of FTO. Meanwhile, the incorporation of SFTO and TAETO will retain the same hardness level as the neat alkyd resin. The data in the Figure 4-6 was fitted with linear mixture model. The model F-value of 38.97 implied the model was significant. There was only a 0.01% chance that a model F-Value this large could occur due to noise. Values of prob > F less than 0.0500 indicated model terms were significant. In this case, Values of prob > F was less than 0.0001. Other important ANOVA statistical information about the plot includes: standard deviation = 0.58, R-squared = 0.8863, mean = 7.74, adj R-squared = 0.8635, PRESS = 7.17, adeq.precision = 20.688. Adeq,precision measures the signal to noise ration. A ratio greater than 4 was desirable. The ratio in Figure 4-6 of 20.688 indicated an adequate signal. This model can be used to navigate the design. The final equation in terms of real component is:

Pencil hardness= \(-8.94973 \times \text{FTO} + 8.66222 \times \text{SFTO} + 7.76669 \times \text{TAETO} + 9.25923 \times \text{Alkyd}\).
Figure 4-6: Contour Plot of Pencil hardness and standard error containing 70w% of alkyd in the formulation
4.7.4 Viscoelastic Properties

The viscoelastic properties of the film were measured using Dynamic Mechanical Analyzer (DMA) at the strain frequency of 1 Hz and temperature range from -55 °C to 150 °C with the temperature ramp 3 °C/min. The film specimens were rectangular (16mm long, 10mm wide). The average thickness was 0.05mm. The gap distance for the measurement was around 5mm. The glass transition temperature was determined at the maximum value of the tan delta. The crosslink density \( (\nu_e) \) was determined by utilizing the minimum) storage modulus \( (E') \) at the rubbery plateau beyond the \( T_g \). \( R \) is the gas constant and \( T \) is the absolute temperature.

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

The storage modulus and tan delta of all samples exhibited the similar trends with the increasing of temperature. For demonstration, the DMA spectra of the three formulations are shown in Figure 4-7. The Design ID of the three samples is 1, 2, 3 respectively, which correspond to each of the three reactive diluents incorporated with the alkyd resin separately. The weight percentage of reactive diluent was all 30 w% for all three formulations. From the plot, the modulus displayed a small decreasing trend between -50 °C – 45 °C and then a significant drop between 45 °C – 90 °C. This region corresponds with the glass transition of the film. As the temperature continued to increase, the modulus of each sample continued to fall into the rubbery plateau region. From the storage modulus in rubbery plateau, the crosslink density can be determined.
Figure 4-7: Modulus ($E'$) and tan $\delta$ as a function of temperature of the Design ID=1, 2, 3.

Besides the common trends, the different behavior of three reactive diluents could be observed. The formulation with 30 w% FTO showed the lowest storage modulus at the rubbery plateau while the formulation with 30 w% of TAETO showed
the highest storage modulus at the rubbery plateau. This result was expected as the TAETO tends to provide the additional autoxidative crosslink functionalities while FTO would decrease the number of crosslink functionalities. SFTO consists additional \textit{in situ} polycondensation of alkoxy silane thus would also increase the crosslink density \cite{46}. The glass transition temperature would increase with the incorporation of TAETO and SFTO. The increase in glass transition temperature was also due to the addition of crosslinking density \cite{47}. The values for $E'_{\text{min}}$, $\nu_e$ and $T_g$ for all the formulations are shown in Table 4-4.

Table 4-4: Viscoelastic properties of each formulation

<table>
<thead>
<tr>
<th>Design ID</th>
<th>Storage Modulus (MPa)</th>
<th>XLD (mol/m$^2$)</th>
<th>$T_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.13 ± 0.34</td>
<td>237.08 ± 37.55</td>
<td>37.2 ± 0.7</td>
</tr>
<tr>
<td>1</td>
<td>1.67 ± 0.24</td>
<td>186.97 ± 26.5</td>
<td>35.1 ± 0.5</td>
</tr>
<tr>
<td>2</td>
<td>3.92 ± 0.19</td>
<td>437.17 ± 20.98</td>
<td>36.5 ± 0.3</td>
</tr>
<tr>
<td>3</td>
<td>4.8 ± 0.35</td>
<td>518.86 ± 38.65</td>
<td>47.9 ± 1.2</td>
</tr>
<tr>
<td>4</td>
<td>2.01 ± 0.22</td>
<td>225.98 ± 24.29</td>
<td>33.6 ± 1.3</td>
</tr>
<tr>
<td>5</td>
<td>1.79 ± 0.28</td>
<td>220.79 ± 30.92</td>
<td>34.5 ± 0.9</td>
</tr>
<tr>
<td>6</td>
<td>3.46 ± 0.45</td>
<td>383.42 ± 40.7</td>
<td>38.8 ± 0.5</td>
</tr>
<tr>
<td>7</td>
<td>2.43 ± 0.31</td>
<td>268.68 ± 34.23</td>
<td>39.6 ± 0.7</td>
</tr>
<tr>
<td>8</td>
<td>4.65 ± 0.13</td>
<td>506.06 ± 14.35</td>
<td>45.4 ± 1.6</td>
</tr>
<tr>
<td>9</td>
<td>4.87 ± 0.15</td>
<td>536.11 ± 16.56</td>
<td>41.2 ± 1.4</td>
</tr>
<tr>
<td>10</td>
<td>4.3 ± 0.38</td>
<td>406.96 ± 41.97</td>
<td>51 ± 0.8</td>
</tr>
<tr>
<td>11</td>
<td>3.56 ± 0.22</td>
<td>384.76 ± 24.29</td>
<td>43.2 ± 1.1</td>
</tr>
<tr>
<td>12</td>
<td>2.88 ± 0.17</td>
<td>321.82 ± 18.78</td>
<td>35.8 ± 0.3</td>
</tr>
<tr>
<td>13</td>
<td>2.84 ± 0.26</td>
<td>316.64 ± 28.71</td>
<td>36.6 ± 0.6</td>
</tr>
<tr>
<td>14</td>
<td>4.22 ± 0.34</td>
<td>457.65 ± 37.55</td>
<td>46.7 ± 1.6</td>
</tr>
<tr>
<td>15</td>
<td>2.53 ± 0.17</td>
<td>283.18 ± 18.78</td>
<td>35.2 ± 0.6</td>
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<tr>
<td>16</td>
<td>1.52 ± 0.12</td>
<td>116.28 ± 13.25</td>
<td>43.5 ± 0.7</td>
</tr>
<tr>
<td>17</td>
<td>3.47 ± 0.23</td>
<td>381.78 ± 25.4</td>
<td>41.4 ± 0.3</td>
</tr>
<tr>
<td>18</td>
<td>2.19 ± 0.27</td>
<td>239.25 ± 29.82</td>
<td>44 ± 1.1</td>
</tr>
</tbody>
</table>

The crosslink density model calculation is shown in Figure 4-8. As discussed before, crosslink density would decrease with the incorporation of FTO. The minimum value of crosslink density was located at the apex of FTO. The maximum
value of crosslink density was located at the apex of TAETO. The crosslink density data in Figure 4-8 were fitted with a linear model. The model F-value of 5.33 implies the model was significant. There is only a 1.06% chance that a model F-Value this large could occur due to noise. Values of “prob > F” less than 0.0500 indicates model terms were significant. In this case, linear mixture components are significant model terms. Values greater than 0.1000 indicated the model terms are not significant. Other important statistical information about the plot area is listed as following: standard deviation = 91.68, R-squared = 0.5162, mean = 343.09, adj.R-squared = 0.4194, PRESS = $1.917 \times 10^5$, adeq.precision = 8.714. The ratio adeq.precision of 8.714 indicated an adequate signal. This model can be used to navigate the design space.

The final equation in terms of real components is:

$$\text{Crosslink Density} = -157.76132 \times \text{FTO} + 630.29867 \times \text{SFTO} + 1064.10125 \times \text{TAETO} + 293.99160 \times \text{Alkyd}$$

![Diagram showing crosslink density withfluorine, siloxane, and allyl ether components.
Figure 4-8: Contour Plot of Crosslink density and standard error containing 70w% of alkyd in the formulation

The glass transition temperature model is shown in Figure 4-9. The result shows $T_g$ would increase with the incorporation of TAETO. The maximum value of $T_g$ appears at the apex of TAETO. In opposite, the minimum $T_g$ shows at the apex of FTO. The glass transition temperature data in Figure 4-9 was fitted with a linear model. The model F-value of 6.07 implies the model was significant. There was only a 0.65 % chance that a model F-Value this large could occur due to noise. Values of prob > F less than 0.0500 indicates model terms were significant. Other statistics of interest are listed as following: standard deviation = 3.75, R-squared = 0.5481, mean = 40.38, adj.R-squared = 0.4578, PRESS = 406.16, adeq.precision = 9.593. A ratio greater than 4 was desirable. The ratio in Figure 4-9 of 9.593 indicates an adequate signal. This model can be used to navigate the design space. The final equation in terms of real components is:
\[ T_g = +15.74686 \times \text{FTO} + 39.06029 \times \text{SFTO} + 70.70208 \times \text{TAETO} + 39.95581 \times \text{Alkyd} \]

* Alkyd

Figure 4-9: Contour Plot of Tg and standard error containing 70w% of alkyd in the formulation
4.8 Conclusion

The tung oil reactive diluents have shown the ability to dilute the alkyd system as well as alter the number crosslinking sites in the system. Film properties of the three tung oil based reactive diluents with long oil alkyd system were investigated via a quaternary simplex-centroid experimental design. Crosslink density and glass transition temperature of the film would alter with the different types and amount of reactive diluents. The incorporation of TAETO and SFTO in the formulation resulted in improved $T_g$ and crosslink density while the incorporation of FTO tended to decrease $T_g$ and crosslink density. In addition, the film tended to dry significantly faster with the incorporation of TAETO. As the crosslink density was altered with the incorporation of different types and amount of reactive diluents, general coating properties, such as hardness, MEK double rub were altered correspondingly.
CHAPTER V

CONCLUSIONS

In this thesis, four different acrylate monomers: 3-methacryloxypropyl trimethoxysilane (MAS), 2,2,2-trifluoroethyl methacrylate (TFM), triallyl ether acrylate (TAEA), and glycidyl methacrylate (GMA) were used to modify tung oil via Diels-Alder reaction. The reaction was conducted at atmospheric pressure and elevated temperature. The reaction condition was determined by the individual properties of each acrylate monomer. The acrylate modified tung oil was used as reactive diluents in alkyd system. For the first three acrylate modified tung oils, a quaternary experimental design was employed to determine the influence of reactive diluents on the alkyd coating system. It was found that the incorporation of three reactive diluents in alkyd binder would alter the thermal and mechanical properties of alkyd system. Through mathematical fit of empirical models generated by experimental design technique, the anticipated coating properties can be achieved by adjusting proportions of each modified tung oil in alkyd binder.
REFERENCES


