Development of Efficiently Produced, Renewable Polycarbonates from Fatty Acids, CO2, and Propylene Oxide for Plastic Film Applications

Thesis

Presented in Partial Fulfillment of the Requirements for the Degree Master of Science in the Graduate School of The Ohio State University

By

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2017

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Abstract

Dwindling fossil resources and climate change caused by increasing atmospheric CO₂ have spurred technological developments worldwide. Some help address this problem while producing another. One example is the overproduction of glycerol from a still growing biodiesel industry. This research investigates the production and properties of a novel polymer that could help address all three aforementioned issues.

Through the use of a ring opening reaction involving CO₂ inclusion, epoxides can be used to produce polycarbonates. In 2015, researchers from Ohio State’s department of food, agricultural, and biological engineering successfully produced glycidyl epoxides from soybean oil and epichlorohydrin (from glycerol). They also demonstrated that these monomers could be used to produce polycarbonates. Unfortunately, these fatty acid based (FAB) monomers were low yielding, at 31.7% polycarbonate yield (Chang, Qin, Luo, & Li, 2017). It was thought that yield could be increased through the use of propylene oxide (PO); whose high yielding nature is already well established. To assess PO’s effect on FAB polycarbonate’s yield and properties, polycarbonates were made from glycidyl oleate (GO) or glycidyl linoleate (GL), with or without the addition of PO at two FAB monomer to PO volume ratios.

Yield was evaluated using FT-IR and proton ratios calculated from relevant ¹H-NMR resonance integrals. FT-IR spectra indicated that, while all samples showed good conversion, only terpolymer samples showed evidence of high yield. ¹H-NMR results corroborated these findings. All samples showed monomer conversion in excess of 98%, and it was found that calculated yield could be increased roughly four times over
using only 20% PO by volume, reaching nearly 97% at its highest. There was not a significant difference in the yields of GO and GL based polycarbonates and it did not appear that FAB monomer or PO were preferentially polymerized, as calculated polymer composition was in agreement with the relative quantities of monomer used.

The polycarbonates’ molecular weights were measured using GPC. Molecular weight showed bimodal distribution and low dispersity (1.28±0.09). It was found that increasing relative quantities of PO increased molecular weight and that GO samples were consistently higher molecular weight than GL samples. Though, it remains uncertain as to whether FAB monomer type was responsible the differences.

After purifying the polycarbonates, they were applied to PTFE coated aluminum substrates and left to cure in an open air environment for two weeks. Changes in the polycarbonates’ FT-IR spectra showed good evidence of curing. Peaks associated with double bonds were either eliminated or significantly reduced, indicating crosslinking between polymer chains. Moreover, the appearance or intensification of other peaks was associated with a number of products formed through chain scission and free radical reactions known to occur during oxidative curing. There was also evidence to suggest that trace residual catalyst inadvertently served as a drying agent.

DSC revealed that increasing relative quantities of PO significantly increased glass transition temperature and that GL based samples had a significantly higher glass transition temperature than GO based samples. This also is evidence of superior crosslinking among GL based polymers. All samples had a glass temperature below 25ºC. Also, all sample thermograms showed an exotherm around 150 ºC attributable to
film degradation, as was made evident by the significant drop in glass transition temperature seen in a subsequent heating cycle.

TGA corroborated that degradation occurred around 150 °C, as there was a peak in the TGA curves around 145 °C. Entirely FAB samples showed five distinct peaks in total. They were associated with various curing byproducts and cyclic carbonates produced during polymer degradation. Samples made with PO were very similar, but showed intensification and conflation of two adjacent peaks seen in entirely FAB sample curves.

Tensile Tests showed that both tensile strength and percent elongation to break of GL based samples increased with increasing relative quantities of PO. Unfortunately, adhesion to the PTFE substrate prevented the testing of GO based samples. Tensile strength of GL based films ranged from 12.5 MPa to 18.0 MPa, and percent elongation to break ranged from 86.5% to 209.1%. These property values are similar to film grade linear low density polyethylene (LLDPE), a popular material for making plastic wraps. However, unlike LLDPE, the films’ stress-strain curves were more characteristic of natural rubber. By leveraging PO’s polymerizability, these efficiently produced FAB polymers showed potential to substitute for popular petrochemical derived products.
Acknowledgements

I would like to thank my advisor, Dr. Fred C. Michel for agreeing to take on his advisory role at short notice. I would also like to thank Dr. Katrina Cornish and Dr. Mark D. Soucek in addition to Dr. Michel for offering their time and guidance.

I would like to thank Dr. Shaoqing Cui for assisting me with material preparations, instrument use, and supporting me throughout my project. Her patient and helpful nature was of vital importance to the completion of my project. I would also like to thank her for providing some pertinent data that really strengthened my thesis.

I would like to thank Dr. Yusheng Qin for his guidance and for providing me with the catalyst necessary for my work to proceed. I would also like to thank Dr. Chun Chang in addition to Dr. Yusheng Qin for their research, which serves as the foundation for my own. Without their efforts, my project would not have been possible.

Of the members of the Department of Food, Agricultural and Biological Engineering, I would like to give special thanks to design engineers, Mike Klingman and Scott Wolfe, for preparing a number of custom assets used during my project, and for promptly providing maintenance and repair assistance when needed; Peggy Christman, for administrative assistance; and Zhe Liu, for troubleshooting a number of equipment failures.

Finally, I would like to thank my family for their unyielding support throughout my academic career.
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Chapter 1: Introduction

Polycarbonates are widely used polymers that have myriad applications. Defined by the carbonate moieties within its backbone (Fig.1), polycarbonates are generally tough, transparent materials. Traditional polycarbonates are made from phosgene and bisphenol A (BPA) and are commonly used in the auto industry for door and instrument panels, headlight lenses, and bumpers (Idrees, 2014). They are also used in electronics, as film sheets, and in home appliances (Idrees, 2014). Recent innovations in catalytic technologies have enabled new polycarbonate production strategies that address concerns over dwindling fossil resources and climate change caused by increasing atmospheric CO₂. These new polycarbonates can use byproduct glycerol from the growing biodiesel industry as well as atmospheric CO₂. They are products of epoxides and CO₂, and can be synthesized from monomers derived from fatty acid sources, like vegetable oil (Chang et al., 2017). However, details regarding the yield and applicability of these fatty acid based polycarbonates are limited.

![Carbonate Group](image)

Figure 1: Polycarbonate of BPA

Biodiesel is a renewable fuel that boasts a nearly 80% reduction in life cycle CO₂ emissions as compared to its petroleum derived counterpart (Coronado, Andrade, Jr, &
Silveira, 2008). Its use is on the rise too; in 2016, 1.9 billion gallons of biodiesel were produced in the United States, with the EPA mandating an additional 100 million gallons for 2017 (Meyer, 2016). While the use of biodiesel reduces dependence on fossil resources, a drawback is the production of a glycerol byproduct. For every 9 kg of biodiesel produced, approximately 1 kg of crude glycerol is made (Dunn, 2010). From 2003 to 2006, between 180 and 200 million kg of glycerol were consumed per year in the USA (Dunn, 2010). Considering that Americans only account for about 25% of the world’s glycerol consumption (Dunn, 2010), the global consumption should amount to roughly 800 million kg/yr. As of 2011, the biodiesel industry alone was producing glycerol in excess of 2 billion kg/yr (Ciriminna et al., 2014). It is for this reason that crude glycerol has been rendered a waste product (Ciriminna et al., 2014). At first glance, it would be logical to think that producing polycarbonates from vegetable oil would exacerbate this surplus, but a thoughtful gaze reveals that this is not so. This is because in order to generate polycarbonates from vegetable oils, the oil’s fatty acids must first be reacted with epichlorohydrin (EPCH) to yield glycidyl esters. EPCH, which is both an organochlorine compound and an epoxide, can be synthesized from glycerol using a two-step process involving the formation of dichlorohydrins from glycerol and anhydrous hydrochloric acid, with subsequent reaction with sodium hydroxide (Guzman, 2011), Stoichiometrically, this means that there would be a net loss of two glycerol molecules per triglyceride used to produce fatty acid based epoxides. Thus, polycarbonates from these monomers would actually consume some of the excess glycerol supply.

With the growth of the biodiesel industry over the past decade, consumption of vegetable oil has increased dramatically. The source of all this oil is largely dependent on
factors such as climate, geography, and economics, but in America, soybean oil reigns supreme. In fact, soybean oil contributed nearly 67% of the total oil input for biodiesel production in 2015 (U.S. Energy information administration, 2016) and nearly 25% of the soybean oil produced in America was used for biodiesel (United Soybean Board, 2016). The crops needed to provide this oil serve to decrease net CO$_2$ emissions (Coronado et al., 2008). Polycarbonate synthesis as an additional application for vegetable oil, soybean based or otherwise, would increase demand for oilseed crops, thus further increasing CO$_2$ uptake on the farm.

By synthesizing polycarbonates from epoxide monomers, CO$_2$ can also serve as a feedstock off the farm. Polycarbonates of epoxides and CO$_2$ are becoming increasingly popular due to advances in catalytic technologies. Polypropylene carbonate, made from propylene oxide and CO$_2$, is a common example. Compared to a polyether chain formed from propylene oxide in the absence of CO$_2$, an equally long polypropylene carbonate has been estimated to yield a nearly $800/ton savings in terms of feedstock cost (econic technologies, 2013). Concentrated, low cost sources of CO$_2$ include corn ethanol plants and coal and natural gas burning power plants.

Recent research has demonstrated that epoxide monomers from soybean oil can be used to create polycarbonates. However, the results indicate a poor yield (Chang et al., 2017). Moreover, previous studies have provided little information regarding the properties of polycarbonates made from fatty acids.
**Purpose and Scope**

The primary goal of this project was to investigate a more efficient fatty acid based (FAB) polycarbonate production method. The aforementioned polycarbonates were made from FAB monomers using a process established by former Ohio State University researcher Dr. Yusheng Qin (Chang et al., 2017). The FAB monomers were glycidyl esters made using a process also established by researchers within OSU’s Department of Food, Agricultural, and Biological Engineering (Chang et al., 2017). Polycarbonate yield from these FAB monomers is, thus far, low (~32% (Chang et al., 2017)), yet yield from propylene oxide using the same reaction parameters is high, >95%. An objective of this project was to demonstrate that using propylene oxide in addition to FAB monomers increases FAB polycarbonate yield, thereby improving production efficiency. To accomplish this, monomers derived from the two most prevalent fatty acids in soybean oil, oleic and linoleic acid, were separately polymerized with or without the addition of propylene oxide at multiple monomer ratios.

To measure polymer yield, qualitative and quantitative yield assessments were made using FT-IR and $^1$H-NMR spectroscopy. The chemical and physical properties of these polymers were also evaluated. Analyses included polymer composition, via $^1$H-NMR; molecular weight, via HPLC(GPC); thermal properties of purified polycarbonate samples after being dried as a film, via DSC and TGA; chemical changes that occurred while curing, via FT-IR; tensile strength, and % elongation to break, via tensile testing performed using a DMA. The results of these secondary tests were used to explore the suitability of these novel polycarbonates for various product applications. Ultimately, it is hoped that this project will result in materials that can displace those made from fossil sources using low cost byproduct glycerol, thereby contributing to sustainability efforts.
Chapter 2: Literature Review

Fatty acid based polycarbonates are enticing since they are catabolized from renewable feedstocks such as CO₂, vegetable oil, and glycerol. However, there is little information available on their production or properties. This review seeks to summarize current and promising polycarbonate production strategies and establish their applicability to the production of polycarbonates from vegetable oils. It will then elaborate on the structure and properties of vegetable oils and means of their modification, with emphasis on using them to produce polycarbonates. At the end of the review, a means of producing a polycarbonate from vegetable oil that warrants further development is proposed.

2.1 Polycarbonate Production and Use

While the term “polycarbonate” is most often used to refer to polycarbonates of bisphenol A, the term accurately encompasses any polymer possessing carbonate linkages. It was during the 1890s that the first polycarbonates were prepared by reacting resorcinol and hydroquinone with phosgene in pyridine. However, the resulting crystalline polymers were brittle and difficult to process (Antonakou & Achilies, 2013). It wasn’t until 1953 that Dr. Hermann Schnell and his team at Bayer first produced polycarbonates suitable for commercial purposes (Bayer, 2015). Being a strong, durable, and easy to mold material possessing optical transparency, BPA based polycarbonates have found many applications in the automotive, electronic, and architectural industries.
as various types of windows, films, and casings (Bayer, 2015). The current focus on carbon emissions control and sustainability, has led to the consideration of alternative feedstocks like vegetable oil for polycarbonate production.

2.1.1 Phosgenation of Diols

Most polycarbonates produced commercially are derived from BPA. In this process, BPA, an aliphatic diol, is treated with NaOH and then mixed with phosgene, a deadly gas (Fig. 2). The hydroxy groups of the diol donate a proton to the hydroxides, turning the alcohol into a salt and the hydroxides into water. Then the bisphenol-derived salt reacts with the phosgene to form the polycarbonate (PSLC 2016). However, BPA has come under scrutiny due to its prevalence in plastics and its potential as a human carcinogen. Research from the Centers for Disease Control and Prevention shows that more than 90% of Americans have BPA in their urine, most likely from plastic bottles and cans (NIH, 2017). A review published in 2013 concluded that exposure to BPA and other endocrine-disrupting chemicals has probably contributed "to the increase in the incidence of breast cancer observed over recent decades." (Soto, Brisken, Schaeberle, & Sonnenschein, 2013). The FDA has banned BPA-based products for use in baby bottles and toddler cups due to BPA leaching issues (FDA, 2014).
Vegetable oils could also probably be used to manufacture polycarbonates via phosgenation. For instance, vegetable oils with an abundance of naturally occurring hydroxy groups, like castor oil, would likely work well as a feedstock. However, the relatively low number of carbonate groups that would be found in such a “polycarbonate” world make it less deserving of the name. There is very little literature describing polycarbonates made from vegetable oil and phosgene; perhaps due to the limited number of viable feedstocks or the fact that phosgene is highly toxic and deadly with only a brief exposure. Manufacturing polycarbonates from vegetable oil, CO₂ and glycerol offers a more sustainable, less toxic option.

2.1.2 Ring-Opening Polymerization

In an attempt to improve biodegradability, and safety, alternative polymerization mechanisms, such as ring opening polymerization (ROP), have been studied. ROP is a form of chain-growth polymerization, wherein the terminal end of a polymer chain serves as a reactive center from which other cyclic monomers may react by opening their rings, thus forming a longer chain. In contrast to the aromatic backbones of BPA based polycarbonates, those made through ROP are usually aliphatic. The more flexible and
less bulky backbone of these polycarbonates is more accessible to microbial enzymes, hence their greater susceptibility to biodegradation (Artham & Doble, 2008). One example of ROP is the polymerization of cyclic trimethylene carbonate (Fig. 3). It has been evaluated for use in drug delivery systems, as it is very susceptible to biological degradation, yielding no toxins (Engelberg & Kohn, 1991). Other common examples include poly(butylene carbonate), and poly(hexamethylene carbonate) (Artham & Doble, 2008).

![Figure 3: Polycarbonate from cyclic trimethylene carbonate](image)

However, since they lack a carbonate ring, vegetable oils cannot undergo ring opening polymerization to form polycarbonates when used alone. However, vegetable oils, or any of their derived products that possess epoxide groups, are capable of undergoing ring opening polymerization to form polyethers (J. Zhang & Tang, 2015).

2.1.3 **Copolymerization of CO$_2$ and Epoxide**

Polycarbonate synthesis strategies that don’t rely on toxic chemicals were developed in the late 1960’s. In 1969, Dr. Shohei Inoue made the landmark discovery of alternating copolymerization of CO$_2$ and propylene oxide using a ZnEt$_2$-H$_2$O binary catalyst to produce polypropylene carbonate (Fig. 4) (Inoue, Koinuma, & Tsuruta, 1969).
Since Dr. Inoue’s discovery, a variety of other catalytic systems have been
developed for this process. Such catalysts are either heterogeneous, like zinc glutarate
and double metal cyanide (DMC), or homogeneous. Heterogeneous catalysts generally
have higher activity, but demonstrate poorer CO$_2$ uptake (Trott, Saini, & Williams, 2016).
Therefore, they tend to form polyethers. Homogeneous catalysts can be classified under
two groups, bicomponent or dinuclear (Trott et al., 2016). Bicomponent catalysts are
metal(III) complexes usually comprised of Co(III), Cr(III), Mn(III) or Al(III) coordinated
by porphyrin or salen ligands (Fig.) (Trott et al., 2016); “salen” is a contraction
salicylaldehyde and ethylenediamine. They are usually used in tandem with ionic co-
catalysts, the most common of which is bis(triphenylphosphine)iminium chloride
(PPNCl) (Trott et al., 2016). Dinucleaer catalysts are metal(II/III) complexes tethered by
“mononucleating” ligands (Fig. 5) and have shown higher turnover frequencies compared
to their mononuclear counterparts (Nakano, Hashimoto, Nakamura, Kamada, & Nozaki,
2011).
During the polymerization reaction (Fig. 6), the oxygen of an epoxide group weakly binds to the metal center of the catalyst and is subsequently attacked by a nucleophile (usually from the catalyst or co-catalyst), resulting in an alkoxide ligand that can rapidly react with CO$_2$ to afford a weakly bound carbonate (Darensbourg, 2016). This carbonate reacts with the epoxide in a rate determining step to continue the polymerization process (Darensbourg, 2016). It should be noted that if the metal catalyst is too electrophilic, the metal alkoxide formed post ring opening won’t be sufficiently nucleophilic for CO$_2$ insertion (Darensbourg, 2016). The nucleophile of co-catalysts, such as the chlorine anion of PPNCL, can coordinate with the metal centers, helping to temper electrophilicity, yielding nearly perfect alternating polycarbonates (Pescarmona & Taherimehr, 2012). This reaction can also yield a cyclic byproduct, as will be discussed in section 2.1.4.
2.1.3.1 Polypropylene Carbonate

The most heavily researched polycarbonates involving CO\textsubscript{2} inclusion are propylene oxide based (aka polypropylene carbonate or PPC). Propylene oxide is traditionally derived from propylene (propene), a byproduct of oil refining and natural gas processing. However it can also be synthesized from glycerol by hydrogenating the glycerol to form propylene glycol, which can then undergo cyclic dehydration to form propylene oxide (Yu et al., 2009). Using Co-Salen catalysts, PPC selectivity can exceed 97\%, even at elevated temperatures (Rieger et al., 2012). A transparent thermoplastic polymer, PPC has demonstrated a fairly large elongation at break (~300\%) (Luinstra & Borchardt, 2012). The yield strength of PPC is typically between 10–20 MPa (Luinstra & Borchardt, 2012) and is reminiscent of the low-density polyethylene commonly used for
plastic bags and wraps. However, its glass transition temperature regularly exceeds 40°C (Luinstra & Borchardt, 2012), which may render it too inflexible for such applications. It is also biodegradable via acid catalyzed hydrolysis, yielding CO₂ and propylene glycol (Luinstra & Borchardt, 2012). Fatty acid based polycarbonates would degrade into monoglycerides which, like propylene glycol, pose little to no health concerns; they are both popular food additives (FDA, 2014b).

2.1.4 Cyclic Backbiting

One problem with catalyzed CO₂ inclusion reactions is byproduct formation. Given enough energy, linear polymerization will falter in favor of the production of cyclic carbonates (Fig. 5). With respect to PPC, reaction parameters tend to be sufficiently well controlled to avoid byproduct formation but this may not be the case with vegetable derived products. As an example, if the vegetable oil or its derived products were highly saturated, they may exist as a solid at room temperature. Assuming that solvents aren’t a viable solution, they would need to be melted for the reaction to proceed. The needed rise in temperature may provide enough energy to bias the reaction towards the formation of cyclic carbonates. While such products may possess useful properties, if forming polymer chains is the goal, the fatty acids based monomer may pose a challenge. The use of ring opening polymerization with these cyclic carbonates is not possible because the ring is one carbon short of being large enough to undergo such a reaction (Nuyken & Pask, 2013).
2.2 Vegetable Oils

In 2016, roughly 187 million tons of vegetable oil was produced worldwide (USDA, 2017). Beyond the kitchen, vegetable oils are used to produce a myriad of industrial products including but not limited to, biodiesel, glycerol, coatings, lubricants, solvents, and plasticizers (United Soybean Board, 2016).

2.2.1 Structure and Properties

Biologically derived oils are known as triglycerides. They consist of three fatty acids of varying lengths and or degrees of saturation bound together by glycerol (Fig. 7).

The types of fatty acids bound to a given molecule of glycerol depend on the organism from which the triglyceride was acquired. An oil’s fatty acid profile dictates the oil’s properties. For example, oils with higher portions of unsaturated fatty acids will
generally have lower melting temperatures. This difference is a result of the one or more cis-type double bonds within the oil’s unsaturated fatty acids, which introduce kinks into their shape that make it harder for molecules to pack together into a stable crystalline lattice. The more kinks present, the looser the packing, and the lower the melting point. Average chain length also influences melting temperature, though to a lesser extent. Longer chain lengths allow for more intermolecular attraction and, therefore, result in increased melting points (Table 1).

<table>
<thead>
<tr>
<th>Saturated</th>
<th>Unsaturated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Common Name</td>
<td>Melting Point</td>
</tr>
<tr>
<td>Lauric acid (12:0)</td>
<td>45 ºC</td>
</tr>
<tr>
<td>Myristic acid (14:0)</td>
<td>55 ºC</td>
</tr>
<tr>
<td>Palmitic acid (16:0)</td>
<td>63 ºC</td>
</tr>
<tr>
<td>Stearic acid (18:0)</td>
<td>69 ºC</td>
</tr>
<tr>
<td>Arachidic acid (20:0)</td>
<td>76 ºC</td>
</tr>
</tbody>
</table>

Assuming that polycarbonates derived from vegetable oils maintain the general structure of the fatty acid side chains (i.e. binding from the chains’ end), they would be expected to reflect the properties of the fatty acids. For example, polycarbonates derived primarily from unsaturated fatty acids would generally have lower melting temperatures than those derived from saturated fatty acids.

2.2.2 Crosslinking

Crosslinking is the process of joining two molecules via chemical or physical bonding. It serves to modify the mechanical properties of bulk matter, with the resulting
changes depending on cross-link density. Lower densities might only increase the viscosity of a given fluid polymer, whereas intermediate densities can alter polymers such that they demonstrate elastomeric properties with higher yield strengths (Gent, 2012). High densities will tend to make materials very rigid or glassy (Gent, 2012).

Traditional polycarbonates demonstrate high toughness, but they tend to be relatively soft, thus they show poor abrasion resistance (Antonakou & Achilias, 2013). Also, while polycarbonates tend to be heat resistant, their molecular weight can drop as a consequence of thermal degradation caused by the higher temperatures required for processing steps like extrusion, injection molding, or any other processes that require the polymer to remain in or near its molten state (Rawlings, 1971). This degradation can reduce its viscosity as a fluid, which is disadvantageous for molding processes (Rawlings, 1971). Polycarbonates are also at risk of dissolution caused by organic solvents. These disadvantages can sometimes be surmounted by crosslinking. With its pervasive existence in the food and biodiesel industries, most wouldn’t think of vegetable oils as forming solid or networked structures, however, some will do just given the right conditions. In fact, the same feature responsible for the liquid state of many oils at room temperature, somewhat ironically, is what enables this ability.

2.2.2.1 Oxidative Crosslinking

Humans have been making use of oil’s ability to crosslink since at least the 5th century, when medical writer Aetius Amidenus made note of the use of drying oils as paint and varnish (Mills & White, 1987). Despite its namesake, evaporation isn’t a component of the oil’s “drying” process (more properly termed “curing”). This “drying”
actually refers to the autoxidation of certain oils after contact with oxygen; typically resulting in an insoluble thermoset.

The more double bonds present in an oil, the more susceptible it is to autoxidation. It is for this reason that Englishman Fredrick Walton took notice of linseed oil’s propensity to solidify and went on to use the oil as the key component in Linoleum production, which he patented in 1863 (Powell, 2003). The degree of unsaturation found in an oil’s fatty acids can be captured by its iodine value (IV). The IV is the mass of iodine (mg) that reacts with the carbon–carbon double bonds in 100 g of a given vegetable oil, with larger IVs indicative of more double bonds. If an oil’s IV is less than 100, it is classified as a “non-drying oil”; if greater than 130, it is deemed a “drying oil”; those with an IV that fall between these two values are “semi-drying” (Xia & Larock, 2010). It is important to note that, while IV is closely related to an oil’s ability to cross-link, it can be somewhat deceptive in that it accounts for monounsaturated fatty acids, which do not readily undergo autoxidation. This is because rapid autoxidation is predicated on the presence of abstractable hydrogens located on an oil’s fatty acid chains. The most readily abstractable hydrogens exist as a component of methylene groups seated directly between two double bonds, as in linoleic acid. It is for this reason that an oil’s “Drying Index” is widely accepted as the means to define “cross-linkability”, with drying values greater than 70 classified as a drying oil. An oil’s drying index is calculated as follows:

\[
\text{Drying index} = (\% \text{ Linoleic Acid}) + 2(\% \text{ Linolenic Acid})
\]
Drying ability can also be assessed based on the average number of methylene groups situated between two double bonds, and if the average is equal to or greater than 2.2, it is deemed a “drying oil”. As shown in Table 2, Walton’s chosen linseed oil reigns supreme under all aforementioned drying metrics.

Table 2: Composition of common vegetable oils (adapted from Wicks, Jones, & Pappas, 1992)

<table>
<thead>
<tr>
<th>Oil</th>
<th>Saturated</th>
<th>Oleic (C18:1)</th>
<th>Linoleic (C18:2)</th>
<th>Linolenic (C18:3)</th>
<th>Theoretical Iodine Value*</th>
<th>Drying Index</th>
<th>Avg. # of Methylene Groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coconut</td>
<td>91</td>
<td>7</td>
<td>2</td>
<td></td>
<td>9</td>
<td>2</td>
<td>0.1</td>
</tr>
<tr>
<td>Linseed</td>
<td>10</td>
<td>22</td>
<td>16</td>
<td>52</td>
<td>172</td>
<td>120</td>
<td>3.6</td>
</tr>
<tr>
<td>Soybean</td>
<td>15</td>
<td>25</td>
<td>51</td>
<td>9</td>
<td>126</td>
<td>69</td>
<td>2.1</td>
</tr>
<tr>
<td>Sunflower, Mn</td>
<td>13</td>
<td>26</td>
<td>61</td>
<td></td>
<td>121</td>
<td>61</td>
<td>1.8</td>
</tr>
<tr>
<td>Sunflower, Tx</td>
<td>11</td>
<td>51</td>
<td>38</td>
<td></td>
<td>104</td>
<td>38</td>
<td>1.1</td>
</tr>
</tbody>
</table>

*Calculations made under the assumption that all saturated fatty acids are stearic acid

The drying process begins with induction, when ambient oxygen is absorbed into the oil. During this step, there is negligible change in the oil’s physical or chemical properties because the freshly absorbed oxygen is quickly consumed by any antioxidants present within (Soucek et al., 2012). As the oil continues to absorb oxygen, the autoxidation reaction is initiated when the oxygen begins to react with fatty acid chains which have abstracted hydrogens (singlet oxygen can react directly), forming peroxide groups (Soucek et al., 2012). These peroxides tend to degrade, forming alkoxide and hydroxyl radicals which serve to abstract more hydrogens, thus propagating the oxidation process and demonstrating its autocatalytic nature (Fig. 8). Autoxidation is terminated once all the free radicals combine through a number of secondary and tertiary reactions.
Some of these reactions can result in a cross-link between two fatty acid chains, as in the case of an alkoxide radical reacting with an unsaturated fatty acid (Soucek et al., 2012).

Initiation

\[
\text{H} - \text{H} \quad \text{H}^\cdot \quad \text{H} - \text{H}
\]

Peroxide Formation

\[
\text{O}_2 \quad \text{O}^\cdot - \text{O} \quad \text{R} - \text{H} \quad \text{HO} - \text{O} \quad \text{R}^\cdot
\]

Peroxide Decomposition

\[
\text{O}^\cdot \quad \text{H} - \text{H} \quad \text{O} - \text{H} \quad \text{H} - \text{H} \quad \text{H} - \text{H} - \text{H}
\]

Secondary Reactions

\[
\text{R} - \text{H} \quad \text{O} - \text{H} \quad \text{C} = \text{C}
\]

Figure 8: Autoxidation reactions (adapted from Soucek et al., 2012)

Oxidative crosslinking could prove useful as a post-processing step for polycarbonates synthesized from vegetable oils if such polymers show poor tensile strength or scratch resistance. If said polymers were to be used as a film or coating, the expectation of oxidative crosslinking would also allow for the polymer to be stored, transported, and applied as a liquid.
2.2.3 Epoxidation

A broadly used term, “Epoxy”, denotes the cured end products of epoxy resins, as well as being an informal name for molecules possessing one or more epoxide functional groups. Epoxides are capable of reacting with a wide variety of substances, including acids, polyfunctional amines, thiols, alcohols and phenols, as well as other epoxides (Sienel, Rieth, & Rowbottom, 2000). When these substances possess multiple functional groups, they can serve to cross-link the epoxides. Epoxy products are commonplace in the adhesives industry, where their fast curing time and exceptional binding strength are put to good use (Sienel et al., 2000).

Vegetable oil based epoxies have become more common in recent years. The main method used for epoxidation involves the mixture of functionalizable oils with concentrated hydrogen peroxide and acetic or formic acid in the presence of a mineral acid that acts as a catalyst (Sienel et al., 2000). The hydrogen peroxide reacts with the acid to form a peroxy acid which then reacts spontaneously with the double bonds found in the side chains to form epoxide groups (Fig. 9).

![Figure 9: Triglyceride epoxidation](image)

\[
\text{Figure 9: Triglyceride epoxidation}
\]
Polyols derived from epoxidized soybean oil (ESO) have been used to synthesize polyurethanes comparable with polyurethanes obtained from petrochemical polyols (Lligadas, Ronda, Galià, & Cádiz, 2010). However, because ESOs tend to have lower epoxide content than their petroleum-derived counterparts, they tend to have lower cross-link density. Furthermore, unreacted epoxide groups and saturated fatty acid chains self-plasticize and reduce reactivity, resulting in poorer thermal and mechanical properties (Xu, Liu, Erhan, & Carriere, 2004). Therefore, ESO’s industrial uses tend to be limited to nonstructural, additive applications where they act as plasticizers and or stabilizers. Polycarbonates that rely on cross linking to form solid structures may possess similar shortcomings.

2.2.3.1 Epichlorohydrin from Glycerol

An organochlorine compound and an epoxide, Epichlorohydrin (EPCH) is predominantly converted to bisphenol A diglycidyl ether, used in the production of epoxy resins (Pham & Marks, 2005). EPCH is also a precursor to monomers used for other resins and polymers. In fact, it was once used to produce synthetic glycerol, but with the glut of glycerol produced as a byproduct of the biodiesel industry, the producer has become the product. Dow Chemicals has had ongoing glycerol to EPCH production from its facility in Shanghai since 2012, with an annual capacity of 150,000 metric tons (Guzman, 2011). Solvay International chemical group has followed suit with its own Chinese plant in 2012, boasting a similarly impressive 100,000 metric ton per year capacity (Guzman, 2011). Between 2009 and 2015, EPCH from glycerol grew from 1% to 12% (Ciriminna et al., 2014). As will be explained in section 2.3, EPCH can serve as a
key reactant for the production of vegetable oil derived monomers capable of forming polycarbonates, thus encouraging further growth of the EPCH market.

2.2.4 Separating Fatty Acids from Glycerol

While triglycerides have many applications, there are benefits to working with the building blocks that comprise them, namely the fatty acids and the glycerol that binds them. For instance, in 2013, crude glycerol acquired from the biodiesel industry was used in conjunction with di-isocyanates to produce polyurethane foam (Luo, Hu, Zhang, & Li, 2013). There is also the potential to bind more than glycerol’s maximum of three fatty acids through the polymerization of fatty acid based glycidyl monomers. Doing so may compensate for the lower cross-linking potential of some fatty acid profiles. But, in order to take advantage of each component’s unique properties, they must first be separated.

2.2.4.1 Transesterification

One means of separating fatty acids from their glycerol backbone is via transesterification; the process used in the biodiesel to transform fatty acids into methyl esters. Fatty acid methyl esters (FAMEs) have lower boiling points than their respective fatty acids and are more resistant to oxidative degradation (Farris, 1979). FAMEs are also non-corrosive, so they can be processed in carbon steel equipment, rather than the more expensive stainless steel equipment recommended for fatty acids (Farris, 1979). However, their lack of a carboxyl group does reduce their functionality.

The transesterification process can be catalyzed by acid or base; however, base catalysis is more popular because it proceeds more rapidly and is less corrosive.
(Schuchardt, Sercheli, & Matheus, 1998). Given this, only the base catalyzed reaction will be discussed here. The reaction requires one mole of triglyceride per three moles of alcohol (typically methanol), though an excess of alcohol is used to improve yields and to allow for the physical separation of the two end products, glycerol and FAME (Dunn, 2010). The process consists of four sequential and reversible reactions (Fig. 10).

\[
ROH + B \rightleftharpoons RO^- + BH^+ \quad (1)
\]

\[
R''O\text{C}R' + \text{OR} \rightleftharpoons R''O\text{C}R' + O^- \quad (2)
\]

\[
R''O\text{C}R' \rightleftharpoons R\text{C}R' + R''O^- \quad (3)
\]

\[
R''O^- + BH^+ \rightleftharpoons R''OH + B \quad (4)
\]

Figure 10: Mechanism for base catalyzed transesterification reactions. (R’ is a fatty acid side chain, R” is the glycerol backbone)

In brief, alcohol first reacts with the base, producing an alkoxide along with the protonated catalyst. Next, the carbonyl group of the triglyceride is attacked by the alkoxide, forming a tetrahedral intermediate that results in an alkyl ester and the corresponding anion of what is now a diglyceride. The diglyceride then deprotonates the catalyst, allowing the former to react again. The reaction proceeds until the fatty acids have been completely separated from their glycerol backbone (Fig. 11).
Figure 11: Transesterification of a triglyceride

Of all the alkaline catalyst used, metal alkoxides are the most active, providing yields in excess of 98% in a little as 30 min (Schuchardt et al., 1998). This remains true even at low molar concentrations (0.5 mol%) (Schuchardt et al., 1998). Though, they are less appealing in some respects, as they require the absence of water and are expensive (Freedman, Pryde, & Mounts, 1984). Alkaline metal hydroxides, like KOH and NaOH, are considerably cheaper; however, they are less active. Even so, they remain the economical choice when they are used at molar concentrations that provide yields on par with alkoxides (1 or 2 mol%). (Freedman et al., 1984). There is, however, a secondary disadvantage to using hydroxides in that they produce water if they react with alcohol. Water has the tendency to hydrolyze triglycerides, producing other products, details of which will be discussed in the next section.

Today the most notable use for FAMEs is biodiesel, of which soybean oil is the primary feedstock (at least in the US). In 2016, nearly 25% percent of soy oil harvested underwent transesterification to become biodiesel (United Soybean Board, 2016). FAMEs have also begun to prove their worth in the polymer industry; in 2013, unsaturated fatty acid methyl esters were successfully self-metathesized to produce long-chain aliphatic diesters and their polyesters (Mutlu, Hofsa, Montenegro, & Meier, 2013).
There could also be some unexplored polycarbonate options. For instance, if the transesterification process were to be performed on epoxidized vegetable oils high in oleic acid content, mid-chain cross-linking via CO₂ inclusion could result in relatively symmetrical polycarbonates with saturated side chains.

2.2.4.2 Hydrolysis and Saponification

While there are benefits to methylating the fatty acid side chains during separation, the resulting methyl group lacks the reactivity of a carboxyl group. So if one desired to polymerize the side chains from that end, the task would be difficult. To maintain the carboxyl groups of the fatty acids, hydrolysis or saponification could be used instead. Saponification can be carried out as a one or two step process. As a one step process, the triglyceride’s ester bonds are cleaved after being treated with a strong base (typically NaOH), thus separating the fatty acids from their glycerol backbone. The process occurs in three stages (Fig. 12). First, a hydroxide anion attacks the carbonyl group of one of the triglyceride’s esters, producing an orthoester. The orthoester then releases an alkoxide, generating a carboxylic acid (McMurry, 2007). Given that the alkoxide is a strong base, the carboxylic acid’s proton is transferred to it, producing an alcohol (McMurry, 2007). The process would need to repeat twice more to completely separate the fatty acids from glycerol. While the process is fairly straightforward, it can difficult to recover the fatty acids. Recovery is typically done by precipitating the fatty acid salts (the soap) by adding copious amounts of NaCl (McMurry, 2007). Alternatively the soap could be reacted with a mineral acid to produce a free fatty acids layer that can be separated from a lower layer of glycerol and salt (Wang & Schuman, 2012).
Figure 12: General overview of the hydrolysis/saponification process (R is a fatty acid side chain, R’ is the glycerol backbone)

If one desired to obtain fatty acids directly, they would need to use steam hydrolysis instead. The process occurs in much the same manner as that just described, except water molecules attack the ester bonds rather than hydroxides. Given water’s relative weakness as a base, the reaction proceeds much slower, which is why water is heated into its gaseous phase. As a two-phase saponification process, an alkali substance would then be used to neutralize the fatty acids and produce the soap (Archuleta, 1991).

2.2.5 Hydrogenation

While there are clear benefits to being able to link fatty acid chains, cross-linking can have its drawbacks. With regards to oxidative crosslinking, if and when a vegetable oil derived product is too quick to cure, post processing can be a challenge; a product may be of little to no use if it crosslinks before the catalysts and or solvents used to make it are removed. Crosslinking also reduces a material’s recyclability. As with any thermoset, the covalent linkages between cross linked polymer chains cannot be broken without risking the chains themselves. Therefore, the thermoset cannot be melted down and reused. For these and other reasons, it may useful to limit a vegetable oil’s potential
to cross-link by eliminating or reducing the number of double bonds along the fatty acid side chains. This can be accomplished via hydrogenation.

2.2.5.1 Traditional Means of Hydrogenation

Hydrogenation of vegetable oils is not a new idea; in the food industry, it was once widely performed via a fairly straightforward process. Unfortunately for the food industry, the process tends to isomerize unsaturated fat into unhealthy trans fats (FDA, 2006), which caused its popularity to wane. While it has lost its appeal in the food industry, the method may still have potential in the polymer industry. For the reaction to proceed, vegetable oil is first preheated and then combined with a heterogeneous catalyst, nickel being the most popular choice (Farr & Proctor, 2012). Being a two-phase reaction, hydrogen gas is then added to a pressurized vessel containing the oil. When hydrogen gas enters the aqueous phase, it binds to the catalyst and an unsaturated point on a fatty acid side chain. Subsequently, the double bond on the chain breaks, and the now saturated point is freed from the catalyst’s surface (Farr & Proctor, 2012). Saturation tends to follow a bell-shaped curve, increasing with temperature and decreasing with iodine value (IV); while hydrogenation in this manner tends to be effective at saturating polyunsaturated fatty acids, like linoleic and linolenic acid, it does a poor job at saturating monounsaturated fatty acids like oleic acid. It is for this reason that hydrogenation tends to cease once IVs reach around 85 (Farr & Proctor, 2012). Again, some of the remaining unsaturated fatty acids would be trans fats, although there is currently a lack of research pertaining to trans fat’s propensity to crosslink. Trans-fats were once popular in the food industry because they improved shelf-life (Kimbrough, 2006). In other words, trans-fats
are less likely to undergo oxidative breakdown (Kimbrough, 2006), this may mean that they may also be less likely to crosslink, at least oxidatively.

### 2.2.5.2 Aqueous Phase Reformation (APR)

The underlying issue with the traditional hydrogenation is the solvation of hydrogen; being such a volatile gas, it doesn’t dissolve well. Raising the pressure and or temperature during hydrogenation helps, but the effect is limited. One way to circumvent the issue of transferring hydrogen into the aqueous phase is generating it in situ. This can be accomplished by first hydrolyzing vegetable oil into glycerol and fatty acids. Glycerol can then undergo a process known as aqueous phase reformation, wherein glycerol is converted to CO\textsubscript{2} and hydrogen gas. This method was described by researchers from GREENTEC Laboratory, Brazil. Over a 3 hours period at 270°C, the hydrogen produced in situ was able to decrease the IV by 66%, down to 47.7% (Díaz, 2011). With higher temperatures and or allotted reaction time, complete saturation may be possible.

Aside from being a more effective methodology, APR has other advantages. First, hydrolysis and saturation are accomplished simultaneously. Moreover, post processing becomes easier since glycerol is completely converted to gas, which is also beneficial given the surplus of glycerol from the biodiesel industry. With regards to polycarbonate formation, the CO\textsubscript{2} generated could also be used to carry out polymerization via CO\textsubscript{2} inclusion later in the process stream.
2.3 Polycarbonates from Vegetable Oil

The number of published papers regarding polycarbonates derived from vegetable oils are few; a thorough search found only two. Both involve copolymerization of CO$_2$ and epoxides, but differ in their monomer synthesis strategies. The first is from researchers at the Zhejiang University of Hangzhou, China (Y. Zhang et al., 2014). They described the formation of epoxides from fatty acids possessing a terminal double bond, specifically, 10-undecanoic acid; this acid can be obtained via pyrolysis of the ricinoleic acid found in castor oil (Fig. 13) (Anneken et al., 2006). To produce their epoxides, 10-undecanoic acid was methylated and subsequently reacted with meta-chloroperoxybenzoic acid (m-CBCA), a strong oxidizing agent (Fig. 14) (Y. Zhang et al., 2014).

![Diagram of Ricinoic acid methyl ester pyrolysis](image)

Figure 13: Ricinoic acid methyl ester pyrolysis (adapted from Lligadas, Ronda, Galià, & Cá, 2010)
Polycarbonates were formed using a Zn–Co(III) DMC catalyst at various pressures and temperatures over a 12-hour period. Average molecular weight and % weight cyclic carbonate of the crude polymers negatively correlated with temperature, 18.6 kg/mol to 7.1 kg/mol and 4.8% to 20.0% from 30 ºC to 100 ºC, respectively. Percent conversion was effectively 100% above 40ºC (Y. Zhang et al., 2014). Other works that assessed the influence of monomer length on polycarbonate yield help explain the high yields from the Zhejiang experiment (Y. Zhang et al., 2014). One involved copolymerization of 1, 2-butene oxide, 1,2-hexene oxide and 1,2-octene oxide with CO₂ while also using a SalenCoCl and PPNCl catalyst system. Here, the selectivity towards polycarbonate formation was 97-99% (Lu et al., 2006). A separate experiment using a Zn–Co(III) DMC catalyst also showed decreasing % weight cyclic carbonate with increasing with monomer alkyl length, 14.2-1.1% from 0-10 alkyl carbons (X. Zhang, Wei, Du, & Fan, 2015). Increasing resistance toward backbiting with increasing
monomer length was thought to be a result of intramolecular steric repulsion between two neighboring carbonate units (X. Zhang et al., 2015).

Zhejiang’s research clearly shows that Zn–Co(III) DMC catalysis is an effective means for polycarbonate synthesis from methyl 10-undecenoate, but the product’s applicability has yet to be thoroughly explored.. The polycarbonates are described are clear and viscous liquids, but otherwise, the only notable observation was that water present in their unreacted monomer caused chain transfer reactions that resulted in a hydroxy group forming at each end of their polymers’ backbone. This indicates potential in the polyurethane industry, where these polymers could react with diosocyanates, but because this monomer synthesis strategy is only readily applicable to one type of fatty acid, abundant in only one type of vegetable oil, this strategy doesn’t seem commercially viable..

A second, more recent paper from researchers at the Bioproducts and Bioenergy Research Laboratory at OSU’s OARDC campus (Chang et al., 2017) details synthesis of glycidyl monomers (Fig. 15) from soybean oil. Unlike monomers from 10-undecanoic acid, this method is effective for all fatty acids, and by extension, all vegetable oils. Moreover, it retains the functionality of whatever fatty acids are used to make them. This may generate a large range of polycarbonate properties, tunable based on the monomer’s fatty acid profile, thus expanding the number of product applications. The monomers were produced by mixing a dry soybean oil soap with EPCH, the epoxide mentioned in section 2.2.3.1, and a phase transfer catalyst (Cetrimonium bromide) (Chang et al., 2017). A three factor Box Behnkin experiment, varying molar ratio of EPCH to soap, catalyst loading, and reaction time, found that all first and second order factors were significant.
A model was generated and used to optimize reaction parameters for a batch test, which attained a monomer yield of 94.26%.

![Figure 15: Glycidyl esters from vegetable oil](image)

These monomers were polymerized using a SalenCoCl and PPNCl catalyst and co-catalyst to produce polycarbonates with an almost perfectly alternating structure (carbonate linkages >99%) although at relatively low yield (31.7%). This soybean oil based polycarbonate had a molecular weight of 5.1 kg/mol with a dispersity of 1.22.

![Figure 16: Aliphatic polycarbonate from glycidyl epoxies derived from vegetable oil](image)

Like the aforementioned 10-undecanoic based monomers, these glycidyl monomers should be well suited for copolymerization with CO₂ (Fig. 16); their terminal epoxides offer superior reactivity in comparison to internal epoxides, as they’re less sterically hindered (Sienel et al., 2000). Moreover, the long FAB chains should hinder backbiting. So, the low polycarbonate yields were unexpected. The fact that the fatty based monomers used in the OSU experiment were glycidyl esters, unlike Zhejiang’s
monomers, could have been an influential factor. For epoxides like propylene oxide, nucleophilic attack occurs predominantly at the less sterically hindered α-carbon of the epoxide ring. This bias is a result of its superior accessibility and the electron-donating effect of its methyl group (Wu et al., 2011). On the contrary, epoxides such as styrene oxide tend to be attacked at the β-carbon because of the electron-withdrawing effect of the phenyl group (Wu et al., 2011). By comparing NMR spectra, the resonance associate with the hydrogen of the methine group in the OSU polycarbonate backbone was 5.12 ppm vs Zhejiang’s 4.86 ppm(Yu et al., 2009). This shift downfield is evidence of glycidyl esters having greater electron withdrawing ability, thus they would be more likely to experience nucleophilic attacks at their β-carbon. After integration into the polymer, electron withdrawing groups at the β-carbon to the unreacted carbonate group can also drive the reaction towards backbiting (Fig. 17) (Pescarmona & Taherimehr, 2012). Also, increasing monomer length significantly decreases turnover frequency (TOF). For instance, the TOF for 1,2-Octene oxide was found to be about a fifth of 1,2-Butene oxide’s (Lu et al., 2006). With regioselectivity that favors backbiting and a low turnover frequency, there is ample opportunity for byproduct formation when using fatty acid based glycidyl esters.
Figure 17: Most likely positions for nucleophilic attack and their respective backbiting reaction

2.4 Path Forward

Epoxide monomers can be produced from vegetable oils, and EPCH, which can be synthesized from a currently overabundant glycerol supply. Moreover, they can be broadly applied to all types of vegetable oils. However, regioselectivity favors backbiting, resulting in low yield of the glycidyl ester monomers. Use of a high yielding comonomer, such as propylene oxide, which has a relatively fast turnover frequency could serve to quickly propagate a polycarbonate chain before it backbites onto a preceding fatty acid based unit, and increase yield.

Polycarbonate terpolymers can be made from diverse vegetable oils, variable monomer ratios, and can be modified in many ways, creating a wide range of properties, and thus are likely to have many useful applications. Coupled with their consumption of waste CO₂ and glycerol, these terpolymers are promising as sustainable polycarbonate materials.
Chapter 3: Efficient Fatty Acid Based Polycarbonate Production

Polycarbonates were synthesized from one of two distinct glycidyl monomers with or without the addition of propylene oxide for the purpose of evaluating propylene oxide’s influence on polycarbonate yield. These glycidyl monomers were produced from soybean oil’s two most prevalent fatty acids, oleic and linoleic acid. FT-IR analysis of samples made using propylene oxide indicate a marked decrease in byproduct formation with intensification of peaks associated with the desired polycarbonate. Analysis of $^1$H-NMR spectra corroborated these findings; purely oleic and linoleic polycarbonates were low yielding, at 24.8% and 22.7%, respectively, whereas, a 1:0.25 glycidyl monomer to propylene oxide volume ratio increased fatty acid based polycarbonate yields dramatically, to 90.8% and 84.3%, respectively. Additional propylene oxide did not have a statistically significant effect. The average percent of fatty acid based units of all samples were in agreement with the relative amounts of FAB monomer used to make each one, indicating no bias towards polymerization of any one type of monomer. Average molecular weight was found to increase with increasing amounts of propylene oxide. Samples had fairly narrow dispersity (between 1.17 and 1.40) and showed bimodal molecular weight distribution.
3.1 Introduction

Polycarbonates are made with CO$_2$ via ring opening reactions with epoxides, and, until recently, the epoxides were solely derived from petrochemical processes. Such polycarbonates have value in and of themselves, but are neither sustainable nor renewable. Glycidyl epoxides have recently been synthesized from soybean oil and epichlorohydrin (EPCH) (Chang et al., 2017) and used to produce polycarbonates. Unfortunately, these fatty acid based (FAB) monomers were low yielding, at 31.7% polycarbonate yield (Chang et al., 2017). Although these soy oil-derived glycidyl ester monomers create conditions more favorable for cyclic byproduct formation, their resulting regioselectivity likely encourages backbiting, while their large size and shape likely restricts the rate at which the polymer can propagate, both limiting yield. Propylene oxide (PO) was the first epoxide to undergo ring opening polymerization with CO$_2$ and has since shown consistently high yields using a myriad of modern catalysts and reaction parameters (Klaus, 2011). PO, as a co-monomer, may increase polycarbonate yield by compensating for FAB monomers’ poor yielding properties.

3.2 Materials and Methods

3.2.1 Experimental design

Polycarbonates were produced from glycidyl oleate (GO) and glycidyl linoleate (GL) either alone or in combination with PO at two FAB monomer to PO volume ratios (Table 3). Each polycarbonate was produced in triplicate.
3.2.2 Materials

Chemicals were sourced as follows:

Actetone (67-64-1), Fisher
Bis(triphenylphosphine)iminium chloride (PPNCL) (21050-13-5), Alfa Aesar
Calcium Hydride, (7789-78-8) extrapure, 0-20mm grain size, up to 15% powder, Arcos Organics
Cetyl trimethylammonium bromide (CTAB) (57-09-0) 99+%%, Arcos Organics
Chloroform-d (865-49-6) 99.80+%% atoms contains 0.03v/v %TMS, Arcos Organics
CO₂ (124-38-9) 99.99% purity, Praxair Inc
Dichloromethane 99.9, Extra Dry (75-09-2), Arcos Organics
Ephichlorohydrin (EPCH) (106-89-8), Arcos Organics
Ethanol (64-17-5) Absolute, Anhydrous, Pharco-aaper
Linoleic Acid (60-33-3) 99% Fisher ACROS Organics™
Salen Cobalt(III)-Cl, provided by Dr.Yusheng Qin, Changchun Institute of Applied Chemistry
Sodium Oleate (143-19-1) 97.0+%%, TCI
Tetrahydrofuran (HPLC) (109-99-9), Fisher

Table 3: Polycarbonate samples

<table>
<thead>
<tr>
<th>FAB Monomer</th>
<th>FAB Monomer:PO Ratio (mL:mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1:0</td>
</tr>
<tr>
<td>GO</td>
<td>1:0.25</td>
</tr>
<tr>
<td></td>
<td>1:0.5</td>
</tr>
<tr>
<td>GL</td>
<td>1:0</td>
</tr>
<tr>
<td></td>
<td>1:0.25</td>
</tr>
<tr>
<td></td>
<td>1:0.5</td>
</tr>
</tbody>
</table>


3.2.3 Catalyst Preparation

Both the Salen-CoCl and PPNCL were dried prior to use. Each catalyst was placed into its own 5 mL ampule, attached to a vacuum pump via a rubber hose, placed into a 60°C environment, and left to vacuum dry for 24h. The ampules were subsequently filled with nitrogen and transferred to a glove box devoid of oxygen and moisture.

3.2.4 Monomer Preparation

FAB monomer was produced as described by (Chang et al., 2017), except that certain initial saponification and acidification steps were omitted because the chemicals used in this experiment were not triglycerides, briefly, glycidyl linoleate (GL) production began by dissolving linoleic acid in acetone with a weight ratio of 1:8. Then, 110% stoichiometric sodium hydroxide was added dropwise while the solution was vigorously stirred. After mixing for 4h, sodium linoleate was filtered from the acetone and dried at 25°C under vacuum to a consistent weight (~48h). Sodium oleate was purchased outright for glycidyl oleate (GO) production.

In order to produce FAB monomer from these soaps, ~50g of each was added to its own 250 mL three neck flask. EPCH was then added at a 10:1 (EPCH:Soap) molar ratio. The systems were flushed with nitrogen, sealed, and placed in oil baths heated to 115°C. Under constant mixing with a magnetic stirbar, CTAB was added at a 0.02:1 (CTAB:FAB Monomer) molar ratio as soon as refluxing was observed. Immediately afterwards, the systems were quickly flushed with nitrogen and resealed. After 2 hours of mixing, the mixtures were allowed to cool to 70°C, then centrifuged for 10 min at 10,000
rpm to precipitate any remaining soap and CTAB. In order to remove excess EPCH, the supernate was evaporated in a 250mL rotovap flask with a small stir bar to help prevent bumping, using a a rotary evaporator, spun at 60 rpm at 90°C under vacuum until no more evaporation was noted (30-45 min). To remove residual soap, DI (deionized) water was added to the rotovap flasks and the contents were poured into separatory funnels. Once the funnels were filled, sealed, and shaken, the monomer was allowed to separate from the water and the newly formed lower water layer was subsequently removed. This washing process was performed an additional 6 times. Finally, in order to remove residual water from the FAB monomers, they were distilled under vacuum. After distillation, the distillate was placed in a nitrogen filled glovebox until use.

PO was dried as described for drying dichloromethane (Kinard, Kasper, & Mikos, 2012). Briefly, PO was dried under nitrogen and over calcium hydride for six hours at 50°C. It was then distilled and placed in the glovebox with the other monomers.

3.2.5 Polymer synthesis

The polymerization process used was adapted from the highest yielding process previously described (Chang et al., 2017). To summarize, within a nitrogen filled glove box, 0.0260 g (0.04 mmol) of Salen-CoCl and 0.0230 g (0.04mmol) of PPNCl were added to a pre-dried 10ml autoclave (Fig. 18) equipped with a magnetic stir bar. A total of 3ml of liquid epoxide monomer(s) was transferred to the autoclave using a 1mL syringe. The autoclave was then pressurized to 4 MPa with CO₂ and then magnetically stirred at 600 rpm for 30 min. The autoclave was repressurized to 4 MPa after 30 min to
compensate for the drop in pressure caused by the rapid dissolving of the CO\textsubscript{2} into the monomer solution. The reaction was allowed to run for 24 h after the initial fill.

Figure 18: Pressurized Reaction Vessel used for polymerization reaction

At the end of the reaction time, excess CO\textsubscript{2} was slowly released through an outlet valve on the autoclave. One drop of the crude product was immediately analyzed via FT-IR. Another two drops were placed into two separate 1mL vials containing 0.5mL of THF or 0.5 mL of chloroform-d for GPC and NMR spectroscopy; the vials were kept at -20°C until their contents were analyzed. The remainder of the crude product was dissolved in dichloromethane and poured into an 8 oz. jar along with the magnetic stir bar used during the reaction. In an attempt to reduce the products’ exposure to atmospheric oxygen and moisture, a lid designed to connect to a pressure equalizing drip funnel and nitrogen source was attached to the jar (Fig. 19).
Once attached, the drip funnel was quickly filled with 50mL of ethanol, seated in the lid, and the system flushed with nitrogen. The ethanol was then added dropwise to the dichloromethane solution over ~25min while the solution was stirred at 600 rpm. Once all the ethanol was added, the drip funnel was removed from the lid while the jar was slowly flushed with nitrogen. The jar was then sealed and stored in a freezer overnight to allow the product to solidify and precipitate. The purification process was repeated a second time the following day. Post purification, the supernate was removed from the jar and a small amount of purified sample was allocated for FT-IR analysis, GPC, and NMR spectroscopy as described earlier.

Figure 19: Polymer purification system
3.2.6 *FR-IR Analysis*

Fourier transform infrared (FT-IR) spectra were obtained using a Spectrum Two IR spectrometer (Perkin Elmer Inc., MA, USA), equipped with an attenuated total reflectance accessory. The FT-IR spectra were produced using 16 scans and a measuring resolution of 4 cm\(^{-1}\) in the range of 450-4000 cm\(^{-1}\). Data analysis was performed using Perkin-Elmer’s own Spectrum 10™ Software.

3.2.7 \(^1\)H-NMR Analysis

Conversion, yield, and product composition were evaluated using proton ratios calculated from relevant \(^1\)H-NMR resonance integrals (Fig. 20). To prepare the samples, both crude and purified product was dissolved in chloroform-d containing 1% (v/v) TMS. \(^1\)H-NMR spectra were obtained using a Bruker Avance-III 400 MHz spectrometer (Palo Alto, CA, USA). Data analysis was performed using TopSpin 3.5.
3.2.7.1 Yield and Conversion Calculations

The proton bound to the methine group of polycarbonate units show distinct resonances at 5.00 ppm and 5.12 ppm, from PO and FAB monomer, respectively. PO and FAB cyclic carbonates share a resonance associated with one of the hydrogens bound to the ring’s methylene group at 4.55 ppm. Likewise, they shared a resonance associated with the methylene group of the epoxide, at 2.67 ppm. After integrating these resonances, percent conversion was calculated as shown in the following equation.

\[
\%\text{Conversion} = 100 \times \frac{\int b_{11} + \int b_{12} + \int a_{2X}'}{\int b_{11} + \int b_{12} + \int a_{2X}' + \int a_{3X}''}
\]
In order to isolate PO’s influence on FAB monomer polymerization, yields were evaluated both as a percent yield of polycarbonate (\%Yield_{\text{Overall}}), or “overall yield”; and as a percent yield of FAB polycarbonate (\%Yield_{\text{FAB}}), or “FAB yield”. Given near complete conversion, the signal to noise ratio of unreacted monomer was consistently low, and thus it was difficult to obtain a consistent value for their associated integral. Therefore, said integral was excluded from the \%Yield_{\text{Overall}} calculation, shown below.

\[
\%\text{Yield}_{\text{Overall}} = 100 \times \frac{\int b_{11} + \int b_{12}}{\int b_{11} + \int b_{12} + \int a_{2X'} + \int a_{3X'}}
\]

Given that FAB monomer, FAB cyclic carbonate, and FAB polycarbonate units all share the same pendent chain, the integral of the resonance associated with the chain’s double bonds divided by its respective number of protons was used to represent the sum of all three. As such, \%Yield_{\text{FAB}} was calculated as follows.

\[
\%\text{Yield}_{\text{FAB}} = 100 \times \frac{\int b_{11}}{1/n \int j} \quad n = 2 \text{ if GO was used}
\]

\[
\%\text{Yield}_{\text{FAB}} = 100 \times \frac{\int b_{11}}{1/n \int j} \quad n = 4 \text{ if GL was used}
\]

The average percent FAB polycarbonate units within the polymers was calculated via the equation below

\[
\%\text{FAB Polycarbonate} = 100 \times \frac{\int b_{11}}{\int b_{11} + \int b_{12}}
\]
3.2.8 GPC

The molecular weights of the polycarbonates were determined via gel phase chromatography (GPC). GPC was performed with THF as the mobile phase, eluting at a rate of 1.0 mL/min. The system was comprised of a Shimadzu LC-20 AB (Shimadzu, Columbia, MD, USA) upstream of a Waters Styragel HR1 column (7.8 × 300 mm), a Phenogel 5 μm 10E4 Å LC column (7.8 × 300 mm), and an RID-10A refractive index detector; The columns and detector were held at 35°C. Seven polystyrene standards, between 770-35,500 g/mol, were used for calibration. Each sample was eluted for 30 minutes. Data analysis was performed using LabSolutions™ GPC Software.

3.3 Results and Discussion

3.3.1 Monomer Conversion and Polycarbonate Yield

Averaged FT-IR spectra of unreacted FAB monomer and crude product (Fig. 21) indicate the characteristic peaks of the glycidyl esters’ epoxide groups at 855 and 910 cm⁻¹. Peaks associated with the FAB ester chain are at 1739, 2894, 2925, and 3006 cm⁻¹. These were attributed to the ester’s carbonyl group, symmetrical and asymmetrical stretching of C-H bonds, and C-C double bond(s), respectively. There were a number of new peaks that appeared in the polycarbonate products’ spectra: the peaks at 1120 and 1805 cm⁻¹ were attributed to the C-O bonds and carbonyl group of cyclic byproduct. The C-O bonds of the polycarbonate were associated with the peak at 1240, and its carbonyl group at 1744.
Figure 21: FT-IR Spectra of unreacted monomer and crude product
The peaks characteristic of the glycidyl esters’ epoxide groups were not apparent in FT-IR spectra of entirely FAB polycarbonate, indicating complete FAB monomer conversion. In the case of the crude terpolymers, changes in the fingerprint region distorted the epoxide peaks, so degree of conversion is less clear. These peaks are present, though reduced, indicating that at least some monomer conversion has taken place. Analysis of corresponding purified terpolymer and polypropylene carbonate samples also show these peaks, and so they may not be solely representative of the monomers. Spectra of entirely FAB polycarbonates show relatively intense peaks associated with cyclic byproduct with little evidence of the desired polycarbonate, confirming poor polycarbonate yield. The terpolymers show only weak byproduct peaks and a strong peak associated with the C-O bonds of a polycarbonate. The carbonyl peak of polypropylene carbonate appears at 1745 cm\(^{-1}\) (Narang, Macova, Berek, Upadhyay, & Mehta, 2016) and is conflated with the carbonyl peak of the FAB esters (Fig. 21). However, given the intensification and shift of the ester peak, polycarbonate formation is evident when PO is used.

Calculated monomer conversion ranged between 98.4% and ~100% across all samples (Fig. 22), similar to a polypropylene carbonate sample made by fellow researcher Shaoqing Cui (unpolished data) using the same procedure.
Polycarbonate yields (Fig. 23) were more disparate. As expected, the lowest calculated yields were associated with polymerization reactions involving only FAB monomer, with 24.8% yield and 22.3% yield for GO and GL based reactions, respectively. The addition of PO was found to increase the overall percent yield significantly. Yields from the 1:0.25 FAB monomer to PO volume ratio were calculated to be 93.4% and 87.7% for GO and GL based samples, respectively. The calculated percent FAB monomer converted to polycarbonate also increased, to 90.8% and 83.2%. A 1:0.5 volume ratio increased the overall yield to 94.0% for GO and 96.5% for GL based polycarbonate. Their respective FAB polycarbonate yields decreased for GO based polycarbonate, to 82.2%, and increased for decreased for GL based polycarbonate, to 89.4%. The overall yields of the terpolymers were on par with the polypropylene carbonate sample described earlier, at 96.7%.
Figure 23: Polycarbonate yield. *Only one PO sample was produced.

At a significance level of 0.05, a Tukey’s test revealed that the overall and FAB yields of GO and GL samples were not significantly different at the same FAB monomer to PO ratios. Moreover, the average yields of the 1:0.5 groups were not significantly different from the 1:0.25 groups. However, the relative change in overall and FAB yields of the GO based 1:0.5 group did not align with the corresponding GL group. Two of the three GO based 1:0.5 samples had abnormally low FAB yields at 78.6% and 74.08%, whereas the third was in better agreement with overall yield, at 93.9%. This incongruous drop in FAB yield relative to overall yield was likely a result of propylene oxide self-polymerizing, forming polyethers. Examination of the these samples’ NMR spectra indicates the presence of polyether units (Fig. 23). However, the rest of the samples were either devoid, or showed inconsequential evidence, of polyether units. The reason for this isn’t clear, though it was noted that these were the first two samples made. More importantly, they were the only GO samples made from a different batch of GO; all GL
samples were made using the same batch of GL. Recalculating the group’s overall yield after incorporating the ether region reduced it to 88.1%, thus aligning it with the downward trend of FAB yield.

![NMR spectrum of polyether units](image)

Figure 24: NMR evidence of polyether units

### 3.3.2 Terpolymer Composition

A t-test ($\alpha = 0.5$) to determine if the percent FAB units in the terpolymer backbones were in agreement with their theoretical values revealed that, while they were significantly lower statistically (~2.1%), they were actually practically identical (Table 4). The consistently lower calculated values could easily be accounted for by erroneous addition of PO. PO is a volatile liquid which creates an air pocket when withdrawn into a syringe, thereby eliminating the interface between the syringe’s plunger and the PO. The grading on syringes are designed to account for the volume of the plunger, so using this grading to make measurements when the plunger PO interface is broken would result in excess PO and, therefore, relatively less FAB monomer. This result indicates that there was no bias in producing polycarbonate units from PO over FAB monomer.
Table 4: Terpolymer composition

<table>
<thead>
<tr>
<th>FAB Monomer</th>
<th>FAB Monomer:PO Ratio (mL:mL)</th>
<th>Theoretical % FAB Units</th>
<th>% FAB Units (Crude)</th>
<th>% FAB Units (Pure)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO</td>
<td>1:0.25</td>
<td>43.8</td>
<td>41.3</td>
<td>41.0</td>
</tr>
<tr>
<td></td>
<td>1:0.5</td>
<td>28.1</td>
<td>27.2</td>
<td>27.5</td>
</tr>
<tr>
<td>GL</td>
<td>1:0.25</td>
<td>44.0</td>
<td>40.8</td>
<td>41.3</td>
</tr>
<tr>
<td></td>
<td>1:0.5</td>
<td>28.2</td>
<td>26.3</td>
<td>27.1</td>
</tr>
</tbody>
</table>

One other noteworthy point regarding PO’s volatility is the possibility of unreacted PO escaping from the autoclave after the polymerization reaction. This would raise the calculated conversion and overall yield. Given that the composition results suggest percent yields of FAB and PO polycarbonate units are equivalent, this action could explain the consistently higher overall yield relative to FAB yield (Fig. 23).

3.3.3 Molecular Weight, Polydispersity, and Degree of Polymerization

Increasing the relative amount of PO increased the resulting polycarbonates’ average molecular weight (Table 5). The GO based polycarbonates had higher average molecular weights than their GL based counterparts, and that the polypropylene carbonate (made by Shaoqing Cui) had a significantly higher average molecular weight than the rest. Dispersity was narrow for all polymer samples. However, terpolymers consistently had greater dispersities than polymers made without PO. Also, every GO based polymer had a greater polydispersity than its GL based counterpart. Interestingly, the polypropylene carbonate had the lowest dispersity of all.

While $^1$H-NMR analysis indicated that polymer composition was in agreement with the relative amounts of monomer used, it is unclear whether the monomers were actually
integrated into the same polymers. Purification altered the average molecular weight while retaining composition. Increasing relative amounts of PO decreased the percent change in molecular weight (Table 5). When comparing the molecular weight distribution of purified samples to crude samples, the high molecular weight peak intensified relative to the low molecular weight peak for entirely FAB polymers, whereas the opposite occurred for polypropylene carbonate. This might indicate changes in solubility brought on by differing properties of PO and FAB polymer units. In this case, one would expect polymers comprised more of one monomer to be selectively precipitated, thus changing the average composition. However, this did not occur (Table 4).

Assuming that the calculated compositions were representative of each polymer chain, PO substantially increased the degree of polymerization with a relatively modest change in the total number of fatty acid pendant chains along each polymer chain’s backbone.
Table 5: Purified sample GPC results

<table>
<thead>
<tr>
<th>FAB Monomer</th>
<th>FAB:PO Ratio (mL:mL)</th>
<th>Mₙ (kg/mol)</th>
<th>Mₚ/Mₙ</th>
<th>DPᵃ</th>
<th>Avg. # FAB Units per Polymerᵇ</th>
<th>Average MWₜ (kg/mol)</th>
<th>Average MWₜ (kg/mol)</th>
<th>Average MWₜ/MWₜ</th>
<th>% Change Mₙ(Crude to Pure)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO</td>
<td>1:0</td>
<td>8.8</td>
<td>1.27</td>
<td>23</td>
<td>--ᵈ</td>
<td>24.10</td>
<td>13.28</td>
<td>1.81</td>
<td>36.7</td>
</tr>
<tr>
<td></td>
<td>1:0.5</td>
<td>17.7</td>
<td>1.39</td>
<td>99</td>
<td>27</td>
<td>25.72</td>
<td>13.89</td>
<td>1.85</td>
<td>3.8</td>
</tr>
<tr>
<td>GL</td>
<td>1:0</td>
<td>6.6</td>
<td>1.18</td>
<td>17</td>
<td>--ᵈ</td>
<td>17</td>
<td>8.86</td>
<td>1.93</td>
<td>14.6</td>
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<tr>
<td></td>
<td>1:0.25</td>
<td>10.5</td>
<td>1.30</td>
<td>49</td>
<td>20</td>
<td>17.10</td>
<td>8.86</td>
<td>1.93</td>
<td>14.6</td>
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<tr>
<td></td>
<td>1:0.5</td>
<td>13.7</td>
<td>1.29</td>
<td>77</td>
<td>21</td>
<td>21.93</td>
<td>11.82</td>
<td>1.86</td>
<td>5.5</td>
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<tr>
<td>NA</td>
<td>0:1ᶜ</td>
<td>57.1</td>
<td>1.17</td>
<td>559</td>
<td>0</td>
<td>68.27</td>
<td>36.11</td>
<td>1.89</td>
<td>-22.3</td>
</tr>
</tbody>
</table>

ᵃDP = \( \frac{M_n}{(\% \text{FAB Unit})(\text{MW}_{\text{FAB Unit}})+(\% \text{PO Unit})(\text{MW}_{\text{PO Unit}})} \)

ᵇMW_{\text{Monomer Unit}} = MW_{\text{Monomer}} + MW_{\text{CO₂}}

c³Only one PO sample was analyzed

dᵈSecond peak could not be discerned

MWₜ= Molecular weight of high molecular weight peak
MWₜ= Molecular weight of low molecular weight peak
3.3.4 Molecular Weight Distribution

GPC analysis revealed bimodal terpolymer weight distributions but this bimodality was not consistent among all samples (Fig. 25). Entirely FAB distributions show only a small to moderate high molecular weight shoulder. Bimodality may have resulted from trace adventitious water, which is known to act as a bifunctional initiator (Fig. 26). When a water molecule dissociates, its hydroxide can act as a nucleophile and initiate the polymerization reaction. The resulting terminal hydroxy group on the backbone can then dissociate to form an alkoxide, which, as a nucleophile itself, can initiate a second line of propagation (Hostalek, 2016). This phenomenon would result in the formation of an ether group within the backbone. ¹H-NMR analysis showed little evidence of ether groups, but considering the degree of polymerization across all samples, ether resonances from bifunctional initiation could only exist as a small fraction of corresponding polycarbonate unit resonances (<6%). Therefore, the absence of ether resonances in the NMR spectra isn’t surprising. Also worth noting is that the aberrant GO based 1:0.5 samples didn’t have abnormally high molecular weights nor a relatively large high molecular weight peak, so it is unlikely that rampant bifunctional initiation was to blame for the ether groups observed in their NMR spectra.

In samples where multiple peaks could be easily discerned, the average ratio of the high and low molecular weight peaks was ~1.87. This was very near to the value of 2 expected when assuming immediate bifunctional initiation. The differences in bimodality could be attributed to varying degrees of success in drying the monomers. The method used to dry PO appears to have been the least successful, given the more overt bimodality
observed in all samples made with PO, except for the polypropylene carbonate.

However, this sample was produced from a different batch of PO (Shaoqing Ciu, personal communication) which was dried overnight instead of for 6 h. This may help account for the lower polydispersity of her polypropylene carbonate sample compared with the terpolymers.

Figure 25: Representative molecular weight distributions of purified samples
Figure 26: Bifunctional Initiation

GO based samples consistently showed stronger high molecular weight shoulders and peaks than GL based samples. Therefore, more frequent bifunctional initiation could help explain their higher molecular weights and number of fatty acid pendant chains per polymer. Interestingly, the molecular weight of the GO’s lower peak was also higher than the GL’s. Varying levels of bifunctional initiation should have less influence on the lower peak, so other factors are probably involved. While there wasn’t a statistically significant difference in yield between entirely GO or GL based polycarbonate, GL yields were still lower. If GL is indeed poorer yielding than GO, that fact could help account for GO samples’ higher molecular weight. Less monomer converted to polycarbonate would result in a lighter polymer given equal catalyst loading and monomer molarity; GL actually has a slightly higher molarity (~0.7%).
3.4 Conclusions

The results of this research clearly show that PO is capable of markedly increasing polycarbonate yield. PO successfully increased the conversion of FAB monomers to polycarbonate units roughly four times over. At only 20% PO by volume, overall yields were indistinguishable from entirely PO based polycarbonate’s. Furthermore, the chosen catalyst did not appear to bias polymerization of PO over FAB monomers. While not conclusive, it is possible that FAB monomer type had an appreciable effect on molecular weight, though the differences could be explained by extraneous factors, such as the presence of adventitious bifunctional initiators. These results demonstrate the potential of these novel polycarbonates. It was proven that they can be produced efficiently, and that their average molecular weight is highly tunable through the choice of different epoxides. Characterization of these terpolymers’ thermal and material properties would be a logical next step to assess their value.
Chapter 4: Properties of Fatty Acid Based Polycarbonate Films

4.1 Introduction

As a readily renewable resource, vegetable oils are an enticing option for the production of value added products. According to the USDA’s 2017 oil crops yearbook, roughly 70% of the vegetable oil produced in America is derived from soybeans (USDA, 2017). The United Soybean board’s 2016 product guide states that approximately 10% of soybean oil was used for purposes other than food and biodiesel, including films, plasticizers, lubricants, and other products (United Soybean Board, 2016). In the paints and coatings industry, vegetable oil based products primarily take the form of alkyds, a polyester derived from fatty acids, polyols and a dicarboxylic acid or carboxylic acid anhydride. Alkyds account for roughly 12% of the global architectural coatings market (Researchnester, 2017). Yet, in 2016, only about 3% of soybean oil produced in the USA was used for films and coatings (United Soybean Board, 2016). Clearly, only a small portion of vegetable oil production is enough to establish it as a major constituent of a widely used product.

While demonstrating success in a number of chemical supply chains, vegetable oil’s potential as a petrochemical substitute, that can deliver performance that meets or exceeds industry standards, isn’t clear. Having proven that fatty acid based (FAB) polycarbonates can be produced efficiently (Chapter 3), ascertaining their properties is a good step towards understanding this potential. The research contained herein assesses some properties of oxidatively cured films made from the FAB polycarbonates described
(Chapter 3). The cured films are qualitatively assessed by FT-IR, their glass transition and degradation temperatures are quantified by DSC, thermal stability by TGA, and tensile strength and percent elongation to break determined by DMA. These data should inform the potential of the polycarbonates in one or more product applications and encourage further research.

4.2 Methods

4.2.1 Film Preparation

Polycarbonate films were produced directly from the purified polycarbonates described in Chapter 3. As stated, polycarbonates were made solely from glycidyl oleate (GO) and glycidyl linoleate (GL) or were terpolymers from propylene oxide (PO) and a FAB monomer at two FAB monomer to PO volume ratios (Table 6). Each polycarbonate was produced in triplicate.

<table>
<thead>
<tr>
<th>FAB Monomer</th>
<th>FAB Monomer:PO Ratio (mL:mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO</td>
<td>1:0</td>
</tr>
<tr>
<td>GL</td>
<td>1:0.25</td>
</tr>
<tr>
<td></td>
<td>1:0.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>GL</td>
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</tr>
<tr>
<td></td>
<td>1:0.25</td>
</tr>
<tr>
<td></td>
<td>1:0.5</td>
</tr>
</tbody>
</table>

Purified polycarbonate was transferred to a 6” x 6” sheet of PTFE coated aluminum. After allowing residual supernatant to evaporate (~5min), films were created via a single slow draw down with a square metal applicator with a 152.4mm (6mil) gap.
clearance. The films were allowed to cure for two weeks in an open air environment at approximately 25°C before testing.

4.2.2 *FT-IR*

Fourier transform infrared spectroscopy was used to assess chemical changes that occurred during the two-week cure. Spectra were obtained using a Spectrum Two IR spectrometer (Perkin-Elmer Inc., MA, USA) equipped with an attenuated total reflectance accessory. The FT-IR spectra were produced using 16 scans and a measuring resolution of 4 cm⁻¹ in the range of 450-4000 cm⁻¹. Data analysis was performed using Perkin-Elmer’s own Spectrum 10™ Software.

4.2.3 *DSC*

Differential Scanning calorimetry (DSC) was used to determine the degradation temperature, and glass transition temperatures, pre and post degradation, of the films. Between 5 and 10 mg of cured film was placed into standard aluminum Tzero pans and crimp sealed. Samples were loaded into a TA instruments Q20 DSC (Newcastle, DE) and equilibrated at 40°C under a nitrogen atmosphere for 5 minutes. A number of temperature ramps were then performed at 10°C/min. To eliminate the samples thermal history, samples were first heated to 95°C. The first measurement cycle involved cooling the sample to -70°C, where temperature was held for 5 min. Subsequently, the samples were heated to 200°C at 10°C/min. A second, identical, measurement cycle was then performed. Data analysis was performed using TA Universal Analysis 2000™.
4.2.4 TGA

Thermogravimetric analysis (TGA) was performed using a TA instruments Q50 (New castle, DE) to assess degradation behavior of the cured films. Between 5 and 15 mg of cured film was loaded onto a platinum pan. Samples were equilibrated at 40°C for 5 min then heated to 700°C at 10°C/min. Data analysis was performed using TA Universal Analysis 2000™.

4.2.5 Tensile testing

Tensile testing procedures were adapted from ASTM D882 – 12 (ASTM International, 2017), a standard test method for measuring tensile properties of thin plastic sheeting. Due to poor film uniformity and equipment limitations, a number of test parameters did not fall within the recommended ranges; the samples were shorter, and the strain rate was slower, than suggested. From the cured film samples, 10mm x 5mm strips were cut from the cured film samples using a parallel cutting razor. The polycarbonate strips were carefully removed and their thicknesses were measured with a Byko-Test 8500 film thickness gauge. Film thickness was calculated by averaging the thickness at all four corners and center of the middle 5mm of the strip. The film strips were loaded onto a TA instruments Q800 dynamic mechanical analyzer (New castle, DE) with a free length of 5mm. Tensile values were calculated from the mean of nine measurements obtained from three separate strips per polycarbonate film sample. The strain rate was 5mm/min and data analysis was performed using TA Universal Analysis 2000™.
4.3 Results and Discussion

4.3.1 Qualitative Film Assessment

The films were soft and pliable. GL based films were notably glossier than GO samples, while GO samples had a grippier, almost sticky, texture; as was apparent from the greater applied force needed to overcome static friction when sliding one’s finger over them. An example of a GL based film can be seen below.

![Example of polycarbonate film (1:0.5 GL:PO)](image)

Figure 27: Example of polycarbonate film (1:0.5 GL:PO)

An FT-IR analysis (Fig. 28) of the cured films revealed less evidence of the double bonds once present on their polymers’ pendent chains, as their associated peaks, at 3006 cm\(^{-1}\) and \(~715\) cm\(^{-1}\), disappeared or were significantly reduced. A broad band associated with hydroxy groups manifested around 3461 cm\(^{-1}\), and the peak associated with C-O bonds, at 1150 cm\(^{-1}\), intensified. These changes are all reminiscent of oxidative curing, during which a number of products are formed through chain scissions and free radical reactions. These products include water and a number of relatively short chain
linear aldehydes, alcohols, alkanes, and carboxylic acids (Choe & Min, 2006). The loss of double bonds can be accounted for by their reaction with radical species during the autoxidation process; some of which take part in the desired crosslinking reactions, where C-C, C-O-C (ether) and C-O-O-C (peroxide) cross-links are formed (Soucek et al., 2012).

Figure 28: FT-IR spectra of purified polycarbonates and their respective cured film
It was surprising to see such strong evidence of GO autoxidation in the FT-IR results, as monounsaturated fatty acids lack the readily abstractable hydrogens needed for quick oxidation (Wicks, Jones, & Pappas, 1992). As a supplemental, albeit simple, proof of curing, GO and GL based films were left immersed in dichloromethane to see if they would dissolve (dichloromethane was the solvent used to dissolve these polycarbonates for purification). Both films remained intact (Fig. 29), indicating that they had successfully formed networked structures.

Figure 29: Dyed FAB Films immersed in dichloromethane for 48h

The degree to which the GO films cured could be explained by the presence of residual Salen Cobalt(III) catalyst. Cobalt is capable of catalyzing oxygen absorption and the formation and decomposition of hydroperoxides (Soucek et al., 2012). Multivalent
metals like cobalt are capable of combining with double bonds to form species more susceptible to oxidation; oxidation of unsaturated chains requires a tenth of the activation energy in the presence of cobalt (Oil and Colour Chemists’ Association, 1993). As a surface drier, cobalt is known to cause a gradient in cross-link density due to its top to bottom drying action. It was noted that GL films would curl back onto themselves and roll up after being stretched, thus indicating asymmetry in the film’s structure. Given the evidence of cobalt activity, its presence may explain why GO based polycarbonates oxidized so successfully. Salen-type ligands are known to promote solubility in apolar paint mixtures (R. E. Boomgaard, H. Schier, E. J. J. Kirchner, R. P. Klaasen, F. Hartl, R. P. C. Van der Leeuw & Bakkeren, 2003), therefore, the Salen Cobalt(III) used to catalyze the polymerization reaction may have inadvertently doubled as a drying agent.

4.3.2 **Thermal Analysis**

DSC revealed two distinct curves from two successive heating cycles (Fig. 29). The glass transition temperatures ($T_g$) of corresponding GO and GL samples indicate more crosslinking in GL samples, because $T_g$s were always significantly higher for GL samples (Table 7). This is contrary to each samples respective fatty acid, where oleic acid has the higher melting temperature due to its lower number of cis bonds; $T_m$ of oleic acid is 13°C vs. linoleic acid’s -5 °C (Reusch, 2013). The significance of this temperature difference is compounded by the fact that GO samples consistently had higher molecular weights than their GL counterparts (Chapter 3). According to the Flory-Fox equation, $T_g$ is dependent on free volume, or the “elbow room” between polymer chains, which depends on the average molecular weight of the polymer; internal polymer units exhibit
less free volume than end groups. As the molecular weight of a polymer increases, its end
groups comprise less of the sample’s total volume, and total free volume decreases.
Therefore, given GO sample’s higher molecular weight, its $T_g$ should be higher than
GL’s, not lower.

The $T_g$’s of GL films were so close to room temperature that the films would not
be suitable for some applications. For instance, if GL films were used as a stretchable
wrap in a facility with limited climate control, a change in season or time of day could
render the films useless. Fortunately, a truly vegetable oil based film should possess its
oil’s fatty acid profile, most of which include a percentage of saturated and
monounsaturated fatty acids that could serve to keep the $T_g$ lower, as is apparent in the
GO films. While soybean oil is comprised of roughly 60% polyunsaturated fatty acid
(51% Linoleic), it is about 25% oleic and 15% saturated fatty acid (Wicks et al., 1992).

Above the initial $T_g$, an exotherm appeared at roughly 150°C. This exotherm
was attributed to polymer degradation. This was made evident by the significant drop in
$T_g$ and absence of said exotherm during the second heating cycle. The existence of this
exotherm provides further evidence for catalyst being present within the film, as polymer
degradation is known to result from this. Approximately 56% of a 200 kg/mol
polypropylene carbonate produced with a cobalt salen catalyst degraded after 1 h at
150°C (Kodiyan Varghese et al., 2010). However, the polymer did not degrade under this
conditions once residual catalyst was removed (Kodiyan Varghese et al., 2010). This
catalyst induced degradation is primarily an unzipping process wherein the polymer will
continue to backbite to form cyclic carbonate until the polymer has been completely
undone (Kodiyan Varghese et al., 2010). Although Shaoqing Cui was able to provide DSC data for her polypropylene carbonate sample, her test was limited to one heating ramp up to 100°C. Therefore, her DSC data could not provide a degradation or secondary glass transition temperature.

![Figure 30: Representative DSC thermogram (1:0 GO:PO)](image)

Table 7: Glass transition and degradation temperatures

<table>
<thead>
<tr>
<th>FAB Monomer</th>
<th>FAB:PO Ratio (mL:mL)</th>
<th>Tg₁</th>
<th>Td</th>
<th>Tg₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO</td>
<td>1:0</td>
<td>-6.6</td>
<td>147.7</td>
<td>-23.4</td>
</tr>
<tr>
<td></td>
<td>1:0.25</td>
<td>8.9</td>
<td>147.0</td>
<td>-6.4</td>
</tr>
<tr>
<td></td>
<td>1:0.5</td>
<td>9.6</td>
<td>150.4</td>
<td>-4.6</td>
</tr>
<tr>
<td>GL</td>
<td>1:0</td>
<td>16.7</td>
<td>149.0</td>
<td>4.2</td>
</tr>
<tr>
<td></td>
<td>1:0.25</td>
<td>18.5</td>
<td>150.6</td>
<td>8.3</td>
</tr>
<tr>
<td></td>
<td>1:0.5</td>
<td>21.9</td>
<td>153.3</td>
<td>13.1</td>
</tr>
<tr>
<td>NA</td>
<td>0:1&lt;sup&gt;a,b&lt;/sup&gt;</td>
<td>20.5</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

<sup>a</sup>Method for PO involved only one temperature ramp from -50°C to 100°C after a preliminary ramp from 40°C to 100°C

<sup>b</sup>Only one PO sample was analyzed
Degradation appears to begin around 90°C. If FAB polycarbonates were to be used as plastic gloves, bags, or wraps, this threshold should be sufficient. Said products are typically made from blends of film grade low density and or linear low density polyethylene (LDPE/LLDPE), which generally have a maximum operating temperature of 60°C (Chem-Tainer Industries, 2014). However, this degradation temperature would be unacceptable using traditional plastics processing techniques, where extrusion and die temperatures regularly exceed 150°C (Formosa Plastics, 2014). Though, LLDPE enters a molten state between of 106°C to 112°C (Prasad, 1998). Uncured FAB polycarbonate’s fluid state at room temperature obviously isn’t in need of liquefying during the process stream. This could yield some energy savings.

TGA thermograms showed multiple peaks (Fig 30). Those of GO and GL based samples look very similar, with five distinct peaks around 145°C, 250°C, 286°C, 416°C, and a small peak above 500°C. The first peak was attributed to chemical species lost during degradation, as was evident in the DSC results. These may have been entrapped chemicals being released as the film was destroyed. Said chemicals likely include the oxidation products mentioned earlier, many of which have boiling points near or below the peak (Table 8). The second and third peaks were possibly associated with various cyclic carbonates, given their close proximity. While boiling point information for the various cyclic carbonates formed via oxidation and degradation is unavailable, those of corresponding methyl esters are shown in Table 8. If the last two peaks were of cyclic carbonates, the peak around 416°C was likely associated with crosslinked cyclic carbonates; At roughly double the molecular weight, such a significant difference in
temperature is unsurprising. The compound(s) associated with the fifth and final peak is/are less certain.

Compared to GO films, GL films had a relatively more intense “crosslinked cyclic carbonates” peak. This is expected given linoleates’ greater propensity for crosslinking. The polypropylene carbonate showed only one peak at 204°C. This was well below the boiling point of polypropylene carbonate, which is 242°C (PubChem, 2005). This could simply be a case of evaporation.

Unlike entirely FAB polycarbonate, with peaks around 250°C and 286°C, Terpolymer degradation curves had one, much more intense peak, around 264°C. This peak was likely associated with an amalgam of different uncrosslinked cyclic carbonates from FAB and PO units. In the case of propylene carbonate, the presence of less volatile species may have prevented its evaporation, keeping it in place until it reached its boiling point.
Figure 31: Averaged TGA Thermograms
Table 8: Boiling points of oxidation/degradation byproducts of fatty acid methyl esters \(^a\)(Choe & Min, 2006), \(^b\)(ChemSpider, 2017)

<table>
<thead>
<tr>
<th>Class</th>
<th>Chemical(^a)</th>
<th>Boiling Point(^b) (°C)</th>
<th>Class</th>
<th>Chemical(^a)</th>
<th>Boiling Point(^b) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aldehydes</td>
<td>Octanal</td>
<td>169.0</td>
<td>Aldehydes</td>
<td>Pentanal</td>
<td>102.0</td>
</tr>
<tr>
<td></td>
<td>Nonanal</td>
<td>191.0</td>
<td></td>
<td>Hexanal</td>
<td>130.0</td>
</tr>
<tr>
<td></td>
<td>Decanal</td>
<td>208.0</td>
<td></td>
<td>2-Octenal</td>
<td>85.0</td>
</tr>
<tr>
<td></td>
<td>2-Decanal</td>
<td>229.0</td>
<td></td>
<td>2-Nonenal</td>
<td>90.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2,4-Decadienal</td>
<td>110.0</td>
</tr>
<tr>
<td>Methyl esters</td>
<td>Methyl heptanoate</td>
<td>174.0</td>
<td>Methyl esters</td>
<td>Methyl heptanoate</td>
<td>174.0</td>
</tr>
<tr>
<td></td>
<td>Methyl octanoate</td>
<td>192.9</td>
<td></td>
<td>Methyl octanoate</td>
<td>192.9</td>
</tr>
<tr>
<td></td>
<td>Methyl 8-oxooctanoate</td>
<td>230±23.0*</td>
<td></td>
<td>Methyl 8-oxooctanoate</td>
<td>230±23.0*</td>
</tr>
<tr>
<td></td>
<td>Methyl 9-oxononanoate</td>
<td>249±23.0*</td>
<td></td>
<td>Methyl 9-oxononanoate</td>
<td>249±23.0*</td>
</tr>
<tr>
<td></td>
<td>Methyl 10-oxodecanoate</td>
<td>268±23.0*</td>
<td></td>
<td>Methyl 10-oxodecanoate</td>
<td>268±23.0*</td>
</tr>
<tr>
<td></td>
<td>Methyl 10-oxo-8-decenoate</td>
<td>292±33.0*</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Methyl 11-oxo-9-undecenoate</td>
<td>306±25.0*</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alcohols</td>
<td>1-Heptanol</td>
<td>176.0</td>
<td>Alcohols</td>
<td>1-Pentanol</td>
<td>137.0</td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td>Heptane</td>
<td>98.4</td>
<td></td>
<td>1-Octene-3-ol</td>
<td>174.0</td>
</tr>
<tr>
<td></td>
<td>Octane</td>
<td>125.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Other</td>
<td>Water</td>
<td>100.0</td>
<td>Other</td>
<td>Water</td>
<td>100.0</td>
</tr>
</tbody>
</table>

\(^*\)Predicted
4.3.3 *Tensile Strength and Percent Elongation to Yield*

Both GO and GL samples adhered to the PTFE substrate. Samples made with PO required less force to remove than those without PO. Adhesion prevented the clean removal of GO based strips from the PTFE - the GO strips easily tore, and were self-adherent, making these films untestable. GL based strips could be removed without issue and one-way analysis of variance ($\alpha=0.05$) indicated that increasing PO relative to FAB monomer increased the cured films’ tensile strength and percent elongation to break (Table 9).

<table>
<thead>
<tr>
<th>FAB Monomer</th>
<th>FAB:PO Ratio (mL:mL)</th>
<th>Tensile Strength at Break (MPa)</th>
<th>% Elongation at Break</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>GL</td>
<td>1:0</td>
<td>12.5</td>
<td>86.5</td>
</tr>
<tr>
<td></td>
<td>1:0.25</td>
<td>13.5</td>
<td>142.1</td>
</tr>
<tr>
<td></td>
<td>1:0.5</td>
<td>18.0</td>
<td>209.1</td>
</tr>
</tbody>
</table>

The tensile strength of 1:0.25 and 1:0.5 samples compared to 1:0 samples increased by $\sim$8% and $\sim$44%, respectively. This could be explained in part by a greater number of FAB units in the polycarbonate. As discussed in chapter 3, the percent increase in GL units in corresponding samples averaged $\sim$18% and $\sim$24%. These additional units lend greater opportunity for interchain crosslinking. While GO samples consistently had a greater average number of FAB units per chain than GL samples, the fact that these units possess half the number of double bonds reduces their crosslinking potential. It was interesting to note that the percent increase in tensile strength, relative to
the percent increase in FAB units, was appreciably less for the 1:0.25 samples compared to the 1:0.5 GL samples. Additional space between FAB units resulting from additional PO units might help explain this. If intrachain FAB units are farther apart, they may be less likely to crosslink with themselves and more likely to crosslink with pendant chains on neighboring polymers. Covalent bonding between polycarbonate chains is of chief importance in increasing a thermoset’s tensile strength, as these bonds prevent polymer chains from slipping past one another (Nielsen, 1968).

While a polypropylene carbonate film was not available for testing in this research, a similar film reported as polypropylene carbonate, with a molecular weight ($M_n$) of 50kg/mol and dispersity of 1.05, had a tensile strength of 21.5 MPa with a 330% elongation to break (Du et al 2006). While their polypropylene carbonate films had a similar tensile strength and higher percent elongation to break as compared to our GL films, their stress-strain response lacked features characteristic of GL based films, which will be discussed later.

It should be noted that the applied films weren’t particularly uniform. Films ranged between 20 and 60 µm in thickness, well below the 152.4mm (6mil) clearance of the applicator. Poor wettability and high viscosity made application difficult. Pinhole defects were also apparent in the majority of samples, possibly caused by residual solvent trapped within the polycarbonate. When obtaining test strips, effort was made to avoid areas with poor uniformity and defects, though poor film quality could still refute the reliability of the tensile measurements. The average thickness of the test strips was ~38µm ±15%, however, ASTM D882 – 12 procedures dictate that strips at such a
thickness be uniform to within ±5% of the thickness over their length. Consequences of poor film quality are apparent in the data. For instance, the average relative standard deviation of tensile strength for all the tested strips was nearly 21%. One 1:0 measurement even possessed a tensile strength greater than any of the 1:0.25 measurements (Fig. 31). Unfortunately, limited quantities of viable film prevented additional testing.

Regardless of whether these polycarbonate films demonstrated their full potential, they performed competitively. Both properties are well within the range of linear low density polyethylene (LLDPE), whose ultimate tensile strength generally falls between 10.0-37.3 MPa (~22.9 MPa on average), and whose percent elongation at break can range between 19.0% and 550% (~193% on average) (Automation Creations Inc., 2017). Much
like the polycarbonates produced herein, LLDPE is an aliphatic polymer with a large number of pendant chains (Ceresana, 2014). As a thin film, the material is commonly used to make bags, disposable gloves, plastic wraps, and stretch wraps (Ceresana, 2014). In fact, roughly 81% of total demand (2013) is for films (Ceresana, 2014). FAB polycarbonates could potentially fill these roles.

Although loading and unloading tests were not performed, it was noted that manually stretched strips would return to their unstretched length over a few seconds. As an elastomer, the GL films demonstrated a stress-strain response characteristic of natural rubber (Fig. 32). This response follows an S-shaped curve and can be divided into three regions, which are most apparent in 1:0.5 samples. Stress-strain curves have a knee region ending at about 6% strain. Samples made with PO possessed a more distinct knee, most of which had an overt yield point reminiscent of polypropylene carbonate (Chan, Wu, Li, & Cheung, 2002). At the start of the second region, increased strain only modestly increased stress. As the films continued to stretch, their elastic modulus increased until it stabilized, forming a more linear third region.

In the first region, polymer chains resist uncoiling and their stress response comes predominantly from intermolecular forces. After a certain threshold, stress is high enough to uncoil chains with relatively low resistance, forming the second region. Once polymer chains approached their contour length, bonds begin to stretch, gradually increasing the elastic modulus until the polymers completely uncoil. The increase could also be a sign of strain induced crystallization, wherein polymer chains in amorphous regions align, effectively increasing the intermolecular forces at play, thus raising the tensile strength of
the film parallel to its applied force. Polypropylene carbonate films respond like a typical thermoplastic, with a narrow elastic region and no evidence of strain induced crystallization (Chan et al 2002).

As said, the tensile test results indicate that the addition of PO increased the percent elongation to break. Additional PO units within the polymer chains may have provided more “slack” within the polymer, thus increasing the amount of uncoiling before the third region. In other words, crosslinking density would be lower, which is known to be inversely related to elongation to break (Nielsen, 1968). This explanation also helps verify that PO and FAB monomer were being integrated into the same chains.

Figure 33: Representative stress-strain curves of GL based films
4.4 Conclusions

The results of this research demonstrate that the thermal and tensile properties of FAB polycarbonate films are highly tunable using different quantities of PO and/or different types of FAB monomer. More importantly, there is evidence that they can compete well with film grade polyethylene products like LLDPE. Given FAB polycarbonate’s thermosetting nature, manufacturing strategies for polyethylene product analogues will need to be rethought. These new production strategies could be advantageous in that they may require less energy input due to FAB polycarbonate’s fluid state at room temperature. Moreover, there is a useful drying agent built right into the process stream.

In 2014, global demand for polyethylene resins was anticipated to rise to 99.6 million metric tons by 2018, valued at $164 billion (Freedonia, 2014). Polyethylene film accounts for roughly half of its global demand, and LLDPE is expected to overtake the more traditional LDPE’s market share (Freedonia, 2014). The prospect of using FAB polycarbonates as a LLDPE substitute that can deliver performance that meets or exceeds industry standards is extremely exciting. Given the wide variety of vegetable oils and postposing techniques that can be used on them, the potential of these FAB polycarbonates could extend well beyond that demonstrated here. For instance, from literature pertaining to polypropylene carbonate degradation, there is evidence to suggest that FAB films are biodegradable (Luinstra & Borchardt, 2012), a trait that LLDPE does not share (The Dow Chemical Company, 2014).
Chapter 5: Conclusions and Recommendations

The fatty acid based (FAB) polycarbonates discussed herein have shown great potential as an outlet for both CO₂ and glycerol. It was shown that propylene oxide (PO) acting as a co-monomer to FAB monomers can substantially increase polycarbonate yield. There is evidence to suggest that only 20% PO by volume can raise yield four times over, elevating it over 90%. Thus, this research proved that FAB polycarbonate can be made efficiently. More importantly, it was demonstrated that FAB polycarbonates could potentially be used to make valuable products. Likely due to an effective drying agent built into an already efficient process stream. Of the FAB polycarbonate films produced, their tensile properties compete well with film grade LLDPE. As thermosets with a sub-ambient glass transition temperature, they also demonstrate rubbery behavior that could be beneficial for wrapping applications, whose industry is currently dominated by LLDPE.

While this project successfully met its objectives, there remain a number of unanswered questions. For one, it isn’t certain as to whether PO and FAB monomer terpolymers were actually being created. \(^{13}\)C-NMR spectroscopy could be used to prove this by assessing the tacicity of the polycarbonates; \(^{13}\)C-NMR spectroscopy can identify resonances associated with different head/tail configurations along the polymer backbone. The chemical shift of these resonances would be altered by adjacent PO and FAB units. GPC-NMR analysis can also help answer this question, as it can identify whether polycarbonate have the same average composition at all molecular weights. This
is unlikely unless PO and FAB monomer are integrated into the same chains in accordance with the relative quantities used.

Another point of uncertainty is the identities of the chemical species evolved during TGA. Although their speculated identities were logically sound, it would take combined TGA-Mass spectroscopy (TGA-MS) to prove them. Routing evolved gas from the sample to a mass spectrometer would identify the molecular weights of the species lost in response to temperature elevation. The molecular weights of the speculated identities can easily be determined from literature or through direct calculation, and would need to align with the TGA-MS results to support the original conclusions. It might also be useful to perform TGA-MS with uncured, entirely FAB polycarbonate for comparison. If in accordance with polypropylene carbonate degradation, the first derivative of their degradation curve should show only one peak associated with the FAB monomer’s unaltered cyclic carbonate. It would prove that oxidative curing was responsible for the additional peaks observed in the cured samples.

Furthermore, stress-strain curves indicate that FAB polycarbonates experience strain induced crystallization. X-ray crystallography could be used to observe this phenomenon directly. Crystals are arranged in a highly ordered microscopic structure, known as a lattice. In contrast, amorphous materials are comprised of randomly distributed atoms. When there is an ordered arrangement of atoms, X-rays will scatter in only certain directions when they hit lattice planes. This causes high intensity peaks in the X-ray’s diffraction pattern. By performing X-ray crystallography on stretched FAB
polycarbonate strain induced crystallization would be made evident by peak intensification with increasing strain.

Concern over rising CO₂ emissions and limited fossil resources have generated great interest in the development of products that serve to address these concerns. While efforts to use renewable resources have been commendable, they often create issues of their own, such as biodiesel’s glycerol byproduct. It was shown herein all three issues might be addressed by renewable polycarbonates from fatty acids and CO₂. It was shown that propylene oxide could be used to produce them efficiently, and that they have potential in applications currently dominated by fossil based products. It is recommended that future work focus on resolving the uncertainties of this research. Then, the influence of different FAB monomers on other properties relevant to LLDPE applications should be determined. Also, the use of FAB monomer produced directly from vegetable oils, should be explored as they will ultimately serve as the feedstock; soybean oil would be a good first choice given the scale at which it is produced. There are many questions that need to be answered, though, for this research to matter, there is but one. Who will have the gumption to carry it forward?
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