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Sustainable Manufacturing of Natural Fiber Reinforced Green Composite

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SUSTAINABLE MANUFACTURING OF NATURAL FIBER REINFORCED GREEN COMPOSITE

A Dissertation
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
Automotive Engineering

by
Kousaalya Bakthavatchalam
December 2018

Accepted by:
Dr. Srikanth Pilla, Committee Chair
Dr. Beshah Ayalew, Co-Chair
Dr. Igor Luzinov
Dr. Philip Brown
ABSTRACT

Amidst growing concerns about environmental sustainability, the renewed push towards adoption of circular economy has increased focus among several manufacturing sectors on using renewable resources and improving process efficiencies. From the materials standpoint, use of bio-based polymers and natural fibers as sustainable reinforcements are increasingly gaining market share. However, conventional processing methods for fiber reinforced composites are usually energy-intensive and often involve long processing times, which may lead to detrimental environmental impacts. In this context, a holistic attainment of sustainability makes it imperative to adapt sustainable practices not only for raw materials but at every stage of the product. Hence, this work provides a detailed exploration of the potential power of photons for sustainable processing of natural fiber-reinforced bio-polymer composites.

To select a more sustainable matrix material, a comprehensive life-cycle assessment of existing bio-epoxies was carried out. The assessment demonstrated that triglyceride-based epoxies possess the potential to be highly sustainable epoxies if their epoxy equivalent weight is reduced to values of conventional Diglycidyl ether of Bisphenol-A. Hence, triglycerides sourced from perilla oil that possess higher functionality were selected and epoxidized. To obtain epoxidized triglyceride with minimal oxirane cleavage, epoxidation kinetics was systematically studied, and optimal synthesis conditions were determined. A pseudo two-phase model was developed that would demonstrate the variation in reactivity of individual double bonds based on their position.
as the reaction proceeds. Synthesized epoxidized perilla oil exhibited epoxy equivalent weight of ~164 g/eq which was comparable to Diglycidyl ether of Bisphenol-A.

Photo-curing was explored as potential sustainable manufacturing technique due to its fast cure; however, UV attenuation is a major hurdle in curing thicker parts (> 1 mm). Since free-radical mechanism was traditionally studied in photo-cure literature, acrylated epoxidized triglyceride was selected to cure thicker parts. Initially, cure kinetics was studied via photo-calorimetry and appropriate process parameters were selected to cure acrylated triglyceride. In order to process natural fiber-reinforced composite, three different natural fibers, possessing diversified composition of cellulose, hemi-cellulose and lignin content, were selected to understand the effect of fiber constituent on photo-curability. Acrylated epoxidized soybean oil was chosen as matrix material and processed via both thermal- and photo-curing, and their thermal and mechanical performance was evaluated. Photo-curability of natural fiber-reinforced composites was demonstrated for the first time.
ACKNOWLEDGMENTS

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Special thanks are also reserved in particular to Rakesh K. Iyer and Sai Aditya Pradeep, my research group colleagues who have been an immense source of support as friends and colleagues. Additionally, I am also grateful to my teachers, particularly Dr. Terry Tritt (formerly from Department of Physics at Clemson University), for having trusted me, constantly motivated me and helped me to build a strong foundation for my future. I am also grateful to Ms. Kimberly Ivey of the Material Science and Engineering Department for having helped me in characterizing samples and giving useful insights on my research.
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<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full form</th>
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<tbody>
<tr>
<td>AELO</td>
<td>Acrylated epoxidized linseed oil</td>
</tr>
<tr>
<td>AESO</td>
<td>Acrylated epoxidized soybean oil</td>
</tr>
<tr>
<td>AIER</td>
<td>Acidic ion-exchange resins</td>
</tr>
<tr>
<td>BPA</td>
<td>Bisphenol-A</td>
</tr>
<tr>
<td>DGEBA</td>
<td>Diglycidyl ether of bisphenol-a</td>
</tr>
<tr>
<td>DMPA</td>
<td>2,2-dimethoxy -2- phenylacetophenone</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>ECH</td>
<td>Epichlorohydrin</td>
</tr>
<tr>
<td>EEW</td>
<td>Epoxy equivalent weight</td>
</tr>
<tr>
<td>ELO</td>
<td>Epoxidized linseed oil</td>
</tr>
<tr>
<td>ENLO</td>
<td>Epoxynorbornene linseed oil</td>
</tr>
<tr>
<td>EPeO</td>
<td>Epoxidized perilla oil</td>
</tr>
<tr>
<td>EPO</td>
<td>Epoxidized palm oil</td>
</tr>
<tr>
<td>ESO</td>
<td>Epoxidized soybean oil</td>
</tr>
<tr>
<td>EV</td>
<td>Epoxy value</td>
</tr>
<tr>
<td>EVO</td>
<td>Epoxidized vegetable oil</td>
</tr>
<tr>
<td>FE</td>
<td>Freshwater ecotoxicity</td>
</tr>
<tr>
<td>FPM</td>
<td>Fine particulate matter formation</td>
</tr>
<tr>
<td>FRS</td>
<td>Fossil resource scarcity</td>
</tr>
<tr>
<td>Acronym</td>
<td>Definition</td>
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<tr>
<td>---------</td>
<td>------------</td>
</tr>
<tr>
<td>FWE</td>
<td>Freshwater eutrophication</td>
</tr>
<tr>
<td>GW</td>
<td>Global warming</td>
</tr>
<tr>
<td>HCPK</td>
<td>1-hydroxycyclohexyl phenyl ketone</td>
</tr>
<tr>
<td>HCT</td>
<td>Human carcinogenic toxicity</td>
</tr>
<tr>
<td>HNT</td>
<td>Human non-carcinogenic toxicity</td>
</tr>
<tr>
<td>ICTAC</td>
<td>International Confederation for Thermal Analysis and Calorimetry</td>
</tr>
<tr>
<td>IR</td>
<td>Ionizing radiation</td>
</tr>
<tr>
<td>IV</td>
<td>Iodine value</td>
</tr>
<tr>
<td>KF</td>
<td>Kinetic factor</td>
</tr>
<tr>
<td>LCA</td>
<td>Life-cycle assessment</td>
</tr>
<tr>
<td>LU</td>
<td>Land use</td>
</tr>
<tr>
<td>ME</td>
<td>Marine ecotoxicity</td>
</tr>
<tr>
<td>MEPOL</td>
<td>Methyl esters of palm olein</td>
</tr>
<tr>
<td>MRS</td>
<td>Mineral resource scarcity</td>
</tr>
<tr>
<td>OHH</td>
<td>Ozone formation – human health</td>
</tr>
<tr>
<td>OHV</td>
<td>Hydroxyl value</td>
</tr>
<tr>
<td>OOC</td>
<td>Oxirane oxygen content</td>
</tr>
<tr>
<td>OTS</td>
<td>Ozone formation – terrestrial ecosystems</td>
</tr>
<tr>
<td>P2P</td>
<td>Pseudo two-phase model</td>
</tr>
<tr>
<td>P-H</td>
<td>Pseudo-homogeneous</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
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<td>--------------</td>
<td>--------------------------------------</td>
</tr>
<tr>
<td>PI</td>
<td>Photo-initiator</td>
</tr>
<tr>
<td>RMS</td>
<td>Root mean square</td>
</tr>
<tr>
<td>ROC</td>
<td>Relative oxirane conversion</td>
</tr>
<tr>
<td>RSS</td>
<td>Residual sum of least squares</td>
</tr>
<tr>
<td>RT</td>
<td>Room temperature</td>
</tr>
<tr>
<td>RT-FTIR</td>
<td>Real time Fourier Transform Infra-red spectroscopy</td>
</tr>
<tr>
<td>SCC</td>
<td>Stepped-concurrent curing</td>
</tr>
<tr>
<td>SOD</td>
<td>Stratospheric ozone depletion</td>
</tr>
<tr>
<td>TA</td>
<td>Terrestrial acidification</td>
</tr>
<tr>
<td>TBPB</td>
<td>Tert-butyl perbenzoate</td>
</tr>
<tr>
<td>TE</td>
<td>Terrestrial ecotoxicity</td>
</tr>
<tr>
<td>TEAB</td>
<td>Tetraethyl ammonium bromide</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetry analysis</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra-violet</td>
</tr>
<tr>
<td>WC</td>
<td>Water consumption</td>
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CHAPTER ONE

INTRODUCTION

1. Sustainable Composites: Challenges and Opportunities

The rise in public awareness has strengthened the hands of policymakers and governments to formulate stringent regulations for monitoring and protecting our environment. This has pushed organizations, industries and institutions across multiple sectors towards implementing measures to enhance the environmental sustainability of their products and services at each step\(^1\). In particular, the aerospace and automotive sectors have been working towards the use of natural fiber-reinforced composites as alternatives to existing materials in order to achieve the twin goals of superior performance (through lightweight) and enhanced ecological sustainability\(^2,3\). Among the different choices that exist for the matrix material of such composites, thermosets are preferred for their combination of superior mechanical properties and high thermal and chemical resistance that they offer. However, several critical challenges exist with regard to obtaining a truly sustainable high-performance thermoset composite, beginning with material selection and extending to its manufacturing, as shown in Figure 1-1.

From the standpoint of selection of matrix material, epoxies have a major stake among all thermosets due to their versatility and an optimal balance of mechanical and thermal properties\(^4-6\). However, conventional epoxies suffer from two issues that impact their ecological sustainability. First, these are usually petroleum-derived epoxies, i.e., they are dependent on a non-renewable resource. Second, such epoxies, e.g. Diglycidyl ether of
bisphenol-A (DGEBA) – the most commonly used epoxy chemistry\textsuperscript{4} – involve the use of most hazardous and toxic chemicals such as Bisphenol-A (BPA) and Epichlorohydrin (ECH)\textsuperscript{7–9}, making them hazardous for both human health and environment\textsuperscript{10}. To address these issues, a plethora of research initiatives have been undertaken in recent years towards elucidating the synthesis of bio-based epoxies as alternatives to conventional epoxies\textsuperscript{5,11,12}. However, these initiatives have remained confined to the development of eco-friendly replacements solely for BPA\textsuperscript{4–6}, while neglecting the need to address the toxicity of ECH, which has been classified as class 1B carcinogen\textsuperscript{7}. Hence, there exists a need to synthesize epoxies derived from biological resources that are completely free of toxic chemicals\textsuperscript{10,13}, yet also exhibit properties comparable to those of DGEBA-based epoxies. While there are several different chemical moieties that can be sourced from various biological sources, triglycerides are increasingly being used as potential alternative for different polymers\textsuperscript{14,15}. Conventionally, triglycerides can be categorized as non-drying oils, semi-drying oils and drying oils based on the number of unsaturated groups present in their respective fatty acid chains\textsuperscript{16}. Among these, non-drying and semi-drying oils do not exhibit auto-oxidation behavior. In contrast, drying oils are conventionally used in paints and coating applications due to their auto-oxidation behavior (formation of three-dimensional crosslinked network when exposed to oxygen and/or sunlight)\textsuperscript{17}, but the poor reactivity of internal double bonds in these oils renders them unsuitable (due to inferior properties) for any application. Hence, chemical modification of these double bonds with a highly reactive functional group (such as epoxies and acrylates) has been traditionally carried out to utilize these triglycerides as potential alternatives to conventional petroleum-based polymers\textsuperscript{18,19}.
Figure 1-1: Challenges that exist in both state-of-the-art and alternative paradigms in selection of matrix material and manufacturing technique for processing natural fiber-reinforced composites.

Figure 1-2: Key aspects of sustainable manufacturing
However, amidst growing concerns about environmental sustainability, it is not enough that the material is sustainable, non-toxic and derived from natural resources\textsuperscript{20}; its manufacturing or processing method also needs to be sustainable\textsuperscript{21,22} (Figure 1-1). Sustainable manufacturing encompasses a diverse range of aspects, such as reduced energy consumption, costs, and environmental impacts, good operational safety and ensuring the health of employed workers\textsuperscript{23} (Figure 1-2). On applying this notion of sustainable manufacturing to the processing of natural fiber-reinforced composites, the use of conventional thermal curing route poses two major challenges. The primary challenge is the difficulty in obtaining a good balance between processability and property, since any increase in processing temperature beyond 180°C results in deterioration of properties due to the degradation of fiber, while processing at lower temperatures results in poor properties due to high interfacial gap between the fiber and resin\textsuperscript{24}. Another challenge is the highly energy-intensive nature of the process, which when coupled with longer processing times, higher processing costs, and the possible emission of volatile organic compounds, further reduces the ecological attractiveness of thermal curing\textsuperscript{25}.

In this regard, photo-curing (i.e., ultra-violet or UV curing) emerges as an excellent alternative to thermal curing as it possesses a multiplicity of advantages, such as faster curing at room temperature, superior performance, and reduced emission of volatile organic compounds. Together, these advantages may lead to reduction in energy consumption\textsuperscript{25} as well as its associated impacts and costs of employing photo-curing vis-à-vis thermal curing. Photo-curing is commonly employed in several commercial applications, such as in coatings, paints, photo-lithography, screen printing and dental
filings, but in all these cases, this technique is used only for thin specimens (< 1 mm)\textsuperscript{26}. This is because UV attenuation constitutes a major hurdle in using photo-curing for manufacturing composites with higher thickness (> 1 mm)\textsuperscript{25}, thereby hampering its application for processing thick natural fiber-reinforced composites. Moreover, the addition of natural fibers (mainly containing lignin) that are not UV-transparent can accelerate UV attenuation, thereby reducing the extent of photo-curing. To address the aforementioned concerns, novel techniques such as stepped-concurrent curing (SCC)\textsuperscript{25} have been developed in recent times. Yet, while the SCC technique has demonstrated the capability to process 10 mm-thick glass fiber-reinforced unsaturated polyester composite\textsuperscript{25}, its applicability for their natural fiber-reinforced counterparts remains unknown. Consequently, despite its potential as an alternative to thermal curing, existing knowledge on photo-curing cannot be directly applied towards processing thicker (i.e., > 1 mm) natural fiber-reinforced composites for structural applications.

The aforementioned points thus highlight the existence of several research gaps mentioned below (exemplified in Figure 1-3):

1. To date, there does not exist a single non-toxic sustainable epoxy that possesses desirable properties in order to render it a viable alternative to petroleum-based epoxies.
2. There remains a clear lack of fundamental understanding on the UV processability of natural fiber-reinforced sustainable composites that possess thickness > 1 mm.
3. No systematic analysis has been undertaken to understand the effect of natural fibers on the extent of UV attenuation during the processing of sustainable composites.
Finally, no study has focused on comparing the impact of the nature of curing process—thermal or UV—on the properties of natural fiber-reinforced sustainable composites.

![Figure 1-3: Various research gaps and the proposed tasks to address them](image)

This study seeks to address the aforementioned research gaps via the primary objective of “Processing natural fiber-reinforced triglyceride-based green composites via sustainable manufacturing method” via several tasks as outlined in Figure 1-3.

### 1.1. Organization of Thesis

The remainder of this chapter comprehends the current state-of-the-art with regard to both the synthesis of sustainable epoxy as well as photo-curing as a potential sustainable manufacturing technique, while the rest of this thesis is organized as described henceforth. Chapter 2 provides the details of experimental plan carried out in this work. Chapter 3 describes the life-cycle assessment (LCA) of epoxies that are sourced from different bio-derived materials and compares their performance on several environmental impact.
categories. This LCA study demonstrates the potential of triglycerides as sustainable epoxies that can be an alternative to conventional DGEBA.

However, in order to compete with DGEBA, existing triglyceride-based epoxies also need significant improvement in their functionality. Hence, Chapters 4 and 5 detail the epoxidation kinetics of triglycerides that possess higher functionality and can thereby exhibit superior performance. Subsequently, Chapters 6 and 7 respectively describe the photo-cure and thermal-cure kinetics of acrylated epoxidized triglycerides cured via free radical mechanism. Further, Chapter 8 details the potential of photons in processing natural fiber-reinforced green composites and demonstrates the mechanical and thermal performance of the processed composites. Chapter 9 describes the performance of thermally cured natural fiber-reinforced green composites. Various natural fibers, containing varying amounts of chemical constituents (such as cellulose, hemi-cellulose, and lignin), were selected in order to understand the effect of each chemical constituent on the curing technique. Finally, Chapter 10 provides a brief summary of the entire work and also sheds light on the directions in which future research can be undertaken.

1.2. Sustainable Epoxy: Panoramic View

In the endeavor towards developing sustainable ecofriendly alternatives to petroleum-based epoxies, epoxidized triglycerides or epoxidized vegetable oils (EVOs) – synthesized via Prilezhaev reaction\textsuperscript{27-30} – have gained significant attention over the past two decades\textsuperscript{31,32}. Their potential is buttressed by the commercialization of epoxidized soybean oil (ESO) and epoxidized linseed oil (ELO) as the only two fully bio-based epoxies (i.e., 100 % bio-epoxy) that are currently available\textsuperscript{33,34}. Regrettably, such epoxies
are characterized by poor mechanical properties due to the presence of fewer chemically modifiable groups, resulting in higher values of epoxy equivalent weight (EEW > 250 g/eq) (Table 1-1) (lower crosslinking density), and longer aliphatic chains\textsuperscript{35}. Since EEW of epoxies is directly related to their mechanical properties, such high EEW values hinder the use of EVOs as sustainable alternatives to conventional petroleum-based epoxies in structural applications\textsuperscript{33,34,36}.

One way to address this issue is through increasing the number of epoxy groups in EVOs by selecting triglyceride molecules with high unsaturation content in order to reduce the EEW of EVOs to $<175$ g/eq. Such reduction can be achieved by selecting triglyceride molecules with larger proportion ($>90\%$) of chemically modifiable groups – namely, oleic (C18:1), linoleic (C18:2) and linolenic (C18:3) acids. However, the occurrence of oxirane cleavage in the presence of acids during Prilezhaev reaction – a commonly used reaction in industries for synthesizing EVOs\textsuperscript{37-39} – makes it impossible to obtain theoretically predicted EEW values for any EVO (Table 1-1). Hence, a comprehensive knowledge on reaction kinetics of epoxidation of triglycerides is vital for selecting the appropriate reaction conditions that would help obtain EVOs with the maximum number of epoxy groups and minimal occurrence of side reactions.

Further, even though epoxidation kinetics of EVOs synthesized via Prilezhaev reaction\textsuperscript{27,28} have been extensively studied in the past, all these studies involve vegetable oils with no linolenic acid (C18:3) and negligible linoleic acid (C18:2) content – barring one on soybean oil (5-11 wt. % linolenic acid)\textsuperscript{39-48}. Also, it is well known that double bonds in linolenic acid (C18:3) are three times more reactive than those in the other two acid
groups (oleic and linoleic) of a triglyceride molecule due to the elimination of both steric and electronic effects\textsuperscript{49}. Hence, it is necessary to understand the epoxidation reaction kinetics of oils with significant amount (> 50 %) of highly-reactive linolenic acid groups. Also, most studies on epoxidation kinetics of EVOs have focused either solely on oxirane ring formation\textsuperscript{41,43,50} or on oxirane cleavage\textsuperscript{51}, while it is imperative to focus on both types of reactions given the occurrence of oxirane cleavage as a side reaction.

Table 1-1: Theoretical and experimentally-determined parameters for triglyceride-based EVOs studied in literature

<table>
<thead>
<tr>
<th>Vegetable Oil</th>
<th>Iodine Value (g/100 g)</th>
<th>Theoretically Possible</th>
<th>Experimentally Attained</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Oxirane Oxygen (Wt. %)</td>
<td>EEW (g/Eq)</td>
</tr>
<tr>
<td>Mahua\textsuperscript{43}</td>
<td>88.0</td>
<td>5.26</td>
<td>304.41</td>
</tr>
<tr>
<td>Castor\textsuperscript{44}</td>
<td>81.5</td>
<td>4.89</td>
<td>327.41</td>
</tr>
<tr>
<td>Rubber seed\textsuperscript{45}</td>
<td>155.6</td>
<td>8.93</td>
<td>179.15</td>
</tr>
<tr>
<td>Karanja\textsuperscript{48}</td>
<td>89.0</td>
<td>5.31</td>
<td>301.17</td>
</tr>
<tr>
<td>Jatropha\textsuperscript{46}</td>
<td>105.0</td>
<td>6.21</td>
<td>257.71</td>
</tr>
<tr>
<td>Cotton seed\textsuperscript{41}</td>
<td>105.0</td>
<td>6.21</td>
<td>257.71</td>
</tr>
<tr>
<td>Hemp\textsuperscript{47}</td>
<td>133</td>
<td>7.74</td>
<td>206.83</td>
</tr>
<tr>
<td>Perilla (this study)</td>
<td>197.0</td>
<td>11.05</td>
<td>144.83</td>
</tr>
</tbody>
</table>
Hence, the epoxidation kinetics of perilla oil – a vegetable oil with high linolenic acid (> 65 %) content – in the presence of homogeneous catalyst (i.e., inorganic acid) via Prilezhaev reaction was studied to address the aforementioned gap, while also focusing on both oxirane formation and cleavage reactions during epoxidation to minimize the occurrence of side reactions. Rate constants of both these reactions during epoxidation were determined under different reaction conditions to analyze the effect of reaction temperature and time. Further details on the entire experiment, as well as a detailed discussion of the results obtained have been provided in Chapters 2 and 4 respectively.

Interestingly, among the studies undertaken on epoxidation kinetics of triglycerides via Prilezhaev reaction, such research has been widely studied in the presence of inorganic acids (Sulfuric, nitric, hydrochloric acids) as catalyst. However, these studies are often critiqued for the role of acid in causing extensive oxirane cleavage observed during the reaction. This has led to a shift in recent years towards the use of solid acidic ion-exchange resins (AIER) as alternatives to liquid inorganic acids. AIER possesses the ability to trap various reactants that can react with epoxy, such as formic acid and hydrogen peroxide, thus allowing the obtainment of EVOs with minimal oxirane cleavage. Yet, such a shift is marked by enhanced complexity in epoxidation reaction kinetics due to the occurrence of chemical reactions in three phases: oil, water and solid catalyst.

In order to understand reaction kinetics amidst such complexity, epoxidation kinetics of triglyceride (obtained from fish oil) in the presence of ion-exchange resin as catalyst was first studied by Wisniak and Navarrete. However, their model failed to adequately explain epoxidation reaction kinetics on account of its simplistic assumption of
the reaction being homogeneous, thereby neglecting the effect of various reactants on epoxy formation and cleavage\textsuperscript{44,58}. Since then, numerous kinetic models have been proposed\textsuperscript{39,44,47,54,56}, which can be mainly be classified into two categories\textsuperscript{59} – the pseudo-homogeneous (P-H) model\textsuperscript{44}, and the pseudo two-phase model (P2P)\textsuperscript{56}. The P-H model\textsuperscript{44} accounts solely for the reaction occurring between the two liquid phases (oil and water), while assuming that solid AIER catalyst dissolves completely and acts only as a source of protons\textsuperscript{50}. In contrast, the P2P model\textsuperscript{56} considers reactions that occurs between solid AIER and liquid phases, and is developed on the basis of Langmuir-Hinshelwood-Hougen-Watson (L-H-H-W) postulates. The P2P model has been shown as being superior in predicting the epoxidation kinetics of heterogeneously-catalyzed reactions when compared with the P-H model\textsuperscript{39}.

A common feature of all these models\textsuperscript{39,44,47,54,56} is that they have focused solely on vegetable oils rich in oleic acid (C18: 1) content (i.e., containing a double bond only in the 9\textsuperscript{th} position of fatty acid chain). As a result, such models ignore any differences in the reactivity of double bonds based on their position in the triglyceride molecule\textsuperscript{49,60}. This becomes critical given that Janković et. al\textsuperscript{60} have demonstrated that a modified version of the P-H model that accounts for fatty acid composition is more accurate in predicting epoxidation kinetics of soybean oil containing 10 \% linolenic acid (C18:3). However, the Janković model\textsuperscript{60} does not dwell into details on the extent of accuracy, the reasons for higher accuracy of the model upon taking into consideration the composition of constituent fatty acids, and the extent of variation with change in reaction times and temperatures.
Hence, Chapter 5 of this thesis details a pseudo two-phase model that considers the variation in reactivity of double bonds based on their position during both epoxy formation (main reaction) and cleavage (side reaction due to attack by formic acid). High-linolenic perilla oil, containing > 65 wt. % linolenic acid, was epoxidized via Prilezhaev reaction\textsuperscript{28} in the presence of a heterogeneous catalyst (AIER). Reaction kinetics was constantly monitored by experimentally determining the variation in iodine and epoxy values at regular time intervals. Various reaction kinetic parameters were determined by fitting experimentally obtained data using genetic algorithm, which was selected given the flexibility and simplicity it offers in optimization\textsuperscript{61}. A good fit was observed between experimentally obtained results and values predicted by the model, indicating good accuracy of the proposed model. Together, the outcome of the work on both homogeneously- and heterogeneously-catalyzed epoxidation of triglycerides with high linolenic content can enable the synthesis of triglyceride-based sustainable epoxies that are superior to conventional DGEBA chemistry in the future.

1.3. **Photo Curing as Alternate Sustainable Manufacturing for Acrylated Epoxidized Triglycerides**

Photo-curing can take place either via free radical or cationic mechanisms\textsuperscript{62}. Thermosets such as acrylates and vinyl ethers cure via free radical mechanism, while epoxies on the other hand cure via cationic mechanism\textsuperscript{63}. Traditionally, the lack of suitable photo-initiators for curing materials via cationic mechanism has led to enhanced focus on free radical-based curing\textsuperscript{64}. Hence, acrylated epoxidized vegetable oil – that can be cured via free radical mechanism – was selected for this work. Previously, Scala and Wool\textsuperscript{65} have
shown that mechanical properties of acrylated triglycerides tend to level-off (i.e., remain constant) beyond 3 acrylate groups per triglyceride molecule (Figure 1-4) due to the occurrence of intermolecular cyclization (Figure 1-5). Theoretically, acrylated epoxidized perilla oil will possess ~ 9 acrylate groups per triglyceride molecule. Since acrylated epoxidized soybean oil is commercially available and possesses 4.2 acrylate groups per triglyceride molecule, and its cure behavior is not expected to differ significantly from that of its perilla oil acrylated (or triglyceride) counterpart, acrylated epoxidized soybean oil was chosen to understand the cure kinetics of acrylated triglycerides.

While DSC (Differential Scanning Calorimetry) is commonly used to understand cure kinetics of thermally activated processes, both photo-DSC and RT-FTIR (Real time Fourier Transform Infra-red spectroscopy) have been commonly used to study photo-cure kinetics. Cure kinetics is generally monitored using DSC (both photo- and thermal-DSC) by measuring the change in enthalpy during curing, while RT-FTIR monitors the change in intensity of IR absorption spectra of a specific functional group. DSC (photo-DSC or thermal-DSC) remains the oldest technique available for analyzing the photo-cure kinetics of any reaction in a more reliable and robust manner. In addition, photo-DSC also helps us obtain the average degree of cure for the material as a whole.

However, a true study of reaction kinetics necessitates the marriage of experimental observation of cure behavior with its analysis using kinetic models. Typically, any reaction kinetics is studied either via model-fitting method and/or model-free isoconversional method. Among the two types of methods, model-free isoconversional methods are well known for being more realistic and accurate in predicting reaction kinetics as they are free
from any assumptions and determine the variation in effective activation energy with the progression of the reaction\textsuperscript{72–74}. Nevertheless, since their inception, such isoconversional methods have been mainly used to understand non-isothermal reaction kinetics, with model-fitting methods used predominantly in case of their isothermal counterparts\textsuperscript{72,75}. This can be ascribed to the premise of isoconversional methods being inaccurate for isothermal reaction kinetics vis-à-vis their relatively higher accuracy for non-isothermal reactions – an outcome of the initial application of isoconversional methods for thermal degradation reactions\textsuperscript{72,75}. However, isothermal curing of any thermoset may lead to gelation and vitrification of the polymer – an isoconversional phenomenon\textsuperscript{76}. This suggests that determining the photo-cure reaction kinetics via isoconversional methods may provide useful insights about the reaction that may otherwise not be obtained via use of model-fitting methods.

Figure 1-4: Variation in (a) tensile strength and (b) tensile modulus with acrylate functionality (no. of acrylate groups per triglyceride molecule) for polymers containing 87.5 mol. \% styrene (filled symbols) and no styrene (open symbols)\textsuperscript{65}
Figure 1-5: Number of acrylate groups reportedly lost on account of intramolecular cyclization of triglycerides for polymers that were copolymerized with styrene\textsuperscript{65}

Hence, this work attempts to understand the photo-cure kinetics of a bio-based acrylated triglyceride via photo-DSC (for the first time) and analyzes it using both model-fitting and model-free isoconversional methods to assess their relative suitability in explaining the reaction kinetics of such systems. On the other hand, thermal initiators were used to understand the thermal-cure kinetics of AESO. While few studies have attempted to understand the cure kinetics of chemically modified triglycerides (acrylated or epoxidized)\textsuperscript{31,77–84}, all these studies have either used styrene as a co-monomer or used acrylated/epoxidized triglycerides as a co-monomer for conventional resins (such as DGEBA). No single study exists to date that has studied the cure kinetics of acrylated triglycerides without the addition of any solvent or secondary monomer. Scala and Wool\textsuperscript{65} have shown that the addition of any solvent (such as styrene) does not contribute to the crosslinking density, as such solvents are linear molecules. At the same time, acrylated triglycerides exhibit poorer properties in the presence of styrene when compared to the
properties of such triglycerides without styrene (Figure 1-4). Hence, this study aims at understanding the cure kinetics of acrylated epoxidized soybean oil (AESO) without the presence of any solvent or co-monomer.

The curing kinetics of unsaturated polyester resin was studied earlier via photo-DSC in the presence of 2,2-dimethoxy phenylacetophenone (DMPA) as photoinitiator. In this study, AESO was chosen as the acrylated triglyceride, while two different photo-initiators (PIs) belonging to the Norish Type-I category (that can undergo unimolecular bond cleavage or α-Cleavage), namely, DMPA and 1-hydroxycyclohexyl phenyl ketone (HCPK) were used. While DMPA possesses a short-lived excited triplet state with a yellowing character, HCPK is a non-yellowing PI that is widely used for curing acrylate monomers. Photo-cure kinetics of AESO was monitored via photo-DSC under different conditions by varying PI concentration, temperature and light intensity. For thermal curing, tert-butyl perbenzoate (TBPB) was used as thermal initiator and varying concentration was used to study thermal-cure kinetics under dynamic cure conditions. Hence, Chapters 6 and 7 of this thesis detail the photo and thermal cure kinetics of AESO respectively.

Table 1-2 lists the various photo-cured acrylated triglycerides that have been employed in coatings to date. As can be seen, all these studies have restricted coating thickness to less than 1 mm. At the same time, in case of fiber-reinforced composites, only one study exists that has attempted to cure thicker (i.e., > 2 mm) glass fiber-reinforced composites. Interestingly, this study reports that samples had to be cured on both sides due to poor curing of the bottom layer. Unfortunately, no similar study has been undertaken to date on the UV curability of natural-fiber reinforced green composites. Hence, Chapter 8
describes the processing of natural-fiber reinforced green composites via harnessing the potential power of photons (*for the first time*), while Chapter 9 details the performance of natural-fiber reinforced green composites processed via thermal curing.

Table 1-2: Various acrylated or epoxidized triglycerides that were tested for photo-curability

<table>
<thead>
<tr>
<th>Material</th>
<th>Curing Mechanism</th>
<th>Sample Thickness</th>
<th>Tensile Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>AESO(^{89})</td>
<td>Free radical</td>
<td>35 µm</td>
<td>×</td>
</tr>
<tr>
<td>AELO(^{81})</td>
<td>Free radical</td>
<td>60 µm</td>
<td>×</td>
</tr>
<tr>
<td>AESO(^{90})</td>
<td>Free radical</td>
<td>35 µm</td>
<td>×</td>
</tr>
<tr>
<td>ESO(^{79})</td>
<td>Cationic</td>
<td>0.2 mm</td>
<td>×</td>
</tr>
<tr>
<td>ESO(^{91})</td>
<td>Cationic</td>
<td>25 µm</td>
<td>×</td>
</tr>
<tr>
<td>EPO(^{92})</td>
<td>Cationic</td>
<td>50 µm</td>
<td>×</td>
</tr>
<tr>
<td>ENLO(^{93})</td>
<td>Cationic</td>
<td>28 µm</td>
<td>✓</td>
</tr>
</tbody>
</table>
CHAPTER TWO

EXPERIMENTAL

2. Experimental Methods

2.1. Life Cycle Assessment of Bio-epoxies

2.1.1. Goal Scope and Functional Unit

The goal of this life-cycle assessment (LCA) study is to evaluate the ecological performance of bio-epoxies sourced from different biological sources and compare their impacts with those of conventional petroleum-based epoxy. All these epoxies were evaluated from cradle-to-factory gate, i.e., sourcing of raw material and its subsequent extraction, processing and purification of epoxy, followed by the final manufacture of epoxy panel along with all the input chemicals/materials used. LCA work was undertaken based on the methodology defined in ISO 14040 and ISO 14044 standards. Both the use and end-of-life stages of these epoxies have been excluded from this study (Figure 2-1) – while the use phase is assumed to have no difference on environmental impacts, the end-of-life stage is neglected due to lack of data availability.

Since any LCA involves a like-for-like comparison, the functional unit of this study was chosen as a rectangular panel that has length and width of 1 m each and is designed to withstand a uniform load of 250 N while undergoing a maximum deflection of only 1.5 mm. The choice of this functional unit stemmed from the fact that the idea behind this LCA study was to identify the most ecofriendly type of bio-epoxy among currently available bio-derived epoxies. However, the thickness of rectangular panel will vary based on
mechanical properties of the selected epoxy. Therefore, to design the panel and estimate the desired thickness values for each epoxy panel, its corresponding modulus values – as reported in existing literature\textsuperscript{13,96−98} – were considered and have been shown in Table 2-1. Here, each epoxy has been re-named as per the following convention: bark-based epoxy is B-epoxy; vanillin-based epoxy is actually derived from lignin and is named as L-epoxy; epoxy derived from vegetable oil or triglyceride is termed V-epoxy; and conventional petroleum-based epoxy is termed P-epoxy.

![Diagram](image)

Figure 2-1: System boundary considered in this LCA study
Based on the mechanical properties for each epoxy (mentioned in Table 2-1), the variable thickness of each epoxy panel was calculated using Equation 1 and has also been provided in Table 2-1.

\[
d^3 = \frac{15\omega l^4}{96Eb\Delta} \quad (1)
\]

Where: \(\omega\) - Load applied (N/m), \(E\) – Young’s Modulus (MPa), \(l\) – Length of panel (m), \(b\) – Width of panel (m), \(d\) – Thickness of panel (mm), and \(\Delta\) – Deflection (mm), 1.5 mm. Densities of each of the chosen epoxy systems were obtained from existing literature\(^{13,96-98}\), based on which the weight of epoxy panel was calculated and has been reported in Table 2-1. Finally, \(~10\%\) of material wastage during processing was assumed, and thus the input amount of epoxy required was calculated.

2.1.2. LCA Inventory and Impact Assessment

With regard to bark-based epoxy (B-epoxy), synthesis procedure followed by Kuo et. al\(^{96}\) was considered. Under this procedure, bark chips are initially obtained after cutting softwood, following which these chips are mixed thoroughly with aqueous sodium hydroxide solution. The solution is then filtered and later spray-dried to enable the removal of water and sodium hydroxide as well as any impurities in bark chips. Subsequently, bark extractives were obtained through a two-step process, with the first step involving reaction with epichlorohydrin (added in excess) in the presence of aqueous sodium hydroxide, 1,4-dioxane and catalyst amidst stirring at higher temperature, and the second step of filtering and washing bark-based solution to remove the aforementioned chemicals as well as any
salt formed in the process. Finally, rotary evaporation was undertaken to remove any chemical present in bark epoxy, which was subsequently mixed with petroleum-based epoxy and hardener and then cured to obtain the final epoxy panel.

Inventory data containing the material and energy flow was developed based on the synthesis procedure described in literature. Based on the developed inventory data (and use of Ecoinvent 3.4 database), the environmental impacts of all bio-epoxy panels as well as of the conventional epoxy panel were quantified by applying the hierarchist perspective of ReCiPe midpoint method. Environmental impacts were investigated on all 17 midpoint impact categories, namely: GW (Global warming); stratospheric ozone depletion (SOD); ionizing radiation (IR); ozone formation – human health (OHH); ozone formation – terrestrial ecosystems (OTS); fine particulate matter formation (FPM); terrestrial acidification (TA); freshwater eutrophication (FWE); terrestrial ecotoxicity (TE); freshwater ecotoxicity (FE); marine ecotoxicity (ME); human carcinogenic toxicity (HCT); human non-carcinogenic toxicity (HNT); land use (LU); mineral resource scarcity (MRS); fossil resource scarcity (FRS); and water consumption (WC). For each impact category, the prominent contributing reasons were identified and have been briefly described. A termination criterion of 1% was used in this work to determine the significant contributing reasons for each epoxy.
Table 2-1: Various bio-epoxies selected in this LCA study along with their advantages and disadvantages, mechanical properties, density, epoxy equivalent weight.

<table>
<thead>
<tr>
<th>Epoxy Nomenclature / Source</th>
<th>Advantage</th>
<th>Dis-advantage</th>
<th>Thickness (mm) / Panel Weight (kg)</th>
<th>Density (g/cc)</th>
<th>EEW (g/eq) / Modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-Epoxy/ Bark extractive(^96)</td>
<td>Easy synthesis and manufacturing process</td>
<td>Larger petroleum-based content</td>
<td>30.68 / 11.65</td>
<td>0.38</td>
<td>250 / 1200</td>
</tr>
<tr>
<td>L-Epoxy/ Lignin(^97)</td>
<td>Lignin a by-product of paper industry ensuring enhanced sustainability due to use of waste resource</td>
<td>Very high viscosity and molecular weight makes the process challenging</td>
<td>33.06 / 35.32</td>
<td>1.07</td>
<td>250 / 959</td>
</tr>
<tr>
<td>V-Epoxy / Triglycerides(^13)</td>
<td>Only 100% bio-based epoxy currently available both commercially and academic literature</td>
<td>Aliphatic structure resulting in poor properties</td>
<td>41.07 / 38.20</td>
<td>0.93</td>
<td>264 / 500</td>
</tr>
<tr>
<td>P-Epoxy/ Petroleum(^98)</td>
<td>Conventionally used</td>
<td>Presence of petroleum derived and carcinogenic chemicals</td>
<td>22.87 / 27.61</td>
<td>1.21</td>
<td>174 / 2895</td>
</tr>
</tbody>
</table>
2.2. Synthesis of Sustainable Epoxy from Triglyceride Molecule

Non-edible perilla oil – extracted from non-edible seeds of *Perilla frutescens* – was chosen due to its higher linolenic acid content (~ 62-65 %) compared to other vegetable oils (VOs), along with linoleic acid (~ 13-15 %) and oleic acid (~ 12-15 %)\textsuperscript{100,101}. Epoxidation of perilla oil was carried out via Prilezhaev reaction using performic acid (HCOOOH) generated in-situ as explained by Swern\textsuperscript{28} by maintaining the molar ratio of perilla oil, formic acid (HCOOH) and hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}) as 1.0:3.4:10.3. Two types of catalysts were used, namely: (a) Inorganic acid (sulfuric acid or H\textsubscript{2}SO\textsubscript{4}) as homogeneous catalyst, taken at 2 wt. % of (HCOOH + H\textsubscript{2}O\textsubscript{2}) combination; and (b) Acidic Ion-Exchange resin (AIER) as heterogeneous catalyst, taken at 20 wt. % of perilla oil. Epoxidation was carried out at three different temperatures – 40, 50 and 60°C – for 8 h each.

200 ml of perilla oil was initially taken in a 1000 ml three-neck round-bottom flask and equilibrated to synthesis temperature, followed by the addition of HCOOH and catalyst. The solution was stirred at constant speed of 500 rpm for 30 min using an overhead stirrer. Subsequently, 30% (w/w) H\textsubscript{2}O\textsubscript{2} solution was added drop-wise to the afore-described solution under constant stirring. System temperature was maintained below 110°C during the entire reaction duration, as any further increase in temperature due to heat evolution during the formation of performic acid and epoxy – both of which are highly exothermic reactions – would lead to significant amount of water loss via evaporation.

2.2.1. Epoxidation Kinetics

To determine epoxidation reaction kinetics, the time at which H\textsubscript{2}O\textsubscript{2} addition was completed was assumed to be time zero (t = 0). Aliquot samples were removed from the
solution at intervals of 30 min for the first two hours (0.5, 1, 1.5 and 2 h), followed by removal at intervals of 2 h for the next six hours (4, 6 and 8 h). Extracted epoxidized perilla oil (EPeO) was dissolved in toluene and subjected to several cycles of washing with distilled water until the aqueous phase showed pH of 7. Subsequently, washed EPeO was dried using anhydrous sodium sulfate (Na$_2$SO$_4$) – to remove the presence of water (small amount) – and then filtered. The filtrate was finally vacuum dried at 40°C to ensure complete evaporation of any solvent present. Iodine, epoxy and α-glycol values of extracted and dried EPeO was determined to understand the progression of epoxidation and in-situ oxirane cleavage reaction.

2.2.2. Oxirane Ring Cleavage Kinetics

In order to determine post-oxirane ring cleavage kinetics, initially 100 ml of perilla oil was used to synthesize EPeO, while maintaining the same ratio of other chemical constituents used in epoxidation reaction. Epoxidation was initially carried out for 8 h at three synthesis temperatures (40, 50 and 60°C) while being simultaneously stirred at 500 rpm. EPeO obtained via this step was washed several times using distilled water, then dried and introduced in a round-bottom flask and mixed with HCOOH in weight ratio of 1:3 (dried EPeO: HCOOH) and reacted at the same temperature as that of epoxidation reaction. Aliquot samples were removed from the flask at different intervals (0.5, 1, 1.5, 2, 4, 6, and 8 h) and immediately titrated for determination of epoxy content.
2.2.3. **Characterization**

2.2.3.1. **Iodine Value**

Iodine value of a substance refers to the mass of iodine (I\(_2\), in grams) consumed by 100 g of that substance, and is calculated to determine the extent of unsaturation (i.e., double bonds) in fatty acids\(^{102}\). Iodine value is determined via use of Wijs solution that reacts with double bonds, leading to the evolution of I\(_2\) that is detected using sodium thiosulfate (Na\(_2\)S\(_2\)O\(_3\)). Iodine values for both perilla oil and EPeO (withdrawn at different time intervals) were determined as per ASTM D5768 standard and calculated using Equation 2.

\[
IV = \frac{[(B - V) \times N \times 12.69]}{S} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots (2)
\]

Where:

- \(IV\) : Iodine value of the specimen
- \(B\) : Volume of Na\(_2\)S\(_2\)O\(_3\) required for titration of blank solution (Wijs solution) (ml)
- \(V\) : Volume of Na\(_2\)S\(_2\)O\(_3\) required for titration of sample (Perilla oil/EPeO) (ml)
- \(N\) : Normality of Na\(_2\)S\(_2\)O\(_3\) solution (0.1 N)
- \(S\) : Mass of sample used (g)

2.2.3.2. **Epoxy Content (Oxirane Oxygen Content)**

Epoxy content of a material is measured as per ASTM D1652-11 standard. EPeO was dissolved in dichloromethane (CH\(_2\)Cl\(_2\)) and tetraethyl ammonium bromide (TEAB/\((C_2H_5)_4N)^+Br^-\)), followed by titration against 0.1 N perchloric acid reagent (HClO\(_4\)).
Reaction between TEAB and HClO$_4$ results in in-situ generation of HBr, as shown in Equation 3. HBr reacts subsequently with the epoxy group present in EPeO, resulting in the cleavage of oxirane ring, as shown in Equation 4. Epoxy content in EPeO was calculated using Equation 5\textsuperscript{103}.

\[
((C_2H_5)_4N)^+Br^- + HClO_4 \rightarrow ((C_2H_5)_4N)^+ClO_4^- + HBr \quad \cdots \cdots \cdots (3)
\]

![Equation 3](image)

\[
\text{HBr} + \text{C-O} \rightarrow \text{HO-C} + \text{Br} \quad \cdots \cdots \cdots (4)
\]

\[E = 4.3 \times V \times \left( \frac{N}{W} \right) \quad \cdots \cdots (5)\]

With regard to Equation 5:

- $V$ refers to the volume of HClO$_4$ required for titration (ml),
- $N$ refers to the normality of HClO$_4$ (0.1 N), and
- $W$ refers to the mass of EPeO used for titration (g).

However, experimentally obtained oxirane oxygen ($OO_e$) can be estimated using Equation 6\textsuperscript{103}.

\[OO_e = \left( \frac{16}{43} \right) \times E \quad \cdots \cdots (6)\]

### 2.2.3.3. $\alpha$-Glycol Content

Ring opening (cleavage) of epoxy groups in EVOs results in the generation of $\alpha$–glycol during epoxidation (as side reaction). $\alpha$-glycol content in this study was determined via the method reported by May\textsuperscript{104} and Stenmark\textsuperscript{105}. This method is based on the oxidation of glycol via benzylmethylammonium periodate in a non-aqueous medium, whereby excess periodic acid is reacted with potassium iodide (KI), leading to the liberation of I$_2$.
that is titrated against Na$_2$S$_2$O$_3$. To determine $\alpha$-glycol content, EPeO samples (containing < 0.3 meq. of $\alpha$-glycol) were mixed with 25 ml of chloroform in a stoppered bottle and placed in an ice-bath. Subsequently, 25 ml of oxidation reagent was added to the afore-described solution, mixed thoroughly, and allowed to stand for 2.5 h in ice-bath. After this, 100 ml of ice water was added and shaken vigorously for 60 s. Finally, 5 ml of (20 %) H$_2$SO$_4$ and 15 ml of KI solution were added, after which the solution was titrated against 0.1 N Na$_2$S$_2$O$_3$ to the starch end-point. Experimental $\alpha$-glycol content was calculated via Equation 7$^{104}$, where:

$$\alpha - \text{glycol content} \left(\frac{\text{moles}}{100 \text{ g}}\right) = \frac{(B - S) \times N}{20 \times W} \ldots \ldots \ldots (7)$$

Where $B$ refers to the volume of Na$_2$S$_2$O$_3$ required for titration of blank solution (ml)

$S$ refers to the volume of Na$_2$S$_2$O$_3$ required for titration of the sample (ml)

$N$ refers to the normality of Na$_2$S$_2$O$_3$ solution (N)

$W$ refers to the weight of the sample (oil) used (g)

2.3. Sustainable Manufacturing

2.3.1. Processing of Acrylated Epoxidized Soybean Oil

Acrylated epoxidized soybean oil, containing 4000 ppm of monomethyl ether hydroquinone as inhibitor and purchased from Sigma Aldrich, was cured in the presence of photo-initiator or thermal initiator, as the case may be. While 2,2-dimethoxy phenylacetophenone (DMPA) and 1-hydroxycyclohexyl phenyl ketone (HCPK) were selected as photo-initiators, tert-butyl perbenzoate (TBPB) was used as thermal initiator in this work. Varying wt. % of free radical initiators were used and cure kinetics of AESO in
their presence was studied. Subsequently, their mechanical performance and thermal behavior was also evaluated.

### 2.3.2. Natural Fiber Mat and Composite

Acrylated epoxidized soybean oil (AESO) – of the same kind as that described in Section 2.3.1 – was selected as the matrix material, while three different natural fibers – namely, flax, areca and coir – were selected as reinforcement materials. Unidirectional flax fiber (UD flax tape, 110 gsm that is 15.75” wide) was purchased from Lingrove LLC, USA, while areca and coir fibers were purchased from India. The chemical composition of all three fibers is reported in Table 2-2. Areca and coir fibers were observed to be short as they were directly extracted from the seed, while flax fibers were obtained from the bast. Hence, randomly oriented areca and coir fiber mats were prepared by measuring ~ 15 g of fibers and placing these fibers between two aluminum plates in a randomly oriented manner in dimensions of 25 cm × 15 cm. These randomly arranged fibers were then subjected to simultaneous heat and pressure using a Wabash Press (shown in Figure 2-2). Care was taken to ensure that porosity, density and thickness (~ 1 mm) of these mats were consistent across different samples. In order to maintain uniformity, as-purchased flax fibers were also compressed under the same conditions. The varying chemical composition of these fibers helped understand the effect of different constituents, such as cellulose, hemicellulose and lignin, on the processability of these composites.
Table 2-2: Chemical composition of various natural fibers

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Cellulose</th>
<th>Hemicellulose</th>
<th>Lignin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flax</td>
<td>71</td>
<td>18.6-20.6</td>
<td>2.2</td>
</tr>
<tr>
<td>Areca</td>
<td>0.15</td>
<td>35-64.8</td>
<td>13-24.6</td>
</tr>
<tr>
<td>Coir</td>
<td>32-43</td>
<td>0.15-0.25</td>
<td>40-45</td>
</tr>
</tbody>
</table>

Figure 2-2: Step-by-step manufacturing of randomly oriented areca and coir mats

In order to process natural fiber-reinforced composites (Figure 2-3), AESO resin (containing 2% free radical initiator) was cast on natural fibers placed on either polycarbonate or aluminum substrate. Polycarbonate sheets were used as substrate for UV curing, while aluminum substrate was used for thermal curing. Since AESO possesses high viscosity and no solvent was used, in order to ensure good fiber wettability, the resin was cast on the other side as well. To ensure excellent fiber wettability and remove the excess resin, resin-containing fiber was subjected to mechanical load of ~ 5 kg for 30 min. The
excess resin was squeezed out during this process, and the composite was cured in appropriate manner (photo/thermal curing) under inert atmosphere.

![Diagram of composite processing steps]

**Figure 2-3: Step-by-step procedure for processing of composite**

### 2.3.2.1. Photo-curing of Resin and Fiber-Reinforced Composite

Photo-curing of both virgin resin and fiber-reinforced composite was carried out using ELC-4001 UV flood system (Electrolite Corporation, Bethel, CT, USA) that has UV output of 125 mW/cm². The lamp had a peak output in the UV wavelength range of 365 nm coupled with an enclosure. Since the exposure area in this equipment was 7.5” wide and 9” long, ASTM D638 Type 1 specimen were prepared via photo-curing to test their mechanical performance. Photo-curing of pure resin was carried out for 5 min, while for fiber-reinforced composites, curing took place in 10 min with both sides of the composite exposed to UV radiation for 5 min each.
2.3.2.2. Thermal Curing of Resin and Fiber Reinforced Composite

Thermal curing of both AESO resin and fiber-reinforced composites was carried out at 160°C for 3 h in an atmosphere-controlled oven (Across International, USA). The oven was heated from room temperature (RT) to 160°C in 3 h, and it took more than 6 h for the oven to cool down to RT, thereby ensuring that the total processing time for both pure resin as well as its composite was ~ 12 h. Any sample that was taken out of the oven prior to this duration (12 h) was observed to crack due to high temperature differential. Despite the half-life of TBPB being 1 min at 165°C, curing was carried out for 3 h at 160°C, mainly to ensure complete curing.

2.3.3. Characterization

2.3.3.1. Photo Calorimetry

NETZSCH Photo-DSC 204 F1 Differential Scanning Calorimeter (DSC), equipped with a UV lamp (Omnicure S2000) with a single light guide, was used to monitor the photo-cure kinetics of AESO under nitrogen atmosphere with a flow rate of 40 ml/min. Approximately 2-5 mg of samples were taken in an open aluminum pan for each DSC test/experiment. Both the reference pan and sample pan were exposed to UV radiation in the wavelength region of 320-500 nm for 120 s with a delay of 5 s. The influence of photo-initiator concentration (0.5, 1, 2 and 4 wt. %), temperature (25, 50 and 75°C), and light intensity on photo-cure kinetics of AESO was studied. Light intensity was monitored at the end of the light guide and was varied in two batches, namely, a low-intensity batch/regime of 50, 100 and 150 mW/cm², and a medium-intensity batch/regime of 1500, 2500 and 3500 mW/cm², where the intensity experienced by the sample was ~ 50 times lower in case
of both the regimes/batches. To monitor the occurrence of any chemical reaction solely due to thermal energy (i.e., temperature), for each DSC experiment, samples were held in isothermal condition (at their respective temperature profile) for 5 min prior to exposure to UV radiation. Further, for each experiment, the samples were subjected to a second UV irradiation cycle to monitor the occurrence of any residual reaction. No peaks were observed in the second irradiation cycle for any DSC experiment, indicating that the reaction was complete in the first irradiation cycle itself.

2.3.3.2. **Differential Scanning Calorimetry**

Thermally initiated cure kinetics of acrylated epoxidized soybean oil (AESO) in the presence of Tert-butyl peroxybenzoate (TBPB) as thermal initiator was monitored via differential scanning calorimetry (DSC, Q20, TA instruments). Non-isothermal DSC runs were conducted from 25°C to 220°C at varying heating rates (5, 7.5, 10, 15, and 20°C/min) under nitrogen atmosphere (flow rate: 50 ml/min). Approximately 3-8 mg of AESO, containing varying concentration of initiator (1, 2, 4 and 6 wt. %), was measured in an Tzero Aluminum hermetic pan. The samples were subjected to a second heating cycle at the same heating rate (as first heating cycle) after cooling to 20°C at a cooling rate of 20°C/min in order to verify the completion of curing in the first cycle. The absence of exothermic peak during second heating cycle for all samples indicated the completion of reaction during the first cycle. In order to obtain reproducible results, DSC runs were obtained in triplicates.
2.3.3.3. Background on Cure Kinetics

For any chemical reaction that is a thermally activated process, Equation 8 represents the general kinetic equation, where $\alpha$ is the extent of conversion (or curing in this case) while $f(\alpha)$ is a function of $\alpha$, $T$ refers to temperature, $k(T)$ refers to the rate constant as a function of temperature or $T$, and $d\alpha/dt$ is the rate of curing.

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \ldots \ldots \ldots (8)$$

Further, the rate constant $k(T)$ is in turn calculated using Equation 9, where $A$ is pre-exponential factor, $E_a$ refers to effective activation energy (in kJ/mol) and $R$ is universal gas constant (8.314 J/mol K).

$$k(T) = Ae^{-\frac{E_a}{RT}} \ldots \ldots (9)$$

However, any understanding of reaction kinetics – i.e., obtaining values of rate constants ($k$) and effective activation energy ($E_a$) – is typically studied either using model-fitting method and/or model-free isoconversional method\textsuperscript{71}. With regard to model-fitting methods, several phenomenological and mechanistic models have been reviewed in literature, all of which assume that the reaction is a single-step reaction and has a single value of activation energy for the entire duration of the reaction. However, such model-fitting methods may be unreliable when the reactant material undergoes a multi-step complex kinetics reaction.

On the other hand, model-free isoconversional methods are well known for being more realistic and accurate in predicting reaction kinetics, as these methods are free from any assumptions and determine the variation in effective activation energy with the
progression of the reaction. Nevertheless, since their inception, such isoconversional methods have been primarily used to understand non-isothermal reaction kinetics, with model-fitting methods used predominantly in case of their isothermal counterparts\textsuperscript{72,75}. This can be ascribed to the premise of isoconversional methods being inaccurate for isothermal reaction kinetics vis-à-vis their relatively higher accuracy for non-isothermal reactions – an outcome of the initial application of isoconversional methods for thermal degradation reaction\textsuperscript{72,75}.

This study focuses on analyzing both photo-cure and thermal cure kinetics of an acrylated triglyceride system – specifically, acrylate epoxidized soybean oil (AESO). Typically, the isothermal curing of any thermoset leads to gelation and vitrification of the polymer – an isoconversional phenomenon\textsuperscript{76}. This suggests that determining the photo-cure reaction kinetics of AESO via isoconversional methods may provide useful insights about the cure reaction that may otherwise not be obtained via use of model-fitting methods. Further, the possibility of change in effective activation energy with further progress of the reaction retains a significant probability in case of reactions such as isothermal curing of thermosets. It is for such cases that the recent ICTAC Review Committee has recommended the use of model-free isoconversional methods in order to determine reaction kinetics\textsuperscript{71}. At the same time, a definite claim of these methods being superior over model-fitting methods for isothermal reaction kinetics – as experienced by AESO under photo-curing – cannot be made with a high degree of certainty. Contrastingly, thermal curing of AESO represents non-isothermal reaction kinetics, enhancing the
suitability of model fitting methods vis-à-vis model-free methods for understanding thermal curing of acrylated triglyceride systems.

Hence, this study chooses two different procedures with regard to modeling both photo-cure and thermal cure kinetics of AESO. While both the model-fitting and isoconversional methods are used to fit experimentally obtained data for photo-cure kinetics (from photo-DSC), only isoconversional methods are used to analyze experimental data obtained for thermal cure kinetics of AESO. While the choice of both sets of methods for photo-DSC stems from the need to ascertain the relative suitability of both methods when compared against each other, the use of only isoconversional methods for thermal curing is based on its definite suitability for non-isothermal reaction kinetics as established in literature. In addition, model-free isoconversional methods also help in gaging and predicting the nature or mechanism of curing reaction – be it chemical reaction controlled, or diffusion controlled.

2.3.3.4. Photo-DSC: Model-fitting Method

In general, heat flow – measured using photo-DSC – is assumed to be occurring solely due to one reaction, namely, the crosslinking of acrylate groups that are present in the AESO molecule. This assumption is valid in this study due to the absence of any solvent and/or co-monomer. Hence, the rate of conversion (or crosslinking) \( R_p \) or \( d\alpha/dt \) is calculated using Equation \( 10^{108} \), where \( \Delta H_{total} \) is the total enthalpy of the reaction at 100 % crosslinking, and \( dH/dt \) is the heat flow measured under isothermal DSC condition.

\[
R_p = \frac{d\alpha}{dt} = \frac{1}{\Delta H_{total}} \left( \frac{dH}{dt} \right) \quad \ldots \ldots \ldots \ldots (10)
\]
Upon integrating Equation 10, the degree of conversion ($\alpha$) can be obtained from Equation 11, where $\Delta H_{total}$ is the total enthalpy of a reaction at 100% crosslinking (i.e., $\alpha = 1$).

$$\alpha = \frac{1}{\Delta H_{total}} \int_{0}^{t} \left( \frac{dH}{dt} \right) \, d\tau \quad \ldots \ldots (11)$$

In order to understand the variation in $\alpha$ with time, i.e., the progression of the reaction (or its kinetics), several cure kinetics models – both phenomenological as well as mechanistic ones – have been proposed and well discussed in literature. These models can be primarily categorized into two groups: $n^{th}$ order models that can be further sub-classified into accelerating and decelerating reaction models, and autocatalytic reaction models. However, according to the ICTAC Review Committee recommendations, for a cure kinetics model to be reliable and robust, it is necessary that the model is capable of taking into account the variation in extent of conversion ($\alpha$) via both the $n^{th}$ order and autocatalytic reaction models. One such model which has been widely used for understanding the cure kinetics of various systems is the Kamal-Sourour model that is expressed using Equation 12. Here, $d\alpha/dt$ is the rate of crosslinking, $k_1$ and $k_2$ are rate constants that correspond to the $n^{th}$ order and autocatalytic reaction models respectively, while $m$ and $n$ are the orders of crosslinking reaction and monomer consumption reaction respectively.

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1 - \alpha)^n \quad \ldots \ldots (12)$$

However, it is widely known that thermosets exhibit vitrification behavior – a phenomenon that refers to the ceasing of curing reaction due to the formation of glassy
phase and prevents the curing reaction from reaching its completion (i.e., \( \alpha \neq 1 \)). Henceforth, the Kamal-Sourour\textsuperscript{110} model was modified to capture this vitrification phenomenon (as expressed in Equation 13), where the term “1” in Equation 12 is replaced by \( \alpha_{max} \), which refers to the maximum degree of conversion that can occur (such that \( \alpha_{max} < 1 \)) during the reaction.

\[
\frac{d\alpha}{dt} \text{ (or } R_p\text{)} = (k_1 + k_2\alpha^m)(\alpha_{max} - \alpha)^n \ldots \ (13)
\]

The objective of this study – with regard to photo-cure kinetics – is to determine the optimal values of the four parameters of curing reaction, i.e., reaction rate constants \((k_1, k_2)\) and reaction orders \((m, n)\), such that the model-predicted \(d\alpha/dt\) (defined by Equation 13) matches the experimentally measured \(d\alpha/dt\) as closely as possible through curve-fitting. Mathematically, this is defined using the cost function (Equation 14) as shown below, where \(RSS\) is the residual sum of least squares, \(N\) is the total number of data samples, \(i\) is the time index, \(R_{p\ exp}\) is the experimentally measured rate of curing reaction, and \(R_{p\ calc}\) is the model-predicted rate of curing reaction.

\[
RSS = \min_{k_1,k_2,m,n} \sum_{i=1}^{N} \left( R_{p\ exp}(i) - R_{p\ calc}(i) \right)^2 \ldots (14)
\]

Upon determining the values of \((k_1, k_2)\), effective activation energy \((E_a)\) of the curing reaction can be calculated using the Arrhenius equation (Equation 15) – similar to Equation 9 – where \(A\) is pre-exponential factor, \(R\) is universal gas constant (8.314 J/mol.K), and \(T\) is temperature (K).

\[
k_1 \text{ or } k_2 = Ae^{-\frac{E_a}{RT}} \ldots (15)
\]
2.3.3.5. Photo-DSC: Model-free Isoconversional Method

Since model-fitting methods are well-known for giving Arrhenius parameter values (of activation energy and rate constants) that are notoriously uncertain, the recent ICTAC Review Committee has recommended the use of model-free isoconversional methods in order to predict the kinetic behavior of a chemical reaction in a more realistic manner. In this regard, the determination of effective activation energy ($E_{a,\alpha}$) at different values of $\alpha$ (= 0.05 to 0.95) with a step size of not more than 0.05 is imperative for a better understanding of cure reaction kinetics over time. Hence, a simplified form of integral isoconversional method (Equation 16) was used to predict the photo-cure kinetics of AESO, where $t_{\alpha,i}$ refers to the time taken to reach a particular value of degree of conversion ($\alpha$) at different temperatures ($T_i$), and $E_{a,\alpha}$ is the effective activation energy of the reaction for the specific $\alpha$ value.

\[
\ln t_{\alpha,i} = f(\alpha) + \frac{E_{a,\alpha}}{RT_i} \ldots (16)
\]

Using a linear-fit for the plot between $\ln(t_{\alpha,i})$ and the reciprocal of isothermal test temperature ($T_i$), the slope was used to determine (and plot) $E_{a,\alpha}$ as a function of $\alpha$ for AESO containing both photo-initiators: DMPA and HCPK.

2.3.3.6. Thermal DSC: Model-free Isoconversional Method

In case of thermal-DSC (i.e., dynamic (non-isothermal) reaction kinetics), model-free isoconversional methods have been established as the most appropriate method to analyze thermal curing. Unlike in case of photo-curing, the use of isoconversional methods for understanding thermal curing is based on the premise that the rate of reaction is only
dependent on temperature at any constant extent/degree of curing (i.e., same value of \( \alpha \)). Hence, if natural logarithm of all parameters mentioned in Equation 8 is taken on both sides, Equation 17 can be obtained, and upon taking a temperature-inverse derivative on both sides, and subsequently Equation 18 will be obtained, where \( \alpha \) refers to a specific value of degree/extent of conversion (i.e., curing).

\[
\ln \left( \frac{d\alpha}{dt} \right) = \ln k(T) + \ln f(\alpha) \ldots \ldots \ldots (17)
\]

\[
\left[ \frac{\partial \ln \left( \frac{d\alpha}{dt} \right)}{\partial T^{-1}} \right]_\alpha = \left[ \frac{\partial \ln k(T)}{\partial T^{-1}} \right]_\alpha + \left[ \frac{\partial \ln f(\alpha)}{\partial T^{-1}} \right]_\alpha \ldots \ldots \ldots (18)
\]

However, since \( f(\alpha) \) is a constant value for isoconversional method, its temperature derivative is zero. Using this information along with Equation 9 in Equation 18, the relationship between the rate of curing reaction \( (d\alpha/dt) \) and effective activation energy \( (E_\alpha) \) (as shown in Equation 19) is obtained.

\[
\left[ \frac{\partial \ln \left( \frac{d\alpha}{dt} \right)}{\partial T^{-1}} \right]_\alpha = \left[ \frac{\partial \ln k(T)}{\partial T^{-1}} \right]_\alpha = \left[ \frac{\partial \ln (Ae^{-E_\alpha/RT})}{\partial T^{-1}} \right]_\alpha = \left[ \frac{\partial \left( \frac{-E_\alpha}{R} \right)}{\partial T^{-1}} \right]_\alpha = \frac{-E_\alpha}{R} \ldots \ldots \ldots (19)
\]

\[
\ln \left( \frac{\beta_i}{T^2} \right) = A' - \frac{E_\alpha}{RT_\alpha} \ldots \ldots \ldots (20)
\]

\[
\ln \left( \frac{\beta_i}{T^{1.92}} \right) = A'' - 1.0008 \left( \frac{E_\alpha}{RT_\alpha} \right) \ldots \ldots \ldots (21)
\]

Various studies have proposed different equations as integral solutions of Equation 19, two of which have been regarded as highly prominent – the Kissinger-Akahira-Sunose...
equation (Equation 20), and Starink equation (Equation 21) – due to their higher accuracy vis-à-vis other alternative methods. For these equations, $\beta$ refers to the heating rate used, $\alpha$ is the degree/extent of curing (and has a specific value at each data point), $T_{\alpha,i}$ is the temperature at the specific value of $\alpha$ for each time step $i$, $A'$ and $A''$ are constants, $E_\alpha$ is the effective activation energy of curing reaction when the degree of curing is $\alpha$, and $R$ is universal gas constant (8.314 J/mol K). Essentially, Equations 20 and 21 express the idea that when samples of same chemical composition are subjected to different heating rates ($\beta$) under thermal-DSC, they exhibit the same extent of curing ($\alpha$) at different temperatures ($T_{\alpha,i}$), but all these temperatures are related to the heating rate used by the kinetic parameter of effective activation energy ($E_\alpha$) that remains constant for a specific value of extent of curing ($\alpha$). Based on this, effective activation energy was determined for AESO mixed with thermal initiator at different concentrations (1, 2, 4 and 6 wt. %) with change in the degree or extent of curing – in line with the model-free method used for photo-DSC.

2.3.3.7. Thermogravimetry Analysis

Both pure resin and fiber-reinforced composite – cured via photo-curing and/or thermal curing – were subjected to thermogravimetry analysis (TGA) from RT to 800°C (at heating rate of 5 °C/min) in order to determine their respective thermal stability and heat resistant temperatures. TGA was carried out using TGA-2950 (TA Instruments, New Castle, DE) in nitrogen atmosphere at a flow rate of 25 mL/min.
2.3.3.8. **UV Transmission Measurement**

The variation in UV intensity with the progression of the reaction was measured using Solarmeter model 5 that has a resolution of 0.1 mW/cm². Variation in intensity was measured both with and without the photo-initiator.

2.3.3.9. **Tensile Testing**

Tensile testing of AESO was carried out at a strain rate of 5 mm/min as per the ASTM D638 standard, while similar testing for fiber-reinforced composite samples was carried out at strain rate of 2 mm/min as per ASTM D3039 standard. Prior to testing, fiber-reinforced composite samples were cut to dimensions of 14 cm × 2 cm, following which tabs were placed based on the procedure recommended by the ASTM D3039 standard.
CHAPTER THREE

LIFE CYCLE ASSESSMENT

3. Life Cycle Inventory

The synthesis procedure selected from literature for bark-based epoxy (B-epoxy) and lignin-based epoxy (L-epoxy) have been shown in Figure 3-1 and Figure 3-2 respectively. With regard to bark-based epoxy (B-epoxy), synthesis procedure described by Kuo et. al\textsuperscript{96} was considered. Under this procedure, bark chips are initially obtained after cutting softwood, following which these chips are mixed thoroughly with aqueous sodium hydroxide solution. The solution is then filtered and later spray-dried to enable the removal of water and sodium hydroxide as well as any impurities in bark chips. Subsequently, bark extractives were obtained through a two-step process, with the first step involving reaction with epichlorohydrin (added in excess) in the presence of aqueous sodium hydroxide, 1,4-dioxane and catalyst amidst stirring at higher temperature, and the second step of filtering and washing bark-based solution to remove the aforementioned chemicals as well as any salt formed in the process. Finally, rotary evaporation was undertaken to remove any chemical present in bark epoxy, which was subsequently mixed with petroleum-based epoxy and hardener and then cured to obtain the final epoxy panel.

With regard to vanillin-based epoxy panels (L-epoxy), lignin produced along with softwood pulp was considered\textsuperscript{112}, after which vanillin was derived from lignin\textsuperscript{113}. Subsequently, vanillin was treated with multiple chemicals – tetrahydrofuran, hydrochloric acid, hydrogen peroxide, sodium chloride, and sodium hydroxide – to produce
methoxyhydroquinone, which in turn was modified to produce its diglycidyl ether. Following this, methoxyhydroquinone and its diglycidyl ether were chemically reacted in the presence of catalyst to produce an oligomer that was subsequently mixed with an amine hardener to obtain the desired L-epoxy panel.

Figure 3-1: Step-by-step procedure for synthesis of bark-based epoxy (B-Epoxy)

For conventional petroleum-based epoxy (P-epoxy), the inventory for the appropriate resin was chosen from Ecoinvent 3.4 database and combined with hardener to produce the conventional petroleum-based epoxy panel. Finally, for vegetable oil-based epoxy (V-epoxy), inventory was calculated based on available literature\textsuperscript{13,114}. Basically, soybean oil was assumed to be combined with formic acid and hydrogen peroxide in the presence of an inorganic acid (sulfuric acid) as catalyst. The reaction yielded epoxidized
soybean oil along with other chemicals that were subsequently washed away using distilled water. The left-over epoxidized oil was subjected to rotary evaporation to filter the soybean oil-based epoxy resin. This resin was subsequently combined with amine hardener to produce the desired vegetable oil-based epoxy panel.

Figure 3-2: Step-by-step process for lignin-based epoxy (L-Epoxy)
3.1. Life Cycle Impact Assessment – Results

Figure 3-3 (a and b) compare the environmental impacts of all the three bio-epoxy panels considered in this study (B-epoxy, L-epoxy and V-epoxy) on 17 midpoint impact categories. As can be seen, across all environmental impact categories barring two (SOD and LU), V-epoxy (i.e., vegetable oil-based epoxy) exhibits the least amount of impact vis-à-vis the other two bio-epoxies. In contrast, lignin-based epoxy or L-epoxy shows the worst environmental performance among the three systems by exhibiting the highest impact on 12 categories (i.e., except SOD, TE, FE, ME and LU), while B-epoxy shows the highest impact on only 3 categories (TE, FE and ME).
Figure 3-3: Comparison of environmental performance of the three bio-epoxy systems (B-epoxy, L-epoxy and V-epoxy) on 17 impact categories under the hierarchist perspective of ReCiPe midpoint method

Figure 3-4: Comparison of the environmental performance of vegetable oil-based epoxy (V-epoxy) and petroleum-based epoxy (P-epoxy) on 17 impact categories under the hierarchist perspective of ReCiPe midpoint method
Table 3-1: Environmental impacts of vegetable oil-based epoxy and petroleum-based epoxy

<table>
<thead>
<tr>
<th>Impact category</th>
<th>Unit</th>
<th>V-Epoxy</th>
<th>P-Epoxy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Global warming</td>
<td>kg CO₂ eq</td>
<td>83.29</td>
<td>43.51</td>
</tr>
<tr>
<td>Stratospheric ozone depletion</td>
<td>kg CFC11 eq</td>
<td>280.80</td>
<td>165.81</td>
</tr>
<tr>
<td>Ionizing radiation</td>
<td>kBq Co-60 eq</td>
<td>59.48</td>
<td>3.26</td>
</tr>
<tr>
<td>Ozone formation, Human health</td>
<td>kg NOₓ eq</td>
<td>65.66</td>
<td>37.05</td>
</tr>
<tr>
<td>Fine particulate matter formation</td>
<td>kg PM₂.₅ eq</td>
<td>88.39</td>
<td>56.56</td>
</tr>
<tr>
<td>Ozone formation, Terrestrial ecosystems</td>
<td>kg NOₓ eq</td>
<td>63.84</td>
<td>28.03</td>
</tr>
<tr>
<td>Terrestrial acidification</td>
<td>kg SO₂ eq</td>
<td>81.46</td>
<td>49.26</td>
</tr>
<tr>
<td>Freshwater eutrophication</td>
<td>kg P eq</td>
<td>76.93</td>
<td>14.56</td>
</tr>
<tr>
<td>Terrestrial ecotoxicity</td>
<td>kg 1,4-DCB eq</td>
<td>0.28</td>
<td>0.12</td>
</tr>
<tr>
<td>Freshwater ecotoxicity</td>
<td>kg 1,4-DCB eq</td>
<td>2.51</td>
<td>0.75</td>
</tr>
<tr>
<td>Marine ecotoxicity</td>
<td>kg 1,4-DBC eq</td>
<td>40.32</td>
<td>10.21</td>
</tr>
<tr>
<td>Human carcinogenic toxicity</td>
<td>kg 1,4-DBC eq</td>
<td>71.74</td>
<td>43.40</td>
</tr>
<tr>
<td>Human non-carcinogenic toxicity</td>
<td>kg 1,4-DBC eq</td>
<td>79.54</td>
<td>24.36</td>
</tr>
<tr>
<td>Land use</td>
<td>m²/a crop eq</td>
<td>122.73</td>
<td>5.56</td>
</tr>
<tr>
<td>Mineral resource scarcity</td>
<td>kg Cu eq</td>
<td>94.55</td>
<td>24.86</td>
</tr>
<tr>
<td>Fossil resource scarcity</td>
<td>kg oil eq</td>
<td>78.27</td>
<td>55.21</td>
</tr>
<tr>
<td>Water consumption</td>
<td>m³</td>
<td>58.08</td>
<td>2.46</td>
</tr>
</tbody>
</table>

Overall, it can be clearly seen that in terms of holistic environmental performance, V-epoxy is superior than the other two bio-epoxy systems considered in this study. Subsequently, ecological performance of V-epoxy was compared with its conventional epoxy counterpart or P-epoxy, as can be seen in Figure 3-4 and Table 3-1. As the figure shows, P-epoxy panel performs superior than V-epoxy on all impact categories, albeit by
differing amounts. Since the inventory was developed beginning with the extraction of raw materials to the manufacture of the panel for all the considered epoxies, energy consumed during agriculture (in case of V-epoxy), deforestation (in case of B-epoxy and L-epoxy) and extraction of raw materials from petroleum sources (for P-epoxy) were also considered.

3.2. Life Cycle Impact Assessment – Discussion

The most interesting finding from this work is that vegetable oil-based epoxy (V-epoxy) has lower environmental impacts when compared with bio-epoxies derived from other biological sources (such as bark or lignin) (Figure 3-3). It is an interesting finding given that V-epoxy has significantly poorer mechanical properties compared to B-epoxy or L-epoxy (i.e., more amount of V-epoxy is required in the panel compared to the other two bio-epoxies) (Table 2-1). However, these higher impacts of B-epoxy and L-epoxy (over V-epoxy) can be ascribed to two key factors. The first is the use of epichlorohydrin (ECH) – a highly toxic and carcinogenic chemical – in large quantities, with a larger quantity of usage in B-epoxy vis-à-vis L-epoxy (almost twice that of L-epoxy in B-epoxy), which explains the higher toxicity-related impacts in particular for both these bio-epoxies vis-à-vis vegetable oil-based epoxy. The second factor is the larger amount of electricity consumed (during the entire process starting from raw material extraction) to process both B- and L-epoxy when compared to V-epoxy (~ 10315 MJ for B-epoxy and ~ 11406 MJ for L-epoxy vis-à-vis ~ 7577 MJ for V-epoxy). Since this electricity is mostly produced from fossil fuels (coal and natural gas), fossil-based electricity accounts for a significant share of the impacts of these epoxies.
Beyond the aforementioned aspects, individual contributing factors explain the ecological performance of each of the three bio-epoxies considered in this study. As explained earlier, electricity – primarily coal-based electricity – accounts for a significant share of environmental impacts across all three epoxies, especially with regard to B- and L-epoxy. While coal-based electricity generation results in the emission of large amount of greenhouse gases (GW), it is also accompanied by the emission of local atmospheric pollutants such as sulfur dioxide that cause acidification (TA), particulate matter (FPM) and nitrogen oxides that cause multiple impacts (GW, SOD, OHH and OTS). Furthermore, coal-based electricity also involves the use of large amounts of water and land for both mining and washing of coal as well as during electricity generation (LU and WC). Finally, coal mining also produces large amount of toxic elements (such as mercury) which results in high toxicity-related impacts (TE, FE, ME, HCT and HNT) of all these epoxies.

All these indicates that with regard to the choice of a suitable sustainable epoxy form, V-epoxy would easily outperform the other bio-epoxies considered in this work. Coupled with the fact that vegetable oil-based epoxies have been proven as being biodegradable vis-à-vis the lack of biodegradability for other thermosets, one can confidently vouch for V-epoxy as being the desired solution to ensuring sustainability in epoxies from the standpoint of sustainable materials.

However, upon comparison with its conventional epoxy counterpart (P-epoxy), it turns out that V-epoxy performs poorly despite its biodegradability (Figure 3-4). However, this can be ascribed to two factors. First, the inventory considered for P-epoxy resin (excluding the amine hardener) is obtained directly from Ecoinvent 3.4 database. This
inventory is built upon the use of optimum process conditions and material requirements for producing such resin, for it is produced in large quantities on commercial scale. In contrast, the inventory for V-epoxy (or for that matter, all the bio-epoxies considered in this study) is based upon its synthesis at laboratory-scale conditions. Since input chemicals (such as hydrogen peroxide and formic acid) are often required in larger quantities for laboratory-scale synthesis vis-à-vis production on an industrial scale, the inventory for V-epoxy is based on an over-estimate of chemical requirement that may offer possibilities for reduction in case of industrial-scale production. Second, in addition to the challenge with inventory, vegetable oil-based epoxies suffer from the issue of higher epoxy equivalent weight (EEW) vis-à-vis their conventional epoxy counterparts. Higher EEW values result in poorer mechanical properties of V-epoxy compared to P-epoxy, necessitating the use of larger amount of V-epoxy for producing the desired panel and further exacerbating its environmental impacts. Thus, the combination of lack of industrial-scale inventory and poorer mechanical properties (an outcome of higher EEW) lead to V-epoxy panels performing poorly vis-à-vis P-epoxy panels. Hence, the following part of this work focuses on the use of triglycerides as sustainable materials by improving their performance via lowering EEW.
CHAPTER FOUR
SYNTHESIS OF SUSTAINABLE EPOXY FROM A TRIGLYCERIDE MOLECULE

4. Epoxidation Reaction and Conditions

In-situ epoxidation via Prilezhaev reaction is a two-step process: (i) Performic acid formation; and (ii) Conversion of double bond to epoxy, with these steps occurring simultaneously in both oil and aqueous phases\textsuperscript{48,115–117} along with several side reactions. During these reactions, H\textsubscript{2}O\textsubscript{2}, H\textsubscript{2}O and H\textsubscript{2}SO\textsubscript{4} remain in the aqueous phase, while perilla oil and EPeO remains in the oil phase. Only HCOOH and HCOOOH are transferred between the aqueous and oil phase\textsuperscript{116,117}. Hence, oxirane ring cleavage can take place at the oil phase and at the oil/aqueous phase interface\textsuperscript{115} due to the attack of HCOOH, HCOOOH, H\textsubscript{2}O\textsubscript{2} or H\textsubscript{2}O. In addition to oxirane ring cleavage, several other side-reactions occur simultaneously, as shown in Figure 4-1. Hence, the extent of both epoxidation and oxirane ring cleavage reactions is dependent on reaction conditions, such as the molar ratio of H\textsubscript{2}O\textsubscript{2}-to-organic acid-to-double bond and the amount of catalyst (H\textsubscript{2}SO\textsubscript{4}) used\textsuperscript{41,43,48,50,115,117,118}.

High molar ratio of H\textsubscript{2}O\textsubscript{2}-to-organic acid-to-double bond can result in significant oxirane cleavage, while low molar ratio of these entities can cause incomplete epoxidation. Hence, these parameters were carefully chosen based on available literature to synthesize EPeO with minimal in-situ oxirane cleavage. Various studies have shown the optimal amount of HCOOH to be in the range of 0.25-0.5 and H\textsubscript{2}O\textsubscript{2} to be in the range of 1.5-2.0
for one mole of C=C bonds\textsuperscript{32}. Hence, in this work, molar ratio of H\textsubscript{2}O\textsubscript{2}-to-HCOOH-to-ethylenic unsaturation was maintained at 1.5:0.5:1.0.

Figure 4-1: Schematic of epoxy formation and side-reactions during epoxidation of vegetable oils (VOs)

Among different organic acids, formic acid (HCOOH) and acetic acid (CH\textsubscript{3}COOH) are the most widely used due to their high reactivity\textsuperscript{32,39,40,117}. HCOOH is also advantageous as it does not require any catalyst for the occurrence of epoxidation reaction and is the most preferred in industrial epoxidation process\textsuperscript{119}. However, the absence of
catalyst is generally accompanied by rapid increase in reaction temperature to $> 100^\circ$C, leading to the explosion of performic acid at $> 80-85^\circ$C$^{28,32}$. Hence, an inorganic acid had to be used as a catalyst to control the reaction rate and inhibit the detonation of performic acid. Among the four commonly used inorganic acids: sulfuric acid (H$_2$SO$_4$), phosphoric acid (H$_3$PO$_4$), nitric acid (HNO$_3$) and hydrochloric acid (HCl), H$_2$SO$_4$ results in the highest level of oxirane content, followed by H$_3$PO$_4$ > HNO$_3$ > HCl. Hence, H$_2$SO$_4$ was chosen as the inorganic acid catalyst with an optimal concentration of H$_2$SO$_4$ as 2 wt. % of (HCOOH + H$_2$O$_2$) combination$^{41,43}$.

Another critical factor, stirring speed, was observed to play a determining role$^{43,48,54}$ in the reaction rate up to 1500 rpm beyond which its effect on epoxidation kinetics becomes insignificant. However, the stirring speed has significant effect in epoxidation based on the initial volume of oil selected$^{120}$, as the objective was to eliminate both heat and mass transfer during the reaction. Hence to avoid uncontrolled turbulence and chemical spillage associated with high stirring speeds, 500 rpm was chosen for this study.

4.1. Results and Discussion

4.1.1. Rate of Epoxidation

Iodine value (IV) of perilla oil was estimated to be 196.9 g/100 g (of oil), indicating the double bond concentration to be 0.77 moles per 100 g of oil, while the average molecular weight of perilla oil was calculated as $\sim$ 871 g/mole. Rate of progression of epoxidation reaction was determined by estimating the iodine, epoxy, and $\alpha$-glycol content values of extracted EPeO (Figure 4-2). The results presented in Figure 4-2 were within the statistical error of $\pm$ 5 %. Figure 4-2 (a) exemplifies the variation in iodine value, while
Figure 4-2 (b) shows the rate of relative oxirane conversion (ROC), as estimated using Equation 21\textsuperscript{46,48}.

\[
ROC = \frac{OO_e}{OO_t} \ldots \ldots \ldots (21)
\]

Where \(OO_t\) (theoretical oxirane oxygen) was calculated from Equation 22\textsuperscript{46,48}.

\[
OO_t = \left( \frac{IV_o}{2A_i} \right) \left[ 100 + \frac{IV_o}{2A_i} A_o \right] \times A_o \times 100 \ldots \ldots \ldots (22)
\]

Where \(IV_o\) is iodine value of perilla oil = 196.9 g/100 g oil
\(A_i\) is atomic mass of iodine = 126.9 amu, and
\(A_o\) is atomic mass of oxygen = 16 amu

Based on Equation 22, \(OO_t\) was estimated as 11.04 wt. % and \(OO_e\) was experimentally determined and calculated from Equation 6. Figure 4-2 (c) shows the variation in \(\alpha\)-glycol content with change in temperature and time.

From Figure 4-2 (a,b), it is evident that increase in reaction temperature (from 40 to 60°C) led to increase in \(ROC\) (from 58 % to 88 %). This can be attributed to the enhanced rate of formation of peroxyformic acid, along with its enhanced activation, at higher temperatures\textsuperscript{121}. On the other hand, increase in reaction time at constant temperature was observed to be accompanied by the conversion of a significant fraction of double bonds (35-50 %) to epoxy groups in the first 30 minutes, with the extent of conversion dependent on reaction temperature. This is in contrast to the observation of < 30 % conversion in other EVOs, such as epoxidized mahua oil\textsuperscript{43} and epoxidized karanja oil\textsuperscript{48}. Such higher epoxidation rate – in the initial 30 minutes – can be attributed to the higher reactivity of
linolenic acid\textsuperscript{49}. Kousaalya et. al\textsuperscript{122} had shown that all double bonds present at the 15\textsuperscript{th} position (accounting for \(\sim 22\%\) of double bonds) in a triglyceride molecule react completely within the first 30 minutes, resulting in their conversion to epoxy groups. This is also accompanied by the conversion of a few moles of double bonds present at the 9\textsuperscript{th} and 12\textsuperscript{th} positions to epoxy groups. Nevertheless, as time proceeds, the reaction rate was observed to slow down with nearly 9\% conversion (of double bonds) at 40 and 50\textdegree{}C in the next 1 h 30 min, while at 60\textdegree{}C, 24\% conversion was observed in the same duration.

![Graphs of iodine value, relative oxirane conversion, and \(\alpha\)-glycol content as a function of synthesis temperature and reaction duration.]

Figure 4-2: a) Iodine Value b) Relative Oxirane Conversion c) \(\alpha\)-Glycol content of EPeO as a function of synthesis temperature and reaction duration.
Further, it can also be seen that the slope of the reaction curve changes at 2 h for all reaction temperatures, indicating a reduction in reaction rate from this point onwards. This can be ascribed to the fact that during the first 2 h, the observed initial increase in system temperature – due to the highly exothermic nature of performic acid formation – led to vigorous epoxidation for 2 h. Subsequently, significant reduction in epoxidation reaction rate was observed beyond 2 h, which is observed via ~ 15-20 % conversion over a span of 6 h. This reduction in rate of reaction with time can be attributed to two factors: (a) Decomposition of formic acid (HCOOH), performic acid (HCOOOH), and hydrogen peroxide (H₂O₂) with time, resulting in loss of their quantity\(^\text{123}\); and (b) Stabilization in system temperature back to original reaction temperatures after 2 h.

From Figure 4-2 (c), it is clear that with increase in both reaction time and/or temperature, along with the epoxidation reaction, a small-yet-significant amount of oxirane ring cleavage reaction was also observed. While α-glycol values were observed to be similar at reaction temperatures of 40 and 50°C, they were found to undergo a substantial increase at 60°C, indicating the ease of oxirane cleavage at higher temperature. Relative glycol conversion (RGC) can be calculated from Equation 23\(^\text{46,48}\).

\[
RGC = \frac{G_{\text{exp}}}{G_{\text{the}}} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldot
Hence, $G_{the}$ was obtained through calculations as 0.61 moles/100 g (of oil). From Equation 24, the maximum $\alpha$-glycol content was obtained to be in the range of 6-18 %. This is in stark difference to the observation by Goud et. al$^{43,48}$ of minimal oxirane cleavage for many EVOs ($< 10 \%$). However, linolenic acid group – a highly-reactive group present in perilla oil – is likely to undergo ring opening at a faster rate than the other two acid groups (linolenic and oleic) present in a triglyceride molecule. Kousaalya et. al$^{122}$ had shown that the epoxy group formed at 15$^{th}$ position underwent cleavage to form $\alpha$-glycol in a triglyceride molecule due to the higher reactivity of a chemical group that is farther away from the glycerol center. Also, it should be noted that in spite of high oxirane ring cleavage, epoxidized perilla oil possessed higher number of epoxy groups compared to epoxies from other vegetable oils.

4.1.2. Epoxy Equivalent Weight ($W_{eew}$ or EEW)

$W_{eew}$ or EEW refers to the weight of resin (in grams) that contains 1 mole of epoxy, and is directly related to the crosslinking density (number of crosslinks per unit volume) which dictates the structural performance of epoxies$^{13}$. $W_{eew}$ of synthesized EPeO was calculated using Equation 25$^{103}$ and plotted in Figure 4-3.

$$W_{eew} = 43 \times \left(100 \times \frac{1}{E}\right)$$  \hspace{1cm} (25)

Where:

$W_{eew}$ represents epoxy equivalent weight (g/eq),

“43” is the molecular weight of an epoxy ring, and

$E$ represents weight percent of epoxy groups or epoxide (wt. %) as determined via titration.
It can be observed from Figure 4-3 that EEW reduced by a smaller degree with increase in reaction temperature from 40 to 50°C. However, further increase in reaction temperature to 60°C led to significant reduction in EEW (to below 200 g/eq) upon extending synthesis time to beyond 2 h. EPeO synthesized at 60°C for 8 h exhibited EEW of 164 g/eq, which is equivalent to that of conventional DGEBA-based epoxies (EEW = 182 – 192 g/eq)\(^{124}\) – well-known for their high structural performance. Thus, lower EEW of EPeO raises the possibility of their use as a sustainable, ecofriendly alternative to conventional epoxies.

![Figure 4-3: Epoxy equivalent weight (EEW) of EPeO as a function of synthesis temperature and reaction duration](image_url)
4.2. **Kinetics and Thermodynamics**

4.2.1. **Epoxidation Kinetics**

Several studies\textsuperscript{43,118} have shown that among the various reactions in homogeneously catalyzed two-step epoxidation reaction, the first step – formation of HCOOOH – is the rate-determining step, assuming the concentration of performic acid (i.e. peroxyformic acid) to be constant throughout the entire reaction. Based on this hypothesis, Equation 26 shows the applicable rate law, where $k$ is the rate constant (Lmol\textsuperscript{-1}s\textsuperscript{-1}), $[EP]$ is the molarity of epoxy groups formed during the reaction (mol/L) at any given time, and $[H_2O_2]_0$ and $[HCOOH]_0$ refer to molarity of H\textsubscript{2}O\textsubscript{2} and HCOOH respectively at zero time\textsuperscript{43,118}. On integration, Equation 26 changes to Equation 27, indicating that this reaction is possibly a first-order reaction\textsuperscript{40,117}.

\[
\frac{d[EP]}{dt} = k([H_2O_2]_0 - [EP]) \cdot [HCOOH]_0 \quad \ldots\ldots\ldots\ldots\ldots (26)
\]

\[
\ln([H_2O_2]_0 - [EP]) = -k[HCOOH]_0 t + \ln[H_2O_2]_0 \quad \ldots\ldots\ldots\ldots\ldots (27)
\]

As per Equation 27, any graph between $\ln([H_2O_2]_0 - [EP])$ and time ($t$) is expected to be a straight line for the first step of epoxidation reaction, assuming that a negligible amount of oxirane undergoes cleavage. However, the graph between these two variables (Figure 4-4 (a)) shows deviation from the expected linear relationship, indicating that a fraction of epoxy rings underwent cleavage as observed from Figure 4-2 (c).

Kinetic rate constants ($k$) were calculated for the epoxidation reaction (first-step) based on the initial slopes of the curve as the reaction showed first-order nature in this region. Table 4-1 shows rate constants ($k$) of the epoxidation reaction at different synthesis
temperatures, with values for these rate constants being in the order of $10^{-6} \text{ L mol}^{-1} \text{ s}^{-1}$, which is in accordance with rate constants calculated in available literature\textsuperscript{32,39–41,43,46,48,117}. As can be seen, an increase in synthesis temperature leads to increase in epoxidation kinetic rate constant, i.e., increase in the rate of epoxidation reaction, which can be attributed to easier cleavage of ethylenic unsaturation as observed in Figure 4-2 (a,b).

Figure 4-4: a) Plot of $\ln ([\text{H}_2\text{O}_2]_0-[\text{EP}])$ vs time for epoxidation of perilla oil by performic acid b) Arrhenius plot for epoxidation reaction and c) Arrhenius plot for post-oxirane ring cleavage reaction

Figure 4-4 (b) shows Arrhenius plots – rate constants ($k$) v/s reciprocal of temperature ($1/T$) – for in-situ epoxidation reactions to obtain effective activation energy ($E_a$). Based on Figure 4-4 (b), $E_a$ for epoxidation reaction was determined to be 20.10 kJ/mol. This is significantly lower compared to $E_a$ reported in literature for VOs treated
with HCOOH and H$_2$SO$_4$ as catalyst: jatropha oil (68.24 kJ/mol)$^{46}$ and MEPOL (53 kJ/mol)$^{40}$. It is also lower when compared to $E_a$ values reported for VOs treated with CH$_3$COOH, such as cotton seed oil (48.95 kJ/mol)$^{41}$, soybean oil (43.11 kJ/mol)$^{98}$, mahua oil (60.66 kJ/mol)$^{43}$, karanja oil (62.38 kJ/mol)$^{48}$, rubber latex (55.6 kJ/mol)$^{118}$, and palmolein oil (73.64 kJ/mol)$^{40}$. This significant variation in $E_a$ of epoxidation can be explained by the fact that perilla oil contains higher linolenic acid compared to other VOs, imparting it higher chemical reactivity. Scala and Wool$^{49}$ have shown that double bonds present in linolenic acid are thrice more reactive than those in oleic and linoleic acid, possibly due to the individual and combined result of steric and electronic effect. They have shown increase in epoxidation rate constant upon increase in the number of double bonds due to increase in electron density, with double bonds farther from the glycerol center likely to be free from steric hindrance, resulting in their higher reactivity.

Table 4-1: Kinetic rate constant ($k$) of epoxidation reaction at different synthesis temperatures

<table>
<thead>
<tr>
<th>Synthesis Temperature (°C)</th>
<th>$k$ ($\times 10^6$ L mol$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>48.50</td>
</tr>
<tr>
<td>50</td>
<td>53.85</td>
</tr>
<tr>
<td>60</td>
<td>77.52</td>
</tr>
</tbody>
</table>
4.2.2. Oxirane Cleavage during In-situ Epoxidation

Kinetic rate equations used to describe in-situ epoxidation assume that epoxy groups formed during epoxidation remain completely stable, without any ring cleavage reactions taking place. However, this is an ideal case, and in reality, epoxy rings present in oil phase are reactive and can cleave. To determine the extent to which epoxy ring cleavage may have happened via this route, two kinds of tests can be generally undertaken: α-glycol test and hydroxyl test (OHV)\textsuperscript{32,41}. Hydroxyl test is used to detect the presence of -OH groups that form during side-reaction between epoxy phase and HCOOH (Figure 4-2 (c)). However, due to the low concentration of HCOOH used in this study, theoretical calculation shows negligible concentration of hydroxylated-formiated products (< 0.01 wt. %) thereby confirming negligible epoxy ring cleavage via this route. However, presence of excess H\textsubscript{2}O due to several reasons – such as high amount of H\textsubscript{2}O in initially used H\textsubscript{2}O\textsubscript{2} solution and generation of H\textsubscript{2}O during epoxidation reaction as a result of various side-reactions – is likely to have resulted in the occurrence of epoxy ring cleavage. Hence, only α-glycol test was undertaken to understand the degree of epoxy ring cleavage.

The α-glycol content of EPeO (Figure 4-2 (c)) was higher than values observed in literature\textsuperscript{54} by a factor of ~ 10, even as less than 20 % of theoretical α-glycol limit was achieved at reaction temperature of 60°C and duration of 8 h. This indicates that a small-yet-significant fraction of epoxy groups was not stable, with increase in this fraction upon increase in reaction temperature/duration. This can be attributed to mainly two reasons: (1) Higher reactivity of functional groups that are further away from the glycerol group\textsuperscript{13}, and
(2) Higher degradation of H$_2$O$_2$ at higher temperature, resulting in the formation of excess amount of H$_2$O that reacts with epoxy to form α-glycol$^{32,125}$.

### 4.2.3. Post-oxirane Cleavage Kinetics

Unlike epoxidation that involves both oxirane formation (a two-step reaction) and oxirane cleavage (a side-reaction) simultaneously, post-oxirane cleavage kinetics is significantly different. The reaction of oxirane groups with excess HCOOH – resulting in the ring opening of epoxy groups$^{40,51}$.

The general form of the kinetic rate law equation for oxirane ring cleavage is described in Equation 28, where $[EP]$ refers to the molarity of epoxy in EPeO (mol/L), $[FC]$ refers to molarity of HCOOH (mol/L), $t$ is reaction duration (s), $k$ is the kinetic rate constant for ring cleavage reaction, $-d[EP]/dt$ is the rate of oxirane ring cleavage, and $a$ and $b$ refer to the order of the reaction with respect to epoxy groups (in EPeO) and HCOOH respectively$^{40,51}$.

$$-\frac{d[EP]}{dt} = k[EP]^a[FC]^b \quad \ldots \ldots \ldots \quad (28)$$

When excess HCOOH is used – i.e., molar ratio of epoxy groups-to-HCOOH is 1:3 – Equation 28 can be re-written as Equation 29, where $k'$ is a pseudo first-order kinetic rate constant defined as per Equation 30. Previous studies$^{40,51}$ have shown that experimental data on plots of ln$[[EP]_0/[EP]_t]$ against reaction time ($t$) at various reaction temperatures leads to the obtainment of linear curves$^{51}$. This indicates that $a = 1$, meaning that the ring opening reaction is first-order with respect to epoxy group concentration, and that $k'$ is a pseudo first-order rate constant.
\[-\frac{d[EP]}{dt} = k'[EP]^a \quad \ldots \ldots \ldots (29)\]

\[k' = k[FC]^b \quad \ldots \ldots \ldots (30)\]

\[\ln \left(\frac{[EP]_0}{[EP]_t}\right) = k't \quad \ldots \ldots \ldots (31)\]

Hence, Equation 29, upon integration and considering \(a = 1\), reduces to Equation 31, where \([EP]_0\) and \([EP]_t\) are the molarity of epoxy groups at \(t = 0\) and varying time \((t)\) respectively.

With regard to the order of the reaction for HCOOH concentration, Equation 30 can be rewritten as Equation 32 by taking natural log on both sides\(^{40,51}\). Based on Equation 32, the slope of the curve between \(\ln k'\) and \(\ln [FC]\) is the value of \(b\). Prior studies on oxirane ring cleavage of EVOs have shown that such plots lead to straight lines with the value of \(b\) as 2 at different temperatures\(^{40,51,98}\). Hence, the overall kinetic rate equation for oxirane cleavage can be rewritten as Equation 33\(^{40,51}\), showing that the reaction is first-order with respect to epoxy concentration and second-order with respect to HCOOH concentration.

\[\ln k' = \ln k + b \ln [FC] \quad \ldots \ldots \ldots (32)\]

\[-\frac{d[EP]}{dt} = k[EP][FC]^2 = k'[EP] \quad \ldots \ldots \ldots (33)\]

For this study, Equations 29-33 were used to determine both pseudo-rate constant \((k')\) and actual rate constant \((k)\) by measuring \([EP]\), using titrations of the EPeO-HCOOH mixture against perchloric acid for aliquot samples drawn at different reaction temperatures.
and time intervals. Table 4-2 shows the values of $k'$ and $k$ at different reaction temperatures, with the values for $k$ being in the order of $10^{-8} \text{ L}^2\text{ mol}^{-2}\text{ s}^{-1}$, which is in accordance with literature$^{40,51}$. As can be seen from Table 4-2, both rate constants – pseudo first-order kinetic rate constant ($k'$) as well as kinetic rate constant for oxirane cleavage ($k$) – show an increase with increase in reaction temperature, indicating a reduction in oxirane ring stability with increase in reaction temperature$^{40,51}$.

Table 4-2: Rate constant ($k$) and pseudo-rate constant ($k'$) for oxirane cleavage at different synthesis temperatures

<table>
<thead>
<tr>
<th>Synthesis Temperature (°C)</th>
<th>$k'$ ($\times 10^{-6} \text{ L mol}^{-1}\text{ s}^{-1}$)</th>
<th>$k$ ($\times 10^{-6} \text{ L}^2\text{ mol}^{-2}\text{ s}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>15.71</td>
<td>0.04</td>
</tr>
<tr>
<td>50</td>
<td>33.64</td>
<td>0.09</td>
</tr>
<tr>
<td>60</td>
<td>42.24</td>
<td>0.11</td>
</tr>
</tbody>
</table>

Figure 4-4 (c) shows Arrhenius plots – rate constants ($k$) v/s reciprocal of temperature ($1/T$) – for oxirane cleavage reactions. These plots were used to obtain activation energy ($E_a$) of oxirane cleavage reactions and assess the stability of epoxy groups formed during epoxidation. Based on Figure 4-4 (c), $E_a$ for oxirane ring cleavage was obtained through calculations as 43.11 kJ/mol. This is significantly lower than $E_a$ values reported for palm olein oil (73.5 kJ/mol)$^{40}$ and soybean oil (66.27 kJ/mol)$^{51}$. However, it should be noted that the cleavage reaction mentioned in these studies was the reaction between CH$_3$COOH and EVO. Hence, the lower $E_a$ value for oxirane cleavage of
EPeO could be due to either/both higher reactivity of HCOOH\textsuperscript{32,41} or easier cleavage of epoxy groups in perilla oil when compared to the aforementioned two oils.

Furthermore, $E_a$ of oxirane cleavage (43.11 kJ/mol) was observed to be significantly higher than $E_a$ of in-situ epoxidation (20.10 kJ/mol) in this work. This is in line with the trend observed upon comparing Table 4-1 and Table 4-2, whereby at all reaction temperatures, first-order rate constant for epoxidation is significantly higher than pseudo first-order rate constant for oxirane cleavage. This shows that in-situ epoxidation was preferred to epoxy ring cleavage, and epoxy groups formed during epoxidation were stable and less likely to form $\alpha$-glycol.

### 4.2.4. Epoxidation Thermodynamics

$E_a$ values obtained using Figure 4-4 (b,c) respectively for epoxidation and oxirane cleavage reactions were used to calculate thermodynamic parameters for both reactions. Enthalpy change ($\Delta H$) of both reactions was calculated using Equation 34, where $R$ is universal gas constant (8.314 J mol\textsuperscript{-1} K\textsuperscript{-1}) and $T$ is absolute temperature (K). Equation 35 was used to obtain change in entropy of activation ($\Delta S$), where $k$ is kinetic rate constant of the reaction (L mol\textsuperscript{-1} s\textsuperscript{-1}), $N_A$ is Avogadro’s number (6.023 x 10\textsuperscript{23}), and $h$ is Planck’s constant (6.623 x 10\textsuperscript{-34} Js). Finally, Equation 36 was used to determine the free energy change of the reaction ($\Delta G$)\textsuperscript{41,43,46,48}.

\[
\Delta H = E_a - RT \quad \ldots \ldots \ldots (34)
\]

\[
k = \frac{RT}{N_A h} \cdot e^{\frac{\Delta S}{R}} \cdot e^{-\frac{E_a}{RT}} \quad \ldots \ldots \ldots (35)
\]

\[
\Delta G = \Delta H - T \Delta S \quad \ldots \ldots \ldots (36)
\]
Table 4-3: Thermodynamic parameters for epoxidation and post-oxirane cleavage reaction

<table>
<thead>
<tr>
<th>Thermodynamic Parameters</th>
<th>Epoxidation Reaction</th>
<th>Post-oxirane Cleavage Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthesis temperature (°C)</td>
<td>40       50       60</td>
<td>40       50       60</td>
</tr>
<tr>
<td>Enthalpy of activation (ΔH, kJ/mol)</td>
<td>17.98   17.89   17.81</td>
<td>56.37   56.29   56.20</td>
</tr>
<tr>
<td>Entropy of activation (ΔS, J/mol.K)</td>
<td>-262.18 263.61 262.75</td>
<td>-194.72 -198.60 -202.33</td>
</tr>
<tr>
<td>Gibbs free energy of activation (ΔG, kJ/mol)</td>
<td>100.08 103.08 105.34</td>
<td>117.35 120.46 123.61</td>
</tr>
</tbody>
</table>

Table 4-3 shows the thermodynamic parameters – activation enthalpy, activation entropy and activation free energy – for epoxidation reaction and oxirane ring cleavage reaction respectively – at all reaction temperatures (40, 50 and 60°C). As can be observed from the values for different thermodynamic parameters mentioned in Table 4-3, both epoxidation and ring opening reactions are endothermic, and are also non-spontaneous as Gibbs’ free energy change (ΔG) for both reactions is positive. It can also be seen that increase in synthesis temperature leads to an increase in non-spontaneous nature of both reactions, thereby reducing the possibility of their occurrence. However, sections on kinetics (epoxidation and oxirane cleavage) show the very opposite of this trend – increase in reaction rates for both epoxidation and oxirane reaction.
cleavage reactions with increase in synthesis temperature. This can be attributed to the external heat supplied for occurrence of both reactions, as well as excess heat generated due to the formation of performic acid during epoxidation reaction. However, since the Gibbs’ free energy of activation (ΔG) is lower for epoxidation over oxirane cleavage, reaction rates are higher for epoxidation compared to those for oxirane cleavage, as has been seen in the section on oxirane cleavage kinetics. ΔG values for epoxidation reaction were also observed to be significantly lower compared to values reported in other literature: jatropha oil (126-133 kJ/mol)\textsuperscript{50}, karanja oil (130 kJ/mol)\textsuperscript{48}, and cottonseed oil (117.5 kJ/mol)\textsuperscript{41}. This indicates easier formation of oxirane groups for perilla oil compared to other VOs studied in literature, which can be explained by the presence of higher linolenic acid content and its higher reactivity and can be correlated with results presented in other sections of this study.
CHAPTER FIVE

INFLUENCE OF DOUBLE BOND POSITION ON

EPOXIDATION KINETICS

5. Kinetic Model

Epoxidation of triglycerides via Prilezhaev reaction is a two-step process: (a) Perforinic acid formation (via acid catalysis, Scheme I, Figure 5-1 (a)), and (b) Epoxidation reaction (Scheme II, Figure 5-1 (a))27. These two steps are accompanied by the simultaneous occurrence of multiple side reactions such as the cleavage of epoxy rings and decomposition of reactant molecules. Among these side reactions, the most predominant is epoxy cleavage due to the attack of formic acid, resulting in the formation of hydroxylated-formiated products (Scheme III, Figure 5-1 (a))56. Reaction kinetics of these reactions (shown in) is expressed by multiple first-order differential equations (Equations 37-40), assuming negligible mass and heat transfer resistance due to intense stirring.

\[
\frac{d[F]}{dt} = \frac{d[H]}{dt} + \frac{d[E]}{dt} \quad \ldots \ldots (37)
\]

\[
\frac{d[P]}{dt} = -\frac{d[H]}{dt} + \frac{d[D]}{dt} \quad \ldots \ldots \ldots \quad (38)
\]

\[
\frac{d[W]}{dt} = -\frac{d[H]}{dt} \quad \ldots \ldots \ldots \quad (39)
\]

\[
\frac{d[HA]}{dt} = -\left(\frac{d[E]}{dt} + \frac{d[D]}{dt}\right) \quad \ldots \ldots \ldots \quad (40)
\]
Figure 5-1: (a) Major reactions occurring during the epoxidation of triglyceride: (i) Reaction I: Acid-catalyzed formation of performic acid; (ii) Reaction II: Formation of epoxy groups via reaction between performic acid and double bond; and (iii) Reaction III: Ring-opening reaction due to attack of formic acid on epoxy groups; and (b) Triglyceride molecule that indicates the position of double bonds in different fatty acids.
Here, square bracket “[]” denotes the concentration of a particular chemical species (in moles per 100 g of oil). Thus, formic acid \([F]\), performic acid \([P]\), water \([W]\), hydrogen peroxide \([H]\), hydroxyl acetate \([HA]\), double bond \([D]\) and epoxy \([E]\) are denoted respectively.

To understand the influence of the position of double bond on its reactivity, four scenarios (S1, S2, S3 and S4) were considered in the proposed model (Figure 5-1 (b)), each of which assumes the reactivity of double bond and epoxy at any position to be the same. For the aforementioned kinetic equations (Equations 37-40), double bond concentration \((d[D]/dt)\) and epoxy concentration \((d[E]/dt)\) were expanded for different scenarios as explained below:

a) Scenario 1 (S1) considers the reactivity of double bonds to be highly influenced by their position, i.e., double bonds at various positions exhibit differences in their reactivity. Hence:

\[
\frac{d[D]}{dt} = -k_{2a}[P][O_1] - k_{2b}[P][O_2] - k_{2c}[P][O_3]
\]

\[
\frac{d[E]}{dt} = \{k_{2a}[P][O_1] - k_{3a}[EO_1][F]^2\} + \{k_{2b}[P][O_2] - k_{3b}[EO_2][F]^2\} + \{k_{2c}[P][O_3] - k_{3c}[EO_3][F]^2\}
\]

b) Scenario 2 (S2) considers the reactivity of double bonds at positions 9 and 12 to be equal, while assuming the reactivity of double bond at the 15\(^{th}\) position to be different from those at the 9\(^{th}\) and 12\(^{th}\) positions. Hence:

\[
\frac{d[D]}{dt} = -k_{2d}[P][O_4] - k_{2c}[P][O_3]
\]
\[
\frac{d[E]}{dt} = \{k_{2d}[P][O_4] - k_{3d}[EO_4][F]^2\} + \{k_{2c}[P][O_3] - k_{3c}[EO_3][F]^2\}
\]

c) Scenario 3 (S3) considers the reactivity of double bonds at positions 12 and 15 to be the same, and that of double bond at the 9th position to be different from those at the 12th and 15th positions. Hence:

\[
\frac{d[D]}{dt} = -k_{2a}[P][O_1] - k_{2e}[P][O_5]
\]

\[
\frac{d[E]}{dt} = \{k_{2a}[P][O_1] - k_{3a}[EO_1][F]^2\} + \{k_{2e}[P][O_5] - k_{3e}[EO_5][F]^2\}
\]

d) Scenario 4 (S4) considers the reactivity of double bonds at all positions (9, 12 and 15) to be equal. Hence:

\[
\frac{d[D]}{dt} = -k_{2f}[P][O_6]
\]

\[
\frac{d[E]}{dt} = \{k_{2f}[P][O_6] - k_{3f}[EO_6][F]^2\}
\]

Here, \(k_{2a}, k_{2b}, k_{2c}, k_{2d}, k_{2e}, k_{2f}\) are the rate constants that correspond to epoxy formation, while \(k_{3a}, k_{3b}, k_{3c}, k_{3d}, k_{3e}, k_{3f}\) are the rate constants that correspond to epoxy cleavage reaction, at different bond positions for different scenarios.

The following initial conditions (@ time, \(t = 0\)) were used in model computations (where total double bond concentration \([D]\) is 0.77 moles/100 g of oil):

Scenario S1: \([D] = [O_1] + [O_2] + [O_3] = 46.5\% \text{ of } [D] + 30.7\% \text{ of } [D] + 22.8\% \text{ of } [D] \]

Scenario S2: \([D] = [O_4] + [O_3] = 77.2\% \text{ of } [D] + 22.8\% \text{ of } [D] \]

Scenario S3: \([D] = [O_1] + [O_5] = 46.5\% \text{ of } [D] + 53.5\% \text{ of } [D] \]

Scenario S4: \([D] = [O_6] = 100\% \text{ of } [D] \]
Among the three reactions mentioned in Figure 5-1 (a), formation of performic acid (Scheme I) occurs in three steps amidst the presence of AIER catalyst: (a) Adsorption of chemicals onto the surface of solid catalyst; (b) Reaction between these adsorbed chemicals on the catalytic surface; and (c) Desorption of products from the surface of the catalyst\textsuperscript{39,54}. Also, unlike homogeneous catalyst-based reactions where performic acid formation is the rate-determining step, either of these three steps (adsorption, surface reaction or desorption) can be the rate-determining step in case of heterogeneous catalyst-based reaction\textsuperscript{39}.

Hence, the kinetic rate equation for such a complex reaction (performic acid formation) was developed based on the L-H-H-W postulates. The general form of this equation is shown in Equation 41, where $k$ is kinetic rate constant, $KF$ is kinetic factor, $DF$ is driving force group, and $AG$ is the adsorption group. While the rate coefficient of rate-determining reaction is included in $KF$, displacement from chemical equilibrium is explained by $DF$. Further, variation in the rate of reaction is explained by variation in the number of active catalytic sites.

$$k = \frac{KF \times DF}{AG} \ldots \ldots (41)$$

Hence, it is assumed that during chemisorption mechanism, all chemicals in the aqueous phase (formic and performic acids, hydrogen peroxide, and water) were adsorbed onto the surface of the catalyst. Among these chemicals, adsorption of formic acid was assumed to be the rate-determining step for reasons explained by Janković et. al\textsuperscript{39}. Based on these assumptions and the L-H-H-W postulates, rate of consumption of hydrogen peroxide during the formation of performic acid was obtained from Equation 42\textsuperscript{39}, where,
$M$ is the mass of catalyst (in grams), and $C_s$ is the number of moles of active catalytic sites per gram of catalyst.

\[
\frac{d[H]}{dt} = \frac{-\left\{MC_s k_{a,F} \left( [F] - \frac{[P][W]}{K_1[H]} \right) \right\}}{1 + \frac{K_F[P][W]}{K_1[H]} + K_H[H] + K_P[P] + K_w[W]} \ldots \ldots (42)
\]

Here, $K_F$, $K_H$, $K_P$, $K_w$ are the respective adsorption equilibrium constants for formic acid, hydrogen peroxide, performic acid and water, while $k_{a,F}$ refers to the adsorption rate constant for formic acid. $K_1$ refers to the chemical equilibrium constant for performic acid formation, and is obtained from Equation 43 as described by Santacesaria et.al\textsuperscript{123}.

\[
K_1 = 1.6 \exp \left[ -\frac{10000}{R} \left( \frac{1}{298} - \frac{1}{T} \right) \right] \ldots \ldots \ldots (43)
\]

Schwaab et.al\textsuperscript{61,126} had shown the existence of strong correlation of kinetic parameters in mathematical models containing more than one temperature-dependent kinetic constant. Such correlation makes the task of precise estimation of different kinetic parameters more onerous\textsuperscript{127,128}. In such cases, re-parametrized form of Arrhenius equation is known to significantly reduce computational effort by reducing the correlation between parameters\textsuperscript{129}. Hence, temperature-dependency of various kinetic rate coefficients and adsorption equilibrium constants in the proposed model was determined using the re-parametrized form of Arrhenius equation (Equation 44). In Equation 44, $K_i$ refers to the rate coefficient of reaction $i$, $K_{i,0}$ is the constant related to frequency coefficient, $K_{i,Ea}$ is the constant related to activation energy of a reaction, $R$ is universal gas constant (8.314 J/mol. K), and $T$ is temperature (in Kelvin).
\[ k_i = \exp \left[ k_{i,0} - \frac{k_{i,Ea}}{R} \left( \frac{1}{T} - \frac{1}{323} \right) \right] \ldots \ldots (44) \]

### 5.1. Parameter Estimation and Model Validation

To determine the various rate constants, experimentally determined \([D]\) and \([E]\) values were used as input parameters in the proposed model for all four scenarios (S1, S2, S3 and S4). First-order differential equations (Equations 37-40) were integrated using Forward-Euler method with a step size of 1 s. Genetic algorithm was used to minimize the cost function \((J)\) (Equation 45) by running 1000 iterations that had the same boundary conditions for all kinetic parameters in all scenarios. Initially, various rate constants were determined for the epoxidation reaction at 40, 50 and 60°C for all four scenarios.

\[
J = \frac{1}{n} \sum \left( \frac{[D]_{\text{exp}} - [D]_{\text{model}}}{[D]_{\text{exp,max}}^2} \right) + \frac{1}{n} \sum \left( \frac{[E]_{\text{exp}} - [E]_{\text{model}}}{[E]_{\text{exp,max}}^2} \right) \ldots \ldots (45)
\]

Where \([D]_{\text{exp}} = IV/(2*126.9), \text{mol}/100 \text{ g of oil}\) and \([E]_{\text{exp}} = EV/16, \text{mol}/100 \text{ g of oil}\), and \(n = 8\).

To estimate the robustness of the proposed model and obtain a clear understanding of the influence of double bond position on its reactivity, all scenarios were validated. Under the model validation process, pre-calculated rate constants were used as input parameters and the model was allowed to predict \([D]\) and \([E]\) values, which were then compared with their corresponding experimentally determined values.

Model predicted rate constants at 40 and 60°C for various reactions in each scenario were used to obtain the pre-exponential factor and activation energy of the generalized
Arrhenius equation (Equation 46). From this, rate constants at 50°C were calculated and used as inputs for model validation.

\[ k = A e^{-\frac{E_a}{RT}} \]  

(46)

Where \( k \) – rate constant, \( A \) – pre-exponential factor and \( E_a \) – activation energy.

Error percentage (%) between experimentally determined and model-predicted iodine value (IV) and epoxy value (EV) was calculated using Equations 47 and 48.

\[
\% D\ Error = \frac{RMS(D_{exp} - D_{model}) \times 100}{Mean(D_{exp})} \quad \ldots \ldots (47)
\]

\[
\% E\ Error = \frac{RMS(E_{exp} - E_{model}) \times 100}{Mean(E_{exp})} \quad \ldots \ldots (48)
\]

5.2. Results and Discussion

Figure 5-1 (b) shows the chemical composition of perilla oil\textsuperscript{130,131}. While the average molecular weight of triglyceride (perilla oil) was estimated to be \(~ 871\) g/mol, its double bond functionality (i.e., average no. of double bonds per mole of triglyceride) was calculated as \(~ 7\). Iodine value of perilla oil was experimentally determined to be 196.6 g/100 g of oil, (i.e 0.775 mol/100 g of oil)\textsuperscript{132}.

5.2.1. Influence of Double Bond Position on its Reactivity

Experimentally determined (shown as points) and model-predicted (shown as lines for all scenarios) IV and EV, along with their respective error % (using Equations 47 and 48) are shown for 40°C (Figure 5-2 (a,b)) and 60°C (Figure 5-2 (c,d)) respectively. Further, Figure 5-2 (e,f) show IV and EV predicted at 50°C during the validation of the proposed
model, while Figure 5-2 (g) gives the values of optimized cost function at all reaction temperatures obtained during parameter estimation and model validation (at 50°C) for all the four scenarios.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Method of parameters obtained</th>
<th>Optimized cost function</th>
</tr>
</thead>
<tbody>
<tr>
<td>40°C</td>
<td>Parameter estimation</td>
<td>0.031 0.037 0.051 0.048</td>
</tr>
<tr>
<td>50°C</td>
<td>Model validation</td>
<td>0.116 0.059 0.117 0.776</td>
</tr>
<tr>
<td>50°C</td>
<td>Parameter estimation</td>
<td>0.048 0.048 0.054 0.056</td>
</tr>
<tr>
<td>60°C</td>
<td>Parameter estimation</td>
<td>0.043 0.051 0.065 0.065</td>
</tr>
</tbody>
</table>

Figure 5-2: Experimentally obtained and model-predicted (for all four scenarios): a) Iodine values and b) Epoxy values at reaction temperature of 40°C; c) Iodine values and d) Epoxy values at reaction temperature of 60°C; e) Iodine values and f) Epoxy values during model validation at reaction temperature of 50°C; and g) Optimized cost function
(RMS value) of the developed model for all four scenarios at the three reaction temperatures

As can be seen (Figure 5-2 (a-d, g)), both error % and optimized cost function obtained during parameter estimation were observed to be higher for scenarios S3 and S4 at all three temperatures. In contrast, scenarios S1 and S2 showed the least error and cost function values, with S1 predicting experimental observations more accurately when compared to S2 during parameter estimation. However, upon the validation of the model (Figure 5-2 (e-g)), scenario S2 was observed to predict experimental observations accurately with least error (< 10%) and cost function (0.06). Conversely, scenario S4 exhibited very high error (> 50%) and cost function (0.776), thereby failing completely in validating itself as a likely scenario, while scenarios S1 and S3 had higher error (≥ 15%) compared to S2, even though their predicted values were close to those observed experimentally when compared to S4.

Based on these observations (from Figure 5-2 (a-g)), the model indicates that the assumptions made in scenario S2 are the most likely to explain experimentally observed epoxidation behavior. In other words, the reactivity of double bonds at the 9th and 12th positions are the same, while that of double bond at the 15th position is different. This is in line with similar findings reported earlier by Scala and Wool49. They attributed this to the high influence of steric and electronic effects of glycerol center on double bonds closer to them (i.e., 9th and 12th positions), with no influence of such effects on double bonds that are farther from the glycerol center (i.e., 15th position).
Conventionally, epoxidation kinetics of various triglycerides has been modelled using scenario S4 in existing literature\textsuperscript{39,44,47,50,54,56}, indicating that models based on this scenario are highly robust and accurately predict epoxidation of different triglycerides. However, the model indicates that scenario S4 is the least likely to explain experimentally observed epoxidation behavior of high-linolenic perilla oil. This stark contrast is due to the absence of linolenic acid (C18:3) – that possesses double bond in the 15\textsuperscript{th} position – in triglycerides used in aforementioned studies, while perilla oil has high linolenic content (> 50\%). This means that scenarios S2 (the most accurate) and S4 (the least accurate) in this study are same for high-oleic triglycerides that have been studied to date.

Together, these explanations highlight the vital need for developing a model that robustly captures the variation in reactivity of double bonds for synthesizing EVOs with higher oxirane content – an aspect achieved by the model. In addition to capturing this variation, the model also provides further insights into their epoxidation behavior. An explanation of some such insights for two scenarios (S1 and S2) is provided henceforth.

5.2.2. Reactivity of Double Bond and Epoxy Groups at Different Bond Positions – Scenario S1

Figure 5-3 shows the variation in double bond and epoxy concentration – based on their bond position – as predicted by the proposed model for scenario S1 at all three reaction temperatures. Figure 5-3 (a) indicates sluggish reactivity of the double bond present at the 9\textsuperscript{th} position. Nevertheless, almost all double bonds at this position are predicted to participate in epoxidation reaction at both 50 and 60°C. On the other hand, significant amount of residual double bond content is predicted to exist at 40°C, indicating that the
epoxidation reaction is incomplete even after 8 h. Conversely, Figure 5-3 (c,e) indicate high reactivity of double bonds present at the 12th and 15th positions at reaction temperatures of 50 and 60°C, showing that they get consumed within the first 50 minutes of the reaction. However, at 40°C, the double bond at 12th position is predicted to react slowly when compared to the double bond at the 15th position. Contrastingly, the reactivity of epoxy group – which indicates its stability or the probability of cleavage of epoxy groups – is shown in Figure 5-3 (b,d,f) (corresponding to the 9th, 12th and 15th positions respectively). As can be seen, at all reaction temperatures, epoxy groups formed at the 15th position (Figure 5-3 (f)) are predicted by the proposed model to have undergone cleavage. However, epoxy groups formed at the 9th and 12th positions (Figure 5-3 (b,d)) are predicted to have not participated in the ring-opening reaction.

Nonetheless, as mentioned earlier, scenario S1 shows a higher error when compared to S2 during model validation (at 50°C), indicating that it is not the most accurate scenario for explaining the experimentally observed epoxidation behavior. Hence, variation in the reactivity of double bond and epoxy groups at different positions, as predicted in scenario S2, is explained in the subsequent section.

### 5.2.3. Reactivity of Double Bond and Epoxy Groups at Different Bond Positions – Scenario S2

Figure 5-4 (a-d) highlight the variation in double bond and epoxy concentration with increasing reaction duration at all three reaction temperatures, as predicted by scenario S2. As can be seen (Figure 5-4 (a)), double bonds at the 9th and 12th positions exhibit sluggish reactivity at 40°C, resulting in a significant number of un-reacted double bonds.
However, the rate of reactivity of double bonds at these positions showed increase with increase in temperature to 50 and 60°C. At the same time, Figure 5-4 (b) indicates that epoxy groups formed at the 9th and 12th positions did not undergo cleavage. These observations are comparable to the predictions made for variation in epoxy value (EV) in scenario S1 (Figure 5-3 (b,d)).

Figure 5-3: (a to f) Variation in the reactivity of the double bond and epoxy groups, based on their position at different reaction temperatures and reaction durations, for scenario S1.
Figure 5-4: (a to d) Variation in the reactivity of the double bond and epoxy groups, based on their position at different reaction temperatures and durations, for scenario S2

On the other hand, Figure 5-4 (c) indicates that double bond at the 15th position reacts completely within the first 50 minutes of epoxidation reaction, while the epoxy group formed at this position is prone to undergo cleavage (Figure 5-4 (d)). Hence, for both double bond and epoxy group at the 15th position, rate of reactivity is comparable across both scenarios S1 (Figure 5-3) and S2 (Figure 5-4 (c,d)). This is a divergent outcome from that observed in most studies on reaction kinetics of EVOs to date, which show significant epoxy cleavage (at 9th and/or 12th positions) in oleic-rich vegetable oils\textsuperscript{41,45,46,48,50,117}. Hence, the behavior (predicted by the model) of epoxy groups present at the 9th and 12th positions – of not undergoing oxirane cleavage via attack by formic acid – could be due to the combination of three factors.
The first factor is the possible steric effect of the hydroxylated group present at the 15th position (formed due to oxirane cleavage) on incoming formic acid. This effect is hypothesized to prevent any interaction between formic acid and the epoxy groups present at the 9th and 12th positions, thereby preventing their cleavage.

The second contributing factor is the combination of steric and electronic effects as reported by Scala and Wool125 in their study on reaction kinetics of acylation reaction (i.e., cleavage of epoxy groups and formation of acrylic group) of EVOs. They observed that oleic-rich vegetable oils exhibited higher reaction rates for acylation reaction when compared to oils containing higher amount of linoleic (C18:2) and linolenic acid (C18:3) groups, a finding they attributed to steric and electronic effects. Steric effect was generated by the presence of multiple epoxy groups in the same fatty acid chain that hindered other chemical species from attacking these groups. Simultaneously, electronic effect generated due to the glycerol center was considered responsible for preventing the cleavage of epoxy group present at the 9th position in fatty acids.

A third interesting factor that explains the low levels of oxirane cleavage, as observed via decrease in kinetic rate constant for oxirane cleavage (at 9th and 12th positions) with increase in reaction temperature (Table 4-1 and Table 4-2), is the degradation of formic acid at higher temperatures due to the higher reactivity of hydrogen peroxide32,133. Such degradation is likely to reduce the possibility of oxirane cleavage via attack by formic acid on epoxy groups, especially for epoxy groups at relatively less-accessible positions (i.e., 9th and 12th positions).
CHAPTER SIX

PHOTO-CURE KINETICS OF ACRYLATED EPOXIDIZED SOYBEAN OIL

6. Results and Discussion

6.1. Change in Enthalpy and Reaction Time Under Different Process Conditions

Table 6-1 and Table 6-2 provide the respective reaction enthalpies and peak times for photo-curing of AESO under different processing conditions (varying PI concentration, UV light intensity, and temperatures), as obtained from photo-DSC, for the low-intensity batch (50, 100 and 150 mW/cm²) and medium-intensity batch (1500, 2500 and 3500 mW/cm²). As can be seen from both the tables, increase in intensity from the low-intensity (50-150 mW/cm²) to medium-intensity (1500-3500 mW/cm²) regime resulted in an increase in reaction enthalpy along with significant reduction in reaction time. This observation was consistent, irrespective of the type of PI, UV light intensity and/or temperature used. Since a broadband lamp with a wide UV wavelength ranging from 320-500 nm was used in photo-DSC, the effect of UV wavelength on the extent of curing was not studied. Further, the reaction time for HCPK-initiated reaction was higher than for DMPA-initiated reaction at lower PI concentration and temperature in both low- and medium-intensity regimes. In order to determine the extent of conversion ($\alpha$) under all conditions, Equation 11 was employed.
Table 6-1: Enthalpy of reaction and peak time for photo curing of AESO at different photo-initiator concentration, intensity and temperature obtained from Photo-DSC for low-intensity regime.

<table>
<thead>
<tr>
<th>Intensity (mW/cm²)</th>
<th>Temp (°C)</th>
<th>Concentration of PI (%)</th>
<th>Enthalpy (J/g)</th>
<th>Peak Time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>DMPA</td>
<td>HCPK</td>
</tr>
<tr>
<td>50</td>
<td>25</td>
<td>0.5</td>
<td>-89.85</td>
<td>-59.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1</td>
<td>-113.2</td>
<td>-87.24</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>-121.2</td>
<td>-116.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4</td>
<td>-127</td>
<td>-124.7</td>
</tr>
<tr>
<td>50</td>
<td>50</td>
<td></td>
<td>-143</td>
<td>-124.3</td>
</tr>
<tr>
<td>75</td>
<td>2</td>
<td></td>
<td>-155.7</td>
<td>-128.3</td>
</tr>
<tr>
<td>100</td>
<td>25</td>
<td>2</td>
<td>-134.4</td>
<td>-133.8</td>
</tr>
<tr>
<td>150</td>
<td>25</td>
<td></td>
<td>-139.2</td>
<td>-141</td>
</tr>
</tbody>
</table>

In case of photo-cure kinetics, for Equation 11, the general practice is to consider the enthalpy value of a reaction obtained at the highest reaction temperature as its total enthalpy value (ΔH_{total}), in order to calculate the extent of the reaction (i.e., conversion or crosslinking in this study)^{108,109}. From Table 6-1, it is evident that by this logic, the highest enthalpy value of crosslinking reaction (-155.7 J/g) was obtained at the highest temperature (75°C) for AESO sample containing DMPA (2 wt. %) as photo-initiator (negative sign indicates that the reaction is exothermic). On the contrary, for AESO samples containing HCPK as photo-initiator (Table 6-1), increase in UV radiation intensity (from 50 to 150
mW/cm²) led to a higher increase in enthalpy value (-141 J/g) when compared to that observed via an increase in temperature (-128.3 J/g).

Table 6-2: Enthalpy of reaction and peak time for photo curing of AESO at different photo-initiator concentration, medium-light intensity and temperature obtained from Photo-DSC

<table>
<thead>
<tr>
<th>Intensity (mW/cm²)</th>
<th>Temp (°C)</th>
<th>Concentration of PI (%)</th>
<th>Enthalpy (J/g)</th>
<th>Peak Time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>DMPA</td>
<td>HCPK</td>
</tr>
<tr>
<td>1500</td>
<td>25</td>
<td>0.5</td>
<td>-132.73</td>
<td>-123.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1</td>
<td>-143.36</td>
<td>-131.98</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>-149.79</td>
<td>-130.83</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4</td>
<td>-144.80</td>
<td>-163.89</td>
</tr>
<tr>
<td>50</td>
<td>25</td>
<td>2</td>
<td>-173.52</td>
<td>-178.46</td>
</tr>
<tr>
<td>75</td>
<td></td>
<td></td>
<td>-187.28</td>
<td>-179.3</td>
</tr>
<tr>
<td>2500</td>
<td>25</td>
<td></td>
<td>-155.75</td>
<td>-180.32</td>
</tr>
<tr>
<td>3500</td>
<td></td>
<td></td>
<td>-153.35</td>
<td>-162.19</td>
</tr>
</tbody>
</table>

A similar result is observed for DMPA and HCPK samples in the medium-intensity batch (Table 6-2). Also, upon comparison between Table 6-1 and Table 6-2, it is evident that for the same PI concentration and temperature, reaction enthalpy value showed increase with increase in light intensity (to 1500/2500/3500 mW/cm²). This exemplifies that any further increase in reaction temperature and/or UV intensity – beyond the values used in this study – may lead to a higher value of enthalpy than the values obtained in this work. Hence, the conventional practice (as specified in literature) of choosing the highest
enthalpy value obtained as the total enthalpy value ($\Delta H_{total}$) of the reaction can lead to unrealistic conclusions about the kinetics of curing reaction. Therefore, to obtain a more realistic understanding of the extent of conversion ($\alpha$), it is critical to calculate the reaction enthalpy value at 100 % conversion using a theoretical method.

6.2. Theoretical Heat of Reaction

While the theoretical heat of reaction has been previously calculated in literature for simple molecules such as acrylates and diepoxyxides$^{134}$, there still exists lack of clarity on determining the theoretical heat of reaction for complex molecules such as triglycerides. Typically, Equation 49 can be used to calculate the theoretical heat of reaction ($\Delta H_{theoretical}$) for a complex molecule (such as triglyceride), where $f$ is the number of sites per mole of monomer, $C$ is the fraction of monomer used in the chemical composition, $H$ is the energy (in Joules) per mole of reactive site, and $MW$ is the molecular weight of the monomer (in grams/mole).

$$\Delta H_{theoretical} = \frac{f \times C \times H}{MW} \quad \ldots \ldots \ldots (49)$$

In case of acrylated epoxidized soybean oil (AESO), there can only be a maximum of 4.2 acrylate groups in the molecule$^{65}$ (i.e., $f = 4.2$), resulting in the total molecular weight ($MW$) of the monomer being 1290 g/mol$^{135}$. Enthalpy of the reaction ($\Delta H$) was considered to be -86.2 kJ per acrylate double bond$^{134,136}$, while the value of $C$ (fraction of monomer) was assumed to be 1 as no solvents or co-monomers were used in this study. Based on these details, the theoretical heat of reaction ($\Delta H_{theoretical}$) for 100 % conversion of double bond in AESO was calculated to be -280.65 J/g. Using this value as $\Delta H_{total}$, the
degree or extent of conversion ($\alpha$) was calculated using Equation 11 for all the test conditions and has been plotted for the low-intensity and medium-intensity batches in Figure 6-1 (a-f) and Figure 6-2 (a-f) respectively.

### 6.3. Effect of Photo-Initiator Type and Concentration on Extent of Cure

From Figure 6-1 and Figure 6-2, it is evident that the extent of crosslinking did not reach unity ($\alpha \neq 1$) under any DSC condition. Upon comparing these two figures, it is clear that the reaction reached completion within 40 s for the medium-intensity regime, while it continued beyond 120 s in the low-intensity regime despite the UV irradiation on sample for only 120 s under both scenarios. As can be seen from Figure 6-1 (for low-intensity regime), the extent of cure is observed to increase with increase in PI concentration (be it DMPA or HCPK), UV intensity, and/or temperature. However, in case of the medium-intensity regime/batch (Figure 6-2 (a,b)), it can be seen that while increase in DMPA concentration did not alter the extent of curing ($\alpha$), significant increase in $\alpha$ was observed with increase in HCPK concentration. On the other hand, Figure 6-2 (c,f) show that $\alpha$ increased with increase in DSC temperature – irrespective of the PI used. This can be attributed to the probable reduction in viscosity of the resin precursor (AESO), thereby enabling increased diffusivity of the PI that in turn would result in increased conversion\(^{137}\). Further, the rate of reaction was also observed to differ in both intensity regimes, being slower in the low-intensity regime vis-à-vis the medium-intensity regime (Figure 6-1 and Figure 6-2). Additionally, for both the low- and medium-intensity regimes, DMPA-containing samples exhibited a higher reaction rate (i.e., faster reaction) when compared to
HCPK-containing samples. In contrast, for both the PIs, increase in intensity beyond 1500 mW/cm² did not influence either the curing rate (\(da/dt\)) or the extent of curing (\(\alpha\)).

<table>
<thead>
<tr>
<th>Photo Initiator</th>
<th>Varying Concentration</th>
<th>Varying Intensity</th>
<th>Varying Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMPA</td>
<td><img src="image1" alt="Graph" /></td>
<td><img src="image2" alt="Graph" /></td>
<td><img src="image3" alt="Graph" /></td>
</tr>
<tr>
<td>HCPK</td>
<td><img src="image4" alt="Graph" /></td>
<td><img src="image5" alt="Graph" /></td>
<td><img src="image6" alt="Graph" /></td>
</tr>
</tbody>
</table>

Figure 6-1: Extent of conversion (\(\alpha\)) as a function of time during photo curing of AESO at varying photo-initiator concentration, intensity and temperature for two different photo-initiators in the low-intensity regime.

<table>
<thead>
<tr>
<th>Photo Initiator</th>
<th>Varying Concentration</th>
<th>Varying Intensity</th>
<th>Varying Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMPA</td>
<td><img src="image7" alt="Graph" /></td>
<td><img src="image8" alt="Graph" /></td>
<td><img src="image9" alt="Graph" /></td>
</tr>
<tr>
<td>HCPK</td>
<td><img src="image10" alt="Graph" /></td>
<td><img src="image11" alt="Graph" /></td>
<td><img src="image12" alt="Graph" /></td>
</tr>
</tbody>
</table>

Figure 6-2: Extent of conversion (\(\alpha\)) as a function of time during photo curing of AESO at varying photo-initiator concentration, intensity and temperature for two different photo-initiators in the medium-intensity regime.
6.4. Kinetic Analysis

6.4.1. Model-fitting Method

In order to determine the cure kinetics of acrylated epoxidized soybean oil (AESO), experimentally obtained $\frac{da}{dt}$ values were fitted using Equation 12 (Kamal-Sourour model) as a function of $\alpha$ (Figure 6-3). As can be seen from the figure, model-predicted values did not show a good fit for experimentally obtained values, indicating that this model cannot accurately predict the experimental observations for curing of AESO. This is due to the assumption made by the Kamal-Sourour model that $\alpha$ always reaches unity (i.e., complete crosslinking)$^{138,139}$, while Figure 6-1 and Figure 6-2 clearly show that crosslinking of AESO was not completed under any cure condition – largely as a result of vitrification. Hence, to account for the vitrification that occurs in AESO upon photo-curing, the modified Kamal’s model (Equation 13) was used to fit experimentally obtained $\frac{da}{dt}$ values and determine the reaction rate constants and activation energy. Figure 6-4 shows the model-predicted and experimentally obtained $\frac{da}{dt}$ values as a function of $\alpha$. As can be seen, the model shows a good fit with experimental values, indicating that the modified Kamal’s model can well explain experimental observations during the photo-curing of AESO. Based upon this fitting, the values of rate constants ($k_1$, $k_2$) and reaction orders ($m$ and $n$) were obtained and have been reported in Table 6-3.
Figure 6-3: Experimental and model-fitted (Kamal-Sourour model) values of $d\alpha/dt$ as a function of $\alpha$ for AESO containing 2 wt. % DMPA photo-cured at 25°C and UV intensity of 30 mW/cm².

Figure 6-4: Experimental data for $d\alpha/dt$ as a function of $\alpha$ at 25, 50 and 75°C, fitted with the modified Kamal’s model, for two photo-initiators: (a) DMPA and (b) HCPK.
As can be seen from Table 6-3, at all temperature conditions (25, 50 and 75°C), the value of $k_1$ is obtained as zero, indicating that the reaction has no $n^{th}$ order component and is solely a chain reaction\textsuperscript{110}. Also, $m + n \cong 2$ indicating that the reaction order is 2. Hence, effective activation energy ($E_a$) of the auto-catalyzed reaction was calculated via Arrhenius equation (Equation 15) and the obtained values are provided in Table 6-3.

Table 6-3: Rate constant and reaction order predicted by modified Kamal’s model

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temp (°C)</th>
<th>$k_1$ (s$^{-1}$)</th>
<th>$k_2$ (s$^{-1}$)</th>
<th>$m$</th>
<th>$n$</th>
<th>$m + n$</th>
<th>$\alpha_{max}$</th>
<th>Sum of Squares</th>
<th>Activation Energy (kJ/mol)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMPA</td>
<td>25</td>
<td>0</td>
<td>1.035</td>
<td>0.57</td>
<td>1.37</td>
<td>1.98</td>
<td>0.54</td>
<td>0.000585</td>
<td>1.12</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0</td>
<td>0.988</td>
<td>0.59</td>
<td>1.5</td>
<td>2.1</td>
<td>0.63</td>
<td>0.000833</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>0</td>
<td>0.97</td>
<td>0.59</td>
<td>1.55</td>
<td>2.14</td>
<td>0.67</td>
<td>0.000938</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCPK</td>
<td>25</td>
<td>0</td>
<td>0.658</td>
<td>0.5</td>
<td>1.35</td>
<td>1.85</td>
<td>0.47</td>
<td>0.000249</td>
<td>7.39</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0</td>
<td>0.831</td>
<td>0.56</td>
<td>1.48</td>
<td>2.03</td>
<td>0.64</td>
<td>0.00052</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>0</td>
<td>1.01</td>
<td>0.59</td>
<td>1.54</td>
<td>2.13</td>
<td>0.65</td>
<td>0.000647</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 6.4.2. Model-free Isoconversional Method

In order to understand the variation in effective activation energy with the progression of the reaction, and to also determine cure reaction kinetics in a holistic manner, model-free isoconversional method was employed in this study. Using Equation 16, plots between $\ln t_{\alpha, i}$ and $1000/T_i$ were plotted (as shown in Figure 6-5 for DMPA as PI). Based on the linear-fit for experimentally obtained values, effective activation energy
values $(E_{\alpha,\alpha})$ at different values of $\alpha$ were calculated for both the PIs and have been shown in Figure 6-6.

Figure 6-5: Isoconversional plots of the extent of conversion in the range of 0.05-0.50 for AESO containing 2 wt. % of DMPA as photo-initiator.

Figure 6-6: Variation in effective activation energy with extent of conversion for AESO samples photo-cured using two different photo-initiators (DMPA and HCPK).
6.5. **Light Intensity Exponent – Termination Mechanism**

In addition to the use of model-fitting and model-free isoconversional methods to test their relative suitability for analyzing the cure reaction kinetics of AESO, termination mechanism of cure reaction was also analyzed via the light intensity exponent method. Under this method, the termination mechanism of curing reaction was determined by fitting experimentally obtained \( \frac{d\alpha}{dt} \) v/s \( \alpha \) values to estimate the light intensity exponent \( (\beta)^{26,140} \) using Equation 50. Here, \( \frac{d\alpha}{dt} \) is the rate of crosslinking, \( k(p) \) is a parameter that depends on the extent of conversion \( (\alpha) \), \( x \) and \( \beta \) are exponents, and \( I_0 \) refers to the intensity of the UV radiation incident on the sample (in mW/cm\(^2\)).

\[
\frac{d\alpha}{dt} = k(p)(1 - \alpha)^x I_0^\beta \quad \ldots \quad (50)
\]

With regard to this method, in general, the value of \( x \) is assumed to be 1 during modeling in order to determine the value of the light intensity exponent \( (\beta)^{26,141} \), while keeping in mind the RSS principle (Equation 14), i.e., obtaining the least sum of squared errors. Based on this assumption (i.e., \( x = 1 \)), \( \beta \) was obtained in the range of 0.1-0.3 for all conditions, i.e., \( \beta \leq 0.5 \), indicating that the termination of curing occurred via the combination of two mechanisms: (a) Primary radical termination, or the reaction between free radicals derived from AESO molecule and photo-initiator radicals that prevent crosslinking between two AESO-based free radicals; and (b) Second-order termination, or the reaction between two AESO-based molecular radicals that actually leads to the ceasing of further crosslinking.
6.6. Discussion

6.6.1. Vitrification and Steric Hinderance on Extent of Cure

Multiple studies have reported incomplete curing (i.e., $\alpha \neq 1$) during isothermal cure conditions, irrespective of the material used and/or the cure mechanism\textsuperscript{78,86,109,142}. Such behavior is commonly known as “vitrification”, which refers to the transformation of a polymer from its liquid/rubbery state to its glassy state. Vitrification occurs due to increase in the molecular weight of the polymer – an outcome of its crosslinking – and is typically accompanied by an increase in polymeric viscosity, leading to a drastic decrease in the rate of crosslinking reaction due to the reduced mobility of both PI and AESO species. As a result, the reaction stops prior to reaching the maximum degree of conversion theoretically possible ($\alpha_{max} < 1$), with the remaining functional groups left behind as unreacted groups\textsuperscript{143}. In addition, steric hindrance experienced by the free radicals – due to the presence of glycerol group in triglycerides – also hinders their segmental mobility and ceases the curing reaction, thereby preventing $\alpha$ from reaching unity. Thus, the simultaneous occurrence of vitrification and steric hindrance experienced by free radicals explains the lack of completion of the curing reaction ($\alpha \neq 1$).

It is widely known and understood that for any photo-curing reaction, increase in any one of the three processing parameters – light (UV) intensity, photo-initiator (PI) concentration, temperature – will increase the rate and extent of curing ($da/dt$ and $\alpha$) due to the increase in number of free radicals available for reaction propagation. However, for the medium-intensity batch in this study, DMPA (PI) concentration is observed to be ineffective in causing any change in either the cure rate or the extent of curing (Figure 6-1).
Similar observations have also been reported by Mucci and Vallo\textsuperscript{144} in their work on analyzing the photopolymerization of methacrylate monomers using DMPA as PI. They attributed this behavior to the screening effect on account of increase in UV absorbance in samples containing $\geq 0.25$ wt. % of DMPA. In other words, at higher UV intensities (similar to those in the medium-intensity batch in this study), the optimum PI concentration for obtaining the maximum extent of curing is 0.25 wt. % for DMPA, beyond which any further increase in PI concentration will accelerate the termination process and not contribute towards the propagation reaction (i.e., curing). Since this study employs DMPA at higher concentrations (0.5, 1, 2 and 4 wt. %) than this limit (0.25 wt. %), change in DMPA concentration is observed to have a negligible effect on crosslinking-related parameters for the medium-intensity batch.

In contrast with the non-influence of DMPA concentration, temperature is observed to play a determining role with regard to the curing rate and extent of cure for the medium-intensity batch (Figure 6-2 (c)). This can be explained by the fact that increase in temperature enhances the rate of reaction by increasing the mobility of both PI (photo-initiator) and AESO species that have hitherto remained unreacted at lower temperatures. This in turn improves the ability of PI molecules to cause photo-curing of AESO. On the other hand, for the low-intensity batch, the curing reaction is observed to occur beyond 120 s (Figure 6-1), indicating that the AESO molecule had undergone dark-polymerization despite its slower rate of curing. This demonstration of the existence of dark polymerization, albeit at retarded rates, is at odds with conventional thought that considers free radical polymerization to cease upon switching off the UV light. However, such dark
cure in free radical polymerization has also been reported lately in difunctional methacrylate\textsuperscript{145}. This dark cure was hypothesized to occur due to the activity of free radicals that were trapped inside the crosslinked polymeric network. While conventional thought believed these radicals to be inactive, the dark-cure hypothesis assumed that these radicals retained some portion of their reactivity and cured any cross-linkable molecule that was available and freely accessible to them. This led to further progression of the reaction (i.e., curing), albeit at a highly retarded rate due to the highly-reduced activity of the trapped free radicals.

A stark difference is also observed in the reactivity of the two PIs (DMPA and HCPK) used in this study, as corroborated by lower peak times (Table 6-1 and Table 6-2) and higher/equivalent extent of curing ($\alpha$), (Figure 6-1 and Figure 6-2) for DMPA-containing AESO samples vis-à-vis their HCPK-containing counterparts. This can be ascribed to the faster cleavage of DMPA that takes place within 100-200 ps\textsuperscript{146,147} (as obtained through measurement using Electron paramagnetic resonance spectroscopy that has a picosecond resolution)\textsuperscript{148}. The decomposition rate constant ($k_a$) was estimated as $10^{11}$ s\textsuperscript{-1} by Kurdikar and Peppas\textsuperscript{149}. Such high rate constants indicate faster reaction. Conversely, HCPK needs more time for cleavage and reaction with triglyceride molecules\textsuperscript{87}.

Lastly, despite observing the vitrification phenomenon under all photo-DSC conditions, the acrylated triglyceride system (AESO) employed in this study has exhibited the highest rate constant to date among all acrylates that are commonly used in photo-cure coatings. A high rate constant means faster reaction, thereby highlighting that AESO undergoes faster curing (i.e., over less time) in comparison to other existing acrylates. Yet,
at the same time, no AESO sample showed complete curing under any condition, which can be explained by the sole major limiting factor with such systems – their higher functionality \( (f = 4.2) \). This is also in line with existing literature\(^{150} \) which shows the inversely proportional relationship between the functionality of an acrylate \( (f) \) and its extent of conversion (or curing, \( \alpha \)). This can be understood as the logical outcome of the combination of increase in total enthalpy \( (\Delta H_{\text{total}}) \) of the acrylate due to its higher functionality (Equation 49) and the occurrence of vitrification phenomenon in the acrylate system upon its curing.

### 6.7. Activation Energy Dependence on Conversion

Based on the model-free isoconversional method used in this work (Figure 6-6), effective activation energy \( (E_{a,\alpha}) \) of the curing reaction was initially observed to increase linearly with \( \alpha \), but subsequently showed a drastic increase during the later stages of the reaction. This increase was observed irrespective of the PI used (DMPA or HCPK) and can be entirely attributed to the occurrence of vitrification in AESO due to its curing. An additional complementing factor is the trapping of primary radical into the molecular network of AESO which inhibits its availability for further curing, thereby ceasing the entire cure reaction. Interestingly, effective activation energy is observed to be higher for HCPK-containing samples in comparison to DMPA-containing samples when determined from both model-fitting and model-free techniques. This can be ascribed to the fact that since the photolysis product of HCPK is bulkier than that of DMPA, HCPK molecules may experience severe steric hindrance from the glycerol center upon migrating to acrylate groups for undergoing crosslinking reaction. Hence, HCPK-containing samples find it
difficult to undergo crosslinking at higher \( \alpha \) values vis-à-vis their DMPA-containing counterparts, which explains the difference in their respective activation energies at higher \( \alpha \). The variation in effective activation energy with increase in the extent of crosslinking (\( \alpha \)) also highlights the high complexity of the crosslinking reaction – as reported elsewhere\textsuperscript{71} – from the point of view of cure kinetics, for it means that a single rate equation cannot be used to explain or describe the cure kinetics of AESO. This is because vitrification of a polymer is accompanied by a shift in the reaction mechanism (from chemical- to diffusion-controlled) on account of change in its effective activation energy\textsuperscript{71}. Hence, the combination of vitrification, primary radical trapping, and the subsequent transformation in the nature of cure reaction leads to significant differences in the effective activation energy (\( E_{a,a} \)) values obtained at different degrees of conversion (\( \alpha \)) vis-à-vis the effective activation energy (\( E_a \)) value obtained using the modified Kamal’s model (reported in Table 6-3). Further, it also establishes that the model-free isoconversional method is more accurate and realistic in predicting cure reaction kinetics of AESO in comparison to the model-fitting method, as it can capture the complexity of the entire curing process. Thus, this study establishes the relatively higher suitability of isoconversional methods over model-fitting methods with regard to analyzing the cure phenomenon of acrylated triglycerides.
CHAPTER SEVEN

THERMAL CURE KINETICS OF ACRYLATED EPOXIDIZED SOYBEAN OIL

7. Results and Discussion

7.1. Effect of Thermal-initiator Concentration on Heat Flow

Figure 7-1 (a,b) shows the heat flow recorded under dynamic conditions at varying heating rates for two different thermal initiator concentrations – 1 wt. % and 2 wt. % of TBPB – as a representative image of thermal DSC curves obtained in this study. As can be seen, at higher initiator concentration (i.e., 2 wt. % and above), two peaks were observed irrespective of the heating rate employed. In contrast, at lower initiator concentration (1 wt. %), two peaks (in the heat flow curve) are only observed for samples that were heated at higher heating rates (15°C/min or more), while samples heated at lower heating rates (< 15°C/min) exhibited a single peak.

Conventionally, a single peak is observed during thermoset curing, but the presence of two peaks in Figure 7-1 (a,b) indicates the occurrence of secondary reaction. A similar observation has been made by various other researchers upon the use of tert-butyl perbenzoate (TBPB) as free radical initiator\textsuperscript{151,152}, irrespective of the material system used. TBPB possesses half-life of 10 h at 104°C and of 1 min at 165°C\textsuperscript{153}. However, the second peak in this study is consistently observed at temperatures > 150°C, while conventionally,
the decomposition of TBPB (to form radicals) is well known to start at temperatures < 100°C (as also indicated via its half-life).

Figure 7-1: Heat flow as a function of temperature for AESO samples containing (a) 1 wt. % and (b) 2 wt. % of thermal initiator at different heating rates

From all the aforementioned observations, the first peak can be said to correspond to the occurrence of curing reaction of AESO due to the formation of radicals at < 100°C\(^\text{154}\). While some of these radicals initiate curing of the polymer, this onset of reaction results in the trapping of TBPB molecules within the three-dimensional crosslinked network. This leads to incomplete decomposition of initiator molecules, and it is this incomplete decomposition at lower temperatures that is referred to as the “cage effect”. This effect is also known to impact the mechanical performance of resin\(^\text{152}\). However, with further increase in temperature, such trapped molecules gain additional thermal energy due to which they can further decompose and lead to the formation of newer radicals. These newly formed radicals in turn enhance the rate and extent of curing reaction by reacting with the resin precursor, leading to the observance of the second peak at higher temperatures that corresponds to the progression of further curing of AESO.
At the same time, a comparison of Figure 7-1 (a,b) shows that the second peak is prominent at higher initiator concentration but is less prominent (or even absent) at lower initiator concentration. The prominence of second peak for higher initiator concentration can be explained by the availability of significant number of radicals for curing of AESO upon the receipt of thermal energy (i.e., higher temperatures). In contrast, at lower initiator concentration and slower heating rate, initiator molecules may not undergo “cage effect” due to the simultaneous occurrence of decomposition to form radicals that in turn react with AESO and lead to its curing. However, at lower initiator concentrations and faster/higher heating rates, the increased supply of thermal energy means that curing occurs at a faster rate and leads to the trapping of initiator molecules, which can then escape this ‘cage’ to cause curing at higher temperatures. The lower prominence of second peak in this scenario can be explained by the low content of trapped radicals in the cured network.

### 7.2. Extent of Cure

Figure 7-2 shows the variation in extent of conversion (i.e., curing or $\alpha$) with time for AESO samples containing 1 wt. % of thermal initiator (TBPB) at different heating rates. The extent of curing was calculated using Equation 11 that has been described earlier. With regard to $\alpha$, $\Delta H_{total}$ was calculated as the average value of heat flow/enthalpy for all samples corresponding to the same chemical composition (i.e., initiator concentration) but subjected to different heating rates. This is at variance with the methodology used for UV-cured samples, where $\Delta H_{total}$ was calculated as the theoretical maximum value of enthalpy possible (for $\alpha = 1$, based on Equation 49). However, this variation is mainly due to the assumption that in photo-curing, photolysis of initiator (i.e., photo-decomposition of
initiator) does not result in any heat generation. In contrast, it is well known that decomposition of the thermal initiator used in this study – TBPB – results in heat evolution of \(~-1300 \text{ J/g}\)\textsuperscript{154}. While, decomposition or breakage of bond is an endothermic reaction, TBPB exhibits an self-accelerating decomposition behavior at 65.8°\textdegree C resulting in an highly exothermic thermal run-away reaction\textsuperscript{155}. Given the occurrence of both exothermic curing of AESO and exothermic decomposition of TBPB (to form radicals), it is practically difficult to calculate $\Delta H_{\text{total}}$ theoretically. This is also evident from Table 7-1 which shows the heat of reaction (enthalpy or heat flow) obtained (through calculations) for AESO at different initiator concentrations. As can be seen from this Table 7-1, the total heat of reaction shows increase with increase in initiator concentration, further confirming the evolution of heat due to thermal decomposition of initiator molecules.

![Figure 7-2: Variation in the extent of curing ($\alpha$) as a function of time for AESO resin precursors containing 1 wt. % of initiator concentration at different heating rates](image)

Figure 7-2: Variation in the extent of curing ($\alpha$) as a function of time for AESO resin precursors containing 1 wt. % of initiator concentration at different heating rates.
Furthermore, as can be seen in Figure 7-2, increase in heating rate also causes significant shift in the time required for initiation of curing of AESO as well as in the rate of this reaction. This can be ascribed to the fact that at same initiator concentration, increases in heating rate enhances the rate of radical formation, thereby enhancing the probability of its (radical’s) subsequent reaction with the resin precursor to increase its degree of cure. Similar results were also observed for other AESO samples containing higher levels of thermal initiator concentration.

Table 7-1: Heat flow values for AESO samples at varying initiator concentration

<table>
<thead>
<tr>
<th>Heating Rate (°C/min)</th>
<th>1 % TBPB</th>
<th>2 % TBPB</th>
<th>4 % TBPB</th>
<th>6 % TBPB</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>-204.4</td>
<td>-239.0</td>
<td>-255.4</td>
<td>-296.7</td>
</tr>
<tr>
<td>7.5</td>
<td>-206.2</td>
<td>-235.0</td>
<td>-266.1</td>
<td>-283.4</td>
</tr>
<tr>
<td>10</td>
<td>-196.5</td>
<td>-234.6</td>
<td>-262.8</td>
<td>-289.3</td>
</tr>
<tr>
<td>15</td>
<td>-188.2</td>
<td>-233.4</td>
<td>-258.8</td>
<td>-286.5</td>
</tr>
<tr>
<td>20</td>
<td>-213.9</td>
<td>-233.5</td>
<td>-267.7</td>
<td>-290.4</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td><strong>-201.84</strong></td>
<td><strong>-235.12</strong></td>
<td><strong>-262.16</strong></td>
<td><strong>-289.26</strong></td>
</tr>
</tbody>
</table>

7.3. **Cure Kinetics**

Figure 7-3 (a&b) shows the plots for both Kissinger and Starink methods used to evaluate the reaction kinetics of thermal curing of AESO at low initiator concentration (1 wt. %). As is well understood, time (t) and temperature (T) in thermal-DSC are related to each other via the use of constant heating rate (β). Thus, for thermal curing, plots between the extent of conversion (α) and time (t) were used to obtain temperatures corresponding
to the different degrees of curing ($\alpha = 0.05$ to 0.95) in step of 0.05, based on the recommendations of the ICTAC Review Committee\textsuperscript{71}. Subsequently, these temperatures were used to generate plots between $\ln \left( \frac{\beta_i}{T_{\alpha,i}^2} \right)$ or $\ln \left( \frac{\beta_i}{T_{\alpha,i}^{1.92}} \right)$ and the reciprocal of temperature (Figure 7-3) for AESO resin containing different levels of thermal initiator concentration. Linear curve-fitting was undertaken on the aforementioned plots and the slope was used to calculate effective activation energy ($E_\alpha$) at different values of $\alpha$.

### 7.4. Effect of Initiator Concentration on Activation Energy

Based on Figure 7-3, effective activation energy ($E_\alpha$) of thermal curing reaction was calculated at different degrees of conversion ($\alpha$) using the Kissinger method (Equation 20), as described earlier. Subsequently, these effective activation energy values were plotted as a function of $\alpha$ for different levels of initiator concentration from 1 to 6 wt. % (Figure 7-4). Effective activation energy values ($E_\alpha$) obtained using Starink method (Equation 21) were observed to be nearly the same as those obtained using Kissinger method – with a variation of less than 5 %. Interestingly, $E_\alpha$ values obtained for thermal curing were observed to be ~ 2-3 times higher than those obtained for UV curing, irrespective of the amount of thermal initiator concentration used. As can be seen in Figure 7-4, effective activation energy ($E_\alpha$) does not show a consistent trend with $\alpha$ at all levels of initiator concentration. At lower initiator concentrations (1 wt. % or less), $E_\alpha$ shows increase with increase in $\alpha$ – a behavior also observed for photo-cured samples (Chapter 6). In the case of thermal curing though, this behavior can be ascribed to the lower likelihood of trapping of initiator-derived free radicals in the cured AESO network. This
reduced probability of radical trapping means that all radicals formed via decomposition of initiator molecules immediately lead to curing reaction at lower temperatures (or lower values of $\alpha$). This in turn reduces the likelihood of availability of free radicals at higher temperatures/values of $\alpha$, thereby increasing the effective activation energy of the reaction by making it more difficult to occur.

Figure 7-3: Plots for application of (a) Kissinger and (b) Starink methods to evaluate reaction kinetics for curing of AESO at initiator concentration of 1 wt. %
However, at higher initiator concentration (2 wt. % and above), effective activation energy was higher, indicating that the reaction is very difficult to occur despite the presence of larger number of free radicals. This can be ascribed to the possible recombination of radicals resulting in the killing of free radicals. Also, a clear and consistent trend was not observed for $E_\alpha$ as a function of $\alpha$. This is because at higher initiator concentration, the previously described cage effect has a pronounced influence on the curing reaction.

Initially, high initiator concentration translates to a higher concentration of free radical formation via thermal decomposition of initiator molecules, resulting in the initiation of curing of AESO. However, the cage effect delays a prominent chunk of curing reaction from occurring by trapping initiator-derived radicals within the cured AESO network, as mentioned earlier. Upon further increase in temperature, these radicals receive higher amount of energy, upon which they either lead to curing of AESO within the trapped region or zone or escape out of this zone to cause the curing of resin precursor. These two events – curing within trapped zone vis-à-vis curing outside the trapped zone – may not have the same probability of occurrence due to a variety of factors, such as the lack of bonds in the trapped zone for curing to occur, or the inability of radicals to escape out of this trapped zone. In addition, the effect of either of these events on effective activation energy is not monotonous, for their effect on the rate of curing reaction depends on the probability of the trapped radical obtaining a favorable reaction site on the AESO molecule. Hence, depending on the nature of curing reaction through overcoming the cage effect at higher temperatures, the rate of curing may enhance or reduce at higher values of $\alpha$, leading to inconsistent variation in effective activation energy as a function of the extent of curing.
Figure 7-4: Variation in effective activation energy ($E_\alpha$) as a function of the extent of conversion ($\alpha$) for thermally cured AESO at different initiator concentrations.
CHAPTER EIGHT

PHOTO CURABILITY OF NATURAL FIBER-REINFORCED

ACRYLATED EPOXIDIZED SOYBEAN OIL

8. Results and Discussion
8.1. Photo-curing of Thicker Parts

Figure 8-1 shows tensile specimen (thickness > 3 mm) processed via photo-curing. Photo-curing has been traditionally known to be restricted to use in coatings (thickness < 1 mm) due to the attenuation of UV light\textsuperscript{25,81,146,156}. In this work, unreinforced AESO samples of thickness > 3 mm were cured via Photo-curing. Conventional UV curing formulation contains 1-3 % of photo-initiator, 25-90 % of oligomer/monomer, and 15-60 % of diluent or solvent that is added to adjust the viscosity of coating formulation\textsuperscript{157}. However, no diluent/solvent was used in this study, and casting formulation was instead maintained as 96-99 % of acrylated epoxidized soybean oil (AESO) and 1-4 % of photo-initiator.

Further, it is well known that aromatic hydrocarbon compounds – such as benzene and styrene – tend to absorb more UV radiation compared to aliphatic hydrocarbons\textsuperscript{158}. Also, in conventional photo curing, the presence of styrene molecule (or similar molecules) will lead to absorption of incident UV radiation on the sample, thereby accelerating the cure reaction and resulting in the formation of a highly cured surface layer that further screens UV from penetrating deeper\textsuperscript{144}. On the other hand, in the absence of aromatic
hydrocarbons along with the long aliphatic chain of AESO used in this study might enable higher photon penetration across the sample, thereby resulting in higher cross-section. When trial experiments were carried out with the use of ethyl lactate as solvent for AESO, complete curing up to thickness > 3 mm was observed – it is important to note here that ethyl lactate is an aliphatic molecule.

Figure 8-1: Representative photo cured tensile specimens both prior to and after the tensile test

To understand the extent of curing, UV intensity was measured at the bottom layer of the sample for pure AESO (without photo-initiator) and AESO (with 2 wt. % photo-initiator). Figure 8-2 shows that AESO is more transparent to UV, thereby increasing the number of photons that reach up to the bottom layer of the resin precursor\textsuperscript{144}. Furthermore, AESO was also observed to cure completely in 5 min despite the absence of any initiator. However, both photo-initiators (DMPA and HCPK) generated photon-absorbing radicals, as is evident from the decrease in intensity. This is in line with the observation made by Yebi et.al\textsuperscript{159} when DMPA was used as photo-initiator for UV curing of unsaturated polyester resin reinforced with glass-fiber.
8.2. *Photo-curing of Natural Fiber-Reinforced Composite*

It is well known that processing of natural fiber-reinforced composites via thermal curing poses two prominent challenges. On one hand, higher processing temperatures result in the degradation of natural fibers, thereby causing deterioration in the properties of the composite\textsuperscript{24}. On the other hand, use of lower processing temperatures causes high interfacial gap between the fiber and resin precursor, again resulting in poor properties of the composite\textsuperscript{25}. Since these challenges hinder the obtainment of sustainable composites with superior performance, UV curing was explored as an alternative technique for processing natural fiber reinforced composites for the first time. Hence, natural fiber-reinforced green composites were processed via UV curing for 10 min, and their mechanical and thermal performance was analyzed.
On processing composites as per the procedure detailed in Figure 2-3, it was observed that flax fibers exhibited superior wettability – with the resin precursor flowing through the plane – when compared with their areca and coir fiber counterparts. Given the high viscosity of AESO that in turn must have hindered fiber wettability, this difference in wetting behavior between the three different natural fibers can be easily ascribed to their respective surface tension\textsuperscript{160}. Since flax fiber contains the highest amount of cellulose among the chosen fibers (\textasciitilde70 \%), it possesses higher surface tension\textsuperscript{161}. Natural fibers that possess high surface tension are known for exhibiting higher wettability, thereby leading to improved interfacial adhesion between the fiber and resin precursor\textsuperscript{161}. On the other hand, coir and areca fibers contain lesser or negligible amounts of cellulose vis-à-vis flax fibers, resulting in the relatively poor wettability of these fibers during casting (Figure 8-3). Hence, AESO resin precursor (containing 2 \% of initiator) was cast on both sides of these fibers and a load of \textasciitilde5 kg was applied on the resin precursor-impregnated fiber for 30 min to ensure higher wettability of these fibers. Flax fiber-reinforced composite was a long fiber unidirectional composite, while areca and coir fiber-reinforced composites were randomly oriented mats, with areca fibers in the range of 5-8 cm long while coir fiber length varied from 8 to 12 cm.

8.3. \textit{Mechanical Performance of AESO}

Tensile strength of AESO (Table 8-1) was obtained as \textasciitilde4 \pm 0.5 MPa for all cure conditions irrespective of initiator concentration (1, 2 or 4 wt. \%). This is explained by the fact that tensile strength of such resins is directly related to their crosslinking density. On the contrary, tensile modulus and toughness were observed to decrease with increase in
initiator concentration, when DMPA was used as photo initiator. When HCPK was used as photo initiator, varying concentration did not alter the modulus or toughness.

Under isothermal processing conditions, thermosets (such as AESO) exhibit vitrification or transition from liquid to glassy state. Hence, as curing reaction proceeds the bulkier initiator molecules and/or initiator-derived radicals get trapped within the vitrified polymeric network resulting in a cage effect. In turn, these molecules/radicals alter the local bonding structure and might create higher void/free volume due to steric hindrance. Figure 8-4 depicts the aforementioned explanation.

Figure 8-3: Challenges encountered with respect to fiber wettability during the impregnation of fiber with resin precursor
Figure 8-4: Influence of the trapped initiator radicals on the mechanical performance of the material

Table 8-1: Strength, Young’s modulus and Tensile toughness of AESO with varying photo-initiator concentration (1, 2 and 4 wt. %)

<table>
<thead>
<tr>
<th>Content of initiator</th>
<th>Strength (MPa)</th>
<th>Modulus (MPa)</th>
<th>Toughness (J/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DMPA</td>
<td>HCPK</td>
<td>DMPA</td>
</tr>
<tr>
<td>1 %</td>
<td>4.67 ± 0.45</td>
<td>3.94 ± 0.53</td>
<td>71.59 ± 4.70</td>
</tr>
<tr>
<td>2 %</td>
<td>4.23 ± 0.36</td>
<td>3.98 ± 0.63</td>
<td>64.09 ± 2.44</td>
</tr>
<tr>
<td>4 %</td>
<td>3.73 ± 0.55</td>
<td>3.86 ± 0.37</td>
<td>55.50 ± 4.91</td>
</tr>
</tbody>
</table>

Since Initiators reside within the network, their size/bulkiness dictates the free volume.
8.4. Mechanical and Thermal Performance of Natural Fiber-Reinforced Composites

Thermogravimetry analysis of UV-processed natural fiber-reinforced composites were carried out in nitrogen atmosphere to understand their thermal stability (Figure 8-5). The figure shows a single decomposition peak, indicating that both the resin precursor and fibers decompose together. Table 8-2 provides mechanical properties and heat resistant index ($T_s$) values for the composites and unreinforced AESO. Heat resistant index was calculated using Equation $51^{162}$, where $T_5$ refers to the temperature corresponding to 5 % of mass loss, $T_{30}$ refers to the temperature corresponding to 30 % of mass loss. Heat-resistant index is defined as the ability of a material to withstand decomposition.

$$T_s = 0.49 \left( T_5 + 0.6 \left( T_{30} - T_5 \right) \right) \quad \cdots \cdots \ (51)$$

Tensile strength of areca-reinforced and coir-reinforced composites exhibited performance poorer than the pure AESO resin (Table 8-2). This can be attributed to short fiber length, presence of porosity in the fiber mats and the randomized orientation of fibers. Such short fibers tend to produce higher stress concentration regions, resulting in reduction in strength of resultant composites$^{24}$. However, superior performance was observed for flax-reinforced composites, which is mainly due to the inherent high strength of flax fibers$^{163}$, their unidirectional nature and lower or negligible porosity in the fiber mat.
Figure 8-5: Thermo-gravimetry analysis of natural fiber-reinforced composites cured via UV radiation

Table 8-2: Mechanical properties and heat-resistant index of UV-cured natural fiber-reinforced composites

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Strength (MPa)</th>
<th>Modulus (MPa)</th>
<th>Ts (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure AESO (2 % DMPA)</td>
<td>4.22± 0.35</td>
<td>64.09± 2.43</td>
<td>173.4</td>
</tr>
<tr>
<td>Flax (unidirectional) – reinforced composite</td>
<td>50.96 ± 5.9</td>
<td>24001 ± 3900</td>
<td>167.55</td>
</tr>
<tr>
<td>Areca (Random oriented) – reinforced composite</td>
<td>1.29 ±0.1</td>
<td>600 ± 70</td>
<td>165.69</td>
</tr>
<tr>
<td>Coir (Random oriented) – reinforced composite</td>
<td>1.27 ±0.37</td>
<td>820 ± 20</td>
<td>166.16</td>
</tr>
</tbody>
</table>
CHAPTER NINE

THERMAL CURING OF NATURAL FIBER REINFORCED
ACRYLATED EPOXIDIZED SOYBEAN OIL

9. Results and Discussion

Prior to processing, thermogravimetry analysis of natural fibers were carried out to understand their thermal stability. Table 9-1 provides the $T_5$, $T_{30}$ and heat resistant index ($T_s$) (calculated using Equation 51) values for pure fibers. From Table 9-1, it can be seen that $T_5$ values for all the three natural fibers were > 200°C. Hence, it is unlikely that the fibers would have undergone degradation during processing at 160°C for 3 h. This is also evident from the absence of any discoloration of the processed composites. Therefore, processing was not carried out at varying cure temperatures.

Table 9-1: Heat resistant index/temperature ($T_s$) and other important temperatures ($T_5$, $T_{30}$) for chosen fibers (flax, areca and coir)

<table>
<thead>
<tr>
<th>Fiber</th>
<th>$T_5$ (°C)</th>
<th>$T_{30}$ (°C)</th>
<th>$T_s$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flax</td>
<td>248.94</td>
<td>344.56</td>
<td>150.09</td>
</tr>
<tr>
<td>Areca</td>
<td>253.03</td>
<td>317.22</td>
<td>142.86</td>
</tr>
<tr>
<td>Coir</td>
<td>205.71</td>
<td>319.97</td>
<td>134.39</td>
</tr>
</tbody>
</table>

9.1. Mechanical and Thermal Performance of AESO and Composites

Mechanical performance (i.e., tensile strength, modulus and toughness) of AESO with varying initiator concentration is shown in Table 9-2. It can be seen that while
increasing initiator concentration did not alter strength and toughness, modulus was observed to increase. Table 9-3 provides the mechanical properties and heat resistant index of fiber-reinforced composites. It can be seen that the tensile strength of areca and coir fiber-reinforced composites was inferior compared to pure AESO, which was in line with the observation made in UV-cured composites. However, the modulus of natural fiber-reinforced composite was observed to be higher than that of pure AESO. This can be attributed to the higher modulus of natural fibers (modulus of coir is ~ 6000 MPa and that of flax is 60000 MPa\textsuperscript{163}) than pure AESO. Figure 9-1 shows thermogravimetry analysis (TGA) of fiber-reinforced composites processed via thermal curing. Similar to photo-cured composites, thermally cured composites also exhibited single decomposition peak, indicating that both the resin and fibers decompose together. Also, it can be seen from Table 9-3 that thermal resistance or heat resistance index of composites did not alter irrespective of the natural fiber used or the processing method employed.

Table 9-2: Strength, Young’s modulus and Tensile Toughness of AESO with varying photo-initiator concentration (1, 2 and 4 wt. %)

<table>
<thead>
<tr>
<th>Content of initiator (Benzo)</th>
<th>Strength (MPa)</th>
<th>Modulus (MPa)</th>
<th>Toughness (J/m\textsuperscript{3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 %</td>
<td>3.71 ± 0.10</td>
<td>67.05 ± 3.62</td>
<td>1.95 ± 0.18</td>
</tr>
<tr>
<td>2 %</td>
<td>4.01 ± 0.32</td>
<td>87.88 ± 4.43</td>
<td>1.54 ± 0.39</td>
</tr>
<tr>
<td>4 %</td>
<td>4.04 ± 0.41</td>
<td>110.05 ± 3.79</td>
<td>1.32 ± 0.32</td>
</tr>
</tbody>
</table>
Table 9-3: Mechanical properties and heat resistant index/temperature ($T_s$) of fiber-reinforced composites

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Strength (MPa)</th>
<th>Modulus (MPa)</th>
<th>$T_s$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure AESO</td>
<td>4.00 ± 0.32</td>
<td>87.87 ± 4.43</td>
<td>169.35</td>
</tr>
<tr>
<td>Flax (unidirectional) –</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>reinforced composite</td>
<td>25.48 ± 2.7</td>
<td>22900 ± 3900</td>
<td>170.42</td>
</tr>
<tr>
<td>Areca (Random oriented) –</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>reinforced composite</td>
<td>0.6 ± 0.075</td>
<td>400 ± 48</td>
<td>167.56</td>
</tr>
<tr>
<td>Coir (Random oriented) –</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>reinforced composite</td>
<td>1.43 ± 0.41</td>
<td>830 ± 70</td>
<td>167.66</td>
</tr>
</tbody>
</table>

Figure 9-1: Thermogravimetry analysis of fiber-reinforced composites processed via thermal curing.
9.2. Effect of Interface on Mechanical Performance

It is well known that interfacial gap between the fiber and resin arises in any natural fiber-reinforced composites on account of the difference in surface energies of fiber (Polar) and resin (non-polar) given the presence of moisture in fibers\textsuperscript{164}. Further, during curing reaction, the resin typically experiences cure shrinkage\textsuperscript{165} due to crosslinking, while the presence of moisture (in fibers) may result in the formation of air bubbles upon increasing temperature. Such air bubbles tend to grow with increase in temperature and result in the formation of interfacial gap. Hence, it is hypothesized that the nature of curing process might significantly influence the magnitude of this interfacial gap. Specifically, while UV curing is undertaken for a very short duration (\(\sim 10\) min) immediately after the wetting of fiber, thermal curing is undertaken for longer duration (\(\sim 6\) h). Thus, given the mismatch in surface energies of fiber and resin, coupled with prolonged curing duration (\(\sim 6\) h), thermally cured composites are expected to exhibit higher cure shrinkage and stronger repelling of resin precursor (AESO) from the interface with natural fibers. As a result, UV-cured composites are expected to possess reduced interfacial gap vis-à-vis their thermally cured counterparts. This interfacial gap (between fiber and resin) inhibits the transfer of mechanical stress (load) from the resin to the fiber, thereby lowering the mechanical properties of natural fiber-reinforced composites that are thermally cured. However, it is vital to conduct detailed studies i.e. curing at varying process conditions such as different time-temperature combinations for thermal curing and varying UV wavelength, intensity for UV curing to further elucidate the above hypothesized phenomenon.
CHAPTER TEN

SUMMARY AND FUTURE WORK

10. Conclusions

10.1. Life Cycle Assessment

Vegetable oil-based epoxy was compared with two other bio-derived epoxies (bark-based and lignin-based) as well as conventional petroleum-derived epoxy via cradle-to-factory gate LCA to assess the extent of their eco-friendliness and assess the best material from the perspective of sustainability. The results of this work showed that across most impact categories, vegetable oil-based epoxy showed the best ecological performance among all the three bio-epoxies on account of two factors: significantly higher electricity consumption during the processing of B- and L-epoxy vis-à-vis V-epoxy, and the use of epichlorohydrin in producing other bio-epoxies except V-epoxy. Further, a comparative evaluation of the impacts of vegetable oil-based epoxy vis-à-vis conventional epoxy showed its poor performance, which was ascribed to the use of laboratory-scale inventory for V-epoxy that utilizes chemicals in larger proportions when compared to the optimized industrial-scale inventory used for P-epoxy. This is further compounded by poorer mechanical properties of V-epoxy when compared to P-epoxy. In sum, this work highlights the potential for vegetable oil-based epoxy to constitute the base for synthesis of sustainable epoxies for structural applications. Simultaneously, it also shows the need for optimizing the synthesis of such epoxies to reduce the input chemical requirement as well
as reducing their epoxy equivalent weight in order to enhance their resultant mechanical properties so as to make them competitive with respect to petroleum-based epoxies.

### 10.2. Synthesis of Sustainable Epoxy

This work witnesses the first-ever successful synthesis of green epoxy with high epoxy content and low EEW (< 175 g/eq) – comparable to that of DGEBA-based epoxies, thereby raising the possibility of EPeO as being an ecofriendly and sustainable alternative to conventional epoxies. With regard to homogeneously-catalyzed epoxidation of perilla oil produced via in-situ generation of performic acid in the presence of H₂SO₄ as catalyst, higher epoxy content (relative oxirane conversion of ~ 88 %) was observed. This was mainly due to higher unsaturation content in perilla oil (i.e., higher double bond content) as confirmed by its high iodine value (196 g per 100 g of oil), thereby enhancing its reactivity when compared with other vegetable oils. Reaction kinetics for epoxidation and ring opening reactions under homogeneously-catalyzed scenario showed activation energies of 20.10 kJ/mol (for epoxidation) and 43.11 kJ/mol (for ring opening) reactions respectively. This indicates higher stability of epoxy groups and lower probability of α-glycol formation, as confirmed by results obtained using the α-glycol content test that showed its molar concentration at < 20 % of epoxy molar concentration. Thermodynamic parameters – obtained through calculations – further confirmed higher stability of oxirane groups compared to α-glycol given the lower free activation energy for epoxidation vis-à-vis oxirane cleavage reactions.

In contrast, for the heterogeneously-catalyzed reaction, a pseudo two-phase model that captures the variation in reactivity of chemical groups based on their position was
developed to study epoxidation kinetics of perilla oil under such condition. Four different scenarios were considered to understand the reactivity of chemical species at different positions in the triglyceride molecule. The results clearly indicated that chemical groups present at the 9th and 12th position in the triglyceride molecule exhibit the same reactivity that was significantly different from that exhibited by groups present at the 15th position. Further, the robustness of the model was validated by calculating different kinetic parameters (rate constant and activation energy) as well as predicting the iodine and epoxy values of EPeO at 50°C under the heterogeneously-catalyzed reaction.

Upon combining both homogeneously- and heterogeneously-catalyzed reactions, this study can be said to bring novelty in at least three respects. One, it is the first attempt at analyzing the effect of high linolenic acid content – both via presence of larger number of double bonds and their enhanced reactivity compared to those in other acid moieties – of VOs on their epoxidation reaction through a detailed understanding of reaction kinetics and thermodynamics. Second, it also remains the first and only attempt to date to have focused on all three critical aspects related to EVOs – epoxidation, in-situ ring cleavage (side-reaction during epoxidation), and ex-situ ring cleavage – while analyzing the stability of epoxy groups during both epoxidation and ring cleavage reactions for the same EVO through data on reaction kinetics and thermodynamics parameters. Finally, this study also sheds light on the synthesis of EVOs with EEW equivalent to that of conventional epoxy. Together, the combination of these three aspects is expected to help advance vigorous research with regard to multiple aspects, including on the use of homogeneous and heterogeneous catalysts, accounting for the rates of side-reactions in different phases, and
also contribute towards a better understanding on the relation of stability of epoxy groups with the nature and content of different acid moieties present in the initially chosen VO.

10.3. Cure Kinetics of Acrylated Triglycerides

Beyond epoxidation kinetics, this study also involved comparing the cure kinetics of acrylated epoxidized soybean oil processed via different curing methods (photo-curing and thermal curing). Photo-cure kinetics of AESO – a bio-based acrylated triglyceride – was studied via photo-DSC by using two different photo-initiators (DMPA and HCPK). Irrespective of the photo-initiator used, AESO exhibited chain reaction behavior with the reaction order obtained as ~ 2, while under no condition was the extent of curing observed to be complete (i.e., \( \alpha \neq 1 \)). For the medium-intensity regime, DMPA-containing samples showed increase in reaction enthalpy with increase in UV intensity and/or temperature, with their HCPK-containing counterparts exhibiting similar behavior for increase in photo-initiator concentration and/or UV intensity. Modified Kamal’s model that takes vitrification into account was observed to well-fit experimentally obtained values for the extent of curing (\( \alpha \)) and was therefore used to determine the average activation energy (\( E_a \)) of cure reaction. On the other hand, model-free isoconversional plots were developed to study the variation in effective activation energy (\( E_{a,a} \)) as the reaction proceeds, showing increase in \( E_{a,a} \) with increase in \( \alpha \) for AESO samples containing either of the two photo-initiators. Given its ability to highlight change in effective activation energy as a function of the extent of curing (\( \alpha \)) on account of vitrification of the triglyceride, the isoconversional method was considered more apt vis-à-vis model-fitting method for understanding the photo-cure kinetics of acrylated triglycerides. Finally, light intensity exponent method
indicated that termination of curing reaction occurred via the combination of primary radical termination and second-order termination mechanisms.

Simultaneously, thermal cure kinetics of the same resin precursor (AESO) was also studied using tert-butyl perbenzoate as thermal initiator (in varying concentrations). Heat flow curves obtained using thermal DSC were used to calculate the extent of curing ($\alpha$) at different heating rates. Subsequently, two methods – Kissinger and Starink – were used to determine the variation in effective activation energy ($E_{a,\alpha}$) of curing reaction as a function of $\alpha$ using the isoconversional method. Both methods gave similar values of $E_{a,\alpha}$ at each $\alpha$ with a difference of less than 5 %, indicating the robustness of both models. Further, AESO samples showed irregular behavior with regard to their effective activation energy as a function of thermal initiator concentration. While lower initiator concentration was observed to result in enhancement of effective activation energy with increase in the extent of curing, higher initiator concentration showed inconsistency in effective activation energy behavior as a function of $\alpha$ due to the pronounced influence of the cage effect.

10.4. Mechanical Properties of Acrylated Triglycerides

Mechanical properties – tensile strength, Young’s modulus and toughness – were measured for both thermally cured and UV-cured AESO, as well as for their respective composites (reinforced with natural fibers – flax, areca and coir). Regarding properties of AESO-based composites, three natural fibers – flax, coir and areca – were chosen to evaluate the impact of chemical composition of fibers on mechanical and thermal properties of their respective composites. Among the three fibers, flax fiber exhibited the best wettability of resins, followed by areca fibers with the coir fiber showing the least
amount of wettability. Tensile strength of areca and coir reinforced composites exhibited inferior performance compared to pure AESO irrespective of the curing method employed. However, the tensile modulus of the fiber reinforced composite was higher than the pure AESO irrespective of the type of fiber and the curing method. However, the curability and performance of natural fiber reinforced composite cured via two different techniques need to be studied to a greater extent by varying the various process parameters. In case of UV curing, varying UV wavelength and in case of thermal curing, varying the curing temperature and time may impact the performance of the composites. Further, semi-empirical models could be used to determine mechanical properties.

10.5. Future Work

This work began with epoxidation and oxirane cleavage kinetics of triglyceride-based epoxies, but then shifted towards analyzing the cure kinetics along with thermal and mechanical behavior of acrylated triglycerides. This shift was undertaken in light of limited information availability for cure kinetics of triglyceride-based epoxies and their associated composites. However, any subsequent attempt towards improving the potential of vegetable oils, specifically perilla oil, as sustainable sources for alternatives to conventional epoxies would necessitate a whole host of studies on diverse research fronts.

The first immediate task would have to be the measurement of mechanical properties of epoxidized perilla oil (EPeO) in order to assess its performance vis-à-vis conventional DGEBA, since this study has restricted itself to comparing only their epoxy equivalent weights (EEW). Further studies would also be required with regard to selecting novel triglycerides that can help achieve lower EEW values than those exhibited by perilla
oil, followed by measurement of their mechanical properties. This would potentially yield sustainable epoxies with superior mechanical properties.

The second task would focus on understanding cure kinetics of epoxies derived from biological precursors (e.g. vegetable oils) – one immediate example in this regard can be EPeO. This task is especially relevant in light of the difference in curing mechanism of epoxies (via cationic mechanism) when compared to acrylated triglycerides (free radical mechanism). In particular, photo-cure kinetics of such epoxies would need an exhaustive study given the lack of sufficient literature on this domain.

The third task would involve in analyzing the effects of sizing and/or treating natural fibers on both cure kinetics as well as thermal and mechanical properties of such composites. Also, it is important to determine the UV curability by varying UV wavelength and in case of thermal curing, varying the curing temperature and time and evaluate the impact of process conditions on the performance of composites. Also, it was hypothesized that there exists some interfacial gap between the fiber and matrix. Hence, such surface modification (sizing) of these fibers may further reduce this interfacial gap and thereby enhance the mechanical properties of such composites. However, the effect of such modification on UV attenuation and curability remains to be understood. Additionally, experimentally obtained properties for such composites should also be modeled using semi-empirical models (such as Halpin-Tsai model) to enable better prediction of mechanical properties vis-à-vis fiber loading.

As stated in Chapter 1, the stepped concurrent curing (SCC) technique remains key to developing thicker composites (i.e., > 1 mm thick). However, this work did not dwell
further on the relevance of SCC technique for developing thicker UV-cured natural fiber reinforced composite. The fifth task emanating from this study would evaluate the suitability of SCC technique, since any possibility for use of bio-derived composites requires its commercial applicability, that can be used in structural applications. Finally, even as this study highlighted the superior ecological performance of vegetable oil-based epoxy systems, it has not shed light on the ecological performance of the two curing methodologies (photo and thermal curing). This can be the sixth task that emerges from this work, given the need to establish the ecological credentials of UV curing prior to declaring it as a sustainable manufacturing technique in its truest sense.

In sum, while this work demonstrates the potential power of photons towards processing natural fiber-reinforced sustainable thermoset composites, it also highlights the need for several key steps that must be undertaken to advance this effort towards the commercial application of such composites for futuristic products. These efforts are required at every life-cycle stage of such composites to enhance their true sustainability. To begin with, novel polymers need to be synthesized in an eco-friendlier manner while adhering to the 12 principles of green chemistry. Subsequently, it must be understood that most commercially used components have highly complex shapes, and hence the UV curability of such complex-shaped parts needs to be evaluated. Such understanding would hasten the manufacturing of composites at reduced cycle times and costs, while also fostering the culture of environmental benchmarking in industrial production, thus making our world truly sustainable.
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