

**DEVELOPMENT OF FLAXSEED OIL-BASED BIO-RESIN FOR  
FLAX FIBER REINFORCED BIOCOMPOSITES**

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in the Department of Chemical and Biological Engineering

University of Saskatchewan

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By

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## ABSTRACT

Researchers have extensively studied the use of triglyceride oils to develop biopolymers for various applications, such as coatings, paints, inks, plasticizers, and lubricants. Because of its wide availability and high unsaturated fatty acid content, soybean oil has usually been the focus of studies to develop biopolymers for the composite industry. However, like soybean oil, flaxseed oil is also comprised of mostly unsaturated fatty acids (more than 90% w/w), and although it has not been studied as much as soybean oil, it can also be used to develop bio-resin for composite applications. As a leading producer and exporter of flaxseed, Canada has abundant flaxseed oil and flax fiber available to produce renewable value-added products.

In this research, Saskatchewan-grown flaxseed oil was used to develop a bio-resin, which was investigated for its application in developing flax fiber-reinforced biocomposites. Flaxseed oil contains high levels of unsaturated fatty acid (linolenic acid = 54% w/w as shown by  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra) and has double bonds that can be used for polymerization (shown by FTIR spectra). In this research, flaxseed oil-based bio-resin was synthesized via epoxidation and acrylation reactions. There were 3.7 epoxy groups per triglyceride molecule present in the epoxidized flaxseed oil (EFO) and 2.6 acrylate groups per triglyceride molecule present in the acrylated epoxidized flaxseed oil (AEFO). A vacuum-assisted resin transfer molding (VARTM) process was used to produce the AEFO-based biocomposite test specimens.

The AEFO resin was compared to one of the commercially available versatile biopolymers, polylactic acid (PLA), and to two commonly used petroleum-based polymers, polypropylene (PP) and high-density polyethylene (HDPE). The density of the AEFO resin

(1.166 g/cm<sup>3</sup>) was found to be higher than the densities of PP (0.906 g/cm<sup>3</sup>) and HDPE (0.946 g/cm<sup>3</sup>), but it was slightly lower than the density of PLA (1.189 g/cm<sup>3</sup>). Less than 1% w/w of water was absorbed by all four polymer-based samples tested in this study. DSC results showed that AEFO has a glass transition temperature ( $T_g$ ) of 62 °C, which is similar to the  $T_g$  (56 °C) of PLA; this indicates a high cross-link density. The mechanical properties of the developed AEFO bio-resin are as follows: tensile strength =  $29.8 \pm 1.5$  MPa; Young's modulus =  $373 \pm 19$  MPa; flexural strength =  $53.5 \pm 2.3$  MPa; flexural modulus =  $2.84 \pm 0.15$  GPa; and Rockwell hardness number =  $90 \pm 4$ . PLA was found to be the strongest and hardest of the four polymers tested; it had the highest tensile strength, Young's modulus, flexural strength, and flexural modulus. However, the mechanical properties of AEFO indicated that it was stronger than PP and HDPE, and its properties were closer to those of PLA. The stress-curve of the AEFO sample showed some ductility as well. The mechanical properties of the AEFO bio-resin were also comparable to the mechanical properties of the acrylated epoxidized soybean oil (AESO) resin found in the literature.

Silane-treated flax fiber-based biocomposites were developed using the AEFO bio-resin produced by the VARTM process. The effect of fiber loading was investigated by varying the amount of flax fiber as follows: 2%, 5%, and 10% w/w. To enhance the strength of the polymer matrix, styrene was added at five different levels (10%, 20%, 30%, 40%, and 50% w/w). The mass increase percentage was found to be less than 1.5% for the maximum flax fiber content used in this study (10% w/w). The addition of styrene had no effect on the water absorption characteristics of the AEFO-based biocomposites. The flax fiber served as reinforcement in the AEFO biocomposites. The mechanical properties of the

AEFO-based biocomposites (i.e., tensile strength, Young's modulus, flexural strength, and flexural modulus) improved with an increase in the flax fiber content. The mechanical properties of the AEFO-based biocomposite with maximum flax fiber content in this study (10% w/w) were as follows: tensile strength =  $31.4 \pm 1.6$  MPa; Young's modulus =  $520 \pm 26$  MPa; flexural strength =  $53.5 \pm 2.3$  MPa; flexural modulus =  $2.98 \pm 0.17$  GPa; and Rockwell hardness number =  $97 \pm 5$ . Adding styrene to AEFO enhanced the hardness of the AEFO biocomposite material as well as its tensile strength, Young's modulus, and flexural modulus; however, adding styrene also decreased the composites' flexibility, thus decreasing its flexural strength.

The AEFO-based biocomposites were compared with the PLA-, PP-, and HDPE-based biocomposites. The PLA, PP, and HDPE polymer matrices were reinforced with the silane-treated flax fiber via extrusion and injection molding processes. The densities of all four types of biocomposites were proportional to the densities of their respective polymers. It was found that the AEFO, PP, and HDPE biocomposites had very low density deviation from their respective ideal densities. However, the PLA biocomposite showed a higher density deviation of 13% from its ideal density, thus indicating a large amount of porosity in its test specimen. The mass increase observed during the water absorption tests was similar for all biocomposites, and it was less than 2% w/w for each biocomposite. The tensile properties (tensile strength and Young's modulus) and the flexural properties (flexural strength and flexural modulus) of the AEFO-, PP-, and HDPE-based composites increased with an increase in the flax fiber content. However, tensile strength and flexural strength of the PLA-based biocomposites decreased with an increase in the flax fiber content due to the poor fiber-matrix interfacial adhesion. Based on the study and the

mechanical test results, AEFO proved to have the potential to replace PP- and HDPE-based biocomposite material. The PLA-based natural fiber biocomposite might need some compatibilizer to improve the interfacial adhesion between fiber-matrix.

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## DEDICATION

*I dedicate this thesis to my parents, my wife, my daughter and my parents-in-law.*

*Thank you very much for your love and encouragement throughout my life.*



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## LIST OF ABBREVIATIONS

$^{13}\text{C}$ NMR	carbon nuclear magnetic resonance spectroscopy
$^1\text{H}$ NMR	hydrogen nuclear magnetic resonance spectroscopy
AAMSO	acetic anhydride modified soybean oil
<i>ADF</i>	acid detergent fiber
<i>ADL</i>	acid detergent lignin
AEFO	acrylated epoxidized flaxseed oil
AEFO10S	AEFO resin with 10% styrene content
AEFO20S	AEFO resin with 20% styrene content
AEFO30S	AEFO resin with 30% styrene content
AEFO40S	AEFO resin with 40% styrene content
AEFO50S	AEFO resin with 50% styrene content
ALA	alpha linolenic acid
ASEO	acrylated epoxidized soybean oil
ASTM	American Society for Testing and Materials
BaF <sub>2</sub>	Barium fluoride
CDCl <sub>3</sub>	Deuterated chloroform
DSC	Differential scanning calorimetry
EFO	epoxidized flaxseed oil
ESOCA	cinnamate esters of epoxidized soybean oil
$F_{18:3}$	represent the amount of linolenic acid
FF	flax fiber content by weight
FTIR	Fourier transform infrared spectroscopy

HDPE	high-density polyethylene
HSO/MA	maleinized hydroxylated soybean oil monoglycerides
$I_{\text{exp methyl,18:3}}$	represent the integration value of terminal methyl protons of linolenic acid determined experimentally,
$I_{\text{exp methyl,rest}}$	represent the integration value of terminal methyl protons of all other fatty acids determined experimentally.
KGF	kilogram force
LDPE	low density polyethylene
LLDPE	linear low density polyethylene
$M_f$	weight of test sample after 24 h immersion in water (g)
$M_i$	initial weight of test sample (g)
MSO	methacrylated soybean oil
MMSO	methacrylic anhydride modified soybean oil
<i>NDF</i>	neutral detergent fiber
PE	polyethylene
$P_I$	pressure reading after pressurizing the reference volume (psi)
$P_{II}$	pressure reading after including $V_C$ (psi)
PLA	polylactic acid
PP	polypropylene
ppm	parts per million
PS	polystyrene
PVC	polyvinyl chloride
rpm	revolutions per minute

SEM	scanning electron microscope
SOMG/MA	maleinized soybean oil monoglycerides
$T_g$	glass transition temperature
UV	ultra violet
$V$	volume of sample ( $\text{cm}^3$ )
VARTM	vacuum assisted resin transfer molding
$V_C$	volume of sample cell ( $\text{cm}^3$ )
$V_R$	reference volume ( $\text{cm}^3$ )
$\rho$	density ( $\text{g}/\text{cm}^3$ )
$m$	mass (g)
$\delta$	chemical shift
$\sigma_t$	tensile strength (MPa)
$F_{max}$	maximum load value (N)
$A$	cross-sectional area ( $\text{mm}^2$ )
$E$	Young's modulus (MPa or GPa)
$\Delta\sigma$	change in tensile stress before the material yields
$\Delta\varepsilon$	change in tensile strain before the material yields
$S$	flexural strength (MPa)
$P'$	load (N)
$L$	length of span (mm)
$b$	width of specimen (mm)
$d$	thickness of specimen (mm)
$E_H$	Flexural modulus (MPa or GPa)

$s$  slope of the tangent to the initial straight line portion of the load deflection curve (N/mm)

# Chapter 1

---

## 1. Introduction and Objectives

### 1.1 Introduction

A large amount of plastics ( $\approx$  280 million tonnes) are manufactured and used annually worldwide. The source for most of the polymers that are used to develop various plastic products is petroleum, a non-renewable resource. In recent years, researchers have been driven to develop alternatives to petroleum-based products due to the steady growth of energy consumption and the rapid reduction of fossil fuel resources (Dutta *et al.*, 2004). To find a sustainable alternative to petroleum-based materials, several researchers have started developing carbon-neutral polymers from renewable plant and animal sources (Avella *et al.*, 2002; Avérous, 2004; Yu *et al.*, 2006).

Polymers that are derived from renewable natural sources are known as “biopolymers” (Sharma & Kundu, 2006). Sources used to develop biopolymers include starch, cellulose, sugar, and plant oil (Avérous, 2004). Biopolymers have several advantages over synthetic polymers; for example, they are renewable, non-toxic, commercially cheaper, and eco-friendly since they are fully or partially biodegradable (Mallik *et al.*, 2002). Numerous studies have reported that vegetable oil-based biopolymers have shown noticeable properties such as biodegradability and desired viscosity (Erhan *et al.*, 2003). The main constituents of natural plant oils are triglycerides, which have various active sites open to polymerization. The main primary sites in a triglyceride are the double bond, the allylic carbons, the alpha carbon of the ester group, and the ester group (Knot *et al.*, 2001). Similar to the synthesis of petroleum-based

polymers, a polymerizable group can be added to the triglyceride molecule on these active sites (Sharma & Kundu, 2006; Nayak, 2000; Knot *et al.*, 2001; Guner *et al.*, 2006).

Many researchers have worked on developing bio-resins from soybean oil because of its wide availability and high levels of unsaturated fatty acids. Different grades of soybean oil-based biopolymers have been developed based on their physical and mechanical properties (O'Donnell *et al.*, 2004; La Scala and Wool, 2005; Lu and Wool, 2008). Biodegradable composites have also been developed from soybean-based bio-resin; these composites have shown potential for application in the packaging and indoor panel industries (Netravali and Chabba, 2003).

Similar to soybean oil, flaxseed oil (otherwise known as linseed oil) can also yield good results because it also contains high amounts of linolenic and other long-chain unsaturated fatty acids. These unsaturated fatty acids are the primary components that can be polymerized to produce a biopolymer. The polymerization reactions of plant oils have been reported since 1830, when thermal polymerization of linseed oil was first attempted (Kavitha *et al.*, 2010). Most studies indicate that the polymerization of unsaturated fatty acids starts with the formation of a dimer or polycondensation with catalysts at higher temperatures. Modification of the catalyst and the process conditions can provide the desired product. Currently, vegetable oil-based resin is blended with synthetic resin and then cured with a hardener. Free fatty acids are obtained by lipolysis of triglycerides. Free fatty acids can be used to develop polymers for several applications by following various polymerization reactions (Kavitha *et al.*, 2010). Flaxseed oil has mostly been used for its drying characteristics; however, in recent years, it has also been used for its nutritional

value. It has n-3 fatty acid and alpha linolenic acid (ALA), which is used to prevent and cure various human diseases (Zhang *et al.*, 2008).

Flaxseed is an important crop grown in Western Canada. Canada has been the leading producer and exporter of flaxseed oil since 1994. More than half of the Canadian flax is produced in Saskatchewan, and the remaining is grown in Manitoba and Alberta. Across Canada, the total acreage under flax production was 805,000 hectares in 2006-2007, but it declined to 692,000 hectares by 2009 (Canadian Grain Commission, 2009). This decrease in flax acreage was due to an increase in the acreage of the versatile crop, such as canola. To increase flax acreage and boost the value of flax, new flax-based value-added products should be explored and developed. The use of Canadian flaxseed oil for polymeric and biocomposite applications have not been studied yet. Therefore, the primary objective of this research is to develop a flaxseed oil-based bio-resin and to investigate its application in the development of flax fiber based-biocomposites. The outcome of this study will also help reduce our dependency on the depleting petroleum resources and will provide a direction towards the development of new biopolymers and renewable alternate materials.



## 1.2 Literature Review

### 1.2.1 Natural oil/Plant oil

Natural oil can be extracted from worldwide available renewable sources, such as plants and animals. Several studies have been done developing biopolymers from plant oils such as soybean, corn, castor, linseed, sesame, sunflower, safflower, and walnut (Sharma & Kundu, 2006; Nayak, 2000; Knot *et al.*, 2001; Guner *et al.*, 2006). All these oils mainly contain triglyceride molecules with different levels of unsaturation (Knot *et al.*, 2001; Guner *et al.*; 2006, Wool & Sun, 2005). The level of unsaturation can be modified genetically. Triglyceride is an ester product comprised of three fatty acids connected at a glycerol juncture. The carbon length varies from 14 to 22, and has 0 to 3 double bonds in most of the plant oils (Knot *et al.*, 2001; Wool & Sun, 2005). The saturated and unsaturated fatty acid composition of different plant oils is shown in Table 1.1.

Table 1.1 Typical fatty acid composition of different plant oils

Plant oil	Palmitic acid (wt %)	Stearic acid (wt %)	Oleic acid (wt %)	Linoleic acid (wt %)	Linolenic acid (wt %)	Ricinoleic acid (wt %)
Soybean oil	12	4	24	53	7	-
Flaxseed/Linseed oil	5	4	22	17	52	-
Castor oil	1.5	0.5	5	4	0.5	87.5
Rapeseed oil	4	2	56	26	10	-
Sunflower oil	6	4	42	47	1	-
Palm oil	39	5	45	9	-	-

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Triglycerides are mainly used to produce coatings, paints, inks, plasticizers, lubricants, and other agro-chemicals (Knot *et al.*, 2001; Guner *et al.*, 2006; Wool & Sun, 2005). However, extensive research has only been done on soybean and corn oil (Sharma & Kundu, 2006; Knot *et al.*, 2001; Guner *et al.*, 2006; Wool & Sun, 2005; Li & Larock, 2000; Li & Larock, 2001; Li & Larock, 2002; Li *et al.*, 2001; O'Donnell *et al.*, 2004; La Scala and Wool, 2005; Lu and Wool, 2008). Many researchers have investigated soybean oil because of its abundant availability and high level of unsaturated fatty acid contents (Sharma & Kundu, 2006). Soybean and flaxseed oil can be compared as both of them contain high amounts of unsaturated fatty acids, such as linoleic and linolenic acid. The degree of unsaturation is the most important factor affecting different properties of the fatty acid and the oil, and it is measured by the iodine value (Guner *et al.*, 2006). A higher iodine value indicates better drying characteristics of the oil. Some natural oils contain fatty acid having functional groups, such as hydroxyls, cyclic group, epoxies, and furanoid groups (Sharma & Kundu, 2006). Castor oil contains hydroxyl groups and, therefore, is used as a reactant for interpenetrating the polymer network (Nayak, 2000; Guner *et al.*, 2006). The thermal and the mechanical properties of vegetable oil-based polymers depend on the level of unsaturation of oil (Nicolau *et al.*, 2009).

### **1.2.2 Flaxseed oil**

Flax (*Linum usitatissimum*, L.) is one of the oldest oilseed crops grown in Canada and is an integral part of Canadian agriculture (Flax Council of Canada, 2009). Flaxseed oil is also commonly known as linseed oil (Zhang *et al.*, 2008). Flax is a dicotyledon, belonging to the linacea family. This plant is mainly used for triglyceride oil, omega-3

fatty acid, fiber, textiles, paper, and composite products. Flaxseed oil is extracted from the plant seeds (Carter *et al.*, 2008), is yellowish to brown in color, and is obtained mainly by cold pressing; however, solvent extraction process can also be used sometimes (Zhang *et al.*, 2008; Oomah & Mazza, 1998). The oil content in Canadian flaxseed is 43.5-44.7% (dry basis), and its iodine value is 192-193 units ([www.grainscanada.gc.ca](http://www.grainscanada.gc.ca)). The high oil content and high iodine value are the result of longer daylight and cool temperature in Canada ([www.grainscanada.gc.ca](http://www.grainscanada.gc.ca)).

Traditionally, flaxseed oil was mainly used to produce paint and linoleum. However, recently there has been an increase in the use of flaxseed in human and animal diet because of its nutritional benefits. Flaxseed oil contains a high percentage of  $\alpha$ -linolenic acid, which is an essential fatty acid beneficial in the treatment of heart disease, cardiovascular disease, and inflammatory bowel disease (Daleprane *et al.*, 2010; Goyal *et al.*, 2014). Flaxseed also has antioxidant properties and can protect against certain kinds of cancer (Eilati *et al.*, 2013). After the extraction of oil from flax seeds, the remaining by-product serves as animal feed. Flaxseed oil is an edible oil and can be consumed in the human diet, but presently it is being used as a nutritional supplement and not for cooking because of its strong odour and flavour. However, in the recent decade, food-grade flaxseed has been developed, which contains higher levels of omega-3 fatty acids.

Flaxseed oil contains long chains of unsaturated fatty acids, which oxidize very quickly when exposed to air and form a three-dimensional network. Flaxseed oil is a well-known drying oil that is widely used in paint formulation (Mallegol *et al.*, 2007). The presence of triglycerides with various reaction sites makes flaxseed oil polymerize easily, and the polymerization reaction is exothermic. The drying characteristic of

flaxseed oil has mainly been used for applications such as oil, varnish, paint and linoleum (Zhang *et al.*, 2008; Savoire *et al.*, 2008).

### 1.2.3 Flaxseed oil composition and structure

The main content of flaxseed oil is fatty acid ester triglyceride; Table 1.2 details the typical composition of flaxseed oil. As shown in Table 1.2, flaxseed oil contains mostly unsaturated fatty acids having one or more carbon double bonds (88-92%) and few saturated fatty acids (7-12%). The principal constituents of flaxseed oil are highly unsaturated linolenic and linoleic acids.

Table 1.2 Typical composition of flaxseed oil

Fatty Acid	#NC:#NDB*	Percentage (wt %)
Palmitic acid	16:0	5.5-6
Stearic acid	18:0	2-6
Oleic acid	18:1	10-22
Linoleic acid	18:2	12-18
Linolenic acid	18:3	53-71

*Sharma and Kundu, 2006; Boquillon and Fringant, 2000; Knot et al., 2001; Guner et al., 2006*

\*#NC indicates the number of carbon

#NDB indicates the number of double bonds

Flaxseed oil contains triglyceride molecules that have three unsaturated fatty acids. Typically a triglyceride is an ester, which is obtained from three molecules of unsaturated fatty acids and one molecule of glycerol (Figure 1.1). The unsaturated fatty acids contain carbon double bonds, whereas saturated fatty acids do not have any double bond. The

double bond in unsaturated fatty acids can be isolated or conjugated based on the separation of double bonds in the carbon chain. Double bonds separated by two or more carbon atoms are called “isolated,” and double bonds separated by one carbon atom are called “conjugated” (Guner *et al.*, 2006).

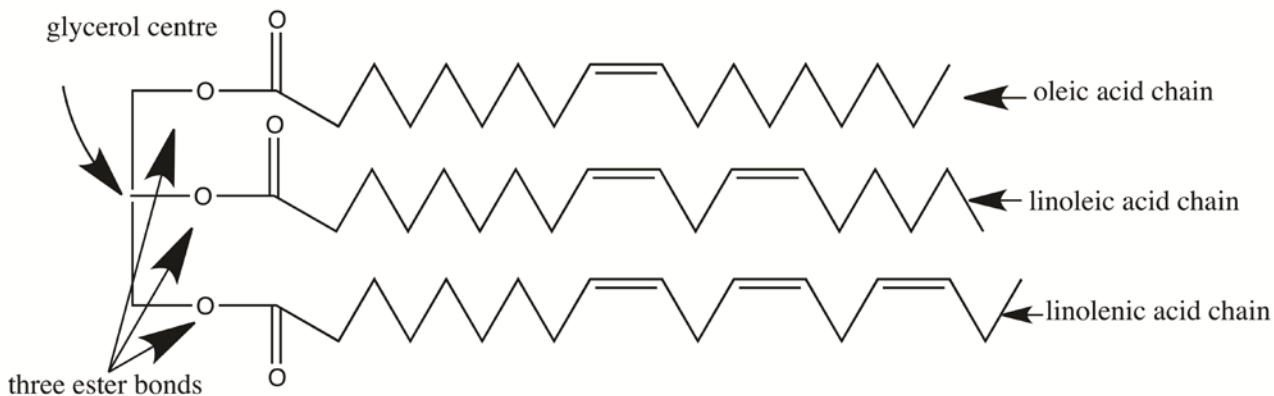


Figure 1.1 Typical triglyceride molecule

Some of the physical properties of flaxseed oil are given in Table 1.3. The melting point of flaxseed oil is low due to high levels of unsaturated fatty acids.

Table 1.3 Typical properties of flaxseed oil

Viscosity (cSt at 37.8 °C)	293.4
Specific gravity (20 °C/4 °C)	0.925-0.932
Refractive index	1.480-1.483
Melting Point (°C)	-20

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#### 1.2.4 Plant oil-based polymers

The development of polymers from bio-based renewable resources is of significant economic and scientific interest. In most polymer studies, epoxidized plant

oils have been used as toughening agents. Only soybean oil has been extensively studied for developing biopolymers. The high soybean yields in the United States and the high levels of unsaturated fatty acids present in the oil are the main factors for extensive research on soybean oil-based polymers in North America. Plant oils are made up of triglycerides as discussed earlier. Triglyceride oils have been used to develop various polymers, such as oxypolymerized oils, acrylic resins, polyamides, polyesters, epoxy resins, polyesteramides, and polyurethanes (Guner *et al.*, 2006; Sharma & Kundu, 2006; Nicolau *et al.*, 2009).

Triglycerides can be synthesized by three different methods to develop various types of polymers. The first method involves functionalizing the unsaturated sites like the double bonds (Khot *et al.*, 2001). In this method, polymerizable chemical groups are added to break the double bonds present in the triglyceride molecule. Polycondensation polymerization of triglycerides is possible after the transformation of the unsaturated triglyceride by the addition of epoxy or hydroxyl functionalities. The hydroxyl groups can be introduced in the triglyceride oils by various methods, including attacking the carbon-carbon  $\pi$ -bond to form different polyol structures.

The second method involves converting the triglycerides to monoglycerides through chemical reactions, such as glycerolysis and amidation reactions (Khot *et al.*, 2001). Monoglycerides are also referred as alkyd resins by various researchers and are used for surface coating (Wool and Sun, 2005). Monoglycerides can further react with alcohol and co-monomers, such as epoxy or anhydride, via a polycondensation reaction. Another polymerization process for monoglycerides is by reacting it with maleate half esters via free radical polymerization.

The third method involves both functionalizing the unsaturation and converting the triglycerides to monoglycerides (Wool and Sun, 2005). With these three methods, different types of polymers are developed from different types of triglyceride oils.

Most of the polymers produced from triglyceride oils involved the epoxidation process. In an epoxidation reaction, an oxygen atom is added to the triglyceride molecule, where it forms a three-member ring with the unsaturated carbon-carbon bond. The carbon-carbon double bonds are reactive due to their relatively high electron density (McMurray, 2007). This property makes the epoxidation of vegetable oils possible. The epoxidation of plant oils is carried out primarily with peroxyacetic and peroxyformic acids on an industrial scale (Gamage *et al.*, 2009). The epoxidized product is used typically in the PVC industry as a plasticizer. The epoxidation reaction is performed to attain maximum epoxy yield, which is beneficial when the product is to be used for further chemical transformations. The epoxidation of plant oils can be carried out in solution or in bulk with homogeneous or heterogeneous catalysts (Zehar *et al.*, 1989; Sinadinovic-fiser *et al.*, 2001).

Epoxidized oils can be polymerized in different ways; cinnamate esters of the epoxidized soybean oil (ESOCA) are formed when cinnamic acid is added to the epoxidized soybean oil. ESOCA can be prepared by free radical polymerization, photopolymerization, and copolymerization (Esen & Kusefoglu, 2003). Acrylated epoxidized soybean oil (ASEO) is a commercial biopolymer (Ebecryl 860, UCB Chemical Co., Atlanta, GA) developed by adding an acrylic acid to the epoxidized soybean oil (Wool & Sun, 2005; Hong & Wool, 2005). Similarly, two other triglyceride monomers developed from soybean oil have also shown good results: maleinized soybean oil monoglycerides

(SOMG/MA), and maleinized hydroxylated soybean oil monoglycerides (HSO/MA) (Wool and Sun, 2005). Epoxynorbornane-modified linseed oil was developed by photo-initiated cationic polymerization (Sharma and Kundu, 2006).

Alkyd resin is a common polymer developed from triglyceride oil; it is obtained via esterification of polyhydroxyl alcohols with the polybasic acids and fatty acids (Guner *et al.*, 2006). Alkyd resins are used in the manufacturing of offset printing inks (Blayo *et al.*, 2001). Oxypolymerized oil is one of the polymers obtained from triglyceride oils, which is commercially used in oil-based binder. Oxidized oils are developed by the polymerization reaction that occurs during the oxidation of carbon double bonds (Guner *et al.*, 2006). Plant oil-based polyamides are used in the paint industry; soybean oil dimer acids can be used to produce thixotropes, a modifier used for changing paint flow (Guner *et al.*, 2006). Polyurethanes are produced by the reaction of di-isocyanates with the hydroxyl functional triglyceride. The hydrophobic nature of triglycerides affects the properties of the polyurethanes prepared from vegetable oils (Guo and Petrovic, 2000; Koprululu *et al.*, 2008). Linseed oil, castor oil, and sunflower oil have been used to develop polyurethane, which is used in making paint (Guner *et al.*, 2006). Different polymerization techniques have been used to develop different grades of vinyl polymers from various plant oils. Linseed oil-based polymer has been developed via cationic polymerization of the linseed oil with styrene and divinyl benzene. Conjugated linseed oil, acrylic acid, styrene, and divinyl benzene have been used to prepare polymers by thermal polymerization (Sharma *et al.*, 2008). Various linseed oil-based polymers have been successfully developed by oxidative polymerization, cationic



photo-polymerization, and thermal polymerization (Sharma *et al.*, 2008; Sharma & Kundu, 2006).

### 1.2.5 Flax fiber and its role in biocomposite applications

Flax fiber is one of the oldest natural fibers and is mainly used in textiles, paper, and composite products. Flax fiber is obtained from the stem of the flax crop, and it is mainly comprised of cellulose and low amounts of hemicellulose, pectin, lignin, and waxes. The chemical composition of the flax fiber depends on the source of the fiber, the age of the crop, and the extraction conditions (Hearle and Peters, 1963). Table 1.4 compares the chemical compositions of flax fiber and other available natural fibers.

Table 1.4 Chemical compositions of natural fibers

Fiber	Cellulose (wt %)	Hemicellulose (wt %)	Pectin (wt %)	Lignin (wt %)	Wax (wt %)
Flax	64.1	11.0-20.6	1.8-2.3	2.0-2.9	1.5
Hemp	57.0-77.0	3.7-13.0	14.0-22.4	0.9	0.8
Jute	45.0-71.5	12.0-26.0	13.6-21.0	0.2	0.5-2.0
Kenaf	31.0-57.0	15.0-19.0	21.5-23.0	-	2.0-5.0
Ramie	68.6-91.0	0.6	5.0-16.7	1.9	-
Sisal	47.0-78.0	7.0-11.0	10.0-24.0	10.0	0.6-1.0

(Baley 2002; Mohanty *et al.* 2001)

Flax fiber is hydrophilic, leading to poor fiber-polymer interfacial bonding. This hydrophilic nature of flax fiber is a main disadvantage in developing high quality biocomposite products. The cellulose and hemicellulose content in the flax fiber are hygroscopic due to the presence of hydroxyl groups. Many researchers have worked on improving the fiber-polymer bonding by treating the fiber with different chemical processes. Most of the surface waxes and other non-cellulosic materials are removed

during chemical treatment processes (Li *et al.*, 2007). Some of the chemical treatments used to treat natural fibers are alkaline treatment (Morrison *et al.*, 2000; Jacob *et al.*, 2004; Sarkar and Ray, 2004), silane treatment (Valadez *et al.*, 1999; Agrawal *et al.*, 2000), acetylation (Hill *et al.*, 1998; Xu *et al.*, 2002), potassium permanganate treatment (Joseph *et al.*, 1999), and chemical coupling method (Joseph *et al.*, 1996; Sreekala *et al.*, 2003; Joseph *et al.*, 2003; Zafeiropoulos *et al.*, 2002). Alkaline and silane treatments are the most common chemical treatments adopted by many researchers for surface modification of different natural fibers.

The durability and mechanical properties of natural fibers, including flax fiber, mainly depend on the cellulose, hemicellulose and lignin content. It has been reported that flax fiber has the potential to replace glass fiber for developing high-performance composites (Joffe *et al.*, 2003). Synthetic fibers such as glass fiber have disadvantages in that they have a low elastic modulus and pose potential health risks due to skin irritation (Matthews and Rawling, 1999).

Plant fibers have several advantages over synthetic fibers, including low density, recyclability, renewability and biodegradability. Jahn (2002) reported that plant fiber properties have a direct effect on the physical properties of plant fiber-based biocomposites. Table 1.5 compares the density and tensile properties of flax fiber with other natural and synthetic fibers. Flax fiber is one of the strongest fibers among the bast fibers available worldwide. Flax fiber is also exceptional in that during processing, it can survive high temperatures (up to 250 °C) (Sreekala *et al.*, 2000).

Table 1.5 Comparison of flax fibers' physical and mechanical properties with other natural and synthetic fibers

Fiber	Density (g/cm <sup>3</sup> )	Tensile Strength (MPa)	Young's Modulus (GPa)
Flax	1.40 – 1.50	345 – 1500	27.6 – 80.0
Hemp	1.48	550 – 990	70
Cotton	1.50 – 1.60	287 – 597	5.5 – 12.6
Jute	1.30 – 1.46	393 – 800	10.0 – 30.0
Ramie	1.50	400 – 938	61.4 – 128.0
Sisal	1.45	400 – 700	9.0 – 38.0
Coir	1.15	131 – 175	4.0 – 6.0
E-glass	2.50	2000 – 3500	70.0
Carbon	1.70	4000	230.0 – 240.0
S-glass	2.50	4570	86.0
Aramid	1.40	3000 – 3150	63.0 – 67.0

(Bledzki and Gassan 1999; Paul et al. 1997; Mohanty et al., 2001; Wallenberger and Weston 2004)

Flax fiber has been investigated by various researchers as a reinforcement in producing different biocomposites (Hornsby et al., 1997; Harriette et al., 2005; Singleton et al., 2003; Voorn et al., 2001; Weyenberg et al., 2006; Wollerdorfer and Bader 1998). In most of the studies, it was confirmed that adding flax fiber increases the tensile strength of the biocomposites; however, in other studies, it was reported that the tensile properties of the biocomposite decreases if the flax fiber content exceeds a certain level (Thomason, 2005). This decrease is because the flax fiber behaves as reinforcement up to a certain amount, and after that, it may just behave as a filler material. It has been reported that tensile strength is more dependent on the fiber properties and tensile modulus is more sensitive to the polymer matrix properties (Saheb and Jog, 1999). Sometimes defects such

as nodes can be the break points during mechanical tests, which can adversely affect the mechanical properties (Davies and Bruce, 1998).

A hollow lumen is present in flax fiber, which decreases its bulk density and makes it lightweight. The empty cavity also makes flax fiber behave as an acoustic and thermal insulator (Reddy and Yan, 2005). These properties are preferable in the automotive and construction industries, where natural fiber-based lightweight composites can be used because of their insulating properties (Netravali and Chabba, 2003). The short natural fiber-based composites can be manufactured by using molding processes, such as extrusion, compression molding, rotational molding, and injection molding. The long fiber-based biocomposites can be produced by various techniques, such as sheet forming, pultrusion, resin mold transfer, and tape lay-up process (Advani and Sozer, 2002).

### **1.2.6 Application of plant oil-based resins in different biocomposites**

A considerable amount of work has been done on natural fiber using petrochemical polymer matrices, and now there is a growing interest in developing and using plant oil-based resins in natural fiber-reinforced biocomposite materials. Soybean oil-based polymer has been extensively investigated to develop natural fiber-based biocomposite materials. Soybean-based polymers such as AESO and HSO/MA have been used with glass, flax, and hemp composites to develop different composites (Knot *et al.*, 2001; O'Donnell *et al.*, 2004; Morye and Wool, 2005).

O'Donnell and co-workers (2004) developed and studied biocomposites made of AESO resin and natural fiber mat, and they reported that the developed biocomposite

materials had potential use in housing materials, furniture, and automobile components. Liu and co-workers (2001) investigated composites made from epoxidized soybean oil, glass, carbon, and mineral fiber, and determined that glass-reinforced composites showed better results than carbon-filled composites.

Soy-based bio-resins showed potential for developing biodegradable biocomposites (Netravali and Chabba, 2003). The epoxidized plant oil (EFO) resin has been also used for developing natural fiber-based composites. EFO has also been identified as a potential alternative material for flooring to replace PVC (Carter *et al.*, 2008). Flax fiber-reinforced biocomposites were developed using soybean oil-based resin, such as methacrylic anhydride modified soybean oil (MMSO), methacrylated soybean oil (MSO), and acetic anhydride modified soybean oil (AAMSO) (Adekunle *et al.*, 2010). Hong and Wool (2005) used keratin feather fibers and soybean oil to produce biocomposite material, and they found that keratin feather fibers significantly improved the mechanical properties of the biocomposite material; the mechanical properties of biocomposites were acceptable for composite applications, electronic casing, and aeronautical and automotive applications.

A study has also been done to develop hybrid biocomposites using a soybean oil-based resin and different levels of glass/flax fiber and their arrangements (Morye and Wool, 2005). Biocomposites produced using cellulose fibers and terpene-based acid anhydride cured epoxidized soybean oil (ESO) showed good potential as a biodegradable structural building material (Takahashi *et al.*, 2008).

Resin mold transfer (Knot *et. al.*, 2001), vacuum assisted resin transfer mold (O'Donnell *et. al.*, 2004), and sheet molding (Lu & Wool 2008) processes have been used to develop biocomposites from plant oil-based polymers.

### **1.2.7. Research gap**

Plant oils have been used to develop different types of polymers for various applications. Extensive research has been performed on soybean oil, and various grades and types of soybean oil-based biopolymer have been studied. Flaxseed oil-based polymers have mainly been developed and characterized for coating and paint formulation. Flaxseed oil contains a high level of unsaturated fatty acids similar to soybean oil and has the potential for polymeric applications. Soybean oil-based polymers have mostly been used to develop composites with man-made fibers, such as glass and carbon fiber, and only a few studies have been done with natural fiber. The main focus of the plant oil-based polymer studies done in the past has been on the polymer structure, composition, and success of the chemical reactions. Canada is the leading producer and exporter of flaxseed. Total acreage of flaxseed in Canada in 2009 was 692,000 hectares. However, in Western Canada, flaxseed is getting an enormous competition from the new versatile crop, canola.

Over the last decade, continuous and innovative research on flaxseed and flax fiber has been started in Western Canada. However, no flaxseed oil-based biopolymer is used or has been developed to produce a biocomposite material with flax fiber. There has been no study performed that provides detailed physical and mechanical characterization of AEFO bio-resin and its biocomposite. No study is performed on effect of flax loading in AEFO based biocomposites. Canada has an abundant availability of raw material:

flaxseed oil and flax fiber; therefore, it is important to develop and investigate different flaxseed oil and flax fiber based value-added products. Flaxseed oil-based polymers can be prepared and studied for polymeric applications similar to soybean oil-based resin. A detailed characterization of flaxseed oil for polymeric applications is needed to develop new biopolymers via different polymerization techniques. It is important to investigate whether flax fiber can reinforce flaxseed oil-based bio-resin.

This study will examine the role of flax fiber and flaxseed oil in flaxseed oil bio-resin-based biocomposites. Comparing several physical and mechanical properties of flaxseed oil-based bio-resin with a commercially available biopolymer and common petroleum-based polymers can predict its potential as a polymer matrix for various applications. No comparative study has been done on AEFO bio-resin with other commercially successfully polymer matrices used in composite industry. Polylactic acid (PLA) is a versatile biopolymer and has second highest consumption worldwide in bioplastic applications (Ceresana, 2011). Therefore, PLA was identified as a commercial biopolymer for comparison. Among petroleum based polymers, HDPE and PP have the greatest consumption and they are most commonly used polymers to manufacture a wide range of plastic products. Over the last two decades, these polymer matrices have also been studied extensively for developing various biocomposite materials. Hence these two polymer matrices were selected for comparison. Comparing the flaxseed oil-based bio-resin with these three globally used polymer matrices will predict the success of the bio-resin as a polymer matrix and its potential use commercially. This research can provide an alternative value-added use of flaxseed oil and flax fiber. Overall, this study will

facilitate the development of partially or fully biodegradable biocomposites for industrial applications.

### **1.3 Hypotheses of the Research**

1. Flaxseed oil contains a high level of unsaturated fatty acids which can be used to develop bio-resin via epoxidation and acrylation reactions.
2. Flax fiber has good mechanical properties and it can serve as reinforcement when it will be added to flaxseed oil-based resin to develop biocomposite material.

### **1.4 Objectives of the Research**

The overall goal of this research is to develop a flaxseed oil-based bio-resin using Saskatchewan-grown flaxseed and to investigate its use in developing a natural fiber-based biocomposite. To achieve the primary goal, the following specific objectives were set for the research:

1. To characterize (spectroscopically) and determine the potential double bond reaction sites in flaxseed oil;
2. To develop a flax oil-based bio-resin for natural fiber reinforced biocomposites;
3. To measure the following physical and mechanical properties of the developed bio-resin: density, glass transition temperature, water absorption, tensile strength, Young's modulus, flexural strength, flexural modulus, and Rockwell hardness;
4. To compare the properties of the flaxseed oil-based bio-resin measured in objective 3 with a biopolymer polylactic acid (PLA) and two commonly used synthetic polymers: HDPE and PP;



5. To develop a biocomposite using a flax oil-based bio-resin and flax fiber for plastic casing and furniture applications;
6. To measure the physical and the mechanical properties of the developed biocomposite as per objective 3;
7. To compare the properties of biocomposite developed using a flaxseed oil-based bio-resin measured in objective 6 with PLA-, HDPE-, and PP-based biocomposites.

### **1.5 Organization of the Thesis**

In this research, a flaxseed oil-based resin and its flax fiber-reinforced biocomposite were developed for biocomposite applications. The bio-resin and its biocomposite were characterized and compared to three other polymers and their biocomposites. This thesis is comprised of 7 chapters.

Chapter 2 presents the characterization of the raw material used in this research (i.e., flaxseed oil and flax fiber). Flaxseed oil was characterized spectroscopically to study the fatty acid profile and the potential reaction sites. The compositional study of the flax fiber was performed using a fiber analyzer. The density and thermal properties of the flax fiber were studied before using it to develop the biocomposite.

Chapter 3 mainly focuses on the synthesis and the characterization of the acrylated epoxidized flaxseed oil (AEFO) resin. The spectroscopic characterization discusses the changes in the unsaturated fatty acid profile of flaxseed oil along with the reaction mechanism. Physical, thermal, and mechanical properties were measured and compared to similar biopolymer values available in the literature.

Chapter 4 compares the developed flaxseed oil-based resin with a commercial biopolymer, PLA, and two commonly used polymers in biocomposite industry, HDPE and PP. All tests were carried out in the same laboratory under the same testing conditions to give a true comparison of the properties of the flaxseed oil resin.

Chapter 5 explains the development and the molding procedure of the flaxseed oil resin-based biocomposite. The flax fiber was chemically treated and characterized for the biocomposite development. The morphological changes were studied via SEM images of the untreated and chemically treated flax fiber. The physical, thermal, and mechanical properties were measured and compared to similar biopolymer values in the literature.

Chapter 6 discusses the development of different biocomposites using PLA, HDPE, and PP with flax fiber and compares them with a flaxseed oil resin-based biocomposite. The interaction of flax fiber with the flaxseed oil resin and different polymers was studied and discussed. The physical, thermal, and mechanical properties of different biocomposites were measured and compared.

Chapter 7 summarizes the entire thesis and states the main conclusions drawn from the results discussed in preceding chapters. Important recommendations for future studies on flaxseed oil resin and biocomposite applications are also given in this chapter.

## Chapter 2

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### 2. Characterization of Flaxseed Oil and Flax Fiber

#### 2.1 Chapter Overview

In this chapter, the main raw materials (flaxseed oil and flax fiber) used in this research are characterized. This chapter also contains manuscript #1 (*Spectroscopic characterization of flaxseed oil for biopolymer application, (submitted and in review)*). Spectroscopic characterization of flaxseed oil was necessary to understand its fatty acid profile. The plant oil content varies due to growing and extraction conditions. An appropriate polymerization method was selected based on the characterization results and literature review. It was important to characterize the flax fiber used to develop the flaxseed oil resin-based biocomposite.

The contributions of this chapter to the overall study are twofold: i) to meet objective 1 through spectroscopic characterization and determination of the potential double bond sites in the flaxseed oil and; ii) to characterize the other raw material flax fiber to be used in biocomposite development.

The PhD candidate's contribution to manuscript #1 were: a) sample preparation and performing the spectroscopic tests of the flaxseed oil via  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and FTIR techniques, b) generating the graphical results of  $^1\text{H}$ NMR,  $^{13}\text{C}$  NMR and FTIR techniques, and c) writing the paper and replying to reviewers' comments.

References for this chapter are presented in the references section of the thesis.

## 2.2 Abstract

Flax is harvested for its oil and fiber. Flaxseed oil contains high levels of unsaturated fatty acids. The unsaturated fatty acids profile in flaxseed oil can be studied via hydrogen nuclear magnetic resonance spectroscopy ( $^1\text{H}$  NMR), carbon nuclear magnetic resonance spectroscopy ( $^{13}\text{C}$  NMR), and Fourier transform infrared spectroscopy (FTIR). The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra quantify and characterize the unsaturated fatty acids (linolenic, linoleic and oleic) present in the oil. The integration values of the peaks of different groups present—such as terminal methyl group, allylic, and bis-allylic protons—help in determining and quantifying the amount of linolenic, linoleic, and oleic acid present in the flaxseed oil. The  $^1\text{H}$  NMR spectra showed that the flaxseed oil contains 54% (w/w) linolenic acid (C18:3), which coincides with the fatty acid profile of the flaxseed oil. The FTIR spectra showed the peaks for the double bond  $=\text{C}-\text{H}$ ,  $\text{C}=\text{O}$  and  $\text{C}=\text{C}$  stretching at  $3012\text{ cm}^{-1}$ ,  $1746\text{ cm}^{-1}$ , and  $1654\text{ cm}^{-1}$  respectively. The  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and FTIR spectra provided a complete fatty acids profile of the flaxseed oil.

Flax fiber contains high amounts of cellulose and low amounts of hemicellulose and lignin. The density of flax fiber was found to be  $1.46\text{ g/cm}^3$ . Below  $300\text{ }^\circ\text{C}$ , there was only one exothermic peak observed in the DSC curve of the flax fiber, which can be attributed to the degradation of lignin or hemicellulose.

## 2.3 Introduction

Flax (*Linum usitatissimum* L.) is one of the oldest oilseed crops grown in Western Canada, mostly in Saskatchewan and Manitoba. In many regions of the world, flaxseed oil is commonly called linseed oil (Zhang et al., 2008). Flaxseed oil contains unsaturated

long fatty acids, and it oxidizes quickly when exposed to air. Flaxseed oil has been studied and used by various researchers and industries for its drying characteristics (Zhang *et al.*, 2008; Savoie *et al.*, 2008; Mallegol *et al.*, 2007). Several researchers have studied biopolymers derived from various natural sources, such as cellulose starch, plant oils, and sugar, for developing materials that can be a sustainable alternate source for plastic. Plant oils from such crops as soybean, corn, linseed, sesame, castor, walnut, sunflower, and safflower have been studied for developing different grades of biopolymers (Sharma and Kundu, 2006; Nayak, 2000; Khot *et al.*, 2001; Guner *et al.*, 2006).

Most plant oils contain mainly triglyceride molecules with different amount of unsaturated fatty acids (Khot *et al.*, 2001; Guner *et al.*, 2006; Wool and Sun, 2005). Triglyceride is an ester product that is comprised of three fatty acids connected at a glycerol juncture. The carbon length of triglycerides varies from 14 to 22 and has 0 to 3 double bonds (Khot *et al.*, 2001; Wool and Sun, 2005). Triglyceride oils have been mainly used in inks, coatings, paints, lubricants, plasticizers, and other agro-chemical applications (Khot *et al.*, 2001; Guner *et al.*, 2006; Wool and Sun, 2005). Along with the polymerization process, the fatty acid profile of a triglyceride-based plant oil is an important influencing factor on the chemical and physical properties of the resulting biopolymer.

Analytical methods such as FTIR,  $^{13}\text{C}$  NMR and  $^1\text{H}$  NMR have been widely used to characterize and study the chemical microstructure of natural oils (Nayak, 2000; Khot *et al.*, 2001; Guner *et al.*, 2006; Nicolau *et al.*, 2009; Sharma and Kundu, 2008; Blayo *et al.*, 2001; Li and Larock, 2000; Sharma *et al.*, 2008; Knothe and Kenar, 2004; Gullen and

Ruiz, 2001; Gullen and Ruiz, 2003; Gunstone, 1993). Gas chromatography has also been used to determine and analyze fatty acids (Eder, 1995; Jalali-Heravi and Vosough, 2004). Several researchers have studied  $^1\text{H}$  NMR spectra to determine the fatty acid profile of vegetable oils (Fauhl *et al.*, 2000; Knothe and Kenar, 2004; Gullen and Ruiz, 2001).

Natural fiber mainly contains cellulose, hemicellulose, lignin, and small traces of pectin and waxes. The composition of flax fiber plays a significant role in determining fiber strength and durability. Fiber analysis can determine the flax fiber composition. To select the molding technique and processing conditions of the biocomposite, knowledge of the thermal properties of the fiber is important. Thermally degraded fiber can produce a biocomposite with poor physical and mechanical properties.

In this chapter, flaxseed oil composition was analyzed using  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and FTIR to identify the potential sites for the polymerization process. A fiber analyzer was used to examine the composition of the flax fiber. Density and thermal properties of the flax fiber were also measured.

## **2.4 Materials and Methods**

### **2.4.1 Materials**

This study used Saskatchewan-grown, 100% cold-pressed flaxseed oil from Herbal Select and 99% pure flax fiber. The flax fiber used in this research was provided by Biolin Research Inc. (Saskatoon, SK, Canada). Deuterated chloroform ( $\text{CDCl}_3$ ) used for  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR analysis was bought from Sigma Aldrich (St. Louis, MO, USA); for the FTIR study, barium fluoride ( $\text{BaF}_2$ ) windows were purchased from ISP Optics (NY, USA).

#### 2.4.2 Characterization of flax fiber and flaxseed oil

The flaxseed oil fatty acid profile was studied via  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and FTIR spectra. The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were obtained using a Bruker 500 MHz Avance Spectrometer at the Saskatchewan Structural Sciences Centre, Saskatoon, Canada. Samples were prepared by dissolving 10-20 ml of oil in 0.4-0.5 ml of deuterated chloroform ( $\text{CDCl}_3$ ). The chemical shifts in  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra are given in ppm. FTIR spectra were obtained using a Bruker 66v/S spectrometer at Canadian Light Source, Saskatoon, Canada. A thin layer of oil (approximately 7-8 micron in thickness) was obtained by placing a drop of flaxseed oil between two  $\text{BaF}_2$  windows and the spectra were obtained in scanning range of  $600\text{-}4000\text{ cm}^{-1}$  for 16 scans.

The composition of the flax fiber was determined by a fiber analyzer (ANKOM Technology, Fairport, NY, USA). The cellulose, hemicellulose, and lignin content in the flax fiber were determined by the following equations:

$$\text{Lignin (\% dry matter)} = ADL \quad (2.1)$$

$$\text{Cellulose (\% dry matter)} = ADF - ADL \quad (2.2)$$

$$\text{Hemicellulose (\% dry matter)} = NDF - ADF \quad (2.3)$$

where:

$ADL$  = acid detergent lignin,

$ADF$  = acid detergent fiber, and

$NDF$  = neutral detergent fiber.

A Galaxy 160D weighing scale (OHAUS Scale Corporation, USA) was used to measure mass ( $m$ ) of the flax fiber samples at room temperature. A gas-operated pycnometer (Quantachrome Corporation, USA), shown in Figure 2.1 was used to measure the volume of the flax fiber samples. A pycnometer is an instrument that measures the true volume of solid materials. This device uses Archimedes' principle of fluid displacement; it measures the pressure difference when a known amount of gas penetrates the finest pores of test material. The volume of a test material was determined by the given equation:

$$V = V_C - V_R \left( \frac{P_I}{P_{II}} - 1 \right) \quad (2.4)$$

where:

$V$  = volume of sample ( $\text{cm}^3$ ),

$V_C$  = volume of sample cell ( $\text{cm}^3$ ),

$V_R$  = volume of reference cell ( $\text{cm}^3$ ),

$P_I$  = pressure reading after pressurizing the reference volume (pa), and

$P_{II}$  = pressure reading after including  $V_C$  (pa).

The density ( $\rho$ ) of the flax fiber samples was determined as mass per unit volume and expressed in grams per cubic centimetre:

$$\rho = \frac{m}{V} \quad (2.5)$$





Figure 2.1 Gas-operated pycnometer

Thermal analysis of the flax fiber and the flaxseed oil was performed using a thermo-analytical technique, DSC, Model Q2000 (TA Instruments, New Castle, DE, USA), shown in Figure 2.2. In this technique, heat flow is measured as a function of time or temperature. Sample weighing between 5 to 10 mg were used for testing different specimens. The DSC system was operated in a dynamic mode with a heating scheme of 40 to 300 °C and heating rate of 10 °C/min. A heat flow versus temperature curve was produced to study the phase transition. The thermograms were then analyzed for any changes in the thermal behaviour of the flax fiber and flaxseed oil.



Figure 2.2 Differential scanning calorimetry (Model Q2000)

## 2.5 Results and Discussion

### 2.5.1 Spectroscopic characterization of flaxseed oil

The signal from different fatty acids present in the flaxseed oil was used to identify and quantify the compounds in the oil via  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra. The main unsaturated fatty acids present in the flaxseed oil were linolenic (C18:3), linoleic (C18:2), and oleic acid (C18:1). The  $^1\text{H}$  NMR spectrum shown in Figure 2.3 confirms the presence of different functional groups. Table 2.1 lists the main compounds present in the flaxseed oil. The peaks indicate that the unsaturated fatty acids are composed of olefinic protons (5.31 ppm), protons attached to *bis*-allylic carbons (2.76 ppm), protons attached to the allylic carbons (2.02 ppm), and protons attached to the terminal methyl group (0.94 ppm and 0.85 ppm). Peaks at 1.2-1.3 ppm indicate the presence of methylene ( $\text{CH}_2$ ) protons, which can be used to determine the saturated fatty acids.  $^1\text{H}$  NMR spectra have

been effectively used to study and quantify the fatty acid profile of a vegetable oil (Knothe and Kenar, 2004; Gullen and Ruiz, 2001). The fatty acid composition of flaxseed oil was determined by the method of integrating the different peaks to giving the area per proton. The following equation was used to determine the main unsaturated fatty acid (C18:3) composition in the flaxseed oil (Knothe and Kenar, 2004):

$$F_{18:3} = I_{\text{exp methyl, 18:3}} / (I_{\text{exp methyl, 18:3}} + I_{\text{exp methyl, rest}}) \quad (2.6)$$

where:

$F_{18:3}$  represent the amount of linolenic acid,

$I_{\text{exp methyl, 18:3}}$  represent the integration value of peak of terminal methyl protons of linolenic acid determined experimentally,

$I_{\text{exp methyl, rest}}$  represent the integration value of peaks of terminal methyl protons of all other fatty acids determined experimentally.

$^1\text{H}$  NMR spectrum gave the values of  $I_{\text{exp methyl, 18:3}}$  as equal to 0.388 and  $I_{\text{exp methyl, rest}}$  equal to 0.330. Using equation (2.6),  $F_{18:3}$  content was determined to be 54%. This value of linolenic acid matches closely to the known fatty acid composition of flaxseed oil (Sharma and Kundu, 2006).

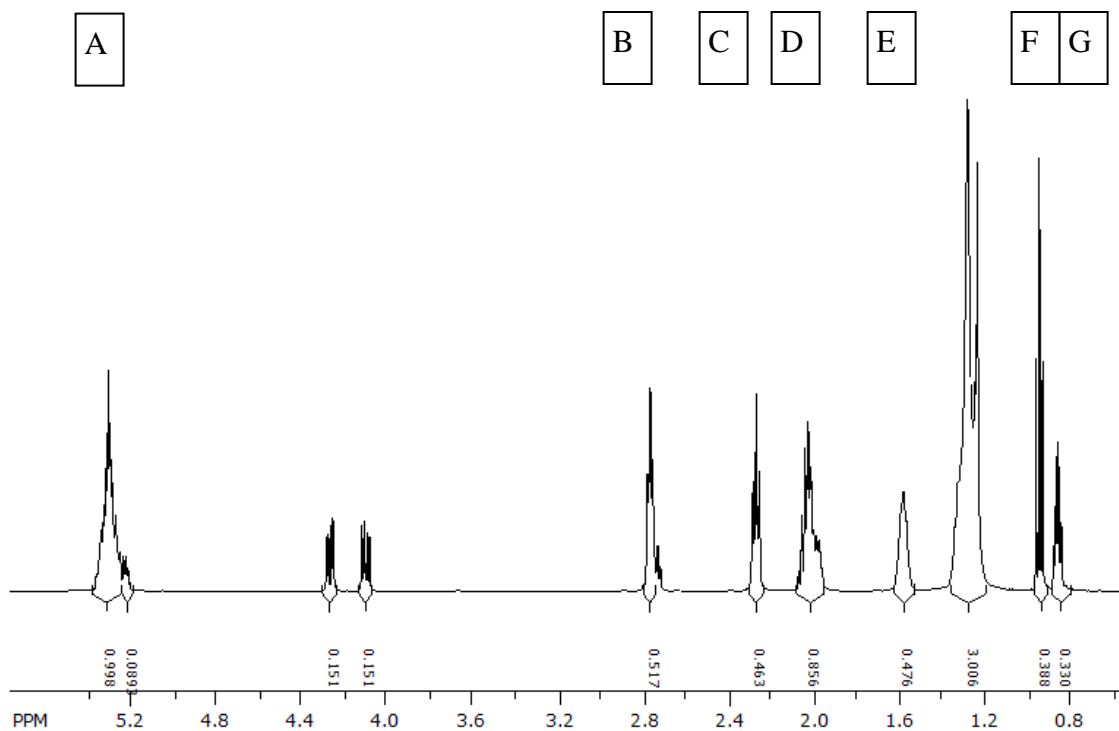


Figure 2.3 Measured <sup>1</sup>H NMR spectra of flaxseed oil with integration values

Table 2.1 Chemical shifts and assignment of main resonances in the <sup>1</sup>H NMR spectra of flaxseed oil

Peak	Chemical shift (ppm)	Functional group
A	5.31	-CH=CH-
B	2.76	-CH=CH-CH <sub>2</sub> -CH=CH-
C	2.27	CH <sub>3</sub> OOC-CH <sub>2</sub> -
D	2.02	-CH <sub>2</sub> -CH <sub>2</sub> -CH=CH-
E	1.58	CH <sub>3</sub> OOC-CH <sub>2</sub> -CH <sub>2</sub> -
F	0.94	-CH=CH-CH <sub>2</sub> -CH <sub>3</sub>
G	0.85	-(CH <sub>2</sub> ) <sub>y</sub> -CH <sub>3</sub>

The  $^{13}\text{C}$  NMR spectrum given in Figure 2.4 confirms the presence of unsaturated fatty acids resonating in the frequency region of 127-131 ppm. Figures 2.5 and 2.6 indicate the different unsaturated carbon atoms present in the region of 127-131 ppm and 171.5-174 ppm respectively. The peaks at 128.15 ppm, 128.13 ppm, and 127.70 ppm confirm the presence of linolenic acid; the peaks at 128.02 ppm, 127.84 ppm, 130.02 ppm, and 172.87 ppm confirm the presence of linoleic acid; and the peaks at 172.9 ppm confirm the presence of oleic acid.

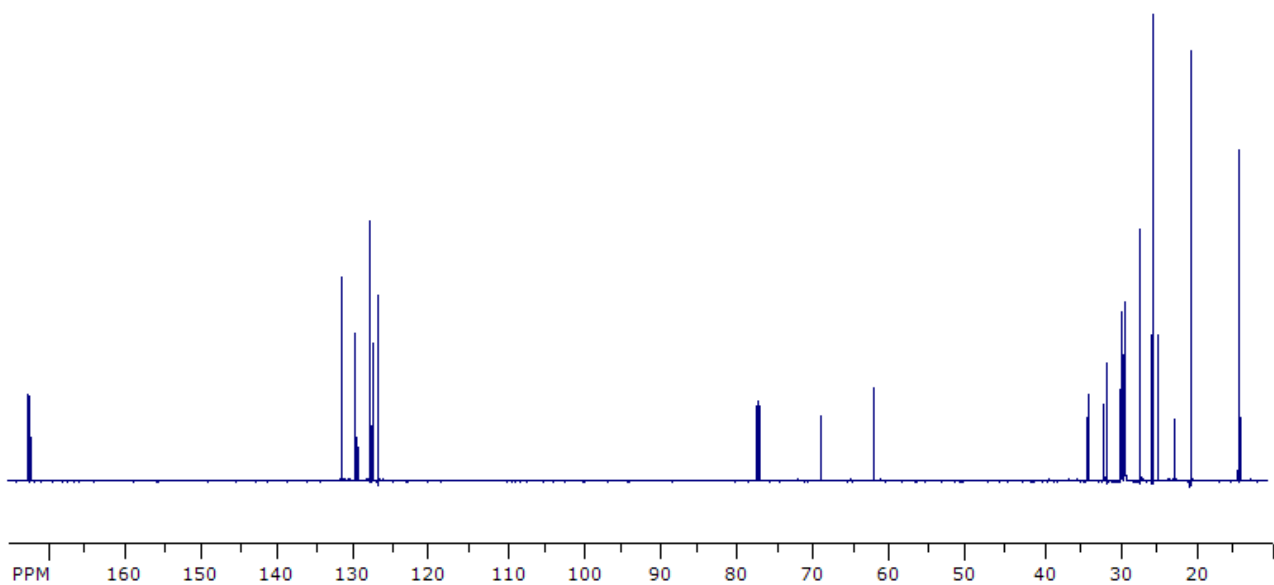


Figure 2.4 Measured  $^{13}\text{C}$  NMR spectra of flaxseed oil

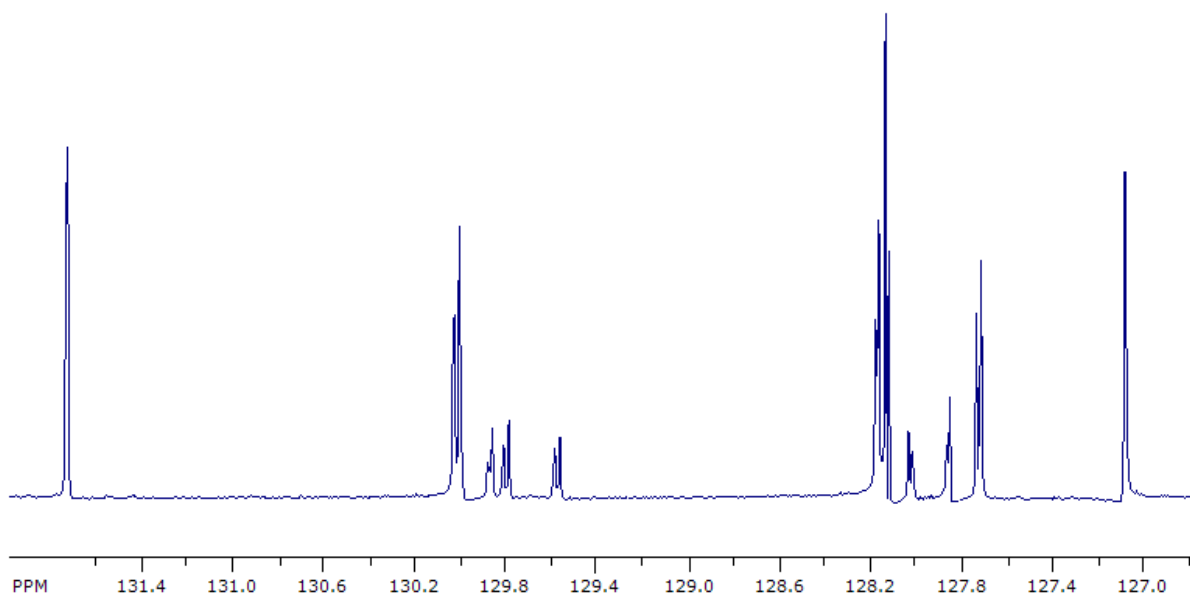


Figure 2.5 Measured <sup>13</sup>C NMR spectra of flaxseed oil for unsaturated carbons (127-131 ppm)

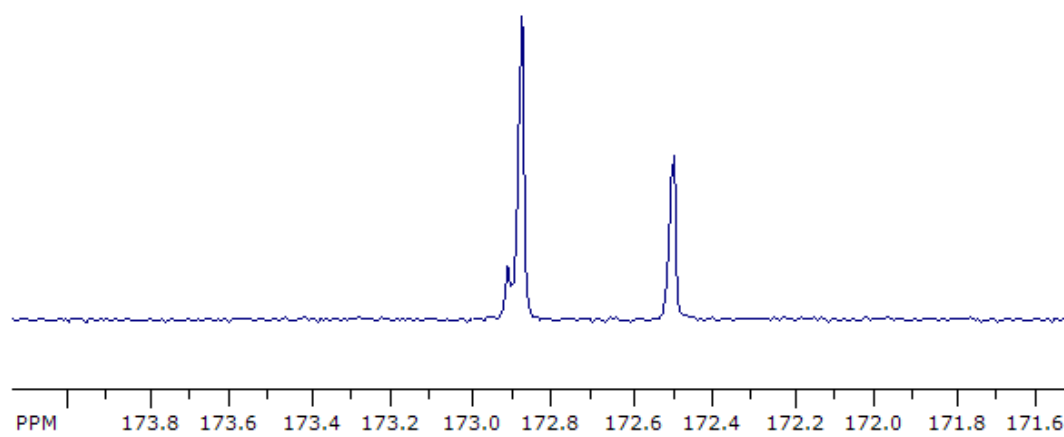


Figure 2.6 Measured <sup>13</sup>C NMR spectra of flaxseed oil for unsaturated carbons (171.5-174 ppm)

The FTIR spectrum of the flaxseed oil is shown in Figure 2.7. The methylene group ( $\text{CH}_2$ ) confirmed the presence of saturated fatty acid, which corresponds to the pair of peaks observed at  $2855$  and  $2927\text{ cm}^{-1}$ . The peak at  $3012\text{ cm}^{-1}$  indicates the double bonds  $=\text{C-H}$ . The  $\text{C=O}$  stretching and  $\text{C=C}$  stretching are at the peaks shown at  $1746\text{ cm}^{-1}$  and  $1654\text{ cm}^{-1}$  respectively.

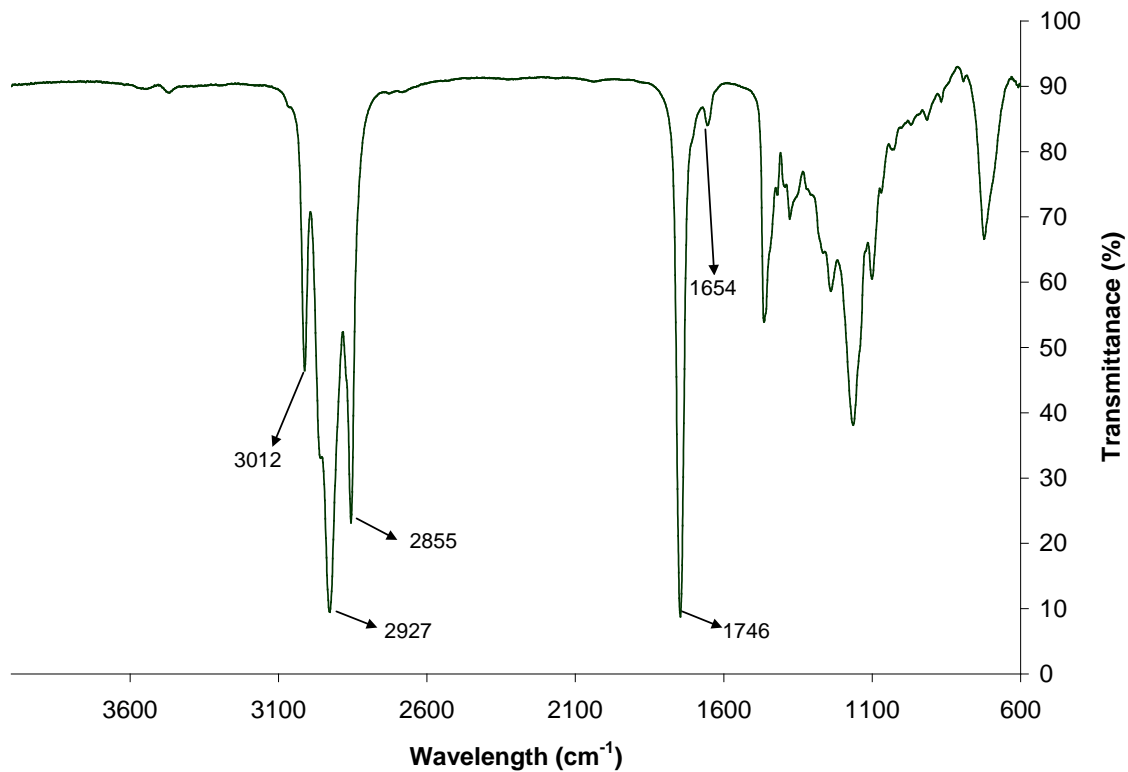


Figure 2.7 Measured FTIR spectra for flaxseed oil

### 2.5.2 Chemical composition of flax fiber

The results of chemical composition analysis are shown in Table 2.2. The flax fiber sample had high cellulose content and low lignin content. Cellulose content imparts high strength to the fiber. Similar flax fiber chemical compositional results were also reported by Sain and Fortierb (2002).

Table 2.2 Chemical composition of flax fiber

	Materials	(wt %)
1.	Cellulose	79.0
2.	Hemicellulose	6.1
3.	Lignin	4.2

Cellulose content in the flax fiber can vary from 65% to 87% (Wiener *et al.*, 2003). High cellulose content makes flax fiber one of the strongest natural fibers used in the biocomposite industry. The variation in composition of flax fiber is due to the different varieties of flax crop, the growing conditions, and the processing techniques adapted.

### 2.5.3 Density of flax fiber

The density of natural fiber plays an important role in developing lightweight and durable biocomposite materials. The density of the flax fiber was determined using the described method, and it was found to be 1.46 g/cm<sup>3</sup>. Similar results have also been reported in the literature, with flax fiber reported as having a true density of 1.53 -1.54 g/cm<sup>3</sup> (Baley, 2002). Flax fiber has higher density than some other natural fibers and lower density than common synthetic fibers such as glass fiber (Mohanty *et al.*, 2000).

### 2.5.4 Thermal characterization of flax fiber

The flax fiber was subjected to heat during the DSC test. The thermogram obtained from the DSC test revealed the thermo-chemical activity occurring in the flax fiber during exposure to the heat. Figure 2.8 shows the DSC curve for the flax fiber. Natural fiber's high affinity for water can be verified by the flax fiber DSC curve. The broad endothermic peak shown in Figure 2.8 confirms the presence of water in the flax



fiber. A similar endothermic peak was obtained for hemp fiber at the temperature range of 50 to 175 °C (Aziz and Ansell, 2004).

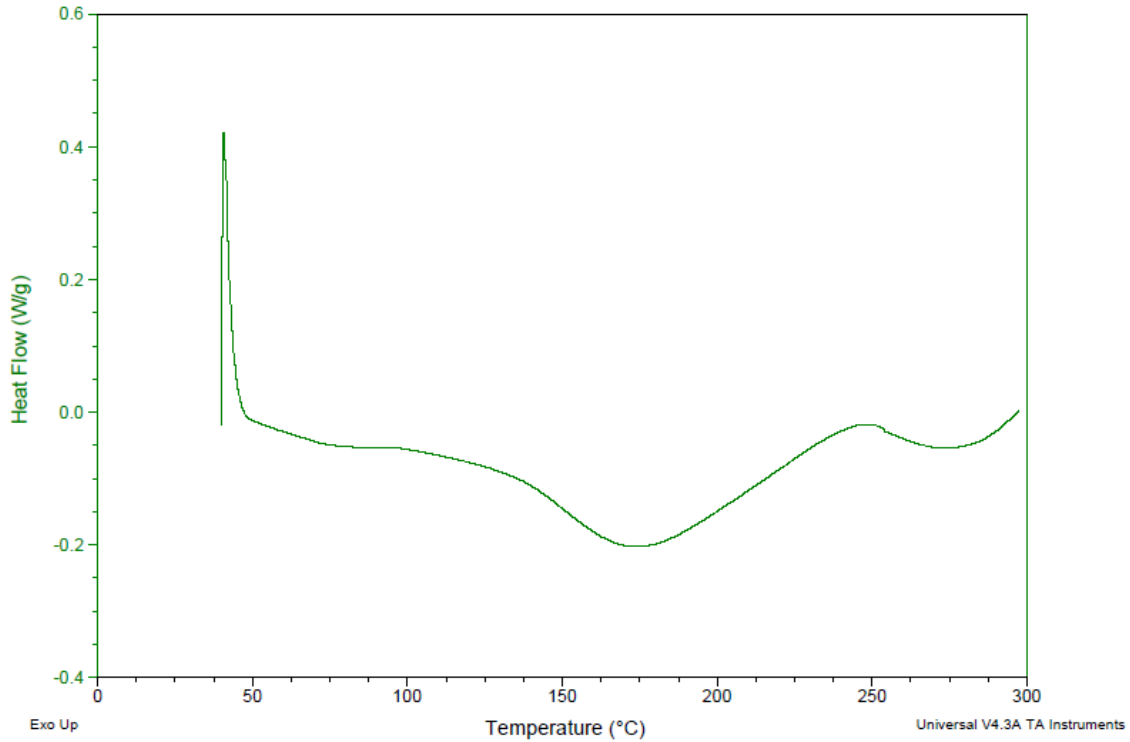


Figure 2.8 DSC thermogram of flax fiber

The degradation of natural fiber is different at temperatures below 300 °C than at temperatures above 300 °C (Van de Velde and Kiekens, 2002). Below 300° C, fiber degradation occurs due to decomposition of  $\alpha$ -cellulose, thermal depolymerisation of hemicellulose, and degradation of lignin (Manfredi *et al.*, 2006; Van de Velde and Kiekens, 2002). In the tested temperature range of 40 to 300 °C, there was only one exothermic peak visible at around 250 °C. This exothermic peak could be due to lignin or hemicellulose degradation in the flax fiber sample. In this research, the flax fiber was

exposed to a maximum temperature of 200 °C during the different biocomposite preparations and the various physical and mechanical tests.

## **2.5 Conclusions**

The fatty acid profile of flaxseed oil was studied using  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectroscopy. The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra confirmed the presence of the following unsaturated acids: oleic, linoleic, and linolenic acids. The flaxseed oil had a high percentage of linolenic acid (54%), which has the highest level of unsaturated carbons. The FTIR spectrum also confirmed the presence of double bond sites, which can be the reaction site for the epoxidation process to start polymerization.

The flax fiber samples contained a high amount of cellulose (79%) and a low amount of hemicellulose (6%) and lignin (4%). The density of the flax fiber was 1.46 g/cm<sup>3</sup>. No degradation occurred in the flax fiber below the temperature of 200 °C, and only one exothermic peak was observed in the range of 40 to 300 °C, at around 250 °C. This exothermic peak can be attributed to the degradation of lignin or hemicellulose present in the flax fiber.

## **2.6 Summary of Chapter 2**

This chapter presents the spectroscopic characterization of flaxseed oil and the composition characterization of flax fiber. It also discusses the density and thermal properties of flax fiber. This characterization of flaxseed oil helped in selection of suitable polymerization technique. The Saskatchewan-grown flaxseed used in this study has high levels of unsaturation, as shown by the linolenic acid content (54%). The

thermal characterization of the flax fiber will help in the selection of process parameters while developing the biocomposite product.

In the next chapter, synthesis and characterization of the acrylated epoxidized flaxseed oil (AEFO) is discussed in detail.  $^1\text{H}$  NMR and FTIR techniques were used to study the change in the fatty acid profile of triglycerides in flaxseed oil, EFO, and AEFO; they also were used to determine the success of each reaction performed.

## Chapter 3

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### 3. Synthesis and Characterization of Acrylated Epoxidized Flaxseed Oil

#### 3.1 Chapter Overview

In this chapter, the synthesis of acrylated epoxidized flaxseed oil (AEFO) is described along with the reaction mechanism. The formation of the epoxy ring after epoxidation process was confirmed by FTIR and <sup>1</sup>HNMR spectra. Further change in fatty acid profile of the triglycerides and formation of the AEFO was also discussed and reported. This chapter contains manuscript # 2 (*Synthesis and Characterization of Acrylated Epoxidized Flaxseed Oil for Biopolymeric Applications. International Polymer Processing. (2015) Vol. 30, No 3, pp. 331-336 (doi: 10.3139/217.2961)*).

The contributions of this chapter to the overall study are twofold: i) to meet objective 2 through development a flaxseed oil-based bio-resin and; ii) to characterize the flaxseed oil-based bio-resin to understand the change in the fatty acid profile and success of each reaction.

The PhD candidate's contributions to manuscript # 2 were: a) performing the synthesis of AEFO in laboratory, b) testing the EFO and AEFO via FTIR and <sup>1</sup>HNMR techniques, c) data processing and generating the graphical results of FTIR and <sup>1</sup>HNMR spectra, and d) writing the paper and replying to reviewers' comments.

References for this chapter are presented in the references section of the thesis.

### 3.2 Abstract

In this study, acrylated epoxidized flaxseed oil was synthesized and characterized by spectroscopic techniques. Triglycerides are the main constituents of flaxseed oil and the carbon-carbon double bond was the reaction site for epoxidation reaction. The flaxseed oil was epoxidized by adding formic acid and hydrogen peroxide. Acrylic acid was then added to produce the acrylated epoxidized flaxseed oil (AEFO). The change in the structure of the fatty acids chain after the epoxidation and the acrylation reactions was studied and characterized by hydrogen nuclear magnetic resonance spectroscopy ( $^1\text{H}$  NMR) and Fourier transform infrared spectroscopy (FTIR). The FTIR spectra of the epoxidized flaxseed oil and the flaxseed oil shows the disappearance of the  $=\text{C-H}$  ( $3012\text{ cm}^{-1}$ ) and  $\text{C=C}$  ( $1654\text{ cm}^{-1}$ ) peaks, and peaks present at  $822$  and  $1244\text{ cm}^{-1}$  confirms the formation of epoxy rings. The FTIR spectra confirmed the formation of AEFO since the presence of hydroxyl group ( $-\text{OH}$ ) was shown by the peak at  $3455\text{ cm}^{-1}$  and the acrylate group ( $-\text{CH}=\text{CH}_2$ ) was indicated by the peaks at  $1406$ ,  $984$  and  $812\text{ cm}^{-1}$ . The changes in peaks of the  $^1\text{H}$  NMR spectra also confirmed the formation of AEFO. The number of acrylate groups per molecule of triglyceride was found to be 2.6 from  $^1\text{H}$  NMR spectra.

### 3.3 Introduction

During the last 38 years, the worldwide consumption of plastic has increased from 50 million tonnes to over 240 million tonnes (Nkwachukwu *et al.*, 2013). The main source of polymers is fossil fuel, which is depleting day by day. Over the last two decades, researchers have been working to identify other renewable sources that could overcome environmental concerns, and provide alternative solution to rising demand and depleting

resources (Dutta *et al.*, 2004). Bio-based polymers have been identified as potential alternative material that can reduce the dependence on fossil fuel (Averous, 2004; Avella *et al.*, 2002; Yu *et al.*, 2006). Various researchers have studied triglyceride-based plant oils as a renewable source for developing several biopolymers (Guner *et al.*, 2006; Averous, 2004; Erhan *et al.*, 2003; Shabeer *et al.*, 2007; Sharma and Kundu, 2006; Nayak, 2000).

Unsaturated fatty acids contain one or more carbon double bonds whereas saturated fatty acids do not have any double bonds (Guner *et al.*, 2006). Most of plant oils contain unsaturated fatty acids that have a chain length of 14 to 22 carbons and have 0 to 3 double bonds per fatty acid (Khot *et al.*, 2001; Wool and Sun, 2005). Triglyceride oils have been used to develop various polymers, such as oxypolymerized oils, polyesters, polyurethane, polyamides, acrylic resins, epoxy resins, and polyesteramides (Guner *et al.*, 2006; Sharma and Kundu, 2006; Nicolau *et al.*, 2009). These polymers are mostly used to produce coatings, plasticizers, and lubricants (Guner *et al.*, 2006; Khot *et al.*, 2001; Wool and Sun, 2005). It has been reported that synthetic lubricants and esters can be replaced by plant oil such as rapeseed and sunflower oils (Wu *et al.*, 2000; Asadauskas *et al.*, 1996; Randles and Wright, 1992). Linseed oil along with sunflower oil and castor oil has also been used to develop polyurethane for paint formulation (Guner *et al.*, 2006).

Different plant oils such as soybean, linseed, corn, castor, sesame, sunflower, safflower, and walnut oil have been used for biopolymers development (Guner *et al.*, 2006; Sharma and Kundu, 2006; Nayak, 2000; Khot *et al.*, 2001). However, extensive research has only been done on soybean and corn oil (Guner *et al.*, 2006; Sharma and Kundu, 2006; Khot *et al.*, 2001; Wool and Sun, 2005; Li and Larock, 2000; Li *et al.*,

2001; Li and Larock, 2001, Li and Larock, 2002; O'Donnell *et al.*, 2004; La Scala and Wool, 2005; Lu and Wool, 2008). Many researchers have investigated the soybean oil because of its abundant availability and high levels of unsaturated fatty acids (Sharma and Kundu, 2006). Similar to soybean oil, the flaxseed oil also contains mostly unsaturated fatty acid having one or more carbon double bond (88-92%) and low amounts of saturated fatty acid (7-12%) (Sharma and Kundu, 2006; Khot *et al.*, 2001; Boquillon and Frignant, 2000). Typically the unsaturated fatty acid composition in the flaxseed oil is about 21% oleic (18:1), 17% linolenic (18:2) and 54% linolenic acid (18:3). The carbon-carbon double bonds are the main reaction sites in the plant oils during different polymerization reactions (Wool and Sun, 2005).

Most plant-based bio-resins are synthesized via a process known as epoxidation (Kiatsimkul *et al.*, 2008; Guo *et al.*, 2000; Petrovic *et al.*, 2000). This process enhances the conversion rate of polymerization over direct methods. The epoxidation reaction is usually carried out by mixing plant oils with hydrogen peroxide and low concentrations of acetic or formic acid. The hydrogen peroxide acts as an oxygen donor and the acid as an oxygen carrier during epoxidation (Dinda *et al.*, 2008; Goud *et al.*, 2006). In this reaction, a three-member ring known as epoxide or oxirane is formed when oxygen is added to the carbon-carbon double bond compound (McMurray, 2007).

Epoxidized soybean oil resin has been studied for use in natural fiber based biocomposites (Khot *et al.*, 2001; Liu *et al.*, 2002; Liu *et al.*, 2006). Thermoset resins have also been developed by polymerizing the epoxidized oil with styrene (Li and Larock, 2000; Li *et al.*, 2001; Li and Larock, 2001, Li and Larock, 2002). The literature shows that adding acrylic acid to the epoxidized oil to produce acrylated epoxidized oil

improves several properties of the resin (Tanrattanakul and Saithai, 2009; Saithai *et al.*, 2011). Acrylated epoxidized soybean oil (AESO) resin had been reported as a suitable alternative to petroleum-based resin (Behera and Banthia, 2008). AESO has also been successfully investigated to develop coating that was cured by UV (Habib and Bajpai, 2011). The acrylate double bonds present in the acrylated epoxidized oil can be polymerized with styrene to produce strong thermoset resin using a free radical initiator. These materials have mechanical properties that are comparable to polyester and vinyl ester resin (Wool *et al.*, 2000; Lu and Wool, 2005). The fatty acid profiles of the plant oil, epoxidized oil and acrylated epoxidized oil have been studied and characterized by different analytical methods, such as  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, GC, and FTIR (Guner *et al.*, 2006; Sharma and Kundu, 2006; Li and Larock, 2000; Saithai *et al.*, 2011; Sharma and Kundu, 2008; Colak and Kusefoglu, 2007; La Scala and Wool, 2002; Knothe and Kenar, 2004; Guillen, 2001; Gunstone, 1993; Eder, 1995; Jalali-Heravi and Maryam, 2004).

In this research, acrylated epoxidized flaxseed oil was synthesized from flaxseed oil via epoxidation and acrylation reactions. A conventional epoxidation method involving formic acid and hydrogen peroxide were used to produce EFO. The EFO produced was converted to AEFO by adding acrylic acid. The change in flaxseed oil profile during the synthesis of EFO and AEFO was studied and characterized by FTIR and  $^1\text{H}$  NMR techniques.



### **3.4 Materials and Method**

#### **3.4.1 Materials**

Saskatchewan grown flaxseed oil was used in this study. Formic acid (85%), hydrogen peroxide (30% v/v aqueous solution) and ethyl ether were purchased from Fisher Scientific (NJ, USA). Sodium chloride, sodium bicarbonate, and anhydrous sodium sulfate were from EMD Chemical Inc. (Gibbstown, NJ, USA). Acrylic acid was from Sigma-Aldrich (St. Louis, MO, USA). Deuterated chloroform ( $\text{CDCl}_3$ ) used for  $^1\text{H}$  NMR tests was bought from Sigma-Aldrich (St. Louis, MO, USA). Barium fluoride ( $\text{BaF}_2$ ) windows (BF-W-25-1, dimension of 25.4 mm diameter and 1 mm thickness) were purchased from ISP Optics, (NY, USA) for the FTIR studies.

#### **3.4.2 Characterization of acrylated epoxidized flaxseed bio-resin**

FTIR spectra were obtained using a Bruker 66v/S spectrometer at the Canadian Light Source, Saskatoon, Canada. A thin layer of oil (approximately 7-8 micron in thickness) was obtained by placing a drop of flaxseed oil between two  $\text{BaF}_2$  windows and the spectra were obtained in scanning range of  $600\text{-}4000\text{ cm}^{-1}$  at  $4\text{ cm}^{-1}$  resolution for 16 scans for each sample. Opus 6.5 software (Bruker opticsinc., Billerica, MA) was used to collect and analyze the FTIR data.

The  $^1\text{H}$ NMR spectra were obtained using a Bruker 500 MHz Avance Spectrometer at the Saskatchewan Structural Science Centre, Saskatoon, Canada. Samples were prepared by dissolving 10-20 ml of flaxseed oil, EFO and AEFO in 0.4-0.5 ml of deuterated chloroform ( $\text{CDCl}_3$ ) respectively. The chemical shifts in  $^1\text{H}$  NMR spectra are given in ppm. SpinWorks 4.0 was used to analyze the  $^1\text{H}$  NMR data.

### **3.4.3 Synthesis of acrylated epoxidized flaxseed bio-resin**

To produce the acrylated epoxidized flaxseed oil (AEFO) resin, the first step was to epoxidize the flaxseed oil. The flaxseed oil was mixed with formic acid and hydrogen peroxide in a volume ratio of 50:15:45; the flaxseed oil was first mixed with formic acid (85%), and then hydrogen peroxide (30% v/v) was added drop-wise to the solution. The solution was vigorously stirred at 45°C for 18 h using a magnetic stirrer at 200 rpm. This process generated epoxidized flaxseed oil (EFO). The EFO was then dissolved in ethyl ether and washed with saturated sodium bicarbonate solution until a pH of approximately 7 was reached. The mixture was further washed with a saturated sodium chloride solution and dried over anhydrous sodium sulfate. The washing step was to remove the hydrogen peroxide and formic acid remaining in the epoxidized oil (Stauffer, 1996). The oil and water phase was separated using separation funnel. Then the ether was removed by heating the oil to the temperature of 50°C for 10 minutes.

In the second step, the EFO was mixed with acrylic acid in a weight ratio of 1:3 in an Erlenmeyer flask. Excess acrylic acid was added to ensure complete level of acrylation. The mixture of EFO and acrylic acid was stirred at 250 rpm using a magnetic stirrer at a temperature of 75°C for 6 h. It has been reported that adding acrylic acid in aliquots during the acrylation reaction reduces the epoxy homo-polymerization; hence during the acrylation reaction, the acrylic acid was added in aliquots (Wool, 2005).

### 3.5 Results and Discussion

#### 3.5.1 Reaction mechanism of synthesis of acrylated epoxidized flaxseed oil

The reaction mechanism of the epoxidation reaction and acrylation reaction are shown in Figure 3.1 (Wool and Sun, 2005). During the epoxidation reaction, the carbon-carbon double bonds were broken, and oxygen was added to form the oxirane or epoxy ring. Further, when acrylic acid was added to epoxidized flaxseed oil, the epoxy ring opens up, and the acrylate and hydroxyl groups were attached to the triglyceride molecule.

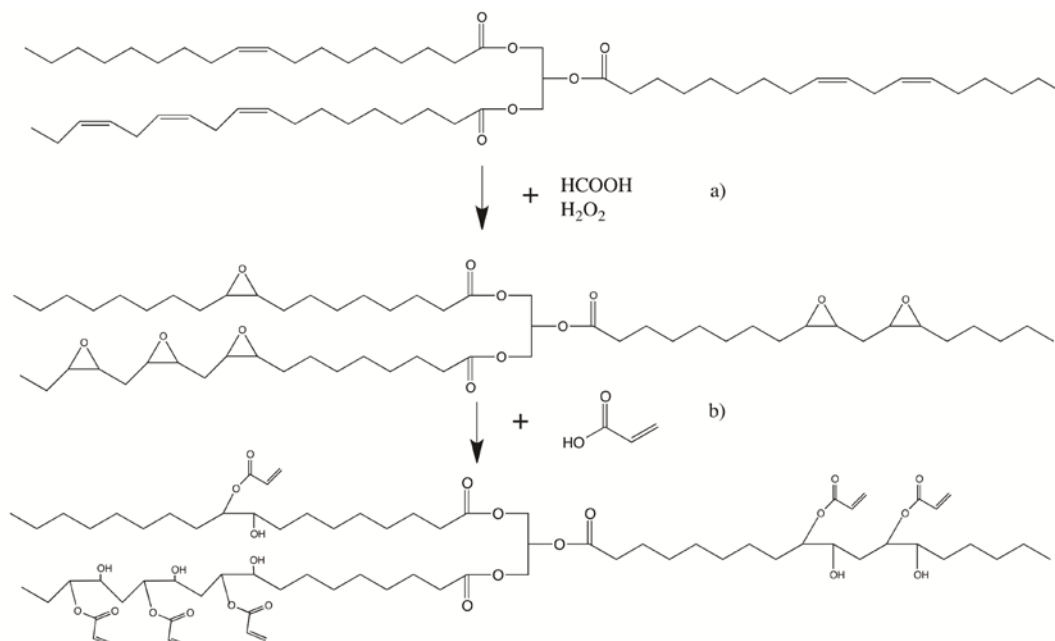


Figure 3.1 a) Epoxidation reaction mechanism b) Acrylation reaction mechanism

#### 3.5.2 FTIR analysis of epoxidized flaxseed oil and acrylated epoxidized flaxseed oil

The flaxseed oil, epoxidized flaxseed oil, and acrylated epoxidized flaxseed oil were characterized via FTIR analysis specifically to examine the change in the structure of the triglyceride molecule. The FTIR spectrum of the flaxseed oil is given in Figure 3.2.

The different functional groups present in the flaxseed oil are shown by the various peaks; the CH<sub>2</sub> group is shown by the pair of peaks observed at 2855 and 2927 cm<sup>-1</sup>; the peak at 3012 cm<sup>-1</sup> is due to the presence of the =C-H group; the C=O stretching and C=C stretching occurs at 1746 cm<sup>-1</sup> and 1654 cm<sup>-1</sup> respectively.

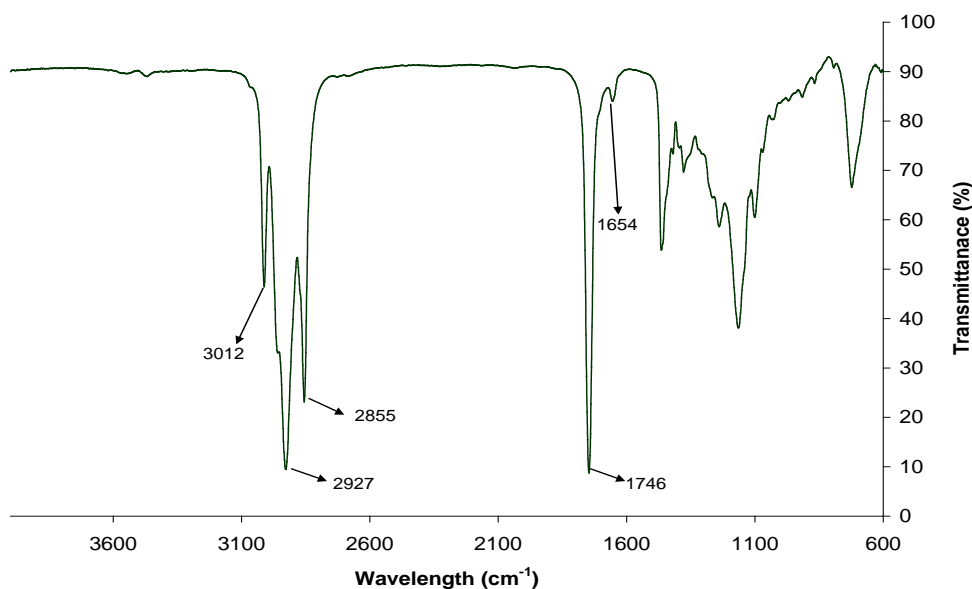


Figure 3.2 Measured FTIR spectra for flaxseed oil

The epoxidized flaxseed oil (EFO) was synthesized by blending the flax oil with formic acid (HCOOH) and H<sub>2</sub>O<sub>2</sub>. This reaction breaks the double bonds of the fatty acid using formic acid. Synthesis of epoxidized soybean oil by a similar scheme has been discussed by Wool and Sun (2005). The FTIR spectrum of epoxidized flax oil is given in Figure 3.3. The FTIR spectra of the EFO and the flax oil (Figures 3.3 & 3.2) were compared to determine the change in the structure of the unsaturated fatty acids of the triglyceride molecule. The double bond peaks at =C-H (3012 cm<sup>-1</sup>) and the C=C stretching (1654 cm<sup>-1</sup>) present in flaxseed oil FTIR spectra (Figure 3.2) disappeared in EFO FTIR Spectra (Figure 3.3). Epoxy rings were formed which was confirmed by the

peaks at 822 and 1244  $\text{cm}^{-1}$  in EFO FTIR Spectra (Figure 3.3). Similar FTIR results have also been reported for flaxseed oil and EFO in preliminary work of this research by Panigrahi and Li (2011). In the literature, absorption peaks at 912 and 881  $\text{cm}^{-1}$  have been reported for confirmation of oxirane in epoxidized soybean oil (Sharma and Kundu, 2008).

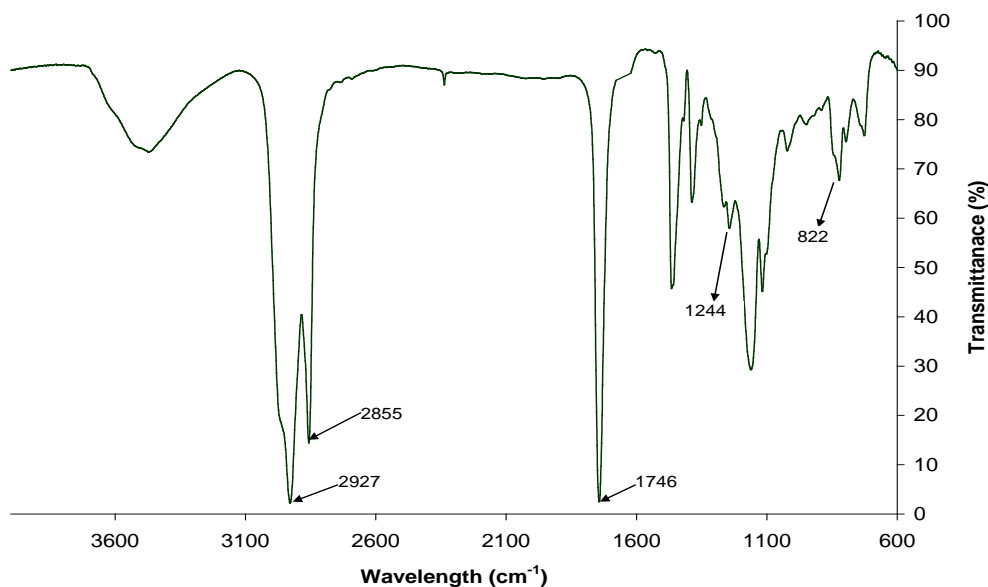


Figure 3.3 Measured FTIR spectra for epoxidized flaxseed oil

The FTIR spectrum shown in Figure 3.4 confirms the formation of AEFO via the peaks at 3455  $\text{cm}^{-1}$  (-OH); the strong absorption band for the carbonyl group (C=O) is shown by the peak at 1730  $\text{cm}^{-1}$ ; and the -CH=CH<sub>2</sub> vibration in acrylate is shown by the peaks at 1406, 984 and 812  $\text{cm}^{-1}$ . The C=C stretching is shown by the peak at 1634  $\text{cm}^{-1}$ .

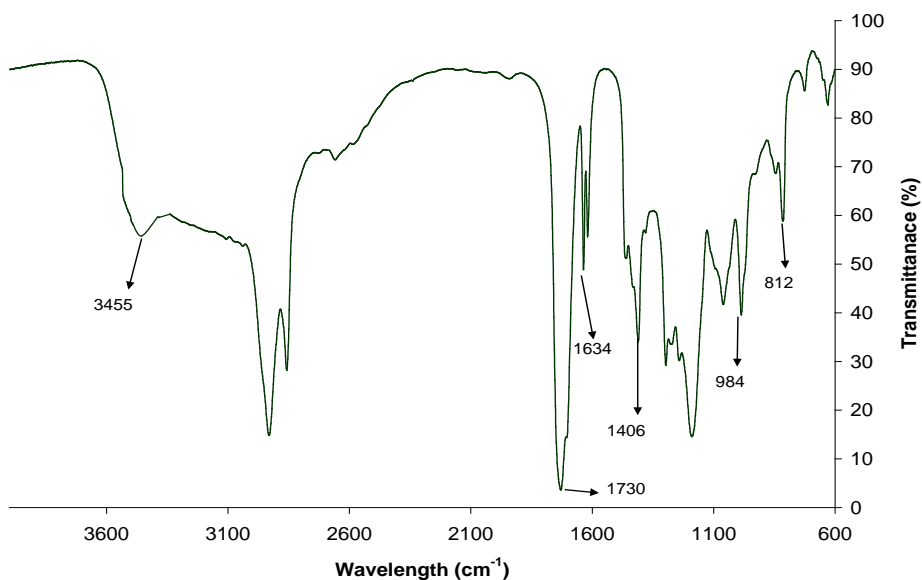


Figure 3.4 Measured FTIR spectra for acrylated epoxidized flaxseed oil

Similar absorption peaks were reported for FTIR spectra of acrylated epoxidized soybean oil polymers (Sharma and Kundu, 2008; Saithai *et al.*, 2013).

### 3.5.3 $^1\text{H}$ NMR analysis of epoxidized flaxseed Oil and acrylated epoxidized flaxseed oil

The structures of epoxidized flaxseed oil and acrylated epoxidized flaxseed oil were also examined by  $^1\text{H}$  NMR spectroscopy. Several researchers have studied different epoxidized oils by  $^1\text{H}$  NMR spectroscopy (La Scala and Wool, 2005; Wu *et al.*, 2000; Dinda *et al.*, 2008; Goud *et al.*, 2006; Behera and Banthia, 2008; Saithai *et al.*, 2011; Meher *et al.*, 2008; Saithai *et al.*, 2013; Espinoza-Perez *et al.*, 2009). The  $^1\text{H}$  NMR spectrum with chemical shift ( $\delta$ ) of epoxidized flaxseed oil is given in Figure 3.5.

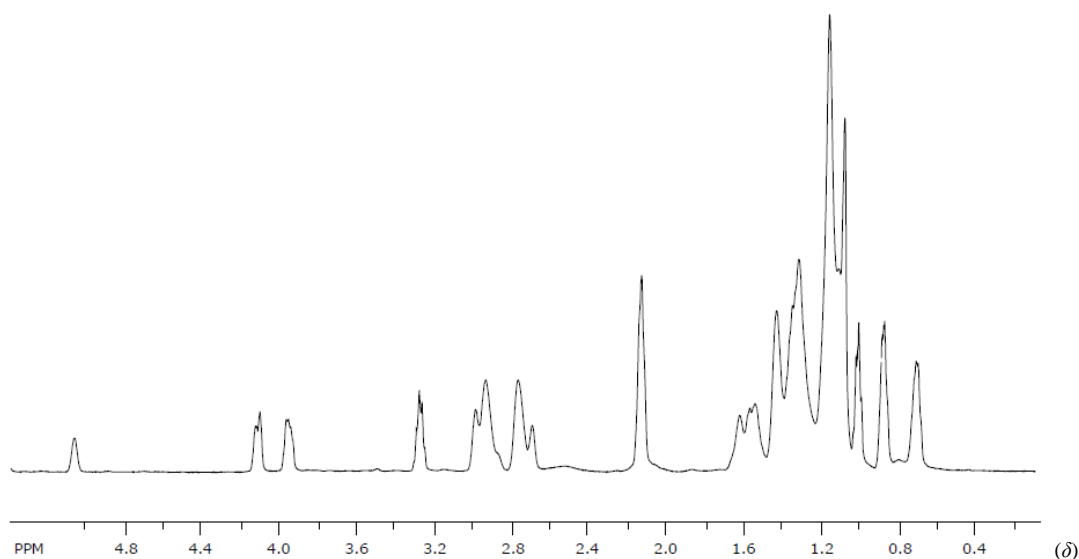


Figure 3.5 Measured  $^1\text{H}$  NMR spectra for epoxidized flaxseed oil

The peaks at  $\delta = 4.0 - 4.4$  ppm represent the glyceride backbone, and the peaks at  $\delta = 2.8 - 3.3$  ppm confirm the formation of epoxy ring (Saithai *et al.*, 2013). The ratio of the intensity of epoxide peaks to the peaks of glycerides gives the value of the number of epoxide groups per molecule, which was found to be 3.7 epoxides per triglyceride molecule.

It has been reported in the literature that epoxidized jatropha oil, canola, linseed, hemp and soybean oil have 3.0, 3.8, 3.4, 5.1 and 2.4 - 4.6 epoxy groups per triglyceride molecule respectively (Meher *et al.*, 2008; Saithai *et al.*, 2013; Espinoza-Perez *et al.*, 2009; Francucci *et al.*, 2013; Lopez Tellez *et al.*, 2009). The peaks at  $\delta = 0.8 - 1.0$  ppm represents the terminal methyl ( $\text{CH}_3$ ) group, and peaks at  $\delta = 1.1 - 1.2$  ppm confirms the methylene ( $-\text{CH}_2$ ) protons. The small peak at  $\delta = 5.1$  ppm indicates that there are small traces of unsaturated fatty acid left in the EFO.

Various researchers have extensively studied the acrylated epoxidized soybean oil (Behera and Banthia, 2008; Lu and Wool, 2005; La Scala and Wool, 2002; Saithai *et al.*,

2013, Lopez Tellez *et al.*, 2009). The  $^1\text{H}$  NMR spectrum with chemical shift ( $\delta$ ) of acrylated epoxidized flaxseed oil is given in Figure 3.6. The  $^1\text{H}$  NMR spectra of EFO (Figure 3.5) and AEFO (Figure 3.6) show that the epoxy ring peaks at  $\delta = 2.8 - 3.3$  ppm were reduced during acrylation reaction and acrylate groups added are indicated by peaks at  $\delta = 5.6 - 6.4$  ppm (Figure 3.6).

These peaks confirm the presence of three protons attached to the C=C of the acrylate esters (La Scala and Wool, 2005; Lu and Wool, 2005; La Scala and Wool, 2002; Francucci *et al.*, 2013). The small peak at  $\delta = 5.1$  ppm indicates that there are small traces of unsaturated fatty acid remaining in the AEFO. The number of acrylate groups per molecule of triglyceride was found to be 2.6. Some of the epoxide groups must have been lost in homo-polymerization.

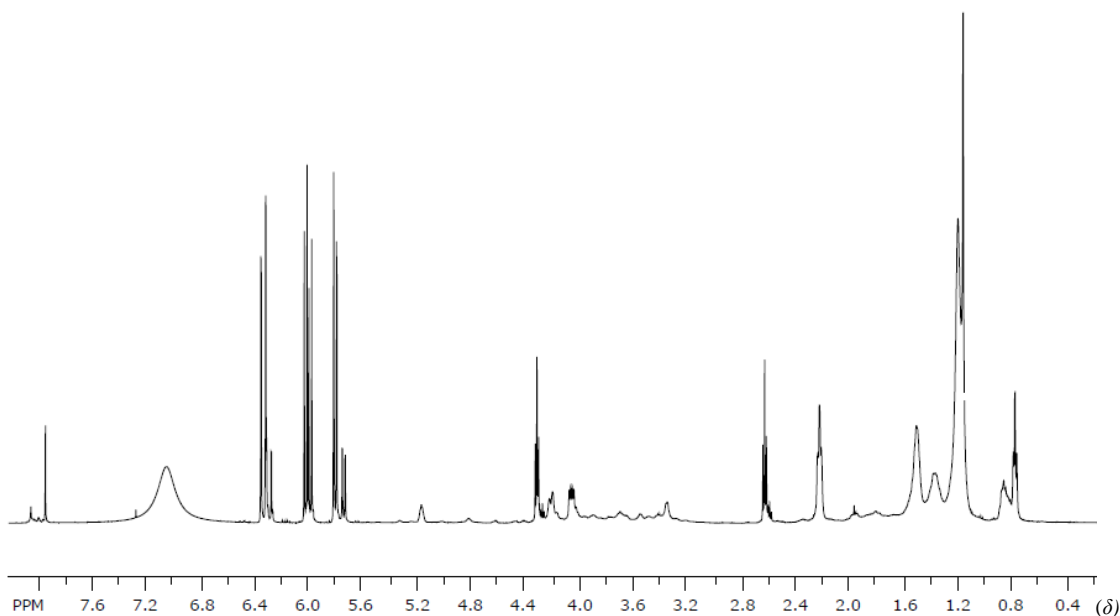


Figure 3.6 Measured  $^1\text{H}$  NMR spectra for acrylated epoxidized flaxseed oil



### 3.6 Conclusions

The acrylated epoxidized flaxseed oil was synthesized via epoxidation and acrylation reactions. The results of FTIR and  $^1\text{H}$  NMR spectra confirm the formation of epoxy rings during epoxidation. It was determined that the epoxidized flaxseed oil has 3.7 epoxy groups per triglyceride molecule. During the acrylation reaction, the epoxy ring breaks, and acrylate and hydroxyl group are added to the molecule. This result is confirmed by the FTIR spectra of the AEFO; the peak at  $3455\text{ cm}^{-1}$  was due to  $-\text{OH}$  group and peaks at  $1406$ ,  $984$  and  $812\text{ cm}^{-1}$  were due to the acrylate group. This is also supported by the  $^1\text{H}$  NMR spectra of the acrylated epoxidized oil that shows peaks at  $\delta = 5.6 - 6.4$  ppm representing the acrylate group, and the epoxide peaks at  $\delta = 2.8 - 3.3$  ppm are diminished which are present in the  $^1\text{H}$  NMR spectra of EFO. Finally, FTIR and  $^1\text{H}$  NMR techniques were able to characterize the change in the triglyceride molecule during different reaction, and hence these are recommended as suitable techniques for future structural/compositional studies of the plant oil based biopolymer characterization.

### 3.7 Summary of Chapter 3

This chapter presents a description of the synthesis of acrylated epoxidized flaxseed oil via epoxidation and acrylation processes. The EFO and AEFO were characterized spectroscopically via FTIR and  $^1\text{H}$ NMR spectra. The change in structure of the triglyceride was shown by the reaction mechanism and confirmed by the peaks in FTIR and  $^1\text{H}$ NMR spectra.

In the next chapter, the characterization of AEFO-based bio-resin is presented. Three more polymer matrices (PLA, HDPE, and PP) were selected for the comparative

study; the physical, thermal and mechanical properties of AEFO bio-resin were compared to those of PLA, HDPE and PP. The test samples for all four polymer matrices were prepared and tested in the Chemical and Biological Engineering Department, University of Saskatchewan.

# Chapter 4

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## 4. Characterization and Comparative Study of Flaxseed Oil Bio-Resin (AEFO) with PLA, PP and HDPE

### 4.1. Chapter Overview

In this chapter, the AEFO resin was molded by the vacuum assisted resin transfer molding (VARTM) process and several physical, thermal and mechanical properties were compared with that of a commercially available biopolymer (PLA) and two of the most commonly used polymers (PP and HDPE). The following properties were examined: density, glass transition temperature, tensile strength, Young's modulus, flexural strength, flexural modulus, and Rockwell hardness. This chapter contains manuscript # 3 (*Characterization and Comparative Study of Flaxseed Oil Bio-Resin with PLA, HDPE and PP. (submitted and in review)*).

The contributions of this chapter to the overall study are twofold: i) to meet objective 3 through measurement of the physical, thermal and mechanical properties of the developed bio-resin and, ii) to meet the objective 4 through comparative analysis of characteristics of AEFO bio-resin with PLA, HDPE, and PP.

The PhD candidate's contributions to manuscript # 3 were: a) developing the VARTM molded test samples using AEFO, b) preparing injection molded test samples for PLA, HDPE and PP matrices, c) conducting the physical, thermal and mechanical tests for all four polymer samples, d) data processing and generating graphical and tabular results of all the test performed, and e) writing the paper and replying to review's comments.

References for this chapter are presented in the references section of the thesis.

## 4.2 Abstract

The developed acrylated epoxidized flaxseed oil resin (AEFO) was compared with the polylactic acid (PLA), high-density polyethylene (HDPE) and polypropylene (PP) for determining its potential application in the polymer industry. The comparison was done by measuring several important physical, thermal and mechanical properties. The density of the AEFO was found to be  $1.166 \text{ g/cm}^3$ , which was lower than that of the PLA and higher than the densities of HDPE and PP. All four polymers showed a minimal mass increase during the water absorption tests (less than 1%). The glass transition temperature ( $T_g$ ) of the AEFO was found to be  $62^\circ\text{C}$ , which was higher than all the other three polymer samples. The AEFO exhibited mechanical properties as follows: tensile strength of  $29.8 \pm 0.1 \text{ MPa}$ , Young's modulus of  $373 \pm 9 \text{ MPa}$ , flexural strength of  $53.5 \pm 1.3 \text{ MPa}$ , and flexural modulus of  $2838 \pm 12 \text{ MPa}$ . The AEFO developed in this research has a tensile strength and Young's modulus higher than that of HDPE and PP, but lower than PLA. The flexural strength and flexural modulus were highest for PLA followed by the AEFO, PP, and HDPE. Rockwell hardness test showed that PLA was the hardest material among the four polymers.

## 4.3 Introduction

Materials developed from renewable resources have been a research focus for more than two decades (Avella *et. al.*, 2002; Averous, 2004; Yu *et. al.*, 2006; Dutta *et. al.*, 2004; Guner *et. al.*, 2006; Sharma and Kundu, 2006). Also, biopolymers are being developed as replacement material for traditional fossil fuel based polymers (Avella *et. al.*, 2002; Averous, 2004; Yu *et. al.*, 2006; Dutta *et. al.*, 2004). These renewable plastics

include materials such as polylactic acid (PLA), poly hydroxyl butyrate, cellulose esters and so on.

Many researchers are working on replacing synthetic fibers such as glass or carbon fiber with natural fibers in composite material. For manufacturing natural fiber reinforced biocomposite, a low processing temperature is required to avoid fiber degradation during different molding processes. Polyethylene (PE) is a thermoplastic used extensively in consumer products; over 80 million tonnes are produced worldwide every year (Piringer and Baner, 2008). It is a suitable polymer for developing biocomposites since it has a lower melting point and lower processing temperatures than other thermoplastics (Van de Velde and Kiekens, 2001). The most common synthetic polymers used in natural fiber reinforced composites are; polypropylene (PP), high-density polyethylene (HDPE), low-density polyethylene (LDPE), and linear low-density polyethylene (LLDPE). These polymers are thermoplastic in nature. Thermoplastics are amorphous and semi-crystalline. They can be used for producing various products depending upon the properties of the different polymers (Strong, 2006).

LDPE has appreciable properties, such as water resistant, resistant to many chemicals except oxidizers and low power factor (Beadle, 1971). LLDPE has noticeable properties such as good impact, flexible, tear, and puncture properties. It has the density and melt index similar to LDPE, and it can be used to produce flexible products such as films (Charrier, 1991). HDPE has several advantages over LDPE, such as it is resistant to several solvents that attacks the LDPE and is also harder and more brittle than LDPE (Beadle, 1971). HDPE and LLDPE have a greater Young's modulus than LDPE (Strong, 2006). HDPE also has good chemical resistance and excellent stiffness over a large range

of temperatures; from 20°C to 100°C (Crawford and Throne, 2000). HDPE is mainly used in the extrusion and blow molding applications. HDPE is used widely in the wood plastic composites.

PP has several desirable properties, such as lightweight, good hardness, high stiffness, stain resistance, heat resistance, chemical resistance, stress-crack resistance, and better dimensional stability. These properties make polypropylene and propylene copolymers a distinct raw material for molding items, such as housewares, electronic parts, automobile parts and accessories, laboratory ware, hospital ware, toys, and sporting goods (Beadle 1971). Thermoplastics, such as PP, PE, polystyrene (PS), and polyvinyl chloride (PVC), are the most common thermoplastics that are workable at low temperatures (Schartel *et al.*, 2003). The glass transition temperature ( $T_g$ ) of the polymer is important during polymer processing since it influences the mechanical properties of the product. The glass transition temperature ( $T_g$ ) also affects other things, such as degree of crystallinity, degree of branching, and length of side chains. Higher  $T_g$  results in higher cross-link density of a polymer, which enhances the mechanical properties as well (Wool and Sun, 2005). Thermally stable polymers have high  $T_g$ .

These fossil fuel based polymers can be replaced by the renewable biopolymers derived from various sources such as plant oil (Averous, 2004). PLA, poly hydroxyl butyrate, cellulose esters, acrylated epoxidized soybean oil (AESO) and maleinized hydroxylated soybean oil (HSO/MA) are some of the renewable plastics that are currently used in some commercial applications (Khot *et al.*, 2001). PLA is a commercially available rigid thermoplastic biodegradable polymer with good mechanical properties

(Vink *et. al.*, 2004; Henton *et. al.*, 2005). It is a cost effective alternative material that can be used in synthetic polymers applications.

Over the past two decades, the triglyceride-based plant oils such as soybean, corn, castor, linseed, sunflower, sesame, walnut, and safflower oil, have been studied as a raw material for the production of different biopolymers (Averous, 2004; Guner *et. al.*, 2006; Erhan *et. al.*, 2003; Shabeer *et. al.*, 2007; Sharma and Kundu, 2006; Nayak, 2000; Khot *et. al.*, 2001). Thermoset resins such as epoxidized triglyceride oil and acrylated epoxidized triglyceride have been copolymerized with the styrene to develop different grades of polymers (Sharma and Kindu, 2006; Esen and Kusefogh, 2003; Wool and Sun, 2005; Hong and Wool, 2005). Rigid Polyurethanes were also been prepared from vegetable oils due to the hydrophobic nature of the triglycerides (Petrovic *et. al.*, 2000; Koprululua *et. al.*, 2008). Several plant oils, such as linseed oil, castor oil, and sunflower oil, have been studied for developing a polyurethane used in paint formulation (Guner *et. al.*, 2006). Hybrid polymers are also being developed by adding a vinyl ester to the acrylated epoxidized soybean oil (Grishchuk *et al.*, 2013; Grishchuk and Karger-Kocsis, 2012). Polymers are also being developed by thermal polymerization using a conjugated linseed oil with acrylic acid, styrene, and divinylbenzene (O'Donnell *et. al.*, 2004). Several linseed oil-based polymers have been developed by oxidative polymerization, cationic photo-polymerization, and thermal polymerization (Sharma and Kundu, 2006; Sharma *et. al.*, 2008).

Soybean based polymers, such as AESO and HSO/MA, have been used with glass, flax, and hemp fibers to develop composites (Khot *et. al.*, 2001). Processes such as resin transfer molding, vacuum assisted resin transfer molding (O'Donnell *et. al.*, 2004),

and sheet molding (Lu and Wool, 2008), have been used to develop composites from plant oil-based polymers.

In the literature, there is very little information on the various physical, thermal and mechanical properties of linseed/flaxseed oil-based biopolymers for biocomposite application. In this research, AEFO resin was developed compared with a commercially available biopolymer (PLA) and two commonly used petroleum-based polymers (PP and HDPE). The following properties of the AEFO bio-resin, PLA, PP and HDPE polymer matrices were measured; density, water absorption characteristics, glass transition temperature, tensile strength, Young's modulus, flexural strength, flexural modulus and Rockwell hardness.

## **4.4 Materials and Method**

### **4.4.1 Materials**

In this study, Saskatchewan grown flaxseed oil was used for the biopolymer development. For comparison, PLA was bought from Jamplast Inc. (Ellisville, MO, USA); HDPE (HD- 8760.29) from Exxon Mobil (Toronto, ON, Canada); and PP (Pro-fax 7823) from Equistar Chemicals LP (TX, USA). Acrylated epoxidized flaxseed oil resin was developed in the Chemical & Biological Engineering Laboratory (U of S, Saskatoon) using the following chemicals: hydrogen peroxide (30% v/v aqueous solution), formic acid (85%) and ethyl ether from Fisher Scientific (NJ, USA); sodium bicarbonate, sodium chloride and anhydrous sodium sulfate from EMD Chemical Inc. (Gibbstown, NJ, USA); and acrylic acid from Sigma- Aldrich (St. Louis, MO, USA).



#### 4.4.2 AEFO, PLA, PP and HDPE sample preparation

To produce the acrylated epoxidized flaxseed oil (AEFO) resin, the flaxseed oil was mixed with the formic acid and hydrogen peroxide in a volumetric ratio of 50:15:45; the flaxseed oil was first mixed with the formic acid, and then hydrogen peroxide was added drop-wise to the solution. The solution was vigorously stirred at 45°C for 18 h using a magnetic stirrer at 200 rpm. This process generated epoxidized flaxseed oil (EFO). To remove any unreacted hydrogen peroxide and formic acid, the EFO was dissolved in ethyl ether and washed with saturated sodium bicarbonate solution until a pH of approximately 7 was reached. The mixture was then washed with a saturated sodium chloride solution and dried over anhydrous sodium sulfate (Guner *et. al.*, 2006). The oil and water phase was separated using a separation funnel; the ether was then removed by heating the epoxidized oil to a temperature of 50°C for 20 minutes.

The EFO was mixed with acrylic acid in a weight ratio of 1:3 in an Erlenmeyer flask. Excess acrylic acid was added to ensure complete level of acrylation. The mixture of the EFO and the acrylic acid was stirred at 250 rpm using a magnetic stirrer at a temperature of 75°C for 6 h. During the acrylation reaction, the acrylic acid was added in aliquots to EFO to eliminate the chances of epoxy homo-polymerization.

After completion of the acrylation reaction, the AEFO-based samples were prepared via vacuum assisted mold and cured at 100°C for 1 h and then post cured at 125°C for 2 h. The cured solid AEFO resin board was cut into the test sample as per ASTM standards for the different tests mentioned in the next section.

The PLA, HDPE, and PP-based test samples were prepared via injection molding process using a standard mold which gives a dog bone shape and other size test specimen

directly. The injection molding machine use to develop the molded sample is shown in Figure 4.1.



Figure 4. 1 Injection molding machine

#### 4.4.3 Characterization of AEFO, PLA, PP and HDPE

Five rectangular samples (approximate dimensions of  $76.2 \pm 0.2$  mm x  $25.4 \pm 0.2$  mm x  $3.2 \pm 0.2$  mm) of each polymer were used to determine the density of the respective polymer after molding. Galaxy 160D weighing scale (OHAUS Scale Corporation, USA) was used to measure the mass ( $m$ ) of the polymer samples at room temperature. A gas-operated pycnometer (Quantachrome Corporation, USA) was used to measure the volumes of the test samples. The density of the polymer samples was determined as mass per unit volume and expressed in grams per cubic centimeter.

The water absorption characteristics were studied using the ASTM D570 test method. Rectangular test specimens (approximate dimensions of  $76.2 \pm 0.2$  mm x  $25.4 \pm 0.2$  mm x  $3.2 \pm 0.2$  mm) were used during the test and the increase in mass after 24 h immersion in water was calculated to the nearest 0.01%.

$$\text{Mass Increase (\%)} = \frac{(M_f - M_i)}{M_i} \times 100 \quad \% \quad (4.1)$$

Where,

$M_f$  = Weight of test samples after 24 h immersion in water (g)

$M_i$  = Initial weight of dry test sample (g)

Thermal analysis of the flax fiber and flaxseed oil was performed using a thermo-analytical technique, DSC (Model Q2000, TA Instruments, New Castle, DE) shown in Figure 2.2. In this technique, heat flow is measured as a function of time or temperature. Samples weighing between 5 to 10 mg were used for testing different specimens. The DSC system was operated in a dynamic mode with a heating scheme of 40 to 300°C and heating rate of 10°C/min. A heat flow versus temperature curve was produced to study the phase transition. The resulting thermograms were studied for changes in the thermal behaviour of the polymer resin.

The test samples were subjected to the tension test described in ASTM D638 using Instron testing machine shown in Figure 4.2. A familiar dog bone type specimen of thickness of  $3.2 \pm 0.2$  mm was machined for the test (shown in Figure 4.3). The test specimens were conditioned at a temperature of  $23 \pm 2^\circ\text{C}$  and relative humidity of  $50 \pm 5\%$  for 40 h prior to the test. The tensile test was performed at a crosshead speed of 5 mm/min for five samples and each test was performed until tensile failure occurred. The tensile strength ( $\sigma_t$ ) was calculated using the following equation:

$$\sigma_t = \frac{F_{\max}}{A} \quad (4.2)$$

Where,

$A$  = the cross-sectional ( $\text{mm}^2$ ), and

$F_{max}$  = maximum load value (N)

Young's Modulus ( $E$ ) was determined using the following equation:

$$E = \frac{\Delta\sigma}{\Delta\varepsilon} \quad (4.3)$$

Where,

$\Delta\sigma$  = change in tensile stress before the material yields

$\Delta\varepsilon$  = change in tensile strain before the material yields



Figure 4.2 Instron testing machine

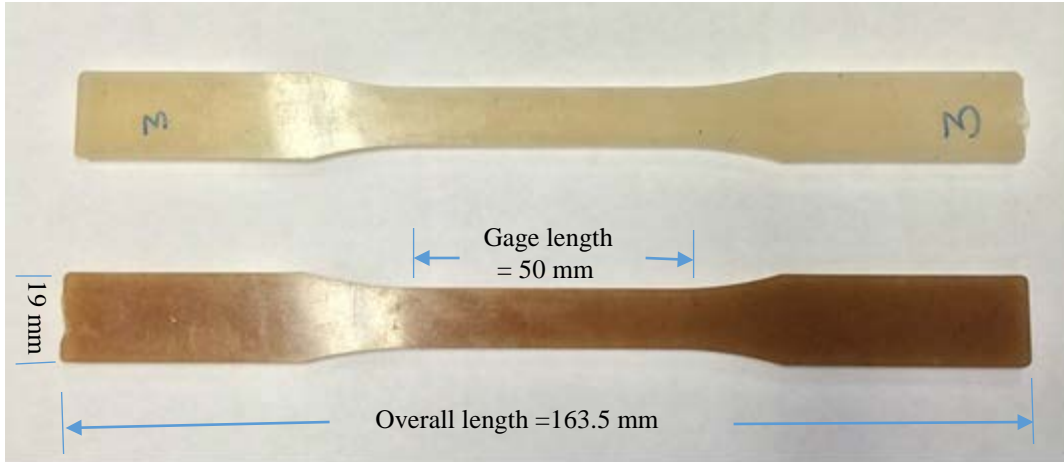


Figure 4.3 Tensile test specimens

The test samples were subjected to the flexural test according to ASTM D790 using Instron testing machine shown in Figure 4.4. Five rectangular cross-section samples of dimension  $64 \pm 0.2$  mm x  $12.7 \pm 0.2$  mm x  $3.2 \pm 0.2$  mm were tested (shown in Figure 4.4). The test specimens were conditioned at a temperature of  $23 \pm 2^\circ\text{C}$  and relative humidity of  $50 \pm 5\%$  for 40 h prior to the test. The test samples behaved as a beam during the test. The flexural strength ( $S$ ) was determined using the following equation:

$$S = \frac{3P'L}{2bd^2} \quad (4.4)$$

Where,

$S$  = flexural strength (MPa),

$P'$  = load (N),

$L$  = length of span (mm),

$b$  = width of specimen (mm), and

$d$  = thickness of specimen (mm).

The flexural modulus was determined using the following equation:

$$E_H = \frac{L^3 s}{4bd^3} \quad (4.5)$$

Where,

$E_H$  = modulus of elasticity in bending (MPa), and

$s$  = slope of the tangent to the initial straight line portion of the load deflection curve (N/mm).

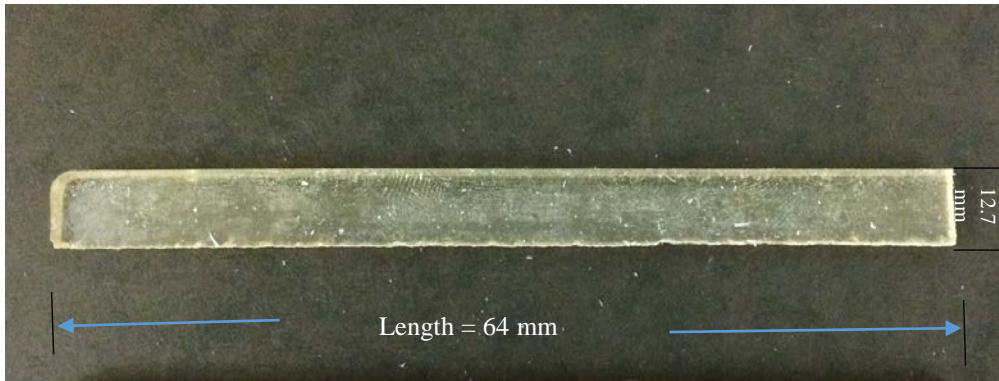


Figure 4.4 Flexural test specimen

The hardness of the test samples was measured by determining the Rockwell hardness number by following ASTM D785. The test specimens of thickness  $6.4 \pm 0.2$  mm, were conditioned at a temperature of  $23 \pm 2^\circ\text{C}$  and relative humidity of  $50 \pm 5\%$  for 40 h prior to the test. A HRLW tester, 60 KGF forces and 1/4" ball indenter was used to evaluate the hardness. The hardness of each sample was reported as an average of ten readings.



Figure 4.5 Instron Rockwell hardness Tester

## 4.5 Results and Discussion

### 4.5.1 Density measurement and comparison

The density of the polymeric resin plays an important role in the development of composite material applications; polymers with low density and high strength are desired in most of the applications. The density of the polymer depends on both composition and the packing arrangement of the chains and branches. Often a higher degree of crystallinity in the polymer makes the density higher. Table 4.1 shows the density of AEFO along with that of PLA, PP, and HDPE. The AEFO density ( $1.166 \text{ g/cm}^3$ ) was found to be higher than that of the PP ( $0.906 \text{ g/cm}^3$ ) and HDPE ( $0.946 \text{ g/cm}^3$ ) but lower than that of the PLA ( $1.189 \text{ g/cm}^3$ ). Properties such as stiffness, hardness and yield point,

increases with crystallinity and density of most of the polymer materials. The tensile and the hardness test results confirm this effect of the density.

Table 4.1 Measured densities of polymer samples

S. No	Polymer Sample	Density (g/cm <sup>3</sup> )
1.	AEFO	1.166 ± 0.004
2.	PLA	1.189 ± 0.003
3.	PP	0.906 ± 0.006
6.	HDPE	0.946 ± 0.004

#### 4.5.2 Water absorption characterization and comparison

Most of the polymer matrices are hydrophobic in nature. Figure 4.6 shows the water absorption characteristics of AEFO, PLA, PP, and HDPE. The water absorption of AEFO was found to be slightly higher than the other three polymers, but it was still less than 1% w/w.

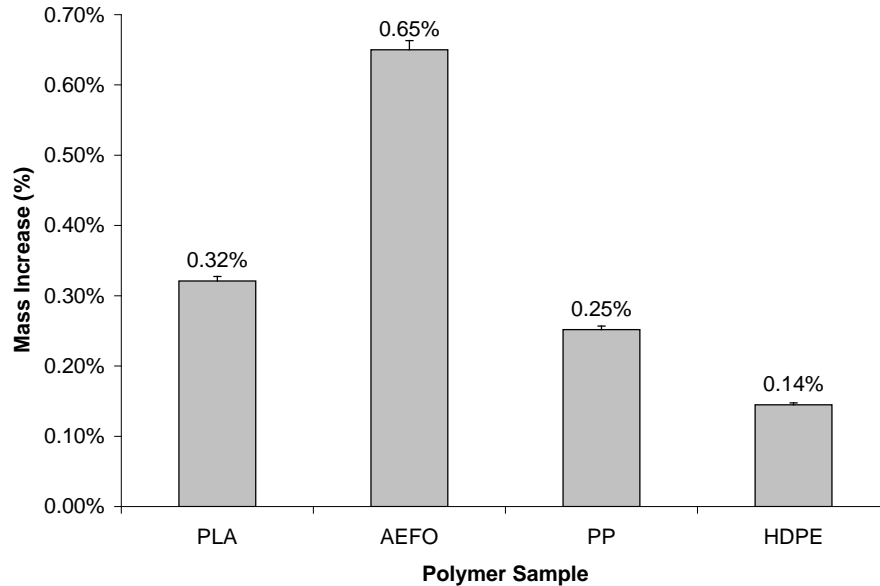


Figure 4.6 Mass increase (wt%) during water absorption test for AEFO, PLA, PP & HDPE polymers samples. The uncertainty presented in the figure is at the 95% confidence level



### 4.5.3 Thermal properties measurement and comparison

Table 4.2 shows the glass transition temperature value of the AEFO, PLA, PP and HDPE. The AEFO has a higher glass transition temperature (62 °C) similar to the PLA (56 °C) compared to the other two polymers (PP,  $T_g = -8$  °C; HDPE,  $T_g = -74$  °C). The higher glass transition could indicate a higher cross-link density; since it has been found in the literature that the glass transition temperature is directly proportional to the cross-link density of a polymer (Wool and Sun, 2005). Polymers with high cross-link density also showed better mechanical properties.

In the literature  $T_g$  for several plant oil-based resins have been reported:  $T_g$  of AESO was at 36.4 °C – 43.6 °C (Fu *et al.*, 2010);  $T_g$  of different conjugated linseed – styrene–DVB-based polymers ranged from 72°C – 120°C;  $T_g$  of soybean oil monoglycerides (SOMGs) was at 135 °C (Kundu and Larock, 2005).

Li and co-workers (2010) developed an AESO resin using acrylation of EFO having different epoxy contents and found that the glass transition temperature of these synthesized polymers is dependent upon the epoxy value; they found that with an increase in the epoxy value, the  $T_g$  also increases.

Table 4.2 Measured thermal properties of polymer samples

S. No	Polymer Sample	Glass Transition Temperature (°C)
1.	AEFO	62
2.	PLA	56
3.	PP	-8
4.	HDPE	-74

#### 4.5.4 Tensile properties measurement and comparison

Most of the thermoset materials are brittle in nature. Figure 4.7 shows the stress-strain behaviour of the AEFO resin during a tensile test. Initially, the stress increase is linear before the sample enters the plastic region. The Young's modulus value was found to be 373 MPa, and the peak of the stress-strain curve gave the tensile strength value of 29.8 MPa. The elongation at break was found to be 9.2 mm. The AEFO resin exhibits some ductility, which is evident from stress-strain graph (Figure 4.7). The ductility of AEFO can be due to the long fatty acid chain of the triglyceride molecules. Sample raw data for AEFO Bio-resin tensile test is given in Appendix B.

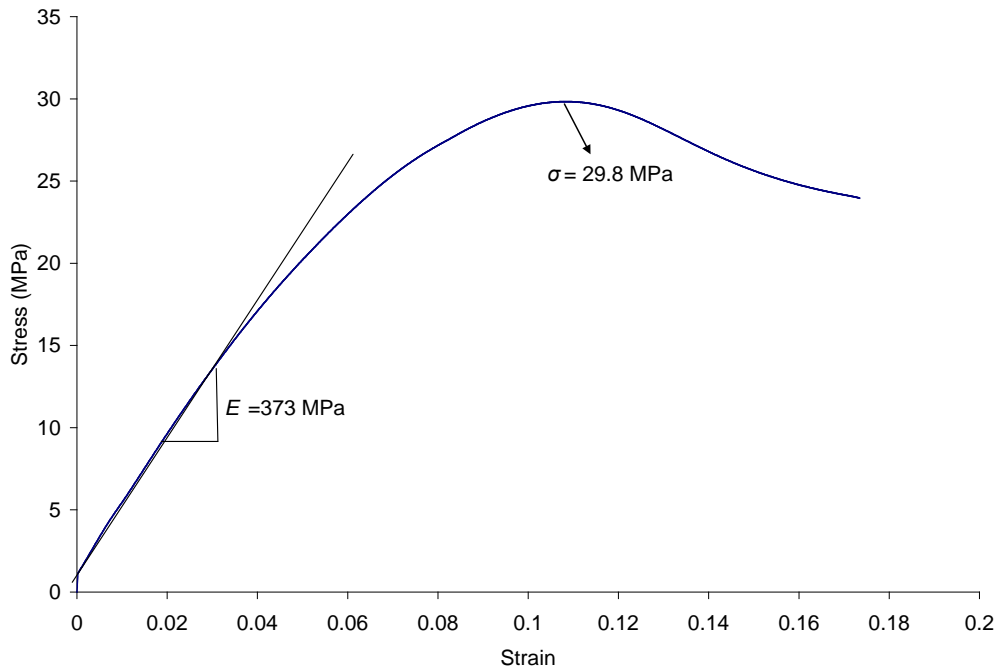


Figure 4.7 Stress-Strain curve of AEFO bio-resin showing AEFO to have some ductility

Figure 4.8 displays the tensile strength of the AEFO compared with the PLA, PP, and HDPE. The tensile strength of the AEFO was 44% lower than that of PLA and 43-47% higher than that of PP and HDPE. The tensile strength of several plant oil-based resin reported in the literature are; for AESO,  $\approx 30$  MPa (Khot *et. al.*, 2000); MAESO, 41-44 MPa (Wool and Sun, 2005); SOMG maleates, 29.36 MPa;

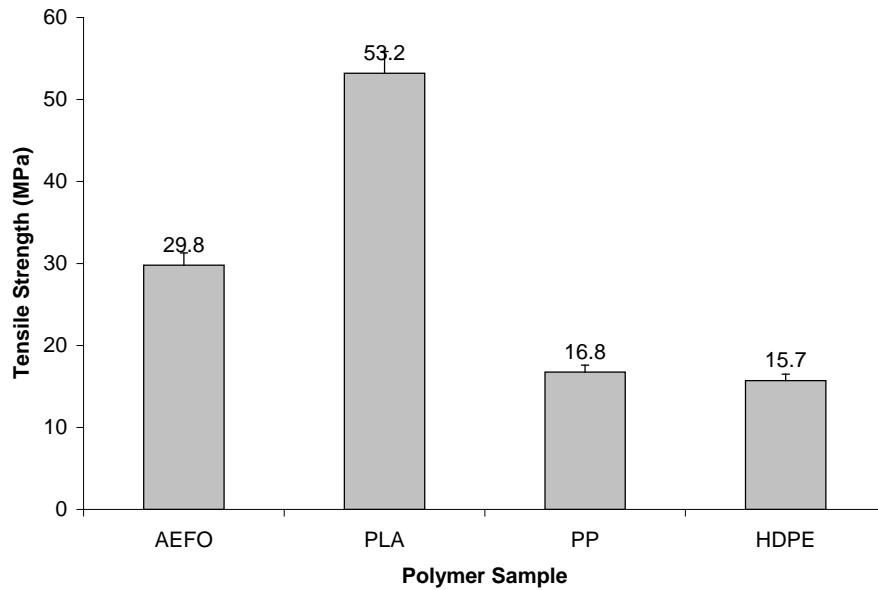


Figure 4.8 Tensile strength of AEFO, PLA, PP & HDPE polymers samples. The uncertainty presented in the figure is at the 95% confidence level.

Thermoset polymers have higher stiffness than the thermoplastic polymer. The Young's moduli of all four polymer resins are shown in Figure 4.9. The modulus of AEFO (373 MPa) was found to be less than that of PP (434 MPa) and PLA (598 MPa), and higher than that of HDPE (316 MPa). To enhance the modulus, styrene can be added to AEFO resin since it has been reported that addition of styrene improves stiffness and impart additional rigidity to the triglyceride-based resin (Fu *et. al.*, 2010). It has also been reported that a lower acrylic content causes rubbery behaviour, and a higher content shows plastic behaviour in AESO resin (Fu *et. al.*, 2010). The Young's modulus of

different conjugated linseed –styrene –DVB-based polymers was reported having a wide range of values (11.7 MPa to 438.1 MPa) (O'Donnell *et. al.*, 2004).

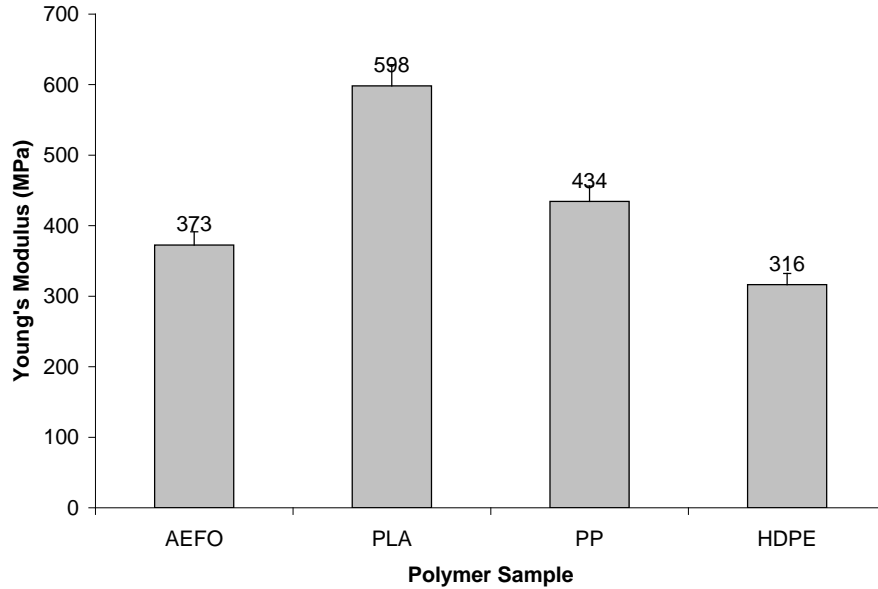


Figure 4.9 Young's Modulus of AEFO, PLA, PP & HDPE polymers samples. The uncertainty presented in the figure is at the 95% confidence level.

#### 4.5.5 Flexural properties measurement and comparison

Figure 4.10 and 4.11 shows the flexural strength and the flexural modulus of the AEFO resin compared to the PLA, HDPE and PP respectively. The AEFO has flexural strength and flexural modulus higher than that of HDPE and PP, but both flexural strength and flexural modulus of the AEFO were lower than that of the PLA. The AEFO (2838 MPa) has a flexural modulus close to that of the PLA (3338 MPa). The AEFO developed in this research showed good flexibility. A similar observation has been reported for the triglyceride oil-based polymer, i.e. AESO; AESO have good flexibility due to the long fatty acid chain (Li *et. al.* 2004).

Flexural strength and modulus of the AEFO and PLA test samples were significantly higher than that of the PP and HDPE due to higher cross-link density.

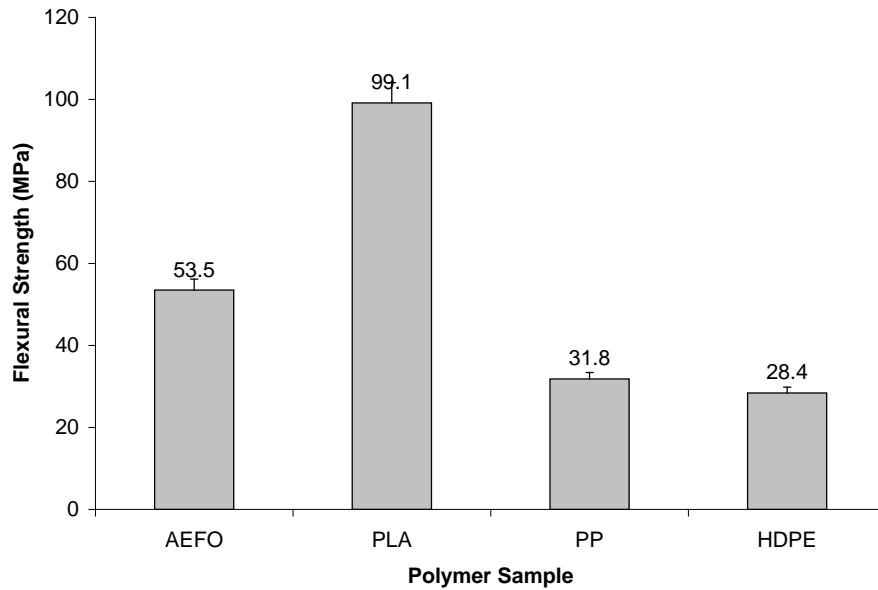


Figure 4.10 Flexural strength of AEFO, PLA, PP & HDPE polymers samples. The uncertainty presented in the figure is at the 95% confidence level.

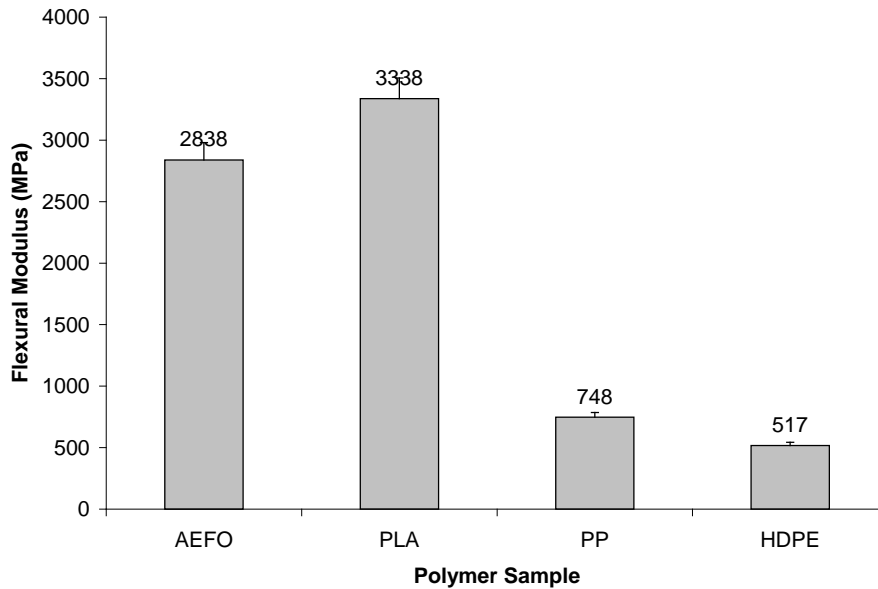


Figure 4.11 Flexural modulus of AEFO, PLA, PP & HDPE polymers samples. The uncertainty presented in the figure is at the 95% confidence level.

#### 4.5.6 Rockwell hardness measurement and comparison

Thermoset resins are usually harder than thermoplastic materials due to a high cross-link density. Lower cross-link density often results in lower hardness (Laskoskie *et al.*, 2006). Compressive stress was induced during the hardness test. Figure 4.12 shows the Rockwell hardness number for the AEFO, PLA, HDPE and PP, and higher hardness number corresponds to the harder material. It was found that both PLA and AEFO have similar hardness. AEFO had significantly higher Rockwell hardness number than those of HDPE and PP.

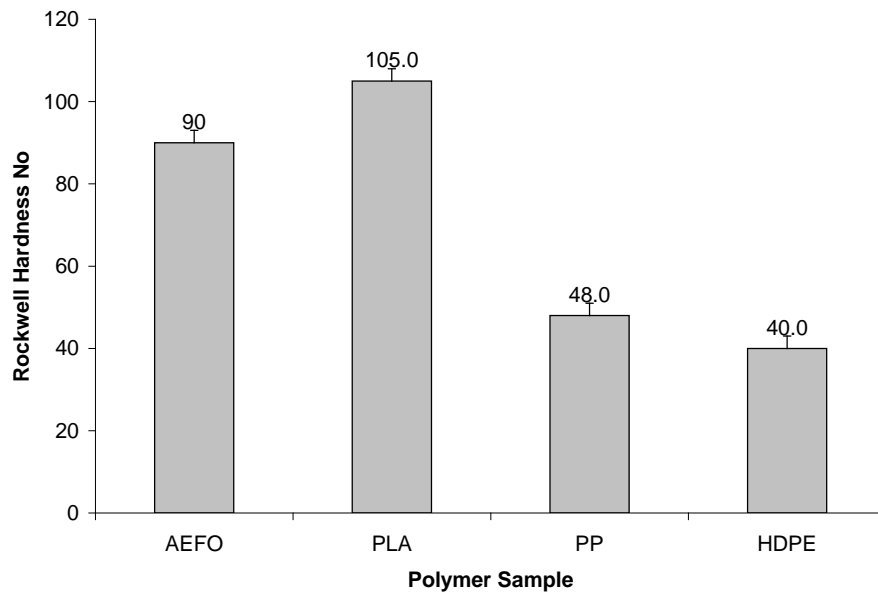


Figure 4.12 Rockwell Hardness of AEFO, PLA, PP and HDPE polymers samples. The uncertainty presented in the figure is at the 95% confidence level.

## 4.6 Conclusions

The acrylated epoxidized flaxseed oil (AEFO) resin synthesized from the flaxseed oil in this study showed comparable physical and mechanical properties. The density of the AEFO resin ( $1.166 \text{ g/cm}^3$ ) was found to be lower than that of the PLA ( $1.189 \text{ g/cm}^3$ ) and higher than both PP ( $0.906 \text{ g/cm}^3$ ) and HDPE ( $0.946 \text{ g/cm}^3$ ). As expected, all the polymers (AEFO, PLA, HDPE, and PP) have low water absorption characteristics with mass increase of less than 1 % w/w. The DSC results showed that AEFO has  $T_g$  of  $62^\circ\text{C}$  indicating a high cross-link density. The results of mechanical properties exhibited by AEFO were: tensile strength of  $29.8 \pm 0.1 \text{ MPa}$ ; Young's Modulus of  $373 \pm 9 \text{ MPa}$ ; flexural strength of  $53.5 \pm 1.3 \text{ MPa}$ ; and flexural modulus of  $2838 \pm 12 \text{ MPa}$ . The tensile strength and the flexural strength of the AEFO were higher than that of the HDPE and PP. PLA was found to be the strongest and hardest polymer amongst the four polymers that were tested.

## 4.7 Summary of Chapter 4

This chapter presents the physical, thermal and mechanical properties of the AEFO bio-resin. These properties were compared to those of PLA, HDPE, and PP matrices. Mass increase percentage during water absorption test was less than 1 % for all polymer matrices. Overall, PLA was found to be the hardness and strongest polymer. However, the AEFO showed significantly higher tensile and flexural properties than PP and HDPE, and comparable properties to that of PLA. The test samples for the AEFO and PLA, PP and HDPE were molded and tested in Chemical and Biological Engineering Department, University of Saskatchewan.

In the next chapter, the development of flax fiber reinforced biocomposites using the AEFO resin is presented. The role of flax fiber and AEFO in the biocomposite was studied by measuring the main physical and mechanical properties of the biocomposites. In this phase of research, styrene was also added to enhance physical and mechanical properties of the biocomposite. The detailed discussion about the impact of flax fiber and styrene on various properties of resulting biocomposite is also presented in the next chapter.



## Chapter 5

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### 5. Development and Characterization of Flax Fiber Reinforced Biocomposite using Flaxseed Oil Bio-Resin

#### 5.1 Chapter Overview

In this chapter, the acrylated epoxidized flaxseed oil-based resin developed in this research was used to produce flax fiber reinforced biocomposites. This chapter contains manuscript # 4 (*Development and Characterization of Flax Fiber Reinforced Biocomposite Using Flaxseed Oil Bio-Resin. Journal of Applied Polymer Science. (2015) Vol. 132, Iss. 15 (doi: 10:1002/app.41807)*). In this research, the flax fiber was added as reinforcement to the AEFO resin-based biocomposite. The role of styrene in enhancing the physical and the mechanical properties is also discussed. The results of physical and mechanical testing of the AEFO-based biocomposites are also presented in this chapter..

The contributions of this chapter to the overall study are: i) to meet objective 5 through development of a biocomposite using flaxseed oil-based bio-resin and flax fiber, and ii) to meet objective 6 through characterization of physical, thermal and mechanical properties of the developed biocomposite.

The PhD candidate's contributions in manuscript # 4 were: a) performing the development of AEFO-based biocomposite in laboratory, b) testing the AEFO and flax fiber reinforced biocomposite, c) data processing and generating the graphical results of physical and mechanical properties of AEFO-based biocomposite, and d) writing the paper and replying to reviewers' comments.

References for this chapter are presented in the references section of the thesis.

## 5.2 Abstract

In this study, acrylated epoxidized flaxseed oil (AEFO) resin was synthesized from flaxseed oil, and flax fiber reinforced AEFO biocomposites was produced via a vacuum assisted resin transfer molding technique (VARTM). Different amounts of flax fiber and styrene were added to the AEFO resin to improve its mechanical and physical properties. Both flax fiber and styrene improved the mechanical properties of these biocomposites, but the flexural strength decreased with an increase in the styrene content. The mass increase during water absorption testing was less than 1.5 % (w/w) for all of the AEFO-based biocomposites. The density of the AEFO resin was  $1.166 \text{ g cm}^{-3}$ , which increased to  $1.191 \text{ g cm}^{-3}$  when reinforced with 10% (w/w) flax fiber. The flax fiber reinforced AEFO-based biocomposites have a maximum tensile strength of  $31.4 \pm 1.2$  MPa and Young's modulus of  $615 \pm 31$  MPa. These biocomposites also have a maximum flexural strength of  $64.5 \pm 2.3$  MPa and a flexural modulus of  $2.98 \pm 0.12$  GPa.

## 5.3 Introduction

During the last two decades several studies have been performed on natural fiber reinforced biocomposite materials (Guner *et al.*, 2006; Bledzki and Gassan, 1999; Mohanty *et al.*, 2000; Paul *et al.*, 1997). Biocomposites have been developed using both synthetic polymers and biopolymers (Guner *et al.*, 2006; Bledzki and Gassan, 1999; Mohanty *et al.*, 2000; Paul *et al.*, 1997; Netravali and Chabba, 2003). Synthetic polymers are derived from non-renewable sources; hence there is a paradigm shift towards developing renewable materials such as biopolymers. Biopolymers have been derived from various sources, such as starch, sugar, cellulose, and plant oils (Averous, 2004).

There have been several studies done on the synthesis of polymers using vegetable oils, and these biopolymers have shown comparable properties at reduced cost (Erhan *et al.*, 2003). Natural plant oils are predominantly made up of triglycerides. Triglycerides contain many active sites available for polymerization reactions; these include the allylic carbons, the double bond, the ester group, and the carbon alpha to the ester group (Khot *et al.*, 2001). Functional groups can be added to the triglyceride molecule via these active sites, which is similar to the synthesis of synthetic polymers (Guner *et al.*, 2006; Khot *et al.*, 2001; Sharma and Kundu, 2006; Nayak, 2000). Most of the polymers that are developed from the triglyceride oil involve intermediate process such as the epoxidation (Sinadinovic-Fiser *et al.*, 2001; Zaher *et al.*, 1989). During the epoxidation reaction, an oxygen atom is introduced into a compound containing an unsaturated carbon-carbon bond to form a three-member ring (McMurray, 2007).

Plant oils have been used to produce different polymers such as polyurethane, polyester, polyether and polyolefin (Miao *et al.*, 2014; Lligadas, 2013; Liu *et al.*, 2014). Significant research has been performed on bio-resin produced from soybean oil because large quantities of soybean oil are produced in North America, and soybean oil also have high amounts of unsaturated fatty acids. Different grades of soybean oil polymers have been developed and they are categorized based on their physical and mechanical properties (La Scala and Wool, 2005; Lu and Wool, 2008; O'Donnell *et al.*, 2004). Several vinyl polymers have also been developed from the plant oil by various polymerization techniques (Sharma *et al.*, 2008). Flaxseed oil has a high level of unsaturation similar to the soybean oil since its main content is also linolenic acid (Guner *et al.*, 2006). Linolenic acid contains three double bonds, which is advantageous for

initiating polymerization reactions. Flaxseed oil is also known as linseed oil in most parts of the world (Zhang *et al.*, 2008). Flaxseed oil has been studied by many researchers for its drying properties for commercial applications, such as in oil-based paint, varnish, putty, and linoleum (Zhang *et al.*, 2008; Savoire *et al.*, 2008). Sunflower oil, castor oil, and linseed oil have been investigated for their potential for polyurethane production in paint formulation (Guner *et al.*, 2006). It has been reported in the literature that sometimes triglyceride-based oil polymers show low rigidity and strength (Khot *et al.*, 2000). To impart additional rigidity and strength to the resin, styrene can be used as an additive (Fu *et al.*, 2010).

Natural fiber can be used to reinforce plant-based bio-resin. Flax fiber possesses the highest strength amongst reported different natural fibers (Bledzki and Gassan, 1999; Mohanty *et al.*, 2000; Paul *et al.*, 1997). The principal constituent of the flax fibers is cellulose, with low amounts of hemicellulose, pectins, lignin, oils, and waxes (Li *et al.*, 2007). The physical and the mechanical properties of the natural fibers depend upon the internal structure and the chemical composition (Mohanty *et al.*, 2001; Reddy and Yan, 2005). Natural fibers are hydrophilic in nature due to the presence of cellulose and hemicellulose, which is a major problem in biocomposite development. The hydrophilic natural fiber and hydrophobic polymer matrices have poor interfacial adhesion. Several chemical treatments have been studied to improve the fiber-polymer interface by surface modification (Li *et al.*, 2007; Capelletto *et al.*, 2000). Most of the researchers commonly adopt alkaline and silane treatments. Adding a coupling agent improves the chemical compatibility at the fiber/matrix interface (Li *et al.*, 2007).

Different grades of biocomposites have been developed using natural fiber and various biopolymers (Netravali and Chabba, 2003; Khot *et al.*, 2000; Sharma and Kundu, 2006; O'Donnell *et al.*, 2004; Oksman *et al.*, 2003; Morye and Wool, 2005). PLA has been investigated to develop various biocomposites with different natural fibers such as kenaf and flax fiber (Faruk *et al.*, 2012). Studies on biodegradable biocomposites from soy-based bio-resin have indicated its potential commercial use in packaging and the production of interior panels for the construction industries (Netravali and Chabba, 2003). Epoxidized soybean oil and cellulosic fiber have been used to develop biodegradable biocomposite for structural building material (Takahashi *et al.*, 2008).

Canada is the largest producer of flax worldwide and hence abundant raw material is available for developing new renewable flax-based bio-products for commercial application. In this study acrylated epoxidized flaxseed oil (AEFO) resin synthesized from flaxseed oil was used to develop flax fiber reinforced biocomposites. Different amounts of silane treated flax fiber and styrene content were added to the AEFO bio-resin to develop several biocomposites via vacuum assisted resin transfer molding process. Physical (density, water absorption) and mechanical (tensile, flexural, hardness) properties of the AEFO-based biocomposites were determined. In this chapter, the effects of flax fiber and styrene content on these properties are presented.

## **5.4 Materials and Methods**

### **5.4.1 Materials**

In this research, Saskatchewan grown 100% pure cold-pressed flaxseed oil from Herbal Select and 99 % pure flax fiber provided by Biolin Research Inc. (Saskatoon, SK)

was used. Hydrogen peroxide (30% v/v aqueous solution), formic acid (85%) and ethyl ether were from Fisher Scientific (NJ, USA). Sodium bicarbonate, sodium chloride and anhydrous sodium sulfate were from EMD Chemical Inc. (Gibbstown, NJ, USA). Acrylic acid and triethoxyvinylsilane (97%) were from Sigma-Aldrich (St Louis, MO, USA). Styrene (99%) was purchased from Alfa Aesar (Heysham, UK), and t-butyl peroxybenzoate (98%) was from Acros Organics (NJ, USA).

#### **5.4.2 Chemical treatment of flax fiber**

The flax fiber was treated with 5% (w/w) NaOH solution and later treated with an alcohol water mixture (60:40) containing 2.5 % (w/w) triethoxyvinylsilane as a coupling agent for 1 h. The treated flax fiber was placed in a dryer for 24 h at 50°C to reduce the moisture content to 2% (w/w).

#### **5.4.3 Development of acrylated epoxidized flaxseed oil-based biocomposite**

Flaxseed oil was used to produce the acrylated epoxidized flaxseed oil (AEFO) resin. The flaxseed oil was mixed with formic acid and hydrogen peroxide at a volume ratio of 50:15:45; the flaxseed oil was first mixed with formic acid (85%), and then hydrogen peroxide (30% v/v) was added drop-wise to the solution. The solution was vigorously stirred at 45°C for 18 h using a magnetic stirrer at 200 rpm. This process generated epoxidized flaxseed oil (EFO). The EFO was then dissolved in ethyl ether and washed with saturated sodium bicarbonate solution until a pH of approximately 7 was reached. The mixture was further washed with a saturated sodium chloride solution and dried over anhydrous sodium sulfate. The washing step was to remove the hydrogen

peroxide and formic acid remaining in the epoxidized oil (Khot *et al.*, 2000). The oil and water phase was separated using separation funnel, and the ether was then removed by heating the oil at a temperature of 50°C.

The epoxidized flax oil was mixed with the acrylic acid in a weight ratio of 1:3 in an Erlenmeyer flask. Higher amount of the acrylic acid was added to maximize the level of acrylation. The mixture was stirred at 250 rpm using a magnetic stirrer at a temperature of 75°C for 6 h. The acrylic acid was added in aliquots to reduce the amount of epoxy homo-polymerization during the course of the reaction. The resin was produced then by adding the styrene to the AEFO with 1.5 % (w/w) of the free radical initiator, *t*-butyl peroxybenzoate. Styrene was added to the AEFO biocomposite in five different weight ratios as presented in Table 5.1.

Table 5.1 Investigated AEFO: Styrene weight ratios

S.No		Weight Ratio	Sample ID
1	AEFO: Styrene	100%:0% *	AEFO
2	AEFO: Styrene	90% :10%	AEFO10S
3	AEFO: Styrene	80% :20%	AEFO20S
4	AEFO: Styrene	70% :30%	AEFO30S
5	AEFO: Styrene	60% :40%	AEFO40S
6	AEFO: Styrene	50% :50%	AEFO40S

\*Control Sample with 0% styrene

All styrene based biocomposite were prepared having same flax fiber content (10% w/w).

The AEFO-based resin was reinforced with the silane treated flax fiber. The silane treated flax fiber was placed in the vacuum assisted mold (Figure 5.1). The resin was transferred to the vacuum assisted mold containing the flax fiber and, the mold was cured

at 100°C for 1 h and post cured at 125°C for 2 h. Three levels of flax fiber content (2%, 5%, and 10% w/w) were used to investigate the effect of flax fiber content on the biocomposite. The biocomposite was prepared using a single batch of bio-resin and single batch of silane-treated flax fiber. Test specimens were cut and machined from multiple biocomposite samples produced from the above batches.

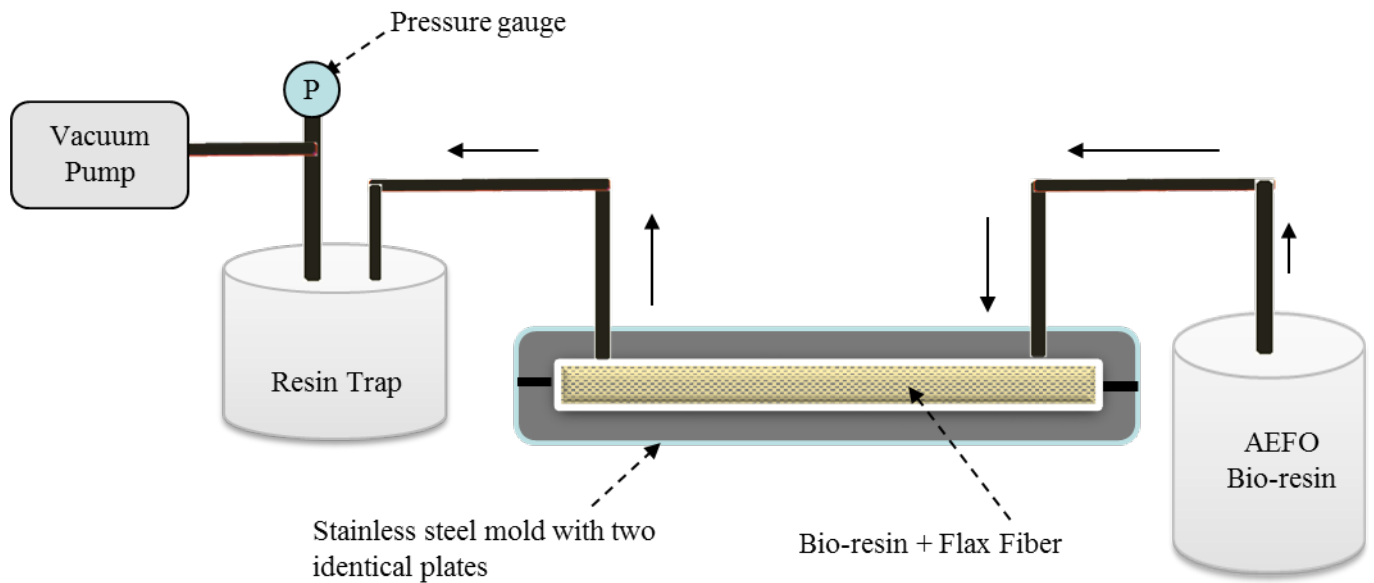


Figure 5.1 Schematic diagram of the vacuum assisted resin transfer molding process

#### 5.4.4 Characterization of acrylated epoxidized flaxseed oil-based biocomposite

The effect of silane treatment on flax fiber surface was studied using the images captured by scanning electron microscope-SEM 505 (Philips, Holland). The fiber surface was coated with a thin layer of gold in vacuum using a S150B sputter coater (BOC Edwards, Wilmington, MA). This was done to provide required electrical conductivity to capture SEM images. The SEM and sputter coater is shown in Figures 5.2 and 5.3 respectively



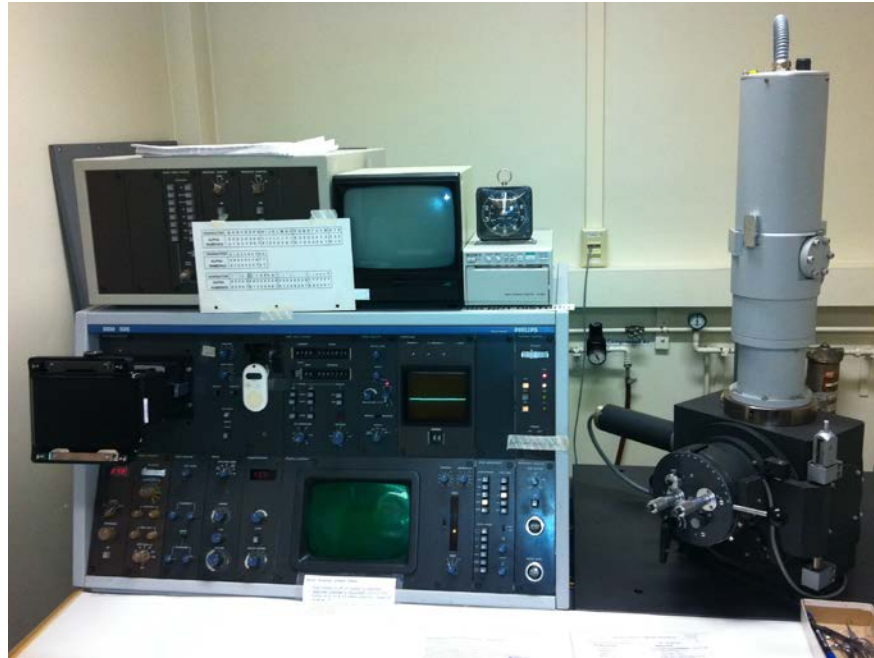


Figure 5.2 Scanning electron microscope



Figure 5.3 Sputter coater

The water absorption characteristics were studied using the ASTM D570 test method (2003). Rectangular test specimens (approximate dimensions of  $76.2 \pm 0.2$  mm x  $25.4 \pm 0.2$  mm x  $3.2 \pm 0.2$  mm) were used during the test and the increase in mass after 24 h immersion in water was calculated to the nearest 0.01%.

Five rectangular samples (approximate dimensions of  $76.2 \pm 0.2$  mm x  $25.4 \pm 0.2$  mm x  $3.2 \pm 0.2$  mm) were used to determine the density of the biocomposite. Galaxy 160D weighing scale (OHAUS Scale Corporation, USA) was used to measure mass ( $m$ ) of the flax fiber samples at room temperature. A gas-operated pycnometer (Quantachrome Corporation, USA) was used to measure volume of the test samples. The density of biocomposite samples was determined as mass per unit volume and expressed in grams per cubic centimeter. The actual density was compared with the ideal density. Ideal density was determined using the following equation (Stroshine, 2000)

$$\rho_{ideal} = \frac{1}{\frac{m_{polymer}}{\rho_{polymer}} + \frac{m_{fiber}}{\rho_{fiber}}} \quad (5.1)$$

Where,

$\rho_{ideal}$  = ideal density (g/cm<sup>3</sup>)

$\rho_{polymer}$  = density of polymer (g/cm<sup>3</sup>)

$\rho_{fiber}$  = density of fiber (g/cm<sup>3</sup>)

$m_{polymer}$  = mass fraction of polymer

$m_{fiber}$  = mass fraction of fiber

The biocomposite samples were subjected to the tension test described in ASTM D638 (2003). A dog bone type specimen of thickness of  $3.2 \pm 0.2$  mm was machined for the test. The test specimens were conditioned at a temperature of  $23 \pm 2^\circ\text{C}$  and a relative humidity of  $50 \pm 5\%$  for 40 h prior to the test. The tensile test was performed at a crosshead speed of 5 mm/min for five samples and each test was performed until tensile failure occurred. The tensile strength and the Young's modulus were determined from the test results.

The biocomposites samples were subjected to the flexural test according to ASTM D790 (2003). Five rectangular cross-section samples of dimension  $64 \pm 0.2$  mm x  $12.7 \pm 0.2$  mm x  $3.2 \pm 0.2$  mm were tested. The test specimens were conditioned at a temperature of  $23 \pm 2^\circ\text{C}$  and relative humidity of  $50 \pm 5\%$  for 40 h prior to the test. The test samples behaved as a beam during the test. The flexural strength and flexural modulus were determined from the test results.

The hardness of the biocomposites was measured by determining the Rockwell hardness number using ASTM D785 test method. The test specimens of thickness  $6.4 \pm 0.2$  mm, were conditioned at a temperature of  $23 \pm 2^\circ\text{C}$  and relative humidity of  $50 \pm 5\%$  for 40 h prior to the test. An HRLW tester, 60 KGF force, and 1/4" ball indenter were used to evaluate the hardness. The hardness of each biocomposite sample was reported as an average of ten readings.

## 5.5 Results and Discussion

### 5.5.1 Water absorption characteristics of AEFO biocomposites

Water absorption by the biocomposite may affect its dimensional stability and mechanical properties; hence, low water absorption characteristics are desirable. The water absorption of the AEFO-based biocomposite increased with an increase in flax fiber content as shown in Figure 5.4. Since natural fibers are hydrophilic in nature, adding them to polymers will increase the amount of water absorption of the polymer (Sreekala *et al.*, 2002).

It was found that the biocomposite with the highest flax fiber content (i.e., 10% w/w flax fiber) had an increase in mass of less than 1.5 % (w/w) which is acceptable for most biocomposite applications; the water absorption ability of flax fiber was reduced by silane treatment. The coupling agent triethoxyvinylsilane provides a coating on the flax fiber surface that reduces water absorption.

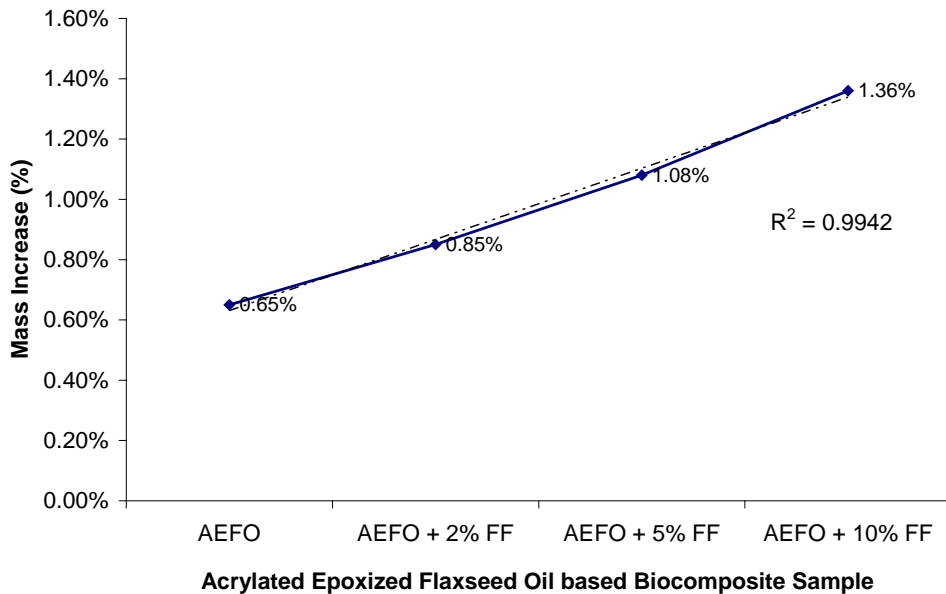


Figure 5.4 Effect of flax fiber content on water absorption characteristics of AEFO biocomposites

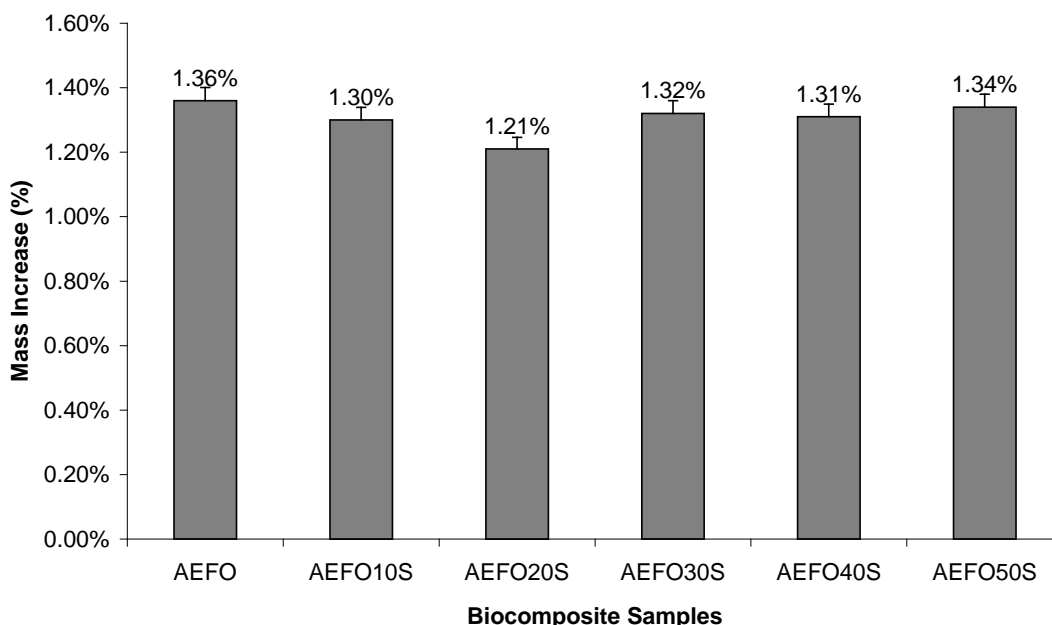


Figure 5.5 Effect of styrene content on water absorption characteristics of AEFO biocomposite. The uncertainty presented in the figure is at the 95% confidence level.

No significant effect was found on the water absorption characteristics by changing the styrene percentage from 0 to 50% (w/w) in AEFO-Styrene resin formulation (Figure 5.5). In the literature, the mass increase during the water absorption test for similar biopolymer acrylated epoxidized soybean oil (AESO) was given as 0.5% (Hong and Wool, 2005).

### 5.5.2 Morphological characterization of silane treated flax fiber

SEM images of the untreated and silane treated flax fiber are shown in Figure 5.6. The SEM image of the untreated flax fiber shows the presence of waxy substances like lignin and pectin on the fiber surface. After silane treatment, the waxy material is removed, and layer of coupling agent triethoxyvinylsilane is more readily coated on flax fiber surface. This chemical treatment helps in improving the fiber-polymer matrix interfacial adhesion and reduces the water absorption as well. The reaction mechanism of

the silane treatment is shown below in equations 5.2 and 5.3 (Agrawal *et al.*, 2000; Xie *et al.*, 2010).

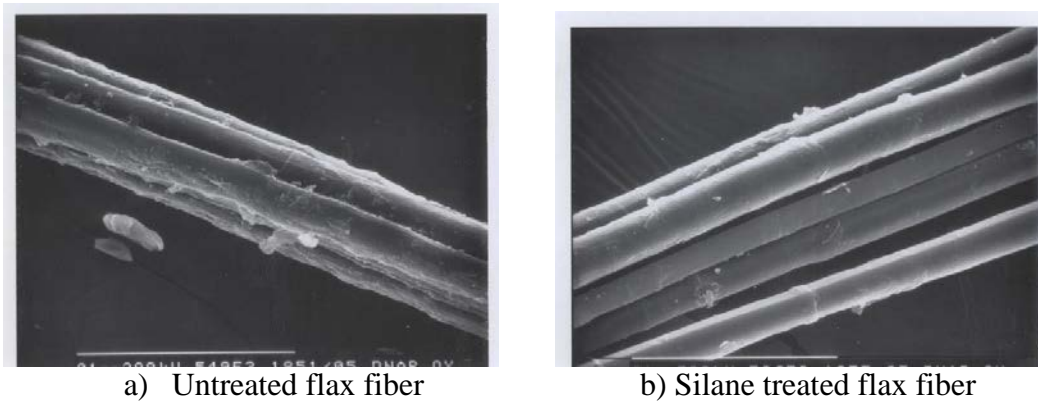
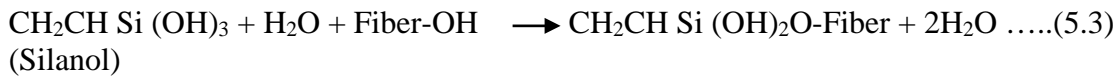


Figure 5.6 SEM images of untreated and silane treated flax fiber

### 5.5.3 Density of AEFO biocomposites

The density of the biocomposite plays an important role in commercial applications to develop low density and high strength products. The densities of the AEFO biocomposites with different flax fiber contents are shown in Figure 5.7. The flax fiber has higher density (1.461 g/cm<sup>3</sup>) than that of the AEFO resin (1.166 g/cm<sup>3</sup>). Therefore, as expected, the density of the AEFO-based biocomposite increases with an increase in the flax fiber content.

The comparison of the measured density and the ideal density is also shown in Figure 5.7. It can be inferred from the comparison results that the biocomposite did not have any significant cavity or pores since the density determined was as expected; the

vacuum assisted resin transfer molding technique eliminates most of the air bubbles during the molding process and develops a high quality product. Table 5.2 indicates that the density of the AEFO biocomposite decreases with increasing styrene content due to the lower density of styrene (0.909 g/cm<sup>3</sup>).

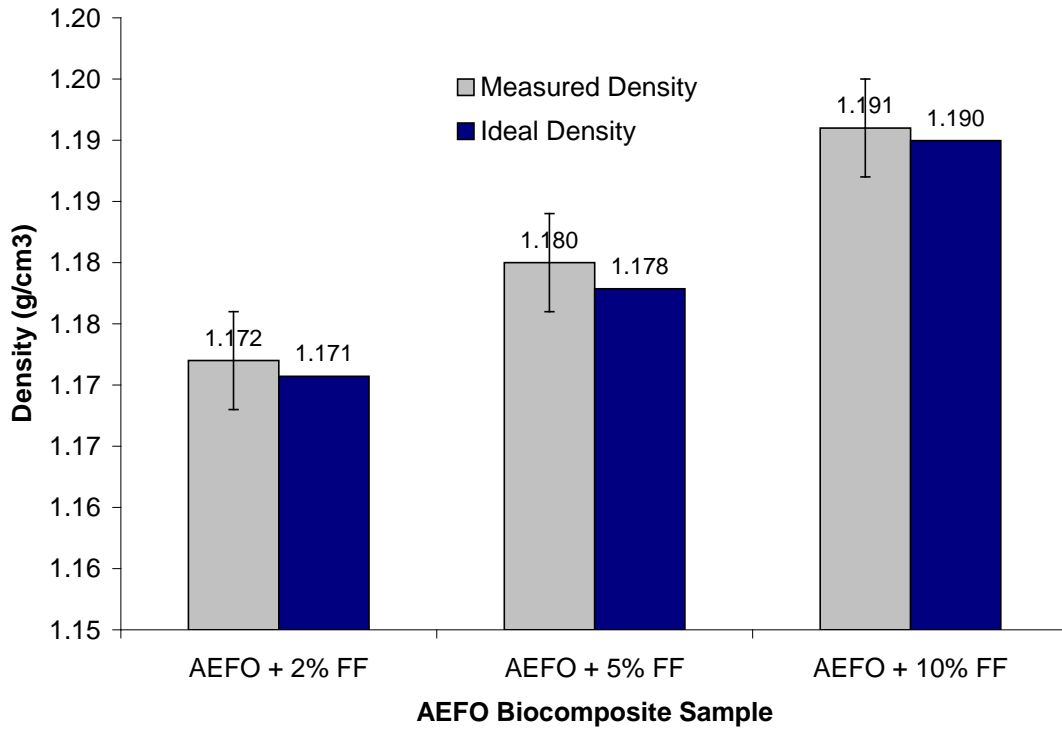


Figure 5.7 Effect of fiber loading on density of AEFO-based biocomposite samples. The uncertainty presented in the figure is at the 95% confidence level.

Table 5.2 Effect of styrene on density of AEFO-based biocomposite samples

S. No	Biocomposite Sample	Density (g/cm <sup>3</sup> )
1.	AEFO + 10% FF	1.191 ± 0.004
2.	AEFO10S + 10% FF	1.180 ± 0.005
3.	AEFO20S + 10% FF	1.170 ± 0.004
4.	AEFO30S + 10% FF	1.166 ± 0.005
5.	AEFO40S + 10% FF	1.156 ± 0.003
6.	AEFO50S + 10% FF	1.151 ± 0.006

*% FF: percentage of flax fiber content (w/w)*

### 5.5.4 Tensile properties of AEFO biocomposites

The tensile strength of the AEFO biocomposites developed with different flax fiber contents is shown in Figure 5.8. Increasing the flax fiber from 0 to 10 % (w/w) increased the tensile strength of AEFO biocomposite from 29.8 MPa to 31.4 MPa. The flax fiber has high tensile strength and hence it serves as reinforcement in the biocomposite.

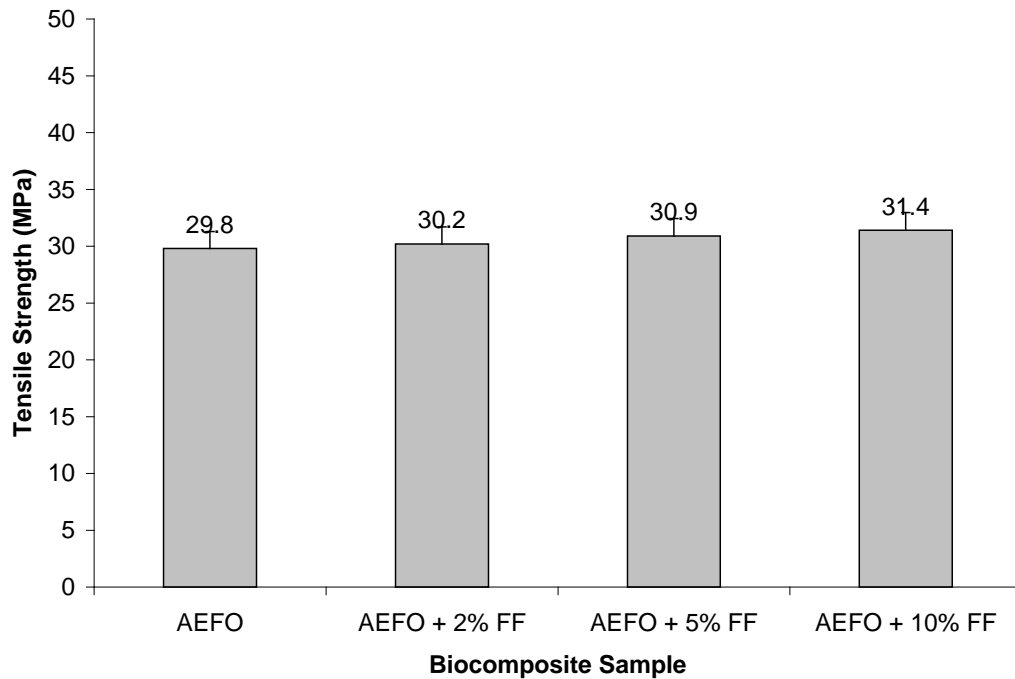


Figure 5.8 Effect of flax fiber content on tensile strength of AEFO biocomposites. The uncertainty presented in the figure is at the 95% confidence level.

Silane treatment also improves the interfacial adhesion and the tensile strength because this treatment creates a cross-linked network of fiber and polymer due to covalent bonding (Li *et al.*, 2007; Valadez-Gonzalez *et al.*, 1999). Many studies have also confirmed that the addition of natural fiber to polymer matrices increases the tensile strength (Herrera-Franco *et al.*, 1997; Oksman *et al.*, 2003, Fung *et al.*, 2003).

To improve the tensile strength of AEFO the biocomposites, styrene was added to the AEFO biocomposite. Styrene imparts rigidity to the polymer and hence improves the



tensile strength of the biocomposites. As expected, an increase in the styrene content significantly increases the tensile strength (Figure 5.9). There was approximately a 21% increase in the tensile strength with an addition of 50% (w/w) styrene to the AEFO biocomposites. The tensile strength of the AEFO was found equivalent to the literature values of tensile strength ( $\approx 30$  MPa) of AESO resin (Khot *et al.*, 2001).

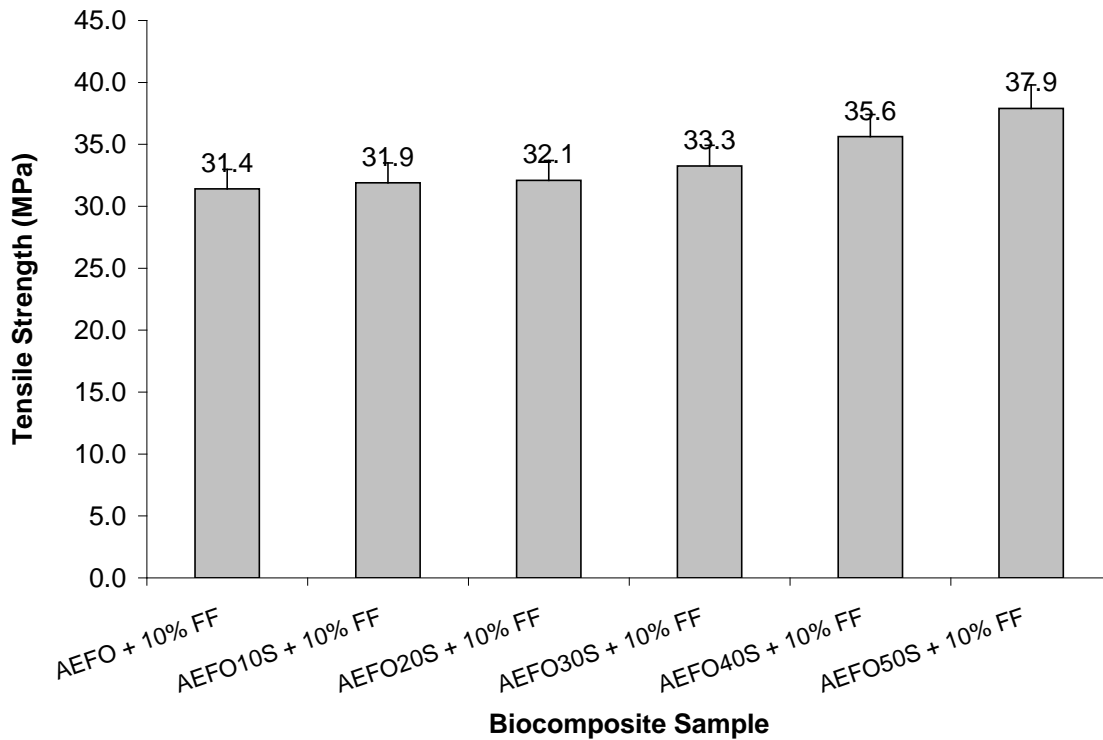


Figure 5.9 Effect of styrene content on tensile strength of AEFO biocomposites. The uncertainty presented in the figure is at the 95% confidence level.

Similarly, the flax fiber also increases the Young's modulus significantly. Figure 5.10 shows that increasing the flax fiber content from 0 to 10 % (w/w) increased the Young's modulus from 373 MPa to 520 MPa. It has been reported that the Young's modulus increases significantly when cellulosic material is added to acrylated epoxidized soybean oil resin (O'Donnell *et al.*, 2004). The addition of styrene to the composite-polymer matrix also increases the rigidity of the composite (Khot *et al.*, 2001).

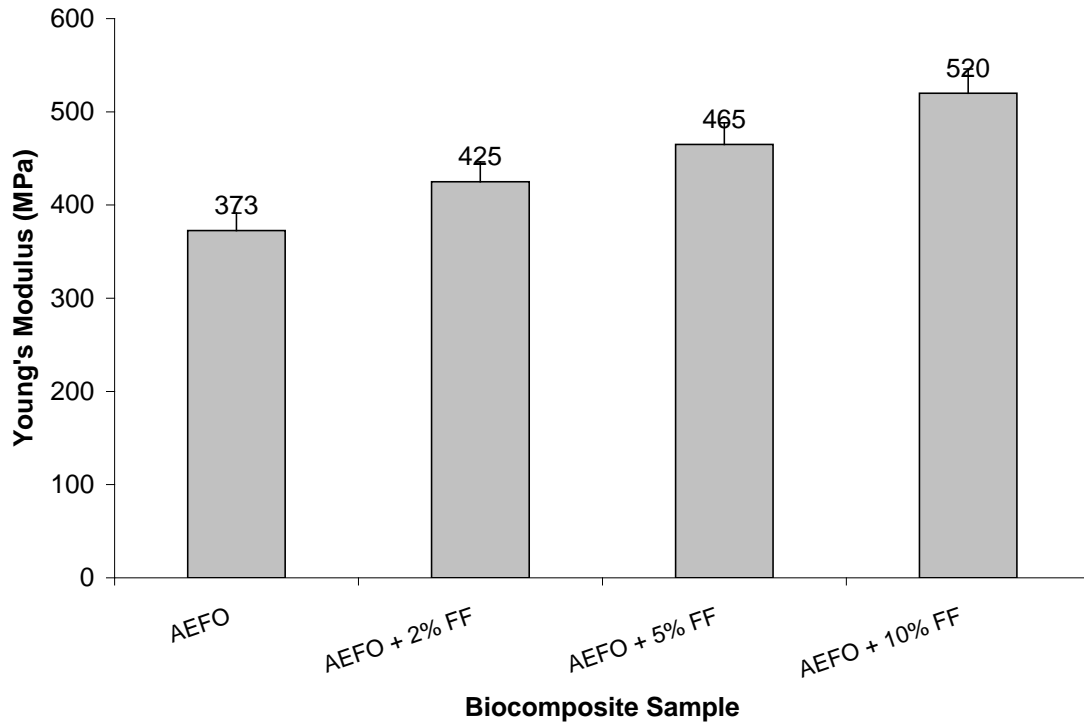


Figure 5.10 Effect of flax fiber content on Young's modulus of AEFO biocomposites. The uncertainty presented in the figure is at the 95% confidence level.

Figure 5.11 illustrates that an increase in styrene content in the AEFO biocomposite increases the Young's modulus significantly. However, an increase in rigidity also increases the brittleness of the AEFO biocomposite.

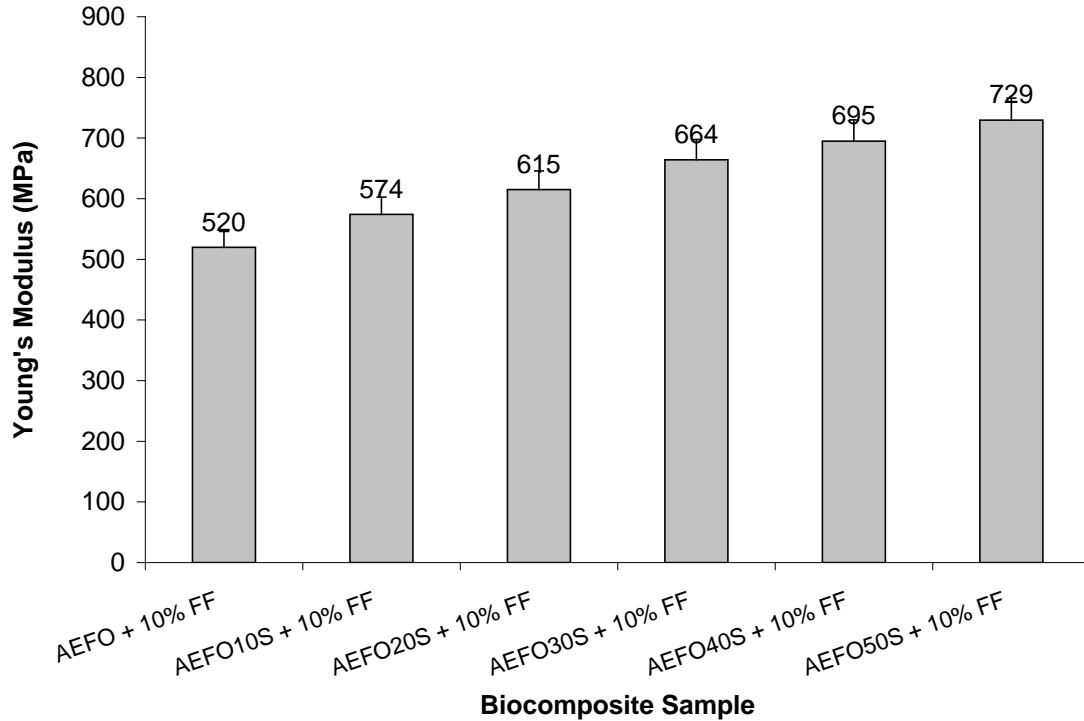


Figure 5.11 Effect of styrene content on Young's modulus of AEFO biocomposites. The uncertainty presented in the figure is at the 95% confidence level.

### 5.5.5 Flexural properties of AEFO biocomposites

The flexural test was used to determine the flexural strength and the flexural modulus of the AEFO biocomposite. It was found that, as with tensile strength, an increase in the flax fiber content increased the flexural strength significantly (Figure 5.12). Similar observations were reported for other natural fiber based biocomposites by several researchers (Li *et al.*, 2007; Sain *et al.*, 2005; Khanam *et al.*, 2007). The flexural strength of AEFO biocomposite increases from  $53.5 \pm 2.3$  MPa (0% flax fiber) to  $64.5 \pm 2.3$  MPa (10 % flax fiber) when flax fiber was added to AEFO resin.

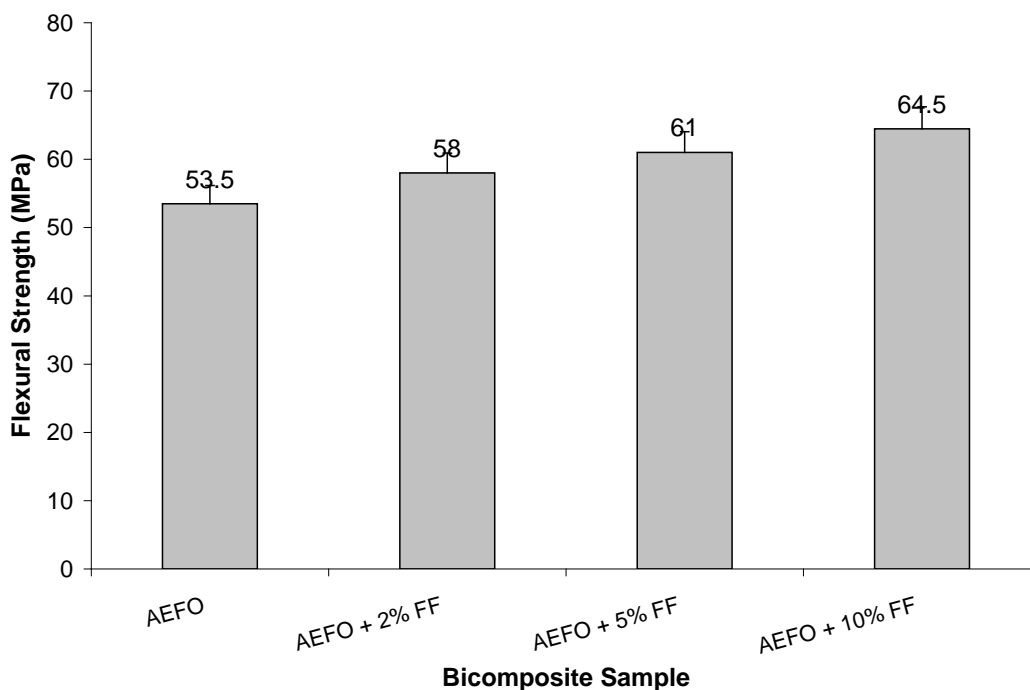


Figure 5.12 Effect of flax fiber content on flexural strength of AEFO biocomposites. The uncertainty presented in the figure is at the 95% confidence level.

Researchers also reported that the flexural load induces both compressive and tensile stresses during the flexural test (Li *et al.*, 2007). Flax fiber possesses high strength and, the silane treatment further improves the fiber-polymer interfacial adhesion. The results presented in Figure 5.12 shows that flax fiber has good interfacial bonding with the AEFO polymer. Similar results have been reported for biopolymer like AESO; AESO composite with 0% fiber has a flexural strength of 34.8 MPa (Hong and Wool, 2005).

As reported earlier, the addition of styrene increases the rigidity and brittleness. The addition of styrene to the AEFO biocomposite decreased the flexural strength as shown in Figure 5.13. This can be explained by the fact that an increase in brittleness decreased the flexibility; hence the flexural strength also decreased.

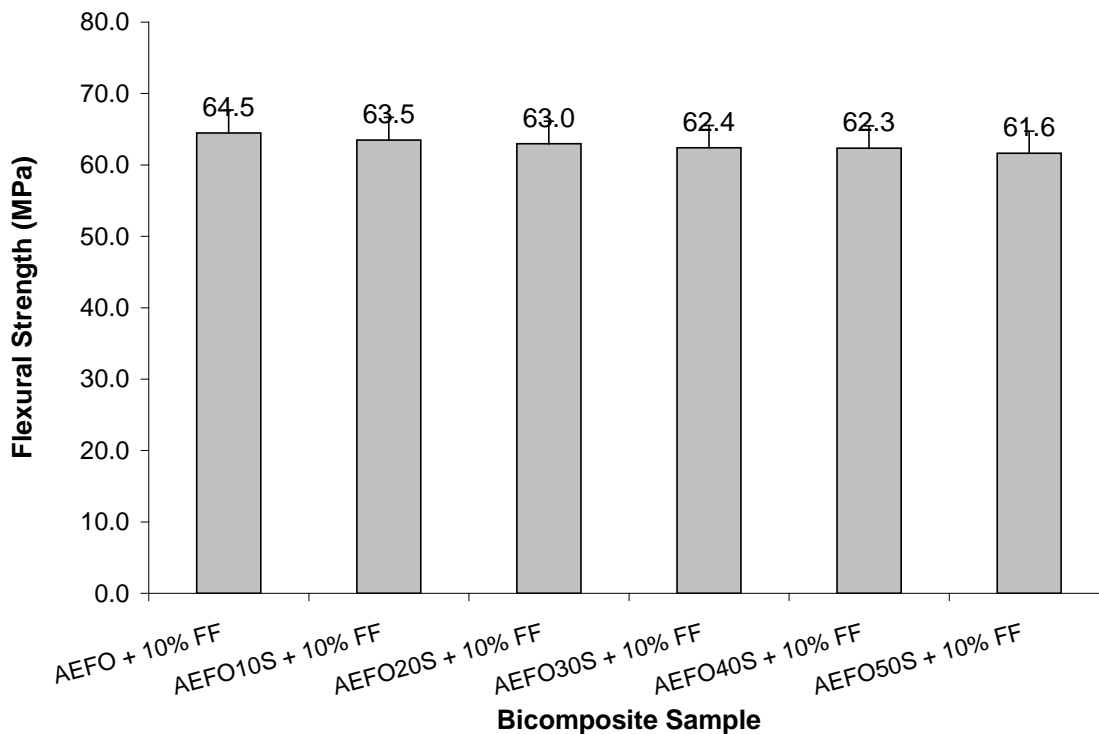


Figure 5.13 Effect of styrene content on flexural strength of AEFO biocomposites The uncertainty presented in the figure is at the 95% confidence level.

The trends in flexural modulus were similar to those of the Young's modulus. It was found that the flexural modulus increased with an increase in the flax fiber and styrene content as indicated in Figures 5.14 and 5.15 respectively. The flexural modulus of the pure AEFO sample (0% flax fiber) was found to be  $2.838 \pm 0.121$  GPa and it increases to  $2.979 \pm 0.121$  GPa with 10% flax fiber loading. This result can be also attributed to the better fiber-polymer interfacial adhesion and rigidity provided by the styrene. In the literature, the flexural modulus of AESO is reported as 0.896 GPa (Hong and Wool, 2005).

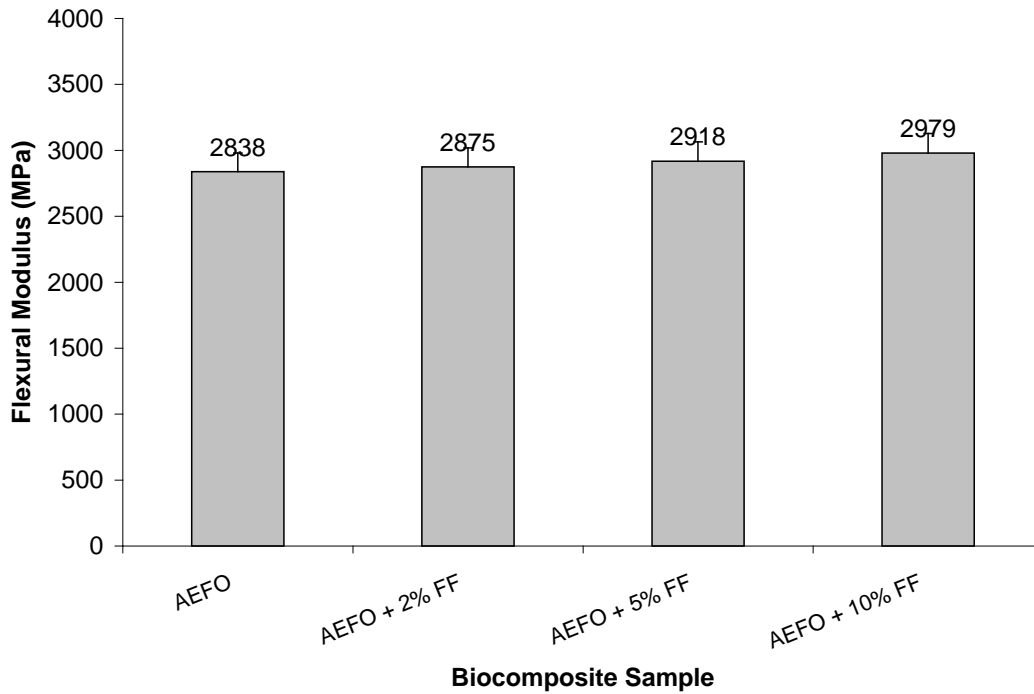


Figure 5.14 Effect of flax fiber content on flexural modulus of AEFO biocomposites. The uncertainty presented in the figure is at the 95% confidence level.

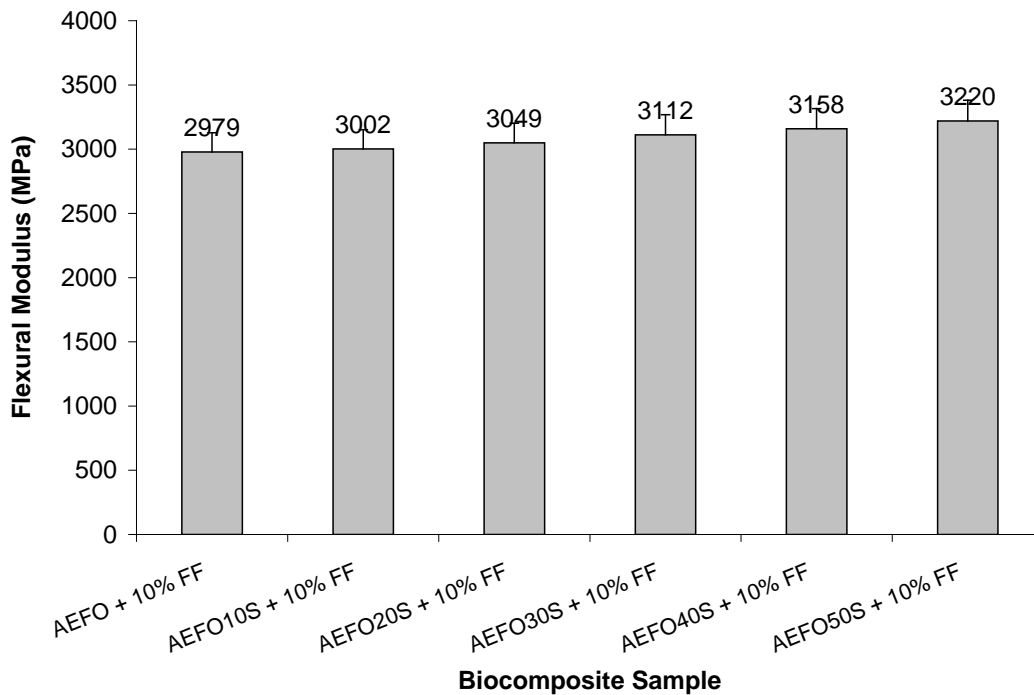


Figure 5.15 Effect of styrene content on flexural modulus of AEFO biocomposites. The uncertainty presented in the figure is at the 95% confidence level.

### 5.5.6 Rockwell hardness of AEFO biocomposites

Hardness measures the resistance to bending, scratching, abrasion and indentation. The Rockwell hardness number measures the indentation hardness, which helps in characterizing the visco-elastic behaviour of the material. Intermolecular forces have a significant effect on the hardness. The results shown in Figure 5.16 illustrate that the addition of flax fiber increased the Rockwell hardness number of the AEFO biocomposites, which implies that the hardness of the biocomposites has increased. It has been reported that similar behaviour has been observed for polypropylene-based biocomposites (Lai *et al.*, 2005). The hardness of a material is related to the modulus in such a way that an increase in modulus will increase the hardness too (Lai *et al.*, 2005).

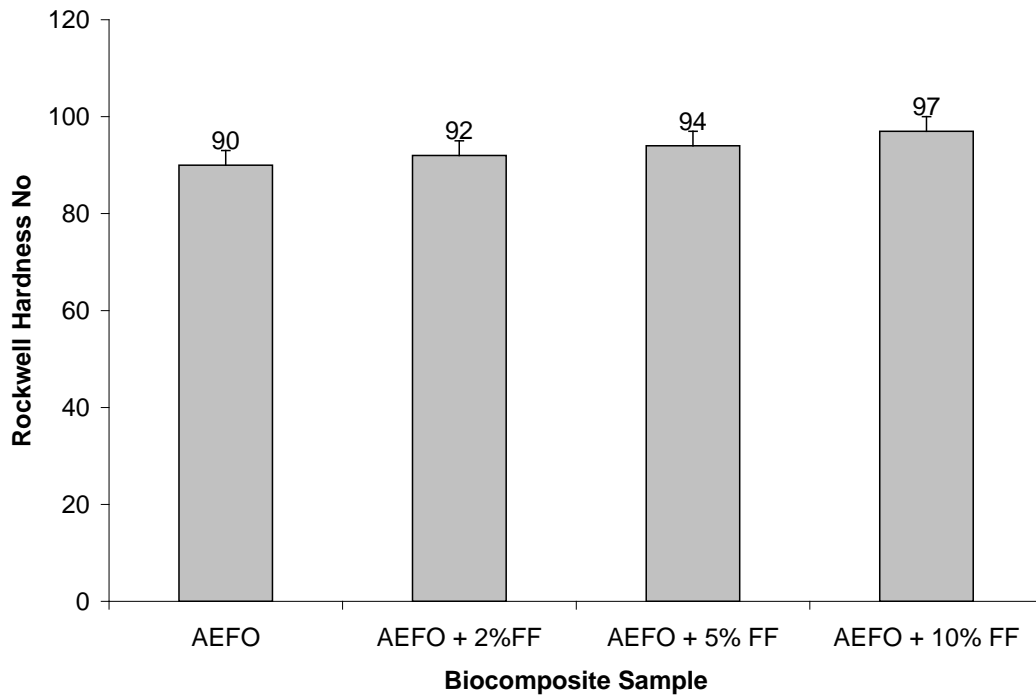


Figure 5.16 Effect of flax fiber content on hardness of AEFO biocomposites. The uncertainty presented in the figure is at the 95% confidence level.

Hardness is also directly related to rigidity. Since the styrene content increases the rigidity of the biocomposite, the hardness of composite will also increase. Figure 5.17 illustrates the hardness of the composite materials with different styrene amounts. As expected, the Rockwell hardness number increases with an increase in the styrene content.

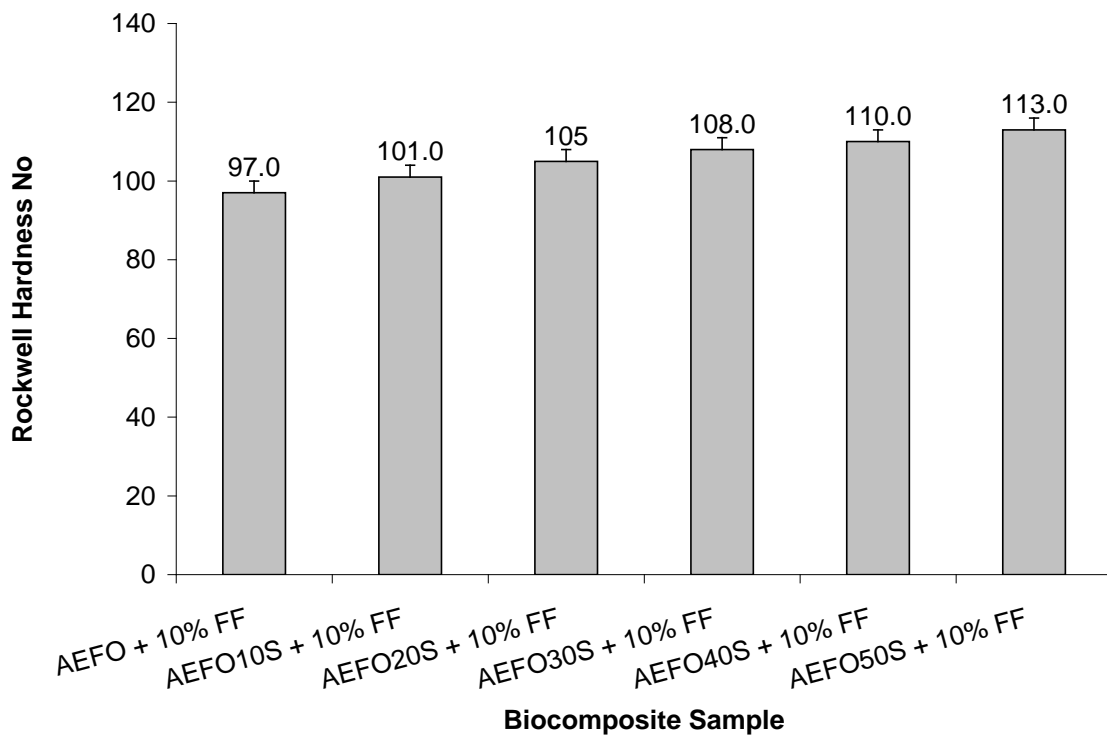


Figure 5.17 Effect of styrene content on hardness of AEFO biocomposites. The uncertainty presented in the figure is at the 95% confidence level.

## 5.6 Conclusions

In this study, acrylated epoxidized flaxseed oil (AEFO) resin synthesized from flaxseed oil was used to develop flax fiber reinforced biocomposites via vacuum resin



transfer molding method. The biocomposites exhibited good physical and mechanical properties.

The mass increase during the water absorption test was found to be less than 1.5 % (w/w) for all AEFO-based biocomposites, which is generally acceptable in biocomposite industries. The styrene content had no significant effect on the water absorption characteristics. The density of the AEFO resin ( $1.166 \text{ g/cm}^3$ ) was found to be higher than that of the styrene ( $0.909 \text{ g/cm}^3$ ) and lower than that of the flax fiber ( $1.461 \text{ g/cm}^3$ ). Flax fiber loading improved the mechanical properties of the AEFO biocomposite. An increase in flax fiber content increased the tensile strength, the Young's modulus, flexural strength, flexural modulus and hardness of the AEFO biocomposite. It was found that styrene improves the tensile strength and the Young's modulus of AEFO biocomposites but decreases the flexural strength. Both flax fiber and styrene content were found to increase the hardness of AEFO-based biocomposite.

The AEFO biocomposite with 10 % (w/w) flax fiber had a tensile strength of  $31.4 \pm 1.2 \text{ MPa}$  and a Young's modulus of  $520 \pm 26 \text{ MPa}$ . It also exhibited a flexural strength of  $64.5 \pm 2.3 \text{ MPa}$  and a flexural modulus of  $2.98 \pm 0.12 \text{ GPa}$ .

## **5.7 Summary of Chapter 5**

This chapter presents the development of AEFO-based biocomposites via VARTM molding process. The biocomposites were characterized using several physical and mechanical tests in order to predict the influence of flax fiber and styrene content on the biocomposite properties; these properties include density, water absorption, tensile strength, Young's modulus, flexural strength, flexural modulus and hardness number.

Addition of flax fiber increased the biocomposite density; whereas addition of styrene decreased the biocomposite density. Both styrene and flax fiber improved the tensile properties and the hardness of the biocomposite. But the styrene content however decreased the flexural strength.

In the next chapter, comparison of the flax fiber reinforced biocomposites developed using AEFO, PLA, HDPE, and PP is presented. The comparison was performed by determining the following physical and mechanical properties of these four different polymer matrices based biocomposites: density and density deviation, mass increase during water absorption test, tensile strength, Young's modulus, flexural strength, flexural modulus and hardness.

# Chapter 6

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## 6. Comparative Studies of Different Biocomposite Developed from AEFO, PLA, HDPE and PP

### 6.1 Chapter Overview

This chapter presents a comparison of biocomposites prepared using AEFO, PLA, PP, and HDPE matrices. The following properties among the biocomposites were compared: density, mass increase percentage during water absorption characteristics, tensile strength, Young's modulus, flexural strength, flexural modulus, and Rockwell hardness.

The contribution of this chapter to the overall study is to meet objective 7 through comparison of biocomposites developed using AEFO, PLA, HDPE and PP polymers. This comparative study will give a clear picture of the potential of AEFO compared to the available commercial biopolymer (PLA) and the synthetic polymers (PP and HDPE) for biocomposite applications.

The PhD candidate's contributions to this chapter were: a) developing injection-molded flax fiber-reinforced biocomposite samples using PLA, HDPE, and PP matrices, b) conducting physical and mechanical tests for the four biocomposites, c) data processing and generating graphical and tabular results of all the tests performed, and d) discussing the results and summarizing the main findings.

References for this chapter are presented in the references section of the thesis.

## 6.2 Abstract

The physical and mechanical properties of the AEFO biocomposites were compared with those of PLA, PP, and HDPE biocomposites. All biocomposites were developed with 10 % (w/w) silane-treated flax fiber. The following properties were measured for all four types of biocomposites: density, water absorption, tensile strength, Young's modulus, flexural strength, flexural modulus, and hardness. All biocomposite samples showed good water absorption characteristics, having a mass increase of less than 2% (w/w). The density of the AEFO biocomposites ( $1.191 \text{ g/cm}^3$ ) was lower than that of the PLA biocomposites ( $1.369 \text{ g/cm}^3$ ) and higher than that of the PP ( $0.957 \text{ g/cm}^3$ ) and HDPE ( $0.972 \text{ g/cm}^3$ ) biocomposites. The AEFO biocomposites had no density deviation from their ideal density, whereas the PLA biocomposites had a higher density deviation of 13%. The addition of flax fiber increased the tensile strength, Young's modulus, flexural strength, and flexural modulus of the AEFO, PP and HDPE biocomposites. However, in the PLA biocomposite, tensile and flexural strength decreased with the addition of flax fiber. The AEFO biocomposite had the highest tensile (31.4 MPa) and flexural strength (64.5 MPa), the HDPE biocomposite had the lowest tensile strength (17.4 MPa), and the PLA biocomposite had the lowest flexural strength (27.2 MPa). The PLA biocomposite had the highest stiffness ( $E = 921 \text{ MPa}$ ,  $E_H = 4.6 \text{ GPa}$ ) and hardness (Rockwell hardness number = 110). Overall, PLA was the strongest polymer matrix, but after flax fiber loading, AEFO exhibited higher tensile and flexural properties. The AEFO-based biocomposite was the strongest among all the biocomposites compared.

### 6.3 Introduction

Renewable source-based composite materials have been studied and used worldwide (Paul *et al.*, 1997, Bledzki and Gassan, 1999; Mohanty *et al.*, 2000). Traditionally, petroleum-based polymers have been reinforced with glass and carbon fiber to produce high-quality products for various applications. However, over the last two decades, researchers have identified natural fibers as a substitute for man-made fibers in the automotive, housing, and packaging industries (Arbelaiz *et al.*, 2005; Bos and Mussig, 2006; Cantero *et al.*, 2003; Singleton *et al.*, 2003; Pervaiz and Sain, 2003). Natural fibers have several advantages over man-made fibers: they are low-density, eco-friendliness, economic, renewable, and biodegradability (Alix *et al.*, 2008; Mohanty *et al.*, 2003; Van de Velde and Kiekens, 2002).

Flax is one of the strongest natural fibers, and it has properties comparable to many synthetic fibers (Bledzki and Gassan, 1999; Mohanty *et al.*, 2000; Wallenberger and Weston, 2004). Flax fiber has been primarily used for textiles and paper, but due to its high strength, it has been recently used to develop biocomposites for commercial applications.

Initially, thermoset polymers were used to develop natural fiber-based biocomposites (Garkhail *et al.*, 2000). However, interest has now shifted to thermoplastic polymers for biocomposite development. One study identified PP, LDPE, and HDPE as suitable matrices for natural fiber-based biocomposite materials among 12 commonly used thermoplastics (Van de Velde and Kiekens, 2001).

A limiting factor in flax fiber-reinforced biocomposite processing is that the processing temperature should remain relatively low to avoid possible degradation of the

fibers, which occurs at higher temperatures (Soleimani *et al.*, 2008). Thus, polyethylene (PE) and PP are the commonly available thermoplastic matrices suitable for biocomposites manufacturing since they have lower melting points and processing temperatures than other thermoplastics (Van de Velde and Kiekens, 2001). Several researchers have studied PP-based fiber-reinforced composites and have found them to have low cost and good thermal stability (Arbelaiz *et al.*, 2005; Wielage *et al.*, 2003). HDPE have been widely studied for developing natural fiber-based biocomposites (Salleh *et al.*, 2014; Sever *et al.*, 2011; Li *et al.*, 2008)

Recently, the focus has shifted to developing renewable or bio-based polymers derived from natural sources like plants and animals. Among the biopolymers developed, PLA is one of the most multipurpose. It is produced from agricultural raw material and has been used to develop commercial biodegradable products (Wallenberger and Weston, 2004).

Several soy-based biopolymers have also been developed and used in the production of biocomposites (Knot *et al.*, 2001; O'Donnell *et al.*, 2004; Liu *et al.*, 2001; Netravali and Chabba, 2003; Lu and Wool, 2008). Flaxseed oil has been extensively studied due its rapid drying characteristics, and it is used in paint, varnish, and linoleum (Zhang *et al.*, 2008; Savoire *et al.*, 2008). Flaxseed oil contains high levels of unsaturated fatty acids, and it can be used to develop bio-resins similar to the different soybean oil-based bio-resins. In this research, a flaxseed oil-based resin was developed and used to produce flax fiber-reinforced biocomposites. The physical and mechanical properties of the biocomposites vary depending on both the fiber and polymer matrix characteristics.

In this chapter, the physical and mechanical properties of acrylated epoxidized flaxseed oil (AEFO) resin-based biocomposite are compared to those of PLA, PP and HDPE biocomposites. A commercially available biopolymer PLA was selected for developing a flax fiber reinforced biocomposite material along with AEFO for comparing their potential as a polymer matrix for developing commercial composite products. Since extensive research has been performed on PP- and HDPE-based biocomposites, those polymer matrices were also selected for comparison with the AEFO-based biocomposite.

## **6.3 Materials and Method**

### **6.3.1 Materials**

The AEFO bio-resin developed in this research was used to produce flax fiber-reinforced biocomposites. Biocomposites were also prepared using three polymer matrices: PLA from Jamplast Inc. (Ellisville, MO, USA); HDPE, HD-8760.29 from Exxon Mobil (Toronto, ON, Canada); and PP, Pro-fax 7823 from Equistar Chemicals LP (TX, USA). For reinforcing the composites, 99% pure flax fiber from Biolin Research Inc. (Saskatoon, SK, Canada) was used. For the silane treatment, the following chemicals were used: sodium hydroxide from EM Industries (Gibbstown, NJ, USA), ethanol from Commercial Alcohols Inc. (Brampton, ON, Canada), and triethoxyvinylsilane from Sigma-Aldrich (St. Louis, MO, USA).

### **6.3.2 Biocomposite sample preparation**

AEFO bio-resin was prepared as presented in Chapter 5. The AEFO-based resin was reinforced with silane-treated flax fiber; the silane treatment process is presented in

Chapter 5. To produce the biocomposite, the silane-treated flax fiber was placed in a vacuum-assisted mold, and then the resin was transferred into the mold. The vacuum system was used to reduce the number of air bubbles in the composite. The mold was then cured at 100 °C for 1 h and post-cured at 125 °C for 2 h. Three levels of flax fiber content (2%, 5%, and 10% w/w) were used to investigate the effect of flax fiber content on the biocomposite.

The PLA-, HDPE-, and PP-based biocomposite test samples were prepared in two steps. In the first step, the flax fiber and the polymer matrix were mixed in a rotating blender (Waring Products, New York, NY) and then fed into a twin-screw extruder. Images of the blender and twin-screw extruder are shown in Figures 6.1 and 6.2 respectively.



Figure 6.1 Rotating blender





Figure 6.2 Twin-screw extruder

The extrusion process was used to compound the polymer matrix and the flax fiber. Next, the extrudates were pelletized, and the pellets were then injection molded using a standard mold, which produced a dogbone shaped and rectangular test specimen.

### 6.3.3 Characterization techniques

Five rectangular samples (approximate dimensions of  $76.2 \pm 0.2$  mm x  $25.4 \pm 0.2$  mm x  $3.2 \pm 0.2$  mm) of each polymer-based composite were used to determine the density of the respective polymer-based composite after molding. A Galaxy 160D weighing scale (OHAUS Scale Corporation, USA) was used to measure the mass ( $m$ ) of the biocomposite samples at room temperature. A gas-operated pycnometer (Quantachrome Corporation, USA) was used to measure the volumes of the test samples. The densities of the biocomposite samples were determined as the mass per unit volume and expressed in grams per cubic centimeter.

The actual density was compared with the ideal density. The ideal density was determined using the mass fraction and the density of the polymer matrix and the flax fiber (Stroshine, 2000).

The water absorption characteristics were studied using the ASTM D570 test method (2003). Rectangular test specimens (approximate dimensions of  $76.2 \pm 0.2$  mm x  $25.4 \pm 0.2$  mm x  $3.2 \pm 0.2$  mm) were used during the test. The increase in mass after 24 h of immersion in water was calculated to the nearest 0.01%.

The biocomposite samples were subjected to the tension test described in ASTM D638 (2003). A familiar dog-bone type specimen of thickness of  $3.2 \pm 0.2$  mm was machined for the test. The test specimens were conditioned at a temperature of  $23 \pm 2$  °C and relative humidity of  $50 \pm 5\%$  for 40 h prior to the test. The tensile test was performed at a crosshead speed of 5 mm/min for five samples, and each test was performed until tensile failure occurred. The tensile strength ( $\sigma_t$ ) and Young modulus ( $E$ ) were determined from the test results.

The biocomposite samples were subjected to the flexural test described in ASTM D790 (2003). Five rectangular cross-section samples of dimension  $64 \pm 0.2$  mm x  $12.7 \pm 0.2$  mm x  $3.2 \pm 0.2$  mm were tested. The test specimens were conditioned at a temperature of  $23 \pm 2$  °C and relative humidity of  $50 \pm 5\%$  for 40 h prior to the test. The test samples behaved as a beam during the test. The flexural strength ( $S$ ) and flexural modulus ( $E_H$ ) were determined from the test results.

The hardness of the test samples was measured by determining the Rockwell hardness number by following ASTM D785. The test specimens of thickness  $6.4 \pm 0.2$  mm were conditioned at a temperature of  $23 \pm 2$  °C and relative humidity of  $50 \pm 5\%$  for 40 h prior

to the test. An HRLW tester, 60 KGF force, and 1/4-inch ball indenter were used to evaluate the hardness. The hardness of each biocomposite sample was reported as an average of ten readings.

## **6.4 Results and Discussion**

The results of the physical and mechanical tests for the AEFO-, PLA-, PP-, and HDPE-based biocomposites are summarised in bar graphs presented in this section. All graphs used for comparison show the control sample and biocomposite samples. The control sample has no flax fiber and is purely made of polymer resin, and the biocomposite samples have 10 % (w/w) flax fiber. AEFO, PP, and HDPE properties changed linearly with an increase in flax fiber content. However, PLA biocomposite properties did not change linearly with the flax fiber content; hence, additional graphs for PLA biocomposite are shown and discussed in this section.

### **6.4.1 Water absorption measurement and comparison**

Water absorption is one of the main problems with natural fiber-reinforced biocomposites. Mass increase percentage during water absorption tests was measured for all AEFO-, PLA-, PP-, and HDPE-based biocomposites. All biocomposites in this study were reinforced with 10% (w/w) silane-treated flax fiber. The results are shown in Figure 6.3.

Most of the polymers are hydrophobic, and their water absorption values is less than 1% w/w. Adding natural fiber always increases the water absorption since natural fiber has a higher affinity for water. Several researchers have adopted a number of

chemical treatments to decrease water absorption. Figure 6.3 showed that the AEFO-based biocomposites along with the PLA-, HDPE-, and PP-based biocomposites had less than 2% mass increase when reinforced with 10% flax fiber. The variability shown in water absorption by the polymer matrix could be because of different structure of each polymer. This might also have influenced interfacial bonding with the flax fiber. The fiber dispersion in the biocomposite can also have an effect on the water absorption. However, the silane treatment was effective in limiting the water absorption to less than 2%. Several researchers have reported that chemical treatments, including silane treatment, are effective in reducing the water absorption of natural fiber-reinforced biocomposites such as in flax fiber-PE composites and flax fiber-PP composites (Paul *et al.*, 1997; Bledzki and Gassan, 1999; Mohanty *et al.*, 2001; Wang *et al.*, 2003).

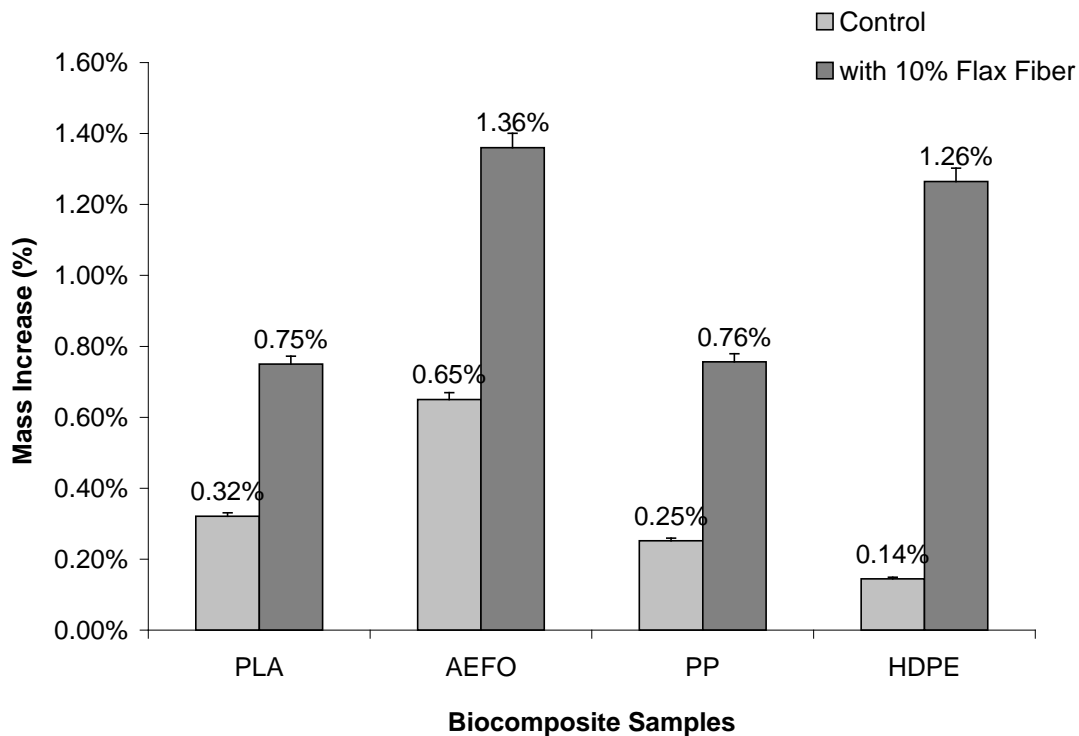


Figure 6.3 Mass increase during the water absorption tests of AEFO, PLA, PP and HDPE matrices and their biocomposites. The uncertainty presented in the figure is at the 95% confidence level.

#### 6.4.2 Density measurement and comparison

Table 6.1 shows the measured and ideal densities for the biocomposites with 10% (w/w) flax fiber content. As discussed in Chapter 4, AEFO has higher density than PP and HDPE and lower density than PLA. The densities of the biocomposites also followed the same pattern: the AEFO biocomposites had higher density than the PP and HDPE biocomposites but lower density than the PLA biocomposites. There was no density deviation between the ideal and measured densities of the AEFO biocomposites. Hence, the VARTM process was successful in removing the majority of the air bubbles and producing good quality AEFO biocomposites.

PP- and HDPE-based biocomposites showed a low density deviation of 2% and 1% respectively. A 13% density deviation from the ideal was found in the PLA biocomposite, possibly because the flax fiber might not have completely bonded with the PLA matrix, which could cause some porosity in the PLA biocomposite. Similar observations of weak interfacial bonding between natural fibers and PLA have also been reported in the literature (Wallenberger and Weston, 2004).

Table 6.1 Densities of different biocomposites

S. No	Biocomposite Sample	Measured Density (g/cm <sup>3</sup> )	Ideal Density (g/cm <sup>3</sup> )	Density Deviation (%)
1.	AEFO + 10% FF	1.191 ± 0.004	1.190	0
2.	PLA + 10% FF	1.369 ± 0.006	1.211	13
3.	PP + 10% FF	0.957 ± 0.005	0.942	2
4.	HDPE + 10% FF	0.972 ± 0.006	0.980	1

### 6.4.3 Tensile properties measurement and comparison

Figure 6.4 compares the tensile strengths of the AEFO-, PLA-, PP-, and HDPE-based biocomposites. When reinforced with 10% flax fiber content, the tensile strength of the AEFO composites increased from  $29.8 \pm 1.5$  MPa to  $31.4 \pm 1.6$  MPa. Among all the biocomposites, the AEFO-based biocomposites had the greatest tensile strength, followed by the PP, PLA, and HDPE biocomposites. Adding flax fiber increased the tensile strength of AEFO-, PP-, and HDPE-based composites, but it did not increase the tensile strength of the PLA composites. The increase in tensile strength of the AEFO, PP, and HDPE biocomposites is due to good fiber-polymer interfacial adhesion and the higher tensile strength of the flax fiber (Joesph *et al.*, 2000).

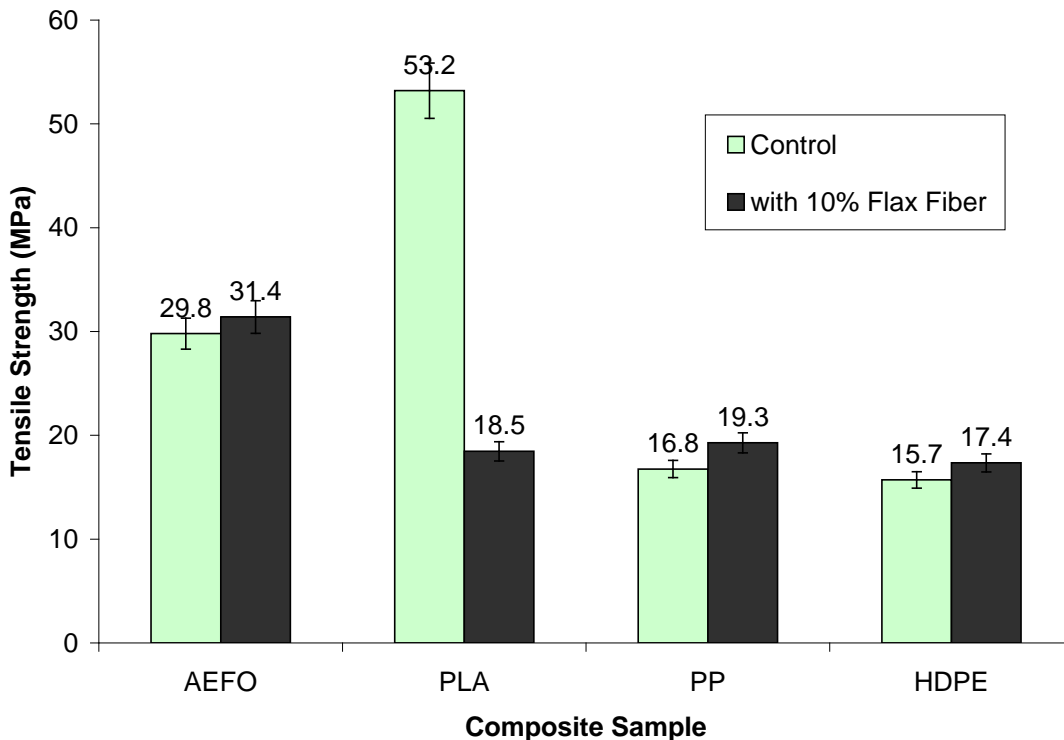


Figure 6.4 Tensile strength of AEFO, PLA, PP and HDPE matrices and their biocomposites. The uncertainty presented in the figure is at the 95% confidence level.

The PLA composites decreased in tensile strength with the addition of flax fiber (Figure 6.5). This decrease may be due to poor adhesion between the flax fiber and the PLA matrix, leading to inadequate stress transfer to the fiber from the polymer matrix (Soleimani *et. al.*, 2008). Oksman and co-workers (2003) reported similar results for PLA-flax composites. Usually, tensile strength varies linearly with natural fiber content to a limit. However, the initial sudden decrease in tensile strength of the PLA composite with 2% flax fiber may be due to poor fiber dispersion, which might have resulted in low stress transfer from fiber to the polymer matrix. Adding more flax fiber (5% w/w) increased the tensile strength, possibly because adequate fiber was then available for stress transfer. But further increasing the flax fiber to 10% w/w decreased the tensile strength, possibly due to poor matrix-fiber interfacial adhesion, which plays an important role where there is a higher fiber content within the composite.

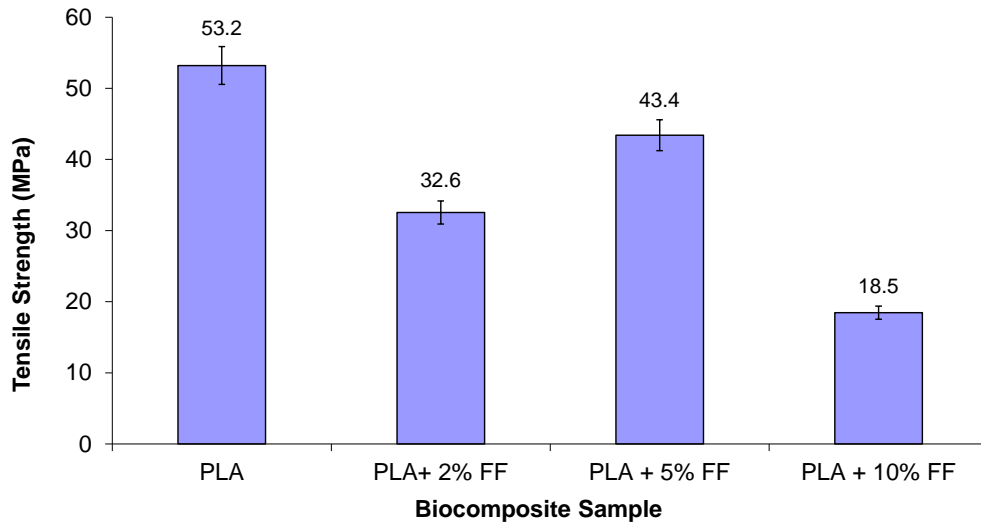


Figure 6.5 Effect of flax fiber on tensile strength of PLA biocomposites. The uncertainty presented in the figure is at the 95% confidence level.

The Young's modulus of all the biocomposites is shown in Figure 6.6. The PLA biocomposite had the highest Young's modulus, followed by the AEFO, PP, and HDPE biocomposites, in that order. With 10% (w/w) flax fiber content, the Young's modulus of the AEFO composite was 520 MPa, which was around 44% lower than that of the PLA biocomposite (921 MPa). However, the AEFO biocomposite had greater stiffness than did the PP and HDPE biocomposites, because it had higher density and fewer weak spots like air voids (0% density deviation).

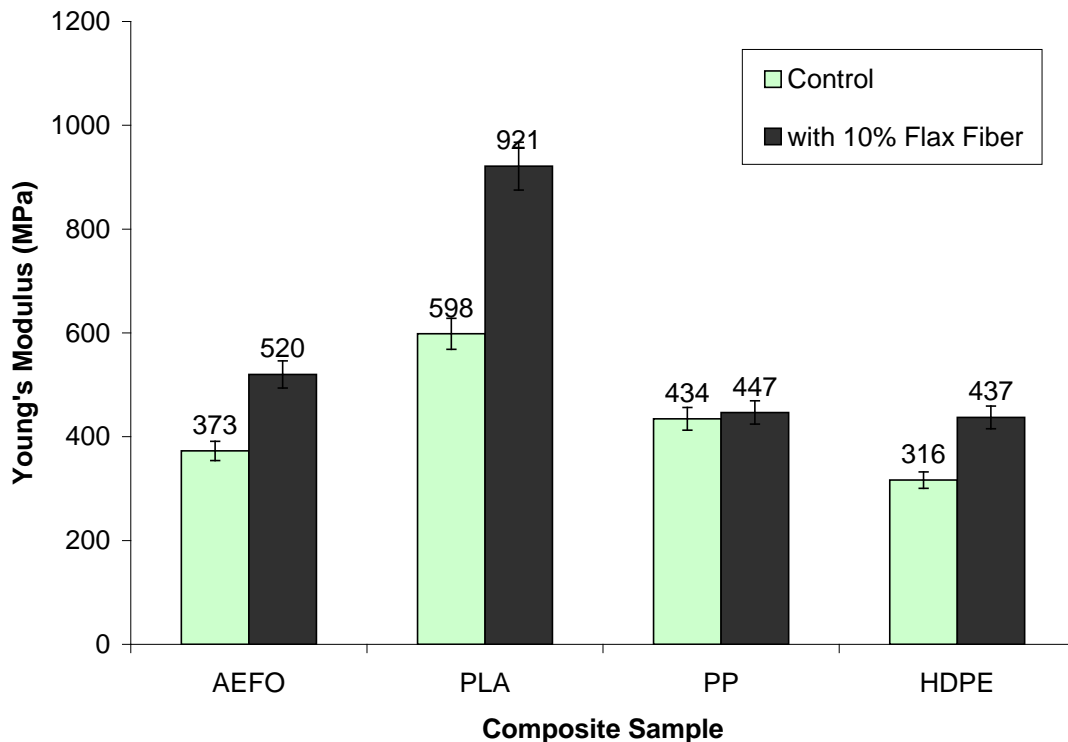


Figure 6.6 Young's Modulus of AEFO, PLA, PP, and HDPE matrices and their biocomposites. The uncertainty presented in the figure is at the 95% confidence level.

When the flax fiber content increased from 0 to 10% w/w, a corresponding steady increase in the Young's modulus of the PLA, AEFO, PP, and HDPE composites was observed. The effect of fiber loading on the AEFO composites is discussed in Chapter 5, and the effect of flax fiber on the PLA composites is shown in Figure 6.7. Similar



increases in the Young's modulus with an increase in natural fiber have been reported for PP and HDPE composites (Soleimani *et. al.*, 2008, Herrera-Franco *et. al.*, 1997). In contrast to the aforementioned decreased tensile strength shown by the PLA biocomposite, the Young's modulus for the PLA composite steadily increased with an increase in flax fiber content. Thus, even with weak interfacial bonding between PLA and flax fiber, the PLA biocomposite increased stiffness with an increase in flax fiber possibly due to the high modulus of flax fiber.

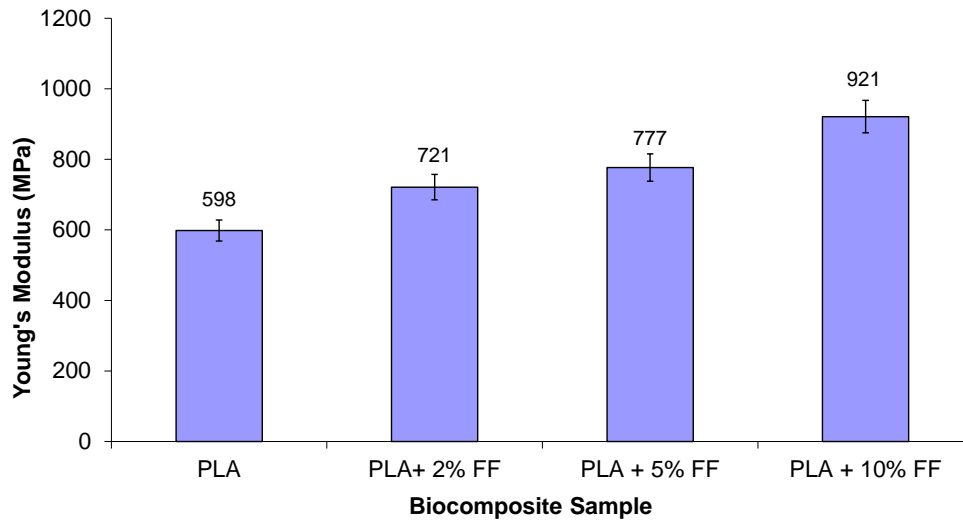


Figure 6.7 Effect of flax fiber on Young's modulus of PLA biocomposites. The uncertainty presented in the figure is at the 95% confidence level.

#### 6.4.4 Flexural properties measurement and comparison

The flexural strengths of the AEFO-, PLA-, PP-, and HDPE-based biocomposites are shown in Figure 6.8. The addition of flax fiber to the polymer matrices increased the flexural strength of the AEFO, PP and HDPE biocomposites and decreased the flexural strength of the PLA biocomposite. The AEFO biocomposite had the highest flexural

strength, at 64.5 MPa. AEFO has a high flexural strength of 53.5 MPa, and it was increased by the addition of the flax fiber. The higher flexural strength can also be attributed to better interfacial adhesion of flax fiber and the AEFO polymer matrix. The other biocomposites had the following flexural strengths: PLA biocomposite, 27.2 MPa; PP biocomposite, 32.4 MPa; and HDPE biocomposite, 29.1 MPa.

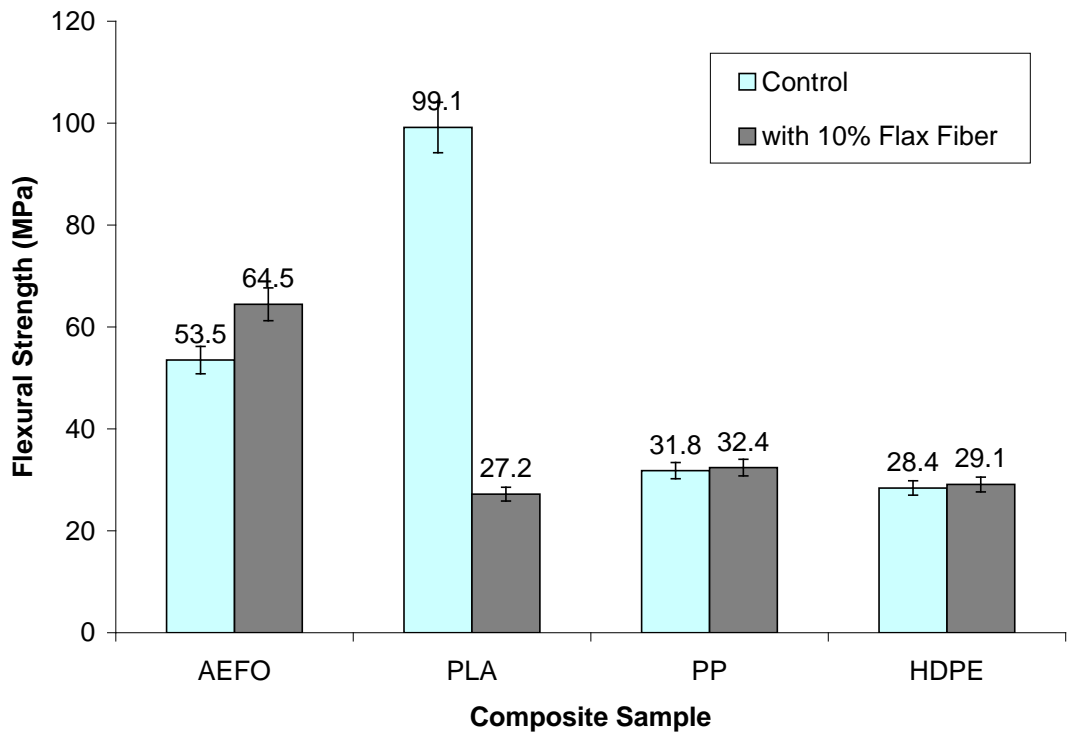


Figure 6.8 Flexural strength of AEFO, PLA, PP and HDPE matrices and their biocomposites. The uncertainty presented in the figure is at the 95% confidence level.

When the flax fiber content was increased from 0 to 10% w/w, the flexural strength of the PLA composite decreased significantly from 99.1 MPa to 27.2 MPa (Figure 6.9). PLA is a brittle polymer, and adding flax fiber increases the brittleness of

the biocomposite (Wallenberger and Weston, 2004); an increase in brittleness decreases its flexural strength. This decrease in flexural strength of the PLA composite with flax fiber loading also followed a similar trend as with tensile strength, which was discussed earlier in section 6.4.3. This decrease in the flexural strength of the PLA composite can be due to weak spots (e.g., air voids), since these biocomposites had a high density deviation from its ideal density; it may also be due to poor interfacial adhesion. Weak spots and poor adhesion may have caused a lack of shear strength transfer from the PLA matrix to the flax fiber.

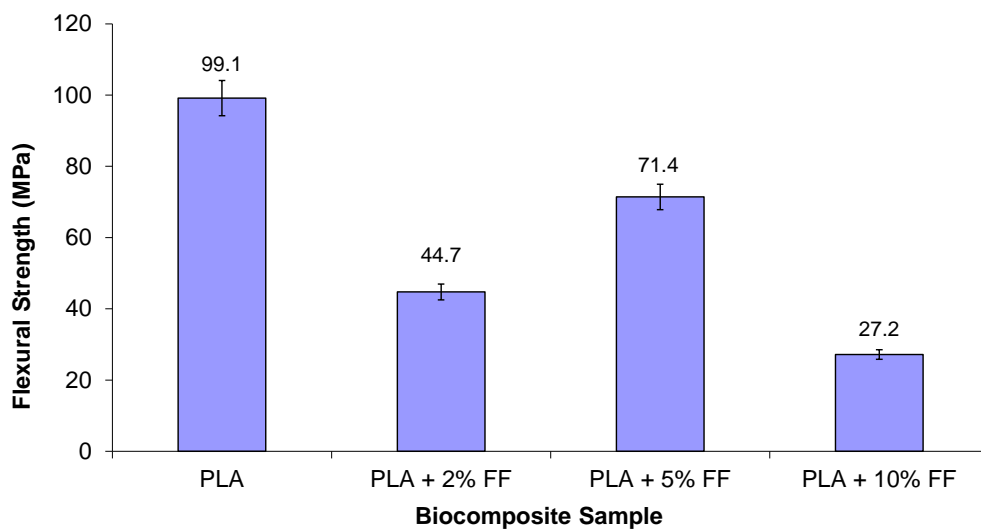


Figure 6.9 Effect of flax fiber on flexural strength of PLA biocomposites. The uncertainty presented in the figure is at the 95% confidence level.

The flexural modulus of the AEFO-, PLA-, PP-, and HDPE-based biocomposites are shown in Figure 6.10. While comparing, the PLA composites were found to have the largest flexural modulus (4.6 GPa, with 10% flax fiber content). This is because PLA is a stiff material and has a high flexural modulus of 3.34 GPa; adding the flax fiber further

increased the modulus. The AEFO-based biocomposite had a high flexural modulus of 2.98 GPa, which was significantly higher than that of the PP biocomposite (0.92 GPa) and the HDPE biocomposite (0.72 GPa). With each of the four polymer composites, the flexural modulus increased with an increase in the flax fiber content. However, with the AEFO composite, the increase in flexural modulus was not statistically significant.

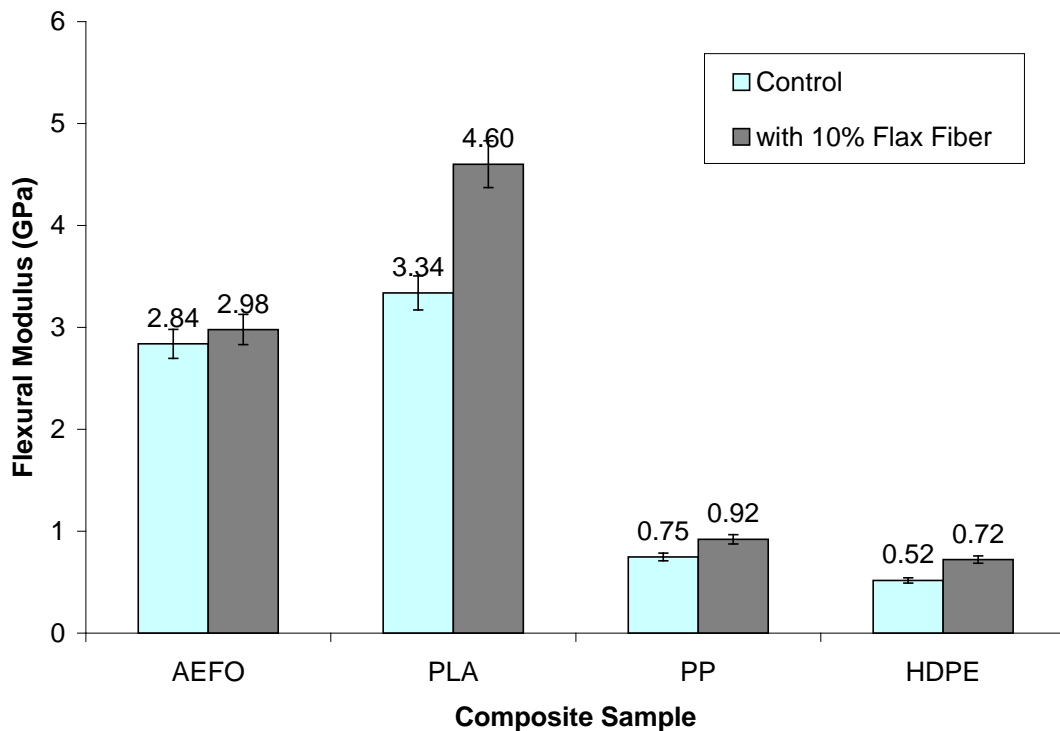


Figure 6.10 Flexural modulus of AEFO, PLA, PP and HDPE matrices and their biocomposites. The uncertainty presented in the figure is at the 95% confidence level.

As shown in Figure 6.11, there is a linear increase in the flexural modulus of the PLA composites with an increase in flax fiber content. (A similar trend was observed with the flexural modulus of the AEFO composites, as shown in Figure 5.13 in the previous chapter.)

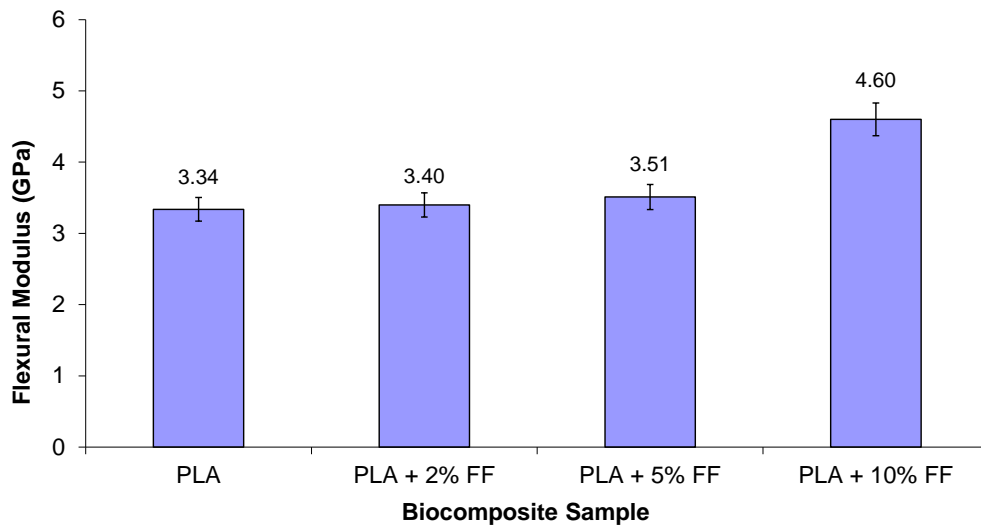


Figure 6.11 Effect of flax fiber on flexural modulus of the PLA biocomposites. The uncertainty presented in the figure is at the 95% confidence level.

### 6.5.5 Rockwell hardness measurement and comparison

The results of the Rockwell hardness tests for all four polymer-based biocomposites are shown in Figure 6.12. With 10% flax fiber loading, the Rockwell hardness number was found to increase for all four polymer composites. The increases in the hardness of the PLA and AEFO biocomposites were not statistically significant because these resins already have high hardness on their own. The increases in the hardness of the PP and HDPE composites can be explained by the increase in stiffness. Hardness is directly proportional to stiffness; hence, an increase in the stiffness will also mean an increase in hardness. It has already been shown in Figure 6.7 that the Young's modulus increases with an increase in the flax fiber content.

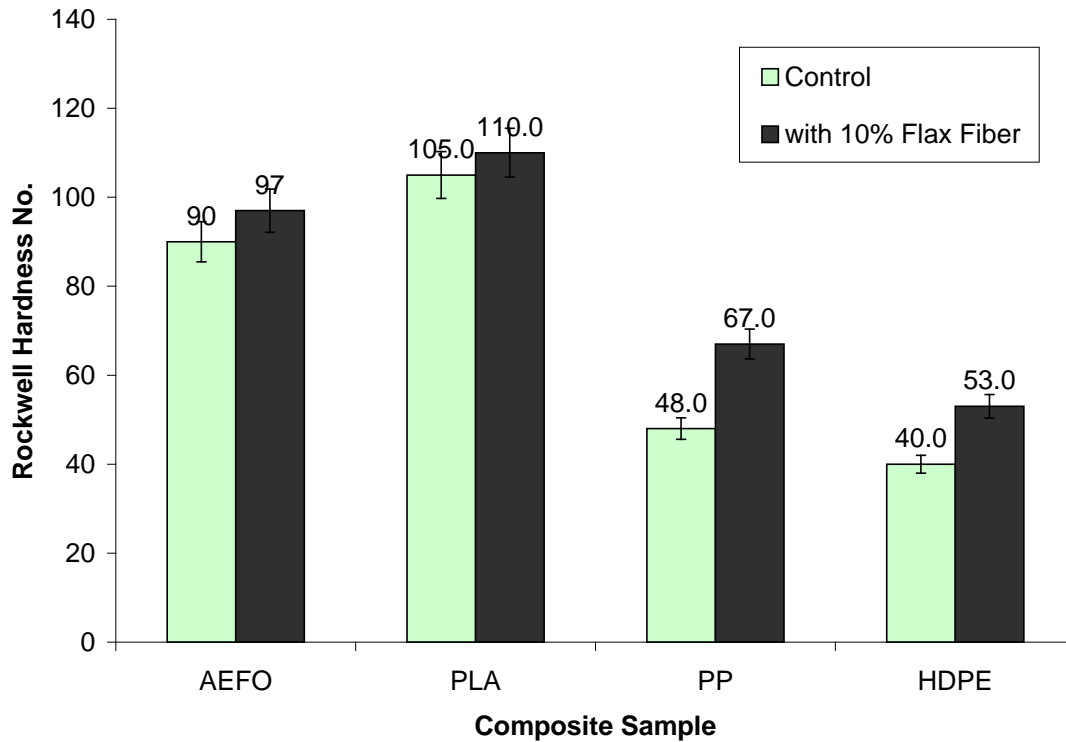


Figure 6.12 Rockwell hardness results of AEFO, PLA, PP and HDPE matrices and their biocomposites. The uncertainty presented in the figure is at the 95% confidence level.

## 6.6 Conclusions

All four polymer matrices-based biocomposites showed good water absorption characteristics, with a mass increase of less than 2% (w/w). The density of the AEFO biocomposites ( $1.191 \text{ g/cm}^3$ ) was found to be lower than that of the PLA biocomposites ( $1.369 \text{ g/cm}^3$ ) and higher than that of the PP ( $0.957 \text{ g/cm}^3$ ) and HDPE ( $0.972 \text{ g/cm}^3$ ) biocomposites. The PLA biocomposites had a higher density deviation of 13% from the ideal density.

Flax fiber served as reinforcement in the AEFO, PP, and HDPE biocomposites by enhancing their mechanical properties. However, the tensile strength and the flexural strength of the PLA composites were reduced with the addition of flax fiber. The Young's modulus, flexural modulus, and hardness of all four polymer-based

biocomposites increased with flax fiber reinforcement. The AEFO biocomposite had the highest tensile strength (31.4 MPa) and flexural strength (64.5 MPa), the HDPE biocomposite had the lowest tensile strength (17.4 MPa), and the PLA biocomposite had the lowest flexural strength (27.2 MPa). The PLA biocomposite had the highest Young's modulus (921 MPa), flexural modulus (4.6 GPa), and hardness (Rockwell hardness number = 110), followed by the AEFO biocomposite ( $E = 520$  MPa;  $E_H = 2.98$  GPa; Rockwell hardness number = 97), PP ( $E = 447$  MPa;  $E_H = 0.92$  GPa; Rockwell hardness No. = 67), and HDPE biocomposite ( $E = 437$  MPa;  $E_H = 0.72$  GPa; Rockwell hardness number = 53). Overall, the AEFO biocomposite was the strongest among the four biocomposites tested.

From these results, it can be concluded that the AEFO biocomposites have real potential for replacing PP- and HDPE-based biocomposites. PLA failed to develop a high quality biocomposite with flax fiber.

## **6.7 Summary of Chapter 6**

This chapter compares the physical and the mechanical properties of the AEFO biocomposite with those of the PLA, PP and HDPE biocomposites. For comparison, all biocomposites were reinforced with 10% silane-treated flax fiber. The mass increase percentage due to the water absorption was found to be less than 2% for all biocomposites. The measured density of the AEFO biocomposite was equal to its ideal density, whereas the PLA biocomposite had the highest density deviation of 13% from its ideal.

The results showed that the AEFO biocomposite was the strongest among all the tested biocomposites. The PLA composite had poor tensile and flexural results due high-density deviation and poor interfacial bonding with the flax fiber.

In the next chapter, a detailed summary of the entire thesis is presented, along with conclusions for each objective and recommendations for future work.



# Chapter 7

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## 7. Summary, Conclusions and Recommendations

### 7.1 Thesis Summary

With a rising demand for polymer and plastic materials, there is an urgent need for the development of sustainable, alternative biopolymer and bio-based composite materials. Plant oil-based resins and natural fibers have the potential to develop renewable biomaterials that can replace plastic materials.

Canada is a leading producer of flaxseed and other grains and therefore has ample raw material available that can potentially be used to develop renewable value-added products such as biopolymer and biocomposites. Currently, a very small amount of flax fiber and shives are being used for composite development in Canada. Saskatchewan-grown flaxseed oil and flax fiber were the principal raw materials used in this study. In this research, Saskatchewan-grown flaxseed oil was used to develop flax fiber-reinforced biocomposites. The fatty acid profile of the flaxseed oil was studied using  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR. The flaxseed oil contained high levels of unsaturated fatty acid (linolenic acid content was 54% w/w), and the FTIR confirmed the presence of the double bonds that make it amicable for polymerization. The flax fiber used in this work contained mainly cellulose (79 % w/w), and the density of the fiber was found to be  $1.46 \pm 0.01 \text{ g/cm}^3$ . The DSC results showed no degradation in the flax fiber below 200 °C, and hence it could be used for developing biocomposites using a VARTM process where the raw materials are exposed to a maximum temperature of 150 °C.

Flaxseed oil-based bio-resin was synthesized via epoxidation and acrylation reactions. The success of these reactions was determined by FTIR and  $^1\text{H}$  NMR techniques. Peaks at  $822\text{ cm}^{-1}$  and  $1244\text{ cm}^{-1}$  in the epoxidized flaxseed oil FTIR spectrum confirmed the formation of epoxy rings during epoxidation. The  $^1\text{H}$  NMR spectrum confirmed 3.7 epoxy groups per triglyceride in the epoxidized flaxseed oil. The peaks at  $1406$ ,  $984$ , and  $812\text{ cm}^{-1}$  in the AEFO FTIR spectrum indicate the acrylate group. The  $^1\text{H}$  NMR spectra showed 2.6 acrylate groups per triglyceride in the AEFO. The AEFO was molded into rectangular test specimens via the VARTM molding process.

To evaluate the potential use of the AEFO resin developed in this research, it was compared to one of the commercially available versatile biopolymers (i.e., PLA) and to two commonly used petroleum-based polymers for biocomposites (i.e., PP and HDPE). The test specimens for the comparative study (samples of PLA, PP, and HDPE) were prepared in the Department of Chemical and Biological Engineering, University of Saskatchewan. The AEFO resin was compared to these three polymers by measuring the following properties: density, water absorption, glass transition temperature, tensile strength, Young's modulus, flexural strength, flexural modulus, and Rockwell hardness.

The density of the AEFO resin ( $1.166\text{ g/cm}^3$ ) was found to be higher than the densities of both PP ( $0.906\text{ g/cm}^3$ ) and HDPE ( $0.946\text{ g/cm}^3$ ), and it was slightly lower than the density of PLA ( $1.189\text{ g/cm}^3$ ); density plays an important role in developing lightweight composites for various applications. Most plastic-based composite materials are frequently exposed to water, and hence water resistance is an important property to be considered during the selection of a polymer for a given application. Similar to common thermoplastic materials (PP and HDPE), PLA and AEFO bio-resin also have low water

absorption characteristics. Less than 1% w/w of water was absorbed by all four polymer samples tested in this study. Crystallinity plays an important role in the strength and the density of the polymer. The DSC results showed that the AEFO had a glass transition of 62 °C, which is similar to PLA; this indicates a high cross-link density.

Of the four polymers tested, PLA was found to be the strongest and the hardest. It had the highest tensile strength, Young's modulus, flexural strength, and flexural modulus. However, AEFO had mechanical properties that indicated it was stronger than PP and HDPE, and its properties were close to those of the PLA sample. The stress-curve of the AEFO sample showed that it had some ductility as well. Both PLA and AEFO had higher cross-link densities than did the PP and HDPE. AEFO mechanical properties were also comparable with those of the acrylated epoxidized soybean oil resin found in the literature.

After comparing the above properties of the AEFO samples with three commercially used polymers, it was important to assess the capability of AEFO to act as a matrix for natural fiber-based biocomposites. Flax fiber is one of the strongest natural fibers available in Canada, and it was chosen for this study to develop biocomposites with AEFO as the matrix. To improve the interfacial adhesion with the polymer matrix, the flax fiber was subjected to silane treatment. Several studies have shown that chemical treatment improves the matrix-fiber bonding and the strength of the resulting biocomposite. Silane-treated flax fiber-based biocomposites were developed using an AEFO resin via the VARTM process. The effect of fiber loading was investigated by varying the amount of flax fiber as follows: 2%, 5%, and 10% w/w. The physical and mechanical properties of the biocomposites obviously depend on the properties of both

polymer matrix and natural fiber. To enhance the strength of the polymer matrix, styrene was added at five different levels (10%, 20%, 30%, 40%, and 50% w/w).

Water absorption usually increases with an increase in the natural fiber content, and this was observed in the AEFO-based biocomposite. However, the mass increase percentage was found to be less than 1.5% for the maximum flax fiber content used in this study (10% w/w); an acceptable maximum amount for commercial use is less than 2%. It was found that the addition of styrene had no effect on the water absorption characteristics of the AEFO-based biocomposites.

Flax fiber serves as reinforcement for these AEFO biocomposites. All mechanical properties of the AEFO-based biocomposites (i.e., tensile strength, Young's modulus, flexural strength, and flexural modulus) improved with an increase in the flax fiber content. Adding styrene also improved the tensile strength, the Young's modulus, and the flexural modulus, but the styrene content decreased the flexibility of the composites by decreasing their flexural strength. Increasing the styrene content also increased the hardness of the biocomposite material.

A comparative study was done for the AEFO-based biocomposites with the PLA-, PP-, and HDPE-based biocomposites. The PLA, PP, and HDPE polymer matrices were also reinforced with silane-treated flax fiber. The flax fiber was mixed and compounded with these three polymer matrices via an extrusion process using a twin-screw extruder. The extrudates were pelletized and fed into an injection-molding machine to produce the biocomposite test samples.

The physical and mechanical properties of the AEFO-based biocomposites were compared to those of the PLA, PP, and HDPE biocomposites. The densities of all four

types of biocomposites were proportional to the densities of their respective polymers. It was found that the AEFO, PP, and HDPE biocomposites had very low density deviation from their respective ideal densities. However, the PLA biocomposite showed a higher density deviation of 13% from its ideal density, indicating a large amount of sample porosity. The mass increase observed during the water absorption tests was similar for all biocomposites, and it was less than 2% w/w for each. The tensile properties (tensile strength and Young's modulus) and the flexural properties (flexural strength and flexural modulus) of the AEFO-, PP-, and HDPE-based composites increased proportionally to the amount of flax fiber. However, the tensile strength and the flexural strength of the PLA-based biocomposites decreased with an increase in the flax fiber content. As well, with the PLA-based biocomposites, both the Young's modulus and the flexural modulus increased with an increase in the flax fiber content.

## 7.2 Main Conclusions

In this research, flaxseed oil was used to develop an acrylated epoxidized flaxseed oil (AEFO) bio-resin, which was then used to develop flax fiber-reinforced biocomposites. Several properties of the bio-resin and its biocomposite were tested and compared to a natural polymer (PLA) and to two synthetic polymers (HDPE and PP) and their respective biocomposites. There were seven objectives for this research, and conclusions were drawn for each.

Objective 1: To characterize (spectroscopically) and determine the potential double bond reaction sites in the flaxseed oil.

Conclusions drawn for this objective are as follows:

1. The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of the flaxseed oil revealed the presence of unsaturated fatty acids such as oleic, linoleic, and linolenic acids.
2. Flaxseed oil has a high level of unsaturated fatty acid (linolenic acid = 54%) that can be targeted for bio-resin development.
3. The FTIR spectrum of flaxseed oil showed the presence of double bond ( $=\text{C-H}$ ,  $\text{C=O}$ ,  $\text{C=C}$ ) sites that can be the reaction sites for the epoxidation process to start polymerization.

Objective 2: To develop flaxseed oil-based bio-resin for natural fiber reinforced biocomposites.

Conclusions drawn for this objective are as follows:

1. An acrylated epoxidized flaxseed oil-based resin can be synthesized by epoxidation and acrylation reaction for biocomposite application.
2. The results of the FTIR and  $^1\text{H}$  NMR spectra confirmed the success of epoxidation and acrylation reactions.
3. The epoxidized flaxseed oil has 3.7 epoxy groups per triglyceride molecule.
4. The number of acrylate groups per molecule of triglyceride was found to be 2.6.

Objective 3: To measure the following physical and mechanical properties of the developed bio-resin: density, glass transition temperature, water absorption, tensile strength, Young's modulus, flexural strength, flexural modulus, and Rockwell hardness.

Conclusions drawn for this objective are as follows:

1. The density of the developed AEFO bio-resin is  $1.166 \text{ g/cm}^3$ .
2. The mass increase during the water absorption test is less than 1%.
3. The glass transition temperature of the developed AEFO bio-resin is  $62 \text{ }^\circ\text{C}$
4. The mechanical properties of the AEFO bio-resin are as follows: tensile strength =  $29.8 \pm 1.5 \text{ MPa}$ , Young's modulus =  $373 \pm 19 \text{ MPa}$ , flexural strength =  $53.5 \pm 2.3 \text{ MPa}$ , flexural modulus =  $2.84 \pm 0.15 \text{ GPa}$ , and Rockwell hardness number =  $90 \pm 4$ .

Objective 4: To compare the properties of the flaxseed oil-based bio-resin measured in objective 3 with a biopolymer (PLA) and two commonly used synthetic polymers (HDPE and PP).

Conclusions drawn for this objective are as follows:

1. The AEFO developed in this research has a higher density than PP and HDPE, and a lower density than PLA.
2. The water absorption characteristics of AEFO are comparable with PLA, PP, and HDPE since all polymer samples had less than 1% mass increase during the water absorption test.
3. The tensile strength of the flaxseed oil-based polymer (AEFO) is 44% lower than PLA but 43-47% higher than PP and HDPE.
4. The flexural strength of the flaxseed oil-based polymer (AEFO) is 46% lower than PLA but 40-47% higher than PP and HDPE.
5. The PLA is the hardest resin, followed by AEFO, PP, and HDPE, respectively.
6. Based on the overall comparison, as a polymer matrix, PLA shows better mechanical properties compared to the AEFO and other polymers HDPE and PP; the AEFO showed better properties than HDPE and PP.

Objective 5: To develop a biocomposite using the flax oil-based bio-resin and flax fiber for plastic casing and furniture applications.

Conclusions drawn for this objective are as follows:

1. The flaxseed oil-based bio-resin was used to develop flax fiber reinforced biocomposites via vacuum-assisted resin transfer molding process.



2. Biocomposites were developed using 3 flax fiber loading (2%, 5%, 10% w/w) and 5 styrene content levels (10%, 20%, 30%, 40%, 50% w/w).

Objective 6: To measure the physical, thermal, and mechanical properties of the developed biocomposite as per objective 3.

Conclusions drawn for this objective are as follows:

1. Flax fiber serves as reinforcement in the AEFO-based biocomposite, and it improves all mechanical properties as well as increases the density and water absorption.
2. The addition of styrene improves the tensile strength and the Young's modulus of the AEFO biocomposite but decreases its flexural strength.
3. The density of the AEFO-based biocomposite (flax fiber 10% w/w) is 1.191 g/cm<sup>3</sup>.
4. There was a slight increase in mass during the water absorption test when flax fiber was added to each of the four polymer matrices; but still, the mass increase percentage was less than 2% for all AEFO-based biocomposites, which is in the acceptable range of various biocomposite industries.
5. The mechanical properties of the AEFO-based biocomposite with maximum flax fiber content in this study (10% w/w) are as follows: tensile strength =  $31.4 \pm 1.6$  MPa, Young's modulus =  $520 \pm 26$  MPa, flexural strength =  $53.5 \pm 2.3$  MPa, flexural modulus =  $2.98 \pm 0.17$  GPa, and Rockwell hardness number =  $97 \pm 5$ .

Objective 7: To compare the biocomposite developed using the flaxseed oil-based bio-resin measured in objective 6 with the PLA-, HDPE-, and PP-based biocomposites.

Conclusions drawn for this objective are as follows:

1. The water absorption characteristics are similar for all biocomposites tested; the mass increase percentage is less than 2 % w/w for each.
2. The AEFO biocomposites have no density deviation (0%) between the measured and the ideal densities; HDPE (1%) and PP (2%) biocomposites have a very low density deviation, whereas the PLA biocomposites have a high density deviation of 13%.
4. Fiber loading decreases the tensile and flexural strengths of the PLA biocomposite, whereas the same properties of the AEFO-, PP-, and HDPE-based biocomposites increase with an increase in the flax fiber. The flax fiber serves as reinforcement for the AEFO, PP, and HDPE biocomposites; however, it may have weak bonding with the PLA matrix and thus cannot develop a biocomposite with greater strength.
5. The tensile and the flexural properties of the AEFO-based biocomposites were found to be better than that of PP and HDPE.
6. Amongst the biocomposites developed from the AEFO bio-resin, the PLA, PP, and HDPE, biocomposites made of AEFO bio-resin showed better results than the PLA, HDPE and PP-based biocomposites.

Based on the mechanical test results, AEFO has the potential to replace PP and HDPE-based biocomposite material. The PLA-based natural fiber biocomposite showed poor properties and it might need some compatibilizer to improve the interfacial adhesion between matrix-fiber.

### **7.3 Recommendations for Future Work**

1. Biodegradability assessment of the flaxseed oil-based bio-resin:

It is important to assess whether the bio-resin is biodegradable since it is a thermoset material, which cannot be recycled. Studies on conducting biodegradation tests such as ASTM D5988 - 12 are suggested for future work.

2. Additional properties should be measured:

Some of the other properties of AEFO such as impact strength, UV-resistance, thermo-electrical properties must also be investigated in future; results from these studies will be helpful in predicting its potential commercial application.

3. More comparative studies should be performed:

More studies are needed to compare AEFO with other commercial biopolymers derived from soybean and other plant oil. This will help in determining the potential of flaxseed-based bio-resin in commercial industries.

4. Commercial application of the flaxseed oil-based bio-resin:

Based on the physical and mechanical properties of the flaxseed oil-based bio-resin and its biocomposite, studies must be conducted to develop commercial products like plastic casing or structural panels.

5. Life cycle analysis of AEFO and the AEFO-based biocomposite:

There is no literature on life cycle analysis of plant oil-based bio-resins and their biocomposites. Therefore, it is essential to conduct a full cradle-to-grave life cycle analysis of AEFO and its biocomposite to assess the environmental impact at different stages; this will help in improving the different processes and making viable decisions for commercial production.

6. Other grades of the flaxseed oil-based bio-resin should be developed:

Other polymerization reactions such as glycerolysis and amidation reaction should be investigated to develop other grades of the flaxseed oil-based resin.

7. A study on flaxseed oil and flax fiber quality is also recommended:

The effect of flaxseed oil quality on the quality of the bio-resin should be studied. Flax fiber quality should also be studied in order to determine its effect on the physical properties of the biocomposites.

8. A study of moisture uptake and loss in the biocomposites should be performed:

To date no study has been performed on the effect of water adsorption/desorption cycles on the mechanical and physical properties of the biocomposites. For real-world application it is important to know how adsorption/desorption cycles affect the properties of the biocomposite.

9. It would be ideal if a dimensionless number representing the quality of a biocomposite was developed. This would aid in classifying biocomposites in terms of their utility.

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## APPENDIX A

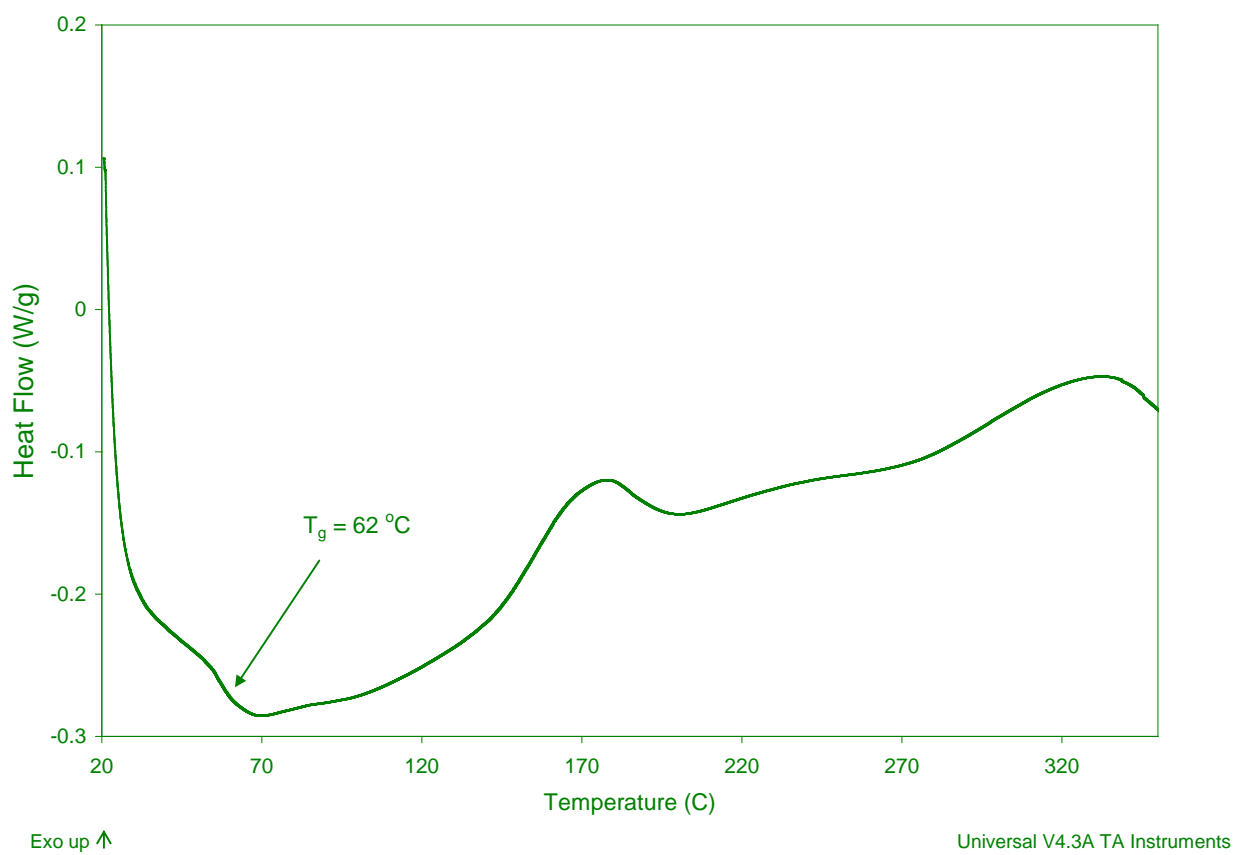


Figure A.1 DSC thermogram of AEFO

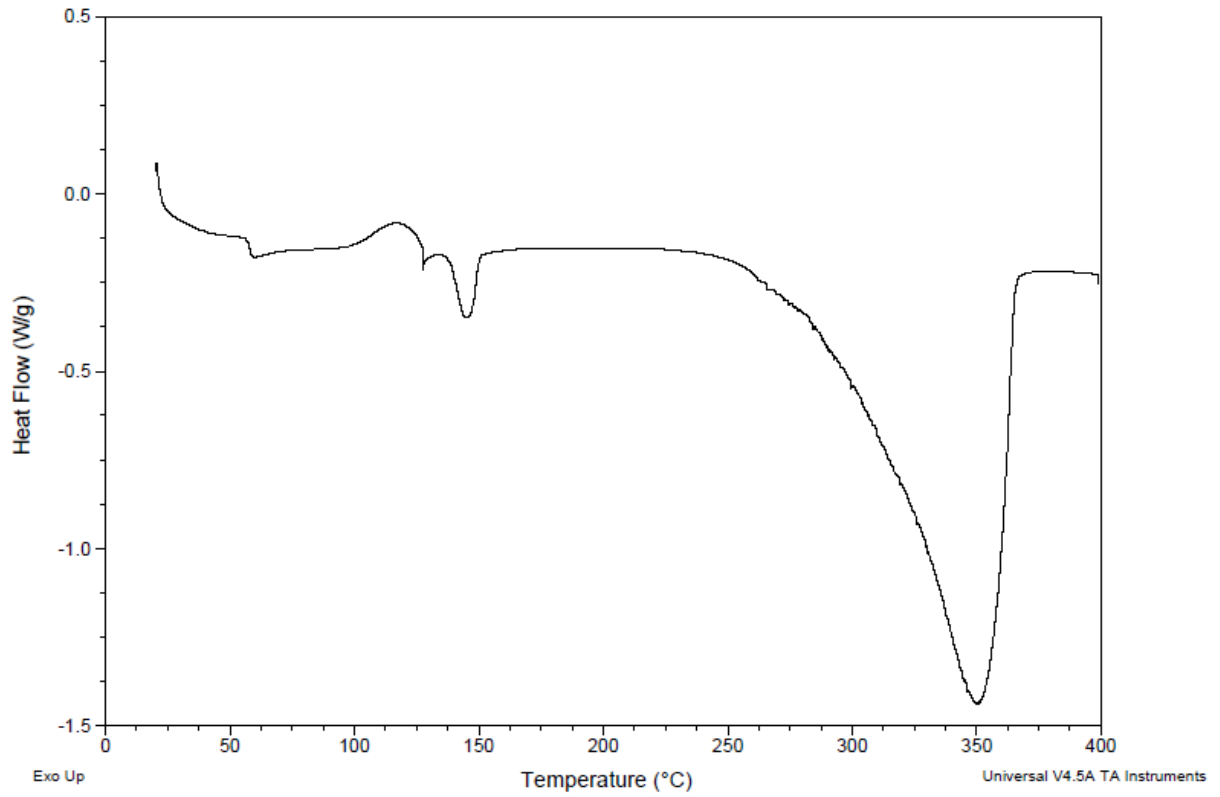


Figure A.2 DSC thermogram of PLA

Table A.1 Measured properties of AEFO bio-resin and AEFO-based biocomposites

Material	Density (g/cm <sup>3</sup> )	Mass Increase during water absorption test (%)	Tensile Strength (MPa)	Young's Modulus (MPa)	Flexural Strength (MPa)	Flexural Modulus (GPa)	Rockwell Hardness No.
AEFO Bio-resin	1.166	0.65	29.8	373	53.5	2.84	90
AEFO + 2% FF	1.172	0.85	30.2	425	58.0	2.86	92
AEFO + 5% FF	1.180	1.08	30.9	465	61.0	2.92	94
AEFO + 10% FF	1.191	1.36	31.4	520	64.5	2.98	97
AEFO + 10% Styrene + 10% FF	1.180	1.30	31.9	574	63.5	3.00	101
AEFO + 20% Styrene + 10% FF	1.170	1.21	32.1	615	63.0	3.05	105
AEFO + 30% Styrene + 10% FF	1.166	1.32	33.3	664	62.4	3.11	108
AEFO + 40% Styrene + 10% FF	1.156	1.31	35.6	695	62.3	3.16	110
AEFO + 50% Styrene + 10% FF	1.151	1.34	37.9	729	61.6	3.22	113



Table A.2 Measured properties of PLA polymer matrix and PLA-based biocomposite

Material	Density (g/cm <sup>3</sup> )	Mass Increase during water absorption test (%)	Tensile Strength (MPa)	Young's Modulus (MPa)	Flexural Strength (MPa)	Flexural Modulus (GPa)	Rockwell Hardness No.
PLA	1.189	0.32	53.2	598	99.1	3.34	105
PLA + 2% FF	1.253	0.49	32.6	721	44.7	3.40	106
PLA + 5% FF	1.308	0.60	43.4	777	71.4	3.51	108
PLA + 10% FF	1.369	0.75	18.5	921	27.2	4.60	110

Table A.3 Measured properties of PP polymer matrix and PP-based biocomposite

Material	Density (g/cm <sup>3</sup> )	Mass Increase during water absorption test (%)	Tensile Strength (MPa)	Young's Modulus (MPa)	Flexural Strength (MPa)	Flexural Modulus (GPa)	Rockwell Hardness No.
PP	0.906	0.25	16.8	434	31.8	0.75	48
PP + 10% FF	0.957	0.75	19.3	447	32.4	0.92	67

Table A.4 Measured properties of HDPE polymer matrix and HDPE-based biocomposites

Material	Density (g/cm <sup>3</sup> )	Mass Increase during water absorption test (%)	Tensile Strength (MPa)	Young's Modulus (MPa)	Flexural Strength (MPa)	Flexural Modulus (GPa)	Rockwell Hardness No.
HDPE	0.946	0.14	15.7	316	28.4	0.52	40
HDPE + 10% FF	0.972	1.26	17.4	437	29.1	0.72	53

## APPENDIX B

### Sample Raw Data for AEFO Bio-resin

#### B.1 Tensile Test

Table B.1.1 Tensile test break point of AEFO Bio-resin

Break (Standard) : Load at Break (Standard)	12.105 N
Break (Standard) : Extension at Break (Standard)	9.175 Mm
Break (Standard) : Time at Break (Standard)	220.2 Sec

Table B.1.2 Tensile test data of AEFO Bio-resin\*

Time (sec)	Extension (mm)	Load (N)	Stress (N/mm <sup>2</sup> )	Strain	
0.0	0.00	0.07	0.00	0.00	
5.0	0.21	29.65	0.69	0.00	
10.0	0.42	78.67	1.83	0.01	
15.0	0.63	162.10	3.76	0.01	
20.0	0.83	236.07	5.48	0.02	
25.0	1.04	310.69	7.22	0.02	
30.0	1.25	386.39	8.97	0.03	
35.0	1.46	459.76	10.68	0.03	
40.0	1.67	530.42	12.32	0.03	
45.0	1.88	598.09	13.89	0.04	
50.0	2.08	663.21	15.40	0.04	
55.0	2.29	724.96	16.84	0.05	
60.0	2.50	783.65	18.20	0.05	
65.0	2.71	839.20	19.49	0.05	
70.0	2.92	891.76	20.71	0.06	
75.0	3.12	942.26	21.88	0.06	
80.0	3.33	990.19	23.00	0.07	
85.0	3.54	1035.10	24.04	0.07	
90.0	3.75	1076.61	25.00	0.07	
95.0	3.96	1114.13	25.88	0.08	
100.0	4.17	1147.06	26.64	0.08	
105.0	4.37	1175.81	27.31	0.09	
110.0	4.58	1203.14	27.94	0.09	
115.0	4.79	1228.23	28.53	0.10	
120.0	5.00	1249.10	29.01	0.10	
125.0	5.21	1265.74	29.40	0.10	
130.0	5.42	1277.31	29.67	0.11	
135.0	5.62	1283.45	29.81	0.11	
<b>140.0</b>	<b>5.83</b>	<b>1283.98</b>	<b>29.82</b>	<b>0.12</b>	←Max Stress

145.0	6.04	1278.70	29.70	0.12
Time	Extension	Load	Stress	Strain
(sec)	(mm)	(N)	(N/mm <sup>2</sup> )	
150.0	6.25	1267.54	29.44	0.13
155.0	6.46	1250.99	29.05	0.13
160.0	6.67	1230.17	28.57	0.13
165.0	6.88	1206.70	28.03	0.14
170.0	7.08	1182.07	27.45	0.14
175.0	7.29	1157.82	26.89	0.15
180.0	7.50	1135.16	26.36	0.15
185.0	7.71	1114.44	25.88	0.15
190.0	7.92	1096.24	25.46	0.16
195.0	8.13	1080.29	25.09	0.16
200.0	8.33	1066.34	24.77	0.17
205.0	8.54	1054.27	24.49	0.17
210.0	8.75	1043.88	24.24	0.18
215.0	8.96	1034.47	24.03	0.18

*\*only partial data of 5 sec interval is presented whereas data was collected for each 0.1 sec interval by Instron Bluehill software*

Sample Calculations:

$$\begin{aligned} \text{Tensile Strength, } \sigma_t &= \frac{F_{\max}}{A} \\ &= 29.82 \text{ (N/mm}^2 \text{ or MPa)} \end{aligned}$$

$$\begin{aligned} \text{Young's Modulus, } E &= \frac{\Delta\sigma}{\Delta\varepsilon} \\ &= \frac{(15.90 - 11.21)}{(0.043 - 0.030)} \\ &= 373 \text{ (N/mm}^2 \text{ or MPa)} \end{aligned}$$

## B.2 Bending Test

Table B.2 Bending test data of AEFO Bio-resin\*

Time (sec)	Extension (mm)	Load (N)	Flexural stress (MPa)
0	0.00	0.0	0.0
5	-0.10	0.0	0.0
10	-0.36	-5.2	3.8
15	-0.72	-11.5	8.5
20	-1.03	-17.4	12.8
25	-1.34	-22.9	16.9
30	-1.63	-28.1	20.8
35	-1.90	-33.1	24.4
40	-2.20	-37.8	27.9
45	-2.44	-42.4	31.3
50	-2.65	-46.8	34.5
55	-2.86	-50.9	37.6
60	-3.07	-55.0	40.6
65	-3.28	-58.9	43.5
70	-3.47	-62.3	46.0
75	-3.67	-65.5	48.3
80	-3.85	-68.3	50.4
85	-3.98	-70.6	52.1
90	-4.12	-72.3	53.3
91.15	-4.18	-72.5	53.5

← Max stress

\*only partial data of 5 sec interval is presented whereas data was collected for each 0.05 sec interval by Instron Bluehill software

### Sample Calculations:

$$\begin{aligned} \text{Flexural Strength, } S &= \frac{3P'L}{2bd^2} \\ &= 53.5 \text{ MPa} \end{aligned}$$

$$\text{Flexural Modulus, } E_H = \frac{L^3 s}{4bd^3}$$

where, s= 18.02 , L = 64 mm, b= 12.7 mm, d=3.2 mm

$$E_H = \frac{64^3 \times 18.02}{4 \times 12.7 \times 3.2^3} = 2838 \text{ MPa}$$

### B.3 Hardness Test Results for AEFO

Table B.3 Hardness test data of AEFO Bio-resin

Trial	Rockwell Hardness No.
1	89
2	85
3	92
4	92
5	88
6	86
7	90
8	93
9	93
10	90
Average Rockwell Hardness No.	90
Standard Deviation	2.7

## APPENDIX C

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