Vacuum Infusion Molding of Natural Fibre Reinforced Biobased Resin Composite

by

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A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy
Faculty of Forestry
University of Toronto

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Doctor of Philosophy

Center for Bio material and Bio composite Processing, Faculty of Forestry
University of Toronto

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Abstract

The increasing demand in the field of bio material research for an in-depth understanding of processing phenomenon to convert it into a useful product is essential. Besides, there is inadequate information regarding the dependency between their processing mechanism and mechanical performance. The main focus of this work is to address the issues of the resin flow behavior of natural fibre in vacuum infusion molding, the determination of permeability and validation of the proposed contact angle model with experimental data. The proposed model shows greater accuracy when validated with experimental observation. The outcome of this research emphasizes the wetting mechanism and fibre network of sisal mats are the major factors that reduces 26% of permeability as compared to glass fibres. In addition, it is observed that the swelling phenomenon had a minimal influence on the permeability of the sisal fibre mat.

The complex phenomena occurring during wetting of natural fibres with epoxidized soybean oil (ESO) in terms of contact angle and surface energy are investigated. The fibres are treated with various reagents to improve the wetting behavior. It is noted that NaOH treatment provides considerable amount of increase in surface area of the exposed cellulose that aids in enhancement of wettability characteristics by increasing the surface energy from 18 mN/m to
23.5 mN/m while reducing the contact angle from 53° to 31°. Conversely, there is a formation of virtual layer on the fibre when treated with silane and isocyanate. Moreover, isocyanate treated fibre exhibits improved wetting behaviour in terms of increase in surface energy from 18 mN/m to 25.5 mN/m when wetted with ESO.

The kinetics study of the curing reaction of the resin is performed by differential scanning calorimetry. A new empirical model is proposed to analyze the kinetic data obtained experimentally. The results highlighted that the proposed model attained significant improvement to predict the experimental cure kinetic data qualitatively and quantitatively. The addition of 30% ESO in the conventional system increases the activation energy of the system up to 108 kJ/mol. The effect of the surface treatments of natural fibre, fibre loading direction, and resin flow direction on the tensile properties of developed composites are investigated. The longitudinal tensile strength of developed composites demonstrated a 7-8 fold increment, as compared to the transverse direction tensile strength. The flow along the fibre provides 10% increment in tensile strength due to higher permeability.
Acknowledgments

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<tr>
<td>K</td>
<td>Permeability</td>
</tr>
<tr>
<td>Q</td>
<td>Volumetric flow rate</td>
</tr>
<tr>
<td>ΔL</td>
<td>Preform length</td>
</tr>
<tr>
<td>A</td>
<td>Mold cavity transverse area</td>
</tr>
<tr>
<td>ΔP</td>
<td>Pressure gradient</td>
</tr>
<tr>
<td>d_f</td>
<td>Fibre diameter</td>
</tr>
<tr>
<td>k</td>
<td>Kozeny constant</td>
</tr>
<tr>
<td>n</td>
<td>Experimental parameter</td>
</tr>
<tr>
<td>C</td>
<td>Experimental parameter</td>
</tr>
<tr>
<td>a,b,c</td>
<td>Empirical constants</td>
</tr>
<tr>
<td>W_A</td>
<td>Work of adhesion</td>
</tr>
<tr>
<td>ΔE_A</td>
<td>Activation energy</td>
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### Greek Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>µ</td>
<td>Viscosity of the resin</td>
</tr>
<tr>
<td>φ</td>
<td>Porosity of the mat</td>
</tr>
<tr>
<td>θ</td>
<td>Contact angle</td>
</tr>
<tr>
<td>γ</td>
<td>Surface free energy</td>
</tr>
<tr>
<td>α</td>
<td>Degree of cure</td>
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1 Introduction

1.1 Overview

Modernization inclines towards the utilization of green products in the field of composites which promotes the limited usage of synthetic materials in many engineering applications. This is due to their positive features, such as high strength/stiffness to weight ratio, economical aspect, competitive specific mechanical strength, reduced energy consumption, CO₂ reduction, biodegradability, and favorable non-brittle fracture on impact (Joshi et al., 2004; Oksman 2001; Faruk et al., 2012, 2014). The compound annual growth rate of biomaterial market is forecasted to grow 14.85% from 2012 to 2016 in North America, Europe, and Asia, which are accounted as the major global markets (Global Biomaterial Market, 2012–2016). The increasing demand in the field of biomaterial research for an in-depth understanding of processing phenomenon to convert it into a useful product is essential. These bio materials are fabricated by using well established molding techniques such as hand layup, press molding, pultrusion, resin transfer molding, and vacuum infusion molding (Mei-po Ho et al., 2012; Francucci et al., 2009).

The current trend is towards increased use of vacuum infusion molding owing to its excellent repeatability, cost effectiveness, environmental benefits, and better mechanical properties. The basic principle of the method is that a stack of dry fabrics is placed between rigid mold half and flexible bag. The bag is sealed to the mold except at certain positions being open for resin supplies and outlets. Liquid resin is then forced into the stack by a reduction of the pressure at the outlets, while keeping the atmospheric pressure at the inlets (H.M. Andersson, 2001). To effectively use this technique, conceptual understanding of natural fibres, its impact on process parameters, and structure-property characteristics is an imperative. Sisal fibre is considered as a suitable reinforcement for the composites because it has high permeability and good interface with thermoset material (Francucci et al., 2009, 2011; Schmidt et al., 2009). In engineering applications, thermoset matrix composites are preferred due to their effective performances in terms of its mechanical behaviour which institutes ESO (epoxidized soy bean oil) resin employment in the matrix material being environmental friendly.

Most of the studies have been devoted to mechanical properties of the natural fibre based composites and few studies pertaining to flow prediction in terms of permeability for glass fibre
is available. The studies on aspects concerned with the permeability of natural fibre for vacuum infusion processes are inadequate.

The main purpose of this research is to create a detailed knowledge base of vacuum infusion process by proposing a new model describing the permeability of a sisal/ESO blended resin system. While employing traditional manufacturing process, it is observed that the wetting is non-uniform and indicates insufficiency. Moreover, the resin distribution is inadequate, leading to non effective performance of the composite. Hence, in this study an attempt is made to design and develop a fibre wetting process with higher efficacy to enhance the fibre/matrix interface. Subsequently, to develop natural fibre reinforced composite with superior mechanical strength, it is essential to reduce hydrophilic behaviour of the fibers through surface modifications. Therefore, it is imperative to modify the fibre and/or the matrix to improve the wetting of fibre and achieve optimum fibre/matrix properties.

One of the basics for optimizing the process parameters for vacuum infusion process is the development of a suitable kinetic model. Scanty information available creates barriers in understanding and corresponding prediction of the curing behaviour of bio based system which is a major constraint in their applicability for high performance engineering structures. To address these issues, another objective is framed in this work to predict the curing behaviour of the resin during the molding process. The cure behaviour of the bio based resin is elucidated by proposing a model to access cure progress of the resin during the molding process. Another aim of this research is to investigate tensile properties of the manufactured bio based composites to facilitate commercialization.

1.2 Problem statement

Study of flow characteristics in vacuum infusion of natural fiber bundles poses complexity as it involves macro and micro infusion taking place within and along the fibres. The key factor in the performance of the composite during production is facilitated by good wetting of the fibre by the matrix. This problem is called as permeability.

The permeability study of natural fiber in vacuum infusion process demands consideration of the undesirable resin flow occurring through natural fiber that is used as reinforcement. In addition,
the resin flow path deviates from the standard path which is attributed to the unpredictable variations in the fibre preform mat.

Traditionally, flow prediction in liquid molding processes is a trial-and-error approach which is expensive and time consuming. Further, there is an ambiguity in achieving desired properties. Incorporation of proposed approach demands greater understanding of the interdependencies between the various process parameters (Han et al., 2000; Hammami et al., 2000). Hence in this study, an attempt is made to determine the governing parameters, causes, methodology for bio fibre and bio resin while employing vacuum infusion process. Subsequently, the wetting, fibre network, and swelling parameters are considered. Expressing the permeability with respect to fibre network structure is complicated (Chih-hsin et al., 1998).

The generalization of wetting behaviour of natural fibre is difficult due to swelling, extraction, macromolecular rearrangement, intricate microstructure for the presence of cellulose, hemicelluloses, lignin, pectin, and etc., which poses difficulties in prediction of wetting behaviour (Barsberg 2001). Further, natural fibres do not effectively adhere to non-polar resins due to these polar groups. This may be addressed by chemical modification. Hence in this study, an attempt is being made to determine the effect of different chemical treatments carried out in sisal fibre surfaces on wetting properties targeting the potential applications of these fibres.

Cure kinetics of bio-based epoxy plays a prominent role in this infusion process. During the cure of a bio based resin a number of complex chemical and physical changes occur as the material turns from a viscous liquid to a highly cross linked solid. A good understanding of the kinetic parameters is essential to control and optimize the cure schedule, material properties and processing conditions of thermosetting materials. Determination of the kinetic parameters such as the reaction orders, activation energies, and the kinetic rate constants are elucidated.

1.3 Research Hypothesis and Objectives

1.3.1 Hypothesis:

It is to be hypothesized that wetting behavior of natural fibre and porosity will majorly affect the permeability during composite processing.
1.3.2 Research Objectives

Overall objective:

The main objective of this research is to study the effective parameters on the performance of natural fibre reinforced bio-based epoxy composites manufactured by vacuum infusion process.

Sub objective:

1) Investigate the processing factors influencing the flow behavior of biobased epoxy resin over the porous natural fibres in vacuum infusion process.
2) Study the cure kinetics of bio-based epoxy resin without natural fibre.
3) Explore the effect of fibre surface modifications on natural fibre/biobased epoxy interactions.
4) Characterize the mechanical, thermal, and morphological properties of natural fibre reinforced bio-based epoxy composites manufactured by vacuum infusion process.

1.4 Research approaches

The mold filling and curing processes play an important role in vacuum infusion and are governed by the following key factors: permeability, porosity, preform architecture, viscosity, temperature, part geometry, and resin inlet location. In order to achieve the primary goals of this project, the permeability and cure kinetics of resin were investigated. Subsequently, the wetting, fibres network, and swelling parameters were analyzed to study the permeability of natural fibres.

Permeability needs to be viewed with two perspectives:

a. Contact angle and time are considered initial phenomena influencing permeability at the micro level;
b. Flow front and filling time gradually taking centre stage as secondary governing phenomena following the micro-level.

In an infusion process the driving force for the micro flow is the capillary pressure developed in the intra tow region due to the imperfect and hollow configuration of natural fibers which
provides more capillary channels for micro-flow. Therefore, this should be added in flow prediction equation to improve their accuracy.

The outcome of this study is expected to provide a parameter window and database encompassing the extent of interdependency of parameters for vacuum infusion processes employed for natural fibre. Detailed results of the permeability modeling are discussed in chapter 3.

The hydrophilic nature of natural fibres leads to poor adhesion between fibre and matrix that reduce the strength of the composite. This may be addressed by chemical modification. The outcome of this study is expected to improve the understanding and assist in arriving at effective design of the surface of fibre to a liquid molding process and thus improving the reliability in flow prediction of the process. The cure kinetics of epoxy resins and triethylene tetramine (TETA) hardener in the presence of ESO are studied by DSC, and the dependence of the curing activation energy with conversion for different analytical approaches are identified to propose the new models of the cure process if desirable. If the experimental data show that the existing models are not accurate to describe the cure process, the development of new models is necessary. Another aim of this research is to investigate tensile properties of the newly manufactured composites. This study also addresses the effect of fibre orientation, flow direction, and process parameters on tensile strength of composites. The proposed work flowcharts of this research are as follows in Figure 1.1.
1.5 Outline of the thesis

This thesis focuses on the manufacture of natural fibre composites using a vacuum infusion molding process with bio based resin. A technical discourse on the fundamentals of natural fibre composites and their manufacturing processes are presented in Chapter 2. This chapter briefly presents a review of permeability modeling, surface chemistry and cure kinetics. In the industry the processing time is a key parameter and the mold filling stage is therefore critical for a vacuum infusion system.

In Chapter 3, a study of the permeability of the sisal fibre mats when exchanged with a glass fibre mat and subsequently, the wetting, fibre network, and swelling parameters are considered. An empirical model is introduced to predict the permeability of sisal fibre mat in a vacuum infusion process. The proposed model is compared to experimental measurements and the results
are discussed. The findings in this chapter were published in the Canadian journal of chemical engineering.

In order to improve the wetting properties of the sisal fibre in vacuum infusion process various fibre treatments are investigated. The impact of these treatments on the contact angle and surface energy are reported in chapter 4. This chapter also presents the complex phenomena occurring during wetting of natural fibres with bio based resin. These results were published in the Journal of reinforced plastics and composites.

In Chapter 5, a kinetic study of the bio based epoxy is performed to describe the curing behavior of the resin using differential scanning calorimeter (DSC). An empirical model is introduced to predict the cure kinetics of the resin. Details about the experimental procedure and data analysis method are given. These results were published in the Canadian journal of chemical engineering.

In chapter 6, in order to improve the surface properties and mechanical properties of the natural fibre various fibre treatments are performed. The influence of the surface treatments of natural fibre, fibre loading direction, resin flow direction and process behaviour on the tensile properties of developed composites is also presented in this chapter. The outcome of the studies is published in the polymer composites. Chapter 7 gives a summary of all the results found in the previous chapter and recommendations for future work.
2 Literature Review

Although natural fibre-reinforced bio based plastics is a relatively new progress in recent trend of composite materials. The subsequent sections present some of the important literatures relevant to the natural fibre, surface modification, and processing and cure kinetics of bio based system by vacuum infusion. Understanding the physical and chemical nature of reinforcing natural fibres is an important in developing appropriate processes for their inclusion in composite system. These directly affect the flow characteristics (Karbhari et al., 1997; Rodriguez et al., 2007) during liquid molding processes as well as the wetting properties with the matrix. The subsequent sections present the physical and chemical of natural fibres.

2.1 Physical nature of natural fibre

The structures of natural fibres are relatively complex, with each fibre having a compound of cellulose micro fibrils embedded in a soft lignin and hemi cellulose (Dicker et al., 2014). The structure is shown in Figure 2.1.

![Figure 2.1 Structure of natural fibre](image)

The single fiber (primary fiber) resembles a hollow composite. Cellulose fibrils act as reinforcements. Hemicelluloses, pectin, lignin and the other amorphous components form the
matrix which holds these fibrils together (Fuqua et al., 2012). The hydrogen bond in natural fibre provides good mechanical properties of the fibres. Hemi cellulose is responsible for the thermal degradation, moisture absorption and biodegradation of the fibre. Lignin is responsible for the UV degradation of the fibre (Rouison et al., 2004). The thermal stability of the reinforcing fibres is a key parameter in composite processing, especially in the case of thermosetting resins and their exothermic curing behavior (Rouison et al., 2004).

Generally, each fibre contains a primary wall and three secondary walls. The interlayer of the secondary wall governs the mechanical properties of fibre (Azwa et al., 2013). The microfibrils orientation has a greater effect on the elastic modulus of the fibers (Khalil et al., 2012). The central axis of the natural fibre is hollow nature and is termed lumen. It reveals that, due to the unique morphology of natural fibres, there is a noticeable impact in the liquid molding processing. In specific, the hollow structure provides greater channels for flow which lead to a complex transverse elastic behaviour resulting in plastic deformation causing the fracture of the lumen (Francucci et al., 2012).

Density is also a key factor for calculating volume fraction of fibre and void content. This dictates the mechanical properties of a composite material (Jones 1999; Judd et al., 1978). Differences in fibre diameter also alter the mechanical performance. Decreasing fiber diameter yields improved mechanical behavior and wetting. In general, mechanical properties of natural fibres are lower to those of synthetic fibres, nevertheless, may be improved by suitable surface treatment of fibre. The specific modulus of natural fibres is comparable to that of synthetic fibres (Bajpai et al., 2012). The prominent properties of natural fibres are listed in Table 2.1. The tensile properties of natural fibres improves with increasing cellulose content while reduces with increasing content of lignin, pectin, hemi-cellulose, and wax. Besides, the structure, diameter, angle of the microfibrillar, and various defects affects the fibre properties. The physical properties of natural fibers are also altered by their several other factors viz., fibre source, size, age, location of the fibers in the plant, processing methods and maturity of the fibers (Bajpai et al., 2012).

Major challenge in natural fibres is depend on cultivation methods and location, the composition of natural fibres is different. In addition, natural fibre is completely incompatible with the majority of polymers due to their non-polar nature. It can absorb a certain amount of water,
which leads to swelling and low dimensional stability of composites. Moreover, due to their low thermal stability and degradation, natural fibres cannot be processed at high temperatures (Ku et al., 2011).

**Table 2.1** Typical properties of some natural fibres

(Dicker et al., 2014; Fuqua et al., 2012; Sathishkumar et al., 2013; Bajpai et al., 2012; Aji et al., 2012; Francucci et al., 2011; Rouison et al., 2004; Phillips et al., 2013)

<table>
<thead>
<tr>
<th>Natural fibre</th>
<th>Diameter (µm)</th>
<th>Microfibrillar angle (degree)</th>
<th>Length (mm)</th>
<th>Density (g/cm³)</th>
<th>Tensile strength (Mpa)</th>
<th>Permeability (m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bast fibre/Stem fibre</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jute</td>
<td>20-200</td>
<td>8</td>
<td>1.5-120</td>
<td>1.44-1.52</td>
<td>400–860</td>
<td>6.95×10⁻¹¹</td>
</tr>
<tr>
<td>Hemp</td>
<td>25-500</td>
<td>2-6</td>
<td>5-55</td>
<td>1.47-1.52</td>
<td>550–920</td>
<td>10⁻¹⁰</td>
</tr>
<tr>
<td>Banana</td>
<td>50-250</td>
<td>11-12</td>
<td>770-1370</td>
<td>1.35</td>
<td>600</td>
<td>-</td>
</tr>
<tr>
<td>Flax</td>
<td>12-600</td>
<td>5-10</td>
<td>5-900</td>
<td>1.42-1.52</td>
<td>750–940</td>
<td>9.42×10⁻¹¹</td>
</tr>
<tr>
<td>Kenaf</td>
<td>70-250</td>
<td>2-15</td>
<td>-</td>
<td>1.30-1.50</td>
<td>195–666</td>
<td>10⁻¹⁰ to 10⁻¹³</td>
</tr>
<tr>
<td>Ramie</td>
<td>20-80</td>
<td>7.5</td>
<td>900-1200</td>
<td>1.45-1.55</td>
<td>500–680</td>
<td>-</td>
</tr>
<tr>
<td><strong>Leaf fibre</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sisal</td>
<td>8-200</td>
<td>10-22</td>
<td>900</td>
<td>1.40-1.50</td>
<td>550–790</td>
<td>2.1×10⁻⁹</td>
</tr>
<tr>
<td>Pineapple</td>
<td>20-80</td>
<td>14</td>
<td>-</td>
<td>1.44-1.56</td>
<td>413-1627</td>
<td>-</td>
</tr>
<tr>
<td><strong>Seed/Fruit fibre</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coir</td>
<td>10-460</td>
<td>30.45</td>
<td>20-150</td>
<td>1.15-1.22</td>
<td>135-240</td>
<td>-</td>
</tr>
<tr>
<td>Cotton</td>
<td>10-45</td>
<td>-</td>
<td>10-60</td>
<td>1.52-1.56</td>
<td>350–800</td>
<td>-</td>
</tr>
</tbody>
</table>

2.2 Chemical Aspects of natural fibre

The chemical composition of natural fibres shows variation from fibre to fibre based on its type. The bonding characteristics and the wetting behaviour of the fibres rely on the chemical properties (Bajpai et al., 2012).
2.2.1 Surface chemistry

The surface chemistry of fibres governs their wetting behaviour and is important in the study of liquid molding processes. The study of surface chemistry demands the measurement of contact angle (Aranberri et al., 2003).

2.2.1.1 Contact angle

The contact angle is defined as the angle between the surface and the external angle of tangent to the surface of the resin drop (Figure 2.2). The contact angle is an important parameter in surface science. The contact angle directly relate to wettability and the adhesion between the fibre and resin.

![Diagram of contact angle](image)

**Figure 2.2** A schematic depicting the balance of forces on a liquid droplet based on Young’s equation

The contact angle gradually reduces as the resin spreads on the surface. The equation adopted to estimate the forces that balances drop on the surface is provided by Young.

\[ \sigma_S = \sigma_{SL} + \sigma_L \cos \theta \]

(2.1)

where, \( \sigma_L \) is surface tension of the wetting liquid, \( \sigma_S \) is surface tension of the solid, \( \sigma_{SL} \) is interfacial tension between the solid and the liquid, and \( \theta \) is the contact angle between the liquid and the solid (Adamson, 1990). Contact angle less than 90° depicts that the wetting of the surface is appreciable and the resin uniformly spreads over a large area on the surface. In
contrast, contact angles greater than 90° shows unfavorable wetting which forces the resin to minimize its contact with the surface and form a compact resin droplet (Yuan et al., 2013).

2.2.1.2 Capillary pressure

The investigation on the resin impregnation majorly focuses on the permeability. The capillary effect is an important parameter in the resin flow. According to the Washburn theory, flow of resin into the pores of the solid medium results from capillary forces provided any porous solid medium in contact with a resin. During infusion, an evaluation of the wicking phenomenon via the measurements of axial resin impregnation rates, surface tension, and contact angle properties is essential as good wetting is imperative for attaining better adhesion between the resin and fibre systems (Ayça Ertekin et al., 2008).

Patel et al., (1993) investigated the effects of material variables and the corresponding processing on the fibre - resin interface. They examined the wetting behavior of unsaturated polyester and other resins in the fibre glass mat. It was observed that lower surface tension of resins and lower fibre porosity resulted in higher capillary pressures. Capillary pressure has significant impact on the impregnation of natural fibers owing to their hollow nature (Patel et al., 1993; 1996).

Thermodynamically, the capillary pressure is defined as:

$$\Delta P_y = -S_f \gamma_{ma} \cos \theta $$

(2.2)

Where $\gamma_{ma}$ is surface tension between the liquid, and the fibre, and the surrounding gas, $S_f$ is area of resin–fibre interface per unit volume of liquid, and $\theta$ is dynamic contact angle (Mortensen et al., 1990).

2.3 Surface modification of natural fibre

Certain engineering applications demand an improved property of the identified fibre along with the permeability concept through surface modification techniques elucidated in this section. Natural fibres do not efficiently adhere to non-polar resins due to these polar groups. This difficulty can be overcome by chemical modification of fibres. Chemically modified surfaces increase tensile strength, decrease moisture absorption, and wettability of fibres by resin. Coupling agents are commonly used chemical substances for improving adhesion. They form a
bridge between the fibre and resin by chemical bonds. The coupling agents attaches to the OH group of the natural fibre at one end, while the other end reacts with the matrix functional groups (Rouison et al., 2004; Kabir 2012).

There are number of techniques to modify the natural fibres such as physical treatments (corona treatment and cold plasma treatment) and chemical treatments (Maleic anhydride, sodium hydroxide, silane, isocyanates, permanganate, and peroxide). The physical treatments modify the surface and structural properties of fibres, and therefore the mechanical bonding increases with the matrix. Further, these treatments do not alter the chemical composition of fibres. The chemical treatments are mainly used to modify the surface properties of fibres. Chemical modifications increase the compatibility between fibres and matrix which leads to enhanced stress transfer at the fibre-matrix interface (Wambua et al., 2003; Behzad et al., 2007).

The main purpose of the NaOH treatment on natural fibres is to dissolve part of the impurities and waxes present on the fibres surface. This leads to the fibres surface become coarser and provide more wetting surface area, and better interaction with the matrix. During NaOH treatment, initially the alkalized groups react with hydroxyl groups (-OH) of the natural fibre and produce H₂O which are consequently extracted from the fibre. Subsequently, the remaining alkalized groups (Na-O-) are reacts with the wall of fibre cell and yields fibre-cell-O-Na groups (John et al., 2008). Brígida et al (2010) observed that the fibre treatment with NaOCl/NaOH resulting in more hydrophilicity nature for natural fibre. Kabir (2012) treated natural fibres with silane agent and recorded that the silane act as surface coatings that promote penetration in pores, decrease in moisture absorption, and greater tensile strength.

The various researchers found that the isocyanate treated natural fibre provides increased thermal stability, reduced water absorption, better mechanical properties, and etc. During isocyanate treatment, the functional group of isocyanate (-N=C=O) reacts with the hydroxyl groups of the fibres, and consequently, a urethane linkage is formed. This chemical linkage provides strong covalent bonds between the fibre and matrix. Further, the isocyanate reacts with the moisture present on the natural fibre surface and forms urea which can further react with the hydroxyl groups (-OH) of the fibre (George et al., 2001). This reaction results in greater moisture resistance of the natural fibre and provides enhancement in bonding with the matrix (Kalia et al., 2009). Ly et al treated (2007) fibre with isocyanate and observed that the contact angle of a drop
of water is increased and concluded that enlightened performances of composites is attainable with isocyanate treated fibre. Permanganate treatment improves chemical interlocking at the interface and provides greater natural fibre adhesion with the matrix (Rahman et al., 2007).

2.4 Processing of natural fibre-reinforced composites

The composites of natural fibre are manufactured by conventional techniques designed specifically for thermoplastic and thermoset fibre reinforced composites. These techniques comprises of vacuum infusion, direct extrusion, resin transfer molding (RTM), compounding, compression molding, and injection molding. This section basically focuses on injection molding in thermoplastic composites and RTM, Vacuum infusion in thermoset composites. Thermoplastics composites are inexpensive and recyclable. Nevertheless, these thermoplastics have limited mechanical properties and demands higher tooling cost. Added to this, the use of short natural fibres oriented randomly incompletely utilizes the directional properties of the fibres (Gassan et al., 1999, Gning et al., 2011, Oksman 2001). This forces the choice of high performance thermosetting resins such as epoxy. They offer the advantages such as easy processing, requirement of less processing temperature, less expensive system, requirement of lower pressure, easy wetting which is viscosity dependent and facilitate higher loading of the fibers (Thakur et al., 2014).

2.4.1 Injection molding

This processing technique is usually employed for high-volume and low-cost component manufacturing. Either of thermoset and thermoplastic is subjected to injection molding. Thermoplastic material is initially melted and subsequently forced through an orifice into the mold which is relatively lesser temperature. The thermoplastic material solidifies in the mold and consequently removed. In contrary, in thermoset injection molding, high temperature is essential for solidification. Hence, a reaction material is forced into a considerable warm mold wherein the material advances solid part after suitable polymerization. The method is limited to short fibres (Shubhra et al., 2011).

Dickson et al., (2014) reported that the injection molded samples in all trials illustrated significant reductions in fibre length. During injection molding, the melt is subjected to high pressure and temperature. This causes high shear, elongation, and deformation rates. This
reduces the fibre length that deteriorates mechanical properties. Besides, the damage of the fibre walls was also prominently recorded. The damaged region showed a distorted structure that indicates crack initiation and swelling of the fibre outwardly due to fibre wall delamination. Sallih et al., (2014) also established that feeding fibres into these machines poses complexities viz., poor feed regulation and funnel flow deficiency (Francucci et al., 2012, Rong MZ et al). Longer fibres demands stringent conditions to be dispersed satisfactorily in an injection molding. This is attributed to the fact that the final fibre lengths are lesser than those of the initial input lengths. Injection moldings are preferred for small to medium sized components because of their simplicity and speed of processing. Fibre orientation and residual stress are also the critical issues which affect the modulus distribution of the injection molded composites (Mei-po Ho et al., 2012).

2.4.2 Liquid molding process

The liquid molding process is a composite manufacturing technique with a variety of applications. The liquid molding process has a many number of processing variables and with complex flow behavior during resin flow to the mold and cure stage. Among various methods for manufacturing of polymer composite materials, liquid molding is one of the best suitable processes for complex geometries. Generally, natural fibre reinforced thermoset composites are fabricated by using traditional liquid molding techniques which are designed for synthetic fibre reinforced polymer composites. These techniques include resin transfer molding (RTM), vacuum infusion, injection/compression molding, sheet molding, pultrusion, reaction injection molding, and etc (Mei-Po et al., 2012). In liquid molding processes a dry fibre preform is placed as reinforcement within a mold cavity where resin is made to flow into the mold. Among the existing technique, RTM, and vacuum infusion attract considerable interest in many fields such as aero industries, automobile sector, shipping industries, and wind power plants.

2.4.2.1 Resin Transfer Molding (RTM)

Resin transfer molding (RTM) is one of the most popular manufacturing process to produce complex shape products for a high volume production. In RTM process; a porous fibrous preform is placed into the mold cavity. Two stiff mold halves (Cavity & Core) are tightly enclosed to avoid any leakage of resin during the injection stage. Then, using dispensing head, a
Pressurized molten plastic is injected into the cavity of the mold using the feeding system (single or multiple inlet ports) in the mold until the mold is filled with resin. After cooling, the product is removed from the mold (Sreekumar et al., 2007).

The pressure required to inject the resin into the mold in RTM is low compared to compression/injection molding processes. Manufacturing process cycle time of RTM is low compared to other composite process and the end product has a good surface finish on both sides (Class-A). The uniform thickness of the part is practicable, RTM is a viable process for mass production of composites parts, and low capital investment. The major parameters that influence the resin flow in RTM are a geometry of mold, injection pressure, resin viscosity, mold temperature, feeding system design (position of the injection ports), and the permeability of the reinforcement (Shojaei et al., 2003; Wen-bin et al., 2009).

2.4.2.2 Vacuum infusion (VI)

The vacuum infusion technique is developed and patented by Marco in 1950. The vacuum infusion process has a high potential for manufacturing high performance fibre reinforced polymer composites at a reasonable price. The Vacuum Infusion Process (VIP) is a very simple closed molding process that uses vacuum to drive resin into a fibre perform and very similar to resin transfer molding (RTM). The experimental setup of vacuum infusion process is shown in Figure 2.3. This process is normally applied with fabrics (woven or non woven). The multiple layers required for the natural fibre fabrics are first cut in the mold shape and then placed over the die. Fibres and mold are then vacuum-bagged. The resin is allowed to infuse into the fabric smoothly and slowly for wet out, assisted by the vacuum. To improve the resin impregnation and surface finishing of final product, gel coat is required over an area of the infusion mold. The peel ply is placed over the fibre fabrics and flow media (green mesh)/core layer is placed over the peel ply, to accelerate the resin flow. Regarding flow media, three types of structure are generally used 1) Continuous strand mat (CSM) 2) Thermoplastic sandwich core 3) 3D knitted glass core. After completing the resin infusion, the natural fibre composites are left to cure under vacuum for 24 h at room temperature, after which they are unpacked and taken for inspection (Andersson et al., 2001; Ragondet et al., 2005).
The vacuum infusion process having many benefits over traditional liquid molding process such as i) Higher fibre-to-resin ratio, ii) Less wasted resin, iii) Very consistent resin usage, iv) Unlimited set-up time and v) Cleaner (Mei-Po et.al., 2012; Hammami et al., 2000). Vacuum infusion is increasingly popular in the transportation, marine, and wind power generation industries. The vacuum infusion process modeling is so far not completely satisfactory because the behavior of the process is not fully understood due to undesirable flow fashion and also that resin flow path is deviating from the standard path due to unpredictable variations in the fibre preform mat (Justin et al., 2010). Flow characteristics are important factor in vacuum infusion which makes it essential to be addressed in order to completely visualize the process.

### 2.4.2.3 Issues in liquid molding process

The conventional hand lay-up process is very slow, labor intensive process, and this process is only suitable for simple geometric parts. In reaction injection molding (RIM) the resin and catalyst are injected separately into the mold cavity by two separate streams. The mixing as well as chemical reaction occurs in the mold at a very fast rate. The RIM process needs large injection pressure due to the high reactivity of the resin system for reducing manufacturing process cycle time. The pultrusion is a process which is used for produce the continuous fibre composite products having constant cross-section profiles such as flat sheets, rods, hollow tubes, channels, beam having a constant cross section. The pultrusion process is a continuous, rapid process and product length variations of pultrusion process are restricted to shipping capabilities. The pultrusion process needs high capital investment compare to hand lay-up/filament winding. The filament winding process is mainly used for producing tubular composite products. The geometry of the filament winding products is limited mostly to the symmetric products (Hakan ipek et al., 2005).
The achievement of high fibre volume fraction in RTM is increasing processing time due to slow rate of resin flow into the fibre preform. The higher injection pressure of RTM may lead to the fibre washing problem or deformation of the preform. Another most important problem is edge flow which is mainly created by the clearance between mold and preform. This problem affects uniformity of flow and rate of flow (the resin flow in near the edge is faster than center area) (Richardson et al., 2000).

Mold filling stage in RTM is very difficult with increasing fibre volume fraction, and hence RTM is not suitable for producing larger parts with higher fibre volume fraction (Rouison et al., 2004; Richardson et al., 2000). However, for large size product structure, the RTM process is not effective in terms of economical perspective as it incurs high equipment costs and molds. The injection strategies developed for manufacturing large size structure products with higher volume fraction emphasizes that vacuum infusion is the appropriate option (Hammami et al., 2012). Considering the pros and cons of all the processes, vacuum infusion was chosen for this investigation owing to the merits the process offers.

2.5 Previous flow modeling work on vacuum infusion process

This part of the review presents a comprehensive of the literature relevant to flow modeling during the vacuum infusion using natural fibres as reinforcement. The motion of fluid is described by the governing equations for the conservation of mass, momentum, and energy. These equations (2.3 – 2.5) can be expressed in the following vector form, which is independent of coordinate systems:

2.5.1 Governing Equation

Continuity : \( \frac{\partial p}{\partial t} + \nabla \cdot (\rho V) = 0 \) \hspace{1cm} (2.3)

Momentum : \( \rho \frac{dV}{dt} = \rho g - \nabla p + \nabla \cdot \tau_{ij} \) \hspace{1cm} (2.4)

Energy : \( \rho \left( \frac{du}{dt} + p \nabla \cdot V \right) = \nabla \cdot (k \nabla T) + \phi \) \hspace{1cm} (2.5)

During the infusion process the resin is forced into the fibre preform network. In order to predict the resin filling time for a certain volume of pore space between fibres, the corresponding filling pattern, analytical expressions, and mold filling simulation is necessity (Correia et al., 2004). All
flow based analytical expressions of vacuum infusion is based on conservation of mass equation and Darcy’s law. The Darcy’s law is the most commonly used for describing the flow behavior through porous fibre preform (Hammami et al., 2000).

2.5.2 Permeability model for synthetic fibre

Permeability is the measurement of the ability of a fluid to pass through a porous medium. In-plane unsaturated permeability is an essential processing parameter for modeling any liquid molding process. The permeability is most difficult parameter to achieve and therefore it is the key parameter to obtain any flow prediction model. Even though many techniques to compute the permeability have been proposed and investigated by several researchers but there is still not a standardized technique to obtain permeability due to anisotropic fibre preform reinforcement (Rouison et al., 2004).

The very simple method to calculate the permeability is that the resin is injected at constant pressure or constant flow rate into the mold half and then flow front is recorded as a function of time by using a video camera. Many other parameters such as clamping pressure, compaction, and capillary effects also have an influence on the permeability. In this case flow can be divided in two streams 1) flow inside each layer and 2) flow between layers (Ken et al., 2000).

2.5.2.1 Darcy Law

\[ K = \frac{(Q \cdot \mu \Delta L)}{(A \cdot \Delta P)} \]  

(2.6)

Where K is permeability (m²), Q is the volumetric flow rate (m³/s), ΔL is the preform length (m), A is the mold cavity transverse area (m²), ΔP is the pressure gradient (Pa), and μ is the viscosity of the resin (Pa.s).

Limitation: The change of permeability behind the flow front is not explained clearly and Darcy model not clarifies the partial saturation of fibre porous reinforcement. Darcy’s law is applicable only for the following conditions: Low Reynolds number, Newtonian and incompressible fluid. Several researchers report that the flow rate of the liquid molding is not a linear function with the pressure gradient, which is in disagreement with Darcy’s law (Gebart et al., 1992).
2.5.2.2 Kozeny – Carman model:

Kozeny – Carman developed a flow model on array of channels of varying cross section in 1927. This model is generally used to find a relationship between porosity and permeability in porous media. This relationship is mainly used to predict the flow behavior of resin in a fibre porous medium. The basic assumptions stated by Kozeny for simplification of the problem are: 1) Interconnected pore space, 2) Randomly distributed pore, 3) Uniform pore size, 4) Porosity is very large and 5) No slip at solid-resin interface (Julian et al., 2007).

The Kozeny – Carman model has the following expression:

\[ K = \frac{d_f^2}{c} \frac{\phi^3}{(1-\phi)^2} \]  \hspace{1cm} (2.7)

Where \( K \) is permeability \( (m^2) \), \( d_f \) is the fibre diameter, \( c \) is the Kozeny constant, and \( \phi \) is the porosity of the mat (Julian et al., 2007; chih-hsin et al., 1998). Here, the permeability is modeled as a function of the porosity, which is the easiest model to determine permeability.

Limitation: Application of Carman equation (2.7) for porous flow problem has been limited. Due to that the nature of permeability is very complex; it has generally determined by experimental technique for the particular application. The experimental technique is not standardized till now, still some issue over whether these measurement techniques should be done with already saturated medium (impregnated) or an advancing flow front. Some researchers found differences in permeability values with different similar viscosity fluids, a phenomenon which is not accounted in the Carman equation. As for the value of Kozeny constant calculated that is approximate value only (chih-hsin et al., 1998). It is clear that the derivation of Kozeny constant is actually considered as a weak function of \( V_f \) and not as a constant (Bizet et al., 2008).

This model is only valid for flow along the fibre mats in unidirectional fibre reinforcement and the permeability predicted from this model is isotropic, which is not actually applicable for unidirectional fibre reinforcement due to transverse flow across the mat which is more constricted than flow along the fibres (Julian et al., 2007).
2.5.2.3 Improved Carman–Kozeny model:

The assumptions made by the Kozeny – Carman model are not satisfied with many types of fibre preform and this model is not able to accurately predict the permeability values from experiment. The basic Carman model prediction can be improved by modifying the Carman–Kozeny equation by varying kozeny constant in the different direction.

\[ K = \frac{\phi^{n+1}}{c(1-\phi)^n} \quad (2.8) \]

Where \( n \) and \( c \) are experimental parameters (Francucci et al., 2009).

Limitation: This modified Carman-Kozeny model cannot fit all the data well unless both \( n \) and \( c \) parameters are changed for each fibre reinforcement mat. It is a complex model to relate fibre architecture of each mat to the values of the other parameters (Gebart et al., 1992). Another important common limitation of both models is that the transverse permeability is greater than zero for \( V_t > V_{f_{\text{max}} \text{ theoretical}} \) which is obtained when flow in transverse direction is blocked due to fibre entanglements.

2.5.2.4 Gutowski model:

\[ K = \frac{R^2}{4k'} \left( \frac{\sqrt{\frac{v'_a}{v_f}} - 1}{\sqrt{\frac{v'_a}{v_f} + 1}} \right)^3 \quad (2.9) \]

Where \( v'_a \) and \( k' \) are experimental parameters, \( R \) is the fibre radius and \( v_f \) is the fibre volume fraction. This model shows a qualitative behavior in agreement with experiments.

Limitation: The most common limitation is that the model parameters are only linked to one fibre parameter that is radius (\( R \)) and the model does not consider any other parameter such as porosity, orientation, and surface properties (Gebart et al., 1992).
2.5.2.5 Gebert model (1992)

It is based on Kozeny-Carman model for predicting the flow longitudinal and perpendicular to fibre alignment.

Two of these models are expressed in terms of the fibre volume fraction \( V_f \) and the fibre radius \( R \) as follows:

\[
K_{||} = \frac{8}{c} \frac{(1-v_f)^3}{v_f^2} R^2 \quad (2.10)
\]

\[
K_{\perp} = C \left( \sqrt{\frac{V_{f_{\text{max}}}}{V_f}} - 1 \right) \frac{5}{2} R^2 \quad (2.11)
\]

Where, \( V_{f_{\text{max}}} \) is maximum fibre volume fraction, \( c \) and \( C \) are constants dependent on the actual fibre arrangements, and \( R \) is radius of the filaments in the bundle. These models were found to fit experimental data for the unsaturated impregnation of unidirectional fibre reinforcements parallel and perpendicular to fibre alignment by providing suitable choice of the parameters (Endruweit et al., 2010).

Limitation: A number of assumptions made by Gebert for simplification of the problem as following 1) the inertia effect is negligible 2) the channel geometry (curve) formed by the fibre reinforcement is approximated with a parabolic curve and 3) the integral of the \( \Delta P \) along the resin flow is completely acceptable and is provided that \( \Delta/R \ll 1 \). (\( \Delta \) is a gap between fibres and \( R \) is radius of the fibre). In some cases with RTM process, \( \Delta/R \) value may be slightly smaller than unity mainly depends on the volume fraction of fibres. The accurate value of the shape factor \( c \) is still unknown for different fibre volume fractions and arrangements (Endruweit et al., 2010).

A few conclusions from these models can be derived: 1) The higher the porosity of the fibre performs, the higher the permeability 2) The higher fibre volume fraction, the lower the permeability 3) The smaller the pore size, the larger exposed surface area of the flowing resin, the lower the permeability. Therefore, a more mechanistic model enabling to correlate the natural fibre mat permeability with its fibre bundle architecture is needed.
2.6 Analysis of Vacuum infusion molding process

Liquid molding process is a very complex process with many numbers of processing variables and complex flow behavior during resin flow and cure. In order to obtain an economical, mass production, process parameters needs to be optimized to obtain the desired properties in the final part. The basis of all the mathematical models for liquid molding is the conservation of mass and momentum equation. In order to make a model from the conservation equations for vacuum infusion, assumptions have to be made to simplify the problem (Saad et al, 2011).

2.6.1 Assumptions stated by several researchers (Hammami et al., 2000, Amico 2000, Correia 2004):

i. The resin is Newtonian incompressible fluid.
ii. The preform remains rigid during mold filling
iii. Inertia effects are neglected due to low Reynolds number
iv. The effect of the surface tension is negligible due to high viscous force
v. The transverse flow along the mold thickness direction is neglected.

2.6.2 Governing equation-based on assumptions

In vacuum infusion (VI) process, the thickness of the composite is not pre-determined by the mold geometry and it may be a function of pressure and therefore changes with time.

The continuity equation is the basis of all the mathematical models of vacuum infusion. Applying conservation of mass equation to one dimensional along x where the control volume is defined over the whole thickness h of the laminate results in:

$$\frac{\partial h}{\partial t} = - \frac{\partial (u,h)}{\partial x}$$

(2.12)

Where h is laminate thickness (m), u is the superficial velocity (m/s), t is time (s), and x is the in plane direction distance (m).

Momentum balance equation or Darcy law: 

$$u = \left( \frac{-K}{\mu} \right) \nabla P$$

(2.13)
Where \( u \) is the superficial velocity (m/s), \( K \) is permeability (m\(^2\)), \( \nabla P \) is the pressure gradient (Pa) and \( \mu \) is the viscosity of the resin (Pa.s).

From Darcy's law, the following conclusions can be obtained about the behavior of the resin flow:

a) The higher the pressure difference, the faster mold filling; b) The lower the resin viscosity, the faster mold filling; c) The higher the permeability, the faster mold filling (Correia et al., 2004).

The first two parameters, pressure difference over the mold and resin viscosity, may be considered constant during infusion of the product and can be approached similarly to the ordinary RTM process.

Combine the above two equations (2.12 and 2.13) by substituting \( u \) value in mass equation, results the following equations:

\[
\frac{\partial h}{\partial t} = - \frac{\partial ((-K/\mu) \nabla P.h)}{\partial x} \tag{2.14}
\]

Assume that the flow is quasi-stationary, i.e. that the cavity height have time to approach its static equilibrium value at every instant in time during the infusion process. This approximation corresponds to neglect \( \frac{\partial h}{\partial t} \) and then integrate above equation to obtain the flow front position as a function of time.

\[
x(t) = \frac{\sqrt{2Kp_i}}{\varphi \mu} \cdot t \tag{2.15}
\]

\[
t_{\text{fill}} = \frac{\mu}{2} \frac{L^2}{\left(\frac{K dp}{\varphi d\xi}\right)_{\alpha=1}} \tag{2.16}
\]

Where \( x(t) \) is the x coordinate of liquid front, \( \varphi \) is the initial porosity (which is a constant here), and \( p_i \) is the constant inlet-pressure (Labordus et al., 2000).

In a circular mold, the filling time and a flow front position for a constant injection pressure is given by the following relations.
2.6.3 Scheidegger–Han model

\[
\frac{\partial h}{\partial t} = - h_0 \frac{\partial u}{\partial x} 
\]

Where \( h \) is laminate thickness (m), \( u \) is the superficial velocity (m/s), \( t \) is time (s), and \( x \) is the in plane direction distance (m).

This approach requires moving the time differential inside the volume integral, which is incorrect in VI since the volume is time dependent (Saad et al., 2012).

2.6.4 Kang model

The following equation gives a relation between the flow front velocity and superficial velocity.

\[
v = \frac{u}{\phi} \text{ or } v = \frac{u}{v_f} 
\]

Using the above relation and combine it with Darcy with these. The result will be

\[
- \frac{1}{v_f} \frac{\partial v_f}{\partial t} = - \frac{\partial}{\partial x_i} \left( \frac{K_{ij}}{\mu} \nabla P \right)
\]

Where, \( i \) and \( j \) denote \( x \) and \( y \) direction only, not transverse direction. Since the vacuum bag is not rigid, the stress is created by fibre deformation and the resin pressure. The fibre volume fraction and the thickness of the fibre preform are varied throughout the composite because of the variation of pressure (Hammami et al., 2000).

2.7 Previous modeling work on natural fibre

Recently, some investigations of resin flow through natural fibre mats in mold filling are reported. For any swelling of natural fibre porous mat, the basic continuity equation is modified to the following form (Reza Masoodi et al., 2009):
\[ \nabla \cdot \mathbf{u} = -S \frac{\partial \phi}{\partial t} \] \hspace{1cm} (2.21)

Where \( \phi \) is porosity of the porous medium, which defined as the ratio of pore volume to the total volume, \( S \) is sink or source effects due to liquid absorption, \( \nu_f \) fibre volume fraction and \( u \) is superficial velocity (Darcy velocity), which takes into account the porosity of the medium.

\[ S \propto \frac{d\phi_0}{dt} \] \hspace{1cm} (2.22)

\[ S = b \times \frac{d\phi_0}{dt} \] \hspace{1cm} (2.23)

Where \( \phi_0 \) is the ratio of solid volume to the total volume, and \( b \) is the coefficient of absorption.

Momentum balance equation or Darcy law:

\[ u = \left( \frac{-K}{\mu} \right) \nabla P \]

By Combining modified conservation of mass equation and momentum and further assumptions leads to the following equation:

\[ x(t) = \frac{2 p_i}{K_0 \phi_i} \left( \frac{\phi}{\phi_i} \right) \frac{t^{b-1} \phi}{p_i} \int_0^t e^{(b-1) \phi} K(t') dt' \] \hspace{1cm} (2.24)

### 2.7.1 Permeability model for natural fibre

Since the porosity is not constant in a swelling porous medium, permeability variable for solving Darcy’s law is needed. Apply this condition to Kozeny equation; the permeability will be as follow (Languri et al., 2010):

\[ K = D_f (t^2) K_0 \left( \frac{\varepsilon_f}{\varepsilon_{f0}} \right)^3 \frac{1-\varepsilon_{f0}}{1-\varepsilon_f} \] \hspace{1cm} (2.25)

Where \( K \) is the permeability, \( D_f \) is swelling fibre diameter, \( K_0 \) is the initial permeability, \( \varepsilon_{f0} \) is the initial porosity, and \( \varepsilon_f \) is the porosity of a swelling porous medium is a function of time.
Limitation: This model is not universal and the parameters such as fibre architecture/fibre bundle, tortuosity is not accounted in this model, therefore, the calculated permeability should be approximated.

From the intense literature survey, it was hypothesized that, the parameters namely the swelling, wetting in terms of contact angle and fibre architecture plays a significant role in permeability. Therefore, there is a discussion on those aspects is presented in this section.

2.8 Swelling

Generally when a solid swells it results in: 1) Its dimensions increasing by absorption of a liquid, 2) It remains homogeneous at the microscopic level, and 3) Its cohesion is decreased but not destroyed. The swelling of the natural fibre (Sisal) mainly due to water absorption may effect on the porosity and permeability of mats; hence such a swelling may play an important role in mold-filling. Swelling may reduce pore size and thus increases the viscous-flow resistance, which results permeability reduction (Mantanis et al., 1994).

Natural fibers obtained from plants are cellulose-based materials that swell on coming in contact with water and organic liquids. The swelling of natural fibers depends on several parameters of the wetting liquid and fibres. From the wetting resin point of view, hydrogen bonding capability, molecular size, cohesive energy, viscosity, density, and basicity and from the fibre point of view, surface coating and treatment, density, porosity, and crystalline structure of the fibres are the main effective parameters. Therefore, in this research various synthetic and natural based thermoset resins as a matrix material were used to study the sisal fibre swelling. The natural fibers also significantly swell when exposed to various resins with different functional groups such as alcohol amines, and benzene rings (Pillai et al., 2012).

2.9 Wetting analysis

Generally, the fibre/resin interactions depend on the wettability of the fibres, resin property, surface geometry of the mat, the capillary geometry, and externally applied pressure. The wetting is majorly governed by the surface chemistry. The surface treatment of fibre alters the chemical properties of the surface that changes the contact energy of the surface. Besides, the surface chemistry, the surface forces also plays important role in wetting phenomenon (Bonn et al., 2009). In a good wetting, greater contact area between the fibre and the resin prevails.
Generally, the adhesion mechanism at the interface can be explicated by the following interactions: 1) physical adhesion related to surface energies of the fiber and the resin, 2) chemical bonding and 3) mechanical locking created on rough fiber surfaces. Good interfacial adhesion initially requires a good wetting between the fiber and the resin, which leads to an extensive and proper interfacial contact. The surface energy of a fiber generally should be higher than that of the resin for a good wetting to take place during composite processing. Moreover, the surface energies will play an important role for keeping a stable contact after consolidation of the composite (Tran et al., 2013).

Therefore, a proper match of the surface properties of resins to reinforcements is one of the key concerns achieving successful wetting during infusion molding. Typically, a low resin surface tension is necessary for good and fast fibre impregnation (Gennes 1985).

The literature reviews showcased the research gap in the studies pertaining to the effects of treatments on the wetting of thermosetting resin. Further, the literature reports the evaluation and effects of treatment on the viewpoint of mechanical behavior. Besides, the contact angle tests to analyze the moisture absorption are most commonly presented. There has been scanty report for extrapolating this analysis for inter-wettability studies between fibres and resins respectively.

2.10 Cure Kinetics

Cure kinetics is an important stage in vacuum infusion which makes it essential to be addressed in order to completely visualize the process.

2.10.1 Kinetic modeling

The degree of cure (\(\alpha\)) indicates the extent of the resin chemical reaction. It is proportional to the amount of heat given off by bond formation, and is usually defined as:

\[
\alpha = \frac{H}{H_U}
\]  

(2.26)

Here H is the accumulative heat of reaction up to a given time t during the curing process, and \(H_U\) is the ultimate heat released during a complete reaction. For an uncured resin, \(\alpha = 0\), whereas for a completely cured resin, \(\alpha = 1\)
Cure kinetics of an epoxy resin shows a relationship of heat release rate with the temperature and the degree of cure, and can be directly applied into formulation of heat transfer and heat generation models (Varley et al., 1996).

The curing rate is assumed to be proportional to the rate of heat generation and is calculated by the following expression:

$$\frac{d\alpha}{dt} = \frac{1}{H_U} \left( \frac{dH}{dt} \right)$$

(2.27)

For cure kinetics numerous models have been developed to characterize the curing for different resin systems. The simplest one is the $n^{th}$-order equation: (Barral et al., 1995; Cai et al., 2008).

$$\frac{d\alpha}{dt} = K(1 - \alpha)^n$$

(2.28)

Where $n$ is the reaction order, $\alpha$ is the conversion or degree of cure, and $k$ is the curing rate constant defined by Arrhenius equation.

A study on cure kinetics/ flow has been inadequately reported in the literatures for natural fibre/bio based polymer system during the infusion molding process. In the past, most of the natural fibre reinforcement studied manufactured by hand lay-up or press molding. Scanty research reports are available for vacuum infusion. Most of the papers focus on the mechanical properties obtained using VI and only few researchers given information about the flow of the process. The understanding of the resin impregnation behaviour in natural fibre reinforcement in the vacuum infusion is less documented in the open literature. Further, no significant work has been reported concerning the effect of chemical treatments on permeability of the natural fibre in the vacuum infusion and the studies on the effect of flow direction on tensile strength of composite in infusion process is lacking. This prompted in undertaking this research study.
Studies on Permeability of Sisal Fibre Mat during Thermoset Resin Filling in Vacuum Infusion Process

3.1 Abstract

The focus of this study is to investigate the resin flow behaviour (dictating permeability) in a sisal based natural fibre mat when exchanged with a glass fibre mat. This mainly deploys the fibre reinforced plastics subjected to a vacuum infusion process. The outcome of this research emphasizes the wetting mechanism and fibre network of sisal mats, which significantly reduces the flow characteristics. In addition, it is observed that the swelling phenomenon had an insignificant or minimal influence on the permeability of the sisal fibre mat. However, employment of bio-based resin provides a considerable change in the swelling phenomenon. Hence, this factor is important to consider in permeability studies to attain higher accuracy.

3.2 Introduction

Recently, research on replacement of glass fibres with natural fibres as composite reinforcement has increased dramatically, owing to its assets such as lower cost, non-toxicity, and high strength-to-weight ratio, which are some of the important factors to be considered for automotive, construction, aerospace, and other industrial applications (Joshi et al., 2004; Oksman 2001; Faruk et al., 2012; Faruk et al., 2012). The natural fibre reinforced thermoset composites that are fabricated using traditional liquid molding techniques are designed for glass fibre reinforced polymer composites (Ho et al., 2012). To efficiently use the traditional technique, a conceptual understanding of natural fibre and its impact on process parameters is essential. O’Donnell et al., (2004) suggested that the vacuum infusion process is more suitable for processing and manufacturing of bio-composites. The mold filling and curing processes play an important role in vacuum infusion and are governed by the following factors: permeability, porosity, preform architecture, viscosity, temperature, and resin inlet location. The permeability study of the vacuum infusion process is not clear, due to undesirable resin flow through fibre reinforcement. In addition, the resin flow path deviates from the standard path which is attributed to the unpredictable variations in the fibre preform mat (Johnson et al., 2003; Rouison et al., 2006). Traditionally, flow prediction in liquid molding processes was a trial-and-error approach which was expensive and time consuming. Further, there is an ambiguity in achieving desired properties. Incorporation of this proposed approach demands greater understanding of the
interdependencies between the various process parameters (Han et al., 2000; Hammami et al., 2000). Rouison et al., (2006) presented the following steps to optimize the liquid molding process: pre-pressing for high fibre volume, filling, curing, and post-curing.

Francucci et al., (2009 & 2011) studied the permeability of jute fibre fabrics. No concrete fibre washing or race tracking problems in the infusion process were observed. They noticed that the fluid (water/glycerin) absorption phenomenon affected the permeability, as it removes fluid from the main stream while traversing through the reinforcement. The same authors further investigated and observed that the permeability of sisal mats is almost five times greater than that of jute fabric. On similar lines, Schmidt et al., (2009) studied the permeability of hybrid reinforcement (glass and sisal). They found that the flow medium is important for higher fibre volume composites in resin transfer molding (RTM) and recommended that sisal mat is a good alternative to commercial flow media in many engineering applications owing to it maintaining a high permeability for more packed fibrous beds. Rodríguez et al., (2004) studied the mold filling process in RTM with natural fibres and random glass fibre mats. Race tracking for low porosities was observed due to less friction in the mold edges with the absence of fibres. Identical trends were observed for permeability and porosity for each type of mat.

Masoodi et al., (2012) studied the swelling of jute fibre in epoxy and bio-based epoxy. The swelling in bio-based epoxy specimens was remarkably high due to the cellulose and hydroxyl groups in its composition. Mohseni Languri et al., (2010) observed the change in kenaf fibre diameter due to swelling and they also noticed good flow-front prediction for natural fibre with the addition of swelling as a function of time in permeability model. Sun et al., (2012) observed that the jute fibres were not easily wetted by thermoplastic resin and recorded that external pressures are necessary to speed the wetting. Tran et al., (2013) estimated the surface energy of coir fibre through equilibrium contact angle to analyze the coir fibres that seem to be hydrophobic with a less polar fraction of the surface energy. Fuentes et al., (2011) studied the wetting behaviour of bamboo fibre and concluded that the lignin content in bamboo fibre is responsible for its wetting properties. Barsberg et al., (2001) derived an inference that the generalization of wetting behaviour of natural fibre is impossible due to swelling, extraction, macromolecular rearrangement, etc. Ma et al., (1999) observed that the influence of test liquids such as corn syrup, vinyl ester resin, and epoxy on the permeability measurement is small
compared to that of fabric architecture. Shih et al., (1998) emphasized that relating the permeability to a particular fibre network structure is difficult.

Having reviewed the literature, it may be observed that there are several studies pertaining to flow prediction in terms of permeability for glass fibre. Various parameters and their interdependencies governing flow behaviour have been reported. However, the studies on aspects concerned with the permeability of natural fibre for vacuum infusion processes are inadequate. Most of the studies have been devoted to mechanical properties of the natural fibre based composites. Hence in this study, an attempt is made to determine the flow characteristics that distinguish natural and glass fibres. Subsequently, the wetting, fibre network, and swelling parameters are considered. The outcome of this study is expected to provide a parameter window and database encompassing the extent of interdependency of parameters for vacuum infusion processes employed for natural fibre.

3.3 Experimental

3.3.1 Raw Materials

In this study, the commercial unsaturated orthalate polyester resin from Naptha Resins and Chemicals Pvt. Limited (Bangalore, India) is chosen. The chosen catalyst is methyl ethyl ketone peroxide (MEKP). The unidirectional sisal fibre mat (woven) with an areal weight of 577 g/m² is used as reinforcement. The average filament diameter and thickness of the mat of sisal fiber are 0.35 mm and 1.2 mm, respectively. A random E-glass fibre mat (non-woven) with an areal density of 450 g/m² is used to as a reference. Besides, water, epoxy, unsaturated polyester, epoxidized soy bean oil, polyol, bio-curing agent, and cashew-based epoxy resin are used for swelling study.

3.3.2 Experimental Setup

The study uses a 900 × 600 × 50 mm³ dimension infusion mold which is surface treated by a releasing agent (PVA). To improve the resin flow and surface finishing, a gel coat is applied over an area of 510 × 310 mm² on the mold. The fibre mat (natural or glass) is prepared to the required size of 500 × 300 mm². The peel ply is placed on the top layer of the fibre mat (preform). Green mesh (flow media) is placed on top of the peel ply to accelerate the resin flow. It may be noted here that the peel ply surface finish determines product finishing. A vacuum bag
sealed by tacky sealant tape is chosen according to the resin system that is fixed on the corners of the mold. The vacuum bag is used to cover the whole top of the mold including the sealant tape. It is important that the vacuum bag being used must be 25.4 cm greater than the sealant tape to accommodate the shrinkage factor. The mold is connected with a vacuum pump and resin inlet on its sides. Air is evacuated from the mold by the application of 735 mm vacuum pressure of mercury. In the midst of this, orthophthalic resin that cures at room temperature is poured into a beaker. This is followed by the addition of 1 wt. % of methyl ethyl ketone peroxide (MEKP) catalyst stir mixed for a few minutes. Subsequently, the resin beaker is moved inside the inlet reservoir tank and connected to the inlet tubing for resin infusion. The resin is given ample time to infuse completely over the mat, followed by closing off of the resin supply. The vacuum is permitted to persist until the resin has gelled. The experimental setup is shown in Figure 3.1.

![Experimental Setup](image)

**Figure 3.1** Experimental Setup

### 3.3.3 Infusion Experiments

Two different preforms (random glass fibre and unidirectional natural fibre) are used to carry out the infusion process to determine the permeability. Infusion experiments with identical thickness of the preform layers and resin types are performed. The process is tested for precision by increasing the number of trials. A high definition camera with 1000 frame split-up capability is employed for this study. The pictures were captured by fitting the camera to monitor the progress of flow front position in the mold from an elevated top angle view. There are significant differences in flow (pattern and time) between the experiments. The differences observed
between these experiments illustrate the influence of the natural fibre on the impregnation phase. Initially during infusion, differences in flow rate are remarkably high and decrease gradually with the progress in the process. This may be attributed to the flow resistance increasing prominently, which leads to the minimal difference in the flow rate. A real image of infusion process carried out is also presented in appendix 3.1.

3.3.4 Permeability Analysis

Permeability is an essential parameter for flow prediction of any liquid molding process (Hammami et al., 2000). All flow-based analytical expressions of RTM and VI are based on the conservation of mass equation and Darcy’s law. Well established and reliable models frequently used in the literature are adopted for this study (Han et al., 2000). The resin enters at a constant flow into the mold half and then flow front is recorded as a function of time, given in Equation (3.1).

\[
K = \frac{(Q \cdot \mu \cdot \Delta L)}{(A \cdot \Delta P)}
\]  

(3.1)

Where \( K \) is permeability (m\(^2\)), \( Q \) is the volumetric flow rate (m\(^3\)/s), \( \Delta L \) is the preform length (m), \( A \) is mold cavity transverse area (m\(^2\)), and \( \Delta P \) is the pressure gradient (Pa). In this, the permeability is measured by measuring the resin volumetric flow rate (Francucci et al., 2009).

Following this, Carman-Kozeny developed a flow model on an array of channels of varying cross section. The Carman-Kozeny relationship is mainly used to predict the flow behaviour of the fibre porous medium, while relating the porosity and permeability.

\[
K = \frac{d_f^2}{k} \frac{\varphi^3}{(1 - \varphi)^2}
\]  

(3.2)

where \( d_f \) is the fibre diameter, \( k \) is the Kozeny constant, and \( \varphi \) is the porosity of the mat. The nature of permeability is complex, which limits the applicability of the Carman equation for porous flow problem. The Kozeny constant is an approximate value only. This model is only valid for flow along the fibre mats and the permeability predicted from this model is isotropic (Shih et al., 1998; Pillai et al., 1998).
The basic Carman model prediction can be improved by modifying the Carman-Kozeny equation by varying Kozeny constant in a different direction, as in Equation (3.3)

\[ K = \frac{\phi^{n+1}}{C(1-\phi)^n} \]  

Where \( n \) and \( C \) are experimental parameters. This model does not represent the behaviour of the fibre reinforcements with complete accuracy and this modified Carman-Kozeny model may not accurately fit for all data sets, until the \( n \) and \( C \) parameters are modified for each fibre reinforcement mat. It is a complex model to relate the fibre architecture of each mat to the values of the other parameters (Hammami et al., 2000; Schmidt 2009; Gebart 1992).

### 3.3.5 Investigations on Swelling

To understand swelling of sisal fibre, the swelling of individual natural fibres (sisal) in water and various resins such as epoxy, unsaturated polyester, soy based epoxy oil, polyol, bio-curing agent, and cashew-based epoxy resin are initially measured using an optical microscope coupled to the host system. The average fibre diameter and the standard deviation for the sample are measured. After recording the initial diameter, a drop of water and the above-mentioned resins are poured onto the fibres while the microscope captures the images. The images captured from optical microscope are further imported to the Computer Aided Design and Drafting (CADD) package for measuring the variation in the diameter of fibres (Masoodi et al., 2012).

### 3.3.6 Infrared Spectroscopy Analysis of Sisal Fibre

Fourier transform infrared (FTIR) spectroscopy is carried out to qualitatively identify the constituents of epoxidized soybean oil. Both the epoxy and epoxidized soybean oil are examined to explain the variations in the swelling rate.

### 3.3.7 Wetting Analysis

Contact angle significantly governs the wetting phenomenon. Hence, in this study, the contact angle is measured by goniometer. In a goniometer, a line is drawn from the point of contact of the surface of the mat tangentially such that it coincides at a single point on the resin. This tangential line helps to measure the contact angle. It may be emphasized here that the measurement of contact angle is carried out with respect to left and right planes. To attain an
accurate value, the averages of these are recorded (Neumann et al., 2010). Further, the impacts of contact angle on permeability are examined.

3.3.8 Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDX)

Weaving is used in the net-like structure with each tow (fibre bundle) consisting of 30–40 individual fibres. The tows are in the order of millimeters, whereas the individual fibres are of a few microns in diameter. There are two types of pores in the sisal fibre mats. One is the gap between the tows typically termed a larger pore, and the other is the gap inside the tow, considered a smaller pore. Pore size and fibre network of sisal and glass fibre mats respectively are analyzed using SEM (Shih et al., 1998; Slade et al., 2001). Further, the chemical compositions of the fibres are examined using EDX.

3.4 Results and Discussion

3.4.1 Fibre Volume Fraction (FVF) in the Composite

The fibre volume fraction is determined from mat weight, mat volume, and material density. The fibre volume fraction shows a lower value (31 %) for sisal fibre composite in comparison with glass fibre (42 %), which is mainly due to fibre packing of the sisal mat. Glass fibre mat can achieve high fibre volumes due to the uniform arrangement. Five samples of identical experimental scenario are tested to access the repeatability and average value of fibre volume fraction is taken for further calculation. The detailed calculation is given in Table 3.1.

Table 3.1 Calculation of fibre volume fraction and porosity from weight measurements

<table>
<thead>
<tr>
<th>Glass mat</th>
<th>Sisal mat</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>226</td>
<td>31.15</td>
<td>Mat weight in gram</td>
</tr>
<tr>
<td>2.55</td>
<td>1.3</td>
<td>Fibre density g/cm³</td>
</tr>
<tr>
<td>88.62</td>
<td>23.96</td>
<td>Volume mat in cm³</td>
</tr>
<tr>
<td>362.0</td>
<td>90.1</td>
<td>Weight composite in gram</td>
</tr>
<tr>
<td>136.12</td>
<td>58.95</td>
<td>Weight resin in gram</td>
</tr>
<tr>
<td>1.11</td>
<td>1.11</td>
<td>Density of resin</td>
</tr>
<tr>
<td>122.52</td>
<td>53.10</td>
<td>Volume of resin</td>
</tr>
<tr>
<td>211.15</td>
<td>77.06</td>
<td>Total volume</td>
</tr>
<tr>
<td>42%</td>
<td>31%</td>
<td>Avg. fibre volume fraction</td>
</tr>
<tr>
<td>0.58</td>
<td>0.69</td>
<td>Porosity((\varphi = 1 - V_f))</td>
</tr>
</tbody>
</table>
Sisal fibres are soft and compressible, which may reduce the fibre volume fraction. During a vacuum infusion process, there are many aspects to ensure the desired fibre volume fraction. Resin feeding system is too wide that leads to overfill the bag, resulting in a low fibre volume fraction. Reducing the flow rate (tertiary factor) into the bag and restricting the amount of resin entering the mold leads to alteration in the fibre volume fraction (Simacek et al., 2012). The porosity value determined is 0.69 for sisal fibre mat and 0.58 for glass fibre mat. Factors that influence the distribution of porosity include fibre stiffness, number of fibres in the fibre bundles, degree of misalignment, and the presence of sizing. The sisal fibre mats studied had higher porosity values than the glass fibre mats. The higher porosity of the natural fibre mat was due to more open channels or pathways of bundled fibres (Williams et al., 1974).

3.4.2 Permeability of Glass Fibre and Natural Fibre Mats

To obtain permeability, a modified Carman–Kozeny equation appears to be more suitable for natural fibre as the Darcy equation demands more data from an experimental analysis. The experimental parameters depend on material or preform structure variation. The values of C ($4.8 \times 10^8$ m$^{-2}$, 0.0103) and n (1.48, 2.04) are adopted from the literature (Rodriguez et al., 2004; Shih et al., 1998). It is observed that the material variation constant yields accurate prediction in case of glass fibre. Whereas, for natural fibre the preform structure variation yields better permeability. Micro observation at elemental level shows that fibrous reinforcements used in composite manufacture have inherent heterogeneity, which can influence the infusion process in an unpredictable manner. This model allows for the structural differences between the random glass and unidirectional natural fibre mats. This results in differences of micro-flow processes which are responsible for the heterogeneous nature of the natural fibre mats. The natural fibre bundle contains unidirectionally aligned 30 numbers of filaments. In contrast, the commercially available random mats show disorderly placed fibre filaments such that their alignment envisages a homogeneous porous medium (Williams et al., 1974; Pillai 2004).
The permeability for a sisal fibre preform measured is $1 \times 10^{-9}$ m$^2$. The permeability of sisal fibres under similar conditions and volume content is derived from the improved Kozeny model as $4.77 \times 10^{-9}$ m$^2$. On similar lines, when the same measurement incorporates the identical technique for glass fibres, it yields a result with a noticeable difference as compared to the natural fibres. Figure 3.2 illustrates the comparative plots for permeability with respect to the various models that are being used. The Kozeny constant for Kozeny model is 20.52 as recorded in the literature (Pillai et al., 1998). As observed from the statistical data (Figure 3.2) none of the model predicts the permeability accurately while they show greater deviations which promote the development of the new model as proposed in this study.

This distinctly provides evidence of external factors modifying the permeability performance apart from porosity, pressure gradient, and viscosity of the resin. Permeability needs to be viewed with two perspectives:

(a) Contact angle and time are considered initial phenomena influencing permeability at the micro level;

(b) Flow front and filling time gradually taking center stage as secondary governing phenomena following the micro-level.

**Figure 3.2** A comparison of permeability value for natural fibre and glass fibre.
It is imperative that the two phenomena are incorporated into the equation, to develop a model for permeability. A comprehensive model representing the empirical version may be extrapolated with the addition of external factors, namely swelling (which is negligible due to the use of synthetic resin), wetting, and fibre network, which enable the determination of permeability with higher accuracy and precision as presented in Equation 3.4.

\[
K = \frac{c\phi}{a+b\left(\frac{1}{\theta} + \frac{\theta^2}{2} - \frac{\theta^2}{2\theta} - 1\right)}
\]  

(3.4)

Where \(\phi\) represents porosity, \(\theta\) is contact angle, and \(a\), \(b\), and \(c\) are empirical constants; \(a = 1.01 \times 10^5\) for vacuum infusion process, \(b = 860\), and \(c = 2.08 \times 10^{-4}\) for a unidirectional sisal fibre mat wetted with polyester resin in axial direction (See appendix 3.2).

To derive this permeability equation, a capillary pressure formula estimated from the Young-Laplace equation (Sun et al., 2012) is employed in Darcy’s equation (Hammami et al., 2000). Further, the contact angle is simplified using the Taylor series with appropriate simplification to suit the physical conditions; the desired Equation (3.4) is evolved. This equation appears to satisfy the data attained in this study. The closeness in terms of SSD (sum of squared deviation) to the experiments results are achieved repeatedly with the proposed comprehensive model. The results clearly highlight that there is a reasonable percentage of improvement in the flow characteristics of natural fibre (Figure 3.3).
Figure 3.3 A comparison of the theoretical prediction of flow front as a function of time with the experimental observations for sisal fibre and glass fibre.

3.4.3 Swelling Tests

The swelling of natural fibres depends on the wetting liquid and the fiber properties. From the wetting resin, the factors influencing swelling are hydrogen bonding capability, molecular size, viscosity, cohesive energy density, and basicity. In parallel the effects of the fibre on swelling include surface coating and treatment, density, porosity, and crystalline structure of the fibres. In this case, various synthetic thermoset and natural thermoset matrix materials are used and the results are compared (Masoodi et al., 2012) and presented in Figure 3.4.
Here, two types of liquids are used to find the effect of the swelling behaviour on permeability: (1) a synthetic such as epoxy, polyester and (2) natural-based liquids such as water, polyol, epoxidized soybean oil, cardonol based curing agent, and resin. From these experiments, swelling of sisal fibre is negligible, i.e. only 1.5% for synthetic material, while there is a substantial increase in the swelling percentage of sisal fibre up to 6% for natural-based liquids. The chemical composition of bio-based resin, confirmed by FTIR analysis, may be the influencing factor. The graph shows enlargement of the average diameters of sisal fibre when exposed to water. The sisal fibers comprises of 66% to 77.2% cellulose. The cellulose molecule has a polar group which attracts water molecules through hydrogen bonding, which in turn leads to moisture build-up in the cell wall that appears as fibre swelling. In contrast, the swelling drastically reduces for synthetic epoxy, unsaturated polyester and that minimal swelling owes to the presence benzene rings and viscosity. Usage of ESO also shows a lesser swelling as compared to water due to the absence of any free OH group and amine group.

Figure 3.4 Sisal fibre swelling in various resin.
3.4.4 Chemical Analysis of Synthetic and Bio-based Resin by FTIR

Epoxidized soybean oil (ESO) (with 6.5 % epoxy content) is analyzed by FTIR to comparing its swelling effect with synthetic epoxy. The presence of a peak in the FTIR spectra of ESO at 825.93 cm\(^{-1}\) is attributed to the epoxy group. The peaks at 2992 and 2854 cm\(^{-1}\) are assigned to C-H stretching vibration in the hydrocarbon backbone of both soybean oil and epoxy, as in Figure 3.5; nevertheless the intensity of the peak is strong compared to epoxy. This suggests that ESO has a long hydrocarbon chain in the backbone. The peaks at 1456, 1502, and 1604 cm\(^{-1}\) correspond to C-C aromatic stretching in the backbone of the epoxy. The non-polar aromatic hydrocarbon backbone causes a resin weaker affinity towards polar sisal fibre surface.

![FTIR spectra of a) Epoxy b) Epoxidized soy bean oil](image)

**Figure 3.5** FTIR spectra of a) Epoxy b) Epoxidized soy bean oil

The strong peak at 1740 cm\(^{-1}\) corresponds to C=O stretching in carboxylic function group. The increase in the swelling behaviour of sisal fibre mat in bio-based epoxy compared to synthetic epoxy is due to the polar carboxylic group present in the bio-based epoxy.
3.4.5 Wetting Tests

The contact angles between random glass fibre mat/polyester and sisal fibre mat/polyester are shown in Figure 3.6. The experimental results reveal that the resin spread over the mat surface which favors wetting at particular time. The polyester on the random glass fibre mat gives excellent wetting behaviour compared to sisal fibre.

![Figure 3.6](image)

**Figure 3.6** Contact angle between fibre and matrix a) Polyester/Glass b) &c) Polyester/Sisal

The fibre and resin interactions depend on the wettability of the fibres, resin property, surface geometry of the mat, capillary geometry, and externally applied pressure. The contact area is directionally proportional to the wetting. The mold filling of the reinforcement, between wetting in the periphery, inner configuration, and between the tows becomes a major role, which controls processing time and quality of the product.

The experimental observations reveal facts that are contrary to the anticipated phenomenon, in which the wettability is enhanced. Figure 3.7 indicates that the sisal fibers are not easily wetted by the resins. The wetting behaviour of sisal fibre is far different from that of glass fibre. This response may be due to surface heterogeneity, packing of fibres in the mat, and chemical composition of sisal fibre. Validation is carried out with the EDX results shown in Figures 3.8–3.9. The contact angle used for this analysis is incorporated into the permeability model to further enhance its accuracy while measuring the permeability.
Figure 3.7 The comparison of contact angle versus time for sisal fibre and glass fibre

3.4.6 Element Analysis

The EDX results of the fibre surface (Figures 3.8–3.9) are given in Table 3.2. Silicon, oxygen and calcium are the main elements in an E-glass fibre surface.

Table 3.2 EDX results of atomic concentrations of glass fiber surface and sisal fibre.

<table>
<thead>
<tr>
<th>Elements</th>
<th>C</th>
<th>O</th>
<th>Si</th>
<th>Ca</th>
<th>Al</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass</td>
<td>12.52</td>
<td>42</td>
<td>24.08</td>
<td>14.39</td>
<td>5.38</td>
<td>1.62</td>
</tr>
<tr>
<td>Sisal</td>
<td>54.83</td>
<td>43.97</td>
<td>-</td>
<td>1.20</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Peaks indicate the presence of C and O in prominence in natural fibre. In addition, the presence of Si may appear to slightly influence the wettability of glass fibre as a contrast to natural fibre where Si is missing, apart from the packing and surface heterogeneity of the fibres.
For random glass fibre mats, Darcy’s law appears to be suitable as the flow profile results in a straight line. Nevertheless, a drooping curve is observed for natural fibre mats. This suggests that the difference in the local flow velocity pertinent to micro- and macro-flow may be the cause for
the observation. There are two types of pores in the fibre mats: small and large pores. Random glass fibre mats have many large pores that are not connected to each other (Shih et al., 1998). The flow from one large pore to another is envisaged through pores of different sizes. Accordingly, the flow in the random fibre mat can be described as large and small pores being connected together in series, as shown in Figure 3.10.

![Figure 3.10](image)

Figure 3.10  a) Glass fibre random mat b) SEM photograph of glass fibre c) Pore connection in glass fibre mat d) Flow pattern of resin over glass fibre e) Experimental photograph of glass fibre mat impregnation.

In the natural sisal fibre mat, all fibre tows are aligned in one direction, and the flow pattern may be dominated by the orientation of the fibre tows. The micro scale flow path for natural fibre (sisal) can be theoretically treated as macro and micro pores connected together in parallel as shown in Figure 3.11.
The sisal fibre spacing inside the tows is much smaller than the spacing between the tows. During the course of characterizing their properties, it has become evident that flow of resin in these types of mats is fundamentally different from the flow in random mats. This aspect has already been incorporated into the improved Carman-Kozeny as a fitting parameter.

3.4.8 Model Validation

This investigation is primarily focused to study the effect of fiber network on the permeability in vacuum infusion molding process. The unsaturated permeability of several natural fiber mats with different networks is measured. The experimental permeability’s are fitted by the kozeny model and contact angle model. The outcome highlighted that the contact angle model shows more precise results as compared to kozeny model. The obtained permeability for the random fiber mats shows higher values than directional fiber mat.
3.4.8.1 Pore analysis

The pore sizes are typically categorized as: the micro-pores, located inside the fiber tow, and the macro-pores, present in the gaps between the fiber tows. These pore sizes are non-uniform and has its own distribution. For the bidirectional fiber mat (Figure 3.12), the macro-pore is much larger as compared to the micro-pore and these pores are interconnected. It is assumed that the micro-scale flow path is treated as a macro-pore and micro-pore parallel connection. Hence, the resin flows mainly through the macro-pore and the permeability is governed primarily by the flow resistance in the macro-pore. For the random fiber mat (Figure 3.12) the macro-pores in the fiber reinforcement are not connected to each other. It is hence assumed that the resin flows through some mid-sized pores. Subsequently, the flow in the random fiber mat can be described as a macro-pore and midsized pore existing as series connection. Therefore, the permeability of such fiber mat is mainly decided by the flow resistance in the midsized pore. For the unidirectional fiber mat (Figure. 3.12), its structure is identical to that of the bidirectional fiber mat, nevertheless, there is presence of micro-pore and midsized pore. It is assumed that midsized pore and micro-pore are connected in parallel.

![Figure 3.12 Conceptual diagrams for a) Random mat b) Unidirectional mat c) Bidirectional mat](image)

The permeability of this type of fiber mat is altered by the flow resistance in the midsized pore. The permeability of the bidirectional fiber mat is higher than that of the unidirectional fiber mat as its flow channel is larger. The lower permeability of uni-directional fiber mats is due to the dual scale nature of the fiber mat structure. In unidirectional mat, once the resin enters the mold, the fiber tows close to the resin inlet are impregnated prior to the tows near the downstream due to the flow resistance inside the fiber tows. The flow behavior in directional mats is anticipated to be basically different from the random fiber mats leading to the above observation.
3.4.8.2 Permeability modeling

In this study, improved kozeny model and contact angle model is adopted to analyze the flow behaviour in terms of permeability of the fiber mat. This model is validated with the experimental data. It clearly illustrates that the contact angle model provides better accuracy while predicting permeability for all types of fiber mats. Adding capillary pressure in terms of contact angle gives good correlation with experimental observations because natural fiber has more impacts of capillary due to its hollow nature of lumen. Hence, it is an important parameter to be considered for unsaturated permeability calculation, especially with the usage of natural fiber and low injection pressure processing system. The process, fiber and experimental parameters are considered to describe the overall behavior of permeability in the contact angle model. These parameters are derived for each fiber network category. This model establishes a generic format and can be extended for permeability prediction for liquid molding process simulation.

![Graph comparing experimental data with model predictions of unidirectional sisal fibre mat](image)

Figure 3.13 Comparisons of experimental data with model predictions of unidirectional sisal fibre mat
In this experimental investigation, the permeability of a fiber preform is measured by the unsaturated measurement method. The bidirectional mat and random mat have good flow properties. It is feasible to complete the resin infusion of 250 mm fiber mat in less than a 25 sec interval. For the unidirectional mat, the resin filling time is longer than the other mats. In these mats, while resin is entered into a mold, it initially passes through the fiber inter-tow channels without impregnating the fiber tows. After the flow front has passed, resin from the surrounding gap region continues to impregnate the fiber tows. This delayed impregnation of tows leads to longer resin filling time.

In contact angle model, the parameter a considers the process; b takes into account fiber nature while c depends on experimental parameters.

Figure 3.14 Comparisons of experimental data with model predictions of bidirectional jute fibre mat

This study accounts for the influence of fiber architecture on the flow pattern in terms of micro-scale and permeability of fiber reinforcements, i.e., bidirectional and unidirectional stitched, and continuous random fiber mats. Carman-Kozeny model is employed to validate the proposed model in this study. Carman-Kozeny relationship is typically developed to predict the flow behavior in porous medium, and it is deduced by assuming that the medium is an arrangement of parallel tubes. However, there is higher deviation in the permeability with the experimentally recorded values owing to irregular orientations in natural fibers. The Carman-Kozeny model also predicts permeability for bidirectional mat with good agreement with experimental results owing to uniform cross flow and longitudinal flow during impregnation phase (Figure. 3.13). While in
unidirectional, (Figure 3.14) the cross flow (transverse flow) is much more constricted than flow along the fibers. Carman-Kozeny equation is valid only for uniform flow and invalid for unidirectional mat. In the case random mats, both the models are shown (Figure. 3.15) higher deviation in flow prediction. It is due to that the longitudinal and transverse flow occurring simultaneously, pore analysis and flow pattern is basically different from directional mats. The above fact leads to difficulties in prediction of the parameters value for contact angle model.

![Graph](image)

Figure 3.15 Comparisons of experimental data with model predictions of random sisal fibre mat

### 3.5 Conclusions

The permeability of natural fibre from improved Kozeny model is $4.77 \times 10^{-9}$ m$^2$ and the measured value of permeability from fitting curve methods is $1 \times 10^{-9}$ m$^2$. The deviation of $3.77 \times 10^{-9}$ m$^2$ in the permeability values appears to be influenced by the preform structure, wetting properties, and swelling. It is concluded that swelling does not alter the flow behaviour of synthetic resin over natural fibre in infusion process compared to fibre network and wetting behaviour. When bio-epoxy is used as a matrix material, swelling is considered one of the factors to predict the flow behaviour of bio-based resin over a natural fibre mat with higher accuracy. The experiments show that the sisal fibres which give various complex wetting behaviour are not present in glass fibres. Consequently when this parameter is included in the adopted model, there will be a considerable improvement in the accuracy. The closeness to the experiments results are
achieved repeatedly with the proposed contact angle model is almost 5 times better than kozeny model in terms of SSD value. Further, it is concluded that external pressures (negative or positive pressure) are essential to accelerate the wetting of sisal fibres; particularly with high viscosities of resins, the impregnation must be performed using large external pressures. In addition, the fibre network analysis provides the causes and behaviour details of the natural fibre as a conclave. The permeability of three different natural fiber mats is measured and compare with models. The kozeny and contact angle model are employed as tools in order to determine the permeability of various natural fiber networks. The contact angle model parameters can be related to the fiber networks, the model is validated with respect to experimental values and excellent agreement is found. The natural fiber mats studied here (bidirectional jute and unidirectional/random sisal) demonstrated similar behavior in terms of permeability.
4 Wetting behavior of soy based resin and unsaturated polyester on sisal fibre mat modified surface.

4.1 Abstract

This chapter presents the complex phenomena occurring during wetting of natural fibres with epoxidized soybean oil (ESO) and polyester in terms of contact angle and surface energy. The fibres are treated with various reagents to improve the wetting behavior. The observations demonstrate that NaOH treatment removes hemicelluloses and other impurities to a greater extent as observed through Fourier transform infrared spectroscopy (FTIR) and Scanning electron microscopy (SEM). Besides, it is further noted that there is a considerable amount of increase in surface area of the exposed cellulose that aids in enhancement of wettability characteristics. Conversely, there is a formation of virtual layer on the fibre when treated with silane and isocyanate. An evaluation indicates coherence for silane and isocyanate treated fibre when expressed in terms of contact angle and surface energy. Moreover, isocyanate treated fibre exhibits good wetting in ESO resin which may be attributed to change in polarity. Thermogravimetric analysis (TGA) studies reveal that there is an appreciable enhancement in thermal stability for all the treatments.

4.2 Introduction

In modern years, research on the replacement of synthetic materials with bio materials in fibre reinforced composites industry has increased dramatically due to low carbon footprint and the capability of being made to completely degrade. The compound annual growth rate of biomaterial market is forecasted to grow 14.85% from 2012 to 2016 in North America, Europe and Asia, which are accounted as the major global markets (Faruk et al., 2012; Ho et al., 2012; Global Biomaterial Market, 2012–2016).

Natural fibers extracted from different parts of plants typically have different surface chemistry i.e degree of hydrophilicity and physico-chemically heterogeneous. The fiber surface property governs the fiber–matrix interactions in the composite (Aranberri et al., 2003). Natural fibres do not effectively adhere to non-polar resins due to these polar groups. This may be addressed by chemical modification. Chemically modified surface reduces the moisture absorption, increases the tensile strength and wettability between fibres and matrix through microstructure
modification, and enhances surface topography and chemical groups. This creates bonds between the fibre and matrix (Rouison et al., 2004; Rout et al., 2001; Silva et al., 2000). Few compounds appears to endorse adhesion chemically to surface such as sodium hydroxide, silane, acetic acid, acrylic acid, maleated coupling agents, isocyanate, potassium permanganate, peroxide, etc., as observed from available literatures (Li et al., 2007; Sreekala et al., 2003). Apart from this, it is well established that the cross linking system itself may provide an impact on the interfacial adhesion e.g. anhydride curing of epoxidized plant oil (Fejős et al., 2013).

NaOH treatment enhances the roughness of the fibre surface, which also improves fibre-matrix adhesion by providing mechanical interlocking, Mechanical and thermal behaviors of the composite gradually improves by this treatment (Ly et al., 2007; Kabir 2012). Brigida et al., (2010) discussed the possibility of fibres treated with NaOCl/NaOH resulting in more hydrophilic nature than the natural fibre. Zhong et al., (2011) presented the fact that OH group on the surface of the fibre yields good wettability with water and resulted in increased contact angle after various treatments namely amino silicone oil, silane coupling agent and emulsified wax.

Cantero et al., (2003) studied the effects of the treatments on the contact angles of natural fibre and they noticed that the treatments increase the contact angle of fibre with water due to its polarity changes. Kabir treated natural fibres with silane agent and reported that silane act as surface coatings that facilitate penetration in pores, reduction in moisture absorption and higher tensile strength/modulus (Kabir 2012; George et al., 1999; Ly et al., 2008). They evidently proved fact that the contact angle of a drop of water increases and concluded that fully sustainable composites with enlightened performances is attainable with isocyanate treated fibre. Alternatively, low pressure plasma treatment may also be used to improve the bonding between the reinforcement and matrix (Aguilar et al., 2014).

The literature reports the evaluation and effects of treatment on the viewpoint of mechanical behavior. Besides, the contact angle tests to analyze the moisture absorption are most commonly presented. The literature reviews showcased the research gap in the studies pertaining to the effects of treatments on the wetting of thermosetting resin. There has been scanty report for extrapolating this analysis for inter-wettability studies between fibres and resins, respectively.

Hence in this study, an attempt is being made to determine the effect of different chemical treatments carried out in sisal fibre surfaces on wetting and thermal properties targeting the
potential applications of these fibres. Three different chemical treatments are being used namely NaOH, Silane and Isocyanate and the characteristics like morphology, chemical composition, element analysis, wettability and thermal stability from natural and treated sisal fibre are evaluated. The outcome of this study is expected to improve the understanding and assist in arriving at effective design of the surface of fibre to a liquid molding process and thus improving the reliability in flow prediction of the process.

In this study, epoxidized soybean oil is used as a bio resin due to its availability in abundance and economical factor. Besides, soy-oil is highly unsaturated oil (reactive double bond) which presents itself as a good source for bio based resin synthesis. Added to this, the conventional polymeric matrix (polyester) is also tested and compared with the result of the epoxidized soybean oil (Miyaki et al., 1998). Wang et al., (2013) illustrated that epoxidized soybean oil (ESO) possess less viscosity, and good compatibility with diglycidyl ether of bisphenol A (DGEBA) at high cure temperature and favorable mechanical strength up to 30%. This enables ESO and their derivatives to be utilized as reactive diluents for the partial replacement of DGEBA resin which are having relatively high viscosity in liquid processing.

4.3 Materials and Methods

4.3.1 Materials

The commercial unsaturated polyester resin used was ‘orthophthalic’ containing 38 wt. % of styrene purchased from naptha resins & chemicals pvt limited, Bangalore, India with specific gravity of 1.12, viscosity of 550 cps at 25°C. Epoxidized Soybean Oil (ESO; trade name Makplast SNS) [6.5 wt% epoxy oxirane content and specific gravity of 0.987] are used as the base resin was supplied from Makwell organics pvt. ltd., Mumbai, India. The unidirectional sisal fibre mat (woven) with an area density of 577 g/m² manufactured by Women’s development organisation, India. The average filament diameter and thickness of the mat of sisal fiber are 0.35 mm and 1.2 mm respectively.
4.3.2 Surface treatment of sisal fibre mat

Alkali Treatment (NaOH). The sisal mats (300 mm $\times$ 300 mm) are soaked in a 2 wt % solution of NaOH at room temperature for one h. The fibres are washed thoroughly until NaOH is removed completely and the pH of the water reaches a steady value. Then the mats are dried for 12 h at 80°C (Aguilar et al., 2014).

Silane coupling agent. In this process, 1 wt. % of 3-aminopropyltriethoxysilane is dissolved in distilled water. The fibres are immersed in the solution for 30 min at room temperature to permit the hydrolysis of the silane. This is followed by drying of fibres in an oven at 100°C prior to its exposure for 12 h at 80°C (Kabir 2012; Rouison 2004).

Isocyanate Treatment. In this process, 6 % of Methylene diphenyl diisocyanate (MDI) solution is prepared using toluene solvent. Then, 150 g of sisal fibre mat is placed in the reaction kettle and the mat is immersed in the MDI solution of about 2000 ml. The resulting suspension is then heated to 50°C for about 30 min. After completion of the reaction, the mat is decanted and dried in air oven at 70°C for 2 h (George et al., 1998).

4.3.3 Fourier Transform Infrared (FTIR) Spectroscopy

Fourier transform infrared (FTIR) spectroscopy is carried out to qualitatively identify the constituents of sisal fibre. Both the untreated (raw) and treated sisal fibers are examined to understand the differences in chemical characterization of their surface.

4.3.4 Scanning Electron Microscopy (SEM)

The surface texture of sisal fibres are analyzed by scanning electron microscopy (SEM).

4.3.5 Element analysis by Energy dispersive X-ray spectrometry

EDX examinations of the sisal fibres are carried out using a FEI Quanta 200 FEG scanning electron microscope combined with an ultra-thin window energy dispersive X-ray (EDX) detector for qualitative elemental analysis.
4.3.6 **Wettability measurements**

In this study, the contact angle is measured by goniometer. In this technique, initially the videos are obtained from goniometer followed by its conversion to picture. These are further imported to computer-aided design and drafting (CADD) software which assists in drafting. This enables the measure of the size accurately. The wettability which is a contact angle dependent parameter is measured in sisal fibre subjected to polyester and epoxidized soya bean oil for various treatments. The surface tension of the ESO resin is estimated from pendant drop. This technique uses the drop profile of the resin resting on a syringe tip for the calculation of surface tension of the resin based on a balanced forces acting on the surface of the drop.

4.3.7 **Sisal fibre surface energy estimation**

Contact angle measurements of a natural fibre mat (solid) already discussed in the previous section reveal the thermodynamics relationship of the solid–liquid interactions. In this section, attempt is made to estimate the surface free energy of sisal fibre mat while ESO resin wets mat and the same resin is used for sessile drop measurement and the contact angles attained are used together with the Young’s and Neumann’s equations to determine the surface free energy of sisal mat, as given in equation 4.1.

\[ \gamma_{sv} = \gamma_s + \gamma_l \cos \theta \]  

(4.1)

There are two unknown \( \gamma_{sv} \), surface free energy of the interface solid/liquid and \( \gamma_s \), surface free energy of the solid and \( \theta \) is the contact angle in the Young’s equation. Young’s equation is solved by Neumann concept in this section.

Neumann’s Equation of state for interfacial tension (Free Energy) is given in equation 4.2.

\[ \gamma_s = \frac{(\sqrt{\gamma_{sv}} - \sqrt{\gamma_l})^2}{1 - 0.015 \sqrt{\gamma_{sv} \gamma_l}} \]  

(4.2)

Where \( \gamma_s \) the surface free energy of the solid is, \( \gamma_{sv} \) is surface free energy of the interface solid/liquid and \( \gamma_l \) is surface free energy of the liquid.
From Neumann’s equation (Neumann et al., 1974), when the denominator tends to zero, the entire equation becomes infinity. To evaluate the surface free energy of fibre mat, substitute equation (4.2) to (4.1).

\[ \gamma_{sv} = \frac{\left(\sqrt{\gamma_{sv}} - \sqrt{\gamma_{l}}\right)^2}{1 - 0.015 \sqrt{\gamma_{sv} \gamma_{l}}} + \gamma_{l} \cos \theta \]  

(4.3)

Then, the right parameters moved to the left:

\[ \gamma_{sv} - \frac{\left(\sqrt{\gamma_{sv}} - \sqrt{\gamma_{l}}\right)^2}{1 - 0.015 \sqrt{\gamma_{sv} \gamma_{l}}} - \gamma_{l} \cos \theta = 0 \]  

(4.4)

The iteration of assumed values of surface energy of mat is introduced in equation 4.4. Surface energy estimated from this method is also verified with Young-Dupre equation.

\[ \gamma_{s} = \gamma_{sv} + \gamma_{l} - W_{a} \]  

(4.5)

By combining equation 4.1 and 4.5:

\[ W_{a} = \gamma_{l} (1 + \cos \theta) \]  

(4.6)

Equation 4.5 is the Young-Dupre equation. The work of adhesion (\( W_{a} \)) can be estimated from equation 4.6 using accessible quantities \( \gamma_{l} \) and \( \theta \). After the evaluation of \( W_{a} \), the surface energy of the solid \( \gamma_{s} \) is evaluated from equation 4.7 (Chaudhury 1993).

\[ \gamma_{s} = 0.25 \gamma_{l} (1 + \cos \theta)^2 \]  

(4.7)

### 4.3.8 Measurement of pore size and their distribution

The pore sizes and their distribution are measured for various treatments by a capillary flow porometer, based on the principle of the liquid extrusion porometry technique. The test liquids used in the porosimeter is GalwickTM (Propene,1,1,2,3,3,3-hexafluoro, oxidized, polymerized, Porous Materials Inc.) (Patanaik et al., 2009) Galwick has surface tensions of 15.9 mN/m and it is anticipated that this facilitates complete wetting in the samples tested and hence a contact angle of 0° is taken for calculations of pore diameter using the Young–Laplace equation.
\[ P \cdot d = 4 \sigma \cos \theta \]  

(4.8)

Where \( P \) is extrusion pressure in MPa, \( d \) is pore diameter in µm, \( \sigma \) is surface tension of Galwick in N/m, and \( \theta \) is contact angle of Galwick with the sample, in degrees.

### 4.3.9 Thermal Gravimetric Analysis (TGA)

Thermo gravimetric analysis (TGA) is conducted to evaluate the thermal stability of the fibers. TGA is carried out by using a NETZSCH STA 409PC/PG. The mass of the samples is between 5 and 6 mg. This experiment is carried out at a temperature interval of 30–650°C at a heating rate of 10°C/min.

### 4.4 Results and Discussion

#### 4.4.1 Chemical characterization

The chemical modification of surface was characterized by FTIR. The spectra of untreated sisal fibre (see Figure.4.1 a) illustrate a broad and intense peak at 3200-3300 cm\(^{-1}\) thereby denoting the hydrogen-bonded (O-H) stretching from the cellulose and lignin structure of the sisal fiber. Peaks in the region of 1030–1150 cm\(^{-1}\) are mainly due to the C–O–C and C–O symmetric stretching of primary and secondary hydroxyl group. Peak near to the 1724 cm\(^{-1}\) corresponds to –C=O stretching due to the presence of aliphatic carboxylic acid (Kabir 2012; Cantero et al., 2003).

**NaOH treated fibre.** The characteristic bands of hemicellulose, observed in the natural sisal fiber around 1724 cm\(^{-1}\), are not present in NaOH treated sisal fibers. This is the outcome of the decomposition of hemicelluloses and partial leaching out of lignin by NaOH. The band at 1238 cm\(^{-1}\) is related to the vibration (C-O) of carboxylic groups attributed mainly due to the presence of waxes and the subsequent disappearance of this band in the treated fibers results from the removal of those waxes. This phenomenon has been verified by various literatures that employed NaOH in the treatment of natural fibre surfaces (Brigida et al., 2010; Favaro et al., 2010; Kalaprasad et al., 2004).

**Silane treated fibre.** It is hard to fully assign the existence of Si-O-C (cellulose of sisal fibre), because of the strong absorption of the two wave bands in the region of 1000–1200 cm\(^{-1}\) from
cellulose. However, the peak at 1023 cm\(^{-1}\), which is an overlap of Si-O-C band and the C-O stretching of cellulose, increases after silane agent treatment illustrating the presence of Si-O-C. The silane had no reactivity with the lignin constituents as it had a similar peak to the untreated fibre.

![FTIR spectra of different chemically modified sisal fibre: a) Untreated b) NaOH treated c) Silane treated, and d) MDI treated](image)

**Figure 4.1** FTIR spectra of different chemically modified sisal fibre: a) Untreated b) NaOH treated c) Silane treated, and d) MDI treated

The FTIR spectra do not clearly show the effect of silane on the transmittance bands. From the literatures, the peaks are identified at 766 cm\(^{-1}\) and 847 cm\(^{-1}\) are corresponding to Si–C symmetric stretching. Generally the concentration of silane on the fibre surfaces may be too small to be detected by FTIR (The reaction between the silane and chemical components are weak).

**MDI treated fibre.** The FTIR spectra of MDI treated sisal fibre shows peaks at 1732 cm\(^{-1}\) corresponding to carbonyl (C=O) stretching. The peaks at 1696 cm\(^{-1}\) attributed to urethane carbonyl group. The presence of peaks at 1367 cm\(^{-1}\) in both treated and untreated sisal fibre assigned to C-H bending vibration. However, the peaks in treated sisal fibre are strong, owing to the overlapping of C-H bending and C-N stretching vibration. The peaks at 1602 cm\(^{-1}\), 1580 cm\(^{-1}\)
and 1513 cm\(^{-1}\) attributed to aromatic C-C stretching vibration present in the MDI. The above discussion confirmed that the sisal fibre is treated with MDI (Ly et al., 2008).

### 4.4.2 Morphological characterization

Untreated sisal fibre surface appears to be rough due to the presence of impurities, and others constituents such as lignin, hemicelluloses and waxes of the fibres (Figure 4.2.a). SEM micrographs (Figure 4.2.b) indicate a significant change in surface topography after NaOH treatment. The NaOH treated samples show the scratch formation and disintegration existent on the surface. The fact attributing to this observation may be the removal of hemi-cellulose and lignin interconnecting the cellulose fibrils. The alkali treatment leads to fibrillation of the fibre bundle into smaller fibres, leading to a reduction in the diameter. Chemical treatment cleans the fibres from impurities which are mostly non-polar. This enhances the adhesion between fibre and matrix when used in reinforcing composite materials (Kabir 2012; Brigida et al., 2010).

**Figure 4.2** Sisal fibre, a) untreated fibre b) NaOH treated fibre c) Silane treated fibre d) MDI treated fibre
The SEM image of Figure 4.2.c shows the presence of silane on the sisal fibres. The silane impinged surface covers the space between the cellulose micro fibrils giving it a smooth outlook (Kabir et al., 2012). Similar observations are recorded with MDI (Figure 4.2.d).

4.4.3 Wetting Test Analysis

Generally, the fibre mat/resin interactions are influenced by the wettability of the fibres, resin property, surface geometry of the mat, the capillary geometry, and externally applied pressure. Wetting is proportional to the spreading of resin on fibre surface and inversely proportional to contact angle. Typically, in liquid molding process as adopted for this study, the resin filling of the reinforcement, between and inside tow wetting, controls the processing time and improves the product features.

The wetting behavior analysis of this mat is important task due to its intricate microstructure for the presence of cellulose, hemicelluloses, lignin, and pectin etc., in these experiments; sisal fibre consists of bundles of more than 30 elementary fibres. An elementary fibre consists of several layers of fibrils aligned in different angles with respect to the longitudinal fibre axis bound together with hemi-cellulose and lignin. Starova et al., (2003) emphasized that while resin spreads on the porous surface, penetration and spreading are phenomenon occurring in parallel. One of these two processes is faster than the other depending upon the porosity of the substrate, impact velocity of the droplet and the surface tension of the liquid.
Figure 4.3 Effect of fibre treatments on contact angles of sisal fibres wetted with polyester

Figure 4.4 Effect of fibre treatments on contact angles of sisal fibres wetted with ESO
Contact angle is measured by placing a drop of polyester & epoxidized soy bean resin on the untreated and treated sisal fibre mat surface respectively, as shown Figures 4.3 and 4.4, which enables, the determination of wettability. It is clearly evident that the surface treating agent applied creates a difference in the interaction of fibre-resin. In untreated sisal fibre mat, the wettability between the non-polar resin molecules and presence of polar OH group on the untreated sisal fibre mat curbs resin spreading and it remains as a droplet on the mat surface. Inversely, when a resin drop is placed in contact with a sisal mat, it spreads instantaneously towards its equilibrium shape when treated with NaOH as against the untreated fibres. When natural fiber is treated by NaOH, the initial contact angle decreases to 53° wetted with polyester resin.

Figure 4.5 ESO resin on the treated sisal fibre a) Untreated b) NaOH treated c) Silane treated d) MDI treated

In NaOH treatment, the polar OH groups on the surface of the fibre are reduced, which enables the sisal fibre mat to exhibit a non-polar behavior. Due to the fact the wettability between polyester and sisal mat is improved. The similar trend observed for ESO resin also. This also
causes roughness behavior on the surface. The decrease of contact angle leads to the appreciation in wettability. The Figure 4.5 Shows the ESO resin wetted with treated and untreated sisal fibre. The contact angle is increased from 72 to 88° (Figure observation on the columnar portion from 4a to 4d), after silane treatment wetted with ESO which indicates high repelling action attained initially. The appearance of polar molecule on the surface is consistent as seen from the FTIR spectroscopic. The contact angle of the resin drop decreased rapidly for MDI-treated samples. Besides, the contact angle of a drop of the resin deposited on the surface of sisal fibre mat before and after treatment shows that the penetration of the resin increases significantly after MDI treatment. The MDI treated surface illustrates greater adhesiveness to epoxidized soybean oil which may be the reason of interaction between the non-polar mat surfaces/resin layers enabling good wetting. Contrasting observation are recorded for silane treated fibres wetted with epoxidized soy bean oil due to polarity difference between N-C-O linkage in MDI and Si-O linkage of silane.

Table 4.1 Fit parameters from the exponential model for sisal fibre/ESO system.

<table>
<thead>
<tr>
<th>Fibre Type</th>
<th>Parameter</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
<td>c</td>
<td>$\chi^2$</td>
</tr>
<tr>
<td>Untreaed SF</td>
<td>4.26±0.02</td>
<td>-1.51×10^{-4}</td>
<td>-1.73×10^{-8}</td>
<td>03.18</td>
</tr>
<tr>
<td>NaOH treated SF</td>
<td>4.43±0.02</td>
<td>-6.15×10^{-4}</td>
<td>-6.59×10^{-8}</td>
<td>20.75</td>
</tr>
<tr>
<td>Silane treated SF</td>
<td>4.46±0.02</td>
<td>-1.50×10^{-4}</td>
<td>-3.85×10^{-8}</td>
<td>12.86</td>
</tr>
<tr>
<td>MDI treated SF</td>
<td>4.53±0.02</td>
<td>-6.88×10^{-4}</td>
<td>-9.33×10^{-8}</td>
<td>41.21</td>
</tr>
</tbody>
</table>

To have an in-depth and clear understanding, the effects of the surface modification on the spreading behavior, employing an exponential model of the following form is fitted to the experimental data,

$$\theta = e^{a+bt+ct^2}$$  (4.9)
where a, b, and c are empirical constants determined by the best fit. For all the treatments, a good agreement is observed between the experimental data and the fits. The values of the fit parameters with their 95% confidence intervals, as well as the sum of the squared deviations of the theoretical values from the experimental values which is called $\chi^2$ from the best fit, are shown in Table 4.1. The $\chi^2$ values increases for treated fibres and shows maximum for MDI treated fibres.

### 4.4.4 Surface energy of sisal fiber

The surface tension of the ESO resin as estimated from pendant drop technique is $= 27.3$ mN/m while the surface free energy of sisal mat is unknown. From the iteration results, a graph of assumed values of $\gamma_s$ vs solution of equation 4.4 is plotted to estimate the real value of surface free energy of mat. The accurate value of the surface energy yielding zero for equation 4 is identified. In this paper, the dynamic contact angle (contact angle with specific time period) is used to calculate the surface energy of the fibre mat. From Figure 4.6, the surface free energy of mat is deduced and presented in Table 4.2.

![Figure 4.6](image)

*Figure 4.6* A graph of assumed values of surface energy Vs Solution of equation 4
Table 4.2  Calculated surface free energies and work of adhesion of sisal fibres.

<table>
<thead>
<tr>
<th>Fibre</th>
<th>Untreated SF</th>
<th>NaOH treated SF</th>
<th>Silane treated SF</th>
<th>MDI treated SF</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma_s [\frac{mN}{m}]$</td>
<td>18</td>
<td>23.5</td>
<td>15.35</td>
<td>25.5</td>
</tr>
<tr>
<td>$W_A [\frac{mN}{m}]$</td>
<td>43.73</td>
<td>50.70</td>
<td>40.12</td>
<td>52.61</td>
</tr>
</tbody>
</table>

The surface energy of the various treated sisal fibres is significantly different due to surface treating agent effect. Untreated fibers exhibit less surface energy, which can be attributed to surface contamination of the sisal fibres by remaining extractives and lignin fragments (Sever et al., 2012). Decrease in contact angle for alkali treated fibres correspond to the increase in surface free energy component which is due to extraction of lignin, hemicellulose, other derivatives and reduction of the polar OH groups from the surface of the fibre. The similar trend is observed for surface energies and contact angles of MDI treated fibres while wetted with ESO resin. The Silane treated fibres exhibits less surface energy probably due to polarity difference between silane treated fibre and ESO resin. Based on this study, the alkali and MDI treatments is appears as a top priority in choice to improve the sisal fiber/ESO resin adhesion.

4.4.5  Element Analysis

The EDX results for treated and untreated fibres are tabulated in (Table 4.3). Explanation for various behaviors may be viewed from O/C ratio. The higher O/C ratio indicates lower lignin (Zhong et al., 2010). EDX Peaks indicate the presence of C and O in prominence in natural fibre. Small amounts of calcium are also present sisal fibre. Cellulose, hemicellulose and pectin have an O/C ratio of 0.83 (Brigida et al., 2010).
Table 4.3 The EDX analysis of atomic concentrations of the sisal fiber surface, before and after modification with various chemical treating agents.

<table>
<thead>
<tr>
<th>Elements</th>
<th>C</th>
<th>O</th>
<th>Si</th>
<th>Ca</th>
<th>N</th>
<th>Na</th>
<th>O/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>61.83</td>
<td>36.97</td>
<td>-</td>
<td>1.20</td>
<td>-</td>
<td>-</td>
<td>0.59</td>
</tr>
<tr>
<td>NaOH</td>
<td>56.46</td>
<td>42.34</td>
<td>-</td>
<td>0.51</td>
<td>-</td>
<td>0.69</td>
<td>0.74</td>
</tr>
<tr>
<td>Silane</td>
<td>60.26</td>
<td>36.26</td>
<td>1.47</td>
<td>1.51</td>
<td>-</td>
<td>0.5</td>
<td>0.60</td>
</tr>
<tr>
<td>MDI</td>
<td>68.79</td>
<td>29.77</td>
<td>-</td>
<td>0.69</td>
<td>0.75</td>
<td>-</td>
<td>0.43</td>
</tr>
</tbody>
</table>

The O/C ratio of any natural fibre is limited to 0.83. This enforces the surface to possess significant proportion of lignin and waxes. In this work, it is noted that 0.59 O/C ratio leads to non-oxidized carbon atoms from various impurities of sisal fibre. However, considering the increase in the O/C ratio observed for most treated fibres (Table 4.3).

It may be interpreted that the various chemical treatments reduced the proportion of waxes on the surface, while increasing cellulose quotient. The increase in cellulose on the fibre surfaces provides more hydroxyl groups that can react with epoxide groups (Brigida et al., 2010). MDI has induced a decrease of the O/C value as it is richer in carbon atoms. Besides, they are more reactive compared with silane, which induces a better coverage of the surface. The silane shows negligible alternation in the O/C value, as they bear an O/C ratio close to that of pristine cellulosic substrate (Ly et al., 2008).

4.4.6 Pore analysis

Generally, three types of pores present in nonwoven mat namely, through pores, closed pores, and blind pores. Closed pores are not accessible and therefore do not allow passage of liquid and air. The blind pores terminate inside the material and therefore do not permit fluid flow (Patanaik et al., 2009). Through pores are open and allow the flow through the medium and so are important for any liquid molding (infusion) process. The capillary flow porometer is considered only to measure through pores.

Comparison between treated and untreated sisal mat, indicated that the porometer could detect the finer pores in the sisal mat in addition to some of the bigger pores shown. Figure 4.7
shows that smaller pores contribute more to the pore volume than bigger pores. The pore distribution is presented in Figure 4.7 is following the distribution function (f):

$$f = (-d(F_w/F_d) \times 100)/dD$$  \hspace{1cm} (4.10)

Where $F_w$ and $F_d$ are flow rates through wet and dry samples respectively at the same differential pressure, $D$ is measured pore diameter, $d$ is the largest particle diameter that can pass through the elliptical pore (Jena et al., 2003).

Figure 4.7 shows the pore size distribution of the sisal mat from the porometry analyses. Since, there are much smaller pores than larger pores and also the resin has high surface tension, the capture of all the pore volume, especially in finer pores is limited. Consequently, such mat geometry and resin property would restrict “wetting out” of the entire pore volume present without exceedingly high applied pressures.

![Figure 4.7 Pore size distribution of the sisal mat, before and after modification with various chemical treating agents](image)

Untreated sisal fibre mat exhibited mean pore size of 19.8 μm whereas the corresponding value for NaOH treated was 23.18 μm. The experimental results indicate that the combined increase in constricted pore size and diameter may contribute to an increase in porosity for these classes of
mat. In this work, the pore size distribution was divided into three different regions of pore diameters: 0–40 µm, >40-80 µm and >80-120 µm (small, medium, and large sized pores respectively). The percentage contribution of pores in the above three different regions for untreated, NaOH, Silane and MDI treated fibres are as follows: 60%, 20%, 20%; 55%, 25%, 20%; 60%, 30%, 18% and 58%, 22%, 20%. These larger pores (>80 µm) mainly govern the permeability, as the fluid passes easily through the structure without unnecessary pressure built-up. During the process, some of the medium sized pores are converted into smaller pores and larger pores are converted into medium pores due to the entanglement action. Application of external pressure or force leads to creation of entanglement action which acts in the direction of load. Hence, the resize of pores occurs only at specific area and does not affect the size in the entire mat in the absence of centripetal force (Patanaik et al., 2009; Manickam et al., 2012). In the mat structures, the pore size distribution obtained from experiment are identical as observed from Figure 4.7. The sum of squared deviation (SSD) values between the untreated and chemically treated fibre is very less. It is concluded that physical changes of the mat during treatment with various treating agent shows negligible effects in the wettability.

4.4.7 Thermal analysis

The two step degradation is observed in TG curves. The first weight loss around 110°C is due to moisture loss. The second relates to the degradation of the material. On comparing the weight losses at 550°C, it is seen that the values are 83, 75, 71 and 78% for untreated, NaOH, Silane and MDI treated fibre respectively shown in Figure 4.8. Thermal stability of the fibre is increases noticeably. Weight loss at this temperature decreases for treated fibres than that of untreated fibre justifying the experimental observation.
Figure 4.8 Thermo gravimetric analysis of untreated and treated sisal fibre

The NaOH treated fibre showed less weight loss than the untreated fibres due the removal of hemicelluloses and lignin constituents from the fibre. Therefore, the decomposition process mainly occurred on the cellulose which in turn increased the overall degradation temperature of the treated fibres. During silane treatment, silane molecules formed couplings with the hemicelluloses and lignin constituents of the fibre. These chemical couplings acted as a covering layer on the fibre surface (Figure 4.2-c). This silane covering protected the fibre from thermal decomposition at higher temperatures. These actions prevented the breakdown of the fibre’s molecular structure thus enhancing the overall thermal stability of the silane treated fibres at higher temperatures as compared to the untreated fibres.

The slightly higher thermal stability of MDI treated fibre may be due to the formation of covalent bond between the -N=C=O group of MDI and --OH group of cellulose. TGA helps in confirming that the chemical modifications do not induce an undesirable change on the thermal resistance of the fibres (George et al., 1996).
4.5 Conclusions

The sisal fibre is treated with NaOH, Silane and MDI for analyzing the wettability with various resin, thermal stability, pore analysis and surface morphology. The extent of the treatment is confirmed with FTIR, SEM/EDX. The various tests are conducted and the results are summarized as follows.

Treatment with NaOH yield good wettability for both resins (Polyester and ESO). Silane and MDI shows a reasonable enhancement of thermal stability. In connection with the pore distribution it is noted that uniformity and integrity is upheld while a minute modification is visible in the pore size as seen from porometer analyzing. Owing to the fact that the pore size remains reasonably unaltered, wettability phenomenon is maintained almost the same for polyester resin. In contrast, for MDI treatment, there is a significant change in wettability for ESO resin due to occurrence of polar - non-polar interaction. The most prominent observation from this study indicates an appreciable improvement in the flow characteristics for MDI treated fibre exclusively w.r.t wettability with ESO. The outcome of the surface energy analysis illustrates direct proportionality between surface energy and wetting.
5 Cure kinetics characterization of soy-based epoxy resins for infusion molding process

5.1 Abstract:

This study presents the kinetics of the reaction of diglycidyl ether of bisphenol A (DGEBA) based epoxy resin in the presence of epoxidized soybean oil (ESO) cured with Triethylene tetramine (TETA). Isothermal differential scanning calorimetric (DSC) study is carried out to propose a model to analyze the reaction kinetic data obtained experimentally. The proposed model is also compared with the prominent kinetic model available in the literature. The results clearly highlighted that the proposed model is attained reasonable percentage of improvement to accurately capture both the degree of cure and rate of cure qualitatively and quantitatively. The addition of ESO in the conventional system decreases the enthalpy of reaction and increases the activation energy of the system. The outcome of the study confirms the feasibility of the proposed material system for infusion process.

5.2 Introduction

In the recent years, bio-based products is gaining greater attention in technical applications due to their advantages such as low energy consumption, low density, low cost, high strength to weight ratio, and recyclability (Faruk et al., 2012; Joshi et al., 2004). Soybean-oil can be used for bio based resin schema due to its higher degree of unsaturation compare to other vegetable oils. (Miyake et al., 1998). Zhu et al., (2004) reported through experimental investigations that the pultrusion epoxy resin formulation may contain a maximum of 30 wt. % soy based resin to retain or improve the mechanical properties. The dynamic curing and the isothermal curing experiments are the two different approaches for cure kinetic study. In specific, the isothermal mode is preferred because of its ability to produce the heat flow as a function of time without the occurrence of thermal gradients during the cure stage (Arrillaga et al., 2007).

Kamal et al., (1976) developed a kinetic model elaborating the cure kinetics of epoxy/diamine systems and they found that the model is well agreed with the experimental results. Nevertheless, it was observed that the model is not valid for the later stages of cure where the reaction mechanism is diffusion-controlled. When three dimensional cross linking network is attained during the curing, an enormous portion of the reactive functional groups attach to the gel and
the mobilities of these functional groups were limited due to the higher viscosity such that the curing reactions become diffusion controlled which is generally termed as critical stage of conversion (Chern et al., 1987). Barral et al., (1995) found during the first stage of cure, the experimental data indicating an autocatalytic behaviour. Park et al., (2000) noticed slight deviation in kamal model. This deviation is initiated by the vitrification where the mobility of the reacting groups is hindered and the rate of conversion is governed by diffusion instead of autocatalytic kinetic factors. Cole et al., (1991) made significant improvement in their model while accounting both the epoxide-amine reactions and the subsequent observed etherification reaction. Further, the inclusion of diffusion factor enables calculation with greater precision in degree of conversion over the whole range of cure. The kamal model partially fits at low conversion indicating a rather complex mechanism for autocatalysis than the bimolecular or termolecular system existing. Additionally, with the increasing temperature the conversion at which diffusion-control kinetics begins to dominate occurs at a higher value. This is due to the resin ability to stay mobile longer at the higher temperatures (Varley et al., 1996). It was evident that the cure processes under dynamic and iso-thermal conditions were not identical (Karkanas et al., 1996).

This section presents some of the curing analysis done previously for epoxidized soybean oil (ESO) based system. Mustafa et al observed that the maximum peak temperature shifts to higher values with the increase of heating rate and ESO content. Further, they recorded that the low viscosity of the ESO samples, permits an enhanced contact between the epoxy ring and active protons of the cross linking agent (Mustata et al., 2011). Samper et al., (2012) showed that as the quantity of ESO in the system increases, the reaction enthalpy decreases since ESO has a considerably less epoxy groups in its structure. Altuna et al., (2011) revealed the fact that increasing amounts of ESO leads to polymerization at higher temperatures compared with diglycidyl ether of bisphenol A (DGEBA) owing to less reactive oxirane rings centrally placed in long aliphatic chains of ESO. Mashouf et al., (2014) observed that the addition of different amounts of ESO can change the kinetics of curing. In addition, it was found that the higher the amount of ESO, the higher is the activation energy of reaction.

In depth explorations of the literature survey indicate a void in the research area pertaining to cure kinetics of bio-based epoxy which plays a prominent role in the infusion process. In this paper, the curing kinetics of epoxy resins and triethylene tetramine (TETA) hardener in the
presence of ESO are studied by DSC, and the dependence of the curing activation energy with conversion for different analytical approaches are identified. Determination of the kinetic parameters such as reaction orders, activation energies and the kinetic rate constants are elucidated. TETA is selected as a curing agent for this work since it cures ESO blend at atmospheric temperature in shorter time. In addition, the viscosity is considerably less compared to other curative which facilitates the impregnation phase of the infusion process and lesser quantity is sufficient to cure designed material system due to more active hydrogen present in these curative.

5.3 Experimental

5.3.1 Materials

Araldite GY 257, the diglycidyl ether of bisphenol A, used as a resin base component was supplied from Javanthee enterprises, Guindy, Chennai. An amount of 30% Epoxidized Soybean resin [6.5 wt.% epoxy oxirane content and specific gravity of 0.987] obtained from Makwell organics pvt. ltd., Mumbai, India is added to the base resin. Triethylene tetramine (TETA) is used as a curing agent and the amount of curing agent is calculated theoretically based on the stoichiometry. The stoichiometry ratio of the resin to curing agent is calculated to be 12.40. (Appendix 5.1)

Selection of curative

The following points may be highlighted:

1) (p-aminocyclohexyl) methane (PACM): This amine requires high temperature for curing ESO blended resin at which the natural fibre gradually degrades. The infusion process necessitates special accessories and setup for the above mentioned temperature. Irrespective of the application of higher temperature, the final product appears more flexible due to the flexible methylene linkage in cyclic ring (Zhu et al., 2004; Lu et al., 2001).

2) Methylhexahydrophthalic anhydride (MHHPA): The anhydride needs higher temperature to cure the epoxy while a catalyst is essential for promoting breakage of the hydrogen linkage from the curative which finally reacts with epoxy group. Adding catalyst will affect the gel time and the material system which cause some trouble at times (Tan et al., 2011).
3) Polyamidoamine (Aradur 140): These curatives have more viscosity and require higher molar ration between resin/curative, which is approximately 50% of the system due to less active hydrogen compared to amine curative. The predominant high viscosity nature causes the difficulty in infusion setup as it necessitates higher vacuum pressure to impregnate the resin on the fibre and secondly, the disintegrating possibility of bio composite concept due to more percentage of the synthetic being higher.

4) Triethylene tetramine (TETA): It cures ESO blend at considerably low temperature in shorter time, which eliminates the need for any special accessories in infusion process. The viscosity of TETA is considerably less compared to other curative that facilitates the impregnation phase of the infusion process and improves the wettability between fibre and resin system (Lu et al., 2001). Less quantity is sufficient to cure designed material system due to more active hydrogen present in these curatives. These observations emphasizes that this particular curative is appropriate for the infusion process as well as designed material system.

5.3.2 Modelling of Cure Kinetics

For cure kinetics numerous models have been developed to characterize the curing for different resin systems. The simplest one is the \( n \)th-order two parameter rate equations:

\[
\frac{d\alpha}{dt} = K (1 - \alpha)^n
\]  
(5.1)

\[
K = A \exp \left( -\frac{E_a}{RT} \right)
\]  
(5.2)

Where \( E_a \) is the activation energy, \( A \) is the pre-exponential factor, \( R \) is the gas constant (8.314 J/mol K) and \( T \) is the absolute temperature (K). The \( n \)th-order kinetics model does not account for any autocatalytic effects (Liang et al., 2006).

For autocatalytic thermosetting resin systems, the following equation has been applied:

\[
\frac{d\alpha}{dt} = K \alpha^m (1 - \alpha)^n
\]  
(5.3)

Here \( m \) and \( n \) are reaction orders determined by experimentally, and \( K \) is the reaction rate constant. Rather than at the starting of the reaction process as in equation. (5.1), the maximum
reaction rate takes place in the middle of the conversion stage for equation (5.3), it results in bell-shaped reaction rate curve versus time for an autocatalytic reaction process (Milanese et al., 2011).

The \( n \)th order rate model given by equation 5.1 manages to predict the curing reaction rate at initial stages of cure. However, this model fails to predict the kinetics of resin systems that attain a maximum reaction rate at some intermediate degree of cure. A modification to the \( n \)th order kinetic model as autocatalytic model was proposed by Kamal and Sourour, given by:

\[
\frac{d\alpha}{dt} = (K_1 + K_2 \alpha^m)(1 - \alpha)^n
\]  
(5.4)

Where \( K_1 \) and \( K_2 \) are the rate constants, \( \alpha \) is the degree of cure and \( m \) and \( n \) are the orders of reaction. However, Kamal and Sourour autocatalytic model does not consider incomplete cure reaction, and it fails to predict the behavior at the later stages of the curing reaction (Kamal et al., 1976; Park et al., 2000).

Cole et al., (1991) modified the equation (5.3) by adding a term to clearly account for the shift from kinetics to diffusion control in an autocatalytic resin system; the modified equation has the following form:

\[
\frac{d\alpha}{dt} = \frac{K \alpha^m (1-\alpha)^n}{1+e^C(\alpha-(\alpha C_0+\alpha C_T T))}
\]  
(5.5)

Here \( C \) is diffusion constant; \( C_0 \) is critical degree of cure at absolute zero temperature. The constant \( C_T \) is accounts for an increase in critical resin degree of cure with temperature. \( K \) represents reaction rate constant, and \( m \) and \( n \) are reaction orders determined experimentally (Liang et al., 2006).

Cole et al., (1991) improved their model significantly while accounting both the epoxide-amine reactions and the subsequent etherification reaction. Further, the inclusion of diffusion factor enables calculation with greater precision in degree of conversion over the whole range of cure. The kamal model partially fits at low conversion indicating a rather complex mechanism for autocatalysis than the bimolecular or termolecular system existing. Additionally, with the increasing temperature the conversion at which diffusion-control kinetics begins to dominate
occurs at a higher conversion. This is due to the resin ability to stay mobile longer at the higher temperatures (Liang et al., 2006).

An extension to Kamal’s model that accounts for increased accuracy at the later stages of cure has been developed by Karkanas et al., shown below:

\[
\frac{d\alpha}{dt} = (K_1 + K_2 \alpha^m)(\alpha_{max} - \alpha)^n
\]  

(5.6)

Here \(\alpha_{max}\) is the maximum degree of cure at a given temperature. The constants \(m\) and \(n\) are reaction orders determined experimentally, while \(K_1\) and \(K_2\) are reaction rate constants. The modified Kamal model incorporates the term \(\alpha_{max}\), so that the fractional conversion will not exceed the degree of cure associated with vitrification at the specific temperature (Karkanas et al., 1996).

The following model is proposed by the authors:

\[
\frac{d\alpha}{dt} = (K_1 + K_2)e^{m+n_1\alpha+n_2\alpha^2}
\]  

(5.7)

(Complete derivation details provided in appendix 5.2)

Here, \(K_1\) and \(K_2\) are temperature dependent kinetic rate constants, \(m\), \(n_1\) and \(n_2\) are the empirical parameters. The parameters of the proposed model are obtained by fitting the experimentally obtained cure rate versus degree of cure data with the help of nonlinear regression. In this paper, the kamal model is adopted to compare with proposed model for cure rate versus degree of cure data, to obtain the empirical constants involved.

5.3.3 Differential Scanning Calorimetry

DSC measurements are performed by a NETZSCH DSC-200F3 supported by a computer for data acquisition. The mixture is stirred at room temperature, and samples of about 5-6 mg weight are enclosed in aluminum capsules. Isothermal and dynamic-heating experiments are conducted under a nitrogen flow of 40 mL/min.
5.3.3.1 Dynamic scan

In experiments with dynamic loading, the samples are heated from 25 to 275°C with a heating rate of 10°C. This is mainly carried out to measure the temperature during the exothermic reaction and use dynamic DSC to determine the curing temperature range for isothermal conditions.

5.3.3.2 Isothermal scan

In these set of experiments, the thermal program initialized by increasing the temperature from 25°C to the preferred temperature with the heating rate of 60°C/min following the isothermal condition. The reaction exothermic data with time, obtained from the isothermal DSC experiments, are converted into degree of cure, $\alpha$, and rate of cure, $d\alpha/dt$, using the following steps:

Total heat of reaction, $\Delta H_T$, which is given by following equation, is determined by calculating the area under the isothermal heat flow with time curve at a particular temperature.

$$\Delta H_T = \int Q(t) \, dt \quad (5.8)$$

$\Delta H_{(t)}$ is the instantaneous heat of reaction which is the amount of heat released by the curing reaction until a particular time, $t$, and is computed by performing a similar numerical integration up to that time $t$. This is mathematically expressed as:

$$\Delta H(t) = \int_0^t Q(t) \, dt \quad (5.9)$$

where $Q(t)$ is the heat flow value at time ‘$t$’.

The instantaneous degree of cure, $\alpha$ (t), is estimated using equation 5.10, resulting in degree of cure $\alpha$ versus time $(t)$:

$$\alpha(t) = \frac{\Delta H(t)}{\Delta H_T} \quad (5.10)$$

The rate of cure $d\alpha/dt$, which is the slope of the degree of cure versus time curve, is computed by numerically differentiating the degree of cure versus time data.
5.4 Results & Discussion

5.4.1 Process feasibility

Several types of resins have been used for vacuum infusion process, including epoxy, unsaturated polyester, phenolic resin, and vinyl ester. Generally, a resin mixture for infusion process demands suitable properties such as low viscosity (up to 2000 cps), long pot life, and high reactivity (Hammami et al., 2000; Ragondet et al., 2005). Typically, the viscosity of the resin formulation considerably drops as the proportion of soy resin additive is increased. The reduced viscosity allows resin to penetrate into the fiber reinforcement with ease and results in good wet-out in the flow stage. Gel time has considerably increased due to addition of ESO resin. This enables easy fabrication of product with bigger dimensions by this resin as it enhances the processing time. The proposed material system cures at room temperature and the gel time is increased from 12 min (90°C) to 33 min for room temperature. Overall, these resin systems performed well for the infusion process.

5.4.2 Dynamic scan analysis

The dynamic scan of resin cure (Figure 5.1) shows that the reaction initiates at around 60°C and the heat flow reaches the peak at around 100°C. Therefore, the isothermal scans are carried out at the selected temperatures of 80, 85, 90 and 95°C. This particular range is chosen considering the fact that for temperature less than 80°C, the reaction is slow leading to a delayed completion while for temperature above 100 °C; the reaction speed is going to shoot up eventually leading to completion before the attainment of the isothermal temperature. Consequently, the selected temperature range is generally adopted for curing of epoxy resins in vacuum infusion process.
5.4.3 Isothermal curing analysis

The isothermal heat flow variation, normalized by the sample weight for varying temperature is presented in Figure 5.2. It is clearly concluded that the time taken for peak heat flow reduces with an increase in curing temperature. This indicates that the curing temperature is proportional to the heat flow. The degree and rate of cure with time are presented in Figure 5.3 & 5.4, respectively.
Figure 5.3 Degree of cure of Epoxy/ESO/TETA at different temperatures with cure time.

Figure 5.4 Rate of cure of Epoxy/ESO/TETA at different temperatures with cure time.

It is evident from Figure 5.3 that the degree of cure has a sharp and a steep rise in the initial stages of curing. The higher the isothermal temperature leads the higher degree of cure. The fact supporting the observation is the drift velocity attained by the molecules with the rising temperature. These energized molecules improve the reaction rate, which consequently increases the heat flow and reduces the time for curing (Milanese et al., 2011).
5.4.4 Kinetic model and activation energies

The variations of the rate of cure with the degree of cure at varying temperatures are obtained from equation 5.10 shown in Figure. 5.5. From Figure 5.5, it can be concluded that the rate of cure rises with the degree of cure at the initial stages of curing, attains a maximum, and then gradually decreases. Such behaviors indicate that the curing reaction of ESO is autocatalytic in nature (Tan et al., 2013). This curve typically resembles the normal behaviour as reported in several literatures (Barral et al., 1995; Sudip et al., 2014). The autocatalytic reaction initially need not be zero as there is an occurrence of the reaction via alternative paths, mainly due to the presence of impurities. However, the critical conversion occurs prior to the anticipated degree of cure. Subsequent to this, the reaction rate drops considerably.

![Variations of experimental rate of cure at different temperatures of Epoxy + ESO resin with degree of cure.](image)

**Figure 5.5** Variations of experimental rate of cure at different temperatures of Epoxy + ESO resin with degree of cure.

The presence of internal structure and functionality of the epoxy ring in soya epoxy governs the reaction and is the cause of reaction rate reduction. A nonlinear regression analysis is performed on the rate of cure versus the degree of cure experimental data for fitting the proposed model and kamal model, respectively. The non-linear regression is being used to minimize the value of the squared sum of the difference between data and fit. The boundary conditions are assigned based on the literatures and Least Square Method. The boundary condition implies on the mathematical
phenomenon as a constraint. The chosen value provides a confident interval of more than 90% and appears to possess the best fit $\chi^2$ value by multiple iterations for proposed model.

![Figure 5.6 Arrhenius plot of the rate constants $K_1$ and $K_2$.](image)

Comparison between the degree of cure, cure rate data and the kamal model prediction shows good agreement for the entire range of the cure, apart from the end of the cure where some deviation is observed (Figure 5.7-5.10). Comparisons of the proposed model (Equation 5.7) with experimental data reveal that the model is capable of predicting the reaction kinetics satisfactorily over the range of cure (Table 3.1).
Table 5.1 Estimated parameters of kinetic models as determined by isothermal DSC runs

Values of parameters for Kamal model (Equation 5.4), obtained from non linear regression analysis at different temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>K₁ (min⁻¹)</th>
<th>K₂ (min⁻¹)</th>
<th>m</th>
<th>n</th>
<th>Reduced chi-sqr</th>
<th>Ea₁(kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>0.082</td>
<td>0.32</td>
<td>0.28</td>
<td>1.04</td>
<td>7.31E⁻⁵</td>
<td>108</td>
</tr>
<tr>
<td>85</td>
<td>0.109</td>
<td>0.49</td>
<td>0.13</td>
<td>1.24</td>
<td>8.26E⁻⁵</td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>0.231</td>
<td>0.79</td>
<td>0.24</td>
<td>2.22</td>
<td>6.35E⁻⁴</td>
<td>Ea₂(kJ/mol)</td>
</tr>
<tr>
<td>95</td>
<td>0.345</td>
<td>0.86</td>
<td>0.17</td>
<td>1.82</td>
<td>1.10E⁻⁴</td>
<td>73</td>
</tr>
</tbody>
</table>

Values of parameters for proposed model (Equation 5.7), obtained from non linear regression analysis at different temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>K₁(min⁻¹)</th>
<th>K₂(min⁻¹)</th>
<th>m</th>
<th>n₁</th>
<th>n₂</th>
<th>Reduced chi-sqr</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>0.07</td>
<td>0.33</td>
<td>1.90</td>
<td>3.07</td>
<td>1.20</td>
<td>1.75E⁻⁶</td>
</tr>
<tr>
<td>85</td>
<td>0.09</td>
<td>0.44</td>
<td>1.98</td>
<td>1.60</td>
<td>1.24</td>
<td>6.33E⁻⁶</td>
</tr>
<tr>
<td>90</td>
<td>0.20</td>
<td>0.64</td>
<td>1.79</td>
<td>3.46</td>
<td>2.41</td>
<td>8.68E⁻⁵</td>
</tr>
<tr>
<td>95</td>
<td>0.31</td>
<td>0.80</td>
<td>1.96</td>
<td>3.2</td>
<td>2.35</td>
<td>2.42E⁻⁴</td>
</tr>
</tbody>
</table>

It is concluded that the application of this proposed model, following the same evaluation procedure, resulted in a more accurate fit. The parametric values of both the models for all the isothermal temperatures are presented in Table 5.1. From Table 5.1, it can be observed that the rate constants K₁ and K₂ are increased by the increase in the curing temperature. Fast polymerization is the basis for this observation. In order to study the kinetics, it is imperative to
analyze the activation energy for characterizing the curing reaction determined by using the kamal method.

\[ K = A \exp \left( -\frac{E_a}{RT} \right) \]

Figure 5.6. Illustrates the Arrhenius-type plot for rate constants, \( K_1 \) and \( K_2 \). The activation energies of the ESO system is determined from the y-intercepts of the plots of \( \ln k_1, k_2 \) against \( 1/T \), respectively. As shown in Table 5.1, The \( E_{a2} \) value is also found to be lower than the \( E_{a1} \) value. This observation is instigated by the propagation step (\( K_2 \)) in this system that involves less activation energy than the previous step (\( K_1 \)).

The activation energy of this particular material system is higher than that of conventional system (Aykanat et al., 2008) due to functionalities and chemical structures of the ESO resin system. The proposed model (Equation 5.7) clearly emphasizes its strength in all aspects as seen from Figures 5.7 to 5.10. The increase in the number of parameters and the corresponding order of reaction leads to better accuracy and precision as compared to kamal model for this particular complicated material system. This is anticipated to material system involve more reactions for attainment of the above observation.

**Figure 5.7** Comparison of experimental and model predicted rate of cure with degree of cure at 80°C.
Figure 5.8 Comparison of experimental and model predicted rate of cure with degree of cure at 85°C.

Figure 5.9 Comparison of experimental and model predicted rate of cure with degree of cure at 90°C
Figure 5.10 Comparison of experimental and model predicted rate of cure with degree of cure at 95°C.

5.5 Conclusions

The kinetics of the curing reaction of a biobased thermoset system, i.e., an epoxy resin in the presence of ESO cured with TETA, is investigated in this study employing isothermal DSC scans. The kamal model and a proposed model are used as tools in order to determine the activation energy and other kinetic parameters of the system. The results showed that the reaction rate is significantly reduced after completion of 50% of the degree of conversion due to epoxy value and inexistence of ESO. It is observed that, the addition of epoxidized soybean oil alters the kinetics of curing. The addition of ESO yields higher activation energy as recorded owing to its chemical structure and functionality of epoxy in ESO. The proposed model shows more precise results as compared to kamal model. On the basis of the comparison of the results between experimental and analytical data, it may be concluded that the present study provides clarity, in the isothermal reaction kinetics characteristics of the ESO/TETA system for infusion process.
6 Permeability and mechanical property correlation of bio based epoxy composite reinforced by unidirectional sisal fibre mat through vacuum infusion molding technique

6.1 Abstract

The present investigation is focused to study the permeability of natural fibre during vacuum infusion process and the effect of the surface treatments of natural fibre, fibre loading direction, resin flow direction and process parameter on the tensile properties of developed composites (sisal/bio based epoxy). The bio based resin exhibits good flow characteristics in NaOH and isocyanate treated fibres which may be attributed to change in polarity. The surface treatments appear to provide an appreciable enhancement in tensile strength through enhanced bonding between fibre and matrix. The longitudinal tensile strength has been found to be higher than that of the transverse direction and the flow along the fibre provides maximum tensile strength. It has also been demonstrated that vacuum infusion process provides improved mechanical properties as compared to hand-layup process. Morphological studies of fractured developed composites were performed by scanning electron microscopy (SEM) to understand the de-bonding of fibre/matrix adhesion.

6.2 Introduction

Bio materials in composite industry are introduced to overcome the critical issues such as environmental pollution, ecological issues, degradability, maintenance, and weight reduction (Faruk et al., 2012; 2014). The increasing demand in the field of bio material research for an in-depth understanding of processing phenomenon to convert it into a useful product is essential. These bio materials are fabricated by using well established molding techniques such as hand layup, press molding, pultrusion, resin transfer molding, and vacuum infusion molding (Ho et al., 2012; Francucci et al., 2009). The lack of fibre wetting and insufficient resin distribution in traditional manufacturing processes leads to inferior composite performance. To efficiently use these techniques, conceptual understanding of natural fibres, its impact on process parameters and structure-property characteristics is enviable. Donnell et al. recommended that infusion molding process is more suitable for manufacturing of bio composite (Donnell et al., 2004). Considering the significance of naturally available materials in societal/scientific applications,
this study targeting the understanding of processing phenomenon such as permeability/wettability and mechanical characterization of these composites is undertaken.

The permeability study of vacuum infusion process is difficult task due to that the resin flow path is deviating from standard path which is attributed the unpredictable variations in the fibre preform mat (Alms et al., 2011). Yula ma et al., (1999) observed that the effect of resin such as vinyl ester, corn syrup and epoxy on the permeability is less as compared to fibre architecture. The flow profile is differing with the fibre-mat orientation and appears to be strongest along the inter-tow channels direction (Roy et al., 2005). Reza Masoodi et al. (2012) observed that the swelling of fibre in bio based epoxy were more intense than conventional epoxy, which attributed to more interaction of cellulose fibre with bio based epoxy resin. E. Languri et al., (2010) also observed change in natural fibres diameter due to swelling and improvement in flow-front prediction with the addition of swelling as a function of time in permeability model. Dungan et al. (2002) claimed that the flow among the fibre filaments decrease the overall permeability by increasing penetration times due to the required wetting of the tows. Albuquerque et al. (2000) demonstrated that NaOH treated jute fibre shows superior mechanical properties, due to better fibre surface wettability. Barsberg et al. (2001) derived a conclusion that, the generalization of wetting behaviour of natural fibre is more complex due to macromolecular rearrangement swelling, and extraction. Shih et al. (1998) highlighted that connecting the permeability to particular fibre architecture is difficult.

The tensile strength of woven fibre composites depends on the fiber orientation, weave style, and the bonding between the fiber and matrix (Alavudeen et al., 2015). Fibre reinforced composite are fabricated with the key objective of attaining a superior mechanical properties. Literatures have focused on this critical issue by subjecting the specimen to chemical treatment which reduces hydrophilic behaviour of fibres and moisture absorption respectively instituted by enhanced bond interaction between matrix and fibres (Edeerozey et al., 2007; Tajvidi et al., 2006, Rouison et al., 2004; Rout et al., 2001). The NaOH chemical modification causes stronger fiber–matrix adhesion by increasing roughness of the fibre surface and better mechanical anchoring. Mechanical and thermal behavior of the composite gradually was improved by this treatment (Sreekala et al., 2003; Lopattananon et al., 2008). Silane molecules form a chemical link between the fibre surface and the matrix through a siloxane bridge. Silane forms silanol in the presence of fibre moisture. The one end of silanol reacts with the cellulose hydroxyl group of
the fibre and the other end reacts with the matrix functional group (Kabir 2012, George et al., 2001). Kabir modified natural fibres with silane agent and stated that the silane covering a layer on the surface that assists penetration in pores, higher tensile strength and reduction in moisture absorption (Kabir 2012). Ly et al. treated natural fibre with isocyanate. In these composites, it was found that an enlightened performance is attainable with treated fibre (Ly et al., 2008).

The plain weave fibre composite shows higher tensile strength than randomly oriented composites (Alavudeen et al., 2015). The reinforced composite exhibit de-bonding between the fibre and the matrix due to the lack of adhesion which cause pull-out (Pinto et al., 2013). Oksman et al. (2001) achieved higher mechanical properties of sisal fibres composites manufactured by resin transfer molding process. To attain multidirectional isotropic behaviour, correct fibre orientation in different angle is essential, which can only be done by multiply laminate preparation (Corrales et al., 2007). Hossain et al. observed that the tensile properties of the developed composites are strongly dependent on the tensile strength of fibre (Hossain et al., 2012). Khan et al. found that tensile strength in the warp direction are superior than those in the weft direction (Khan et al., 2013).

The understanding of the behaviour of natural fibre reinforcement in the vacuum infusion is less documented in the open literature. No significant work has been reported concerning the effect of chemical treatment on permeability of the natural fibre in the vacuum infusion and there are no such studies about the effect of flow direction on tensile strength in infusion process. Hence, a sincere effort has been made to evaluate the effect of chemical modification on permeability of natural fibres in the vacuum infusion process and finally on tensile properties of developed composites. This study also tries to give a hypothesis by correlating the permeability and tensile strength. The present investigation also addresses the effect of fibre orientation, flow direction, and process parameters on tensile strength of composites.

6.3 Experimental

6.3.1 Materials

The diglycidyl ether of bisphenol A (DGEBA) is used as a base component of epoxy resin. An amount of 30% epoxidized soybean oil (ESO) with 6.5 wt% epoxy oxirane content and specific gravity of 0.987 is added to the resin base. Triethylenetetramine (TETA) is used as a curing
agent and the stoichiometry relation between the blended resin to curing agent is calculated to be 12.40. The woven sisal fibre mat with an areal density of 575 g/m² is the reinforcement. The average filament diameter and thickness of the mat of sisal fiber are 0.35 mm and 1.2 mm, respectively.

6.3.2 Fibre surface treatment

To investigate the influences of chemical treatments in terms of the flow characteristics and tensile characterization, the fibres are treated chemically with different chemicals namely NaOH, silane, and isocyanate.

In alkali treatment, the woven sisal mats were soaked in a 2 wt. % solution of NaOH at room temperature for 1 h. Then, the mats were dried for 12 h at 80°C (Rouison et al., 2004). For silane treatment, 1 wt. % of 3-aminopropyltriethoxysilane is dissolved in distilled water. The fibres are immersed in the solution for 30 min at room temperature to permit the hydrolysis of the silane. This is followed by drying of fibres in an oven at 100°C prior to its exposure for 12 hr at 80°C (Rouison et al., 2004; Kabir 2012). In isocyanate treatment, 6% of methylene diphenyl diisocyanate (MDI) solution is prepared using toluene solvent. The woven sisal fibre mat (150 g) is placed in the reaction kettle and the mat is immersed in the MDI solution of about 2000 ml. The resulting suspension is then heated to 50°C for about 30 min. After completion of the reaction, the mat is decanted and dried in air oven at 70°C for 2 h (George et al., 1998).

6.3.3 Permeability measurements

Permeability is a key parameter for flow prediction in infusion molding process (Hammami et al., 2000). Well established and reliable models frequently used in literatures i.e. Darcy’s law (Equation 2.6) and improved Carman–Kozeny (Equation 2.8) are adopted for this study (Han et al., 2000) to compare our proposed contact angle model (Equation 6.1). The proposed contact angle model for determine the permeability which includes porosity and contact angle to improve the flow prediction accuracy.

\[
K = \frac{c\phi}{a+b\left(1+\frac{\theta^2}{2}+\frac{\theta^2}{20}\right)}
\]

(6.1)

Where \(\phi\) is porosity, \(\theta\) is contact angle, \(a, b,\) and \(c\) are empirical constants.
6.3.4 Mechanical characterization

Tensile Testing was performed according to ASTM D3039 using an INSTRON 3382 testing machine. Rectangular test specimens cut to 25 mm × 255 mm as specified by the standard, were tested at a crosshead speed of 2 mm/min. For statistical significance, 5–6 samples were characterized for each case. The specimens for tensile testing were fabricated by vacuum infusion process. The flexural strength is determined by applying bending load on rectangular specimen of size 60 mm x 10 mm x 4 mm as per ASTM D 790. The Izod impact strength of all the samples were measured using an Tinius olsen impact pendulum tester of model 104 according to ASTM D256 (2010).

6.3.5 Scanning electron microscopy (SEM)

The fracture surface of the specimens were investigated using SEM (EVO15, Carl Zeiss, Germany) operating in the high vacuum mode at accelerating voltage of 10–15 kV.

6.4 Results and discussion

6.4.1 Permeability study

Permeability of natural fibres is mainly important in low pressure injection techniques like vacuum infusion where void formation and filling time can be increased dramatically when the permeability decreases. The experimental analysis involves resin flow front measurements with filling time during the resin impregnation. Untreated sisal fibre mat shows lesser permeability which may be attributed to weak interaction between non-polar ESO blended resin and polar OH group on the untreated sisal fibre. When sisal fibre is treated by NaOH, the initial contact angle decreased to 40° wetted with ESO blended resin. NaOH treatment increases surface roughness resulting in better mechanical interlocking and the amount of cellulose exposed on the fibre surface. This increases the number of possible active sites. Consequently, the surface free energy may increase, probably due to the decrease of contact angle and allows better fibre wetting. Thus, increase the permeability of sisal fibre mat. Besides, during NaOH treatment the polar OH group on the fibre surface may reduce which allow better wetting. The similar trend is observed for permeability of isocyanate treated fibres. The permeability of mat is decreased after silane treatment which indicates high repelling action attained and polarity difference between interaction of fibre and matrix.
The Table 6.1 shows identical behavior between wettability and permeability. It is well known fact that the mold filling time is related to permeability, resin injection pressure, geometry of the mold, resin viscosity, and other parameters. Once wettability is improved, the permeability will increase this will leads to the quicker filling as shown in Figure 6.2, it showed that mold filling time is decreased with the increase of permeability. The Figure 6.3 presents two models, Kozeny and proposed contact angle model to predict the flow front versus filling time to compare with experimental results to verify the accuracy of the model.

The subsequent model comprises of contact angle which illustrates the role of the contact angle in predicting accurate results. The outcome of the contact angle model proposed in this study unfolds the relativity with respect to capillary pressure that insights a greater magnitude in natural fibre as compared to synthetic fibre. This may be due to that the imperfect and hollow configuration of natural fibres provides more capillary channels for micro-flow. It is also evident from Figure 6.1 that prediction of flow is better in the case of untreated fibre whereas treated fibres (NaOH, Silane, Isocyanate) the flow prediction is poor. This may be attributed to the fact that static contact angle taking place within the system. Instead of static contact angle, if there is a dynamic contact angle then flow prediction may be better for treated samples. The contact angle model clearly emphasizes its strength in all aspects as seen from Figure 6.2a-6.2d. The sum of squared deviation (SSD) value obtained for contact angle model proposed in this study provides results that are deviating from the kozeny model by almost 2 times. Nevertheless, the closeness to the experiments results are achieved repeatedly with the proposed contact angle model. The adding contact angle in permeability model leads to better accuracy and precision as compared to kozeny model. The contact angle model appears to possess the best fit value. Therefore we can conclude by saying that contact angle model gives good accuracy as compared kozeny model.
Figure 6.1 A comparison of flow front as a function of time for untreated and chemically treated sisal fibre.

Table 6.1 Permeability and contact angle of untreated and treated sisal fibres

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Permeability (m$^2$)</th>
<th>Fibre volume fraction (%)</th>
<th>Contact angle (Radians)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>7.38 ×10$^{-10}$</td>
<td>33</td>
<td>1.13</td>
</tr>
<tr>
<td>NaOH</td>
<td>1.46 ×10$^{-9}$</td>
<td>35</td>
<td>0.69</td>
</tr>
<tr>
<td>Silane</td>
<td>6.07 ×10$^{-10}$</td>
<td>33</td>
<td>1.30</td>
</tr>
<tr>
<td>Isocyanate</td>
<td>1.21×10$^{-9}$</td>
<td>30</td>
<td>0.69</td>
</tr>
</tbody>
</table>
6.4.2 Mechanical properties of the composites

6.4.2.1 The effect of chemical treatment on mechanical properties

6.4.2.1.1 Tensile strength

The effect of different chemical treatments on the tensile strength of sisal/ESO based composites is shown Figure 6.3. It is clear that in all cases an improvement is observed. The NaOH treatment takes out certain portion of hemicelluloses, lignin, wax, and other impurities present on the fibre surface. Consequently, the fibre bundles are disintegrated to single fibres. Further, it reduces fibre diameter, thereby increases the aspect ratio which leads to the development of a rough surface that results in enhanced interfacial bonding between fibre and matrix and an increase in tensile properties.
The tensile strength improvement in the case of silane treated fibre composite due to the amino silane helps to bond with hydroxyl groups through hydrolysable alkoxy groups and amino groups capable of interacting with the epoxy resin. It emphasized that, the silane creates a bridge between the natural fibre and the resin that may improve the interfacial adhesion between the fibre and matrix. The formation of strong covalent bonds between the isocyanate and hydroxyl groups of cellulose may leads to significant improvement in strength for isocyanate treated fibre. The hydrophilic nature of the sisal fibre can be reduced by isocyanate treatment. The isocyanate treatment makes fibre hydrophobic, compatible and highly dispersible in the matrix. This will result in a strong interfacial bond between the fibre and the matrix. The silane treated fibre based composites have shown lesser permeability and higher tensile strength. These findings may be attributed to the effect of transverse (z direction) permeability and unsaturated permeability which may influence more the longitudinal and saturated permeability.

**Figure 6.3** Tensile properties of treated and untreated sisal/bio based composites.

### 6.4.2.1.2 Flexural strength

All types of surface modifications result in a flexural strength increase as compared to the untreated fiber samples (Figure 6.4). The flexural properties of composites are governed by the resistance to inter laminar failure. The explanation for these results is the same as for
tensile strength increases because the flexural strength is mainly influenced by the fiber/matrix interface interaction. Therefore, the higher flexural strength treated fiber composites owing to the better interfacial adhesions in the composite.

**Figure 6.4** Flexural properties of treated and untreated sisal/bio based composites.

### 6.4.2.1.3 Impact strength

Figure 6.5 shows the impact strength of the untreated and treated composites. It is clear that the impact strength decreases slightly with NaOH, silane and isocyanate treatments. The NaOH treatment broke the structure of natural fibers and the blended epoxy resin is filled the gaps between the fibrillations, thus the impact energy absorbed by them is lower. Due to the surface treatment with highly reactive reagents such as silane and isocyanate lead to strong chemical bonds with the natural fibre. The chemically modified surface can further bond with epoxy system and initiates a good bonding. When there is good bonding/adhesion at the interface, the contribution of this work is lesser, resulting in a reduced impact strength.
Figure 6.5 Impact strength of treated and untreated sisal/bio based composites.

6.4.2.2 Effect of fibre loading direction on tensile strength

It is clear from Figure 6.6 that, in transverse direction the tensile strength is significantly lower than that of the longitudinal direction. This may be attributed to that, the bundle of fibres is aligned perpendicular to the load direction and these fibers are weak in the transverse direction, they cannot contribute efficiently to the strength in that direction (Pinto et al., 2013).

These composite generally exhibit behaviour between the isostrain and isostress conditions. Strength and stiffness are generally much higher along the fibre direction (isostrain) than perpendicular to the fibre direction (isostress). In the isostrain case, the contribution of a constituent is directly proportional to its volume fraction. In the case of isostress, the fibres are much less effective in raising the composite modulus. Unidirectional composites are inherently anisotropic in that maximum strength and modulus are achieved along the direction of fibre alignment.
Figure 6.6 Effect of fibre loading on tensile properties.

6.4.2.3 Effect of flow direction on tensile strength

The key characteristic of unidirectional fibre mats is that the fibre tows are aligned in one direction. In unidirectional fibre mats, when resin is injected into a mold, it firstly passes through the fibre inter-tow channels without impregnating the fibre tows. After the front has passed, resin from the surrounding gap region continues to impregnate the fibre tows. This delayed impregnation of tows leads to the unsaturated flow in liquid molding process. According to the unsaturated flow theory, if these fibre mats are placed such that their tows are in the x direction with flow taking place in this direction as well, then the resin will flow easily through the inter-tow channels aligned with the fibre. The above fact leads to good wettability and higher permeability of the system. Good wetting can enhance the adhesive bond strength between fibre and matrix, which is leads to better tensile strength. This is clear evidence from Figure 6.7 that the fibre have higher permeability, good wetting characteristics and formation of strong bonds have to be assured for higher tensile strength. A correlation coefficient of 0.78 is obtained between permeability and tensile strength of composites (See appendix 6.1).
Decreasing in tensile strength in y-direction is because of low flow ability of resin, less impregnation of fibres and subsequently low wetting and therefore low strength of composite.

![Flow direction diagram](image)

**Figure 6.7** Effect of flow direction on tensile strength.

Decreasing in tensile strength in y-direction is because of low flow ability of resin, less impregnation of fibres and subsequently low wetting and therefore low strength of composite.

### 6.4.2.4 Effect of fiber network on tensile strength

The tensile strength of natural fiber composites depends on the fiber orientation, fiber network (architecture), and the interfacial bonding between the fiber and matrix. Figure 6.8 shows the tensile strength of various fiber networks of jute and sisal composites.

The directional network composites demonstrated higher tensile strength as compared to randomly network sisal composites. The lower tensile strength of random mat may be the reason for non uniform stress transfer along the fiber direction due to discontinuous structure of fibers in the random network. The unidirectional sisal mat shows higher tensile strength than the bidirectional jute fiber mat. This is attributed to the longitudinal orientation of sisal fiber, which results in greater and uniform stress uptake capacity. In bidirectional mat, only one half of the fibers contributes to each direction and the fibers are loosely packed as compared to
unidirectional fiber mat. Besides, the crimping of the weft and warp fiber filaments at the cross points in the mat also leads to reduction in the tensile strength. The results are contrary with respect to permeability factors i.e. higher permeability of random sisal mat achieved lower tensile strength. It may be concluded that the fiber orientation, weaving pattern and mat manufacturing methods play dominant role as compared to permeability effects on tensile.

**Figure 6.8** Tensile strength for different natural fibers composites tested: S(sisal); U(unidirectional); T(transverse flow); L(longitudinal flow); J(jute); B(bi-directional); and R(random)

6.4.2.5 Comparing VI and hand-layup process on tensile strength of composite

From Figure 6.9, it can be observed, the vacuum infusion sample shows the better mechanical properties than hand layup technique. It may be attributed to decreasing of voids due to applied compression force (vacuum pressure) and maintained until the resin cures completely for infusion process. In addition, the resin infusion process involves vacuum which cause less moisture content while the resin sucked into the mold. Reducing the moisture content of the infusion sample during the curing phase will contributed to better mechanical properties of composites. The hand lay-up technique is carried out in environment that exposed to the moistures and gaseous which adversely affect the performance of the composites.
Figure 6.9 Effect of process parameters on tensile properties.

6.4.3 SEM characterization

The SEM images of untreated and treated composites are shown in Figure 6.10. As it can be observed from Figure 6.10-a, a poor bonding between the fibre and matrix exists in untreated composite. SEM characterization of sisal reinforced composites shows the brittle character of the fracture at a macroscopic level with significant presence of pull-out representing weak fibre/matrix interface and presence of fibrillation. Many hollow portions after the fracture can be seen in the micrograph, indicating that the phenomenon of fiber ‘pull-out’ occurred to a large extent. The reduction in tensile strength of untreated composite is possibly due to more number of voids present and large gap between the fiber and the matrix (Alavudeen et al., 2015).
After NaOH treatment, the gap between the sisal fibre and epoxy is closer than in the untreated sisal fibre composite (see Figure 6.10-b) due to fact that the epoxy resin will easily permeate into the gaps of fibrillation and subsequently strongly joint the fibers together. A good link between the isocyanate treated fibers and the epoxy could be seen from the fracture of the composite. Figure 6.10-c presents lesser voids due to fibre pull out and closed packing between the fibre and resin which results higher strength compare to NaOH treated fibre. The occurrence of enriched resin surrounding the fibers restricts the sliding motion of fibers by shearing action at the interface. The closely packed interfacial bonding between fiber and matrix is evident from Figure 6.10-d. Better bonding and absence of fibre pullout is mainly attributed to higher strength of
silane treated fibre. Thus, it can conclude that the improvement in tensile strength may be attributed to excellent interfacial adhesion between sisal and matrix.

6.5 Conclusion

Bio based resin exhibit good flow ability in NaOH and Isocyanate treated fibre composites compare to untreated fibres due to increase the surface energy. Significant enhancement in the tensile properties of the developed composites has been observed after various surface treatment processes which may be because of excellent interfacial bonding between sisal fibre and matrix. Vacuum infusion samples depict better mechanical properties as compared to hand layup due to less number of voids and moisture absorption. It has also been seen that the tensile strength is more in longitudinal direction of fibre as compare to transverse direction of the fibre. This may be because of the isostrain behaviour of the composite. Longitudinal flow also supports the enhancement of tensile strength as compared to transverse flow because of unsaturated flow theory. The SEM micrographs of treated samples demonstrated that there is improved interfacial bonding between the reinforcement and matrix. This might be the reason that there is appreciable enhancement tensile strength of the treated samples as compared to untreated sample. It can be concluded from the present study that vacuum infusion is also a promising technique to fabricate bio-based composites with superior mechanical properties.
7 Conclusions, recommendations and contribution of the thesis

7.1 Conclusions

This study concentrates on investigating the manufacturing of sisal fibre/ESO (Epoxidized soy bean oil) blended composites using a vacuum infusion process and explore the behavioral changes with respect the process parameters and controlling input/output parameters. Multiple aspects of the vacuum infusion process such as resin impregnation, fibre wetting, cure kinetics, and tensile strength were analyzed. The overall objectives of this work were successfully achieved.

1. In order to predict the flow behaviour, the permeability of the sisal fibre reinforcements was evaluated.

- The permeability for a sisal fibre preform measured was $1 \times 10^{-9}$ m$^2$ is lower than glass fibre.
- The permeability of sisal fibres derived from the improved kozeny model was $4.77 \times 10^{-9}$ m$^2$. The deviation in the permeability values appears to be influenced by the preform structure, wetting properties, and swelling.
- Swell does not alter the flow behaviour of natural fibre in infusion process as compared to that of fibre network, wetting parameters.
- The proposed model was comprehensive as it involves the addition of wetting factors namely contact angle, capillary pressure and fibre network, thoroughly validated with the experimental results as compared to kozeny model.

2. The sisal fibre is treated with NaOH, Silane and MDI for analyzing the wettability.

- The treatment with NaOH yields good wettability by decreasing the contact angle.
- The isocyanate treated surface indicates greater adhesiveness to epoxidized soybean oil due to the interaction between the non-polar mat surfaces/resin layers enabling good wetting.
- Wettability was poor for silane treated fibres subjected to epoxidized soy bean oil.
3. The kamal model and proposed model were employed to analyze the cure kinetics.

- The experimental results fitted well with the proposed model which indicated that an increase in the number of parameters and the reaction order leads to higher accuracy.
- The activation energy (108 kJ/mol) was higher than that of the conventional epoxy system owing to chemical structure and functionality of epoxy in ESO.

4. Mechanical properties were investigated for natural fibre reinforced bio-based epoxy composites manufactured by a vacuum infusion process.

- The NaOH, silane and isocyanate treatments resulted in slight increase of about 1-7% in tensile properties due to the interfacial bonding between sisal fibre and matrix.
- Tensile strength of 10 MPa in transverse direction was significantly lower than that of the longitudinal direction which was 80 MPa. Fibres aligned perpendicular to the load direction exhibited weaker strength in the transverse direction.
- Flow in y-direction decreases the tensile strength to about 10% due to low rate of flow of resin, less impregnation of fibres and low wetting.
- Vacuum infusion samples shows better tensile strength (80 MPa) as compared to hand layup (63 MPa) due to less number of voids and moisture absorption.

While summarizing the conclusions, it was established that all the objectives framed for this research study were successfully achieved. It was clearly observed that vacuum infusion is a promising technique to fabricate bio-based composites with superior mechanical properties. Some key parameters such as the wetting property, permeability, gate location, and curing conditions are to be maintained in an optimized range to attain production parts meeting commercial standards. This research lays valuable information enabling the commercialization of these composites.
7.2 Recommendations

The following are recommendations for improving and extending the current study:

- Tortuosity in fibrous porous media under microscope may be investigated and used for estimating the porosity and permeability changes in fibre mats.
- Numerical simulation of flow analysis in the porous media during infusion process may be performed.
- Studying the effect of fibre on the curing behaviour and kinetics parameters of the ESO blended resin is essential.
- Manufacturing 100 % biodegradable composites by combining natural fibres and biopolymers, and studying the performance of the composite is suggested.
- A study of the fracture behaviour of bio based composites produced by vacuum infusion and comparison of the same with the fracture behaviour of synthetic composites is recommended.

7.3 Scientific and Engineering Contribution of the thesis

Some of the important scientific contribution resulting from this Ph.D. work, published in established technical journals is as follows:

- The novelty in this thesis is the development of a new expression for permeability in biobased resin infusion system based on the wetting kinetics of natural fibre.
- Scientific knowledge derived from this work is original and makes a novel contribution to the better understanding of the wetting theory and practices of bio based epoxy resin impregnate in a natural fibre system that renders to improve the flow prediction in an infusion process by modifying Darcy’s law.
- Modification of the Darcy’s law based model for modelling of resin infusion through young’s equation with contact angle parameters expressed as mathematical formulations for permeability. The proposed model predicts the experimental results and has good coherence with the conventional Darcy’s model.
- An improved understanding of the permeability in relation to contact angle and surface energy also generated new knowledge to this field. Measurement of permeability in terms of contact angle parameters is a novelty to the science of resin impregnation.
A new model is also proposed to estimate the cure kinetics of bio based resin. The model and the kinetic data provided in this research may be extrapolated to design vacuum infusion equipment and formulate the procedures for the production of bio based composites.

This investigation is a pivotal attempt to correlate permeability of natural fibre with tensile properties of bio based composite.

The information compiled in this thesis is of immense significance to designers of infusion mold for the bio based composite production.
References


Appendices

Appendix 3.1: Infusion experiments carried out to find the flow behaviour

Natural fibre(Sisal)/Unsaturated Polyester system-Longitudinal infusion strategy
Appendix 3.2: Detailed calculation for proposed model

The theoretical value for the capillary pressure is estimated from the Young–Laplace equation. The capillary pressure may be comparable to the applied mechanical pressure as well as the vacuum pressure.

\[
\text{Capillary pressure (Pc)} = \left( \frac{F}{\phi} \right) \left( \frac{1-\phi}{\phi} \right) (\sigma \cos \theta)
\]

where \( F \) is a form factor which depends on the flow direction. For axial flow, it has been derived that \( F = 4 \).

Network resin flow in sisal fibre mat

The process of fibers impregnation in any liquid molding techniques has been historically described using Darcy’s law, Unsaturated permeability from Darcy law shows equation 2:

\[
K = \frac{x^2 \mu \phi}{2 \ell_f \Delta P}
\]

Thus, a more accurate expression of Darcy’s law can be written if the capillary pressure is considered on the pressure term in equation 2. A more accurate expression for permeability through the impregnated fibers can be written as follows:

\[
K = \frac{x^2 \mu \phi}{2 \ell_f \left( \rho m + \left( \frac{F}{\phi} \right) \left( \frac{1-\phi}{\phi} \right) (\sigma \cos \theta) \right)}
\]
Where \( F \) – constant is 4 for unidirectional flow, \( d_f \) – fibre filament diameter, \( P_m \) – Applied pressure, \( \phi \)–porosity of mat, \( \sigma \)–Surface tension of resin, \( \mu \)–Viscosity, \( x \)–flow front, \( \theta \)–Contact angle

Here, the Taylor series used to simplify the \( \cos\theta \)

\[
\cos\theta = 1 - \frac{\theta^2}{2^1} + \frac{\theta^4}{4!} - \ldots
\]

This value substitute in equation 3 ,

\[
K = \frac{x^2\mu\phi}{2t_f\left(P_m + b\left(\frac{1-\phi}{\phi}\right)\left(1-\frac{\theta^2}{2}\right)\right)}
\]

Generally, the capillary pressure is reliant on flow velocity and fiber–resin system, it may vary from negative values (where flow is enhanced) to positive values (where flow is impeded).

\[
K = \frac{x^2\mu\phi}{2t_f\left(P_m + b\left(\frac{1-\phi}{\phi}\right)\left(1-\frac{\theta^2}{2}\right)\right)}
\]

\[b = 860\] (for unidirectional sisal fibre mat wetted with polyester resin in axial direction)

\[0 < \phi < 1\]

\[0 < \theta < \frac{\pi}{2}\]

\[
K = \frac{c\phi}{a+b\left(\frac{1}{\phi} + \frac{\theta^2}{2\phi} - \frac{\theta^2}{2\phi} - 1\right)}
\]

\[a = 101325\] for vacuum infusion process

\[c = 2.08\times10^{-4}\] for unidirectional sisal fibre mat wetted with polyester resin
Appendix 5.1: Detailed calculation of stoichiometry ratio

Resin: DGEBA + Epoxidized soybean oil

Curative: TETA (Triethylene tetramine)

Amine active hydrogen Equivalent = Molecular weight/Number of active amine hydrogen

Amine active hydrogen Equivalent = 24.3 grams/equivalent

Epoxy equivalent weight of DGEBA = 186 g equiv-1

Epoxy equivalent weight of ESO = 238 g equiv-1

In this work, 100 parts of DGEBA and 30 parts of ESO is chosen. Therefore, the epoxy equivalent weight = Total parts/ ((DGEBA parts/EEW of DGEBA) + (ESO parts/EEW of ESO))

= 130/ ((100/186)+ (30/238)) =195 g equiv-1

Stoichiometry ratio between resin and curing agent = Amine active hydrogen Equivalent/epoxy equivalent of the blend

=24.3/195*100 = 12.40
Appendix 5.2: Detailed for proposed kinetic model

\[
\frac{d\alpha}{dt} = cf(\alpha) \text{ Differential equation}
\]

\[
f(\alpha) = e^{(a + b\alpha + c\alpha^2)} \text{ Function of alpha}
\]

\[
\frac{d\alpha}{dt} = ce^{(a + b\alpha + c\alpha^2)}
\]

\[
e^{a + b\alpha + c\alpha^2} = c \int dt \quad \text{Method of variable separable}
\]

Integrating

\[
\int e^{a + b\alpha + c\alpha^2} \, d\alpha = c \int dt
\]

Let \( a + b\alpha + c\alpha^2 = p \)

Differentiate with respect \( \alpha \)

\[
(0 + b + 2c\alpha) = dp/d\alpha
\]

\[
d\alpha = \frac{dp}{b + 2c\alpha}
\]

\[
\frac{1}{b + 2c\alpha} \int \frac{dp}{e^p} = c \int dt
\]

\[
\frac{1}{b + 2c\alpha} (-e^{-p}) = ct + d (\text{constant})
\]

Boundary condition

When \( t=0, \alpha=0 \), also \( p = a + b\alpha + c\alpha^2 \)

When \( \alpha=0, p=a \)

\[
\frac{1}{b + 0} (-e^{-a}) = 0 + d
\]
Where $d = \frac{-e^{-a}}{b}$

When $\alpha = 1$ then, $P = (a+b+c)$

$$\frac{1}{(b+2c)}(-e^{-(a+b+c)}) = 100c - \frac{e^{-a}}{b}$$

$$c = \frac{1}{100} \left[ \frac{1}{(b+2c)}(-e^{-(a+b+c)}) + \frac{e^{-a}}{b} \right]$$

$$\frac{d\alpha}{dt} = \frac{1}{100} \left[ \frac{e^{-a}}{b} - \frac{e^{-(a+b+c)}}{(b+2c)} \right] e^{a+b\alpha+ca^2}$$

$$y = (K_1 + K_2)e^{m+n_1\alpha+n_2\alpha^2}$$
**Appendix 6.1:** Correlation between permeability and tensile strength

![Graph showing correlation between permeability and tensile strength](image)

**Figure:** Correlation between tensile strength and permeability of the investigated materials.

The tensile strength of the fabricated composites that determined using tensile testing are correlated well ($R^2 = 0.78$) with the permeability as shown in above Figure. The high correlation coefficient between tensile strength and permeability suggests that higher permeability, good wetting characteristics and formation of strong bonds have to be assured for higher tensile strength.
Appendix 7: Natural Fiber Composites in Automotive Applications

The data obtained and referred from the literature reported on mechanical properties of the composite related to this research are tabulated in Table 1.

Table 1: Comparison of mechanical properties of composites

<table>
<thead>
<tr>
<th>Composite</th>
<th>Izod notchd Impact strength (kJ/m²)</th>
<th>Flexural strength (Mpa)</th>
<th>Tensile strength (Mpa)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyester-Glass composite</td>
<td>70± 2</td>
<td>180± 5</td>
<td>92± 2</td>
<td>D Shanmugam 2014/ Rouison, David 2004</td>
</tr>
<tr>
<td>Epoxy-Glass composite</td>
<td>85± 2</td>
<td>190± 5</td>
<td>120± 3</td>
<td>Latha, P. S et al., 2015</td>
</tr>
<tr>
<td>Bio based epoxy –Sisal fiber composite</td>
<td><strong>58± 5</strong></td>
<td><strong>103± 8</strong></td>
<td><strong>82 ± 5</strong></td>
<td>Rajkumar et al.,2015</td>
</tr>
<tr>
<td>Polyester-sisal composite</td>
<td>28± 1</td>
<td>91± 5</td>
<td>59± 2</td>
<td>Rodri´guez et al., 2005, Sreekumar et al., 2007</td>
</tr>
</tbody>
</table>

The viscosity of the matrix significantly drops as the proportion of ESO resin additive is increased. The reduced viscosity allows matrix to penetrate into the reinforcement without any difficulty and results in good wetting characteristics. Good wetting can enhance the adhesive bond strength between fibre and matrix, which is leads to better tensile strength. Gel time has considerably increased due to addition of ESO resin. This enables easy fabrication of product with bigger dimensions by this resin as it enhances the processing time. Overall, these resin systems performed well for the infusion process.

It is clearly evident from this table that bio composite has lower strength properties than synthetic fiber composite due to high strength properties of synthetic fibers. The tensile and flexural strengths of the glass fiber-polyester based composite and the sisal/ESO composite manufactured in the current project can be comparable. Besides, the higher volume of composite is replaced with natural fibers/ESO resin which are much cheaper
and safer than glass fibers and synthetic polymers (Figure 1 and 2). The automotive sector needs composite materials that meet the performance criteria as decided by numerous investigations such as tensile strength, impact strength, flexural properties, moisture absorption, and crash behaviour.

![Figure 1: Actual cost of thermoset, fibers, and curing agent](image1)

![Figure 2: Cost comparison for various composites.](image2)
The OEM requirements for a series of different manufactured industrial plastics and synthetic fiber reinforced composites used for automotive applications such as steering housing, lamp holders, ignition distribution caps, car electrical, and electronics parts are studied in terms of mechanical characteristics.

These commercial products are tabulated in Table 1. These requirements are compared with the mechanical performance of the manufactured sisal fiber/ESO composite in this research. The result of the tensile strength is shown in Figure 3. The sisal fiber/ESO composite shows the maximum value compared to the OEM requirement for different products.

Table 2: Commercial products used in the auto industry (https://hexion.com/products)

<table>
<thead>
<tr>
<th>S.No</th>
<th>Commercial Name/Grade</th>
<th>Material</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Keripol RW 1411</td>
<td>Polyester</td>
<td>H4 lamp holders</td>
</tr>
<tr>
<td>2</td>
<td>Bakelite® UP 802</td>
<td>Polyester</td>
<td>Ignition distributor caps, distributor fingers, spark plug connectors</td>
</tr>
<tr>
<td>3</td>
<td>Bakelite® EP 8412</td>
<td>Epoxy</td>
<td>Encapsulation of electric parts</td>
</tr>
<tr>
<td>4</td>
<td>Bakelite® PF 2874</td>
<td>Phenolic Resin</td>
<td>Steering housings</td>
</tr>
<tr>
<td>5</td>
<td>Bakelite® EP 8414</td>
<td>Epoxy</td>
<td>Car electronics, reflectors, spark plug connectors</td>
</tr>
<tr>
<td>6</td>
<td>Bakelite® UP 3620</td>
<td>Polyester</td>
<td>Lamp housings</td>
</tr>
</tbody>
</table>

The flexural strength and impact strength results are shown in Figures 4 and 5. The flexural/impact strength of the manufactured sisal fiber/ESO composite is an adequate for most of the OEM products. The conventional material shows higher strength in few cases compared to the sisal fiber/ESO composite, however; the differences are not significant. The overall mechanical properties of the sisal fiber/ESO composite are in acceptable level for many different automotive components. Other important properties such as moisture absorption, flammability, and crash behaviour of the composite have to be investigated.
Figure 3: Tensile strength of the sisal fiber/ESO composite in comparison to the standard value of different commercial products.

Figure 4: Flexural strength of the sisal fiber/ESO composite in comparison to the standard value of different commercial products.
Figure 5: Impact strength of the sisal fiber/ESO composite in comparison to the standard value of different commercial products