Characterization of Flax Fibres and the Effect of Different Drying Methods for Making Biocomposites

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ABSTRACT

As the environmental concern grows, researchers try to find material which can be environmental friendly and biodegradable to some extent. At present, flax fibre cannot fully replace glass fibre. Some attempts have been made to replace the glass fibre.

Studies show the physical and mechanical properties of natural fibres are comparable with glass fibre, so it can replace glass fibre in the process of making biocomposites.

The properties of biocomposites depend on the fibre used. Research shows that to get a better biocomposite, the fibre has to be chemically treated to improve adhesion between fibre and polymer matrix. After the chemical treatment, the fibre has to be dried to minimum moisture content so the drying of flax fibre is essential in the process of making biocomposites.

In this research, oilseed flax fibre is dried and drying characteristics were investigated. After drying, the physical properties of the fibre were tested and analysed.

The fibre was dried using three different drying methods, namely, microwave, microwave-convection, and microwave-vacuum environments. Curve fitting with four empirical methods has been carried out to determine the drying constant, coefficient of determination and standard error values.

The results showed that microwave-vacuum drying method is more efficient (in terms of final moisture content) than microwave and microwave-convection drying. Although microwave-vacuum drying took the most time and did not result in promising colour

values, the maximum moisture removal is achieved because fibres can be dried for a longer period of time with a comparatively low temperature.

The results of physical properties were analysed for untreated and treated and dried flax fibre. The tensile strength and elastic modulus of untreated and treated fibre did not show any significant change. Because the diameter of flax fibre cannot be consistent, a range of values can be obtained. The diameter range of fibre bundle 30-300 μm was examined for these tests. The tensile strength obtained from these fibre bundles ranged between 16 to 667 MPa and elastic modulus values were 2 GPa up to 63 GPa.

The scanning electron micrograph (SEM) was also analysed for untreated and treated-dried fibre. The fibre which was dried with high power or longer period of time showed black spots, probably due to local heating. The fibre dried with microwave-vacuum developed some black spots which were clearly seen in the SEM.

Differential scanning calorimetric data showed a shift in temperature of degradation. In this research, degradation temperature of cellulose was found 350(± 10)°C for the treated and dried flax fibre.

In conclusion, the flax fibre has a potential to be used in biocomposite production. The microwave-vacuum works best for drying where the fibre can be dried up to a less than 1% of moisture content.

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DEDICATION

DEDICATED TO MY LOVING WIFE REENA

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

MC	Moisture Content (%)
MR	Moisture Ratio
w.b	Wet Basis
d.b	Dry Basis
k, k_0, k_1	Drying Velocity Constants (min^{-1})
a, b	Drying Constants (dimensionless)
W	Unit of Power (Watts)
V	Voltage Unit (Volts)
P4, P6	Microwave Power Levels (in-built)
Vac20	Vacuum Pressure of 20” Mercury (~67.72kPa)
SEM	Scanning Electron Microscope
MW	Microwave
DAQ	Data Acquisition
I/O	Input / Output
L	Lightness Indicator (White to Black)
a	Chromacity Coordinates (Red to Green)
b	Chromacity Coordinates (Yellow to Blue)
ΔE_{ab}	Total Colour Difference
MHz	Unit of Frequency (Mega Hertz)

GHz	Unit of Frequency (Giga Hertz)
MPa	Unit of Pressure (Megapascal)
GPa	Unit of Pressure (Gigapascal)
DSC	Differential Scanning Calorimetry
NAF	Natural Agricultural Fibre
HDPE	High Density Polyethylene
LDPE	Low Density Polyethylene
LLDPE	Linear Low Density Polyethylene
PVC	Polyvinyl Chloride
PP	Polypropylene
PE	Polyethylene
FAOSTAT	Food and Agriculture Organization of United Nations Statistical report
PC	Personal Computer
SD	Standard Deviation
SE	Standard Error
MSE	Standard Error of Mean
C1	Combination 1 (max 130 ºC)
NaOH	Sodium Hydroxide (alkali)
Silane	Vinyltriethoxysilane 97%,

[Molecular formula: $H_2C=CHSi(OC_2H_5)_3$]

Abbreviated sample name

Sample Name	Drying Condition	Chemical Treatment
UNTRT	Raw flax (not dried)	Raw flax(untreated)
Apx	MW P4	NaOH (5%)
Apy	C1(5min)+ MW P4	NaOH (5%)
Apz	MW P4,Vacuum pressure (67.73kPa)	NaOH (5%)
Aqx	MW P6	NaOH (5%)
Aqy	C1(5min)+ MW P6	NaOH (5%)
Aqz	MW P6,Vacuum pressure (67.73kPa)	NaOH (5%)
Bpx	MW P4	NaOH+ Isopropyl alcohol :Water(60:40) + 1% Silane
Bpy	C1(5min)+ MW P4	NaOH+ Isopropyl alcohol :Water(60:40) + 1% Silane
Bpz	MW P4,Vacuum pressure (67.73kPa)	NaOH+ Isopropyl alcohol :Water(60:40) + 1% Silane
Bqx	MW P6	NaOH+ Isopropyl alcohol :Water(60:40) + 1% Silane
Bqy	C1(5min)+ MW P6	NaOH+ Isopropyl alcohol :Water(60:40) + 1% Silane
Bqz	MW P6,Vacuum pressure (67.73kPa)	NaOH+ Isopropyl alcohol :Water(60:40) + 1% Silane

Legend: Apx: A- NaOH treated, p- microwave power level P4, x- dried with microwave

CHAPTER 1

INTRODUCTION

1.1 Overview

Natural fibre has been used since prehistoric times. Presently, the diversified uses of natural agricultural fibre make it very important. In the past, natural fibre was used for clothes, but now it is used for automotive and aerospace applications (Huang et al., 2007). The diversification of natural agricultural fibres (NAF) is important in the composite industries. The non-corrosive, light weight, economical, and comparable physical and mechanical properties have drawn a lot of attention to natural fibre based composite research. From the textile industry to the automotive industry, natural fibres are utilized in many different ways. Use of plastic and synthetic fibre is a big concern today. They are not cheap or environmentally safe. However natural fibres are bio-degradable, environmentally friendly, renewable, non-abrasive, low in cost, and available abundantly in Western Canada (Ghazanfari et al., 2006). Natural fibres are used in the development of new materials used for construction, furniture, packaging, ropes, bags for grain storage, and even in automotive industries. Presently most of the interior parts of an automobile are petrochemical-based. These parts are disposed of either in landfills or by burning where both contribute to environmental pollution (Chen et al., 2005). Thus auto manufacturers are now trying to use parts made of materials that are fully recyclable or biologically degraded. According to European commission guidelines, carmakers should use up to 95% recyclable parts by the year 2015. They can

either use interior parts made of single polymer or material which can easily be biologically degraded like biocomposites. Biocomposites are composite materials, which contain plastics and natural fibre. The application of biocomposites in automotive manufacturing can improve mechanical properties, lower the product weight, speed up processing time, enhance passenger safety, withstand extreme temperature, improve the insulation, and improve biodegradation (Kemper and Hobi, 2003).

Fibre plants are cultivated in almost all the regions of the world. These are flax, hemp, jute, sisal, coir, Manila hemp, etc. There are about 800,000 acres of flax (Linseed) grown every year in Saskatchewan (FAOSTAT, 2007). The degradation of flax straw is very slow; farmers usually burn them to get rid of biomass which causes environmental pollution and health hazards. These fibre plants can be developed to replace wood, which would add value to the crop. Flax fibre can replace wood fibre in some applications and also can be combined with plastics, such as HDPE (high density polyethylene), LDPE (low density polyethylene), LLDPE (linear low density polyethylene), PVC (polyvinyl chloride), PP (polypropylene), and PE (polyethylene) to produce biocomposites used in different industrial applications.

Natural fibre works as a reinforcement material in biocomposites. Natural fibres have high aspect ratio, high strength-to-weight ratio, and good insulation properties. Although the tensile strength of glass fibre is higher than that of natural fibre, the elastic modulus of natural fibres is close to or even better than that of glass fibre. This gives tremendous advantage to natural fibre for competition with glass fibre (Saheb and Jog, 1999). Natural fibres are not popular in composite industry because of its incompatibility with matrix and hydrophilic nature. To improve the compatibility on the surface of the fibre, chemical modification is needed. Fibre adsorbs moisture from the atmosphere due to its

hydrophilic nature. In the process of making biocomposites, pores are created due to the presence of moisture so drying is necessary prior to the compounding process of biocomposites. Studies show that the adhesion between polymer matrix and natural fibre will be enhanced if it is treated by chemical reagents such as sodium hydroxide, trimethoxy silane, acetic acid, acrylic acid, maleated coupling agents, isocyanates, potassium permanganate, or peroxide (Ghazanfari et al., 2006; Li et al., 2007). After chemical treatment, the natural fibre has to be washed with water. In this process, the fibre absorbs a large amount of water that has to be removed prior to further processing. Therefore, there is a strong need for effective drying processes in order to remove excess water and at the same time, retain the physical and mechanical properties of the natural fibre. Some researchers use thin layer drying as a conventional process, but there is very little literature available on the drying of natural fibres using microwave, microwave-convective, and microwave-vacuum technology although these technology used in food and pharmaceutical industry for a long time.

Traditionally, natural fibres are dried under the sun, but this process is time consuming and drying conditions are difficult to control. It also does not produce good quality fibre. Drying is necessary because the moisture inside the fibre forms bubbles during the mixing process of making biocomposites (Panigrahi et al., 2006). So, prior to the extrusion process (compounding), the fibre must be dried properly.

There are different drying methods that have been developed. The conventional drying method is very inefficient due to its improper utilization of energy. This is because it takes a lot of time and consumes energy for heating the air (Panigrahi et al., 2006).

Microwave drying is fast, but due to uneven distribution of heat, hot spots may develop but the use of a rotating table may help maintain a uniform moisture distribution within

the material to some extent (Panigrahi et al., 2006). This study also concluded that discolouration was noticed at drying temperatures less than 190^{o}C and moisture content fell below 2 and 1% at 200 and 300 W power levels, respectively. Farmer and Brusewitz (1980) investigated the use of a household microwave for alfalfa drying and for moisture determination.

Temperature should not be very high during drying to get a better quality of fibre. If the temperature is high, it can cause degradation of the material and reduction in quality. Microwave-vacuum technology is often used for heat sensitive materials to avoid degradation. The use of vacuum pressure to the microwave environment offers great advantages of dielectric heating at a reduced processing temperature. In addition, a volumetric heat transfer mechanism coupled with drying in vacuum provides an ideal low-temperature drying technique resulting in better quality of dry fibre.

Microwave and microwave-vacuum technologies have been used for a long time in the processing of agricultural products such as fruits and vegetables. There is no efficient method reported for drying oilseed flax fibre. Very little information on the drying of natural fibres using microwave, microwave-convective, and microwave-vacuum technology has been reported. This type of drying has been used in food industry for energy conservation and drying, so it can be applied for drying of flax fibre.

Since the physical properties of flax fibre play an important role in the biocomposite process, these properties must be understood in order to process the flax fibre for the purpose of developing biocomposite.

1.2 Objectives

The main objective of the study is to evaluate the effect of different drying methods on the physical and mechanical properties of dried flax fibre for biocomposite production, and to study the drying behaviour of flax fibre under microwave and microwave-vacuum methods. The following are the specific objectives of this research:

1. to evaluate the drying characteristics of flax fibre using microwave, microwave-convective, and microwave-vacuum conditions at 2.45 GHz frequency in terms of the moisture content, moisture ratio, and drying rates;
2. to study the physical properties of flax fibre in terms of;
    - tensile strength,
    - colour profile,
    - morphology,
    - thermal degradation characteristics; and
3. to compare different drying methods and to select an appropriate drying method for flax fibre used for biocomposites.

1.3 Organization of the Thesis

This thesis has six Chapters which include; Introduction, Literature Review, Materials and Methods, Results and Discussion, Summary and Conclusions, followed by Recommendations for future work.

In this research, flax fibre has been chemically treated and dried with microwave, microwave-convection, and microwave-vacuum drying conditions. Physical properties

like tensile strength, colour profile, structural analysis (SEM), and thermal properties (DSC) of flax fibre were also determined. In Chapter 2, literature review was given for flax fibre, its structure, quality parameters and three drying conditions. Chapter 3 discusses about the materials and equipment used in conducting the experiments and tests were done to achieve the objectives. The results obtained from drying process, curve fitting, test results for physical properties, and its validation referencing to different literatures were discussed in Chapter 4. The Chapter 5 summarizes major findings and gives a brief comparison of three drying methods. Chapter 6 gives the recommendation for the future work. At the end of the chapters, there is a list of references given which is used in this thesis with additional tables and figures in the Appendices.

CHAPTER 2

LITERATURE REVIEW

This section will focus on the review of literature on the physical structure and chemical composition of fibres and its characterization of physical properties, chemical treatment, and different drying methods.

2.1 Natural Agricultural Fibres (NAF)

Studies show that replacement of synthetic fibre with natural agricultural fibre has increased in the field of biocomposites. Natural agricultural fibres are low in density, cheap, and biodegradable. But the big disadvantage of natural fibres is that they do not have same consistency in quality as compared to synthetic fibres. This inconsistency is due to variety of reasons such as climate, crop variety, retting process, and processing equipment used for fibres (Thomsen et al., 2006). In natural fibres, climatic conditions play an important role in fibre production. Low temperature and high relative humidity during growing season contribute to fineness and length of fibre (Elhaak et. al, 1999). Different crop variety has different cellulose and non-cellulosic contents which are key factors for retting and fibre quality (Sharma and Faughey, 1999). Retting is very important factor for processing of fibre and ultimately fibre quality. Type of retting and duration and bacterial species used in retting are responsible for quality of fibre in terms of strength and fineness. It has reported that, the flax fibre desiccated at midpoint flowering followed by stand-retting and high speed decortications process yielded fine

and strong fibre with low lignin content. Complete degradation of lignin and separation of fibre bundles are possible due to low lignin content which yields a finer elementary fibre (Sampaio et al, 2004). Decortication process makes the fibre free from shives and separate fibre bundles resulted strong and fine quality fibre. The quality of the fibre depends upon parameters like strength, fibre morphology, and composition (Kesler et al., 1997).

There are three types of natural fibres available, namely, vegetable fibre, animal fibre, and mineral fibre. The vegetable fibres are also divided into four categories; stem or bast fibre, leaf fibre, seed fibre, and fruit fibre. Flax, hemp, kenaf, jute, and ramie are known as bast fibre. Cotton and kapok are seed fibre. Manila hemp and sisal are leaf fibre. Coconut is a fruit fibre.

2.1.1 Natural agricultural fibre structure

The structure of fibre is very complicated. Flax has a non-uniform structure. It is semi-cylindrical in shape where the fibre diameter becomes narrower towards the end (Grishanov et al., 2006; Moskaleva et al., 1981). Natural fibre is a composite structure. Hemicelluloses, pectin, and lignin act like a matrix whereas, cellulose acts like reinforcement to the matrix. This is the reason why it is difficult to separate a single fibre from a bundle. It always comes with 4-10 fibres sticking together in a bundle (Baley, 2002) and can be separated individually for different characterizations. Fig 2.1 shows the longitudinal view of a fibre bundle.

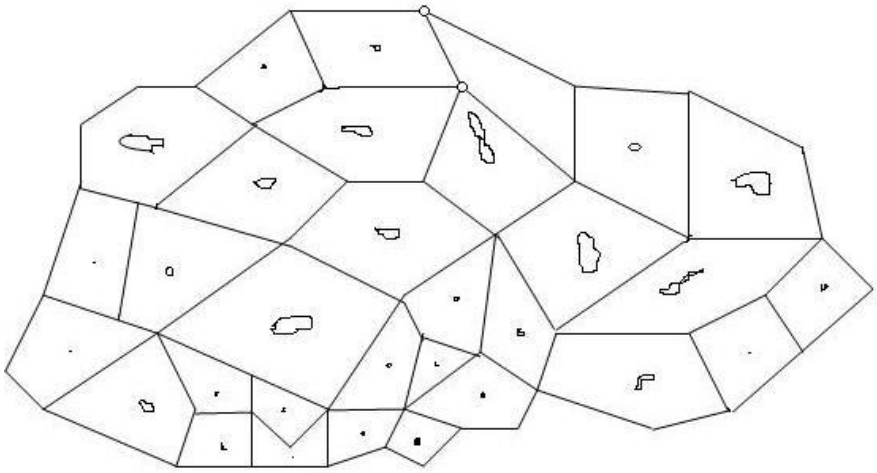


Figure 2.1 Longitudinal view of a fibre bundle (reproduced from Baley, 2002)

In the mesoscopic scale (the length scale from which somebody can discuss the properties of material without having to go for the properties of individual atoms), the fibre structure shown here has two cell walls, known as primary and secondary cell walls that are concentric with the middle lumen, which helps in water absorption. Crystalline cellulose fibrils go around with a tilt angle of 10º (Figure 2.2).

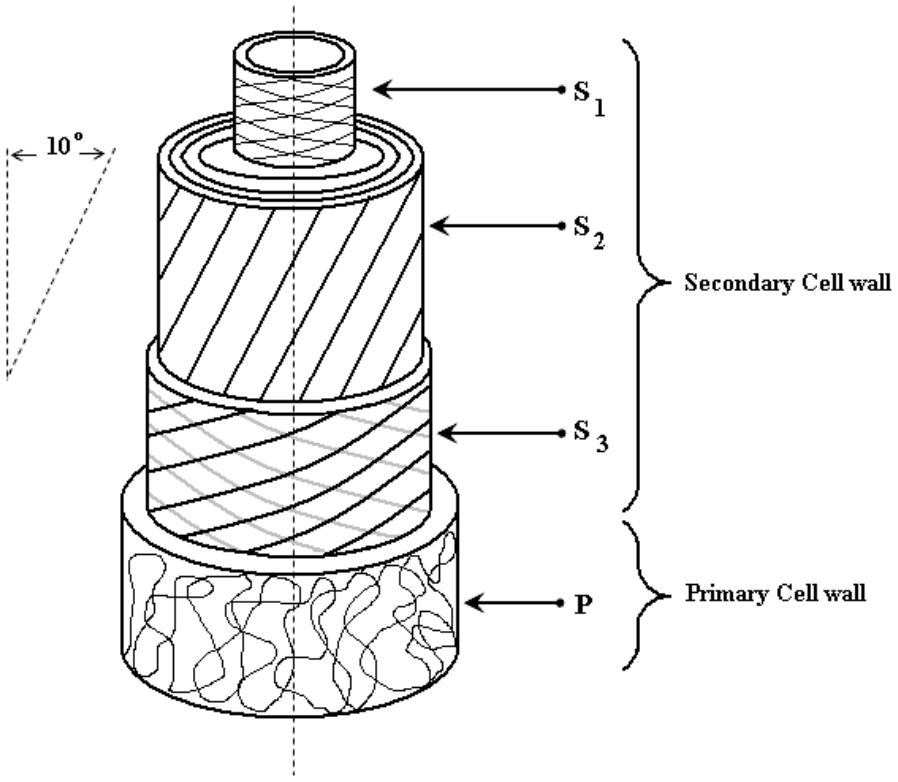


Figure 2.2 Atlas of a plant structure (reproduced from Bowes, 1996)

Some researchers have found that flax fibre consisted of macrofibrils, microfibrils, and elementary fibrils. The macrofibrils are 0.5 mm in diameter divided further into microfibrils which are up to 10 to 20 nm. The microfibrils are further divided into elementary fibrils which are further divided into micelles. Fifty to 100 molecules of cellulose form these micelles (Baley, 2002).

2.1.2 Chemical composition of natural fibres

Chemical composition is similar for all types of plant fibres. Plant fibre consists of cellulose, hemicelluloses, and lignin in different proportions (Thygesen, 2006). In addition to these components, there are other compounds in plant fibre such as pectin, wax, minerals, and water soluble compounds. Cellulose content of fibres varies from 60-

82% for jute, flax, hemp, ramie, sisal, palf, henequen and cotton fibres however kenaf, coir and wood fibres have less percentage (30-47%) of cellulosic materials (Mohanty et al, 2000).

Above all other components of fibre, cellulose is the main component that contributes strength to the material. For composite production, fibre with high cellulose content gives more strength to the product (Klinke et al., 2001). The study also found that retted hemp fibre gave more strength than the unretted fibre because its cellulose content is high (Thygesen, 2006).

2.1.3 Flax

Flax (*Linum usitatissimum*) is a plant from which linen is obtained. In Saskatchewan, 800 000 acres of flax was grown in the year 2005 (FAOSTAT, 2007). After the seed has been harvested for oil, farmers burn the flax straw in the field. Because the flax fibre plants are very strong, it takes a longer time to disintegrate (Keijzer et al., 1992). From prehistoric times, people have used flax fibre for clothing, rope, and other household applications. It is found in Egypt, Greece, Rome, Belgium, Ireland, China, the former Soviet Union, and Western Europe.

Flax grows in cool climates, to a height of 0.91 to 1.22 m (Flax, 2006). This height gives a good quality of fibre used for fabrics. The shorter ones grown in Saskatchewan are used for oilseed. Oilseed flax has a height of 0.40 to 0.91 m (Growth and Development, 2007). The height of the plant depends on variety, plant density, and soil fertility. Plant morphology, anatomy, growth condition, maturity, and retting factors contribute to the quality of fibre. The textile fibre undergoes different processes like retting, breaking,

scutching, and hackling after harvest. Flax used for yarn has to go through spinning, bleaching, and weaving processes.

2.1.4 Physical properties of natural fibre

Manmade or artificial fibres are very high in cost and hazardous to the environment. Natural fibres have almost the same strength as artificial fibre, but they are cheaper and environmentally friendly. Therefore, natural fibre has gained popularity for use in composites. Natural fibre gives good reinforcement, which is comparable to glass fibre in biocomposite. At the same time, the density is lower than that of glass fibre, so it contributes lighter weight to biocomposite material. For the production of composites, the fibre strength is more important than the fibre fineness (Foster et al., 1997; Norton et al., 2006). Researchers (Mohanty et al., 2000) compared the mechanical properties of natural fibres with artificial fibres. The density of flax fibre is 1.5 g/cm^3 whereas synthetic fibre has a value ranged 1.4-2.5 g/cm^3 that contribute to higher weight to synthetic fibres. The tensile strength of E-glass is very high (2000-3000 MPa) with comparison to flax (ranges 345-1100 MPa), but the elastic modulus of flax ranges between 12-85 GPa (Baley, 2002) that are very close to E-glass of 70 GPa (Mohanty et al., 2000). Some researchers suggested that glass fibres can be replaced by flax fibres because of the very good mechanical properties of flax; it can also be used in polymer composites (Joffe et al., 2003).

2.2 Fibre Quality and its Microstructure

There are four factors affecting strength and fineness of fibre. These are plant morphology, plant anatomy, growth conditions, and the retting process. Table 2.1 shows

each of the factors affect the strength and fineness in different ways. Fibre strength depends on stem diameter, stem branching, and leaf density of the plant. If there is too much of branching (oilseed flax), it has more nodes and kinks where the fibre will be not continuous as in textile grade fibres. The anatomy of plant also plays an important role in the strength and fineness of fibre. Cell diameter and cell wall thickness contribute to the strength of the fibre. If the bundle diameter is small, it gives a more fine fibre because fibre splitting will be easier. Growth conditions also contribute to the strength and fineness. If plants are denser, it will not get enough nutrients to grow bigger and will be branched and fibre will be not stronger. Harvest date shouldn't be very late or very early; because unmatured plant does not produce strong fibre and when plant is older, fibre will be stiffer. Retting method also played an important role on fibre quality. The fibre plants cannot be put in retting for a long time to get good fibre. If plants laid for a good amount of time, bacteria can destroy fibres instead of eating the lignin and pectin materials which help freed up from stem. In a controlled environment, enzymatic retting always gives a better quality of fibre although it is not economically viable.

Table 2.1 Factors affecting fibre quality (Keijzer et al., 1992).

Factors	Fibre strength	Fibre fineness
Plant morphology	Stem diameter	Stem diameter
	Stem branching	
	leaf density	
Plant anatomy	Cell diameter	Cell diameter
	Cell wall thickness	Bundle diameter
		(ability of fibre to split)
Growth	Sowing date	Sowing date
conditions	Climatological factors	Climatological factors
	(Plant density, Nutrients,	(Plant density, Nutrients,
	Harvest date)	Harvest date)
Retting	Method	Method
	Duration	Bacterial species

The composition of the multi-cellular structure of fibre is almost the same as reinforced composites. Fibre polymer is composed of cellulose, hemicelluloses, lignin, and pectin. Lignin and pectin act like bonding agents to cellulose.

2.3 Characterization of Natural Fibres

Characterization usually means to know internal structures and properties of material by using external techniques. It can mean using actual material testing and analysis. Before using natural fibres in composites, the fibre has to be chemically treated and dried.

Because different methods are used for drying, characterization can be done to help optimise drying conditions and methods for a better quality fibre. There are different techniques available to characterize the natural fibre properties. These are colour, tensile strength, degradation temperature, and morphological structure.

Natural fibres are chosen for their mechanical properties for the manufacture of biocomposites. As fibre is processed in different processing stages, damage occurs. Andersons et al. (2005) suggested that a single fibre fragmentation (SFF) test was a better method for the efficient evaluation of fibre strength. Nechwatal et al. (2003) studied that there is a need for reliable and exact measurement of tensile strength and elastic modulus for the reinforcing element. Two procedures are available to measure these properties for fibre materials; the single fibre test and bundle test. Studies have suggested that, the single fibre test is more accurate and should be used for evaluations (Andersons et al., 2005).

2.4 Moisture Adsorption Characteristics

The hydrophilic property of natural fibres is a drawback when using it in biocomposites (Wang, 2005). Adsorption of moisture has a deleterious effect on composite properties because of its chemical composition.

Mechanical property of natural fibre depends on moisture content of fibre. Water inside the fibre molecules behaves like a plasticizer. It allows cellulose molecules to move freely, which causes low elastic modulus and tensile strength. The decrease in mechanical property might be also because of fungus development due to internal moisture of fibre (Stamboulis et al., 2001).

2.5 Chemical Treatment of Fibre

The main disadvantage of natural fibre is poor compatibility with matrix and high moisture absorption. Therefore, chemical treatment of natural fibres is essential before the fibres are used as a reinforcing material in biocomposites. There are different chemical treatments available for producing a good quality fibre. The silane treatment is one of the treatments which will be discussed here because it increases the fibre matrix interface.

Dry flax fibre usually contains 8% of moisture, but because it is hydrophilic in nature, it absorbs water from the atmosphere. Plastics are hydrophobic in nature, so if the composite is made by mixing natural fibre with plastic without chemical treatment, it may not yield a high quality product. Therefore, the moisture should be removed totally from the fibre (Li et al., 2007).

2.5.1 Silane treatment

Silane is a chemical compound with chemical formula SiH_4. This works as a coupling agent between fibre and polymer matrix. This reduces the number of cellulose hydroxyl groups in the fibre matrix interface. It improves the degrees of cross-linking in the interface region, which results in a perfect bonding (Wang et al., 2007).

Various studies show that different coupling agents are effective in improving interface properties of wood-propylene, mineral filled elastomers, fibre-reinforced epoxies, and phenolic composites. Studies show that silane coupling agents are effective in modifying natural fibre-polymer matrix interface and increasing the interfacial strength. Researchers have also found that the interaction between the silane coupling agent modified fibre and matrix is much stronger than that of alkali treatment, which leads to a

composite with higher tensile strength when silane treated fibre than alkali treated fibre are used (Li et al., 2007). This treatment can increase the interface adhesion and decrease the water absorption.

2.6 Drying of Fibre

Drying is a process of removing moisture from materials through evaporation by means of heat. Fibre is usually dried after chemical treatment for further processing of biocopmosites. Troeger and Butler (1980) concluded that when drying agricultural material, the rate of drying depended on i) water removal from the surface and ii) movement of moisture from the interior to the surface. This is due to the vapour pressure difference between the interior and surface.

The drying process affects the quality of the fibre being used for processing biocomposites. During the drying process, physical and chemical changes occur which may lead to changes in the physical characteristics of the material such as strength, texture and colour. At one point in this process, biochemical reactions take place, which may be responsible for the deterioration of compounds.

Physical and mechanical properties of cellulose fibre should be thoroughly investigated before using them in composite materials. Soykeabkaew et al. (2004) concluded that the reinforcement effect increases with increase in fibre content and fibre aspect ratio. The flexural strength and flexural modulus increases with the longitudinal orientation of the fibre.

When the fibre is exposed to heat, thermal degradation starts. At 120°C, decomposition of waxes starts. At a temperature of about 150-180^{o}C, decomposition of pectin and

hemicelluloses may occur. At 350-500°C decomposition of cellulose occurs (Knothe and Folster, 1997).

It has been found that hemicelluloses are degraded at lower temperatures (250-350°C), reported by Raveendran et al. (1996) which caused degradation of fibres into cellulose microfibrils and leads to weaker strength of fibre bundle (Thygesen, 2006).

Powell et al. (2002) also found that the pure flax fibre starts degrading at a temperature 200-210°C and continue degrading till reached a temperature of 400°C.

Presently, there are only a few drying methods reported for natural fibre drying. They are convection drying and microwave drying. Microwave drying is occasionally involved because it is not very economically beneficial. In this study, more effective drying methods of biological material will be proposed and evaluated. These are:

1. convection drying,
2. microwave drying,
3. microwave-convection combination drying, and
4. microwave- vacuum drying.

2.6.1 Conventional drying (thin layer cross-flow dryer)

Drying of fibre is necessary in the process of making the composites. To get a better product, the fibre should be properly dried. Like other agricultural processes, drying is an energy consuming process. Flax fibre is currently dried using tray or rotary dryers, but there is no literature available on enhancing the drying process. Ghazanfari et al. (2006) concluded in their experiment that layer thickness has a major impact on drying time. If the thickness of a layer is increased, drying time will be decreased but the role of thickness is not significant if the thickness of the layer is increased more than 15 mm.

The drying air temperature has also a major effect on the drying time. By increasing the drying air temperature, the drying time will be shorter. The coefficient of diffusion for all layers is a linear function of drying air temperature and thickness of the layer. Ghazanfari et al. (2006) have used thin-layer drying method to dry the flax fibre, but it took 4-10 hours, depending on drying conditions and the moisture content (M.C.) of the material. Jayas and Sokhansanj (1989) also indicated that temperature plays an important role in drying barley increasing the temperature a little gives a significant result whereas relative humidity and airflow rate have no significant effect.

2.6.2 Microwave drying (MW drying)

Microwave energy is used for drying not only in food industry but also in industrial drying applications. MW is used for the drying of food, wood, paper, and textiles and even for the curing of resins in plastic processing. MW has a penetrating effect, which causes volumetric heating. When MW energy comes in contact with the molecules of water in the material, they start oscillating and due to friction, heat is developed. The generated heat depends on frequency, strength of the electromagnetic field, and dielectric properties of the material (Beaudry et al., 2003). The increase in internal pressure causes the moisture to move out from interior to the surface where it evaporates. That is why sometimes conventional drying is combined with MW to accelerate the drying process.

Alibas (2007) studied the drying of nettle leaves using MW and found a reduction in drying time by increasing the MW power level. He also reported that MW was the most energy efficient method in comparison to vacuum and convective oven drying.

Due to the dielectric properties of material, they absorb the microwave and radio frequency and heat is generated throughout the material. The energy is absorbed by the material and the material is dried. When internal heat is generated by microwave fields, internal pressure increases causing diffusion of water to the surface. This water can be removed by flow of air or convectional heat.

Soysal et al. (2006) reported that drying using MW is a better approach than conventional drying. They also found that there is no significant difference in the colour of herbs after drying with a MW. His research claims that there is a significant reduction of drying time compared to the conventional oven. This study also shows that, with a higher material load, there is a longer drying time but that specific energy consumption is lower and hence there is an increase in efficiency.

Due to the vapour pressure inside, water vapour comes to the surface and the material becomes soggy. This is one of the drawbacks of microwave oven. Additionally, in microwave drying, hot and cold spots are generated. This is due to the non-uniformity of the electromagnetic field (E-field). This non-uniform E-field creates non-homogeneous temperature patterns, which cause the hot and cold spots. One of the solutions recommended by Kelen et al. (2006) was the intensification of mixture motion and/or the reduction of microwave power but the reduction of microwave power can cause an increase in the processing time.

The usual way of using MW is to apply at the end of the falling rate period. Therefore, it is a good idea to put in hot air first, and then at the end of falling rate, MW energy can remove moisture very quickly. Some researchers also recommend that (Yongsawatdigul and Gunasekaran, 1996) two power ON times (30,60s) and three power OFF times (60,

90,150s) were the two most suitable settings for maximum efficiency when drying cranberries.

2.6.3 Microwave-convection combination drying

At present, the microwave has been improved to evaporate moisture from the outer layers of the material when combined with convectional heating. The heating may take place at the same time or separately. Microwaves accelerate the dying process, so it is effective when it is applied at the later stage of drying (falling-rate drying period). Microwave drying has been used for a long time for the drying of food materials. It improves product quality and increases the rate of dehydration. The internal temperature of the material is higher than the surface temperature as result moisture moves out to the surface. Microwave drying combined with hot air creates a synergistic effect and offers uniformity of heating. Also, this reduces the drying time and retains the original quality of fibre. Pereira et al. (2007) also found that increasing the air velocity and temperature improves product appearance and quality.

2.6.4 Microwave with vacuum drying

MW-vacuum technology allows the boiling point of water to be reduced by lowering the atmospheric pressure in the drying chamber. The atmospheric pressure within the chamber is controlled by a vacuum system. When the proprietary microwave system is turned on, microwaves are directed into the chamber at controlled levels (pre-set by the user, end product specific) and absorbed by the water in the sample. The energy from the absorbed microwaves combined with the vacuum conditions in the chamber cause the water to evaporate quickly at relatively low temperatures.

Microwave-vacuum drying has advantages over microwave drying. The vacuum created inside the chamber reduces the boiling point and affects drying at a reduced temperature. The results show that the target moisture content could be achieved in a greatly reduced drying time when the vacuum is supplemented with microwave drying (Mishra et al., 2006). Durance and Wang (2002) dried tomatoes in MW-vacuum and hot-air convection and concluded that MW-vacuum is much faster than hot air dehydration during the second phase of drying.

2.6.5 Drying characteristics

In biological products, drying takes place in two phases; one is the constant-rate drying period and the second is the falling-rate drying periods (Soysal et al., 2006). In the first phase of drying, the product loses moisture quickly and in the second phase, moisture loss is very slow and takes a lot of drying time to complete. The study of drying chard leaves showed that the combined microwave-convective drying is the most efficient method with respect to the drying period, average drying rate, and colour criteria when comparing microwave only and convection only drying method. Researchers also found the best drying parameters for chard leaves drying are 500 W of MW power, 75°C temperature with a drying period of 4.5 min (Alibas, 2006). Yongsawatdigul and Gunasekaran (1996) also suggested that microwave drying is a better method to dry biological material than conventional drying where there is no significant colour change in the green leaves. Quantity of material also plays an important role in microwave drying. Drying of parsley leaves takes more time if the load is increased because the power density of the microwave is less on unit mass of material dried (Soysal et al., 2006). Therefore, the drying coefficient decreased with an increase in material load.

With the decrease of moisture in the material, microwave energy absorption also decreases due to the moisture decrease inside the material. Panigrahi et al. (2006) dried flax in a microwave oven and found that the Page model was best for predicting the drying characteristics of flax fibre. They also found that the moisture content could not be dropped below 2 and 1% at P2 (154 W) and P3 (234.5 W) power level (Mishra et al., 2006).

2.6.6 Effect of microwave on the colour on flax fibre

Cellulose is a linear polymer of D-glucose molecules (poly[β-1,4-D-anhydroglucopyranose], ($C_{6n}H_{10n+2}O_{5n+1}$). Two adjacent glucose units are linked by elimination of one water molecule between their hydroxyl groups at carbon atoms 1 and 4 (Thygesen, 2006). When it is exposed to microwave for a longer period of time, the break down of glucose molecules resulted in brown colour because the molecules have undergone Maillard reaction. "The Maillard reaction is a chemical reaction between an amino acid and a reducing sugar, usually requiring heat. Like caramelization, it is a form of non-enzymatic browning. The reactive carbonyl group of the sugar reacts with the nucleophilic amino group of the amino acid, and forms a variety of interesting but poorly characterized molecules responsible for a range of odours and flavours" (Glomb and Monnier, 1995). Panigrahi et al. (2006) also studied the colour profile of flax fibre drying with microwave resulted brown colour after 9.5 min when exposed to microwave of power level 400 W.

2.7 Summary

This chapter reviewed structure, composition, physical properties, and chemical treatment of natural fibre. One section of this chapter was also dedicated to drying methods of biological materials. Although there are different drying methods available and has been used for a long time for other biological materials (food and pharmaceuticals), fibre drying with drying methods like microwave, microwave-convection, and microwave-vacuum is a new era of research. Because fibre is a heat sensitive material, physical characteristics has to be studied to determine the effect of drying methods of flax fibre. Effects of microwave, microwave-convection, and microwave-vacuum drying on physical properties like colour also discussed.

This research mainly focuses on three innovative drying methods for flax fibre, its drying characteristics and physical properties after drying. These physical properties are very essential for developing biocomposite products in the future. Morphological and thermal properties were also measured using scanning electron microscopy and differential scanning calorimetry of raw and dried and treated fibre.

CHAPTER 3

MATERIALS AND METHODS

This chapter describes the materials, chemical treatments, drying techniques, and characterization of dried flax fibre. The experimental plan and techniques related to drying of natural fibre are also discussed.

3.1 Overview of Research Methodology

The step by step experimental procedure can be developed starting from flax fibre procurement, chemical treatment, drying and physical characterization. The plan is developed to meet the overall objectives of the research as follows.

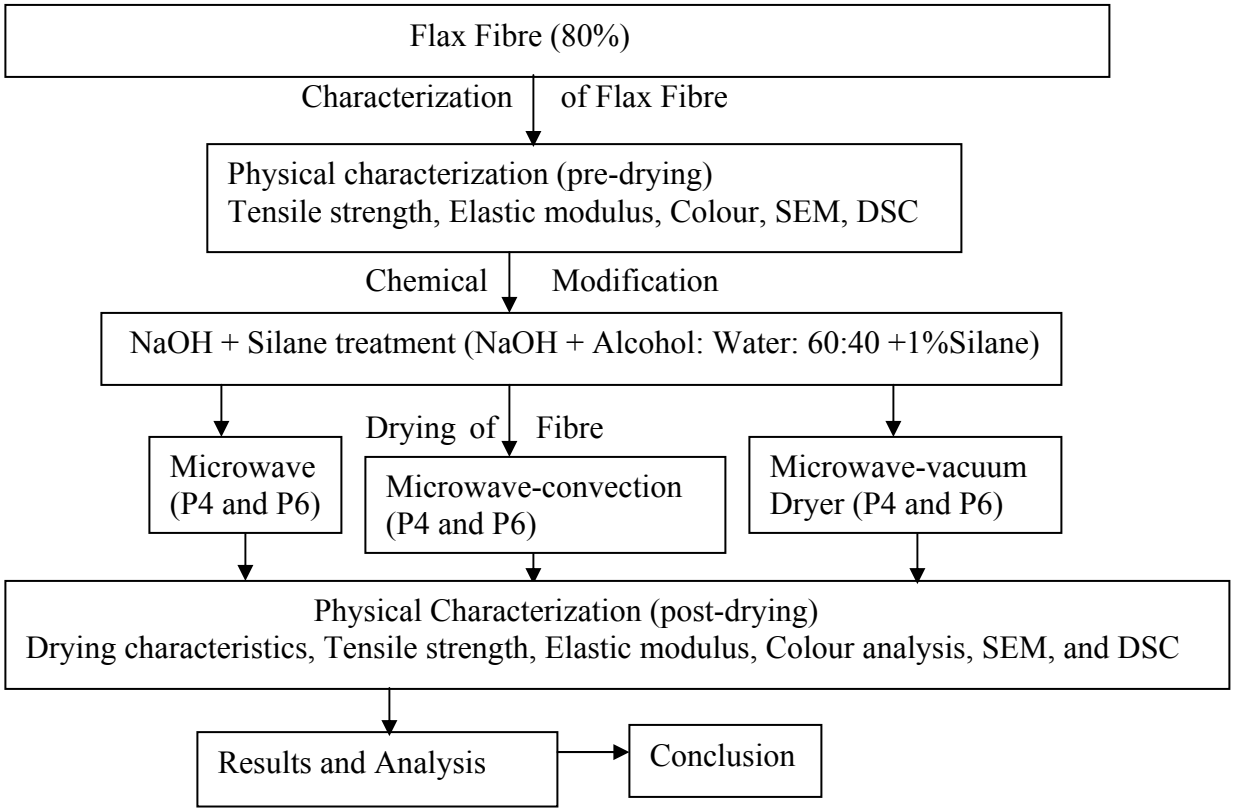


Figure 3.1 The schematic diagram of research methodology.

3.2 Materials

This section particularly describes materials and the equipment used for drying and characterization of flax fibre. This includes oilseed flax fibre, different drying systems and related equipment used for characterization of physical properties.

The raw materials used for preparing samples, chemical treatments and drying:

1. Oilseed flax fibre;
2. Isopropyl alcohol -ACS grade (EMD Chemicals Inc, Gibbstown, NJ); and
3. Five-minute epoxy (Henkel Canada Corp., Brampton, ON) to glue the flax sample with paper sample holder)

In this experiment, oilseed flax fibre was obtained from Saskatchewan Ministry Research Chair program in Engineering at University of Saskatchewan. The fibre was extracted from Saskatchewan grown oilseed flax. The flax straw was collected by Biolin Research Inc, Saskatoon, SK and decorticated by USDA, Clemson, SC.

3.2.1 Initial moisture content determination

There is no exact standard (or reported standard) for determining the initial moisture content of flax fibre. However, American Society of Agricultural and Biological Engineers (ASABE) has developed some standards for measuring the moisture content of forage crops ASAE S358.2 Dec 93. Flax fibre samples of 25 g were dried in a vacuum oven at 103ºC for 24 h and by calculating initial weight and moisture content percentage on wet basis was calculated

3.2.2 Purity measurement for flax fibre

The Saskatchewan oilseed flax fibre was used in this experiment. One hundred grams of raw flax fibre was taken and combed with metallic brush. It was cleaned so that the fibre

was totally free from any kind of shives. Then the cleaned fibre was weighed again. The new cleaned fibre weight divided by the raw weight was multiplied by 100 to give the purity of fibre. The tests were made in 3 replications and average was reported. The purity of the flax fibre found by above method was approximately 80%.

3.2.3 Chemical treatment

Natural fibre without any pre-treatment was procured. The fibre was cleaned from shives using metallic brushes. This fibre was taken as untreated fibre in this research. After, two equal amounts of cleaned flax fibre subjected to two chemical treatments (alkali and silane treatment).

First, the flax fibre was treated with sodium hydroxide. Flax fibre was immersed with 5% NaOH for 30 min. Then fibre was washed with double distilled water.

Second treatment was silane treatment. Silane (Vinyltriethoxysilane 97%, molecular formula $H_2C=CHSi(OC_2H_5)_3$, Sigma-Aldrich Canada) treatment is usually performed after treating with sodium hydroxide (NaOH). Flax fibre was dipped into 5% NaOH for 30 min and then thoroughly washed. The treated fibre again dipped into alcohol (isopropyl alcohol) and water (60:40) with 1% containing vinyltriethoxysilane coupling agent for 30 min. Then fibre was washed in distilled water and an industrial spinner was used to get rid of excess of water. Then the fibre was ready for drying.

3.3 Experimental Setup for Drying Using MW and MW-convectional oven

A microwave convectional dryer was used for drying. A little modification has been made to suit our measurement needs. For the temperature measurement inside the microwave, two holes were made on the side wall of the microwave. Through these

holes, fibre optics probes were inserted. Neoptix fibre optics signal conditioner was used to monitor temperature of the sample. The Neoptix signal conditioner was connected to a laptop with Neolink software, which comes with the signal conditioner. The result was stored in a MS (Microsoft) Excel readable format. Because fibre optic sensors were used to measure temperature in the sample, it was difficult to use a turntable. This was because of the fragile nature of fibre optic probes that made it impossible for a rotating tray to be used while drying. The online weight loss measurement was also made difficult when using a rotating tray. To make the design simple, a hole was made on the top of the microwave, a Teflon tube was passed through the hole to avoid sharp edge cutting through the Teflon thread. Teflon thread was connected to the polypropylene tray and suspended from the weighing tray passing through the Teflon tube. Because the temperature is high inside microwave, Teflon thread was used that can sustain the temperature up to 220^{o}C. The Figure 3.2 shows the microwave-convection dryer, weighing machine, and personal computer for temperature data acquisition.

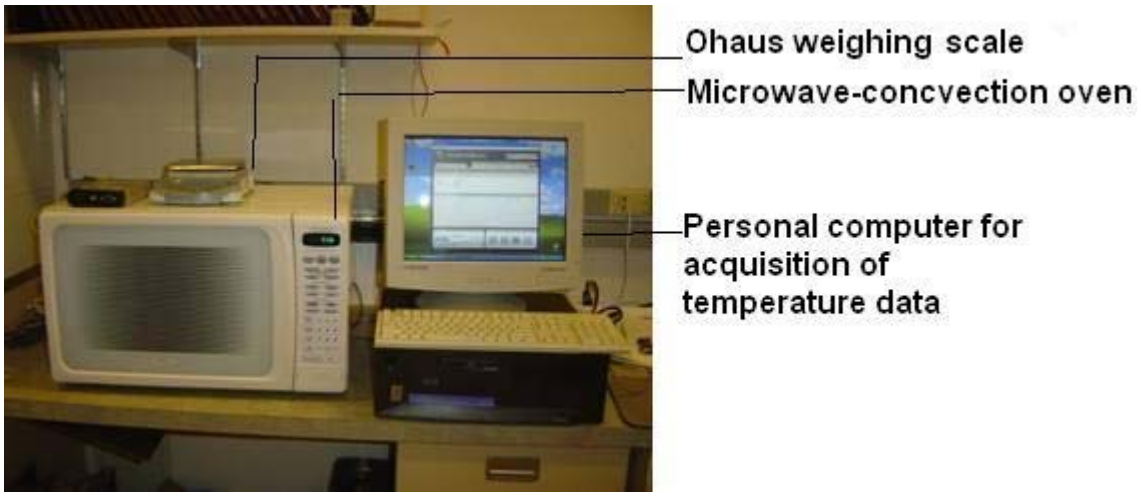


Figure 3.2 Experimental setup – microwave (Panasonic® model NNC980W), weighing scale (Ohaus® Corp, Model Adventure Pro), and data logger (Neoplex), PC with Assistant software to acquire data**.**

Figure 3.3 Sample holders suspending from weighing machine through Teflon tube inside microwave.

3.3.1 Temperature acquisition

Neoptix Reflex-4 (Neoptix Inc., Quebec City, QC) signal conditioner was used to acquire temperature data from the microwave convection oven. Fibre optic temperature sensors were kept inside the MW and data were acquired by using the Assistant software (Neoptix- Assistant version 3.3 for Windows, Neoptix Inc., Quebec City, QC) (Figure 3.4). Assistant software gives the data in the form of MS Excel worksheet (Figure 3.5), which makes it easier to process the data later.

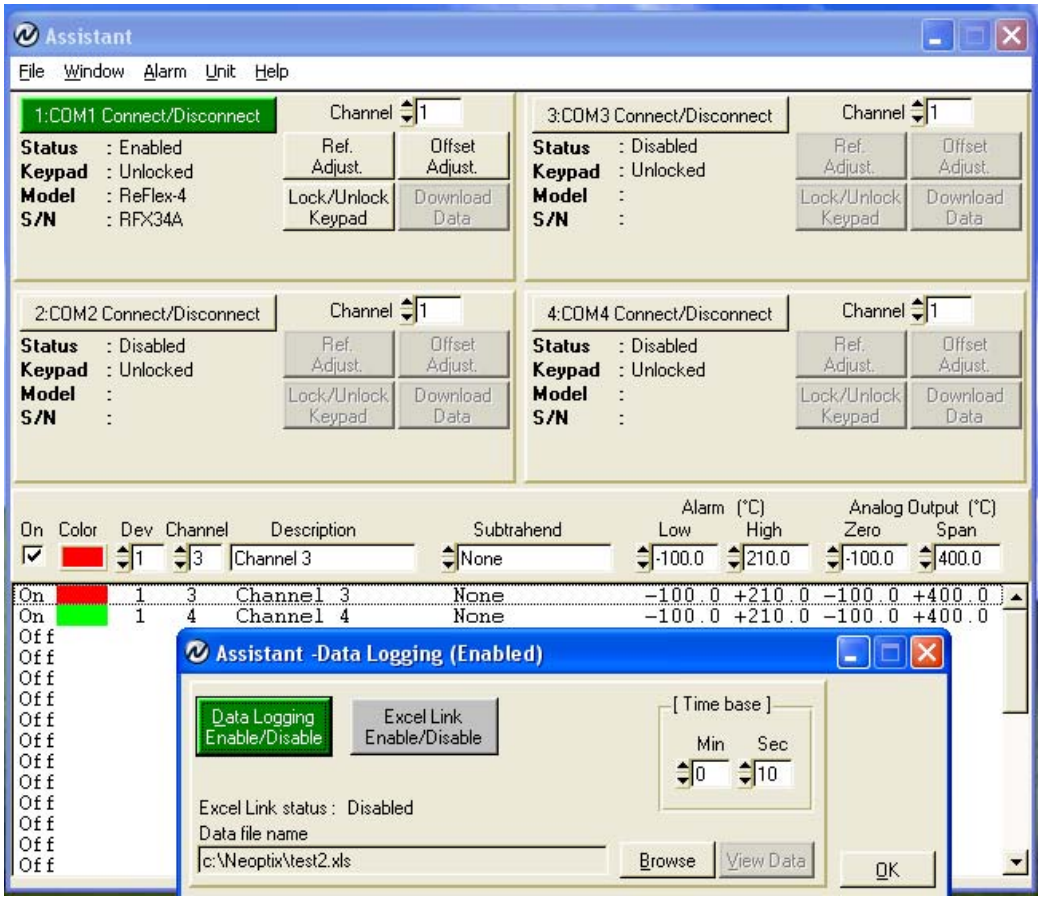


Figure 3.4 Data logging window of Assistant software.

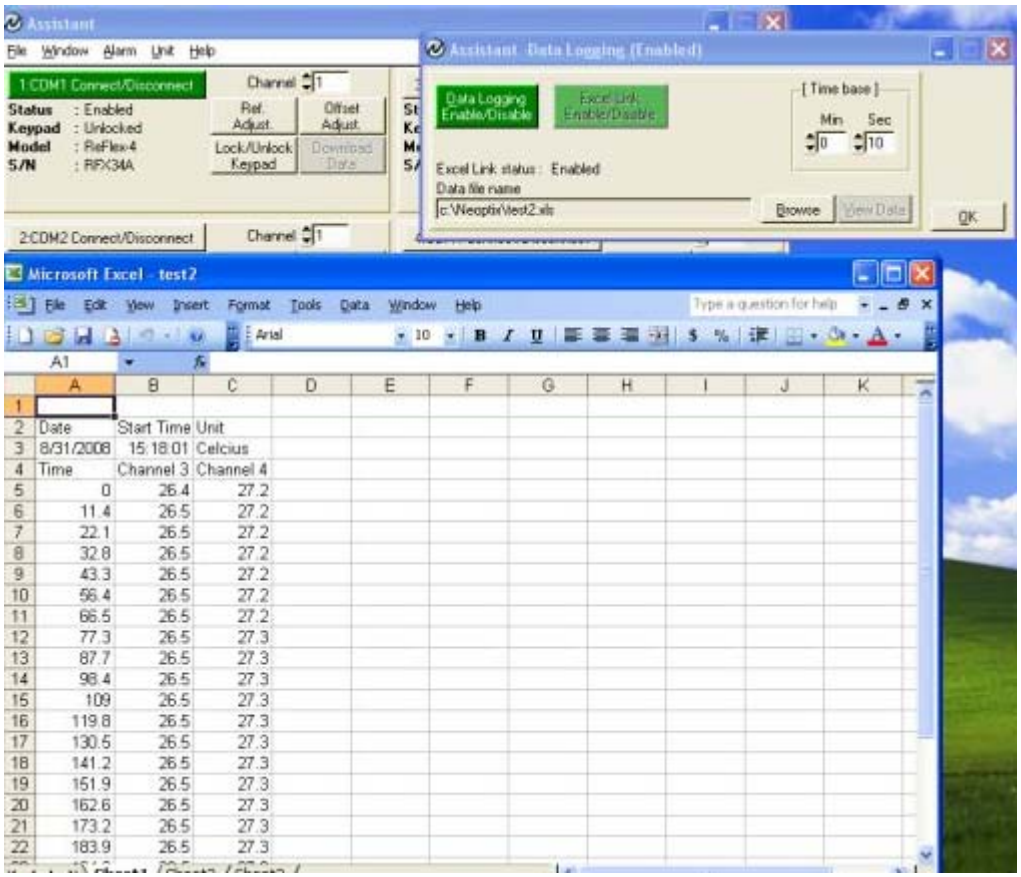


Figure 3.5 Assistant program with Excel sheet show the data when the experiment is running on data logging window.

3.3.2 Weighing scale setup

Adventurer Pro (Model AV812, Ohaus® Corporation, Pinebrook, NJ, USA), was used for online weight measurement during the flax drying. A serial port RS-232 was used to connect the weighing machine to the laptop for data acquisition. Labview version 6.2 was used for getting the data from the weighing machine to the laptop. The Figure 3.6 shows the screen shot of Labview software acquiring the weight loss data from the weighing machine.

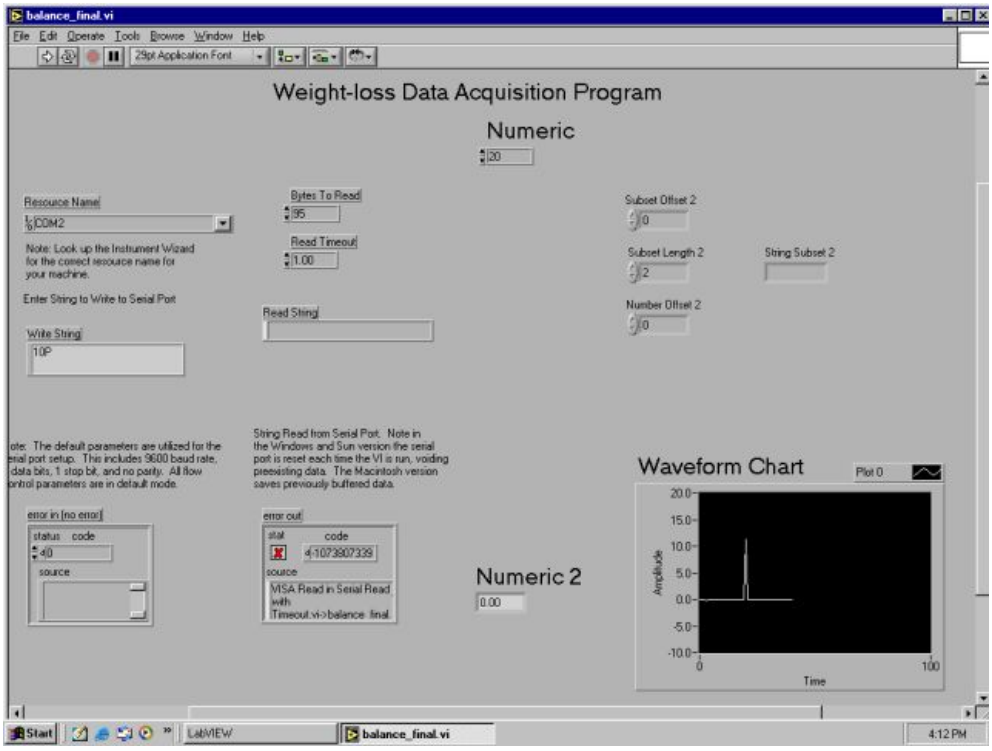


Figure 3.6 Data acquisition screen shot for weight loss data acquisition from weighing machine.

3.3.3 Weighing scale calibration

There is airflow turbulence inside the microwave when the material is drying. Therefore, when the data is acquired, there might be errors due to the air movement and contact friction between the suspended string and the wall of the tube. Specific measures were taken to avoid this problem. Wider Teflon pipe was used and the Teflon string was suspended exactly in the middle so that there wouldn't be any friction between the suspended string and wall of Teflon tube.

Because of air movement inside the dryer, the string might touch the edge of the tube. To avoid this, the Ohaus® (Adventure Pro) balance was calibrated. After each reading was taken, the error could be subtracted and the actual reading could be obtained. A measured weight (50 g) of flax fibre was placed on the tray and the microwave dryer

was run. Data was acquired on the PC while microwave-convection combination was running. The weight obtained was the weight of material with error factor. Then final weight could be calculated by total weight subtracting the error factor.

3.4 Procedure of Drying

For the composites, different drying techniques are needed to get a bone dry material (almost 0-2% moisture content depending on the method of drying) for the biocomposites. Two different dryers were used:

1. Microwave-convection combinational dryer and
2. Microwave-vacuum dryer

The microwave only drying and microwave-convection combination drying were done using Panasonic® combinational dryern (model NN-C980W) and microwave-vacuum drying was done using Enwave® microwave-vacuum dryer (Model VMD1.8).

3.4.1 Microwave-convection combination dryer

For all the microwave and microwave-convectional combination drying studies, a Panasonic® microwave-convection oven that was developed into a stand-alone drying system was used. This section discusses the experimental setup and drying of treated fibre using above mentioned microwave-convection dryer. Figure 3.7 shows the schematic diagram of microwave-convection dryer.

There are four combinations available, which are built-in and cannot be changed. C1 combination is the lowest where convection goes to a temperature of 130ºC with 30% MW power. Other combinations (C2=150ºC, C3=160ºC, C4=190ºC) are higher and cannot be used for drying flax fibre (Panasonic® User Manual, 2000). The combination

and power settings that were used in this research were given in the experimental design section.

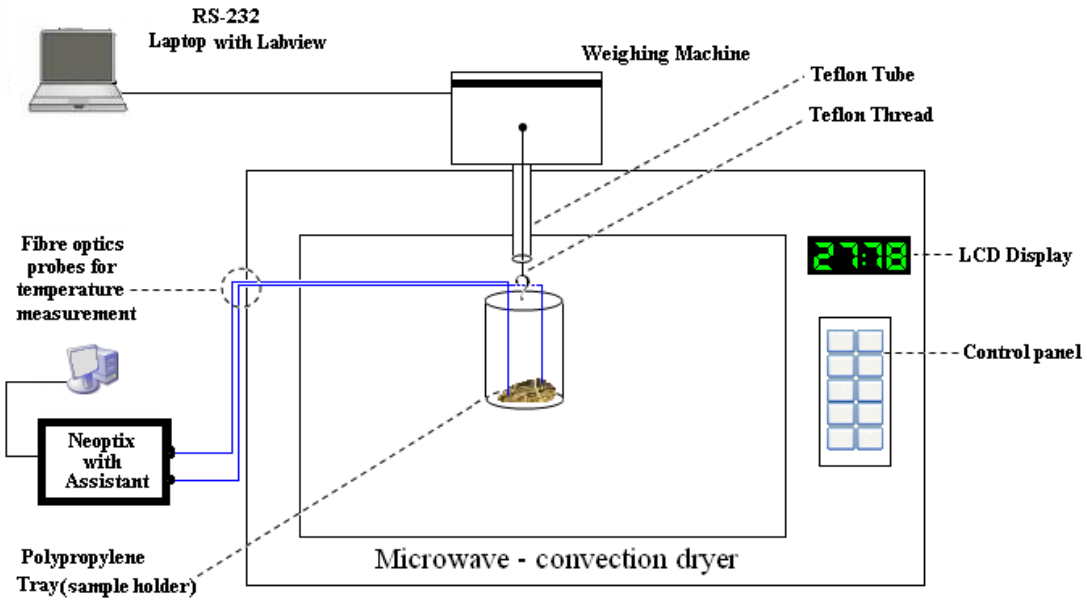


Figure 3.7 Schematic diagram of experimental setup with microwave-convection dryer

3.4.2 Microwave-vacuum (MW-vacuum) dryer

The Enwave® mw-vacuum dryer (Enwave microwave-vacuum dryer, Vancouver, BC, Canada) consists mainly of five different components. These are vacuum system, microwave system, chamber, motor, and venting system. Figure 3.8 and 3.9 show the complete assembly of the microwave-vacuum dryer. The vacuum, microwave and water inlet are engaged properly to the drier before starting the machine. After plugging in the power, the vacuum pump is switched on and the water flow is adjusted by a tap on the water inlet to achieve the desired vacuum pressure.

Water acts as a seal and lubrication for the vacuum pump. The excess vacuum is controlled by the venting system. Then the motor speed controller is adjusted to the selected speed.

Figure 3.8 Enwave® MW-vacuum dryer (from outside) showing the magnetron on the top, top right- control panel, right down- pressure-vacuum scale.

Figure 3.9 Sample holder (flat plastic plate) and control panel of Enwave® MW-vacuum dryer.

3.4.3 MW and MW-convection drying

The sample was carefully selected after the chemical treatment. Three 50 g samples were taken each time from each type of chemical treatment. The wet fibre was uniformly placed in a thin layer on the sample holder before it was dried with MW or MW-convection dryer. The online temperature change was recorded with fibre optic sensors and weight loss due to drying was acquired online and was recorded using a weighing machine which was connected to a personal computer. The data was acquired using Labview software.

3.4.4 MW-vacuum drying

The sample was carefully selected after the chemical treatment. Three 50 g samples were taken each time from each type of chemical treatment. The wet fibre was uniformly placed in a thin layer on the sample holder before it was dried with MW-vacuum. The microwave-vacuum dryer was set to vacuum level of 20 in Hg (67.74 kPa). After vacuum was set, the sample was exposed to microwave for 3 min and vacuum was released and sample was weight was taken. After putting back the sample, vacuum was again adjusted to 20 in Hg, exposed to microwave for 3 min, and same process was repeated until final moisture content of sample was less than 1%. The sample was weighed using a Ohaus® weighing scale with 0.01g resolution to record the weight loss due to drying. The temperature data was acquired through Neoptix signal conditioner with fibre optics sensors.

3.4.5 Power measurement

The power for each level of the system was measured using the IMPI-2 litre test (Buffler, 1993). Two 1-L beakers (Pyrex 1000) filled with water was taken and initial temperatures of water (20 ± 2) °C were measured with a thermometer. Then the water was heated for 122 s with different power level. The water was stirred with a glass rod and again final temperatures were recorded. The power was calculated using the following formula:

$$P = 70 \times \left(\frac{\Delta T_1 + \Delta T_2}{2} \right) \tag{3.1}$$

where P is the power, in watts;

ΔT1 is the temperature rise of the first beaker in °C,

and ΔT2 is the temperature rise of the second beaker, in °C.

The number 70 is used here for approximation for multiplication as stated in the literature (Buffler, 1993). Temperature rise after 122 s was calculated by subtracting the initial water temperature from the final temperature as mentioned in the IMPI-2 litre method. The power measurement was repeated three times and the final power was calculated from the average of the three readings.

Tables 3.1 and 3.2 show that the temperature rises in too beakers along with power measured by IMPI 2-Liter tests at different power levels.

Table 3.1 Measurement of microwave Power in ENWAVE Microwave vacuum environment measured by IMPI 2-Liter test

Power level	ΔT1 (°C)	ΔT2 (°C)	Power, P (watt)
4	4.10	4.40	295.20
6	6.70	7.30	488.80

Table 3.2 Measurement of microwave Power in PANASONIC Microwave environment measured by IMPI 2-Liter test

Power level	ΔT1 (°C)	ΔT2 (°C)	Power, P (watt)
4	5.35	5.25	371.00
6	9.05	8.50	614.00

3.5 Experimental Plan and Data Analysis

This subsection describes about the how the experiments were conducted and data were analyzed.

3.5.1 Experimental plan

Fibre characterization was done before and after the chemical treatment and drying to identify the effect of drying and the change in the quality of the fibre. The following properties were analyzed before and after the chemical treatment and drying of the fibre:

1. Tensile strength,
2. Elastic modulus,
3. Colour criteria,
4. Scanning electron microscopy (SEM), and
5. Differential scanning calorimetry (DSC).

The flax fibre used in the experiment was of 80% purity. After the fibre was selected, it has undergone two types of chemical treatments. These were NaOH and silane

treatment. After being treated with sodium hydroxide (NaOH), the fibre was subjected silane treatment (60:40 isopropyl alcohol: water plus 1% trimethoxy silane). Fibre treated with only alkali was used as the control and compared to the fibre treated with silane. After the treatment, the whole fibre was washed and dried with three drying methods such as microwave only, microwave-convection combination, and microwave-vacuum. So the three factors were

1. Chemical treatment type (2 levels-alkali and silane),
2. Microwave power level (2 levels-P4 and P6), and
3. Drying methods (3 levels-MW, MW-convection, and MW-vacuum).

Therefore, the experimental design plan will look like a three way-factorial shown in the Table 3.3.

Table 3.3 Experimental design for drying and characterization of fibre.

Factor 1 (chemical treatment)	Factor 2 (power level)	Factor 3 (drying methods)	Treatment combination	Number of replications of different tests			
				Tensile strength	Young's Modulus	Colour	DSC
A (NaOH)	p (P4)	x (MW only)	Apx	9	9	3	3
		y (MW-convectio	Apy	9	9	3	3
			Apz	9	9	3	3
	q (P6)	combination)	Aqx	9	9	3	3
		z (MW-Vacuum)	Aqy	9	9	3	3
			Aqz	9	9	3	3
B (NaOH+ Silane)	p (P4)	x (microwave only)	Bpx	9	9	3	3
		y (MW-convectio	Bpy	9	9	3	3
			Bpz	9	9	3	3
	q (P6)	combination)	Bqx	9	9	3	3
		z (MW-Vacuum)	Bqy	9	9	3	3
			Bqz	9	9	3	3

Legend: P4: MW power P4 and P6: MW power P6; A-alkali treated, B-Silane treated; p-power P4, q-power P6; x-MW, y-microwave with convection C1, z-MW-vacuum dried (20 in Hg).

For the calculation of tensile strength and elastic modulus, the diameter of fibre is needed. Because the diameter of fibre was not consistent (within a range of 30- 300µm), it was not possible to conduct an analysis of variance (ANOVA). Tukey's Multiple range test can be performed on colour test and differential scanning calorimetry. Tukey's test was done to compare the each pair of means, if there is any significant difference in the ANOVA. The Tukey's honestly significant difference (HSD) test was chosen because of following reasons. First, it is very simple and relatively reliable; second, it controls the familywise error rate; and third, it uses Q-distribution. Although Duncan's multiple range tests is powerful, it is complicated because sets of treatments are high and there are critical values at each step, Tukey's HSD takes into account all pairs of treatment means. Although it is less sensitive to differences between treatment means, it does fewer calculations and is easier to report. The results of scanning electron micrographs were analysed separately. All this analysis was done using statistical application SPSS 14.0 for Windows.

3.5.2 Mathematical modelling of drying characteristics

After getting the drying data, drying models were fitted to the drying using four different thin layer drying equations.

Table 3.4 Mathematical models applied to drying curves.

#	**Model name**	**Model**	**Reference**
1	Page	$MR=exp(-kt^n)$	Midilli and Kucuk (2003)
2	Henderson and Pabis	$MR=a\ exp(-kt)$	Midilli and Kucuk (2003)
3	Two term	$MR=a\ exp(-k_0t) + b\ exp(-k_1t)$	Midilli and Kucuk (2003)
4	Wang and Singh	$MR=1+at+bt^2$	Midilli and Kucuk (2003)

Where

MR = Moisture ratio (Equation 3.2),

k, k_0, and k_1 = Drying rate constants, min^{-1},

n, a, and b = Drying coefficients,

t = Drying time, min, and

the moisture ratio equation is given as:

$$MR = \frac{M_t}{M_0} \tag{3.2}$$

Since the equilibrium moisture content, M_e, equals 0 in both cases of microwave and microwave-vacuum system. The original moisture ratio equation, $MR = \frac{M_t - M_e}{M_0 - M_e}$, reduces to Eq. 3.2.

The correlation coefficient R is used as the criteria for the best fit of the curve. The maximum R^2 (coefficient of determination) value will be taken as the best fit and it is calculated as:

$$R^2 = 1 - SSM/SSE \tag{3.3}$$

Where SSE = sum of squared errors (residuals),

SSM = sum of squares of the mean

In addition to that standard error has been calculated through TableCurve2D method and defined as Fit Standard Error (Root MSE)

$$SE = \sqrt{SSE/(n-p)} \tag{3.4}$$

Where n = number of samples or pairs

and

p is the number of parameters

If the coefficient of determination is very close or equal to 1 and the model having least standard error value closes to 0 gives the best fit.

3.5.3 Curve fitting

After the data has been gathered, the moisture ratio has to be determined. By using the *TableCurve2D (*TableCurve version 5.01 for Windows, Systat Software Inc., Chicago, IL), the curve fitting was done. A different R^2 and standard error (SE) values are determined for different equations and highest R^2 value with lowest standard error selected as the best model.

3.6 Physical Characterization of Fibre

The physical and chemical characterization of untreated and treated flax fibre is needed to study the quality of fibre after chemical treatment and drying. The indicators that give the overall fibre quality for textile flax fibres are fibre quality, fineness, length and shape of flax process, strength, density, lustre, colour, handle, alignment of strands, and absence of naps and knots. The four indicators of fibre quality that are major contributing factors for making biocomposites were focused on a) fibre strength, b) colour, c) morphology, and d) thermal degradation temperature.

3.6.1 Diameter measurement of flax fibre

To measure the tensile properties of the material, the length and diameter of the flax fibre had to be measured. Physical property of a natural fibre depends upon a wide variety of conditions. It depends on the type of flax, environmental conditions, processing type, and its chemical treatment. In this research, bundle of flax fibre was

selected. The diameter is not uniform along its length. It is wider at one end and shorter at the other, but in this research it was assumed that the fibre is cylindrical shape and the diameter is circular for the convenience of experiment.

A single bundled fibre was selected manually from bunch of fibre treated with alkali and silane. Samples from untreated and undried fibre were also selected. The schematic diagram of the sample was shown in Figure 3.10.

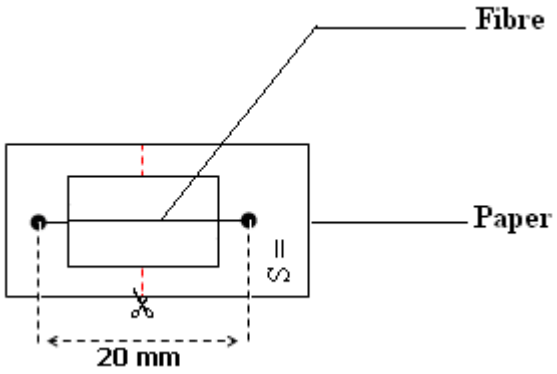


Figure 3.10 Schematic diagram of sample prepared for tensile test.

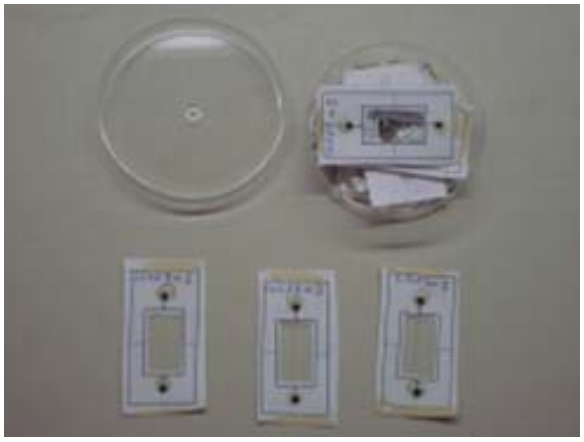


Figure 3.11 Prepared samples for measuring tensile strength of flax fibre.

The prepared sample for the tensile measurement is shown in Figure 3.11. The fibre was selected manually by hand to obtain minimum number of fibres in a bundle and then glued onto a prepared paper sample holder that had a square hole in the middle. It was then glued with epoxy carefully by gluing two ends of the fibre. It was then left for 4-6 h for curing at ambient temperature. After the glue has been cured, the fibre diameter was measured using Canon microscope fitted with PAX-IT digital camera. Nine replicates of single bundled fibres were chosen for each of sample.

The image was then magnified 100 times using a microscope. Each of the fibre samples was placed on a slide with a white background and eight readings were taken for each sample along the length of fibre and focusing on different parts of the fibre. Because the fibre is not cylindrical the diameter of the fibre varies from place to place. The fibres were chosen in such a way that there would not be a big difference in the readings and a more uniform diameter of fibre would be selected. Figure 3.12 shows the experimental setup for the measuring the diameter of flax with Canon microscope, Pax-it camera and Pax-it image acquiring and processing software.

Figure 3.12 Experimental setup for measuring the diameter of flax fibre

The experimental setup consisted of a Canon microscope with a 100X lens (10x10), and a Pax-it digital camera fitted on the top interfaced with a PC with Pax-it image capturing software. After the image was focused and image was acquired, it was then analysed using Pax-it imaging software. The obtained diameter was used for further calculation of tensile strength and elastic modulus of the treated and dried fibre for characterization. Figure 3.13 shows the measured diameter of a single bundled fibre with Pax-it camera and software.

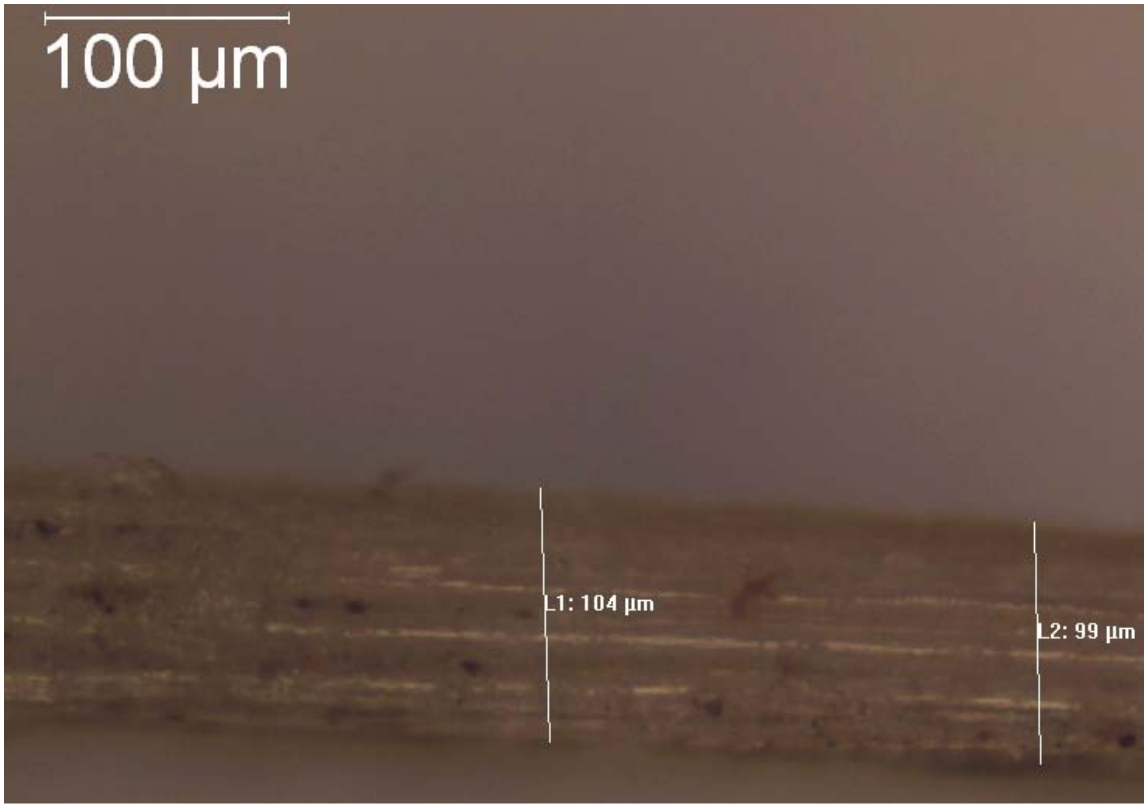


Figure 3.13 A single bundle of flax fibre prepared for measuring diameter and tensile strength on a Canon microscope with Pax-it digital camera

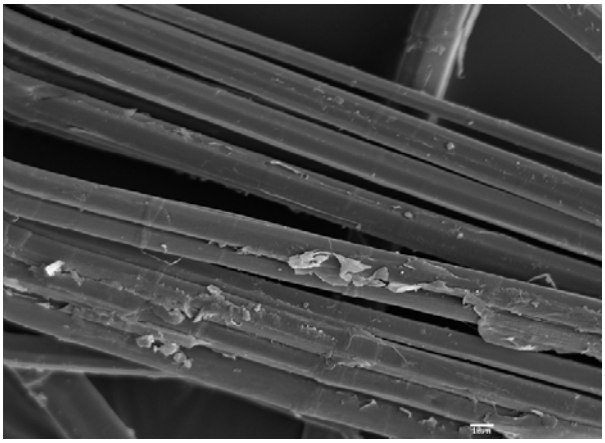


Figure 3.14 Image of a single fibre bundle consists of 10 individual fibres- image from electron microscope

3.6.2 Fibre strength measurement (Tensile)

Fibre is used as a reinforcement material in biocomposites, so the tensile strength of the fibre must be measured before it is put into the composite product (Morrison III et al., 2000). In the literature reviewed above, it was found that the Single Fibre Fragmentation test is a better method than the bundled fibre fragmentation test. Because a single fibre is very fine, it is very difficult to measure tensile strength using Instron 1011 machine (Instron Corporation, Canton, MA, USA). Therefore, the tensile test was conducted using the Texture Analyser (Texture Technologies Corp., Scarsdale, NY) shown in Figure 3.15) by using software TA Exceeds. Manual clamps were used to hold the sample. Ten replicates were done for each sample. After each step of the chemical treatment and drying process, a sample was analysed. After the diameter had been measured, the tensile strength of flax fibre was measured. The data was acquired through Texture Expert Exceed software, and saved in a text file. The test was done each time until the fibre breaks. The crosshead speed of 0.05 mm/s, the gauge length of 20 mm, and the pre-test speed was 0.02 mm/s was used in this experiment. The maximum force

(F_{max}) was recorded from the text file through Texture Expert Exceed software and the tensile strength was calculated using the formula below:

$$\sigma_t = F_{\max} / A \tag{3.5}$$

where F_{max} was maximum load value (N) and A was the area of cross section (mm^2).

The elastic modulus (E) was also calculated by following formula:

$$E = \Delta\sigma / \Delta\varepsilon \tag{3.6}$$

where $\Delta\sigma$ was the change in tensile stress and $\Delta\varepsilon$ was the change in tensile strain.

Figure 3.15 Experimental setup for measuring the tensile strength of flax fibre.

3.6.3 Colour profile

Because colour is vital part of the product development process, the colour analysis of the fibre after drying is necessary. The colour of the final product depends on the colour of the fibre. Colour measurements were done using the HunterLab spectrocolorimeter model LABSCAN2 (Hunter Associates Laboratory Inc, Reston, VA) (Figure 3.16). The colour change of the dried flax was determined by measuring the *L*, *a,* and *b* coordinates. . The scales used were L (0=black to white=100), a (-a=green to +a=red) and b (-b=blue to +b=yellow).

After initial calibration against a standard white ceramic surface plate, three measurements for each sample were taken. The viewing area of 12.8 mm and a port size of 25.4 mm were used in this experiment. After the calibration was done, the sample was prepared by weighing fibre of 2.46 g each time and put inside a transparent plastic petri dish. The petri dish was stuffed fully to avoid airspace and transmission of light through it. After each measurement was taken, the petri dish was cleaned thoroughly with alcohol. Each time three measurements were taken in different locations of sample and repeated on both sides.

L is the lightness indicator and a and b are the chromacity coordinates. The untreated fibre sample was taken was standard and changed were measured after fibre being treated and dried. Colour difference values ΔL, Δa and Δb were calculated according to the following equations

$$\Delta L = L_0 - L_1,\ \Delta a = a_0 - a_1,\ \Delta b = b_0 - b_1 \tag{3.7}$$

where:

L_0, a_0 and b_0 are the measured values of the specimen (treated and dried sample),

L_1, a_1, and b_1 are values of the target colour (untreated sample).

The target colours in this experiment are L, a, and b of the untreated flax fibre. The total colour difference ΔEab is measured using the L, a, b colour coordinates and as defined by equation 3.4 (Minolta, 1991):

$$\Delta Eab = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{0.5} \tag{3.8}$$

Figure 3.16 Hunter lab colour analyzer (Lab Scan II).

The analysis was carried out with help of statistical package SPSS 14.0 for Windows.

3.6.4 Morphology

The scanning electron microscopy (SEM) gives a clear idea about the morphology of the fibre internal structure. Therefore, samples of fibres treated using the different chemical treatment and drying processes were analysed using SEM (JEOL 840A, JEOL Ltd, Tokyo, Japan) at an accelerating voltage of 15 kV to examine the change in morphological structure. Through this analysis, the change in the internal structure of the material can be studied before and after drying with different dying methods. As we know microwave drying generates localized hot spots; SEM can find if any hot spots appear after drying with microwave, microwave convection and microwave-vacuum dryers.

3.6.5 Thermal degradation temperature

Differential scanning calorimetric (DSC) analysis was used for studying thermal stability, decomposition, dehydration, oxidation, determination of volatile material, binder burnout, and high temperature gas corrosion. The decomposition or the degradation temperature is very important for the processing of natural fibre based biocomposite material. In this research, the degradation characteristics of flax fibre was analyzed using the DSC (DSC model Q2000, TA Instruments, New Castle, USA).This is necessary to determine how much temperature the flax withstand when making biocomposites. The fibre can degrade when it is processed with plastics at a higher temperature in the injection moulding and compression moulding processes. This analytical technique can measured the heat flow with the function of time. Three replicates of thirteen samples are prepared for thermal analysis of untreated and treated-dried fibre. Sample of 6 to 12 mg was placed inside hermetic aluminium pan and sealed with standard sealing process. The testing was done in dynamic mode with heating rate of 20°C/min with heating range of 20 to 400°C and chart of heat flow with temperature was obtained. Three secondary peak temperatures were taken and analyzed with statistical software SPSS 14.0 for Windows.

CHAPTER 4

RESULTS AND DISCUSSION

In this chapter, the drying characteristics of treated flax fibre for three different drying methods and the characterization of the physical, mechanical, thermal, and morphological properties of flax fibre are presented and discussed. The experimental data were measured and analysed to find out the influence of different drying conditions (microwave, microwave-convection, and microwave-vacuum environments) on untreated and chemically treated flax fibre. The results of physical characteristics such as tensile, colour, thermal, and the morphological characteristics are also discussed.

4.1 Drying Characteristics

After chemical treatment, the fibre was dried using microwave, microwave-convection and microwave–vacuum dryers. In chapter III, all three dryers were described. Drying step is very important in the process of making biocomposites. Since the flax fibre is hydrophilic in nature, moisture should be removed to a minimum level enabling the fibre to mix well with the plastic, for further processing. After the chemical treatment, flax fibre had moisture content 75-85% wet basis. Bringing down the M.C. from 85% to less than 1% in a very short period of time requires a very fast drying method. Microwave, microwave-convection combination, and microwave-vacuum were used and proved to be very effective drying processes to remove moisture from the material.

Table 4.1 Drying time for treated and dried flax fibre at different drying conditions with 5% final moisture content (w.b).

Drying Method	Approximate Mean Drying Time (min)
Microwave	
P4	15
P6	10
Microwave-convection	
C1-P4	18
C1-P6	12
Microwave-vacuum	
Vac20 P4	24
Vac20 P6	21

The drying time in microwave, microwave-convection, and microwave-vacuum are given in Table 4.1. Microwave-vacuum drying took approximately 24 min when dried with power level P4 of microwave, whereas at power P6, it took 21 min. Because it took longer, this type of drying process could produce a better product, since it lowered the boiling point while maintaining temperature at a minimum level. The M.C. of the final product was found to be less than 1%. But the time taken for different drying methods calculated up to 5% final moisture content for comparison purposes (Table 4.1). In microwave drying, it took approximately 15 min at MW P4 whereas at MW P6, it took approximately 10 min. In microwave-convection drying at MW P4 with combination level 1, it took approximately 18 min and at MW P6 with same combination level, it took approximately 12 min. More time was taken with microwave-convection drying than microwave drying but less than with microwave-vacuum drying. The power calculation in Table 3.1 and 3.2 in Chapter III shows that the microwave power in

microwave-vacuum dryer is lower than that of microwave power in microwave convection oven. This might be one of the reasons why microwave-vacuum drying took more time than microwave and microwave-convection dryer. In drying, microwave plays a significant role than vacuum. Microwave-convection drying also kept the temperature lower than the microwave process, so took more time to reach the same final M.C. In the beginning, when the moisture level was high, the moisture on the surface was removed easily with convection drying, and then in the second phase of drying where drying is slow, microwave drying continued effectively. In microwave-convection drying, only 30% of microwave power (Panasonic® User Manual, 2000) was used with combination of convection heating and air circulation by fan. This might be one of the reasons that temperature rise in microwave-convection drying was not high as microwave and took more time than microwave drying. Figure 4.1 shows the drying characteristics of flax in microwave, microwave-convection and microwave-vacuum dryers.

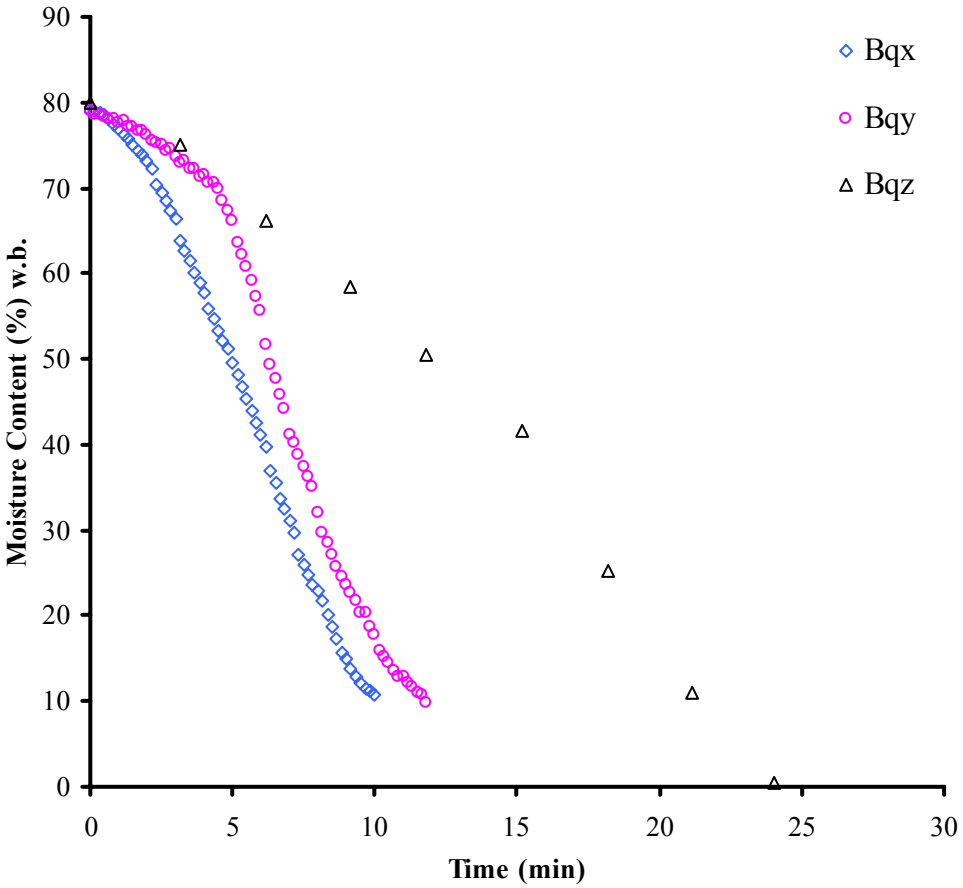


Figure: 4.1 Graph shows microwave (P4), microwave-convection (C1-P4) and microwave-vacuum (P4) moisture loss with time (Legend: Bpx - Silane treated flax sample with MW P4; Bpy - Silane treated flax with MW P4 and convection C1; Bpz - Silane treated sample with MW P4 and vacuum pressure 67.7 kPa).

At the beginning, drying is usually faster than at later stages. When the time increases, the drying rate decreases. In the first phase of drying, the drying occurs faster because it is similar to the evaporation of water. This is due to the free water available in the material held by capillary forces (Stanish, 1988). In the second phase, the drying rate becomes slower and microwave drying can be implemented, which is more efficient. This is due to the properties of material and the bound water (hygroscopic water) which is bound with hydrogen bonds (Can, 2000). Because the flax fibre contains cellulose,

hemicellulose, and lignin molecules, the hydroxyl group within it attracts, and holds water by hydrogen bonding (Stanish, 1986). In combination microwave-convection drying (Table 4.1), convection drying followed by microwave drying gave better results in terms of drying time. It enhances the drying rate and the quality of material as well (Alibas, 2007; Torringa et al., 1996). The drying time with MW P6 is shorter than P4 and the same results were found for combination drying with P4 and P6. Microwave power has a greater effect than other types of drying. The time taken for microwave-vacuum drying was more than that of microwave drying at the same level of microwave power. One of the reasons is that, there is difference in power output between microwave and microwave-vacuum ovens. Another reason is that, the cavity is bigger in microwave-vacuum than in microwave, so power needed to heat up microwave vacuum will be more and might take longer time. In microwave-vacuum drying, fibre can be dried for a longer period of time and therefore more moisture can be removed without compromising the quality of the fibre.

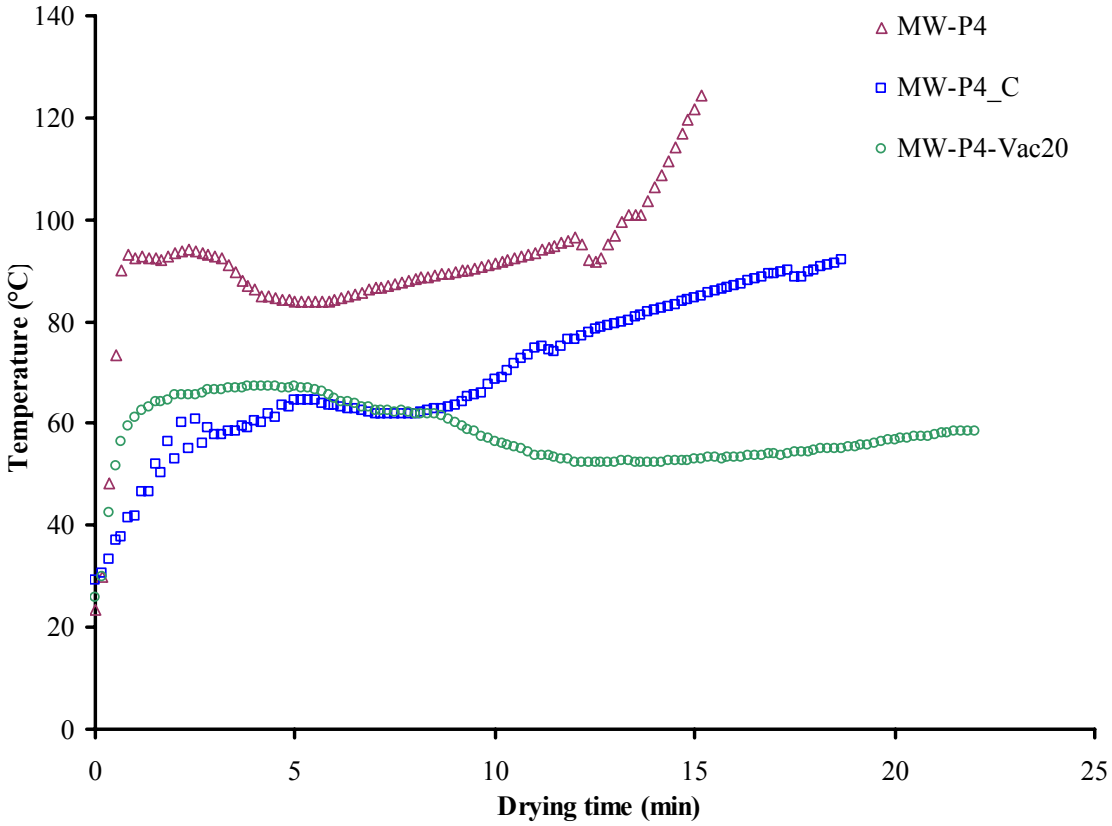


Figure 4.2 Different drying times for the flax fibre (Alkali treated) in MW P4, MW P4_C (MW P4 with combination C1), and MW-P4-Vac20 (MW P4 with vacuum 67.74kPa).

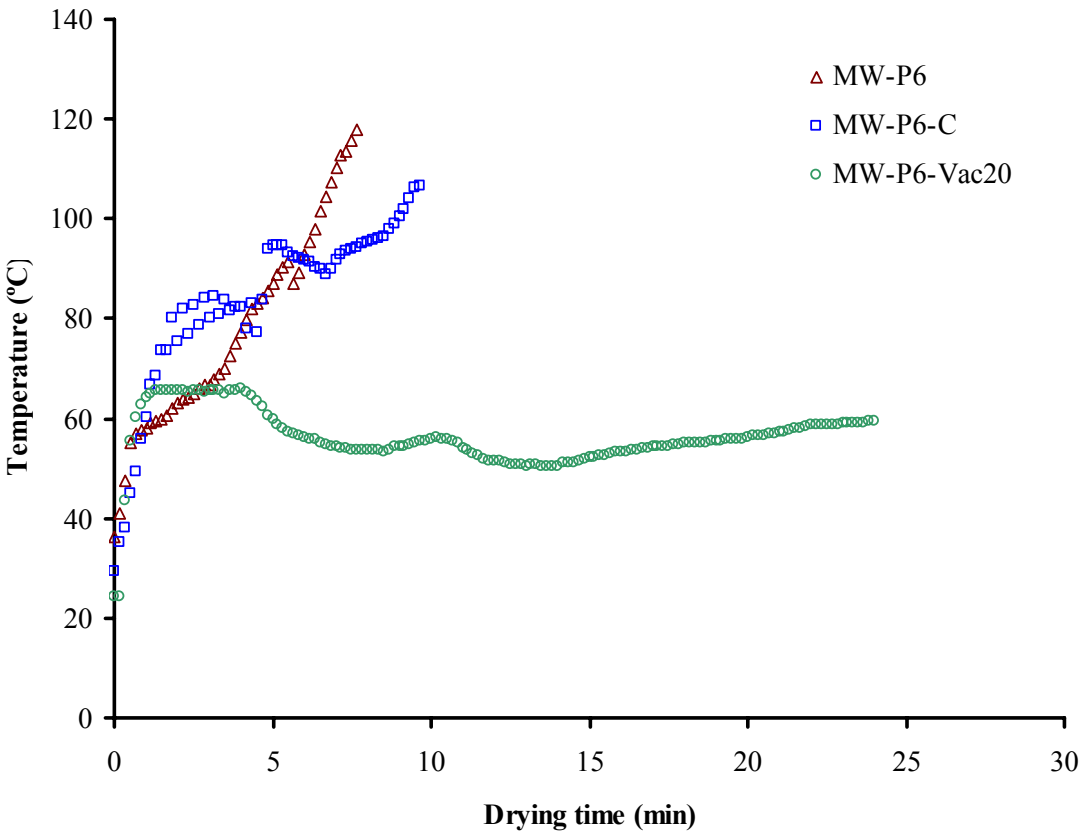


Figure 4.3 Different drying times for the flax fibre (Alkali treated) in MW P6, MW P6_C (MW P6 with combination C1), and MW-P6-Vac20 (MW P6 with vacuum 67.74kPa).

Figure 4.2 and 4.3 show the drying time and temperature rise in different types of drying conditions. Microwave only drying results in the highest rise in temperature although it takes the least time. Because the temperature was very high inside microwave-convection dryer, it was not possible to dry completely or reach to a particular moisture

level. The temperature reached around 110°C in the case of MW P4 and 130°C in the case of MW P6 with MW drying.

In the case of mw-vacuum drying, a more uniform low temperature was observed. The temperature was never more than 70°C in the case of microwave vacuum, so this type of drying resulted in a better quality dried fibre.

4.1.1 Modelling of drying process

Empirical methods are used by researchers for modelling of drying data. In this research, flax fibre was dried using different drying conditions. Microwave, microwave-convection, and microwave-vacuum dryers set at different power levels until particular moisture content. Drying models were fitted to the drying data and then TableCurve2D was used to calculate the drying parameters.

4.1.2 Drying constants

It is reported in literature that the drying constant increases as the microwave power level increases (Alibas, 2007). In Table 4.2, the drying constants and drying parameters are shown for all twelve treatments for four different semi-empirical equations for three different drying conditions using TableCurve 2D and Microsoft Excel. In case of Apz and Aqz (microwave-vacuum P4 and P6), the drying constant k, value increased with increased power level which is in good agreement with research findings (Alibas, 2007).

4.1.3 Mathematical modelling of thin layer drying curves

The chosen models are fitted to the drying data. TableCurve2D was used for fitting using non-linear regression technique. Coefficient of determination (R^2) and standard error (SE) values are shown in Table 4.2 for all four models for all treatments. The Two

term model gave the best fit for three samples (alkali treated microwave-vacuum dried with Power P6 (Aqz), silane treated microwave dried with power P4 (Bpx) and microwave-convection dried with P4 (Bpy). The Page model fits rest of the 9 samples data. Page model best fitted with alkali treated samples with P4 (Apx: R^2=0.9616, SE=0.0470, Figure 4.4) and P6 (Aqx: R^2=0.9951, SE=0.0210, Figure B.1), microwave-convection with power P4 (Apy: (R^2=0.99, SE=0.0279, Figure 4.5) power P6 (Aqy (R^2=0.994, SE=0.0240, Figure B.4); and microwave-vacuum with MW P4 (Apz: R^2=0.9782, SE=0.0310, Figure 4.6). For silane treated samples Page model fits with microwave-vacuum dried with power P6 (Bqx: R^2=0.9948, SE=0.0213, Figure B.3), microwave-convection with P6 (Bqy: R^2=0.9952, SE=0.0231, Figure B.6), and microwave-vacuum with P4 (Bpz R^2=0.9978, SE= 0.0136, Figure B.8), with P6 (Bqz: R^2=0.9896, SE=0.0229, Figure B.9). Two term model fits alkali treated samples microwave-vacuum dried with P6 (Aqz: R^2=0.9998, SE=0.0033, Figure B.7) and silane treated samples microwave drying P4 (Bpx: R^2=0.9973, SE=0.0143, Figure B.2) and microwave-convection drying P4 (Bpy: R^2=0.9938, SE=0.0242, Figure B.5). The Henderson and Pabis model as well as Wang and Singh model did not fit any of the drying data.

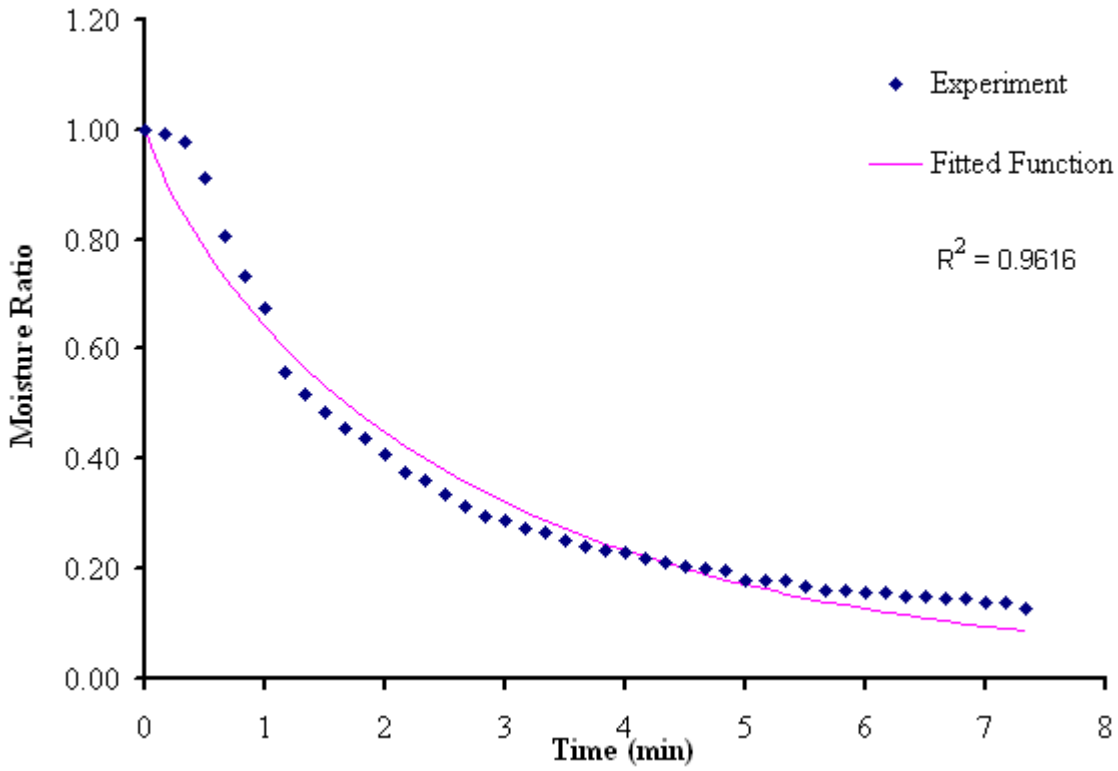


Figure 4.4 Page model fitted to the drying data of alkali treated MW-dried (P4) fibre drying (Apx).

Figure 4.4 shows the drying curve of alkali treated and microwave dried (with power level P4) fibre. In the beginning of drying, it was over predicted, in the middle, it was under predicted and again it was over predicted again. The Page model showed the best fit for this sample.

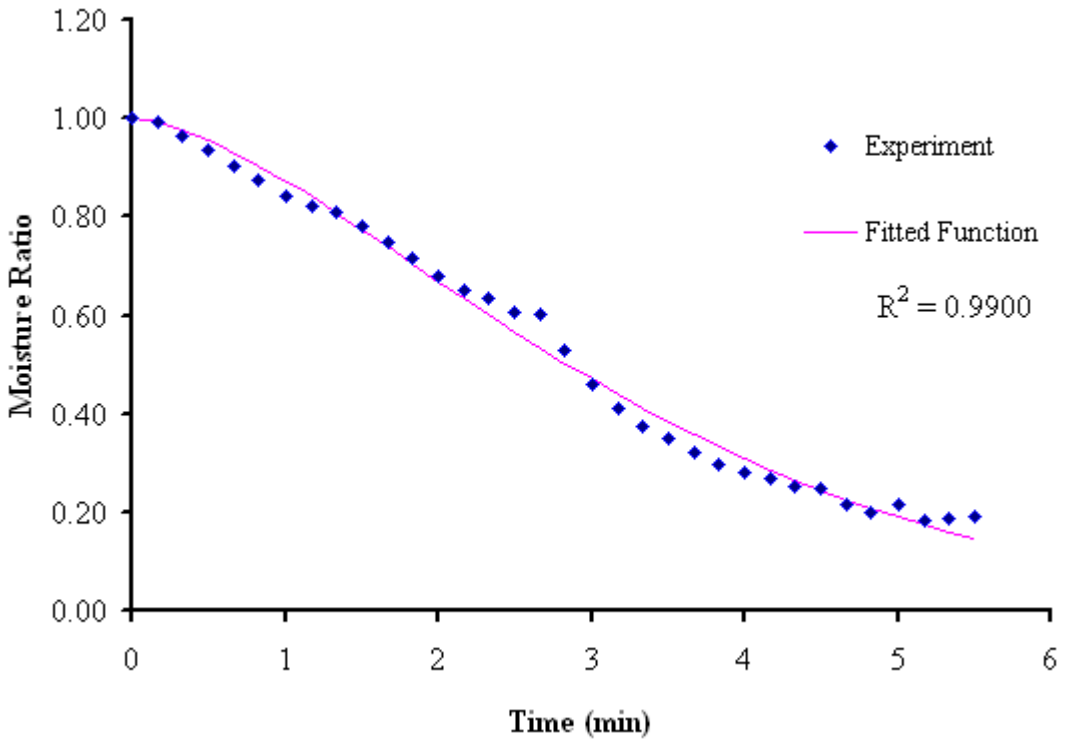


Figure 4.5 Page model fitted to the drying data of alkali treated MW-Convection combination (P4) fibre drying (Apy).

Figure 4.5 shows the drying curve of alkali treated and microwave-convection dried fibre (with MW power level P4 with combination C1). In the beginning of drying, it was under predicted, in the middle it was over predicted some part and then under predicted, again over predicted at the end of drying. Page model best fitted for this type of sample.

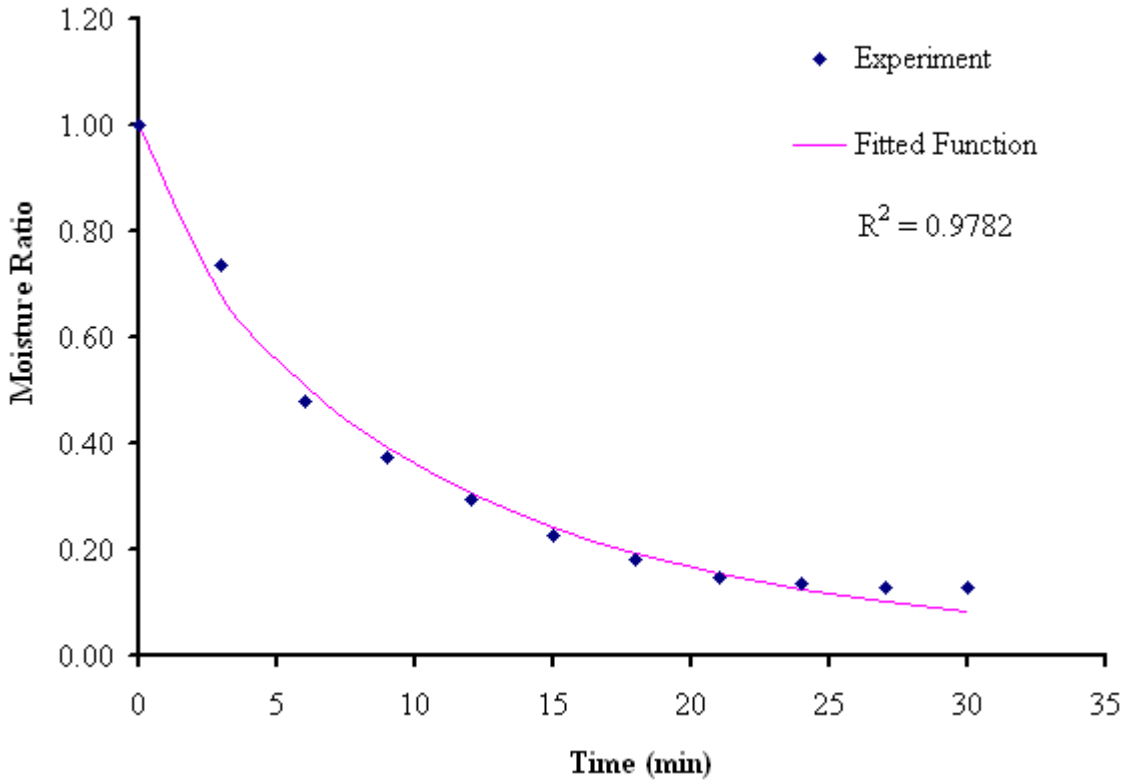


Figure 4.6 Page model fitted to the drying data of alkali treated MW-vacuum (P4-Vac 20) fibre drying (Apz).

Figure 4.6 shows the drying curve of alkali treated and microwave-vacuum dried fibre (with MW power level P4 with vacuum 67.73KPa). In the beginning of drying, it was under predicted, Andover predicted at the rest of the drying. The Page model best fitted for this type of sample.

Table 4.2 Estimated parameters of drying (drying coefficients), co-efficient of determination, and standard error values for different drying models

Samples	Model Name	k	n	a	k_0	b	k_1	R^2	SE (fitted)
Apx	Page	0.4434	0.8581					0.9616	0.0470
	Henderson and Pabis	0.9889		0.3769				0.9495	0.0540
	Two Term			1.1873	0.4359	0.0006	-0.6956	0.9485	0.0550
	Wang and Singh			-0.3205		0.02929		0.9474	0.0551
Aqx	Page	0.0030	1.2423					0.9951	0.0210
	Henderson and Pabis	1.0782		0.0102				0.9891	0.0313
	Two Term			0.9038	0.0101	0.1744	0.0102	0.9891	0.0330
	Wang and Singh			-0.0076		0.0162		0.9912	0.0282
Bpx	Page	0.2309	1.1217					0.9944	0.0200
	Henderson and Pabis	1.0757		0.2946				0.9965	0.0158
	Two Term			1.0992	0.3011	-0.1219	4.1828	0.9973	0.0143
	Wang and Singh			-0.2273		0.0149		0.9941	0.0205
Bqx	Page	0.0005	1.4406					0.9948	0.0213
	Henderson and Pabis	1.1626		0.0064				0.9815	0.0404
	Two Term			1.1450	0.0062	-0.0009	0.2867	0.9811	0.0421
	Wang and Singh			-0.0041		0.0042		0.9820	0.0399

Samples	Model Name	k	n	a	k_0	b	k_1	R^2	SE (fitted)
Apy	Page	0.1372	1.5507					0.9900	0.0279
	Henderson and Pabis	1.1425		0.3087				0.9611	0.0550
	Two Term			5.4457	0.5567	-4.4969	0.6946	0.9898	0.0291
	Wang and Singh			-0.1810		0.0036		0.9774	0.0419
Aqy	Page	0.1595	1.9230					0.9940	0.0240
	Henderson and Pabis	1.2100		0.4473				0.9341	0.0797
	Two Term			14.4857	0.9207	-13.6138	1.0198	0.9889	0.0343
	Wang and Singh			-0.1994		-0.0102		0.9727	0.0513
Bpy	Page	0.0951	1.4167					0.9871	0.0345
	Henderson and Pabis	1.1808		0.2265				0.9827	0.0398
	Two Term			1.4195	0.2641	-0.4391	1.2014	0.9938	0.0242
	Wang and Singh			-0.1510		0.0061		0.9717	0.0510
Bqy	Page	0.0860	2.3271					0.9952	0.0231
	Henderson and Pabis	1.2582		0.4134				0.9051	0.1025
	Two Term			18.8082	0.8827	-17.9557	0.9635	0.9770	0.0527
	Wang and Singh			-0.1282		-0.0250		0.9749	0.0528
Apz	Page	0.1870	0.7941					0.9782	0.0310
	Henderson and Pabis	0.0987		0.8614				0.9632	0.04036
	Two Term			0.0417	-0.0363	0.9885	0.1489	0.9761	0.0393
	Wang and Singh			-0.0913		0.0023		0.9285	0.0562
Aqz	Page	0.2155	0.7925					0.9919	0.0180
	Henderson and Pabis	0.1158		0.8510				0.9856	0.0240
	Two Term			0.0362	-0.0454	1.0060	0.1756	0.9998	0.0033
	Wang and Singh			-0.1052		0.0030		0.9513	0.0477

Samples	Model Name	k	n	a	k_0	b	k_1	R^2	SE (fitted)
Bpz	Page	0.0494	1.3270					0.9978	0.0136
	Henderson and Pabis	0.1303		1.2205				0.9904	0.0287
	Two Term			6.3841	0.1953	-5.4805	0.2291	0.9974	0.0171
	Wang and Singh			-0.0768		0.0015		0.9965	0.0173
Bqz	Page	0.2322	1.0250					0.9896	0.0229
	Henderson and Pabis	0.2441		1.0089				0.9893	0.0232
	Two Term			0.5988	0.2442	0.4100	0.2441	0.9893	0.0403
	Wang and Singh			-0.1613		0.0065		0.9838	0.0355

1

[1]Legend: UNTRT- untreated and undried fibre (raw); A-alkali treated, B- silane treated; p- MW with P4, q- MW with P6; x - microwave oven dried, y microwave-convection, and z- microwave-vacuum dried.[1]

4.2 Physical Characteristics

Physical characteristics are very important for making biocomposite. In this section, physical and mechanical properties are measured and tested after and before drying to find out if there is any change to the quality of fibres.

4.2.1 Diameter measurement

Each of the fibre bundles contained approximately 4-10 single fibres (SEM picture shown in Figure 3.14). This was the reason why the bundle diameter ranged from 33µm up to 310µm depending on how many fibres a bundle contained. Figure 4.7 bar chart shows the distribution of diameter of flax fibre. Major percentage of diameter was in the range of 50-199 µm, whereas diameter range above 200 µm was not very significant percentage.

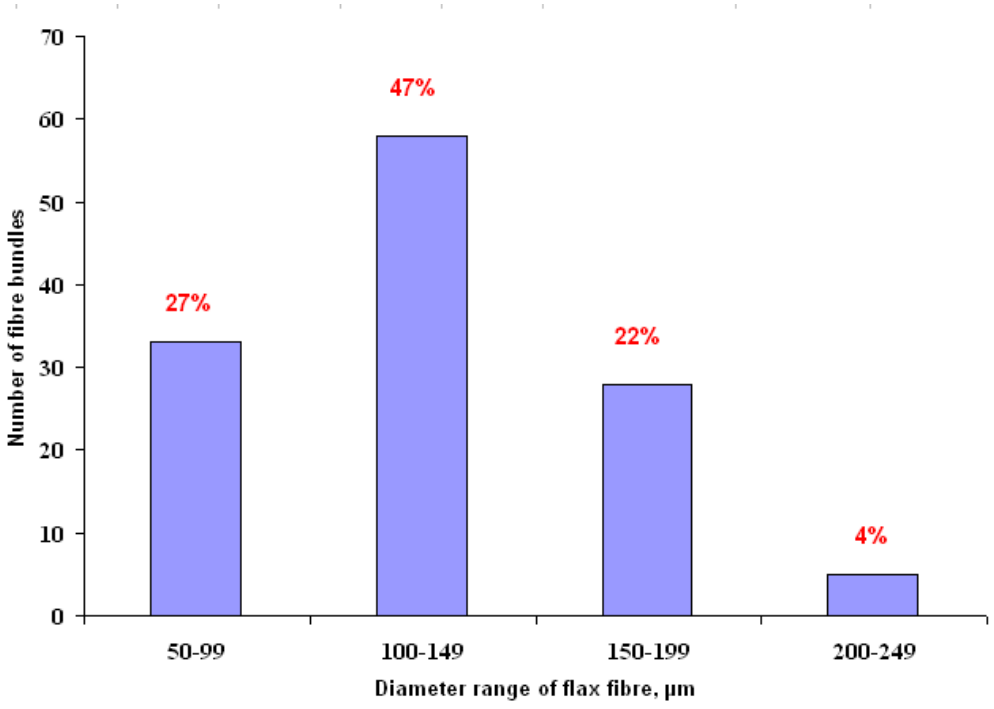


Figure 4.7 Diameter distribution of flax fibre

4.2.2 Measurement of tensile strength and elastic modulus

As stated earlier, the physical properties of flax are very important for the characterization of fibre. In this research, two different chemical treatments of flax had been used with three different drying methods. There were twelve different treatments depending on the combination of chemical treatment, drying method, and power level. Raw fibre (untreated and undried) was also taken as a control to compare with treated and dried fibres. A pre-test was done on 50 fibres to get a range of tensile strength and elastic modulus measurements for the fibre. The range obtained for tensile strength was 16 MPa to 667 MPa. It has been observed that the tensile strength of flax fibre decreased with the increase in diameter. The elastic modulus of fibre also decreases as the diameter of flax fibre increases. Same change can be seen for both untreated and treated fibres but no specific trend on elastic modulus and tensile strength was observed between the values and diameter. The elastic modulus obtained here was in the range of 2 GPa up to 63 GPa. These range of elastic modulus values found here were in good agreement with the values reported in literature (Baley, 2002; Davies et al., 1998; Ganster et al., 1999; Troger et al., 1998). However, the flax fibre used in this experiment was oilseed flax fibre which has more lignin and pectin and a more branched structure. There was also a possibility of more nodes on oilseed flax fibre than regular textile flax fibre, which was used in other reported research experiments.

The stress-strain curve (Figure 4.8) shows the behaviour of fibre under tension. Because the fibre bundle was composed of not only one fibre, but a bundle of 2-20 fibres, all the fibres in the bundle might not have broken at the same time (Figure 4.9).

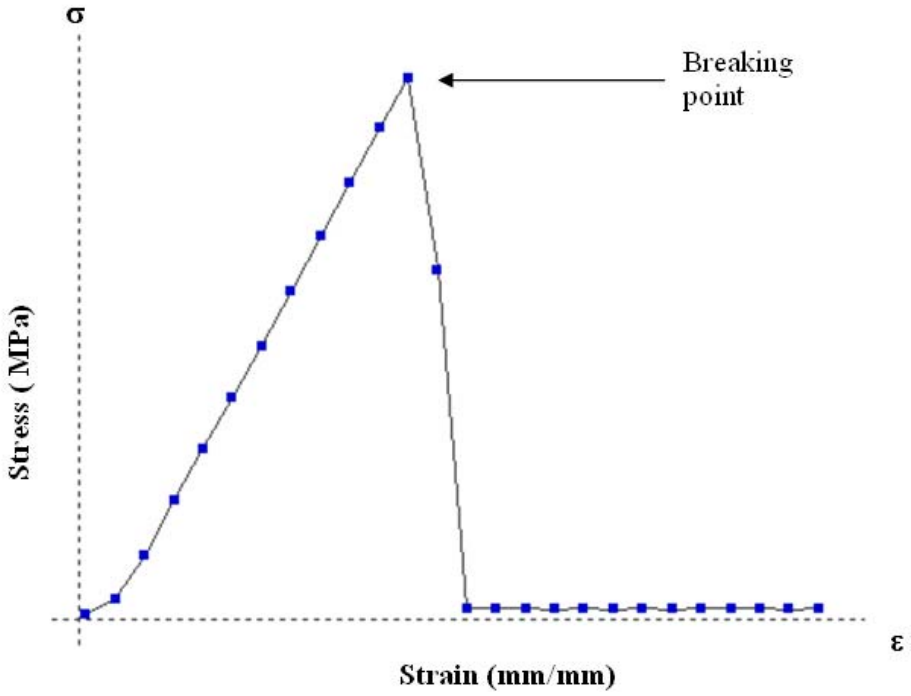


Figure 4.8 Stress ~ Strain curve for measuring tensile strength of dried flax fibre

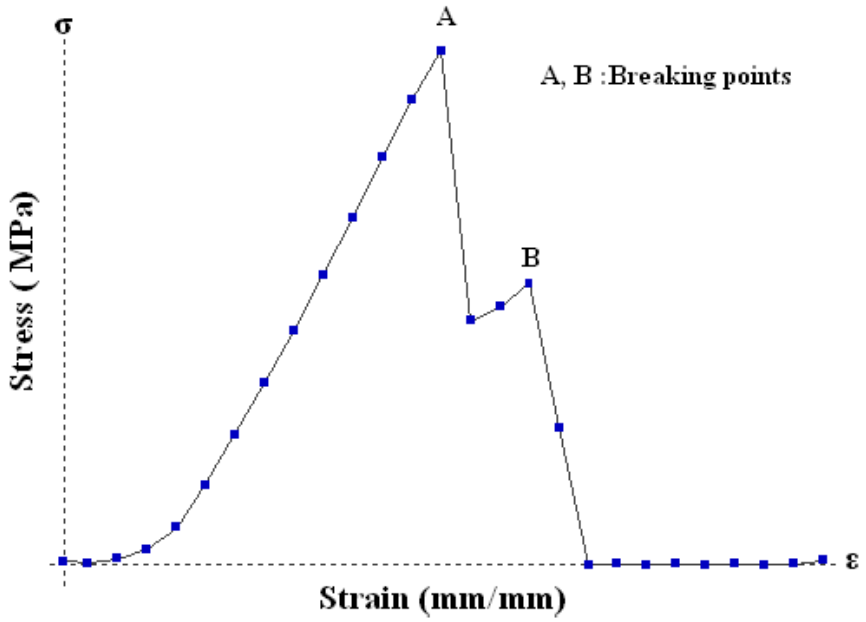


Figure 4.9 Stress ~ Strain curve showing more than one breaking points

In Figure 4.10 and 4.11 shows the tensile strength and elastic modulus of fibre of diameter ranges from 50-199 μm. The fibre diameters are grouped together with a range of 50-99 μm, 100-149 μm, and 150-199 μm in diameter. For ease of comparing and analysing the tensile strength and elastic modulus, data are grouped together within certain range. Since the fibre diameter varies from one to the other, it was difficult to get the same diameter to compare the tensile or elastic modulus property. If it is grouped within a range, it would be a better comparison. Figure 4.10 shows the tensile strength of treated and dried fibres of diameter ranges from 50-199 μm has almost equal or more tensile strength value than untreated fibre. For untreated fibre of diameter 50-99 μm range has an average value of tensile strength 231 MPa, whereas most of the sample with different treatments like Apx, Aqy, Bpx, Bqy, and Bqz are much higher values than untreated one. The tensile strength value of treatments such as Apy, Apz, Aqx, Aqz, Bpy, Bqx are less but closer. Although in bar graph, tensile strength of flax fibre look different, Tukey's HSD test showed that there was no significant difference between their mean of tensile strength (at $p=0.05$).

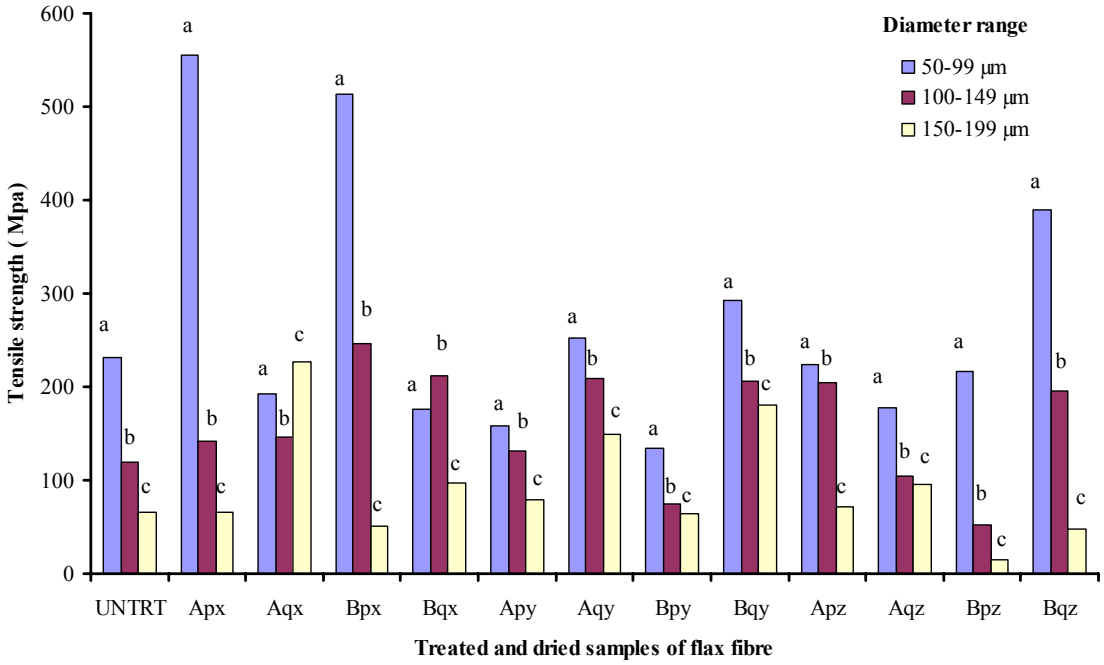


Figure 4.10 Tensile strength of treated and dried fibre of diameter ranges between 50-199 µm. (Legend: UNTRT- untreated and undried fibre (raw); A-alkali treated, B- silane treated; p- MW with P4, q- MW with P6; x - microwave oven dried, y microwave-convection, and z- microwave-vacuum dried).

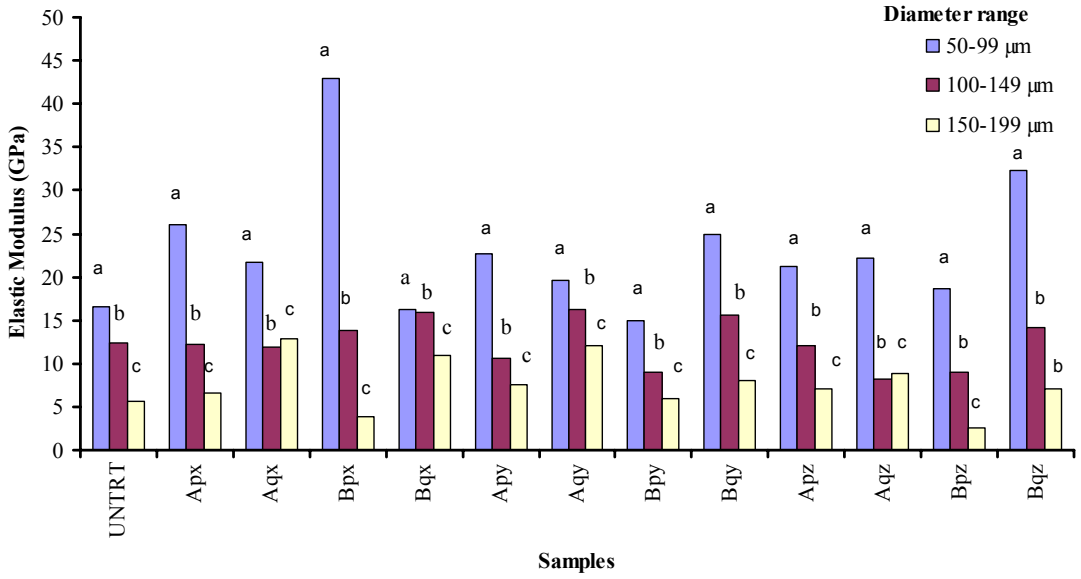


Figure 4.11 Elastic modulus of treated and dried fibre of diameter range between 50-199 µm. (Legend: UNTRT- untreated and undried fibre (raw); A-alkali treated, B- silane treated; p- MW with P4, q- MW with P6; x - microwave oven dried, y microwave-convection, and z- microwave-vacuum dried).

The elastic modulus of untreated fibre of diameter range 50-99 µm has a value of 17 GPa whereas all other treatments except Bpy and Bqx have much higher elastic modulus. Bpy and Bqx samples have smaller elastic modulus value (15 GPa and 16 GPa) but very close to untreated one.

4.3 Physical Properties Analysis

Colour is an important physical property in the process of the characterization of flax fibre. In industry, colour is an important criterion for developing different products. In case of biocomposite, manufacturer had always an issue with the colour of the fibre. If the colour of biocomposite is dark, it will reflect on the final product. So the colour analysis was carried out for different methods of drying flax fibre to determine the colour change for different drying conditions.

4.3.1 Colour analysis treated and dried fibre

The colour measurement was done to determine the effect of different drying methods and chemical treatments on the visual properties of treated flax fibre. The experiment results are shown in the Table 4.3. The colour index change (ΔE), change of L, a, b and subsequently the RGB colour shade were calculated (Table 4.4). The RGB colour shade was determined using OpenRGB program. Study shows that, after chemical treatment of flax fibre, the colour of flax fibre became lighter. It was visually observed that silane treated flax had a lighter colour than alkaline treated flax fibre.

Table 4.3 Colour values L, a, b with treatments.

Sample	L	SD	a	SD	b	SD	ΔE
UNTRT	61.41	0.90	2.38	0.13	10.66	0.22	
Apx	60.48	0.58	1.32	0.06	9.36	0.08	1.92a
Apy	57.96	1.12	1.28	0.04	9.85	0.02	3.71ab
Apz	55.76	0.95	1.45	0.12	10.51	0.20	5.73b
Aqx	58.11	0.35	1.17	0.06	9.53	0.14	3.69ab
Aqy	57.11	1.00	1.10	0.02	9.87	0.27	4.56b
Aqz	51.27	2.13	1.10	0.11	10.03	0.53	6.74c
Bpx	58.05	0.42	1.23	0.04	8.87	0.05	3.98bc
Bpy	59.66	1.17	1.30	0.09	9.52	0.12	2.35ab
Bpz	57.75	0.48	1.32	0.19	9.07	0.39	4.13b
Bqx	59.06	0.53	1.32	0.06	9.43	0.20	2.86ab
Bqy	56.48	1.49	1.39	0.06	9.30	0.33	5.22b
Bqz	58.47	0.64	1.27	0.06	9.07	0.30	3.53b

Legend: UNTRT- untreated and undried fibre; A-alkali treated, B- silane treated;
p- MW with P4, q- MW with P6; x - microwave oven dried, y microwave-convection, and z- microwave-vacuum dried.

After drying in a microwave environment, flax fibre became darker. The reason for being darker colour may be due to browning effect (Maillard reaction). The glucose or sugar from cellulose might be responsible for this reaction.

Table 4.4 RGB colour shade of untreated and treated and dried flax fibre sample

	R	G	B	Colour shades
UNTRT	184	161	148	
Apx	178	159	149	
Apy	172	153	141	
Apz	168	148	134	
Aqx	172	154	142	
Aqy	170	151	139	
Aqz	155	137	123	
Bpx	172	154	144	
Bpy	176	157	147	
Bpz	171	153	143	
Bqx	175	156	145	
Bqy	168	150	139	
Bqz	173	155	145	

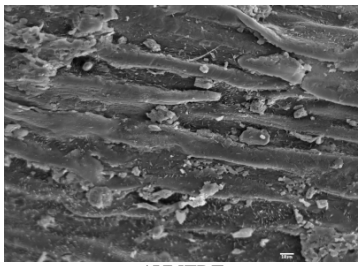
Legend: UNTRT- untreated and undried fibre; A-alkali treated, B- silane treated; p- MW with P4, q- MW with P6; x - microwave oven dried, y microwave-convection, and z- microwave-vacuum dried.

The colour value (L_0) of all the treated and dried fibre decreased compared to the untreated fibre. The lower colour value (L_0) signifies that the colour of fibre was changed from lighter to darker after chemical treatment and drying. When the microwave power level increase, the colour also relatively became darker. This may be caused by higher temperature drying conditions, however microwave-vacuum dried fibre which is dried at a low temperature had a darker colour than microwave and microwave-convectional dried fibre. Microwave-convection drying also resulted in a

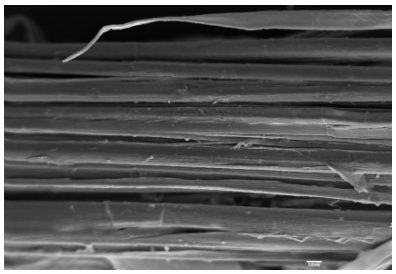
darker colour than microwave alone drying conditions. Microwave only drying conditions resulted in a lighter colour than any other drying method.

4.3.2 Morphological characterization (SEM)

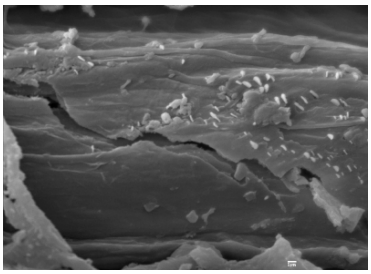
Scanning Electron Microscopy (SEM) analysis was performed on samples of dried fibre that had been subjected to different drying conditions. Fibre microstructure is very important for making the bio-composites. The physical and mechanical properties play an important role for the end product. Usually fibre is dried at a low temperature for a longer period of time but to accelerate the process, fibre was dried in a microwave environment. The heating is non-uniform inside the microwave chamber resulting in local hot spots in Figure 4.12-m). The SEM results showed that, after chemical treatment, untreated fibre which was full of waxy materials was almost cleaned. In the case of silane treated and microwave-vacuum dried sample (Bqz), some black spots appeared on the fibre which might be due to local heating. The black spots could be caused by heating in microwave for a prolonged period of time and with high power (MW with power P6). Because the vacuum lowers the boiling point of water, the fibre can be dried for a longer period for complete removal of water. Microwave power applied here was also high (MW P6), however other samples dried with less power (P4) did not develop local hot spots.



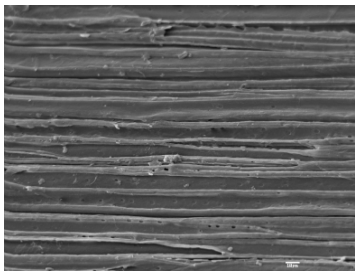
a)UNTRT



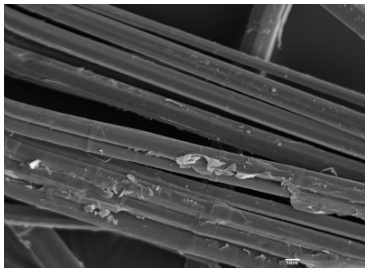
b) Apx



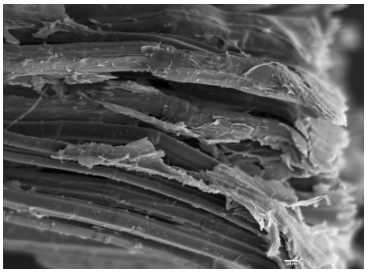
c) Apy



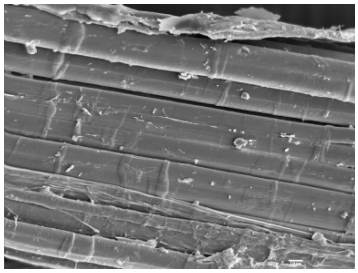
d) Apz



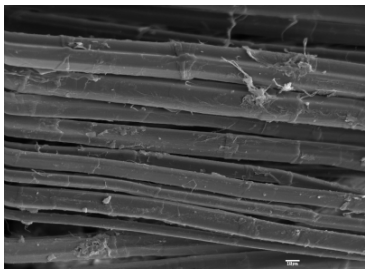
e) Aqx



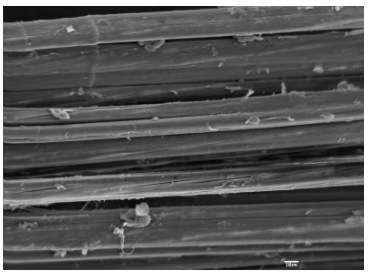
f) Aqy



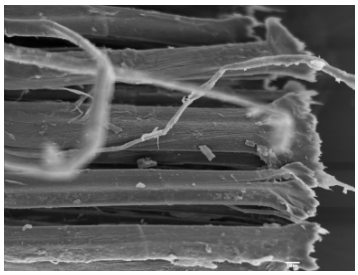
g) Aqz



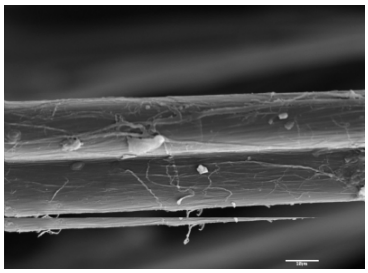
h) Bpx



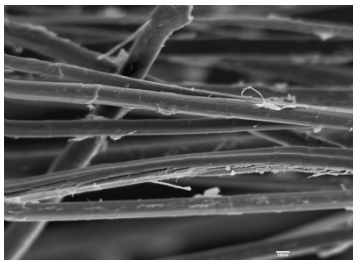
i) Bpy



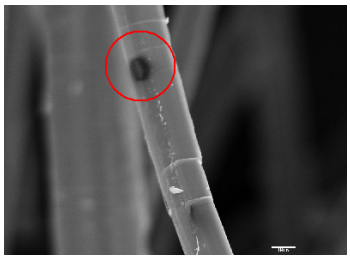
j) Bpz



k) Bqx



l) Bqy



l) Bqz

Figure 4.12 SEM images of untreated and chemically treated and dried flax fibre. Legend: UNTRT- untreated/undried fibre; A-alkali treated, B- silane treated; p- MW with P4, q- MW with P6; x - microwave oven dried, y microwave-convection dried, and z- microwave-vacuum dried.

4.3.3 Thermal characterization (DSC)

Differential scanning calorimetric data describes the nature of the melting point, water evaporation, and degradation temperature of the material. The first endothermic peak indicates the water evaporation temperature of the material (Ansari et al., 1999). These values ranged from 87°C to 135°C. This explains about how much moisture is present in the fibre after the chemical treatment and drying. The second exothermic peak plays an important role, because this temperature is very important at the time of processing of flax fibre. It is necessary to process below the degradation temperature of flax fibre when making the biocomposites.

Table 4.5 Exothermic peak of fibre samples conducted by differential scanning calorimetry

Sample	Degradation temperature (°C)		
	Average temperature	SD	SE
UNTRT	374.00c	5.57	3.21
Apx	378.24c	2.13	1.23
Apy	360.41a	4.06	2.35
Apz	356.88a	1.18	0.68
Aqx	356.57a	1.59	0.92
Aqy	359.89a	0.41	0.24
Aqz	362.34ab	1.53	0.89
Bpx	373.89bc	2.01	1.16
Bpy	375.36c	1.51	0.87
Bpz	377.15c	6.31	3.64
Bqx	375.67c	6.64	3.84
Bqy	372.22bc	5.29	3.06
Bqz	376.94c	4.54	2.62

Legend: UNTRT- untreated and undried fibre; A-alkali treated, B- silane treated; p- MW with P4, q- MW with P6; x - microwave oven dried, y microwave-convection, and z- microwave-vacuum dried. Same letters in the same column are not significantly different at 95% confidence interval (P=0.05)

Table 4.5 shows the degradation mean temperature of flax fibre which ranged from 356.57°C to 378.24°C. The degradation temperature of cellulose falls between 315-400ºC as reported by Yang et al. (2007). The silane treated dried fibre shows a higher

peak than alkali treated fibres. The degradation temperature of lignin is 250-550ºC. The degradation temperature of hemicelluloses is 200-260ºC (Schniewind and Arno, 1989). The peak shown before 300ºC might be due to the lignin decomposition which shows there was still some lignin left after the chemical treatment of the fibre.

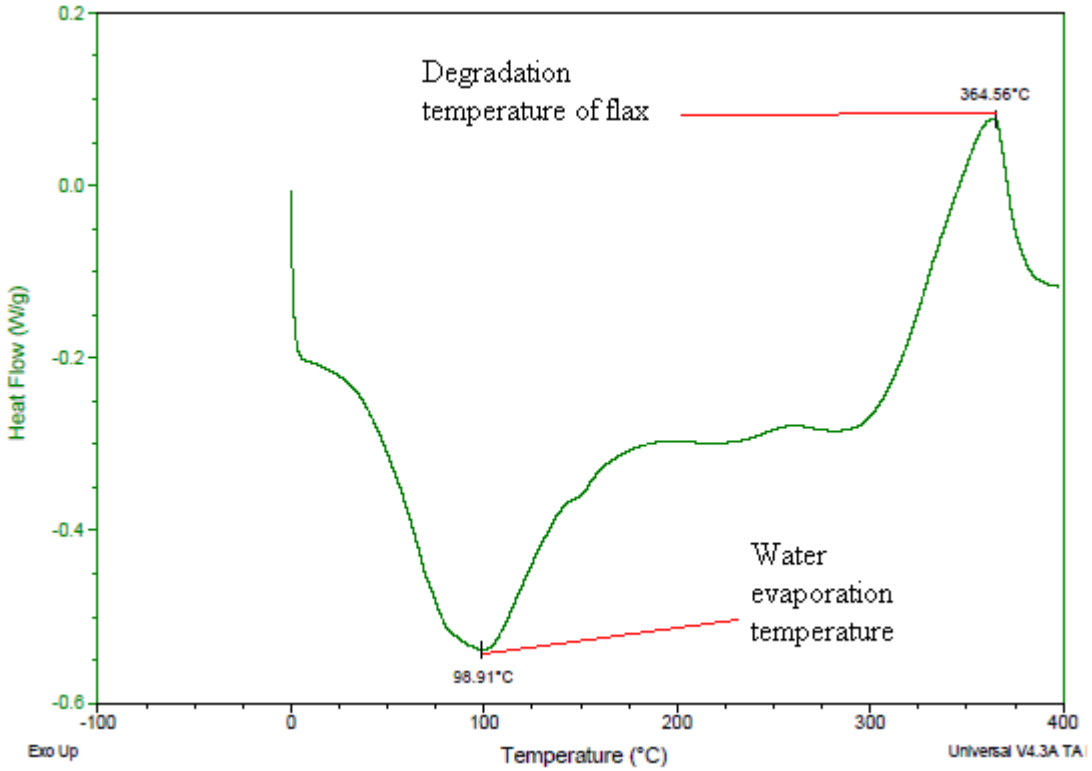


Figure 4.13 Thermogram of alkaline treated flax fibre dried with MW-combination power P4 (Apy)

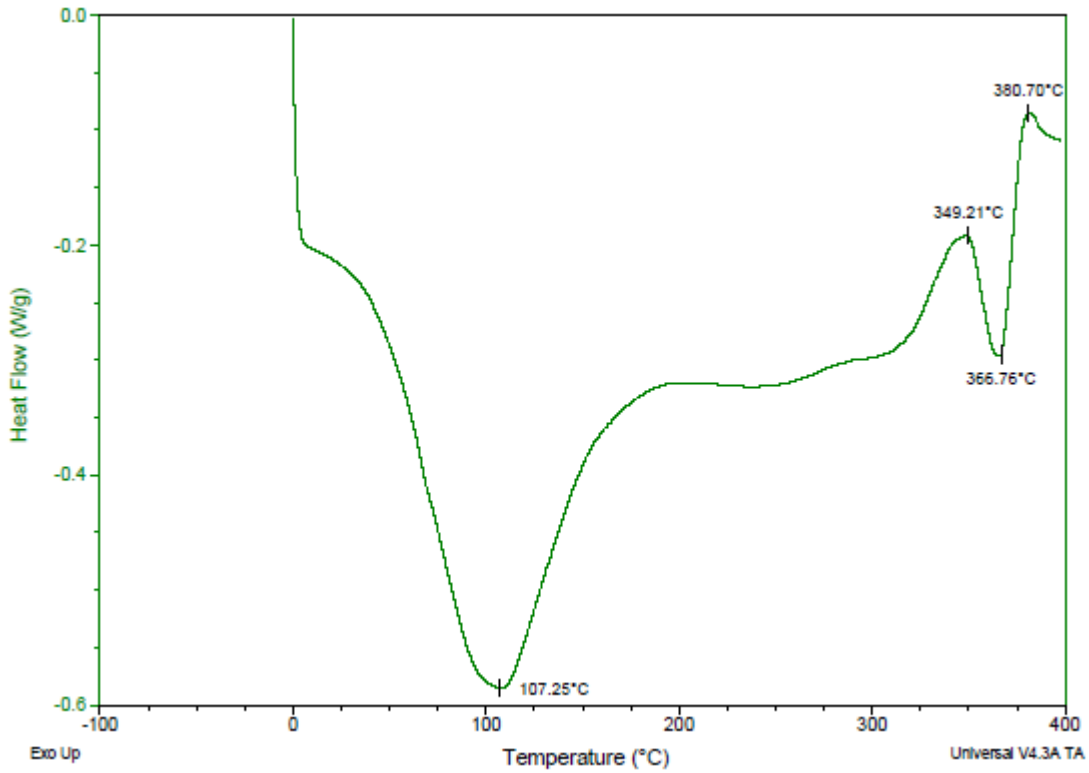


Figure 4.14 Thermogram of untreated flax fibre with endothermic and exothermic peaks (UNTRT)

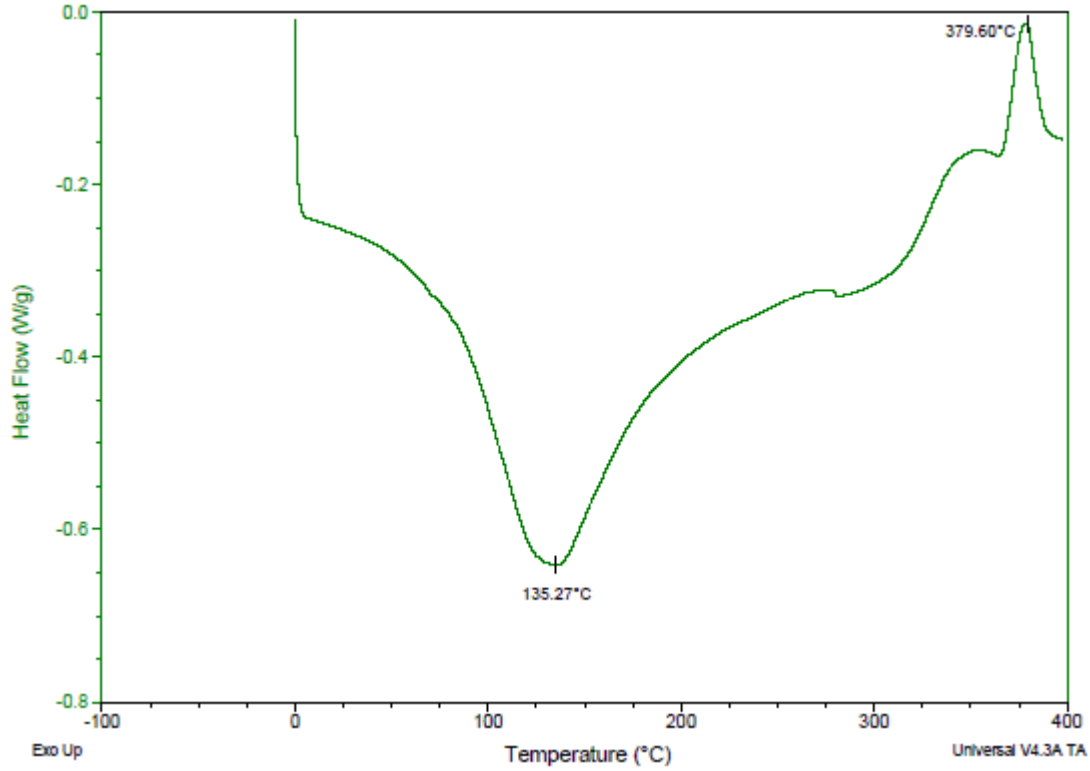


Figure 4.15 Thermogram of alkaline treated flax fibre dried with MW only power P4 (Apx)

In Figure 4.13 shows the graph of degradation peak; this shows part of the material degrading at higher temperatures. According to literature, degradation happens in a temperature range. The alkali treated fibre shows the lower peak than silane treated fibre. This might be because of silane created a layer on surface of fibre; the bound water evaporation takes more energy to degrade the cellulosic component of fibre. Figures 4.13-4-15 and Appendices C.1-C.10 show the endothermic and exothermic peak of flax fibre of different samples. The first peak close to 100ºC was due to the evaporation of water as shown in Figure 4.13 (98.91ºC). The second peak at 364.56ºC was the degradation temperature of fibre, most likely cellulose that falls in the range of cellulose degradation temperature.

Tukey's HSD test (Table 4.5) shows that, there was no significance difference between degradation temperatures of silane treated fibres. For alkali treated fibres, except the microwave treated fibre with power P4 has no significant difference with untreated fibre. It also shows that, the alkali treated fibre has lower degradation peak (cellulosic degradation) temperature than the silane treated fibres.

CHAPTER 5

SUMMARY AND CONCLUSIONS

Oilseed flax fibre was dried using three different methods: microwave, microwave-convection, and microwave-vacuum. The flax fibre was treated chemically with alkali and/or silane and dried with three different drying environments stated above. The conclusions were drawn based upon the experimental results and divided according to specific objectives.

5.1 Evaluation of Drying Characteristics Using Microwave, Microwave-convection, and Microwave-vacuum:

1. Thin layer drying models were fitted to the drying data of three microwave drying environments. The Page model is suitable for most of the drying conditions (i.e. samples: Apx, Aqx, Bqx, Apy, Aqy, Bqy, Apz, Bpz, Bqz). The Two-term fits well with (i.e. samples: Bpx, Aqz, Bpy).
2. Moisture content decreased gradually in the process of microwave-vacuum drying during all the phases (initial falling and constant rate drying period) however sharp changes were observed in the case of microwave and microwave-convection drying.
3. Moisture ratio trend for microwave condition explained decreased linearly throughout drying of the material. In the case of microwave-vacuum, it is sharp but at the end of drying process. It takes longer time to dry the fibre and since the temperature is maintained low, the chance of burning is low.
4. In the case of drying time, MW drying took the least time and MW-vacuum took the maximum time as detailed in Table 4.1., but the minimum moisture content was less

than 1%. The microwave drying took more time than MW-convection drying and less than MW-vacuum. The MW could dry the fibre to the minimum moisture level, but it could burn the fibre and create more localised hot spots. Flax fibre cannot be dried with a microwave for longer duration power and P6; the temperature could exceed beyond 130 °C, which is not a favourable condition for fibre drying.

5.2 Study of Physical Properties

1. Tensile properties

The results showed that the tensile strength and elastic modulus increase as the diameter decreases for treated and untreated flax fibres, which confirms the results of Baley (2002). It also stated in literature that elastic modulus along the fibre axis decreases with increase in spiral angle, and increases linearly with cellulose content. The results are in close agreement with the ones reported by Baley (2002).

2. Colour

After chemical treatment, flax becomes lighter. However, after the flax is dried using the microwave, the treated flax fibre becomes darker than untreated one. This is due to the longer exposure time during microwave drying. The flax that was exposed the most had the darkest colour. Microwave dried fibre had the least colour change; microwave-vacuum had the maximum.

3. SEM

Flax fibre exposed to microwaves usually developed hot spots due to non-uniform distribution of heat. Sometimes, these spots were not visible to the naked eye. The scanning electron microscopy can reveal the morphology of dried fibre and shows the microstructure which may be affected due to local heating (Figure 4.12-m). The temperature of drying in MW-vacuum is very low (50ºC in P4 and 70ºC in P6), however, localised dark spots are observed in a MW-vacuum dried fibre. That might be

due to exposure of microwaves for a longer period and might be result of transfer of lignin and pectin components to the outer surface.

4. DSC

Differential scanning calorimetry (DSC) showed the thermal behaviour of the material. The degradation temperature was lower in case of alkali treatment than in case of silane treatment. So, silane treated fibre seems to be more stable and more suitable in processing the biocomposite.

5.3 Overall Comparison of Drying Methods

Microwave-vacuum drying is one of the suitable methods considering the removal of moisture content up to and less than 1% (d.b.) and time taken to dry the product. Mechanical properties such as tensile strength and elastic modulus were not too much degraded after drying the fibre. MW-vacuum dried fibre can be used for biocomposite where colour is not a concern.

It was found that there was a maximum temperature rise in microwave drying condition, whereas the other two drying conditions; microwave convection and microwave-vacuum had a lower rise in temperature. The temperature rise using microwave power P4 was less than the temperature rise using power P6. Because the boiling point is low in an MW-vacuum oven, it showed the minimum rise in temperature (the minimum temperature was maintained around 50°C in case of MW-vacuum oven). In case of MW and MW-convection drying, the average temperature range of the material was 70-90°C with a maximum temperature of 120°C. Therefore by considering all above facts, the MW-vacuum drying method is the most suitable method for drying of flax fibre.

CHAPTER 6

RECOMENDATIONS FOR FUTURE WORK

In this research, the drying characteristics of flax fibre with different drying methods have been studied. To understand fully, more in-depth study is required for a practical application of flax fibre in the industry. These are the recommendations drawn from this study, which will be beneficial for oilseed flax fibre application in the biocomposite industry;

- Energy consumption and economical benefits have to be measured for MW, MW-convection and MW-vacuum drying and should be compared with thin-layer drying method,
- Dried material has to be tested by making the biocomposites to observe the physical properties and identify the possible implementation in bio-composite industry. The final product has to be prepared to study strength and durability of the product, and it should be compared with the products prepared using the traditional (conventional air drying) method,
- Uneven distribution of heat has to be managed by using the rotating table in the microwave and rotating basket in the case of MW-vacuum,
- The temperature problem has to be resolved by installing fan to regulate temperature inside the microwave oven,
- Because the colour profile did not show a good result (dried fibre was darker than the original one), the implementation of dried fibre should be application

specific and should be used where colour is not a concern for the production of biocomposites

- Dielectric properties of flax fibre need to be determined to understand the heating absorption and dissipation qualities,
- Thorough study on temperature control has to be done, because temperature plays a big role in drying process and should be carefully monitored in order to keep the temperature rise within an allowable range.

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APPENDICES

APPENDIX A

Analyses of Variance (ANOVA)

Table A.1 Analysis of variance of Colour Index ΔE for Treated and Dried Flax Fibre

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	217.911(a)	11	19.81	8.414	0
Intercept	1435.273	1	1435.273	609.637	0
Chemical Treatment	0.219	1	0.219	0.093	0.763
MW Power Level	34.948	1	34.948	14.844	0.001
Drying Condition	72.144	2	36.072	15.322	0
Chemical treatment * MW Power Level	46.399	1	46.399	19.708	0
Chemical Treatment * Drying Condition	34.753	2	17.377	7.381	0.003
MW Power Level * Drying Condition	9.226	2	4.613	1.959	0.163
Chemical Treatment * MW Power Level * Drying Condition	20.221	2	10.111	4.295	0.025
Error	56.503	24	2.354		
Total	1709.688	36			
Corrected Total	274.414	35			

a R Squared = .794 (Adjusted R Squared = .700)

APPENDIX B

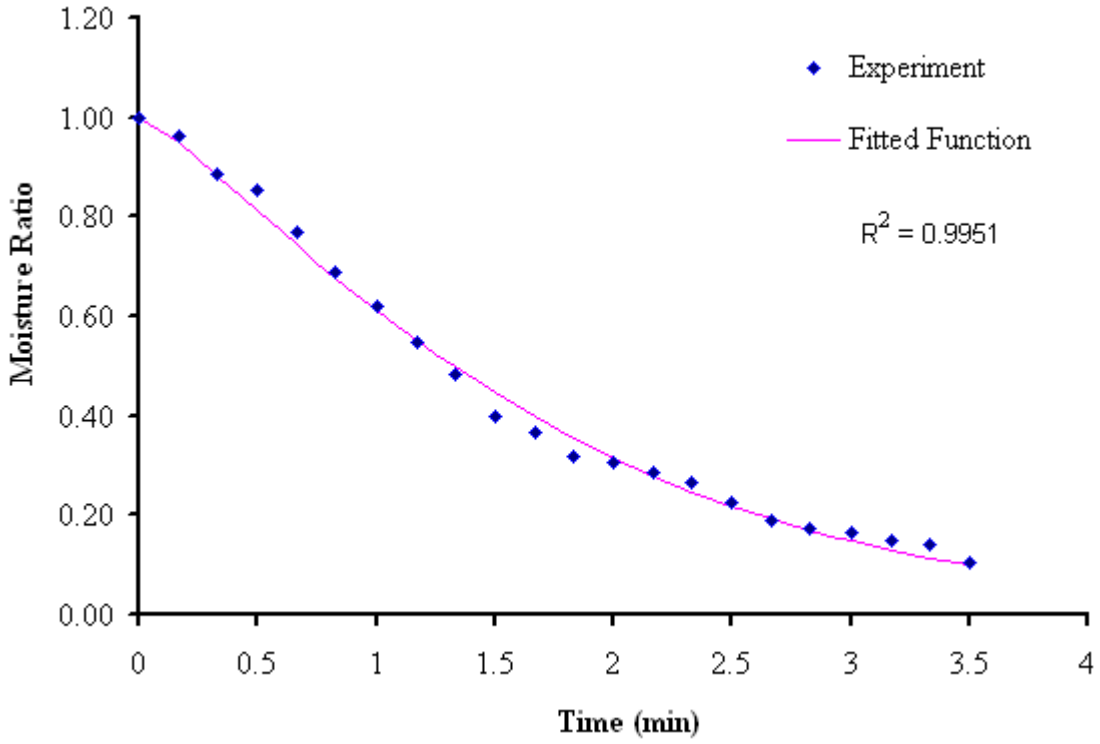

Figure B.1 Page model equation drying curve fit for alkali treated MW-P6 dried fibre drying (Aqx).

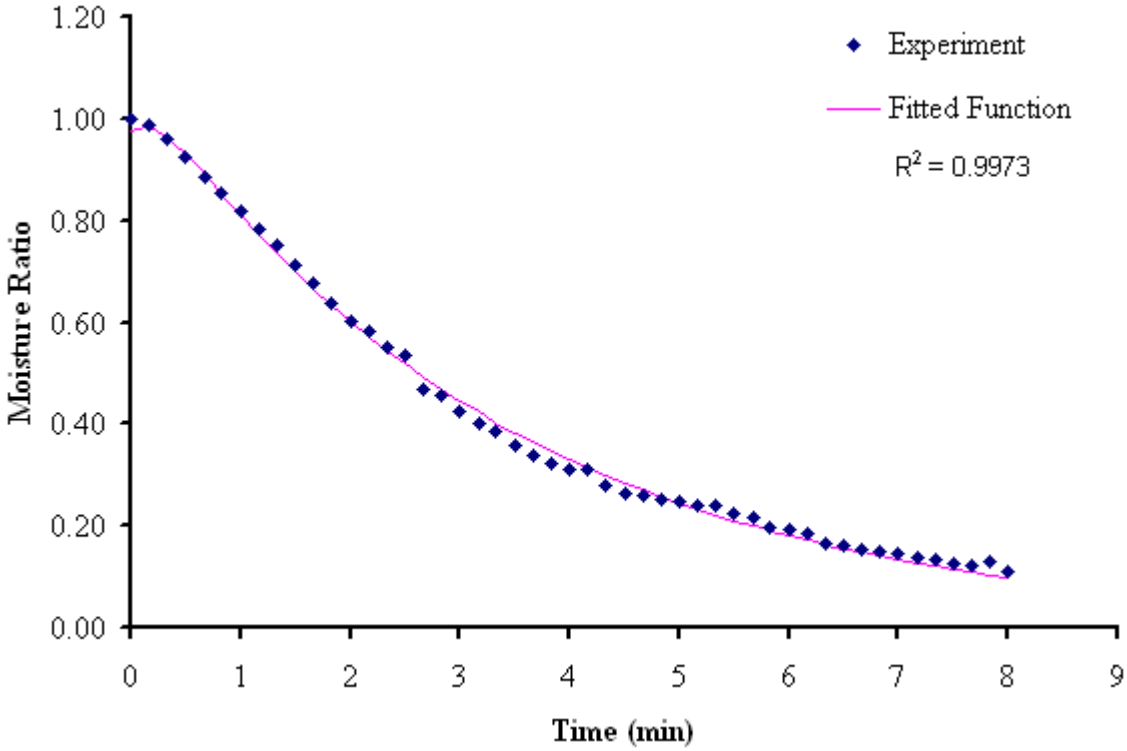

Figure B.2 Two term model equation drying curve fit for silane treated MW (P4) dried fibre drying (Bpx).

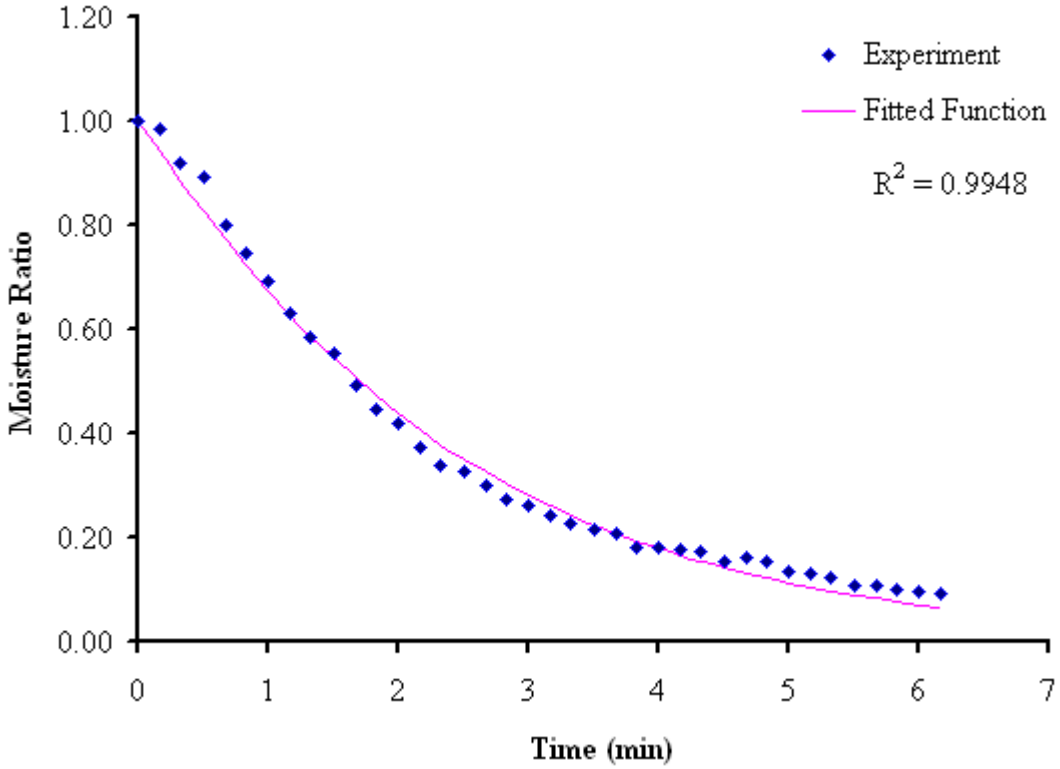

Figure B.3 Page model equation drying curve fit for silane treated MW (P6) dried fibre drying (Bqx).

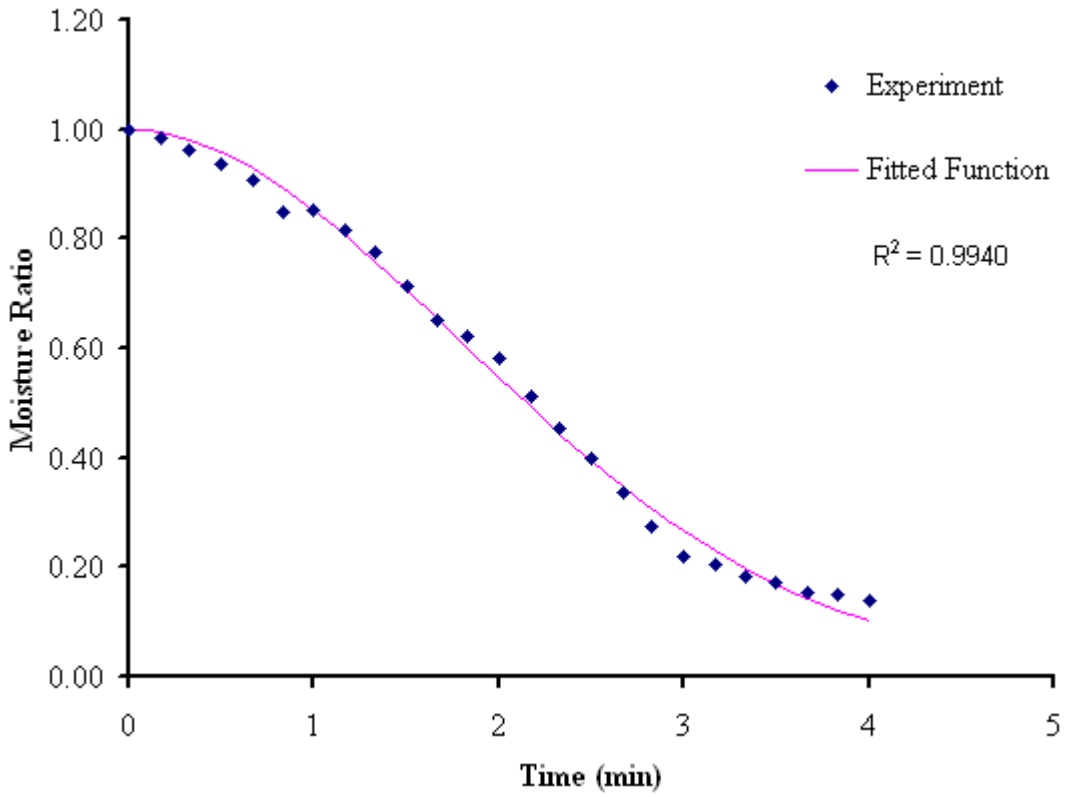

Figure B.4 Page model equation drying curve fit for alkali treated MW-combination (P6-convection) dried fibre drying (Aqy).

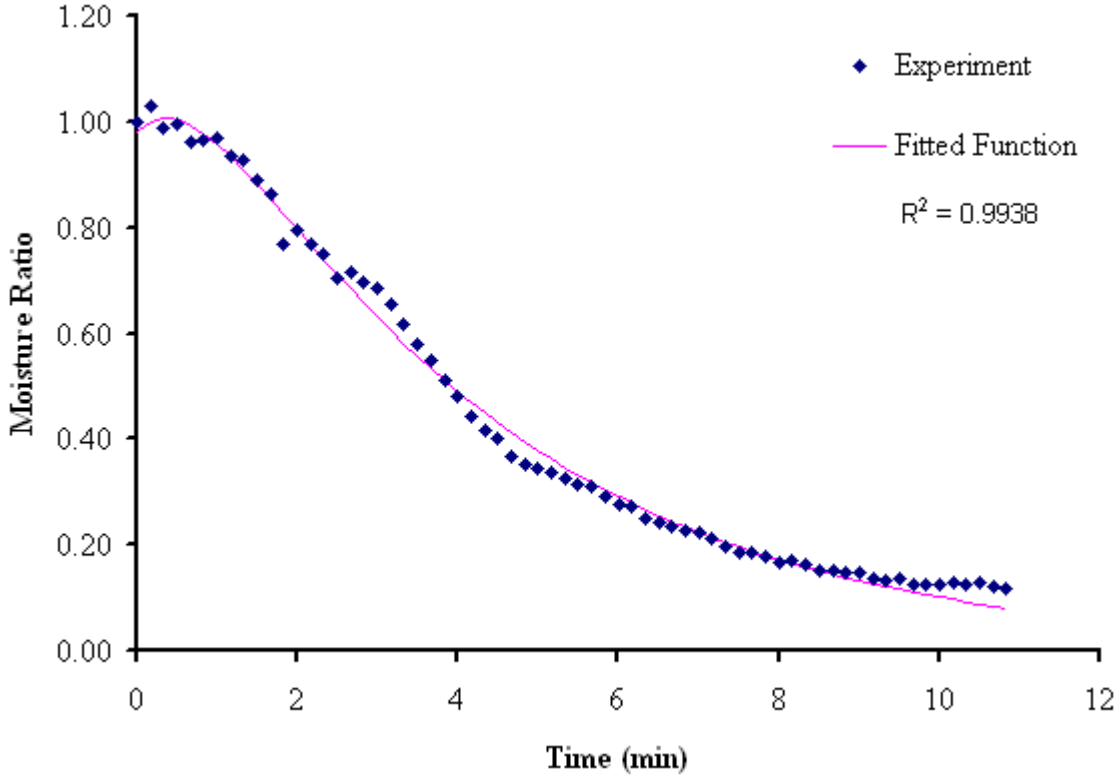

Figure B.5 Two term model equation drying curve fit for silane treated MW- convection (P4) dried fibre drying (Bpy).

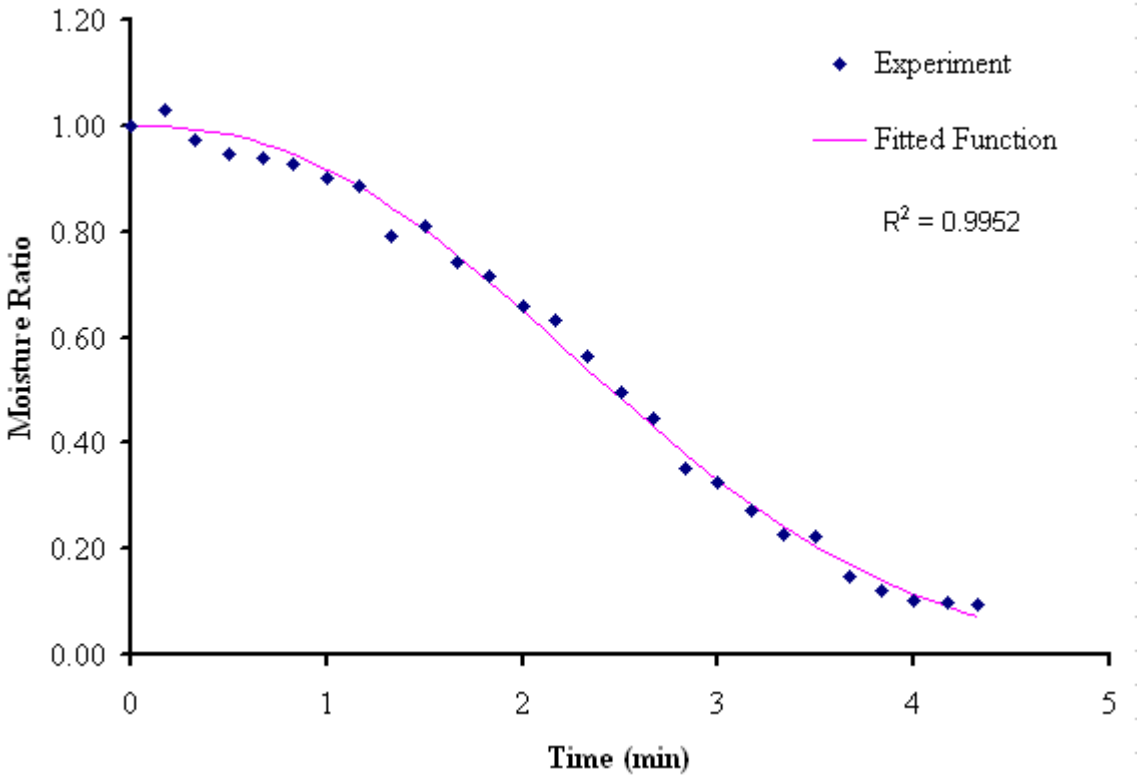

Figure B.6 Page model equation drying curve fit for silane treated MW-convection (P6) dried fibre drying (Bqy).

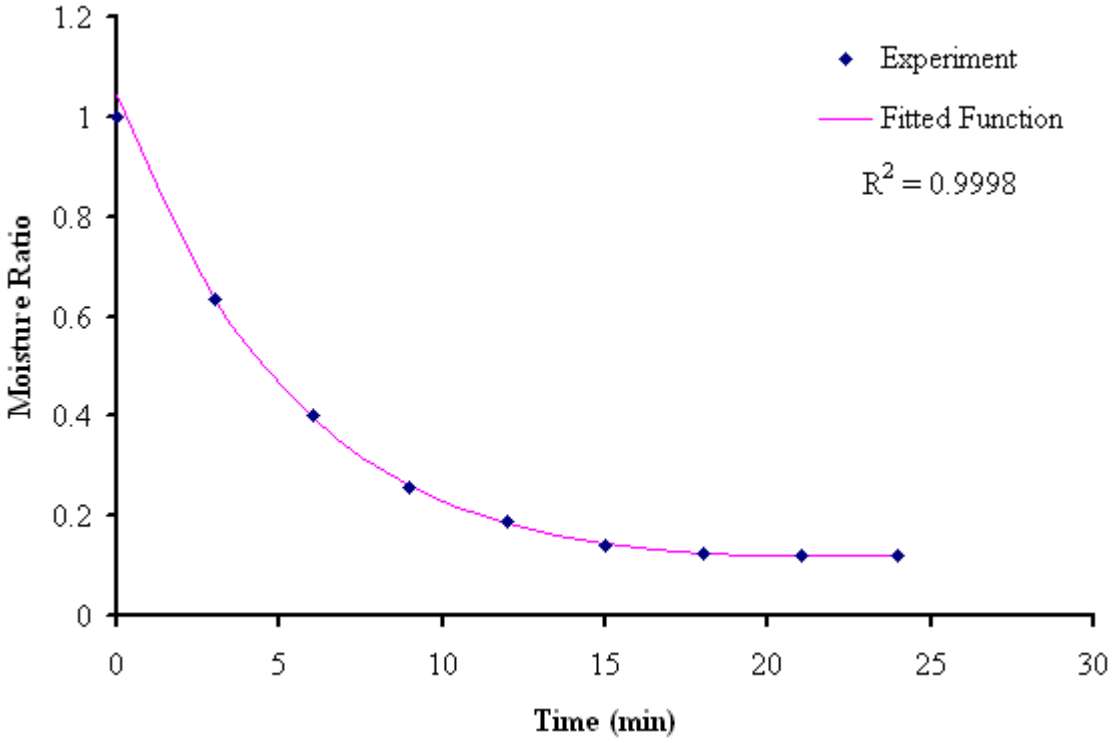

Figure B.7 Two term model equation drying curve fit for alkali treated MW-vacuum (P6) dried fibre drying (Aqz).

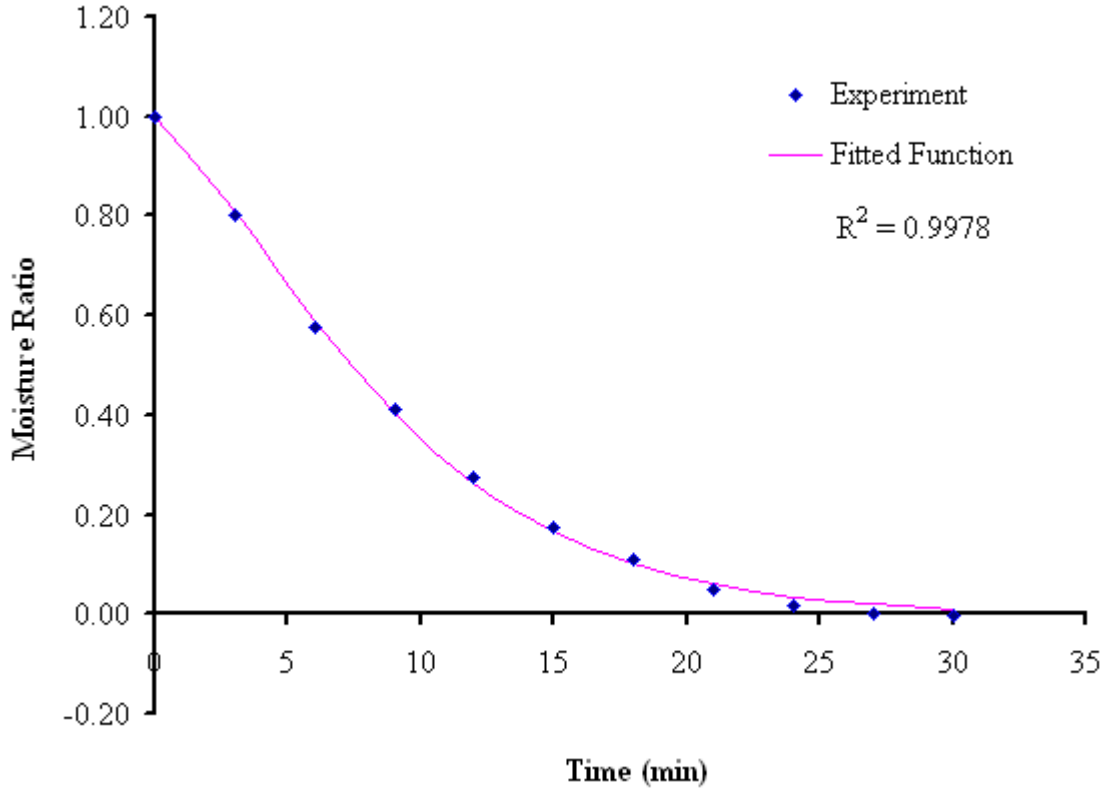

Figure B.8 Page model equation drying curve fit for silane treated MW-vacuum (P4) dried fibre drying (Bpz).

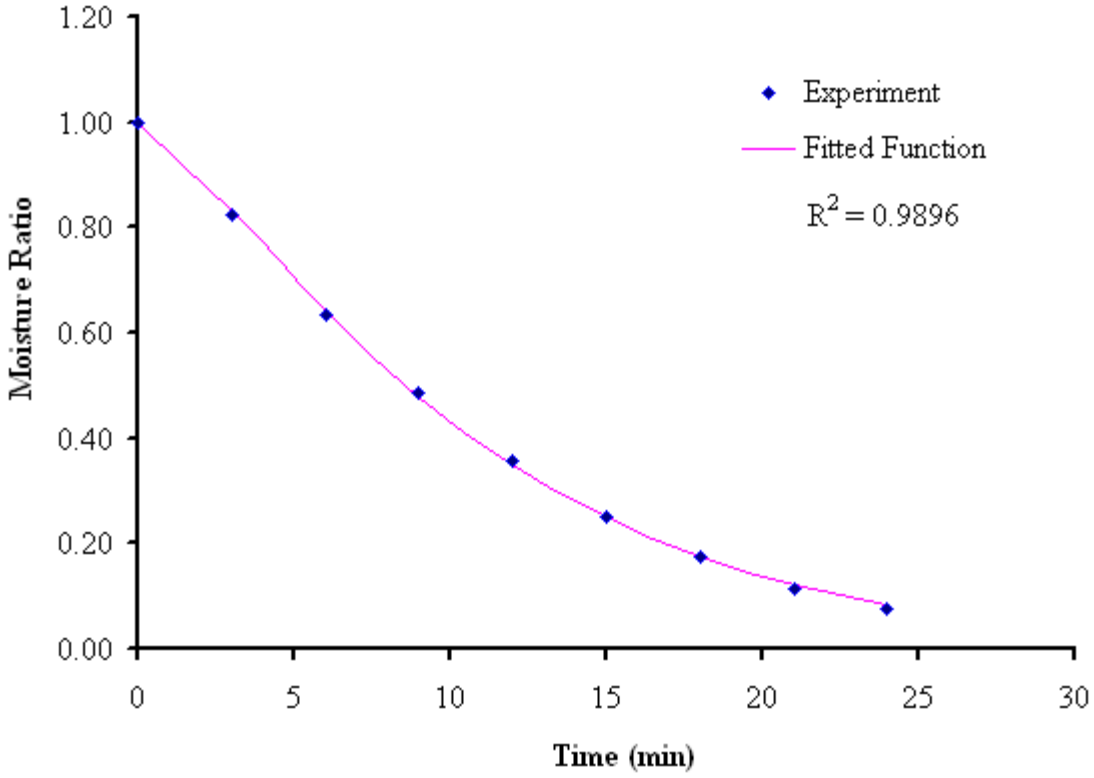

Figure B.9 Page model equation drying curve fit for silane treated MW- vacuum dried fibre drying (Bqz).

APPENDIX C

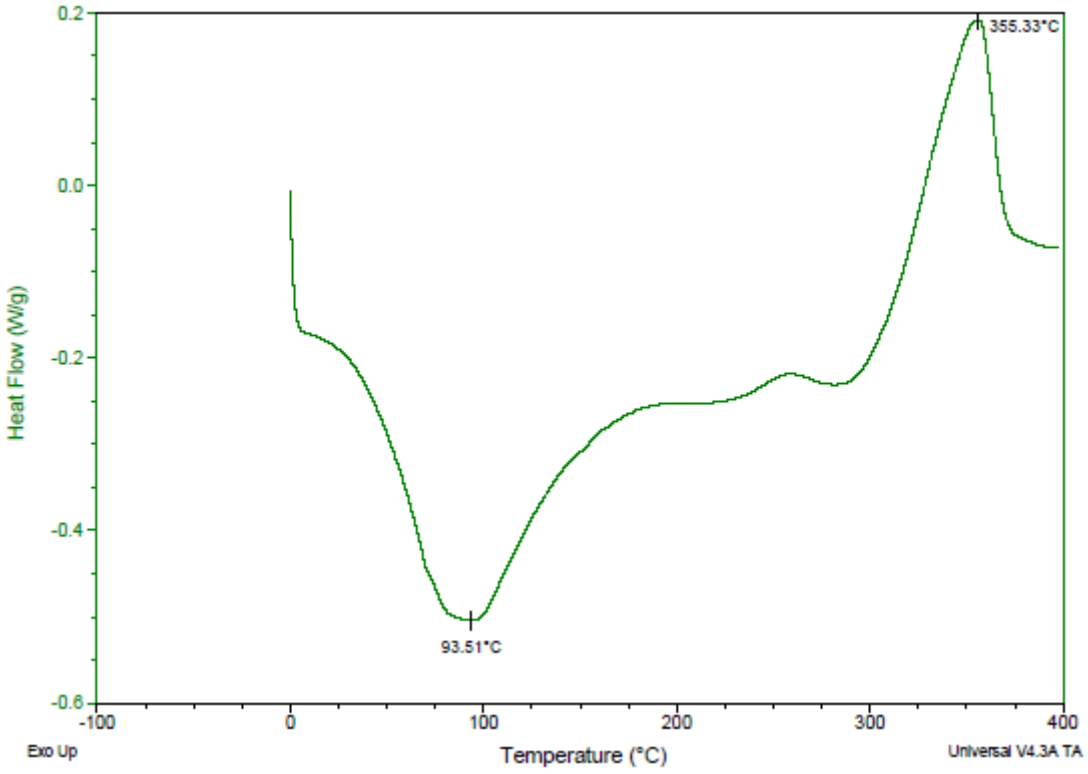

Figure C.1 Thermogram of alkaline treated flax fibre dried with MW only using power P6 (Aqx)

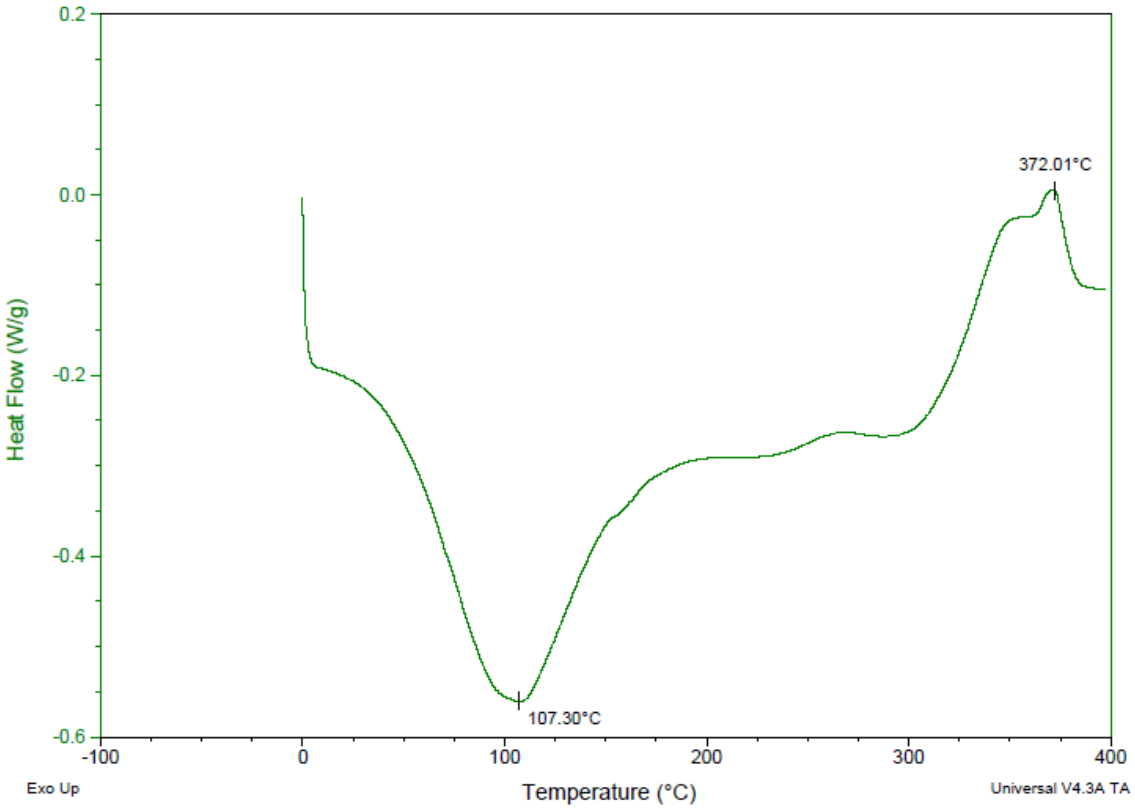

Figure C.2 Thermogram of silane treated flax fibre dried with MW only using power P4 (Bpx)

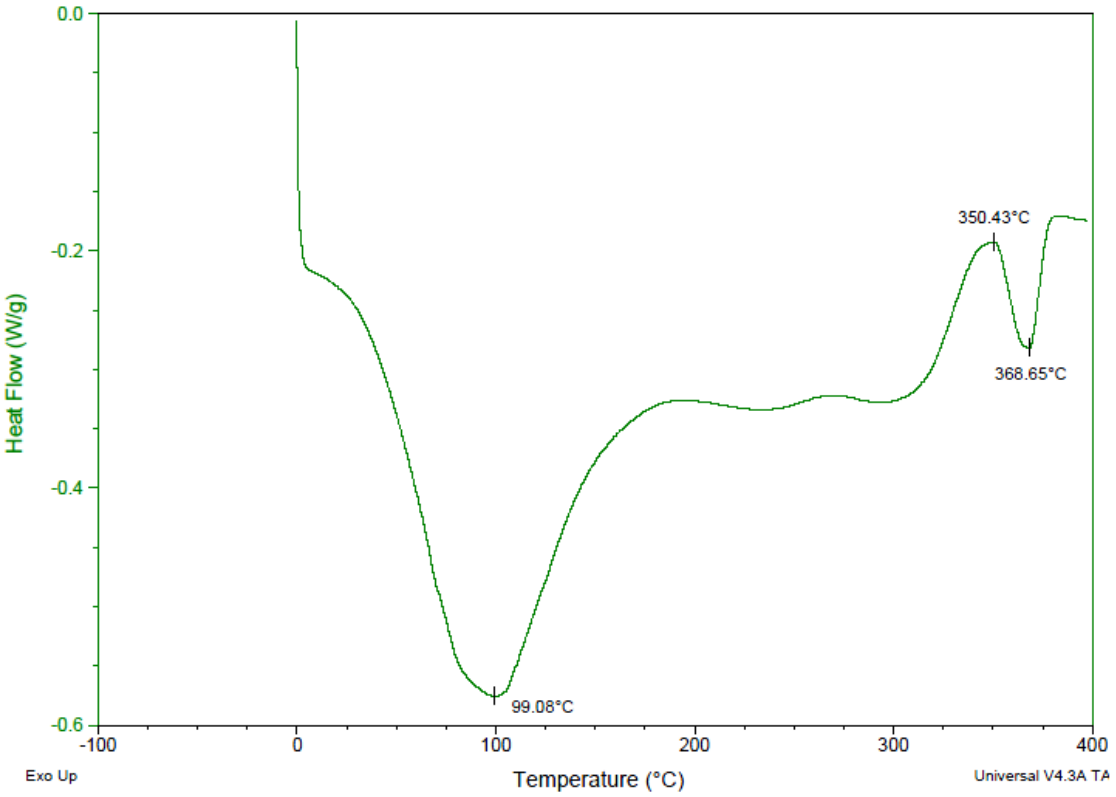

Figure C.3 Thermogram of silane treated flax fibre dried with MW-convection using power P6 (Bqx)

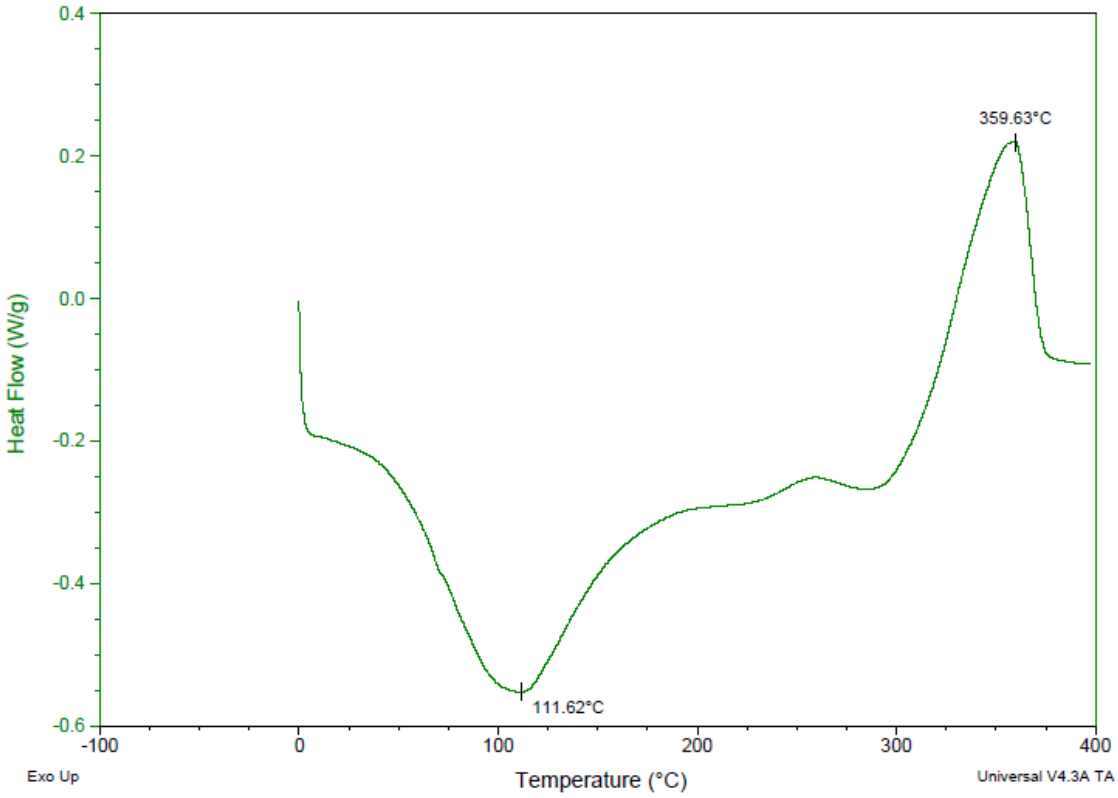

Figure C.4 Thermogram of alkaline treated flax fibre dried with MW-convection using power P6 (Aqy)

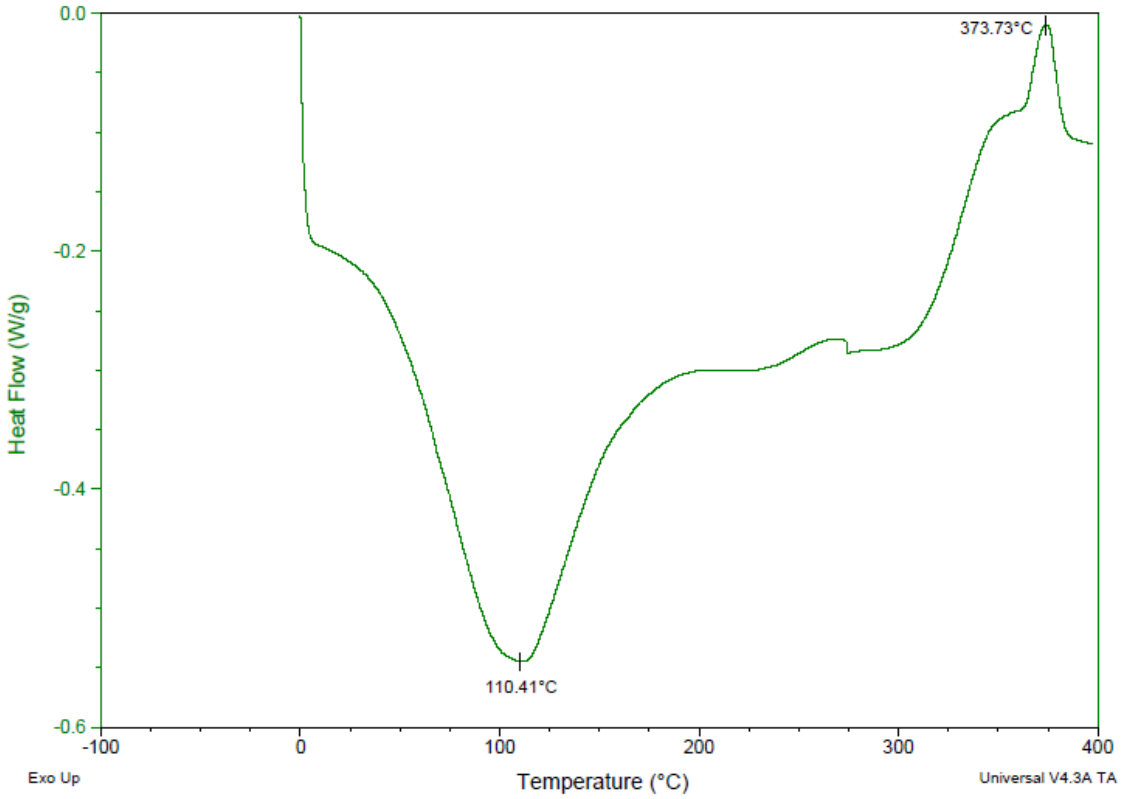

Figure C.5 Thermogram of silane treated flax fibre dried with MW-convection using power P4 (Bpy)

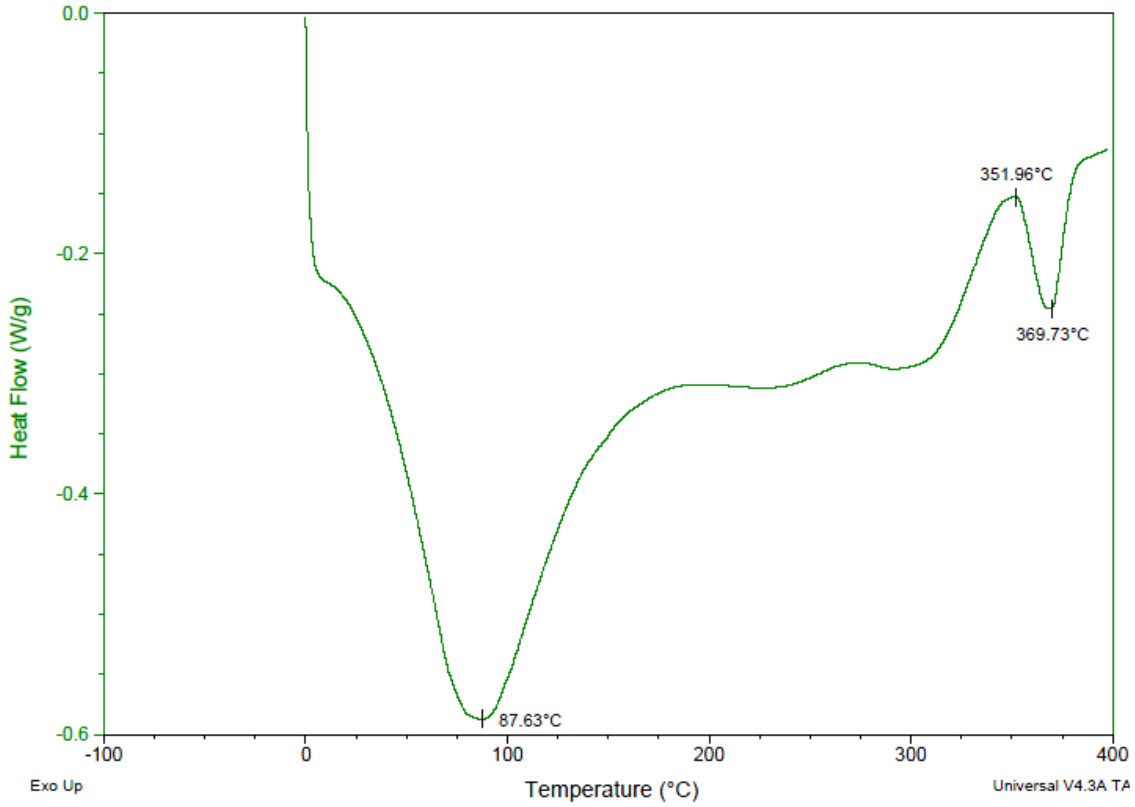

Figure C.6 Thermogram of silane treated flax fibre dried with MW-convection using power P6 (Bqy)

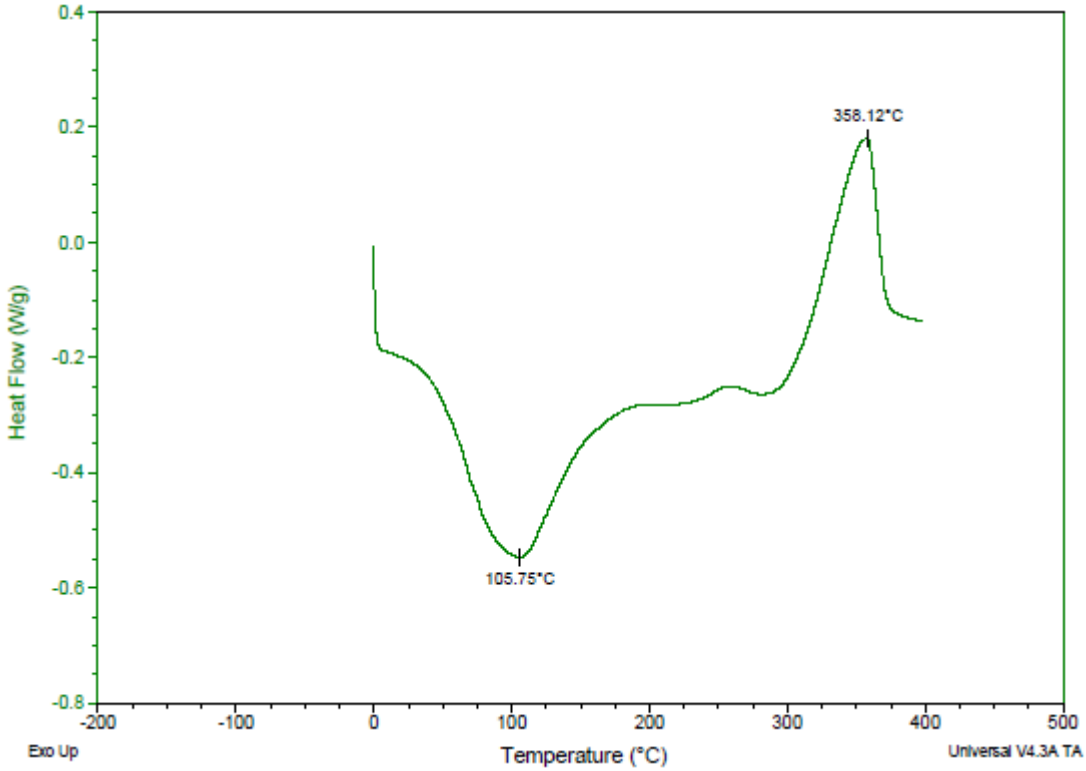

Figure C.7 Thermogram of alkaline treated flax fibre dried with MW-vacuum using power P4 (Apz)

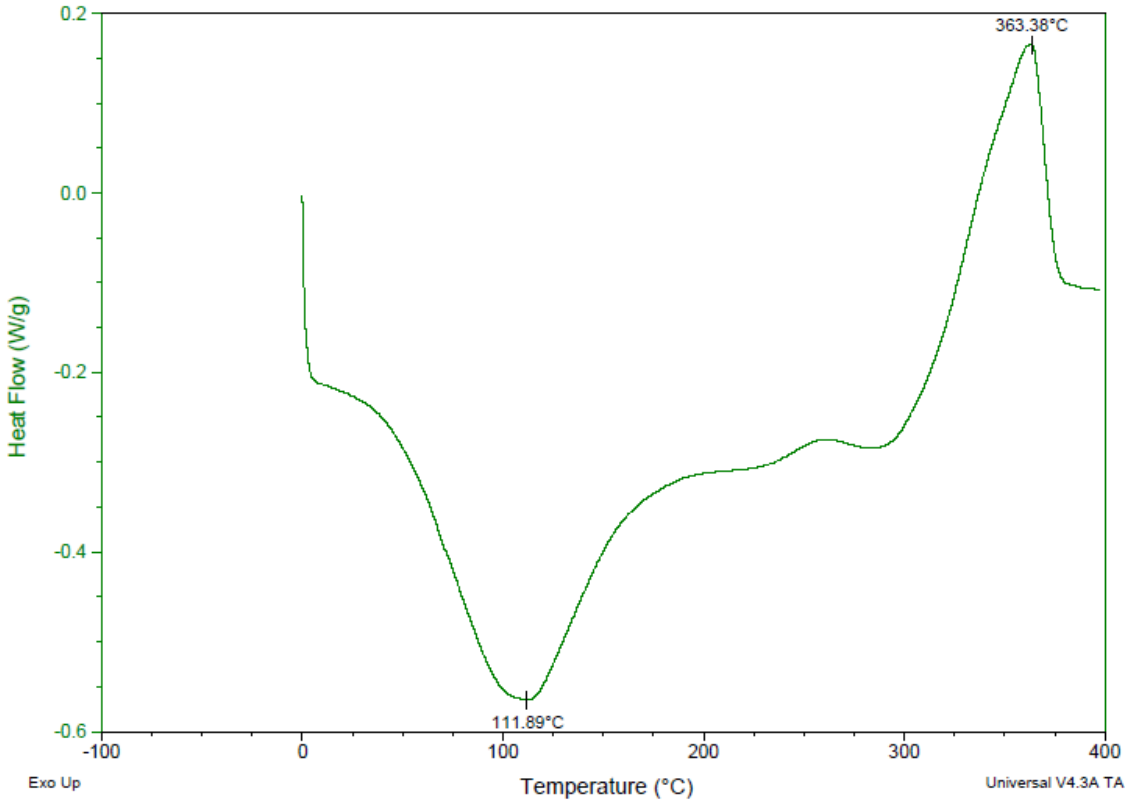

Figure C.8 Thermogram of alkaline treated flax fibre dried with MW-vacuum using power P6 (Aqz)

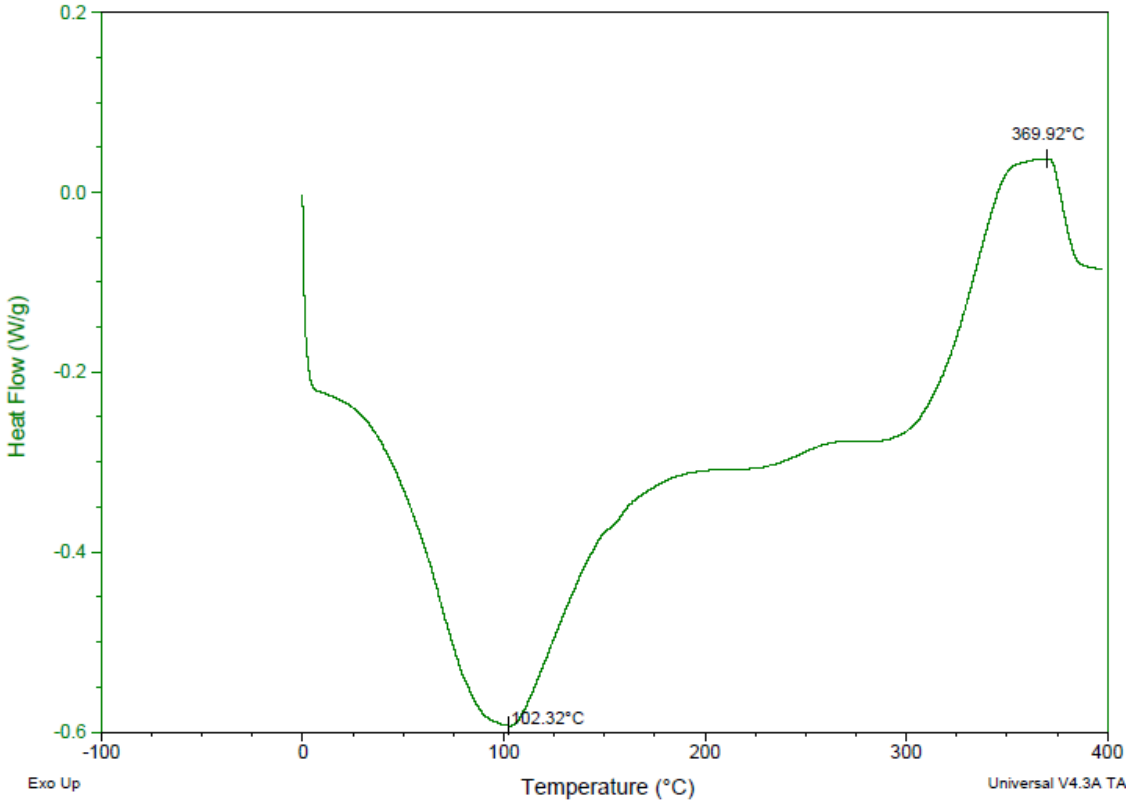

Figure C.9 Thermogram of silane treated flax fibre dried with MW-vacuum using power P4 (Bpz)

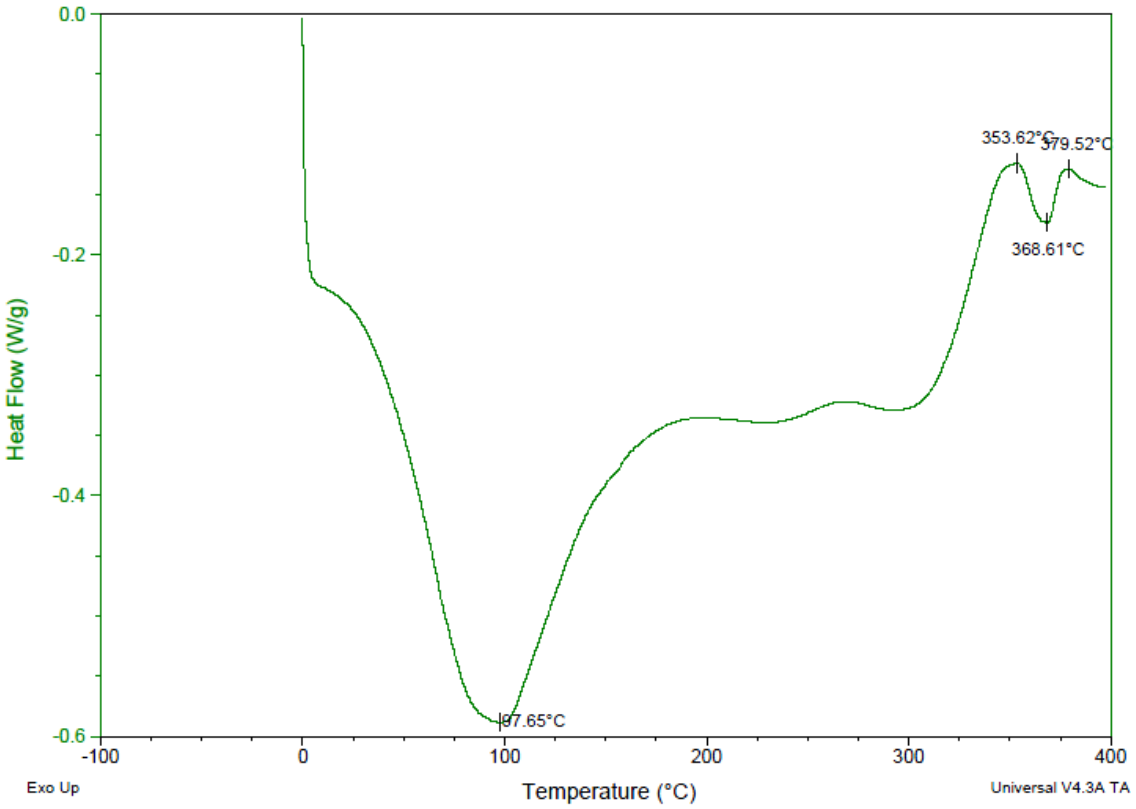

Figure C.10 Thermogram of silane treated flax fibre dried with MW-vacuum using power P6 (Bqz)