STUDIES ON NOVEL NATURAL FIBERS AND THEIR REINFORCED EPOXY COMPOSITES

Ph.D. THESIS

by

GIRDHARI LAL DEVNANI

DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY ROORKEE
ROORKEE - 247667 (INDIA)
MAY, 2019

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A THESIS

Submitted in partial fulfilment of the requirements for the award of the degree

of

DOCTOR OF PHILOSOPHY

in

CHEMICAL ENGINEERING

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ROORKEE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **"STUDIES ON NOVEL NATURAL FIBERS AND THEIR REINFORCED EPOXY COMPOSITES"** in partial fulfillment of the requirements for the award of the Degree of Doctor of Philosophy and submitted in the Department of Chemical Engineering of the Indian Institute of Technology Roorkee is an authentic record of my own work carried out during a period from July, 2016 to May, 2019 under the supervision of Prof. Shishir Sinha, Department of Chemical Engineering, Indian Institute of Technology Roorkee.

The matter presented in the thesis has not been submitted by me for the award of any other degree of this or any other Institute.

(Girdhari Lal Devnani)

This is to certify that the above statement made by the candidate is correct to the best of my (our) knowledge.

(Shishir Sinha)
Supervisor

The Ph.D. Viva-Voce Examination of Girdhari Lal Devnani, Research Scholar, has been held on .....

Chairperson, SRC **Signature of External Examiner**

This is to certify that the student has made all the corrections in the thesis.

Signature of Supervisor **Head of the Department**

Dated: _____

ABSTRACT

Recent economic development and technological growth are inspiring academicians and researchers to look for newer materials which can compete with cutting edge technology and at the same time should be sustainable and safe for environment also. Natural fibers reinforced in different polymer matrices are offering excellent mechanical and thermal properties that is why they are getting more and more attention in this decade as an alternate of synthetic fibers as reinforcement in composites. Traditional lignocellulosic natural fibers like bagasse, wheat straw, jute, sisal, coir, ramie, kenaf, sisal, hemp ,banana, pineapple, flax etc. have been extensively used and exploited as a reinforcement in various polymer matrix because of their biodegradability, easy availability, light weight and outstanding mechanical properties.

The major issues that are noticed with these lignocellulosic natural fibers are their hydrophilic tendency and their poor interaction with hydrophobic polymer matrix. Alkylation is the preferred choice for removal of hemicellulose and lignin to improve the compatibility between polymer matrix and these fibers.

On account of having excellent properties like high temperature stability and resistance to chemicals and corrosion, epoxy resin is preferred to be used as polymer matrix in a number of reinforced composites.

Researchers are looking for various new fibers as reinforcement in polymer matrix and a number of fibers have been tested as reinforcement in epoxy matrix for diverse applications. Alkali treatment is primarily used for the improvement of interaction and compatibility between fiber and matrix. Optimum concentration of alkali for treatment depends upon the nature of these new fibers. Present study is centered on the exploration of two new novel natural fibers/fillers, their extensive characterization and assessment of their suitability as reinforcement in Epoxy matrix

The Teff fiber is treated with different concentrations of alkali NaOH (5% and 10%) to improve the properties and the effect has been observed by Fourier transform infrared (FTIR) spectroscopy, Scanning electron microscope (SEM) analysis, X-ray diffraction XRD, Atomic force microscopy(AFM), Mechanical property tester and Thermogravimetric analysis. Flynn-Wall-Ozawa method (FWO), Kissinger-Akahira-Sunose method (KAS

method) and Friedman method have been used for calculation of activation energy of untreated and treated Teff straw. There is an increase of approximately 31% (280 to 368 MPa) in tensile strength and 21% (136 kJ/mol to 164 kJ/mol) in average activation energy in case of 5% alkali treated fiber as compare to untreated one. This treated fiber can be recommended as reinforcement in polymer composites for light weight applications.

Epoxy based composites reinforced with African Teff straw (*Eragrostis tef*) have been fabricated by simple hand lay-up technique with different fiber loading varying form 5% to 25%. The fiber surface is treated with 5% alkali and 10% alkali to improve the interaction between fiber and matrix. The mechanical, morphological, water absorption and thermal characterization of the untreated and treated, both types of composites have been done to analyze the properties and effect of surface treatment on prepared composites. Water diffusion mechanism has also been studied. Increase in tensile strength by 12% as compared to neat epoxy resin was observed in 5% alkali treated Teff straw based epoxy composites.

The fibers have been extracted from *Saccharum spontaneum* plant stem and subjected to various concentrations of alkali that is 3%, 5% and 7% to improve the properties. Untreated and alkali treated fibers have been characterized by Fourier transform infrared (FTIR) spectroscopy, Scanning electron microscope (SEM) analysis, X-ray diffraction XRD, Atomic force microscopy(AFM), Mechanical property tester and Thermogravimetric analysis (TGA/DTG).Flynn-Wall-Ozawa(FWO), Kissinger-Akahira-Sunose (KAS) and Friedman methods were used to observe the activation energy and thermal kinetics of these fibers before and after treatment. The 5% alkali treated fibers exhibit maximum increase in activation energy that is from 145 KJ/mol to 244 KJ/mol as compared to untreated fibers. Similar improvements are observed in tensile strength of fibers (from 280 to 400 MPa), modulus, crystallinity index, surface roughness and thermogravimetric analysis.

Filler of different sizes that is 0-500 μm, 500-1000 μm and 1000-1500 μm, have been successfully utilised as a reinforcing material in epoxy matrix. Comparable tensile and flexural strength with neat epoxy for 10% and 15% filler loading and 500-1000μ particle size has been obtained. Flynn-wall-Ozawa method has been applied for calculation of activation energy of pure epoxy sheet and its composites reinforced by Kans grass filler at optimum

loading of 15% and optimum size of 500-100 μm. It was found that pure epoxy sheet has an average activation energy of 192 kJ/mol while reinforcement with 15% loading of Kans grass filler having size of 500-1000 μm increased the activation energy from 192 to 227 kJ/mol.

ACKNOWLEDGEMENT

I express my sincere gratitude to my supervisor Prof. Shishir Sinha, Department of Chemical Engineering, Indian Institute of Technology Roorkee, for his help, logical suggestions, motivation and encouragement during the planning and execution of the research work reported in this thesis. He has always been a constant source of inspiration and motivation. I have learned so many things not only related to academics but also related to administration and personal affairs from him and I hope, this work partially satisfies his expectations.

Besides my supervisor, I would like to thank the rest of my Research committee: Prof. B.Prasad, Dr. Prakash Biswas and Dr. Inderdeep Singh for their valuable suggestions and encouragement.

My sincere thanks to all the faculty members of the Chemical Engineering Department at Indian Institute of Technology Roorkee and in particular, Dr. V.C Srivastava for their help and co-operation

A deep sense of admiration acknowledged to the Head, Institute Instrumentation Centre (IIC) and Mechanical Engineering department for their help in extending the necessary facilities during the course of characterization work. Special thanks to all the IIC technical staffs members for giving their full co-operation for all the characterization facilities.

I am thankful to the staffs of Chemical Engineering Department especially Mr. Vipin Ekka, and technical staff of Mechanical and Industrial Engineering Department especially Mr. Kapil Sharma for their kind help during my research work.

I sincerely thank my parent institute HBTU Kanpur, QIP center IIT Roorkee and Ministry of Human Resource and Development, Government of India, for facilitating me to carry on my research work

Several people significantly contributed to make my life and work at Indian Institute of Technology Roorkee a memorable experience. I am greatly indebted to all my labmates beyond words, the list is infinite, but to name a few, Kantilal Chouhan, Kajal Mishra, Brijesh Kumar Yadav, Devendra Rai, Jyoti Jain, Srinivas, Varun Mittal, Prashant Srivastava, Manvendra and Umesh. They have been always there for me with their help and moral support.

Thanks to my father and in-laws for their cooperation during research work. I would also like to thank my brother Kamlesh for being a constant source of inspiration and support even in tough times.

Above all, I pay my prayer to thank the God for giving me courage to complete my work in time.

Last but not the least a special thanks to my beloved wife Anjali and kids Sneha and Daksh for their love, support, patience and sacrifice.

(GIRDHARI)

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NOMENCLATURE

ABBREVIATIONS

TGA	Thermogravimetric analysis
FTIR	Fourier transform infrared spectroscopy
AFM	Atomic force microscopy
XPS	X-ray photoelectron spectroscopy
ASTM	American society for testing and materials
DTG	Derivative thermogravimetry
HDPE	High-density polyethylene
LDPE	Low-density polyethylene
NaOH	Sodium hydroxide

CHAPTER 1

INTRODUCTION

1.1 Background

Importance of composite materials can not be overlooked in today's scenario. Composite materials are formed by the combination of two or more materials on a macro scale, having different properties. Normally these materials are developed by one or more reinforcements phase embedded in a matrix. Application of these composite materials is enormous in various fields like aerospace, automotive, construction, electrical, sports and so many other sectors. Composites are bringing exemplary changes in the field of material world with diverse applications (Babu and Murthy 2017, Babu and Murthy 2018, Chadda et al. 2017, Tan and Tiwari 2011, Yaddanapudi et al. 2016, Patel et al. 2012).Extensive studies on effect of matrix (Praveen et al. 2010) and fillers (Banerjee et al. 2016, Chattopadhyay et al. 2010, Praveen et al. 2008) on these composites are carried out. Different characterization methods have also been used for the performance evaluation of these composites (Ahuja and Kaushik 2017, Basuli et al. 2010, Gautam et al. 2016, Kaushik and Kumra 2014, Kumar et al. 2017, Gautam et al. 2016)

Manufacturing sector and researchers are exploring various environmental friendly and renewable materials that are cost effective and energy efficient (Kumar et al. 2013, Naik et al. 2010, Nanda et al. 2014, Onabanjo et al. 2016, Wu et al. 2013, Yaddanapudi et al. 2017) to produce variety of products for sustainable development. In last few decades, agricultural based materials have drawn attention of the researchers to replace existing nonrenewable materials (Azargohar et al. 2019; Wu et al. 2013). Environmental issues are also perturbing for the scientific community to concentrate on alternative technologies and materials (Anyaoha et al. 2018, Bhosale et al. 2016, Hanak et al. 2016, Kamel H. et al. 2018, Saraswat et al. 2016, Teng et al. 2015, Yin et al., 2017).

Lignocellulosic natural fibers and fillers derived from various parts of the plant are offering numerous advantages like light weight, sustainable, environment friendly cost effective and having good mechanical properties and becoming an alternate of their synthetic counterpart like glass, aramid, as reinforcement in various polymer matrix (Faruk et al. 2012). These

lignocellulosic materials are basically made of cellulose, hemicellulose and lignin (Kaushik et al. 2010). These three key components are another area of interest for scientific community (Ahuja et al. 2018, Ferdous et al. 2002, Singh and Murthy 2017, Singh et al. 2018). Natural fiber and filler based composites are bringing new dimensions and applications in the field of composite world (Gautam et al. 2017, Gautam et al. 2018a, Gautam et al. 2018b)

A good number of reviews are available on extraction and characterization of traditional natural fibers and fillers like coir, bagasse, bamboo, banana, pineapple, wheat straw etc. and their reinforcement in different polymer matrix like Polypropylene (PP), High density polyethylene (HDPE) Low density polyethylene (LDPE), Epoxy etc. (Faruk et al. 2012, Mittal et al. 2016, Saba et al. 2016). The major issues addressed by the scientists are the poor adhesion and the compatibility of these natural fibers and fillers with different polymer matrix. To deal these issues different surface treatment methodologies have been suggested (Li et al. 2007, Mohanty et al. 2001). Addition of some additives like nanofillers have also been experimented to improve the quality of product.(Hui et al. 2010). On account of having excellent properties like high temperature stability and resistance to chemicals and corrosion, epoxy resin is preferred to be used as polymer matrix in a number of reinforced composites (Mittal et al. 2016, Saba et al. 2016). The mechanical, thermal, morphological properties of these new fibers have been studied extensively but comparatively few papers are available on comparison on activation energy of these fibers before and after treatment steps. Thermal kinetic modelling of common natural fibers was analyzed (Oranghi et al. 2014, Yao et al. 2008). Effect of alkali and acid treatment on thermal degradation kinetics of bagasse fiber derived from sugar cane was compared and calculation of activation energy was done in each case and it was observed that alkali treatment improved the activation energy significantly (Motaung and Ananjiwala 2015).

1.2 Surface treatment of natural fibers

The major issue faced by academicians with these natural fibers is their poor compatibility with the polymer matrix. Being lignocellulosic, natural fibers are hydrophilic in nature at the other hand these polymer matrix are hydrophobic so compatibility between these two materials is very important for the better quality of product commercialization. This issue can be remediated using different chemical and surface treatment methodologies. Different

surface treatment methodologies like alkylation, silanization , acetylation etc. have been suggested, experimented and compiled by researchers to improve the compatibility and adhesion between natural fibers and polymer matrix (Li et al. 2007, Mohanty et al. 2001). Few important chemical treatment methodologies which are successfully experimented and exercised by the researchers are as follows.

1.2.1 Alkaline treatment

Treatment of natural fibers with optimum concentration of alkali is very economical and promising treatment methodology. The chemical changes occurs according to the reaction:

$$\text{Fiber}{-}\text{OH} + \text{NaOH} = \text{Fiber}{-}\text{O}{-}\text{Na} + H_2O + \text{surface impurities}$$

The alkali treatment removes a certain amount of lignin, hemicellulose, oils and waxes. The removal of these cementing materials causes the crystallinity index and cellulose content of the fibers to increase. The tensile strength also increases due to increased cellulose content. The improvement in performance of composites because of alkali treatment of natural fibers have been studied by several researchers (Arthanarieshwaran et al. 2016, Rajesh kumar et al. 2017, Balaji and Nagrajan 2017). The increasing roughness and fibrillation is assumed to be responsible for better adhesion between natural fiber and polymer matrix.

1.2.2 Silane treatment

The chemical formula of Silane is SiH_4 and these coupling agents can reduce the hydrophilic tendency of natural fibers by removing the hydroxyl groups. The hydrolyzable alkoxy groups form silanol in the presence of moisture. The hydroxyl group present in fiber then reacts with forming stable covalent bonds.

$$CH_2CHSi\,(OC_2H_5)_3 + H_2O = CH2CHSi\,(OH)_3 + 3C_2H_5OH$$

$$CH_2CHSi\,(OH)_3 + \text{Fiber}{-}\text{OH} = CH_2CHSi(OH)_2O{-}\text{Fiber} + H_2O$$

Silane treatment in the case of hemp fibers was reported more effective as compare to alkali treatment (Sepe et al. 2018).

1.2.3 Acetylation

Acetylation is another important surface treatment method for natural fibers to make it more hydrophobic. It also reduces the swelling tendency of natural fibers in the presence of water. The acetyl group reacts with hydroxyl group of water and reduces the hydrophilic behavior of natural fibers as follows.

$$\text{Fiber}{-}OH + CH_3 - C(=O){-}O{-}C(=O){-}CH_3 = \text{Fiber}{-}OCOCH_3 + CH_3COOH$$

This method also improves the dimensional stability.

1.3 Motivation

Significant amount of work has been reported and reviewed on epoxy composites reinforced with traditional fibers in the last decade, now the researchers are looking for possibility in new natural fibers that are locally available and can be used as a reinforced phase in composites. The exploitation of these locally available fibers not only reduces the burden on traditional lignocellulosic fibers but also will provide job opportunities to the rural areas. Moreover, it will offer diversity of application in the composite world.

Teff straw, a waste material of annual cereal crop Teff in east African countries, majorly produced in Ethiopia. Researchers have used Teff straw for biomethane production (Chufo et al. 2015), waste water treatment (Wassie and Srivastava 2016a, Wassie and Srivastava 2016b) and nano silica production (Bageru and Srivastava 2017).This novel lignocellulosic fiber has never been experimented as reinforcement in polymers. Similarly *Saccharum spontaneum* (Kans grass) is a non wood perennial plant, plentifully available in various part of globe that is Africa, Asia, Untited states, India and Bangladesh, which inadvertently grows in barren lands, near the ponds, lakes and river banks (Barman et al. 2015a, Barman et al. 2015b, Chaudharyet al. 2012, Komolwanich et al. 2014). This novel filler has been used successfully as reinforcement in HDPE and polypropylene and characterization of composites were done (Barman et al. 2015a, Barman et al. 2015b) but still its reinforcement with epoxy has not been reported.

1.4 Objectives of the Research

The research is centered on the exploration of two new novel natural fibers/fillers, their extensive characterization and assessment of their suitability as reinforcement in Epoxy matrix. The specific objectives of the research work are as follows.

- Morphological, mechanical and thermal characterisation including activation energy of African Teff straw before and after surface treatment steps using state of art analysis techniques to asses its suitability as reinforcement in epoxy matrix.
- To optimise the Teff straw fiber loading along with suitable and economical surface treatment methodology with optimum concentration to develop its reinforced epoxy composites.
- Mechanical, thermal and morphological characterisation along water absorption characteristics of Teff straw reinforced epoxy composites before and after surface treatment steps.
- Extraction, characterisation and compositional analysis of locally available *Saccharum spontaneum* (Kans grass) fiber before and after alkali treatment steps.
- To optimise the filler size and loading of Kans grass in epoxy composites for getting improved quality of composites using mechanical, morphological and thermal characterisation.

1.5 Overview of thesis

The thesis has been organized in eight chapters summarized as follows

Chapter 1: In this chapter background and motivation for the use of natural fibers in different polymer matrix, environmental issues and current scenario of composite world has been discussed.

Chapter 2: This chapter reviews some of the latest literature along with previous work reported on new natural fibers and their use in epoxy composites.

Chapter 3: This chapter gives the details of the materials, methods and experimental procedures along with specifications, used for the characterization of fibers and preparation of composite materials. Different characterization techniques used for the compositional, morphological, structural mechanical, water absorption and thermal, analysis with degradation mechanism and activation energy analysis of reinforcing fibers and composite materials are discussed.

Chapter 4: This chapter discusses the characterization and effect of alkali treatment on thermal, mechanical and morphological properties along with calculation of activation energy of Teff straw fiber.

Chapter 5: This chapter focuses on the mechanical, morphological, water absorption behavior and thermal degradation of untreated and alkali treated Teff straw reinforced epoxy composites.

Chapter 6: This chapter deals with extraction, characterisation and effect of alkali treatment on thermal, mechanical and morphological properties of *Saccharum spontaneum* (Kans grass fiber) along with calculation of activation energy from various iso-conversional methods.

Chapter 7: This chapter presents the effect of filler size and loading on the properties of Kans grass reinforced epoxy composites and their thermal degradation behavior.

Chapter 8: This chapter describes about the findings and conclusions of the research work carried out on exploration of novel natural fibers and their utility in epoxy composites along with the opportunities and scope for future research.

CHAPTER 2

LITERATURE REVIEW

The literature review is divided in following parts

1. Available review papers in the field of natural fiber reinforced polymer composites specifically epoxy composites, various surface treatment methodologies of natural fibers to improve their properties and compatibility of polymer matrix and review papers on new natural fibers.
2. Literature on Extraction characterization and effect of surface treatment of various available, new and uncommon fibers.
3. Literature on reinforcement of these new and novel natural fibers in epoxy matrix to develop quality composites.
4. Literature on thermal degradation kinetics and activation energy of natural fibers and their reinforced polymer composites.
5. Literature based on water absorption mechanism related to natural fiber based composites
6. Literature related to Effect of fiber/filler size on the properties of natural fiber/filler reinforced composites
7. Literature available on the fiber and fillers used in the present study.

2.1 Review papers

Substantial work has been done on the reinforcement of traditional natural fibers bagasse, wheat straw, coir etc. in various polymer matrix whether thermoplastic or thermoset. Various academicians and researchers reviewed the available literature for last twenty years in different manner. Some seminal reviews in the field of natural fiber reinforced polymer composites are presented as follows.

Mantia and Morreale (2011) compiled the information on green composites. They discussed about different polymer matrix used for the fabrication of natural fiber composite materials. They studied the various methodologies used for the surface treatment of these

natural fibers for improving the adhesion between fibers and polymer matrix. They also discussed about processing and rheology. They also compiled information on diverse applications of these novel materials and also about sustainability and environmental impact assessment.

Faruk et al. (2012) reviewed all the studies done in the field of natural fiber reinforced composites from 2000-2010. They discussed about various natural fibers like flax, hemp, jute, kenaf, sisal, abaca, pineapple, ramie, coir, bamboo, rice husk, oil palm, bagasse, their chemical composition, structure and properties. They also compiled the various treatment methods, physical as well as chemical to improve the tensile strength, thermal properties and morphology of these fibers. They also collected the papers on different polymer matrix, thermoset as well as thermoplastic used with different natural fibers. They also discussed the factors influencing the processing of of these composites, various fabrication procedures and their advantages and disadvantages. The characterization techniques like tensile testing, flexural and impact properties were also elaborated in this study.

Pickering et al. (2016) discussed about recent developments and specifically mechanical performance of these green composites. They analyzed the effect of various factors like fiber and matrix selection, interface strength, geometry and orientations of fiber, fiber dispersion, porosity on the mechanical characteristics of natural fiber reinforced polymer composites. They also examined the effect of hybridization on the performance of these composites. Influence of moisture and weathering along with applications were also discussed in this review.

Sanjay et al. (2018) did a comprehensive review on properties and characterization of natural fiber reinforced polymer composites. They emphasized on tensile, flexural, impact, inter-laminar, hardness and water absorption properties. Along that they also compiled the studies done on thermal and tribological properties of these novel materials. FTIR, XRD and SEM characterizations were also discussed.

Ku et al. (2011) considered majorly tensile properties of these composites in their review paper. They told about density, tensile strength, elongation, elastic modulus, of these natural fibers. They also collected information on density, water absorption, heat deflection temperature, coefficient of thermal expansion, tensile strength, and elastic modulus of different polymer matrix like PP, LDPE, HDPE, PS. Mathematical modeling, rule of

mixtures, transverse rule of mixtures. Halpin-Tsai equation, shear log theory and their application in composites were also discussed.

Koronis et al. (2013) provided the application aspects of theses composite materials in the field of automobile industry. They discussed about green interior and green exterior composites in automobile industry. Different reinforcing elements like abaca, kenaf, hemp and flax, ramie jute, their mechanical performance and major issues and challenges regarding the application of natural fibers as reinforcement were talked in this study. The importance of matrix materials, mechanical characteristics of natural resins and concerns related to use of bio-based matrices were also analyzed.

Sydow and Bienczak (2018) brought diversity of application of these natural fiber based composites in food packaging in their review. They discussed the barrier properties of these composites which is a very important aspect when we use these composite materials in food packaging.

Thakur and Thakur (2014) targeted only thermoset polymers, based on natural fibers reinforcement in their review. They compiled the papers on natural fibers based phenolic composites, natural fiber based epoxy composites, natural fibers based polyester composites and natural fiber based vinyl ester composites.

Mittal et al. (2016) reported the findings on all the papers related to epoxy matrix reinforced by different natural fibers. Since epoxy has excellent properties like withstanding high temperatures, resistance to chemicals, and corrosion so numerous studies are their with natural fibers as reinforcement. They discussed about reinforcement of various fibers and fillers like cellulose, bamboo, sisal, hemp, piassava, coir, jute, flax, wood dust, kenaf, ramie, sugar palm, weave flax, palm tree, hemp yarn, natural silk, banana, tenax, betelnut, agave, phormium leaf, arenga pinnata, fique, luffa, coconut shealth, and basalt fiber in epoxy matrix.

Saba et al. (2016) also told about applications and recent trends of natural fibers based epoxy composites. Chemistry, structure and synthesis of epoxy resin, its advantages, commercial applications, modification, fire retardancy was discussed. Papers based on different fabrication techniques of these composites, different fibers used along with surface treatment methodology and diverse applications were also compiled in this review.

Mohanty et al. (2001) gave an overview on different surface modification methods and their effect on the quality of biocomposites. They discussed about production, chemical

composition and various properties along with advantages and disadvantages of natural fibers. Mechanism and chemistry of surface treatment methods like alkali treatment, graft copolymerization, etherification, acetylation, treatment with isocynate and maleated polypropylene was explained.

Li et al. (2007) also compiled information on various chemical treatment methodologies of natural fibers for the application in natural fiber reinforced composites. They reported the outcomes and findings of papers based on alkaline treatment, silane treatment, acetylation of fibers, benzoylation treatment, acrylation and acrylonitrile grafted maleated coupling, permanganate treatment, peroxide treatment, isocynate treatment and other chemical treatments.

John and Anandjiwala (2008) described about latest developments of chemical modifications and characterization techniques in the field of natural fiber based composites. They discussed the effect of chemical modification on the performance of aspen fiber composites, abaca fiber composites, bagasse fiber composites, bamboo fiber composites, banana fiber composites, coir fiber composites, date palm fiber composites, flax fiber composites, hemp fiber composites, henequen fiber composites, isora fiber composites, jute fiber composites, kapok fiber composites, kenaf fiber composites, luffa fiber composites, oil palm fiber composites, pine apple fiber composites, ramie fiber composites and sisal fiber composites.

Madhu et al. (2019a,b) reviewed the extraction, characterization, chemical and physical analysis of traditional fibers like bagasse, jute along with some less common natural fibers like acacia leucophloea, elephant grass etc.

2.2 Extraction characterization and effect of surface treatment of various available, new and uncommon fibers.

Over the last few decades, huge amount of work has been carried out by scientific community on reinforcement of traditional fibers which was presented in the various review articles presented earlier. The work done on extraction, characterization, and surface treatment of new and locally available uncommon fibers is as follows.

Ramanaiah et al. (2011) extracted green fibers from sansevieria leaves and treated these fibers with 5% aqueous NaOH solution and performed TGA/DTA analysis and improvement

in thermal stability was observed. Thermal diffusivity, conductivity and specific heat capacity of these fibers were also evaluated. Mechanical properties of fibers also improved after surface treatment with 5% solution of alkali.

Fonesca et al. (2013) evaluated the main properties of jacitara fibers and their potential as a possible reinforcement in polymer composites. Along with chemical, physical and mechanical properties, anatomical and ultrastructural properties were also investigated. The chemical composition of this fiber was estimated and it was found that the average percentage of cellulose, hemicellulose and lignin was 66.9%, 18.4% and 11.6% respectively. Higher modulus of elasticity (1.7 GPa) and tensile strength was observed. The properties were better or at par with traditional lignocellulosic fibers used by researchers.

Reddy et al. (2013) explored the potential of century fibers as a potential reinforcement in various polymer matrix. 5% solution of aq. NaOH was used for the treatment of fiber surface and results indicated removal of hemicellulose, improvement of tensile strength and elongation at break and crystallinity of fiber.

Fiore et al. (2014) characterized new natural fiber *Arundo donax* and studied its possibility as reinforcing material. The fibers were pulled out from the outer part of stem. Electron microscopy was used for the analysis of morphology of the fiber and helium pycnometer was used for real density analysis. Statistical modeling was also used to correlate the mechanical properties like tensile strength and transverse dimension of the fiber.

Indran et al. (2014) did the comprehensive characterization of *Cissus quadrangularis* fiber from the root of the plant. Anatomical analysis, chemical composition, physical properties, SEM, XRD and FTIR studies were done along with thermogravimetric analysis. The excellent results were obtained for its possible reinforcement in composite materials. High cellulose percent (77.17%) with small wax (0.14%) was responsible for high strength and good bonding characteristics. The fiber was found stable up to 230ºC by thermogravimetric analysis and proved to be well within polymerization process temperature.

Sarvankumar et al. (2014) investigated the physico-chemical properties of *Prosopis juliflora* before and after alkali treatment. The optimally treated fibers had cellulose (72.27%), hemicellulose (4.02%) and lignin (12.09%). Higher crystallinity index of 73% was also observed which is a desired characteristic for good reinforcing fiber.

Ticolau et al. (2014) studied the characteristics of gomuti (*Arenga pinnata*) fiber for the application in polymer composites. Diameter of the fiber was found in the range of 81-313μm and density was estimated ~1.40g/cm^3. The average tensile strength of fiber was in the range of 173.9 MPa. Sodium hydroxide, a preferred treatment methodology was applied for the surface treatment of fiber.

Arthanarieshwaran et al. (2015) explored new natural fiber *Acacia leucophloea*, characterized it and concluded that 5% NaOH treatment is an optimum treatment methodology for the best results. The tensile strength of alkali treated fibers was (357-1809 MPa) with Young's modulus (10.45-87.57 GPa).The cellulose content of optimally treated fiber was 76.69% which is quite high and the crystallinity index was found to be 74.27%.

Akintayo et al. (2016) did mechanical, spectroscopic and thermal characterization of untreated and modified Nigerian coir fibers. Fibers were modified by acetylation, oxidation, and mercerization. The NMR spectroscopy was used and it was found that treatment of these fibers did not affect the cellulose of type C-1. All the fibers showed thermal stability until 200°C, mercerated fibers experienced highest thermal stability that oxidized and acetylated fibers. Universal testing machine and scanning electron microscope were also used to justify the findings.

Rajeshkumar et al. (2016) analyzed the outcome of NaOH treatment on the properties of *Phoenix Sp.* fiber. Extraction of fibers was done from petioles of the plant. Three different concentrations of NaOH that is 5%, 10% and 15% was used for the surface treatment of fiber. The tensile testing was done at different gauge length varying from 20-60 mm. Substantial improvement in properties were observed after alkali treatment of the fibers.

Balaji et al. (2017) examined the application of new natural fiber, extracted from Saharan aloe vera cactus plants. Effect of alkali treatment on these fibers was also observed. Standard test methods were used to estimate the contents α cellulose, hemicellulose and wax. Single fiber tensile test was applied for the tensile strength of fiber. Fiber pull out test was also used to have an idea of interfacial strength between fiber and matrix. FTIR analysis confirmed the removal of amorphous materials after alkali treatment. Crystallinity index and crystal size was also improved because of alkali treatment.

Chen et al. (2017) observed effect of chemical treatment on tensile properties of windmill palm fiber. Scanning electron microscopy and Raman spectroscopy were applied for

characterization purpose. Alkali treated fibers had highest tensile strength that is 119.37±27.21 MPa, elongation at break that is 30.58 ±5.87% and elastic modulus 10.75 ±4.30 GPa, respectively. Alkalized samples were the most flexible fibers.

Maache et al. (2017) characterized natural fiber obtained from wild natural plant which is widely available in Algeria known as *Juncus effusus L*. Optical and scanning electron microscopy were used for the morphology of the fiber and functional groups were estimated using FTIR. Weibull distributions of the properties were also analyzed.

Balasundar et al. (2018) extracted and characterized new natural cellulosic *Chloris barbata* fiber. High cellulose content that is (65.37%) and lower density that is (634 kg/m^3) which is desirable for the better reinforcing material was observed. 50.29% crystallinity index was evaluated using X-ray diffraction studies. Fiber diameter was also calculated and it was found that the range of measurement is 180-200 μm. Fibers were found thermally stable until 210°C and findings confirmed the possibility of this fiber for the fabrication of sustainable natural fiber reinforced polymer composites.

Chen et al. (2018) evaluated the outcome of various chemical treatments on the morphology, moisture absorption and mechanical properties of luffa sponge fiber bundles. Three different chemical treatment methodologies were experimented that is application of 5% NaOH and 5% hydrogen peroxide, 10% NaOH and 20% acetic acid , 18% NaOH and 1.6% carbamide for modification of fiber bundles. The findings showed that the treatment with 10% NaOH and 20% acetic acid increased the tensile strength of fibers by 121.3%. The decrease in moisture regain was also observed that is 29%, 16.9% and 12.4% respectively, in each treatment methodology.

Kilinc et al. (2018) investigated the prospects of porous and lightweight natural fiber extracted from *Conium maculatum* as a possible reinforcement for composite materials used in transportation. Along with traditional characterization techniques X-ray photoelectron spectroscopy (XPS) was also used for the compositional analysis. The composition of this fiber was reported as cellulose 49.5%, hemicellulose 32.2% and lignin 8.6%. Tensile strength of this fiber was determined 327.89± 67.41 MPa. XPS studies showed that fiber surface was hydrophobic, which is a desired quality for composites and SEM imaging suggested that fiber has a porous structure which is very important for application in transportation industry.

Manimaran et al. (2018) presented the physico-chemical characterization of *Furcraea foetida* fiber as a reinforcement material in composites for light weight applications. The fiber had high cellulose content (68.35%) with lesser hemicellulose (11.46%) and lignin (12.32%). Atomic force microscopy (AFM) was applied to analyze the topography and quantification of roughness. The kinetic activation energy of fiber was calculated using Brido's method and found to be 66.64 kJ/mol. 52.6% crystallinity index and 28.36 nm crystalline size was reported from X-ray diffraction analysis.

Pouriman et al. (2018) reported the properties of untreated and alkaline treated salago fibers of Philippines which has numerous applications like handmade paper, bank notes, currency papers. They characterized this novel material before and after alkali treatment steps. FTIR analysis revealed the reduced lignin content.

Ramasamy et al. (2018) scrutinized the applications of *Calotropis gigantea* bast fibers as reinforcing material in polymer composites. An alkali solution of 5%, was used for the treatment of fiber surface. Removal of noncellulosic material by this treatment was confirmed by the FTIR studies. Crystallinity index was also found to be increased by this treatment. Substantial increase in mechanical properties was also observed. SEM analysis showed the roughened surface of fiber after surface treatment with 5% alkali

Sari et al. (2018) focused on physical, chemical and mechanical characterization of alkali treated cellulosic fiber from corn husk. The fiber was treated with different concentrations of alkali that is 0.5, 1, 2, 5 and 8% for two hours. Decrease in moisture content along with removal of hemicellulose was observed. Chemical, mechanical and physical properties were greatly improved because of removal of hemicellulose and roughness was also induced on the fiber surface which is very much desirable for the better adhesion and interaction with different polymer matrices.

Senthamaraikannan and Kathiresan (2018) extracted the cellulosic fiber from *Coccinia grandis. L* and performed physical, tensile, chemical, crystalline, thermal and morphological characterization. Alkali treatment was performed to improve the properties of fibers. The thermal stability and decomposition activation energy improved from 213.4°C to 220.6°C and 67.02 kJ per mole to 73.43 kJ per mole respectively. Weibull analysis was also performed to analyze the tensile properties.

Shanmugasundaram et al. (2018) addressed the new natural fiber named Areca palm leaf stalk fiber and treated this fiber with three different concentrations of NaOH that is 5%, 10% and 15.Diameter of the fiber was decreased and density was increased due to alkali treatment.5% alkali treated fiber possessed highest tensile strength that is 486.41±35.57MPa and tensile modulus 9.89 ± 1.46 GPa.

Vijay et al. (2019) discussed various properties of untreated and alkali treated cellulosic natural fibers from *Tridax procumbens.* Alkali treatment improved the tensile strength from 25.75 MPa to 33.82 MPa and crystallite size from 25.04nm to 38.23nm. SEM analysis confirmed the rougher surface in case of alkali treated fibers which is an indication of removal of lignin and waxy substances.

2.3 Reinforcement of new and novel natural fibers in epoxy matrix to develop quality composites

In previous section, articles were related to exploration and characterization of new and locally available fibers. This section deals with the work done on reinforcement of these uncommon fibers in epoxy matrix.

Yeng-Fong Shih (2007) evaluated the mechanical and thermal properties bamboo fiber which was agricultural waste of Taiwan. The elemental composition of fiber was carbon (40.35%), oxygen (46.20%) and hydrogen (6.60%), respectively. Fibers were modified by coupling agents. Better compatibility was observed in case of modified fiber with epoxy resin. 10% fiber or powder addition increased the char yields about 13.5-52.8%. Increment in glass transition temperature of epoxy was also observed by 8-18°C. Improvement of storage modulus of epoxy was about 16.4% and 36.1% by the addition of 10% coupling agent modified fibers and untreated powders respectively.

Bachtiar et al. (2007) studied the outcome of alkaline treatment on mechanical properties of sugar plam fiber reinforced epoxy composites. Different concentrations of alkali and soaking time were used for the improved quality of composites. Tensile modulus values were much higher than untreated fiber composite specimens.

Murillo and Ansell (2009) analyzed the mechanical properties of henequen fiber reinforced epoxy composites. Compression molding technique was used to fabricate the composites and the mechanical properties were investigated in tension, bending and impact loading.

Ali et al. (2010) investigated the effect of aging in *Arenga pinnata* fiber reinforced epoxy composites. Hand lay up process and 10% fiber loading was used for the development of epoxy composites. Properties were evaluated for original and aged samples. 50.4% higher tensile strength was observed in case of aged samples as compared to original ones. Degradation in impact strength by 6.33% was also observed for aged samples.

Yousif et al. (2010) observed the wear and frictional behavior of epoxy composites reinforced by treated betelnut fibers having different particle size (500μm, 714μm and 1430μm). They explained predominant wear mechanism of composites. The composites showed higher values of frictional coefficient when coarse sand was applied. The specific wear rate for three different sand particles followed the order coarse > grain > fine sands respectively.

Amor et al. (2010) prepared new structural composites reinforced by unidirectional natural fibers. Dielectric properties were also evaluated for the composite material.

Mylsamy and Rajendran (2011a) studied deformation, mechanical properties and thermo mechanical properties of untreated and alkali treated Agave fiber reinforced epoxy composites. Dynamic mechanical analysis (DMA) was used along with other characterization technique. Significant improvement in properties was obtained in case of alkali treated composites as compare to untreated composites.

Mylsamy and Rajendran (2011b) also studied influence of fiber length on the mechanical properties of Agave fiber reinforced epoxy composites. Three different lengths of fiber (3 mm, 7 mm and 10 mm) were used for the preparation of composites by simple hand lay up method. The machinability and atomic force microscope (AFM) studies were carried out to observe the fiber-matrix interaction.

Hoyos et al. (2012) fabricated epoxy fique composites and evaluated its applicability for construction applications.18w/v% of NaOH. The matrices used were epoxy and epoxy with 5 wt% of chemically modified montmorillonite. The dimensions of the composites were 90mm x 20mm x 4mm and preparation method was pultrusion processing technique. Loss of flexural properties were observed when composites were placed in three different environments that is water, saturated calcium hydroxide solution and mortar with w/c ratio of 0.45 and 540kg/m^3 of cement which was cured in a saturated lime stone solution.

Appreciable improvement in flexural strength and modulus of composite was obtained that is 40% and 34% in case of fiber treated and montmorillonite added composites.

Alamri and Low (2012) investigated mechanical properties and water absorption response of epoxy composites reinforced by recycles cellulose fibers. 19, 28, 40, 46% of fiber loading was used for the fabrication of composites. Improvement in flexural strength, flexural modulus, impact strength and fracture toughness was observed as we increases the fiber loading.46% fiber loading showed the maximum upgradation in properties. Degradation in properties were observed as a result of moisture absorption.

Fiore et al. (2014) studied static and dynamic mechanical properties of epoxy composites reinforced by novel natural filler *Arundo Donax.* Culms of the plant were grinded and effect of filler content and size was evaluated on the tensile, flexural, storage and loss moduli. Assessment of void content was also done and the optimization of filler content and size was done to have the superior quality composites.

Suresh kumar et al. (2014) analyzed thermal, mechanical and dynamic mechanical properties of raw and surface treated reinforced epoxy composites by coconut sheath fiber. Hand lay up method was used for the preparation of composites. Fabricated samples were cut as per ASTM standard and universal testing machine (UTM) was used for the tensile and flexural testing of composites. Treated composite showed very few voids and better fiber matrix bonding as compared to untreated one.

Arthanarieshwaran et al. (2016) evaluated thermal and mechanical properties of alkali treated *Acacia leucophloea* fiber/epoxy composites. Ten composites samples were fabricated by varying fiber content form 5 to 25%. NaOH solution of 5% concentration and 45 minute soaking time was used for the treatment of fibers. Composites prepared by 20% treated fiber loading exhibited improved mechanical properties. Morphology of the composites was analyzed by Atomic force microscope and SEM.

Oliveira et al. (2017) compared the tensile properties of epoxy and polyester composites reinforced with eucalyptus fibers without any treatment of fiber. Except other mechanical properties only improvement in elastic modulus was experienced and a treatment of the fiber was recommended for enhancement in properties.

Nascimento et al. (2018) did impact characterization of epoxy composites reinforced by untreated and mercerized mallow fibers. Surface treatment with 5% solution of alkali for 24 hours without agitation was applied.

Farzi et al. (2019) used oxamino triazine (OAT) one of common by-product in the petrochemical industry as new reinforcing filler for epoxy composites. The loading of OAT was varied from 0-50%. They concluded that OAT powder can be a promising option for the reinforcement in epoxy matrix.

Sarikaya et al. (2019) produced epoxy composites reinforced by three different natural fibers birch, palm and eucalyptus. Resin transfer molding and molded fiber production technique in combination was applied for the fabrication of composites. The tensile strength was reported as 29.53, 42.24 and 45.28 MPa respectively. Impact energy was 0.105, 0.130, 0.124 J respectively.

Molded fiber production method was recommended for the better quality of these fibers reinforced epoxy composites.

Shah et al. (2019) reinforced biodegradable Acacia Catechu (AC) particles in epoxy/amine system 94% improved impact strength and 14% increase in flexural strength was recorded in case of 1.0% wt addition of AC particles.

2.4 Literature on thermal degradation kinetics and activation energy of natural fibers and their reinforced polymer composites

This section deals with specifically with thermal degradation kinetics and activation energy of the natural fibers and their prepared composites which is a very important parameter when these composite materials are exposed to high temperature atmosphere.

Agrawal et al. (2000) took oil palm fiber reinforced phenol formaldehyde composites. Untreated and treated both type of fibers were used in their work. Crystallization kinetics and energy of crystallization was studied by differential scanning calorimetry. Modified Kissinger equation was used to determine activation energy. Matusita's equation was also applied to determine other crystallization parameters. Various treatments improved the thermal stability of composites.

Yao et al. (2007) evaluated the the activation energy of 10 different fibers used for the composites and studied their thermal decomposition process. The fibers used in the work

were wood, bamboo, agricultural residue and bast fibers. Kissinger, Friedman, Flynn-Wall-Ozawa and modified Coats-Redfern methods were applied to determine the apparent activation energy. The range of activation energy for those fibers was obtained in the range 160-170 kJ/mol.

Poletto et al. (2011) characterized two cellulose fibers, *Eucalyptus grandis* (CEG) and *Penus taeda* which were obtained by Kraft and sulfite pulping process respectively. Kinetic parameters of degradation were determined by TGA at heating rates of 5, 10, 20 and 40°C min^{-1} by applying Avrami, Flynn-Wall-Ozawa (FWO) and Criado methods. The activation energy reported for *Eucalyptus grandis* was higher as compared to *Penus taeda.*

Islam et al. (2014) examined thermal stability and kinetic analysis of epoxy composites which were modified by multiwalled carbon nanotubes. The investigation was done to understand the effect of polyether polyol and multiwalled carbon nanotubes. Activation energy for degradation of these epoxy naocomposites was evaluated by different integral and differential methods that are Horowitz-Metzger, FWO, Kissinger and Coats-Redfern. Activation energy of the modified composites were increased as compare to unmodified epoxy composites.

Ornaghi et al. (2014) studied the thermal decomposition behavior of six different vegetal fibers. Thermogravimetry under nitrogen atmosphere was exercised at four different heating rates (5, 10, 20 and 40 $^{\circ}$C/min). Two integral methods Kissinger, Flynn-Wall-Ozawa and one differential method Friedman were used to calculate the activation energy and frequency factor of the fibers. Criado's method was used to understand the solid state degradation mechanism..

Oza et al. (2014) analyzed the effect of surface treatment on the thermal stability of PLA composites reinforced by hemp fibers. In their work three different chemical surface treatment methods that is alkylation, silanization, and acetylation were applied. Model free FWO method was used to calculate the activation energy of composites. 10-13% higher activation energy was obtained in case of acetic anhydride modified hemp composites. The ranges of activation energy of composites in case of acetic anhydride treated samples were (159-163 kJ/mol).

Song et al. (2014) evaluated activation energy of epoxy resin grafted by polyurethane by applying modified non-linear integral iso-conversional methods. Three samples were heated

at three heating rates that is (10,15 and 20K/min) and a modified non-linear integral iso-conversional method was used for getting the kinetic parameters. Two stages of mass loss were observed between 50-500°C. For α = 0.3 maximum value of kinetic energy was experienced.

Motaung and Anandjiwala (2015) performed studies on effect of acid and alkali treatment on the thermal degradation kinetics of bagasse obtained from sugarcane. Non-isothermal thermogravimetric analysis was used under nitrogen atmosphere. The highest value of thermal degradation activation energy was experienced in case of alkali treated samples.

Karmakar and Shashidhara (2018) assessed thermal decomposition kinetics of jute fiber filled high density polyethylene (HDPE) composites. Jute fiber based HDPE composites experienced degradation of jute at around 375°C and HDPE at around 485°C. Two different methods that is Coates-Redfern and Horowitz-Metzger were utilized. The apparent activation energies obtained in the range of 50 and 95 kJ per mole for jute and 245 and 345 kJ/mol for HDPE. Degradation was reported in two distinct steps.

Abdullahi et al. (2019) used dynamic mechanical analyzer to understand the outcome of sugarcane bagasse on activation energy and viscoelastic parameters of epoxy resin. Hand lay-up method was used for the development of composite material. The decrease in activation energies were observed by increasing the fiber loading from 20-50%. For 20% fiber loading the value was 293.013kJ.mol while for 50% fiber loading it was 201.103kJ per mole.

2.5 Water absoprtion behavior of natural fiber based composites

Study of water diffusion behavior is another important parameter as these lignocellulosic fibers are hydrophilic in nature which is an undesirable characteristic when we talk about quality and commercial application of their finished composites. This section deals with various articles on water absorption mechanism of these novel materials.

Giridhar et al. (1986) compared the moisture absorption tendency under immersion conditions of sisal and jute fiber composites in epoxy matrix. In spite of having more compact structure sisal fiber exhibited more moisture absorption tendency and this behavior was due to high cellulose content.

Espert at al. (2004) performed a comparative study on water absorption behavior of natural cellulosic fibers from wood and a new natural fiber in polypropylene composites and its

effect was also analyzed on the mechanical properties of these composites. Water absorption studies were performed at three different temperatures that is 23, 50 and 70°C . Fick's law was applicable as the water absorption kinetics and mechanism followed the same. Diffusion coefficients estimated by Arrhenius law. Water saturated samples experienced a substantial degradation in tensile properties as compared to dry one. A change in morphology was also observed in case of water exposure.

Hu et al. (2010) studied evolution of microstructure, moisture absorption, tensile strength for short jute fiber/ polylactide composites exposed to hygro-thermal environment. The composites were fabricated by film stacking hot pressed methods. The aging was done for uncoated samples and adhesive tape coated samples. Three different stages were observed that is quick moisture up taking stage then, slow stable stage and the third one quick moisture uptaking stage. Defects like pores, microcracks, delamination of the whole structure.

Masudi et al. (2012) analyzed swelling and moisture absorption behavior in bio-based jute-epoxy composites. Specimens were prepared according to ASTM D 570. It was an important study to understand how these composites behave in wet environmental conditions.

Celino et al. (2013) investigated diffusion phenomena in natural fibers. The samples of four different fibers were put for hygro-thermal aging in total water immersion and in an environmental chamber at a temperature of 23°C and relative humidity of 80%. Various predictive models were used for the simulation of experimental curves.

Hosseinihashemi et al. (2015) assessed long term behavior of water absorption of thermoplastic composites produced by thermally treated wood. In this study wood plastic composites were made from thermally treated beech wood and polypropylene matrix and the method of fabrication was injection molding. Water immersion test was used to study the long term water absorption of composites. The composites which were developed with wood treated at 180°C for 120 min showed the least water absorption. Diffusion coefficient parameter was calculated by fitting the model predictions. It was also observed that theses composites follow Fickian diffusion process.

Mrad et al. (2018) evaluated the water immersion properties of the wood plastic composites which were made by industrial wood residues. Modelling techniques were used to understand the water absorption behavior. Two steps were used for the sample preparation that is extrusion compounding and injection molding. The variations in swelling and water

absorption were understood by applying Fick's law of diffusion. Both numerical and experimental approaches were used in this work. Short term diffusion parameters were also calculated along with long term parameters for better understanding of complex sorption process of wood polymer composites.

2.6 Literature related to Effect of fiber/filler size on the properties of natural fiber/filler reinforced composites

The size of reinforcing fiber or filler also plays a very important role in mechanical and morphological properties of these composites. This section consists of research articles focusing on the size variations of reinforcing fibers and fillers for the development of different thermoset and thermoplastic composites.

Dikobe and Luyt (2006) developed wood-ethylene vinyl acetate copolymer composites. The main purpose of this work was to study the effect of wood fiber content and its particle size on the morphological structure, mechanical and thermal properties and water absorption behavior of and (EGMA) ethylene glycidyl methaacrylate copolymer compatibilized composites. The findings showed that the values of tensile strength decreased with increasing fiber content for the uncompatibilized composites while tensile strength initially decreased but increased after 5% filler content in case of compatibilized composites. One more trend was reported that small that composites containing small particles had higher tensile strength values as compared to the composites containing large wood particles. Degradation behavior was not much influenced by the particle size.

Migneault et al. (2008) analyzed effect of fiber length on various properties and processing on extruded wood fiber based HDPE composites. Fiber length and distribution had a major effect on mechanical behavior of fiber based composites. Fiber quality analyzer was used to characterize length, shape and distribution. Different lengths and fiber loading were used for the composites and result showed the melting properties were also affected by this. Mechanical properties were increased with increasing fiber length.

Onuegbu et al. (2011) fabricated snail shell powder filled polypropylene composites and analyzed the effect of filler content and its size on mechanical performance and end use properties. The snail shell powder loading was varied from 0 to 40% and different particle sizes were used that is 0.150, 0.30 and 0.42μm. Injection molding machine was used for the

preparation of composites. Findings revealed that snail shell powder improved the mechanical performance of composites in a descent manner. However, degradation in flame retardant properties were observed by increasing the filler content.

Raju et al. (2011) did experimental studies on mechanical performance of epoxy composites based on groundnut shell particle. Composite boards were produced by randomly distributed groundnut shell particles having different grain size. Different particle to epoxy ratios were used that is 70:30, 65:35 and 60:40. Sample having 1 mm particle size and particle to resin ratio 60:40 exhibited superior properties as compared to other composites.

Matejka et al.(2013) examined the potential of powderized hazelnut shells to used as natural and biodegradable fillers in composites. CHASE tester was used for the estimation of friction wear properties of composites. Different ratios were tested in order to get the optimum quality of composites.

Salasinska and Ryszkowska (2015) investigated the effect of filler composition and its morphological characteristics on mechanical properties of natural fiber composites. Sunflower husk and pistachio shells were used for the reinforcement in this work. 66% of the sunflower grains were having the size in the range of 180 to 850 μm in size. The size range of 88% of the pistachio shells were in the range of less than 63 μm. Different percentage of filler loading was used for both the reinforcing materials. Mechanical, morphological and other properties were evaluated both for fillers and produced materials.

Zafar and Siddiqui (2017) examined the effect of fiber size and loading for raw natural fiber reinforced polystyrene composites. No surface treatment methodologies were used for the modification of fiber surface. Three different sizes 250-355 μm, 355-500 μm, 500-710 μm, of the natural fillers named rice husk (RH), wheat husk (WH) and mustard husk (MH) were used for the preparation of the samples. Fiber loading was also varied from 5 to 15%. Different mechanical testing like tensile, flexural were used for analysis of the performance of prepared samples. Morphological examination of fractured specimen was done using scanning electron microscopy.

Mohammed et al. (2018) used Mengkuang or *Pandanus atrocarpus* fiber for the production of reinforced natural rubber composites. The fiber was cut, dried and ground to make powder. Sieving was done in order to separate the reinforcing filler according to size. Melt blending was used for filling of fiber into HDPE and natural rubber matrix. The blend of

60% HDPE and 40% natural rubber was used with different size of fiber that is 125μm, 250μm and 500 μm. Samples were prepared for different fiber loadings that is 10%, 20% and 30%. Tensile test, water absorption test and impact test were used to evaluate the properties of composites. Morphology was observed by field emission scanning electron microscopy. The highest tensile properties were observed in case of 10% fiber loading for all the sizes being used for the development of composite materials.

2.7 Literature available on the fiber and fillers used in the present study

In the present work two new natural fibers have been used as reinforcement in epoxy matrix. First one is African Teff straw (*Eragrostis tef*) which is the solid waste material of annual cereal crop of east African countries and other one Kans grass (*Saccharum spontaneum*) is a perennial non-wood plant which automatically grows in barren lands, agricultural fields and bank of rivers ponds or lakes. It is abundantly available in various part of world like Africa, United States and Asia specially, in India, Bangladesh Nepal etc. This section deals with articles on these two novel fibers.

2.7.1 African Teff straw (*Eragrostis tef*)

Chufo et al. (2015) did physicochemical characterization of anaerobically digested Teff straw which was pretreated by sodium hydroxide. Biomethane production was done from this novel material. Different NaOH concentrations that are 1%, 2%, 4% and 6% were used for the pretreatment purpose. Findings showed that structural composition and lignin network was changed due to NaOH treatment and biogas production was improved.

Wassie and Srivastava (2016a) characterized Teff straw and utilized it for chromium removal from waste water. Teff straw was tested as an adsorbent material for hexavalent chromium removal from waste water. XRD, FTIR and SEM analysis were used for the characterization of this adsorbent. Experiments in Batch mode were conducted to observe the effect of pH, initial chromium concentration, time of contact and dose of adsorbent on efficiency of adsorption. Pseudo second order kinetics described the process in realistic manner.

Wassie and Srivastava (2016b) treated Teff straw chemically and tested it as adsorbent for chromium removal. NaOH, H_3PO_4 and $ZnCl_2$ solutions were used for the chemical treatment

of Teff straw. Anatomical characterization was done by XRD and SEM while FTIR was used for the characterization of change in surface. Effect of different operational parameters like pH, intial chromium concentration, contact time, temperature and adsorbent dose were studied.

Wassie and Srivastava (2017) synthesized nano-silica from Teff straw and did its characterization. Combination of heat and acid treatment was applied to produce nano-silica from Teff straw. Presence of high amount of silicon dioxide was confirmed by XRF analysis.

Bageru and Srivastava (2017) prepared and characterized biosilica form Teff straw using thermal method. Three different ashing temperatures was used. Raw Teff straw was subjected for thermal degradation in static air in an electric furnace.

Bageru and Srivastava (2018) used sol gel method to produce biosilica from Teff straw. The effect of ashing temperature on the yield of biosilica produced was observed.

Bageru and Srivastava (2018) developed Teff straw based biocomposites with alginate and chitosan for the efficient removal of pyridine. Biosilica, which was synthesized from Teff straw, was mixed with chitosan and alginate. Adsorption parameters affect the pyridine removal efficiency.

2.7.2 Kans grass (*Saccharum spontaneum*)

Kataria and Ghosh (2011) performed saccharification of Kans grass with the help of enzyme mixture for the production of bioethanol. In this work acid treated Kans grass was put to enzymatic hydrolysis in order to produce fermentable sugars.

Chaudhary et al. (2012) experimented various alkaline treatment methods that is NaOH alone, NaOH with 10% urea and aqueous ammonia for the maximum delignification of Kans grass. Among all the treatment methods applied, superior results were obtained in case of ammonia treated biomas.

Kataria et al. (2013) compared the saccharification of acid and alkali treated biomass of Kans grass for microbial production of bioethanol. Different time and concentrations of alkali treatment were used in the study and parameters were optimized for best results.

Komolwanich et al. (2014) performed a comparative study of Kans grass and giant reed (*Arundo donax*) as lignocellulosic feedstocks for the production of nonnumeric sugars. In this work two stage treatments was performed for the release of monomeric sugars. The optimum

pretreatment conditions were examined and the comparison of monomeric sugar yields was done.

Barman et al. (2015a) reported preparation and characterization of green composites developed from high density polyethylene and *Saccharum spontaneum.* In this study the composites were fabricated from by conventional melt-mixing method utilizing maximum loading of Kans grass filler to achieve acceptable range of properties required. 10% filler loading showed the optimum performance of composites

Barman et al. (2015b) also developed polypropylene composites reinforced by Kans grass filler. Malic anhydride grafted compatibilizer was used to improve the properties of composites. Sight deviation in thermal stability was observed at high loading of Kans grass filler. Substantial improvement was observed in tensile and impact strength of the prepared composites

2.8 Outcome of Literature survey

From the various articles discussed in literature review it is clear that traditional fibers like bagasse, wheat straw, coir sisal etc. have been explored extensively for characterization and reinforcement in different polymer matrix. Substantial number on review articles are also available on characterization, surface treatment methodologies and commercial applications of the composites developed from these fibers. Alkali treatment with optimum concentration and soaking time is well established and economical way to improve the fiber matrix adhesion by inducing roughness on the fiber surface as compared to other treatment methodologies. Understanding of water absorption mechanism is also a very important study for these lignocellulosic fibers and their polymer composites. Thermal degradation kinetics correlated with activation energy is another important analysis to understand the response of these composites subjected to high temperature.

2.9 Research gap

Based on Literature survey following research gaps have been observed

- In contrast with traditional fibers less work has been reported on the reinforcement of locally (specially in underdeveloped countries) available, inexpensive natural fibers or fillers in epoxy matrix to develop composites.
- Only few researchers have given attention to calculate activation energy and to observe thermal degradation kinetics before and after surface treatment steps of these novel natural fibers and their prepared composites which is also a very important aspect when we talk about the quality of end product.
- Not many papers are available on use of advance characterisation techniques like atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS) etc., in the field of natural fibers based composites.
- Fiber/filler size is also a very important factor which plays its role in better mixing of these fibers or fillers with the polymer matrix and needs more emphasis for the development of quality product for end user. Very few articles are available on the effect of mechanical and thermal properties due to size variation of these filler/fiber materials

CHAPTER 3

MATERIALS AND METHODS

This chapter discusses about materials, methods, and analytical procedures used during the experimental studies and analysis for the characterization of Teff straw fiber and Kans grass filler along with their reinforced in epoxy composites.

3.1 Materials

This section deals with the details of the natural fiber: Teff straw and Kans grass; polymer matrix: epoxy resin; surface modifier: sodium hydroxide and the other chemical used for analysis purpose.

3.1.1 Teff straw fiber

Teff is an annual cereal crop of East African countries mainly produced in Ethiopia and Teff straw fiber is the solid agricultural waste of this cereal crop. In Ethiopia, Teff has the largest share in cereal crops, around 3.7 million ton of Teff cereal is produced annually which generates around 2 million ton of Teff straw as a waste (Chufo et al. 2015). The cellulose content of Teff straw is 36.7± 3.2% which is comparable with traditional fibers like coir, bamboo, wheat straw, and rice husk that are successfully reinforced in polymer composites.

Figure 3.1:(a) Teff crop (b) Teff fiber

3.1.2 Kans grass

Kans grass used in this study was collected from the bank of river Ganga near Haridwar in Uttarakhand. The leaves were separated and the stems were cut and immersed for water retting for two weeks. The fibers were separated from the stem internodes manually and dried in the sun after washing with distilled water (Ramanaiah et al. 2011, Ridzuan et al., 2016). The Kans grass and and its extracted fibers are shown in Figure 3.2.

Figure 3.2: Extraction process of Kans grass fiber

3.1.3 Epoxy resin and hardener

On account of having excellent properties such as high temperature stability and resistance to chemicals and corrosion, epoxy resin is preferred choice to be used as a polymer matrix in a number of reinforced composites. In the present study, epoxy system comprised of epoxy resin (AW 106) and the hardener (HV953 which were supplied by Huntsman International (India) Private Limited.

3.1.4 Surface modifier (Sodium hydroxide) and other chemicals

Procurement of Sodium hydroxide (min-assay 98%) was done from M/S Himedia Laboratories Pvt. Limited (Mumbai, India), while other chemicals were provided by SD Fine chemicals India and Thomas Baker India Ltd. and distilled water was produced in the lab itself by a distillation water unit.

3.2 Methods used

This section consists the details of the procedures and methodologies adopted during the experimental studies on the development and characterization of Teff straw and Kans grass reinforced epoxy composites.

3.2.1. Preparation of Teff straw fiber for reinforcement

Teff straw/Kans grass fiber is washed several times with distilled water to remove any unwanted adhered impurities and then put at 70°C for 48 h in an oven for the removal of excess water. The fibers were manually cut to 2-3 mm length. These dried fibers are designated as untreated fibers.

3.2.2 Treatment of Teff straw fiber

Teff straw fibers were soaked in NaOH solution of different concentrations of 5% and 10% that is 5g/100 ml and 10g/100 ml of water for a period of 60 minutes; 20:1 liquor to fiber ratio was maintained (Mittal and Sinha 2015), then distilled water was used for washing of these fibers 3-4 times for the removal of undesired impurities. The fibers were then placed in a hot air oven for a period of 48 hours at a constant temperature of 70°C to remove moisture, these were finally considered as treated fibers.

3.2.3 Treatment of Kans grass fiber

Kans grass fibers were soaked in NaOH solution of different concentrations of 3%, 5% and 7% for a period of 60 minutes and liquor to fiber ratio was kept 20:1.(Maepa et al. 2015, Saravanakumar et al. 2014b), then washing was done with distilled water of these fibers 3-4

times for the removal of undesired impurities. The fibers were then placed in a hot air oven for two days at a constant temperature of 70ºC to remove moisture.

3.2.4 Preparation of Kans grass filler

After drying the fresh plant, the culms were cut into several pieces. These chopped pieces were washed with distilled water to remove the sand, wax and dust particles and dried in an oven at 80ºC for 24 hours to remove the moisture. The dried and chopped pieces were crushed in a high speed mixer/grinder and were sieved into three different sizes (250-500 μm, 500-1000 μm, 1000-1400 μm).

3.2.5 Fabrication of Teff straw and Kans grass composites

Both epoxy resin (AW 106) and the hardener (HV953 IN) were mixed in ratio of 5:4 (recommended by supplier) and after that the fibers/fillers were added. Different loadings of fibers/fillers were used that is 5% , 10%, 15%, 20% and 25% for both untreated and treated fibers in case of Teff straw composites and different size fillers in case of Kans grass composites. The mixture was stirred at 2000 rpm for 10-15 minutes in a mixer to get uniform and homogenous mixture, after mixing; the whole mixture was poured in a mold of size (300 × 300 × 10 mm^3) and allowed for curing at ambient temperature for 24 hours. The simple hand lay-up technique was used for the development of treated and untreated composites, polythene sheets were laid in a clean and dry mould to avoid sticking of epoxy fiber mixture to the wall of mold and the sheets were rolled by a heavy roller in order to remove bubbles and voids. Finally a dead weight of 25 kg was put on the mold for 24 hours and thereafter, prepared composite sheets were withdrawn from the mold for cutting purpose to get sample dimensions as per ASTM standards for the characterization. Figure 3.3 depicts the prepared sheet of Teff fiber reinforced epoxy sheet and samples which were cut for analysis purpose.

Figure 3.3: Teff straw composites and samples for characterization

3.3 Characterization for fibers and composites

Untreated, treated fiber and prepared composite sheets need to be characterized. Following characterization techniques have been used.

3.3.1 Density and diameter measurement of fibers

ASTM D 3800-99 had been used for the measurement of density of the untreated and alkali treated Kans grass fibers. Water, canola oil and benzene were used as immersion liquids and a precise electronic weighing balance along with density determination kit, having accuracy of 0.1 mg was used. The following equation was used for the calculation of density of fibers

$$\rho_f = \frac{\rho_w . W_1}{W_1 - W_2}$$

Where ρ_f is the density of fiber, ρ_w is the density of distilled water and W_1 and W_2 are the weights of fiber in air and water respectively (Jiang et al. 2018). Being non uniform cross section of the fibers, the diameter of each fiber was measured at 5 different places along the gauge length using an optical microscope (Make: Nikon, Model: SMZ-745T) with image analysis software 'ImageJ' and the average of these values was considered for calculation of strength. Strain is calculated by elongation and gauge length of the fiber.

3.3.2 Tensile testing of fibers

The mechanical property tester (Electroforce 3200, Load cell: 225N) had been used at a uniform crosshead speed of 0.1 mm/min for the tensile testing of untreated and treated fibers (25 specimen were used as per ASTM D-3822 standard with a gauge length of 35 mm).

3.3.3 Tensile testing of composites

The tensile test of composite gives the idea about the ability of the material to bear the force that tends to pull apart the sample and the degree to which sample can stretch before breaking. Tensile modulus determines the relative stiffness of the material and can be evaluated from the slope of the stress-strain plot.

Tensile strength and tensile modulus can be calculated numerically as follows.

Tensile strength = Force/Cross section area =F/A

Tensile modulus = Tensile stress/Tensile strain =(F/A)/(ΔL/L)

where

F = Force exerted on the sample under tension

A= cross-sectional area of the sample through which force is applied

ΔL = the amount by which the length of the specimen elongates

L = original length of the specimen

The tensile strength and tensile modulus of the composites are determined with a universal testing machine (UTM) 2716-002 Instron Model 5982. The overview of a machine is shown in Figure 3.5. ASTM D3039 standard has been followed with cross head rate of 2 mm/min. The dimension of a tensile test sample is 250 mm long and 25 mm wide of the material which is cut from a composite sheet of the respective material.

3.3.4 Flexural testing of composites

Flexural strength is the capacity of the material to bear the deflecting force which is applied perpendicular to its longitudinal axis. Flexural modulus is the ratio of stress to strain for flexural deformation, or it is the tendency of a sample to bend. It is evaluated from the slope of a stress-strain curve obtained by a flexural test.

Flexural strength and its modulus are calculated numerically as follows.

Flexural strength $=3FL/2wh^2$

Flexural modulus $= L^3F/4wh^3d$

Where,

L= Length of the support span

F = Force at the fracture point

h = Thickness of the specimen

w = Width of the specimen

d = Deflection due to the load applied at the middle of the specimen

3.3.5 Impact testing of composites

Impact properties of composites were investigated by an impact testing machine (TINIUS OLSEN Model impact104) (Hoorsham, PA, USA); having weight of hammer 4 kg. ASTM D 256 was used for Izod impact strength. The dimensions of the test samples were 63.5 mm long by 12.7 mm wide by the thickness; three samples were tested for each type and average value was taken. Due care was taken to ensure the reproducibility of results.

3.3.6 Scanning electron microscopy (SEM) for fibers and composites

SEM analysis was done using scanning electron microscope LEO 435 VP having acceleration voltage up to 30 kV, with detection mode, magnification range (10X-300,000X). Samples were sputter-coated with gold prior to SEM analysis. It is an excellent tool to understand the morphology of the fibers as well as composites and to observe the morphological changes before and after surface treatment steps. The gold coating prevents electrical charging during examination time.

3.3.7 Fourier transform infrared spectroscopy for fibers and composites

Fourier transform infrared spectroscopy (FT-IR) is an analysis technique which is applied to obtain an infrared spectrum of emission, absorption, photoconductivity of a solid, liquid or gas. FT-IR spectrometer takes spectral data in a wide spectral range at the same time. It is used to analyze the changes that occur in the functional group of the cellulose fibers/composites after chemical treatment. Fibers/Composite specimen were dried, grounded into fine particles and mixed with the potassium bromide (reference substance) then compressed into pellets, and analyzed with Nicolet 6700 series FTIR spectrophotometer, Canada. The fiber/KBr ratio was put 1:9. Fibers were analyzed over the wave range from 4000 to 600 cm^{-1} with a spectrum resolution of 4 cm^{-1} to obtain FTIR spectra.

3.3.8 X-Ray Diffraction (XRD) for fibers and composites

The XRD analysis of untreated and alkali treated fibers/composites was performed using Bruker AXS D8 diffractometer working on Cu-Kα radiation (λ = 1.5406Å) with 40 kV and 30 mA as operating parameters. Samples were put in a holder and scanned with continuous mode in angle 2θ range of 0° -50°C with goniometer speed of 0.02°/s. The CrI (crystallinity index) which gives an idea about the fraction of crystalline material was calculated as-

$$\mathrm{CrI} = \frac{(I_{Total} - I_{Amorphous})}{I_{Total}}$$

CrI can be calculated using intensity at main peak (~21.9° for cellulose) and because of amorphous peak intensity, (estimated at the minimum ~18° between the main peak and the secondary peak at ~16°) (Wassie and Srivastava 2016b). XRD of untreated and treated composites were also studied.

3.3.9 Atomic force microscopy for untreated and treated fibers

The morphology and surface roughness parameters of the fibers were analyzed by Atomic force microscope (AFM) (Model: NTEGRA Prima Make: NT-MDT,) using a tapping mode with silicon nitride cantilever having spring constant 22.5 Nm^{-1} and scan rate of 0.55 Hz. Scan area is 20 μm x 20 μm.

3.3.10 X-ray photoelectron spectroscopy (XPS) analysis for fibers

Surface chemistry of Kans grass filler was investigated by XPS (PHI 5000 versa probe III).

3.3.11 Thermogravimetric analysis (TGA) and Differential thermal gravimetric (DTG) of fibers and composites

Thermal analysis of the composites is as crucial as the mechanical and chemical analysis. Fiber type, fiber loading, surface modification, crystallinity, fiber size, surface and bonding between the fiber & polymer matrix phase, play a major role for the thermal properties of the composite material. These tests are very important for the quality control and application of these materials when exposed to higher temperature. In TGA analysis, the thermal degradation of the composite material is determined by variation in the respective sample weight while the sample is heated at a constant heating rate of temperature or time under air or any inert gas atmosphere like nitrogen. This is a very useful quantitative analysis which depicts thermal reaction accompanying by weight loss due to the evaporation, dehydration, and degradation. In differential thermal gravimetric (DTA) study, the differential of temperature is plotted against time, or against temperature. This methodology gives idea about the temperature at which high rate of degradation takes place. These analysis were performed in a EXSTAR TG/DTA6300 RT (RT Instruments Inc. Woodland, CA, USA), the nitrogen flow rate was kept constant at 200 ml/min. The optimum loaded untreated and treated composites samples (8-10mg) were heated from ambient temperature to 800°C at different heating rates (5,10,20 and 40°C/min)

3.3.12 Thermal degradation kinetics and activation energy

Activation energy of thermal degradation of composites can be evaluated by different methods. There are many iso conversional procedures that can be used in calculation of activation energy.

The first integral method is Flynn-wall-Ozawa model (FWO) which is based on the given equation

$$\ln \beta = c - 1.052 \frac{E_a}{RT}$$

Where β is heating rate in K min^{-1}, E_a is activation energy in kJ mol^{-1} and c is a constant while T is the temperature in K and R is gas constant. The activation energy of fibers can be calculated using slope of graph of ln β versus 1/T.

The second integral method is Kissinger-Akahira-Sunose (KAS) which is based on the equation

$$\ln(\beta/T^2) = \ln(\frac{AR}{E_a \times g(x)}) - \frac{E_a}{RT}$$

Where x is degree of conversion and activation energy can be calculated from slope of graph between ln (β/T^2) and 1/T.

The Differential method is Friedman method

$$\ln(dx/dt) = \ln[Af(x)] - \frac{E_a}{RT}$$

Here x is degree of conversion and slope of graph plotted between ln(dx/dt) and 1/T will give the activation energy

The summary of the used methods for calculation of activation energy in the present work is as follows in Table 3.1

Table 3.1: Different methods for calculation of activation energy of fibers and composites

Method	Expressions	Plots	Reference
Flynn-wall-Ozawa (FWO)	$\ln \beta = c - 1.052\frac{E_a}{RT}$	ln β versus 1/T	(Motaung et al. 2015)
Kissinger Akahira-Sunose (KAS)	$\ln(\beta/T^2) = \ln(\frac{AR}{E_a \times g(x)}) - \frac{E_a}{RT}$	$\ln(\beta/T^2)$ versus 1/T	(Motaung et al. 2015)
Friedman	$\ln(dx/dt) = \ln[Af(x)] - \frac{E_a}{RT}$	$\ln(dx/dt)$ versus $1/T$	(Venkatesh et al. 2013)

3.3.13 Water absorption analysis

The water absorption characteristic of untreated and various treated/loaded epoxy composites were examined according to ASTM D570. The size of the sample was 76.2 mm x 25.4 mm by the thickness of material. The following equation has been used for analysis

$$\% M = \frac{M_f - M_i}{Mi} X\ 100$$

Where, M_i is the dry initial weight and M_f is the weight after immersion in water and % M is water absorption rate. The water absorption behavior in reinforced polymer composites follows Fickian as well as non Fickian diffusion behavior. To analyze diffusion behavior following equation can be used.

$$Fs = \frac{M_t}{M_m} = kt^n$$

Where M_t the percentage of the water is absorbed in the sample at time *t*, M_m is the maximum percentage of the water absorbed, and *k* and *n* are the kinetic parameters. The diffusion coefficient (D) for the water absorption by composite can be calculated using the following equation and mathematical analysis (Celino et al. 2013). Here h is the thickness of sample.

$$\boldsymbol{F_s = \frac{M_t}{M_m} = \left(\frac{4}{h}\right)\left(\frac{Dt}{\pi}\right)^{1/2}}$$

3.3.14 Compositional (Lignocellulosic) analysis of filler

Cellulose, hemicellulose, lignin, extractives, and and ash content of Kans grass filler were determined by these analytical methods earlier used in literature.

3.3.14.1 Ash content

Filler was burnt in muffle furnace for 3 hours at 540°C and difference between original sample and residue, is the ash

3.3.14.2 Extractive content

The Kans grass filler (w_0) was leached with benzene and ethanol mixture having 2:1 volume ratio for 3 hrs keeping temperature fixed at 60°C. After this the residue was dried to a constant weight at 105°C. The dried sample was put in a desiccator and allowed for cooling and then weighed (w_1). The mass of extractives was calculated by difference in w_0 and w_1 and so on the percentage (Varma and Mondal 2016).

3.3.14.3 Hemicellulose content

The hemicellulose content was calculated by boiling extracted (w_1) residue in 0.5M solution of NaOH for 3.5 hours after that the residue was washed and neutralized and dried to a constant weight. The dried sample was put again in desiccator and allowed for cooling and weighed (w_2). The difference in w_1 and w_2 represents the amount of hemicellulose (Kale et al. 2018, Varma and Mondal 2016).

3.3.14.4 Lignin content

Lignin was determined by digesting the fillers in 72% sulphuric acid after that refluxing for 5 hours in boiling water. The residue was washed after filtering lignin containing water. The combined amount of acid insoluble lignin and ash was estimated based on the difference in weight before digestion and weight of residue after extraction of lignin (Vinayaka et al. 2017, Kale et al. 2018). The acid soluble lignin was calculated in hydrolysate with the help of UV spectrophotometer (Schimadzu) (Kale et al. 2018, Sluiter et al. 2010).

3.3.14.5 Cellulose content

Cellulose percentage can be calculated from the difference between 100 and summation of percentages of extractives, hemicellulose and lignin

3.3.15 Experimental and Instrumental errors

Experimental uncertainties are due to either random or systematic errors. Random errors are basically statistical fluctuations (can be in either direction) in the measured value due to the precision limitations of the measurement device. Random errors generates from the

experimenter's inability to take the same measurement in exactly the same way to get exact the same number. Systematic errors are reproducible inaccuracies that are always in the same direction. A proper care is taken to ensure the repeatability of the results and International standards are followed for the analysis and testing.

CHAPTER 4

CHARACTERIZATION AND EFFECT OF 5% AND 10% NaOH TREATMENT ON TEFF STRAW FIBER

4.1 Physical and tensile properties of Teff straw fiber

The density, diameter, tensile strength and tensile modulus of untreated and treated Teff straw are shown in Table 4.1. The density values measured by distilled water as immersion liquid of 5% treated Teff straw has been increased by 6.67% as compare to untreated Teff and density of 10% treated Teff straw shows the increment of 14%. This might be because of of removal of hemicellulose, lignin and waxy layers from the fiber. Similar trend is observed using benzene as immersion liquid. Variation in the results using two different liquids is due to swelling and non covalent interactions between water and cellulose which is not in case of non polar solvent. The density of Teff straw is little higher as compare to the other natural fibers. The diameter reduces in case of treated fiber; this is also due to the removal of lignin, surface impurities and waxy layers from the fiber surface and this is also responsible for improvement in mechanical properties because it leads to increases the amount of cellulose exposed on the fiber surface. The tensile property of Teff straw fiber is better if we compare it to the other natural fibers reported.

Table 4.1: Diameter, Density and Tensile properties of African Teff straw (untreated and alkali treated)

Fiber	Density (g/cm^3) (using water)	Density (g/cm^3) (using benzene)	Diameter (µm)	Tensile strength (MPa)	Modulus (GPa)
Teff straw (untreated)	1.20	1.15	230-270	280-326	9.2-10.7
Teff straw (5% alkali treated)	1.28	1.23	210-250	368- 404	11.3-12.4
Teff straw (10% alkali treated)	1.37	1.31	180-220	312- 338	10.1-10.9

In Table 4.2 like Amazonian vegetable, Phoneix sp., Corn husks etc. and comparable with so many other fibers. 5% alkali treated Teff straw is showing 31% increase in tensile strength and 22 % increase in tensile modulus. This improvement is the result of partial removal of noncellulosic components such as lignin, wax, hemicellulose and impurities. The higher alkali concentration leads to decline in properties which might be because of excess alkali concentration delignify the fiber excessively which can adversely affects the strength of fiber. The two parameter Weibull distribution curve at a confidence level of 95% of strength at break of untreated and alkali treated fibers are shown in Figure 4.1. It can be observed that strength of 25 samples are situated inside the line and fit with Weibull distribution

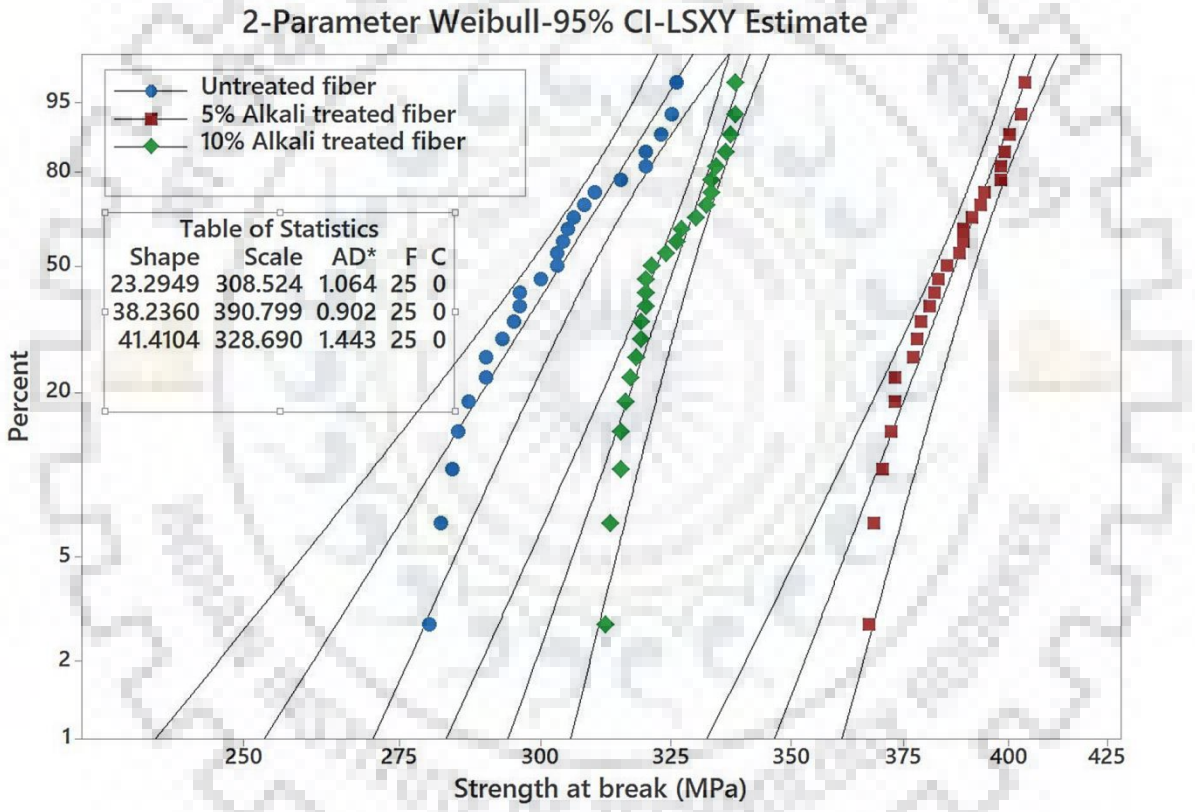

Figure 4.1: Two parameter Weibull distribution plot for tensile strength at break of untreated, 5% alkali treated, 10% alkali treated Teff straw

Table 4.2: Diameter, Density and Tensile properties of reported new natural fibers

Fiber	Density(g/cm^3)	Diameter (µm)	Tensile strength (MPa)	Modulus (GPa)	Reference
Sansevieria	1.41	-	345.174	20.667	(Ramanaiah et al. 2011)
Amazonian Vegetable		10.1-25.9	24.2-113.2	0.4231-0.2806	(Fonesca et al. 2013)
Cissus quadrangularis root	1.51		1857-5330	68-203	(Indran et al. 2014)
Acacia leucophloea			317-1608	8.41-69.61	(Arthanarieshwaran et al. 2015)
Phoenix Sp.	1.2576±0.062	576± 204	120-200	3-6	(Rajeshkumar, et al. 2017)
Corn husks	0.34	186 ±20	160.49±17.12	4.57±0.54	(Sari et al. 2018)
Juncus effusus L.	1.139	280±56	113±36	4.38±1.37	(Maache et al. 2017)
Salago	1.023	6.23	1187	-	(Pouriman et al. 2018)
Windmill palm		225.24±97.77	302.62	2724	(Chen et al. 2017)
Areca palm leaf stalk,.	1.09±0.024	285-330	334.66±21.46	7.64±1.13	(Shanmugasundaram et al. 2018)
Coccinia grandis L	1.243±0.022	27.33±0.3789	273±27.74	10.17±1.261	(Senthamaraikannan et al. 2018)
Conium maculatum	-	-	327.89±67.41	15.77±3.15	(Kilinc et al. 2018,)
Furcraea foetida	0.778	12.8	590.45- 623.52	5.99-6.52	(Manimaran et al. 2018)
Cellulosic Chloris barbata	0.634				(Balasundar et al. 2018)
Calotropis gigantea Bast Fibers	1.324		629	21.3	(Ramasamy et al. 2018)

4.2 SEM observation of untreated and treated fibers

The corresponding SEM images of the untreated and treated Teff straw are shown in Figure 4.2 Figure (a) shows the SEM micrograph of untreated Teff straw. It can be clearly seen that there are considerable impurities, waxes on the fiber surface. Figure (b) and (c) shows the images of Teff straw treated with 5% and 10% wt of NaOH. It can be examined that a clean and rougher surface with less impurities and waxes is there in case of 5% treated fiber without damaging the fiber surface, this might be because of partial removal of hemicellulose, lignin and other impurities. These morphological changes are beneficial for composite manufacture as rougher surface improves the adhesion between the fiber and matrix. However when the fibers were treated with 10% NaOH solution, degradation of fiber surface is observed, this is likely due to fiber surface was affected by high alkali concentration and damaged in surface topography.

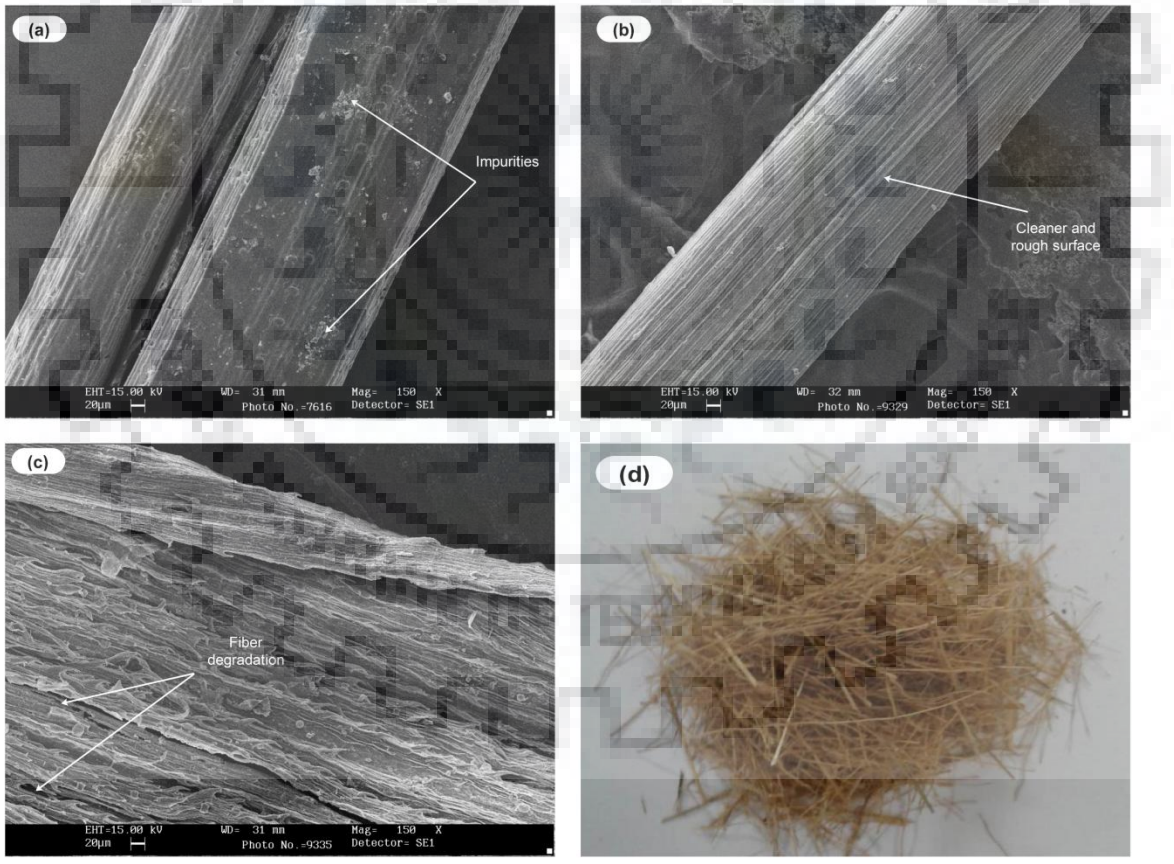

Figure 4.2: SEM images (a) Untreated Teff straw (b) 5% NaOH treated Teff straw (c) 10% NaOH treated Teff straw (d) Fiber samples

4.3 Fourier transform infrared spectroscopy (FTIR)

The untreated and alkali treated fibers were analyzed by Fourier transform infrared spectroscopy. The Figure 4.3 (a) shows the infrared spectra of untreated Teff fiber which has peak at 3328 cm^{-1} because of OH stretch. The peak around 2918 and 2850 cm-^{1} ascribed to CH and CH_2 (Wassie and Srivastava 2016) stretching vibration which is because of cellulose and hemicellulose component. The bands around 1738 cm^{-1} and 1226 cm^{-1} (Motaung and Ananajiwala 2015) cm^{-1} correspond to aromatic skeletal vibrations of hemicellulose and lignin. The peak at 1010 cm^{-1} is because of CO stretching mode of hydroxy and ether groups in cellulose. The 5% NaOH treated fiber in Fig. 4.3 (b) shows similar pattern of bands as untreated one but the peaks at 1738 and and 1226cm^{-1} (Motaung and Ananajiwala 2015) were almost disappeared as a result of removal of lignin and hemicellulose. There is no significant difference between 10% treated Teff fiber in Fig. 4.3 (c) and 5% treated fiber except increase in intensity around at peak 3328 cm^{-1} because of O-H stretching groups.

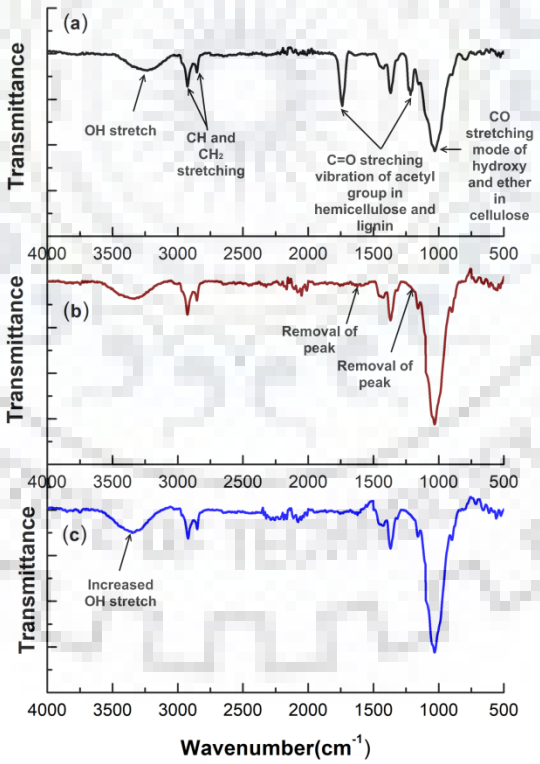

Figure 4.3: FTIR spectra of(a) untreated and (b) 5% NaOH (b) 10% NaOH treated Teff straw fiber

4.4 X-ray diffraction (XRD)

The XRD graphs of untreated and treated Teff straw are presented in Figure 4.4 (a),(b),(c). A broad peak at 2θ~21.9° is present in all the graphs which is associated with the cellulose. The crystallinity index of untreated Teff fiber as 54% (Waasie and Srivastava 2016a). 5% NaOH treated fiber has crystallinity index 72% which is a significant improvement because of removal of amorphous hemicellulose and lignin. There is no further improvement in crystallinity index in case of 10% NaOH treated Teff straw because of degradation in fiber surface which is evident in SEM morphology. The crystallinity index of 10% NaOH treated Teff straw was 71%. High alkali concentration can delignify the fiber excessively and results in onset of degradation of surface which is evident in SEM images that is why after a certain concentration there is no further improvement in crystallinity index.

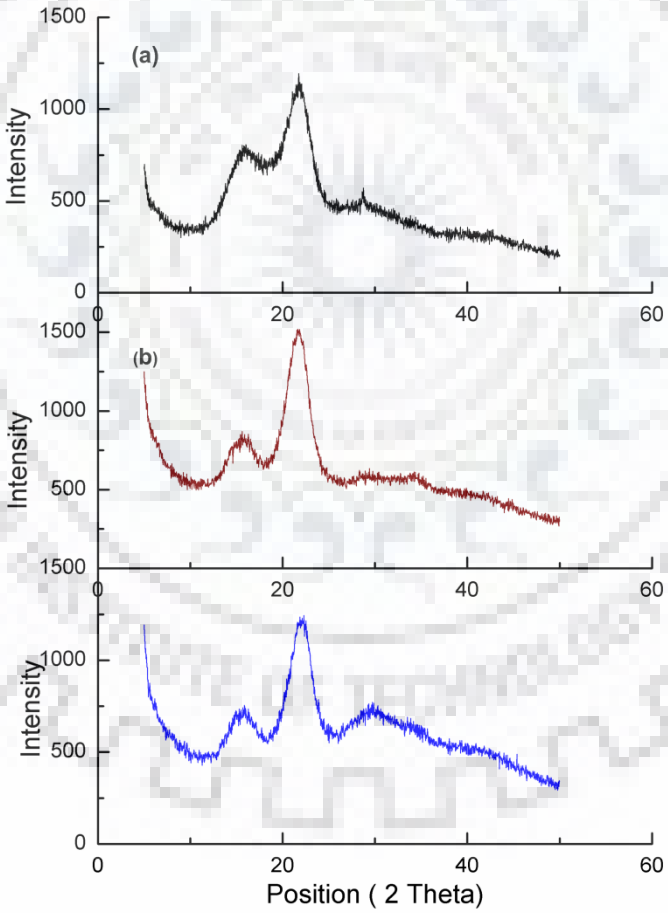

Figure 4.4: XRD spectra of (a) Untreated (b) 5% NaOH (c) 10% NaOH treated Teff

4.5 Atomic force microscopy

Figure 4.5 (a), (b) and (c) shows the images of untreated and treated Teff straw respectively. The root mean square roughness has been increased in case of 5% alkali treated (b) Teff straw which is favorable if we manufacture composite as it will improve the adhesion between fiber and polymer because increased surface roughness leads to better mechanical interlocking between fiber and polymer matrix resulting improved adhesion . There is no further improvement in (c) as degradation of fiber is taking place at high alkali concentration. The value of R.M.S. roughness are given in Table 4.3

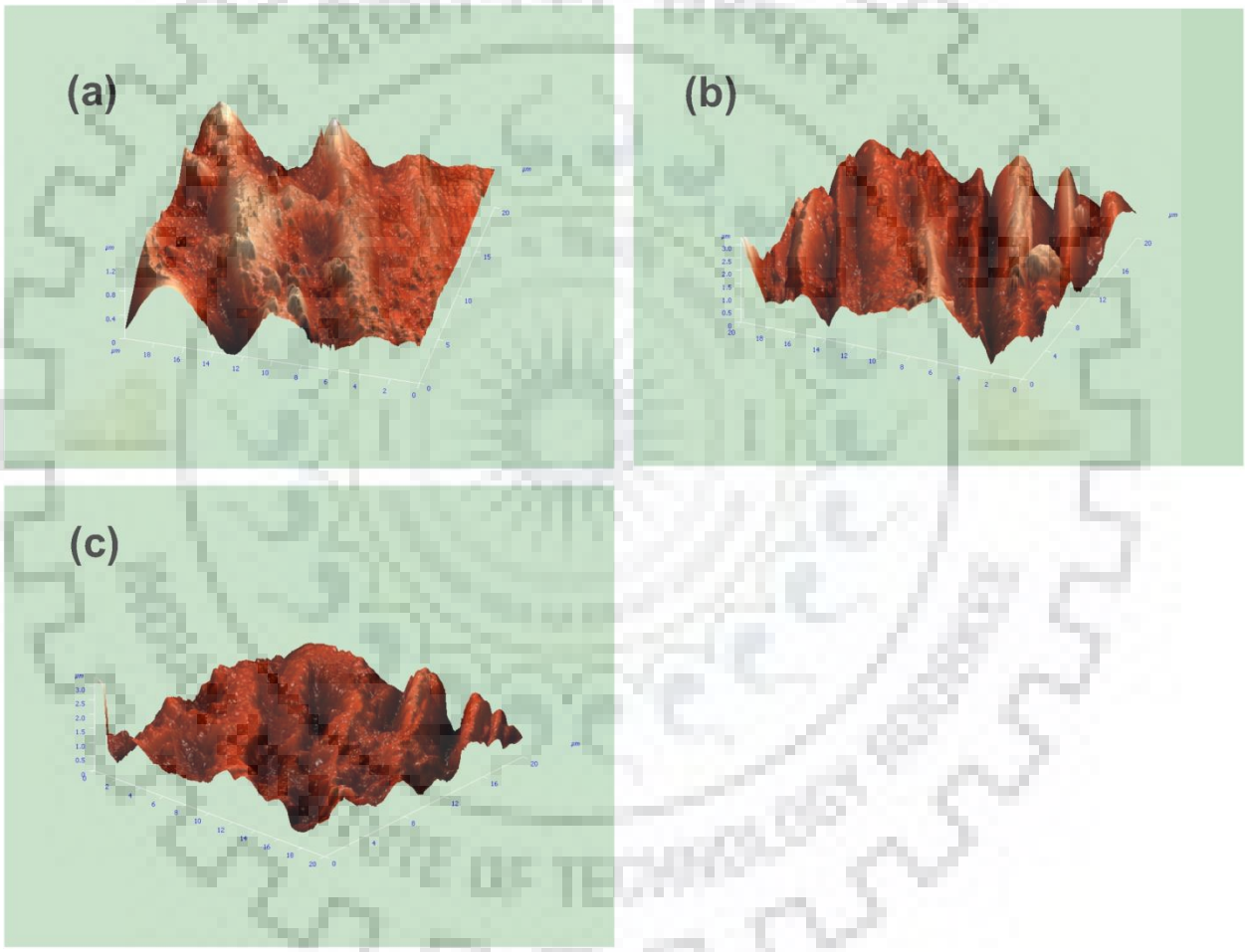

Figure 4.5: AFM images of (a) untreated (b) 5% NaOH (c) 10% NaOH treated Teff

Table 4.3: Average and R.M.S. roughness of untreated and alkali treated Teff straw

Fiber	Average roughness (nm)	R.M.S. roughness (nm)
Teff straw (untreated)	112.774	148.579
Teff straw (5% alkali treated)	353.446	445.429
Teff straw (10% alkali treated)	221.838	287.804

4.6 Thermogravimetric (TGA) and Thermal kinetics analysis

The thermogravimetric and derivative weight curves of the untreated, 5% NaOH treated and 10% NaOH treated Teff straw are presented in Figure 4.6 and Figure 4.7 The middle zone 260-450°C is corresponding to the degradation of hemicellulose. The 5% NaOH treated Teff straw showed enhancement in thermal stability while 10% NaOH treated Teff straw showed opposite. The detailed investigation of activation energy was done by commonly used methods Flynn-Wall-Ozawa (FWO) and Kissinger - Akahira -Sunose (KAS) and Friedman method.

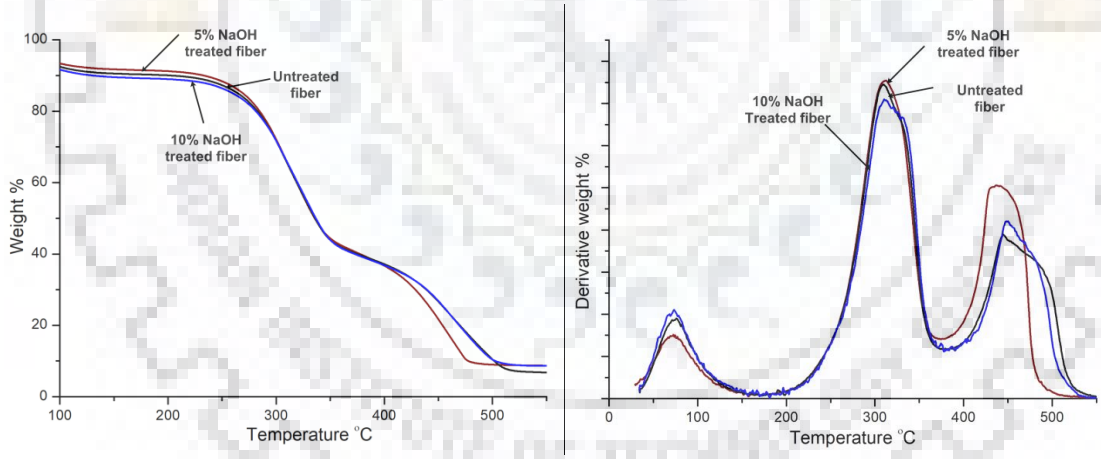

Figure 4.6 and 4.7: TGA and DTG thermogram of untreated, 5% NaOH treated and 10% NaOH treated Teff straw at heating rate 10 °C min^{-1}

From the TGA data of untreated and treated Teff fibers, isoconversional plots according to integral methods were plotted and activation energy values were calculated using the slope of the lines. Figure 4.8 (a-f) showed the graphical representation of untreated, 5% treated and

10% treated Teff straw samples. Figure 4.8 (c and d) showed increase of slope in case of 5% treated fibers the similar observations were also found by (Motaung and Anadjiwala 2015) for sugarcane bagasse.

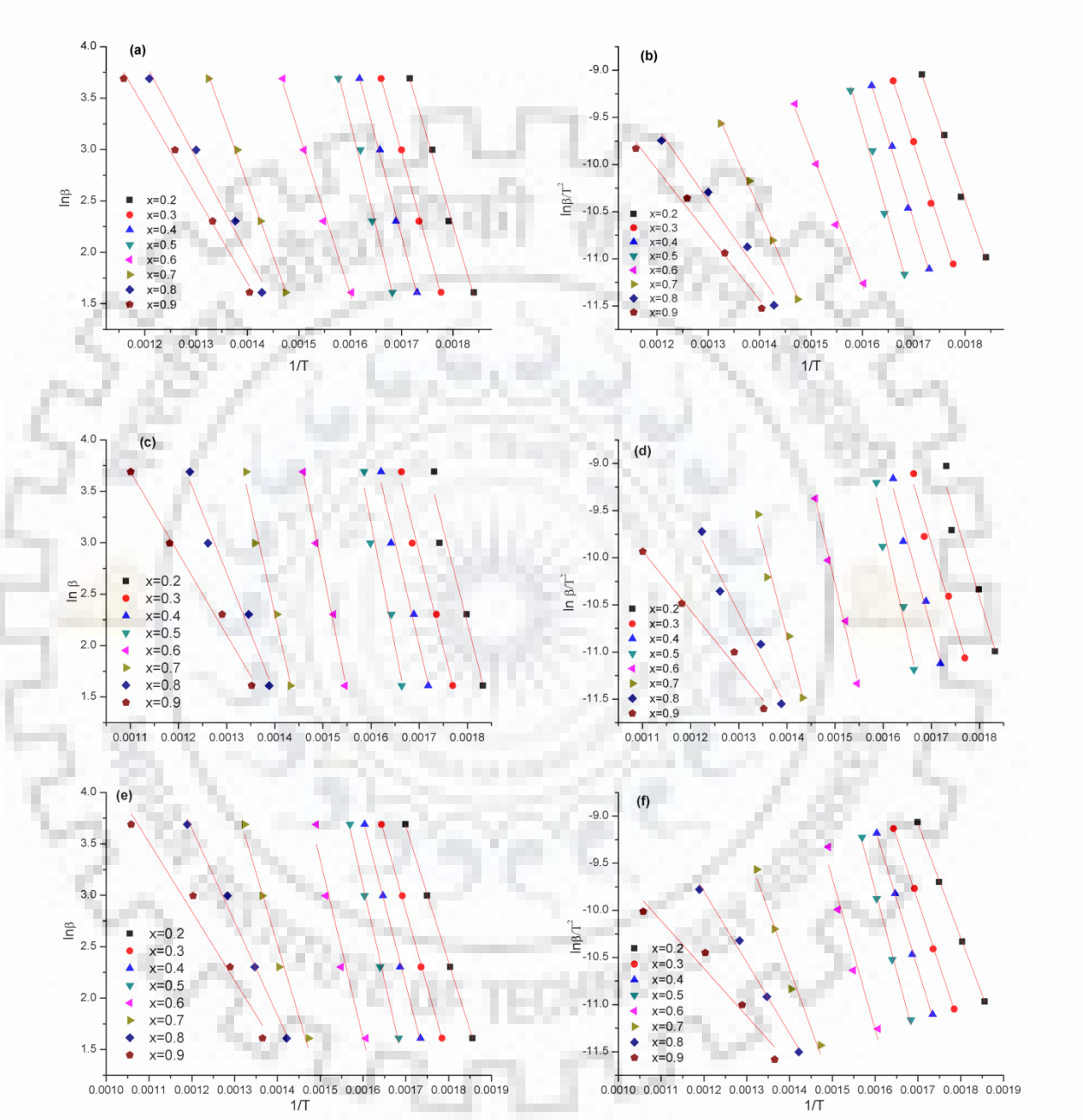

Figure 4.8: FWO plots (a) Untreated Teff (c) 5% NaOH treated Teff (e) 10% NaOH treated Teff straw. KAS Plots of (b) untreated Teff (d) 5% NaOH treated Teff (f) 10% NaOH treated Teff straw

Figure 4.9 (a) and 4.9 (b) are representing the activation energy values of fibers for untreated and treated one as a function of conversion values from two methods namely FWO and KAS . Similar trend is observed in both the methods and for the conversions 0.2 to 0.6 the activation energy values observed within the range of (100-200 kJ/mol) as reported in previous work based on natural fibers (Yao et al. 2008 ; Jr. et al. 2014 ; Moatung and Ananjiwala 2015). It is evident from the both the figures that 5% NaOH treated Teff fibers showed the remarkable increase in activation energy (136 to 164 KJ/mol) which advocates the increased thermal stability while 10% NaOH treated Teff fibers showed decrease in activation energy values because of degradation in surface due to excess alkali concentration.

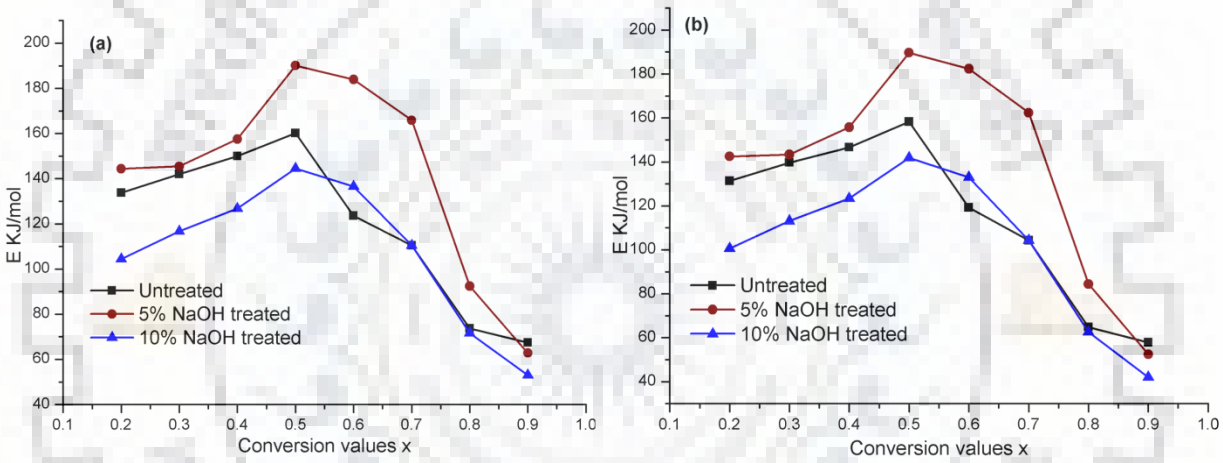

Figure 4.9: Activation energy values of untreated and treated Teff fiber vs degree of conversion (a) FWO method (b) KAS method

Figure 4.10 shows the plots obtained from differential method (Friedman method) described earlier. Slight variations are observed in the values of activation energy from differential method as compared to integral methods because of assumptions used in methods but the trend of variation of activation energy with conversion shown in Figure 4.10 (d) is similar to that of integral methods in Figure 4.9 (a) and Figure 4.9 (b). The lower values of activation energy of 10% alkali treated fiber are likely be due to excessive delignification, depolymerization of native cellulose or degradation of fiber surface.

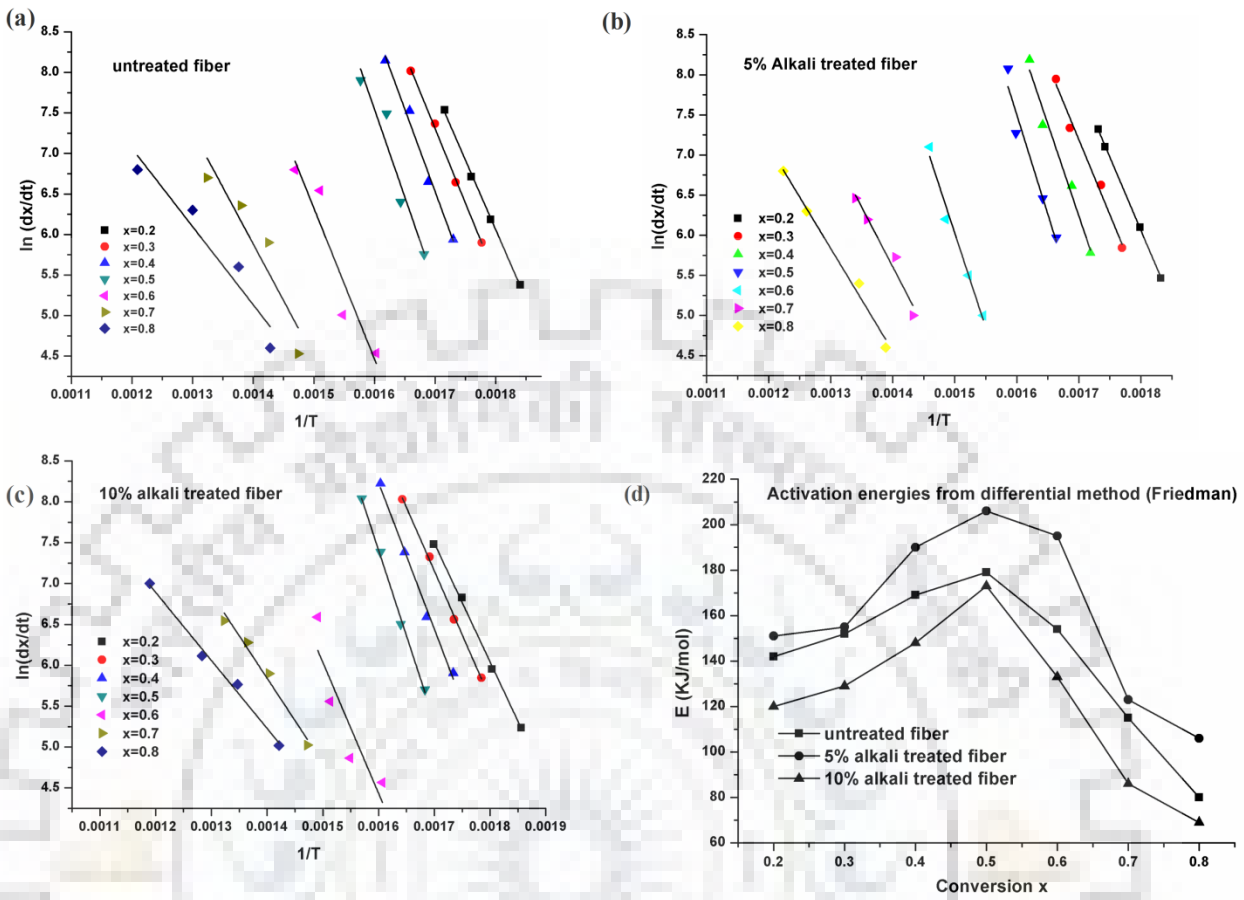

Figure 4.10 Friedman plots (a) Untreated Teff (b) 5% NaOH treated Teff (c) 10% NaOH treated (d) activation energy

CHAPTER 5

EPOXY COMPOSITES REINFORCED WITH TEFF STRAW

5.1 Mechanical properties

The average values of mechanical characteristics that are tensile strength, tensile modulus, flexural strength and flexural modulus for different loading of untreated and treated Teff straw reinforced epoxy composites are represented in Figure 5.1 to 5.4. It can be clearly observed in Figure 5.1 and 5.2 that up to 15 % fiber loading for both untreated and treated composites the value of tensile strength and tensile modulus are increasing and after that both the parameters begin to reduce.

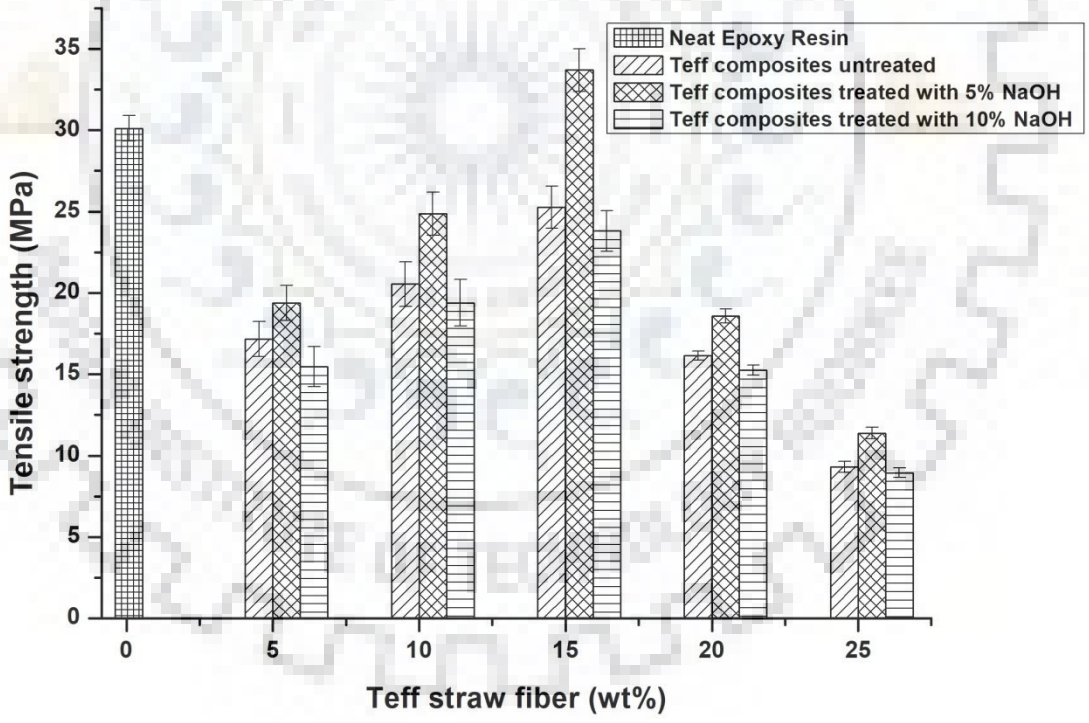

Figure 5.1: Effect of fiber loading and alkali treatment on tensile strength of Teff straw reinforced epoxy composites

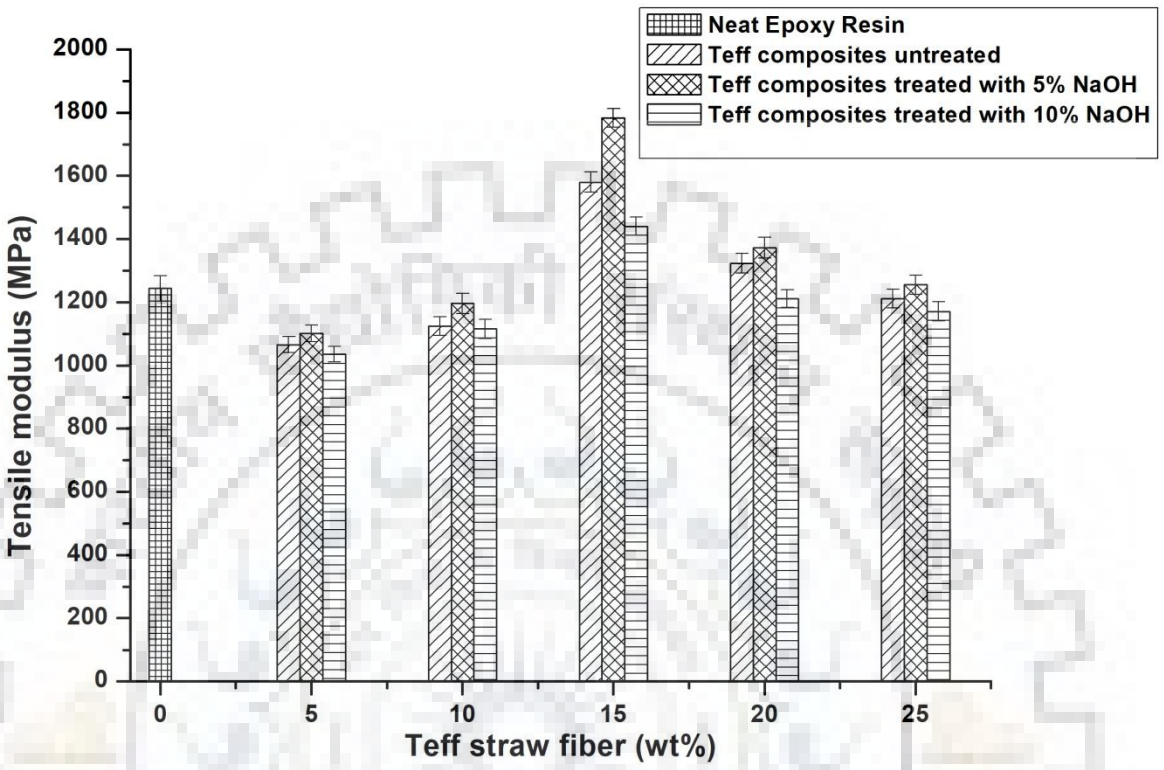

Figure 5.2: Effect of fiber loading and alkali treatment on tensile modulus of Teff straw reinforced epoxy composites

This behavior can be explained by the fiber's capacity to transfer the stress effectively up to 15 % fiber loading and beyond that further improvement of the properties is not taking place. Improvement of more than 10% of tensile strength as compare to neat resin is obtained in case of 5% alkali treated sample and 15% fiber loading. Similar trend was observed in Acacia leucophloea fiber based epoxy composites (Arthanarieshwaran et al. 2016) for 20% fiber loading. 5% NaOH treated samples are showing significant improvement in the properties as compared to untreated one. Samples with 10% NaOH treatment have no appreciable improvement in terms of properties this can be understood by the fact that high concentration of alkali is not suitable for fiber surface.

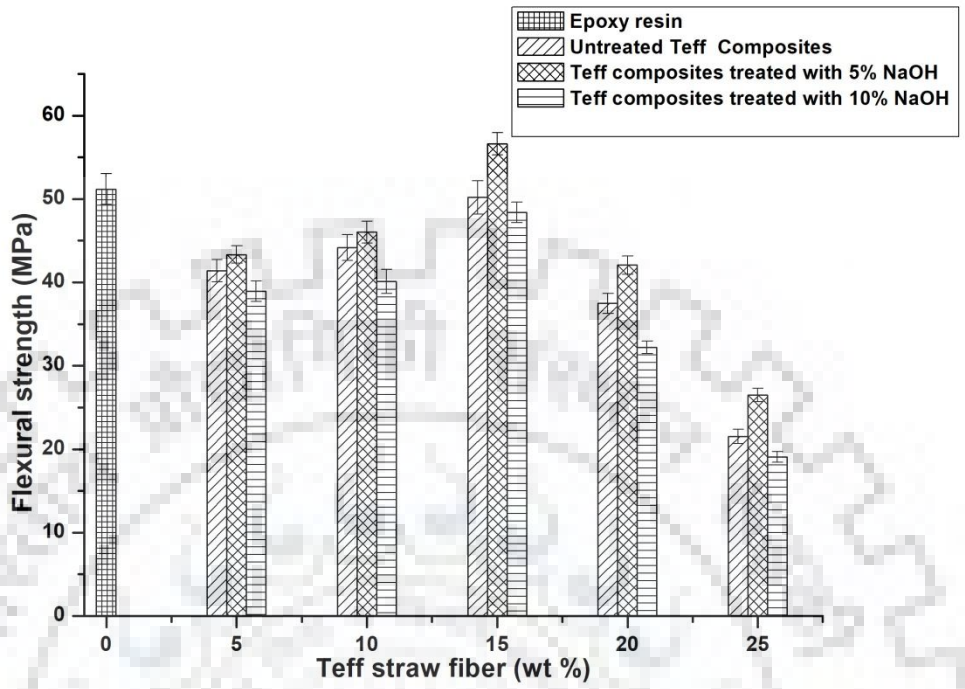

Figure 5.3: Effect of fiber loading and alkali treatment on flexural strength of Teff straw reinforced epoxy composites

Similar trend can also be observed in flexural strength of untreated and treated samples of Teff composites in Figure 5.3. It is clear from the figure that values are improving for both untreated and treated samples upto 15 % fiber loading and beyond that deterioration in properties is taking place, this can be explained that beyond 15% fiber loading, fiber matrix adhesion is poor which is responsible for non uniform stress transfer and agglomeration of fibers within the matrix and ultimately leads to degradation in properties. 5% alkali treated samples have superior values of flexural strength as compared to untreated ones. More than 11% improvement in flexural strength is taking place as compare to neat epoxy resin in case of 15% loading and treatment. High alkali concentration that is 10% is not going to add value in the results, which is because high concentration of alkali causes damage of fiber surface which leads to decrease in the properties. Figure 5.4 represents the effect of fiber loading and alkali treatment on flexural modulus. Flexural modulus values are also increasing up to 15% fiber loading for both untreated and treated samples. Flexural modulus of all the composites are higher as compared to neat epoxy resin , this shows that this reinforcement increase the

stiffness in composites as compare to neat resin. Table 5.1 is giving the comparison of performance of epoxy composites reinforced with various fibers and the fiber used in this study. From the values it can be predicted that 5% alkali concentration is the preferable choice for the researchers and performance of Teff straw is comparable with other new natural fibers

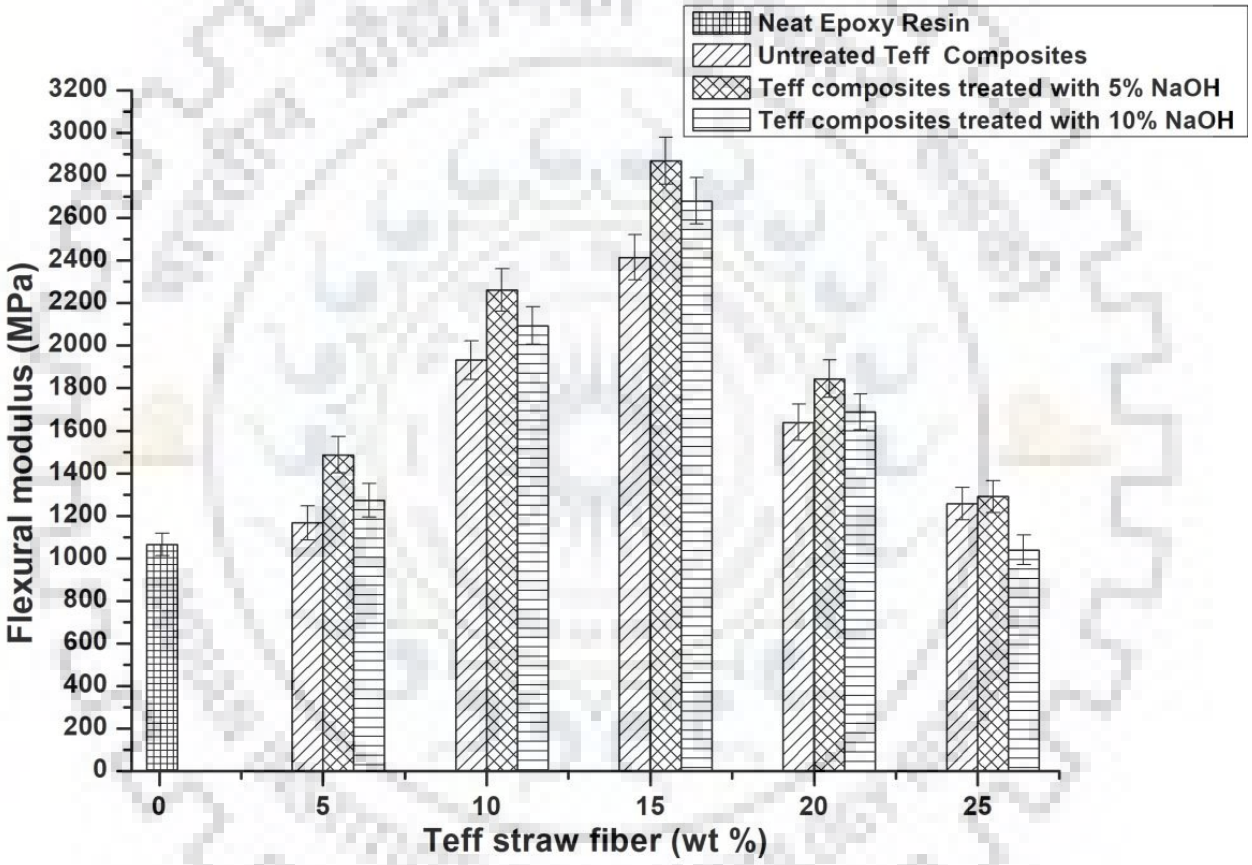

Figure 5.4: Effect of fiber loading and alkali treatment on flexural modulus of Teff straw reinforced epoxy composite

Table 5.1: Comparison of tensile and flexural properties of epoxy composites reinforced with some new natural fibers

Fiber	Matrix	Treatment for Improved properties	Optimum fiber loading	Improvement in tensile strength as compare to neat epoxy resin	Improvement in flexural strength as compare to neat epoxy resin	Reference
Teff fiber	Epoxy	5% alkali treatment	15%	More than 12% improvement	More than 10% increase	Present work
Teff fiber	Epoxy	10% alkali treated	15%	Degradation in properties as compare to 5% alkali	Degradation in properties	Present work
Sugar Palm	Epoxy	0.25 M NaOH for 1 hour	10%	16.4% increase in tensile strength and more than 18% increase in tensile modulus	-	Bachtiar et al. 2008
Henequen	Epoxy	6% NaOH	64%	No significant Improvement	No significant improvement	Murillo et al. 2009
Agave	Epoxy	5% NaOH	30%	Significant improvement	15% improvement as compare to untreated one	Mylsamy et al. 2011
Arundo Donax	Epoxy	None	5,10,15%	Reduction in tensile strength more than 50% in few cases	13.3% improvement in case of 10% loading	Fiore et al.
Acacia leucophloea	Epoxy	5% NaOH	20%	19.98% improvement	6.74% increase	Arthanariesh waran at al. 2016

5.2 SEM Morphology of untreated and alkali treated composites

Figure 5.5 is representing the SEM images of untreated and various surface treated composites at fiber loading of 15%. Figure 5.5 (a) shows the image of untreated composites which has many voids and poor fiber matrix interaction. 5% alkali treated composites in Figure (b) shows the better interaction and fewer voids and improved quality of composites. There is no further improvement in case of 10% alkali treated composites in Figure (c).

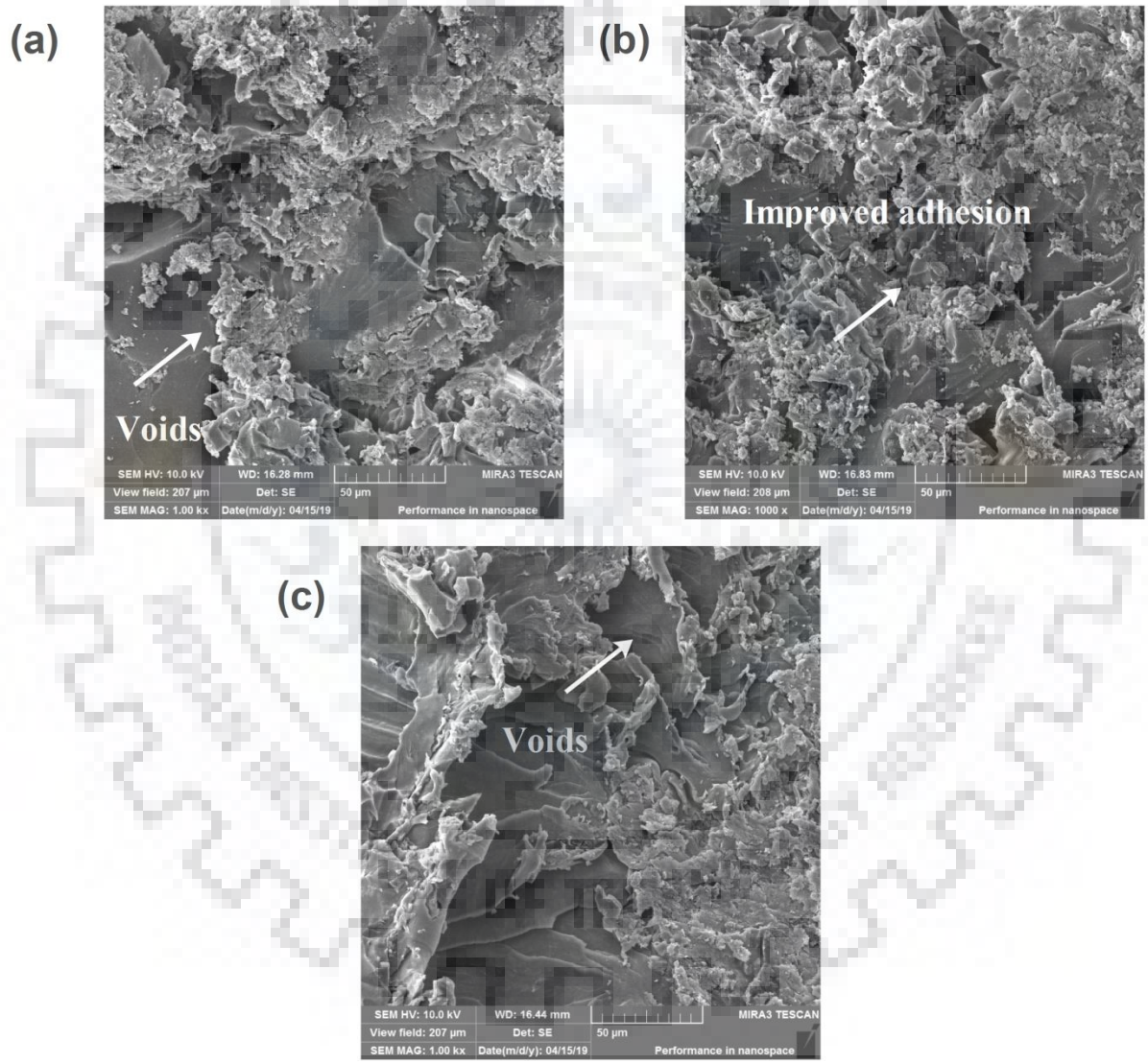

Figure 5.5: SEM images on 15% fiber loading of (a) Untreated composites (b) 5% Alkali treated composites (c) 10% alkali treated composites

5.3 FTIR analysis of untreated alkali treated composites

In the spectra of epoxy composites reinforced with untreated Teff straw at optimum loading of 15% which is shown in Figure 5.6, the presence of epoxy can be confirmed by the additional peak at 2853 cm^{-1} as compare to fiber, which is due to CH_3 of epoxy resin (Almari et al. 2012), the peak at 1508 and 1583cm^{-1} is corresponding to benzene ring of epoxy or C=C stretching of aromatic ring. The only difference between the composites made from untreated and treated Teff straw is the removal of peak at 1738 cm^{-1} (Suresh kumar et al. 2014) in case of treated composites, which is due to the C=O stretching of hemicelluloses. Alkali treatment with 5% NaOH reduced the concentration of hemicelluloses which is evident in IR spectra.

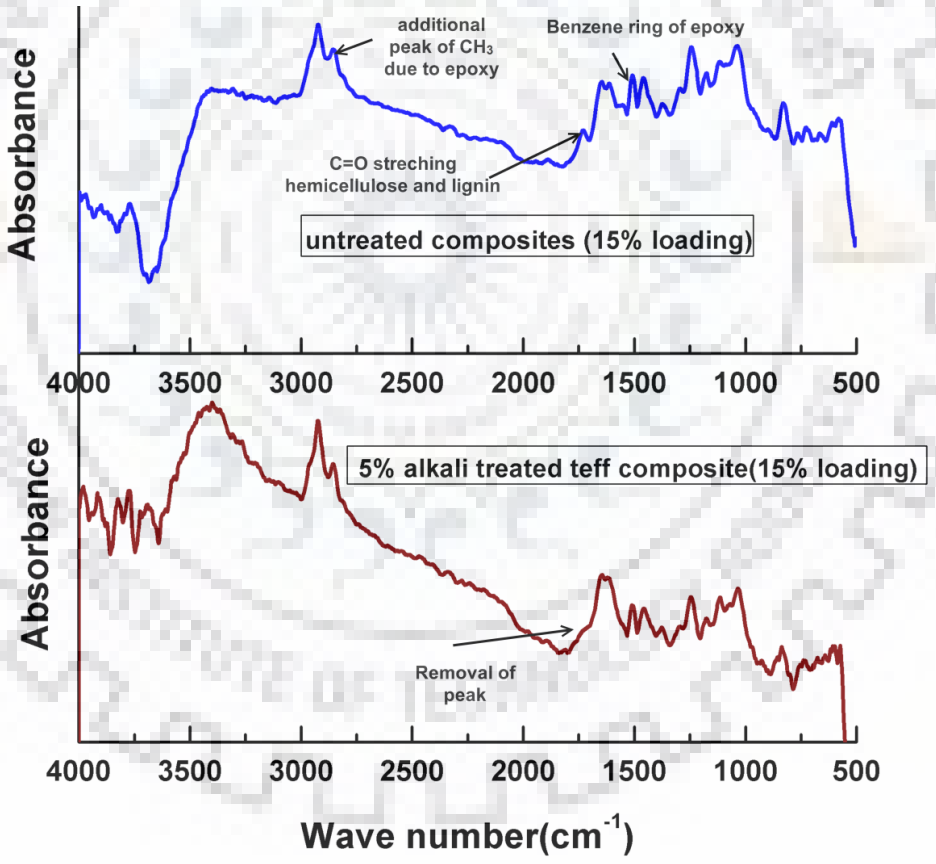

Figure 5.6: FTIR spectra of untreated and 5% alkali treated composite for optimum fiber loading of 15%

5.4 Water absorption

Figure 5.7 depicts the findings of water absorption test on composites developed by untreated fibers and 5% alkali treated fibers. From the Figure it is clear that as we increase the fiber loading, amount of water absorption increases because these lignocelluloses fibers use to be

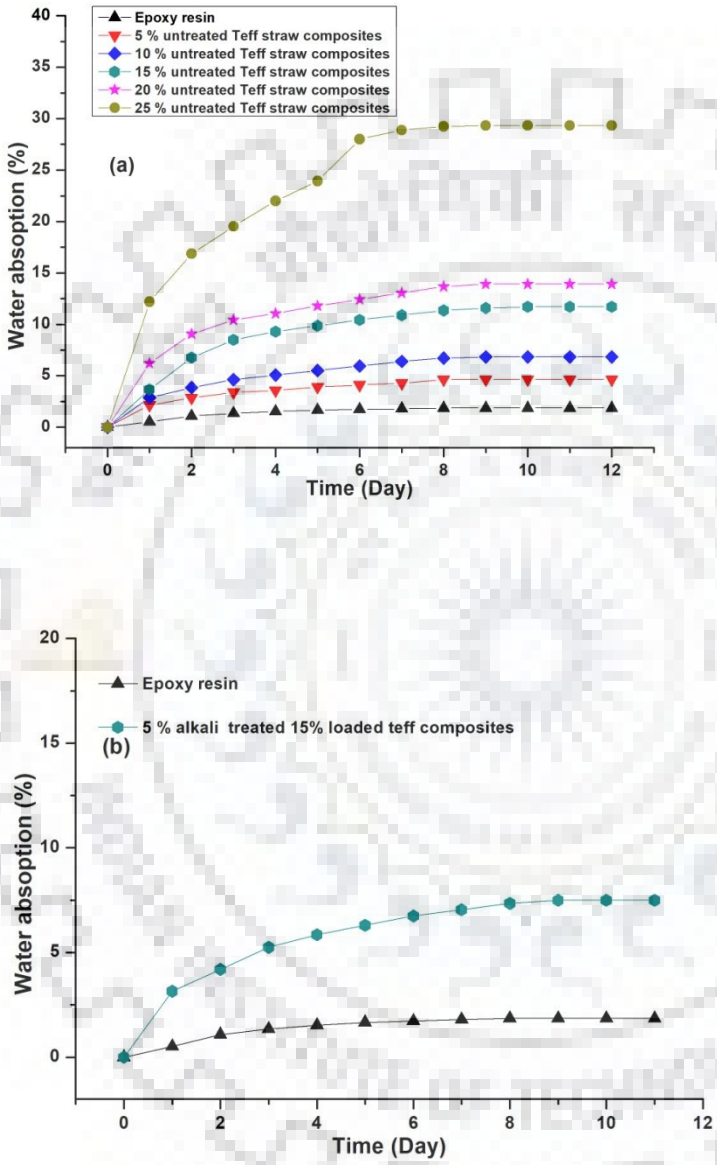

Figure 5.7: Water absorption curve for (a) untreated Teff straw/ epoxy composites (for various loadings) and 5% alkali treated Teff straw/epoxy composites (at 15% fiber loading)

hydrophilic in nature but at the same time if we compare the water absorption between untreated and treated water composites we find that the percentage of water absorption is

less in case of 5% alkali treated samples compare to untreated one (Mittal et al. 2015), this can be understood by the fact that 5% alkali treatment not only improved the morphology of fiber surface but also developed strong adhesion between fiber and matrix and hence produced good quality void free composites which absorbs less water as compared to untreated composites.

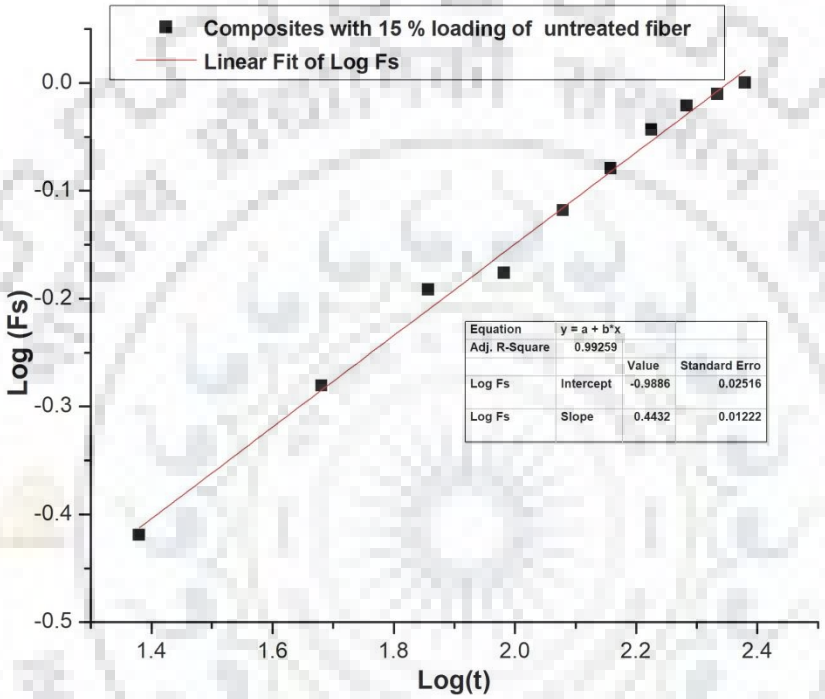

Figure 5.8: Water diffusion curve fitting plot of untreated composite with 15% fiber loading

Figure 5.8 and 5.9 represents the curve fitting graphs of the experimental values used for untreated and 5% alkali treated composite having 15% fiber loading. The parameters n and k were evaluated by curve fitting and the initial diffusivity was estimated with the help of equation described in water absorption test. The Diffusion parameters are shown in Table 5.2, The diffusivity value is reduced from 5.83 to 4.55 in case of treated composite which signifies the improvement in water absorption in case of treated samples.

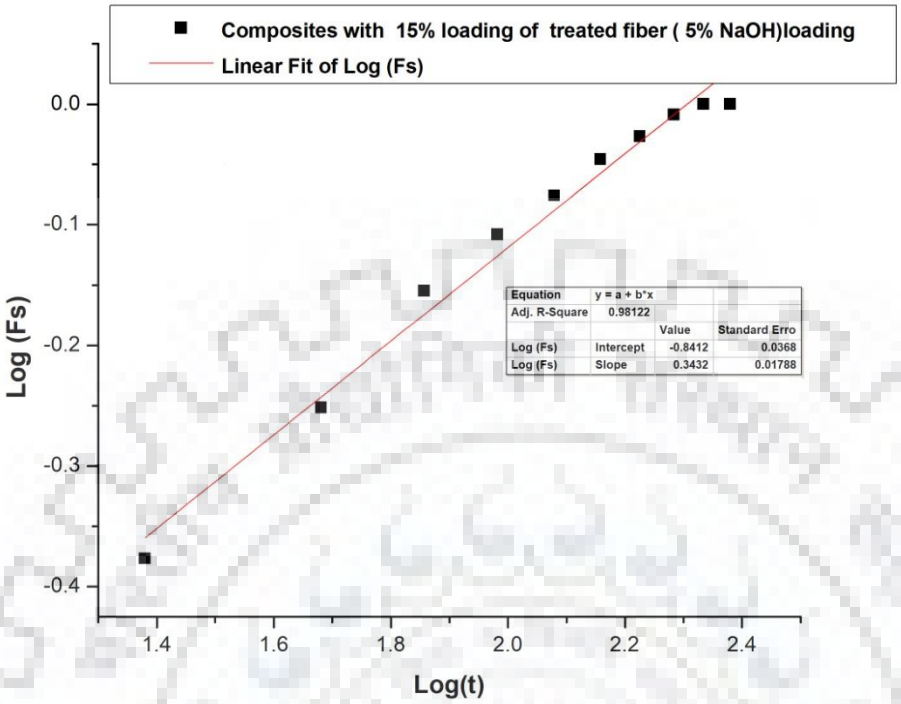

Figure 5.9: Water diffusion curve fitting plot of 5% alkali treated composite with 15% fiber loading

Table 5.2: Kinetic parameters and diffusion coefficient of epoxy composite

Composite	**n**	**k**	**Diffusivity D (m^2/s) *10^{-12}**
15% loading of untreated fiber	0.44	-0.9886	5.83
15% loading of treated (5% alkali) fiber	0.34	-0.8412	4.55

5.5 Thermogravimetric analysis (TGA)

TGA and DTG(Differential thermal gravimetric) curves of epoxy composites reinforced with untreated teff straw and 5% alkali treated Teff straw are presented in figure 5.10. Optimum fiber loading of 15% has been used for both the samples. Three zones of degradation are observed in which first zone 80-100ºC refers to removal of moisture while, second zone 200-470ºC represents degradation of hemicelluloses and other fiber components

and after that degradation of remaining epoxy and lignin take place. The treated fiber based composites have little less residual weight 2.1% as compare to untreated one that is 4.2%, probably because of partial removal of hemicellulose and lignin due to alkali treatment (Arthanarieshwaran et al. 2016). In DTG thermogram it was observed that 5% alkali treated composites have slightly better thermal stability as compared to untreated composites which is evident from the fact that higher rate of weight reduction is observed at 361^{o}C in case of untreated one while at 363 ^{o}C in case of 5% alkali treated samples

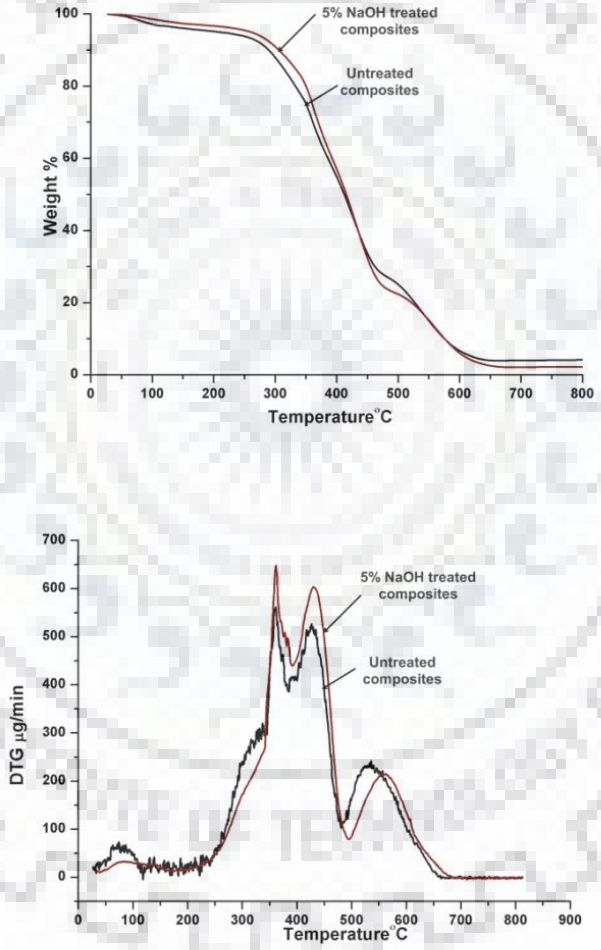

Figure 5.10 TGA and DTG thermograms of untreated and alkali treated Teff reinforced epoxy composites at 15% fiber loading

CHAPTER 6

EXTRACTION, CHARACTERIZATION AND EFFECT OF ALKALI TREATMENT ON KANS GRASS FIBER

6.1 Physical and mechanical properties of Kans grass fiber

The density, diameter and mechanical properties of untreated and various alkali treated (3%, 5%, 7%) fibers along with various other newly explored natural fibers are shown in Table 6.1 The density of 5% alkali treated fiber increased by 7% as compared to untreated fiber while there is a increase of approximately 2.5%, 8.5% in case of 3% and 7% alkali treated fibers. The result gives an inference that alkali treatment increases the density; this is due to partial removal of non cellulosic compounds with alkali treatment. The diameter of untreated fibers is in the range of 310-390 μm which is little high as compared to other natural fibers reported in Table 6.1.The result reveals the reduction of diameter with increasing alkali concentration. This reduction in diameter because of treatment with alkali might be due to removal of waxy layers, surface impurities. The tensile strength of untreated fiber is comparable or better as compared to various other natural fibers presented in Table 6.1. 5% alkali treated fiber has maximum tensile strength which is approximately 24% higher as compared to untreated one. Beyond 5% alkali concentration there is no further improvement in mechanical properties which indicates the optimum level of surface treatment at this concentration. Similar trend is also observed in modulus values.

Table 6.1: Comparison of diameter, density, tensile properties and crystallinity index of Kans grass with other new natural fibers

Fiber	Density(g/cm^3)	Diameter (µm)	Tensile strength (MPa)	Modulus (GPa)	Crystallinity index	Reference
Kans grass fiber	1.188±.008	354±25	337±34	8.91±0.18	53	Present work
3% treated fiber	1.225±.011	305±21	381±17	9.38±.16	66	Present work
5% treated fiber	1.272±.012	238±29	430±16	9.88±.21	76	Present work
7% treated fiber	1.288±.008	172±18	372±25	9.02±.22	74	Present work
Sansevieria	1.41	-	345.174	20.667		(Ramanaiah et al. 2011)
Century		210±50	275±15	8.6±0.31	53.2	(Reddy et al. 2013)
Gomuti (*Arenga pinnata)*	1.40	81-313	173.9±46.9	3.847		(Ticolau et al. 2014)
Prosopis Juliflora	0.58		558±13.4		46	(Sarvankumar et al. 2014)

Acacia leucophloea	1.382		317-1608	8.41-69.61	51	(Arthanarieshwaran et al. 2015)
Nigerian coir	1.097±.0125	369±5	345-440	4.01-4.520		(Akintayo et al. 2017)
Pennisetum Purpureum		240±20	73±6	5.68±0.14		(Ridzuan et al. 2016)
Phoenix Sp.	1.2576±0.062	576± 204	120-200	3-6	57	(Rajeshkumar et al 2017).
Corn husks	0.34	186 ±20	160.49±17.12	4.57±0.54	43.73	(Sari et al. 2017)
Juncus effusus L.	1.139	280±56	113±36	4.38±1.37	33.4	(Maache et al. 2017)
Saharan Aloevera	1.325	91.15	621.8	40.03	52.6	(Balaji et al. 2017)
Salago	1.023	6.23	1187	-		(Pouriman et al. 2017)
Windmill palm		225.24±97.77	302.62±105.02	2.724		(Chen et al. 2017)
Luffa sponge		590±60	33.54±7.18	0.820±0.219	49.1	(Chen et al. 2018)
Areca palm leaf stalk	1.09±0.024	285-330	334.66±21.46	7.64±1.13		(Shamugasundaram et al. 2018)
Coccinia grandis L	1.243±0.022	27.33±0.3789	273±27.74	10.17±1.261	52.17	(Senthamariakannan et al. 2018)
Conium	-	-	327.89±67.41	15.77±3.15	46.4	(Kilinc et al. 2018)

maculatum						
Furcraea foetida	0.778	12.8	590.45- 623.52	5.99-6.52	52.6	(Manimaran et al. 2018)
Arundo donax	1.168		248	9,4		(Fiore et al. 2014)
Cellulosic Chloris barbata	0.634				50.29	(Balasundar et al. 2018)
Calotropis gigantea Bast Fibers	1.324		629±32.6	21.3±2.4	80.9	(Ramasamy et al. 2018)

6.2 FTIR analysis

Figure.6.1 displays The FTIR spectra of untreated and various alkali treated Kans grass fibers. The untreated fiber shows the peak at 3342 cm^{-1} which is because of OH stretching (Manimaran et al. 2018). The peak corresponds to 2894 cm^{-1} represents the CH stretching vibrations of CH and CH_2 which is due to cellulose and hemi cellulose. (Ridzuan et al.2016, Fiore et al. 2014). The peak at 1735 cm^{-1} ascribed to C=O stretching vibrations of acetyl group in hemicellulose (Ridzuan et al.2016, Fiore et al. 2014). The peak around 1596 cm^{-1} is associated with water present in fibers (Fiore et al. 2014). The absorbance peak centered at 1495 cm^{-1} is owed to the C=C stretching of benzene ring of lignin (Chen et al. 2018). The peak at 1422 cm^{-1} is associated with CH_2 symmetric bending (Ridzuan et al. 2016)). The peak noticed at 1368 and 1316 cm^{-1} is attributed to the bending vibrations of CH and CO groups of aromatic ring in polysaccharides (Maache et al. 2017). The band at 1228 cm^{-1} represents the CO stretching vibrations of acetyl group in lignin (Akintayo et al. 2017). The peak centered at 1152 cm^{-1} indicated the CO stretching vibrations of pyranose ring in polysaccharides (Ridzuan et al. 2016) while the peak at 1028, 896 cm^{-1} represents the presence of CO stretching modes of hydroxyl and ether groups, b-glycosidic linkages (Maepa et al. 2015, Ridzuan et al. 2016, Maache et al. 2017, Fiore et al. 2014).The bands for 3% alkali treated fiber are relatively similar to the untreated fiber except there is a reduction in the intensity around the peaks at 1735cm^{-1}, 1495 cm^{-1} and 1228 cm^{-1}, in case of 5% alkali treated there is a complete removal of peaks attributed to 1735 and 1228 cm^{-1} which signifies the partial removal of lignin and hemicellulose because of alkali treatment. In 7% treated fiber there is additional disappearance of of peaks centered at 2894, 1368 and 1152cm^{-1} which represents the degradation in basic structure of fiber along with partial removal of lignin and hemicellulose, also responsible for reducing mechanical properties in case of 7% treated fiber.

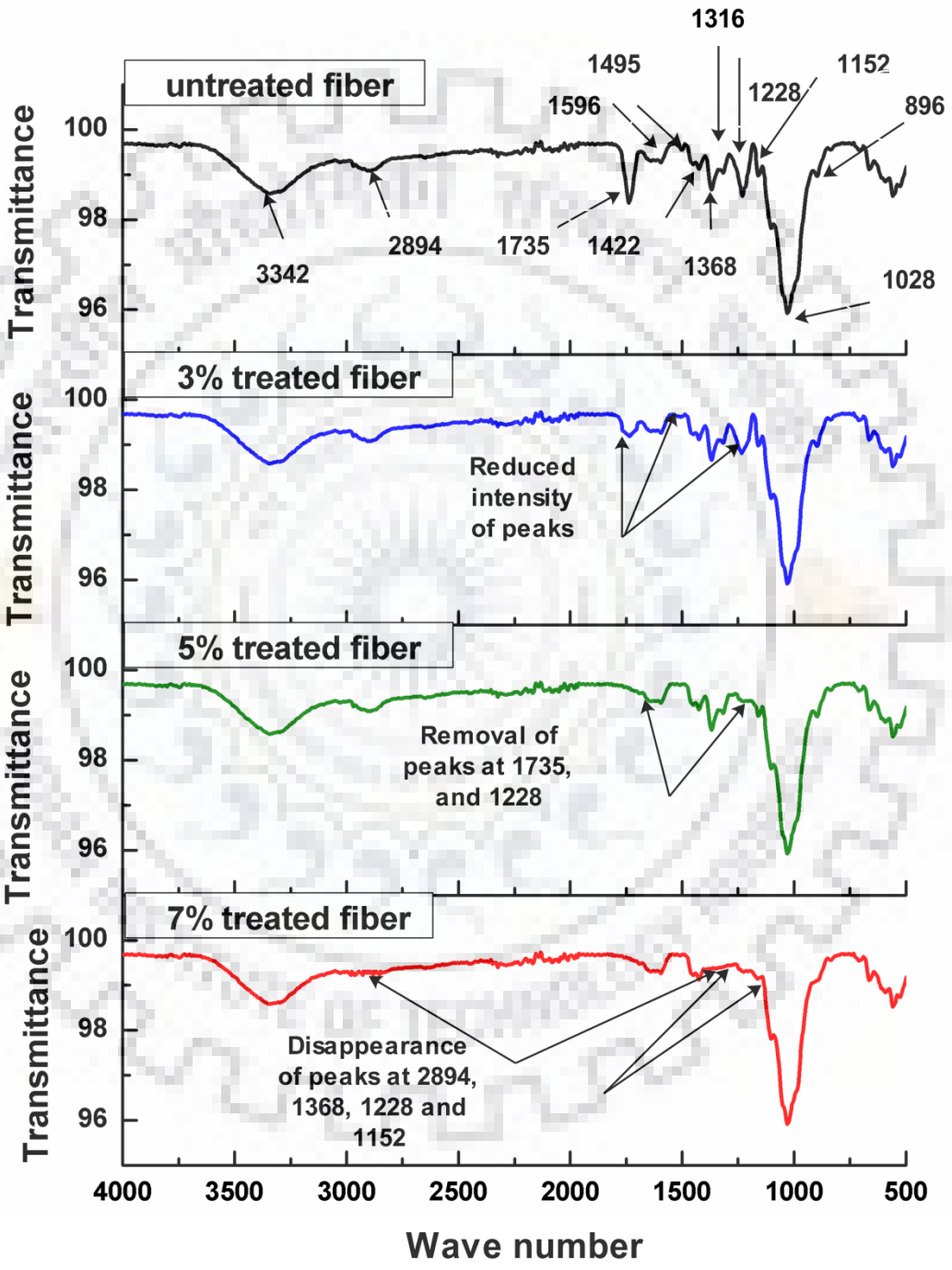

Figure 6.1: FTIR spectra of untreated and treated fiber

6.3 SEM analysis

The SEM images of the untreated and various alkali treated Kans grass fibers are shown in Figure 6.2 It can be observed in the (a) of untreated Kans grass fiber that the filaments of the fibers are joined because of wax, lignin, hemicellulose and oils and a comparatively smooth surface with impurities is visible (Reddy et al. 2017, Balaji et al. 2017). In Figure (b) at 3% alkali treatment the fibrillation starts and roughness is increased around the fiber surface and a cleaner surface is observed which is beneficial for the better interlocking of fiber with the polymer matrix and and exchange of tangential stresses between fiber and matrix (c) is showing fibrilled and rougher surface in case of 5% treated fiber which reflects the change in morphology by the alkalization with optimum concentration of alkali. Fibrillation increases the effective contact surface is which will promote the fiber matrix adhesion (Ridzuan et al. 2016, Rashid et al. 2016, Balaji et al. 2017). Excess alkali concentration can leads to damage of fiber surface and can cause degradation of fiber which is evident in Figure (d) of 7% alkali treated fiber and this degradation and damage of surface is also responsible.

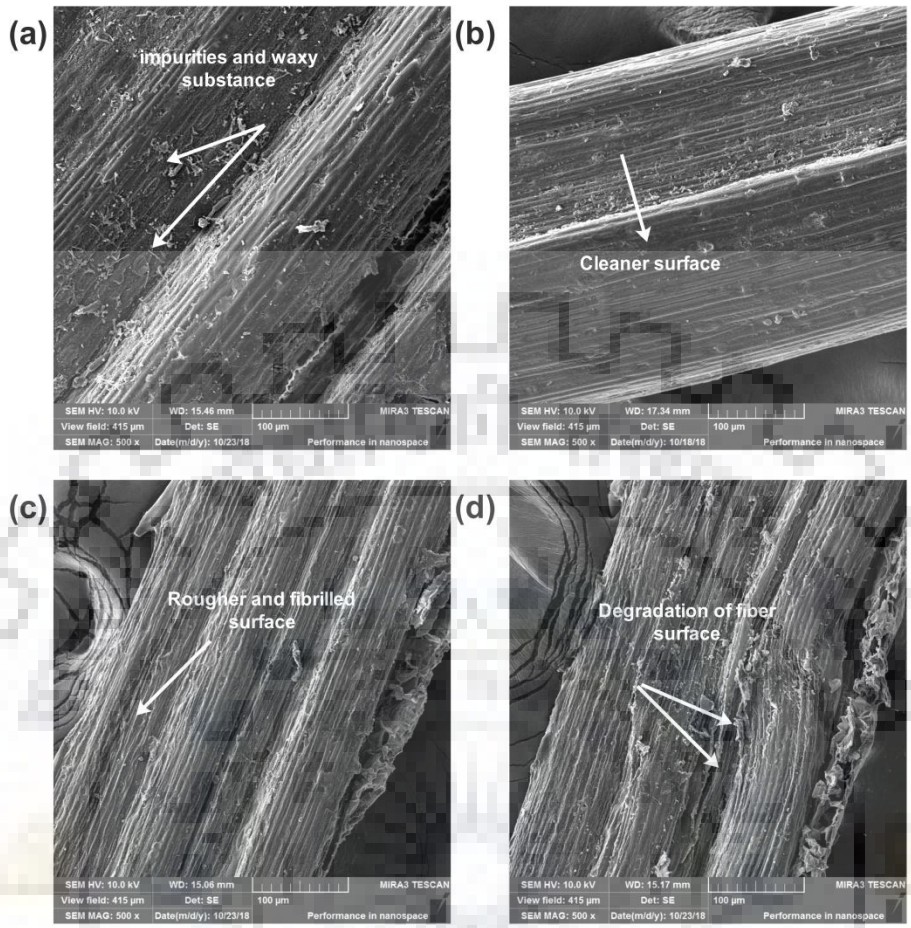

Figure 6.2: SEM images of (a) untreated (b) 3% treated (c) 5% treated (d) 7% treated fiber

6.4 XRD analysis

XRD images of untreated and various alkali treated Kans grass fibers are shown in Figure 6.3. Broad peak at 2θ~21.9° can be observed in all the graphs which is due to the cellulose. The crystallinity index of untreated Kans grass fiber has been calculated as 53% while the crystallinity index of 3% alkali treated fiber is estimated as 66% , this improvement is because of starting of removal of amorphous hemicellulose and lignin. Fiber treated with 5% alkali is showing the maximum crystallinity index, that is 76% possibly because of diminishing amorphous content and rearrangement of crystalline region while there is no further improvement in crystallinity in case of 7% alkali treated fiber which is 74%. That might be because of excessive delignification which leads to degradation of fiber surface.

Similar improvement in crystallinity index of natural fibers due to alkali treatment has also been observed in literature (Arthanarieshwaran et al. 2015, Borchani wt al. 2015)

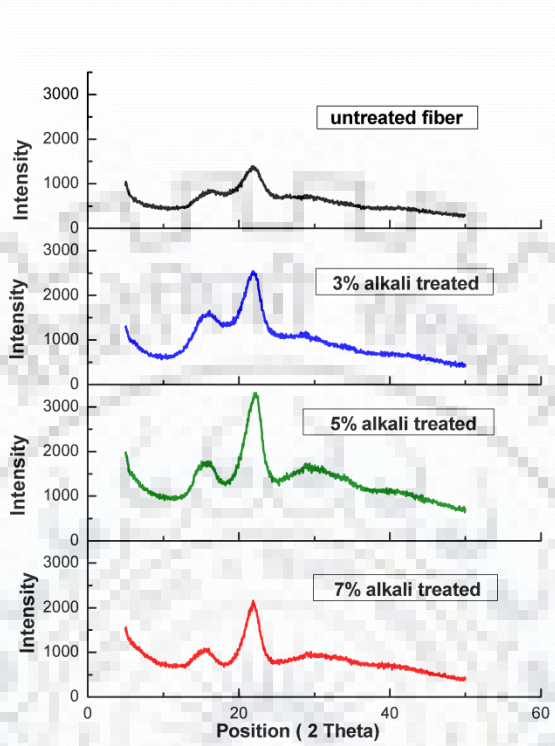

Figure 6.3: XRD spectra of untreated and treated fibers

6.5 AFM analysis

Figure 6.4 displays the 3D, AFM images of untreated and alkali treated Kans grass fibers The untreated fiber in Figure 6.4 (a) has Root mean square roughness of 154 nm which is fairly high as compared to reported value in literature (Arthanareshwaran et al. 2015, Manimaran et al. 2017) . The RMS roughness is 220 nm in case of 3% alklai treated fiber (b) while 321nm for 5% alkali treated fiber (c). Alkali treatment imparted more prominent hills and valleys and increased the roughness which is also evident in SEM images. The higher roughness is favorable for better interlocking between fiber and matrix for application in polymer composites. Marginal increase in RMS roughness has been observed in case of 7% treated fiber (d) which is 334 nm.

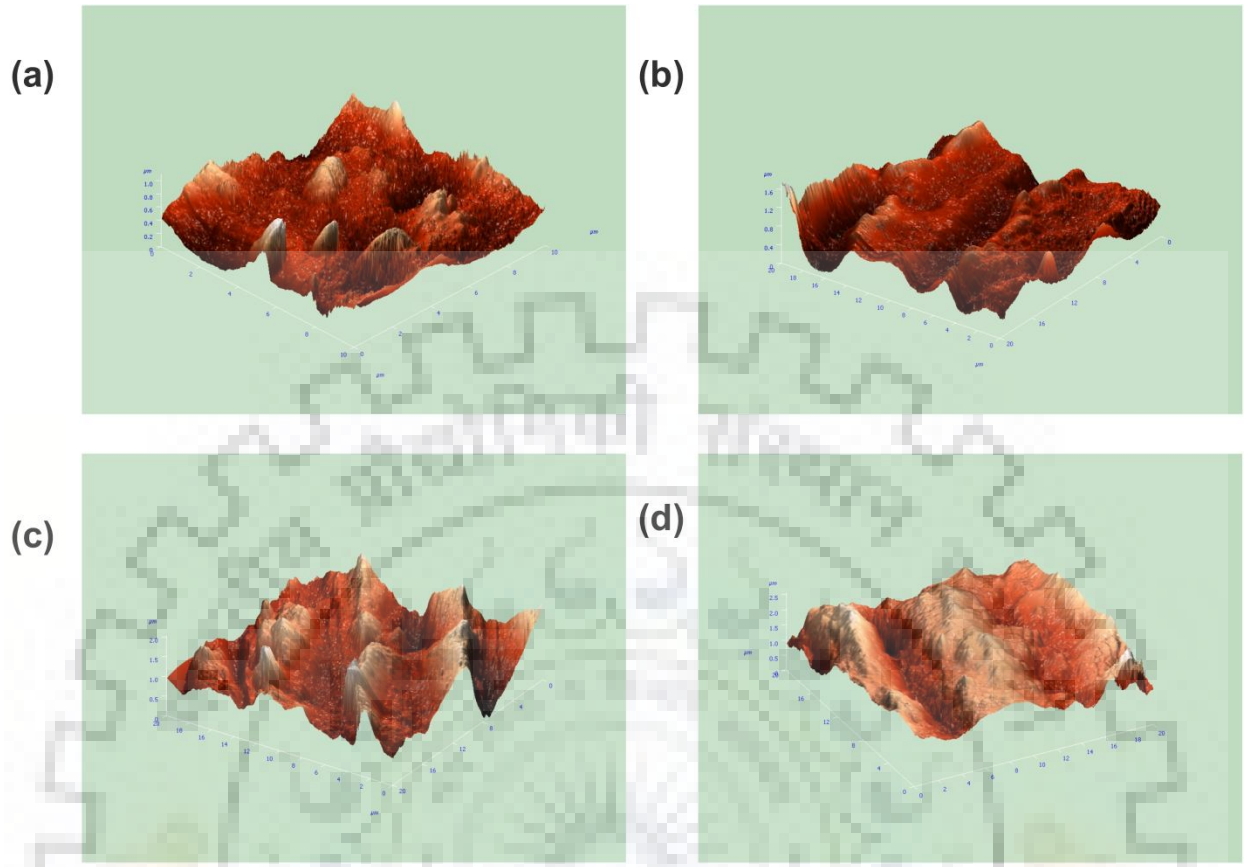

Figure 6.4: AFM images of (a) untreated (b) 3% alkali treated (c) 5% alkali treated (d) 7% alkali treated fiber

6.6 Thermogravimetric analysis, kinetics and activation energy

The thermal stability of untreated and treated Kans grass fibers have been investigated by thermogravimetric analysis and the results are presented in Figure 6.5. Both the TGA graphs and Differential thermal gravimetric graph (DTG) have been plotted as a function of temperature. Initially for the temperature range between 0 to 100°C all the fibers whether untreated or treated loose a small amount of weight because of vaporization of water present in the fiber which is also visible in initial peaks of DTG curves (Balaji et al. 2017, Fiore et al. 2014).

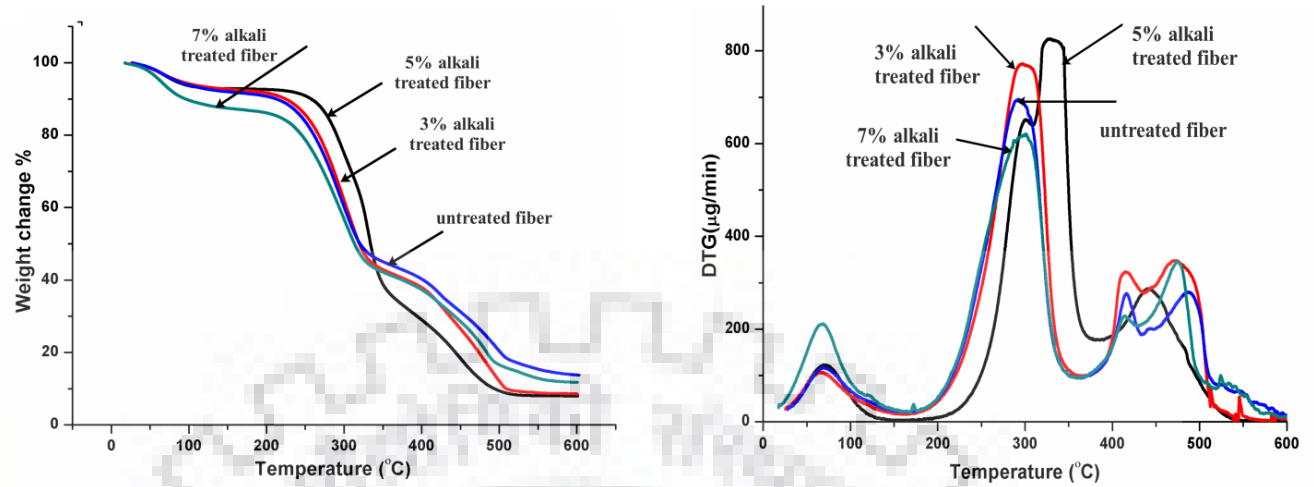

Figure 6.5: TGA and DTG thermograms of untreated and treated fibers

The initial temperature of degradation is higher in case of alkali treated fibers. The first stage of degradation process occurs in the temperature range 254 °C-293 °C in case of untreated fiber while 265 °C -299 °C and 283 °C -323 °C in case of 3% and 5% treated fibers respectively (Borchani et al. 2015, Balaji et al. 2017), corresponding DTG curves are also shown in the Figure. This improvement in thermal stability is because of partial elimination of hemicellulose and removal of surface impurities due to alkali treatment. In case of 7% alkali treated fiber the degradation starts at 258°C and the corresponding peak at DTG curve is observed at 300°C this deterioration is possibly due to excess alkali concentration which is detrimental for fiber surface and its properties. The next peak in case of untreated fiber is noticed at 413°C while in case of 3% and 5% alkali treated fiber it is at 418 °C and 438 °C respectively. These peaks are corresponding to cellulose and lignin decomposition. Lowest residual weight is observed because of optimum delignification in case of 5% alkali treated fiber and this is the appropriate concentration to improve the thermal stability of fiber, beyond that there is no improvement in properties. The observation clearly indicates the suitability of 5% alkali treated fiber as a reinforcement of polymer matrix where processing temperature is below 283 °C.

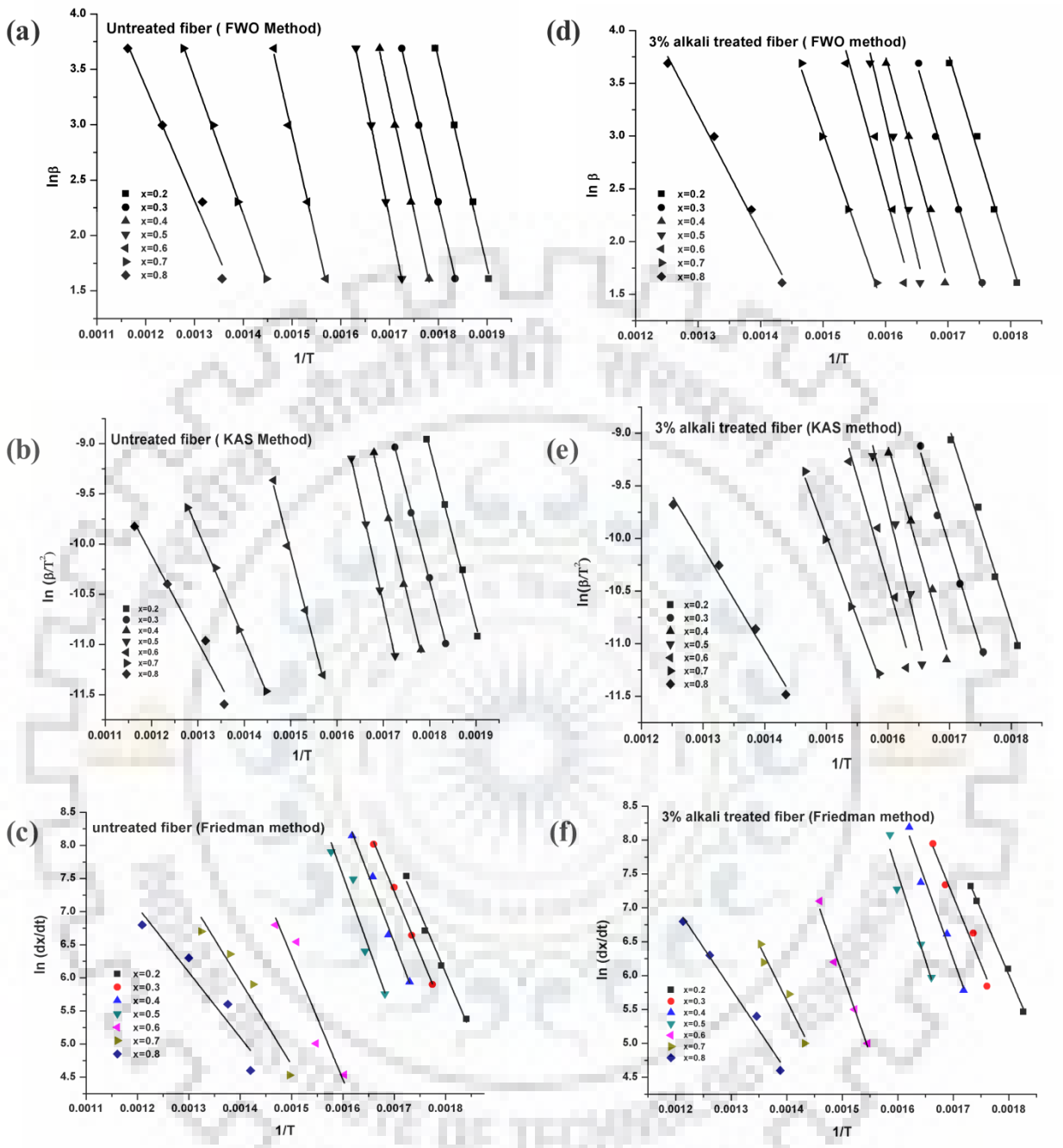

Figure 6.6: (a),(b,(c)FWO, KAS, Friedman plots of untreated fiber, (d), (e), (f) FWO, KAS, Friedman plots of 3% treated fiber

To get deeper understanding of thermal degradation process further studies have been performed using the most popular methods that are Flynn-Wall-Ozawa (FWO), Kissinger-

Akahira-Sunose (KAS) and Friedman method to evaluate the apparent decomposition activation energy.

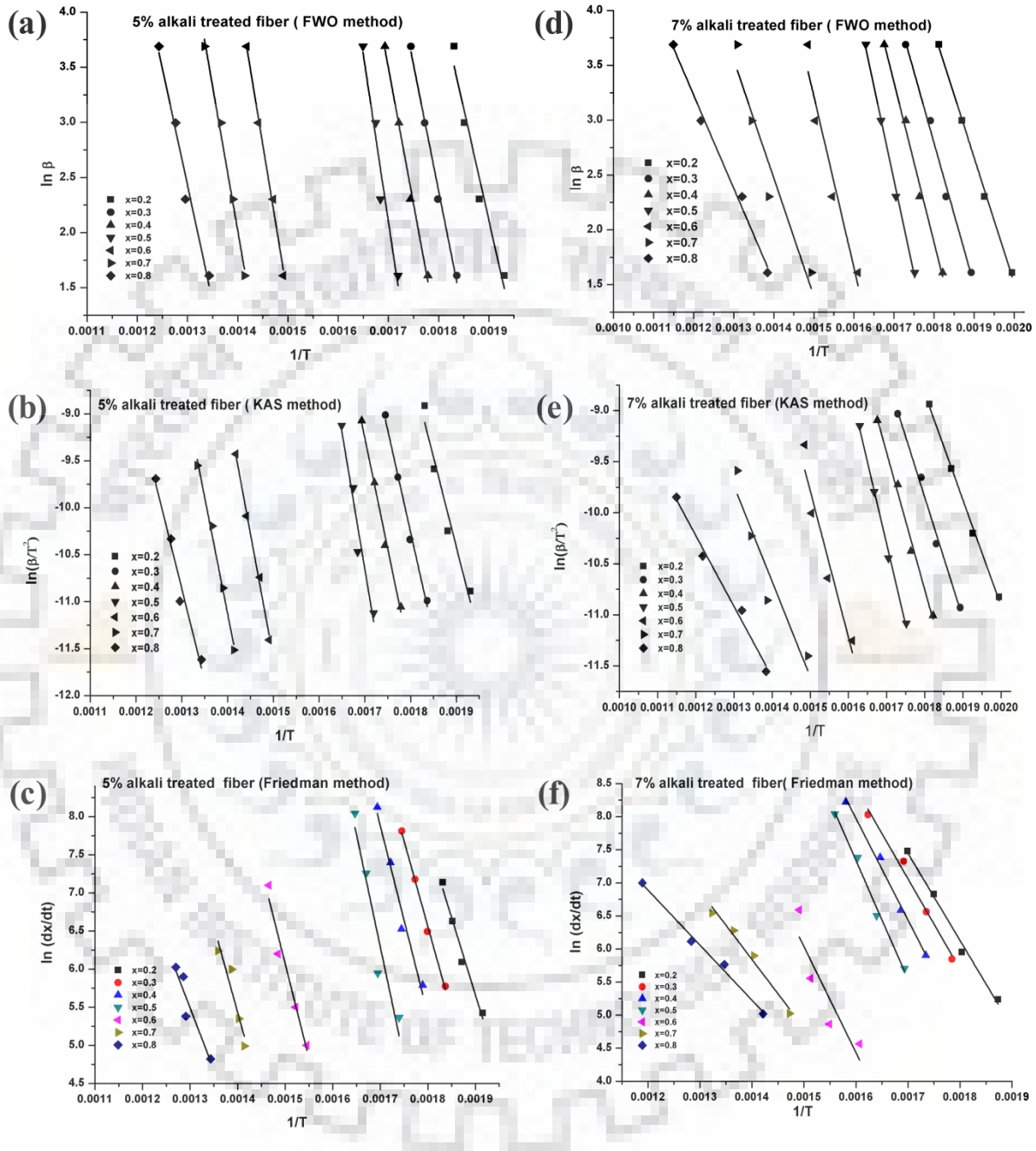

Figure 6.7: (a),(b,(c)FWO, KAS, Friedman plots of 5% treated fiber, (d), (e), (f) FWO, KAS, Friedman plots of 7%% treated fiber

Two different approaches that is integral and differential method have been used to overcome the approximations used in these methods and to have an accurate trend. From the TGA data

of untreated and various alkali treated fibers, graphs were plotted according to equations that are represented in Figure 6.6 and Figure 6.7 and apparent activation energies have been calculated. Mostly the lines are parallel which shows the possibility of single reaction mechanism (Motaung and Anandjiwla 2015)

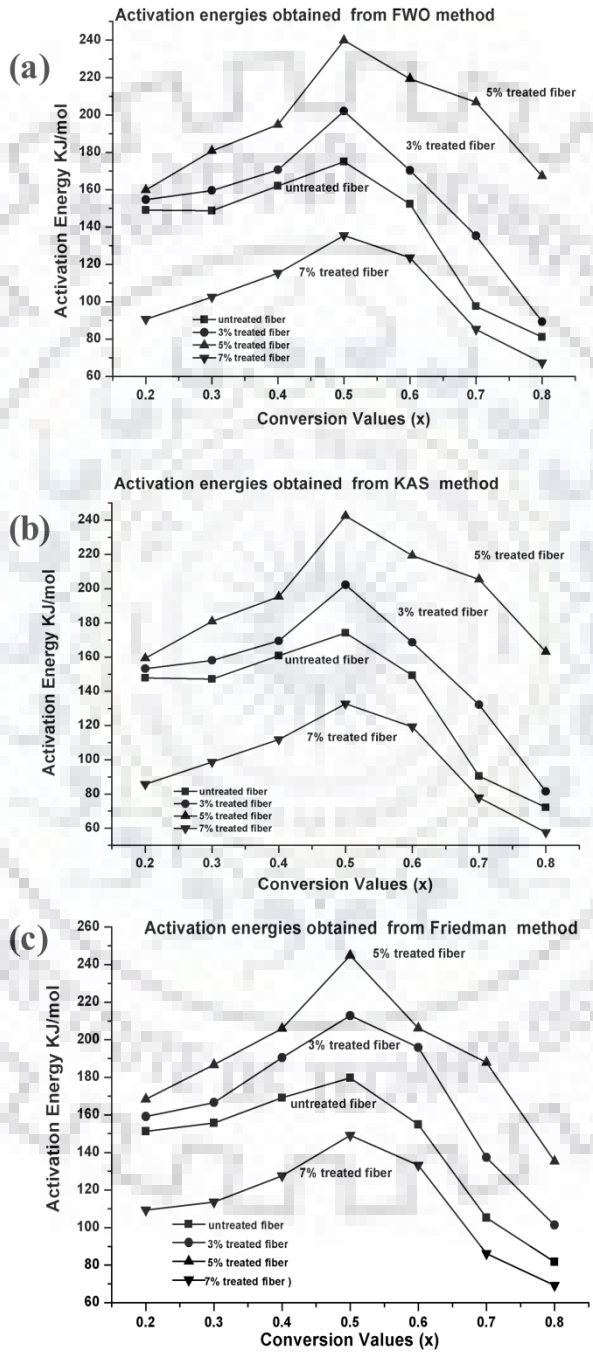

Figure 6.8: Variation of activation energy values with degree of conversion for untreated and various treated fibers, calculated from different methods

Figure 6.8 shows the variation of thermal degradation activation energies versus degree of conversion for both untreated and treated fibers calculated from various methods. The decomposition activation energy of untreated fiber is varying from 81-174 KJ/mol which agrees the reported value of natural fibers in the literature (Ornaghi 2014, Yao et al. 2008) while highest decomposition activation energy values 159-244 KJ/mol are observed in case of 5% alkali treated fiber. Slight variations are observed in the values of activation energies calculated from differential method as compare to integral method because of the assumptions used in these methods but the trend of variation of activation energy with conversion is similar in all the methods within experimental uncertainty. Deterioration of activation energy in case of 7% treated fibers is possibly due to excessive delignification, depolymerization of native cellulose or degradation of fiber surface.

CHAPTER 7

EFFECT OF FILLER SIZE AND LOADING ON KANS GRASS FILLER REINFORCED EPOXY COMPOSITES

7.1 Compositional analysis of Kans grass filler

The compositional analysis of Kans grass filler performed in this study is presented in Table 7.1 and comparison with previous work is also given in the table. The slight variations in the values of components analyzed by various researchers are because of the fact that composition also depends on geographical and seasonal variation of the collected feed stock. The Kans grass filler has average percentage of cellulose is 43.2% which is comparable with so many traditional fibers such as Bamboo (26-43%), Coir (32-43%), Wheat straw (38-45%), Rice husk (35-45%) (Faruk et al. 2012) that have been utilized in various polymer matrix for fabrication of composites.

Table 7.1: Compositional analysis of Kans grass filler

S.No	Cellulose	Hemicellulose	Acid soluble lignin	Acid insoluble lignin	Ash	Reference
1.	**43.2±1.2**	**26.2±0.3**	**22.4±0.3**	**1.6±0.7**	**6.8±0.2**	**Present work**
2.	35.4±0.87	26.7±0.37	14.5±1.82		1.1±0.95	(Komolwanich et al. 2014)
3.	36.8±0.13	23.7±0.04	20.0±0.12		6.6±0.21	(Scordia et al. 2010)
4.	43.7	21.1	25.2±0.6		2.1±0.2	(Kataria et al. 2013)

7.2 XPS analysis of Kans grass filler

The XPS analysis has given the O/C ratio for the filler 0.23, while Carbon and Oxygen concentrations are 75.83% and 17.79% respectively. O/C ratio of the fillers/fibers can give an idea about hydrophilic character of the surface of fiber. A low O/C ratio is an indicative of hydrophobic tendency of fiber (Kilinc et al. 2018). Kans grass filler has low O/C ratio as compare to other natural fibers (Kilinc et al. 2018).

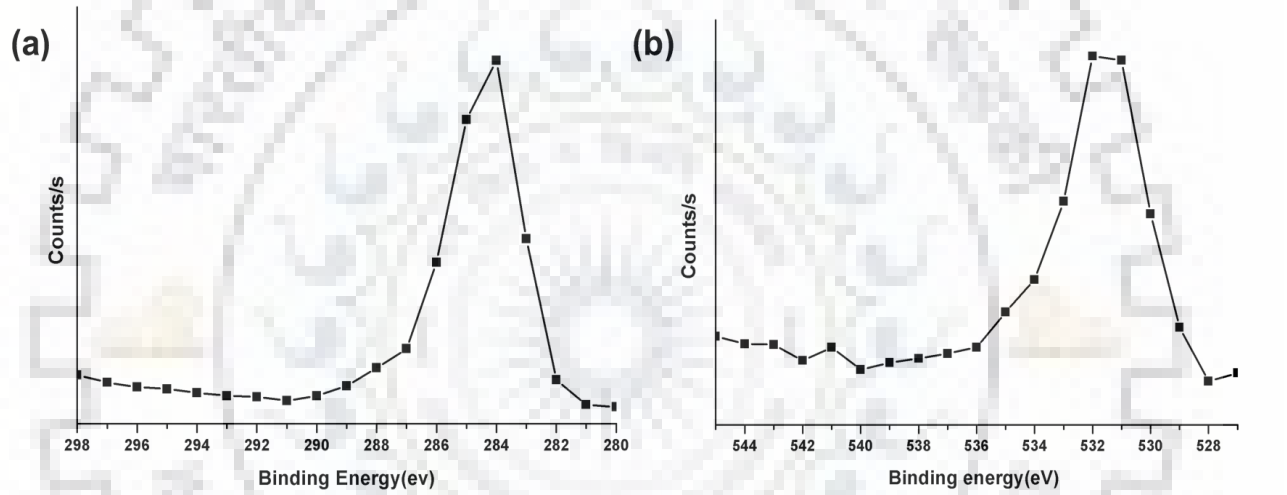

Figure 7.1: XPS spectra showing C1s and O1s envelope for Kans grass filler

7.3 Mechanical Properties of composites

Figure 7.1 and 7.2 are depicting the effect of filler loading and filler size on tensile strength and tensile modulus of Kans grass based epoxy composites. The value of tensile strength decreases as we increase the filler loading beyond 15% for all the size particles but flexural strength is continuously decreases with increase of filler loading. Opposite trend has been observed in case of tensile modulus and flexural modulus values. Hence epoxy composites made from 500-100 micrometer size filler with 15% loading can be concluded to be optimum with repect to maximum tensile strength.

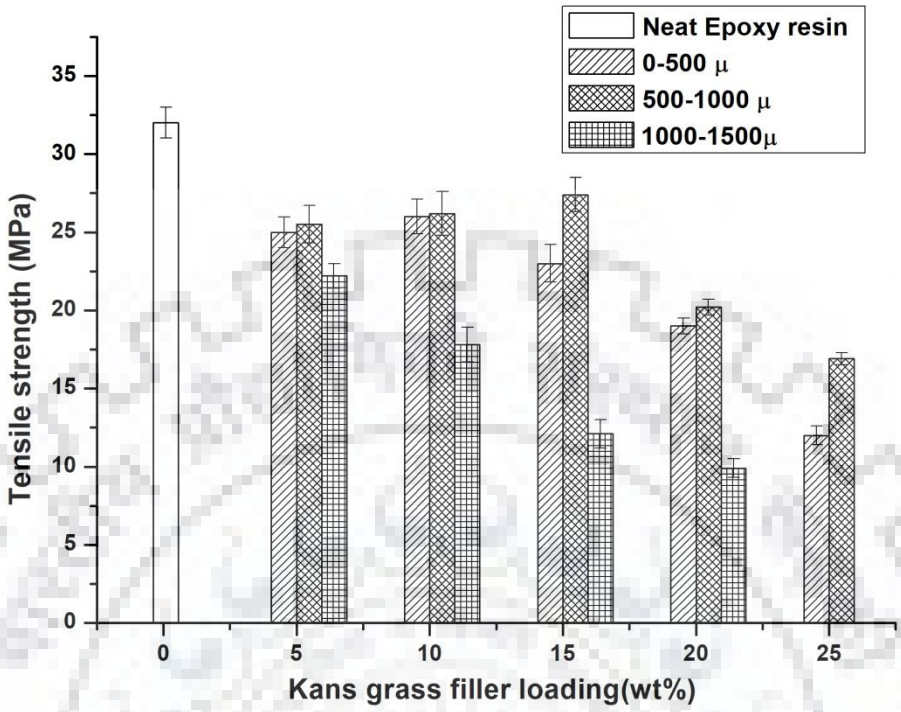

Figure 7.2: Effect of filler size and loading on tensile strength of Kans grass filler reinforced composites

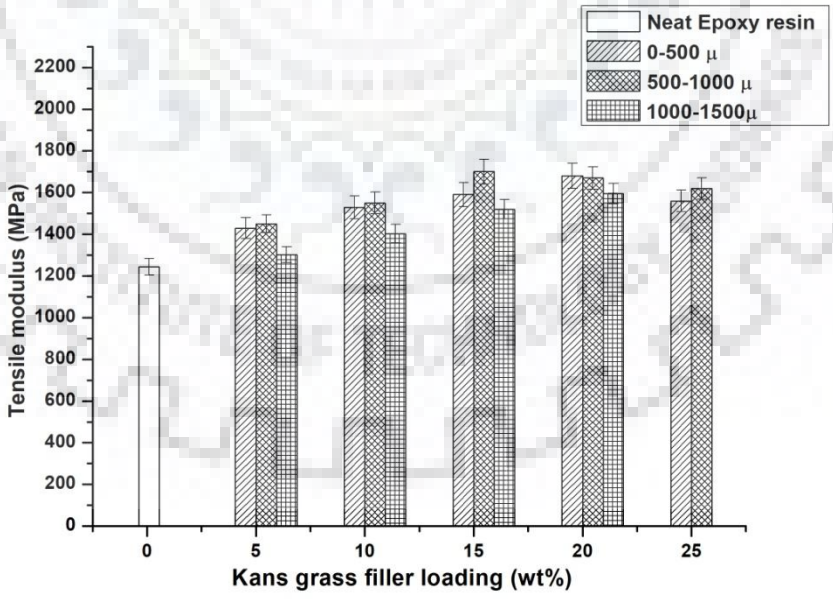

Figure 7.3: Effect of filler size and loading on tensile modulus of Kans grass filler reinforced composites

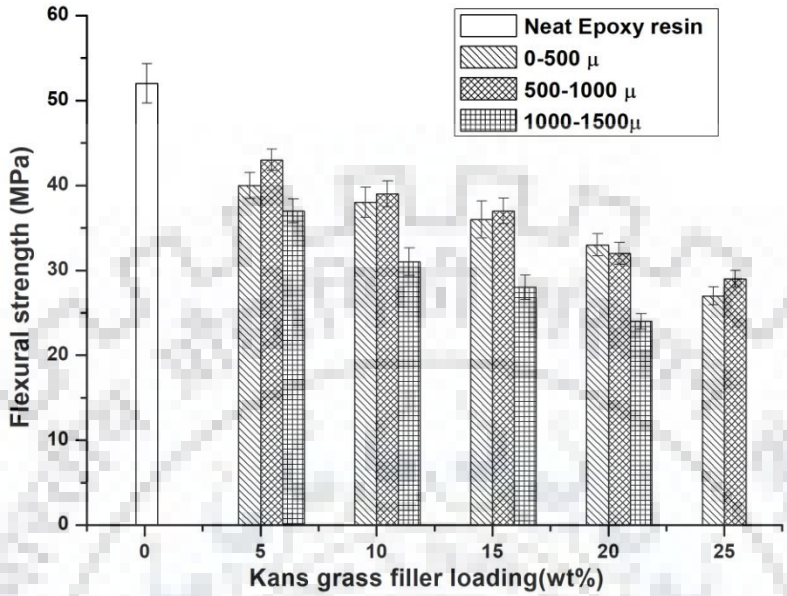

Figure 7.4: Effect of filler size and loading on flexural strength of Kans grass filler reinforced composites

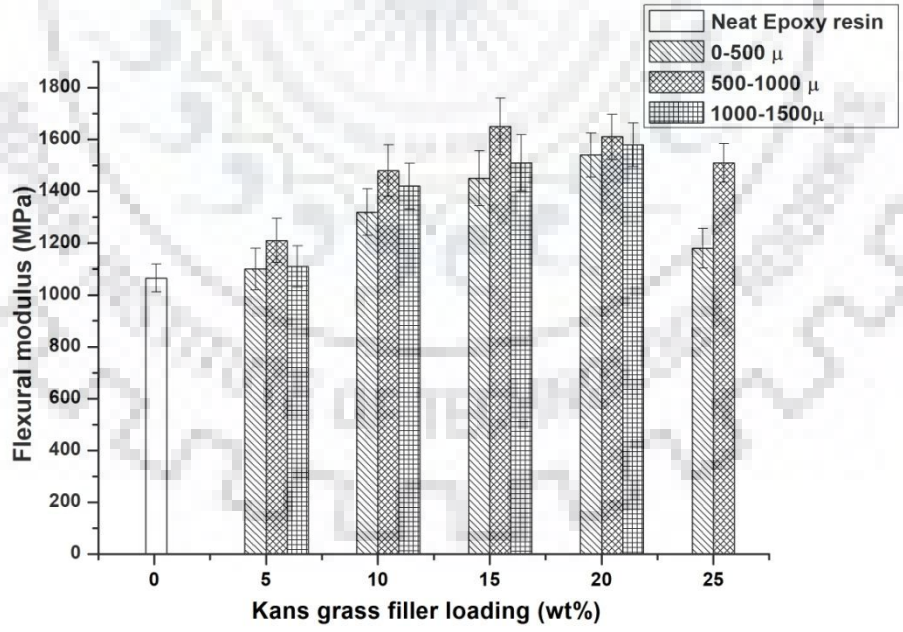

Figure 7.5: Effect of filler size and loading on flexural modulus of Kans grass filler reinforced composites

This behavior can be explained by the fact that beyond 15%, reinforcing filler is not able to transfer the stress properly. Similarly large size of filler is also not suitable for reinforcement in composites as the poor interaction between filler and matrix leads to degradation in properties.

7.4 FTIR analysis

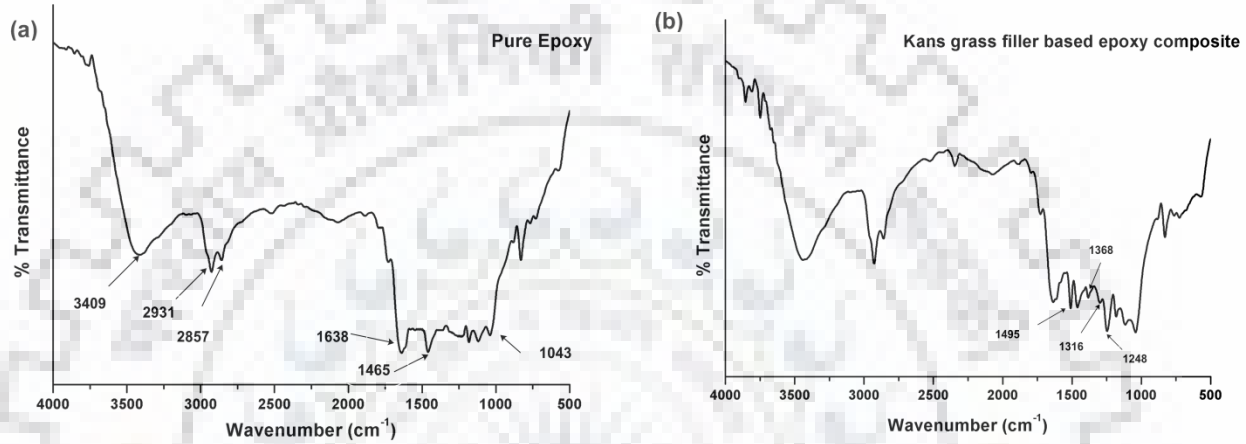

Figure 7.6: FTIR spectra of (a) pure Epoxy (b) Kans grass filler based epoxy composite

FTIR spectra of pure Epoxy and Kans grass filler based composites have been shown in Figure 7.6. In the spectra of pure epoxy OH stretching vibrations are located at 3409 cm $^{-1}$. The peak at 2857 cm $^{-1}$ corresponds to C-H stretching vibrations. The peaks at 1638 and 1507 cm^{-1} ascribed to aromatic ring of epoxy (Shah et al. 2019). Few additional peaks are visible in case of Kans grass based epoxy composites in Figure7.6 (b). The additional peak at 1495 cm^{-1} represents C = C stretching of Benzene ring of lignin. The peaks at 1368 and 1316 confirm the bending vibrations of CH and CO group of aromatic rings of polysaccharide. FTIR analysis of the Figure 7.6 (b) confirms the reinforcement of Kans grass filler in epoxy matrix.

7.5 SEM analysis of composites

Figure 7.7 depicts the high resolution images of Kans grass filler based epoxy composites. It is evident from the figure that there are almost no voids and bubbles which represent the

better interlocking of filler and matrix. A good adhesion between filler and matrix is responsible for the better quality of composite material.

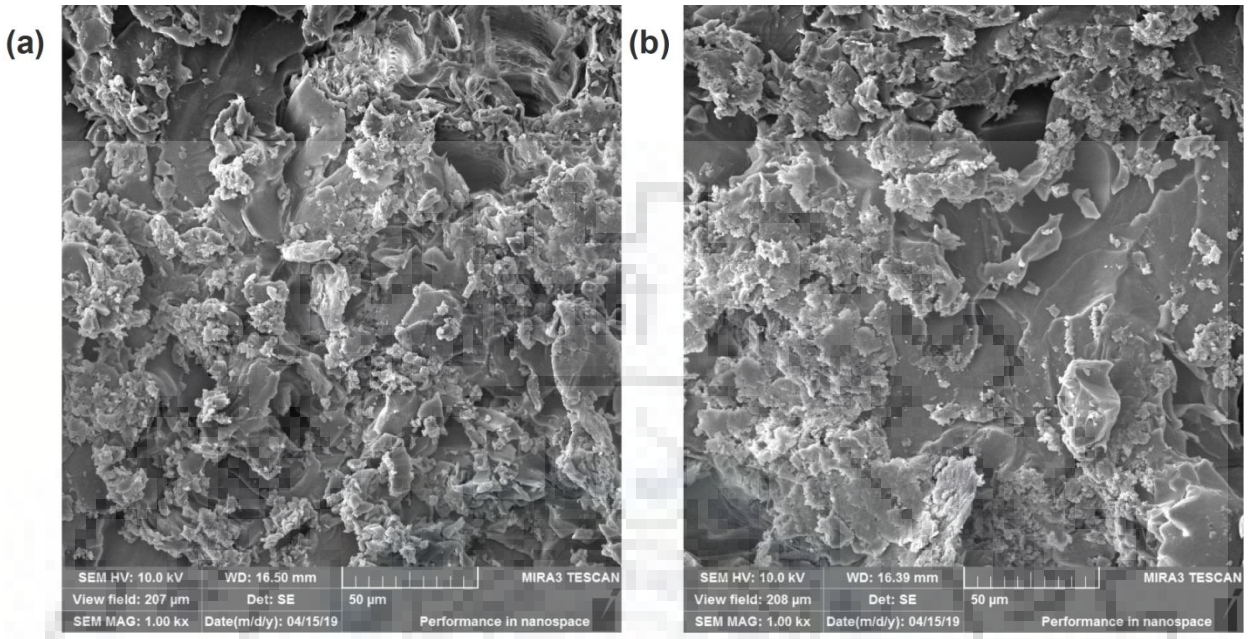

Figure 7.7: High resolution SEM images of Kans grass based epoxy composites

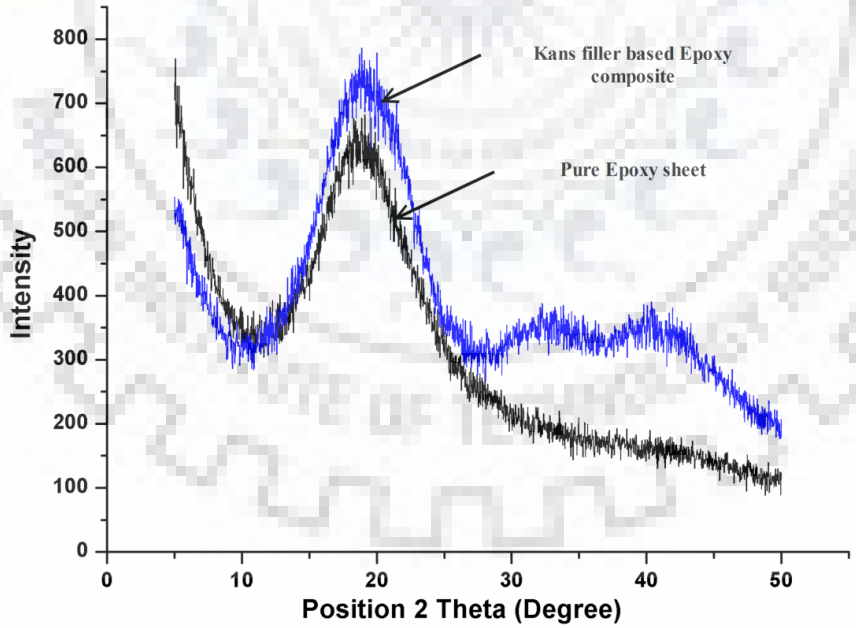

Figure 7.8: XRD spectra of pure epoxy and epoxy composites reinforced by 500-1000 µm size of Kans grass filler at 15% fiber loading

7.6 XRD analysis of composites

XRD images of pure epoxy and Kans grass based epoxy composites for 500-100 μm and 15% filler loading are shown in Figure 7.8. It can be observed from the diffractograph that degree of crystallinity of pure epoxy is retained after reinforcement of Kans grass filler

7.7 Activation energy and thermogravimetric analysis of Kans grass reinforced epoxy composites

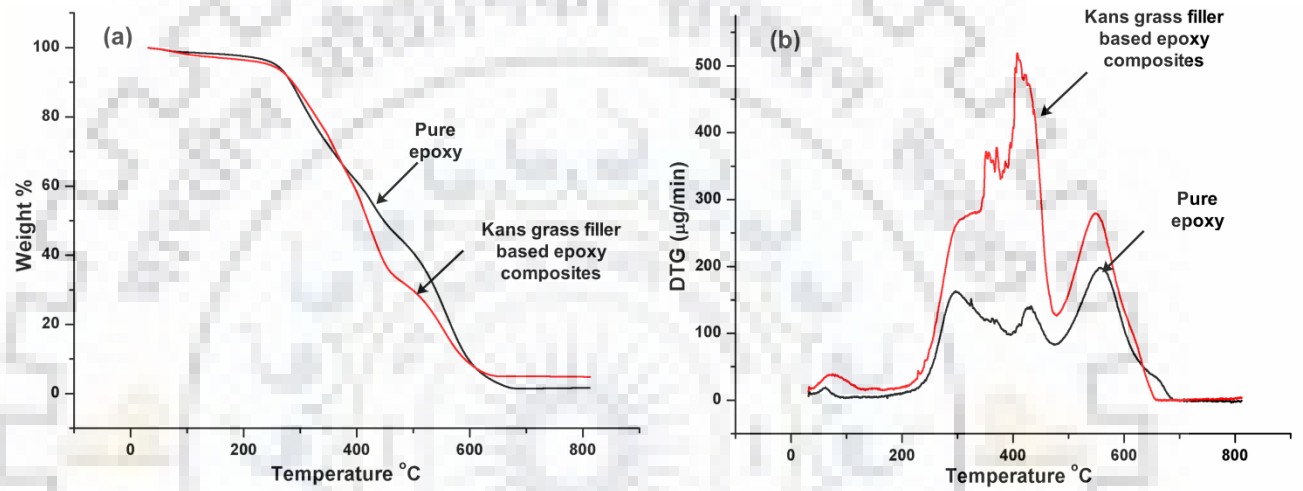

Figure 7.9: TGA and DTG thermograms of pure epoxy sheet and Kans grass based epoxy composites at 15% filler loading and for 500-1000 μm filler size

The thermogravimetric and derivative weight curves of pure epoxy sheet and Kans grass filler based epoxy composite at 15% fiber loading and for 500-1000 μm filler size are represented in Figure 7.9(a) and (b). Two major zones of degradation are observed. Thermal decomposition activation energy analysis of pure epoxy and Kans grass based epoxy composite for optimum filler loading and size will give the better quantitative understanding of thermal stability of these reinforced composites. Figure 7.10 shows the FWO plots of pure epoxy and its composites reinforced by Kans grass. From Figure 7.10 (c) the average value of the activation energy of epoxy comes to be approximately 192 kJ/mol which is very close to earlier reported value (Islam et al. 2014). The average activation energy of Kans grass composite at optimum loading and size is 227 kJ/mol which is high as compare to neat epoxy

sheet. From this analysis it is clear that reinforcement at optimum size and loading of Kans grass filler improves the thermal stability of epoxy composites.

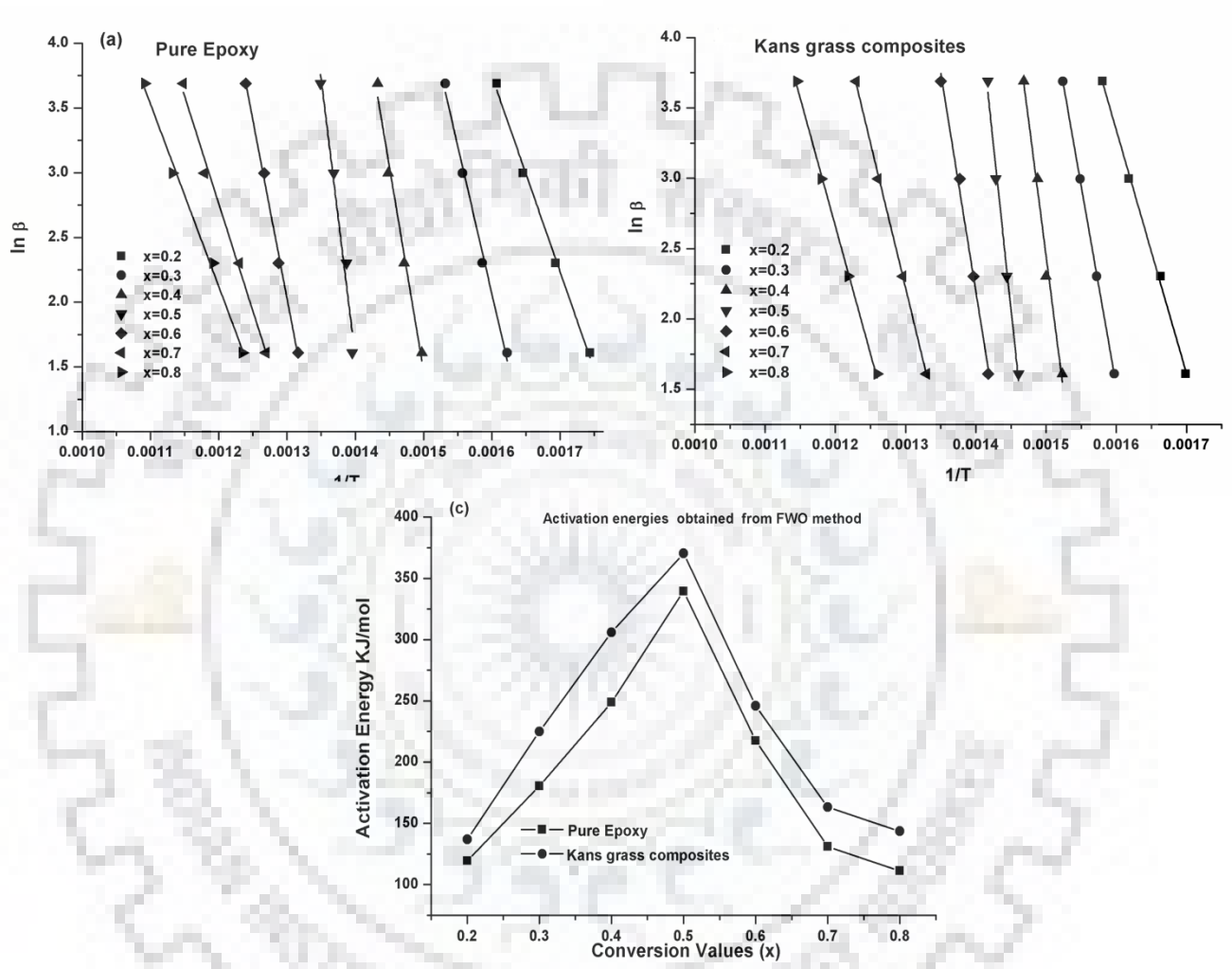

Figure 7.10: FWO plots of (a) Pure epoxy (b) Kans grass based epoxy composites at optimum loading and size (c) Activation energy values of epoxy and its composite for different degree of conversions

CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

This chapter intends to summarize the major findings of the research done and hopefully explore some broader conclusions and future recommendations of research.

8.1 Conclusions

- The agricultural waste material of underdeveloped East African countries has been successfully utilized as reinforcement in Epoxy matrix for the fabrication of composite materials, useful in semi structural or light weight applications.
- Mechanical, morphological and thermal characterization has been done for this novel material using modern analytical equipments. It has been concluded that, Teff straw fiber has better or comparable mechanical and thermal properties as compared to various new natural fibers explored by the academicians and researchers. Treatment with 5% NaOH increased the tensile strength of Teff straw by 31% (280-368 MPa) and average activation energy by 21% (136-164 kJ/mol). Moreover crystallinity index of the fiber has also been improved from 54% to 72% by this surface treatment. Treatment with 10% alkali solution did not improve the properties further.
- Epoxy composites reinforced by untreated and alkali treated Teff straw has been made by simple Hand lay-up process. Mechanical, morphological and thermal characterization of Teff straw reinforced epoxy composites revealed that 15% fiber loading and 5% alkali treatment is optimum to get the improved quality composites. An increment of 12% in tensile strength as compared to neat epoxy resin was observed at optimum loading and surface treatment.
- Another undervalued non wood plant *Saccharum spontaneum* (Kans grass) which automatically grows in barren land, bank of rivers, ponds or lakes has been explored for possible reinforcing filler in polymer matrix.
- Fibers were extracted from the stem by water retting process. Different concentrations of alkali that is 3%, 5% and 7% were used for the surface treatment of fiber. It was

observed that 5% NaOH treatment improved the tensile strength of fiber by 24% which is highest as compared to treatment with another two concentrations of alkali.

- The 5% alkali treated Kans grass fibers exhibited maximum increase in average activation energy that is from 137±3.1 kJ/mol to 194± 2.4 kJ/mol.
- Filler of Kans grass was successfully utilised as a reinforcing material in epoxy matrix with comparable tensile and flexural strength for 10% and 15% filler loading and 500-100 μ particle size with neat epoxy and increased modulus values for 15-20 % fiber loading
- The effect of reinforcement of Kans grass filler on crystallinity and activation energy was also analysed. It was found that pure epoxy sheet has an average activation energy of 192 kJ/mol while reinforcement with 15% loading of Kans grass filler having size of 500-1000 μm increased the activation energy from 192 to 227 kJ/mol.

8.2 Recommendations for future research

- Various new fibers can be explored for their reinforcement in polymer matrices.
- Thermodynamic modelling of water absorption behavior of fiber and their composites can be done by doing water absorption test at three different temperatures.
- Wetting and adhesion properties along with surface energy of fiber and composites can be studied by contact angle analysis.
- Computer programming can be done to calculate the activation energy of fibers and composites from advanced integral methods.
- Finite element modelling can also be done to understand the mechanical properties and water absorption behavior of these composites.

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1. Devnani, G. L., & Sinha, S. **(2019)** Extraction, characterization and thermal degradation kinetics with activation energy of untreated and alkali treated *Saccharum spontaneum* (Kans grass) fiber. **Composites Part B**, 166, 436-445 **(IF. 4.92)**
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