

# PROPERTIES AND PERFORMANCE OF REGENERATED CELLULOSE THERMOSET BIOCOMPOSITES

Sunil Kumar Ramamoorthy



UNIVERSITY  
OF BORÅS

**Thesis for the Degree of Doctor of Philosophy**

**Properties and Performance of  
Regenerated Cellulose Thermoset  
BioComposites**

**Sunil Kumar Ramamoorthy**



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OF BORÅS

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Swedish Centre for Resource Recovery  
University of Borås  
SE-501 90 Borås, Sweden

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## Abstract

Biocomposites have been developed to address the sustainability issues of non-renewable resource based materials. These composites are often produced by reinforcing natural fibres in petroleum based thermoset resins or thermoplastic polymers. Thermoplastic polymers from renewable resources are commercially available, whereas thermoset resins are predominantly derived from crude oil resources. Cellulose fibres have significant importance and potential for polymer reinforcement in lightweight composites. Natural fibres are chemically diverse and their properties vary largely which makes it difficult for them to be used in several applications. The natural fibre based products are limited by their characteristic odour emissions. These issues of natural fibres can be addressed by partly man-made fibres i.e. regenerated cellulose fibre which with little or no compromise in the environmental benefits of the natural fibres can be produced from biomass origin. Natural fibres and their composites have been observed and researched closely for many decades. Study of regenerated cellulose fibres and their composites is, on the other hand, relatively new. Regenerated cellulose fibres are prospective reinforcing material in the composite field due to their even quality and high purity. These fibres have good mechanical properties and also address the odour emission issue of the natural fibres. The development of biocomposites from regenerated cellulose fibre and thermoset resin synthesized from renewable resources has therefore been viewed with considerable interest.

This thesis describes the development of biocomposites from regenerated cellulose fibres (lyocell and viscose) and thermoset resins synthesized from renewable resources (soybean oil and lactic acid). The performance and the properties of the composites were evaluated. Chemical surface treatments, alkali and silane, were performed on the fibres in order to improve the performance of the composites. Hybrid composites were also produced by mixing of two types of reinforcement in order to complement one type of fibre with other.

The developed composites were evaluated through mechanical, thermal, viscoelastic and morphological properties among others. The results showed that the regenerated cellulose fibre thermoset biocomposites have reasonably good properties. Fibres before and after treatment were studied in detail. The silane treatment on these fibres improved the mechanical properties of the composites as the silane molecules act as a link between the fibre and resin which gives the molecular continuity across the interface region of the composite.

**Keywords:** *Regenerated cellulose fibres, Surface modification, Alkali, Silane, Mechanical analysis, Biocomposites, Renewable resources*



## List of Publications

This thesis is based on the results presented in the following publications:

- I. **Ramamoorthy SK**, Di Q, Adekunle K, Skrifvars M. (2012) Effect of water absorption on mechanical properties of soybean oil thermosets reinforced with natural fibers. *Journal of Reinforced Plastics & Composites*, 31(18): 1191-1200
- II. **Ramamoorthy SK**, Kundu CK, Adekunle K, Bashir T, Skrifvars M. (2014) Properties of green composites with regenerated cellulose fiber and soybean-based thermoset for technical applications. *Journal of Reinforced Plastics & Composites*, 33(2): 193-201
- III. **Ramamoorthy SK**, Skrifvars M, Rissanen M. (2014) Effect of alkali and silane surface treatments on regenerated cellulose fibre type (lyocell) intended for composites. *Cellulose*, 22(1): 637-654
- IV. **Ramamoorthy SK**, Bakare F, Herrmann R, Skrifvars M. (2015) Performance of biocomposites from surface modified regenerated cellulose fibers and lactic acid thermoset bioresin. *Submitted to Cellulose*
- V. **Ramamoorthy SK**, Persson A, Skrifvars M. (2014) Reusing textile waste as reinforcements in composites. *Journal of Applied Polymer Science*, 131(17) DOI: 10.1002/app.40687

## Statement of Contribution

The author of this thesis, Sunil Kumar Ramamoorthy, was main author of all the publications and performed most of the experimental work, data analysis and manuscript writing in all publications. Qin Di and Chanchal Kumar Kundu contributed in all the experimental work in publications I and II respectively. Dr. Marja Rissanen performed the tensile testing of the fibres in publication III. Fatimat Bakare and Rene Herrmann supported with the resin synthesis and resonance analysis experimental setup respectively in publication IV. Other co-authors assisted with data analysis and manuscript writing.

SEM analysis in publication II was performed at Chalmers University of Technology, Sweden and contact angle measurements in publication III was done at KTH Royal Institute of Technology, Sweden. The SEM analysis in publication IV was done at Amirkabir University of Technology, Iran.

## **Related publications that are not included in this thesis**

- I. Ramamoorthy SK**, Skrifvars M, Persson A. (2015) A review of natural fibers used in biocomposites: plant, animal and regenerated cellulose fibers. *Polymer Reviews*, 55(1): 107-162
- II. Baghaei B**, Skrifvars M, Rissanen M, **Ramamoorthy SK**. (2014) Mechanical and thermal characterization of compression moulded polylactic acid natural fiber composites reinforced with hemp and lyocell fibers. *Journal of Applied Polymer Science*, 131(15) DOI: 10.1002/app.40534
- III. Bakare FO**, **Ramamoorthy SK**, Åkesson D, Skrifvars M (2015) Characterization of properties for bio-based composites made from a lactic acid thermoset resin and flax and flax/basalt fibre reinforcements. *Submitted to Composites Part A: Applied Science and Manufacturing*

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## Conference Contributions

1. **Ramamoorthy SK**, Di Q, Adekunle K, Skrifvars M. Processing of non-woven lyocell fabric and mechanical properties of non-woven fiber reinforced bio-based composites, *Edana Nonwovens Research Academy 2012 Conference*, Gothenburg, Sweden, April 19-20, 2012 (*oral presentation*)
2. **Ramamoorthy SK**, Di Q, Adekunle K, Skrifvars M. Can the outdoor properties of natural fiber reinforced bio-based composites be improved?, *15<sup>th</sup> European Conference on Composite Materials*, Venice, Italy, June 24-28, 2012 (*oral presentation*)
3. **Ramamoorthy SK**, Kundu CK, Baghaei B, Adekunle K, Bashir T, Skrifvars M. Green composites based on regenerated cellulose textile fibers for structural composites, *AUTEX 2013*, Dresden, Germany, May 22-24, 2013 (*oral presentation*)
4. Lindstrom K, **Ramamoorthy SK**, Persson A. Reuse of waste textiles for composite production, *UN Conference–IPLA*, Boras, Sweden, September 9-11, 2013 (*poster*)
5. **Ramamoorthy SK**, Kundu CK, Adekunle K, Bashir T, Skrifvars M. Regenerated cellulose fiber reinforced composites, *UN Conference–IPLA*, Boras, Sweden, September 9-11, 2013 (*poster*)
6. **Ramamoorthy SK**, Kundu CK, Adekunle K, Bashir T, Skrifvars M. Characterization of wood based fiber reinforced bio-composites, *3<sup>rd</sup> Avancell Conference*, Gothenburg, Sweden, October 8 & 9, 2013 (*poster*)
7. **Ramamoorthy SK**, Thermoset biocomposites from cellulose-based fibers and triglyceride plant oil: properties and improvement by chemical treatments, *The 25<sup>th</sup> Annual International SICOMP Conference*, Pitea, Sweden, June 2 & 3, 2014 (*oral presentation*)



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*I dedicate this thesis to  
my family, relatives, friends and teachers  
for their constant support and unconditional love.  
I love you all dearly.*

Sunil Kumar Ramamoorthy  
University of Borås  
March 2015

## Abbreviations

<b>AESO</b>	Acrylated epoxidized soybean oil
<b>APTES</b>	3-aminopropyl-triethoxysilane
<b>DMTA</b>	Dynamic mechanical thermal analysis
<b>DP</b>	Degree of polymerisation
<b>DSC</b>	Differential scanning calorimetry
<b>ESO</b>	Epoxidized soybean oil
<b>FRC</b>	Fibre reinforced composite
<b>FTIR</b>	Fourier transform infrared spectroscopy
<b>MMSO</b>	Methacrylic anhydride modified soybean oil
<b>MSO</b>	Methacrylated soybean oil
<b>NaOH</b>	Sodium hydroxide
<b>NMMO</b>	N-methylmorpholine N-oxide
<b>PET</b>	Polyethylene terephthalate
<b>PMMA</b>	Poly(methyl methacrylate)
<b>RCF</b>	Regenerated cellulose fibre
<b>SEM</b>	Scanning electron microscopy
<b>TGA</b>	Thermogravimetric analysis

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## 1. INTRODUCTION

### 1.1 Composite material

Composite is a material that has two or more constituent materials with significant properties, when combined yield a material with unique properties. The composites materials are developed to fulfil the need of strong and lightweight materials. The two main constituents in composites are reinforcement and matrix. Reinforcements are fibres or textile structures which give strength to the materials. Synthetic fibres such as glass and carbon are commonly used reinforcement in composite applications. Matrix is a binding material which binds the reinforcement together. Commercially used matrixes are often polyester, polyolefin, epoxy resins etc. that are derived from petroleum resources. Concrete is typical example of composite material where reinforcement stones are held together with cement matrix.

Fibre reinforced composites (FRC) have been used in a number of applications for several years and the market is growing continuously. The performance of the composites has been improved continuously through rigorous research, often through mixing of two or more reinforcements/polymers or fillers (Bunsell and Harris 1974; Harris and Bunsell 1975; Summerscales and Short 1978; Manders and Bader 1981). However, these high-performance composites are difficult to recycle as the separation of the components is not possible.

#### 1.1.1 Reinforcement

Glass or carbon fibres possess high strength and are therefore used as reinforcements in composite materials. These fibres have good mechanical and thermal properties, and are used in materials where strength, stiffness, lightweight and outstanding fatigue characteristics are critical requirements (Brody and Ward 1971; Chand 2000; DiBenedetto 2001). Carbon fibre properties are superior to those of glass fibres; carbon fibres do not suffer from stress corrosion or stress rupture failures at room temperatures whereas the glass fibres do (Chand 2000). The low price of the glass fibres cemented its use in several composite applications such as automobile, bath tubs, boats, surfboards etc. However, carbon fibres are preferred for more demanding applications such as aircraft, racing cars, bearings, gears, fan blades and sporting goods. Due to increasing environmental concerns, there is interest in replacing these conventional reinforcements with bio-based materials in various applications. Bio-based resources include agricultural crops and residues, wood, grass and all other plants as well. Natural fibres such as jute, flax, hemp etc. have environmental benefits over synthetic fibres and have found applications in composite industries. Natural fibres are abundant from renewable resources, biodegradable and lightweight, and are used today mainly in non-structural applications such as automotive headliner as these fibres are not as strong as synthetic fibres. The natural fibres' variable chemical nature, largely varying properties and their odour emission are the biggest drawbacks (Faruk et al. 2012).

## INTRODUCTION

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Regenerated cellulose fibres are produced from natural source with human interference. It cannot be absolutely classified as synthetic fibre as these fibres are produced from biomass origin. Rayon is a regenerated cellulose produced from wood pulp and there are several types of rayon such as viscose, lyocell and modal depending upon manufacturing process. Few authors have explored these fibres and only a low number of pioneering papers are available (Fink et al. 2001; Zugenmaier 2001). Regenerated cellulose fibres are prospective reinforcing materials in the composite field due to their even quality, high purity, low odour emission, reproducibility and as they can be produced in most parts of the world, which is not the case for annual plant fibres. Regenerated cellulose fibres are distinctive as they share beneficial characteristics of both synthetic and natural fibres: uniform mechanical, morphological and physical properties of synthetic fibres and biodegradability, non-abrasiveness to processing equipment, CO<sub>2</sub> neutrality and low density of natural fibres (Ramamoorthy et al. 2015).

### ***1.1.2 Matrix***

Matrix holds the reinforcements together in the composites. It acts as a stress distributor in the composite and transfers the load to the reinforcements. Polymer matrix is divided into two categories, namely, thermoplastic and thermosetting. Thermoplastics are solid at room temperature. They become fluid above the melting temperature and can be remolded or recycled; there is no chemical reaction during this process while only the physical state of the polymers changes. These plastics cannot be used in high temperature applications as the polymers soften when heated. They are also susceptible to high stress. Matrix impregnation is one of the key issues in processing thermoplastic composites as this has to be done at temperature above the polymer's melting point. Most commonly used thermoplastics in composites are based on non-renewable resources, i.e. polypropylene, polyamide etc. Renewable resource based plastics such as polylactic acid has found large-scale commercial non-composite applications in recent times.

Thermosets cure through chemical reactions which cross-link the molecules and form strong bonds, and most often this curing is exothermic. The curing is not reversible and the thermosets produced possess resistance to heat, solvents and good toughness. Thermoset plastics are preferred over thermoplastics in structural composites as it has higher mechanical strength. Most uncured thermoset resins are liquid and their viscosity is substantially lower than the thermoplastics, which make the composite production easier at room temperature using a number of processing methods. It also offers easy fibre impregnation and the possibility of removing air during composite processing. Unsaturated polyester and epoxy resins are commonly used thermosets in composite applications. Epoxy resins are tougher, have better chemical and temperature resistance than unsaturated polyester resins and are used in high-performance applications such as aircraft, boats, wind

turbine blades etc. Lately, thermoset resins are synthesized from renewable resources such as plant oils (Meier et al. 2007).

### ***1.1.3 Biocomposites***

Ecological problems in recent decades have urged the necessity to look for new alternatives which could replace the traditional FRCs with lower environmental impact materials (Bledzki and Gassan 1999; Faruk et al. 2012). This created a renewed interest in natural materials which could be used as reinforcements or fillers in the composites and are thus referred to as ‘natural fibre reinforced composites’ or ‘ecocomposites’ (Bogoeva-Gaceva et al. 2007). They are also termed as ‘biocomposites’ (Mohanty et al. 2000; Ramamoorthy et al. 2015).

Several researchers came up with ideas of reinforcing polymers with different natural fibres to produce ecofriendly composites for several applications which do not require excellent mechanical properties, such as secondary/tertiary building structures, car door panels, packaging, etc. (La Mantia and Morreale 2011). The use of natural fibres as reinforcements in composites has been growing since then and has replaced several synthetic fibre reinforced composites in many applications due to low density, environmentally-friendly/biodegradability character, low tool wear and interesting properties (Bledzki and Gassan 1999; La Mantia and Morreale 2011; Faruk et al. 2012; Ramamoorthy et al. 2015).

The composites from natural fibres gained support due to the environmental-friendly element as considerable reduction of non-renewable resources used in composites by replacing mineral inorganic materials with natural organic materials. The use of natural fibres in composite industry created a new alternative business for the farmers. Furthermore, the possibilities of using recycled plastics like polyolefin succeeded as it reduced the consumption of non-biodegradable polymers (Selke and Wichman 2004). Later, bio-based thermoplastic and thermosets were derived from renewable resources such as plant oils and lactic acid, and the composites were made completely from renewable resources, and were thus referred to as ‘green composites’ (Mohanty et al. 2000; Meier et al. 2007; John and Thomas 2008; La Mantia and Morreale 2011; Faruk et al. 2012; Ramamoorthy et al. 2015).

### ***1.1.4 Regenerated cellulose fibre composites***

Biocomposites from regenerated cellulose fibres are a relatively new field. Regenerated cellulose fibres such as lyocell and viscose were reinforced in thermoplastics to produce composites (Amash and Zugenmaier 1998; Carrillo et al. 2008). The results from the regenerated cellulose composites are promising due to the fibre’s intrinsic properties; high strength of the fibres reflected in the composites. These composites are lightweight, have uniform and good mechanical properties, and could be good alternative for natural fibre composites. These



composites can also be termed as biocomposites owing to its biomass origin (Takahashi et al. 2008; Phuong & Lazzeri A 2012; Ramamoorthy et al. 2015).

### **1.2 Justification**

The non-renewable based materials are replaced by renewable bio-based materials in several applications due to their renewability and sustainability. Environmental legislation (landfill directive) and projects (NATURTRUCK, INNOBITE and BioBuild) of the European Union aims to reduce the negative effects on the environment by reducing the landfilling and using sustainable, renewable and biodegradable materials. Efforts are made to reduce the environmental impact by reducing the fuel consumption in automobiles and aircrafts by introducing lightweight materials as it is estimated that a 1% weight reduction in aircraft corresponds to 0.75% reduction in fuel consumption (Capehart 2007). According to Directive 2000/53/EC, European Union member countries are required to reuse and recover at least 95% by 2015 for all end-of-life vehicles. The European Union funded project, BIOVANT, focuses on developing biocomposites from soybean oil and natural fibres. This thesis falls in line with global interest on producing lightweight biocomposites from cellulosic reinforcement and bio-based matrix.

### **1.3 Aim of this study**

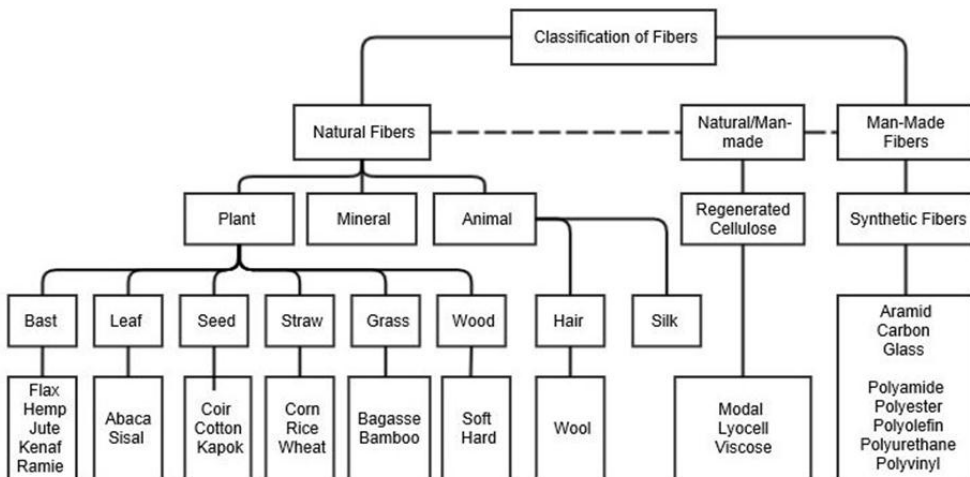
The aim of this thesis was to develop an environmentally friendly lightweight thermoset biocomposite from regenerated cellulose fibres (lyocell and viscose), and bio-based resin synthesized from plant oil (soybean oil) and lactic acid. The study was divided into four parts:

- Develop the biocomposites from regenerated cellulose fibres and bio-based resin
- Evaluate the mechanical, thermal, viscoelastic, morphological properties among others of the developed composites
- Study the effect of fibre surface modification in composites
- Explore alternate reinforcement, discarded cotton blend fabrics

## 2. LITERATURE REVIEW

### 2.1 Cellulose fibres

Fibres are broadly classified as natural and man-made fibres. Figure 1 shows the schematic representation of fibre classification. Natural fibres are categorized into three types based on their origins; plant, animal and mineral fibres. Animal and mineral fibres have not been widely used in composite field whereas plant fibres have been used widely in composites applications (Ramamoorthy et al. 2015). Regenerated cellulose fibres (RCF) fall between natural and man-made fibres and have been used as composite reinforcement in recent times. RCF's primary constituent is cellulose which is from biomass origin. Cellulose fibres, plant fibres and RCF, which are key parts of biocomposites reinforcements, are discussed in this thesis.



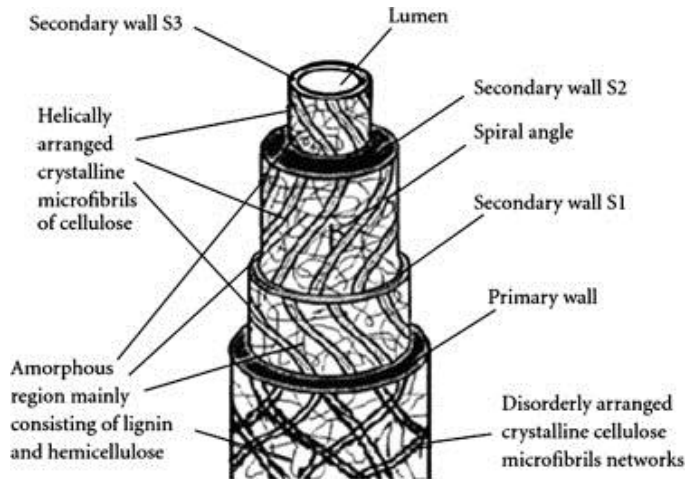
**Figure 1.** Schematic representation of fibre classification (Ramamoorthy et al. 2015)

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#### 2.1.1 Plant fibres

Plant fibres are categorized into six types (bast, leaf, seed, straw, grass and wood) and these fibres can be in the form of hairs (cotton, kapok), hard fibres (coir, sisal), and fibre sheaves (flax, hemp, jute). The plant fibres are classified depending on their utility such as primary and secondary. Plants to be used as fibres for primary utilities include hemp, jute, kenaf, etc., while the byproducts of plants such as coir, pineapple, etc. belong to the secondary group (Faruk et al. 2012). The production of plant fibres primarily depends on geographical location and the quantity of fibres production vary every year due to many reasons, among them weather conditions. The general structure of a plant fibre is shown in Figure 2. The main chemical composition is lignocellulose (cellulose, hemicellulose and lignin) and

the amount of these components differ from plant to plant. These basic components partially determine the physical properties of the fibres. These components could be distributed unevenly throughout the plant cell wall which makes it difficult to know the composition and properties of the fibres, Table 1.



**Figure 2.** Structure of plant fibre (John and Thomas 2008) ©Elsevier. Reproduced by permission of Elsevier. Permission to reuse must be obtained from rightsholder.

The unevenness of the chemical composition of the plant is one concern of natural fibres to be used as reinforcements in composites and influences the mechanical properties of the fibres, see Table 2.

Cellulose is the strongest and stiffest component of the fibre which is linear 1,4- $\beta$ -glucan polymer consisting of D-anhydroglucose ( $C_6H_{11}O_5$ ) repeating units containing hydroxyl groups. The OH groups form inter- and intra-molecular hydrogen bonding making it hydrophilic in nature. The cellulose chemical structure remains the same for all the natural fibres while the degree of polymerization changes, which influences the mechanical properties of the fibres.

Lignin is a phenolic branched polymer which supports the structure of the plant, and it is also resistant to microbial degradation until disturbed through physical/chemical treatment. The chemical structure of lignin is not clear until today even though most of the functional groups and units are identified.

Hemicellulose consists of a group of polysaccharides that are present along with cellulose. It has several different sugar units and exhibit chain branching.

The wax content of the fibre plays a crucial role on processing composites as it influences wettability when the matrix is introduced, furthermore influencing interfacial fibre-matrix adhesion.

Variations in natural fibres' mechanical properties in Table 2 are a result of several factors such as geographical location of the plant, maturity, size, chemical composition, part of the plant from which fibres are extracted, etc. The variation can also be attributed to different stages: growth, harvesting, fibre extraction, and storage, and each stage have several influencing factors. The natural fibres are hydrophilic by nature and have substantial amount of moisture content which influences the mechanical properties. Owing to low density, low cost, renewability and sustainability of natural fibres, these fibres are preferred reinforcements in several applications. (Ramamoorthy et al. 2015)

Natural fibres are widely used in automobile industries as reinforcements for composites. Leading car manufacturers such as Audi, BMW, Mercedes, Volkswagen, Volvo etc. use natural fibres in numerous composite applications, see section 2.8. Currently, most of these composites are used for interior applications as the natural fibres readily absorb moisture and successively deteriorate the composite properties. The methods employed in order to reduce the moisture absorption of the cellulose fibre composites are discussed in section 2.2.

**Table 1.** Chemical composition of some natural fibres (Adapted and developed from Bledzki & Gassan 1999; Mohanty et al. 2000; Hattallia et al. 2002; Hoareau et al. 2004; John and Thomas 2008; Faruk et al. 2012; Ramamoorthy et al. 2015)

<b>Fibre</b>	<b>Cellulose (wt%)</b>	<b>Lignin (wt%)</b>	<b>Hemicellulose (wt%)</b>	<b>Wax (wt%)</b>
<b>Bast</b>				
Flax	71.0	2.2	18.6 – 20.6	1.7
Hemp	70.2 – 74.4	3.7 – 5.7	17.9 – 22.4	0.8
Jute	61.0 – 71.5	12.0 – 13.0	13.6 – 20.4	0.5
Kenaf	31.0 – 39.0	15.0 – 19.0	21.5	–
Ramie	68.6 – 76.2	0.6 – 0.7	13.1 – 16.7	0.3
<b>Leaf</b>				
Abaca	56.0 – 63.0	7.0 – 9.0	20.0 – 25.0	3.0
Curaua	73.6	7.5	9.9	–
Henequen	77.6	13.1	4.0 – 8.0	–
Pineapple	70.0 – 82.0	5.0 – 12.0	–	–
Sisal	67.0 – 78.0	8.0 – 11.0	10.0 – 14.2	2.0
<b>Seed/Fruit</b>				
Coir	36.0 – 43.0	41.0 – 45.0	0.15 – 0.25	–
Cotton	82.7	–	5.7	0.6
Oil Palm	65.0	–	29.0	–
<b>Grass</b>				
Bagasse	55.2	25.3	16.8	–
Bamboo	26.0 – 43.0	21.0 – 31.0	30.0	–
<b>Straw</b>				
Rice	41.0 – 57.0	8.0 – 19.0	33.0	8.0 – 38.0
Wheat	39.0 – 45.0	13.0 – 20.0	15.0 – 31.0	–
<b>Others</b>				
Rice Husk	35.0 – 45.0	20.0	19.0 – 25.0	14.0 – 17.0

## LITERATURE REVIEW

**Table 2.** Mechanical properties of some natural fibres (Adapted and developed from Bledzki & Gassan 1999; Mohanty et al. 2000; Hattallia et al. 2002; Hoareau et al. 2004; John and Thomas 2008; Faruk et al. 2012; Ramamoorthy et al. 2015)

<b>Fibre</b>	<b>Density (g/cm<sup>3</sup>)</b>	<b>Tensile Strength (MPa)</b>	<b>E-Modulus (GPa)</b>	<b>Elongation at break (%)</b>
<b>Bast</b>				
Flax	1.5	345 – 1100	27.6	2.7 – 3.2
Hemp	–	690	30 – 60	1.6
Jute	1.3 – 1.4	393 – 773	13.0 – 26.5	1.2 – 1.5
Kenaf	–	930	53.0	1.6
Ramie	1.5	400 – 938	61.4 – 128.0	1.2 – 3.8
<b>Leaf</b>				
Abaca	1.5	400	12.0	3.0 – 10.0
Curaua	1.4	500 – 1150	11.8	3.7 – 4.3
Pineapple	–	413 – 1627	34.5 – 82.5	1.6
Sisal	1.4	468 – 640	9.4 – 22.0	3.0 – 7.0
<b>Seed/Fruit</b>				
Coir	1.1	131 – 175	4.0 – 6.0	15.0 – 40
Cotton	1.5 – 1.6	287 – 800	5.5 – 12.6	7.0 – 8.0
Oil Palm	0.7 – 1.55	248	3.2	25.0
<b>Grass</b>				
Bagasse	1.25	290	17	–
Bamboo	0.6 – 1.1	140 – 230	11 – 17	–

### 2.1.2 Regenerated cellulose fibres

Regenerated cellulose fibres (lyocell and viscose) are pure cellulose produced from wood pulp through different production methods and have good reinforcement potential, see sections 1.1.1 and 1.1.4.

In 1891 British scientists Charles Cross, Edward Bevan, and Clayton Beadle discovered that cotton or wood cellulose could be dissolved as cellulose xanthate following treatment with alkali and carbon disulphide (Cross et al. 1891). Then, the solution was coagulated in ammonium sulphate and later converted to cellulose (viscose) using dilute sulphuric acid. In 1969, Dee Lynn Johnson initiated the lyocell process by direct dissolution of cellulose in N-methylmorpholine N-oxide (NMMO) solution. The pulp used to produce the fibres determines the chemical composition of the fibres. The pulp used to make RCF has high  $\alpha$ -cellulose content by removal of hemicellulose from the pulp (Zhang et al. 2008). The crystallinity of the lyocell and viscose fibres differs and this affects the mechanical properties of the fibres (Colom & Carrillo 2002; Carrillo et al. 2004; Siroky et al. 2010).

#### *Viscose*

Viscose fibres could be prepared using two different pulps namely kraft and sulphite. Woodings described each step in the viscose process in detail (Woodings 2001). Viscose is important regenerated cellulose fibre in terms of production

volume. Global viscose production increased from 14,000 ton/year in 1920 to 3.5 million ton/year in 2010 (Ramamoorthy et al. 2015). These fibres are used in industrial applications such as tyre cords and textiles. The development of cheap synthetic fibres and environmental concerns in viscose process owing to the use of carbon disulphide are biggest drawbacks of this fibre. Some environmental issues in the viscose process are addressed, namely the usage and recovery of the alkali to the main circuit treatment of effluents and the recovery of carbon disulphide.

The physical properties of viscose fibres: dry tear strength (22 cN/tex), wet tear strength (12 cN/tex) and cellulose degree of polymerisation (~300) were studied by Breier (Breier 1997). These fibres have been used as reinforcement to produce thermoset and thermoplastic composites (Adusumali et al. 2006; Bledzki et al. 2009; Esmaeili et al. 2015; Ranganathan et al. 2015). Viscose fibres were used as impact modifiers to increase the impact strength in composites as these fibres possess high elongation (Ranganathan et al. 2015). The viscose fibre could be used as reinforcement in the biocomposites if the environmental issues during the fibre production are resolved.

### *Lyocell*

Lyocell fibre is produced by wetting the pulp with amine oxide and subsequent removal of water produces a homogenous solution with minimum quantity of undissolved particles and air bubbles (Woodings 2001). The current manufacturing process is designed to recover approximately 99% of the solvent which reduces the effluent. The effluent produced in the lyocell process is non-hazardous making it an environmentally friendly process. Initially, it was developed as Tencel by Courtaulds Fibres and currently, Tencel is owned by Lenzing AG and it is the only producer of these fibres. The annual production of lyocell fibres is around 50,000 tons and the total annual capacity of the industrial units is upgraded to more than 160,000 tons. Lyocell exhibits some unique characteristics such as wrinkle resistance, strong when dry or wet, and easy maintenance (Borbely 2008).

Lyocell fibres exhibit good physical properties; dry tear strength (42 cN/tex), wet tear strength (36 cN/tex) and cellulose degree of polymerisation (~600) (Breier 1997). The crystallinity and the DP of lyocell fibres are higher than for viscose, and this is one of the reasons that lyocell fibres possess higher strength than viscose. RCF under performed when compared to glass and flax fibres in terms of tensile strength and modulus but when the variability was considered, flax and regenerated cellulose fibres performed similarly (Adusumali et al. 2006). The most important difference between regenerated cellulose fibre and the other two fibres is their high failure strain and thus high work to fracture, which makes them useful for composite applications where high fracture toughness is required. The extensibility of the lyocell fibre together with its tensile strength contributes to good impact resistance in composites (Adekunle et al. 2011). The work to fracture of lyocell surpasses the value of flax fibres by a factor of 7 (Adusumali et al. 2006). Lyocell fibres have been used as reinforcement to produce biocomposites and their

properties are promising which makes lyocell a potential reinforcement for composites (Shibata et al. 2004; Carrillo et al. 2008; Johnson et al. 2008).

EU 13432 is a European Standard used to evaluate biodegradability of ligno-cellulosic materials. It states that the biodegradability is a material's capacity to be converted into CO<sub>2</sub> through the action of microorganisms. Using composites produced from biofibres is environmentally friendly as it biodegrades completely, however, the biodegradation of these fibres should be slow so that it can perform efficiently during the lifetime of the application. Cellulosic reinforcements are inherently biodegradable, and their biodegradation can be decelerated with difficulty, normally employing treatments with extra cost. The rate of degradation is an important factor and is governed by the material's chemistry. Cellulose which is the primary constituent of cellulosic fibres is resistant to enzymatic hydrolysis whereas other constituent, hemicellulose, is easily hydrolyzed by dilute acids and base. Degradation is influenced by moisture, temperature, UV radiation and microorganism activities (Azwa et al. 2013).

Moisture absorption influences crystallinity, strength, swelling and porosity of the fibres. Fibres with high amount of cellulose and high degree of crystallinity absorb low amount of moisture and perform well mechanically. Cellulosic fibre absorbs and retains moisture as the moisture interacts with large number of hydroxyl groups present in the cellulose, and also because of amorphous regions in the cellulose. The absorption of moisture along the interface reduces the interfacial adhesion between fibre and matrix as the water molecule establishes hydrogen bonding with the fibre. This results in cracks which could propagate when the swelling of the fibre creates stress in the interface region. This causes the cellulose fibre composites to underperform mechanically on moist conditions. The biological activities degrade cellulosic fibres after a certain period and this restricts the use of cellulosic fibre composites in humid environments. (Azwa et al. 2013)

### **2.2 Fibre surface treatments**

Natural fibres usually undergo treatment before being used as reinforcements in composites. This is mainly to improve the compatibility between fibre and matrix, remove the impurities and to reduce the hydrophilicity of the fibres. Cellulosic fibres are polar and readily absorb moisture as many hydroxyl groups are accessible for interaction with water molecules by hydrogen bonding. The hydrophilic nature of the cellulosic fibres adversely affects the adhesion to the hydrophobic non-polar matrix resulting in poor fibre-matrix interface and poor composite properties (Mohanty et al. 2005). The waxy substances and other impurities on the fibre surface contribute to poor surface wetting and also affect the fibre-matrix bonding as strong fibre-matrix interface is important for good mechanical properties of the composites (Mohanty et al. 2001). Physical or chemical treatments could be performed on the fibre surface in order to overcome the above mentioned issues by reducing the polar component of the fibres,

removing the impurities, changing the crystallinity and chemical composition, improving the fibre-matrix interface and attaining good adhesion between the fibre and the matrix.

Physical treatments such as plasma, corona, ultrasound, ultraviolet and dielectric barrier discharge involve surface fibrillation and electric discharge which alter the structural and surface properties of the fibres. These modifications increase the contact area through roughening of the fibre surface and facilitate the mechanical interlocking. However, these physical methods are not used widely due to inherent complexity and insufficient number of investigations dedicated towards understanding their behavior on fibres (Mukhopadhyay and Figueiro 2009).

Chemical treatments such as alkalisation, silanisation, acetylation, etherification, graft copolymerization, benzylation, isocyanate treatment etc. are studied well to modify the fibre surface of the cellulosic fibres and use the treated fibres as reinforcing material in polymer composites (Mohanty et al. 2001; Kalia et al. 2009). Chemical modifications may activate the hydroxyl groups in the fibre or can introduce new moieties that can interact with the matrix (Kalia et al. 2009). Treatment parameters such as concentration, time and temperature are important to achieve the optimum efficiency of the fibre in biocomposites (Mohanty et al. 2001). Alkali and silane treatments are commonly used treatments to improve the reinforcement potential of cellulosic fibres.

### 2.2.1 Alkali treatment

Alkali treatment which is also named mercerization, is one of the most used chemical treatments on natural fibres. It is an effective low cost process to modify the fibre surface by disrupting the internal hydrogen bonding, which increases the surface roughness. Alkali treatment on natural fibres changes the crystallinity, unit cell structure and orientation of fibrils (Colom and Carrillo 2002). The treatment removes a certain amount of lignin, wax and oils covering the external surface of the fibre cell wall, partly depolymerizes cellulose and exposes short length crystallites (Mohanty et al. 2001). It also removes hemicellulose and increases the amount of cellulose exposed on the fibre surface, thus increasing the number of possible reaction sites.

**Table 3.** Alkali effect on tensile properties of sisal fibre (Adapted from Yang et al. 1996)

Treatment	Tensile Strength (g/tex)	Young's Modulus ( $\times 10^3$ g/tex)	Elongation (%)
Untreated	30.7	1.18	2.5
Alkali	31.7	0.53	7.5
Alkali-thermal	27.6	0.70	4.7
Acetic acid+alkali	9.3	0.39	2.6

Tensile properties of sisal fibre on alkali treatments are shown in Table 3. Several authors have made successful alkali treatment on the natural fibres, enhancing the



mechanical and chemical properties of the composites (Valadez-Gonzalez et al. 1999; Mwaikambo and Ansell 2002; Alvarez et al. 2003). Alkali treatment on RCF changes the surface topography, moisture absorption and the crystalline structure. The increase in the fibre surface roughness enhances the mechanical interlocking with resins, thereby improving the composite properties by strong fibre-matrix bonding.

### 2.2.2 *Silane treatment*

Silane molecules with bi-functional groups are used to link the fibre and the resin by forming a bond with fibre's surface through a siloxane bridge while its organofunctional group forms a bond with the resin, which gives the molecular continuity across the interface region of the composite (Mohanty et al. 2001). These coupling agents have general chemical structure,  $R_{(4-n)}\text{-Si}(\text{R}^1\text{X})_n$ , where R is alkoxy,  $\text{R}^1$  is an alkyl bridge connecting silicon atom and X is organofunctionality (Xie et al. 2010). The most common organofunctional groups are amino, vinyl, mercapto or methacryloxy, whereas the common silanes are trialkoxysilanes (Xie et al. 2010).  $\gamma$ -aminopropyltriethoxysilane is used widely as coupling agent which reduces the number of hydroxyl groups in the fibre-matrix interface. Silane is hydrolyzed due to hydrolyzable alkoxy group to form silanols and is then adsorbed on the fibre surface (Agarwal et al. 2000). Hydrogen bonds are formed between hydroxyl groups of natural fibres and silanols which may further convert into covalent bonds. These covalent bonds are not stable towards hydrolysis (Xie et al. 2010).

Silane treatment was performed on several natural fibres and the resulting composites performed better than untreated fibre reinforced composites due to high degree of crosslinking in the interface region (Agarwal et al. 2000; Rong et al. 2001; Van de Weyenberg et al. 2003; Xie et al. 2010). The fibre-matrix interaction depends upon the organofunctionality of silane and the matrix. The organofunctionality of silane coupling agent are more reactive with thermoset resins than that of thermoplastic ones. This is because thermosets bear reactive functional groups, which lead to three dimensional networks formation on curing, and react effectively with organofunctionality of silanes (Xie et al. 2010). Silane treatment on natural fibres and their interaction with thermosets such as epoxy and polyester were shown in detail by Xie et al. (Xie et al. 2010). Silane treatments could be more effective on RCF than on natural fibres due to high amount of cellulose exposed to silane molecules.

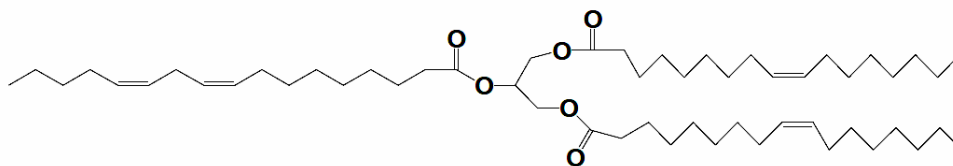
### 2.3 **Bio-based matrices**

Thermoplastics such as polylactic acid and polyhydroxyalkanoate's are developed from renewable resources for composite applications (John and Thomas 2008; Faruk et al. 2012; Koronis et al 2013). Thermosetting polymers from renewable resources are relatively new and the use of these bio-based matrices in composite applications has attracted several researchers. A critical review on thermoset bio-

based matrices has been made by Raquez et al. (Raquez et al. 2010). Plant oils (soybean oil, linseed oil etc.) are commonly used raw materials for the synthesis of bio-based matrix.

### 2.3.1 Plant oil based thermoset matrix

Plant oils are triglycerides which are composed of three fatty acids that are linked to glycerol by ester bonds, Figure 3. The composition of the fatty acids varies with oil source and the growing conditions. The plant oil triglycerides could contain various fatty acids with different degrees of unsaturation. The degree of unsaturation of the fatty acid plays a vital role in developing thermoset resins from plant oils as these oils have to be functionalized before being used as thermoset resin. Some fatty acids and their iodine values together with number of double bonds are listed in Table 4. Iodine values and double bonds reflect the amount of unsaturation in fatty acids; high values indicate high degree of unsaturation. Reactive sites are introduced by modifying the unsaturated fatty acids, which then can undergo chemical reactions during the thermoset curing process.



**Figure 3.** Triglyceride molecule (Adapted from Wool and Sun 2005)

**Table 4.** Fatty acids and their iodine value (Adapted and developed from Bailey 1996)

Fatty acid	Number of C atoms	Number of double bonds	Iodine value
Palmitoleic acid	16	1	99.8
Oleic acid	18	1	89.9
Ricinoleic acid	18	1	85.1
Linoleic acid	18	2	181.0
Linolenic acid	18	3	273.5
Licanic acid	18	3	261.0

**Table 5.** Fatty acid composition (%) of various plant oils (Adapted and developed from Deligny and Tuck 2000)

Fatty acid	Soybean oil	Linseed oil	Rapeseed oil	Palm oil	Sunflower oil
Palmitoleic	12	5	4	39	6
Oleic	24	22	56	45	42
Linoleic	53	17	26	9	47
Linolenic	7	52	10	-	-
Others	4	4	4	7	5

Table 5 shows the fatty acid composition of various plant oils and among those, soybean and linseed oils have high degree of unsaturation. This is because the soybean and linseed oils have large percentages of linoleic and linolenic acids respectively in their triglycerides. Linoleic and linolenic acids have two and three carbon-carbon double bonds respectively in their chain which could be used to create reactive sites during modification. The unsaturated fatty acids are susceptible to modification or functionalization, and a high percentage of these fatty acids will make the process easier.

Epoxy, alkyd, polyurethane and acrylate resins among other resins could be produced from plant oils (Meier et al. 2007). Adekunle et al. synthesized various thermoset resins from soybean oil (Adekunle et al. 2010). Acrylated epoxidized soybean oil (AESO) is one of the common plant oil thermoset resins available commercially for reasonable price. The chemical modification of soybean oil to produce AESO involves two steps; soybean oil is first epoxidized to form epoxidized soybean oil (ESO) and further functionalized with acrylate groups to form AESO, Figures 4 and 5. Other modifications can be done to ESO to yield methacrylated soybean oil (MSO), methacrylic anhydride-modified soybean oil (MMSO), etc. (Adekunle et al. 2010).

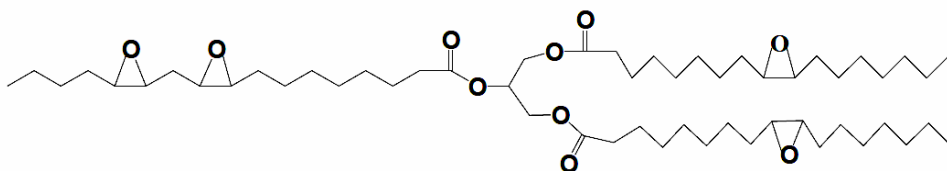


Figure 4. Epoxidized soybean oil (ESO)

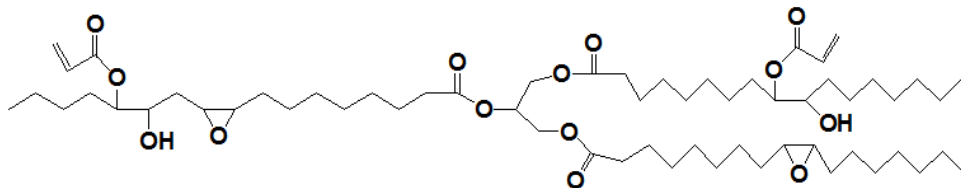


Figure 5. Acrylated epoxidized soybean oil (AESO)

Many researchers have illustrated the potential and importance of the soybean oil based resins, and their ability to be used as matrix in composites. Similarly, thermoset plastics were synthesized from linseed, cottonseed, oilseed radish, castor, olive, canola, corn and peanut oils, and their importance in polymer science is highlighted (O'Donnell et al. 2004; Scala and Wool 2005; Can et al. 2006; Güner et al. 2006; Kim and Sharma 2012;). Plant oils and their thermoset resins are reviewed in detail by Güner et al. (Güner et al. 2006).

### 2.3.2 Lactic acid based thermoset matrix

Lactic acid (2-hydroxy propionic acid) is produced commercially by fermentation of carbohydrates such as glucose, maltose, sucrose or lactose. The carbohydrate

source is often corn, sugarcane or beet (Garlotta 2001). It can also be produced by chemical synthesis. In 1780, the Swedish chemist Carl Wilhelm Scheele refined lactic acid for the first time and it has been produced commercially since 1895. It has found applications in food, pharmaceutical, and polymer industry among others and estimated that the overall lactic acid production will raise over 1 million tonnes per year by 2020 (Jem et al. 2010). Biodegradable polylactic acid (PLA), a thermoplastic polymer, from renewable lactic acid has been focused profoundly but there is only little emphasis on thermoset matrix from lactic acid on a large scale.

As lactic acid has both hydroxyl and carboxyl groups, it can undergo intramolecular or self-esterification and form linear polyesters, lactoyllactic acid, polylactic acid or cyclic dimer dilactide (Datta and Henry 2006). Åkesson et al. synthesized thermoset resin by reacting lactic acid based oligomer with methacrylic anhydride (Åkesson et al. 2010). This resin was prepared by introducing reactive groups in lactic acid polymer chains which can be cross-linked through free-radical polymerisation. Bakare et al. synthesized thermoset resins from lactic acid and their composites had good strength (<sup>a</sup>Bakare et al 2014; <sup>b</sup>Bakare et al 2014). One of the resins was synthesized by reacting lactic acid with glycerol in direct condensation and the resulting branched molecule was later functionalized with methacrylic anhydride and the biocontent of about 92% was achieved (<sup>a</sup>Bakare et al 2014). Lactic acid is a good alternative to produce thermoset bio-based matrices for the composite applications in terms of renewability.

## **2.4 Biocomposites**

Biocomposite is a composite material derived by reinforcing biofibre in petroleum based plastic or renewable resource based plastic. Composite material made from synthetic fibre like glass and bioplastic such as polylactic acid could also be called biocomposite (Mohanty et al. 2005). Biocomposites made from synthetic fibres or petroleum-based matrices are not entirely eco-friendly as only part of the composite is from renewable resources. In recent times, ‘green composites’ are produced from biofibre and bio-based matrix. Green composites possess a high biocontent and on disposal, can biodegrade with minimal harm to the environment.

All the cellulosic fibre types mentioned in Figure 1 have been used to produce biocomposites (Ramamoorthy et al. 2015). Bledzki and Gassan have reviewed the natural fibre reinforced polymer composites until 1999, and Faruk et al. reviewed the same topic between 2000 and 2010 (Bledzki and Gassan 1999; Faruk et al. 2012). The production and characterization of these composites were improved substantially through extensive research (Faruk et al. 2012). Biocomposites were also prepared using bio-based matrices as mentioned in section 2.3. Adekunle et al. studied soybean oil based biocomposites (Adekunle et al. 2011; <sup>a</sup>Adekunle et al. 2011; Adekunle et al. 2012). A seat shell was made from AESO and flax fibres (Åkesson et al. 2009). Biocomposites from lactic acid based thermoset resin and

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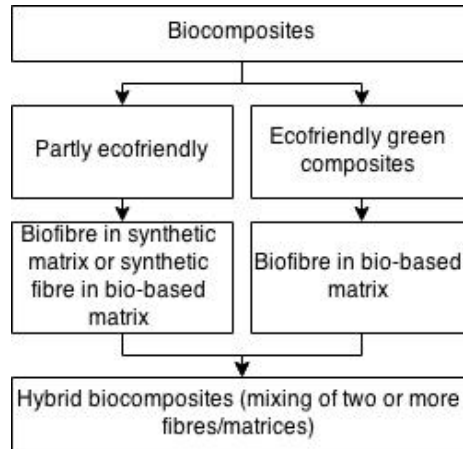
cellulose fibres had good properties (Åkesson et al. 2009; Åkesson et al. 2011; Esmaeili et al. 2015).

Since 2000, a limited number of researchers have considered regenerated cellulose fibres as potential reinforcement in composites as their properties are consistent and encouraging (Amash and Zugenmaier 2000; Seavey et al. 2001; <sup>a</sup>Ganster and Fink 2006; Adusumali et al. 2006; Bledzki et al. 2009; Esmaeili et al. 2015; Ranganathan et al. 2015). Ganster et al. showed that the regenerated cellulose fibre composite properties can be improved by the addition of a suitable coupling agent (<sup>b</sup>Ganster et al. 2006). Seavey et al. discussed regenerated cellulose fibre composite manufacturing, fibre treatment and composite properties (Seavey et al. 2001; Seavey and Glasser 2001; Franko et al. 2001). Many publications including PhD theses reflect biocomposites but there are only few pioneering papers on regenerated cellulose fibre reinforced composites as it is a fairly new field. The reinforcement potential of the regenerated cellulose fibres are explored in the publications I, II and IV in this thesis.

Life cycle assessment (LCA) of biocomposites is essential as several parameters such as raw material consumption, energy utilization etc. from the production to disposal is taken into account to validate the sustainability. The sustainability assessment involves renewability, recyclability, biodegradability and economic viability. Previous LCA studies have clearly shown that the biocomposites outperform the conventional composites and are 'greener' (Nicollier et al. 2001; Patel et al. 2005; Song et al. 2009).

### **2.5 Hybrid biocomposites**

Hybridization is a concept of blending two or more fibres/matrices to produce composites with unique properties, and when some of these materials are from renewable resources, it is termed as hybrid biocomposites, Figure 6. The advantages of each component could complement others and as a result a composite with unique properties could be produced. This concept could be applied either to improve the properties of the composites or to reduce the cost of the composite; or both. While mixing the fibre or matrix, the amount of each component and their compatibility determine the properties of hybrid composites. Several other factors such as each fibre's orientation and arrangement, dimension of each fibre, affinity of each fibre with matrix and the properties of individual fibres play a vital role on composite properties when two or more fibres are mixed. Similarly, matrix blending also includes various factors that influence the composite properties: compatibility between two matrices, physical and chemical properties of each matrix etc. The properties of the hybrid composites could be predicted by the rule of mixtures which is also used to predict the properties of other composites. Hybrid composites and their design is clearly explained in a book chapter (Thomas and Pothan 2009).



**Figure 6.** Schematic representation of biocomposites (Adapted from Mohanty et al. 2005)

**Table 6.** Water absorption of natural fibre and natural/glass fibre composites (Adapted from Rout et al. 2001)

Sample	Water absorption %	
	Coir–polyester (Non-hybrid)	Coir/glass–polyester (Hybrid)
Untreated	8.5	5.2
Alkali treated (5%)	5.0	3.1
PMMA grafted (5%)	4.0	2.7

Glass fibres were mixed with natural fibres to improve the mechanical properties of the composites. The water absorption of these composites was lowered on hybridization and subsequently the properties and the stability improved. A comparison of the water absorption of natural fibre and natural/glass fibre composites with and without treatment of the fibre is given in Table 6. Many studies were made to explore plant/glass fibre hybrid composites and it is summarized (Santulli 2007; Thomas and Pothan 2009). It has been demonstrated that the mechanical, thermal, viscoelastic and morphological properties of the hybrid composites are different from the single fibre composites.

Hybrid biocomposites can be produced without compromising the environmental benefits of the natural fibres by incorporating two or more biofibres. In an interesting study, hybrid composites were produced by mixing banana and sisal fibres (<sup>a</sup>Idicula et al. 2005; <sup>b</sup>Idicula et al. 2005). A positive hybrid effect was reported from the tensile, flexural and viscoelastic properties. Similarly, jute/hemp and sisal/oil palm fibre hybrid biocomposites and their properties were studied (Jacob et al. 2004; Mehta et al. 2005). Regenerated cellulose fibre based hybrid biocomposites were produced recently by mixing together with flax, jute and wood fibres (Johnson et al. 2008; Adekunle et al. 2011; <sup>a</sup>Adekunle et al. 2011).

## 2.6 Reinforcement architecture

Reinforcement architecture or orientation is an important factor and affects the composite properties largely. Reinforcement can be particle, fibre or fabric which can be distributed/layered in the matrix (John and Thomas 2008; Ramamoorthy et al. 2015). Evolution in textile composites brought different textile fabric techniques such as weaving, knitting and braiding to the reinforcement structure; their fibre orientation and production principle is shown in Table 7. The main advantage of fabric reinforcement is their even distribution.

**Table 7.** Fabric production technique (Adapted from Ogale and Alagirusamy 2004)

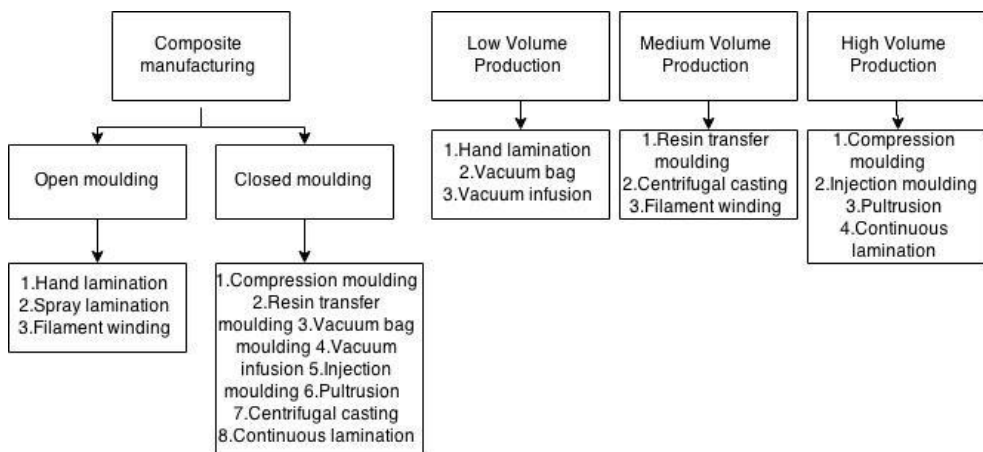
<b>Technique</b>	<b>Direction of yarn feed</b>	<b>Principle of production</b>
<b>Nonwoven</b>	Staple fibres could be used directly (yarn not required); yarn could be used in three or more direction (orthogonal)	Mutual fibre placement
<b>Weaving</b>	Two ( $0^\circ/90^\circ$ ) warp and weft	Interlacing (by selective insertion of $90^\circ$ yarns into $0^\circ$ yarn)
<b>Knitting</b>	One ( $0^\circ/90^\circ$ ) warp and weft	Interlooping (by drawing loops of yarns over previous loops)
<b>Braiding</b>	One (machine direction)	Intertwining (position displacement)

Nonwoven materials possess different structure and properties when compared to woven structure in terms of porosity, bulkiness and fibre arrangement (Das et al. 2012). Fibres are aligned unidirectionally in nonwoven fabrics whereas they are aligned in two directions in woven fabrics ( $0^\circ/90^\circ$ ), Table 7. Composites produced from nonwoven fabrics have high strength and modulus in fibre oriented directions, and low strength in off-axis direction. Woven composite has good strength in both the directions due to fibre arrangement in two directions, but lower than nonwoven composite strength in fibre oriented directions.

## 2.7 Composite processing

A wide range of composite production methods are available and were designed to meet specific manufacturing challenges. Each process has its own benefits and limitations, and can be chosen depending on the reinforcement, matrix and the applications. Several other factors that influence the choice of the process are size and shape of the component, quality required, processing volume and time. Some methods need a high degree of manual handling while few are automated. Some important and frequently used process models are explained in detail (Strong 2008). Figure 7. shows the classification of composite manufacturing based on moulding and production volume. Open moulding such as hand lamination and closed moulding such as compression moulding are most common and well

established techniques used today for thermoset composites due to their low complexity. Hand lamination needs low investment and simple process, however, it is labour intensive. It also causes environment and health problems. The process comprises curing of gel coat in a mould, then addition of reinforcement on the top and finally pouring liquid resin to cure to form the composite. This method is normally performed at ambient temperature and can take several hours to cure. In contrast, compression moulding is automated and the processing time is reduced considerably. This process needs large investments that employs expensive metal moulds, so it is usually chosen when the production quantities are higher than 10,000 mouldings. The resin wetted reinforcement layers are placed in the mould and the metal mould is mounted on a hydraulic press, where pressure and heat are used to spread the resin uniformly and cure the resin respectively. The process is fast and usually takes less than 5 minutes. Hand lamination is a low volume production method whereas compression moulding is a high volume production method. Vacuum infusion and resin transfer moulding methods are used if the curing process involves large amounts of volatile organic compounds emissions.

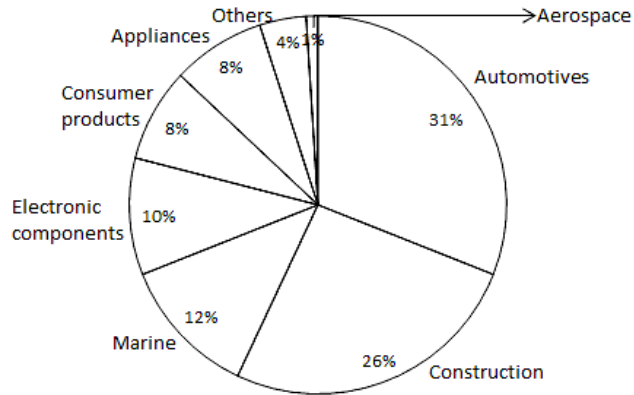


**Figure 7.** Composite manufacturing based on moulding and production volume

## 2.8 Application and market

Figure 8 shows the application areas of fibre reinforced composites (FRC). Automotives and construction industries together comprise 57% of the FRC market. However, these composites are also used in marine, electronic components, consumer products, appliances and aerospace. Glass fibre is the most commonly used fibre, and recent developments have brought biofibres in the composites. The use of biofibre in composite industry has been extended to several applications. Governmental support for ecofriendly products, performance improvement in the materials and unpredictable petroleum price will drive growth of biocomposites in new application areas.





**Figure 8.** Fibre reinforced composite application areas in 2002– $2.28 \times 10^9$  lb (adapted from Mohanty et al. 2005)

Cellulosic fibre content in the composite plays an important role due to its hydrophilicity and it should be limited when the composite is intended for outdoor applications to attain durability of composites (Azwa et al. 2013). It is also common to perform chemical treatments such as alkalization and silanization on fibres to make them less hydrophilic. These treatments are explained in detail in section 2.2. Degradation rate of the fibres can be slowed down but cannot be completely controlled. Nevertheless, biocomposites have already shown good properties by reducing the water absorption of the fibre, thereby increasing the lifetime of the products. A French enterprise, Ekobo, has been manufacturing dishwasher safe home accessories such as cups, plates, bowls, spoons etc. from natural fibre. The durability of these products were extended by using 100% food-grade melamine binder, however, it biodegrades in 2-3 years when buried.

Similarly, the fire retardancy of biocomposites is poor and they cannot be used where inflammability and safety are key issues. Thermal resistance of hemicellulose is low and it starts to decompose between 200 and 260 °C, whereas the cellulose decomposes between 260 and 350 °C (Ahmad et al. 2015). Using high purity cellulose fibres such as regenerated cellulose fibres in biocomposites, extends the durability of the products as hemicellulose is more susceptible to thermal, biological and moisture degradation than cellulose.

Global biocomposite market has reached \$2.1 billion in 2010 with 15% annual growth between 2005 and 2010, and the market is expected to reach \$3.8 billion by the end of 2016 (Lucintel 2011). Europe and America are the largest markets of biocomposites in automotive and construction applications respectively. Automobile applications comprise door panels, seat backs, headliners, dash boards, trunk liners etc. and construction applications comprise door panels, decking, window frames etc. Performance-price ratio (strength/\$) of the biocomposites is significantly higher than the traditional FRC, steel and aluminium, which means

that the biocomposites perform well at low price (Lucintel 2011). Table 8 shows the biocomposites used in cars by leading manufacturers.

**Table 8.** Biocomposites used by leading car manufacturers (Holbery and Houston 2006; Hill 2012; Ahmad et al. 2015)

<b>Manufacturer</b>	<b>Application</b>
<b>Audi (A2, A3, A4, A6, A8, Roadster, Coupe)</b>	Seat backs, door panel, boot lining, hat rack, tire lining
<b>BMW (3, 5 and 7 series)</b>	Door panel, headliner, boot lining, seat backs, noise insulator
<b>Citroen (C5)</b>	Door panel
<b>Daimler/Chrysler (A, C, E and S class; EvoBus)</b>	Door panel, dashboard, pillar cover panel, business table
<b>Ford (Mondeo CD 162, Focus)</b>	Door panel, boot lining
<b>Mercedes-Benz (E-class, Trucks)</b>	Internal engine cover, engine insulation, sun visor, interior insulation, bumper, wheel box
<b>Opel (Astra Vectra, Zafira)</b>	Headliner, door panel, pillar cover panel
<b>Peugeot (406)</b>	Seat backs
<b>Renault (Clio, Twingo)</b>	Rear shelf
<b>Saab</b>	Door panels, seat backs
<b>SEAT</b>	Body panels, spoiler, seats
<b>TOYOTA (Brevis, Harrier, Celsior, RAUM)</b>	Door panels, seat backs, tire cover
<b>Volkswagen (Golf, Passat, Variant, Bora, Fox, Polo)</b>	Door panel, seat backs, boot lining
<b>Volvo (C70, V70)</b>	Seat padding, floor tray

### 3. EXPERIMENTAL

#### 3.1 Materials

##### 3.1.1 Reinforcements

Lyocell fibres were supplied by Lenzing AG. The specific density of the fibres was  $1.5 \text{ g/cm}^3$  and the linear density was 1.7 dtex. The average length and the diameter of the fibre were 38 mm and  $13.4 \text{ }\mu\text{m}$  respectively (*Publications I, II and III*). Viscose nonwoven fabrics were supplied by Suominen Nonwovens Ltd. The surface weight and the thickness were  $60 \text{ g/m}^2$  and 0.66 mm respectively (*Publications I, II and IV*). Woven and nonwoven jute fabrics were supplied by HP Johannesson Trading AB. The nonwoven jute fabric had surface weight of  $810 \text{ g/m}^2$  (*Publication I*). Woven jute fabrics had a surface weight of  $320 \text{ g/m}^2$ , with 46 yarns/10 cm in the weft and 50 yarns/10 cm in warp, the yarn twist was 4.5 turns/inch. Woven glass fabric were supplied by Ahlstrom Corporation and had surface weight of  $500 \text{ g/m}^2$  (*Publication I*). Discarded cotton/PET (1:1) plain-weave bed linen fabrics were obtained from Textilia, Sweden. These cotton blend fabrics had surface weight of  $210 \text{ g/m}^2$  and had been used in hospitals, care centers, or other institutions (*Publication V*).

Chemicals used for fibre treatment were the following: reagent grade NaOH and 3-aminopropyl-triethoxysilane (APTES 99%) were obtained from Scharlau and Sigma Aldrich (*Publications I, III and IV*). Absolute ethanol ( $\geq 99.8\%$ ) was supplied by Sigma Aldrich (*Publications III and IV*).

##### 3.1.2 Matrices

Bio-based matrix from soybean oil, acrylated epoxidized soybean oil (AESO), was supplied by Cognis GmbH. The chemical structure of AESO is shown in Figure 5. (*Publications I and II*) Bio-based matrix from lactic acid was synthesized in lab (*Publication IV*). Bio-based matrix from soybean oil, MSO, synthesized by a colleague was used in Publication V (Adekunle et al. 2010).

Chemicals used in the synthesis were: L-lactic acid (88-92%, Sigma Aldrich), glycerol (99.5%, Scharlau), hydroquinone (99%, Fisher Scientific), toluene (99.99%, Fisher Scientific), methanesulphonic acid ( $\geq 98\%$ , Alfa Aesar) and methacrylic anhydride (94%, Alfa Aesar). (*Publications IV and V*)

Cross-linking initiators used: tert-butyl peroxybenzoate and dibenzoyl peroxide were supplied by Aldrich Chemical Company and Kebo lab respectively. (*Publications I, II, IV and V*)

##### 3.1.3 Chemicals used during characterization

Standard test solvents used for contact angle measurements were: methylene iodide (99%), hexadecane ( $\geq 99\%$ ), formamide ( $\geq 99.5\%$ ) and ethylene glycol (99.8%), and these were supplied by Sigma Aldrich. (*Publications III and IV*)

## 3.2 Methods

### 3.2.1 Fibre treatments

#### *Alkali treatment*

RCF and jute fibres were pre-dried at 105 °C for 2 hours before immersing in seven different concentrations (2, 4, 6, 8, 10, 13 and 15 wt%) of sodium hydroxide solutions. The fibres were treated for six time intervals (0.5, 1, 12, 24, 48 and 72 hours) and at two different temperatures (25 and 50 °C). After the treatment, the fibres were washed thoroughly with distilled water. Then, the fibres were dried at room temperature followed by oven drying at 105 °C to remove any moisture from the fibres. (*Publications I, III and IV*)

#### *Silane treatment*

3-aminopropyl-triethoxysilane (APTES) was used as silane coupling agent to treat the RCF. APTES was added to an ethanol–water mixture (8:2 volume ratio) to make seven different concentrations (2, 4, 6, 8, 10, 13 and 15 wt%). Pre-dried RCF were immersed in the treatment solution for five different time intervals (0.5, 12, 24, 48 and 72 hours) and at two different temperature (25 and 50 °C). After the treatment, fibres were washed and dried similar to alkali treatment. (*Publications III and IV*)

### 3.2.2 Nonwoven fabric manufacturing process

Firstly, RCF fibres were disentangled, put together and aligned by carding process. This process forms a continuous web from staple RCF fibres by aligning all the fibres in one direction. The carding was done using a cylindrical machine supplied by Cormatex, Italy. The frequency of the trolley was 40 Hz; equivalent to 7.5 m/min at the outlet. The cylinder speed and the density of the web influence the quality of the nonwoven fabrics.

Then, the fibres in the web were binded mechanically by needle punching process to form nonwoven fabric. This process entangles the fibres using serrated needles which results in stiff fabric. The needle punching was done using a machine supplied by Certec, France at a frequency of 200 cp/min and the feeding rate was 1.5 m/min. The depth of the needle was 8 mm. The frequency and the needle depth contributed the fibre entanglement. The needle punching was done two times to obtain good fibre interlocking. (*Publications I and II*)

### 3.2.3 Resin synthesis

Lactic acid and glycerol were reacted first in a direct condensation; the product was then end-functionalized with methacrylic anhydride as mentioned in co-author's publication (<sup>a</sup>Bakare et al. 2014). In the first step, 1.08 moles lactic acid and 0.12 mole glycerol were added in toluene to make homogeneous solution. Methanesulphonic acid (0.1 wt%) was used as a catalyst. The condensation

## EXPERIMENTAL

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reaction took place for 5 hours; first 2 hours at 145 °C, followed by 2 hours at 165 °C and finally 1 hour at 195 °C. In the second step, the product was cooled to 110 °C and end-functionalized with 0.396 mole methacrylic anhydride for 4 hours. The whole synthesis was done under nitrogen atmosphere. The byproduct, methacrylic acid, was removed by distillation. The viscosity of the resin was 1.09 Pa.s. (*Publication IV*)

The resins were mixed with 2 wt% peroxides to initiate the cross-linking. Resin viscosity was reduced by heating the resin in an oven at 60 °C for 5 minutes before adding the peroxide as the viscosity influences fibre impregnation and obtained composite porosity. Soybean oil based resins were mixed with tert-butyl peroxybenzoate and lactic acid based resin was mixed with dibenzoyl peroxide. (*Publications I, II, IV and V*)

### **3.2.4 Composite preparation**

Jute, glass and regenerated cellulose fabrics, untreated and treated, were cut to 20×20 cm dimension and conditioned in a vacuum oven for 1 hour at a temperature of 105 °C in order to remove the moisture. The fabrics were impregnated with the peroxide mixed resin to obtain a fibre content between 40 and 70 wt%. For hybrid composites, two fibres are mixed in known ratio in layers. The impregnated fabrics were then stacked between two plates and pressed in a manual heated press. The press used for compression moulding was supplied by Rondol Technology, UK. The impregnated fabrics were subjected to temperature (150–200 °C) and pressure (40–50 bar) for 5–10 minutes. Lactic acid based composites were post-cured at 140 °C for 2 hours. (*Publications I, II, IV and V*)

### **3.2.5 Specimen preparation**

Specimens were cut from the composite laminates according to the ISO test standards using a laser cutter supplied by GCC LaserPro Spirit, Taiwan. Dog bone shaped specimens were used for tensile test and flat specimens were used for other tests as mentioned in section 3.3. The specimens were cut from the centers of the composite laminates, to minimize the edge effects. (*Publications I, II, IV and V*)

## **3.3 Testing and characterization**

### **3.3.1 Fibre and resin characterization**

Fourier transform infrared spectroscopy (FTIR, Nicolet 6700 spectrometer) and Raman spectroscopy (Kaiser optical systems Inc.) were used to see the changes on lyocell fibre surface chemical composition on alkali and silane treatments. FTIR was also used to follow hydroxyl and carboxyl groups during the resin synthesis. (*Publications III and IV*)

Tensile test of individual fibres were done using Textechno Favigraph tensile tester. The load cell used to test fibres was 20 cN while the gauge length and test speed were 20 mm and 20 mm/min respectively. (*Publication III*)

Contact angle measurements were carried out on untreated and treated fibres using a Cahn DCA-322 device to study the change in the hydrophilicity. The fibres were held vertically on the balance and tared before moving towards the wetting agent. A change in the force was detected when the fibre came into contact with the wetting agents and this was recorded as zero depth of immersion. The force changes were recorded when the fibre was immersed deeper. Three dipping liquids (water, ethylene glycol and methylene iodide) were used as the wetting agents. Dynamic contact angles were measured. (*Publication III*)

Moisture regain measurements on different treatments were conducted according to DIN 54 351 using a climate chamber (HPP 108/749) supplied by Memmert GmbH. Pre-dried fibres were placed in the climate chamber and the moisture regain was calculated at two different relative humidities ( $50\pm 2$  and  $65\pm 2\%$ ). Fibre's weight loss after the chemical treatments was calculated by weighing the fibres before and after treatment. Swelling of fibres on treatment was calculated by measuring the diameter of the wet fibres being penetrated by treatment solutions for 30 minutes. (*Publication III*)

Differential scanning calorimetry (DSC) analysis was carried out using Q series DSC from TA Instruments to see the crosslinking reaction efficiency of the resin at the curing temperature. Approximately 10 mg of the resin sealed in an aluminium pan from 20 to 200 °C at a heating rate of 10 °C/min under nitrogen atmosphere. (*Publication IV*)

Thermal decomposition resistance of the fibres and the resin was analyzed using thermogravimetric analysis (TGA, Q series, TA Instrument). The sample weighing approximately 15 mg was heated from 30 to 600 °C in platinum pan at a heating rate of 10 °C under nitrogen atmosphere. (*Publications III and IV*)

Dynamic mechanical thermal analysis (DMTA) was used to study the viscoelastic properties of the resin. The specimen (30×10 mm) was mounted in dual cantilever clamp and the measurement was taken in the temperature range 20–150 °C at a frequency of 1 Hz. Storage modulus, loss modulus and  $\tan \delta$  were analyzed to evaluate the viscoelastic performance. (*Publication IV*)

Scanning electron microscopy images of untreated and treated fibres surfaces were analysed to see the physical changes. The experiment was run on JEOL JSM SEM at 10 kV acceleration voltage. (*Publication III*)

### **3.3.2 Composite characterization**

#### *Mechanical properties*

Tensile testing of the composites was carried out according to ISO 527 using Tinius Olsen H10KT universal testing machine and QMat software. The dog bone shaped specimens were clamped and pulled apart using a 5–10 kN load cell and mechanical extensometer. The overall length of the specimen was 150 mm which

## EXPERIMENTAL

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includes 60 mm parallel sided portion. The parallel sided portion's width was 10 mm and the width at the ends was 20 mm. The gauge length was 50 mm and the rate of loading was 10 mm/min. The tensile properties such as tensile strength, E-modulus and percentage elongation were studied. (*Publications I, II, IV and V*)

Three-point flexural tests were carried out according to ISO 14125 using same machine as tensile test. The flat specimens (80×15 mm) were placed with support at two ends and the force was applied in the middle. The force was detected using same load cell as tensile test. The outer span was 64 mm and the rate of loading was 10 mm/min. Flexural strength and modulus were investigated. (*Publications I, II and IV*)

The Charpy impact test was performed according to ISO 179 using digital Zwick test instrument. The un-notched specimens were tested flatwise. (*Publications I, II, IV and V*)

Non-destructive resonance analysis was done to determine the E-modulus. The apparatus was self-constructed by attaching a piezoelectric transducer to the beam which was connected to a PC's sound card after passing through high pass filter in series. The acoustic signals on vibrating the cantilever composite beam were received using Audacity software and these signals were converted to frequency, and further analysed using Scilab software to determine the modulus. (*Publication IV*)

### *Thermal properties*

DSC and TGA analyses were performed as explained in section 3.3.1. Approximately 10 mg of the composite sample was heated from 20 to 200 °C to detect the resin curing as remaining exothermal heat in the sample. Thermal decomposition resistance of the composites was analyzed by heating 15 mg of the sample from 30 to 600 °C. (*Publication IV*)

Thermal conductivity and diffusivity of the composite specimens were measured according to ISO 22007 using TPS 2500 hot disk. The heating power and the measurement time were 50 mW and 10 seconds. Two identical specimens were placed above and below the sensor and the specimen is heated through heat source. (*Publication IV*)

### *Viscoelastic properties*

Viscoelastic properties of the composites was studied using DMTA as explained in section 3.3.1. Storage modulus, loss modulus and  $\tan \delta$  were examined to evaluate the viscoelastic performance. (*Publications I, II and IV*)

### *Morphological analysis*

Optical (Nikon Instruments, Japan) and scanning electron (AIS2100 Seron Technology; JEOL JSM SEM; FEI Quanta 200F) microscopies were used to see

the cross-section of tensile fractured specimens. Optical microscopy images were taken directly on cross-section without any preparation, whereas SEM images were taken after the specimens were sputtered with a layer of gold at 5–20 kV.

*Density and porosity measurements*

Archimedes principle, buoyancy method, was used to determine the densities of the composite specimens. The specimens were covered with paraffin before immersing in ethanol medium to avoid absorption. The porosity was calculated using the method suggested by Madsen et al. (Madsen et al. 2007). (*Publication IV*)

*Contact angle*

Static contact angle measurement was done on optical tensiometer from Attension Theta Lite, Finland. A liquid drop is placed on flat composite surface and the contact angle was measured from the angle formed between the composite surface and the tangent to the drop. Four wetting agents such as water, ethylene glycol, formamide and hexadecane were used. (*Publication IV*)

*Water absorption*

Gravimetric water absorption tests were carried out on the composite specimens (80×15 mm) to determine the stability of the composites, by weighing the dry samples and placing in water at standard room conditions for 10 days. The percentage water absorption was then calculated.



## 4. SUMMARY OF RESULTS

### 4.1 Fibre properties on chemical treatments (*Publication III*)

Silane treatments on RCF reduced the number of hydroxyl groups and the Si groups were grafted on fibre's surface. Alkali treatment interacted with hydroxyl groups of the cellulose, and also increased the fibre's surface roughness. The crystallinity of the fibres also changed on the treatments. Treatment time, concentration and temperature affected the fibre properties.

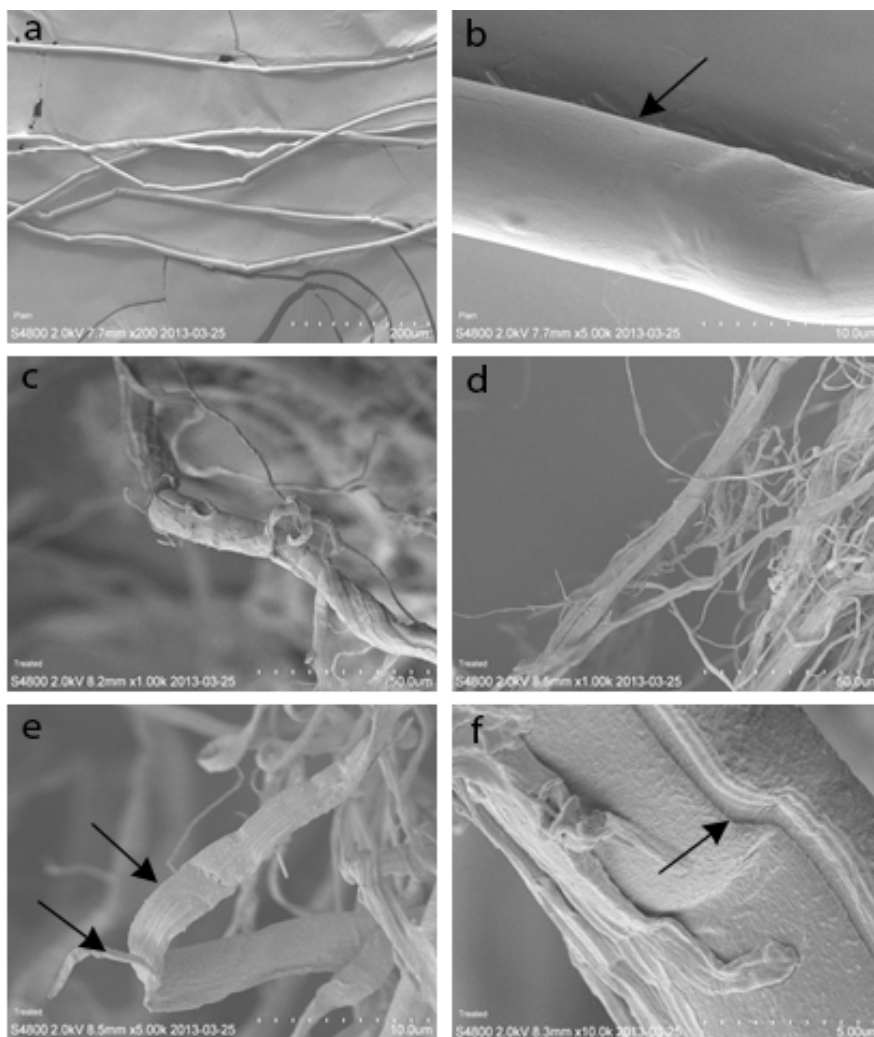
Tensile properties such as fibre strength, toughness and elongation changed depending upon the treatment conditions, see Table 9 and 10. Modulus of the fibre could be improved with appropriate treatment conditions, but the tensile properties decreased on severe alkali conditions. This is due to fibrillation and pore formation on alkali treatment. The splitting of the fibre into finer filaments and progressive fibre damage occurred at high alkali concentrations, which influence the mechanical properties of the fibres. These fibres can give contradictory tensile results in composites; certain degree of fibre fibrillation/pores could increase the composite's mechanical properties as the resin penetrates into the fibre pores and allows good mechanical interlocking.

**Table 9.** Tenacity, modulus and elongation of alkali treated fibres, *Publication III*

NaOH Treatments			Tenacity	Modulus	Elongation
Time	Temp	% Conc	(cN/dtex)	(cN/dtex)	(%)
<i>Untreated</i>			3.27 ±0.63	55.87 ±23.06	8.70 ±2.01
12 h	25°C	4wt	3.22 ±0.59	61.07 ±22.34	10.83 ±1.43
24 h	25°C	4wt	3.05 ±0.55	64.50 ±15.65	9.82 ±2.31
72 h	25°C	4wt	2.96 ±0.55	52.95 ±10.64	10.37 ±1.76
12 h	25°C	15wt	1.65 ±0.53	49.17 ±17.09	7.42 ±3.09
24 h	25°C	15wt	1.64 ±0.44	44.87 ±19.44	7.59 ±2.95

**Table 10.** Tenacity, modulus and elongation of silane treated fibres, *Publication III*

Silane Treatments			Tenacity	Modulus	Elongation
Time	Temp	% Conc	(cN/dtex)	(cN/dtex)	(%)
<i>Untreated</i>			3.27 ±0.63	55.87 ±23.06	8.70 ±2.01
12 h	25°C	4wt	3.17 ±0.43	68.43 ±16.88	9.91 ±1.97
24 h	25°C	4wt	2.82 ±0.45	73.33 ±16.83	7.99 ±1.86
72 h	25°C	4wt	3.10 ±0.56	66.28 ±21.07	9.04 ±1.50
12 h	25°C	15wt	3.30 ±0.28	57.83 ±20.35	11.10 ±1.19
24 h	25°C	15wt	3.06 ±0.35	68.41 ±21.29	8.75 ±1.55



**Figure 9.** SEM images of the RCF (a, b = untreated; c – f= 72h, 50°C, 15 wt% alkali treated) Arrows indicates the change in the surface of the fibre, *Publication III*

The fibres tend to swell and lose weight during the treatment. The swelling causes rearrangement of hydrogen bonds as the cellulose molecules are forced further apart. This reorganization causes the change in the crystallinity, which was confirmed by FTIR. It was found that the alkali treatment caused substantial increase in fibre diameter and the peak swelling was approximately 45% whereas the silane treatment did not increase the fibre diameter more than 14%. High degree of swelling initiates fibre splitting and weight loss. The peak weight loss was approximately 20 wt% on alkali treatment whereas the silane treatment had a negligible loss (~3 wt%). The weight loss affected the tensile properties; higher

## SUMMARY OF RESULTS

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weight loss suggests lower tenacity and vice versa. Fibre fibrillation and void formation have direct impact on moisture absorption.

Microscopy images of untreated and alkali treated fibres show the change in the fibre surface and fibrillation, Figure 9. The micrographs show that the alkali treated fibres suffered oversized fibrillation on harsh treatments whereas the untreated fibre surface was more even and compact. This is consistent with the results from weight loss and tensile test.

Polar and non-polar groups are responsible for the hydrophilicity of the fibres. A less hydrophilic fibre indicates fewer accessible polar groups and vice-versa. The contact angle is a function of the solid's surface energy and liquid's surface tension. The contact angle in water medium was reduced on alkali treatment of fibres, but the contact angle increased on silane treatment. This is mainly due to fibrillation and pore formation on alkali treatment as discussed before, which also makes the fibre less crystalline. The silane treatment on the other hand shields the hydrophilic fibre surface with silane molecules.

The results from each test falls in line with others. Surface treatment is required for the polar cellulose fibres to have good interfacial adhesion with non-polar matrix. The compatibility increases when the components have similar properties. The changes in the fibres on treatment expected to reflect in composites by affecting the fibre-matrix interaction at the interface.

### **4.2 Composites properties** (*Publications I, II, IV and V*)

#### **4.2.1 Effect of fibre treatments** (*Publications I and IV*)

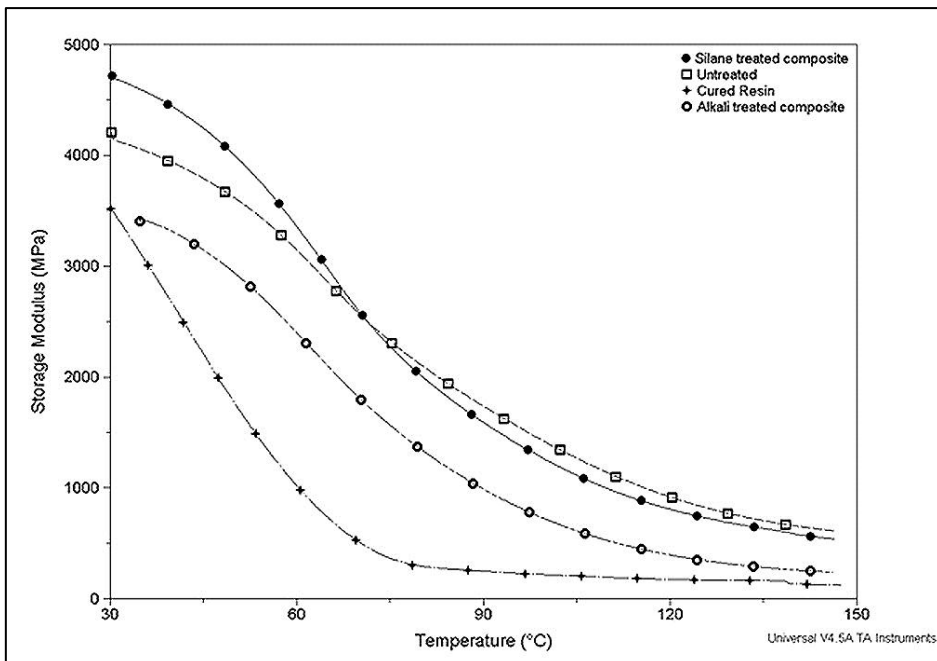
The mechanical properties of the composites were improved by some treatments. High tensile strength (91 MPa) and modulus (9 GPa) were obtained when the viscose fibre was treated with silane, Table 11. The improvement on silane treatment is due to molecular continuity formed in the interface of the composites as silane molecules acts as a link between between the cellulose fibre and the resin. Alkali treatment also altered the properties which is mainly due to increase in surface roughness, hydrogen bonding disruption and resin penetration in the fibre pores. Lyocell fibre reinforced composite's tensile strength and modulus rose from 95 MPa and 17 GPa to 150 MPa and 27 GPa respectively on 4 wt% alkali treatment (*Publication I*). Low alkali concentration showed improvement in tensile strength and modulus whereas at high concentration, strength and modulus deteriorated. The decrease was evident as the tensile strength was 33% lower for the highest alkali concentration (10 wt%), Table 11. The elongation of the composites decreased with increasing alkali concentration due to fibre splitting/fibrillation. A small increase in surface roughness, pore formation and fibrillation in fibres due to alkali treatment improved the composite tensile properties as the pores on the fibres allowed for good interlocking with the matrix,

whereas, high degree of pore formation resulted in failure of fibres as shown in previous section 4.1.

The results from the flexural and impact tests fall in line with the tensile test results; highest impact strength (28 kJ/m<sup>2</sup>), flexural strength (122 MPa) and flexural modulus (6.2 GPa) were obtained when the fibres were treated with silane. Similarly, highest viscoelastic properties were obtained for the composites reinforced with silane treated fibres due to increase in stiffness of composites due to good adhesion between fibre and matrix, and agree with the results from the mechanical tests, Figures 10 and 11. The glass transition of the composites was above 100 °C and increased on introducing fibres to the matrix due to restricted mobility of the polymer chains in the interface.

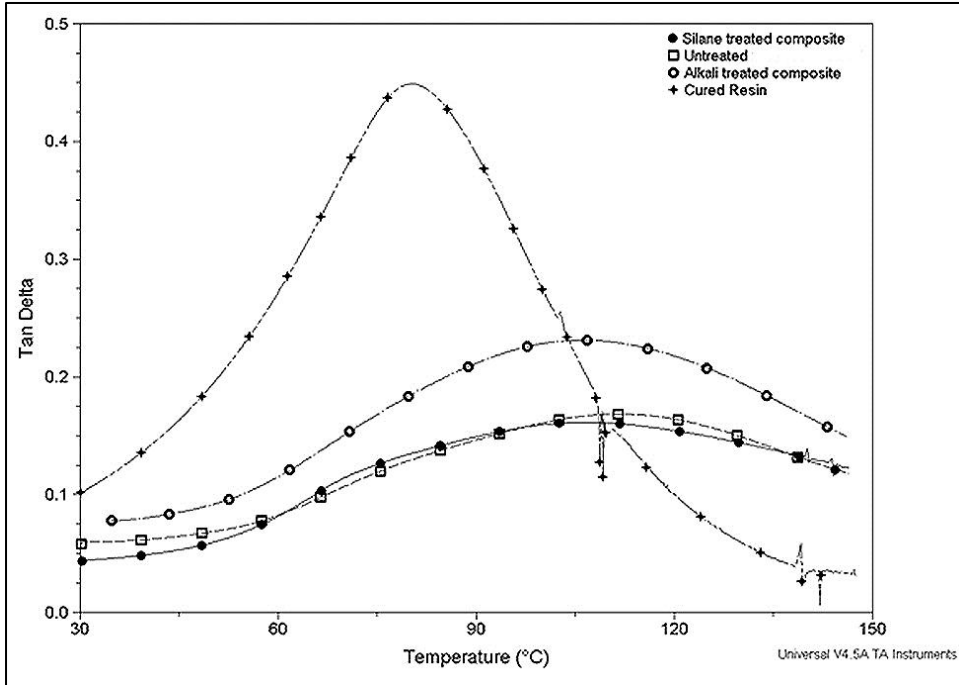
**Table 11.** Tensile properties of the viscose fibre reinforced composites, *Publication IV*

Sample Conditions	Tensile Strength [MPa]	Young's Modulus [GPa]	Elongation [%]
Untreated	80.86 ±6.28	7.80 ±1.41	2.22 ±0.18
Silane treated			
6 wt%	82.41 ±3.82	8.24 ±0.83	1.68 ±0.20
10 wt%	91.43 ±4.69	9.52 ±1.89	1.24 ±0.31
Alkali treated			
6 wt%	83.64 ±5.57	8.10 ±1.61	0.91 ±0.20
10 wt%	60.32 ±7.82	6.90 ±2.09	0.46 ±0.10



**Figure 10.** Storage modulus of cured resin and composites with and without reinforcement surface treatments, *Publication IV*

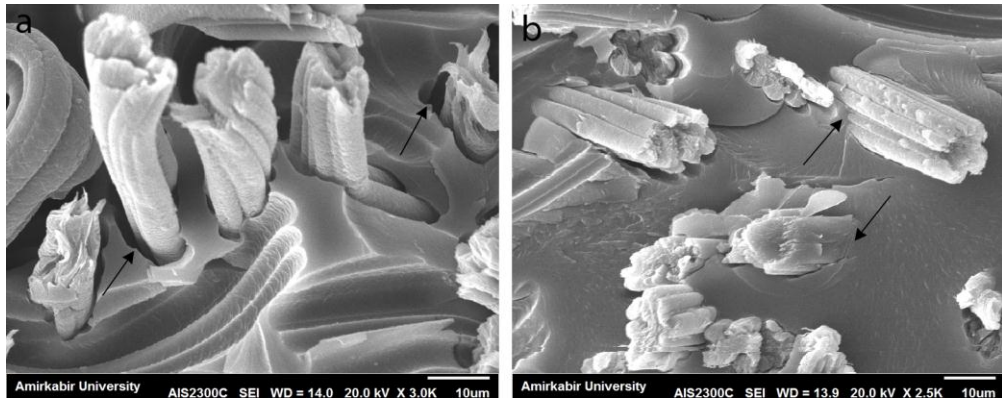
## SUMMARY OF RESULTS



**Figure 11.** Tan delta of cured resin and composites with and without reinforcement surface treatments, *Publication IV*

The contact angle of the composites increased when the reinforcements were treated with the alkali or silane. This is because of the better matrix penetration into the alkali treated fibre, the Si molecules covering the hydrophilic fibre surface on silane treatment, good interlocking of the matrix with the fibres and the improved fibre-matrix adhesion. The porosity was 6.4 vol% when the untreated fibre was reinforced in the matrix, whereas it was less than 2 and 4.5 vol% on reinforcing the silane and alkali treated fibres respectively. The decrease in the porosity indicates good resin penetration and release of air during moulding.

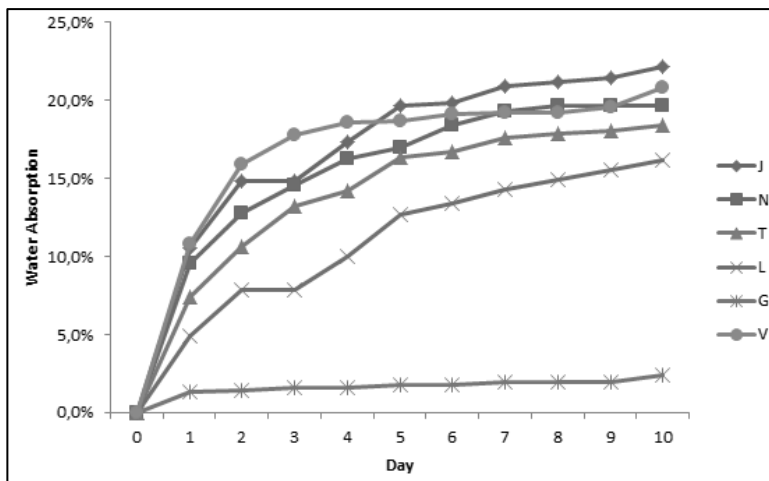
Figure 12 shows the microscopy images of tensile fractured specimens. Untreated fibre reinforced composites had pores between fibre and matrix, and fibre pull-out was noticed, Figure 12a. In silane treated fibre composites, the fibres were well embedded in the matrix and had smaller fibre pull-out, Figure 12b. This confirms the results from tensile test; increase in strength and modulus, and decrease in elongation. Fibre damage and pores were noticed in alkali treated fibre reinforced composites which resulted in low tensile properties. These deductions fit together with the results from porosity tests.



**Figure 12.** SEM images of tensile fractured specimens; (a) untreated (b) silane 10 wt%  
Arrows indicates the change in the interface, *Publication IV*

#### 4.2.2 Effect of water absorption (*Publication I and IV*)

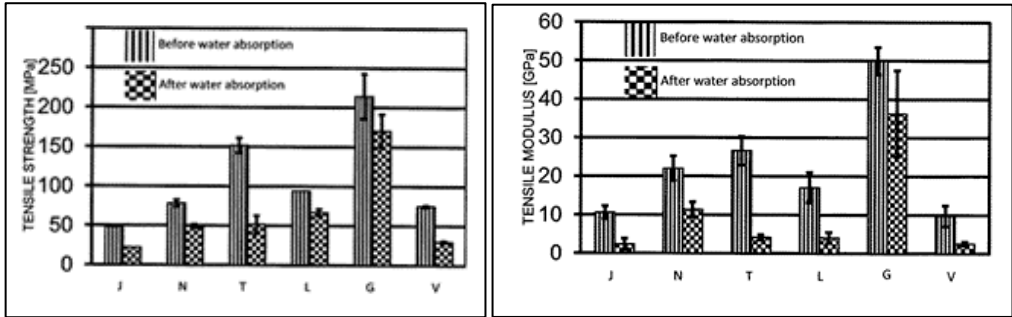
Water absorption of lyocell fibre composites were lower than that of jute fibre composites and this is due to high purity of lyocell fibres together with good fibre-matrix adhesion, Figure 13. The water absorption of the composites was reduced on hybridization, see section 4.2.3. The absorption is primarily influenced by the cellulose reinforcement. It could also be influenced by diffusion of water molecules between the polymer chains, into the pores and into the fibre-matrix interface.



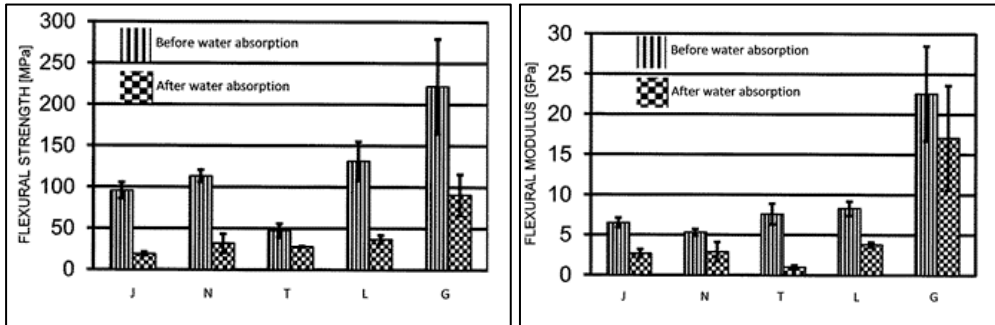
**Figure 13.** Water absorption of the composites (J–woven jute; N–nonwoven jute; T–alkali treated lyocell; L–untreated lyocell; G–glass; V–viscose) *Publication I*

## SUMMARY OF RESULTS

Results (Figure 14) show that the tensile strength and modulus of alkali treated lyocell fibre reinforced composites was comparable and even higher than some natural fibre composites, but the water absorption affected the stability of the composites as the tensile properties of the composites fell drastically due to water uptake. This is because of the fact that the cellulose fibres absorb water which causes fibre-matrix debonding. Similar results were obtained from flexural tests, Figure 15.

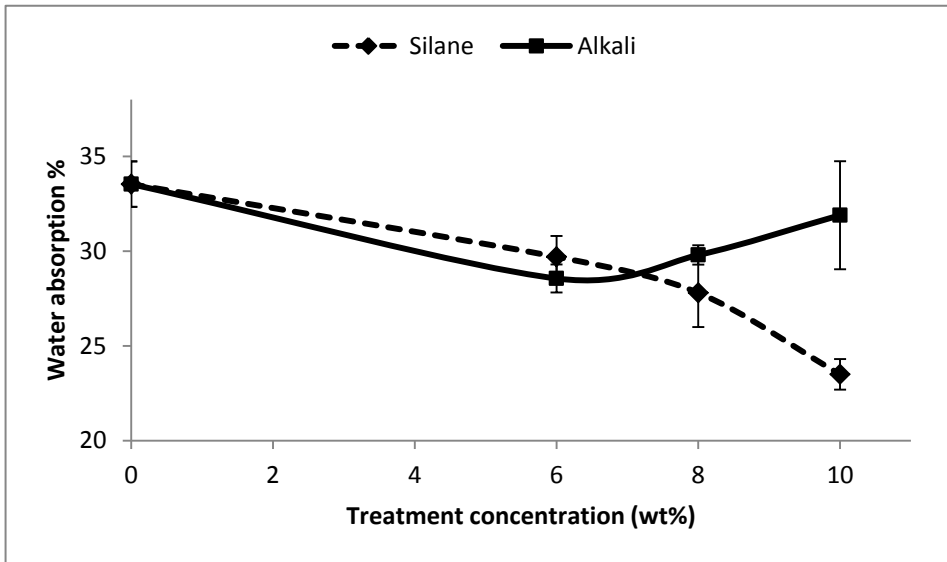


**Figure 14.** Tensile strength and modulus of the composites before and after water absorption (J–woven jute; N–nonwoven jute; T–alkali treated lyocell; L–untreated lyocell; G–glass; V–viscose) *Publication I*



**Figure 15.** Flexural strength and modulus of the composites before and after water absorption (J–woven jute; N–nonwoven jute; T–alkali treated lyocell; L–untreated lyocell; G–glass) *Publication I*

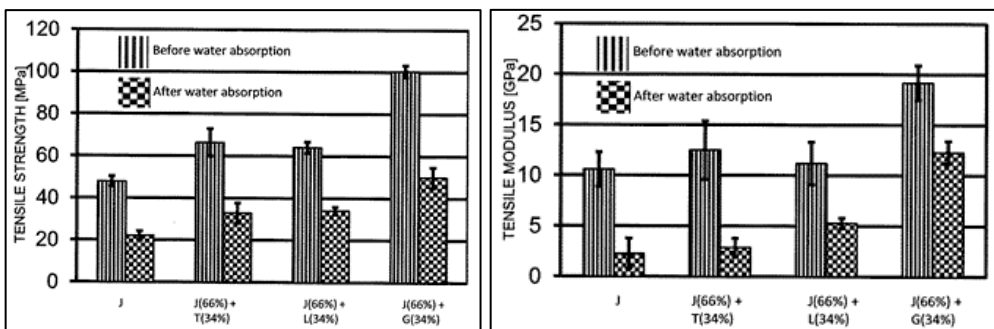
The water absorption of RCF composites was reduced by silane treatment due to decrease in hydrophilicity of fibre surface and good fibre-matrix interface; but the water absorption was still above 20 wt% as the silane molecules interacts only the outer surface of the RCF, Figure 16.



**Figure 16.** Water absorption of alkali and silane treated 50% RCF reinforced composites, *Publication IV*

#### 4.2.3 Effect of hybridization (*Publication I and II*)

Two fibres were mixed to reduce the moisture absorption, improve the mechanical properties and tailor these properties in hybrid composites. Glass fibres were used together with cellulosic fibres to reduce the water absorption of the composites, *Publication I*. The tensile properties were improved by two times on hybridization before and after water absorption, Figure 17.



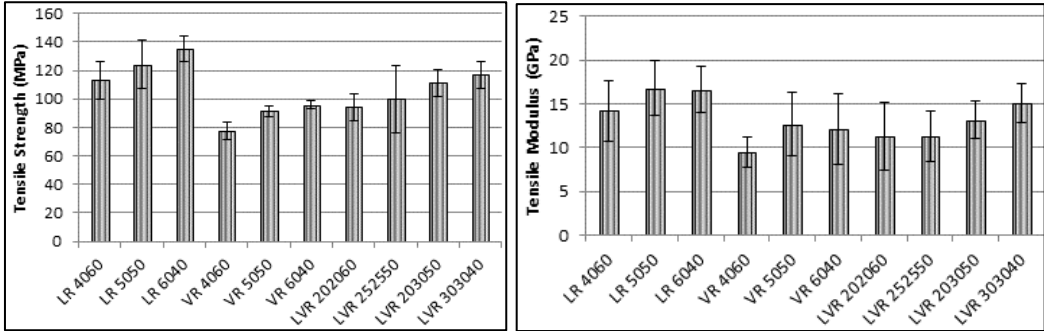
**Figure 17.** Tensile strength and modulus of the hybrid composites before and after water absorption (J–woven jute; T–alkali treated lyocell; L–untreated lyocell; G–glass)

*Publication I*



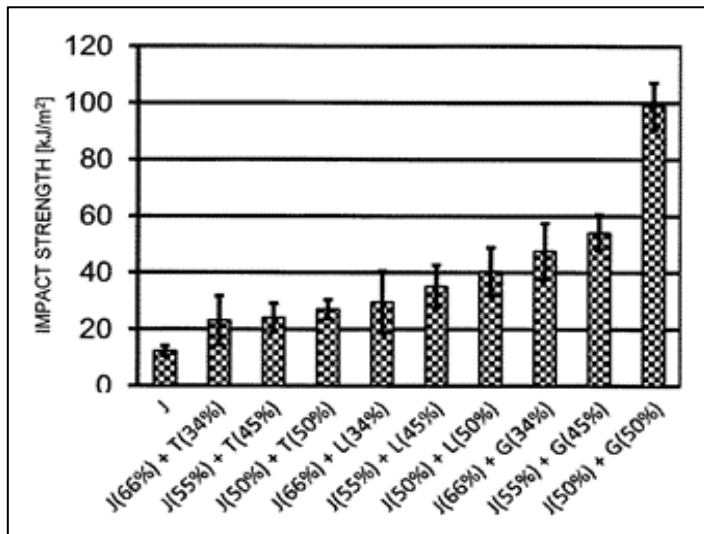
## SUMMARY OF RESULTS

Lyocell and viscose nonwoven composites were investigated in terms of hybridization. Tensile strength and modulus of lyocell composites were better than those of viscose. When part of viscose was replaced by lyocell, strength and modulus of the composites were improved, Figure 18. The elongation of the viscose fibres was almost two times to that of lyocell fibres and it reflected in the composites. Flexural properties followed the similar trend as tensile. The impact strength of RCF composites was between 35 and 50 kJ/m<sup>2</sup> which is higher than some natural fibre composites. High impact strength attributes to high energy absorbed during fracture. High elongation of the regenerated cellulose fibre could



affect impact strength positively. The impact strength of jute fibre composites was improved by inclusion of lyocell and glass fibres. It was possible to tailor the impact properties of the hybrid composites, Figure 19.

**Figure 18.** Tensile strength and tensile modulus of the composites (L–untreated lyocell; V–viscose; R–resin; LR4060 means lyocell 40% and resin 60%) *Publication II*



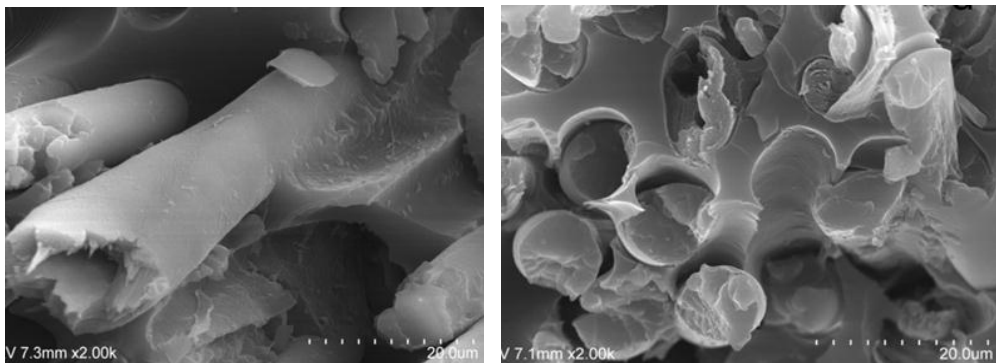
**Figure 19.** Impact strength of the hybrid composites (J–woven jute; N–nonwoven jute; T–alkali treated lyocell; L–untreated lyocell; G–glass) *Publication I*

#### 4.2.4 Effect of reinforcement architecture (Publication I)

Fabric architecture such as woven and nonwoven affected the mechanical properties of the composites; uniaxially fibre alignment in fabric showed better tensile strength and modulus than than biaxial ones in machine direction Figures 14 and 15.

#### 4.2.5 Effect of fibre loading (Publication II and V)

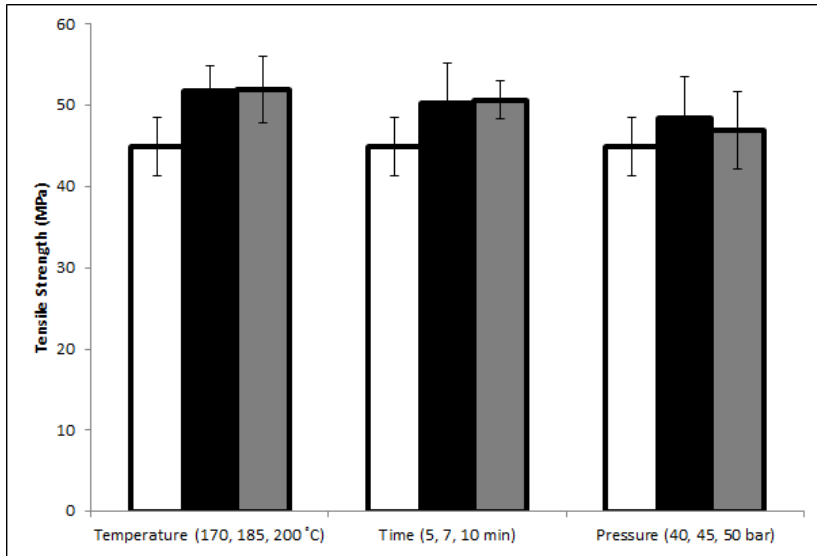
Reinforcement weight % was taken into consideration as it is easy to control in the manufacturing procedure. Increase in fibre weight fraction increases the tensile strength and modulus whereas the pores develop due to improper wetting of fibres. Therefore, fibre content in all the RCF composites was between 40 and 60 wt%. Lyocell, viscose and cotton based composites were investigated in terms of fibre loading. Tensile properties of the composites increased with increasing fibre content which indicates that the stress transfer in the composites due to good fibre-matrix interface. The consistency in the outcomes is attributed to the evenness of the fibre, uniform resin impregnation, fixed curing and testing conditions. Tensile strength and modulus of lyocell composites were better than those of viscose Figure 18. Optimal fibre loading resulted in even spreading of matrix and fibres being well embedded in the matrix, Figure 20. Insufficient matrix lead to improper wetting of fibre and uneven spreading of matrix which caused the composite to fail at lower force.



**Figure 20.** SEM images of the cross-section of the fractured composites, *Publication V*

#### 4.2.6 Effect of processing parameters (Publications IV and V)

The processing parameters such as moulding temperature, pressure and time affected the composites properties marginally, Figure 21. It is not possible to draw any conclusions as the change is small and not statistically significant. Impact strength of the composites followed similar to that of tensile. However, a very low pressure affects the spreading of matrix in the compression molding and a very high pressure forces the matrix to flow out of the system. Similarly, a very low temperature leads to incomplete curing and a very high temperature leads to matrix degradation.



**Figure 21.** Tensile strength of the composites at different processing parameters, *Publication V*

However, the processing conditions affected the resin curing in the composites. DSC analysis showed the need for post-curing of the composites due to incomplete curing shown by small exothermic peak, Table 12. Incomplete resin curing affected the mechanical properties of the composites (*Publication IV*). It is important to fully cure the thermoset resin to obtain stable composite properties.

**Table 12.** DSC characterization of the resin and the composites, *Publication IV*

		Exothermic Heat (J/g)	T <sub>g</sub> (°C)
<b>Resin</b>	Uncured	227.4	–
	Cured	0	85.8
<b>Composite</b>	Before post-curing	13.0	81.8
	After post-curing	0	81.7

#### 4.2.7 Recycling of end of life textiles as reinforcement (*Publication V*)

Composites were produced by three methods using waste cotton blend fabrics in publication V and one method was by reinforcing waste fabrics in soybean oil based matrix (MSO). The composite production was easy because of reinforcement's highly regular woven structure. Tensile strength and modulus of about 60 MPa and 6 GPa were achieved. Composites were explored in terms of fibre loading and processing conditions as mentioned in sections 4.2.5 and 4.2.6.

## 5. DISCUSSION AND CONCLUSIONS

In this thesis, biocomposites were manufactured from regenerated cellulose fibres using compression molding. This work highlights the potential of bio-based thermoset matrices from soybean oil and lactic acid in composite applications. Discarded cotton/PET blend fabrics were used as alternative low cost reinforcement in publication V and three concepts were investigated to reuse these fabrics in composites: compression molding above the melting temperature of PET, use of soybean based thermoset matrix and use of thermoplastic bicomponent fibres as matrix. These composites were tested for mechanical, thermal, viscoelastic and morphological properties. Tensile strength and modulus of about 130 MPa and 16 GPa respectively were attained by reinforcing lyocell fibre in soybean based matrix which can be compared to natural fibre composites. Hybrid composites produced by mixing two fibres reduced the water absorption and increased the composite's mechanical performance. The mechanical properties of the composites were tailored by hybridization. The reinforcement architecture and fibre loading were also studied. Alkali and silane fibre surface modification were investigated in detail, and certain treatments reduced the hydrophilicity of the fibres. Bi-functional silane molecules were grafted on fibre's surface which increased the interaction with the matrix and improved the fibre-matrix interface in the composites.

The issues of natural fibres such as quality variability, low purity, poor durability and uncontrollable properties can be addressed partly by regenerated cellulose fibres such as lyocell and viscose. Although viscose is associated with rather environmentally burdening process, new processes such as lyocell have been developed which have less environmental impact. The properties of these fibres are reproducible with little or no quality variations as the process is highly controlled. Regenerated cellulose fibres are chemically pure which allows for chemical modifications. Results from neat fibres show that lyocell fibres have better tensile properties than natural fibres such as flax, hemp, jute etc., and these fibres can replace natural fibre in composite applications. Similarly, bio-based matrices produced from plant oils and lactic acid have good binding properties and can be used to produce 100% bio-based composites.

Certainly, the performance and the durability of conventional composites from synthetic fibres such as glass, carbon etc. and petroleum based polymers such as epoxy, unsaturated polyesters etc. are superior to most of the biocomposites. But biocomposites' environmental benefits and adequate properties for many applications make them interesting materials. The improvement in biocomposites is necessary for it to be used in more sophisticated products. Using materials from bio-origin reduces the environmental load and promotes sustainable economy. Renewability and sustainability of the biocomposites reduce the dependency of the petroleum products. Biodegradability of products on end-of-life contributes to

## DISCUSSION AND CONCLUSIONS

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effective waste management. However, one must note that the durability is affected by biodegradability of the biocomposites. Several factors responsible for biodegradability can be controlled to prolong the lifetime of the products.

Requirements in automobile industry for composite applications such as rear lift gate and front fenders are 62MPa (tensile strength) and 2 GPa (Young's modulus). Body panel and roof needs tensile strength above 90 MPa and Young's modulus of 8.3 GPa. Several composites prepared in this thesis meet the above mentioned requirements of these applications and could be used as alternative to conventional materials if other properties are explored.

## **6. FUTURE STUDIES**

Future studies should focus on durability, biodegradability and numerical modelling of these biocomposites. Several authors have manufactured biocomposites but there has been only few studies on durability of these composites. Water absorption reduces the lifetime of the biocomposites considerably in relatively short time. There have been several attempts to reduce the hydrophilicity of the cellulosic fibres and increase fibre-matrix interfacial compatibility to improve the durability of the biocomposites, however, this improvement is not enough for it to be used in outdoor applications. The biodegradability of these composites should be investigated along with the environmental impact using life cycle assessment. Numerical modelling helps to predict various properties of the composites in an efficient way.

Various bio-based resins could also be explored and their potential in composite applications could be studied.

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Publications included in this thesis are:

- I. Ramamoorthy SK**, Di Q, Adekunle K, Skrifvars M. (2012) Effect of water absorption on mechanical properties of soybean oil thermosets reinforced with natural fibers. *Journal of Reinforced Plastics & Composites*, 31(18): 1191-1200
- II. Ramamoorthy SK**, Kundu CK, Adekunle K, Bashir T, Skrifvars M. (2014) Properties of green composites with regenerated cellulose fiber and soybean-based thermoset for technical applications. *Journal of Reinforced Plastics & Composites*, 33(2): 193-201
- III. Ramamoorthy SK**, Skrifvars M, Rissanen M. (2014) Effect of alkali and silane surface treatments on regenerated cellulose fibre type (Lyocell) intended for composites. *Cellulose*, 22(1): 637-654
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- V. Ramamoorthy SK**, Persson A, Skrifvars M. (2014) Reusing textile waste as reinforcements in composites. *Journal of Applied Polymer Science*, 131(17) DOI: 10.1002/app.40687

This thesis presents work that was done within the Swedish Centre for Resource Recovery (SCRR). Research and education performed within SCRR identifies new and improved methods to convert residuals into value-added products. SCRR covers technical, environmental and social aspects of sustainable resource recovery.



Biocomposites have been developed to address the sustainability issues of non-renewable resource based materials. These composites are often produced by reinforcing natural fibres in petroleum based thermoset resins or thermoplastic polymers. Thermoplastic polymers from renewable resources are commercially available whereas thermoset resins are predominantly derived from crude oil resources. Cellulose fibres have significant importance and potential for polymer reinforcement in lightweight composites. Natural fibres are chemically diverse and their properties vary largely which makes it difficult for them to be used in several applications. The natural fibre based products are limited by their characteristic odour emissions. These issues of natural fibres can be addressed by partly man-made fibres i.e. regenerated cellulose which with little or no compromise in the environmental benefits of the natural fibres can be produced from biomass origin. Natural fibres and their composites have been observed and researched closely for many decades. Study of regenerated cellulose fibres and their composites is, on the other hand, relatively new. Regenerated cellulose fibres are prospective reinforcing material in the composite field due to their even quality and high purity. These fibres have good mechanical properties and also address the odour emission issue of the natural fibres. The development of biocomposites from regenerated cellulose fibre and thermoset resin synthesized from renewable resources has therefore been viewed with considerable interest.

This thesis describes the development of biocomposites from regenerated cellulose fibres (lyocell and viscose) and thermoset resins synthesized from renewable resources (soybean oil and lactic acid). The performance and the properties of the composites were evaluated. Chemical surface treatments, alkali and silane, were performed on the fibres in order to improve the performance of the composites. Hybrid composites were also produced by mixing of two types of reinforcement in order to complement one type of fibre with other.

The developed composites were evaluated through mechanical, thermal, viscoelastic and morphological properties among others. The results showed that the regenerated cellulose fibre thermoset biocomposites have reasonably good properties. Fibres before and after treatment were studied in detail. The silane treatment on these fibres improved the mechanical properties of the composites as the silane molecules act as a link between the fibre and resin which gives the molecular continuity across the interface region of the composite.

Keywords: Regenerated cellulose fibers, Surface modification, Alkali, Silane, Mechanical properties