DEVELOPMENT OF BIOCOMPOSITES FROM LACTIC ACID THERMOSET RESINS AND CELLULOSE FIBRE REINFORCEMENTS

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This thesis is dedicated in loving memory of my late mother, **Alhaja Tawakalitu Abosede Bakare**, who has been my mentor and support all through my advancement in life. I miss you so much Mummy.

Abstract

Synthesis of polymers from renewable origin has been reported by many authors and it has been found out that it has enormous potential and can serve as alternative to conventional thermoplastics and thermosets in many applications. The use of these renewable resources will provide sustainable platforms to substitute fossil fuel-based materials. To date, efforts made to produce 100% bio-based thermosetting materials have yet to be achieved. Many studies have been reported on increasing the renewability ratio of thermoset materials produced.

A lot of reports have been made on the synthesis of thermoplastic resins from lactic acid for biomedical applications such as tissue engineering but only few reports have been made on composite applications. The issue of high melt viscosity of thermoplastic resins from lactic acid has been of paramount problem because of its difficulty in impregnation into fibre reinforcement. Bio-based thermoset resins have been produced for composite applications from plant oils and improved mechanical properties have been achieved.

In this thesis, an alternative route for synthesis of lactic acid based thermoset resins have been explored to solve the above problem. Thermoset resins were synthesized from lactic acid with different co-reactants and were characterized using NMR, FT-IR, DSC, DMA and TGA. Their rheological properties were also investigated. The resins were reinforced with natural and regenerated cellulose fibres in non-woven and woven form, and with different fibre alignment and fibre loading. The resulting composites were characterized by mechanical testing regarding tensile, flexural and impact strength, and by SEM analysis regarding morphology.

The results showed that these composites could possibly be used in automobile, transport, construction and furniture applications, particularly for interior purposes. The resins produced were found to be promising materials for composite production due to the good mechanical properties achieved.

Keywords: lactic acid, thermoset resin, renewable resources, natural fibre, regenerated cellulose fibre, composite

List of Publications

This thesis is based on the following papers, which are listed in Roman numerals:

  I.   Bakare, F.O., Skrifvars, M., Åkesson, D., Wang, Y., Afshar, S. J. and Esmaeili, N. "Synthesis and characterization of bio-based thermosetting resins from lactic acid and glycerol." Journal of Applied Polymer Science, Volume 131, Issue 13, 2014.
 II.   Esmaeili, N., Bakare, F.O., Skrifvars, M., Afshar, S.J. and Åkesson, D. "Mechanical properties for bio-based thermoset composites made from lactic acid, glycerol and viscose fibers." Cellulose, Volume 22, Issue 1, 2015.
III.   Bakare, F.O., Åkesson, D., Skrifvars, M., Bashir, T., Ingman, P. and Srivastava, R. "Synthesis and characterization of unsaturated lactic acid based thermoset bio-resins." European Polymer Journal, doi: http://dx.doi.org/10.1016/j.eurpolymj.2014.11.045, 2014.
IV.   Bakare, F.O., Ramamoorthy, S.K., Åkesson, D. and Skrifvars, M. "Characterisation 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)

Contribution of the Author

Fatimat Bakare was the principal author of Paper I, III and IV. Some of the experiments and a part of the writing of Paper II were done by the author of this thesis. The ^{13}C-NMR in Paper I and III was done by Andrew Root, Finland. The ^{1}H-NMR in Paper III was done by Rajiv Srivastava, India Institute of Technology Delhi, India.

Other Publications

1. Bashir, T.,Bakare, F.O.,Baghaei, B.,Mehrjerdi, A.K. and Skrifvars, M. "Influence of different organic solvents and oxidants on insulating and film forming properties of PEDOT polymer." Iranian Polymer Journal, 22 (8), 599-611, 2013.
2. Ramamoorthy, S.K., Bakare, F.O., Herrmann, R. and Skrifvars, M. "Performance of biocomposites from surface modified regenerated cellulose fibers and lactic acid thermoset bioresin." Submitted to Cellulose.

Conference Contributions

1. **Bakare, F.O.**, Åkesson, D., Skrifvars, M., Wang, Y., Esmaeili, N. and Afshar, S.J. "The effect of glycerol in the synthesis of a lactic acid based thermoset resin", Nordic Polymer Days Conference, Helsinki, Finland, May 29th – 31st, 2013. (Speaker)
2. **Bakare, F.O.**, Åkesson, D., Skrifvars, M., Wang, Y., Esmaeili, N. and Afshar, S.J. "Bio-based composites prepared from a lactic acid based thermoset resin and a natural-fibre reinforcement", The Third Avancell Conference, Chalmers University of Technology, Gothenburg, October 8th – 9th, 2013. (Speaker)
3. **Bakare, F.O.**, Åkesson, D., Skrifvars, M., Wang, Y., Esmaeili, N. and Afshar, S.J. "Synthesis and preparation of bio-based composites with a novel thermoset resin from lactic acid", 16th European Conference on Composite Materials, Seville-Spain, June 22nd – 26th, 2014. (Poster)
4. **Bakare, F.O.**, Åkesson, D., Skrifvars, M., Wang, Y., Esmaeili, N. and Afshar, S.J. "Morphological and mechanical properties of a bio-based composite from a lactic acid based thermoset resin and viscose fibre reinforcement", SPE Automotive Composites Conference and Exhibitions (ACCE), Novi-Michigan, USA, September 9th – 11th, 2014. (Speaker)

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1.   INTRODUCTION

The focus on sustainability has become a growing awareness among many experts due to rapid population growth, economic growth and consumption of its natural resources which has led the climate and ecological in being fragile. Many activist groups and citizens have become aware of these problems and demand a solution before the earth, its climate and its environments are harmed in irreparable forms [1-2]. Petrochemical-based polymers have been of great use due to their advantages of having low cost, high mechanical performance, good heat seal-ability and good barrier properties, but these petrochemical-based polymers emits volatile organic compounds which have great influence in the health and environmental risks. Also the issue of high and unstable prices of petroleum gives a lot of concern on how long petroleum supply will last. Due to these recent concerns, stringent environmental policies have been made which has led to increased interests in the use of biomass and its derivatives to provide alternative to fossil fuel and material resources [3].

Scientists and researchers in both research and educational institutions are making great efforts to manufacture polymer composites based on renewable resources. These renewable resources are bio-based resins, such as plant seed oils, lactic acids or lactides impregnated into natural fibres/regenerated cellulose fibres, such as flax, hemp, viscose or lyocell fibres. This is done to improve the physical, structural and mechanical properties of the composites produced [4-5]. The development of these bio-based resins have helped in reduction of use of fossil resources and they have been used in different applications such as paints, inks, coatings and plasticizers, due to their biodegradability and inexpensive nature.

The composite manufacturing industries have much concern too in this area that has led them in search of bio-based composite materials from these natural fibre reinforcement and bio-based polymer matrices. The bio-based polymer matrices produced from renewable resources are a relatively new and important research area, which will have the potential to reduce the use of fossil resources. These bio-based polymers are becoming more popular in many technical products such as; housing (doors, composite decking, window frames, hot tubs and spas), aerospace (wings, tails, propellers and fuselages), pipes and fittings, boats, storage tanks and swimming pool panels. In the automotive industry, the main improvement in fuel efficiency is achieved by reducing the mass, which makes manufacturers to put more focus on composite materials because of their low weight to produce lighter components. [6-7].

1.1   Aims of this study

The major aim of this study was to evaluate new synthetic concepts for bio-based thermoset resins from lactic acid. The bio-based resins produced were characterized by using NMR and FT-IR spectroscopy to verify their structure, and by using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA) in order to verify the thermal and viscoelastic properties. The resins were reinforced with cellulose fibres such as warp-knitted viscose fibre, non-woven viscose fibre and woven flax fibre in

different fibre load. Fibre alignment in the unidirectional and bi-directional was also investigated. The obtained composite was characterized by flexural, tensile and Charpy impact testing, by DMA and TGA and by scanning electron microscopy (SEM). The ageing behaviour and water absorption of the composites were also investigated to evaluate their durability performance in composite applications. In order to achieve this goal, the experimental work was divided into two parts:

a. Synthesis and characterization of lactic acid based thermoset resins (Paper I & III).
b. Bio-based composites preparation from the synthesized lactic acid thermoset resins and cellulosic fibre reinforcement and their characterization (Paper II & IV).

1.2   Justification

The project aims at developing novel thermosetting polymers that are derived from lactic acid based resins. The target is to develop a lighter weight, higher strength and more eco-friendly materials, the present reliance on petroleum based materials in making thermoset resins. The benefits of using renewable polymers are basically their cost/performance ratio, low weight, durability, eco-friendly attributes and comparable mechanical properties with non-renewable polymers. Natural cellulose fibres (flax fibres) and man-made cellulose fibres (viscose fibres) were used as reinforcement due to their advantages of being biodegradable, eco-friendly and their renewable origin. Therefore, the combination of these agricultural materials will contribute greatly in sustainability and renewability of the final product. These composites can have multiple applications, but their application in the automotive industry, will be advantageous in energy savings due to the low weight, the reduced carbon dioxide emission and the improve fuel efficiency, which will make great impact in the automotive and ground-transportation markets.

1.3   Outline of the thesis

This thesis is divided into four main chapters:

1. Chapter 1 introduces the thesis, explains the aims of the research and the benefit of the research.
2. Chapter 2 gives a comprehensive overview on literatures on the various synthesis methods for bio-based resins.
3. Chapter 3 gives a comprehensive overview on cellulosic fibres and composites preparation.
4. Chapter 4 describes the experimental work, discusses obtained results, and gives the conclusion and suggestions for future studies.

2. BIO-BASED RESIN SYNTHESIS - AN OVERVIEW

2.1 Bio-based thermoset resins

Resins are used in composites, binders, adhesives, inks, paints and coatings. Examples of these resins are unsaturated polyester resins, epoxy resins, phenol formaldehyde resins and polyurethane resins. Bio-based thermoset resins consist partially or completely of renewable raw materials but can no longer be melted down after a single hardening step (chemical reaction). Several developments of bio-based resins using natural oils, carbohydrates and natural phenolic compounds (such as tannin and lignin) have been done. These involve the epoxidation of vegetable oils for epoxy resins, phenols from lignin for phenol formaldehyde resins, or sugar derivatives such as polyol in polyurethane resins etc.

Bio-based resins from natural oils for epoxy resins have been prepared by several authors as potential use in applications such as composites, adhesives and coatings. Pan et al. [8], prepared high functionality epoxy resins by the epoxidation of sucrose ester resins of vegetable oil fatty acids. About 99% conversions of the double bonds to epoxides were achieved; high functionality of about 8-15 per molecules was also achieved with high density. The resin was crosslinked with liquid cycloaliphatic anhydride to prepare thermoset which are hard and ductile and gave high modulus with high bio-based content between 71 – 77% [9]. Song Qi et al. [10], synthesized a phosphorus containing bio-based resin from itaconic acid and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide as a green flame retardant in the epoxy resin systems. The resin was cured with methyl hexahydrophthalic anhydride which showed comparable glass transition temperature and mechanical properties to diglycidyl ether in a Bisphenol A system. Deng et al. [11] prepared two types of epoxy resins from rosin to obtain triglycidyl ester and glycidyl ethers with increasing flexible chain amounts. The result showed that the glycidyl ether gave good thermal properties, water resistance, acetone resistance and comparable mechanical properties with some petroleum epoxy resins. Deng et al. [12] also prepared a rosin-based siloxane epoxy resin from ethylene glycol diglycidyl ether modified acrylpimaric acid and poly (methylphenylsiloxane) which showed good mechanical properties. Rahman and Netravali [13] extracted a non-edible protein from defatted karanja seedcake and a thermoset resin was developed using a natural α,β-unsaturated aldehyde (named cinnamaldehyde) and sorbitol as a natural plasticizer to reduce the brittleness of the resin. The result showed that 5 % plasticizer content and 12 % cross-linking give comparable mechanical properties to petroleum based resins and can also be an alternative to edible protein-based resins.

The use of carbohydrates in the preparation of bio-based resin has also been done by various researchers. Sadler et al. [14] studied isosorbide derived from renewable carbohydrate feedstock which provides a scaffold for the development of a bio-based resin system. Isosorbide-methacrylate was synthesized by direct esterification of isosorbide using methacryloyl chloride or methacrylic anhydride. The result showed glass transition temperature higher than 240 ℃ with very good mechanical properties. Sadler et al. [15] also prepared a bio-based resin using isosorbide as a structural constituent to provide stiffness from a diol component in unsaturated polyester. The thermoplastic prepolymer was synthesized by polycondensation of a mixture of diols and diacids with the effect of

isosorbide and maleic anhydride being investigated. The result showed high glass transition temperature up to 107 ℃ and storage modulus as high as 1650 MPa. Chai et al. [16] prepared bio-based bark extractive-melamine formaldehyde resin from bark alkaline extractives from the mountain pine beetle to replace 30 wt-% of melamine. The result showed that the addition of the bark extractive gives higher solids contents, higher pH values, higher initial molecular weight and higher viscosities. Paul et al. [17] used the sap from banana plant as a starting material in the preparation of a bio-resin. The result of the cured resin showed that with addition of 50 wt-% banana sap gave comparable mechanical properties with 100 % petroleum-based unsaturated polyester resin. Dastidar and Netravali [18] prepared a soy flour based thermoset resin without using any external crosslinker. Protein of about 55% and 32% sugar present in the soy flour was separated by filtration technique, where the sugar was oxidized and used to crosslink the reactive groups present in the protein to produce the soy protein resin. Results showed that enhanced mechanical and thermal properties were obtained; also reduced moisture absorption was achieved.

Natural phenol compounds such as tannin and lignin have been prepared by many researchers. Ramires and Frollini [19] prepared tannin-phenolic resin using 40 wt-% tannin to replace phenol. The synthesis was done using formaldehyde, phenol, tannin and potassium hydroxide and the resulted resin was cured with resorcinol, and then sisal fibre was added to prepare the composite. The result showed that with 50 wt-% sisal fibre, a high storage modulus was achieved and with good fibre/matrix interaction as confirmed by SEM. Lagel et al. [20] prepared a bio-sourced thermoset material from tannin-furanic thermoset resin as matrix for solid grinding wheels. Result showed that the resin produced does not require high temperature for curing compared to the commercial grinding wheels which need 1000 ℃ for curing and an excellent abrasiveness property was also achieved. Liu et al. [21] synthesized a bio-based UV-curable antibacterial resin by modifying tannic acid with glycidyl methacrylate and a good film-forming property that can be crosslinked under UV irradiation was obtained. Zhao et al. [22] prepared two types of bio-based phenol formaldehyde resins from beetle-infested pine barks, which were synthesized from acid-catalysed phenol-liquefied bark and bark alkaline extractives. The result showed that the introduction of the bark to the phenolic resin have a high effect on the structure and curing reaction of the resins. The liquefied bark had a phenolated structure which had more reactive sites towards formaldehyde than the bark extractive, and an accelerated curing rate was also observed for the liquefied bark. Other types of phenol compounds derived from the use of lignin were also studied. Stanzione et al. [23] prepared a methacrylated lignin-based bio-oil mimic using phenol, guaiacols and catechols which were methacrylated by esterification with methacrylic anhydride. The results showed that it have comparable thermo-mechanical and thermo-gravimetric properties to commercial petroleum and vinyl ester-based thermosets. Wang et al. [24] prepared the synthesis of phenol-formaldehyde resol using organosolv pine lignins in varying ratios (25 to 75 wt-%) by condensation polymerization. The result showed a decreased thermal stability with increasing amount of lignin and it was suggested that less than 50 wt-% of lignin should be used in replacement of phenol and also purification of the lignin could improve the thermal stability. Wang et al. [25] also prepared phenolic resol resins using cornstalk derived bio-oil by direct liquefaction in hot-compression of phenol-water. The result showed an exothermic curing

temperature at about 150 - 160 ℃, which is comparable with a typical thermosetting phenol-formaldehyde resin.

Polyurethane resins were synthesized by Wei et al. [26] from liquefied wood obtained by liquefaction of benzylated wood wastes. Results showed that higher thermal stability was achieved compared to traditional polyurethane resins. Ahmad et al. [27] synthesized polyurethane from linseed oil epoxy for anticorrosive coating. Result showed good physio-mechanical properties and good weather resistance which indicates promising use in effective anticorrosive coating compound. Dutta and Karak [28] prepared polyurethane resins from the monoglyceride of *Mesua Ferrea L.* seed oil with varying NCO/OH ratio. Results showed that higher NCO/OH ratios gives accelerated curing times, harder materials and higher adhesive strength.

Several developments have been on-going in preparation of new bio-based thermoset resin due to their complicated nature. These resins need to be crosslinked which requires the starting materials to contain reactive groups in the molecules. In this thesis, bio-based thermoset resins are synthesized from lactic acid using synthetic concepts involving modification by introduction of reactive groups in the lactic acid polymer chains. These resins are comparable to commercial unsaturated polyester resin, vinyl ester and epoxy resins based on their structures and curing mechanism.

2.2   Lactic acid

Lactic acid (2-hydroxypropanic acid), also called milk acid, is a widely occurring carboxylic acid. It was first isolated by the Swedish chemist Carl Wilhelm Scheele in 1780 and was later commercially produced in 1881 by Charles E. Avery in USA [29-30]. Lactic acid can be produced by either chemical or biotechnological process. The chemical process involves the use of acetaldehyde and hydrogen cyanide (HCN) in the presence of H_2SO_4. The biotechnological process, which involves the fermentation of carbohydrates, can be used to make a variety of useful products (see Figure 1), which is a technique used by manufacturers because of the limitation of the chemical process. Due to the biodegradability and biocompatibility properties of polylactic acid, high market demand for lactic acid for its production has led to discovery of more efficient methods in the production of lactic acid [3,30-32].
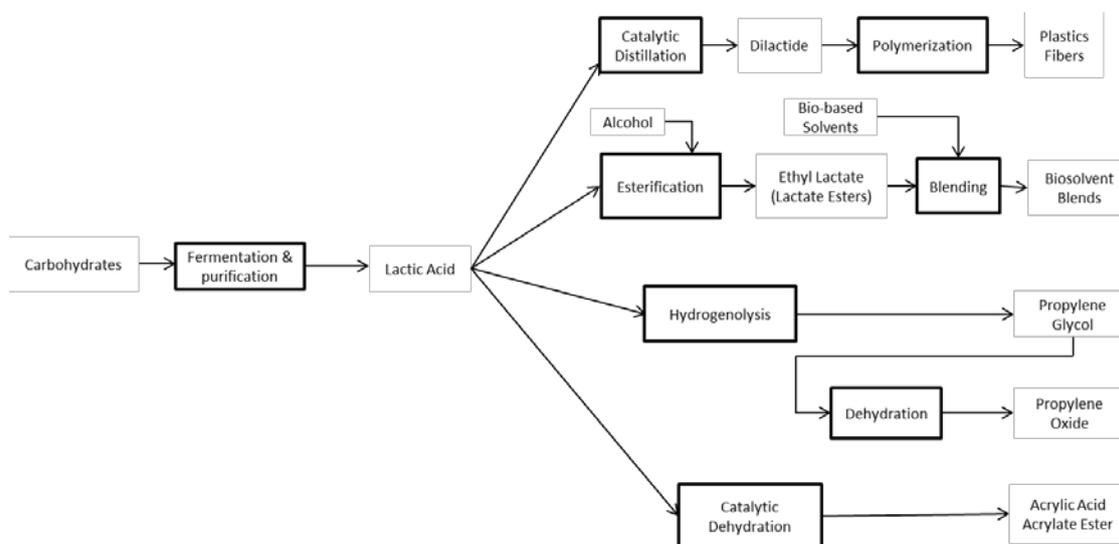
Figure 1. Lactic acid-based potential products and uses [30].

Polylactic acid (also known as PLA) is a polymer derived from the building block of lactic acid monomer. It is biodegradable, bio-absorbable and renewable thermoplastic polyester that have been studied for over several decades. PLA have had limited use because of its low availability, high cost and limited molecular weight. This was the case until the last decade when the formation of a new company by bringing in 1998 two large companies, Cargill and Purac Biochem B.V., together, to produce 34 000 tonne/year lactic acid in the US. This was done with the intention of significantly reducing the cost of its production and making PLA a large-volume plastic [33-34]. PLA has several advantages such as its eco-friendly nature, biocompatibility, excellent processability and good energy savings compared to petroleum-based polymers. It also has its limitations, such as poor toughness, low thermal resistance, slow degradation rate (which is not desired in the medical applications), hydrophobic nature and also its lack of reactive side-chain groups. There have been several studies in solving all these limitations by surface modification to control hydropilicity and toughness and also introduction of reactive groups [29].

2.3   Thermoset resins based on lactic acid

Lactic acid based thermoset resins can be prepared by introducing reactive groups into lactic acid oligomers. This can be done by end-capping lactic acid oligomers with methacrylic or acrylic groups etc. to enable free-radical polymerization of the lactic acid oligomers. These processes have been reported by many researchers for example Xie et al. who polymerized a three-arm oligomeric polyester using glycolic acid and lactic acid and then end-functionalized with methacroyl chloride [35]; see Figure 2. This formed a methacrylated copolymer with compressive yield strength and modulus of about 20.1 MPa and 730.2 MPa respectively.
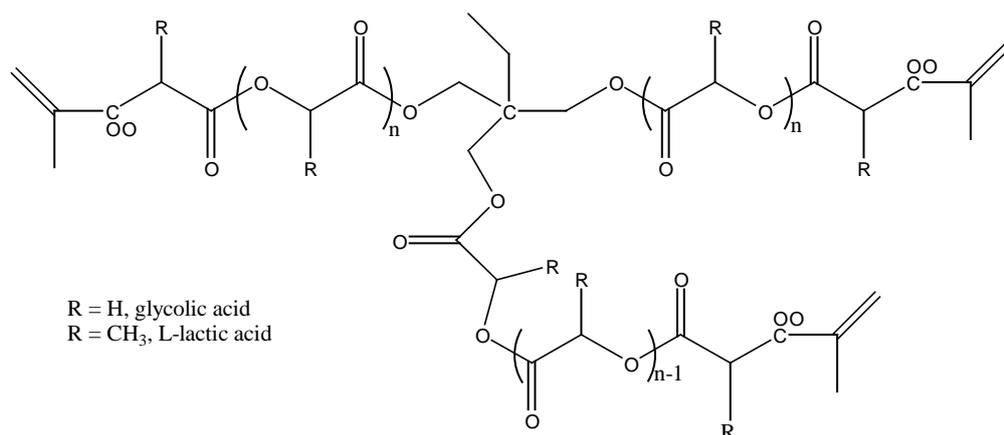
Figure 2. Structure of a synthesized glycolide/lactide based polyester resin.

Ho et al. used methacryloyl chloride for the end-functionalization of the mixture of propylene glycol and lactides in the formation of a triblock poly(lactide-co-propylene glycol) dimethacrylate adhesive [36], see Figure 3.
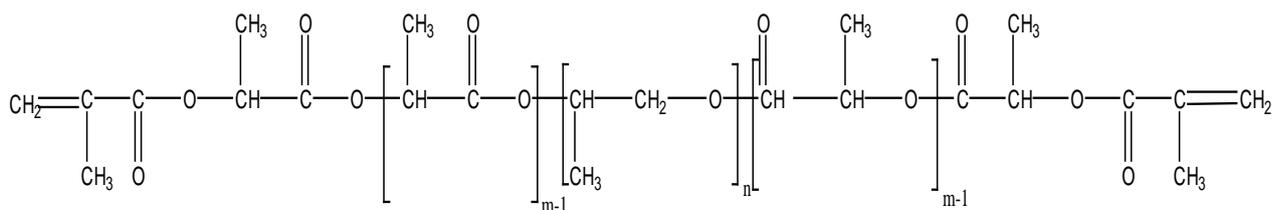
Figure 3. Structure of poly(lactide-co-propylene glycol) dimethacrylate adhesives.

Helminen et al. copolymerized telechelic star-shaped oligomers by ring opening poly-merization and methacrylation with methacrylic anhydride [37]. They also synthesized linear and star-shaped lactic acid oligomers which were end functionalized with methacrylic anhydride which gave a resin with very high tensile strength and modulus of about 120 MPa and 2800 MPa respectively [38], see Figure 4.
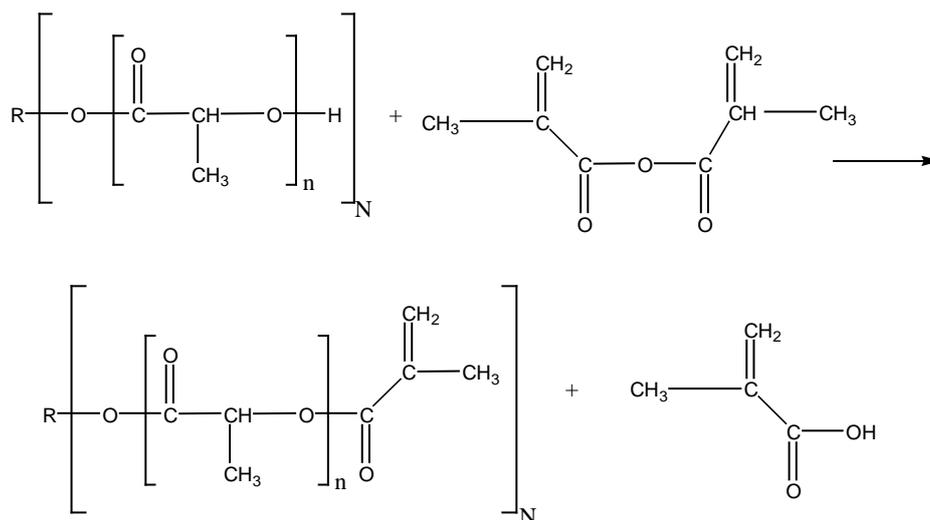
Figure 4. Methacrylated lactic acid oligomers.

Other reports on synthesizing low molecular weight polylactic acid to higher molecular weight by introducing reactive groups was also done by Coullerez et al. by end-capping the telechelic oligomer with acrylate groups in a one-step reaction to increase molecular weight from 700 to 10 000 g/mol [39], see Figure 5.
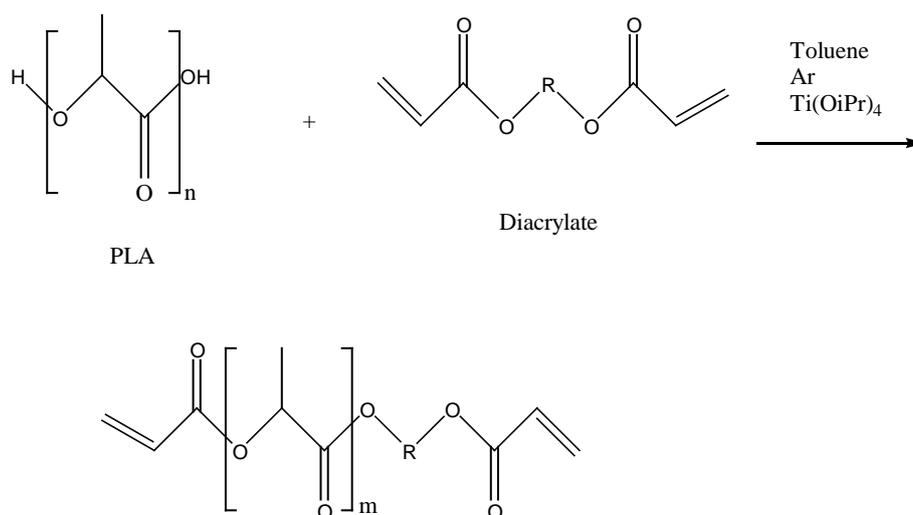
Figure 5. Synthesis of acrylated telechelic oligomers of poly(lactic acid).

Wallach et al. also copolymerized methacrylate-terminated polylactic acid with itaconic anhydride to obtain cyclic anhydride copolymers. High molecular weight from 9 000 to 70 000 g/mol was obtained [40], see Figure 6.
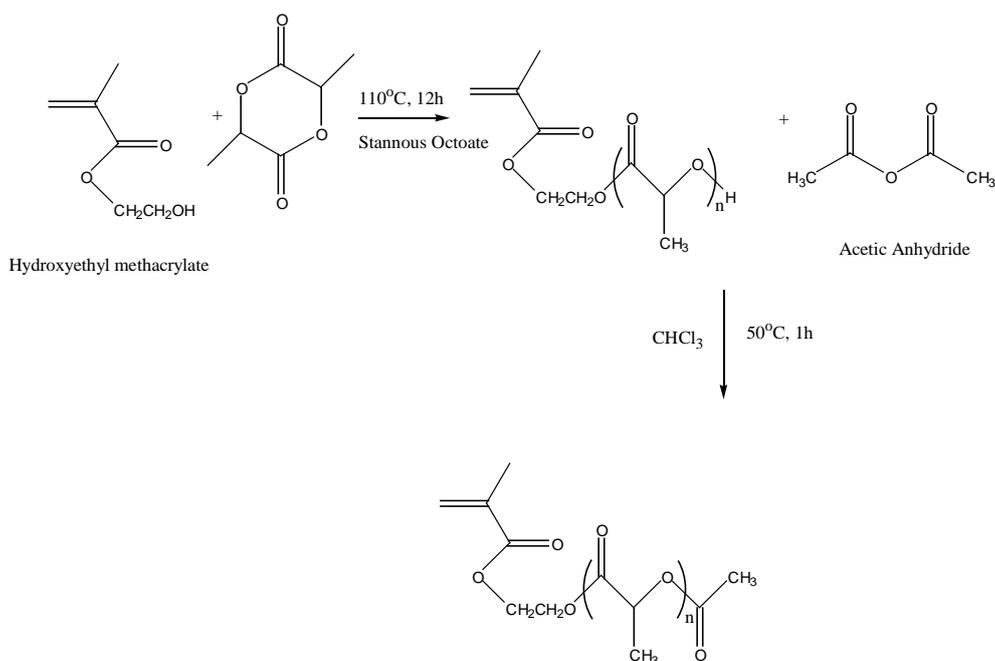
Figure 6. Acetylation of hydroxyl-terminated PLLA with acetic anhydride.

Much of the research made on introducing reactive groups into lactic acid oligomers where done by end-capping the lactic acid oligomers with methacrylate groups but most of these application where intended for medical use [37-38,41]. Based on Åkesson et al. reports [42-43], it is also possible to end-cap lactic acid oligomer with methacrylate groups and crosslink them by free-radical polymerization for composite application. They prepared a thermosetting resin by direct condensation of pentaerythritol, itaconic acid and lactic acid. The obtained star-shaped molecules with pentaerythritol as the core molecule were end-capped by methacrylate groups. This resin had relatively good mechanical properties, but tests also showed that the resin had a relatively high viscosity, which was a drawback in the impregnation of the resin into reinforcement. This led to the idea to synthesize an alternative star-shaped resin from lactic acid, glycerol and methacrylic anhydride as described in Paper I, and further to the idea to synthesize a linear and star-shaped resin from lactic acid, allyl alcohol, pentaerythritol and methacrylic anhydride as described in Paper III.

2.4   Thermoset resins based on glycerol

Glycerol is a renewable material obtained as a by-product in saponification of fats in fatty acid or ester production, in microbial fermentation, soap manufacture and in biodiesel manufacture by trans-esterification of vegetable oils [44-45]. Due to glycerol functionality, availability and competitive cost, it is being used as intermediate in the synthesis of numerous compounds industrially, such as glycerine carbonate used as a solvent or in surfactants and polyethers and in the synthesis of polyurethanes [44]. Yeganeh and Shamekhi [46] prepared polyurethane insulating coatings from the reaction of a polycaprolactone polyol with excess 4,4-methylene-bis-(phenyl isocyanate), and then subsequently reacted glycerine with the NCO-terminated polyurethane. The work showed a high degree of curing and increased mechanical properties with increasing crosslinking density. Another type polyurethane coating was prepared by Vora et al. [47] by synthesizing an AB$_2$-type miktoarm star polymer

by polymerizing butyl acrylate, polyethylene glycol acrylate and N-isopropyl acrylamide monomers by reversible addition-fragmentation chain transfer. The resulting propargylamine was reacted with glycerine carbonate and further reacted with ε-caprolactone and polylactide by ring opening polymerization. The obtained polymer was reacted with azide functional polymers to obtain the miktoarm star polymers with good thermal properties. An hyperbranched aliphatic polyether was prepared by Rokicki et al. [48] from glycerol carbonate (4-hydroxymethyl-1,3-dioxolan-2-one) obtain from glycerol and dimethyl carbonate monomers. A rigid thermosetting polymer was synthesized by Can et al. [49] using soybean oil monoglycerides obtained by the glycerolysis of soybean oils, and was reacted with maleic anhydride. The resulting product was copolymerized with styrene and relatively good mechanical properties were obtained.

2.5   Thermoset resins based on plant oils

Plant oils are one of the most abundant, cheapest, renewable natural resources and are available in various oil seeds [50-52]. These plant oils have been used both for human and animal feeds and also for non-edible use such as for lubricant production, soaps, coating, inks and paints production [50,53]. They are triglycerides composed of three fatty acids with a glycerol centre (Figure 8), and having varying degree of unsaturation. The presence of several C=C bonds in the fatty acid part makes them useful for preparation of polymeric materials. The unsaturation sites on the fatty acids of the triglycerides make them useful crosslinking agents for thermosetting resins [50-51,53]. Several researches have been made on the preparation of thermosetting resin from plant oils. Examples of plant oils used are; soybean oil, linseed oil, tung oil, corn seed oil, etc.
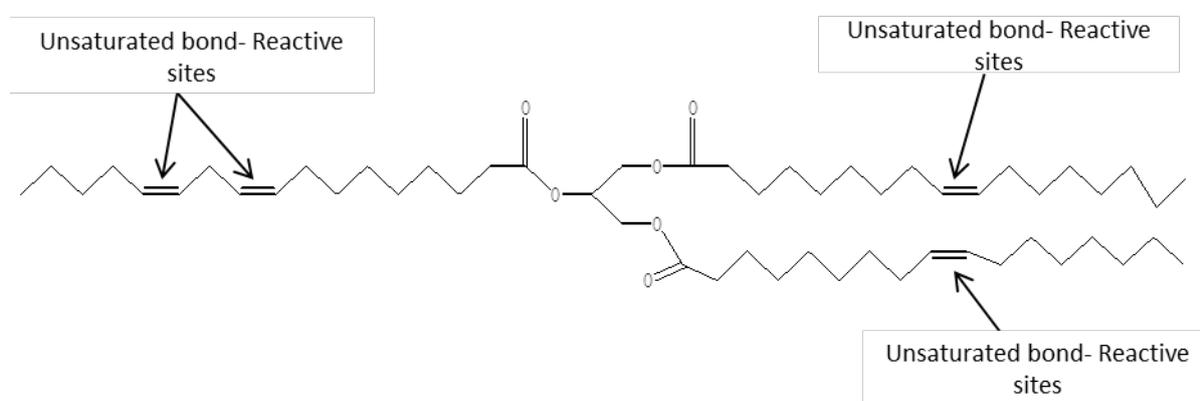
Figure 8. A triglyceride molecule showing its reactive sites.

In order for these plant oils to be useful for radical polymerization, the triglycerides need to be functionalized. Many ways to functionalize the plant oils have been explored by researchers. Examples are epoxidation, malenization and acrylation.

Epoxidation of the carbon double bonds of the soybean oil can be done with peracetic acid or peroxo formic acid [54], there are various research reported on it. Petrovic et al. epoxidized soybean oil in toluene with peroacetic and peroxoformic acids as oxidizing agents [55]. Lu et al. also performed the epoxidation of soybean oil methyl esters in the presence of free fatty

acids [56]. (See Figure 10 for the structure of epoxidized soybean oil.) Acrylation of epoxidized soybean oil is done to modify the epoxidized triglycerides to increase its molecular weight and makes the triglyceride possible to undergo free-radical polymerisation. Fu et al. modified epoxidized soybean oil with acrylic acid to give acrylated epoxidized-soybean oil (AESO) [57]. Adekunle et al. [58] prepared three different modifications of epoxidized soybean oil. First, ring-opening polymerization of epoxidized soybean oil was done using methacrylic acid to give methacrylated epoxidized soybean oil (MSO) (Figure 9).
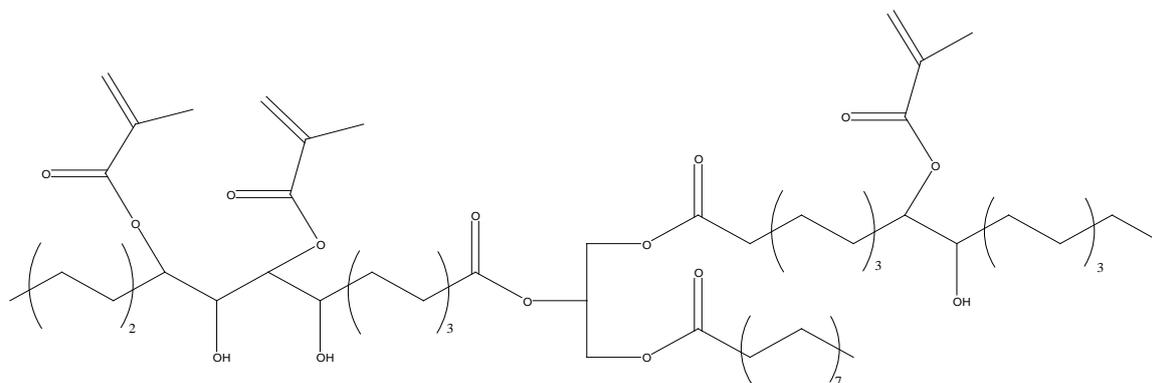
Figure 9. Structure of epoxidized soybean oil (ESO) modigied with methacrylic acid to give methacrylated soybean oil.

The second was the modification of the methacrylated epoxidized soybean oil (MSO) with methacrylic anhydride, giving twice methacrylated epoxidized soybean oil (MMSO). The third was the modification of the methacrylated epoxidized soybean oil with acetic anhydride to give an acetic anhydride modified methacrylated epoxidized soybean oil (AMSO).

Other studies on the epoxidation of linseed oil were also reported by Supanchaiyamat et al., making it possible to use them due to their excellent heat and light stability [59]. They also prepared a thermoset resin from epoxidized linseed oil and bio-derived crosslinker yielding 99.5 % bio-derived resin. Martini et al. modified linseed oil epoxidzed methyl esters with different cyclic dicarboxylic anhydrides to form oligomers with increased entanglement density [60]. Boquillon et al. used epoxidized linseed oil with different catalyst and anhydride hardeners [61]. The result shows that the anhydride hardener from cis-1,2,3,6-tetrahydrophthalic anhydride had a higher crosslinking density than the other anhydride used.

3. CELLULOSIC FIBRES AND COMPOSITE PREPARATION- AN OVERVIEW

Biocomposite materials have gained a lot of interest in the scientific research due to the huge problems of disposing thermoset plastics, which is one of the major environmental problems facing the plastic industries. These biocomposites consist of natural fibres and natural polymer matrix from renewable raw materials for their production [62-64].

3.1 Natural fibres as reinforcement in composite production

Natural fibres are classified into two categories; which are plant-based fibres consisting of polysaccharides, and the animal-based fibres consisting of proteins, as shown in Figure 10. Extraction of the cementing substances such as hemicellulose, wax, lignin and proteins are done before they can be used as reinforcements in composite production [65]. Natural fibres have many advantages over synthetic fibres like low weight, low raw material cost, recyclability, biodegradability, high toughness, high specific strength and stiffness, carbon dioxide neutrality and non-abrasive characteristics [62-64,66]. Plant fibres are of different classes; seed, bast, leaf and fruit. The most commonly used are the leaf and bast fibres in composite production. Examples of leaf fibres includes sisal, abaca, banana, pineapple and henequen, while for bast are kenaf, ramie, jute, hemp and flax representative examples [62,66].
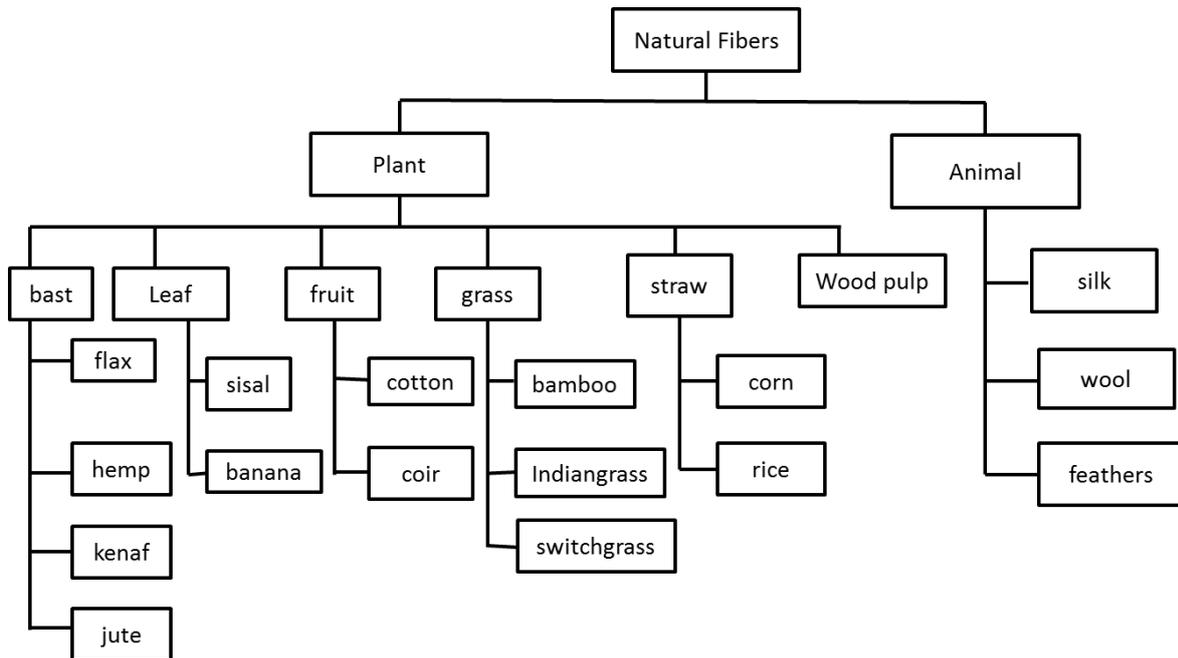
Figure 10. Classification of natural fibres [65].

Table 1 shows the chemical composition of some the natural fibres, while Table 2 shows the mechanical properties compared to the conventional and synthetic fibres.

Table 1. Chemical composition for some natural fibres [62,67-69]

Category	Fibre Type	Species	Cellulose (%)	Hemicellu lose (%)	Lignin (%)	Pectin (%)	Wax (%)	Moisture content (%)
Bast	Flax	Linum usitatissimum	71-81	18.6-20.6	2.2-3	2.2	1.7	10.0
	Hemp	Cannabis sativa	70.2-74.4	17.9-22.4	3.7-5.7	0.9	0.8	10.8
	Kenaf	Hibiscus cannabinus	28-39	21.5-25	15-22.7	-	-	-
	Jute	Corchorus capsularis	61-73.2	13.6-20.4	12-16	0.2	0.5	12.6
	Ramie	Boehmeria nivea	68.6-76.2	13.1-16.7	0.6-1	1.9	0.3	10
Leaf	Sisal	Agave sisilana	56.5-78	5.6-16.5	8-14	10	2.0	11.0
	Abaca	Musa textilis	60.4	20.8	12.4	-	-	-
	Henequen	Agave fourcroydes	77.6	4-8	13.1	-	-	-
	Banana Fibre	Musa acuminate Musa balbisiana	63-67.6	19	5	-	-	-
	Pineapple Fibre	Ananas comosus	70-82	0	5-12.7	-	-	-
Fruit	Cotton	Gossypium sp.	82.7-92	5.7-6	0	5.7	0.6	10
	Oil Palm	Elaeis guineensis	48-65	0-22	19-25	-	-	-
	Coir	Cocos nucifera	32-47	0.3-20	31-45	-	-	-

Table 2. Mechanical properties of some natural fibres compared to conventional fibres [67, 69-70].

Category	Fibre Type	Density (g/cm^3)	Elongation (%)	Tensile strength (MPa)	Young's modulus (GPa)
Bast	Flax	1.5-1.54	2.7-3.2	450-1500	27.6-38
	Jute	1.3-1.45	1.5-1.8	393-773	2.5-26.5
	Hemp	1.48	1.6	690-873	9.93
	Kenaf	-	1.6	930	53.0
	Ramie	1.45	3.6-3.8	400-938	24.5-128
Leaf	Sisal	1.45	2.0-2.5	80-640	1.46-15.8
	Abaca	1.5	3.0-10.0	400	12.0
	Pineapple fibre	-	1.6	413-1627	34.5-82.5
Fruit	Cotton	1.5-1.6	7.0-8.0	287-800	1.1-12.6
	Oil Palm	0.7-1.55	25.0	248	3.2
	Coir	1.1	15.0-40	131-175	4.0-6.0
Conventional	E-Glass	2.5	2.5	2000-3500	70.0
	Aramide	1.4	3.3-3.7	3000-3150	63.0-67.0
	Carbon	1.4	1.4-1.8	4000	230.0-240.0
	S-Glass	2.5	2.8	4570	86.0

Many researches have been made on the potential of natural fibres in composite production. The drawbacks in the performance application of the composite produced are due to environmental factors such as geographical location, climate condition, age of the plant and its extraction and preparation techniques. Examples of the drawbacks in the composite produced are; low thermal stability [63], lower strength properties [71-72], quality variation [72], lack of interfacial adhesion [62,73], poor compatibility with hydrophobic matrix [74-75], hygroscopicity [74], low permissible processing temperature [62,76] and high moisture uptake [71,74-75]. This high moisture uptake is caused by the hydrophilic nature of the natural fibre that has a very high influence on the mechanical properties. Due to these drawbacks, several chemical and physical treatments of fibres are considered to modify the properties of fibres.

3.2 Regenerated cellulose fibre as reinforcement in composite production

Cellulose is the most abundant, renewable, biodegradable, biocompatible, modestly abrasive to ensure longevity of processing tools, and low cost natural polymer which can replace petrochemically derived polymers [77-82]. It has a very high mechanical performance in the plant cell wall due to its high elastic modulus, high degree of polymerization and linear orientation of the cellulose molecules. Increased interest in the use of cellulose fibres for the preparation of biocomposites is due to its high modulus of about 128 GPa, which is higher than for aluminium and glass fibre which are 70 GPa and 76 GPa respectively [77].

Regenerated cellulose fibres, also called man-made fibres, are of two categories, i.e., cellulose fibres (examples; viscose, lyocell and modal) and cellulose derivatives (examples; acetate and

triacetate). Viscose fibres (also called Rayon) are cellulose xathogenate dissolved in sodium hydroxide and which is then spun by wet spinning process in sulphuric acid, zinc sulphate or sodium sulphate [83]. They have wet-strength cotton-like properties and have application as cord yarn in high-performance tires, and as a textile yarn in clothing, apparel and domestic textiles [84]. They also have properties that make them advantageous to replace natural fibres; no seasonal variation, no variation of the fibre diameter, excellent chemical purity and good reproducibility properties [84-85]. A new type of regenerated cellulose fibre (called lyocell fibre) has been discovered, this is also prepared by dissolution of the cellulose but no derivatization is required. It is an environmentally friendly alternative to the viscose fibre process, and is manufactured by cellulose dissolution in N-methyl morpholine N-oxide. The lyocell fibres are biodegradable and are relatively strong which make them useful industrially for ropes, bandages, clothing's, mattresses, automotive filters and abrasive materials [80]. Lyocell has better mechanical properties with higher modulus and tenacity compared to flax fibre [85-86]. Table 3 shows mechanical properties for some regenerated cellulose fibres and reference fibres (flax and glass fibre). It is evident that regenerated cellulose fibres have less strength and modulus but very high extensibility compared to flax and glass fibres. The regenerated cellulose fibres also had a good work to fracture property which makes them suitable reinforcement for composite production in applications where high fractured toughness is required.

Table 3. Mechanical properties of regenerated cellulose and reference fibres [87].

Fibres	Modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)	Work to fracture (J*10^{-3} mm^{-3})
Viscose	10.8 ± 2.5	340 ± 73	15.4 ± 2.2	32.7
Modal	13.2 ± 2.2	437 ± 69	10.4 ± 1.8	37.2
Lyocell	$23.4 (30.5) \pm 3.9$	$556 (790) \pm 78$	8.7 ± 1.6	34.5 (47.1)
Rayon tire cord	22.2 ± 1.0	778 ± 62	10.7 ± 1.4	40.8
Flax	40.0 ± 19.2	904 ± 326	1.4 ± 0.2	6.7
Glass	70.0 ± 9.3	3000 ± 356	$4.3 \pm$	54.3

3.3 Composites prepared from lactic acid thermoset resins

Several reports are dealing with synthesis of lactic acid and lactides for biomedical applications [37,88], tissue engineering applications (e.g. scaffold material) [89], packaging applications [90] and coating applications [42]. There have recently been growing interests in the use of lactic acid thermoset resin for composite applications using different types of natural fibre. Chen et al. [91] produced a composite from lactic acid, pentaerythritol and methacrylic anhydride resin together with ramie fibre. Fibre content of 37 wt-%, 43 wt-%, 48 wt-%, 52 wt-% and 59 wt-% was used. The tensile strength, flexural strength and impact strength showed an increase up to 48 wt-%, while further increase in fibre content caused a decrease in the mechanical properties because of poor dispersion and interfacial bonding between the fibre and matrix. Åkesson et al. [43] prepared composite from flax fibre and a bio-based thermoset resin from methacrylated star-shaped oligomers of lactic acid. The tensile strength and tensile modulus showed an increasing trend with increased fibre ratio up to 70

wt-% and this was also in agreement with the impact resistance test too. The storage modulus of the flax/lactic acid composite with 70 wt-% was 9.32 GPa at 20 °C. The humidity ageing tests showed that the tensile modulus was reduced from 9 GPa to 2.5 GPa and tensile strength was reduced by about 70 % after 1000 h exposure time at 95 % humidity and 38 °C. Åkesson et al. [92] prepared a nanocomposite using a lactic acid-based resin (trade name Pollit) which was cured with ultraviolet radiation in the presence of photo initiators. Methyl methacrylate (MMA) and tripropylene glycol diacrylate (TPGDA) were used as reactive diluents and the resins were then reinforced with layered silicate to form a nanocomposite. The Pollit resin had good thermomechanical properties with storage modulus of about 3 GPa and tensile strength of about 58 MPa. Reinforcement of the resins with 1.5% of nanoclay, improved the storage modulus at room temperature by 27 % of the Pollit with MMA as the diluents. This was not the case for the Pollit/TPGDA which showed decrease in the storage modulus.

3.4   Composites prepared from plant oil-based thermoset resins

There have been several reports on the use of epoxidized soybean oil, linseed oil and other plant oils as matrix in fibre-reinforced composites. Natural and regenerated cellulose fibres were used to produce thermoset composite with high renewable ratio. The use of nanosize reinforcements, which are nanoparticles of less than 100 nanometres, was also reported for the production of bio-based nanocomposites.

Epoxidized soybean oil and different type of modified epoxidized soybean have been reported which showed very good mechanical properties compared to the commercial resins. Williams and Wool [93] produced natural fibre composite from acrylated epoxidized soybean oil blended with styrene and divinyl benzene with both flax and hemp fibres using resin transfer moulding (RTM). The composites were prepared with fibre load up to 40 wt-% and the tensile and flexural properties of the flax and hemp composite show almost the same trend. The tensile strength of the flax composite shows an increased trend up to 34 wt-% at 30 MPa then decreased down to 40 wt-%, but in the case of the tensile modulus there was an increase with increase fibre content up to 40 wt-% of 5 GPa. The flexural strength and modulus shows an increase till 34 wt-% and a decrease to 40 wt-% at 64 MPa and 4.2 GPa respectively.

Thielemans and Wool [94] prepared composites from treated flax fibre and acrylated epoxidized soybean oil blended with styrene. The flax fibre was treated with aqueous sodium hydroxide for about 5 minutes. The result shows improved mechanical properties due to the improved fibre wettability caused by the treatment but the contact angle was decreased. Other reports that used acrylated epoxidized soybean oil are by Hong and Wool [95] with keratin fibres, by Morye and Wool [96] with combination of glass fibre and flax, while O'Donnell et al. [97] used different natural fibre reinforcement. All three reported composite systems also gave good mechanical properties.

Some reports were done on the use of soybean oil and regenerated cellulose fibres for composite preparation. Takahashi et al. [98], used epoxidized soybean oil cured with a terpene-based anhydride with lyocell fabric. The result showed that the tensile strength increases with increasing fibre content up to 75 wt-% with tensile strength and modulus of 65 MPa and 2.3 GP a respectively. Ramamoorthy et al. [99] prepared a lyocell composite, a

viscose composite and a hybrid composite using combinations of lyocell and viscose with acrylated epoxidized soybean oil as matrix, and with the fibre content between 40 to 60 wt-%. The result showed that the lyocell composite had a better tensile strength and modulus of 135 MPa and 17 GPa respectively with fibre content of 65 wt-% than the other composite. The viscose composite also showed a very high percentage elongation than the other composite types. The hybrid composite showed improved impact resistance and comparable flexural strength and tan delta to other composites but the SEM images showed uneven spreading of the matrix and delamination of the composite during manufacturing. Ramamoorthy et al. [100] prepared hybrid composite using acrylated epoxidized soybean oil with non-woven and woven jute, non-woven lyocell and viscose mat and woven glass fibre. The effect of water absorption on the treated and untreated fibre mat was investigated and the result showed that hybridizing jute fibre with glass or lyocell fibre can improve the mechanical properties of the composite and reduce the water uptake of the composite produced. Ramamoorthy et al. [101] used soybean oil thermoset resin with cotton/polyester textile waste as reinforcement in a composite. Four parameters were varied to investigate their effect on mechanical properties of the composite, these were; curing temperature and pressure, fibre ratio and curing time. It was verified by statistical analysis that all factors affects the properties of the composite and contributes to the improvement of the mechanical properties of the composite. This report encourage the use of textile waste as reinforcement for composite production, and tensile strength, modulus, elongation and impact strength of 58 MPa, 6 GPa, 1.7 % and 71 kJ/m^2 respectively can be obtained.

Nanocomposites were also prepared using soybean oil resin. Liu et al. [102] prepared epoxidized soybean oil/ clay nanocomposite with triethylene tetramine as a curing agent, using quaternary alkyl ammonium modified montmorillonite as the reinforcement. The result showed an increase in tensile strength from 1.27 MPa to 4.54 MPa with increasing clay concentration. Lu et al. [103] prepared clay nanocomposite using acrylated soybean oil (AESO), maleinized acrylated epoxidized soybean oil (MAESO) and soybean pentaerythritol maleates (SOPERMA) combined with styrene. The MAESO reinforced with 3 wt-% nanoclay showed the highest storage modulus with 13 % increase compared to other resins. Thielemans et al. [104] prepared carbon nanotubes and carbon soot in acrylated epoxidized soybean oil, the results showed that the storage modulus increased by about 30 wt-% with increasing reinforcement loading.

Linseed oil has also been used to produce fibre-reinforced composites. Mosiewicki et al. used linseed oil resin/styrene reinforced with wood flour to produce a composite and the mechanical properties were measured when varying the percentages of wood flour [105]. An aging study was also done to see its effect on the mechanical properties of the composite produced [106], and also the moisture absorption effects on the thermal and mechanical properties were also studied [107]. The investigations showed that 30 wt-% of wood flour gives a high T_g and good mechanical properties, while the SEM shows excellent interfacial adhesion. A further increase in the weight percentage of the wood flour leads to voids. The aging test showed a reduction in the mechanical properties but did not inhibit the oxidative aging process. The moisture absorption result showed higher mechanical properties compared

to the initial properties before the test. From this it can be concluded that the slow oxidative polymerization of the linseed oil might be responsible. Aranguren et al. [108] prepared two types of resin; a tannin based matrix and a linseed oil/styrene based matrix using pine wood flour as the filler. The study showed that the tannin oil based composite had a higher modulus but it was very sensitive to humid environment while the linseed oil based composite had good mechanical properties at 60 wt-% oil to 40 wt-% styrene, and it also showed excellent adhesion with the pine wood filler. Boquillon [109] prepared a composite from epoxidized linseed oil with tetrahydrophthalic anhydride as hardener and reinforced with hemp fibres. Fibre content was varied from 0 to 65 vol-% and fibre lengths of 1.2 and 6 mm were investigated. Results showed an increased trend for the flexural modulus and strength up to 30 wt-% and a decrease when fibre content was increase beyond 30 wt-%. The longest fibre length (6 mm) showed the best mechanical properties.

Other types of natural oils have been used for composite production with resulting good mechanical performance. Lu and Larock [110] used regular and conjugated corn oil prepared by cationic copolymerization with styrene and divinyl benzene and reinforced with glass fibre. They also in another report used this corn oil based polymer resin with organic montmorillonite clay modified with (4-vinylbenzyl) triethylammonium cations for the production of a bio-based nanocomposite [111]. Boron trifluoride diethyl etherate modified with Norway fish oil was used as initiator and the result showed improved mechanical properties and thermal stability compared to the pure resin.

Tung oil based resin was prepared by bulk free radical polymerization using spent germ as the filler for composite production [112]. The effect of the particle size of the filler were investigated, the amount of crosslinker and molding pressure was also investigated. The result showed improved mechanical properties and thermal stability compared to the pure resin. Jiratumnukul and Intarat [113] used epoxidized sunflower oil with montmorillonite in a cationic exchange process and cured by ultraviolet radiation with either cationic or hybrid initiation.

4. EXPERIMENTAL WORK

4.1 Resin synthesis

4.1.1 Materials

L-Lactic acid (88-92%, Sigma-Aldrich) was purified by using a rotary evaporator. Glycerol (99.5%, Fisher Scientific), allyl alcohol (≥98.5%, Sigma-Aldrich) and pentaerythritol (98%, Sigma-Aldrich) were used as received. Toluene was used as solvent (99.99%, Fisher Scientific) and methanesulfonic acid (98+%, Alfa Aesar) was used as the catalyst in the condensation reaction. Methacrylic anhydride (94%, Alfa Aesar) was used as the reagent for the end-group functionalization. Hydroquinone (99%, Fisher Scientific) was used as inhibitor during the end-group functionalization reaction. An unsaturated polyester resin (Polylite 444-M850, Reichhold AS) was used as a reference when evaluating the synthesized resin properties. This commercial resin is a medium reactive orthophtahlic type resin, which contains approximately 43 wt-% styrene. For the curing of the resins, two different initiators were used; methyl ethyl ketone peroxide (33%, BHP Produkter AB) for room temperature curing, and dibenzoyl peroxide (>98%, Kebo Lab) for curing at 150 °C. N,N-dimethyl aniline was used as accelerator with the dibenzoyl peroxide.

4.1.2 Methods

Three structurally different resins were synthesized from lactic acid namely; glycerol-lactic acid resin (GLA resin) (see Paper I), methacrylated allyl alcohol-lactic acid resin (MLA resin) (see Paper III) and pentaerythritol methacrylated lactic acid resin (PMLA resin) (see Paper III). All reactions were performed under nitrogen atmosphere.

4.1.2.1 *GLA resin (glycerol-lactic acid resin)*

The synthesis was done in two stages. In the first condensation reaction stage, a star-shaped oligomer of glycerol and lactic acid was prepared. Three oligomers with different chain lengths in the glycerol branches (n = 3, 7 and 10) were made in order to study the influence of the length of the chains. This was done by using 9, 21 or 30 moles of lactic acid for each mole of glycerol. The reactants were diluted in 50 g of toluene and 0.1 wt-% methanesulfonic acid was used as catalyst. All components were placed in a three-necked round bottom flask equipped with a magnetic stirrer, nitrogen inlet and a Dean-Stark azeotropic distillation apparatus. The flask was heated for 2 h in an oil bath with a set temperature of 145 °C under constant stirring. The water produced in the reaction was collected by azeotropic distillation. After the initial reaction, the temperature was raised to 165 °C for further 2 h, and finally increased to 195 °C for 1 h. In the second stage, the remaining reactant solution was cooled to 110 °C and maintained at that temperature. Hydroquinone (0.1 wt-%, used as a stabilizer) was then added into the reaction mixture. The end-functionalization was done by adding drop-wise during 4 h, 0.396 mole of methacrylic anhydride (n = 3) while being constantly stirred under nitrogen atmosphere. After the end-functionalization, the formed methacrylic acid and the remaining toluene present in the resin mixture were removed by rotavapor distillation at temperature of 60 ºC and 13 mbar pressure. The chemical reaction for the GLA resin synthesis is shown in Figure 11.
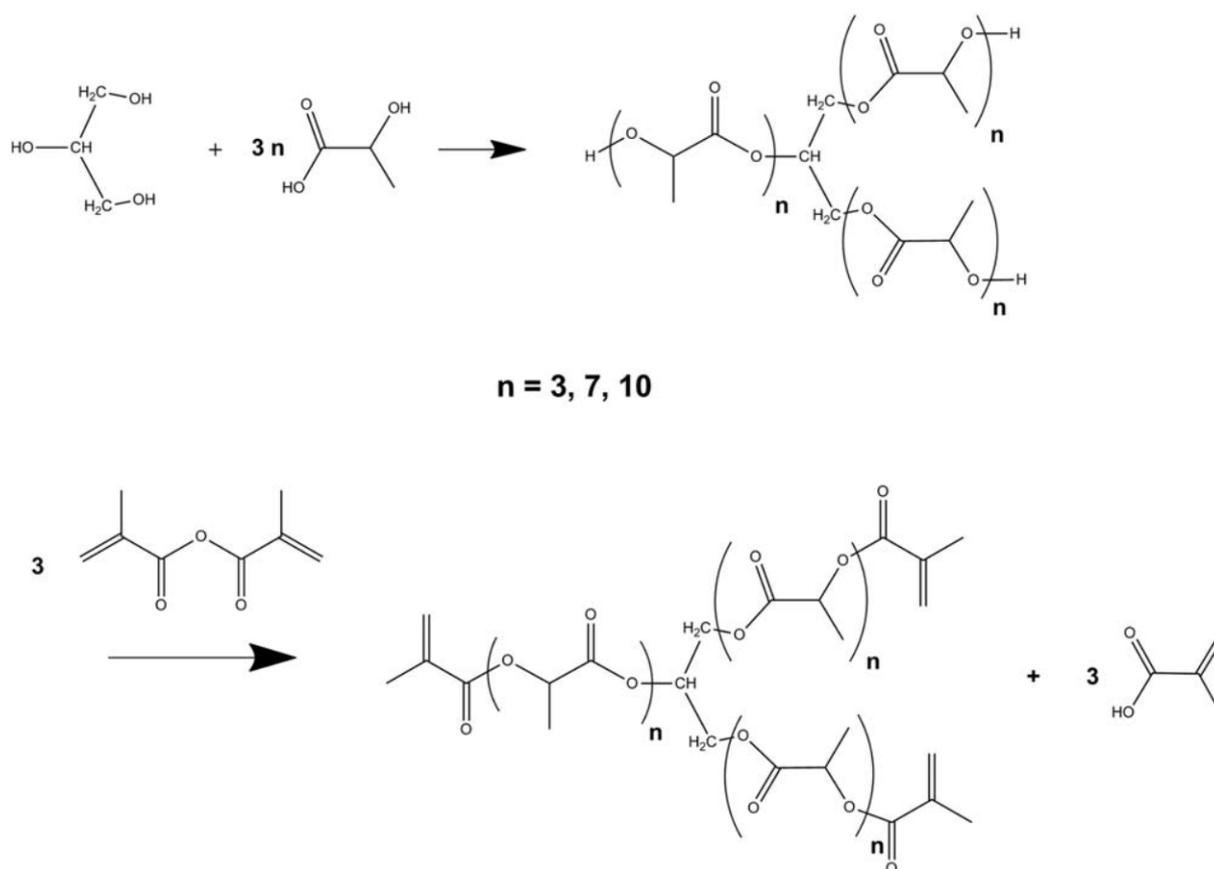
Figure 11. Synthesis reaction for methacrylated glycerol-lactic acid resin (GLA resin) with n = 3, 7 and 10.

4.1.2.2 MLA resin (methacrylated allyl alcohol-lactic acid resin)

The synthesis was performed in two stages. In the first stage, an intermediate allyl alcohol lactic acid oligomer (ALA resin) was prepared from 1 mole of allyl alcohol and 5 moles of lactic acid. The reaction was done in 250 g toluene, and with 0.1 wt-% of methanesulfonic acid as catalyst. All chemicals were placed in a three-neck round bottom flask equipped with a magnetic stirrer, nitrogen inlet and a Dean-Stark azeotropic distilling trap. The flask was heated for 2 h in an oil bath with a set temperature of 145 °C under constant stirring. The water produced in the reaction was collected by azeotropic distillation in the trap. After the initial 2 h, the temperature was raised to 165 °C for further 2 h, and finally increased to 195 °C for 1 h. In the second stage, the obtained ALA resin was reacted with methacrylic anhydride to end-functionalize the oligomer. The intermediate reaction mixture was cooled to 90 °C and a stabilizer of 0.2 wt-% of hydroquinone was added under stirring. Finally 1.1 moles of methacrylic anhydride were added drop-wise during 4 h into the reaction mixture while being constantly stirred under nitrogen atmosphere.

After the second stage, the formed methacrylic acid and the remaining toluene present in the resin mixture were removed by rotavapor distillation at temperature of 60 ºC and 13 mbar pressure. The reaction procedure and the resin structures are shown in Figure 12.

Figure 12. Synthesis reaction for allyl alcohol lactic acid oligomer resin (ALA resin) and methacrylated allyl alcohol-lactic acid resin (MLA resin).

4.1.2.3 PMLA resin (pentaerythritol methacrylated lactic acid resin)

The synthesis was also done in two stages. The first stage was equivalent to the first stage used for MLA resin synthesis. In the second stage, four moles of the ALA resin were reacted with one mole of pentaerythritol. The reaction was done at 90 °C and a stabilizer of 0.2 wt-% of hydroquinone was added into the stirred reaction mixture. Then an excess of 10 moles of methacrylic anhydride was added drop-wise during 4 h while being constantly stirred under nitrogen atmosphere. After the end-functionalization, the formed methacrylic acid and the remaining toluene present in the resin mixture were removed by rotavapor distillation at temperature of 60 °C and 13 mbar pressure. The reaction scheme and the resin are shown in Figure 13.


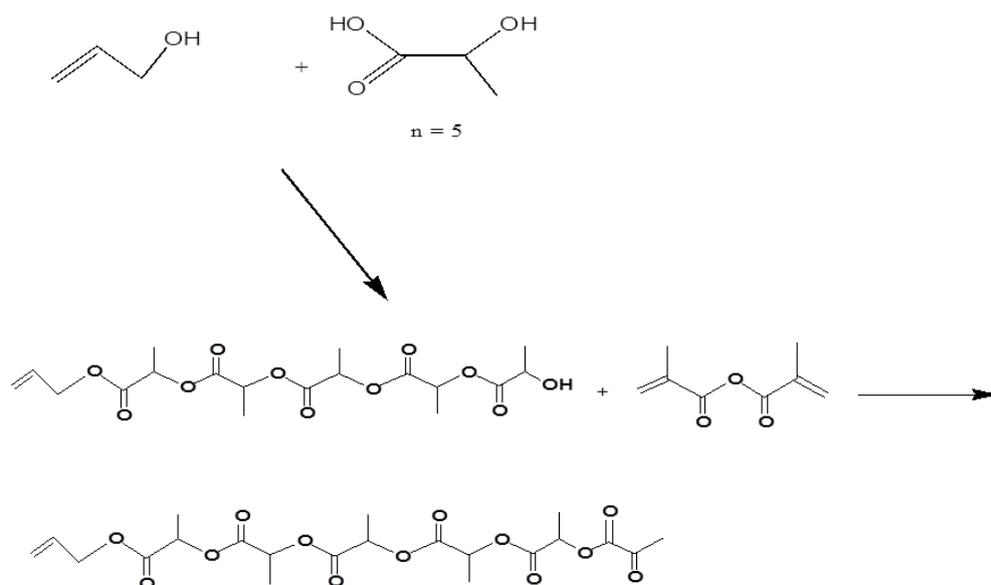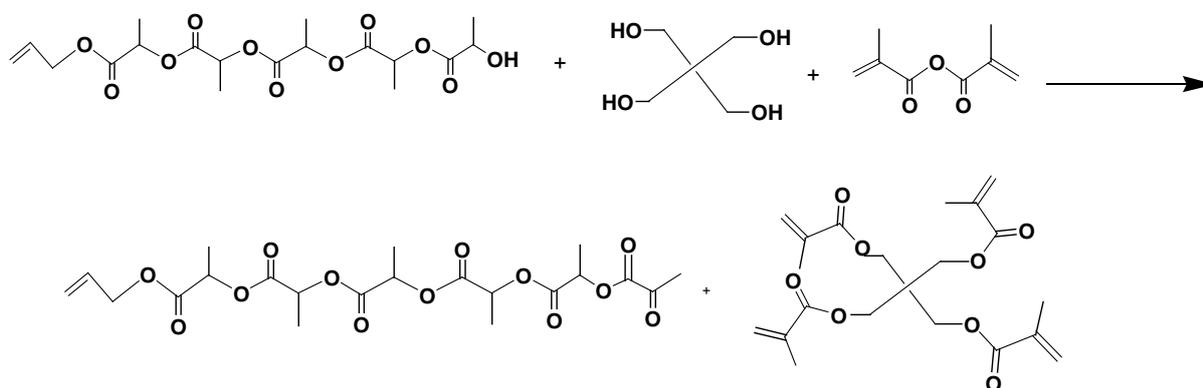**Figure 13.** Synthesis reaction for pentaerythritol methacrylated lactic acid resin (PMLA resin).

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4.1.3   Characterization

The progress of the condensation reaction in stage 1 was followed by titration of the remaining carboxyl groups in the reaction mixture.

The chemical structure for the products from both the first stage and the second stage for all resins were examined using ^{13}C NMR (Chemagnetics CMX respective Bruker AVANCE spectrometers) at 400 MHz. The MLA and PMLA resins were also analysed by 1H NMR (Bruker 300) at 300 MHz. Samples were dissolved in $CDCl_3$.

The neat and cured resins were analysed using Fourier transform infrared (FT-IR) spectroscopy on a Nicolet 6700 spectrometer (Thermo Fisher Scientific).

The neat and cured resins were also analysed by differential scanning calorimetry (DSC) on a TA Instrument Q 1000, from Waters LLC. Samples were placed in sealed aluminium pans and heated from -20 °C to 200 °C at 10 °C /min in a nitrogen atmosphere. Data obtained from the first heating were used to investigate crosslinking reaction efficiency by integrating of the exothermic peaks.

Dynamic mechanical analysis (DMA) was done on a TA Instrument Q800 from Waters LLC on the cured resin and was run in the dual cantilever bending mode with sample dimension of about 35 mm x 2 mm x 8 mm. The temperature ranged from -40 °C to 150 °C with a heating rate of 3 °C/min in a nitrogen atmosphere at frequency of 1 Hz and amplitude of 15 µm.

Thermogravimetric analysis (TGA) on the cured resin was done on a TA Instrument Q500 from Waters LLC. A sample of about 20 mg was heated from 30 °C to 650 °C at a heating rate of 10 °C/min in a nitrogen purge stream.

All cured resin specimens were prepared by thermal curing with 2 wt-% dibenzoyl peroxide as initiator, and 0.5 wt-% N,N-dimethylaniline as accelerator. The resins were first cured at room temperature for 1 h, and then postcured at 150 °C for 20 min.

The flow viscosity of the uncured resin was analysed using a modular compact rheometer, Physica MCR 500. A cone-plate configuration with truncated cone (1mm, 25 °C) was used for all measurements and the measurement was done in rotational mode. Viscosities were measured at temperatures 25 °C, 35 °C, 45 °C, 55 °C and 70 °C. Different shear stress levels were used for the resins.

4.1.4   Results

4.1.4.1   Carboxyl group titration
The first stage of the GLA resin synthesis was followed by the titration, and according to the results, the reaction proceeded well until 360 min reaction time. A longer reaction time did not reduce the number of carboxyl groups.

4.1.4.2   NMR spectroscopy analysis
The ^{13}C-NMR analysis was used to verify for the GLA resin the condensation reaction of the lactic acid with glycerol and also to verify the end-capping reaction of the lactic acid branches

with methacrylic acid. The spectra is shown in Figure 14, where the peaks in the carbonyl area (160 – 180 ppm) for the GLA resin with chain length n = 3 are identified.

The lactic acid carbonyls give two major peaks, of which the end group carbonyl is located at 173.5 – 174.5 ppm. The other lactic acid carbonyls can be seen at 168.5 – 169.5 ppm. From the carbonyl peak areas, it is possible to calculate the length of the lactic acid branches attached to glycerol, and compare with the intended branch length. As discussed in Paper I, the used synthesis condition give slightly longer lactic acid branches.

For the second synthesis stage, the NMR analysis showed that most of the hydroxyl end groups had reacted, as the large peak at 173.5 – 174.5 ppm had disappeared, and instead a peak at 166.0 ppm appeared. This peak is due to the carbonyl in the methacrylate reacted with the lactic acid hydroxyl group. From the spectra the degree of reacted hydroxyl end groups can be calculated, in the resin with n = 3 around 82 % had reacted with methacrylic anhydride, while only 67 and 57 % of hydroxyl groups in the resins with n = 7 and 10 had reacted, respectively.

The MLA resin was analysed by both ^{1}H and ^{13}C NMR spectroscopy. Rather similar carbon spectra as for the GLA resin were obtained, and the intended structures could be verified, as discussed in Paper III. The PMLA resin gave rather complicated spectra, due to the used synthesis procedure. However, a new carbonyl peak was identified at 166.1 ppm indicating that the reaction of pentaerythritol with methacrylic anhydride did occur. From the proton spectra the lactic acid chain length in the ALA resin could be estimated to average 6 lactic acid units. The reaction with methacrylic anhydride could be verified by a peak at 1.9 ppm.
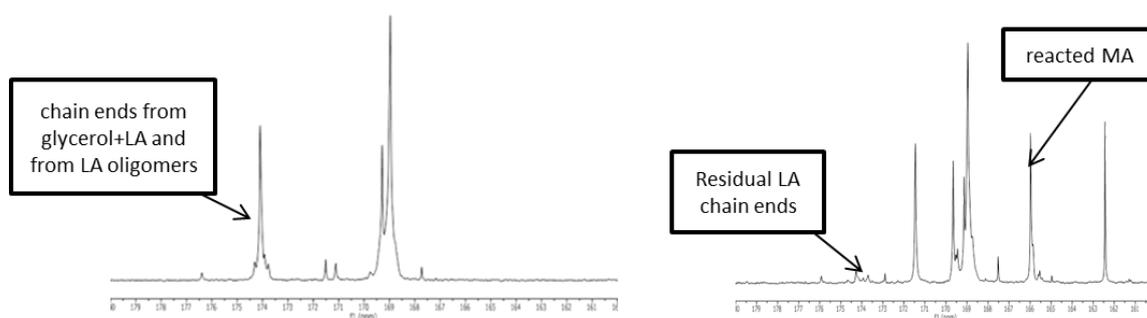
Figure 14. Comparison of ^{13}C-NMR spectra for the carbonyl area (160 – 180 ppm) for the first (left spectra) and second step (right spectra) synthesis of GLA resin for chain length n = 3.

4.1.4.3 FT-IR spectroscopy analysis

The FT-IR spectra were used to verify the GLA resin functionalization with methacrylic anhydride in the second stage by comparing to the resin spectra from the first stage. The cured resins were also analysed to verify the crosslinking reaction from the spectral bands corresponding to the carbon-carbon double bonds. Figure 15 shows the FT-IR spectra of uncured and cured GLA resin with chain length n = 3. In the spectra it can be seen the

unreacted carbon-carbon double bonds at about 1640 cm^{-1} (stretching, C=C) and at 816 cm^{-1} (bending, =CH$_2$) for the uncured resin, these bands were not present in the first step spectra. This indicates that end-functionalization by methacrylic anhydride did occur. The almost complete disappearance of an absorbance at 3500cm^{-1} after reaction with methacrylic anhydride indicates also that almost all the hydroxyl groups were reacted. Therefore it could be concluded that the end-functionalization had proceeded as intended.

The disappearance of the carbon-carbon double bond peak and an increase in the –CH stretch band at about 2900 cm^{-1} in the cured resin indicates that the crosslinking reaction of the resin had occurred. The complete crosslinking reaction was verified for all the cured resins, the spectra showed no band at 1640 cm^{-1} and this clearly indicates that all double bonds had reacted when crosslinked, and therefore the resins could be considered as fully cured.
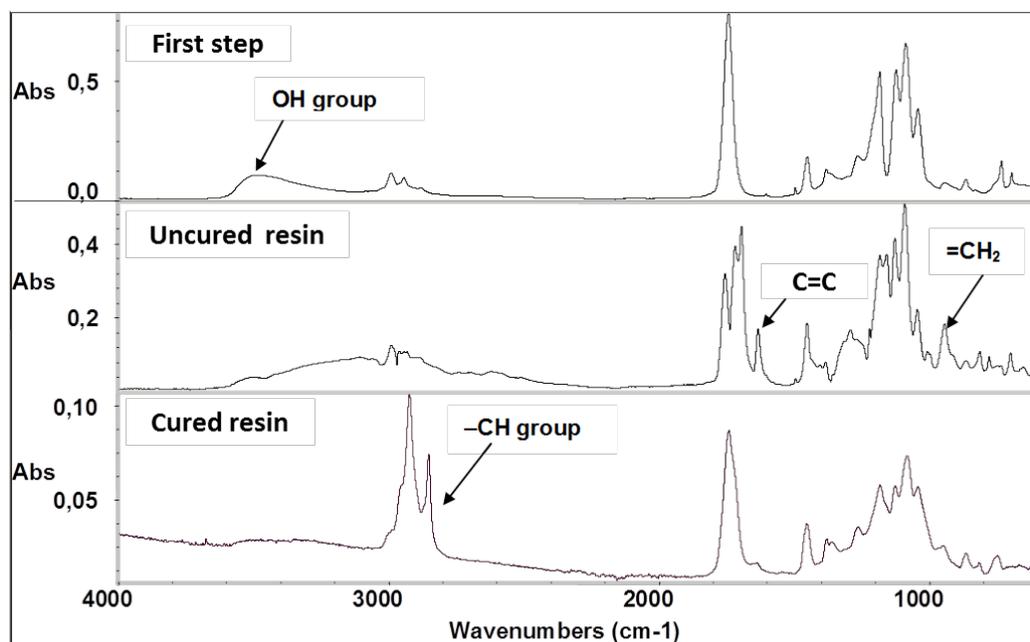
Figure 15. FT-IR spectra of GLA resin with chain length n = 3. The spectra for first synthesis step, second synthesis step and for cured resin are shown.

For the ALA, MLA and PMLA resins the intended resin structures as well as the curing reaction were verified by the FT-IR analysis. The end functionalization of the ALA resin with methacrylic anhydride could be verified by the carbon-carbon double peaks at 1640 cm^{-1} and 816 cm^{-1}, and by the splitting of the carbonyl bond at 1757 cm^{-1}. (See Figure 4 b in Paper III) The curing of the MLA resin could as well be confirmed by the disappearance of the carbon-carbon double bond peaks. Similar conclusions could be made for the PMLA resin.

4.1.4.4 DSC analysis
The DSC was used to investigate the crosslinking-reaction efficiency of the resins, by detecting any residual exothermal heat present in the uncured and cured resins. All results from the DSC analysis are shown in Table 4.

For the uncured GLA resin, the resin with chain length n = 3 gave the highest residual exothermic heat of 227.4 J/g, while for the resins with chain length n = 7 and 10 were 162.2 and 94.3 J/g respectively. The cured GLA resins showed no exothermic peak in the DSC scans. Figure 16 shows the DSC curves for the cured and uncured GLA resins.

The MLA resin had an exothermic peak of about 194 J/g and PMLA resin had about 26 J/g. Exothermic peaks of about 1.40 J/g and 0.03 J/g for MLA and PMLA resin respectively were detected for the cured specimens. This means that the resins are almost fully cured under the conditions used. The PMLA resin had the highest glass transition temperature, which was even about 30°C higher than for the commercial reference unsaturated polyester resin.
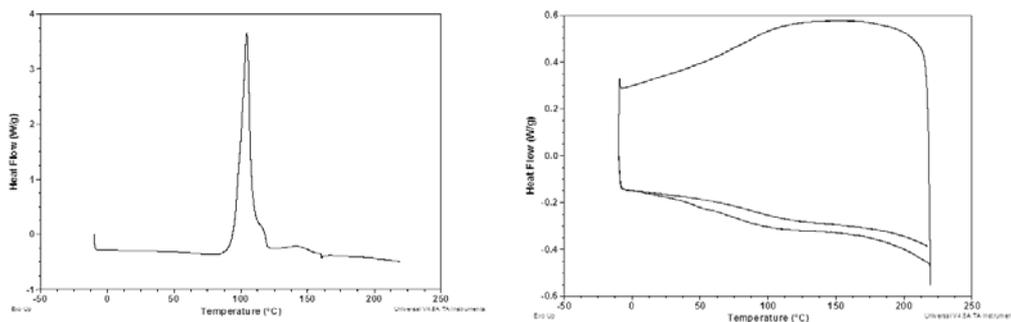
Figure 16. DSC curve of uncured and cured GLA resin with chain length n = 3.

4.1.4.5 Dynamic mechanical analysis

The dynamic mechanical analysis was done to characterize the neat crosslinked resins regarding their viscoelastic properties. Table 4 shows the storage modulus, loss modulus and the peak of tan delta for all synthesized resins compared with a commercial unsaturated polyester resin (UPE). The result showed that GLA resin with chain length n = 3 had the highest storage modulus, due to the short lactic acid branches giving a more crosslinked and rigid resin. The loss modulus values for the GLA resins with different chain length support this conclusion. The tan δ value gives an indication of the glass transition temperature, which could not be detected by the DSC analysis. The GLA resin with n = 3 had the highest glass transition temperature, while the resin with n = 10 had the lowest.

The MLA and PMLA resins had different viscoelastic behaviour than the GLA resin. The PMLA resin had the highest tan delta peak value, which was also confirmed by the glass transition temperature in the DSC result. However, the storage modulus was lower for MLA and PMLA resins compared to the GLA resin, but higher compared to the commercial reference unsaturated polyester resin. All the resins except GLA resin with chain length n = 10 had a higher storage modulus than the commercial polyester resin. This indicates that the synthesized resins should have good mechanical properties when used in a composite.

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Table 4. Thermal characterization results for the resins.

Resin	DSC				DMA			TGA		
	Heat of exotherm uncured resin	Temperature interval for exotherm peak	Heat of exotherm cured resin	T_g	Peak of Tan Delta	Storage Modulus at 25 °C	Loss Modulus at 25 °C	Degradation Temperature at 10 wt-% Loss	Maximum Degradation	Second Derivative Peak
	(J/g)	(°C)	(J/g)	(°C)	(°C)	(MPa)	(MPa)	(°C)	(°C)	(°C)
GLA (n = 3)	227	82 - 160	0	76	97	4312 (± 157)	354 (± 48)	258	375	438
GLA (n = 7)	162	89 - 160	0	70	80	3766 (±215)	229 (±29)	248	366	436
GLA (n = 10)	94	61 - 156	0	50	54	1736 (±59)	482 (±33)	202	357	433
MLA	194	83 - 170	1.40	79	109	3269 (±199)	400 (±145)	290	346	450
PMLA	26	80 - 170	0.03	100	113	3663 (±173)	123 (± 27)	302	344	461
UPE	198	57 - 175	0.45	71	83	2955 (± 5)	135 (± 22)	308	362	388

4.1.4.6 Thermogravimetric analysis of the cured resins

The TGA analysis was done to investigate the thermal stability of the resins by recording the percentage weight loss of the cured samples. The result showed that chain length had an influence in the thermal stability of the GLA resin, with chain length n = 3 having a higher thermal stability than for n = 7 and 10. The MLA resin had slightly higher thermal stability, while the PMLA resin had the best thermal stability, and was comparable to the thermal stability of the commercial unsaturated polyester resin (see Table 4). These results show that the synthesized resins should well meet the thermal requirements for most composite applications.

4.1.4.7 Viscosity measurement

The viscosity of a thermoset resin is of importance regarding how the resin can be processed together with reinforcements. The result showed also that lactic acid chain length had influence on the viscosity of the GLA resin. The resin with chain length n = 3 had a low viscosity which is well suited for processing at room temperature, but chain length n = 7 and 10 gave very high viscosities that make them impossible for reinforcement impregnation. The MLA and PMLA resins had much lower viscosities, even lower than for the commercial polyester resin. This will make them suitable for composite processing at room temperature and an even penetration of the resins into fibre bundles can be achieved. Table 5 shows the viscosities of all resins at different temperature.

Table 5. Viscosity results of the resins at different temperatures.

Resin	Viscosity for all temperature (Pa s)				
	25ºC	35ºC	45ºC	55ºC	70ºC
GLA (n = 3)	1.09	0.47	0.24	0.15	0.09
GLA (n = 7)	4 146	492.40	83.20	19.24	3.56
GLA (n = 10)	63.3×10^6	5.1×10^6	76 600	136.20	8.48
MLA	0.04	0.03	0.02	0.019	0.014
PMLA	0.02	0.018	0.016	0.014	0.012
UPE	0.29	0.22	0.19	0.12	0.07

4.2 Composite preparation

4.2.1 Reinforcements

Viscose non-woven fibre mat with surface weight of 60 g/m^2 and 0.66 mm thickness was supplied by Suominen Non-Wovens Ltd. Warp-knitted uniaxial fabric with surface weight of 182 g/m^2 made from a viscose yarn from Cordenka, (twist Z40, linear density of 2440 dtex with 1350 filaments), was delivered by Engtex AB. A flax fabric with surface weight of 430 g/m^2 made from 100% flax yarn, (warp 8 thread/cm, weft 8 picks/cm, yarn number 263 tex and Twill 2/2 weave type), was supplied by Libeco Technical. A flax/basalt fabric with surface weight of 285 g/m^2 made from 52% flax yarn and 48 % basalt yarn, (warp 16.8/1.67 thread/cm, weft 16.8/1.69 picks/cm, yarn number 42/380 tex and Dobby weave type), was also supplied by Libeco Technical.

4.2.2   Compression moulding

Composites were prepared from four different types of fabrics. In Paper II the fabrics were from regenerated cellulose fibre (warp-knitted and non-woven viscose) and in Paper IV the fabrics were from natural fibre (flax respective flax/basalt woven fabrics). The reinforcement mats were cut in 21×21 cm size and dried in vacuum oven at 15 mbar and 105 ºC for one hour.

For the regenerated cellulose fibre composites, the laminates had 12 layers of warp-knitted viscose fabrics placed in two different configurations. Laminates with all weft yarns in one direction were named as unidirectional or UD and laminates with a 0°/90° alternating weft yarn lay-up were named as bidirectional or BD. Laminates with 34 sheets of non-woven viscose mats were also prepared. Three different fibre loads of 65, 70 and 75 wt-% were investigated for both the warp-knitted and non-woven viscose fabrics. The exact fibre weight load was monitored by weighing the dry fabrics and the cured composite. The GLA resin with chain length n = 3 from Paper I was used as matrix and the impregnation was done by hand lay-up. The resin was first mixed with 2 wt-% of dibenzoyl peroxide and then it was applied onto the surface of the fibre sheet.

For the woven flax composites, laminates of 5 fabric layers were prepared, while laminates of 8 fabric layers were prepared for the woven flax/basalt composite. Composites made from these fabrics with three different fibre loads of 40, 50 and 60 wt-% were investigated. The exact fibre weight load was monitored by weighing the dry fabrics and the cured composite. The PMLA resin from Paper III was used as matrix and the impregnation was done by hand lay-up. The resin was first mixed with 2 wt-% of dibenzoyl peroxide and then it was applied onto the surface of the fibre sheet.

All fabrics stacks were then compression moulded (Rondol hydraulic press) for 5 min at 150 °C and at 0.5 to 4 MPa pressure (depending on the desired fibre content). This gave laminates with an approximate thickness of about 2-3.5 mm.

4.2.3   Characterization

All laminates were cut by laser cutting to obtain specimens for DMA, tensile, flexural, Charpy and water absorption testing.

The DMA was done as described in chapter 4.1.3.

The three point bending flexural testing was done according to ISO 14129 using a H10KT (Tinius Olsen) machine equipped with a 5 kN or 10 kN load cell. The cross head speed was 5 mm/min and the holders distance apart was 64 mm. A minimum of 4 or 6 specimens was tested for each combination of fibre alignment type and load. Standard deviation and mean values were calculated.

For tensile testing 150 mm long dog bone shaped specimens were tested on the same testing machine using a 10 kN load cell and an mechanical extensometer. At least five specimens were tested in the tensile test. Standard deviation and mean values were calculated.

Charpy impact tests were performed using Zwick pendulum type mechanical impact testing machine with 5 J pendulum capacity (Zwick GmbH) according to ISO 179 standard. The un-notched specimens were placed for edgewise impact. Minimum of 10 specimens were tested and mean value and standard deviations were calculated for each material.

Scanning electron microscopy of the laminate cross-sections was done using AIS2100 (Seron Technology) at 20 kV accelerated voltage after the specimens were sputtered with a layer of gold.

For the aging under humid conditions only the viscose composites with 0°/90° alternating lay-up and a fibre ratio of 65 wt-% were tested. The specimens (30 mm length, 10 mm width) were placed in a climate chamber (HPP 108/749 supplied by Memmert GmbH) at 50 ℃ and 85 % relative humidity for 1000 h. The aged specimens were then tested by tensile testing to determine the effect of humidity on the mechanical properties. In the moisture absorption test, the specimen weight was measured before placing in the climate chamber and after keeping in the chamber for 1, 7 and 40 days. Moisture absorption was estimated as the percentage of weight increase from the weight of sample after the moisture absorption and the weight of the dry sample.

The composites made from the flax fabrics were also characterized by DSC and TGA analysis according to the methods given in chapter 4.1.3.

4.2.4   Results

4.2.4.1 Flexural testing
The flexural properties for all made composites are listed in Table 6. The results (Paper II) showed that composites made from the warp-knitted viscose reinforcement can be produced with up to 70 wt-% fibre load for both the unidirectional and bidirectional fibre alignment, while the non-woven viscose reinforcement can be produced with up to 65 wt-% fibre load. Higher fibre load gave no significant improvement of the strength; instead laminates with partly dry areas were obtained. For the flax/basalt reinforcement (Paper IV), it can be produce up to 60 wt-%, while the flax reinforcement can only be produced to 40 wt-%. Increase in fibre load of the flax reinforcement will cause a decrease in the flexural properties. The result also showed that the flax/basalt reinforcement with 60 wt-% fibre load have the highest flexural modulus, with about 2.5 GPa higher than the warp-knitted viscose reinforcement of 70 wt-% fibre load. In the case of the flexural strength, the warp-knitted viscose reinforcement was exceedingly higher with about 160 MPa than the flax/basalt reinforcement.

Table 6. Mechanical properties for all composite types studied.

Composite Type	Fibre Alignment	Fibre content (wt-%)	Tensile Modulus (GPa)	Tensile Strength (MPa)	Flexural Modulus (GPa)	Flexural Strength (MPa)	Impact Resistance (kJ/m^2)
Warp-knitted viscose/GLA	Unidirectional (UD)	65	11.5 (±1.44)	202 (±6.02)	9.9 (±0.32)	217 (±24.62)	132.2 (±30.28)
		70	13.1 (±2.69)	214 (±1.72)	11.6 (±1.21)	228 (±22.19)	148.6 (±29.29)
		75	14.2 (±1.47)	223 (±6.57)	11.3 (±0.46)	223 (±13.71)	110.9 (±16.47)
	Bi-directional (BD)	65	7.0 (±0.62)	83 (±12.34)	5.1 (±0.44)	100 (±2.25)	97.2 (±13.58)
		70	7.9 (±1.83)	107 (±6.52)	6.5 (±0.24)	135 (±4.03)	113.5 (±12.90)
		75	8.5 (±1.09)	114 (±1.72)	5.9 (±0.31)	114 (±24.13)	91.1 (±10.10)
Non-woven viscose/GLA		65	7.5 (±0.53)	85 (±6.02)	6.1 (±0.64)	128 (2.66)	14.0 (±2.40)
		70	5.5 (±0.55)	63 (±10.40)	5.3 (±0.30)	102 (±7.48)	19.5 (±2.26)
		75	5.2 (±1.63)	58 (±29.30)	5.2 (±0.56)	93 (±15.53)	20.0 (±3.96)
Flax/Basalt/ PMLA		40	10.3 (±0.36)	78.3 (±12.17)	10.9 (±0.66)	58.3 (±3.73)	46.0 (±8.71)
		50	10.9 (±1.17)	87.9 (±10.61)	11.4 (±0.90)	67.4 (±12.12)	53.8 (±7.88)
		60	11.6 (±0.94)	90.7 (±15.58)	14.1 (±0.23)	75.2 (±9.97)	49.5 (±10.91)
Flax/PMLA		40	4.8 (±1.65)	32.1 (±6.08)	9.9 (±2.01)	86.2 (±4.67)	33.2 (±3.58)
		50	3.3(±1.30)	25.4 (±1.19)	6.4 (±0.79)	42.6 (±7.92)	31.1 (±3.62)
		60	4.0 (±0,99)	28.9 (±2.13)	6.7 (±0.77)	49.7 (±4.86)	32.2 (±5.56)

4.2.4.2 Tensile testing

Table 6 shows tensile modulus and tensile strength at break for the different composite types. The tensile modulus and strength increases with increasing fibre load from 65 to 75 wt-% for the unidirectional and bidirectional viscose composites (Paper II). For the non-woven composites a decrease in tensile strength and moduli was obtained, which also agrees with the results from the flexural testing indicating it is not possible to use higher fibre ratios than 65 wt-%. For the flax/basalt reinforcement (Paper IV), the tensile modulus and strength increases with increasing fibre load from 40 to 60 wt-%. A decrease in tensile modulus and strength with increasing fibre load from 40 to 60 wt-% for the flax reinforcement was observed, which agrees with the flexural result. The result also showed that the flax/basalt reinforcement have comparable tensile modulus with the warp-knitted viscose reinforcement, while in the case of the tensile strength, the warp-knitted viscose reinforcement was higher with about 132 MPa than the flax/basalt reinforcement.

4.2.4.3 Charpy impact resistance

A relatively high Charpy impact strength (Paper II) for the unidirectional viscose composites which increases with increasing fibre load from 65 to 70 wt-% and decrease when increasing fibre content to 75 wt-%. This can be interpreted as good adhesion between reinforcement and matrix which was confirmed by the SEM result. A lower Charpy impact strength was observed for the non-woven viscose composite, which can be interpreted as the fairly good adhesion between the reinforcement and the matrix. For the flax/basalt reinforcement (Paper IV), an increase in the Charpy impact strength was observed with increased fibre load from 40 to 50 wt-% but a slight decrease when fibre load was increased to 60 wt-%. In the case of the flax reinforcement that had a lower Charpy impact strength than the flax/basalt composite, a decrease in the Charpy impact strength with increase fibre load from 40 to 60 wt-% occurred. All results are listed in Table 6.

4.2.4.4 Dynamic mechanical analysis

Table 7 shows the storage modulus for all composite types with different fibre load. A considerable improvement in stiffness of viscose/GLA composites with the unidirectional alignment compared to the other composite was seen. The storage modulus of all the composites at room temperature is in a very good agreement with their flexural modulus, as expected. The strong increase in the storage modulus of unidirectional viscose/GLA composite can be interpreted as good adhesion between the fibre and the matrix. The results of the storage modulus of the flax/basalt composite have a better stiffness than the flax composite. The strong increase in the storage modulus of 60 wt-% fibre load of the flax/basalt composite can also be interpreted as good adhesion between the fibre and the matrix compared to the 40 wt-% and 50 wt-%. In the case of the flax composite, considering the standard deviation, no significant difference is seen between fibre loads.

The peak of tan delta for all the composites increased by increasing fibre content for almost all reinforcement types which are expected for a composite with good interaction between fibre and matrix.

Table 7. DMA results for all composite types.

Composite Type	Fibre Alignment	Fibre content wt-%	Peak of Tan Delta (ºC)	Storage Modulus at 25 ºC (MPa)
Warp-knitted viscose/GLA	Unidirectional (UD)	65	85 (±3.21)	18335 (±2.76)
		70	99 (±1.53)	16870 (±1.18)
		75	102 (±1.15)	13620 (±0.27)
	Bi-directional (BD)	65	99 (±7.94)	6453 (±0.38)
		70	97 (±1.73)	9239 (±0.19)
		75	102 (±1.73)	8257 (±0.88)
Non-woven viscose/GLA		65	88 (±2.00)	9200 (±0.84)
		70	102 (±2.08)	5743 (±1.13)
		75	106 (±4.58)	5360 (±0.07)
Flax/Basalt/PMLA		40	78.7 (±1.68)	4288 (±80.19)
		50	87.5 (±3.67)	4828 (±681.40)
		60	85.3 (±6.23)	6259 (±329.69)
Flax/PMLA		40	85.3 (±2.16)	3643 (±92.23)
		50	89.7 (±2.36)	3618 (±80.67)
		60	88.4 (±5.59)	3690 (±22.81)

4.2.4.5 Scanning electron microscopy

The SEM micrographs of the cross-sections of the composites were also investigated and are shown in Figure 17. The tensile-fractured viscose/GLA composite with 65 wt-% unidirectional warp-knitted reinforcement showed fairly good adhesion, while the 75 wt-% showed poorly impregnated fibres indicating too high fibre load. The non-woven reinforcement showed debonding between polymer and fibre for the 65 wt-% fibre load, indicating that the adhesion is not optimal. For the flax/basalt and flax composite, the knife-cut surface was investigated. The flax/basalt composite with 60 wt-% fibre load showed fairly good adhesion between fibre and the matrix compared to 40 and 50 wt-%. The flax composite showed poorly impregnated fibre with increasing fibre load. These results agree with the results of the mechanical properties of all the composites.
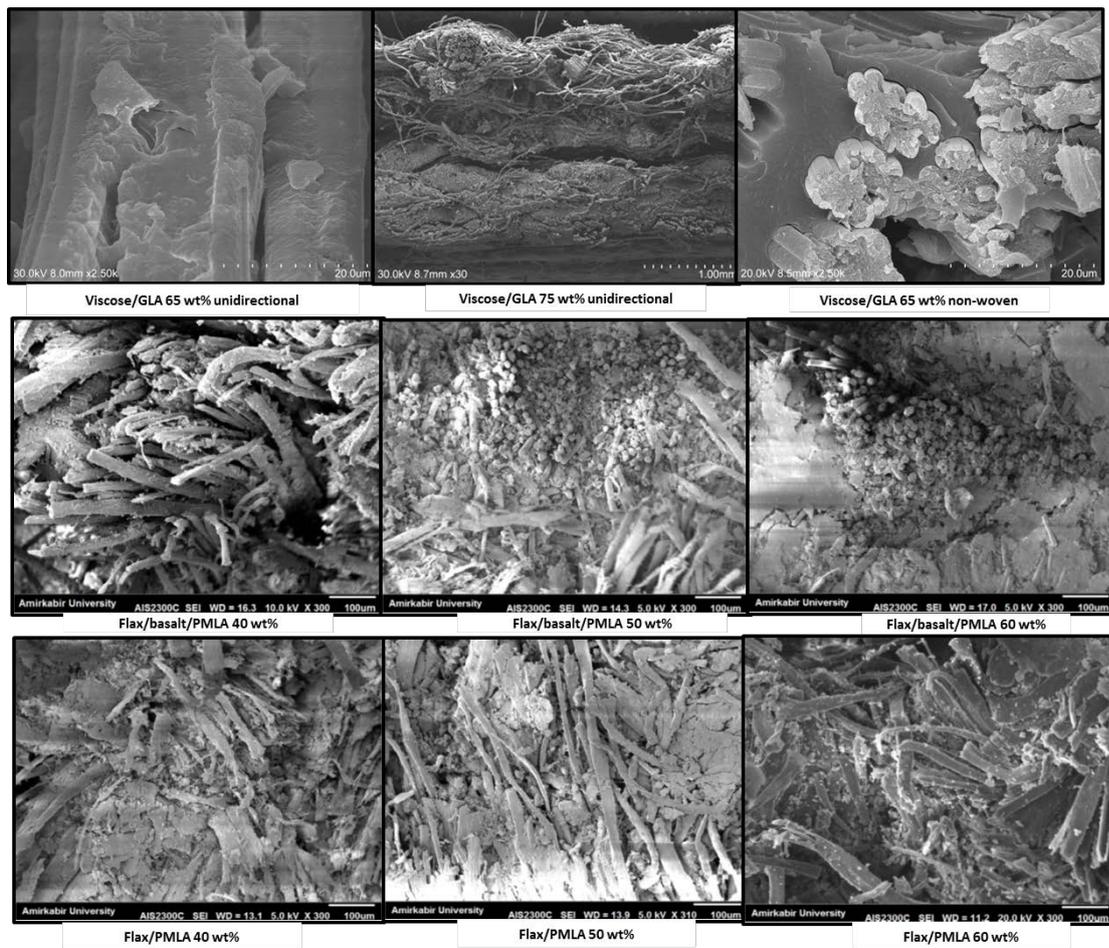
Figure 17. SEM micrographs of the cross-sections for the different composite types.

4.2.4.6 Ageing testing

Ageing test was performed to identify the optimal application fields of the made composites. This is done by subjecting the composite to accelerated ageing condition to make the composite reach the same aged end-state as a real time aged composite but in less time. Due to the evident effect of the ageing on the composite, the possibility of modifying the ageing behaviour of the resin and the composite were investigated. This was done by using styrene as a reactive diluent for the bidirectional composites with 65 wt-% fibre load, and then the mechanical properties and ageing behaviour of the composites were investigated. Also the ageing properties of the flax/basalt and flax composite were investigated.

The results showed in Figure 18 and 19 presents the tensile properties for bidirectional composites with 65 wt-% fibre load with and without added styrene before and after ageing, the flax/basalt and flax composites for all fibre loads. The properties were measured after a 24 h reconditioning at room temperature. For the 65 wt-% bidirectional composite, the tensile strength decreased dramatically after ageing but adding styrene considerably improved the composite`s ageing properties while ageing affect then tensile stiffness of the composites significantly but adding styrene preserved a small portion of the loss. The tensile properties for the flax/basalt and flax composites decreased dramatically after ageing but despite the decrease in the tensile modulus and strength of the flax/basalt composite, its properties were still better than the flax composite before ageing for all fibre loads.
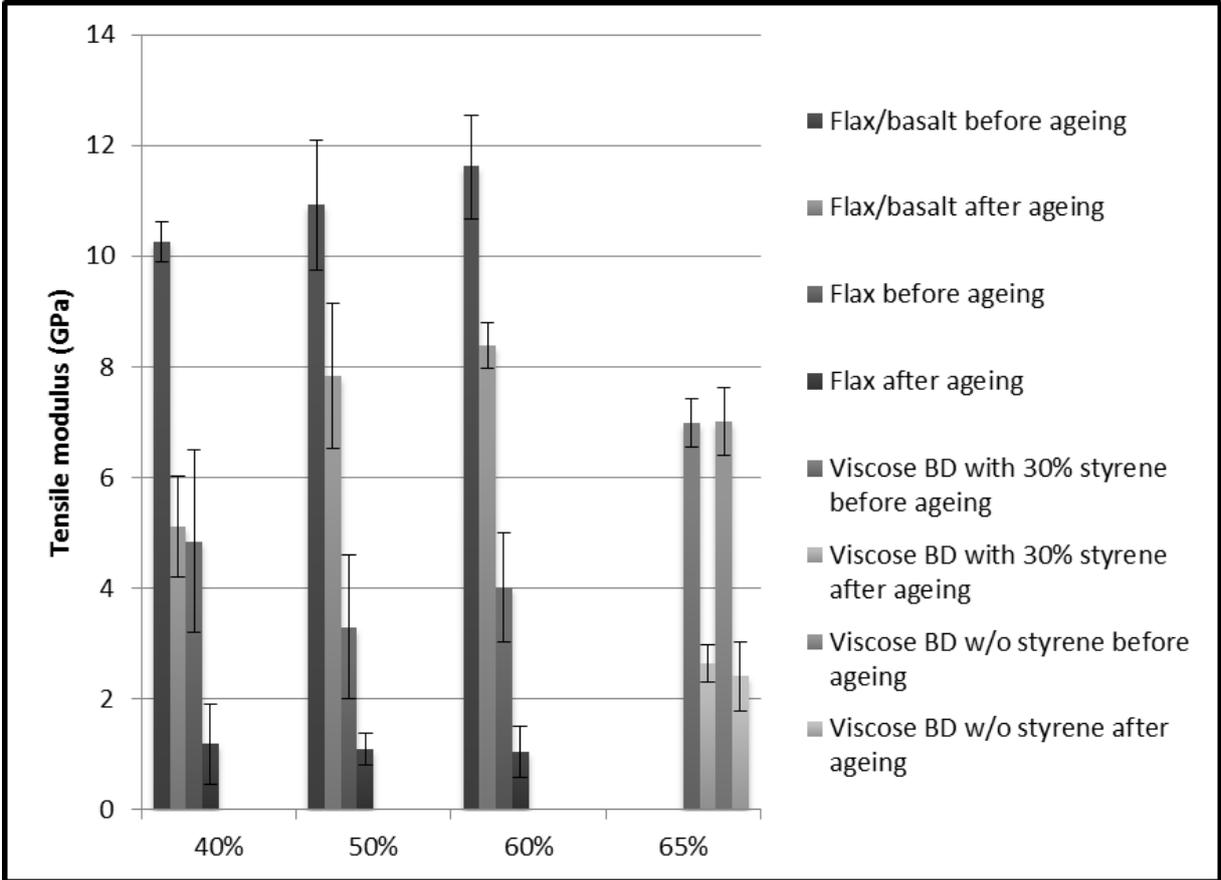
Figure 18. Tensile modulus of all composite before and after ageing in climate chamber.
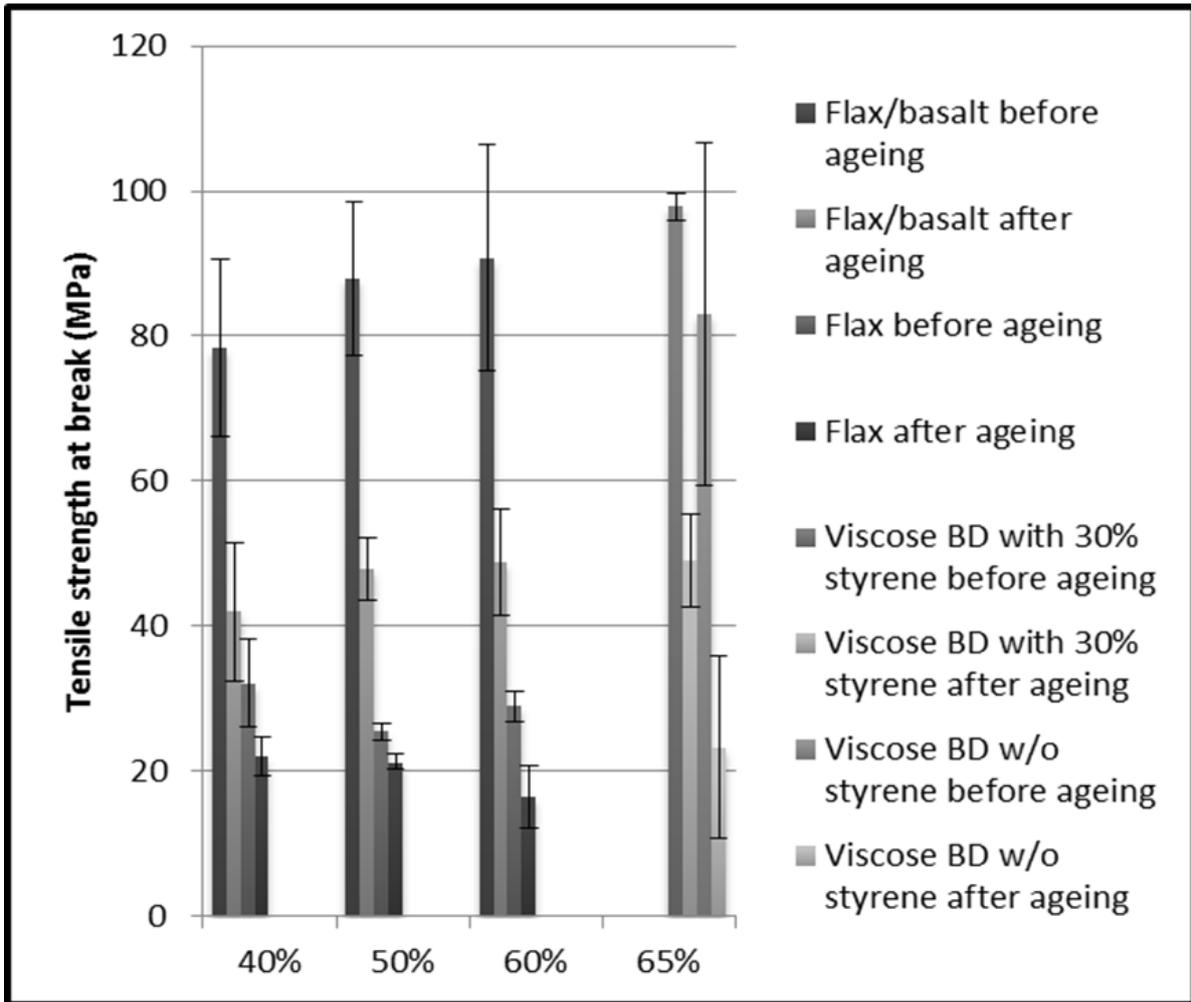
Figure 19. Tensile strength at break of all composite before and after ageing in climate chamber.

4.2.4.7 Water absorption testing

Figure 20 shows the variation of the percentage water absorption with increasing number of days for all fibre loads for flax/basalt composites, flax composite, 65 wt-% fibre load viscose bidirectional type composite with and without styrene. The water absorption in the composite with and without styrene increased rapidly by 7 % by day 2, but for the composite without styrene, there was also a rapid increase between day 2 and day 7 of about 3 %, but a small increase between day 7 and day 40. For the composite with styrene, there was about less than 1% increase in the water absorption between day 2 to day 40. The flax/basalt composite increased rapidly by 5.3 %, 6.2 % and 6.3 % for fibre load of 40 wt-%, 50 wt-% and 60 wt-% respectively by day 2, but for the flax composite a higher percentage of water absorption of 7.4 %, 7.5 % and 7.9 % for fibre load of 40 wt-%, 50 wt-% and 60 wt-% respectively was observed. Between day 2 and day 7, an increase of about 1% or less was observed for the fibre loads of flax/basalt composite while an increase of about 3 % was observed for the fibre loads for the flax composites. By day 40, an increase of water absorption in the range of 1.2 to 1.5 % was observed for both the flax/basalt composites and the flax composite.

After drying of the composites, there was a rapid decrease in the water uptake of the composite without styrene up to about -3 %, -2 % for the flax/basalt composite and about -3 % for the flax composites of its initial weight before it was placed in the climate chamber. This implies that some of the resin as also been washed off during drying but in the case of the composite with styrene, only about less than 1 % of the water uptake was removed.

Figure 20. Water absorption of all composite types.

4.3   Discussion and conclusions

Several reports have been made on the preparation of bio-based thermoset resins with different types of starting materials such as plant oil (soybean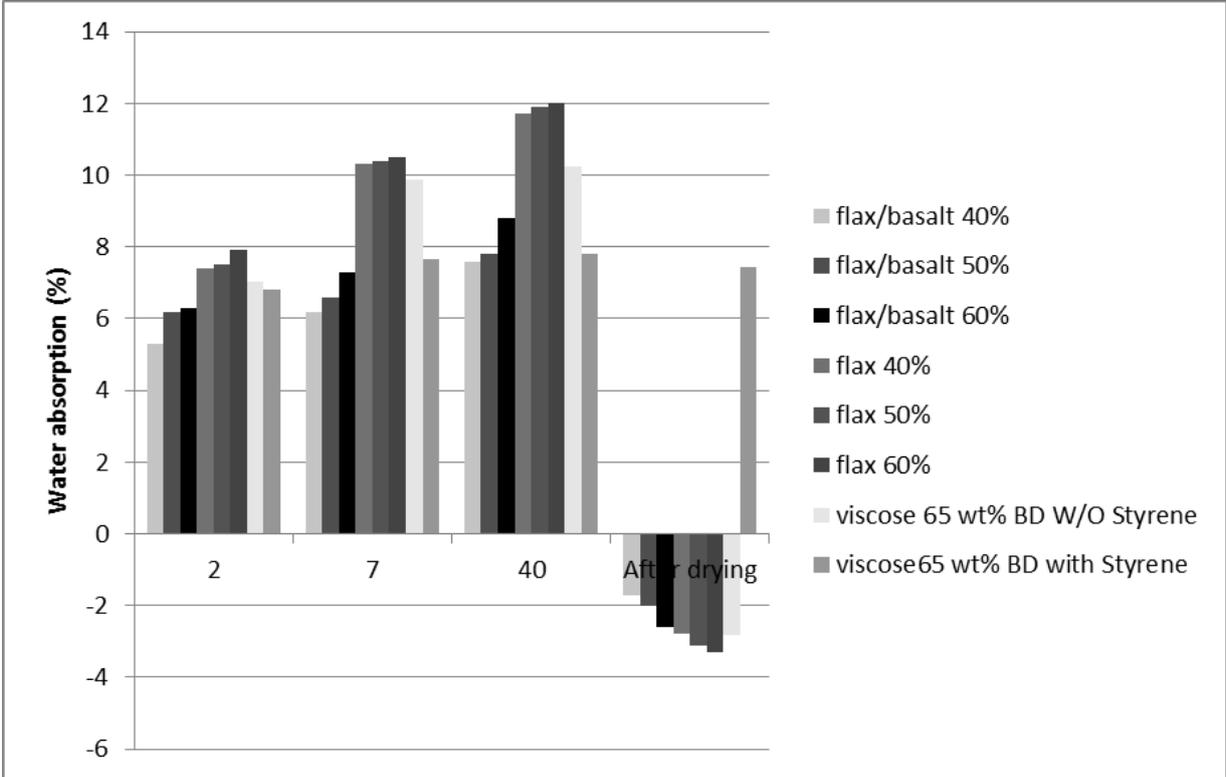 oil, linseed oil) and lactic acid/lactides. Based on these literatures a lot of reports have been written on the production of bio-based composite from soybean oil. Lactic acid and lactide based thermoplastic resins have been used in many biomedical applications but the use of this resin in composite production is relatively a new concept.

In this thesis, three different bio-based thermoset resin was prepared from lactic acid using glycerol (Paper I), allyl alcohol and pentaerythritol (Paper III) as reactant. The first resin with chain length of n = 3, 7 and 10 were synthesized in two synthesis stages. The first stage involved a the direct condensation of lactic acid with glycerol; in the second stage the obtained glycerol-lactic acid oligomers were reacted using methacrylic anhydride to obtain an unsaturated lactic acid polyester (GLA resin). The second resin involved a direct condensation of lactic acid with ally alcohol to form ALA resin; in the second stage this resin was reacted with methacrylic anhydride to obtain an unsaturated lactic acid based (MLA resin). The third resin type was synthesised by mixing the ALA resin with pentaerythritol and then end-functionalized with methacrylic anhydride (PMLA resin).

It was found out that the GLA resin with chain length n = 3 had a lower bio-based content of 78 % than for the resin with n = 7 and 10 but has better mechanical and rheological properties. The MLA and PMLA resin had a higher bio-based content of 86 % and 90 % respectively compared to the GLA resin. The glass transition temperature of PMLA resin and MLA resin was 113 ºC and 109 ºC respectively, which is higher than the GLA resin and the commercial polyester resin at 97 °C and 83 ºC respectively.

The bio-based thermosetting resins demonstrated in this thesis have shown promising mechanical, thermal and rheological properties. They are of high renewable ratio, which encourages the use of renewable reactants and they can compete with many commercial polyester resins. It is a straightforward, relatively cheap methodology and can be up-scaled for industrial production.

Composites have been prepared from these bio-based resin reinforced with natural and regenerated cellulose fibre, which increases the renewability ratio of the composites produced. The mechanical properties of the composites are very good and they can be used in some applications to replace conventional polyester reinforced composites. Based on the aging properties of the composite produced, they can be used for indoor applications such as interiors of automobiles or as furniture applications. These bio-based thermoset resins can possibly be used with synthetic fibres for outdoor application which can reduce its non-renewable ratio and give good mechanical properties. Considering the high renewable ratio of the bio-based resins, promising properties for making strong affordable, biodegradable and renewable resourced composite for many applications can be achieved.

4.4 Future studies

Bio-based composites are gaining increasing interest both in the industrial and academic sectors. They have increasingly found many useful applications commercially and a need to increase research in this sector will highly be encouraged. Further studies that will be established are;

- Using other synthetic methods in the preparation of lactic acid based thermoset resin in composite production in other to increase their potential in industrial applications.
- Due to the problems of aging and moisture absorption of the bio-based composites, other fibre treatments should be investigated to improve the matrix/fibre adhesion, thereby improving their mechanical properties.
- There have been several researches on the use of edible plant oils in the production of bio-based composites which are competing with food consumption. Further research should be made on using inedible plant oil (such as; rubber seed oil, jatropha seed oil) for resin productions.

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APPENDIX

Abbreviations

HCN	Hydrogen cyanide
H_2SO_4	Sulphuric acid
PLA	Polylactic acid
ROP	Ring-opening polymerization
AESO	Acrylated epoxidized soybean oil
MSO	Methacrylated soybean oil
MMSO	Methacrylic anhydride-modified soybean oil
AMSO	Acetic anhydride-modified soybean oil
ESO	Epoxidized soybean oil
RTIL	Room-temperature ionic liquid
DMSO	Dimethyl sulfoxide
DMAc	LiCl/N,N-dimethylacetamide
DMI	LiCl/1,3-dimethyl-2-imidazolidinone
MAESO	Maleinized acrylated epoxidized soybean oil
SOPERMA	Soybean pentaerythritol maleates
MMA	Methyl methacrylate
TPGDA	Tripropylene glycol diacrylate
RTM	Resin transfer moulding
SEM	Scanning electron microscopy
GLA	Glycerol/lactic acid resin
MLA	Methacrylated allyl alcohol/lactic acid resin
PMLA	Methacrylated pentaerythritol/lactic acid resin
NMR	Nuclear magnetic resonance
^{13}C-NMR	Carbon 13 nuclear magnetic resonance
^{1}H-NMR	Proton nuclear magnetic resonance
DSC	Dynamic scanning calorimetry
TGA	Thermogravimetric analysis
DMA	Dynamic mechanical analysis
FT-IR	Fourier transform infra-red
UPE	Unsaturated polyester resin

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.

Synthesis of polymers from renewable origin has been reported by many authors and it has been found out that it has enormous potential and can serve as alternative to conventional thermoplastics and thermosets in many applications. The use of these renewable resources will provide sustainable platforms to substitute fossil fuel-based materials. To date, efforts made to produce 100% bio-based thermosetting materials have yet to be achieved. Many studies have been reported on increasing the renewability ratio of thermoset materials produced.

A lot of reports have been made on the synthesis of thermoplastic resins from lactic acid for biomedical application and tissue engineering but few reports have only been made for composite applications. The issue of high melt viscosity of resin from lactic acid has been of paramount problem because of its difficulty in impregnation into fibre reinforcement. Biobased thermoset resins have been produced for composite applications from plant oils and improved mechanical properties are achieved.

In this thesis, alternative route for synthesis of lactic acid based thermoset resin have been explored to solve the above problem. Thermoset resins were synthesized from lactic acid with different co-reactants and were characterized using NMR, FT-IR, DSC, DMA and TGA. Their rheological properties were also investigated. The resins were reinforced with natural and regenerated cellulose fibres in non-woven and woven form, and with different fibre alignment and fibre loading. The resulting composites were characterized by mechanical testing regarding tensile, flexural and impact strength, and by SEM analysis regarding morphology.

The results showed that these composites could possibly be used in automobile, transport, construction and furniture applications, particularly for interior purposes. The resins produced were found to be promising materials for composite production due to the good mechanical properties achieved.

Keywords: lactic acid, thermoset resin, renewable resources, natural fibre, regenerated cellulose fibre, composite