CHALMERS

Modification of Natural Fibers for Use in Green Biocomposites

The Effect of Chemical Surface Modification

A Bachelor’s Thesis within Chemical Engineering

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DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING
CHALMERS UNIVERSITY OF TECHNOLOGY
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Cover: Dog bones reinforced with modified and unmodified fibers.

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SAMMANFATTNING

Kompositmaterial är en lösning till övergången till helt förnyelsebara material eftersom de radikalt minska användningen av fossila råmaterial. De är vanligtvis en kombination av fossila och förnyelsebara material, men de finns potential att göra dem helt förnyelsebara. Naturliga fibrer har blivit allt populärare som förstärkning i kompsitematerial, men de behöver förbehandlas innan de används för att få en bra vidhäftning. I denna studie studerades effekterna av ytbehandlingar av naturliga fibrer, såsom esterifiering och sampolymerisering, samt mekaniska egenskaper hos naturliga-fiber/PLA-kompositer. Metoderna för ytmodifikationerna skalades upp för att se om liknande resultat som på liten skala uppnåddes. De ytmodifierade fibrerna analyserades av Fourier transform infraröd spektroskopi, termogravimetrisk analys, tepåse-test och dragprovning. Det visades att ytmodifieringar hade olika effekter på hydrofobiciteten, trots att alla metoder lyckades på liten skala. Acetylerade och vattensvullnad DAA förestrade fibrer hade en ökning av vattenabsorptionskapaciteten, vilket indikerar en ökad ytarea, medan sampolymeriserade och alkaliska svullna DAA-esterifierade fibrer hade en minskade absorptionsförmåga, vilket indikerar en ökad hydrofobicitet. Dragspänningen, elasticitetsmodulen och styvheten hos kompositerna ökade vid användning av modifierade fibrer som förstärkning.

ABSTRACT

Composite materials are one solution to completely transition from fossil raw materials to renewable material. They are usually a combination of fossil and synthetic fiber materials, but there are opportunities to make them completely renewable and bio-based. Natural fibers have become increasingly popular as reinforcements in composite materials, but they must be pretreated before use, so they obtain a better adhesion to the matrix material. In this study, the effects of natural fiber surface treatments, such as esterification and copolymerization, was studied as well as the mechanical properties natural-fiber/PLA composites. The modifications were also scaled up to see if similar results as on small-scale was obtained. The surface modified fibers were characterized by Fourier transform infrared spectroscopy, thermogravimetric analysis, tea bag test and tensile testing. It was demonstrated that surface modifications had different effects on the hydrophobicity, despite all methods being successful on small-scale. Acetylated and water swollen DAA esterified fibers had an increase in water absorption capacity, indicating an increased surface area, while copolymerized and alkali swollen DAA esterified fibers decreased its absorption capacity, indicating an increased hydrophobicity. The tensile stress, Young's modulus and stiffness of the composites increased when using modified fibers as reinforcement.

Keywords: Natural fiber; PLA; chemical surface modification; interfacial adhesion

LIST OF ABBREVIATIONS

AA – Acetic Anhydride

AGU – Anhydroglucose Units

DAA – Diketene–Acetone Adduct

TGA – Thermogravimetric Analysis

DTG – Derivative Thermogravimetric

FTIR – Fourier Transform Infrared Spectroscopy

PLA – Polylactic Acid

DS – Degree of Substitution

DP – Degree of Polymerization

ATR – Attenuated Total Reflectance

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1 INTRODUCTION

1.1 BACKGROUND

Some of the most discussed topics nowadays are climate change and the ever-increasing amounts of plastic waste. The effects of these environmental hazards can be devastating, both to mankind and nature. To combat this, there have been substantial efforts to increase the content of renewable and recyclable materials worldwide, even undertaking the ambition to develop completely renewable and/or green CO_2-neutral materials. To achieve such a feat, research and development must be done before they can be implemented and compete with non-renewable materials on a grand scale. When it comes to plastics, bio-based polymers such as thermoplastic starch and polylactic acid are extensively studied and has become more competitive in cost and performance, although not adequate to fully compete with polymers derived from fossil fuel. One approach to this problem is to include inexpensive natural fibers as fillers, decreasing the environmental impact of traditional plastics and making the expensive bioplastics more economically viable. When doing this, the fibers can act as reinforcement, turning the plastic into a composite material (*Šumigin, D. et al.*, 2012).

Composite materials have the advantage of enhanced properties (e.g. mechanical and chemical) as a result of the combining of two different raw materials. This opens new doors since the material properties of composite can be adapted and tailored for the endues. Natural fibers based on cellulose has in recent time been explored as a reinforcement material in composites. It is one of the abundant biopolymers on earth and has some desirable qualities like being biodegradable as well as good thermal and mechanical properties. However, to make a good composite the interfacial adhesion is of utmost importance; neglecting this aspect will avert any improvement (*Murariu, M., & Bubios, P.*, 2016). Unfortunately, cellulose is hydrophilic in nature, resulting in poor adhesion with the most common matrix materials which are hydrophobic. As a consequence, modification of cellulose (chemically or physically) has to be done to overcome this – making it more hydrophobic. This is, however, complex to understand and accurately predict how such modifications will affect the material's structure and properties.

1.2 PURPOSE SPECIFICATION AND SCOPE

The aim of this thesis is to manufacture biocomposite material with PLA (polylactic acid) as matrix material and cellulose-based natural fibers as reinforcement, and to study the effects of surface treatments on natural fibers and mechanical properties of natural-fiber/PLA composites.

The thesis has the vision to use the modified fibers in prototypes the modifications done will start from scalable processes and chemicals. Due to the many alternatives and time constraints only three modifications will be explored − first on smaller scale, then proceeding to scale-up each modification. The fibers are going to be surface modified through either esterification reactions with different reagents or via grafting and polymerization. The aim of the surface modifications is to increase the adhesion of fiber material to the matrix polymer, and thus, also improve mechanical properties of the composite material. The limited time frame for this thesis project, only a few theories, reactions, properties and aspects can be considered and explored. Consequently, the instruments to validify and verify the results will also be limited, and therefore FTIR will be the main analysis method that decisions will be based on.

2 THEORY

This section will introduce theoretical aspects of the experiments, materials and instruments that were used during this thesis.

2.1 Cellulose and Natural Fiber Composition

Cellulose is one of the amplest organic compounds on our planet and is a major structural component of the cell wall in plans (e.g. wood, cotton, and bamboo). It was discovered in the 19th century but have been used for many thousands of years with records of ancient Chinese as well as Egyptian civilizations utilizing it (*Mwaikambo, L.Y.*, 2006).

Cellulose is a linear polysaccharide consisting of D-glucose units linked together with covalent bonds called *β*-1,4-glycosidic bonds. The glucose units are also known as anhydroglucose units (AGU), which are rotated 180° with respect to its neighbor. Two AGUs bonded together is known as cellobiose, the basic repeating unit of the cellulose polymer. The ends of the polymer chain are chemically different and are referred to as a non-reducing and reducing end. On the non-reducing endthe anomeric carbon is involved in the glycosidic linkage, whereas on the reducing end the anomeric carbon is free to react and form an aldehyde; both states of the reducing end being in equilibrium (*Olsson, C., & Westman, G.*, 2013, *Roy, D. et al.*, 2009).

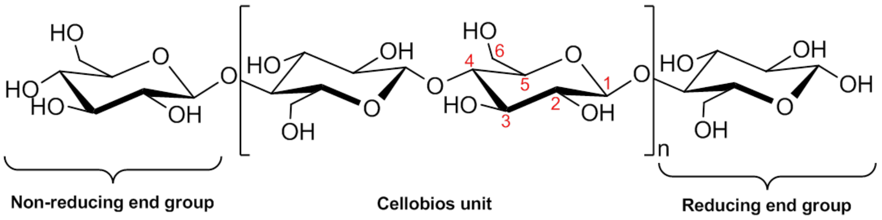

Figure 1. A schematic figure of the structure of cellulose.

As seen in Figure 2, the hydroxyl groups on cellulose are capable of forming extensive inter- and intramolecular hydrogen bonds, which is why the linear chain structure arises in cellulose. Furthermore, the linear structure is the reason for its tendency to have a high crystallinity (*Roy, D. et al.*, 2009).

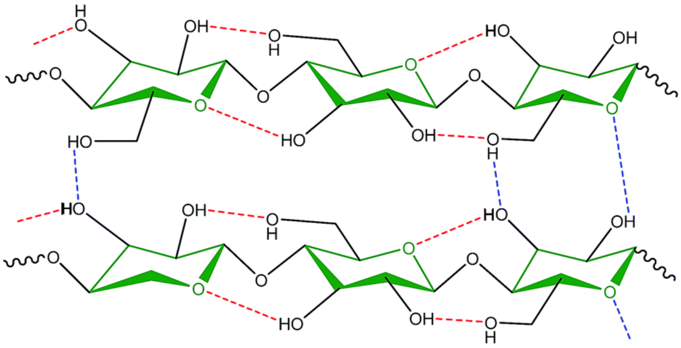

Figure 2. Structure of ordered cellulose chains showing the inter- and intramolecular bonds (blue and red respectively).

Due to the morphology, degree of crystallinity, steric hindrance of the supramolecular structure etc. of cellulose, the countless hydroxyl group on throughout the chain has different reactivity. The primary hydroxyl group at carbon 6 can rotate freely around its axis, making it have the highest reactivity, while the two secondary hydroxyl group at carbon 2 and 3 are more constrained and thus having lower reactivity (*Roy, D. et al.*, 2009). The degree of substitution (DS) is defined as the average number of substituted (reacted) OH-groups per AGU. of 3.0 is the highest average, due to there only being three hydroxyl groups on each AGU, however, due to the supramolecular structure of cellulose fibers some of the hydroxyl groups cannot react, and thus a DS of 3.0 is impossible. This will in turn imply that the DS is unevenly distributed throughout the fiber, considering DS being an average number (*Brodin, M.*, 2013).

To increase the DS and make the hydroxyl groups more reactive, cellulose can undergo an activation treatment. Activation can be done in a number of ways such as opening the surface structure and decrease the degree of crystallinity (i.e. make it more amorphous). The most common and frequently used method is swelling, where the swelling agent penetrates the crystalline regions, splitting the bonds between the polymer chains and fibrils (*Roy, D. et al.*, 2009). Moreover, swelling can be used for dissolution of fibers, which is not desirable in some cases. It has been found that dissolution and swelling coincides, however, to different degrees described with five modes (states): (i) fast dissolution by disintegration into fragments (ii) large swelling by ballooning and complete dissolution (iii) large swelling by ballooning and no complete dissolution (iv) homogeneous swelling and no dissolution (v) no swelling and no dissolution.

What determines the mode attained is mostly attributed to agent used, either swelling or solvating agent. The difference between swelling and solvating agents is the quality of the solvent used and is reflected in such a way that the best solvents act as solvating agents and attain dissolution, while poor solvents act as swelling agents and homogeneously swells the cellulose (*Cuissinat, C., & Navard, P.,* 2006).

Natural fiber, just as cellulose, is a plentiful resource found in throughout the world and has been used by mankind for over 10 000 years. They stem from renewable recourses and are biodegradable, making them an attractive environmentally friendly option to substitute inorganic fibers. The term natural fiber includes fibers from of plant, animal, and minerals, however, in this thesis it refers to fibers from plant.

The many plant species from which natural fibers can be produced has different structures and chemical compositions, resulting in a variety of different characteristics such as degree of polymerization (between 7 000 – 15 000 depending on the plant species) and types of fibers. The fibers are the dominant tissue type in plants being distributed randomly or organized patterns through the plant. They are built from microfibril which are ingrained by a matrix of complex macromolecules (e.g. cellulose, hemicellulose, pectin, lignin) (*Müssig, J.,* 2010). The complex structures they form also contains small amounts of organic compounds (extractives) and inorganic compounds (ash) that can have major impacts on its properties like odor and decay resistance (*Xanthos, M.,* 2010). The chemical composition of these macromolecules for some common fiber sources are listed in Table 1.1.

Table 1.1. Chemical composition of selected natural fibers (*Mwaikambo, L.Y.,* 2006).

Species of Plant	***Cellulose [%]***	***Hemicellulose [%]***	***Lignin [%]***	***Pectin [%]***
Flax	60-81	14-19	2-3	0.9
Jute	51-84	12-20	5-13	0.2
Cotton	82-96	2-6	0.5-1	5-7
Ramie	68-76	13-15	0.6-1	1.9-2
Kenaf	44-57	21	15-19	2
Wood	45-50	23-30	27	2-2.5

Plants cells, the building block of plants, have a cell wall protecting the living parts of the cell. The cell wall consists of several different layers of varying thickness and chemical composition, however, there are only two parts of the cell wall – primary and secondary – which these layers belongs to (as is shown in Figure 3). The latter is the thickest of the two cell walls, consisting of many layers with distinct fibril orientations, while the former being a thinner cell wall, consisting of microfibrils with an irregular pattern, enveloping the cell and secondary wall from the “outside”.

When natural fibers are used as reinforcement, the secondary wall predominantly affects the fibers strength due to its substantial size (*Müssig, J.,* 2010, *Yan, L., Chouw, N., & Jayaraman, K.,* 2014).

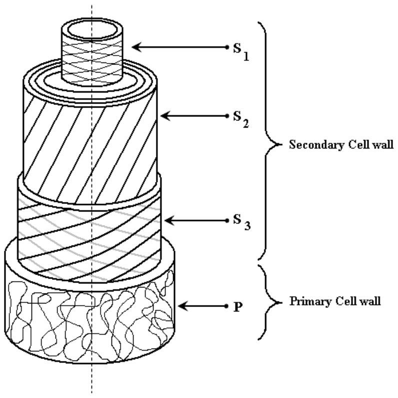

Figure 3. Schematics of the cell wall structure for flax fiber. (*Yan, L., Chouw, N., & Jayaraman, K.,* 2014)

2.2 MODIFICATION OF CELLULOSE

Due to the hydrophilic nature of cellulose, and natural fibers, it introduces major issues in matrix-fiber adhesion when used as reinforcements in composites. Additionally, cellulose has poor solubility in common solvents, and does not melt without degrading. To overcome the issues, it is favorable to (i) chemically modify (ii) physically modify the fibers, or (iii) use a hydrophilic matrix material (*Baiardo, M. et al.,* 2001).

A variety of chemical modifications has been done throughout the decades where the aim has been to substitute the hydroxyl groups on the surface of the cellulose fibers to more hydrophobic functional groups. Acetylation has been the most studied reaction and has been done for both natural fibers and wood/pulp.

2.2.1 Esterification of Cellulose

There are several different methods to produce cellulose esters such as acetylation, alkyl ketene dimer sizing, acetoacetylation etc. Nonetheless, esterification is generally an alcohol reacting with an acid to produce an ester and water (seen in Figure 4). Ester formation is classified as a condensation reaction, where one large molecule and one small molecule is formed; the former one being the desired product and the latter one being the byproduct that is condensed (*Atkins, P., & Jones, L.,* 2013). Esterification is in equilibrium and the procedure can be altered to favor one side of the reaction with Le Chatelier’s principle. To increase ester formation, the reaction can be heated, producing water vapor, or increasing the concentration of acid or alcohol (*Daintith, J.,* 2008).

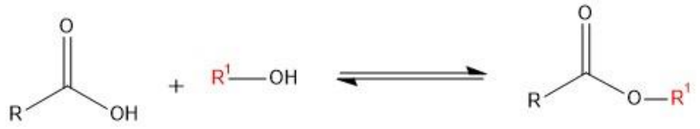

Figure 4. A general esterification reaction between carboxylic acid and alcohol (*Atkins, P., & Jones, L.,* 2013).

2.2.2 Ultraviolet-radiation Induced Graft Copolymerization

Grafting of copolymers onto cellulose has in recent decades become a viable synthesis path in regard to more traditional methods. Graft copolymerization has the advantage of being highly tailor-made for the specific end use and yield specific properties onto the cellulose fibers without destroying the properties of the native material.

A copolymer has a backbone, made up from one monomer, with branches grafted onto the backbone made up from one or more different monomers. The cellulose fibers act as the backbone polymer, and branches of polymerized monomer are grafted onto the backbone. The methods of achieving the grafting process can be split into three major groups, each with its own subgroups: (i) free radical polymerization (ii) ionic and ring opening polymerization (iii) living polymerization (*Roy, D. et al.,* 2009).

UV-radiation induced grafting is a free radical polymerization which is done with the grafting-from approach. The initiation of forming free radicals on the backbone of the cellulose polymer is done through irradiation of UV-radiation. This allows monomers to form covalent bonds to the free radicals, and the free radical is moved to the newly formed monomer branch. Propagation of the branches (the growth of the branches) will be allowed to continue until it is terminated. The formation of the free radicals is generally slow, and thus, photoinitiators are commonly used to accelerate the formation of free radicals when exposed to UV-radiation (*Roy, D. et al.,* 2009).

2.3 CELLULOSE REINFORCED POLYLACTIC ACID COMPOSITES

Polylactic acid (PLA) is one of the most commonly used bioplastics. It is an aliphatic polyester, more specifically, a polymer of lactic acid or lactide, which can be synthesized from petrochemicals or renewable biomass; the latter route is presently the most preferred method, as it is more environmentally friendly. PLA is classed as a thermoplastic polymer, meaning that the polymer can hold its shape at room temperature, however, when heated to elevated temperatures it becomes viscous and thus can be remolded (*Painter, P. C., & Coleman, M. M.,* 1997). PLA is still quite unexplored due to it being implemented in applications recently and has mainly been used in pharmaceutical and medical applications – as a result of its high cost and low availability. However, new strides in the production of PLA has made it available for lower prices resulting in it being used in the packaging and textile sector. PLA has the impressive mechanical properties, even having higher tensile strength and Young's modulus than common polymers like polyethylene and polypropylene (*Murariu, M. & Bubios, P.,* 2016).

In general, composites are man-made multiphase materials (consisting two or more different raw materials that are chemically dissimilar and have different interfaces) exhibiting properties of both constituents such that better properties are obtained. For polymeric composites, reinforcement with different types of fibers (glass, carbon or natural) are done to obtain the strength while still preserve the excellent toughness and flexibility of the matrix (*Callister, W. et al.,* 2014). PLA composites are greatly benefitted by the addition of fibers, increasing its strength, thermal stability and stiffness while still maintaining specific properties like biodegradability and remolded when above melting temperatures (*Murariu, M., & Bubios, P.,* 2016). In spite of the improvements, the introduction of fibers can negatively affect the interfacial adhesion with the usage of a hydrophobic matrix, as a result of natural fibers being hydrophilic. Moreover, the high moisture absorption of natural fibers also affects the interfacial adhesion negatively, consequently by the volume increase and the poor interactions with water (*Xantos, M.* 2010, *Murariu, M., & Bubios, P.,* 2016). As a consequent, the poor adhesion results in an insufficient stress transfer, and thus, making the composites weak. To counteract the poor cohesion, the cellulose fibers is modified.

2.4 NATURAL FIBER MODIFICATIONS REAGENTS

In this section a short reaction theory description is done for the different cellulose modification reagents used in the experiments.

2.4.1 Acetic Anhydride

Acetic Anhydride (abbreviated to AA) is a common acetylation reagent that reduces the polarity of hydroxyl, thiol and amino groups. Despite this, there are some inherent issues when using it as reagent. It has been found that acetic anhydride requires a catalyst (like perchloric acid or sulfuric acid) or pre-activation to reach adequate levels of acetylation (*Akim E.L.,* 1967, *Smith, K. et al.,* 2003). Traditionally, solvents suitable of handling acids are used because of the byproduct acetic acid generates during the acetylation reaction. Preparation of modified fibers via acetylation was based on methods from (*Wahbi, A. K., Galil, F. & Kamel, A.,* 1969).

2.4.2 Diketene–Acetone Adduct

Diketene-Acetone Adduct (also known as 2,2,6-trimethyl-4H-1,3-dioxin-4-one or DAA formed from a reaction between diketene and acetone, hence the name. It is stable at room temperature, however, at temperatures above 100 °C the molecule is known go through pyrolysis (decomposition) yielding an acetone and acetylketene. It has been shown that the resulting acetylketene has the ability to acetoacetylate (a type of esterification) in the presence of a variety of nucleophiles (e.g. aromatic and aliphatic alcohols, and thiols). This reaction is rapid, requiring no catalyst, and only generating volatile byproducts (*Hyatt, J., Feldman, P., & Clemens, R.*, 1984, *Pawlowski, W. et al.*, 1986). When an acetylketene is in the presence of cellulose, the hydroxyl groups on the AGUs acts as nucleophiles resulting in the formation of β-ketobutyric acid cellulose ester seen in figure 5. The preparation of esterification Using DAA as a reagent was based on procedures done by (*Brodin, M.*, 2016).

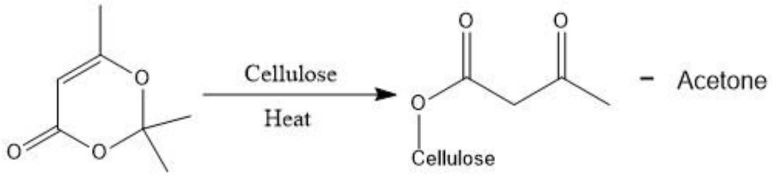

Figure 5. Acetoacetylation of cellulose producing β-ketobutyric acid cellulose ester and acetone (*Hyatt, J., Feldman, P., & Clemens, R.* 1984).

2.4.3 Trimethylolpropane Triacrylate

Preparation of modification via UV-induced grafting of Trimethylolpropane Triacrylate (TMPTA) was based on work done by (*Börjesson, M.*, 2013). A simplified mechanism for how the grafting occurs is seen in Figure 6. TMPTA is a trifunctional monomer with low viscosity liquid monomer commonly polymerized via free radical polymerization. As a result of the three double bonds, TMPTA typically polymerize rapidly. When cured poly-TMPTA offers resistance against weather, water and chemicals (*Khalid, M. et al.*, 2008). It has been found that TMPTA has similar characteristics as other multifunctional monomers, namely trapped radicals in the product due to steric hindrance and prevalent diffusion-controlled termination. The grafting rate of TMPTA is affected by the mass percentage of the reaction system; the higher the mass percentage of TMPTA in the system the higher grafting rate. However, when the mass percentage exceeds 20 wt.% the rates of grafting was limited as a result of radical trapping and diffusion-controlled termination (*Wang, L. et al.*, 2007).

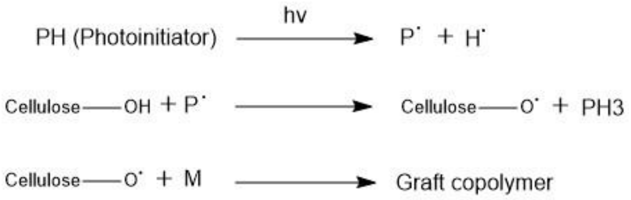

Figure 6. A simplified mechanism for the grating of TMPTA on to cellulose. The TMPTA is presented as M, and the final product is presented as the graft copolymer (*Roy, D. et al.,* 2009).

2.5 ATTENUATED TOTAL REFLECTANCE – FOURIER TRANSFORM INFRARED SPECTROSCOPY

Fourier Transform Infrared spectrometer (FTIR) is a widely used instrument – due to its multitude of ability to analyze practically any sample in any state – to see what molecules are present in a sample as well as its concentration (*Fan, M., Dai, D. & Huang, B.,* 2012). The spectrometer does this by emitting a beam of infrared radiation (light) and measuring how the sample absorbs it. The wavelength of the infrared radiation beam that is emitted can have a large range of wavelengths and has thus been split up into three regions: (i) near infrared (ii) mid infrared and (iii) far infrared. Generally, when using a FTIR the mid infrared region (4000 – 400 cm^{-1}) is used due to most organic and inorganic molecules having their absorption radiation inside this region. When a sample is exposed to the infrared radiation, the molecules in the sample absorbs the radiation of specific wavelengths which in turn change its dipole moment and cause it to vibrate (either stretch, bend, or contract). All molecules have its own complex frequency of vibration, due to their difference in structure, which can be broken down to constituent vibrations that are easier to analyze. The absorbed energy from the radiation transitions the energy level from a ground state to an excited state, and it is the gap between the stated that determines the peaks absorbance frequency. The intensity of the absorption peak is influenced by the change in dipole moment with respect for distance. The energy level gap is represented as wavenumber or wavelength (cm^{-1}) at the x-axis, displaying which functional groups, molecules, and bonds that are present. The intensity is represented as absorption or transmittance at the y-axis, displaying the concentration of the respective functional groups, molecules, and bonds present in the sample (*Chemistry Libre Texts.* 2015 (1-2)).

Carbonyl groups (characterized by the C=O bond) has been found to absorb infrared radiation 1800 – 1600 cm^{-1}, however, depending on if it is an aldehyde, ketone, ester etc., the stretch is different. The ester band of the carbonyl groups in the region of 1750 – 1715 cm^{-1} is the most significant absorption band for this thesis (*Chemistry Libre Texts.* 2015 (2), *Fan, M., Dai, D. & Huang, B.*, 2012, *Lambert, J. B.*, 1998).

There are different sampling techniques to use when doing FTIR spectroscopy, depending on what is sought after. Attenuated total reflection (ATR) is useful for studying the surface structure of a sample, seeing that the sample is put directly on a crystal (without any preparation to the sample). This sampling technique is used in this thesis as it is more suitable for soft flexible materials, for instance textiles, films, polymers, papers etc., which can achieve a good contact between the crystal and the surface of the sample. (*Zafeiropoulos, N. E., 2011*)

2.6THERMOGRAVIMETRIC ANALYSIS

Thermogravimetric analysis (TGA) is widely used to characterize thermal stability of materials by monitoring the change of mass of a sample as a function of time or temperature in isothermal conditions. The temperature is controlled through a pre-programed method that increases the temperature by predetermined value of X K/min. The measured change in mass when the temperature increases giving information about vaporization and decomposition among other characteristics (*Pradyot, P.*, 1995, *Wanger, M.,* 2017).

2.7 COMPRESSION MOLDING

Compression molding of composites reinforced with natural fibers is a common manufacturing process in the automotive industry. It is a most suitable method for larger-sized parts due to lower cost of production, than other types such as injection molding. Usually, the matrix material is thermoplastic because of the better resistance to degradation and thermal stability. Nonetheless, thermoplastic compression molding occurs and is commonly used when fabrics are used as reinforcements (*Müssig, J.*, 2010).

The process can be done in a variety of ways, still, there are similarities between them. Precut parts of the material are heated up to around 160 to 250 °C for a certain amount of time and pressure depending on the material used. The material is then moved to a press and is then molded to a desired form under different amount of time, temperature and pressure (*Müssig, J.*, 2010). For textiles, a film-stacking procedure is done, where precut matrix and fiber is stacked in an alternating pattern whereon, they are molded together in a press (*Huda, M., et al.* 2008).

3 EXPERIMENTAL

Introduction to some of the more general techniques and experimental parts used during this thesis are explained in this part. Modification of substrate and analysis procedures are explained. For further experimental observations see Appendix IV.

3.1 CELLULOSE SUBSTRATE

Three different cellulose substrates were used in different sections of the thesis work. An explanation of the amounts used for each respective substrate during experiments are presented, along with information of the manufactures.

3.1.1 Microcrystalline Cellulose

The substrate first used in the experiments was microcrystalline cellulose (MCC), Sigma-Aldrich, Avicel PH-101 ~50µm particle size, with an average DP of 200.

The microcrystalline cellulose was swelled with deionized water prior to two of the reactions, creating the substrate more accessible for penetration of the reagent.

3.1.2 Jute Fabric

Jute woven fabric sheets were, along with microcrystalline cellulose, was first used in the experiments, bought from Stoff & Stil (article number 9199).

The jute fabric was never dried and swollen with deionized water prior to two of the reactions, creating the substrate more accessible for penetration of the reagent.

3.1.3 Ramie Fabric

Ramie woven fabric sheets were used later in the thesis work and substituted the jute fabric. It was bought from the University of Nottingham in China, sample model ZMPW140-1, and was not chemical surface treated by the manufacturer.

The ramie fabric was never dried and swollen with deionized water or 2 M NaOH solution (alkali solution) prior to each reaction, creating the substrate more accessible for penetration of the reagent.

3.2 REAGENTS

All the reagents used in the modification methods are chemical substances that did not required any further preparation or modification prior to the reaction.

3.2.1 Acetic Anhydride

Acetic Anhydride manufactured by Sigma-Aldrich with CAS 198-24-, with a molar mass of 102.1 g/mole and a density of 1.08 g/mL.

3.2.2 Diketene–Acetone Adduct

Diketene–Acetone Adduct is manufactured by Sigma-Aldrich with CAS 5394-63-8, with a molar mass of 142.15 g/mole and a density of 1.07 g/mL.

3.2.3 Trimethylolpropane Triacrylate

Trimethylolpropane Triacrylate (2,2-Bis[(acryloyloxy)methyl]butyl acrylate) is manufactured by Sigma-Aldrich with CAS 15625-89-5, with a molar mass of 296.3 g/mole and a density of 1.1 g/mL.

3.3MATRIX MATERIAL

Polylactic acid was supplied by NatureWorks, product name Ingeo 3051d, with specific gravity of 1.25 g/cc as well as a T_g of 150 – 165 °C and a T_m of 55 – 65 °C. The PLA was received as pellets and was grinded to a powder before use in the manufacturing of the composite material.

3.4 METHODS OF CHEMICAL MODIFICATION

There were in total three different modification methods done in this thesis. For all the modifications the following raw material was used

a) Avicel Microcrystalline cellulose,
b) Never dried jute woven fabric,
c) Never dried ramie woven fabric.

3.4.1 Production of Ester Using Acetic Anhydride

Two samples of each raw material weighting approximately 1 g were placed in separate beakers and activated by soaking in glacial acetic acid: glacial acetic acid was poured into a beaker until the material were covered, and after the material had swollen for approximately 20 minutes, the samples were then vacuum filtered. This procedure was done twice. Two solutions (based on one-gram AGU) were mixed: (A) 6 ml of AA, 10 ml toluene and 0.01 ml of perchloric acid (B) 0.3 ml AA, 10 ml of toluene and 0.01 ml perchloric acid. After dripping the solutions on the respective samples, they were immediately placed in a conventional oven heated to 50 °C for 2 hours. Afterwards, the MCC was vacuum filtered and then placed in a beaker with distilled water for 45 min. The fabric samples were placed in separate beaker filled with distilled water for 45 minutes directly after the reaction. The samples were vacuum filtered and washed with distilled water mixed with a small amount of 2-propanol, before being bench dried for 16 h.

3.4.2 Scale-up of Production Using Acetic Anhydride

The scale-up was done in a similar way to the procedure of section 3.4.1, however, only ramie fabric was used. A 20x20 cm sheet of ramie fabric of 6 g weight was placed in a large beaker and activated by soaking in glacial acetic acid; soaking for about 20 min the sample was allowed to drip for 30 s and then shaken 5 times to drain excess liquid. This procedure was done twice. Solution A & B from section 4.3.1 was mixed and added to the raw material. The samples were than immediately placed in a conventional oven heated to 50 °C for 2 hours. Afterwards, the fabric was placed in a beaker filled with distilled water for 45 minutes, washed with distilled water mixed with a small amount of 2-propanol, before being bench dried for 16 h.

3.4.3 Production of Ester Using Diketene-Acetone Adduct

One sample of MCC and jute fabric, as well as four samples of ramie fabric were placed in separate forms and either activated with water or a 2 M NaOH-solution at −20 °C for 20 min. The activated with NaOH-solution was washed with a solution of acetic acid highly diluted with deionized water. The reagent DAA (3 mol eq. DAA/AGU) was mixed with a small amount (~2 mL) of 2-propanol – a transport medium – to evenly cover the sheets with reagent. The 2-propanol was allowed to evaporate before the sheets were placed in a conventional oven at either 80 °C for 75 min or 120 °C for 30 min. The sheets were then allowed to cool down to ambient temperature prior to being washed with acetone, ethanol, deionized water, and ethanol once more. The sheets were bench dried for 18 h.

3.4.4 Scale-up of Production Using Diketene-Acetone Adduct

The scale-up was done in a similar way to the procedure of section 3.4.3, however, only ramie fabric was used. A 20x20 cm fabric sheet was placed in an aluminum form and activated with water for 10 min. The reagent DAA (3 mol eq. DAA/AGU) was mixed with 15 mL of 2-propanol. The 2-propanol was allowed to evaporate before the sheets were placed in a conventional oven at either 80 °C for 75 min. The sheets were then allowed to cool down to ambient temperature prior to being washed with acetone, ethanol, deionized water, and ethanol once more. This was done by swirling the sheet around in beakers filled the washing agent before allowing them to drip off excess liquid. The sheets were bench dried for 18 h.

3.4.5 Production of Co-polymerized Skin Using Trimethylolpropane Triacrylate

Samples of each raw material were placed in separate aluminum forms. The TMPTA monomer was added in a concentration of 6, 15, 50, 65 wt.% along with a catalytical amount of the photoinitiator 1-hydroxycyclohexyl phenyl ketone (1-HCHPK). 3 ml 2-propanol was also added to the solution as a transport medium to evenly cover the sheet with reagent and photoinitiator. The solution was stirred until the photoinitiator had dissolve where upon the solution was added to the respective sheets. Prior to the sheets being exposed to UV-radiation, the 2-propanol was allowed to evaporate. A UV-lamp of the model UVG-54 (λ =254 nm) was used at ambient temperature for 40 min, placed 12 cm above the sheets. The sheets were then washed in 2-propanol and bench dried for 18 hours.

3.4.6 Scale-up of Co-polymerized Skin Using Trimethylolpropane Triacrylate

The scale-up was done in a similar way to the procedure of section 3.4.5, however, only ramie fabric was used. A 20x20 cm fabric sheet was placed in an aluminum form. The TMPTA monomer was added in a concentration 65 wt.% along with a catalytical amount of the photoinitiator 1-HCHPK. 15 mL 2-propanol was also added to the solution as a transport medium to evenly cover the sheet with reagent and photoinitiator. The solution was stirred until the photoinitiator had dissolve where upon the solution was added to the respective sheets. Prior to the sheets being exposed to UV-radiation, the 2-propanol was allowed to evaporate. A UV-lamp of the model UVG-54 (λ =254 nm) was used at ambient temperature for 30 min, placed 24 cm above the sheets. The sheets were then washed in 2-propanol and bench dried for 18 hours.

3.5 ANALYSIS

Different types of analysis methods were used during this thesis; all methods analyzing a different property or aspect of the substrates. Each procedure is explained in this section.

3.5.1 Thermogravimetric analysis

The unmodified and surface modified ramie fabric were analyzed with TGA to attain the thermal stability temperature. The analysis was done in N_2 with a flow rate of 60 mL/min, and the temperature was programmed to go from 30 to 500 °C at a rate of 10 °C/min on a Mettler Toledo

TGA/DSC 3+ STAR^e System. The extrapolated onset temperature shown in Appendix II (Figure AII.1) is where the samples are no longer thermally stable and reached its degradation temperature.

3.5.2 Attenuated Total Reflection Fourier Transform Infrared Spectroscopy

The samples analyzed with ATR–FTIR technology was directly placed on in the ATR mount with no pre-modifications or deformation required, due to the modifications being done on the surface of the materials. The ATR mount used was a Pike GladiATRT Mona PerkinElmer FT-IR Spectrometer Frontier, with the settings 20 scans, 4 cm^{-1} resolution and wavelength of 400 – 4000 cm^{-1}. The results and graphs from the FTIR are presented in Appendix I.

3.5.3 Tea Bag Test

A modified tea bag test was constructed on the modified and unmodified materials to analyze the amount of absorbed water per gram of material. The test was carried out by filling the same number of beakers as samples with 100 ml of water rest for 30 min so that it was at ambient temperature. Pre-dried sheets of fabric were then cut into roughly 0.1 – 0.2 g pieces (W_D), placed in the beakers for 45 min before allowed to drip for 10 min. To get rid of excess water, the pieces were gently swiped with a paper towel (as little pressure as possible should be applied when doing this to avoid pressing out absorbed water), afterwards, the water swollen pieces was weighted (W_S).

3.5.4 Tensile Strength Test

The tensile stress test was performed in the machine technology building at Chalmers University of Technology with guidance from Abhijit Venkatesh. The composites were shaped like dog bones and had a thickness between 0.45–0.57 mm. The grip to grip separation was 40 mm, and the samples were exposed to pre-loading of 1 N at a speed of 10 mm/min before the tensile testing started. This is so the samples did not have any slack when starting the test. The machine (a Zwick material testing machine type BZ2.5/TN1S) had a testing speed of 6 mm/min. When the composite broke, the graph showed the stretch at the breaking point and how much force that was applied. Stress-strain graphs are presented in Appendix III.

3.6 COMPRESSION MOLDING

Compression molding of the composite material was done by first hot-pressing PLA films, then film stacking the matrix and fiber in an alternating patter (PLA–fiber–PLA) before hot-pressing them together. This was followed by punching dog bones of each composite, containing roughly 20 wt.% of fiber. To make the films, four pieces of 0.25 mm aluminum spacers were placed like a picture frame making a 9x9 cm square before putting 2.63 g of the grinded PLA powder in the middle. When the pressing machine reached the desired temperature of 160 °C the plates with the spacers and filament was place in the machine for 3 minutes until melted completely. Then, the pressure was slowly increased to 50 kPa and was under pressure for 1 minute before the pressure was released. After the plates were placed on the bench, they were cooled down to room temperature under pressure with metal blocks for approximately 15 minutes.

The composites were done in a similar manner as the PLA films. However, there was some differences partly to the increased thickness of the stacked films, and partly due to the development of bubbles between the layers. The spacers were placed like a picture frame as before, however, 0.5 mm thick spacers were used. The stacked films were heated in 160 °C until melted, then the pressure was increased to 25 kPa and was hold for 20 s before being decreased to 0 kPa. This was repeated twice where on the pressure was increased to 50 kPa and held for 1 minute before letting the pressure down to 0 kPa. The same cool down procedure as the films was used.

4 RESULTS AND DISCUSSION

The main results from the reactions were made by analyzing the FTIR-spectrums, presented in Appendix I.

4.1 ANALYSIS OF THE RESULTS FOR ACETIC ANHYDRIDE

At first the reaction, in which Acetic Anhydride was used, yielded desired results, albeit the ramie fiber did not respond well to the acidic reaction environment. When analyzing the FTIR results (Appendix AI.1), the native material was compared with the modified. Between the two, there are distinct differences in the absorption bands of 3660 – 2880 cm^{-1} as well as 1750 – 400 cm^{-1}. The former absorption range being characteristic for inter- and intramolecular hydrogen bonds (~3333 cm^{-1}) and C–H stretch (~2900 cm^{-1}) of cellulose. The latter absorption range (1750 – 400 cm^{-1}) being bands frequently being attributed to molecules on the cellulose structure such as $–CH_2$, –CH and C–O.

As seen in Figure AI.1, there is a clear peak (that is not present in native substrate) with high intensity found at the wavelength 1738 cm^{-1}, which corresponds to the desired ester functional group substituted on. Further comparison show that the acetylated substrates also have three very distinct peaks around 1030 cm^{-1}, 1215 cm^{-1} and 1350 cm^{-1} that is not found in the native substrates. The ~1030 cm^{-1} and ~1350 cm^{-1} stretches suggests an ester linkage (*Lambert, J. B. et al.* 1998) and is another indicator of the substitution taking place. The nonexistent hydrogen bond stretch means that the inter- and intramolecular hydrogen bonds are broken up, confirming that the substitution has been successful.

Due to the impact on the ramie fiber when using high concentrations of AA, the experiment was later conducted with low concentrations of AA. As a result, the substrates did not decompose to the same degree. Furthermore, the FTIR spectra for low conc. of AA (Figure AI.1) resembles the native fiber much more, with the exception of the weak desired peak at 1735 cm^{-1}. Due to the difference of the fibers with high contra low conc. of AA, it is believed that decomposition did not occur (or at least to only a small extent) at lower conc. of AA, while this is the case for the fibers with high AA concentration. Nonetheless, the intensity of the ester peak at 1735 cm^{-1} became substantially weaker for low AA concentration.

It has previously been found that hydrogen bonding between the carbonyl and hydroxyl group on cellulose esters will lower the frequency of the carbonyl stretch in FTIR results. This correlates with the DS of the cellulose ester; when increasing the DS, Brodin (2013) found that the interaction between the hydroxyl and carbonyl groups decreased, thus increasing the frequency of the carbonyl stretch and lower the intensity of the hydroxyl stretch (~3200−3600 cm^{-1}). However, the effect is subsiding when the reaching higher DS. The carbonyl stretch for the first experiment with the lower conc. of acetic anhydride displayed its peak at 1747 cm^{-1} (along with a lower hydroxyl peak) while other fibers displayed peaks at ~1735 cm^{-1} (along with a high hydroxyl peak).

It should be noted that these results also applies to the jute fiber and MCC, both the FTIR spectra (shown in Figure AI.4) as well as the degradation of the substrates.

4.2 ANALYSIS OF THE RESULTS FOR DIKETENE-ACETONE ADDUCT

The reaction where DAA is used was the most explored modification method and did yield somewhat desirable results on small-scale. As is shown in the FTIR spectra (Figure AI.2) only one peak is present for the jute fibers and ramie fibers (reacting at 80 °C) at 1735 cm^{-1}, while the ramie fiber (reacting at 120 °C) and MCC had two peaks present in the carbonyl stretch. The first peak at ~1705 cm^{-1} shows a ketone and the second peak at 1745 cm^{-1} shows a β-keto ester (in keto form). The β-keto ester (the molecule substituted onto the cellulose) has two forms – keto and enol – which are in equilibrium and both being desired. They have a slightly different bond structure resulting in two peaks at different wavelengths. The peak at ~1666 cm^{-1} is the β-keto ester (in enol form).

What is also evident from the reactions is that the reactions taking place at 120 °C gave better results, which is in accordance with the theory. There are two main differences between water swollen and alkali swollen fibers; (i) the intensity of the peaks and (ii) the frequency of the peaks. For water swollen fibers the frequency of the ketone and ester stretch is lower than the alkali swollen; around 1710 and 1737 cm^{-1} for water swollen, while around 1712 and 1747 cm^{-1} for swollen alkali. This indicates that the alkali swollen fibers have a higher DS than the water swollen. There are some intense peaks at 1030, 1140 and 1358 cm^{-1}; the first and last is caused by the ester linkage, while the middle stretch is due to methyl groups probably on the substituted β-keto ester (*Lambert, J. B. et al.* 1998).

The reagent and ramie fiber did not mix well at first, so activation of the fiber was done with 2 M NaOH-solution instead of water. It was found by Haque M.A. et al. (2017) that 2 M (8 %) NaOH-solution had the best swelling effect on cellulose for any given activation time, something that has been seen in previous studies as well. It was also noted that NaOH mainly swell the fiber by breaking the intermolecular bonds, while water swell by mainly breaking the intramolecular bonds. Thus, water does not swell the fibers as good as the alkali solution does. When swelling the cellulose fibers, they open up, making the hydroxyl groups inside (on C2 and C3) more accessible to react, consequently the reaction environment inside the fiber is different from the outside of the fiber. As seen in the FTIR result, the intensity of the carbonyl stretch is stronger and is an indication that more ketenes are present in the fiber.

A longer in activation time has affects the fibers more, as is evident by comparing the FTIR-spectrums. The ratio between peaks indicates a change that can be interpreted as what time has been the most effective. Activation for 30 minutes has the highest ratio between desired peaks such as the hydroxyl peak at ~3300 cm^{-1} and carbonyl peak at ~1750 to 1700 cm^{-1}.

4.3 ANALYSIS OF THE RESULTS FOR COPOLYMERIZATION OF TMPTA

The reaction where TMPTA was grafted onto the cellulose and polymerized consistently yielded desired results in small-scale. Analyzing the FTIR spectra (Figure AI.3) for each substrate shows that MCC has not responded to the reaction considering there is no ester stretch, while both the jute and ramie fibers displayed the desired peak at 1726 cm^{-1}. Interestingly, a peak at 808 cm^{-1} is seen when 50 wt.% of reagent was used. As Wang et al. (2007) stated, the polymerization rate should be retarded when more than 20 wt.% of TMPTA is used, which was shown to be true in this thesis as well. This has been measured by conversion of grafting (how much has been polymerized) and is shown in Table 4.1. It is seen that the concentration of reagent has the most impact on the conversion rate, however, longer reaction times also results in a higher grafting. Despite the higher conversion rate when using <20 wt.% of reagent, the FTIR spectra displays weaker peaks than for materials using >20 wt.% of reagent. It also shows weaker unsaturated =CH_2 alkene stretch at ~810 cm^{-1}. This is likely due to the completion of the polymerization or conversion of grafting. When the propagation of the monomer occurs not all of the reactive C=C will be able to polymerize due to steric hindrance. As TMPTA is trifunctional, polymerization of it will result in polymer chain consisting of many branches, and thus, steric hindrance is created.

Table 4.1. Table over conversion of grafting as well as mass of grafted monomer for different wt.% of reagent.

Weight percentage of reagent	***Grafting conversion***	***Mass of grafted monomers***
6 wt.%	100% after 30 min	0.05 g
15 wt.%	100% after 30 min	0.11 g
50 wt.%	31% after 30 min.	0.13 g
	47% after 40 min	0.32 g

4.4 ANALYSIS OF THE RESULTS FOR SCALE-UP

After successfully modifying the substrates with all methods, each method was scaled-up around 7 times the small-scale experiments. The scale-up attempts were rushed and was not based on TGA results or complimentary small-scale experiments. Consequently, the reactions did not translate from small to a larger scale due to poorly optimized reaction conditions. The scale-up should be redone with the regard to the newly gained information. FTIR results and physical examination shows that neither of the scale-up attempts was largely successful. The acetylation had the best results when using high conc. of acetic anhydride – which is a logical result due to more reagent being present – while lower conc. of the reagent displayed a small, albeit, a significant peak. Physical signs of degradation were reintroduced at this scale, with smaller holes appearing for lower conc. of reagent and very low strength (both when swollen and dry) of the fibers at higher concentrations – crumbling when not handled gently. The same trend with degradation as in the small-scale was present as well.

The UV-induced grafting of TMPTA did yield some desirable results, however no FTIR spectroscopy was done, therefore only empirical evidence will be used for its analysis. Some regions of the fibers became stiff and got a plastic feel, corresponding to the small-scale, indicating that the reaction had occurred. Note that this only occurred in some regions, which plausibly can be attributed to the initiation not occurring – perhaps due to a modest increase of photoinitiator. As a result of the UV-lamp's limited range the distance between sample and lamp was doubled, which may have retarded the reaction – no increased stiffness or plastic feel.

Esterification using DAA as reagent only small spots on the fibers turn dark brown which occurred in small-scale experiments. This could be due to the reaction taking place at 80 °C instead of 120 °C, verifying that degradation of the reagent is important for the reaction to occurs, as well as poor absorption of the reagent. Nonetheless, the reaction has probably occurred to a small extent, showing minuscule peaks for the desired stretch. Doing TGA before the scale-up this reaction would have been optimal, as it shows that the high degradation temperature and could likely withstand the temperature for 30 min without degrading.

4.5 ANALYSIS OF THE RESULTS FOR TEA BAG TEST

Results of the water absorption capacity of modified and native material shown in Table 4.2 show that the UV-induced grafted material had the lowest water absorption capacity with an average of 70 mg water per gram material, while the acetylated material had the highest average of one-gram water per gram material. Noteworthy, is that the acetylated and the water swollen DAA esterified substrates has much higher absorption capacity than the unmodified substrate. It is assumed to be that they have not become more hydrophilic, instead, the esterification reactions free crystalline parts of the cellulose aggregates when the substitution of hydroxyl groups occurs. The surface area is consequently increased which initially can inhibit water to be absorbed before sufficient substitution has made the fiber too hydrophobic. Brodin (2013) writes that DAA is not hydrophobic and that the produced cellulose ester highly resembles the cellulose backbone. Taking this into account as well as an increased surface area and the different environment of the swollen cellulose between water and NaOH, the result could be an accurate representation of the different absorption capacity. Further analysis would be necessary to better understand it.

Table 4.2. Table of dry weight, swollen weight, and absorption capacity for modified and unmodified ramie fibers. The average absorption capacity for UV-induced grafting has the lowest value, while acetylation has the highest.

Type of Modification	*Dry Weight W_D [g]*	*Swollen Weight W_S [g]*	*Absorption Capacity Qs [g/g]*	*Average Qs*
Unmodified	0.14	0.23	0.59	0.56
	0.16	0.26	0.61	
	0.14	0.21	0.47	
Acetylation Low conc. of Acetic Anhydride	0.09	0.17	0.96	1.00
	0.07	0.13	0.97	
	0.07	0.14	1.08	
Esterified w/DAA at 80°C NaOH treated	0.12	0.18	0.51	0.52
	0.12	0.19	0.52	
	0.14	0.21	0.53	
Esterified w/DAA at 80°C H2O treated	0.09	0.18	1.02	0.96
	0.11	0.22	1.07	
	0.10	0.18	0.80	
UV-induced grafting 50 wt.%	0.12	0.12	0.06	0.07
	0.13	0.14	0.09	
	0.13	0.14	0.06	

4.6 ANALYSIS OF THE RESULTS FOR COMPOSITES

When doing the compression molding for the composites, where were a tendency for bubbles to form between the layers. This is due to the difficulty to get the layers of material to have full contact with each other. Almost all bubbles disappeared when pressing the composite multiple times as was done. Despite this, some bubbles did not disappear which will impact the strength of the composite negatively. A similar observation was done by Brodin (2013) when compounding composites.

The results from the tensile test, seen in Table 4.3, have notably higher Young's modulus, maximum tensile stress and higher elongation at break than the 100% PLA reference. The composite reinforced with acetylated fibers had the highest increase in modulus as well as tensile stress, with an increase of 34% and 22% respectively compared to the PLA + unmodified composite. This is surprising considering that the acetylate fibers showed a relatively weak ester peak in FTIR-spectra, while for example the UV-grafted fibers that had a much stronger peak only showed a slightly higher modulus. The modified composites showed an increase in stiffness compared the unmodified, however, all composites had approximately the same fiber weight percentage, showing that the modifications is the underlying cause.

One problem that occurred during the testing was slippage, affecting the results. The Young's modulus could only be calculated from a small portion of the curve, the straight line at the start of each curve shown in Appendix III (figure AIII.1-AIII.5), making the results misleading.

Table 4.3. Table with biocomposite tensile test values base on 6 samples per type.

Type of composite	***Young's Modulus (MPa)***	***Maximum Tensile stress (MPa)***	***Elongation at break (%)***
100% PLA	28.4	50.1	3.05
PLA + Unmodified	34.4	57.5	3.92
PLA + Acetylated	46.2	70.0	3.25
PLA + Esterificated	36.1	59.1	3.55
PLA + UV-grafted	37.6	54.0	3.40

4.7 ANALYSIS OF THE RESULTS FOR THERMOGRAVIMETRIC ANALYSIS

From analysis of the TGA curves (Appendix AII.1-AII.5on) it is evident that a reaction has occurred for all the modified ramie fibers, although some are more evident than others. This can be observed by the onset temperature (Figure AII.1), which is an extrapolated temperature from the curve that is interpreted as the degradation temperature. The DAA esterified fibers are the only modified fiber showing a large decrease in the onset temperature compared to native fibers. This change is characterized by the effect swelling has on the inter- and intramolecular hydrogen bonds, making it more porous and vulnerable to degradation. The acetylated fibers only had a slight decrease in onset temperature, while the TMPTA grafted fibers did not change in comparison to the native fiber – for the exception of an added degradation interval.

When looking at the derivative thermogravimetry (DTG) the highest rate of mass loss can be ascertained. This gives us some valuable information such as the temperature where the rate of decomposition is high, several decomposition intervals as well as peak decomposition temperature. A breakdown of the DTG curves show that both fibers modified by DAA esterification and acetylation has a slightly lower peak degradation temperature than unmodified fiber (368 °C) at 346 and 351 °C respectively. This is presumably due to the esterification breaking the multitude of strong hydrogen bonds that is present in unmodified fibers, making the decreasing the thermal stability. Fibers where TMPTA has been grafted onto is the only one having two degradation intervals at 260–400 °C and 420–480 °C. This means that two degradation processes occur, in this case the fiber and the TMPTA, providing another proof that the grafting and polymerization has worked. Börjesson (2016) got similar results in her thesis when doing TGA on TMPTA grafted onto paper sheets, supporting the finding in this thesis.

Table 4.4. Table of degradation temperature, peak degradation temperature and total mass loss at 400 °C for modified and unmodified fibers. The two values of peak degradation and degradation temp. for UV-induced grafting due to there being two different types of materials with different thermal stability present.

Type of modification	***Temp. at which Degradation starts [°C]***	***Degradation Temp. [°C]***	***Peak Degradation Temp. [°C]***	***Total Mass Loss at 400 °C [%]***
Unmodified	272	342.4	368	75.5
UV-induced grafting 50 wt.%	274	343.2 432.9	369 454	62.4
Acetylation (low conc. of acid)	300	337.0	346	89.3
DAA esterification (alkali swollen)	200	308.1	351	87.4

5 SUMMARY OF RESULTS

The acetylated fibers at small-scale experiments showed signs of degradation when high conc. of acid was used, with strong peaks at ~1735 cm^{-1}. When low conc. of acid was used, no signs of degradation as seen, however, it had instead weaker peaks at ~1735 cm^{-1}. The scale-up attempts reintroduced degradation even at lower conc. of acid, with the ester peak at ~1735 cm^{-1} following the same pattern between high contra low conc. of acid.

The DAA esterified fibers were successfully modified to some degree at 80 °C, albeit the reaction exhibits higher DS and stronger peaks at 120 °C. Activating the fibers with alkali solution results in a higher DS than activation with water. It was found that longer activation time is favorable, resulting in stronger peaks. The scale-up attempt showed weak peaks at the desired frequency.

All attempts of grafting TMPTA onto the surface of fibers were successful, except for MCC. Higher concentration of monomers in the reaction results in a stronger ester peak at ~1730 cm-1. The scale-up attempt resulted in parts of one fiber sheet getting an increased stiffness and plastic feel. The two other sheets did not have any apparent difference from native material.

The tea bag test shows that the UV-induced grafting of TMPTA has the lowest absorbance capacity, while DAA esterification (activated with water) and acetylation has the highest, believed to be caused by the ability of the increased surface area to hold more water and higher affinity for water.

The TGA showed a slight decrease in degradation temperature for the esterification reactions compared to native fiber, while fibers that had monomers grafted onto it inherited a second degradation interval. The cellulose ester is believed to have broken many hydrogen bonds when substituting the hydroxyl groups, resulting in the lowered degradation temperature, while the new degradation interval is proof of the grafting taking place.

Results from the tensile test shows that the modification has increased some of the mechanical properties of the composite. Comparing the modified to the unmodified reinforcement it is seen that PLA + acetylated fibers has a significant increase in tensile stress and modulus, but, a large decreases in elongation at break. The PLA + DAA fibers slightly increased the modulus and tensile stress while obtaining a higher stiffness. PLA + UV-grafted fibers showed similar results as the DAA fibers but had a slightly decrease tensile stress.

6 CONCLUSION

In this thesis, three different reagents were used (acetic anhydride, DAA & TMPTA) to chemically modify natural fibers (mainly ramie fiber). All three reagents showed promising results on small-scale, however, when scaling up each method the results did not show as desirable results as was hoped.

Acetylated fibers had some negative impact on them, degrading and weakening the fibers when the concentration of acetic anhydride was high. Lower concentrations did result in no visible degradation, nonetheless, the intensity of the ester peak was substantially weaker. Scaling up the reaction, using lower concentrations of acid, introduced visible degradation, yet the ester peak was still weak. There were no direct limitations to the scale-up, so the results indicate that another method should be used to not damage the fibers.

UV-induced grafting of TMPTA affected the fibers in a positive way. The hydrophobic polymer skin that was polymerized on the cellulose did significantly decrease the absorption capacity substantially, which is desirable for reinforcement materials as the problem with swelling fibers practically not occurring. Although being more hydrophobic, this did not greatly improve the mechanical properties of the composite. The poor results from the scale-up attempt was due to unequal scale-up of the reagent and photoinitiator and the limitations of the UV-lamp.

When using DAA esterification to hydrophobize fibers, temperature along with type of pre-activation and activation time plays an extensive role in the success of the reaction. NaOH is a better swelling agent than water as is evident by the higher degree of substitution. The overall modification method yields positive results and does not affect the fibers negatively. Increasing the temperature on the scale-up attempt was probably the reason for the poor results and was shown to be the case on scale experiments.

The high absorption capacity of the acetylated fibers is negative affects the fiber/matrix stress transfer. Although being more hydrophilic, the mechanical properties was improved to a higher degree than the other modifications. Comparing to the more hydrophobic fibers, hydrophobicity does not seem to be the sole factor for improving mechanical strength. Although, it could be argued that elongation at break is affected by hydrophobicity since only the acetylated fibers got a lower result. However, it should not be forgotten that swelling of the fiber already in the composite can have detrimental effects on the mechanical strength, where hydrophobicity is the biggest factor for a lower absorption capacity.

7 FUTURE WORK

In future research, acetylation of ramie fiber should not be further explored, due to the degradation of the fibers when using low conc. of acid at a larger scale and it is difficult to stop the degradation of occurring. However, investigations of modifications in a basic environment such as 1,2-Epoxybutane could be explored to see if the effects are similar.

Optimizing a scale-up of the UV-induced grafting of TMPTA and try to make a design of experiment (DoE) so that better results are obtained and possible to apply in industry. Other hydrophobic monomers could also be investigated due to the relatively general approach of the reaction.

Optimizing the DAA esterification. Try to make a DoE at scale-up so that better results are obtained and possible to apply in industry. Finding another reagent that react in temperature below 100°C when optimized and for a greener reaction that can be an attractive option.

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APPENDIX

APPENDIX I, FTIR-SPECTRUMS

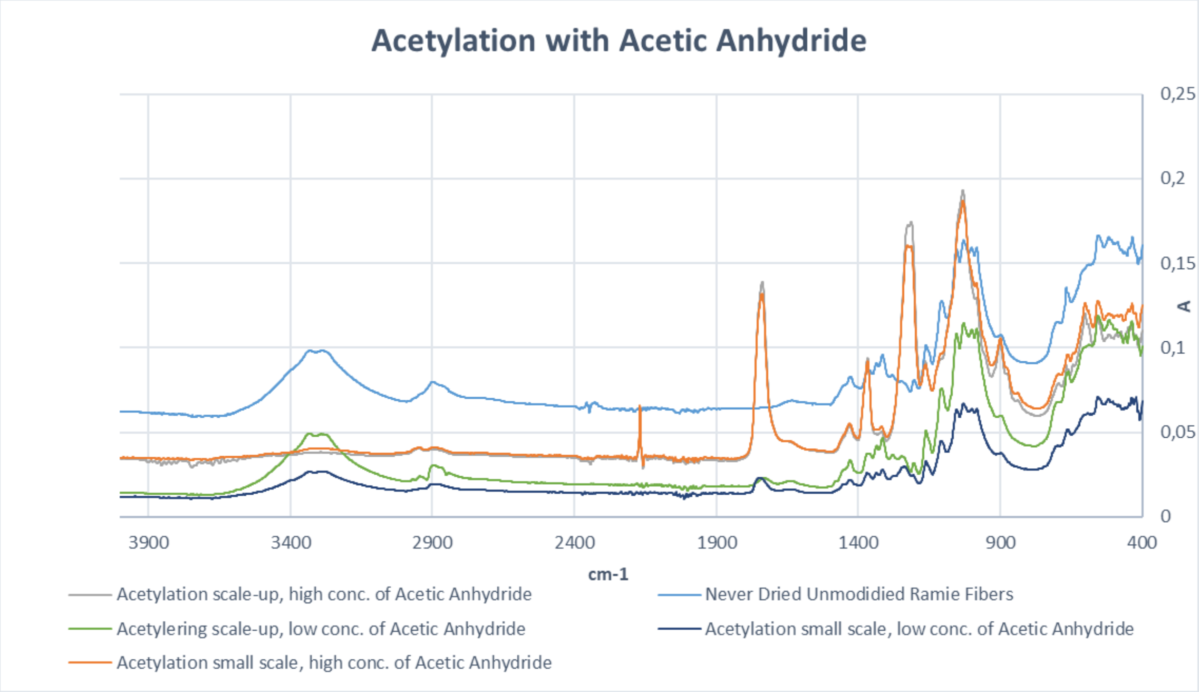

Figure AI.1. FTIR-spectra of acetylated ramie fiber, with different conc. of acetic anhydride.

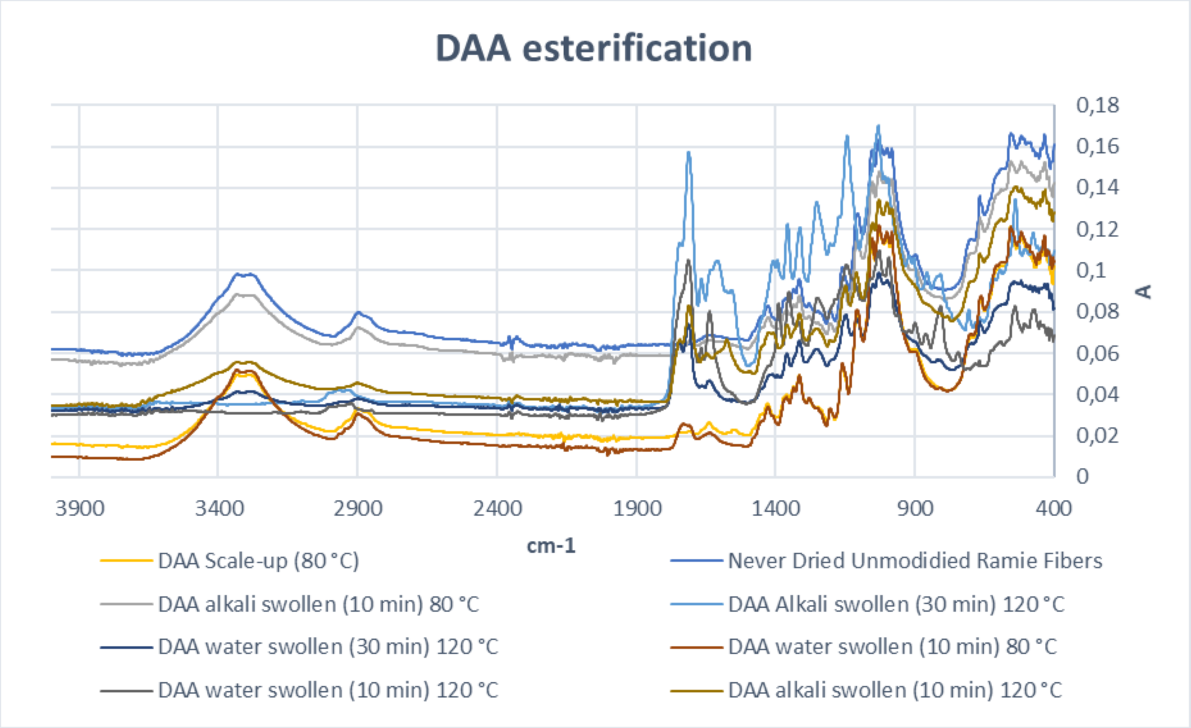

Figure AI.2. FTIR-spectra of DAA esterified ramie fiber, with different swelling agents and activation time.

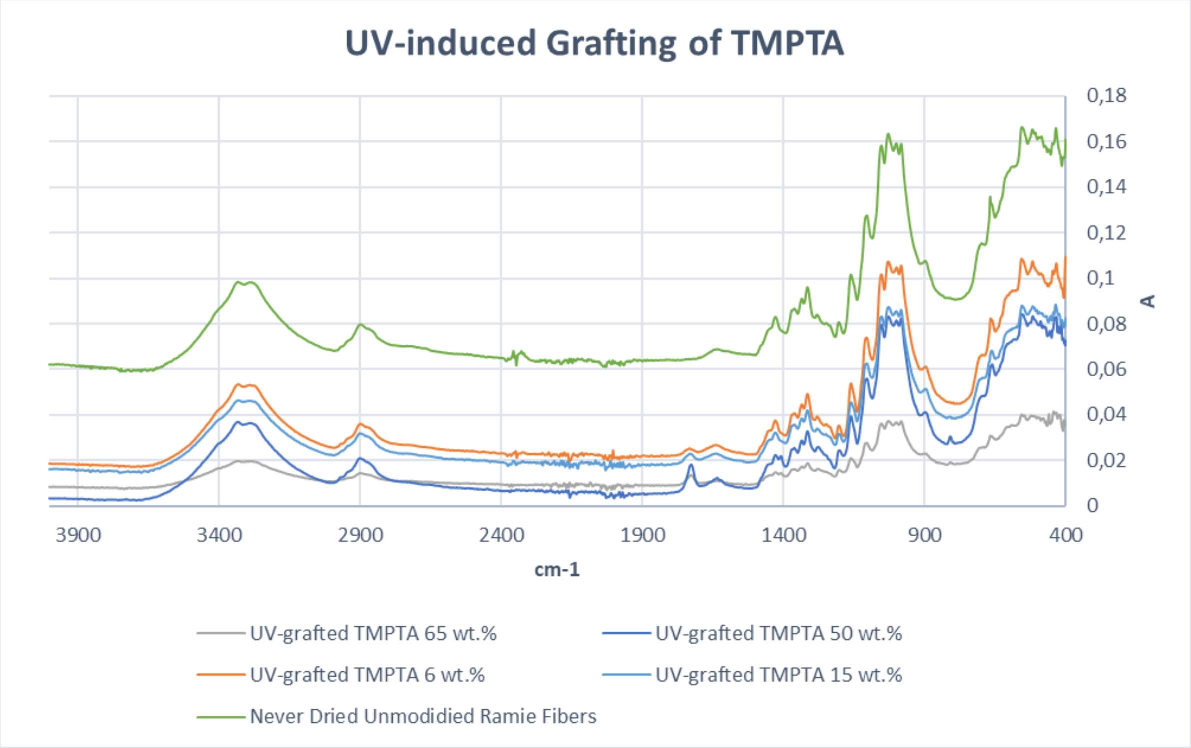

Figure AI.3. FTIR-spectra of UV-induced grafting of TMPTA onto ramie fiber for different weight percentage of TMPTA used.

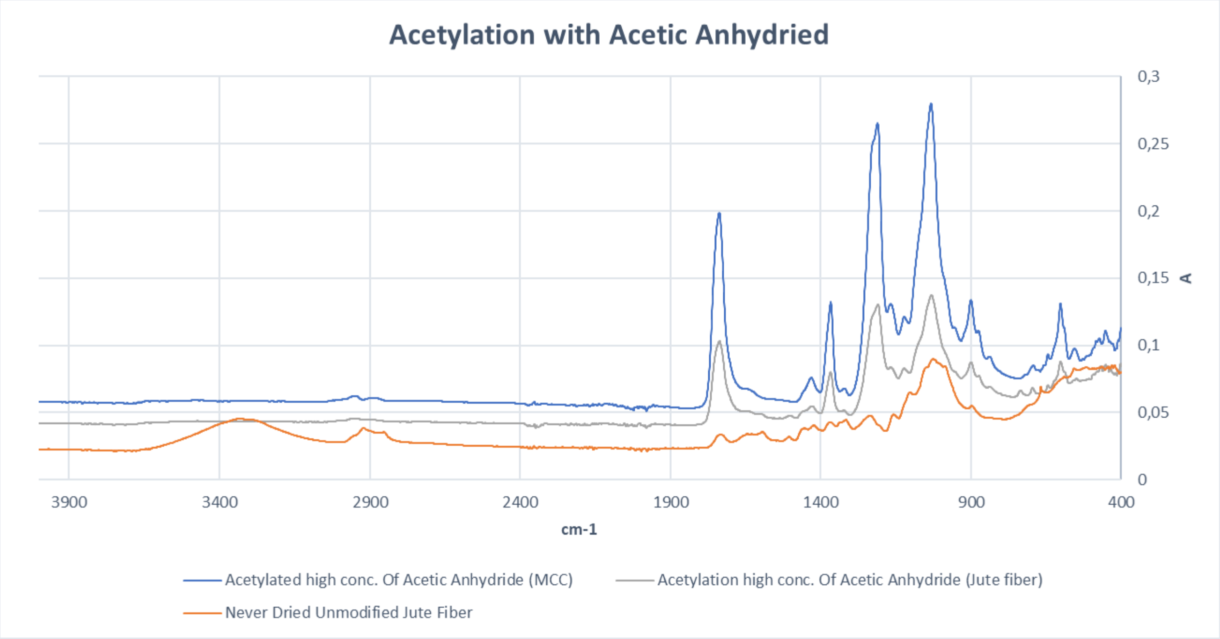

Figure AI.4. FTIR-spectra of acetylated MCC and jute fiber with high conc. of Acetic Anhydride.

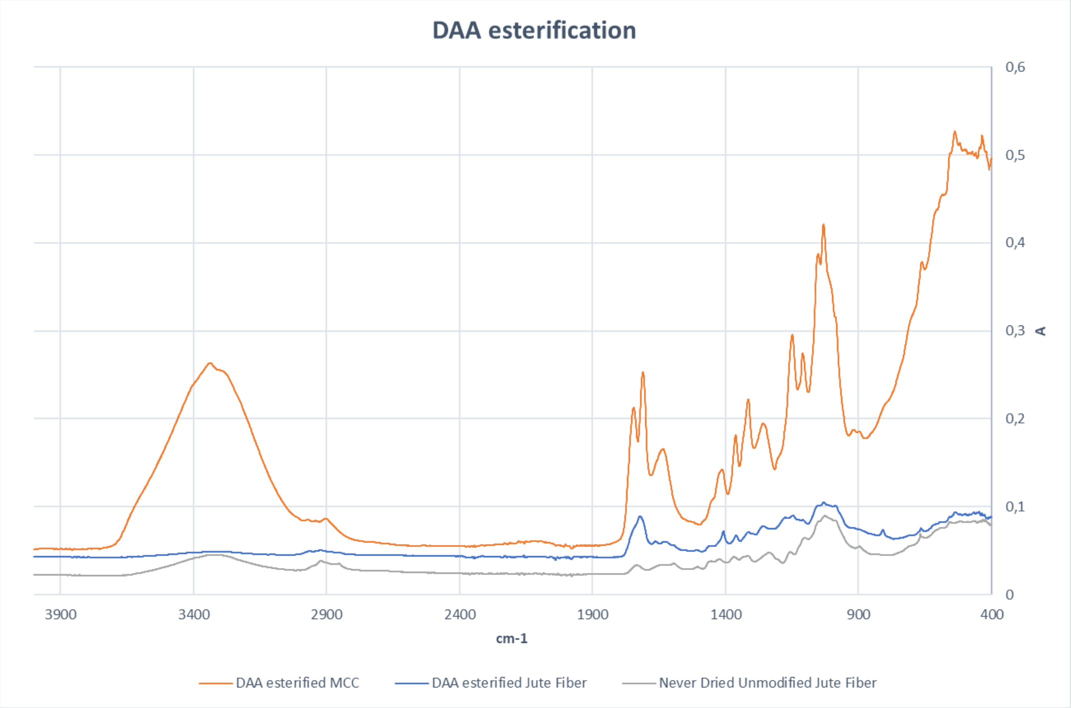

Figure AI.5. FTIR-spectra of DAA esterified MCC and jute fiber, swelled in water.

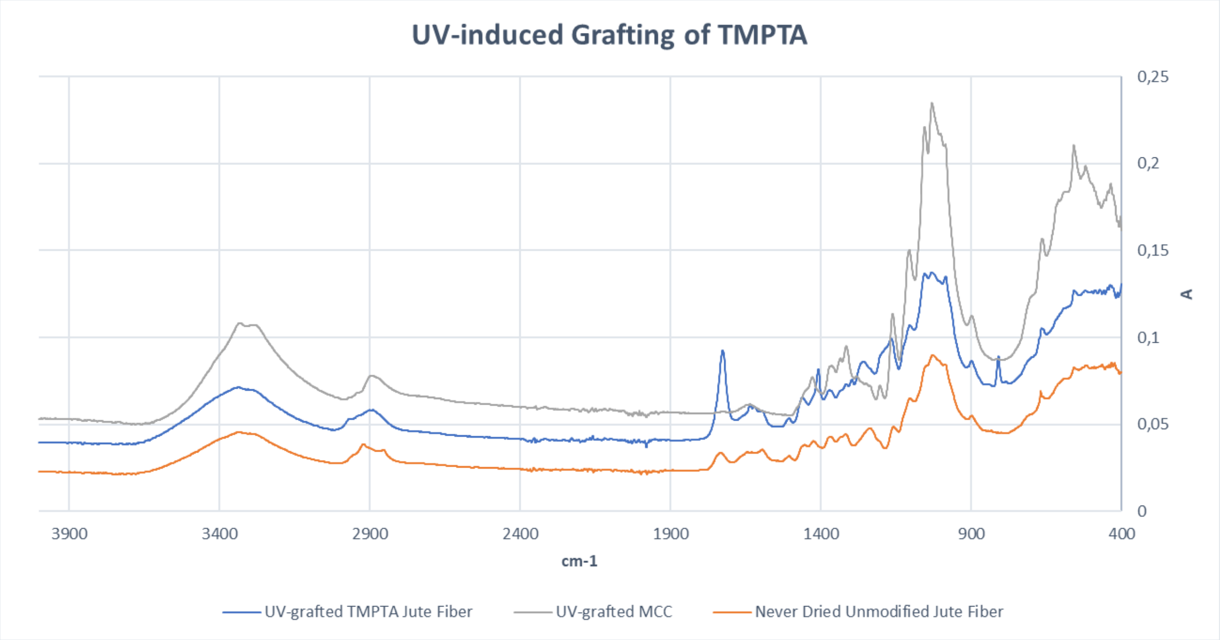

Figure AI.6. FTIR-spectra of UV-induced grafting of TMPTA onto MCC and jute fiber.

APPENDIX II, TGA-GRAPHS

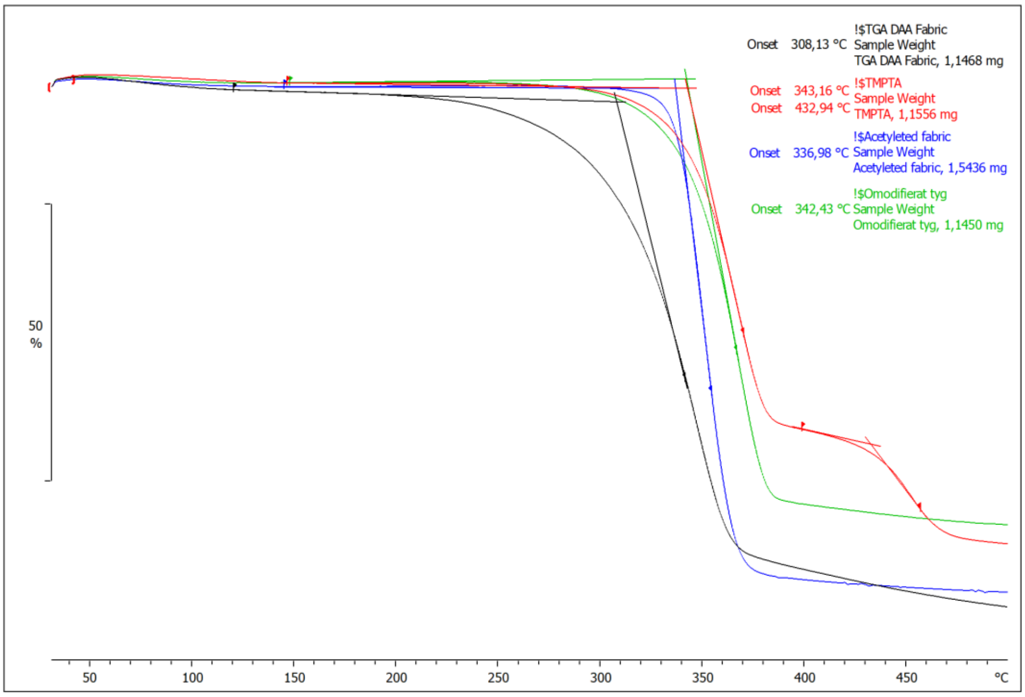

Figure AII.1. Onset temperature for modified and unmodified ramie fiber. The TMPTA fibers used has been modified with 20 wt.% reagent, the DAA fibers used has been activated with alkali solution for 20 min, and the acetylated fiber used has been modified with low concentration of reagent.

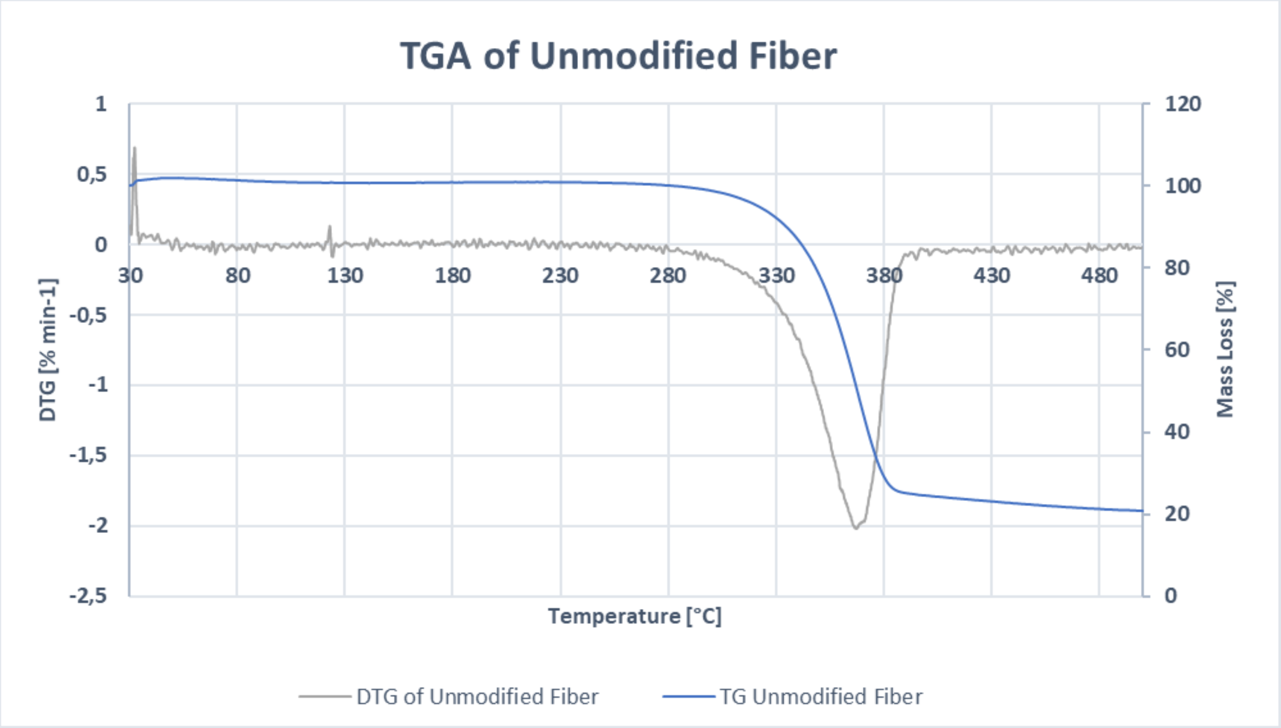

Figure AII.2. TGA and DTG curve for unmodified fiber.

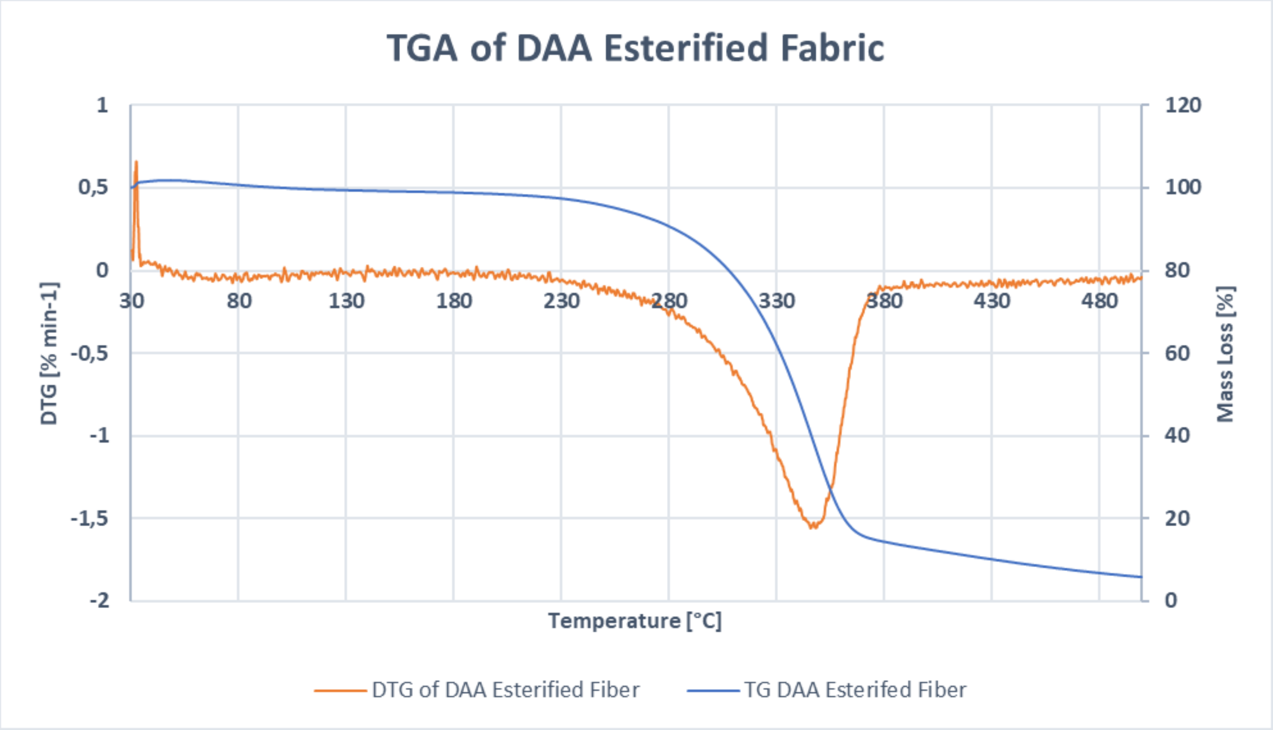

Figure AII.3. TGA and DTG curve for DAA esterified fiber.

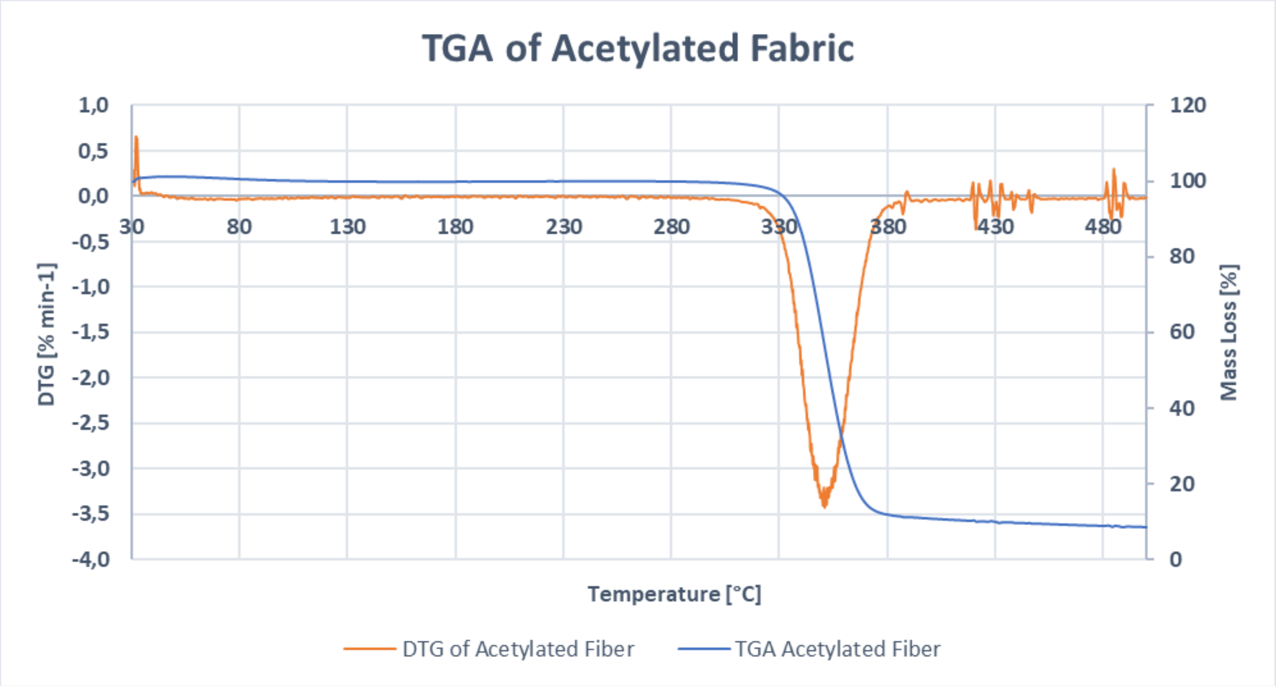

Figure AII.4. TGA and DTG curve for acetylated fiber.

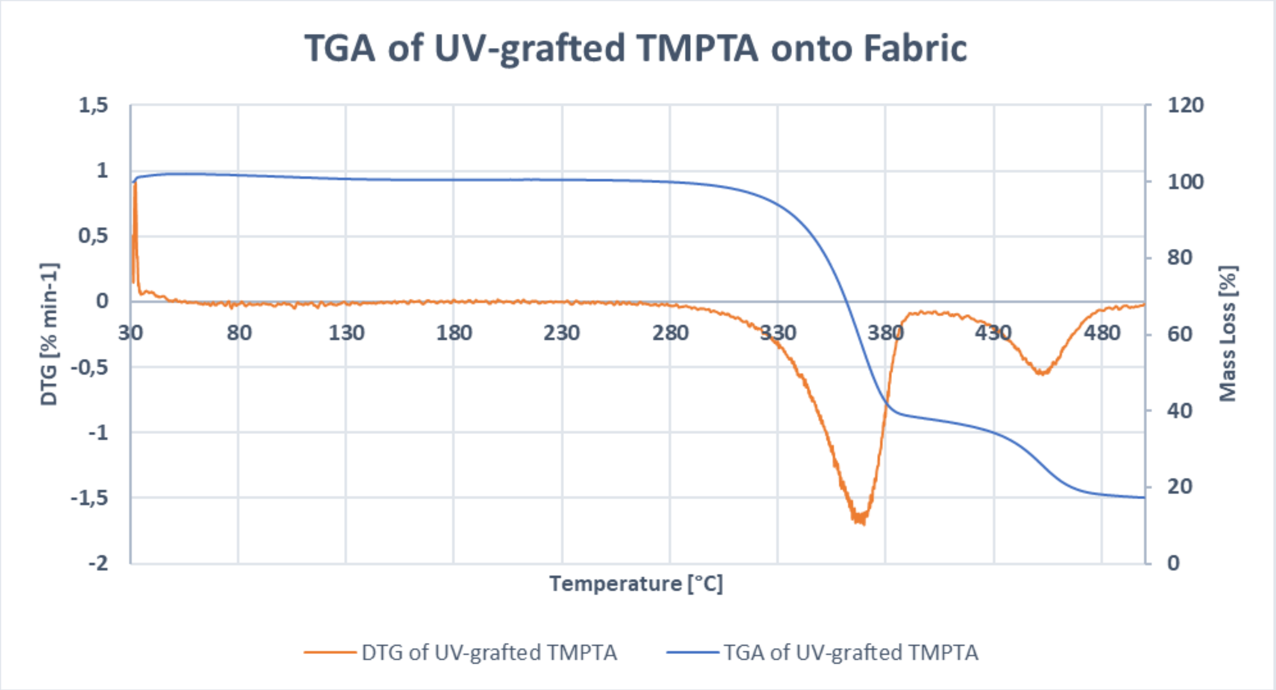

Figure AII.5. TGA and DTG curve for UV-grafted TMPTA fiber.

APPENDIX III, STRESS−STRAIN GRAPHS

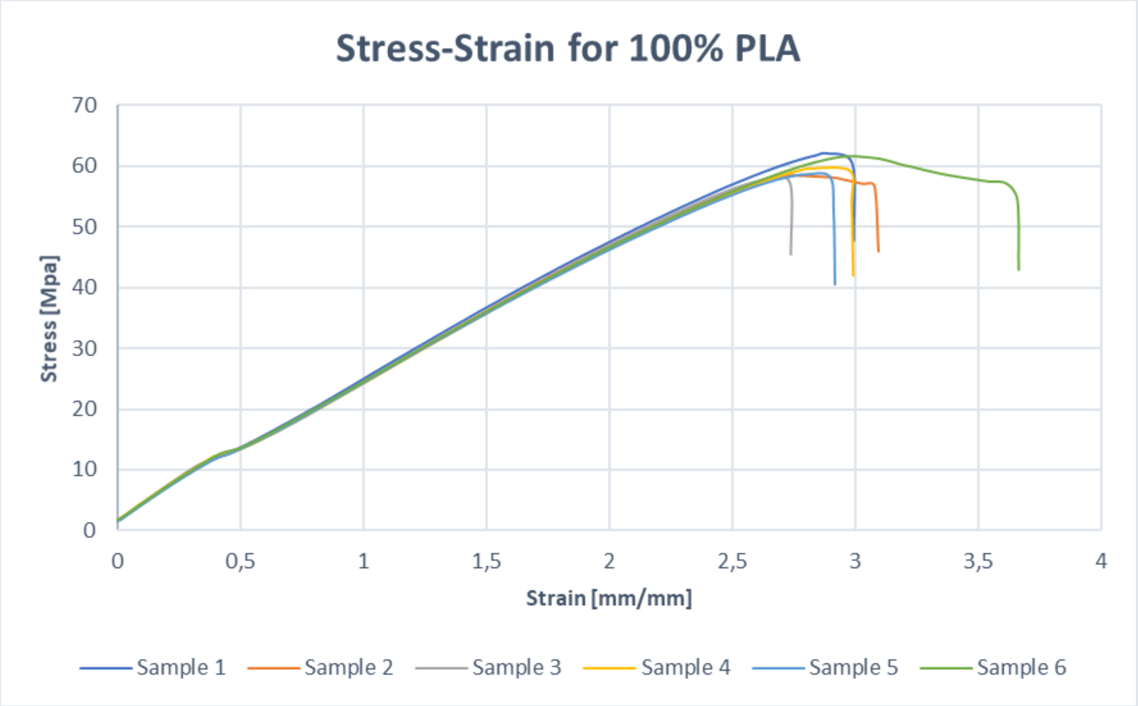

Figure AIII.1. Stress-Strain curves for different samples containing 100% PLA.

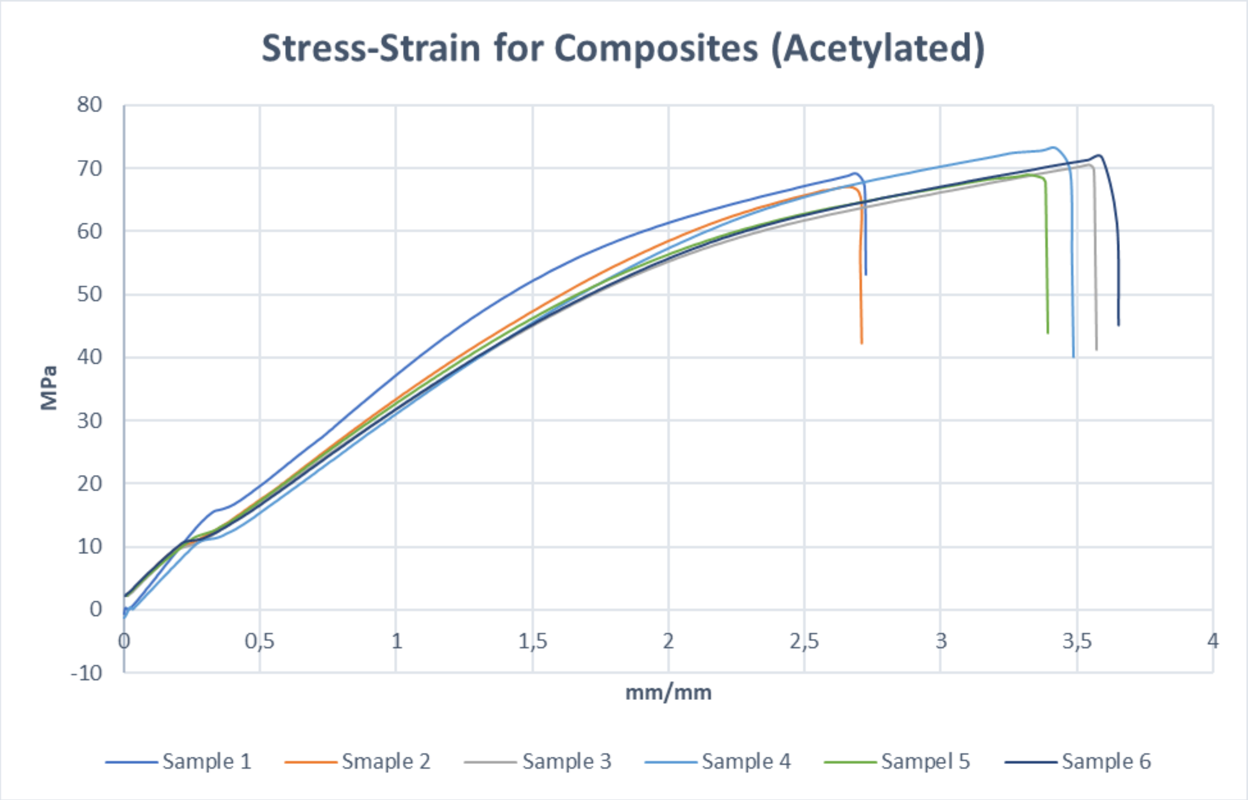

Figure AIII.2. Stress-Strain curves for different samples containing PLA and acetylated fibers. All samples have been modified with low concentration of acetic anhydride.

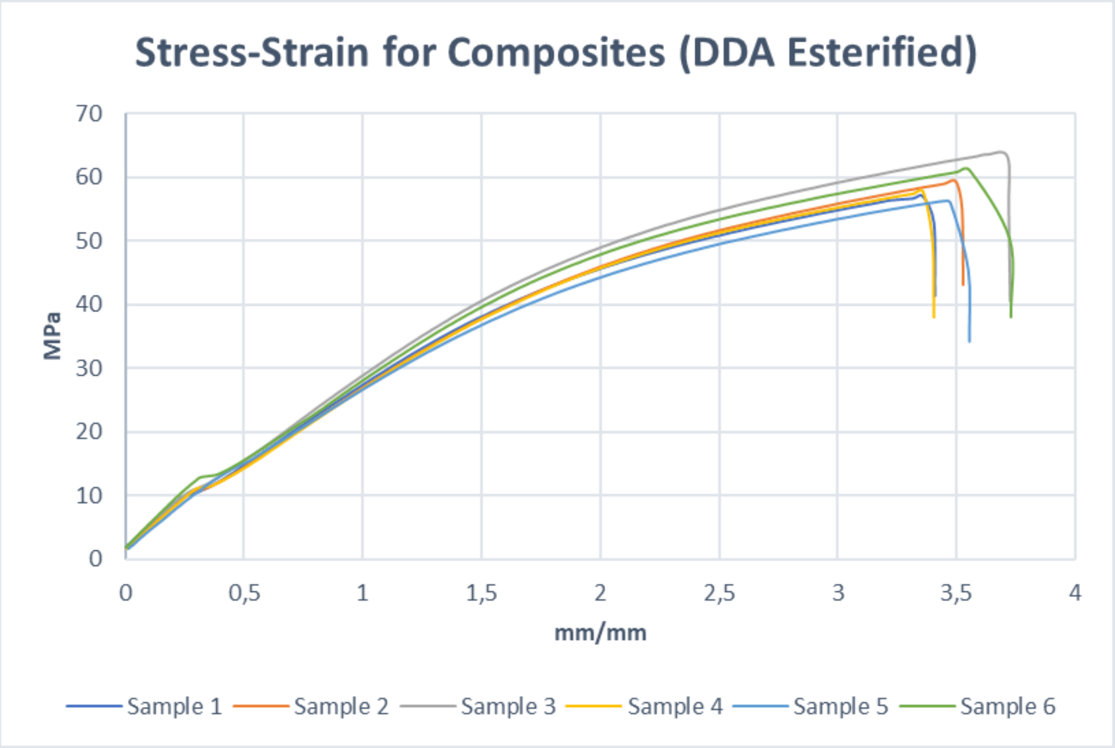

Figure AIII.3. Stress-Strain curves for different samples containing PLA and DAA esterified fibers. All samples have been activated using the 2M alkali solution for 10 min.

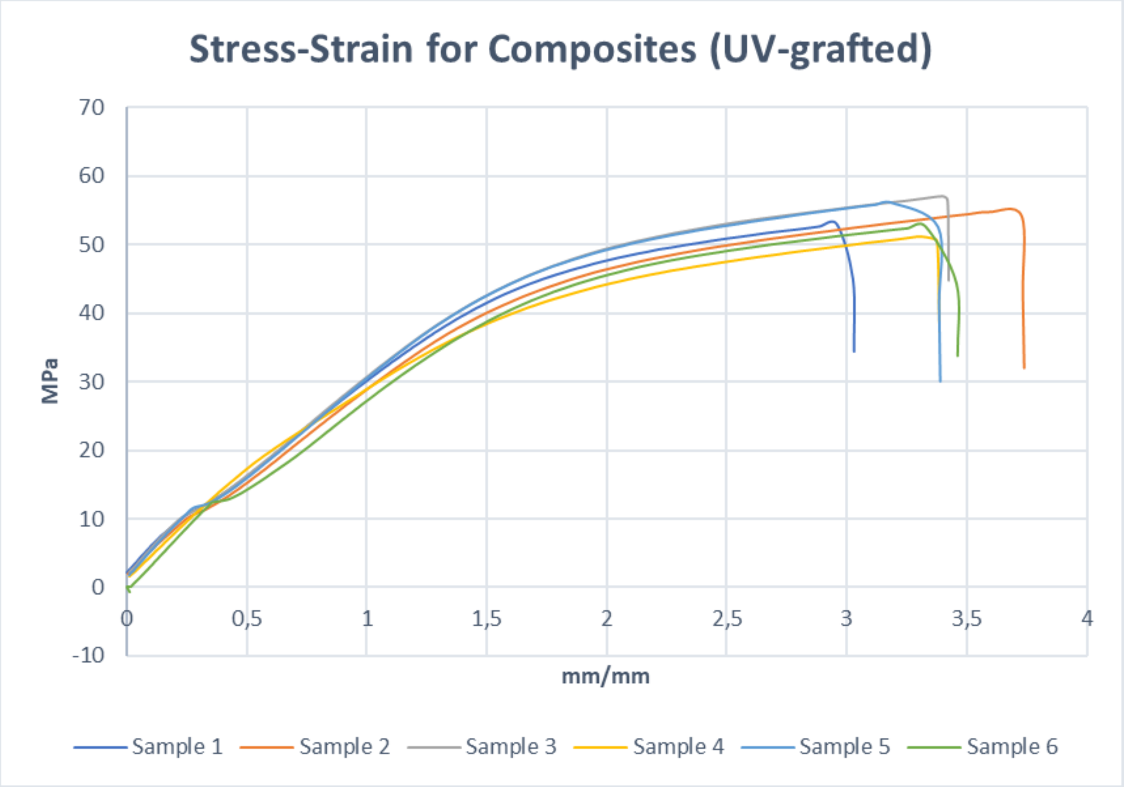

Figure AIII.4. Stress-Strain curves for different samples containing PLA and UV-grafted fibers. All samples have been modified using 20 wt.% of TMPTA.

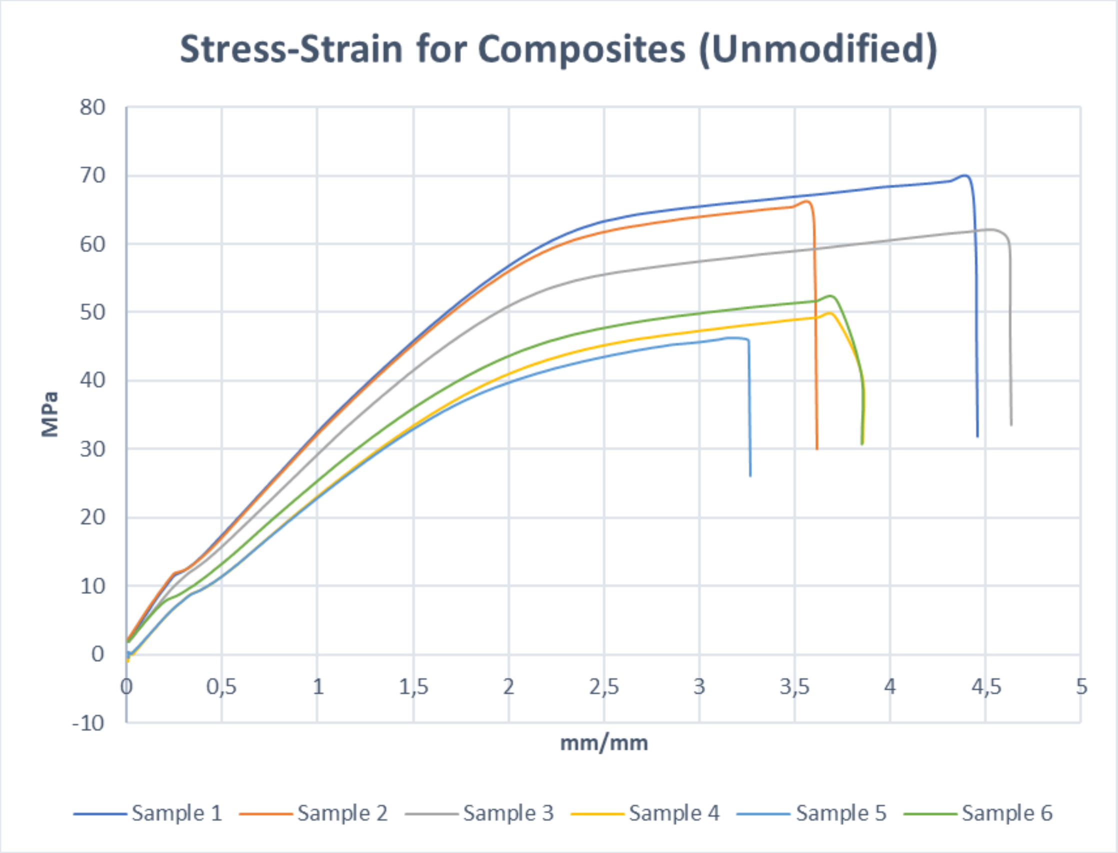

Figure AIII.5. Stress-Strain curves for different samples containing PLA and unmodified fibers.

APPENDIX IV, EXPERIMENTAL OBSERVATIONS

Acetylation with Acetic Anhydride

When using jute fiber and MCC as raw material and high conc. of acid, the material turned dark brown when the solution was poured over the material. This did occur when using high conc. for the scale up of ramie fiber, however, after the reaction the material could not be picked up and was almost gooey-like. The holes that has formed in the scale-up with low conc. of acid had the same dark brown color.

DAA Esterification

The DAA was dark brown and when poured on to the fibers they also turned dark brown (due to absorption of the DAA), however, the fibers that reacted at 80 °C was only very light brown after washing. Fibers reacting at 120 °C did not lose as much color. The water swollen fibers reacting at 120 °C produced a white layer almost immediately after washing. Sometimes the DAA layered itself over the ramie fibers and much of the DAA seemed to not have been absorbed well.

UV-induced grafting

The jute fiber did not turn stiff after the reaction, however, the ramie fibers did; sometimes even forming smaller areas where it felt completely plastic when using >50wt.% monomers. When increasing the height of the UV-lamp, the reaction seemed to not have worked since the material did not gain any stiffness of plastic feel to it.