

THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

# Isolation and chemical modification of arabinoxylan and galactoglucomannan

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Department of Chemistry and Chemical Engineering

CHALMERS UNIVERSITY OF TECHNOLOGY

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Cover: SEM micrograph of arabinoxylan foam, taken together with A. Mårtensson

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## ABSTRACT

Today's society is based on the use of fossil fuels, where oil is used as transportation fuel and as raw material in the petrochemical industry. Efforts are made to increase the use of bio-based materials, since oil is a non-renewable source and a greenhouse gas contributor.

The raw materials used in this thesis are agricultural and forestry by-products. Alkaline extraction was used to isolate the hemicellulose arabinoxylan (AX) from barley husk, while the hemicellulose galactoglucomannan (GGM) was obtained through concentration of pulp process water. Hemicelluloses can be used to produce materials. One way to increase the processability of the hemicellulose is to perform chemical modifications on it. By doing so, the properties of hemicellulose can be altered, such as decreased glass transition temperature ( $T_g$ ), which will change the ability to process the hemicellulose into material.

Two chemical modifications are described in this work; PEGylation of AX and etherification with butyl glycidyl ether (BGE) on GGM. PEG was successfully coupled to AX, acting as an internal plasticiser, resulting in a decreased  $T_g$ . The degree of molar substitution of BGE on GGM affected the thermal and mechanical properties of the modified raw materials. The modified raw materials were investigated for the production of new materials with altered properties compared to the starting materials.

**Keywords:** Hemicellulose, Isolation, Modification, PEGylation, Etherification, Material properties, Films,  $T_g$



# List of publications

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This thesis is based on the studies presented in the following papers, referred to in the text by their Roman numerals.

**I. Arabinoxylan and Nanocellulose from a Kilogram-scale Extraction of Barley Husk**

M. Börjesson, L. Härdelin, F. Nylander, K. Karlsson, A. Larsson and G. Westman

*BioResources*, 2018, 13(3), 6201-6220

**II. Microcellular Foaming of Arabinoxylan and PEGylated Arabinoxylan with Supercritical CO<sub>2</sub>**

L. Härdelin, A. Ström, E. Di Maio, S. Iannace and A. Larsson

*Carbohydrate Polymers*, 2018, 181, 442-449

**III. Altered Thermal and Mechanical Properties of Spruce Galactoglucomannan Films Modified with an Etherification Reaction**

L. Härdelin, D. Bernin, M. Börjesson, A. Ström and A. Larsson

*Submitted*

**IV. Phase separation assisted recovery of modified galactoglucomannan from thermomechanical pulp mill process water**

L. Härdelin, R. Nilsson, D. Bernin, J. Thuvander, M. Börjesson, A. Ström, A-S. Jönsson and A. Larsson

*Manuscript*

# Contribution report

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The author's contribution to the papers presented in this thesis:

**Paper I:** Co-author. Took active part in planning the study. Performed the extraction and the characterisation of the materials together with M. Börjesson. Contributed to the writing of the article.

**Paper II:** Main author. Planned and performed all of the experiments (except for SEM images taken together with Anders Mårtensson). Wrote the article with input from co-authors.

**Paper III:** Main author. Planned and performed all of the experiments. Data analysis of the NMR experiments was done by D. Bernin. Wrote the manuscript with input from co-authors.

**Paper IV:** Main author. Involved in the planning of the study and performed the characterisations. Data analysis of the NMR experiments was done by D. Bernin. Wrote the manuscript with input from co-authors.

## Other publications not included in this thesis

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- A. Electrospinning of Cellulose Nanofibers from Ionic Liquids: The Effect of Different Cosolvents**  
L. Härdelin, J. Thunberg, E. Perzon, G. Westman, P. Walkenström and P. Gatenholm  
*J. Appl. Polym. Sci.*, 2012, 125 (3), 1901-1909
- B. Influence of Rheology and Molecular Weight on Electrospinning Cellulose from Ionic Liquid**  
L. Härdelin, E. Perzon, B. Hagström, P. Walkenström and P. Gatenholm  
*J. Appl. Polym. Sci.*, 2013, 130 (4), 2303-2310
- C. Wet Spun Fibers from Solutions of Cellulose in an Ionic Liquid with Suspended Carbon Nanoparticles**  
L. Härdelin and B. Hagström  
*J. Appl. Polym. Sci.*, 2015, 132 (6), 41417
- D. New Insights on the Influence of Manufacturing Conditions and Molecular Weight on Phase-Separated Films Intended for Controlled Release**  
H. A. Moore, M. Marucci, L. Härdelin, J. Hjærtstam, M. Stading, C. von Corswant and A. Larsson  
*Int. J. Pharm.*, 2018, 536 (1), 261-271

# Abbreviations

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AFM	Atomic force microscopy
AX	Arabinoxylan
BGE	Butyl glycidyl ether
CNC	Cellulose nanocrystals
CNF	Cellulose nanofibrils
CMC	Carboxymethyl cellulose
DMA	Dynamic mechanical analysis
DP	Degree of polymerisation
FTIR	Fourier-transform infrared
GGM	Galactoglucomannan
HPAEC-PAD	High-performance anion-exchange chromatography with pulsed amperometric detection
LC-MS	Liquid chromatography-mass spectrometry
MCC	Microcrystalline cellulose
MS	Molar substitution
<i>m/z</i>	Mass-to-charge ratio
NMR	Nuclear magnetic resonance
PEG	Polyethylene glycol
PLA	Polylactic acid
scCO <sub>2</sub>	Supercritical carbon dioxide
SEM	Scanning electron microscopy
T <sub>g</sub>	Glass transition temperature
T <sub>o</sub>	Onset temperature
TGA	Thermogravimetric analysis
TMP	Thermomechanical pulp

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# CHAPTER 1

## Introduction

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Today's society is based on the use of fossil fuels, where oil is fractionated in an oil refinery before use as transportation fuels or as raw material in the petrochemical industry. Oil is a non-renewable source and a greenhouse gas contributor. To minimize human environmental impact on the planet we need to make a shift from today's petrol-based economy to a bio-based economy [1].

Biomass is a renewable, relatively cheap, and abundantly available potential source for tomorrow's products and chemicals. According to the European Parliament directive 2009/28/EC biomass is defined as a "biodegradable fraction of products, waste and residues from biological origin from agriculture (including vegetal and animal substances), forestry and related industry" [2]. Polysaccharides represent around 75% of the renewable biomass, 20% is lignin and 5% are other natural compounds such as fats and proteins [3].

Plant polysaccharides are cellulose, hemicelluloses, starch, and pectins. Wood has been used to build houses for several hundred years and cellulose has long been used to make paper. Although hemicelluloses are the second most abundant polysaccharide on Earth after cellulose, they are underutilized and are not as widely studied as cellulose [4]. The two main hemicelluloses on Earth are xylans and mannans. Xylans are the most

common hemicellulose in hardwood and annual plants, such as crops and grasses [5]. A great portion of the xylans are found in agricultural by-products and are burnt or used as animal feedstock today. The other main hemicelluloses are mannans, which are the predominant hemicelluloses in softwood [5]. During thermomechanical pulping hemicelluloses are released into the process water. The process water contains less than 1 wt.% total solids [6]. The process water is however available in high quantities and the hemicelluloses in the process water can be recovered by membrane filtration [7, 8].

Hemicelluloses can be used to produce chemicals and materials. One way to increase the processability of hemicelluloses is to perform chemical modifications on it. By doing so, the properties of hemicellulose can be altered, such as decreased glass transition temperature ( $T_g$ ) or increased thermal stability.

## 1.1 Aim and outline of thesis

The main objective of the research presented in this thesis was to evaluate if hemicelluloses can be used for value added products, such as films and foams from modified hemicelluloses. To accommodate that objective, there is a need for supply of raw material. The raw materials used in this thesis are agricultural and forestry by-products. This can be achieved by isolation of hemicellulose from barley husk or by use of the hemicellulose that is released in the thermomechanical pulp (TMP) process water. From a sustainability perspective it is relevant to make use of the different side streams in the extraction process, therefore the possibility of producing nanocellulose from the cellulose fraction isolated during the extraction was looked into.

One specific aim of the work was to investigate the effect of reducing agent on the separation of cellulose and hemicellulose during the alkaline extraction. Also of interest was to determine if the isolation method could be scaled up, since the possibility of having large quantities of extracted hemicellulose is of importance. Efficient ways to concentrate the hemicellulose, which is separated from the cellulose, are of interest for both

the agricultural and the forestry industry. The possibility of increasing the concentration of a hemicellulose and at the same time obtain a modified raw material suitable for production of materials was investigated.

Another aim of the thesis was to reduce the  $T_g$  of hemicelluloses and to alter the mechanical properties. This was achieved by studying the effects of internal versus external plasticisation *via* PEGylation of arabinoxylan. An etherification reaction with an epoxide was employed to reduce the  $T_g$  as a function of the degree of molar substitution. The modified raw materials were investigated for the production of new materials with altered properties.

The work summarized in this thesis has been conducted within the research project SmartFoam. The thesis includes four appended papers. Paper I compares the effect of reducing agent on extraction efficiency and composition of the extracted arabinoxylan. Paper II describes PEGylation of arabinoxylan and how it influences the thermal and mechanical properties of the extracted arabinoxylan. In Papers III and IV galactoglucomannan was modified by an etherification reaction with butyl glycidyl ether and the effect on the material properties was investigated.

The outline of the thesis is that Chapter 2 provides a background and in Chapter 3 a short experimental section is presented. The results from the appended papers are presented and discussed in Chapters 4-6; Chapter 4 presents the results from hemicellulose isolation, Chapter 5 deals with chemical modification of arabinoxylan and in Chapter 6 chemical modification of galactoglucomannan is discussed. In Chapter 7 concluding remarks and future work is discussed.

## CHAPTER 1

# CHAPTER 2

## Background

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### 2.1 The plant cell wall

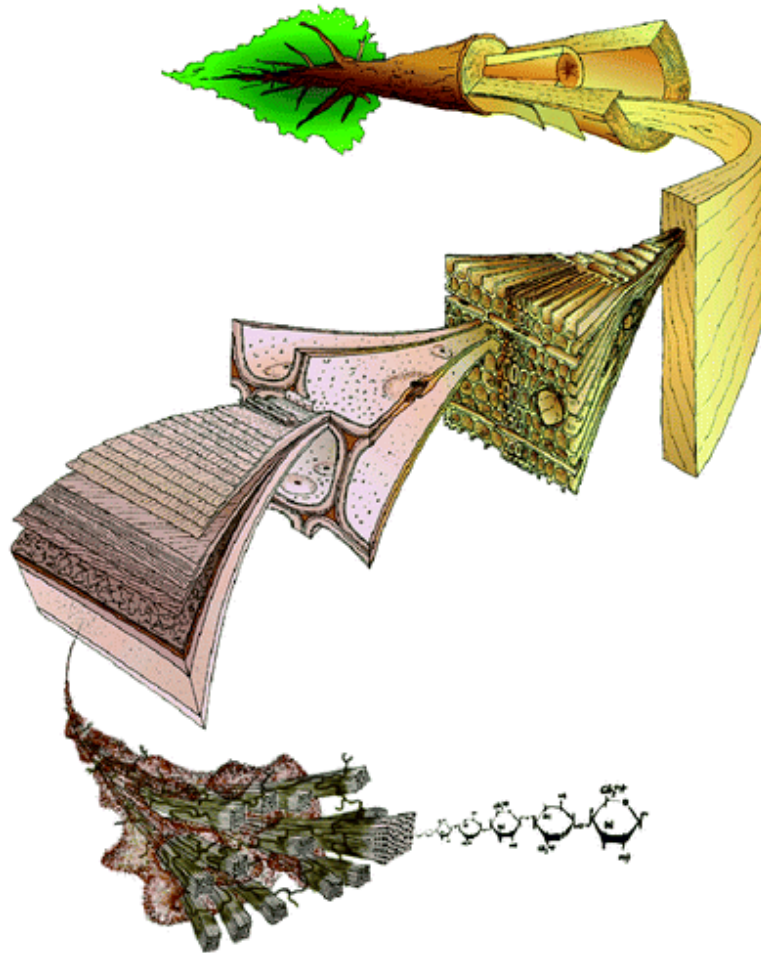
Plant biomass primarily consists of cellulose, hemicelluloses, lignin, and proteins [9]. The cell walls are the major source of biomass in plants and therefore the most important renewable resource. It gives support to the plant so that the plant can stand upright. The plant cell wall is composed of different layers; the middle lamella, the primary cell wall layer, and the secondary cell wall layers which consist of an outer layer ( $S_1$ ), a middle layer ( $S_2$ ), and an inner layer ( $S_3$ ) [10]. The cell wall is a composite material where cellulose acts as fibre reinforcement giving the plant stiffness and rigidity, while the hemicelluloses and lignin together form a matrix surrounding the cellulose [11].

#### 2.1.1 Cellulose

Cellulose was first described by the French chemist Payen in 1838 as a fibrous material that remained after acid treatment of wood. Cellulose is the most abundant biopolymer in the world and can be considered an almost inexhaustible raw material since it is regularly regenerated on Earth. Cellulose is *e.g.* found in wood, grass, and annual plants, where around 35-40% of the dry weight is cellulose. The cellulose molecule is a linear polysaccharide consisting of D-glucopyranose units linked by  $\beta$ -1,4-

glycosidic bonds formed between carbon atom  $C_1$  and  $C_4$  of an adjacent unit. The hydroxyl groups are positioned in the equatorial plane at the  $C_2$ ,  $C_3$  and  $C_6$  atoms and the hydrogen atoms positioned in the axial plane. The degree of polymerisation (DP) of cellulose depends on origin and pre-treatment and varies between 600 and 12 000 [12, 13].

The cellulose chains form microfibrils, which aggregate into macrofibrils. In the microfibrils the cellulose can be arranged in a highly ordered manner, termed crystalline cellulose, and in a less ordered manner, called amorphous cellulose or para-crystalline cellulose [13]. The cell wall in wood has cellulose macrofibrils as the main component and their organization makes up the hierarchical structure of wood as illustrated in Figure 1.



**Figure 1.** Hierarchical structure of wood [14]. © University of Canterbury, 1996. Artwork by Mark Harrington.

### *Nanocellulose*

Cellulose with one dimension in the nanometre range is termed nanocellulose. It is produced by mechanical treatments, enzymes, or hydrolysis of cellulose pulp into *e.g.* nanofibrils or nanocrystals [15, 16]. The cellulose nanofibrils are often termed CNF and the cellulose nanocrystals, CNC [15]. The cellulose nanocrystals consist mainly of the crystalline parts that remain after acid treatment of cellulose. Different cellulose sources and hydrolysis techniques will yield cellulose nanocrystals with various dimensions [17].

Nanocellulose receives a lot of attention as reinforcement in composites due to its unique properties such as high strength and stiffness together with low density, biodegradability, and renewability. These properties can be beneficial in the manufacturing of lighter, stronger materials with improved durability.

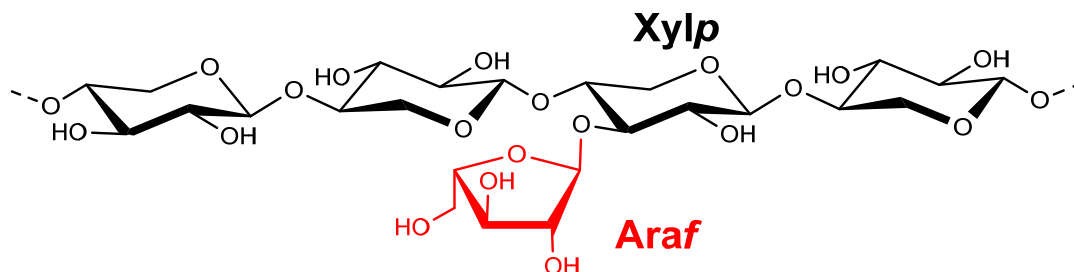
#### 2.1.2 Hemicelluloses

Almost half a century later than cellulose, hemicellulose was discovered. In 1891 Schulze termed this group of polysaccharides hemicelluloses and they were considered to be structurally and chemically related to cellulose [18]. Nowadays the term hemicellulose is used for non-starch polysaccharides found in the cell wall of plants [5]. Hemicelluloses are built up of various monosaccharides, the most common of which are D-xylose, D-mannose, D-galactose, D-glucose, and L-arabinose [19]. The molecular composition of hemicelluloses varies and depends on plant source as well as isolation method. Many hemicelluloses are branched polymer structures with a DP of around 100-200 [9]. The two hemicelluloses used in this thesis are arabinoxylan (AX) and galactoglucomannan (GGM).

#### *Arabinoxylan*

AX has a linear backbone of D-xylopyranosyl (Xyl $p$ ) linked by  $\beta$ -1,4-glycosidic bonds where L-arabinofuranosyl (Araf) side groups are attached with  $\beta$ -1,3-glycosidic bonds [20]. The substituted side groups are situated at positions C<sub>2</sub>, C<sub>3</sub> or both. Arabinoxylans also contain other substituents such

as phenolic acids and acetyl groups [21]. An example of the chemical structure of AX is shown in Figure 2. The structure of AX differs between different species and also depends on where in the plant it is located.

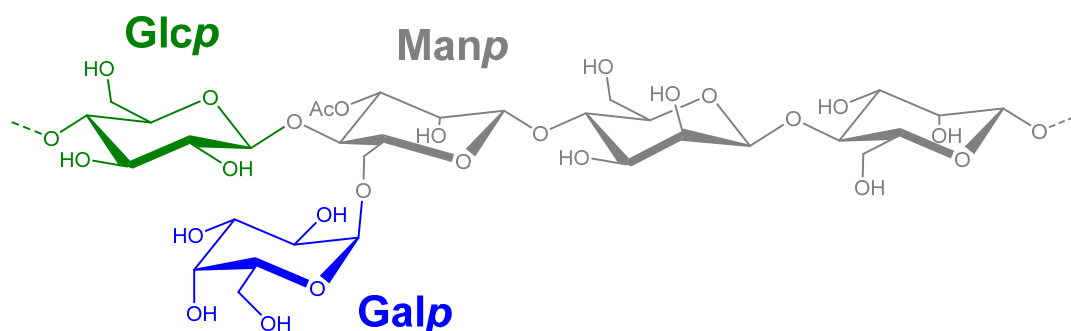


**Figure 2.** Example of a chemical structure of arabinoxylan [21].

The arabinose side groups reduce the interactions between the xylan chains. However, sections of the xylan backbone might be unsubstituted which could cause the chains to interact and aggregate thereby becoming more densely packed [22]. In 1951, Perlin proposed that the solubility of AX was influenced by the amount of arabinose side groups present on the xylan backbone [23]. Andrewartha and co-workers confirmed that a decrease in solubility was seen as the amount of arabinose side groups decreased [24]. The structural features of AX, such as arabinose to xylose ratio, depend on the biomass source but also on the extraction method used [25-27]. The structural characteristics of AX from *e.g.* wheat, rye, and barley, have been studied in detail by several research groups [28-34].

### *Galactoglucomannan*

GGM has a linear backbone of D-mannopyranose (Manp) and D-glucopyranose (Glc<sub>p</sub>) linked by  $\beta$ -1,4-glycosidic bonds randomly distributed where D-galactopyranose (Galp) side groups are attached with  $\alpha$ -1,6-glycosidic bonds [19]. The mannose units are partially acetylated at the C<sub>2</sub> and C<sub>3</sub> positions [35, 36]. An example of the chemical structure of GGM is shown in Figure 3.



**Figure 3.** Example of a chemical structure of galactoglucomannan [9].

Depending on galactose content GGMs are divided into two fractions with low and high galactose content, respectively [9]. The molar ratio between the galactose : glucose : mannose units differs between species, usually 0.5-1.1 : 1 : 3.5-4.5 for water soluble GGM from softwood [8, 9]. The isolation method and starting material will affect the ratios between the sugar monomers [37]. If the galactose side groups are removed the solubility of the GGM is decreased. The acetyl groups also affect the solubility, with more acetyl groups rendering the polymer more soluble in water. Alkaline conditions cleave the galactose groups and the acetyl groups, decreasing the solubility [9, 38].

### 2.1.3 Lignin

The third major component in the cell wall is lignin, where its role is to provide strength by functioning as a glue in the cell wall. It is a complex amorphous polymer network consisting of substituted phenolic units randomly linked to each other. Lignin and carbohydrates form lignin carbohydrate complexes, LCC, which makes it difficult to separate the hemicellulose from the lignin during the isolation process [9, 39, 40].

## 2.2 New materials from biomass

There are several techniques for producing films and foams industrially. In a lab scale environment one of the easiest ways to produce a film is solution casting. The polymer is dissolved in a solvent and the solvent is evaporated leaving a casted film. Larger scale film production is often done with extrusion [41]. Foams can, for example, be produced by freeze drying or

extrusion [42, 43]. Extrusion of foams requires large volumes of raw materials. Small scale techniques, however, such as freeze drying or batch foaming, can be used at lab scale to minimise the amount of material needed.

Synthetic polymer foams have been widely used and were developed in the 1930s and 1940s [44]. Today they are found everywhere in our daily lives *e.g.* in disposable packaging, wound care products, furniture, and insulation [45]. In recent years, interest in biodegradable foams has increased along with awareness of the finiteness of our planet's resources [46]. For production of bio-based products it would be highly beneficial if crude or unrefined streams of raw materials can be utilized [47, 48].

Processing of thermoplastics is a significant industrial and research area. In general, there are three phases during processing of thermoplastics; first the polymer is softened or melted, then it is formed into a shape and then cooled to retain its shape. A variety of processes are used industrially to produce thermoplastic materials where *e.g.* a low glass transition temperature is important. To exemplify; polyethylene terephthalate (PET) which is used to produce plastic bottles has a  $T_g$  of  $75^\circ\text{C}$  [49] and polylactic acid (PLA) used in packaging material has a  $T_g$  of  $60^\circ\text{C}$  [50].

The drawback with processing *e.g.* the hemicelluloses AX and GGM into new materials is that the native hemicelluloses are difficult to process. To increase the processability, a plasticiser can be added to the polymer matrix or the polymer can be modified chemically. External plasticisers are usually added to decrease the interactions between the polymer chains thereby increasing the flexibility. The plasticisers can also be internal plasticisers, meaning that they are attached to the polymer chains [51].

### 2.3 Chemical modifications

Chemical modifications of polysaccharides can be performed by numerous chemical reactions, such as esterification, acetylation, etherification, and oxidation, to name a few [52-54]. The action of attaching polyethylene glycol (PEG) to various molecules is termed PEGylation and has been used extensively in pharmaceutical production [55, 56]. Hydrophilic PEG has also

been used as an external plasticiser to plasticise several compounds, such as chitosan films [57], polylactic acid films [58], and polyvinyl alcohol membranes [59], in order to alter material properties such as elasticity and ductility.

A variety of chemical modifications of GGM have been performed, for example, GGM has been modified using enzymatic crosslinking to produce hydrogels [60]. Oxygen barrier materials have been produced from GGM films [61] and hydrophobic GGM derivatives have been synthesised with esters for barrier applications [62]. Nypelö and co-workers have shown that GGM modified with butyl glycidyl ether (BGE) increased the hydrophobicity of GGM [63]. GGM in wood hydrolysate together with carboxymethyl cellulose (CMC) has been used for production of barrier films with improved oxygen permeability [47, 64, 65].



# CHAPTER 3

## Experimental section

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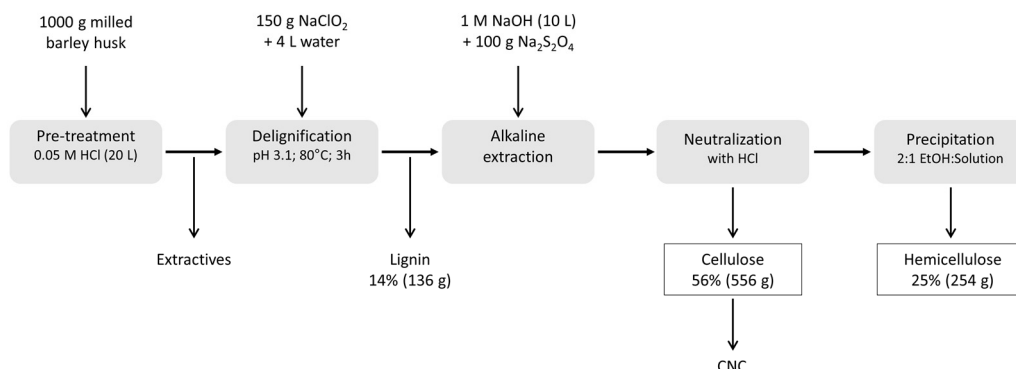
In this chapter a short experimental section is given with more detailed descriptions provided in the appended papers.

### 3.1 Isolation of AX from barley husk

In Paper I, AX was extracted from barley husk and a schematic picture of an example of the extraction process starting from 1000 g barley husk is shown in Figure 4. Extractives in the husks were removed with a 0.05 M HCl pretreatment [66]. Delignification, at 80°C for 3h, was done with NaClO<sub>2</sub> and the pH was adjusted to 3.1 with HCl. This step was optimized in previous work by Claesson *et al.* [67] in which the pH, amount of NaClO<sub>2</sub>, and temperature were varied. The separation of cellulose and hemicellulose was performed in a 1 M NaOH solution containing a reducing agent. Two reducing agents were compared, NaBH<sub>4</sub>, the most commonly used for extractions and the less toxic and lower-cost alternative, Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>. As a reference, extraction without any reducing agent was performed using only a 1 M NaOH solution.

After the alkaline extraction neutralisation was done with HCl, which resulted in two phases. One water soluble phase, rich in hemicelluloses, and one insoluble phase, rich in cellulose. Centrifugation was used to separate the two phases and the solid phase, the cellulose, was washed with deionized water and air-dried for nanocellulose production. The liquid phase was

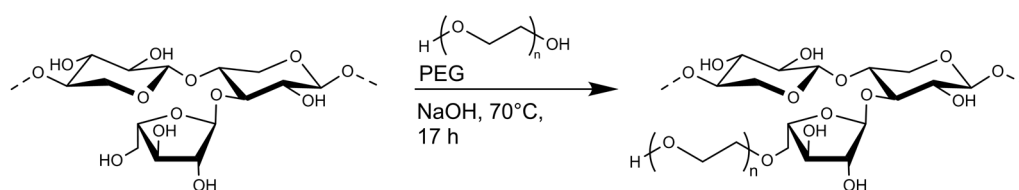
precipitated by dropwise addition to a double volume of ethanol. The hemicellulose was separated through centrifugation followed by air-drying.



**Figure 4.** Schematic example of an extraction process of cellulose and hemicellulose from barley husks starting at 1000 g milled barley husk. The masses given in the schematic are dry weight.

### 3.2 PEGylation of AX

In Paper II, AX was reacted with PEG. In the first step of the PEGylation reaction, the PEG was converted to its chloride derivative by replacing the terminal hydroxyl groups with chloride. This was performed by reacting PEG with HCl, with zinc chloride used as a catalyst for the reaction. NaOH was shown by Jain *et al.* to affect the reactivity of hydroxyl groups [68], therefore, to increase the reactivity of the hydroxyl groups in the AX polymer, the AX was dissolved in a NaOH solution. The PEGylation reaction was done by mixing pre-treated PEG with AX in an alkaline solution with stirring overnight. A proposed reaction mechanism is shown in Figure 5. After neutralisation the PEGylated AX was precipitated by dropwise addition to a double volume of ethanol. The solid material was separated by centrifugation followed by air-drying.



**Figure 5.** Proposed reaction scheme of the PEGylation procedure.

PEG is produced in a variety of molecular weights. It is a mass produced bulk chemical with a low price. Within pharmaceutical science click chemistry has been used for PEGylation reactions [69]. Click chemistry is often performed with expensive chemicals. PEGylation of various compounds have been shown to plasticise and alter the properties of the material [57-59]. The PEGylation reaction employed in Paper II had previously been shown to successfully react PEG with microcrystalline cellulose (MCC) [70]. In this thesis the reaction was adopted to react PEG chains to the AX polymer.

The AX isolated from barley husk was reacted with PEG of two molecular weights, 400 and 1500. The PEG 400 was added at a molar ratio of 1:1 between moles of AX monomer used and moles of PEG 400 used (sample AX-PEG400). Due to practical lab limitations, the PEG 1500 was added at a molar ratio of 1:0.5 to AX monomers (sample AX-PEG1500). A sample was also prepared with 20 wt.% PEG 400 blended with 80 wt.% AX to evaluate if the PEG chains act as an external plasticiser (sample AX + PEG400). Unmodified AX was used as a reference sample (sample AX).

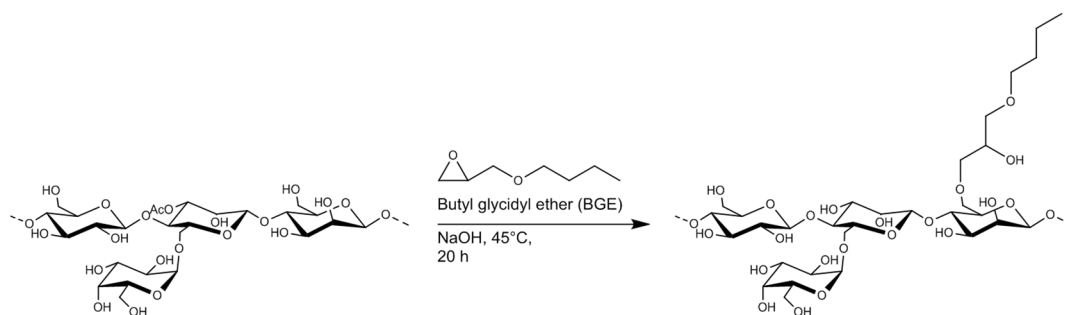
### 3.2.1 Foaming of AX

Films were produced from all four samples by using a hot-press at 130°C with a pressure of 10 MPa for three minutes. To evaluate if the modified AX could produce a stabile solid foam structure, a batch foaming process, with supercritical CO<sub>2</sub> (scCO<sub>2</sub>) as the foaming agent, was used. The foaming procedure, described by Marrazzo *et al.* [71], is such that the samples are inserted into a sealed cylinder, the set foaming temperature and pressure is applied, and the gas, which acts as a foaming agent, is added during the solubilisation time. During this time the gas, here CO<sub>2</sub>, diffuses into the

polymer matrix and when the pressure is released, with a high pressure drop rate, bubbles form within the material. The pressure and temperature applied during the foaming experiments convert the gas to supercritical CO<sub>2</sub>. The foam structure is determined by several factors, *e.g.* the amount of gas dissolved in the polymer matrix, temperature, and pressure [46].

### 3.3 Etherification reaction with GGM

In Papers III and IV, GGM was modified by an etherification reaction with BGE. A proposed reaction scheme is shown in Figure 6. The etherification reaction was performed under alkaline conditions to increase the reactivity of the epoxide. The BGE was added *via* dropwise addition under nitrogen atmosphere and stirred overnight. After neutralisation, dialysis was performed to remove excess BGE and salt.



**Figure 6.** The figure shows one proposed etherification reaction scheme of GGM with BGE.

Films were produced by solution casting. 2 wt.% modified GGM was dissolved in a solvent, poured into a polystyrene petri dish with an inner diameter of 8.7 cm and left to dry at 50% RH and at 23°C until a film was produced.

# CHAPTER 4

## Isolation of hemicelluloses

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### 4.1 Isolation methods

The most common process for extraction of hemicellulose from annual plants is alkaline extraction [72-78] using sodium hydroxide, potassium hydroxide, or barium hydroxide solutions. Alternative methods, such as water extraction [66, 79], dimethyl sulfoxide extraction [80], microwave treatment [81, 82], enzymatic treatment [83, 84], and extrusion [85], have also been explored. Alkaline treatment causes the cellulose to swell, which results in increased hemicellulose solubility [28]. However, although water extraction of hemicellulose preserves the structure of hemicellulose better than alkaline solutions, it has the drawback of relatively low yields of the isolated hemicellulose [26].

The waste water from TMP mills contains less than 1 wt.% total solids, of which 0.2 wt.% is hemicellulose [6], with the main components being: suspended colloidal matter, extractives, hemicelluloses, and aromatic compounds (mainly lignin). By using different fractionation methods, each of these components can be recovered [86]. For example, the suspended colloidal matter can be separated using drum filtration and microfiltration, the extractives can be obtained by microfiltration, the GGM can be recovered *via* ultrafiltration, and the aromatic compounds can be obtained by nanofiltration [7].

In this work the alkaline extraction of AX from the agricultural by-product barley husk is studied. The effect of reducing agent on hemicellulose yield and composition is investigated. The potential of using GGM from waste streams of TMP mills, the process water, as raw material is also investigated. Four different types of GGM have been used in this thesis: (i) GGM from TMP process water filtered with a 75  $\mu\text{m}$  strainer, (ii) GGM from TMP process water microfiltered and ultrafiltered with 10 kDa membranes, (iii) GGM from TMP process water with additional ultrafiltration with 5 kDa membranes, and (iv) GGM from TMP process water that had been chain-extended and spray dried. The composition of the raw materials, *e.g.* the monosaccharide composition and lignin content, were determined.

## 4.2 Effect of reducing agent during extraction of AX from barley husk

In Paper I, the effect of reducing agent on extraction efficiency and composition of extracted AX was evaluated. The process was also evaluated for extracting a cellulose fraction of sufficient quality to be used in further hydrolysis into nanocellulose. To protect the hemicellulose from depolymerisation during alkaline extraction a reducing agent can be added. The role of the reducing agent is to minimize the occurrence of peeling reactions [87].  $\text{NaBH}_4$  is commonly used as reducing agent in small-scale reactions, however, due to its relatively high cost it is seldom used industrially [88]. The lower cost and less toxic  $\text{Na}_2\text{S}_2\text{O}_4$  has been shown to reduce aldehydes [89] and has been used in the pulping process to obtain a pulp with higher yield and higher carbohydrate content [88].

In this study,  $\text{NaBH}_4$  and  $\text{Na}_2\text{S}_2\text{O}_4$  were used as reducing agents during alkaline extraction of AX from barley husk. As a reference, an extraction without reducing agent was also performed. During the neutralisation step, which is done to stop the extraction, addition of  $\text{NaBH}_4$  resulted in foaming, causing this neutralisation step to be delayed. Industrially,  $\text{NaBH}_4$  has been used as a blowing agent for plastics and rubber in many applications [90]. Foaming during the neutralisation step could require larger reaction vessels,

making  $\text{NaBH}_4$  unsuitable for industrialisation. This negative aspect was not seen for  $\text{Na}_2\text{S}_2\text{O}_4$  during the neutralisation step.

The yields from the alkaline extractions are shown in Table 1. The table also shows the Klason lignin content measured in the hemicellulose fraction and the molar ratios between arabinose and xylose in the hemicellulose. When alkaline extraction is performed without a reducing agent the yield of the hemicellulose fraction is reduced. Regarding the two reducing agents,  $\text{NaBH}_4$  and  $\text{Na}_2\text{S}_2\text{O}_4$ , the hemicellulose and the cellulose yields are similar, with a small increase in yield for both the hemicellulose fraction and the cellulose fraction when  $\text{Na}_2\text{S}_2\text{O}_4$  is used. Carbohydrate analysis was employed to determine the monosaccharide composition in the hemicellulose fraction. The main carbohydrates present in all samples were arabinose and xylose, confirming that arabinoxylan is the hemicellulose. The molar ratio between arabinose and xylose were similar for all extractions, as seen in Table 1. To compare, carbohydrate analysis was also performed on the starting material, the barley husk. The results showed that the molar ratio between arabinose and xylose was 0.5:1 in the barley husk, which is similar to the molar ratio determined for arabinoxylan in the hemicellulose fractions. The extraction performed with  $\text{Na}_2\text{S}_2\text{O}_4$  as reducing agent resulted in a somewhat lower lignin content compared to when  $\text{NaBH}_4$  was used. In a thesis presented by Wang, where pre-treatment of spruce was investigated, she also saw that  $\text{Na}_2\text{S}_2\text{O}_4$  had a positive outcome on the hemicellulose yield and a lower lignin content [88].

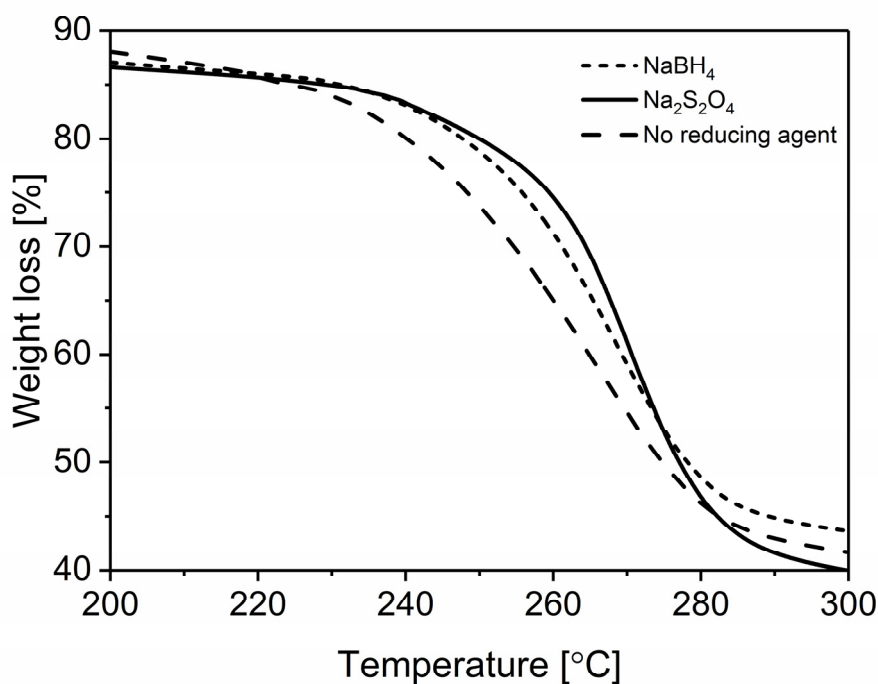
**Table 1.** Yield of cellulose and hemicellulose fractions, Ara:Xyl molar ratio and Klason lignin.

Reducing agent	Yield cellulose fraction	Yield hemicellulose fraction	Ara:Xyl	Klason lignin in hemicellulose fraction
$\text{NaBH}_4$	35%	35%	0.46 : 1	4.0%
$\text{Na}_2\text{S}_2\text{O}_4$	37%	38%	0.48 : 1	3.1%
None	39%	22%	0.46 : 1	2.9%

The Klason lignin is obtained from the hydrolysis of the hemicellulose fraction [91] and is presented in relation to the starting material barley husk.

The thermal stability of the arabinoxylan fractions were analysed using thermogravimetric analysis (TGA) and the decomposition temperatures are illustrated in Figure 7. It has previously been shown that the amount of

arabinose groups on the xylan backbone affected the thermal stability, where a higher arabinose content resulted in a higher decomposition temperature [92, 93]. The chemical composition of a sample will influence the decomposition temperature and differences can be seen in the onset temperature ( $T_0$ ), which is an extrapolated value. Results from the TGA measurements concluded that when extraction was performed without a reducing agent the onset temperature was 240°C. When  $\text{NaBH}_4$  was used the onset temperature increased to 251°C and increased further to 256°C when  $\text{Na}_2\text{S}_2\text{O}_4$  was used. The slightly higher  $T_0$  for  $\text{Na}_2\text{S}_2\text{O}_4$  compared to  $\text{NaBH}_4$  might be related to the small increase in arabinose content and lower lignin content in the sample when  $\text{Na}_2\text{S}_2\text{O}_4$  was used.



**Figure 7.** Partial TGA curves for the hemicellulose fractions isolated from the alkaline extraction.

To accommodate the aim of obtaining large quantities of extracted hemicellulose, several large extraction batches were prepared with  $\text{Na}_2\text{S}_2\text{O}_4$  as reducing agent. Starting from 1000 g milled barley husk around 250 g of AX was obtained, which gives a yield of 25% for the hemicellulose fraction when performed at larger scale. Pilot scale extraction of arabinoxylan from

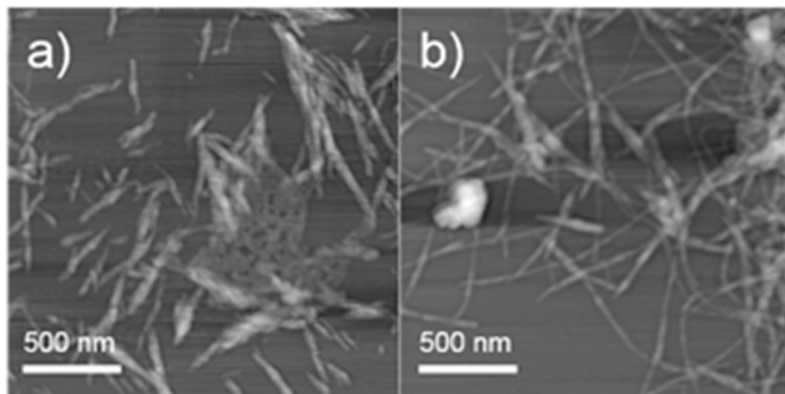
wheat bran starting from 81 kg and 5 kg batches resulted in 13% yield and 16% yield, respectively [76, 94].

In summary, alkaline extraction was performed to extract AX from barley husk, where an alternative reducing agent was evaluated. The less toxic and lower cost alternative  $\text{Na}_2\text{S}_2\text{O}_4$  resulted in higher yields for the extraction, higher arabinose to xylose ratio for the AX, lower lignin content, higher thermal stability, and less foaming at the neutralisation step during the extraction. All combined shows that  $\text{NaBH}_4$  can be replaced with  $\text{Na}_2\text{S}_2\text{O}_4$ .

#### 4.2.1 Nanocellulose from barley husk

MCC and cotton are two common material sources for the production of nanocellulose [15, 16, 95]. The applications for nanocellulose are *e.g.* as reinforcement in renewable nanomaterials. Using barley husk cellulose as the material source would add value, as more side streams generated during the extraction process of AX from barley husk is used for materials production. Previously Espino *et al.* produced nanocellulose from barley husk where alkali combined with a bleaching treatment were used for the isolation of the cellulose, and concluded that the nanocellulose prepared from barley husks gives longer fibrils with a higher aspect ratio than nanocellulose prepared from MCC [96].

In Paper I, the nanocellulose was produced from barley husk cellulose isolated with  $\text{Na}_2\text{S}_2\text{O}_4$  as reducing agent. Nanocellulose prepared from MCC was used as a comparison and the nanocelluloses were analysed with atomic force microscopy (AFM), see Figure 8. The AFM images showed differences in size and shape of the two different types of nanocelluloses, with diameters in the nanometer range for both types. The nanocellulose produced from barley husk cellulose isolated with alkaline extraction where  $\text{Na}_2\text{S}_2\text{O}_4$  was used as reducing agent gives nanocellulose with longer fibres than nanocellulose from MCC. However, different cellulose sources are known to give differences in the size and shape of the nanocelluloses [97].



**Figure 8.** AFM images of nanocellulose prepared using sulfuric acid hydrolysis from a) MCC and b) barley husk cellulose.

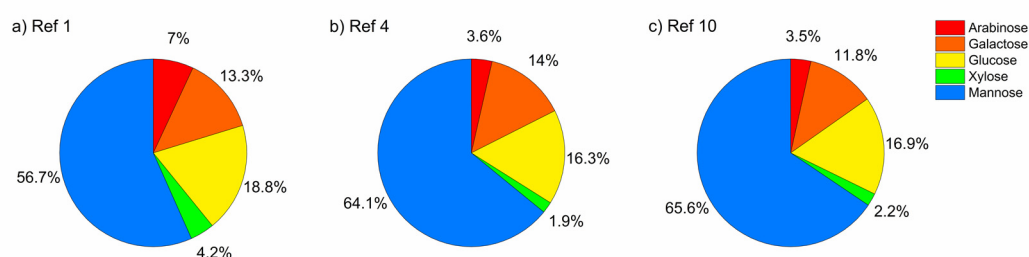
### 4.3 Extraction of GGM from TMP process water

#### 4.3.1 TMP process water

The process water used in Paper IV was received as a gift from a Swedish TMP mill, where spruce is used as the primary raw material. The GGM in the process water was purified and concentrated as described in Thuvander *et al.* [98]. Ultrafiltration was used to remove colloidal extractives. Concentration was performed with membranes with a molecular weight cut-off of 10 kDa and the volume of the GGM solution was reduced by 98%. The hemicellulose solution was further concentrated with membranes with a molecular weight cut-off of 5 kDa and here the volume of the GGM solution was reduced by an additional 66%. This purification and concentration of GGM was performed by colleagues at Lund University and three GGM fractions of varying purity and concentration were received. The dry matter content of the three GGM solutions was determined by drying in an oven until constant weight was achieved, which resulted in 1 wt.%, 4 wt.%, and 10 wt.%. For simplification these fractions are hereafter named Ref 1, Ref 4, and Ref 10 in this thesis.

The dry matter content of the three GGM fractions were characterized with carbohydrate analysis to analyse their respective monosaccharide composition. Sulfuric acid hydrolysis was employed to hydrolyse the samples which were analysed with high-performance anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD) and

the relative carbohydrate composition is shown in Figure 9. The results show that the three samples are similar in carbohydrate composition. Their main carbohydrates are galactose, glucose, and mannose, at an average molar ratio of 0.8 : 1 : 3.5. The molar ratio is in line with what others have determined for water soluble GGM [8, 9]. The total lignin content in the samples was also analysed and the results are shown in Table 2, which shows that the process water contains more lignin than the two membrane filtered fractions *i.e.* 33 wt.% for Ref 1 compared to 9 wt.% and 8 wt.% for sample Ref 4 and Ref 10, respectively. Molar mass was determined by size exclusion chromatography (SEC) to 20 kDa, which gives a DP of 125. Reported DP value for softwood GGM in the literature is 100-200 [9].



**Figure 9.** Relative carbohydrate composition of the three GGM fractions.

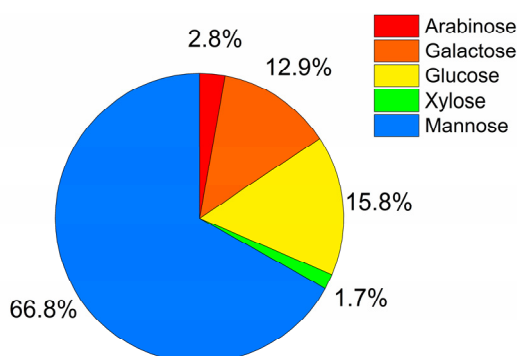
**Table 2.** Lignin content in the three GGM fractions.

Sample	Ref 1	Ref 4	Ref 10
Klason lignin (wt. %)	24.9	4.9	5.3
Acid soluble lignin (wt. %)	8.1	4.0	2.9
Total lignin content (wt. %)	33.0	8.9	8.2

#### 4.3.2 Spray dried GGM

Spray dried GGM was kindly provided by Stora Enso AB (Karlstad, Sweden) and was used as the starting material in Paper III. The GGM had been recovered from a TMP mill and ultrafiltered and enzymatically treated with laccase, resulting in a chain-extended GGM where the polymer chains connect *via* a lignin functionality [99]. The chain-extended GGM was finally spray dried to yield a dry, solid product.

The molar mass of the chain-extended GGM was determined to be 36.5 kDa, which gives a DP of 225. Carbohydrate analysis showed that the molar ratio for the monosaccharides galactose, glucose, and mannose, were 0.8 : 1 : 4.1, which, as for the process water fractions, is in line with previous determinations [8, 9]. The relative carbohydrate composition for the chain-extended spray dried GGM is shown in Figure 10. The Klason lignin was 14 wt.% and the acid soluble lignin 3 wt.%, which gives a total lignin content of 17 wt.%.



**Figure 10.** Relative carbohydrate composition of the chain-extended spray dried GGM.

Comparing the TMP process water fractions and the chain-extended spray dried GGM, some similarities and differences can be seen. The relative carbohydrate composition for spray dried chain-extended GGM is comparable to the ultrafiltered TMP process water with a dry content of 10 wt.%. The lignin content of the spray dried GGM is also higher than both ultrafiltered fractions, however, this is explained by the fact that the spray dried GGM is chain extended *via* a lignin functionality. This chain-extension also contributes to a higher DP, 225 for the spray dried chain-extended GGM compared to 125 for the GGM in the TMP process water.

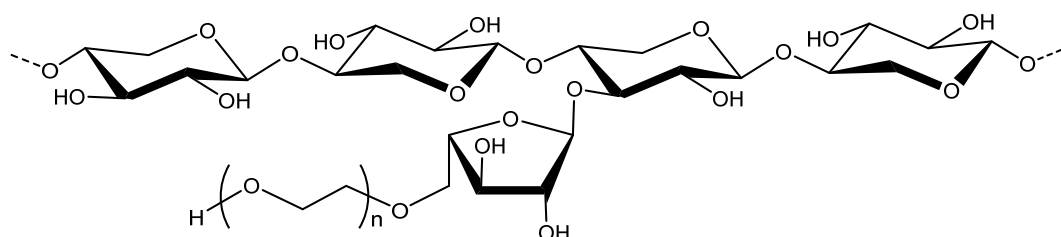
# CHAPTER 5

## Chemical modifications of arabinoxylan

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### 5.1 PEGylation of AX

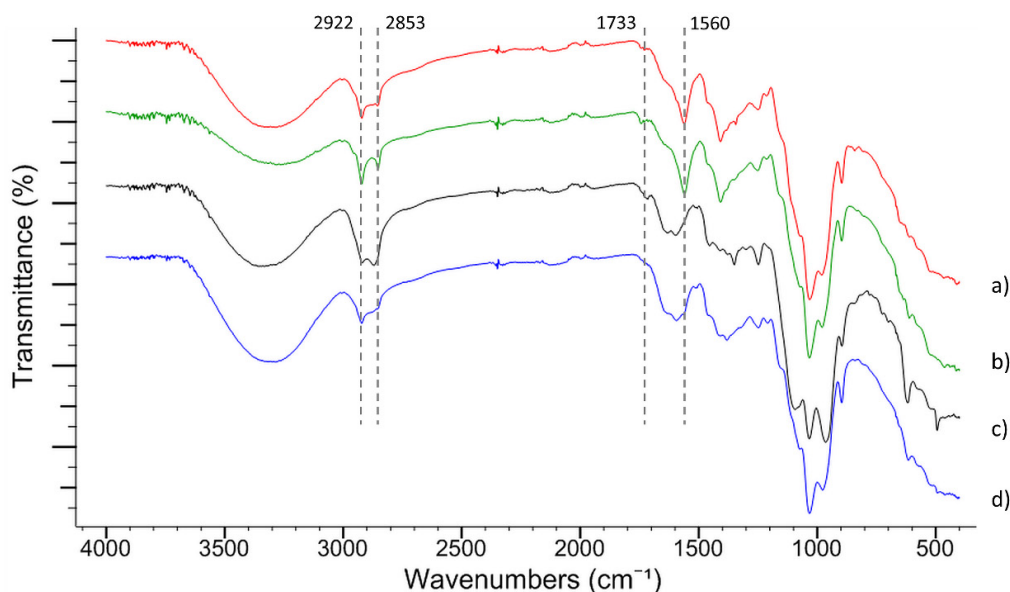
In paper II, PEGylation was performed on AX to study the role of external *versus* internal plasticiser and its effect on  $T_g$ . An example of a PEGylated AX is shown in Figure 11.



**Figure 11.** Example of a chemical structure of PEGylated arabinoxylan.

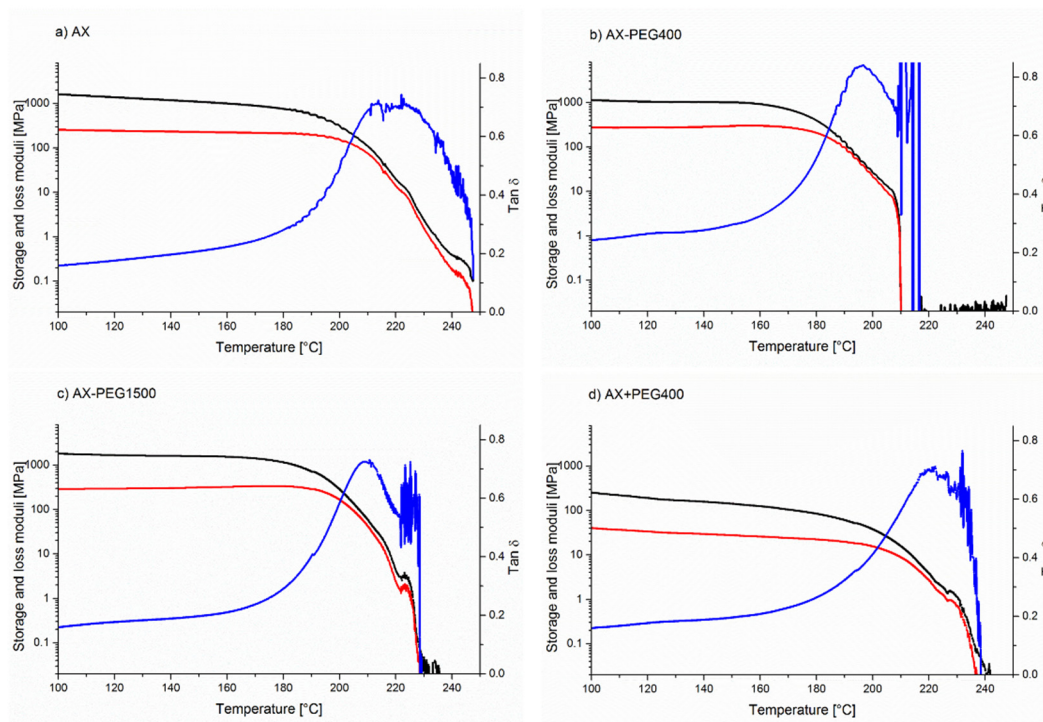
To investigate if PEG was linked to the AX, Fourier-transform infrared (FTIR) analysis was performed, see Figure 12. PEG is linked with  $\text{CH}_2$  bonds and the bonds in the sugar monomers also contain  $\text{CH}_2$  bonds. However, an increase in the intensity of the absorption bands corresponding to  $\text{CH}_2$  stretching, relative to unmodified AX, would indicate that the number of  $\text{CH}_2$  bonds, and thus PEG units, have increased. The absorption bands at  $2922$  and  $2853\text{ cm}^{-1}$  correspond to  $\text{CH}_2$  stretching and show that unmodified AX has the least pronounced absorption bands (Figure 12d). For the sample with PEG 400 blended with AX, the absorption bands have increased (Figure 12c) and the absorption bands for the two PEGylated samples are the most

pronounced (Figure 12a and b), indicating an increased amount of CH<sub>2</sub> bonds in these samples. The hydroxyl group at the end of the PEG molecule is oxidised into an aldehyde which is seen as carbonyl groups in FTIR [100]. For the three samples containing PEG, an absorption band at 1733 cm<sup>-1</sup> attributed to carbonyl groups, is seen, also verifying that PEG molecules are present in the samples. This absorption band is not seen in the AX sample, which does not contain any PEG molecules. To distinguish between PEG coupled to AX, which is expected to give internal plasticisation, and PEG blended with AX, expected to give external plasticisation, absorption bands corresponding to ether bonds were evaluated. The absorption band at 1560 cm<sup>-1</sup> corresponds to ether bonds and is clearly seen for the two samples with PEG coupled to AX (Figure 12a and 12b).



**Figure 12.** FTIR spectra of a) AX-PEG1500, b) AX-PEG400, c) AX + PEG400, and d) AX.

To test the thermal and mechanical properties of the films, dynamic mechanical analysis (DMA) was employed and the results are shown in Figure 13. As seen in the graphs, all samples display insignificant temperature dependence up to around 160–180°C.



**Figure 13.** Thermal and mechanical properties of a) AX, b) AX-PEG400, c) AX-PEG1500, and d) AX + PEG400. Storage modulus (black line), loss modulus (red line), and tan  $\delta$  (blue line).

$T_g$  was defined as where tan  $\delta$  reaches a maximum and was determined for all samples. The unmodified AX displayed a  $T_g$  of around 220°C and the sample where PEG was blended with AX showed a similar transition temperature with a  $T_g$  of around 220°C, however, with decreased moduli compared to the unmodified AX. The sample with 20 wt.% PEG blended with AX consists of 80 wt.% of AX, compared to unmodified AX that constitutes 100 wt.% AX, which could affect the material properties and contribute to decrease in storage and loss moduli. When PLA was externally plasticised with 20 wt.% PEG 400 the storage modulus decreased by half the amount [101].

The  $T_g$  for AX internally plasticised with PEG displayed a reduction in  $T_g$  compared to the unmodified AX and the AX blended with PEG 400. Internal plasticisation with PEG 400 reduced the  $T_g$  to around 190°C and for PEG 1500 to around 205°C. The reduction in  $T_g$  is greatest when PEG 400 is used, compared to when PEG 1500 is used. This could be related to the higher molar ratio during the PEGylation reaction with PEG 400 which could give a

higher substitution of PEG 400 compared to PEG 1500, since a lower amount of PEG 1500 was added. It could also be due to the PEG 400 having a shorter chain than PEG 1500 and therefore a higher reactivity, since the probability of the PEG chain end groups finding an AX polymer to react with is larger.

## 5.2 Foaming of AX and PEGylated AX

Batch foaming with scCO<sub>2</sub> was performed to evaluate if foams could be produced from AX and PEGylated AX. After the foaming was performed the samples were evaluated by their volume expansion during foaming and the results are presented in Table 3. Scanning electron microscopy (SEM) was used to investigate the cross-sectional area of the foamed samples and their foamability was ranked on a scale of 1-5, where 1 represents samples unable to produce foams (represented by the grey background in Table 3). A representative sample of class 1 is shown in Figure 14a. These samples displayed no signs of foamability, instead exhibiting a compact structure and very low to negligible volume expansion. Class 2 is represented by the red background in Table 3, and a representative sample is shown in Figure 14b. These samples started to display some initial small pores but with low volume expansion. In class 3, represented by the orange background in Table 3, a foamed structure is observed in which small pores appear in the samples, as illustrated in Figure 14c. In class 4, represented by the yellow background in Table 3, more and larger pores are seen, as illustrated in Figure 14d. The sample that produced the best foam is represented by the green background in Table 3 and Figure 14e shows a representative sample. Foaming experiments could not be performed at temperatures higher than 170°C.

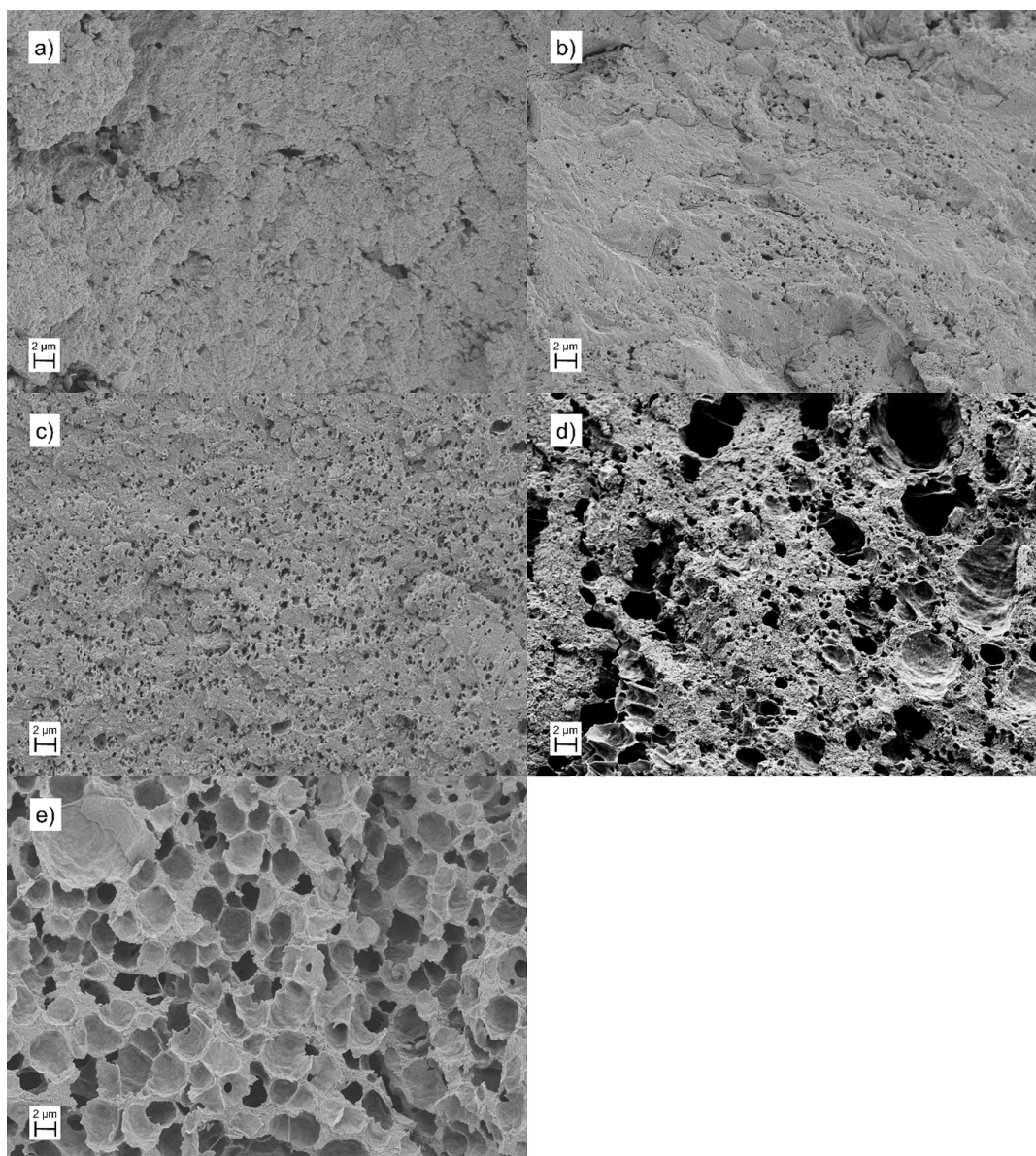
**Table 3.** Foamability and volume expansion (in percent) of foamed samples conducted at different foaming temperatures.

Sample	120°C	130°C	140°C	150°C	160°C	170°C
AX	0	10	0	50*	170**	300***
AX-PEG400	130**	10	0	80	120**	50
AX-PEG1500	0	5	0	0	40*	20
AX + PEG400	0	10	0	30	30	50

\*: One initial bubble in centre of sample

\*\*: One large bubble in centre of sample

\*\*\*: One very large bubble in centre of sample



**Figure 14.** Classification of foamability: a) class 1, AX + PEG400, 150°C; b) class 2, AX-PEG1500, 150°C; c) class 3, AX, 150°C; d) class 4, AX + PEG400, 170°C; and e) class 5, AX, 170°C.

From the classification of the foamability and the morphology of the foamed structures visualised by SEM, it could be concluded that unmodified AX produced the foam with the best foam structure, as illustrated in Figure 14e. When comparing the foamability of unmodified AX with AX blended with PEG, it is the unmodified AX that produces the better foam structure and at a lower processing temperature. This can be due to the interaction of the CO<sub>2</sub> dissolved in the polymer matrix with the PEG molecules instead of it creating

nucleation sites within the polymer [102]. This likely interaction between the CO<sub>2</sub> and the PEG reduces the bubble formation as fewer CO<sub>2</sub> molecules are able to nucleate when the foaming occurs as the pressure is released. This hindering of nucleation sites also seems to happen for the internally plasticised AX, explaining why those samples display a lower foamability than the unmodified AX. However, for the internally plasticised AX with PEG 400, foams with better foamed structure were produced at a lower foaming temperature compared to those for the unmodified AX. This could indicate that foaming can occur at a lower processing temperature when PEG is used as an internal plasticiser and reduces the T<sub>g</sub>. The CO<sub>2</sub> in the process also acts as a plasticiser, for all samples, and lowers the T<sub>g</sub> further, explaining why the foaming can be conducted at temperatures lower than the determined T<sub>g</sub> of the samples.

# CHAPTER 6

## Chemical modification of galactoglucomannan

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### 6.1 Etherification of GGM

In Paper III, the etherification reaction was employed to reduce the  $T_g$  in relation to degree of molar substitution and the modified GGM was investigated for production of new materials with altered properties. GGM was modified with BGE at three molar ratios, *i.e.* 1:1.3, 1:4, and 1:6.7, of moles of GGM monomers used to moles of BGE used.

To determine the molar substitution (MS) for the three reactions performed, nuclear magnetic resonance (NMR) was used. For the two samples with highest theoretical substitution the MS was found to be 1.9 and 2.5, respectively, measured on polymeric samples with  $^{13}\text{C}$  NMR. The polymeric sample with the lowest theoretical substitution did not dissolve sufficiently in the solvent, here  $\text{DMSO-}d_6$ , so the sample was hydrolysed in order to determine the molar substitution by  $^1\text{H}$  NMR and the MS was found to be 1.1. To simplify, the three samples are referred to as  $\text{GGM}_{1.1}$ ,  $\text{GGM}_{1.9}$ , and  $\text{GGM}_{2.5}$ , where the subscript refers to their respective MSs.

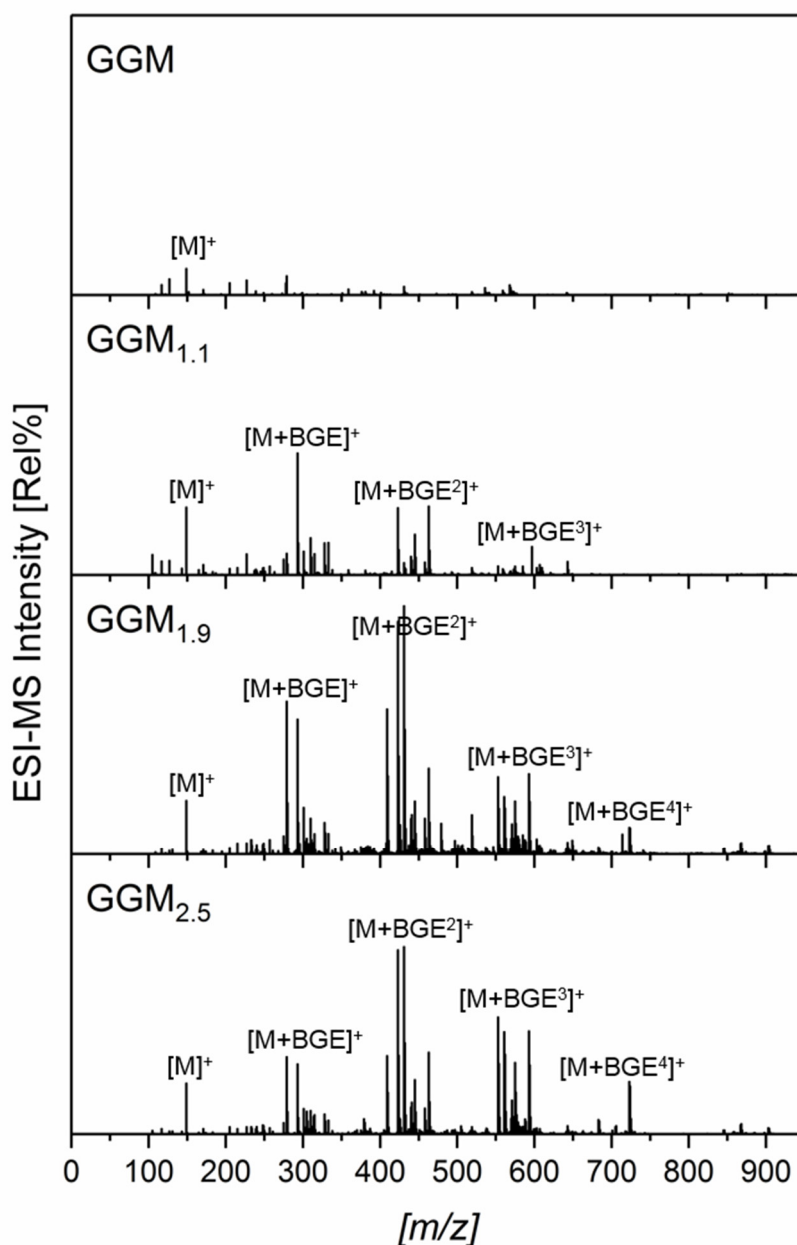
Previously, mass spectrometry has been used to elucidate the fragmentation pattern of spruce GGM [103]. To analyse the mass of the modified samples

liquid chromatography-mass spectrometry (LC-MS) with electrospray ionization (ESI) was used here. The analysis was performed on hydrolysed samples to estimate a degree of substitution. The BGE substituents attached to the monomers would increase the mass and yield a higher mass-to-charge ratio ( $m/z$ ) than monomers without any substituents, which could be used to estimate a degree of substitution *via* mass spectrometry.

The results from the mass spectrometry analysis is shown in Figure 15. It shows that  $m/z$  up to around 900 was detected in samples. GGM monomers are hexoses with a  $m/z$  of 149. Due to the isomeric structure of the monomers in GGM *i.e.* galactose, glucose, and mannose, they cannot be distinguished from each other and therefore they are all detected at the same  $m/z$ . However, monomers substituted with BGE will increase its  $m/z$  by 130 for each substituent that is substituted on the monomer.

Figure 15 shows that GGM monomers are detected ( $[M]^+$ ) and monomers substituted with BGE *i.e.*  $[M+BGE]^+$ ,  $[M+BGE^2]^+$ ,  $[M+BGE^3]^+$ , and  $[M+BGE^4]^+$  is also detected in the analysis. During ionization, ions are formed by adduction of alkali metal to the molecule that is analysed. These ions are known as adduct ions and is the reason why there are several peaks detected in close range of the investigated molecules, *e.g.*  $[M+BGE^2]^+$  [104].

The different masses detected for the samples were used to calculate an alternative molar substitution. The molar substitution determined by NMR was found to be 1.1, 1.9, and 2.5 for the three modified samples. When HPLC-MS data was used, molar substitution values of 1.0, 2.0, and 2.2 were obtained, which are fairly consistent with the MS values determined by NMR.



**Figure 15.** Mass-to-charge ratio  $[m/z]$  on hydrolysed samples. For illustrative purposes the relative intensities are doubled for sample GGM and GGM<sub>1.1</sub>, compared to the other two.

### 6.1.1 Films produced from modified GGM

Films were produced from the chain-extended GGM modified with BGE in order to determine the thermal and mechanical properties of the modified materials. The material with the lowest MS (GGM<sub>1.1</sub>) could not produce any films and the results from that material is lacking from the results that follow.

The reason behind this was that the GGM<sub>1.1</sub> sample could not dissolve sufficiently in water, DMSO, or ethanol, and solution casting from the dispersions resulted in cracked pieces instead of films. Hot-pressing was also attempted but that was unsuccessful. The unmodified GGM is water soluble therefore solution casted films were produced. However, the solution casted films were brittle and difficult to handle. Hot-pressing was also unsuccessful for unmodified GGM since it burned before melting or softening was observed. Solution casted films were prepared from the GGM<sub>1.9</sub> sample, where a mixture of 75% ethanol and 25% water was determined to be the best solvent for this sample when solution casted. Hot-pressing conducted at 110°C directly on the modified material produced a film but better film formation was achieved when the solution casted film was thereafter hot-pressed. The material with the highest MS (GGM<sub>2.5</sub>) dissolves easily in 100% ethanol and films could either be solution casted from ethanol or it could be hot-pressed into films at a temperature of 110°C.

The solubility of a polymer is affected by several parameters [105]. The material with a low MS was insoluble in solvents, such as water, ethanol, and DMSO, which could be related to the acetyl groups and galactose groups being cleaved off during the etherification reaction and the amount of BGE substituted not being enough for it to dissolve in organic solvents. For the other two materials, with a higher MS, dissolution was possible with an ethanol/water solution or ethanol. Nypelö and co-workers noticed a similar behaviour where a low degree of substitution resulted in water solubility and a high degree of substitution decreased the water solubility of the BGE modified GGM [66].

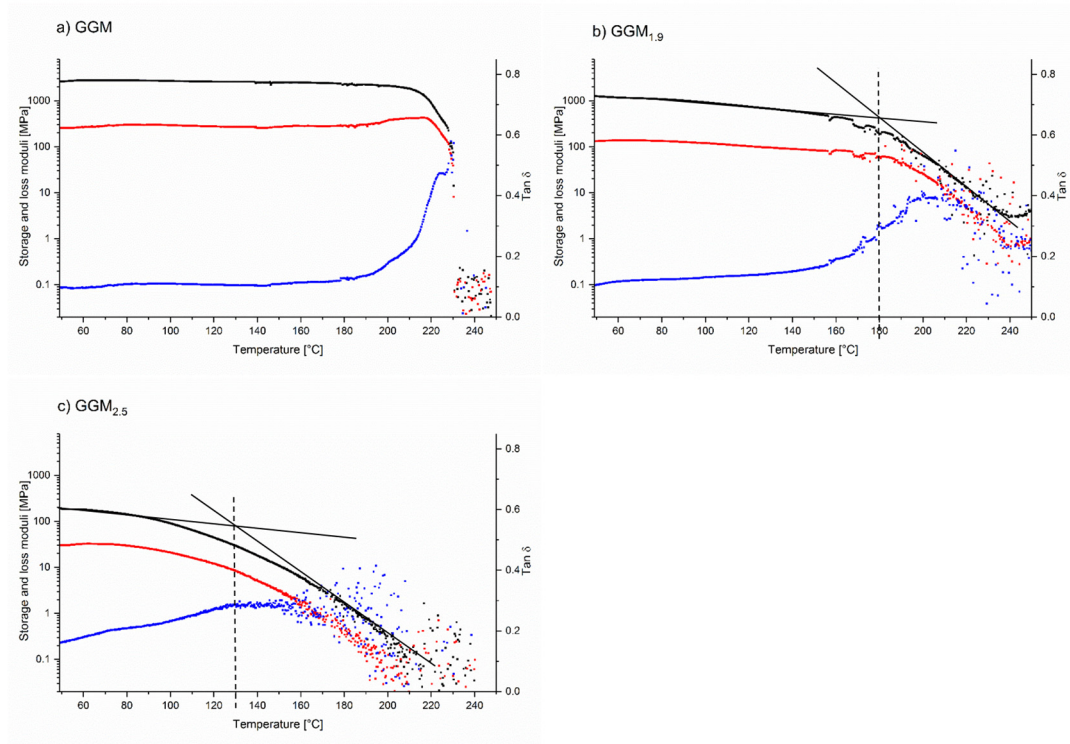
Films were produced from unmodified GGM, GGM<sub>1.9</sub>, and GGM<sub>2.5</sub>, and examples of the films are shown in Figure 16. The unmodified GGM film has sharp edges and is brittle and difficult to manufacture into a specific shape. The films produced from GGM<sub>1.9</sub> and GGM<sub>2.5</sub> can easily be cut into circular shapes. The small colour difference in the samples is due to the different thickness of the films (300-500 µm). The transparency of films indicates that no large-scale aggregations have occurred.



Figure 16. Films produced from GGM, GGM<sub>1.9</sub>, and GGM<sub>2.5</sub>.

### *Thermal and mechanical properties*

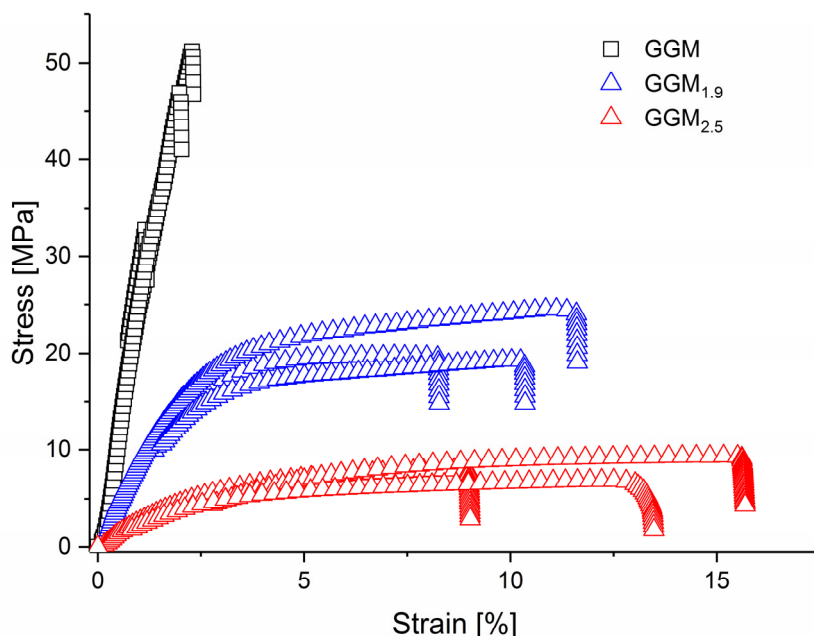
The produced films were analysed with DMA to evaluate their material properties and the results are shown in Figure 17. The material softens as the degree of substitution of BGE increases. The unmodified GGM does not display any transitions and the moduli do not change until the material starts to decompose at 220-230°C. When GGM is substituted with BGE the moduli decreases as the temperature increases. The  $T_g$  is usually defined as a peak in  $\tan \delta$  but a peak in  $\tan \delta$  is not seen in the modified samples. The  $T_g$  was instead determined to be the intersection of two tangent lines from the storage modulus ( $E'$ ) [106], which is the temperature where the stiffness changes rapidly. The GGM<sub>2.5</sub> sample softens rapidly with the increased temperature. What is seen is a continuous reduction in  $E'$  and  $E''$ , which could be related to the increase in mobility of the polymer chains [107]. The  $T_g$  was determined to be 180°C for GGM<sub>1.9</sub> and 130°C for GGM<sub>2.5</sub>. Since the moduli of the GGM<sub>2.5</sub> sample softens so rapidly, that could mean that the  $T_g$  cannot be measured under the conditions used here, and that the  $T_g$  might even be lower than 130°C. In the literature, reported  $T_g$  values for unmodified GGM are given in a broad range, varying between -70°C and 180°C [61, 63, 108].



**Figure 17.** Dynamic mechanical analysis of a) GGM, b) GGM<sub>1.9</sub>, and c) GGM<sub>2.5</sub> with intersection of two tangent lines to indicate  $T_g$ . Storage modulus (black line), loss modulus (red line), and  $\tan \delta$  (blue line).

Tensile tests were performed on the films to analyse their stress strain response. The data is shown in Table 4 and stress-strain curves are shown in Figure 18. Unmodified GGM is stiff and brittle, it fractures at a strain of around 2% but it has the highest stress at break among the tested samples. After modification with BGE the elongation of the samples is improved. The elongation increases from 2% for the unmodified GGM to 7-16% for the modified samples. Plasticisers are usually added to polymers to improve the mechanical properties *e.g.* by increasing the molecular mobility of the polymer [109-113]. Ibn Yaich *et al.* reviewed several studies that report on improved mechanical properties for plasticised hemicellulose films [114]. For example, films produced from the hemicellulose, xyloglucan, containing 20% and 30% sorbitol exhibited improved mechanical properties. The unmodified xyloglucan displayed an elongation of around 2%, a tensile stress of 68 MPa and a Young's modulus of 4 GPa. With sorbitol addition they showed a

ductile behaviour with an elongation of 27%, a tensile stress of 50 MPa and a Young's modulus of 1 GPa [115].



**Figure 18.** Tensile tests performed on triplicates of GGM, GGM<sub>1.9</sub>, and GGM<sub>2.5</sub>.

**Table 4.** Tensile test data (all procedures were performed in triplicate; standard deviations are presented in parentheses).

Sample	Elongation [%]	Tensile stress at maximum load [MPa]	Young's modulus in the linear region [MPa]
GGM	2 (1)	46 (10)	2 700 (250)
GGM <sub>1.9</sub>	9 (2)	21 (3)	600 (150)
GGM <sub>2.5</sub>	12 (3)	8 (1)	200 (50)

The chemical modification of BGE substitution on the GGM affected the material properties of the modified materials. The degree of substitution of BGE affected the solubility of the modified materials as GGM substituted with BGE resulted in an increased solubility in DMSO and a decreased solubility in water. Films were produced from spray dried chain-extended GGM that had been modified with BGE. A higher molar substitution resulted in better film forming abilities. An increased degree of molar substitution lowered  $T_g$  and the moduli of the films decreased with increasing molar substitution. The elongation of the films increased with the degree of molar

substitution and the tensile stress was decreased, meaning that the material exhibits less strength but higher flexibility.

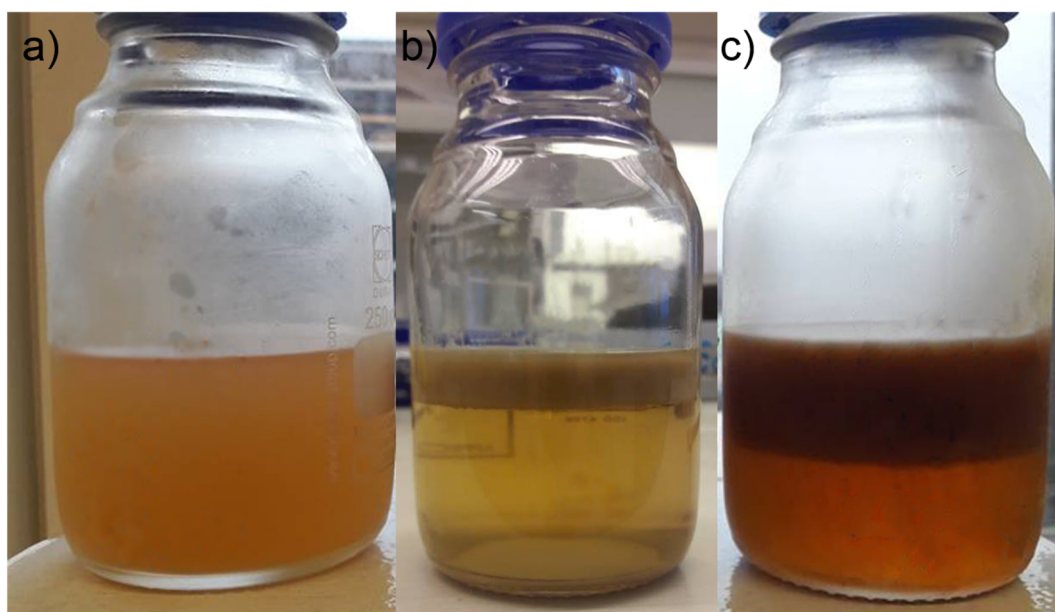
## 6.2 Modification of GGM in process water

Films from modified spray dried chain-extended GGM were produced with altered properties, compared to the starting material. To accompany the aim of increasing the concentration of a hemicellulose in solution and at the same time perform modification reactions, in Paper IV the etherification reaction with BGE was performed on GGM in process water solutions, to evaluate their potential as raw material. The hypothesis was that when GGM is chemically hydrophobized in aqueous solution, the formed hydrophobic modified GGM material will phase separate and can thus be easily separated from the liquid phase for further usage.

The three fractions of process waters with varying concentrations of GGM were modified with BGE. The untreated TMP process water has a solid content of less than 1 wt.%. The membrane filtrations concentrate the process water but the fractions are still in solutions with a high water content. The dry weight of the two membrane filtered fractions were measured to be 4 wt.% and 10 wt.%, respectively. Carbohydrate analysis of the reference materials concluded that the dry matter consisted mainly of the hemicellulose GGM. The etherification reaction between GGM and BGE was done at a molar ratio of 1:5 between moles of GGM monomers used and moles of BGE used. Different concentrations of GGM in the process water could affect the reactivity efficiency since the probability for the BGE unit to find GGM to react with depends on the GGM concentration in the reaction medium. The untreated TMP process water has a low GGM concentration and contains impurities such as salts and lignin, which could negatively impact the reaction yield, compared to the TMP membrane filtered process water fractions with higher GGM concentrations and lower amounts of impurities.

After the modification step with BGE and the neutralisation step, the modified samples appeared different and pictures of the modified samples

are shown in Figure 19. The modified sample using Ref 1 as starting material is noted as modified sample 1 (Mod 1), Ref 4 gave modified sample 4 (Mod 4) and Ref 10 modified sample 10 (Mod 10). Mod 1, depicted in Figure 19a, displayed a one-phase system but Mod 4 and Mod 10, depicted in Figure 19b and c, respectively, displayed two-phase systems with a thicker more viscous non-transparent phase on top.



**Figure 19.** Examples of obtained phases after modification and neutralisation but before dialysis for a) Mod 1, b) Mod 4, c) Mod 10.

The top phase was denoted GGM rich phase as this phase was presumed to mainly consist of modified GGM and was easily separated out from the bottom phase. The bottom phase was denoted “liquid phase” and the respective volumes and dry weight percentages are presented in Table 5.

**Table 5.** Volumes and weight percentages of the samples after modification and neutralisation.

Modified sample	Phase separation after reaction and neutralisation	Volume liquid phase	Volume GGM rich phase	Dry weight percent in the liquid phase <sup>1</sup>	Dry weight percent in the GGM rich phase <sup>1</sup>
Mod 1	No	n.a.	n.a.	n.a	n.a.
Mod 4	Yes (2 phases)	140 mL	32 mL	15 wt.%	38 wt.%
Mod 10	Yes (2 phases)	152 mL	96 mL	20 wt.%	41 wt.%

n.a. = not applicable.

<sup>1</sup> = The dry percent was determined by drying the materials in an oven until a constant weight was achieved.

To investigate the different phases obtained after modification and neutralisation, TGA was run on dried samples. The initial decrease in the TGA measurements is considered to be evaporation of water and the weight loss stabilizes around 150°C. The residual ash was taken as the weight at 500°C. The weight loss between 150°C and 500°C was considered to correlate to the organic material. The results from the TGA measurements from the different phases are seen in Table 6.

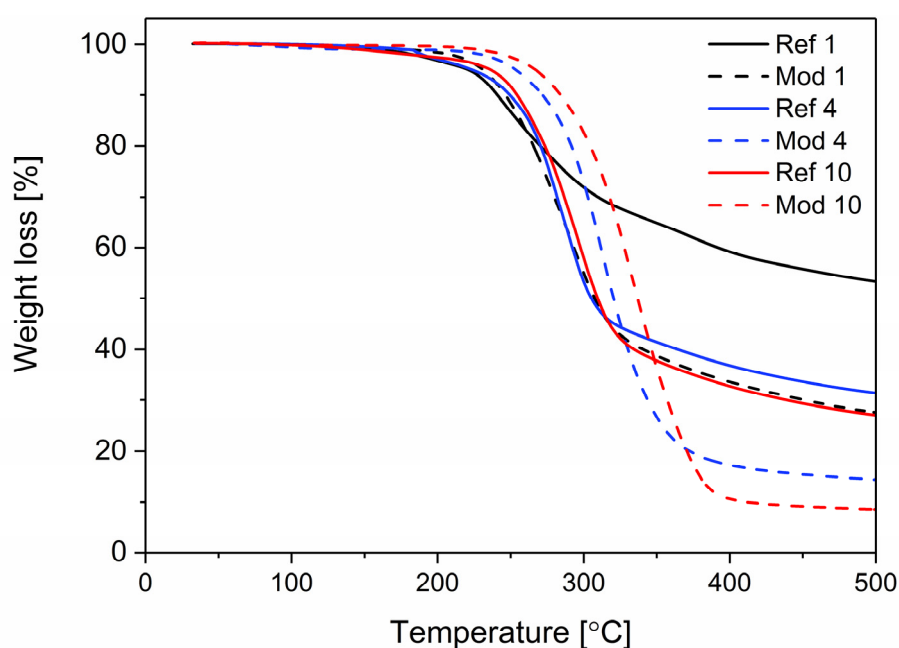
**Table 6.** TGA results from the bottom liquid phase and top GGM rich phase of modified sample 4 and 10 (non-dialysed samples).

Sample	Bottom liquid phases			Top GGM rich phases		
	Water	Organic material	Residual	Water	Organic material	Residual
Mod 4	3.9 wt.%	23.9 wt.%	72.2 wt.%	4.3 wt.%	85.2 wt.%	10.6 wt.%
Mod 10	4.7 wt.%	19.6 wt.%	75.7 wt.%	5.3 wt.%	82.5 wt.%	12.2 wt.%

Comparing the TGA results presented in Table 6, no significant difference was seen between the Mod 4 and Mod 10 samples. The larger part of the bottom liquid phase is residual ash with some minor organic material present. This phase most likely contains salt and other water-soluble material. The major part of the top GGM rich phase contains organic material with 11-12% residual ash. The top phases were put on dialysis for Mod 4 and Mod 10. Since no phase separation was seen for Mod 1 all the material was put on dialysis. The characterisation presented hereafter, for the modified samples, is performed on dialysed samples.

TGA results from the dialysed modified samples and the reference samples are shown in Figure 20 and Table 7. Comparing the reference samples with the modified samples regarding water content, it is seen that the reference samples contain more water than their modified counterparts. The onset temperature ( $T_o$ ) increases after modification for all samples. For the TMP process water the onset temperature is 217°C for the reference sample (Ref 1), which increased to 242°C after modification (Mod 1). Membrane filtration resulted in an increased onset temperature (251°C) for the reference sample (Ref 4) which increased further to 278°C after modification (Mod 4). The second membrane filtration resulted in a small increase in onset temperature to 255°C for the reference sample (Ref 10) and after modification it increased

to 294°C (Mod 10). The membrane filtrations affect the onset temperature seen by the increase in  $T_o$  for the different reference samples. The  $T_o$  also increased with the modification, seen by the increase in  $T_o$  when comparing the modified samples to their respective reference sample. This means that both the membrane filtration and the BGE modification increases the thermal stability of the samples. The total weight loss also increases with modification and filtration. Noticeable is the low total weight loss for the untreated TMP process water. That indicates that the sample (Ref 1) contains high amounts of impurities, *e.g.* salts.

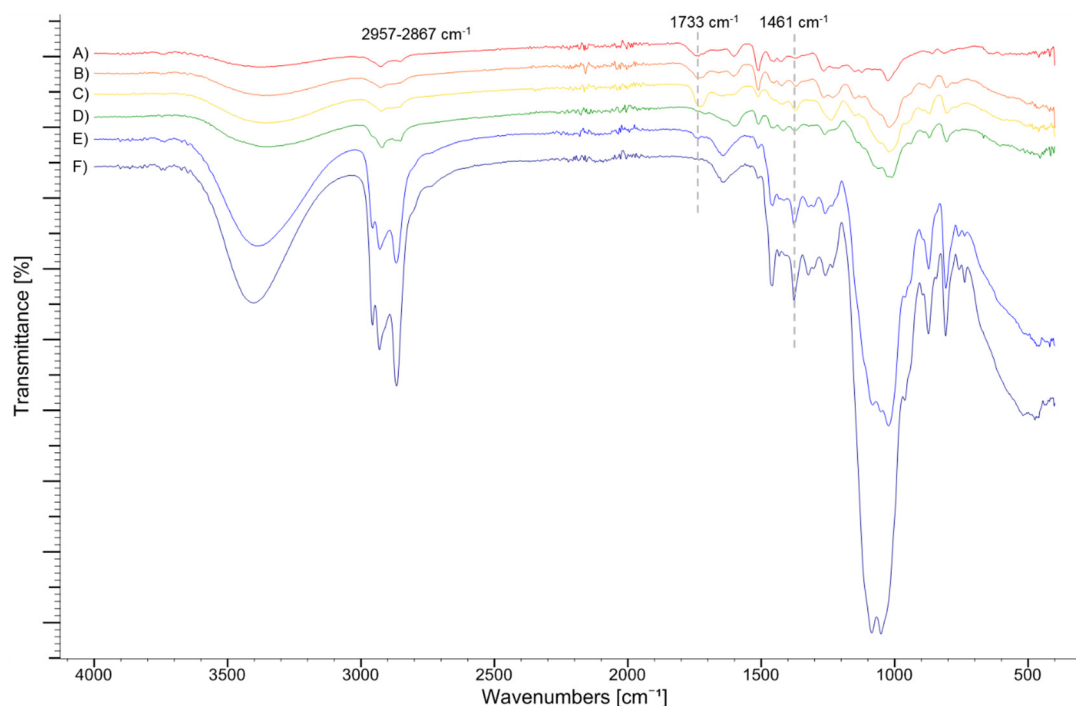


**Figure 20.** Thermogravimetric analysis of the reference samples and the modified samples.

**Table 7.** TGA data of the reference samples and the modified samples.

Sample	Water loss [%]	Total weight loss [%]	T onset [°C]
Ref 1	1.2	49	217
Ref 4	2.2	71	251
Ref 10	1.5	75	255
Mod 1	0.8	74	242
Mod 4	1.4	86	278
Mod 10	0.6	92	294

To characterise if BGE was attached to the GGM, FTIR was performed on the reference samples and the modified samples and the spectrum is shown in Figure 21. The reference samples all display an absorption band at  $1733\text{ cm}^{-1}$  corresponding to acetyl groups in the GGM. Some changes in absorption bands can be seen when the reference samples are compared to the modified samples and a difference is also seen between the modified samples. For Mod 1 the changes in absorption bands is not as pronounced as for Mod 4 and Mod 10. This difference is most likely related to a lower degree of substitution on Mod 1. For Mod 4 and Mod 10 the following changes are seen: the absorption band at  $3600\text{-}3100\text{ cm}^{-1}$  is pronounced and that indicates that the amount of hydroxyl groups have increased. The  $\text{CH}_2$  stretching is seen as a triple peak at  $2957$ ,  $2929$ , and  $2867\text{ cm}^{-1}$ . A new absorption band is located at  $1460\text{ cm}^{-1}$  assigned to C-H scissoring, which is present in the BGE side chain, indicating substitution of BGE in the modified samples.

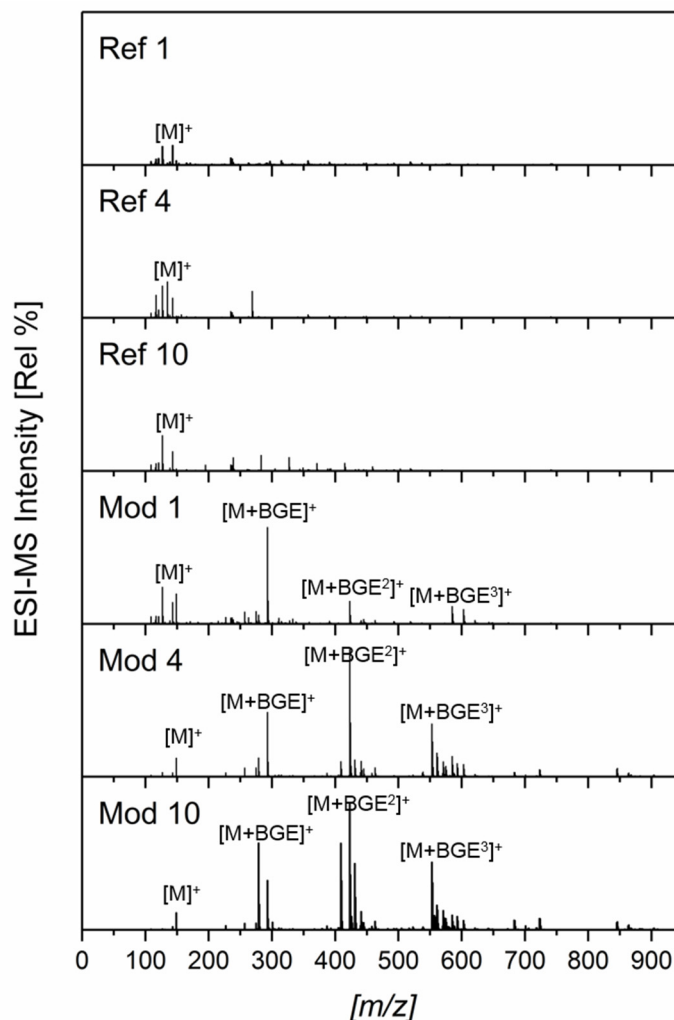


**Figure 21.** FTIR spectrum of a) Ref 1, b) Ref 4, c) Ref 10, d) Mod 1, e) Mod 4, and f) Mod 10.

The molar substitution was determined by  $^{13}\text{C}$  NMR by dissolution of polymeric samples in  $\text{DMSO-}d_6$ . However, the Mod 1 sample could not be dissolved properly therefore acid hydrolysis was performed to produce a

monomeric sample that was dissolved in DMSO- $d_6$ . The  $MS_{\text{NMR}}$  was found to be 0.4 for Mod 1, 2.6 for Mod 4, and 3.8 for Mod 10.

Hydrolysed samples were analysed with liquid chromatography-mass spectrometry (LC-MS) with electrospray ionization (ESI) to analyse the mass of the samples. The results are shown in Figure 22 and the masses detected were used to calculate an alternative molar substitution, where the molar substitution was found to be 0.7 for Mod 1, 2.1 for Mod 4, and 2.3 for Mod 10. Compared to the molar substitution determined by NMR these results differ somewhat. For Mod 1 a higher molar substitution is seen when determined by HPLC-MS but for Mod 4 and Mod 10 a lower molar substitution is found compared to the NMR results. NMR results measure an average degree of substitution of dissolved polymers and mass spectrometry is performed on hydrolysed samples, both of which can influence the results.



**Figure 22.** Mass-to-charge ratio ( $m/z$ ) for the reference samples and the modified samples.

The etherification reaction with BGE was successfully performed on untreated TMP process water as well as membrane filtrated TMP process water. When the reaction was done on filtered TMP process water a phase separation occurred after the modification reaction. This phase separation facilitated easy separation of the modified GGM rich phase, which contained more than 85% of organic material. This shows that membrane filtered TMP process water is preferred compared to untreated TMP process water regarding modification with BGE. It also shows that it is possible to concentrate GGM and perform modification with BGE since a phase separation occurs that allows easy collection of the modified GGM rich phase.

# CHAPTER 7

## Concluding remarks and future work

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The overall focus of this thesis has been on increasing the processability of hemicelluloses in order to increase their industrial utilisation. Processability is a broad concept and in this thesis processability is viewed as lowering of  $T_g$ . The chemical modifications performed, PEGylation of AX and etherification of BGE on GGM, lowered the  $T_g$  and increased the decomposition temperatures. These properties can be desirable when processing polymers as lower processing temperatures can be used thereby reducing costs. The raw materials that are utilised are agricultural and forestry by-products. Today, in industry, they are not used at large scales as raw materials in production of new materials.

Alkaline extraction was investigated for isolation of AX from the agricultural by-product barley husk, where an alternative reducing agent was evaluated. The less toxic and lower cost alternative  $\text{Na}_2\text{S}_2\text{O}_4$  resulted in higher yields for the extraction, higher arabinose to xylose ratio for the AX, lower lignin content, higher thermal stability, and less foaming at the neutralisation step during the extraction. All combined show that  $\text{NaBH}_4$  can be replaced with  $\text{Na}_2\text{S}_2\text{O}_4$ .

Large quantities of extracted AX from barley husk was achieved. Batches starting from 1000 g of barley husk resulted in 250 g dry AX. To utilise more side streams, nanocellulose was produced from the cellulose fraction

obtained during extraction of AX. Compared to nanocellulose produced from MCC, the nanocellulose produced from barley husk cellulose had a higher aspect ratio.

PEG was successfully coupled to AX, acting as an internal plasticiser. The shorter PEG 400 could be added at a higher molar ratio and might also be more reactive than PEG 1500 due to its shorter chain. Thereby PEG 400 is a more suitable option for PEGylation of AX than PEG 1500. Films from all investigated samples could be produced with hot-pressing, showing film forming abilities. A reduction in  $T_g$  was seen when AX was internally plasticised by PEG. However, this was not the case when PEG was blended with AX. Foams were produced with supercritical  $CO_2$  as foaming agent in a batch foaming process. Unmodified AX produced the best foamed structure, possibly due to interactions between PEG and  $CO_2$ , hindering foaming. Foaming of internally plasticised AX could be performed at a lower foaming temperature, which could indicate that a lower processing temperature can be used for processing internally plasticised AX.

The TMP process water contains low amounts of the hemicellulose GGM. As shown earlier, membrane filtration can be used to concentrate water soluble GGM in TMP process water [6]. In this thesis the etherification reaction with BGE was successfully performed on untreated TMP process water as well as ultrafiltered TMP process water. When the reaction was done on ultrafiltered TMP process water, a phase separation occurred after the modification reaction. This phase separation facilitated easy collection of the modified GGM rich phase, which contained more than 85% organic material. This shows that ultrafiltered TMP process water is preferred compared to untreated TMP process water regarding modification with BGE.

Films were produced from spray dried chain-extended GGM that had been modified with BGE. A higher molar substitution resulted in better film forming abilities. The degree of molar substitution of BGE on GGM altered the thermal and mechanical properties of the modified films, where the modified films displayed increased thermal stability and increased elongation in tensile measurements with increased molar substitution. The

degree of substitution of BGE affected the solubility of the modified materials since GGM substituted with BGE resulted in an increased solubility in organic solvents and a decreased solubility in water.

## 7.1 Future work

Possibilities for continuation of the work presented in this thesis:

- Continuation of the study presented in Paper IV to explore if materials with altered properties can be produced from the modified GGM. By using large scale modification of GGM in TMP process water it could be possible to obtain large amounts of modified GGM which can be used for material production, such as films produced by extrusion.
- To investigate the oxygen permeability of the films produced from both PEGylated AX and BGE modified GGM for barrier applications.
- Life cycle analysis (LCA) would be valuable to evaluate the environmental impacts of the chemical reactions.
- The economic aspect of the reactions performed, and the chemicals used, is of interest for potential up-scaling and for industrial application.

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