CHALMERS

Direct Acetylation of Hemicellulose Rich Pulp

On the Effects of Xylan Content on the Properties of Cellulose Acetate

Master's Thesis in Materials Chemistry and Nanotechnology

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CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden 2015

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ABSTRACT

In today's strives towards sustainability and a bio-based economy there is an increasing demand for bio-based plastics. Renewable resources are starting to replace the oil in more and more plastics, with cellulose making a comeback as a plastic raw material. Cellulose acetate is a plastic produced from cellulose and is already today used in a variety of applications ranging from cigarette filters to LCD-screens. To make cellulose acetate, or any plastic, softer and more pliable plasticisers have to be added. There are two main problems with the plasticisers used for cellulose acetate today; they are oil-based and some are classified as hazardous.

Meanwhile, the pulp and paper industry have through diversifying their production qualities and improving energy the efficiency of their process attained new side streams containing hemicellulose. These side streams can be utilised to create new value-adding materials or products, such as plasticisers for cellulose-based plastics, while purer pulp qualities can be used for textiles or plastics. This thesis is aims at investigating the potential of hemicellulose as an internal plasticiser for cellulose acetate by looking at the effect of birch xylan on the thermomechanical properties of direct acetylated xylan-containing cellulose acetate.

Cellulose acetate was prepared by using a method based on the commercial production process for cellulose acetate. The method had to be modified to work with the xylan source. Xylan rich hydrolysates from pre-hydrolysed birch were acetylated together with cotton linters to produce the cellulose acetate. The acetylation was successful, with the cellulose reaching near full substitution. However, only about 15-22% of the xylan remained with the cellulose acetate after the acetylation.

The results for the thermomechanical properties presented in this thesis determine that birch xylan has an effect on the thermomechanical properties of cellulose acetate as it lowers the melting temperature and glass transition temperature of cellulose acetate. There was also a dependence on the amount of xylan added. No optimum cellulose to xylan ratio was found, although the xylan content did not exceed 10%.

The conclusion of this thesis is that acetylated birch xylan produced through pre-hydrolysis shows promise as an internal plasticiser for cellulose acetate.

Keywords: Cellulose acetate, xylan, acetylated xylan, plasticisers, direct acetylation

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1 INTRODUCTION

In today's strives towards sustainability and a bio-based economy there is an increasing demand for bio-based plastics and renewable resources are starting to replace the oil in more and more plastics. A very interesting source for renewable material is wood; consisting mainly of cellulose, lignin and hemicellulose, the most abundant natural biopolymers on earth. Cellulose acetate is a plastic produced from cellulose and is used in a variety of applications. The additives used, such as plasticisers, are however fossil-based.

The traditional utilizers of the wood raw material are the pulp and paper industry and saw mills. However, in the last decades the use of paper for newspapers and printing has declined substantially with many mills closing down as a result. Therefore new applications and markets are needed for the materials and products from the pulp and paper industry. Through diversified production qualities and improved energy efficiency, new hemicellulose rich side streams have formed in the pulp mill. These side streams can be utilised to create new value-adding materials while purer pulp qualities can be used for textiles or plastics.

Peredo et. al. (2015) used bleached Kraft pulp and cotton-xylan blends to produce cellulose acetate in order to investigate if xylan has an impact on the cellulose acetylation and the properties of the acetylated material. It was concluded that xylan did not have a significantly negative effect on the physical properties and that the melting temperature decreased when xylan was added. Similarly (Shaikh, et al., 2009) used hemicellulose and cellulose from sugarcane bagasse for producing cellulose acetate and also came to the conclusion that hemicellulose has potential to act as a plasticiser for cellulose acetate.

1.1 Background

This master thesis is part of the Hemicell project, a collaboration between Fraunhofer Institute for Environmental, Safety and Energy Technology, Innventia, Nova-Institute, Södra, FKuR Kunststoff, ARMINES/Mines ParisTech and OrganoClick. The master thesis is a done in co-operation with Södra, a forest company, which is interested in finding new value-adding applications for side streams in their process.

1.2 Objective

The overall objective of this master thesis is to investigate the potential of hemicellulose as an internal plasticiser for cellulose acetate in order to increase the use of hemicellulose as a renewable, environmentally sustainable resource. The aim is also to investigate possibilities of preparing cellulose acetate from a paper grade pulp, rendering the production of cellulose acetate more resource efficient.

This will be investigated by experimentally producing cellulose acetate from cotton-xylan blends with subsequent material characterisation and evaluation of the material properties.

1.3 Delimitations

Only one hemicellulose, from one source; birch xylan, will be investigated in this project. Therefore conclusions drawn in this report will only be representable for birch xylan and not transferable to other types of hemicellulose.

Only one acetylation method will be used. As the priority is that the cellulose-xylan system works as a whole, no focus will be put on optimising the method with regard to degree of substitution of either components.

Cellulose acetate will be produced by acetylation of a blend of cellulose and xylan, i.e. the xylan will be mixed with cellulose prior to the acetylation rather than acetylating the xylan and cellulose separately with subsequent compounding. This is done to simulate using e.g. Kraft pulp for production of cellulose acetate. The results presented in this report will therefore be limited to xylan as an internal and not external plasticiser.

Due to time constrains only a few select material properties relevant to xylan's plasticising ability will be evaluated as indicators. No regard will be given to other important properties of a plasticiser such as stability, leaching, migration, evaporation or degradation.

1.4 Problem Formulation

The objective of this thesis is articulated as three research questions. These questions focus on how the thermomechanical properties of cellulose acetate are affected by the addition of xylan, as the basic function of a plasticiser is to alter these properties.

How does the addition of xylan affect the thermomechanical properties of cellulose acetate?

Does the ratio between cellulose and xylan affect the thermomechanical properties of cellulose acetate and if so, how?

Does the DP of xylan affect the thermomechanical properties of cellulose acetate and if so, how?

1.5 Disposition of the report

A theoretical background to the master's thesis will be presented in chapter 2, followed in chapter 3 by a description of the experimental and characterising work carried out. In chapter 4 the results of the experimental work will be presented and discussed in relation to relevant literature. Lastly in chapters 5 and 6 conclusions and recommendations for future work will be presented.

2 THEORETICAL FRAMEWORK

This chapter serves to give a theoretical background to the work done in this master's thesis. Areas that will be addressed are; the chemistry and structure of wood components, a brief description of Kraft pulping with its possibilities and challenges, chemical modification of carbohydrates, background and chemistry of cellulose acetate, plasticisers in general and specific for cellulose acetate and lastly the principal for the analytical techniques used for characterisation throughout this project.

2.1 Wood Constituents

Trees are typically divided in to two classes; softwoods and hardwoods were the hardwoods are more evolved than the softwoods and have more advanced reproduction mechanisms, more advanced leaves as well as specialised cells for different functions. This is also reflected in the chemical composition of the trees as this varies between the two classes as well as between species. Wood primarily consists of three biopolymers; cellulose, hemicellulose and lignin. Hemicelluloses have the most apparent variation between the two classes. However, the lignin structure also alters with regard to type of tree.

2.1.1 Cellulose

Cellulose is the main constituent in wood, constituting about 40-45% of dry wood. It is a linear homopolysaccharide, built up by β-D-glucopyranose units, linked with glucosidic bonds, see Figure 1, giving a structure prone to form intra- and intermolecular hydrogen bonds. Cellulose chains display directional chemical asymmetry since the two chain ends are not chemically equivalent; the non-reducing end group has a closed ring structure and is not as reactive as the reducing end group which is a cyclic hemiacetal in equilibrium with the aldehyde which is prone to react. The cellulose chains are bundled together forming elementary fibrils with crystalline and amorphous regions, which in turn build up micro fibrils that are further organized in layered structures forming fibres. The ratio of crystalline and amorphous regions varies in cellulose depending on source, e.g. cotton cellulose is more crystalline than wood cellulose. As a consequence of the strong intra- and intermolecular bonds and fibrous structure cellulose is insoluble in most solvents. Even though the molecular structure is well understood, the morphological and crystalline structure is still debated. The native cotton cellulose chain consists typically of 15,000 glucose residues, which are 5,000 more than native wood cellulose. (Sjöström, 1993)

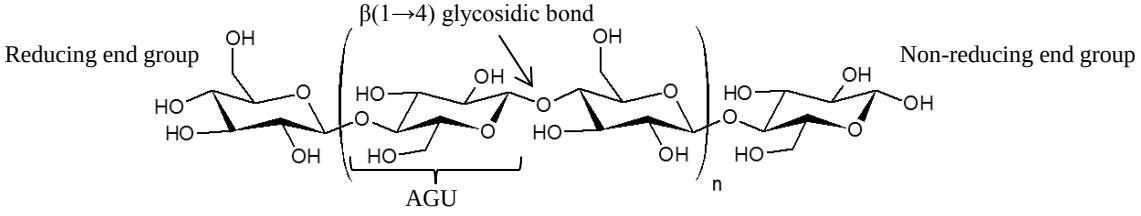

Figure 1. Molecular structure of cellulose with end groups and anhydroglucopyranose unit (AGU).

2.1.2 Hemicellulose

Hemicelluloses are also polysaccharides, but unlike cellulose they are heterogeneous, branched polymers and have a degree of polymerisation of 84-108 (Gellerstedt, et al., 2011). Depending on species the hemicellulose content varies between 20-30 % weight of dry wood. Due to the branching hemicelluloses can be water soluble. More extensive branching as well as lower DP will enhance the dissolution in water. This also makes them more easily hydrolysed by acids as they are more accessible. (Sjöström, 1993)

The hardwood hemicelluloses are distinctively different in composition and structure from the softwood hemicelluloses. The content and composition also varies within a tree, e.g. between stem, branches, roots and bark. The primary softwood hemicellulose is galactoglucomannan but there is also some of arabinoglucoronoxylan present. In hardwood it is the glucoronoxylan that dominates, with smaller amounts of glucomannan. The glucoronoxylan's full name is O-acetyl-4-O-methylglucorono-β-D-xylan, but it is often just referred to as xylan. The backbone consists of β-D-xylopyranose units, linked by the 1→4 xylosicidic bond, with O-acetyl groups at C-2 or C-3 at a ratio of about 4-7 acetyl residues per ten xylopyranosyl residues and 1-2-linked 4-O-methyl-α-D-glucoronic acid residues, on average one glucoronic acid per 8-20 xylose units (Gellerstedt, et al., 2011), see Figure 2. The xylosidic bond is easily hydrolysed while the 1-2-linkage with the glucoronic acid is more resistant. The acetyl group are easily cleaved by alkali (Sjöström, 1993) as well as by acid.

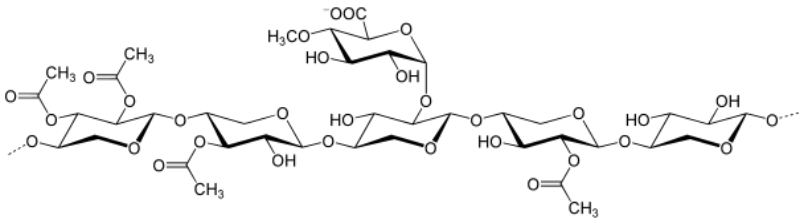

Figure 2. Chemical structure of hardwood xylan.

2.1.3 Lignin

The macromolecule lignin is built up by phenylpropane units covalently bonded with several different types of bonds, mainly ether and ester linkages. The principal structural elements of the lignin molecule are to a great extent elucidated, though the structure of the macromolecule itself is still not clear. A reason for this is that it is very difficult to extract the lignin without degradation or chemical alterations.

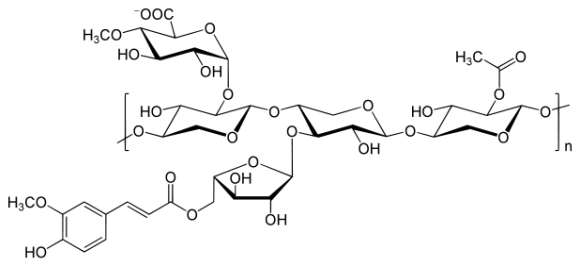

Figure 3. Possible covalent bonding between lignin and xylan.

It has been found that lignin form covalent bonds with carbohydrates, primarily with hemicellulose (Sjöström, 1993), a suggested linkage can be seen in Figure 3. These lignin-carbohydrate complexes must be disjointed in order to achieve a complete separation between the hemicellulose and the lignin. The bond can be hydrolysed in both acidic conditions and alkaline conditions at elevated temperatures.

2.2 Kraft Pulping

Using wood to produce paper has been a commercial process for about 150 years. Paper pulping aims at liberating the fibres from the wood either by mechanical, chemical or semi-chemical treatment. (Sjöström, 1993) Today the dominating process is the Kraft pulping process, a chemical process using sodium hydroxide and sodium sulphide. The fibres are liberated by chemically degrading lignin which holds the fibres together, as well as by introducing charged groups on the lignin fragments, dissolving the lignin fragments and allowing them to be washed away. A mild mechanical treatment is then applied to liberate the fibres. During the Kraft cook there is severe damage to the carbohydrates as the cooking chemicals are not completely selective towards lignin. The cook is therefore not run to completion as the carbohydrate damages would be too extensive. About half of the wood material will be dissolved during the Kraft cook. (Gellerstedt, et al., 2011)

The hemicelluloses are to a greater extent affected by the alkaline degradation compared to the cellulose due to the low DP and amorphous structure. During the beginning of the cook the acetyl groups on hardwood xylan (as well as softwood galactoglucomannan) will be removed by hydrolysis. Peeling will also take place early in the cook, a reaction where the carbohydrate chain is degraded from the reducing end group, peeling off the monosaccharides one by one, see Figure 4. A stopping reaction also takes place, stabilising the reducing end group but this reaction is slower, resulting in approximately 64 monosaccharides being removed by peeling before stabilisation. The glucoronic acids on the xylan chain will also act to stabilise the reducing end group and stop the peeling reaction. The high temperature and alkaline condition will induce alkaline hydrolysis, which cleaves the glucosidic bonds causing a new series of peeling reactions. The carbohydrates will be only partly solvated and degraded as can be seen in Figure 4. However, the solvated polysaccharides will be more or less fully hydrolysed, with mainly monosaccharides and degradation products left. (Gellerstedt, et al., 2011)

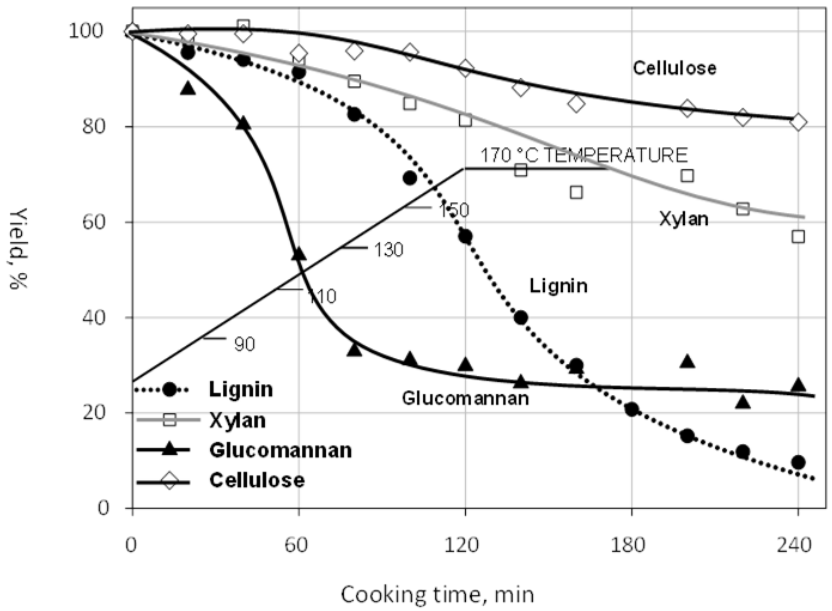

Figure 4. Yield of wood components during Kraft pulping. Data from Aurell and Hartler (1965).

After the cooking the fibres are liberated by rapidly decreasing the pressure and the cooking chemicals with the dissolved lignin fragments and monosaccharides are removed. (Gellerstedt, et al., 2011) If the monosaccharides are separated they can be used to produce alcohol by fermentation. The most common use for the hemicelluloses today is burning them in the recovery boiler together with lignin

and other by-products in the black liquor to produce stream and power, as well as to recover the sodium sulphide in the black liquor. This is however not a very effective use of hemicellulose as the heating value is about half of that of lignin (van Heiningen, 2006). Due to the low heating value and that they do not pose a major part of the black liquor removing them will only have a small impact on the steam and power output. Most modern pulp mills produce an excess of steam and it will thus not pose a problem if the hemicelluloses are removed.

In order to make better use of the hemicelluloses in Kraft pulping, a pre-hydrolysis or autohydrolysis can be implemented prior to cooking to extract hemicelluloses. The pre-hydrolysis uses only water or steam to treat the wood, and it is the hydronium ions from the water in addition to the in-situ formed compounds such as acetic, uronic and phenolic acids that hydrolyses and depolymerises the hemicelluloses. The autohydrolysis reaction can be seen in Figure 5. The hemicelluloses will suffer from degradation processes while the lignocellulosic material will be fairly intact. (Garrote, et al., 1999)

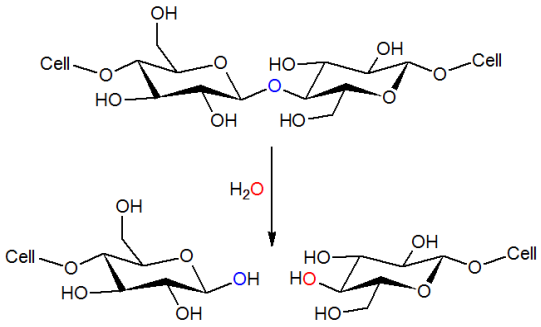

Figure 5. The mechanism for autohydrolysis.

Dissolving pulp is a high purity pulp grade used to produce cellulose acetate, usually made from hardwood. It can be produced using the Kraft process, but the biggest supplier of cellulose acetate grade dissolving pulp is the sulphite process. The reason is that the Kraft process pulp requires more bleaching which makes it a less economically viable process for producing dissolving pulp of that purity. When producing dissolving pulp, the hemicelluloses, and lignin, are nearly completely removed generating an even bigger surplus of hemicelluloses in the black liquor. Pre-hydrolysis prior to producing dissolving pulp would reduce the need for bleaching.

2.3 Chemical Modification of Carbohydrates

Carbohydrates in general and cellulose in particular, have throughout history been a material of interest due to its unique properties. Some of the properties that make cellulose an interesting material is the renewable character, general strength, hydrophilicity, insolubility in water, stability against chemicals, etc. (Sjöström, 1993). Due to this, cellulosic material has been the subject of a great variety of different modifications, both mechanical and chemical. The chemical modifications vary from substitutions with nitrates and acetates to graft polymerisation. The modifications are performed on the hydroxyl groups at C2, C3 and C6 as they are readily available for substitution, see Figure 6. Hemicelluloses have similar chemistry to cellulose, however the hydroxyl groups vary, for instance xylan has just two hydroxyl groups, see Figure 2. Small amounts of aldehydes and carboxylic acids, usually originating from the pulping, can occur and will also be targets for substitution. This has a greater influence on the hemicelluloses as these types of functionalizations are more common. Chemical modifications to cellulose generate a drastic change in the material properties making it a very versatile material. Esterification and etherification are the most common modifications. (Hon & Shiraishi, 2001)

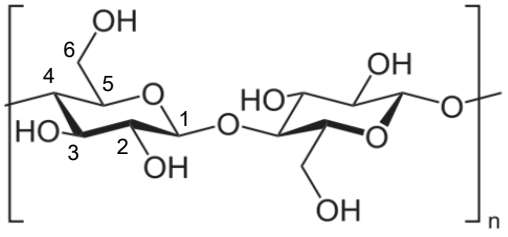

Figure 6. The molecular structure of cellulose with the three hydroxyl groups available for substitution.

2.4 Cellulose Acetate

Acetylated cellulose, commonly called cellulose acetate, was first prepared by Schützenberger in 1865, although a production process of the polymer was not developed until 1894 by Cross and Bevan. A less substituted polymer (cellulose diacetate) that was soluble in acetone and other easily available solvents was developed in 1904 by Miles, see Figure 7. This came to use as safety film and also to waterproof and stiffen fabric covered airplane wings during the First World War. (Rustemeyer, 2004)

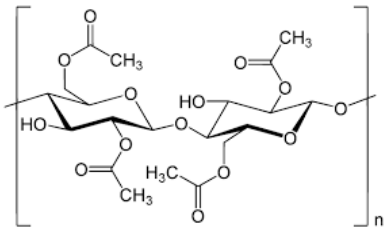

Figure 7. Cellulose diacetate.

The development of cellulose based plastics, including cellulose acetate, came to a halt during the 1960s as the oil based polymers could be produced to a much lower expense, with great variability, easier processing and good properties. (Sjöström, 1993) Cellulose acetate is nevertheless a superb plastic, and is making a comeback as an eco-friendly plastic, as it is produced from renewable raw material. It has applications in a wide range of areas, e.g. lacquers, plastics, composite fabrics (Sjöström, 1993) and LCD screens (Bogard, et al., 2001). The properties, and therefore also applications, depend strongly on if the hydroxyl groups are fully or partially substituted with acetate groups, the distribution of these substituents, the molecular mass and the molecular mass distribution (Hon & Shiraishi, 2001) as well as the cellulosic starting material (Sjöström, 1993). The most favourable position for substitution is C6, substitutions on C2 and C3 occurs statistically (Heinze, et al., 2006). In the case of the cellulosic starting material it has very high requirements for purity and cotton linters or highly pure dissolving pulp are usually used.

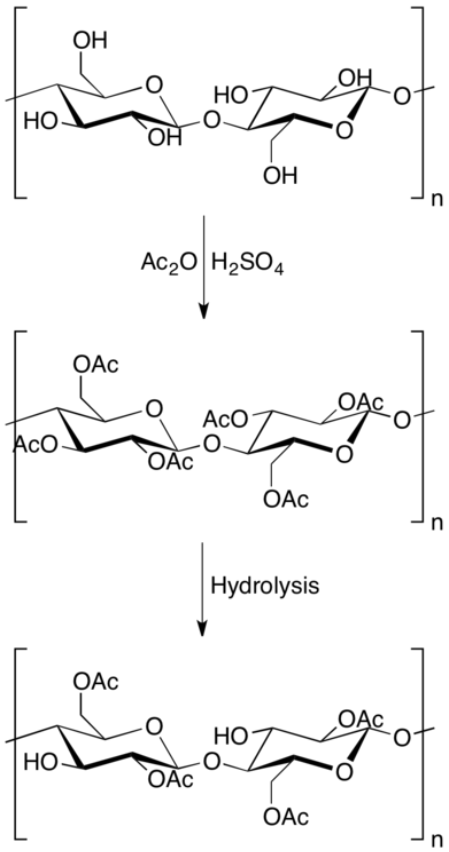

Figure 8. Acetylation of cellulose forming triacetate and the subsequent deacetylation to form of cellulose diacetate.

The most common production process for cellulose triacetate is by pre-treatment of cellulose pulp with acetic acid followed by a condensation reaction with acetic anhydride in the presence of a catalyst, often sulphuric acid, see Figure 8. As the system is heterogeneous the reaction rate is controlled by the diffusion of the reagents into the fibre structure. (Sjöström, 1993; Hon & Shiraishi, 2001) If water is present side reactions between the water and reagents will occur creating by-products as well as lowering the overall reaction efficiency (Hon & Shiraishi, 2001). Cellulose diacetate is produced by partial deacetylation of cellulose triacetate through hydrolysis using an aqueous acetic acid solution resulting in a DS of 2-2.5, see Figure 8 (Sjöström, 1993). It is within this substitution region that cellulose acetate becomes thermoplastic and soluble in acetone and it is this grade that is generally used (Heinze, et al., 2006). The glass transition temperature of cellulose acetate decreases with increasing DS, it is however independent of molecular weight, except for very high degrees of substitution. The melting temperature has a minimum around DS 2.5 (Kamide & Saito, 1985).

2.5 Plastics and Plasticisers

Polymers are large molecules built up by one or more repeating units covalently bonded to each other, where both synthetic and natural polymers, also referred to as biopolymers, exist. Due to the large size of the polymer the properties will differ greatly to the properties of the equivalent monomer. All polymers will be hard, rigid solids at sufficiently low temperatures and adopt different structures with a different level of order depending on intermolecular forces, molecular structure, etc. The level of order varies from amorphous polymers with no order to perfectly crystalline. However, perfectly crystalline polymers do not exist and in reality polymers are semi-crystalline with varying degrees of orders from high to low.

When the temperature is increased beyond the point where the polymer ceases to be hard and rigid, the chains will be able to move more freely making polymer more rubbery. The temperature interval where this occurs is called the glass transition temperature T_g. When the thermal energy of the system is adequate for the all of the chains to move freely the polymer will start to behave as a viscous liquid. The temperature interval where this occurs is called the melting temperature, T_m, and is affected by the thermal history of the polymer material. (Cowie & Arrighi, 2007)

For a polymer to become functional and processable in different applications the properties must be improved. This is accomplished by introducing additives into the polymer material, making it a plastic. An example of such an additive is plasticisers, which make the polymer softer, more flexible and more pliable. Plasticisers can be either low molecular weight compounds with a high boiling-point that are compatible with the polymer, called external plasticisers, or they can be structural groups incorporated into the polymer, called internal plasticisers. These will, in addition to alter the polymer properties as described above, also lower the T_g of the polymer. (Murphy, 1999; Dolbey, 1997) The amount of plasticiser added will affect the extent to which the T_g is lowered. (Cowie & Arrighi, 2007)

2.5.1 Commercial Plasticisers for Cellulose Acetate

Many different plasticisers have been used to plasticise cellulose acetate throughout its history and wide variety of applications. The most common plasticisers used for cellulose acetate are citrates, phosphates, phthalates and glycols with different functionalization. (Wypych, 2004) Examples representing these types of plasticisers are shown in Figure 9. There are two main problems with these plasticisers; they are oil-based and some of them are hazardous, with risk phrases such as *"Dangerous for the environment"*, "*Very toxic to aquatic organisms", "May cause long-term adverse effects in the aquatic environment"* (Sigma-Aldrich, 2013), *Harmful by inhalation* (Sigma-Aldrich, 2014). It is therefore desirable to replace these plasticisers with environmentally friendly, renewable plasticisers.

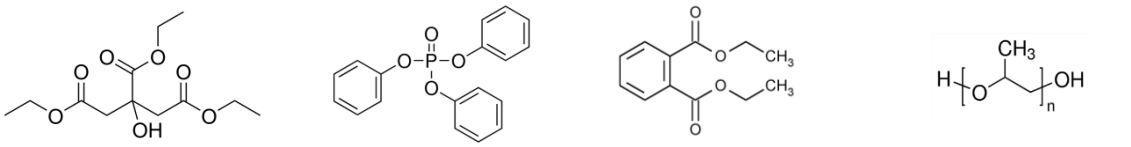

Figure 9. Examples of common plasticisers used for cellulose acetate.

2.6 Analytical Methods

In this section the basic working principals of the analytical methods used in this master thesis will be presented. Six analytical techniques were used for characterisation of starting material and product.

2.6.1 Carbohydrate analysis

The carbohydrate compositional analysis uses acid hydrolysis to degrade the polysaccharides to monosaccharides. In this case the monosaccharides from the hydrolysis are analysed using high performance liquid chromatography. The HPLC technique is based on using pressure to force solvent and solutes through closed columns that are packed with fine particles. The separation of solutes is based on their affinity for the stationary phase. (Harris, 2010)

2.6.2 Methanolysis

Methanolysis can be seen as an alternative method for analysing carbohydrate composition. An acid hydrolysis is performed in an HCl-methanol solution, converting the polysaccharides to methylglucosides. Unlike in the carbohydrate analysis method described in 2.6.1 this method preserves the uronic acid groups much better as they are esterified and cleaved off from the hemicellulose backbone without being degraded (Gellerstedt, et al., 2011) Gas chromatography coupled with a mass spectrometry detector is used to detect the compounds.

2.6.3 Nuclear Magnetic Resonance

Nuclear magnetic resonance, abbreviated NMR, is a spectroscopic technique that uses nuclear spin transitions. For a nucleus to be detected by NMR is has to have an odd number of protons and/or neutrons, as they will have a magnetic moment generated by their spin and charge. Most common is to look at nuclei with spin ½, like ^{1}H or the carbon isotope ^{13}C. The technique uses a strong magnetic field that is applied on the sample causing the nuclei to precess (change orientation of the rotational axis). The charge of the nuclei will, upon precession, generate an oscillating electric field. By applying radiofrequency waves of the same frequency as the oscillating electrical field the energy can be absorbed causing the spin of the nuclei to change, a phenomena called resonance. This can be utilised to obtain information regarding the nature of the immediate environment of each nuclei. The radiofrequencies at which there is absorption generates the peaks in the spectrum, and the absorption depend on the immediate environment of the nuclei.

2.6.4 Gel Permeation Chromatography

Gel permeation chromatography, also known as size exclusion chromatography and molecular exclusion chromatography, is used to look at the molecular weight and molecular weight distribution. In this report it will be referred to as gel permeation chromatography, abbreviated GPC. The technique is based on separating molecules by their size. This is accomplished by passing the mobile phase, either liquid or gaseous, through a porous gel. The smaller molecules will go in to the gel and be delayed as they will have to flow through a larger volume compared to the large molecules that will not enter the pores and therefore pass through the column faster. (Harris, 2010) It is rather difficult to compare results between different GPC systems as the hydrated radius of the molecules will differ depending on the mobile phase and on structure and chemical composition of the molecule. The elution times are calibrated to a standard but the factors mentioned above gives reason to use caution when interpreting the results.

2.6.5 Differential Scanning Calorimetry

In differential scanning calorimetry, abbreviated DSC, a sample is heated at a constant rate and the heat flow to the sample is measured as a function of the temperature. The sample is heated in a heat

sink, with a reference sample heated in a separate heat sink, with individual heaters. The sample and reference will be kept the same temperature by differential heating and any changes in the samples temperature will trigger a response to supply more or less energy to the sample. A phase transition in the sample calls for a significant change in energy supply during the transition, which will then be seen in the thermogram. (Atkins & Jones, 2010)

2.6.6 Thermogravimetric Analysis

By controlled heating of a substance the change in mass for the substance can be measured as a function of temperature. (Harris, 2010) This can for instance be used to follow the decomposition of a material, in order to determine how the decomposition process works, such as which bonds break first etc.

3 MATERIALS AND METHOD

3.1 Raw Material

The chemicals used for the acetylation and pre-treatment were acetic acid (glacial), acetic anhydride (ACS, ISO, Reag. Ph Eur) and sulphuric acid (95-97% reagent grade, ISO). For the NMR chloroform-D (99.8 atom%D), deuterium oxide (99.8 atom%D) and dimethyl sulfoxide-d_6 (99.8 atom%D) were used. Dimethyl sulfoxide (CHROMASOLV® Plus for HPLC ≥ 99.7%) with 1.09 g/L LiBr were used for GCP. All chemicals were purchased from Sigma-Aldrich.

The cotton linters were received from Munktell and were used without further pre-treatments.

The hydrolysates was prepared by Ulf Zander at Södra Innovation through pre-hydrolysis of birch wood chips at 160 °C and 5 bar for 60 and 150 minutes respectively. The hydrolysate from the 60 minutes batch was denoted X_a and the hydrolysate from the 150 minutes batch was denoted X_b. Prior to freeze-drying of X_a most of the water was removed by rotary evaporation. The hydrolysate was then frozen using liquid nitrogen and freeze-dried in a Labconco FreeZone® Triad™ Freeze Dry System 7400030 for six days and was then ground with a mortar to from a more easily dispersible powder. The X_b hydrolysate was freeze-dried without pre-treatment by the project partner Innventia.

3.2 Acetylation

The acetylation was performed based on a method described by Peredo et. al (2015) resembling the commercial acetylation process for manufacturing of cellulose acetate. In order to adjust the method for the addition of hydrolysates the pre-treatment steps were modified as a result of a method optimization also done in this work. Following pre-treatment options have been studied; Addition of hydrolysate prior to impregnation of the cotton linters with acetic acid (3.2.1) and addition of hydrolysate after a completed solvent exchange of cotton linters in acetic acid (3.2.2). The subsequent acetylation is described in 3.2.3. 20 w-% X_a was used in all samples for the optimisation. After the optimisation the acetylation was performed with different hydrolysate to cellulose ratios, varying between 0-50% hydrolysate content using the pre-treatment described in 3.2.2. A flow chart describing the experimental procedure of the acetylation is presented in Figure 10.

3.2.1 Pre-treatment with Hydrolysate

Two different methods of incorporating the hydrolysates were attempted; kneading the cotton and hydrolysate with a small amount of deionised water, and mixing the cotton and hydrolysate with 500 mL deionised water in a blender. The samples were air-dried at room temperatures followed by impregnation in glacial acetic acid. After 18 hours the acetic acid was removed by filtration and the samples were acetylated as described in 3.2.3.

3.2.2 Pre-treatment without Hydrolysate

The flow chart in Figure 10 illustrates the pre-treatment without hydrolysate, in addition to the acetylation. Cotton linters (1–4 g) were suspended in 500 mL deionized water by mixing for 30 seconds with a kitchen blender. A Büchner funnel was used to dewater the cotton that was then dispersed in 50 mL glacial acetic acid, by kneading with a glass rod. After 30 minutes impregnation, the acetic acid was removed by filtration and then re-dispersed in 50 mL acetic acid again. Filtration and re-dispersing in acetic acid was repeated after one hour, 18 hours and one hour respectively, with the exception that there was no re-dispersing after the final filtration. After the final exchange step the freeze-dried hydrolysate was suspended with 2 mL acetic acid before added to the filtered cotton.

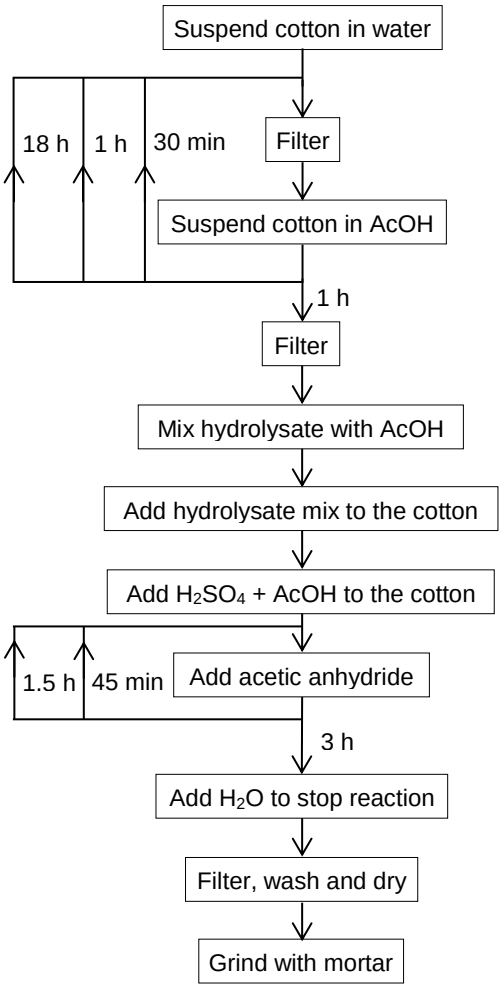

Figure 10. Flow chart describing the acetylation experimental procedure.

3.2.3 Acetylation Following Pre-treatment

To the pre-treated cotton samples 0.2 mL sulphuric acid dissolved in 30 mL acetic acid was added followed by 10 mL acetic anhydride. The samples were then placed in a water bath with a shaker at 40 °C. After 45 min and 90 min respectively 10 mL of acetic anhydride was added. 3 h after the final addition of acetic anhydride approx. 150 mL of deionized water was added to stop the reaction, causing the cellulose acetate to precipitate. The samples were filtered and washed until the filtrate reached neutral pH, dried at room temperature and subsequently ground with a mortar.

3.3 Characterisation of Raw Materials and Products

Six different techniques were used to characterise the hydrolysate and the acetylated samples. The sample preparation and the equipment specifications for the techniques are described in the following section.

3.3.1 Carbohydrate analysis

Carbohydrate composition was analysed using ion exchange chromatography with pulsed amperometric detection. The separation was per formed isocratically in Milli-Q water on a CarboPacTM PA1 column (Dionex, Sunnyvale, CA, USA). The rotary evaporated hydrolysate as well as the acetylated samples containing X_b hydrolysate and samples 5 X_a, 10 X_a, 15 X_a, 20 X_a and 30 X_a were analysed using this technique. The analysis was performed by Linda Svedberg and Lina Turesson at Södra Innovation.

3.3.2 Methanolysis

The samples were hydrolysed using 2.8 mL Ac-Cl in 17.2 mL anhydrous methanol in an oil-bath at 100 °C for three hours. Pyridine was then added as a solvent along with an internal sorbitol standard. The solvent was evaporated followed by silylation overnight using 150 µL hexamethyldisilazane and 80 µL chlorotrimethylsilane as the silylation reagents. After the solvent was evaporated again, 2 mL of diethyl ether was added to the samples that were then filtrated and injected into a gas chromatograph (Agilent 7890A, Stockholm, Sweden) connected to a mass spectrometer (Agilent 5975C, Stockholm, Sweden).

3.3.3 Nuclear Magnetic Resonance

NMR was performed on all samples for qualitative sample information as well as to calculate degree of substitution of the acetylated samples.

NMR was acquired using 15 mg of sample dissolved in 750 µl solvent, chloroform-D ($CDCl_3$) was used for acetylated samples, deuterium oxide/heavy water (D_2O) for non-acetylated hydrolysate and DMSO-d_6 for the filtrates from the improvement of the pre-treatment. The ^1H NMR spectra were recorded in 5mm tubes at 25°C on a Varian-INOVA 400 9,4 T NMR spectrometer operating at a frequency of 400 MHz for ^1H detection. The ^1H spectra were recorded with a 45° pulse angle, 1 s pulse delay, 256 scans and 2.56 s acquisition time. The resulting spectra were automatic phase and the data were processed by ACD/NMR Processor Academic Edition v12.01 software (Advanced Chemistry Development, Inc.).

3.3.4 Gel Permeation Chromatography

GPC was run on both hydrolysates and acetylated samples, but with different GPC systems. The respective systems are described below.

GPC for the hydrolysates was run at pH 13. Quantitative information about the absolute molar mass distribution of the samples was obtained using a system having three Ultrahydrogel columns 500, 250 and 120 (WATERS). A RI detector (model RI-101 SHODEX) and a UV detector with an absorbance at 280 nm (model K-2501 KNAUER) were used as detectors. The loop size was 100 µL. Xylan samples to be analysed were dissolved in a basic solution at a concentration of 5 g/L and the flow rate was 0.8 mL/min (0.3% DMSO, sodium hydroxide 200 mM, sodium acetate 100 mM, pH 13 as eluent). Calculations were carried out using Cirrus GPC Online, GPC/SEC software version 3.1 (VARIAN).

GPC for the acetylated samples was run with a PL-GPC 50 plus integrated system connected with RI detector and UV detector (280 nm, Polymer Laboratories, Varian Inc.) Two series coupled PolarGel-M column and a guard column (300×7.5 mm and 50×7.5 mm) with pore size 8 µm and DMSO/LiBr (10 mM) as mobile phase (0.5 mL/min) was used. A 10-point calibration curve with Pullulan standards was used to determine the molecular weights (Mw) and PDs (708000, 375000, 200000, 107000, 47100, 21100, 11100, 5900, 667 and 180 Da, Polysaccharide Calibrations Kit, PL2090-0100, Varian). Data analysis was performed using Cirrus GPC software Version 3.2. Samples (0.5 mg/mL) were dissolved in mobile phase DMSO/LiBr, 10 mM and filtered through a syringe filter (GHP, Acrodisc, d=13 mm, 0.2 µm GHP membrane).

3.3.5 Differential Scanning Calorimetry

The DSC tests determining the melting temperature were performed by Thibault Cousin at MINES ParisTech. The analysis was carried out in a Perkin DSC 4000, with a ramp of 10°C/min from 25°C to 210°C. The melting point was determined from the minimum of the second peak.

Modulated DSC analysis was performed by Anne-Mari Olsson at Innventia to determine the glass transition temperature. The reversing heat flow was determined with modulated DSC in a DSC Q 1000 from TA Instruments. 2-6 mg sample was put in DSC capsule. A ramp from 20 °C up to 220 °C was performed with a rate of 5 °C/min. A sinusoidal modulation of the temperature of +/- 3 °C/60 s was superimposed on the temperature ramp to enhance the sensitivity. The T_g was determined from the inflexion point of the reversing heat flow decrease.

3.3.6 Thermogravimetric Analysis

The thermogravimetric measurement was performed by Anne-Mari Olsson at Innventia on samples 0 X_a, 5 X_a, 10 X_a, 15 X_a, 20 X_a, 30 X_a, 0 X_b, 5 X_b, 10 X_b, 15 X_b, 20 X_b, 30 X_b and 50 X_b. The measurement was made in a Perkin Elmer TGA 7, with a sample purge of 50 ml/min of nitrogen. The samples were dried in the TGA at 105 °C for 20 min, after which a ramp up to 400 °C was made with a heating rate of 15 C/min.

4 RESULTS AND DISCUSSION

4.1 Raw Material Characterisation

The hydrolysates were characterised with carbohydrate compositional analysis, NMR, GPC and methanolysis analysed by GC-MS. Together these techniques provided information about molecular weight, carbohydrate composition and glucoronic acid and acetate content.

The results from NMR indicate that the pre-hydrolysis mainly extracted carbohydrates. The peaks at 3-5.2 ppm in Figure 11 correspond to the hydrogens bonded to the carbons in the anhydrous sugar units for the different carbohydrates (denoted AGU for cellulose and AXU for xylan). At 6.2-9.4 ppm smaller peaks can be seen, corresponding to the chemical shift for aromatic structures, indicating traces of lignin fragments. Xb has bigger aromatic peaks indicating higher lignin content.

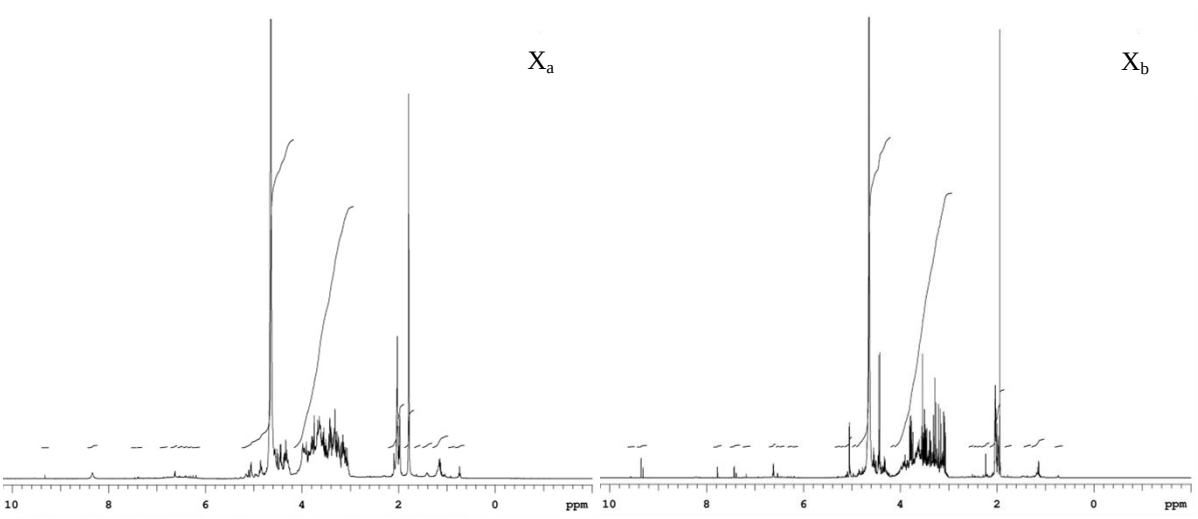

Figure 11. NMR-spectra of the hydrolysates a) X_a and b) X_b.

The carbohydrate compositional analysis results, found in Table 1, shows that that xylose, i.e. xylan, is the main carbohydrate extracted, with smaller amounts of other sugars, likely remnant from glucomannan, pectins and residual cellulose. The high xylan content is expected, and desired, as it is the main hemicellulose in birch. The xylan content increases slightly with the longer hydrolysis time, while the remaining sugars (except galactose) decrease. The error estimation for the xylose is small (coefficient of variation is 2.7%), hence the results can be considered reliable.

Table 1. Results of carbohydrate analysis in weight percent of total sugar content

	Arabinose	Galactose	Glucose	Xylose	Mannose
X_a	3,78%	5,27%	7,51%	78,87%	4,57%
X_b	2,06%	5,84%	6,19%	81,79%	4,12%

The GC-MS analysis of the methanolysis showed that there was approximately 3% glucoronic acid present. Glucoronic acids occupy possible acetylation sites on the xylan backbone and can themselves be acetylated at two positions. However, as the content is so low their contribution to the degree of substitution is of minor importance. The NMR results show that there are acetyl groups present with peaks at 2 ppm corresponding to the methyl groups on the acetyl groups, see Figure 11. By using Eq. 2 an approximate DS for the xylan can be calculated from the NMR. This gives a DS of 0.26 for X_a and 0.24 for X_b. However, integrals from the AXU that are overlapped by the D_2O solvent peak are cannot be considered and there may also be a contribution from other hemicelluloses to the AXU integrals that cannot be excluded. Therefore this can only be used to conclude that the amount of acetate groups on xylan prior the acetylation was low, the absolute values are not reliable enough. The peak at 1.8 ppm corresponds to acetic acid.

The GPC data show three fractions in both hydrolysates with molecular weights corresponding to xylan with a degree of polymerisation of 3, 4 and 6 respectively, see Figure 12. X_a also has a fourth fraction corresponding to polymers and larger oligomers which are not present in X_b, indicating that the longer treatment has hydrolysed the larger polymers. As mentioned in section 2.6.4 GPC results depend on the system used. In this case the systems used for characterisation of hydrolysates and acetylated samples were different but the results where normalized with the same standard allowing for comparisons between the results. Note that the values obtained are means and will vary depending on how they are calculated and how the peak integral is defined.

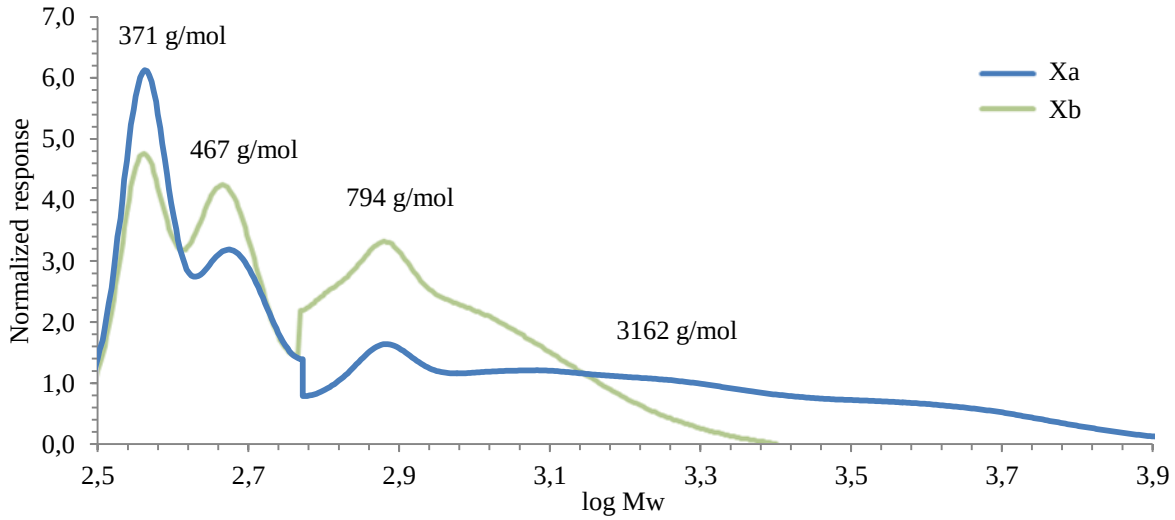

Figure 12. GPC data for the freeze-dried hydrolysates.

4.2 Acetylation

In this section observations regarding the acetylation method and results for the acetylated samples not covered in section 0 will be presented and discussed. The results of the different pre-treatments are presented in section 4.2.1. An attempt to acetylate samples containing 100 % hydrolysate was made, however the sample did not precipitate when the water was added so no characterisation was made.

An unmistakable observation made is that the cellulose acetate became darker with increasing amount of added hydrolysate as can be seen in Figure 13. The colour and colour gradient also remained after the acetylation. Dried, the samples are not as distinctively coloured as the undried samples seen in Figure 13. However, upon dissolution in chloroform a clear colour gradient can be observed from transparent and uncoloured to a transparent brown colour. Xylan does not absorb light in the visible spectrum and is therefore unlikely to give rise to the colour. A possible explanation is that small amounts of lignin remained in the cellulose acetate after the washing, either as free fragments or as lignin-carbohydrate complexes. However, the NMR results, see Appendix I, are not consistent with this as no trend of increasing amounts of impurities with increasing xylan content can be observed. Deduction leads to that xylan will, upon acetylation, become chromophoric. The formation of chromophores from carbohydrates in acidic conditions is described by Theander (1988). One of the reasons the highest purity dissolving pulp is used is because of the yellowing effect the hemicelluloses have on the finished product. If the cellulose acetate is used for other applications that do not require an uncoloured product than the chromophoric effect of the hemicelluloses would be of little concern.

Figure 13. The samples with varying hydrolysate content before acetylation and after the washing following the acetylation.

The GPC results from the acetylated samples showed two fractions, a smaller fraction with lower molecular weight and a larger with higher molecular weight see Figure 36 and Figure 37 in Appendix II. As the 50 X_b sample was the only sample fully dissolved in the solvent (DMSO) it is the only one from which data can be used. Duplicates were run for the 50 X_b sample with the following results; 2 773 g/mol and 2 976 g/mol for the small peak, corresponding to a polymer with 13 and 14 acetylated xylose units, 59 813 g/mol and 63 601 g/mol for the larger peak, corresponding to a polymer with 208 and 221 acetylated glucose units. As the sample is polydisperse, both due to the raw materials and as a result of the acidic environment of the reaction, it is not unexpected to have means varying as much as the ones presented here. It does however mean that the values should not be used as more than estimations.

4.2.1 Pre-treatment

A suspicion that the acetylation method described by Peredo et. al. (2015) was not optimal when using these hydrolysates was raised during initial trials as the permeate from the 18 hours impregnation was discoloured. To determine if this course of pre-treatment was appropriate when using hydrolysate instead of the longer-chained xylan used by Peredo et. al. (2015) two different pre-treatments where performed, described in section 3.2.1. The permeate from the 18 hour impregnation was analysed with NMR to determine if any xylan had been removed during the filtration step after the impregnation. Figure 14 shows photographs of the first and second pre-treatment methods before the drying.

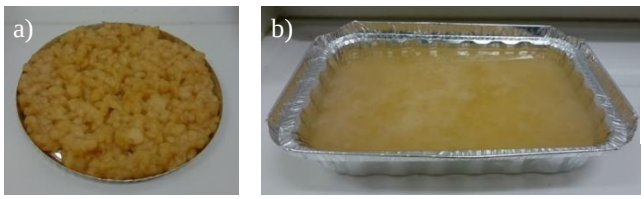

Figure 14. Photographs of a) one of the cotton-xylan blends from first method and b) one of the cotton-xylan blends from second method before drying.

The NMR results of the permeates from the filtration step that followed the impregnation showed minor amounts of carbohydrates, the peaks 3.5-5 ppm seen in Figure 15. The second method, where the hydrolysate and cotton was mixed with a blender, shows more and better resolved carbohydrate peaks. However, the two spectra cannot be compared qualitatively and as no quantitative measurements were performed and therefore no conclusions regarding quantitative comparisons can be drawn. As there were traces of carbohydrates found in the permeate it was decided to use the method described in 3.2.2 where the hydrolysate is added after the filtration steps, to allow as much of the xylan as possible to be acetylated.

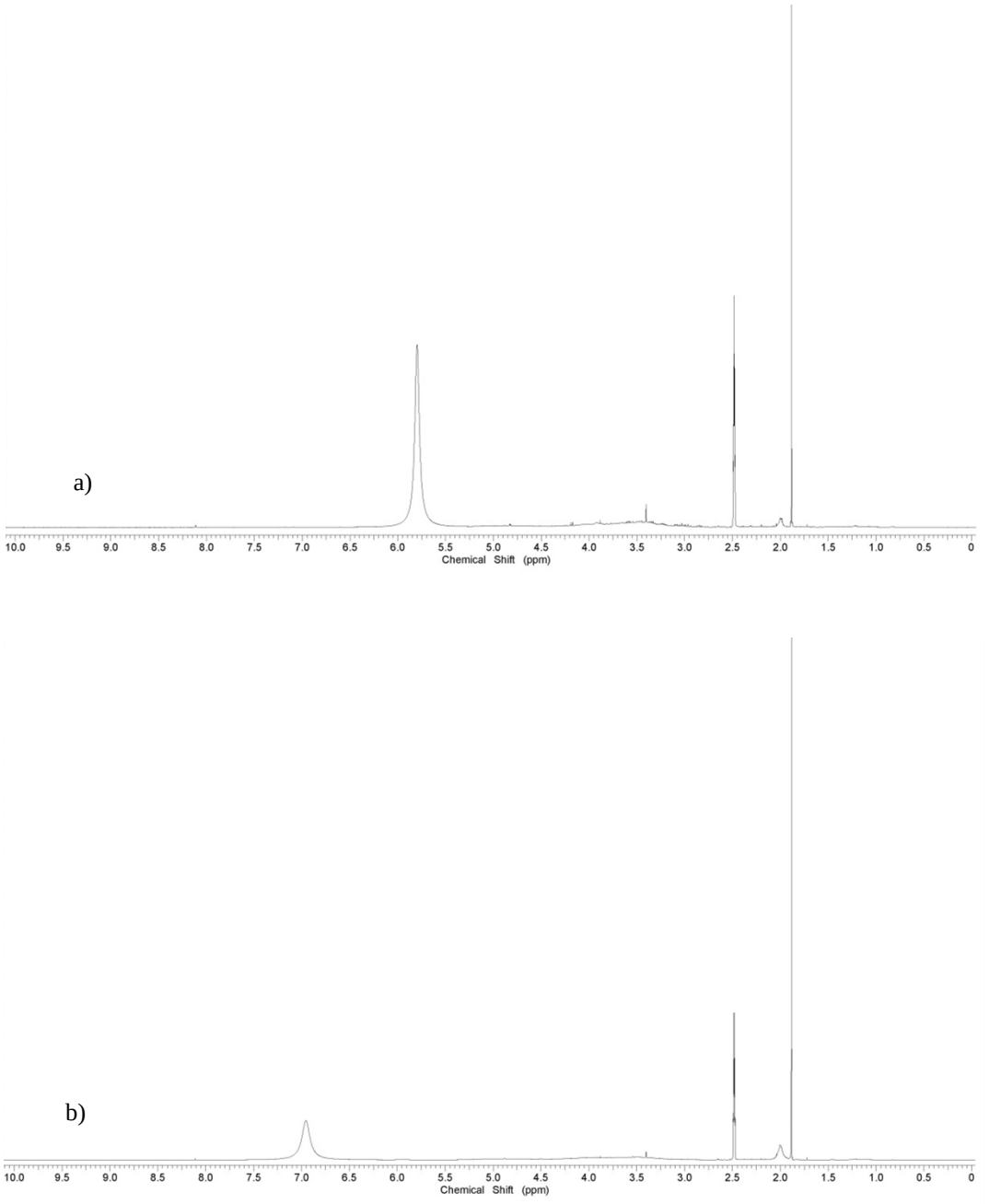

Figure 15. NMR spectra of the a) cotton-xylan blend from first method and b) cotton-xylan blend from second method. The peak at 2.5 ppm is the solvent peak from DMSO, the peak at 2 ppm is acetic acid and the peaks at 5.80 ppm and 6.95 ppm in the respective spectra is water.

4.3 Product Characterisation

A compilation of results of the product characterisation are presented in Table 2, with results from carbohydrate compositional analysis, nuclear magnetic resonance, differential scanning calorimetry, thermogravimetric analysis and gravimetric analysis. The results in Table 2 will be discussed in detail in sections 4.3.1, 4.3.2 and 4.3.3.

Table 2. The table shows xylan content of the acetylated samples, yield, degree of substitution, glass transition temperature, melting temperature and the temperatures where 10% and 50% of the sample mass is lost due to thermal degradation.

Sample	% xylan	Yield %	$DS_{Cellulose}$	T_g (°C)	T_m (°C)	$T_{d\,10\%}$ (°C)	$T_{d\,50\%}$ (°C)
0 X_a	0,00	84	2,81	170	194	351	392
5 X_a	1,00	83	2,87	-	193	342	390
10 X_a	2,03	83	2,87	170	192	339	391
15 X_a	2,97	81	2,93	-	192	323	388
20 X_a	4,01	82	2,94	158	190	315	387
30 X_a	6,58	71	2,84	133	184	249	379
0 X_b	0,00	76	2,81	-	196	347	390
5 X_b	0,93	84	2,75	-	196	363	398
10 X_b	1,53	78	2,78	-	194	355	394
15 X_b	2,26	80	2,77	-	194	353	393
20 X_b	3,07	77	2,82	-	192	351	396
30 X_b	4,38	69	2,73	-	191	333	392
50 X_b	9,77	53	2,81	136	181	305	385

4.3.1 Yield

The yield calculations take into consideration that the hydrolysate contained only about 80 % xylan, and it is thus higher than the yield would have been if it had been calculated based on the entire hydrolysate mass. A clear trend can be seen in the results, presented in Table 2 and illustrated in Figure 16, where the yield of acetylated cellulose and xylan decreases with increasing xylan content. A few factors have been identified that have had a strong influence on the yield. The first one is the inevitable loss of material during the filtration and washing steps that will decrease the overall yield. The second one is that severe degradation occurs during the acetylation, possibly causing formation of chromophores as mentioned in section 4.2. The latter factor is supported by the fact that the yield decreases with increasing xylan content, as well as with shorter xylan chains, see Figure 17. The shorter chains will be completely broken down to degradation products while the longer chains will only be partially degraded, even though the degradation acts equally on both chain types. The material in the filtrate was not isolated and the contribution of this factor can therefore not be determined. The error of the scale used is ±0.1 mg and can therefore be considered small enough to be outweighed by the previously mentioned factors.

The sample 50 X_b had a significantly lower yield which may, in addition to the previously mentioned factors, be attributed to it having a lighter and fluffier consistency compared to the other samples. This made it more vulnerable to gusts of wind and caused material to fly away before it was weighted.

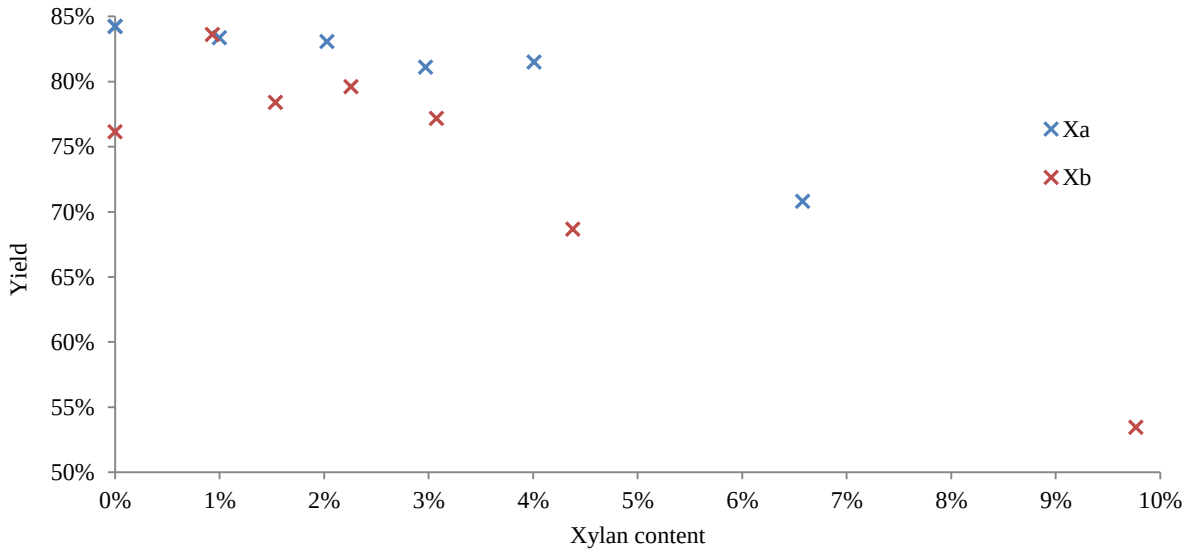

Figure 16. Yield of acetylated cellulose and xylan with respect to the xylan content.

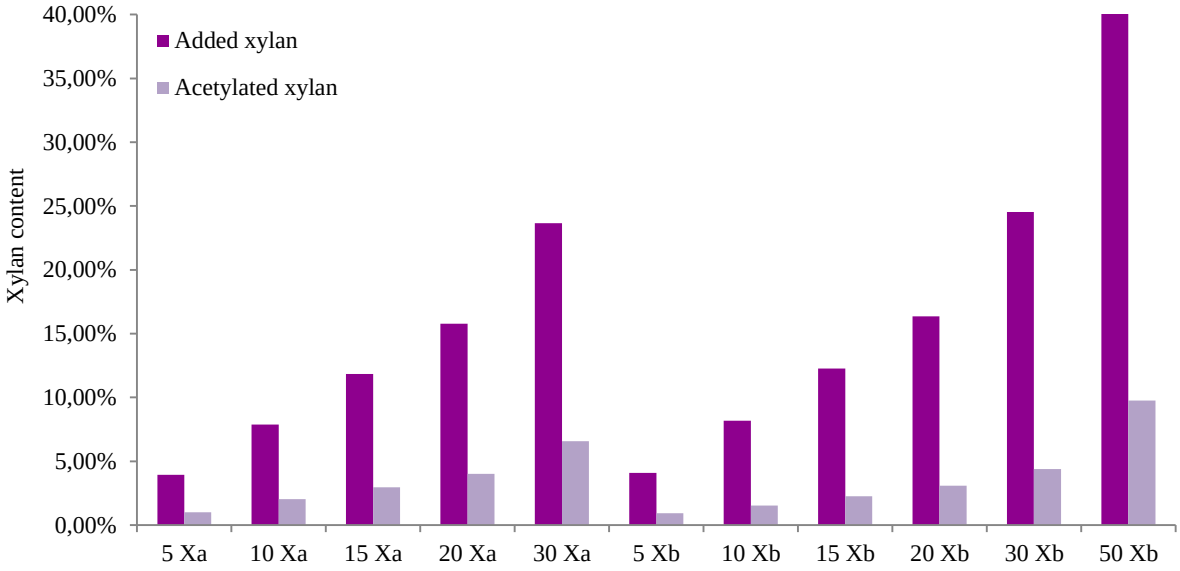

Figure 17. Comparison of xylan content in the sample before the acetylation and in the dried sample after acetylation.

4.3.2 Degree of Substitution

The degree of substitution is calculated differently for xylan compared to cellulose due to the different number of hydrogens of the anhydrous unit as well as the different number of positions available for substitution. The equations are shown below:

$$DS_{acetylated\ cellulose} = \frac{7 * I_{Ac}}{3 * I_{AGU}} \qquad Eq.\ 1$$

$$DS_{acetylated\ xylan} = \frac{2 * I_{Ac}}{I_{AXU}} \qquad Eq.\ 2$$

As the peaks from xylan and cellulose overlap completely, their respective DS cannot be calculated using only NMR. It is known from literature (Efanov, 2001) that the hemicelluloses, being more reactive and accessible, will reach full acetylation first. This knowledge can in combination with the results of the carbohydrate analysis of the acetylated samples (in Table 2) be used to determine an estimate of the degree of substitution for cellulose.

As seen in Figure 18 the degree of substitution for all samples is high, with values between 2.73-2.94. The initial trend with increasing degree of substitution with increasing xylan content may be explained by that xylan has one less position for substitution than does cellulose. The amount of acetic anhydride is the same in all reactions but the amount of substitutable hydroxyl groups decreases with the increasing xylan content with the result that there is more anhydride that can react with the cellulose. This assumption rests on that xylan is acetylated first and that the hydrogens in xylan has the same response in NMR analysis as those in cellulose. If the apparent increase in DS is because of a limit in mass transfer or if a too low amount of acetic anhydride was added to the reactions cannot be determined based on the experiments performed in this project. In samples 30 X_b and 50 X_b, as well as 5 X_1 and 10 X_1 the acetyl peaks were partially overlapped by the peak from the acetic acid which may have caused an over- or underestimated DS. The lower DS for the short-chained hydrolysate may be explained by that the degradation products resulting from the acidic conditions consume a portion of the acetic anhydride. The decreased DS for the samples with higher xylan content may be caused by xylan sorption, making the cellulose less accessible to the acetic anhydride.

NMR is a stable analytical method, however the integral value will depend on how the integration was made; what is defined as the peak and what is left out of the integral. In this case there where ^{13}C satellites present, a phenomena where ^{13}C couples to hydrogen causing peak splitting. ^{13}C satellites make the integration more difficult as it can be hard to distinguish between possible impurities and ^{13}C satellites and the splitting may resulting in the satellites being overlapped by surrounding peaks.

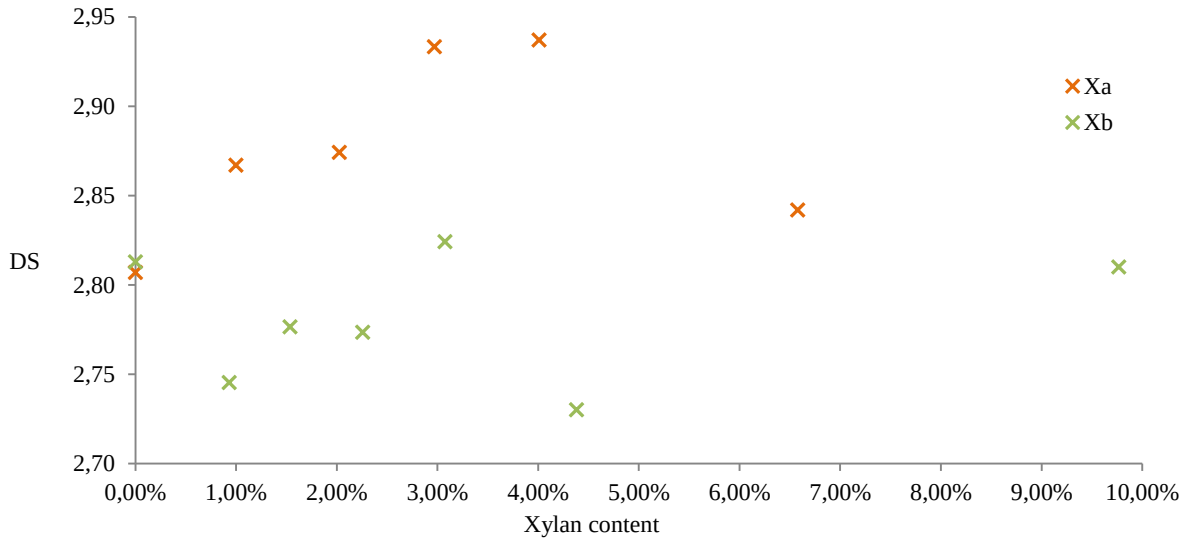

Figure 18. Degree of substitution for cellulose acetate as a function of xylan content.

A solubility study was conducted to confirm the DS results calculated from NMR. The results from the study are presented in Table 3. All samples where soluble in chloroform, supporting the high DS obtained from the NMR. However, the 50 X_b sample was also partially soluble in acetone, indicating it should have a lower DS compared to the other samples. It was also noted that the 50 X_b sample was the only sample completely soluble in DMSO. In addition to the solubility study an FT-IR analysis was performed on the 0 X_b, 15 X_a, 15 X_b and 50 X_b samples to further verify the NMR results. The

results are consistent with the NMR, with exception of the 50 X_b sample. The spectrum, see Figure 19, shows a larger hydroxyl group peak (around 3400 cm^{-1}) for the 50 X_b sample compared to the other samples. The results from the FT-IR analysis together with the solubility study indicate that the DS calculated from the NMR results for the 50 X_b sample is somewhat overestimated. However the DS is nevertheless high as the sample was soluble in chloroform.

Table 3. Results of the solubility study.

	0 X_a	15 X_a	30 X_a	0 X_b	15 X_b	30 X_b	50 X_b
$CHCl_3$	+	+	+	+	+	+	+
Acetone	–	–	–	–	–	–	(+)
DMSO	(+)	(+)	(+)	(+)	(+)	(+)	+

FT-IR was not run on all samples as there was no indication that they would differ significantly from the NMR results based on the solubility study. Note also that the DS cannot be easily calculated from FT-IR. Instead FT-IR can indicate if full acetylation has been achieved by the lack of a hydroxyl group peak or by roughly compare the amount of hydroxyl groups present in different the sample by looking that the quantitative difference in transmission as was done in this case.

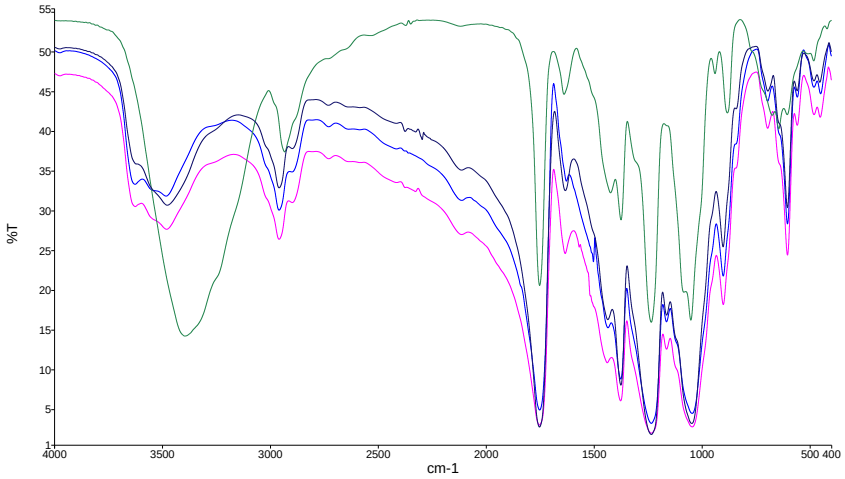

Figure 19. FT-IR analysis of 0 X_b (blue line), 15 X_a (black line), 15 X_b (pink line) and 50 X_b (green line).

4.3.3 Thermal properties

The glass transition temperature for the pure cellulose acetate samples are consistent with results found in literature (Kamide & Saito, 1985) for highly acetylated cellulose acetate. The melting temperatures obtained are however significantly lower to those presented by Peredo et. al. (2015), which may be attributed to the xylan source, as the one used in this project had lower DP. The xylan will create more free volume in the polymer, as the xylan is a smaller, more mobile molecule, resulting in a decreased melting temperature. This can also be observed with the decreasing trend in melting temperature in relation to xylan content. A small difference in melting point can be observed when comparing the two different hydrolysates. Whether the melting temperature difference is caused by the difference in molecular weight, degree of substitution or other factors cannot be determined based on the obtained information. However, the melting temperature of the 0 X_a and 0 X_b samples differs even

though there is no significant difference in DS for the two. This suggests either an uncertainty in the measurement or different thermal histories for the samples. As only one heating cycle was run for each sample it cannot be determined what the underlying factor is.

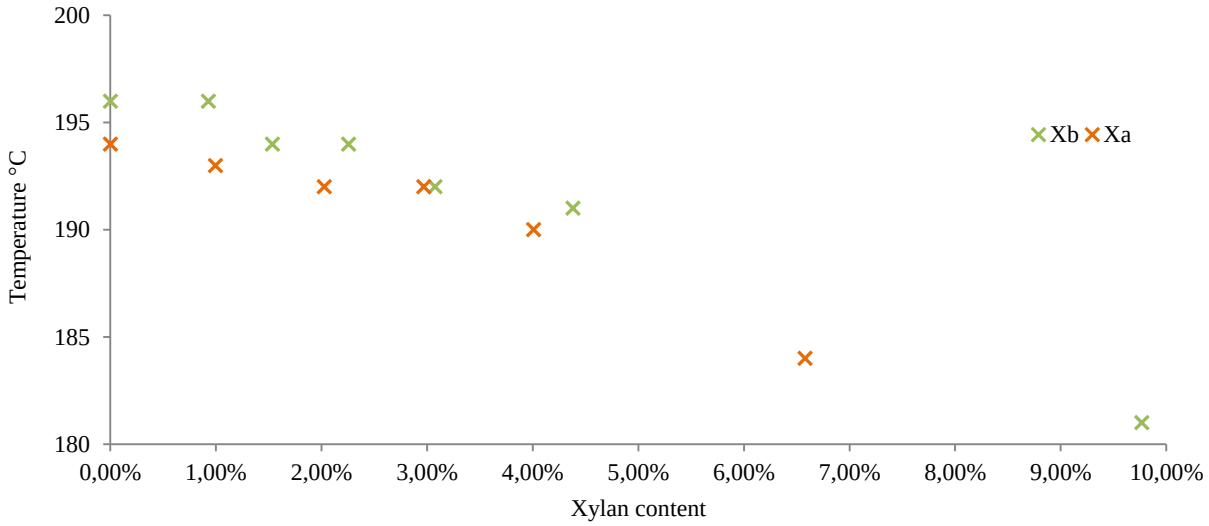

Figure 20. Melting temperature of the cellulose acetate with respect xylan content.

Data for the glass transition temperature could not be obtained for all samples, however for the samples were a T_g was obtained a decreasing trend with increased xylan content was observed, see Figure 21. Decreasing DS should increase the glass transition temperature, however the trend for the DS is not seen in the results of the T_g. The observed difference is also too large to be attributed to any difference in DS (Kamide & Saito, 1985). Therefore it can be determined to be the xylan causing the decreasing trend, showing that xylan has a great impact on the glass transition temperature, a characteristic of a plasticiser. It should also be noted that the glass transition temperature is a temperature interval and the technique used to determine it is of great importance. T_g determined by DSC can differ by up to 15-25 °C compared to values obtained with mechanical measuring techniques such as thermo-mechanical analysis and dynamic mechanical analysis (PerkinElmer, Inc., 2013-2014). If the samples are analysed with the same instrument, as is the case here, they are nevertheless comparable. Because of the aforementioned problems with, T_g no conclusions should be drawn with regard to the absolute values, however the trend is still valid.

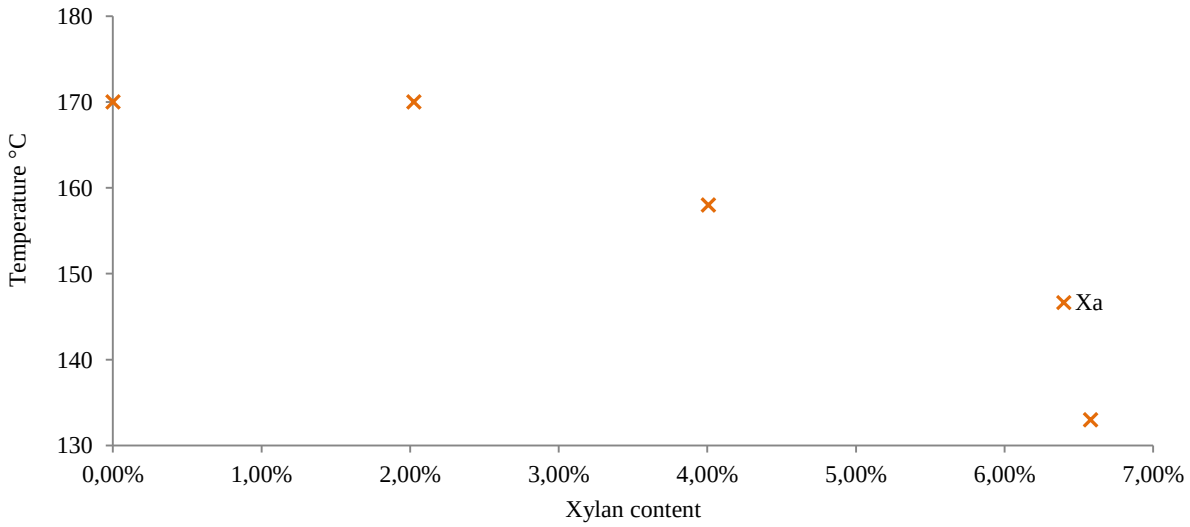

Figure 21. Glass transition temperature of the cellulose acetate with respect to xylan content.

Only one decomposition step is seen in the TGA results, Figure 38 in Appendix III. Removal of the acetyl groups would correspond to a loss in mass of 80% (pure cellulose acetate) to 78% (10% acetylated xylan in the cellulose acetate). It is therefore likely that the decomposition stage obtained in the TGA is from of the removal of acetyl groups, which is in agreement with literature (Kamide & Saito, 1985). However, as the measurements were not carried out to higher temperatures it cannot be said with complete certainty.

The obtained decomposition temperatures are about 15-20 °C higher compared to literature (Peredo, et al., 2015) and as TGA is a sensitive technique this difference must be attributed to material properties, such as molecular weight or degree of substitution. Looking at the decomposition temperatures (both $T_{d10\%}$ and $T_{d50\%}$) there is a deceasing trend with increasing xylan content. This may be due to xylan being less temperature stable than cellulose and therefore speeding up the decomposition.

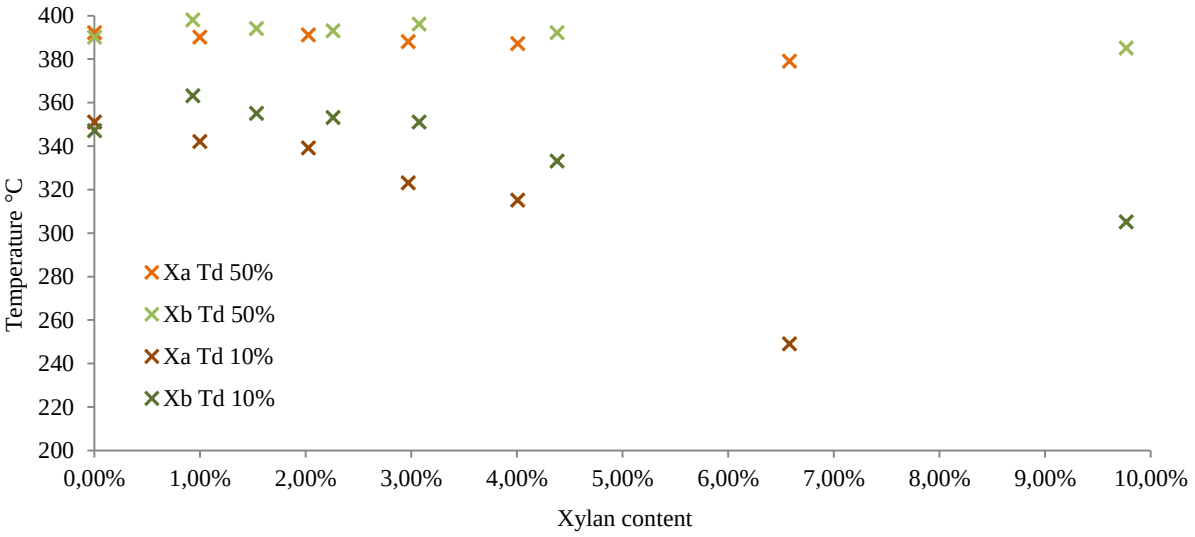

Figure 22. The temperatures were 10% and 50% mass is lost with respect to xylan content.

5 CONCLUSIONS

From the results presented in this master's thesis it is clear that xylan has an impact on the thermomechanical properties, namely the melting, glass transition and decomposition temperatures. In all three cases the transitional temperature is decreased, which is contributed to xylan creating more free volume and thereby increasing chain mobility. The glass transition temperature is the most affected by the increased free volume. As lowering the glass transition temperature is a property inherent of a plasticiser, birch xylan extracted by pre-hydrolysis shows promise.

All the thermomechanical properties measured were correlated to xylan content. The results showed that there was a dependence on the xylan to cellulose ratio, where the respective transitional temperatures all decreased with increasing xylan content. As the xylan content did not exceed 10 %, conclusions drawn from the presented results are only valid for cellulose acetate with birch xylan contents between 0 and 10%.

The results show that there may be an effect of the DP of xylan. The decomposition temperature for 10% mass loss decreases more for the sample containing X_a, i.e. the hydrolysate with a higher molecular weight fraction, compared to the samples containing X_b. The melting temperatures for the samples containing X_a were slightly lower than for the samples containing X_b. However, these differences cannot be concluded to solely depend on the DP, as parameters such as degree of substitution also may play a role.

In conclusion: birch xylan extracted by pre-hydrolysis shows promise as an internal plasticiser and should to be investigated further.

6 FUTURE WORK

During this master's thesis work many interesting questions and issues arose that can and should be further investigated, they are presented below:

- More information about the plasticising ability of acetylated xylan is needed. Mechanical properties such as flexibility, ductility, strength, stress-strain response, etc. should be the focus of further investigations.
- Higher xylan to cellulose ratios should be attempted, to investigate if there is an optimum in xylan content for the properties of cellulose acetate.
- As it proved difficult to reach high xylan content with the chosen acetylation method with water as anti-solvent, other precipitation techniques or acetylation methods could be evaluated for better xylan yield.
- Fractionation of the hydrolysate may lead to better possibilities to investigate the effect of molecular weight/DP on xylan's plasticising ability.

ACKNOWLEDGEMENTS

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- **Kajsa** and **Susanne** for delightful company and small talk.
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APPENDIX I

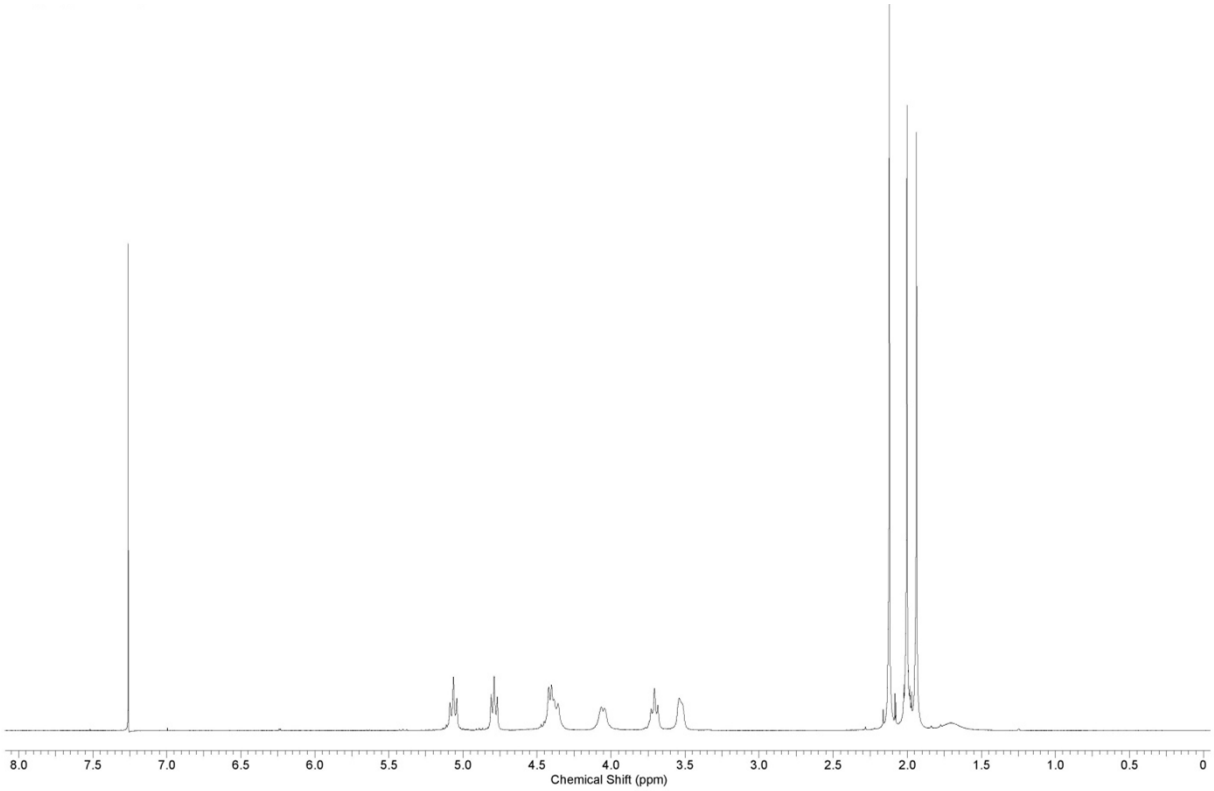

Figure 23. NMR spectrum of 0 X_a.

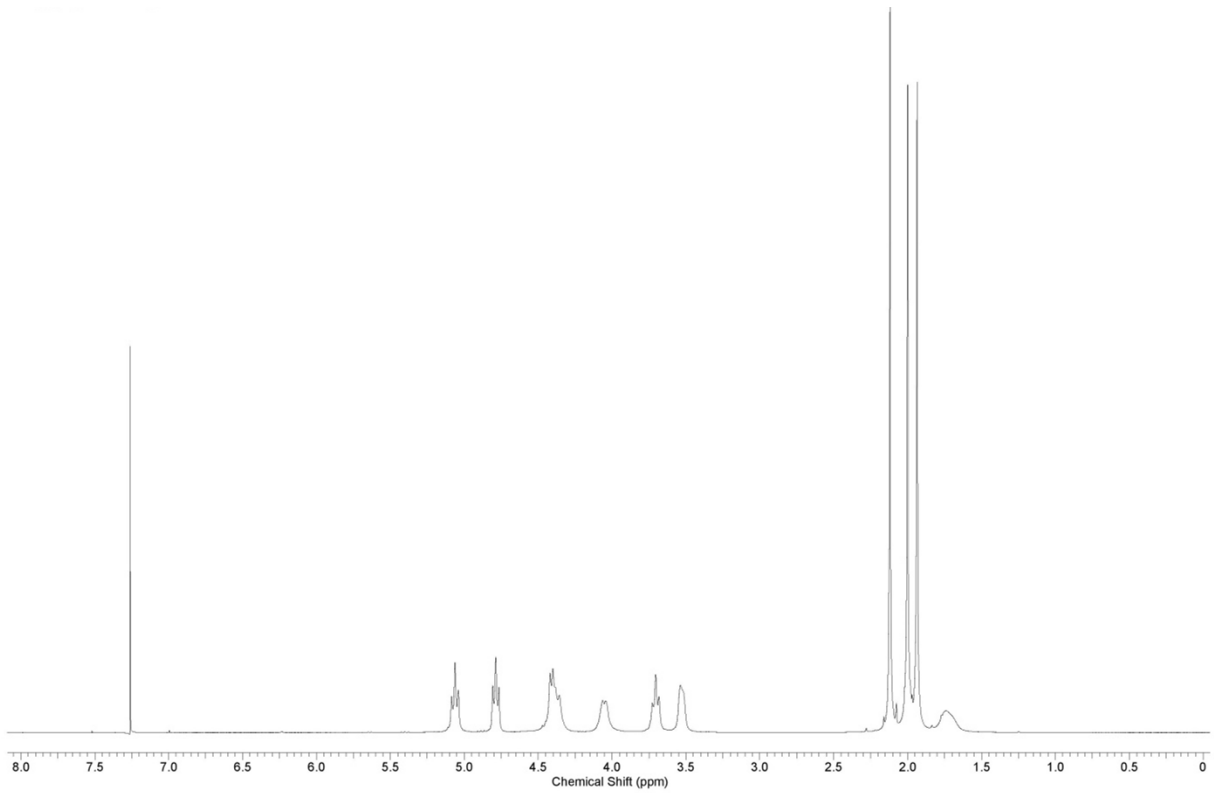

Figure 24. NMR spectrum of 0 X_b.

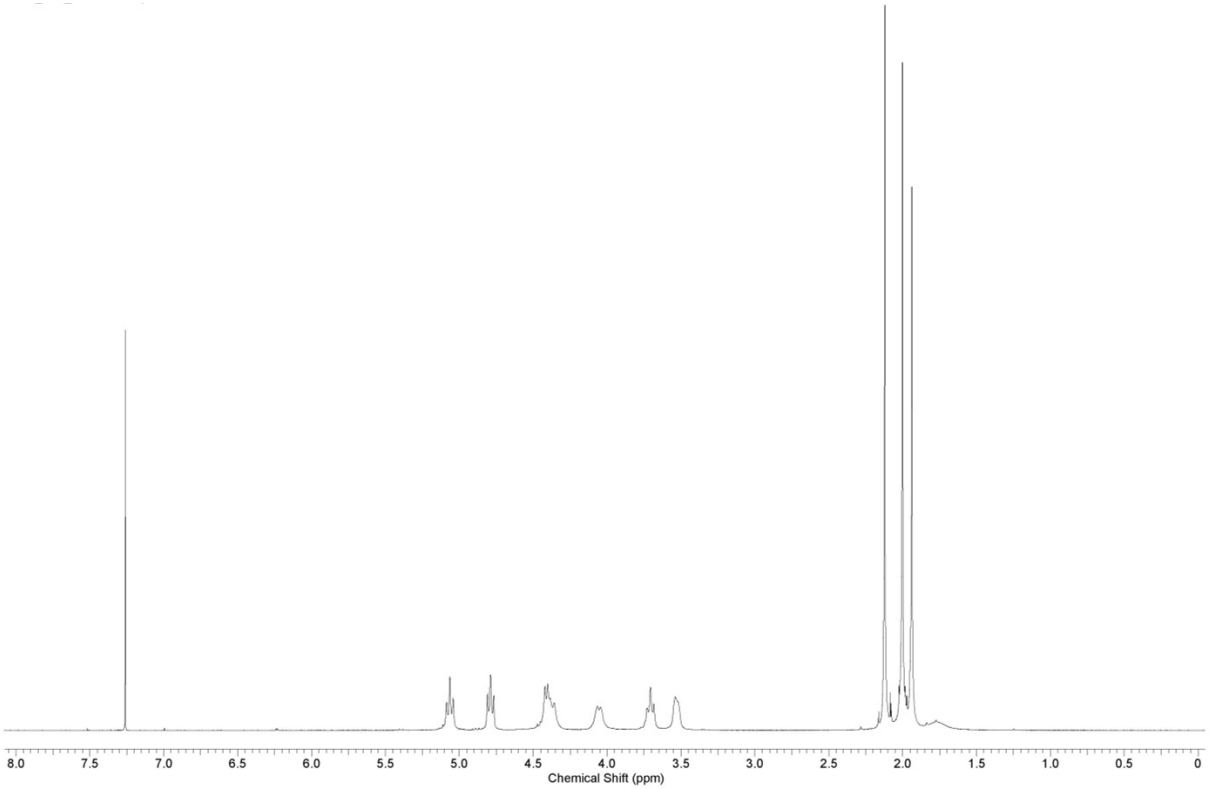

Figure 25. NMR spectrum of 5 X_a.

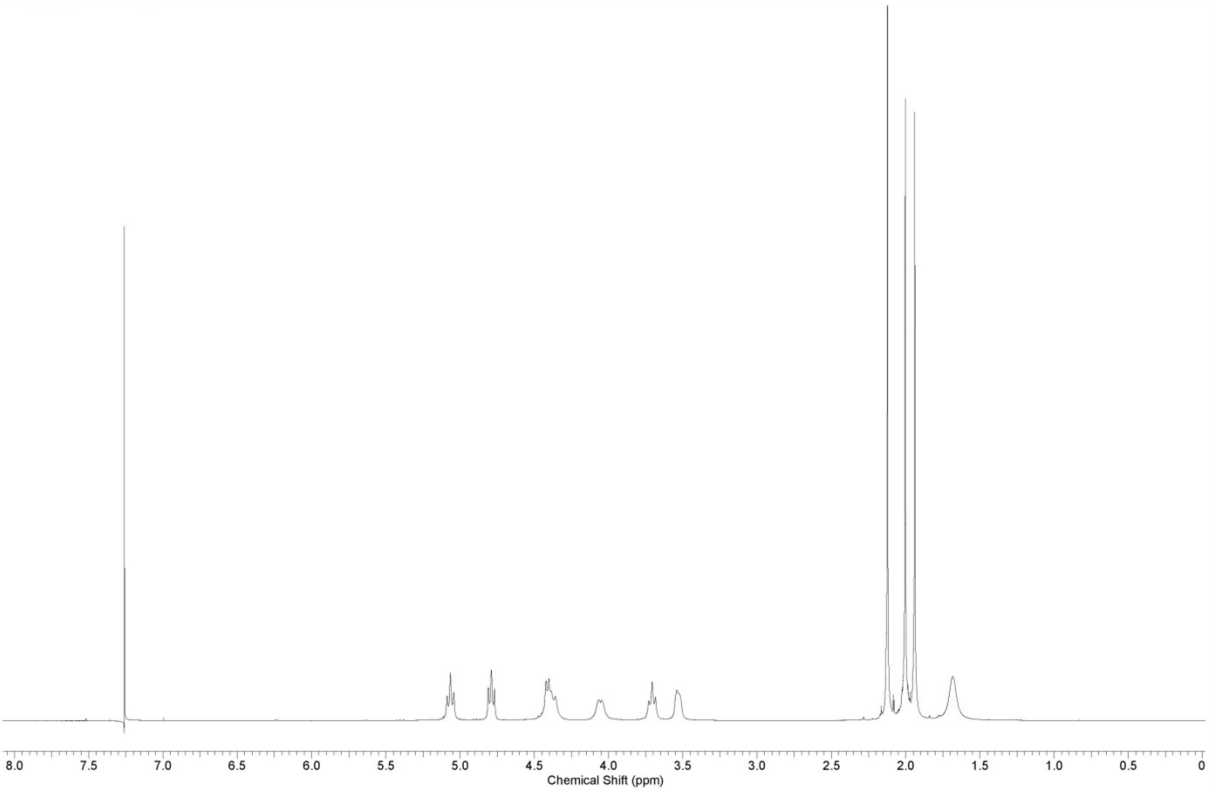

Figure 26. NMR spectrum of 5 X_b.

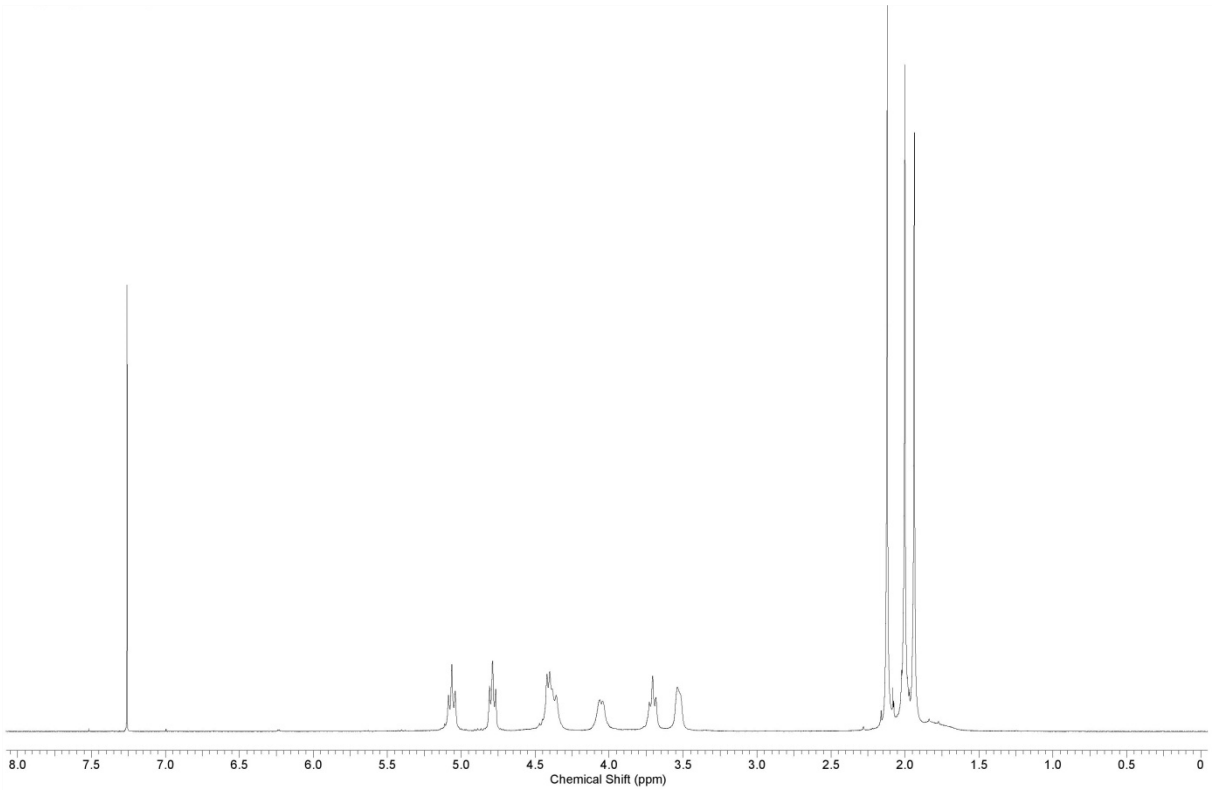

Figure 27. NMR spectrum of 10 X_a.

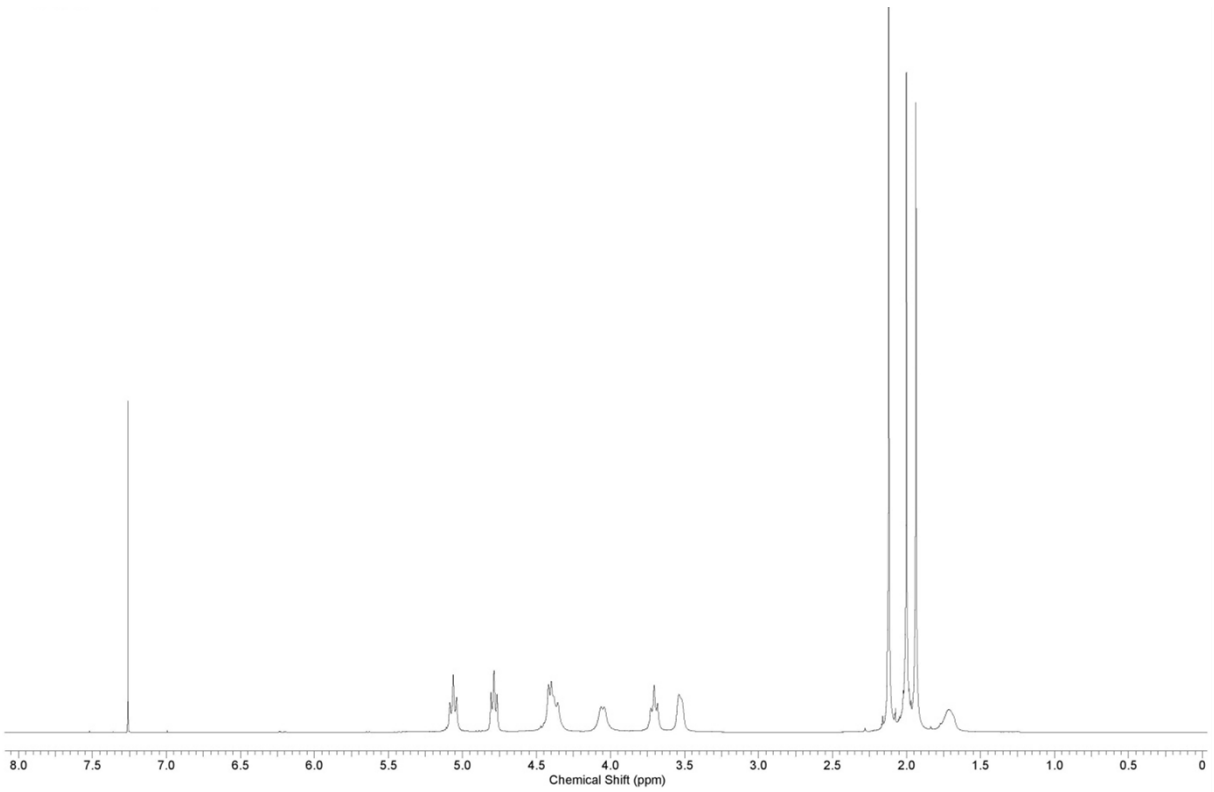

Figure 28. NMR spectrum of 10 X_b.

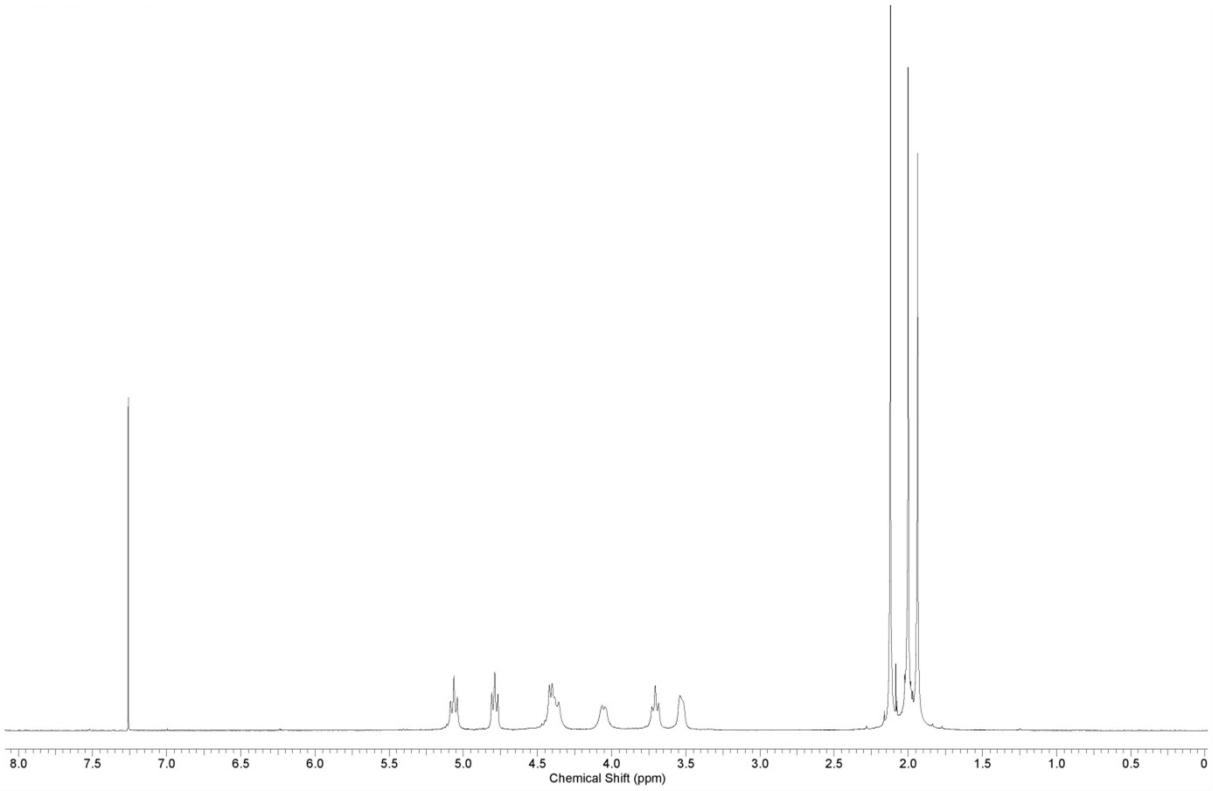

Figure 29. NMR spectrum of 15 X_a.

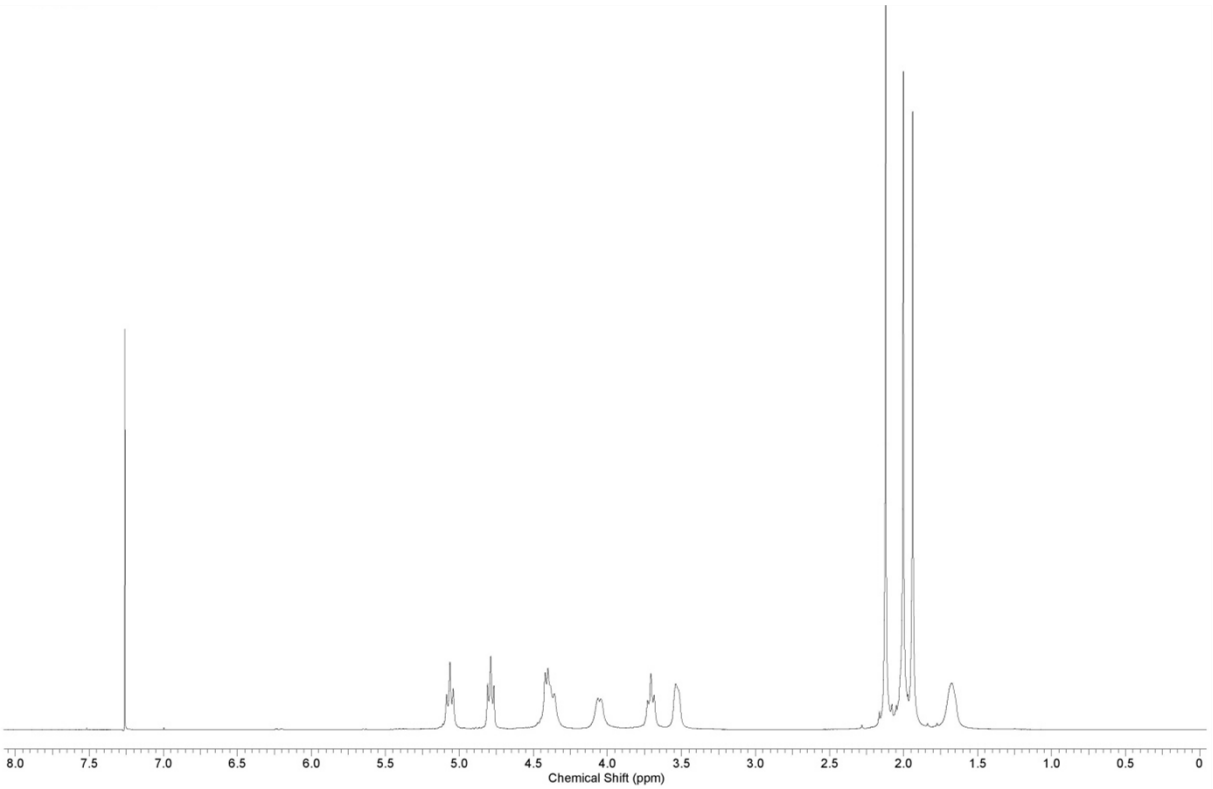

Figure 30. NMR spectrum of 15 X_b.

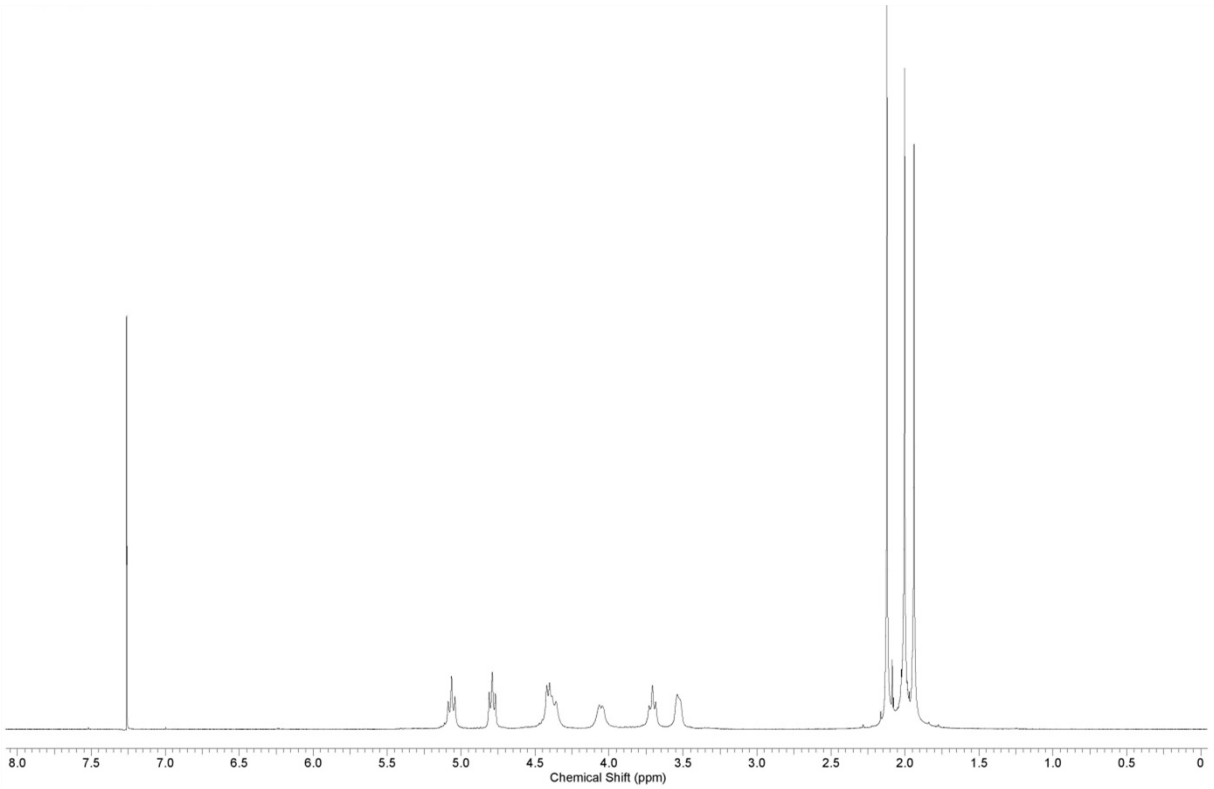

Figure 31. NMR spectrum of 20 X_a.

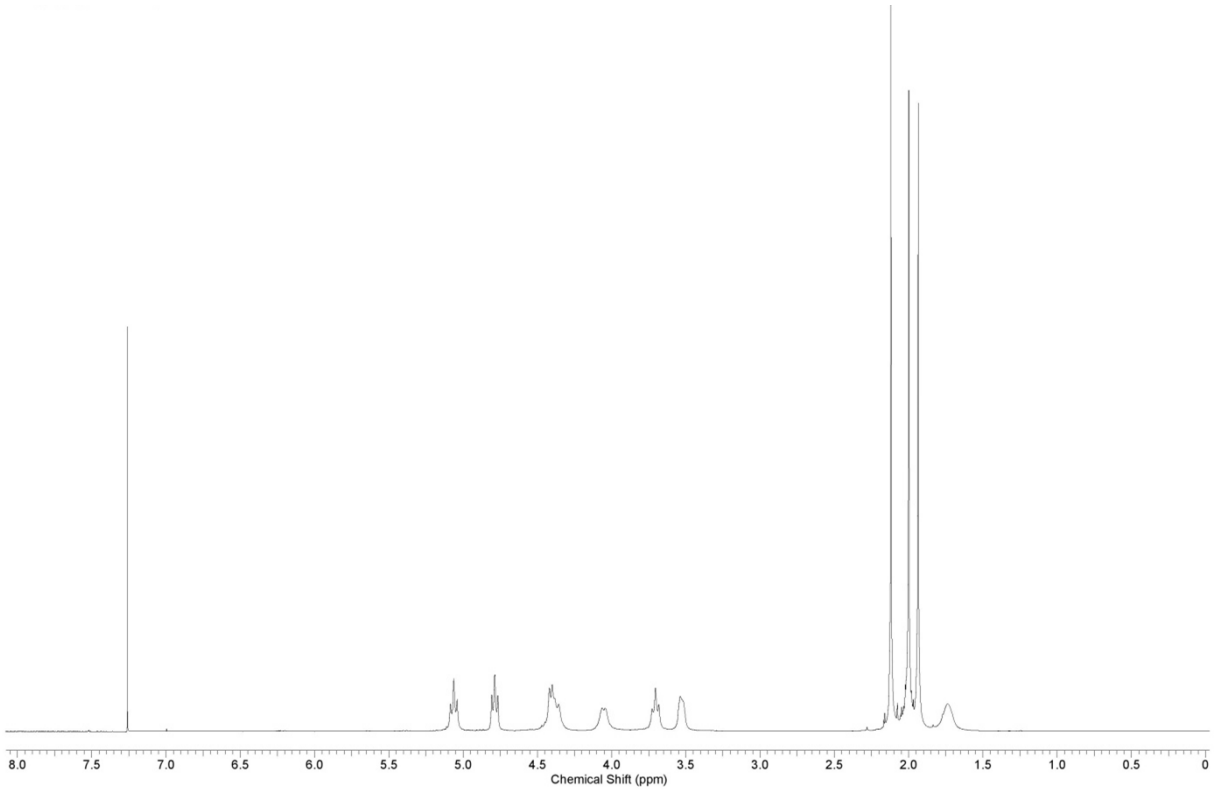

Figure 32. NMR spectrum of 20 X_b.

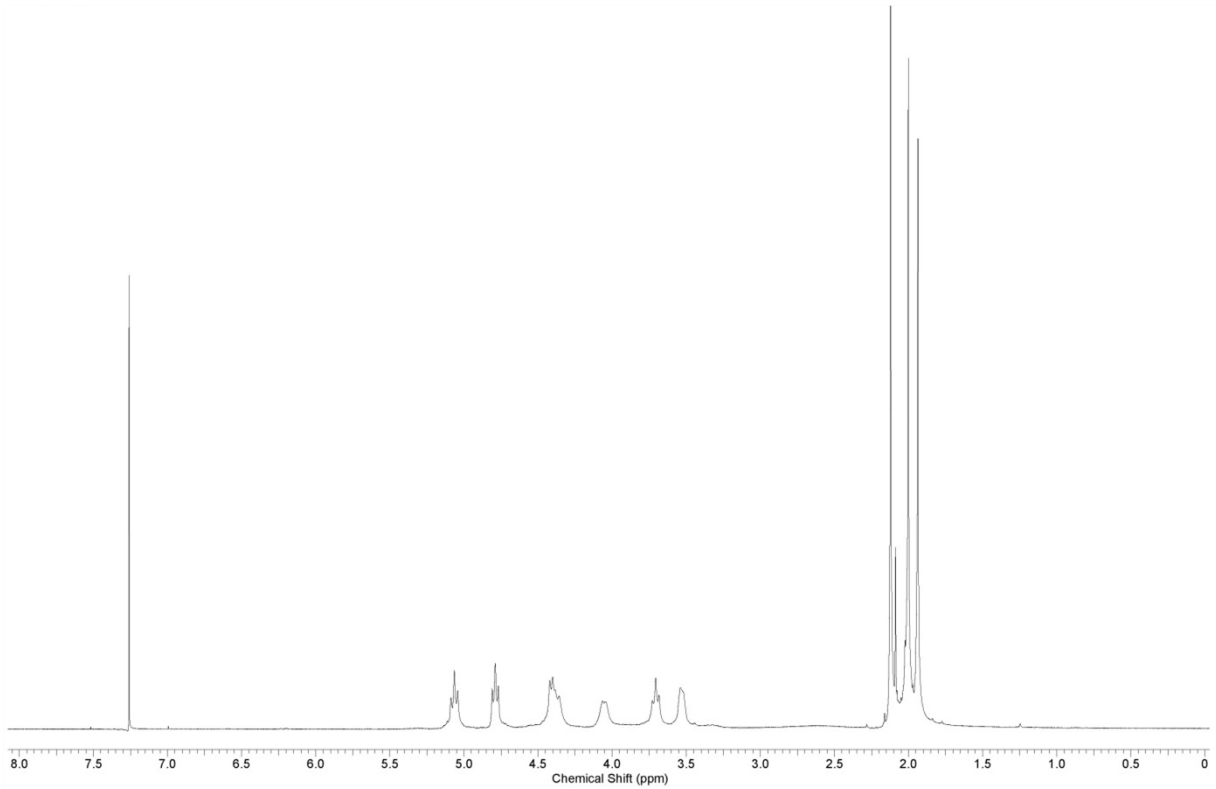

Figure 33. NMR spectrum of 30 X_a.

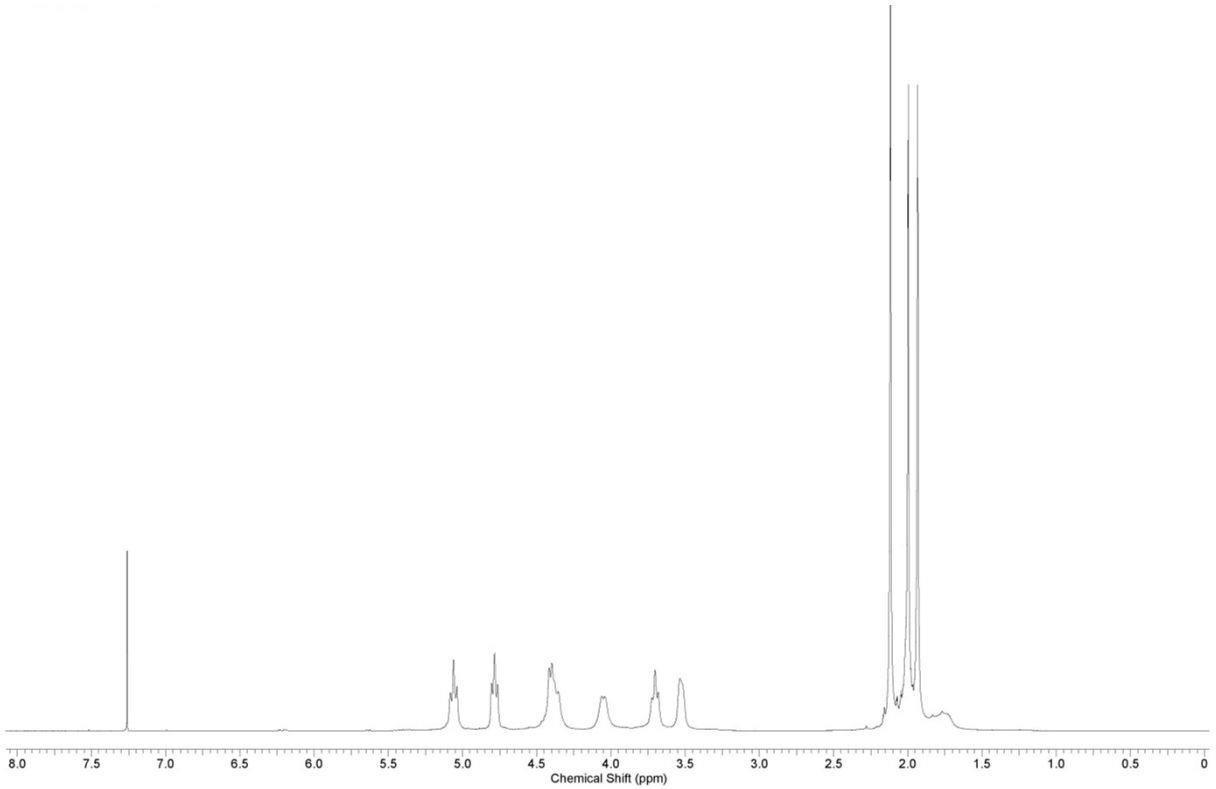

Figure 34. NMR spectrum of 30 X_b.

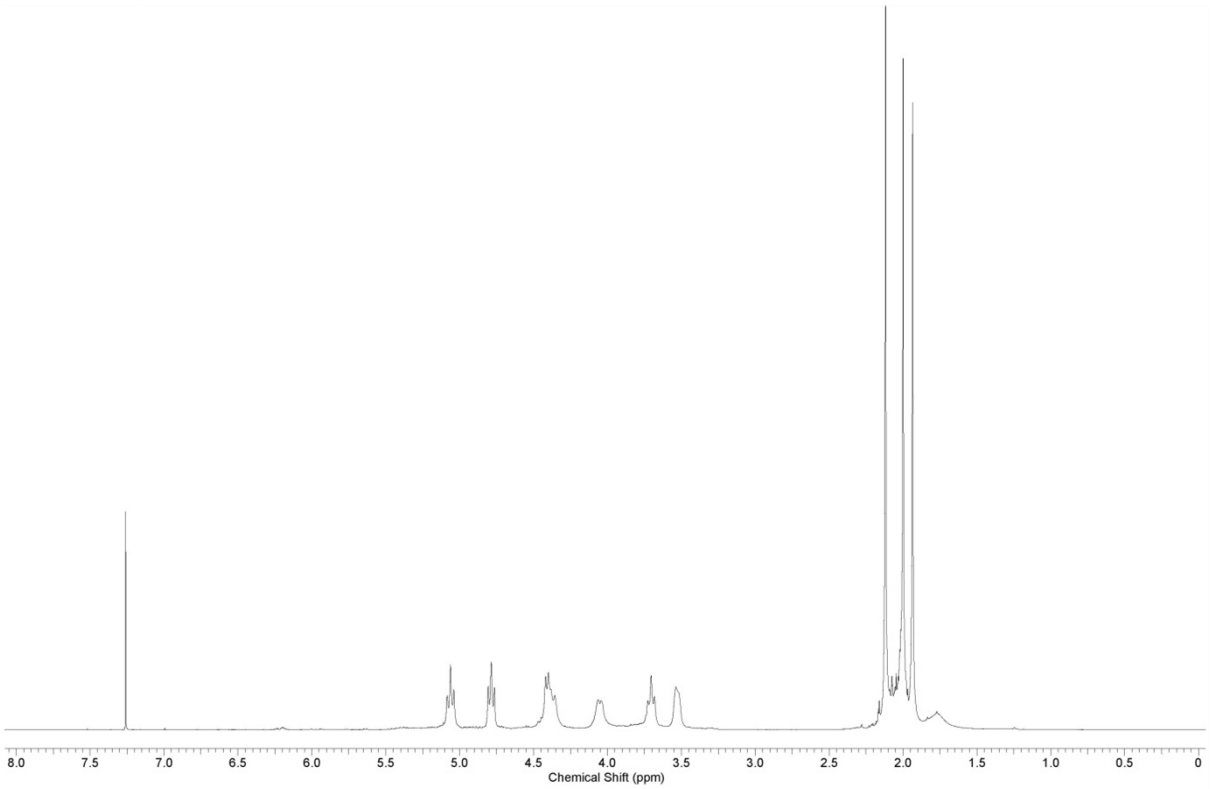

Figure 35. NMR spectrum of 50 X_b.

APPENDIX II

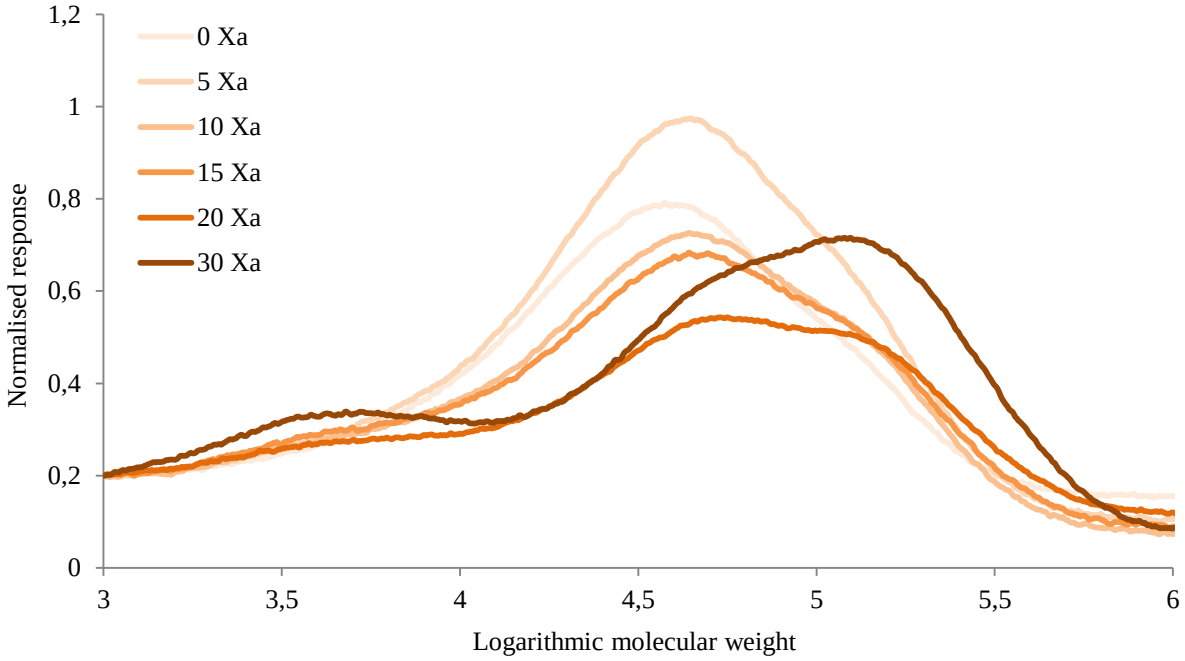

Figure 36. GPC data of the X_a series.

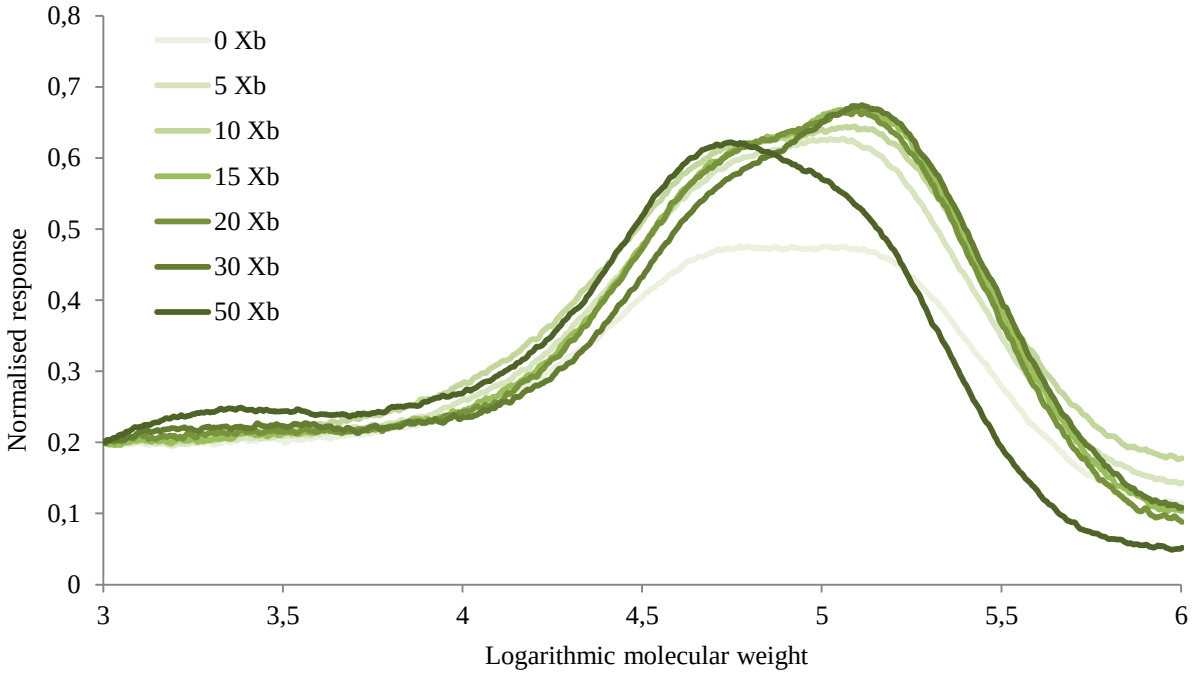

Figure 37. GPC data of the X_b series.

APPENDIX III

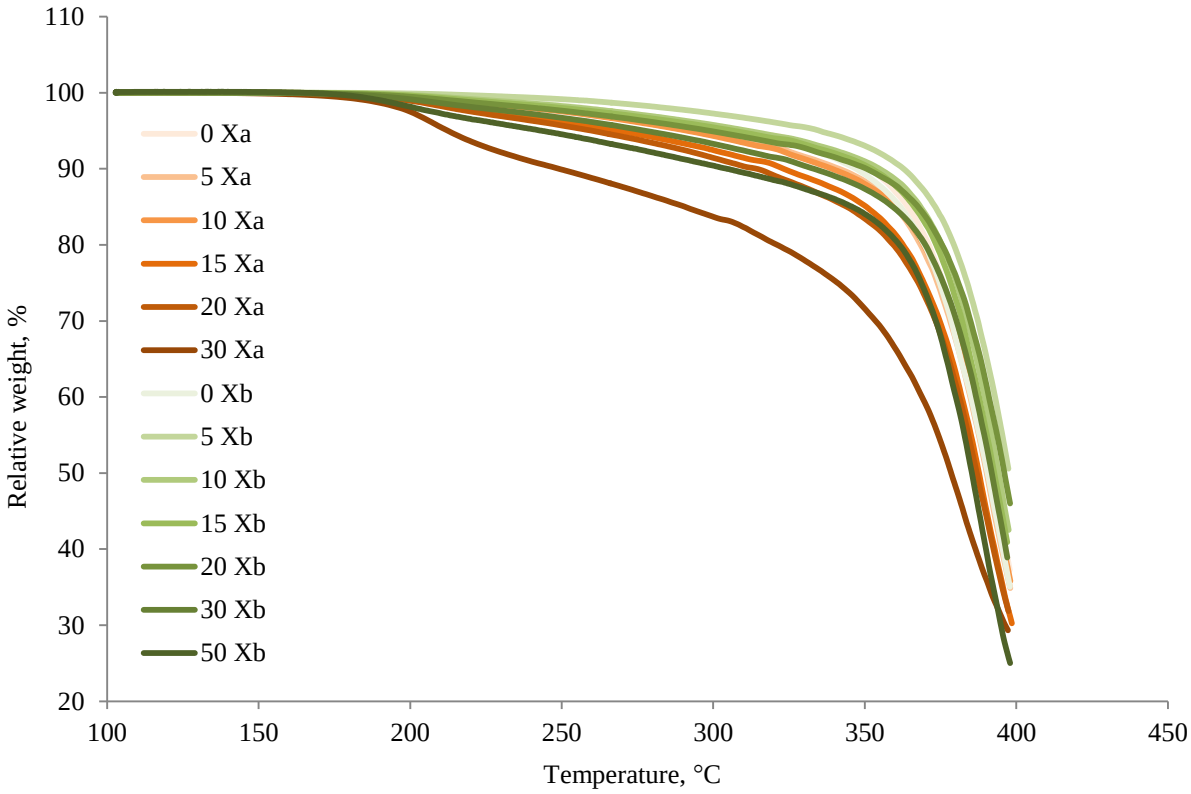

Figure 38. TGA results for the X_a and X_b sample series.