



Branching of hemicelluloses through an azetidinium salt ring-opening reaction



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ABSTRACT

During the last century there has been a steady increase in the number of publications on practical applications of hemicellulose. Due to the water and moisture sensitivity, poor film-forming ability and lack of thermal processability most of the hemicelluloses need to be chemically modified prior to processing into materials. Within this study we present the results of azetidinium salts as a new functional group for conjugation to polysaccharides. The reactivity of three azetidinium salts on xylan, arabinoxylan and galactoglucomannan was investigated. Carbonyl groups were found to be favorable for the reaction with azetidinium salts and thus the glucuronic acid content in the hemicellulose determines the degree of substitution. TEMPO-oxidation of the hemicelluloses was done which successfully increased the degree of substitution. The highly reactive azetidinium salts are easily synthesized from secondary amines and epichlorohydrin and can be used as a new tool toward functionalization of hemicelluloses into the after sought properties.

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1. Introduction

Today the society has become increasingly aware of the limited resource of fossil-fuels and the importance of developing materials from renewable resources with a low environmental impact. The demand for replacing non-renewable products with bio-based products requires knowledge and tools on how to utilize the resources in more efficient ways. Key factors for a shift to hemicellulose-based materials are availability in large quantities at a reasonable price and that the material manufactured from hemicellulose has similar or better properties than the fossil fuel-based material that it will replace. A big difference between fossil fuel-based polymers and biopolymers is the higher content of oxygen in bio-based materials. A consequence of the higher oxygen content is that the material has lower heat value, 13.6 MJ/kg; on the other hand it has the advantage that the reactive oxygen containing groups such as carboxylic acids and alcohol functions can be functionalized to tune the properties of the material.¹ During the 21st century there has been a huge increase in the number of publications on practical applications of hemicelluloses where the main applications have been toward hydrophobized materials such as gels, films and reinforcement in composites.^{2,3} The overall properties of the

hemicelluloses depend on their carbohydrate composition, the degree of polymerization (DP), its branching pattern as well as the chemical structure of added substituents.

Hemicelluloses represent approx. 20–30% of the biomass in nature and are in general shorter than cellulose polymers. The main hemicelluloses found in hardwood are xylans with a DP of 100–400. Xylans consist of a backbone of D-xylopyranose units and are mostly branched with L-arabinofuranose and glucuronic acids and the degree of branching depends on plant species and cell type. The main hemicelluloses found in softwoods are glucomannans, which consist of D-glucopyranose and D-mannopyranose units that are often branched with D-galactopyranose units. The glucomannans are partly acetylated and is shorter than xylans with a DP of ca 100–200. The hemicelluloses found in annual plants such as crops are generally more structurally diverse and complex than the hemicelluloses found in wood. The hemicelluloses in annual plants often consist of mixtures of many different sugar units and can be branched with for example D-xylopyranose, L-arabinofuranose, D-galactopyranose or uronic acid side chains.^{4,5}

Hemicellulose can be utilized from sources like low-value wastewater streams in kraft pulping processes and agricultural crop residues. As said, the type and composition of hemicelluloses are highly dependent on the source, but also the isolation process and chemical reactions during the process can give rise to deacetylation, debranching and/or degradation. As a consequence the hemicelluloses structure depends on its process and fractionation history. Today, isolation of hemicelluloses such as hardwood xylan from the black liquor in kraft pulping processes and galactoglucomannans

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(GGMs) released and accumulated in process waters in the production of thermo-mechanical pulp is often done by membrane filtration.^{6,7} There is also a number of methods available to obtain hemicellulose from different plant sources like extraction with alkali,⁸ dimethyl sulfoxide,⁹ hot-water treatment,¹⁰ microwave treatment¹¹ or extrusion.¹²

Although, being such a close relative to cellulose much less development in chemical modification of hemicellulose has been done compared with cellulose. Traditional modification processes are etherification, esterification, graft polymerization and oxidation which are quite often used as an intermediate for further functionalization. These processes are usually used with the aim to increase the hydrophobicity of the material. Successful acylation of hemicelluloses to increase the hydrophobicity has been reported by several groups.^{13–19} There are also reports on fluorination of hemicelluloses, however thus far; it seems that the water sensitivity of the trifluoroacetyl group limits the use of these derivatives.^{20,21}

Hemicelluloses can find use within the packaging industry,^{22,23} food industry,²⁴ biomedical uses²⁵ and for chemical production.^{26,27} Cross-linked hemicelluloses have also been reported to form hydrogels and are evaluated for drug delivery systems applications.^{28,29}

We have looked into azetidinium salts as new coupling reagents that can be used for functionalization of hemicelluloses. Azetidines are found in a diverse range of natural products and serve as a valuable building block for other structural classes. The four member azetidine-ring can be quarternized to an azetidinium ion and in combination with the ring strain, it is a suitable reagent due to its high reactivity.³⁰ Azetidinium ions can easily be synthesized from secondary amines and epichlorohydrin.^{31,32} Because of the many choices of carbon chains or other functional groups that could be attached to the azetidine-nitrogen, there is a big variety of modifications that can be done. Akzo Nobel Chemicals recently filed a patent for production of azetidinium compounds with carbon chains between 1 and 30 carbon atoms.³³ A difference compared to traditional hydrophobization agents from using azetidiniums is that two substituents in a Y-shaped branching will be formed when the azetidinium ring is opened and covalently linked to the target. Hydrophobization and properties tuning in this way will be a complement to the ones formed by ether and ester conjugation to the polysaccharide. Functionalization with Y-shaped chlorohydrins has recently been investigated showing that longer alkyl chains attached to CNC increase hydrophobicity and enhance the dispersion in low-density polyethylene matrices.³⁴

There are only a few reports on azetidinium ions in the field of polysaccharides. Most of them are found in polyamide amine epichlorohydrin (PAE), which is a water-soluble resins used as wet strength additive for preparing wet strength papers. In a review article by Espy³⁵ potential cross-linking reactions of azetidinium groups are discussed as a possible wet strength agent. In the review it is stated that alcohol groups may play a part in cross-linking reactions as well as carboxylate end groups of cellulosic polymers. Carboxymethylated cellulose (CMC) or other carboxyl-bearing dry strength polymers showed an increased effectiveness in reaction with PAE.³⁶ Also Obokata and Isogai³⁷ found in their study on PAE that TEMPO-oxidized cellulose under alkaline conditions showed an increased reactivity toward PAE resulting in increased wet strength in the cellulose sheets.

Branching of hemicelluloses through azetidinium salts opens up the possibility to attach different functional groups or length of carbon chains and by that gives new properties to the material depending on how the branching is designed. In this study, three different and relatively small azetidinium salts with a 3-hydroxyazetidinium chloride structure have been synthesized and used in reaction with the three different hemicelluloses—xylan, arabinoxylan (AX) and galactoglucomannan (GGM)—to evaluate the branching effect on the different hemicellulose structures. AX and GGM were also TEMPO-

Table 1

Relative carbohydrate compositions (Rel %) in the different hemicellulose samples assuming the samples only consist of detected sugar units. The glucuronic acid (GlcA) content was determined by NMR analysis

Sample	Ara ^a	Gal ^a	Glc ^a	Xyl ^a	Man ^a	GlcA ^b
Xylan	0.7	0.3	3.1	82.5	0.0	13.4
NaOH-xyl	1.0	1.4	3.3	81.0	0.1	13.2
AX	20.9	1.1	7.5	70.5	0.0	–
NaOH-AX	19.2	1.7	10.2	68.7	0.1	–
TEMPO-AX	9.1	1.4	5.8	83.5	0.2	–
GGM	2.1	14.3	16.9	0.1	66.6	–
NaOH-GGM	2.1	10.9	16.4	0.5	70.0	–
TEMPO-GGM	2.0	16.3	16.9	0.7	64.2	–

^a Content detected by ICS.

^b Content detected by NMR.

oxidized to investigate the reactivity of the azetidinium salts. TEMPO-oxidations are known to oxidize primary alcohol functionalities of several polysaccharides. Recently, it has been reported that TEMPO-mediated oxidation is an efficient method for the oxidation of GGM.^{38,39}

2. Experimental procedure

2.1. Materials

Three hemicelluloses were used in the study; a commercial hardwood-xylan (beech wood, Sigma-Aldrich), arabinoxylan (AX) extracted from barley husk (Lyckeby Culinar, Sweden) following the procedure described by Höjje et al.⁴⁰ and galactoglucomannan (GGM) from spruce kindly received as a gift from Stora Enso (Sweden). The hemicelluloses have been analyzed with carbohydrate analysis and NMR to determine the sugar content composition in the samples (Table 1). All chemicals used for the synthesis of azetidinium salts (diethylamine, dihexylamine, morpholine and epichlorohydrin) or treatments of the hemicelluloses with NaOH-activation or TEMPO-oxidation (2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) and bis(acetoxy)iodobenzene (BAIB) as co-oxidant) were purchased from Sigma-Aldrich and used as received.

2.2. Preparation of *N,N*-dialkylazetidinium salts

Preparation of the different azetidinium (Az) salts following previously known synthesis.^{32,41–44} A general reaction scheme is shown in Fig. 1.

The general procedure for preparation of azetidinium salts was dropwise addition of 0.1 mol epichlorohydrin to a solution of 0.1 mol secondary amine and solvent. The temperature was kept below 5 °C during the addition of epichlorohydrin due to an exothermic reaction. The reaction mixture was stirred in an ice bath for 1 h and additional 47 h at room temperature. The solution was purified with diethyl ether and water and solvent was removed in vacuum. Fig. 2 shows the molecular structure of the different azetidinium salts used in this study. For more details see supporting information.

2.3. Pre-treatment of hemicellulose

A pre-treatment of the hemicelluloses was performed before reaction with the azetidinium salts, where a 17.5 wt% NaOH-solution

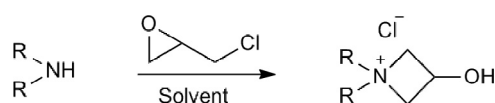


Fig. 1. A secondary amine is converted to azetidinium chloride through reaction with epichlorohydrin.

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