New Aspects in Cationization of Lignocellulose Materials. VIII. Modification of Immitted Spruce Wood with Quarternary Ammonium Groups

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Synopsis

Immitted spruce wood meal (ISWM) was modified with 3-chlor-2-hydroxypropyltrimethylammoniumchloride (CHMAC) or 1,3-bis(3-chlor-2-hydroxypropyl)imidazoliumhydrogensulphate (BCHIHS) in alkaline medium. The obtained material was gradually extracted with water and 5% NaOH. The yields of water-soluble hemicelluloses modified with quartemary ammonium groups were lower in comparison to healthy spruce material obtained under the same conditions but even more material could be obtained from ISWM–holocellulose. The quantity of alkali-soluble polysaccharides from ISWM was the same as obtained from undamaged spruce. The residues after alkali extractions are suitable ion exchangers with low solubility in dilute alkali solutions. The yields of extracts from material modified with BCHIHS were lower than yields of extracts from material modified with CHMAC because ISWM was crosslinked when alkylated with bifunctional chemicals.

INTRODUCTION

In recent years, forest damage of an extent not previously experienced has been observed in a number of countries in the northern hemisphere and particularly in some countries of central Europe. Besides acidifying SO_2 and NO_x from the combustion of great quantities of fossil fuels, the atmosphere is polluted by emission of heavy metals, halogen compounds, and an enormous number of organic compounds. Spruce wood is the most damaged from all species.[1]

The object of the present paper is to study immitted spruce wood from the aspect of its accessibility, extraction, and chemical modification.

EXPERIMENTAL

Materials

Spruce wood meal (*Picea excelsa L.*) from the region Iser Mountains described as damage class 4 (severely damaged, bark pelled during immision and secondarily attacked by fungi prior to felling). The Klason lignin of the sample used was 32.8%. The 50% (vol) aqueous solutions of CHMAC and BCHIHS were used as alkylating agents, as well as 17.5% NaOH for activation.

Journal of Applied Polymer Science, Vol. 34, 2063–2068 (1987)
 CCC 0021-8995/87/062063-06$04.00

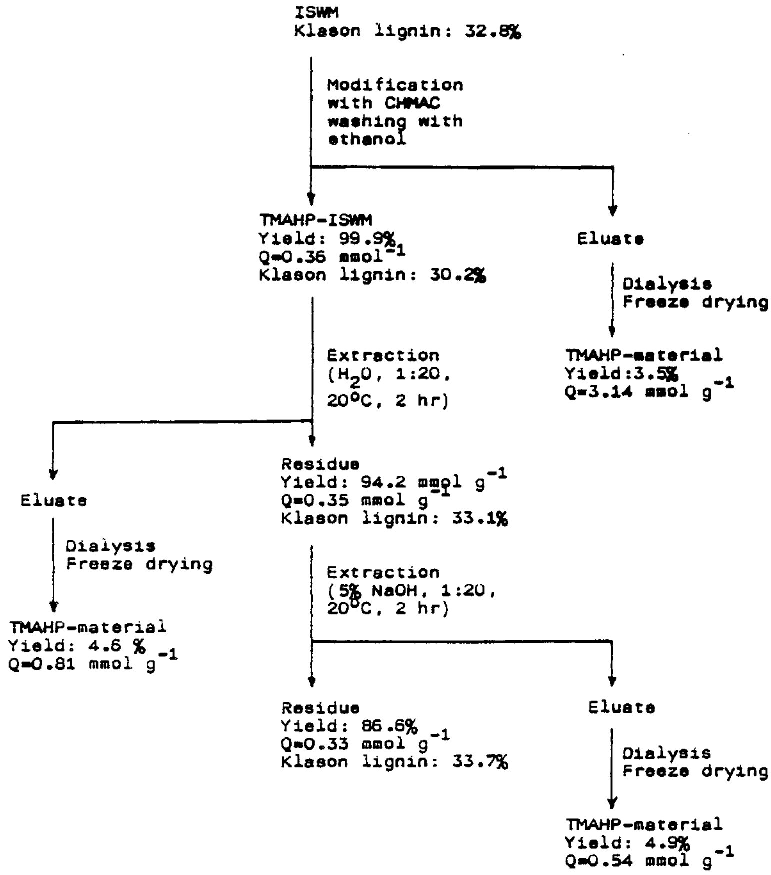

Fig. 1. Fractionation scheme of TMAHP-ISWM.

Methods

The isolation of individual fractions was done according to the schemes in Figures 1–3. The modification with BCHIHS was done under the same conditions as for CHMAC (material:NaOH:alkylating agent = 1:0.32:0.75).[2] All other procedures were described previously.[3]

RESULTS AND DISCUSSION

The yield and quality of pulp from immited spruce are lower in comparison to undamaged spruce.[4] This seems to be in connection with higher Klason lignin content of used material (32.8%, Fig. 1). ISWM was modified with CHMAC and eluted with 80% ethanol. The yield of trimethylammonium-2-hydroxyprophyl (TMAHP) residue was about 8% lower in comparison to spruce wood meal (SWM) and for the dialyzed eluate about 1% higher. It confirms the fact that the immited wood contains more low molecular degradation products. The ^{13}C-NMR spectrum of ethanolic eluate (yield = 3.5%, Q = 3.14 mmol g^{-1}) confirmed the absence of saccharides in anomeric

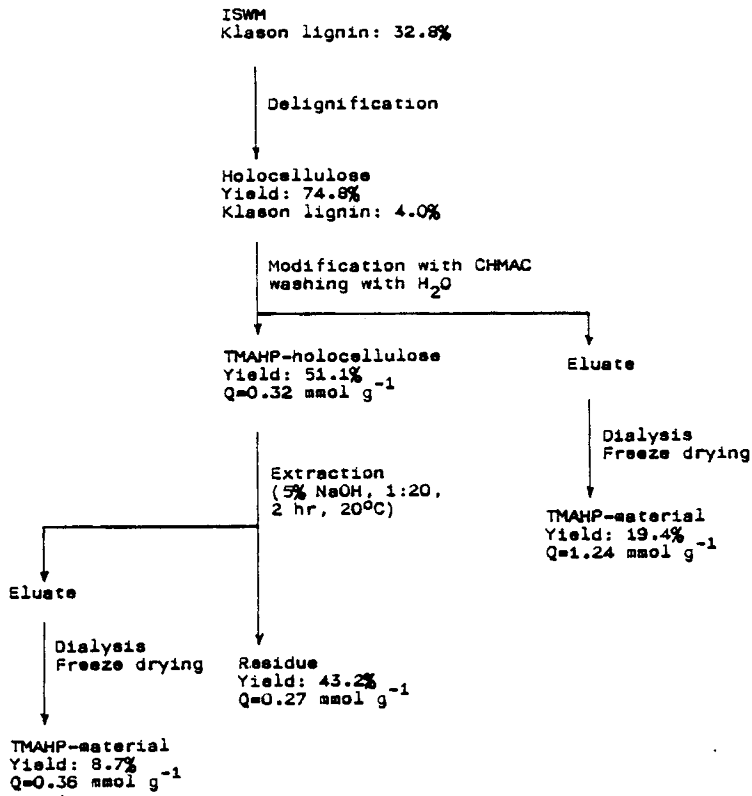

Fig. 2. Fractionation scheme of TMAHP-ISWM holocellulose.

region, as well as aromatic structures from lignin in the region from 100 to 150 ppm.

The water extract from TMAHP-ISWM represented only 4.6% (Q = 0.81 mmol g^{-1}) from ISWM. This was only half of the value obtained under the same conditions from healthy spruce wood.[3] The ^{13}C-NMR spectrum of this fraction showed in the anomeric region the presence of (4-0-methyl-D-glucurono)-D-ylan (102.8, 102.4, and 98.6 ppm)[5] and D-gluco-D-mannan (103.5 and 101.2 ppm).[6] The insoluble residue (yield = 94.2%, Q = 0.35 mmol g^{-1}) contained more Klason lignin (33.1%) than TMAHP-ISWM, as well as ISWM (Fig. 1). This material was extracted with 5% NaOH solution, and the insoluble residue obtained in this way (yield = 86.5%, Q = 0.33 mmol g^{-1}) contained the same quantity of Klason lignin as ISWM. The quantity of NaOH eluate (yield = 4.9%, Q = 0.54 mmol g^{-1}) was the same as for H_2O eluate obtained in this procedure (Fig. 1). The NaOH eluate was soluble in 5% NaOH after dialysis and freeze drying. The IR spectrum of this fraction showed the presence of COO^- groups (1605 and 1420 cm^{-1})[7] from (4-0-methyl-D-glucurono)-D-xylan. The quantity of this fraction was equal when compared to healthy wood.[3]

To eliminate the influence of lignin on the quantity of extracted hemicellulose material, we prepared holocellulose from ISWM. The holocellulose was

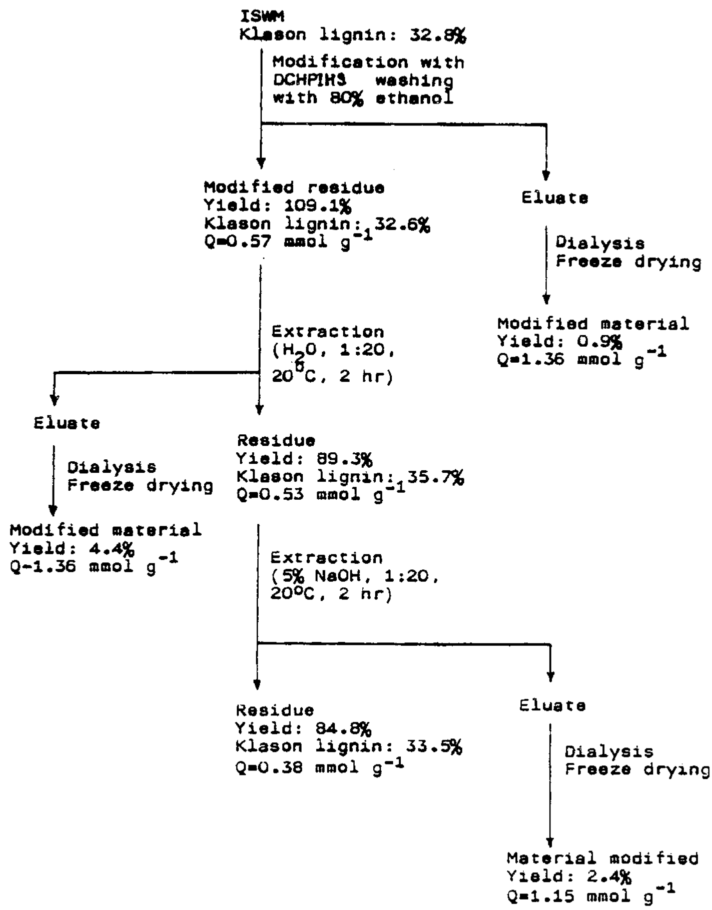

Fig. 3. Fractionation scheme of ISWM modified with BCHIHS.

modified with CHMAC and the reaction stopped by diluting and washing the mixture with water (Fig. 2). The yield (19.4%) of modified, water-soluble material was higher in comparison with undamaged wood.[3] From the ^{13}C-NMR spectrum follows that the composition of this fraction is identical with the water soluble TMAHP material from ISWM. TMAHP–holocellulose was extracted with 5% NaOH solution, and the yield of the obtained eluate was also slightly higher (8.7%) in comparison with NaOH extract from healthy ISWM. These results indicate that also cellulose component of ISWM was degraded and is partially extractable. The IR spectrum of this fraction was identical with the spectrum of NaOH extract from ISWM.

To study the influence of the alkylating agent used on the yield of extracted material from ISWM, the bifunctional chemical BCHIHS was used. ISWM was modified with BCHIHS under the same conditions as used for CHMAC. The yield of obtained material (109.1%) was higher (Fig. 3) than for TMAHP–ISWM, but the yield of ethanol eluate (0.9%) was lower than for TMAHP material eluted from ISWM.

When ISWM modified with BCHIHS was extracted with water only 4.4% of material was obtained after dialysis and freeze drying while the yield of residue was 89.3%. These values are equal to yields obtained when CHMAC was used as alkylated agent. ^{13}C-NMR spectrum of water eluate modified with BCHIHS confirmed the presence of chemically bonded imidazole ring (C_2: 138.0, C_4 and C_5: 124:3 ppm) as well as hydroxypropyl groups (C_1: 53.2, C_2: 71.0, and C_3: 63.7 or 69.4 ppm). These values were in agreement with the spectrum of 1,3-bis(3-chlor-2-hydroxypropyl)imidazoliumhydrogensulfate (C_1: 137.9, C_4 and C_5: 124.2 ppm, of imidazole ring, and C_1: 53.3, C_2: 70.0, and C_3: 46.8 ppm, of 2-hydroxypropyl groups). The difference in chemical shifts of C_3 in 2-hydroxypropyl group of saccharide derivate in comparison to alkylating agent is due to hydrolysis of chlorine atom in the alkylation process. The values of C_3: 63.7 or 69.4 ppm confirm the presence of the C_3—O bond. It is supposed that the presence of two peaks is due to the fact that the alkylating agent was not completely bifunctionally linked to saccharides. In the anomeric region the chemical shifts of (4-0-methyl-D-glucurono)-D-xylan (102.9, 102.5, and 98.5 ppm) and D-gluco-D-mannan (103.6 and 101.3 ppm) were observed. The yields of NaOH extract (2.4%) and the obtained residue (84.8%) were lower in comparison to TMAHP material. These results indicate that ISWM was crosslinked with DCHPAIHS, and the lower quantity of polysaccharides was extracted after modification. On the other hand, the material modified with BCHIHS after eluation with water and NaOH showed higher exchange capacity but twice as high nitrogen content as TMAHP residues. These materials are suitable ion exchangers with high lignin content and low solubility in NaOH solutions. The IR spectra of H_2O and NaOH eluates were identical with bonds at 1603 and 1420 cm $^{-1}$ (COO^- group).

The yields of modified hemicelluloses from immitted spruce meal are lower in comparison to healthy material[3] but higher in comparison to fungi attacked aspen material.[8] We suppose that it is due to lower degradation of lignin in the immitted material in comparison to polysaccharides components of ISWM. The degraded polysaccharides are more accessible to extraction in comparison to undamaged species.

CONCLUSIONS

ISWM was modified with CHMAC and BCHIHS in alkaline medium. The obtained materials were extracted with water and in the second step with 5% NaOH. also TMAHP material from ISWM–holocellulose was prepared and extracted with water and 5% NaOH. The yields of water-soluble hemicelluloses from ISWM were lower in comparison to SWM but more material could be extracted from ISWM–holocellulose. The yields of alkali-soluble polysaccharides from ISWM were equal to the yields from SWM. The residues after alkali extractions are suitable ion exchangers with low solubility in dilute alkali solutions. The yields of extracts from materials modified with BCHIHS were lower than of extracts from TMAHP derivatives because ISWM was crosslinked when alkylated with bifunctional chemicals.

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Received April 30, 1986
Accepted October 1, 1986