Wood modification with maleic anhydride and sodium hypophosphate

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ABSTRACT

The formation of crosslinked bonds between wood constituents is believed to be an effective way to stabilize wood against wet conditions. The possibility to use maleic anhydride (MA) combined with sodium hypophosphate (SHP) as crosslinking agents was studied, using Scots pine sapwood and a model compound. The modified wood showed weight gain and bulking effect after treatment and subsequent Soxhlet extractions, which indicated penetration into the wood cell wall and reaction of the chemicals with the wood constituents. The FTIR spectra confirmed the formation of an ester bond between the wood and MA. Furthermore, a decrease of intensity of band at 1635 cm⁻¹ indicated a reduction of the double bond between carbons in MA after further treatment with SHP, especially at 170 °C. Such reactions were studied using monomethyl maleate (MMM) and SHP. The ¹³C NMR spectra of the reaction product confirmed a reduction of the double bond between carbons. However, we were not able to find clear evidence supporting the formation of the crosslinking C-P bond at this stage.

INTRODUCTION

Replacing artificial biocides in wooden products is of great importance for the sustainable use of wood in exterior conditions. Products that could efficiently reduce moisture uptake could also favour a higher dimensional stability of wood and potentially an increased resistance to microbiological degradation.

Modification with cyclic anhydrides forms an ester bond with wood components without any undesired by-product, providing wood carboxylic moieties capable of further reaction [1]. For these reasons, the reaction between wood and cyclic anhydrides and various subsequent reactions have been extensively studied [1-4]. In previous studies, however, cyclic anhydrides were used as crosslinking agents between wood and chemicals added for subsequent reactions rather than as modification agents of the wood constituents.

In studies of cotton cellulose, it was suggested that sodium hypophosphate (SHP) not only acted as a catalyst but also reacted with the unsaturated carbon of maleic acid to form a crosslink between maleic acid modified cellulose (Fig. 1)[5], resulting in better properties on wrinkle resistance and fire properties after laundry cycles [6].

Fig. 1 Scheme of reaction between cotton cellulose, maleic anhydride and sodium hypophosphite [5].

As wood has a lower crystallinity compared to cotton cellulose and contains other reactive constituents such as hemicelluloses, such modification reactions can be expected in wood. These reactions could improve the performance of wood products at various conditions such as dimensional stability, durability, etc.

In this study, the chemical reaction between wood, MA and SHP was investigated to examine the possibility of using MA combined with SHP as a wood modification system. Furthermore, to study the reaction between wood-MA complex and SHP, reactions using model systems, whereby wood was substituted with methanol, were studied.
EXPERIMENTAL

Materials

Scots pine (Pinus sylvestris L.) sapwood was purchased from a local retailer in Skellefteå, Sweden. Maleic anhydride (MA) and methanol were purchased from Merck and sodium hypophosphite monohydrate (SHP) was purchased from Alfa Aesar.

Modification of wood

Scots pine sapwood blocks of dimension 20×20×10 mm (R×T×L) and an oven-dried density of 583±7 kg/m³ were subjected to Soxhlet extraction using a mixture of acetone: water (4:1, v:v) prior to impregnation with solution of MA in acetone at 15 bar for 1 h. The treated specimens were wrapped with aluminium foil and placed in an oven at 115°C, followed by Soxhlet extraction using acetone for 6 h to remove excess MA. Weights and dimensions of extracted specimens were measured to calculate the weight percentage gain (WPG) and bulking effect (BE) by the MA treatment.

The WPG was calculated as 100×(Wc−Wi)/Wi, where Wc is the oven-dried weight of specimens after impregnation while Wi is the oven-dried weight of specimen before treatment.

The BE was calculated as 100×(Sc−Si)/Si, where Sc is the area of cross-section of specimens after impregnation while Si is the area of cross-section of oven-dried specimen before treatment.

MA treated specimens were vacuum impregnated in aqueous solution of SHP for 0.5 h. For the reaction of SHP and MA treated wood, vacuum impregnated specimens were wrapped in aluminium foil and placed in an oven at 130°C and 170°C for 6 h, respectively.

To remove unreacted chemicals, all specimens were vacuum impregnated with water for 0.5 h and kept immersed under water for 72 h. Water was changed every 24 h. Weights and dimensions of specimens were measured to calculate WPG and BE.

Model compound study

Since wood is a heterogeneous material, it was decided to synthesize a compound to study the possible reaction between wood-MA and SHP by substituting wood with methanol. To synthesize monomethyl maleate (MMM), 0.01 mol of MA was dissolved and reacted in 0.03 mol of methanol at 70°C for 1h. 1mL of product was mixed with 0.05 mol of SHP-H2O and reacted at 170°C for 30 min in a ventilated chamber. A solid foam was formed by this reaction. The product of this reaction will be referred as “PR” in results and discussion.

Chemical analysis

Small shavings of specimens collected from the tangential surface of the treated wood and a small drop of the synthesized model compounds were analysed with Fourier-transform infrared spectroscopy (FT-IR) with an attenuated total reflectance (ATR) (PerkinElmer). IR spectra over the range of 4000 to 450 cm⁻¹ were collected using ten scans with a resolution of 4 cm⁻¹. All spectra were rescaled against the strongest absorption band (1023-1030 cm⁻¹).

To investigate the reaction between synthesized MMM and SHP, the products were analysed with phosphorus nuclear magnetic resonance (³¹P NMR) and ¹³C NMR (Bruker spectrometer, 400 MHz). SHP was dissolved in D₂O, while others were dissolved in deuterated dimethyl sulfoxide (DMSO-d₆).

RESULTS AND DISCUSSION

Modification of wood

Absorption bands at 1723 cm⁻¹ and 1200 cm⁻¹ were observed in the FTIR spectra due to the formation of ester bond and at 1635 cm⁻¹ due to the presence of unsaturated carbons in MA. Spectra of MA treated specimens showed an increased intensity of absorption bands at 1723 cm⁻¹, 1200 cm⁻¹ and 1635 cm⁻¹, which indicated the formation of ester bonds between MA and wood constituents (Fig. 2). The weight gain of MA and BE as a result of treatment suggested there was cell wall penetration of MA (Table 1).

The similar intensity of absorption bands at 1723 cm⁻¹ and 1200 cm⁻¹ was found after further treatment with SHP at 170°C. However, these bands were found to decrease when the reaction was undertaken at a lower temperature (130°C). Considering the low WPG of these specimens (Table 1), it might indicate that the ester bond between wood and MA was not stable during heat treatment. The presence of water and acid groups during the heat treatment could also catalyse the hydrolysis of the ester bond. However, results seemed to suggest that the cleaved maleic acid reacted again with the wood at higher temperature in presence of the SHP catalyst. The decrease of intensity of band at 1635 cm⁻¹ was observed after treating wood with SHP, which might be due to reduction reactions of C=O in MA (Fig. 2).
Table 1 Weight percentage gain (WPG) and bulking effect (BE) after treating wood with maleic anhydride (MA) and sodium hypophosphite (SHP).

<table>
<thead>
<tr>
<th>Treatment</th>
<th>WPG [%]</th>
<th>BE [%]</th>
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<tbody>
<tr>
<td>MA 115°C 2h</td>
<td>19.0 (0.28)</td>
<td>7.5 (0.41)</td>
</tr>
<tr>
<td>MA 115°C 130°C 2h</td>
<td>10.0 (2.08)</td>
<td>3.4 (0.72)</td>
</tr>
<tr>
<td>MA 115°C 170°C 2h</td>
<td>17.0 (0.54)</td>
<td>7.0 (0.32)</td>
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</table>

*The values in the parentheses are standard deviations.

Model compounds

To unravel the reaction mechanisms, reactions using model systems instead of wood were studied. Thus, methanol, which is a primary alcohol, was used, with resultant reactions analyzed using NMR and FTIR.

The chemical shift of CH$_3$ group bonded in the formed ester was observed at 3.6 ppm in $^1$H NMR spectra of synthesized MMM. It was also observed at 51.8 ppm in $^{13}$C NMR spectra of both synthesized MMM and PR (Fig. 3). The chemical shift of methanol at 48.9 ppm was present in $^{13}$C NMR spectra of MMM but not in the spectra of PR. However, new chemical shifts around 29 ppm were observed in the spectra of PR, which suggested the formation of saturated hydrocarbons (Fig. 3). The chemical shifts of carboxylic acid and ester were observed around 166 ppm in $^{13}$C NMR spectra of MMM, while they were found around 174 ppm in the spectra of PR. When comparing chemical shifts of carbonyl group in monomethyl maleate and corresponding ester of succinic acid, a similar tendency was observed.[7]

![Fig. 2](image-url)  
**Fig. 2** Fourier-transform infrared spectroscopy (FT-IR) results of untreated wood, wood treated with maleic anhydride (MA), treated with MA and SHP at 130°C, and treated with MA and SHP at 170°C.

![Fig. 3](image-url)  
**Fig. 3** $^{13}$C NMR spectra of synthesized monomethyl maleate (MMM) (top) and MMM reacted with sodium hypophosphite (PR) dissolved in dimethyl sulfoxide (bottom).

When studying the $^{31}$P NMR spectra, the signal of SHP observed at 7.2 ppm was not present in the spectra of PR, however, new chemical shifts were present in PR that were not observed in SHP. However, a chemical shift around 0 ppm might indicate that SHP was also prone to decomposition in the reaction solution (Fig. 4).
The FTIR spectra of PR showed a decreased peak at 1635 cm\(^{-1}\) compared to MMM (Fig. 5), which indicated reduction of C=C. This was also observed in \(^{13}\)C NMR spectra (Fig. 3). The spectra of PR had a new peak at 1780 cm\(^{-1}\), which might be attributed to the C=O stretching of conjugated anhydride, possibly resulting from the formation of anhydride from maleic acid in MMM solution by SHP (Fig. 5). It could explain the higher WPG and BE of wood treated with SHP at 170°C compared to those treated at 130°C (Table 1): SHP turned maleic acid into the respective anhydride, which further reacted with wood constituents.

**CONCLUSIONS**

From the studies of weight gain and bulking of wood treated with MA and SHP, there appears to be penetration and reaction of chemicals with wood constituents in the cell wall, which suggest the possibility of achieving dimensional stability and potentially more durable wooden products. The model compound study using NMR confirmed the reaction of double bonds between carbons in MA. However, to confirm the crosslinking of esterified MA with phosphorus in SHP, further studies on \(^{31}\)P NMR are needed, possibly using other model compounds than methanol.

**ACKNOWLEDGEMENTS**

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**REFERENCES**


