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Preparation and dimensional stability of wood grafted with alkyl chains

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4,4′-Diphenylmethane diisocyanate and fatty alcohols were reacted with beech blocks. Improvements in dimensional stability were observed for the modified woods obtained probably due to the water repellent properties of the alkyl chains grafted.

Synthese und Dimsionsstabilität von Holz-Pfropfpolymerisaten mit Alkylketten

Buchenklötzchen wurden mit 4,4′-Diphenylmethane Diisocyanat und Fettalkohole umgesetzt. Für die modifizierten Hölzer wurde eine Verbesserung der Dimensionsstabilität beobachtet, die wahrscheinlich durch die wasserabstoßenden Eigenschaften der Alkylketten der Pfropfpolymerisate bedingt ist.

1 Introduction

Various chemicals have been examined to modify wood (e.g. anhydrides, epoxides, aldehydes). However, among all the methods used to modify wood structure, the reaction with isocyanates is one of most popular. Isocyanates react with oven-dried wood to form stable urethane bonds and produce no by-products (Chen et al. 1990; Chen 1992; Weaver and Owen 1995; Pizzi and Owens 1995; Gerardin et al. 1995; Nakashima et al. 1996; Toffey and Glasser 1997; Sun and Hawke 1997).

In this publication, we describe the grafting of bulky alkyl chains on wood using 4,4′-diphenylmethane diisocyanate (MDI) and fatty alcohols (decanol and hexadecanol). The aim of this work is to determine the improvements in dimensional stability of wood obtained by these modifications (Fig. 1).

2 Materials and methods

Beech *(Fagus sylvatica)* blocks, 15 by 25 by 50 mm (radial × tangential × longitudinal), were used in this study. Before treatment, specimens were dried for at least two days at 70 °C, weighed (m_0) and dimensions were measured (V_0).

MDI, decanol and hexadecanol used in this study were purchased from Aldrich. Dichloromethane and acetone were selected as the most appropriate solvents. They were appropriately dried and purified before use. Dichloromethane was dried and distilled over calcium hydride and stored over a 4 Å molecular sieve. Acetone was dried over calcium chloride, distilled over potassium permanganate and stored over a 4 Å molecular sieve.

Infrared spectra of wood and modified woods were recorded on a Mattson Genesis FTIR using potassium bromide disks.

2.1 Reaction of beech blocks with fatty alcohols-MDI mixtures

The monoadduct was prepared when MDI and decanol were used. Due to the poor solubility of the MDI-hexadecanol monoadduct in acetone or dichloromethane, impregnations were realized with mixtures of these reactants.

2.2 Experimental procedure for the preparation of the MDI-decanol monoadduct

The reactions were carried out in a reactor equiped with a magnetical stirrer, a condenser and a nitrogen gas bubbling system. Decanol (23.22 g, 146.9 mmoles) in 100 ml of solvent (CH_2Cl_2 or acetone) was added dropwise to MDI (36.77 g, 146.9 mmoles) in the same solvent. When the addition was completed, the mixture was heated to 40 °C. Advancement of the reaction was monitored by IR spectroscopy (apparition of the urethane C=O bond at 1720 cm^{-1} and partial disappearance of the N=C=O function at 2270 cm^{-1}).

After cooling, the volume of the solvent was adjusted to prepare solutions with a concentration of 10% in mass.

2.3 Blocks impregnation procedure

Blocks were placed in a container inside a dessicator and a vacuum of 5 mbar was drawn for 1 hour using a pump. The blocks were then covered with the solution and the pressure returned to atmospheric. After 1 hour of soaking, the blocks were drained for 5 min. at 25 °C, cured overnight at 105 °C and washed with a Soxhlet extractor during 12 hours with refluxing toluene:ethanol (2:1, v:v) to remove all unreacted chemicals and soluble reaction products. After reovendrying at 70°C, the blocks were weighed (m_1), measured (V_1) and the weight percent gain (WPG) was calculated.

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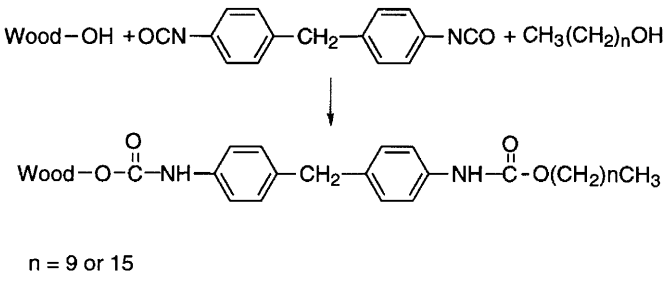

Fig. 1. Synthesis of wood grafted with fatty alkyl chains
Bild 1. Synthese von Holz-Pfropfpolymerisaten mit Alkylketten

2.4
Anti-Swelling-Efficiency measurements

Dimensional stability was determined by the water-soaking method previously reported (Rowell and Ellis 1978). A cycle of five water soakings was applied (changing the water everyday) before determination of the water saturated volume. Blocks were then removed from water, weighted (m_2) and measured (V_2).

The percentage of swelling was calculated from the wet and oven-dried volumes of treated and untreated blocks.

3
Results and discussion

Each result presented in this communication is the average of nine experiments. All the results are shown in Table 1.

Bonding of MDI and alkyl chains to wood was indicated by comparison of infrared spectra of unmodified and modified woods. Spectra are reported in Figs. 2 and 3.

A weak increase of the carbonyl vibration at 1720 cm^{-1} is observed for all the modified woods. For beech blocks grafted with the MDI-decanol monoadduct, the increase of the C-H stretching vibration between 3000 and 2800 cm^{-1} is also weak. However, the absorptions of the C-H bonds at 2921 and 2850 cm^{-1} increased more significantly for wood modified with MDI-hexadecanol mixtures, especially for the impregnation realized in acetone (Fig. 3E). Weight gains of the modified blocks are weak (around 3.5%). Soxhlet extraction with EtOH/Toluene did not remove the reacted chemicals from the wood. No significant increase in volume was found after treatment with the MDI-decanol monoadduct or with MDI-hexadecanol mixtures indicating either that the chemicals are in voids or that the amount of grafted chemicals is too weak to swell the wood structure.

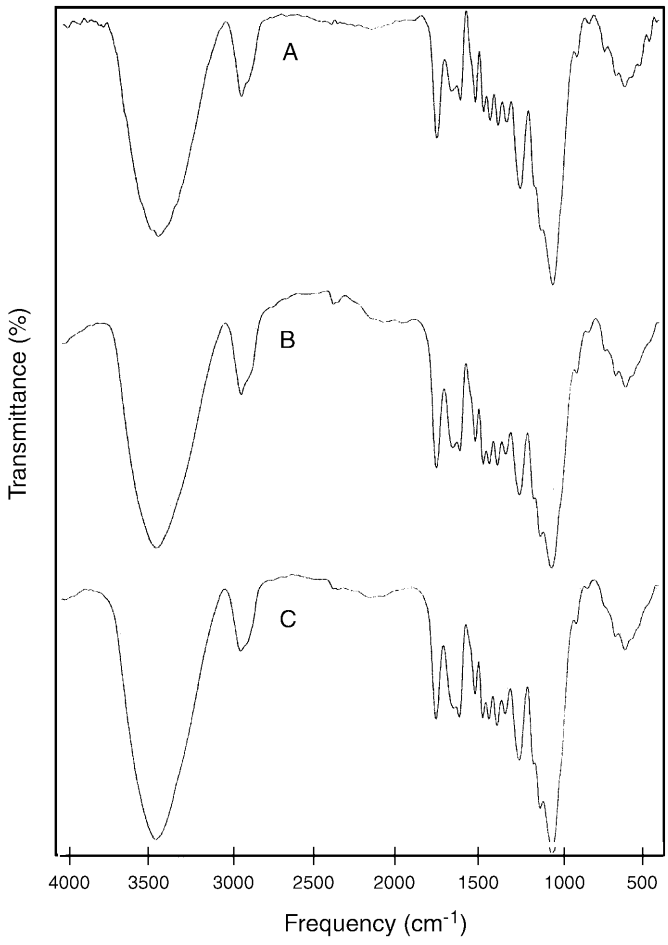

Fig. 2. Infrared spectra of beech blocks reacted with decanol and MDI. **A** Control; **B** 3.76% decanol-MDI bonded on wood; **C** 3.45% decanol-MDI bonded on wood

However, an increase of dimensional stability is observed for all the modified woods. ASE values are higher for impregnations realized in acetone, probably due to its higher swelling coefficient compared to dichloromethane.

Lower dimensional stabilities were obtained for beech blocks modified with the MDI-hexadecanol mixture than for impregnations realized with the MDI-decanol monoadduct (see Table 1). Indeed, grafting of alkyl chains is probably more efficient when a monoadduct is employed allowing thus a greater modification of wood hydroxyl

Table 1. Reaction of beech blocks with MDI and fatty alcohols
Tabelle 1. Reaktion von Buchenklötzchen mit MDI und Fettalkoholen

Impregnation Conditions Reactants/Solvent	m_0 (g)	V_0[a]	m_1 (g)	V_1[b]	WPG (%)	m_2 (g)	ASE (%)
Monoadduct $CH_3(CH_2)_9OH$-MDI/CH_2Cl_2	10.89	18.05	11.27	18.62	3.76	24.20	18.05
Monoadduct $CH_3(CH_2)_9OH$-MDI/Acetone	10.82	18.09	11.16	18.57	3.45	24.25	26.30
Mixture $CH_3(CH_2)_{15}OH$-MDI/CH_2Cl_2	10.95	18.09	11.35	18.38	3.25	24.33	9.43
Mixture $CH_3(CH_2)_{15}OH$-MDI/Acetone	10.75	18.13	11.11	8.55	3.94	24.30	16.88

[a] V_0: Initial volume of dry beech blocks
[b] V_1: Treated volume of dry beech blocks

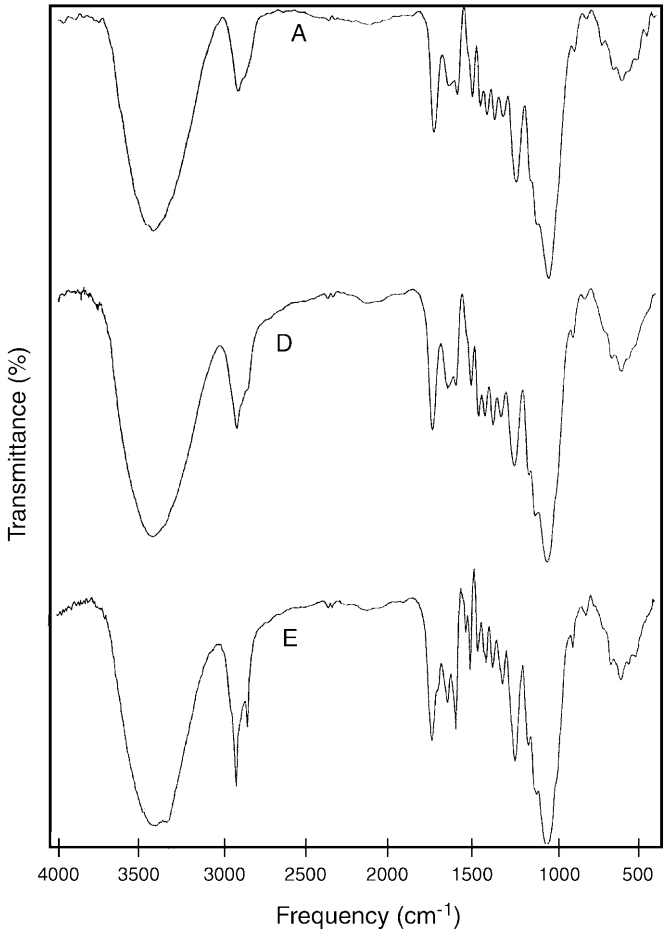

Fig. 3. Infrared spectra of beech blocks reacted with hexadecanol and MDI. **A** Control; **D** 3.25% hexadecanol-MDI bonded on wood; **E** 3.94% hexadecanol-MDI bonded on wood

groups. The use of the MDI-hexadecanol mixture could lead to the competitive reaction of MDI with wood.

4 Conclusion

It was shown that a dimensional stability could be obtained for beech blocks treated with MDI and fatty alcohols. This dimensional stability can probably be attributed to the grafting of bulky alkyl chains on wood which increased its hydrophobicity. Further studies are in progress using the same procedure and compounds possessing strong water repellent properties like perfluoroalkanols.

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