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MDI-bonded hardwood composites: some indications of the impact of MDI on formaldehyde and VOC emissions.

INTRODUCTION

Formaldehyde and VOC emissions from wood and wood-based articles is an issue that increasingly arouses concerns, and regulatory controls and restrictions. It is commonly accepted that the main source of formaldehyde from wood composite panels produced with formaldehyde-based polycondensate resins comes from the resin itself. For this reason producers are devoting resources to limiting and controlling resin-originated formaldehyde and VOC emissions. MDI-based resins do not easily decompose. The question is whether MDI resins impact positively, negatively or indifferently on wood originated-formaldehyde and VOC compounds.

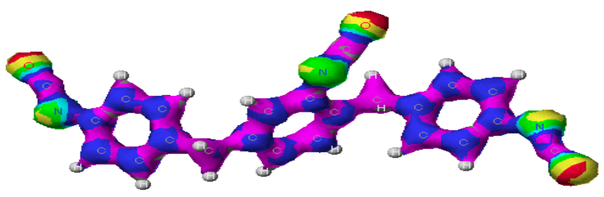
OBJECTIVE

The purpose of this project was twofold: to achieve a better understanding of the chemistry of interaction between isocyanates and wood as related to VOCs in general, and formaldehyde in particular; and to design isocyanate resins promoting interactions that prevent and hinder VOCs.

MATERIALS AND METHODS

Materials

Heartwood from 80cm long / 30 to 40cm diameter softwood (Pinus Sylvestris) trunks (ex-Poland) was ground down to flour. Polymeric MDI was supplied by Huntsman.

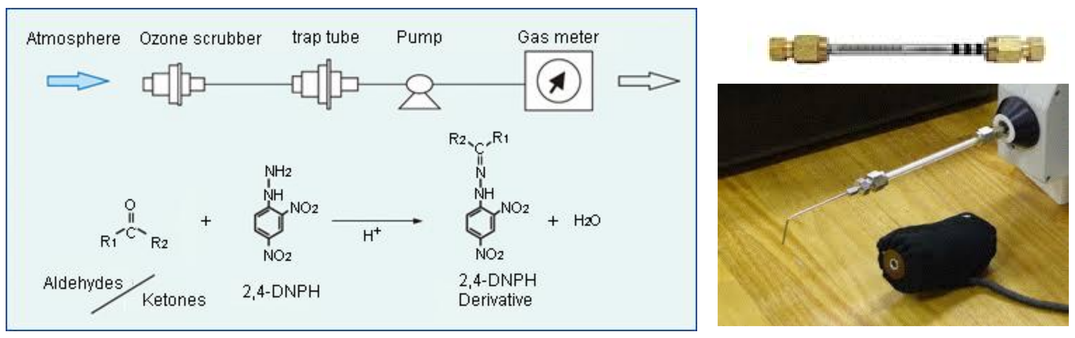


Polymeric MDI is composed of a distribution of functional polyphenylmethane polyisocyanates. The molecule above shows the electron density map for triphenylmethane triisocyanate. The isocyanate groups have the highest electron density, which accounts for the reactivity of these functional groups.

Heartwood flour was used as such or mixed with increasing amounts of MDI and cured for four hours at 120˚C. MDI was applied using an airbrush for low resin loadings (<10 wt%) or simply added drop-wise to the wood flour and agitated with a spatula for higher resin loadings.

Formaldehyde and VOC emissions

Materials were heated by thermogravimetric analyser (TGA) in two steps from room temperature to 230˚C (at 20˚C / min) in an air atmosphere. The eluted gasses were collected in a Tenax tube and a 2,4-dinitrophenyl hydrazine (DNPH) sorbent tube placed in series. Absorbed material in the Tenax tube was thermally desorbed and analyzed by gas chromatography mass spectroscopy (GC-MS). Aldehydes (including formaldehyde) absorbed in the 2,4-DNPH tubes were analyzed by high performance liquid chromatography (HPLC).



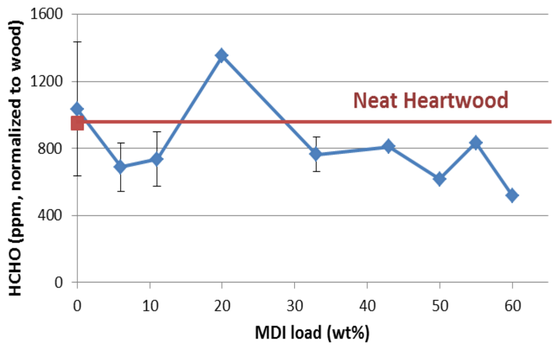
Left: Derivatization of aldehydes with 2,4-DNPH; Right: Tenax tube (top) attached to a TGA (bottom).

RESULTS AND DISCUSSION

Emissions of wood origin formaldehyde and VOC compounds were normalized to the wood content of the composites. NB: All data should be interpreted in a comparative sense.

1. Formaldehyde emissions

Thermally treated wood exhibited similar formaldehyde (HCHO) emissions compared to neat wood. Overall, the addition of MDI did not aggravate but made the release of HCHO slightly decrease (with the exception of the composite made with 20wt% MDI). The authors speculate that the emission data of the latter composite represents a non-resinated fraction of the wood sample. Indeed, when modest amounts of MDI were added, rapid absorption and/or penetration into the wood leads to difficulties in uniform resin distribution, yielding highly resinated and non-resinated regions.

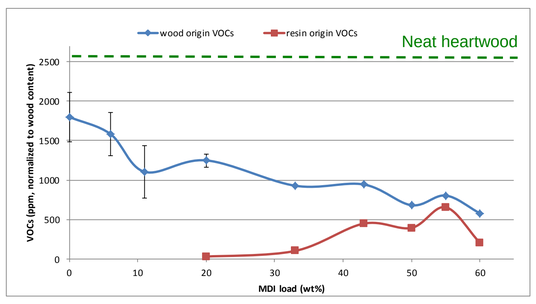


In general, emission tests indicate that HCHO is scavenged or blocked by the MDI binding agent to a small extent.

2. VOC emissions

2.1. Quantitative analysis

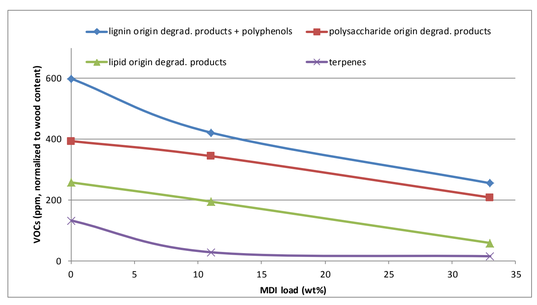
A differentiation was made between wood and resin origin VOCs. Their total amount is plotted below as a function of MDI loading.



VOCs, which are predominantly derived from wood, are significantly reduced as the amount of MDI is increased. Incomplete curing was observed when MDI loadings exceeded 20wt%.

2.2. Qualitative analysis

All VOCs were characterized and could be grouped in four major classes (both in their unaltered and degraded / rearranged forms).



A significant drop in emissions was observed for all classes upon curing with MDI, especially for lignin-polyphenols and terpene origin VOCs at low MDI loadings. The most abundant compounds are summarized below.

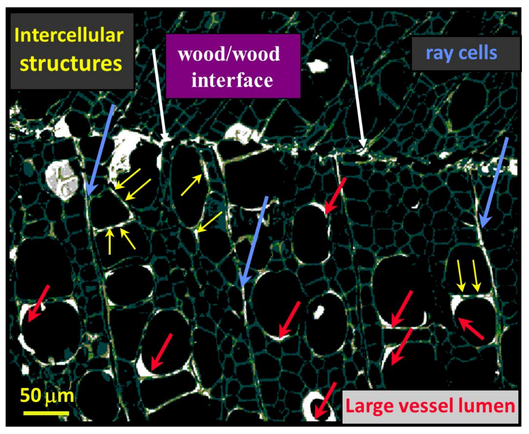
Lignin and polyphenols
- Benzaldehyde
- 3-Methoxy-4-hydroxy benzaldehyde
- 3-Methoxy 4-hydroxy cinnamaldehyde
- 2-Methoxy 4-vinyl phenol

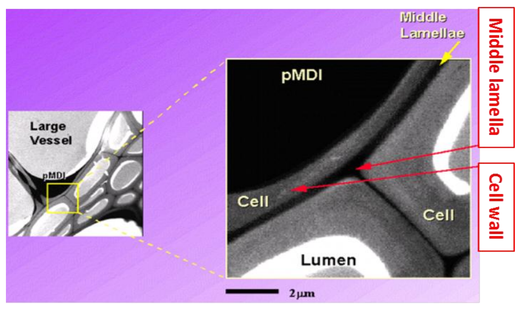
Polysaccharides
- Acetic acid
- Methylfuran
- Furfuraldehyde
- Furfurylalcohol
- Furanone
- Acetylfuran

Terpenes
- Borneol
- Levoglucosenone
- Verbenone
- Terpene derivates

Lipids
- Hexanal
- 2-Propenoic acid
- 2-Cyclopentene-1,4-dione

Earlier studies of the penetration of MDI in wood by scanning x-ray microscopy have demonstrated that MDI diffuses into the wood and locates itself in five specific regions.





Courtesy of Dr. C. Phanopoulos and Dr. C. Buckley: Polyurethane and isocyanates used as adhesives in composite wood products.

X-ray analyses have demonstrated that pMDI is associated with the cell wall. In addition, solid state NMR has identified the lignosic and hemicellulosic components of wood to be affected by the presence of MDI. This suggests interactions of pMDI with the non/semi crystalline cell wall components (lignin and hemicellulosics), through a number of primary and secondary bond interactions. Moreover, pMDI has been shown to react with water (polyurea) and with extractives in many complex reactions.

All these phenomena could alter the volatility and degradation mechanism of the wood extractives, and a polyurea network could act as a physical barrier for wood origin volatiles to emit.

It is suggested that treatment of wood with pMDI results in a diffusion interphase of a multi-component crosslinked polymer, which finally translates into MDI-based wood composites with reduced emission potential.

CONCLUSIONS

1. The amount of wood origin VOCs decreases with increased MDI loadings.

2. Four major classes of VOCs were determined (lignin, polysaccharides, lipids and terpenes origin degradation products), which were quantified and analyzed.

3. Non / semi crystalline cell wall components (lignin and hemicellulosics) have a higher affinity for MDI through the formation of primary and secondary bond interactions.

4. The penetration of MDI into the cell wall was observed by x-ray spectroscopy and confirmed by the decrease of lignin-polyphenols and terpene origin VOCs.

5. MDI does not aggravate wood origin HCHO emissions and may even slightly lower the wood background emissions.

6. Distribution and quality of resination are crucial parameters in controlling formaldehyde and VOC emissions of MDI-based composites.

ACKNOWLEDGEMENTS

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