



Interactions between wood and epoxy functional vegetable oil for use in reactive primer for clear coated exterior wood

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ABSTRACT

The overall aim of the study was to investigate if epoxy functional vegetable oils are able to bind covalently to wood to help protect it from photoinitiated degradation. In the study, two epoxy functional vegetable oils (linseed and soybean oil) were used to investigate their interactions with two different lignin model substances, representing both softwood and hardwood (creosol and 4-methyl-2,6-dimethoxyphenol, respectively). The study also comprises a reactive UV-absorber, 2-hydroxy-4(2,3-epoxypropoxy)-benzophenone (HEPBP), to study its interactions with the two lignin model substances. The results indicate that the proposed reactions do occur for systems using creosol or HEPBP, but for 4-methyl-2,6-dimethoxyphenol the reaction occurs to a lesser extent. No significant difference in reactivity is noticed between the two oils, even though they contain different amounts of epoxy groups. The difference in reactivity between the two lignin model substances, on the other hand, indicates that the treatment might be more effective on softwoods than on hardwoods.

INTRODUCTION

Vegetable oils are among the oldest binders used for paints (Wicks *et al.* 2007). Their use may have decreased over the years but due to their many benefits, such as low price, natural occurrence and large availability, the interest in this raw material is increasing. Vegetable oils can be varied almost infinitely and one way of doing so, and also creating added value to this natural product, is by epoxidation. This opens up for a large variability of use due to change in structure and reactivity. Epoxy functional oils do, however, also occur naturally in nature, *e.g.* suberin which is found in the outer bark of birch trees (Olsson 2012). Suberin acts as a hydrophobising barrier, which is desirable to achieve also in exterior wood products to protect them from degradation due to moist. Since the photodegradation of wood is greater when the cell wall contains water, protecting the wood from moist will also affect the photoprotection of wood (Andersson *et al.* part I and II 1991). In recent studies hydrophobes, such as vegetable oils and waxes, are shown to reduce photoinitiated degradation of wood and also the leaching of chemicals from the wood surface (Lesar *et al.* 2011 and Tomak *et al.* 2011). The latter is a desirable property when it comes to surface protection of wood where leaching of low molecular weight UV-absorbers (UVA) is an issue. Combining with a hydrophobe could hence be useful in protecting the wood from photodegradation. Such combination has

been tested in earlier studies (Olsson *et al.* 2011 and Olsson *et al.* 2012) with the aim to chemically bond the reactive UV-absorber and epoxy functional vegetable oil to the wood substrate for a more long term protection. The studies showed positive results but were not totally conclusive in terms of confirming the covalent bond between the UVA/oil and the wood. Therefore it is of interest to support the results from the earlier study by complementing with a more thorough study on the actual reaction and to what extent it occurs. This is in order to help increase the use of these renewable vegetable oils.

The aim of this study is to study the interactions between the epoxy functional vegetable oils (soybean and linseed oil) and two different lignin model substances representing softwood and hardwood. By choosing two oils with different degrees of unsaturation (hence giving rise to different amounts of epoxy groups on the triglycerides) an intermediate goal is also to study if the amount of epoxy groups on the vegetable oils affects the reaction to wood. The overall aim of the project is, however, to show that it is possible to react the epoxy functionalised vegetable oils covalently to wood since this could result in a new use of these oils.

MATERIAL AND METHOD

Materials

The chemicals used were: Ethanol (99.5%, Kemetyl and 99.5 %, denaturated by isopropanol, Kemetyl), 2,4-dihydroxy-benzophenone (DHBP, 99 %, Aldrich), 4-(dimethylamino)pyridine (DMAP, 99 %, Aldrich), epichlorohydrin (99 %, Aldrich), 3-pentanone (ReagentPlus >99 %, Sigma Aldrich), potassium hydroxide (KOH, 85-87 %, Eka Nobel), epoxy functional soybean oil (Lankroflex E2307, Akros Chemicals), epoxy functional linseed oil (Lankroflex L, Akros Chemicals), creosol (≥ 97 %, SAFC), 4-methyl-2,6-dimethoxyphenol (≥ 98 %, SAFC) and dimethyl sulphoxide (DMSO, 99,9 %, Larodan Fine Chemicals). All chemicals were used as received.

HEPBP synthesis

The synthesis of 2-hydroxy-4(2,3-epoxypropoxy)-benzophenone (HEPBP) was performed according to description in previous literature (Manasek *et al.* 1976) and the reaction path is illustrated in Figure 1.

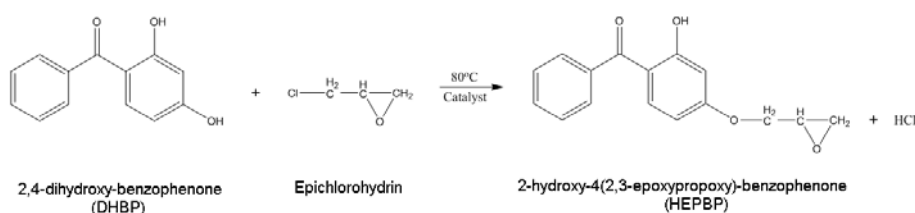


Figure 1: Schematic reaction path of the HEPBP synthesis

Grafting procedure

HEPBP or epoxy functional vegetable oil and lignin model substance were added to a round bottom flask at a molar ratio 1:1. The content of HEPBP or epoxy functional oil was fixed at 1 g or 2 g, respectively, whereas the amount of lignin model substance varied depending on the molar weight of the model substance and HEPBP/epoxy functional oil to achieve the molar ratio 1:1. Forty millilitres of 3-pentanone and 0.02 g of the catalyst DMAP were added and the mixture was left to react for 8 hours at 102 °C with constant stirring. For reactions containing HEPBP half of these amounts were used

due to the low molecular weight of HEPBP, thus leading to a too large volume of HEPBP. After reaction the solvent was evaporated using a rotary evaporator and the solid sample was left in the fume hood for at least 48 h prior to analysis. Figures 2 and 3 illustrates a proposed reaction path of the reaction between the model substance creosol and HEPBP and between linseed oil and creosol. Table 1 shows the reactions performed.

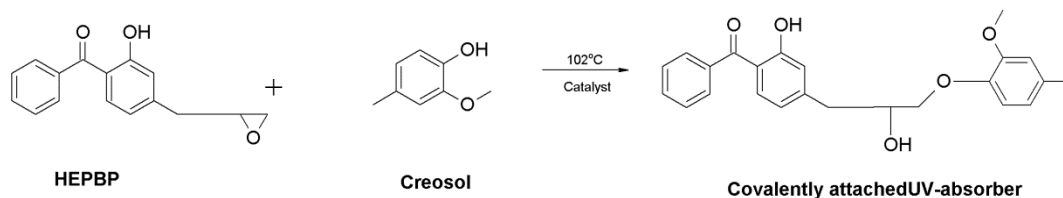


Figure 2: Schematic reaction path of proposed reaction between HEPBP and creosol

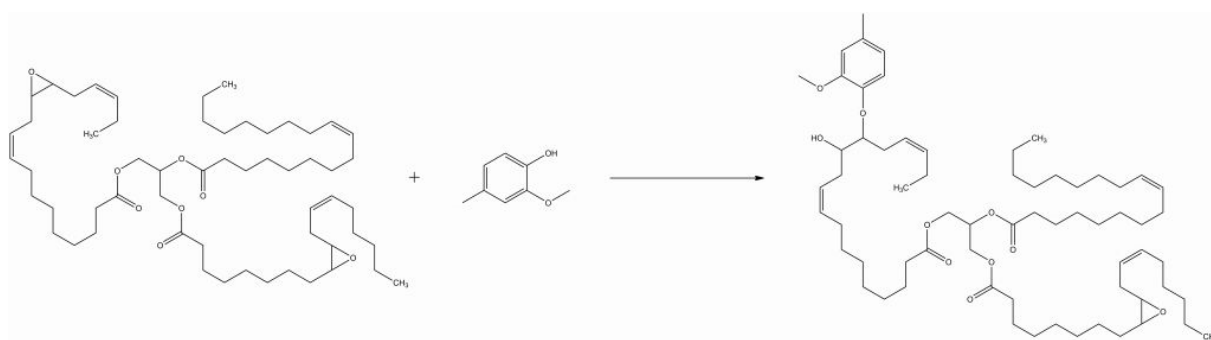


Figure 3: Schematic reaction path of proposed reaction between epoxy functional linseed oil and creosol

Table 1: Content of performed reactions

Batch name:	Reactant	Model substance
Reaction 1	Soybean oil	Creosol
Reaction 2	Linseed oil	Creosol
Reaction 3	HEPBP	Creosol
Reaction 4	Soybean oil	4-methyl-2,6-methoxyphenol
Reaction 5	Linseed oil	4-methyl-2,6-methoxyphenol
Reaction 6	HEPBP	4-methyl-2,6-methoxyphenol

Instrumentation

All products were analysed using Nuclear Magnetic Resonance (NMR). $^1\text{H-NMR}$ spectra were recorded at 400 MHz on a Bruker Avance AM 400 using dimethyl sulphoxide (DMSO) as solvent. The solvent signal was used as internal standard. All peaks were determined using the centre proton on the triglyceride backbone as a reference.

Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy (ATR-FTIR) was used to analyse the chemical composition of the reactants and the product after reaction. All measurements were performed in air at room temperature. The equipment used was a Perkin-Elmer Frontier FT-IR equipped with a Frontier UATR ZnSe with Reflection

Top-Plate and Pressure Arm. The software used was Spectrum 10 software and 4 scans for each sample were used.

RESULTS AND DISCUSSION

Lignin model substances were selected to represent both softwoods and hardwoods. Creosol was hence chosen as a softwood lignin model substance and 4-methyl-2,6-dimethoxyphenol as a hardwood model substance, since their structures are similar to those found in softwood and hardwood lignin respectively. Their structures are shown in Figure 4.

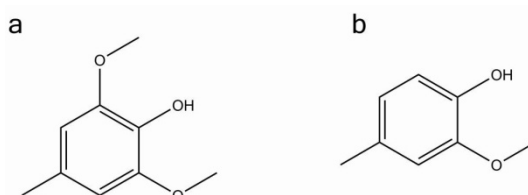


Figure 4: Molecular structures of lignin model substances 4-methyl-2,6-dimethoxyphenol (a) and creosol (b).

Batches were analysed using $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ to determine the number of epoxy groups in the different oils. The number of epoxy groups on the triglyceride of each vegetable oil was determined by the epoxy peaks at 2.9 ppm in the $^1\text{H-NMR}$ (Samuelsson and Johansson 2001, and Liu *et al.* 2012). From $^1\text{H-NMR}$ spectra of the two oils and by using the centre proton on the triglyceride backbone as a reference it was determined that the soybean oil had approximately 4 epoxy groups and the linseed oil had 5 epoxy groups. The result was also supported by FTIR analysis.

In the $^1\text{H-NMR}$ spectra there are several indications of the proposed reactions, illustrated in Figures 2 and 3. **Erro! A origem da referência não foi encontrada.** From the $^1\text{H-NMR}$ spectra of both epoxidised oils it is evident that the hydroxyl proton from the lignin model substances, shown at approximately 8.7 or 8.0 ppm for creosol (Figure 5) and 4-methyl-2,6-dimethoxyphenol, respectively, decreases or disappears after the reaction. This indicates consumption of the hydroxyl group. It is also evident that the protons surrounding the hydroxyl proton, at 6.5-6.8 ppm, have changed slightly in position after reaction, which also indicates that the proposed reaction has occurred. To further strengthen the conclusion that the proposed reaction has occurred the two methyl protons, shown at 2.2 ppm and 3.7 ppm, are determined to remain in the same position after reaction, indicating that these protons have not reacted.

For 4-methyl-2,6-dimethoxyphenol the $^1\text{H-NMR}$ show that all protons in the structure, except for the hydroxyl proton, remain more or less in the same position after reaction, indicating that the proposed reaction has occurred but to a lesser extent. This is likely due to the higher steric hindrance of the 4-methyl-2,6-dimethoxyphenol in comparison to the creosol.

When studying the $^1\text{H-NMR}$ spectra of the oil and the resulting product it can also be noticed that the peak from the epoxy group is still present even after reaction. This is however not to be taken as a sign that the reaction has not occurred, but rather a consequence of adding the reactants in a 1:1 molar ratio. Since the oil contains more epoxy groups than the creosol does hydroxyl groups it becomes clear that the decrease in the epoxy groups of the oil will be much less than for the hydroxyl groups of the creosol.

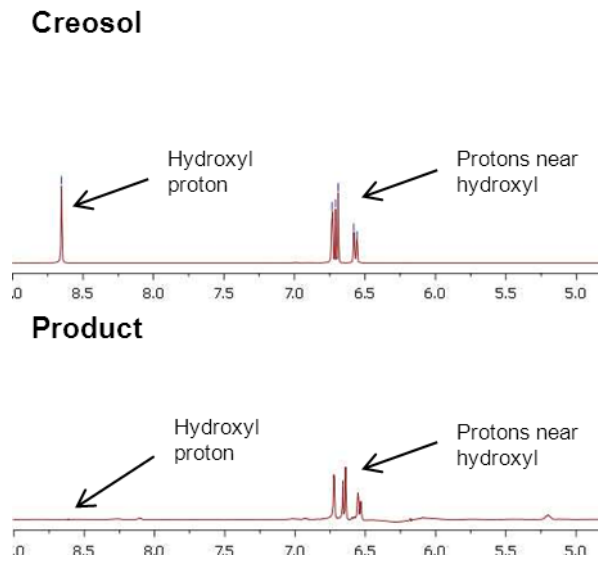


Figure 5: $^1\text{H-NMR}$ spectra of creosol and the product when using epoxidised linseed oil and creosol. Peaks of importance are marked with arrows.

Studying the FTIR spectra of the reactants and products some changes can be noticed that indicate the proposed reaction. Some interesting peaks to study are for example the epoxy peaks at 823 cm^{-1} and 845 cm^{-1} in the FTIR spectrum (Samuelsson and Johansson 2004). Firstly, in the case of linseed oil and creosol a small decrease of the epoxy peak at 823 cm^{-1} is actually noticed after the reaction, which was not evident in the $^1\text{H-NMR}$ spectra. It indicates a slight consumption of the epoxy group and hence that the proposed reaction has occurred (Figure 6). The same pattern can also be seen for soybean oil and HEPBP, showing that creosol seem to react with both oils and HEPBP as proposed. A change in the peak for the hydroxyl group can also be seen but since the reaction both consumes and creates an hydroxyl group it is difficult to use this peak as an indication of the reaction.

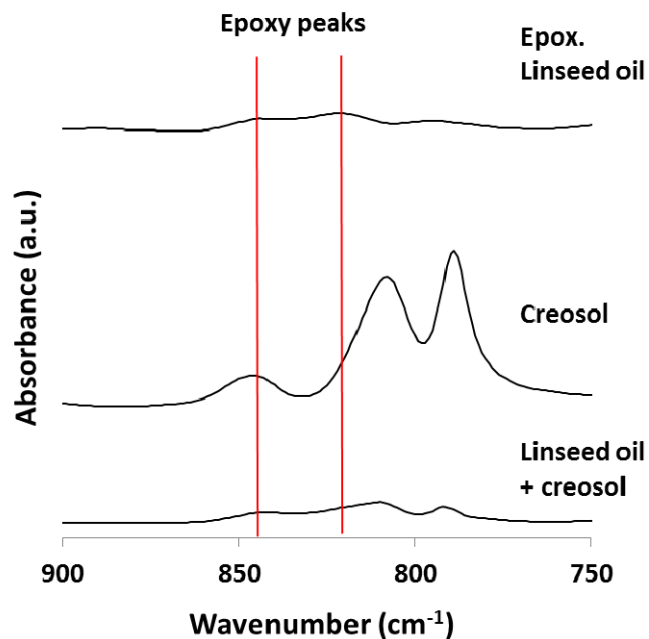


Figure 6: Expanded FTIR spectra of epoxidised linseed oil and creosol, indicating the decrease of the epoxy group after reaction.

When using 4-methyl-2,6-dimethoxyphenol as a model substance the results indicate that the reaction proceeds but to lower extent than when creosol is used (Figure 7). This is most likely a consequence of the lower accessibility of the hydroxyl group of this model substance due to steric hindrance. Since creosol imitates the case of softwoods and 4-methyl-2,6-dimethoxyphenol the case of hardwoods the results imply that the proposed reactions work better on softwoods than on hardwoods.

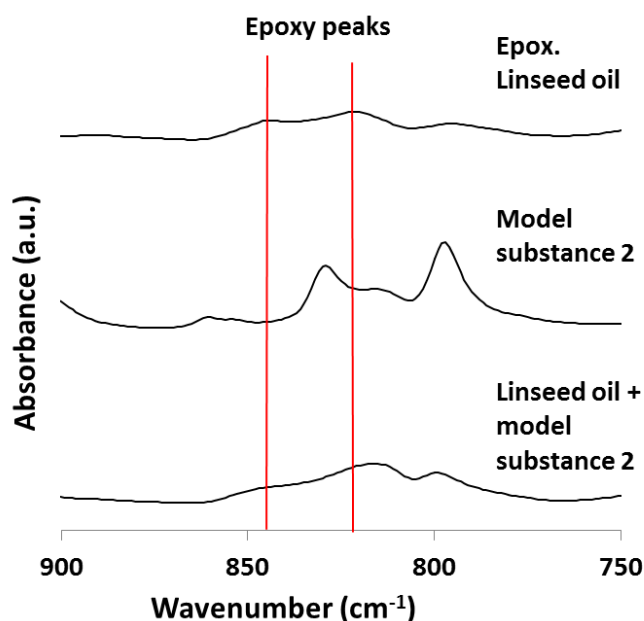


Figure 7: Expanded FTIR spectra of epoxidised linseed oil and 4-methyl-2,6-dimethoxyphenol, indicating the decrease of the epoxy group after reaction.

From the FTIR and NMR results it is difficult to determine if the epoxidised linseed oil, due to the initially higher amount of unsaturations, has reacted more or less than the soybean oil. Using NMR it is, however, possible to determine that the linseed oil appears to have more epoxy groups to start with.

Although the results imply that the proposed reaction does occur for the oils and the HEPBP together with creosol, the lignin in the wood still need to be accessible to the oil/HEPBP in order for the reaction to occur. Hence, it is of importance to study this further by using solid wood.

CONCLUSION

The study investigates the interactions between two lignin model substances and the UV absorber HEPBP or one of the two epoxy functional vegetable oils (soybean and linseed oil). Results from the $^1\text{H-NMR}$ analysis show that the linseed oil together with the softwood-imitating model substance creosol consumes the hydroxyl groups of the creosol during the reaction, indicating that the proposed reaction occurs. Similar results are also seen for the soybean oil and HEPBP together with the creosol. Consumption of the hydroxyl group is also seen for the slightly larger and hardwood-imitating model substance 4-methyl-2,6-dimethoxyphenol, but to a lesser extent. This is likely due to the steric hindrance of the substance. FTIR results confirm the results by showing a

consumption of the epoxy group of the oil and HEPBP. Hence, the proposed reactions are concluded to occur, although to a larger extent for softwood lignin than hardwood lignin.

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