

METHOD TO PREPARE SMOOTH AND EVEN CELLULOSE-LIGNOPHENOL FILMS

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Dissolved cellulose was contacted with dissolved linear or slightly branched lignophenol polymers in alkaline solution, and films were formed through precipitation. Lignophenol is a polymeric lignin derivative isolated from wood meal, and due to its size and chemical structure, it is expected to a better model for natural lignin compared to the previously exploited small lignin model molecules. Smooth and even of cellulose-lignophenol films were achieved, and the interactions between cellulose and lignophenol were tentatively detected. The formed film structures had the crystalline form of cellulose II, and they did not contain any fibril-like material. Although the amount of hemicelluloses was negligible, it seems that the lignin modelling lignophenol tended to positively interact with cellulose.

Keywords: Cellulose; Lignin; Lignophenol; Film; SEM; XRD

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INTRODUCTION

The cell walls of the rigid cells in woody plants can be roughly described as composed of fibrils of cellulose (the world's most abundant natural polymer, about 40 % of the dry weight of the wall) embedded in an amorphous matrix of hemicelluloses and lignin. Together with the hemicelluloses, highly branched and cross-linked lignin (0 to 35 % (w/w) of the material in wood) forms a soft matrix between the cellulose fibrils in the cell wall. Lignin is also the main constituent of the encrusting material that binds individual cells together to form the macroscopic structure of wood. This brief description of the structure of cell walls and wood has been given to highlight the fact that wood is a highly sophisticated composite material into which the cellulose confers tensile strength and the amorphous hemicellulose/lignin matrix confers ductility and flexibility.

Cellulose I is the crystalline form of cellulose chains found in nature, and it occurs in two allomorphs, I_α and I_β. Cellulose II is the crystalline form that emerges after recrystallization or mercerisation with aqueous sodium hydroxide. The dominant intrachain hydrogen bond in both polymorphs is O3-H--O5, which gives the cellulose chain its rigid, linear shape. The interchain bonding is different: in cellulose I O6-H--O3 dominates, whereas in cellulose II it is O6-H--O2 (Langan et al. 1999). Furthermore, cellulose II has an antiparallel packing whereas the chains in cellulose I run in parallel direction (Langan et al. 1999; Nishiyama et al. 2003). Although the Cellulose I structure

has better strength properties compared to Cellulose II, the Cellulose II is thermodynamically the most stable crystalline form (O'Sullivan 1997). Applications related to textiles, films and chemicals require cellulose dissolution and regeneration, and hence the conversion to cellulose II cannot be avoided.

Lignin in nature is a non-linear polyphenol built from three basic phenyl propane precursors: p-hydroxyphenyl, guayacyl, and syringyl alcohol. These are connected to each other via a large number of different linkages, of which the β -O-4 linkage is the most common, leading to the formation of a crosslinked polymeric network. The flexibility of the network is related to the degree of crosslinking. Free methoxyl and free phenolic hydroxyl groups hinder crosslinking and lower the glass transition temperature, thus increasing the flexibility of the structure. Lignin is known to have a low ability to sorb water compared to the hydrophilic hemicelluloses and cellulose, and high lignin content in wood results in lower overall water sorption capacity (Schniewind and Berndt 1991). In addition, the shrinking and swelling behaviour of wood is related to its hygroscopicity and water sorption ability, and therefore lignin is considered to improve the dimensional stability of wood. Thus, the lignin content in wood matrix partly dictates the phenomena related to water interactions.

Lignin is regarded as being associated or linked by covalent bonds to some hemicelluloses (Fengel and Wegener 1984). It is also well established that hemicelluloses are distributed through the lignin network, which strongly indicates that hemicelluloses form a link between cellulose framework and lignin matrix in the cell wall structure (Schniewind and Berndt 1991). The complex network structure of lignin, together with the strong association with hemicelluloses, restricts the exploitation of lignin as a value-added chemical, due to the lack of effective isolation methods in which the polymeric structure and its activity are maintained. So far, apart from a limited number of specialty chemicals, lignin has been mainly used as an energy source. For example, conventional wood fibre delignification processes isolate heterogeneous and dark coloured lignin having sulphuric groups attached to its structure, which impair its further usability as a raw material for lignin based products.

In the extensive work conducted by Funaoka and his co-authors the method to isolate and prepare the lignin model molecules with reasonably high degree of polymerization extracted from wood meal is described (Funaoka and Abe 1989; Funaoka et al. 1995; Funaoka and Fukatsu 1996; Funaoka 1998). The isolated molecules are lignophenols, a class of natural polyethers of coumaryl, coniferyl, and sinapyl alcohols, and they are expected to better imitate natural lignin with respect to reactivity in comparison to the previously used lignin model molecules (Funaoka 1989). They are extracted from lignocellulosics with solvating cresol type compounds and hydrolysing concentrated mineral acids. As a result, linear β -O-4 bonded phenolpolymers having high and controllable reactivity are obtained. Lignophenol itself is a linear aryl-ether linked phenolic lignin polymer, where added solvating cresol is bonded to α -carbon of the phenolic lignin units (Fig. 1).

Lignophenol derivatives are shown to effectively immobilize enzymes. In addition, the presence of lignophenols in lignophenol-cellulose fibre composites clearly decreased water-induced swelling and reduced the water absorption of the composites. Furthermore the original dimensions of the composites were reported to be restored upon

redrying (Funaoka 1998). In a recent study of Nemoto et al. (2010), transparent lignophenol films were used for optical applications.

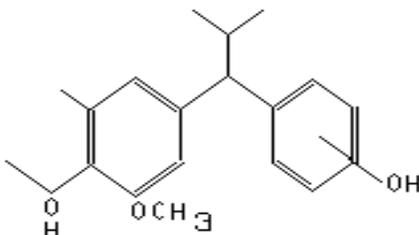


Figure 1. Lignophenol, a 1,1-bis(aryl)propane-type polymer

The aim of this work is to establish a method to prepare cellulose-lignophenol films and tentatively confirm the attractive interactions between regenerated cellulose and soluble lignophenol macromolecules. The motivation for using such combination of these natural polymers and their derivatives arise from:

- 1) Reassembling the cellulose and lignin from solution makes it possible to study the obtained structures with respect to interaction between the polymers. The reassembly could provide, e.g., attractive mechanical properties as well as stable and ductile films.
- 2) Grafting on the polymeric cellulose is demanding and requires in certain cases hard chemical procedures, which may be considered a risk when attempting to achieve high purity and retention of high molar mass. Grafting on lignin, on the other hand, is markedly simpler and enables the use of more sustainable methods such as enzymatic activation. Moreover, lignophenol could be isolated in different forms, depending on the raw material used (softwood, hardwood, grass), solvating compound used, and even using different kinds of mineral acid. These facilitate controlled or tailored reactivity for the lignin fraction, and desired functionality for the desired structures. In order to benefit the easier grafting on lignin in the case of blended films, certain amounts of lignin should be added into regenerated cellulose films, which require understanding of interactions between lignin and cellulose.
- 3) Interaction studies between cellulose and lignin are often restricted to molecular modelling, to the simple model substance approaches (e.g. monolignol, trilignol or other small aromatic compounds), or to research conducted using highly modified lignins (e.g. kraft lignin). This is due to the unavailability of lignin model compounds having reasonably high degree of polymerisation. We believe that this particular lignophenol derivative can facilitate research related to cellulose-lignin interactions.

In the current research dissolved cellulose was contacted with dissolved linear or slightly branched lignophenol polymers in alkaline solution, and films were formed through precipitation in an acid bath. The structure and morphology of the films were characterised using scanning electron microscopy (SEM) and X-Ray diffractometry

(XRD), and the bulk chemistry of the films were characterised by FTIR. On the basis of the results, the cellulose-lignin interactions are tentatively discussed.

EXPERIMENTAL

Materials

Pure cellulose solution

Cellulose raw material was commercial softwood sulphite pulp (Domsjö Fabriker AB, Sweden), produced from a mixture of Norwegian spruce (60%) and Scotch pine (40%) by a two-stage process. Brightness of the pulp was 91.1% (SCAN-P 3:93), viscosity 405 mg/g (SCAN-CM 15:99), R18 and R10 (insoluble fractions in 18% and 10% NaOH) 95.0% and 86.8%, respectively (SCAN-C 2:61), and acetone extractives less than 0.05% (SCAN-CM 49:93). Weight average molecular mass (M_w) measured by the GPC method using LiCl/DMAc as solvent was 280,000 g/mol, and the polydispersity of the molecular weight distribution was 6.8.

In the first stage the pulp was shredded mechanically and treated with a commercial endoglucanase-rich enzyme preparation (AB Enzymes Oy, Finland) at pH 5, 50°C for 3 hours using 250 nkat/g based on the endoglucanase activity of the preparation (IUPAC 1987). The enzymatic treatment released sugars amounting to 17 mg/g of pulp. The M_w of the treated pulp was 170000 g/mol, and the polydispersity of the molecular weight distribution was 5.9.

In the second stage the treated pulp was dissolved into aqueous sodium zincate according to the previously described method (Vehviläinen et al. 2009). The cellulose solution contained 6 wt-% cellulose, 6.5 wt-% NaOH, and 1.3 wt-% ZnO. The solution was visually clear and transparent without any undissolved particles. Falling ball viscosity of the solution at 20°C was 79s (ASTM D 1343-86).

Cellulose xanthate solution

Cellulose xanthate solution was kindly delivered by Kuitu Finland Oy, Finland. The cellulose content of the solution was 9.1 wt-%, and the NaOH content 5.6 wt-%.

Lignophenol derivivate solution

Polymeric lignophenol was prepared from purified softwood (*Japanese cedar*) as described in Funaoka (1998). It was isolated by hydrolyzing extractive-free wood flour (ethanol-benzene, 80 mesh pass) by concentrated sulphuric acid after solvation with cresol (a 2 step process with a cresol/acetone solution). The lignophenol powder was dissolved in 5.5 wt-% NaOH to form a solution containing 13 wt-% of lignophenol. The molecular weight of the dominantly linear alkyl-aryl ether linked lignophenol was 11700 g/mol, and the polydispersity was 3.14. The glass transition temperature (T_g) of the polymer was 156.4 °C.

Other chemicals

All other chemicals were analytical grade and were used without further purification.

Methods

Preparation of cellulose-lignophenol solutions

Solutions containing approximately 95 wt-% of cellulose or cellulose xanthate and approximately 5 wt-% of lignophenol were prepared by adding basic aqueous solution of lignophenol into cellulose/cellulose xanthate solution by mixing at 150 rpm for 5 minutes using a laboratory stirrer.

Preparation of the cellulose-lignophenol films

Solutions of cellulose-lignophenol and cellulose xanthate-lignophenol were evenly spread on the glass plate with the aid of a metal frame to control the layer thickness.

The glass plates were immersed into a coagulation bath containing 10% H₂SO₄ (to precipitate the solution). Finally, the obtained films were transferred to distilled water and washed free from salts until the conductivity of the water was <5 μS/cm. The purified films were dried under tension between the absorbent papers under gentle pressing at ambient temperature (20-22 °C) for 24h.

The absorbent papers were renewed during the drying to avoid the sticking of the films on the paper surface. Although special care was taken to control the shrinkage of the films, slight shrinkage was taking place especially at the edges of the films samples. However, the major part of the films was smooth and the final thickness was approximately 50±10 μm. Smooth films without any wrinkles were used for analysis purposes.

Scanning electron microscopy (SEM)

The structure of the films was analyzed using scanning electron microscopy (SEM, LEO DSM 982 Gemini FEG-SEM). The film samples (ca. 10 mm ×10 mm) were attached on carbon adhesive discs (12 mm Ø) pressed on 12.5 mm (Ø) aluminum stubs. Typically, no conductive coating was applied on the specimen prior to SEM imaging. However, in some cases a thin layer (ca. 10 nm) of platinum was sputter-coated on the film surface to improve conductivity and stability of the specimen. The SEM analyses of the samples were conducted using an electron energy of 2.0 keV.

FTIR

FTIR spectra were collected using a Bruker Equinox 55 spectrometer and Specac Golden Gate MK2 ATR accessory with a 45° diamond crystal. Resolution was 4 cm⁻¹, and 32 scans were collected.

X-Ray diffraction (XRD)

The diffraction patterns of the smooth film samples with constant thickness was recorded by the reflection method using a Philips X'Pert MPD diffractometer with a Cu X-ray tube (λ=1.542Å).

RESULTS AND DISCUSSION

Morphology and Chemistry of the Cellulose-Lignophenol Films

As visually assessed, the precipitated films that had been dried under tension were transparent and smooth, and no pinholes in the film structure were detected. Although still transparent, the lignophenol addition resulted in a slightly brownish film color. The film formation ability was not anyhow deteriorated upon lignophenol addition, and no features of phase separation were observed. A general view of the fine structure of the precipitated films was gained using scanning electron microscopy. The image of the pure cellulose film is shown in Fig. 2a, allowing it to be compared to Fig. 2b, which shows the image of the cellulose film containing approximately 5 wt% of polymeric lignophenol. It is apparent that the film evenness was completely maintained. This aspect is clearly seen, although the image magnification is higher in Fig. 2b.

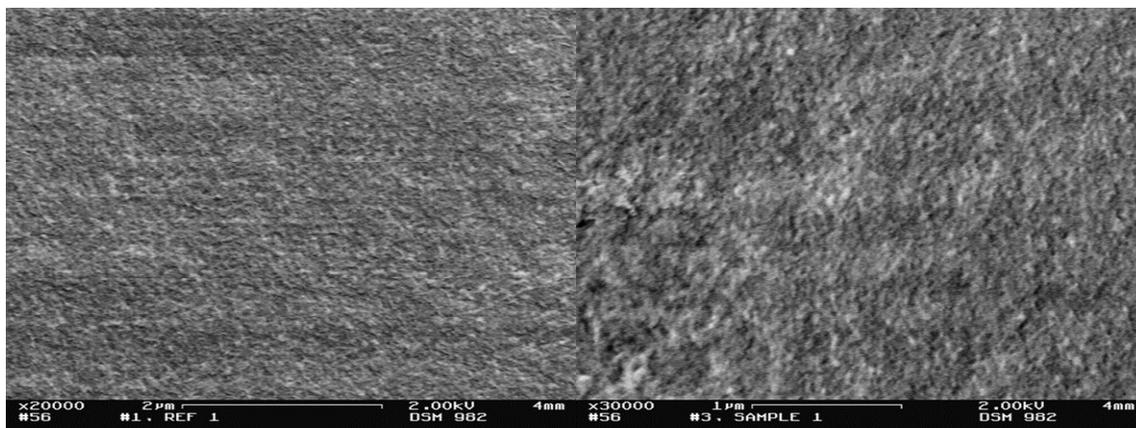


Figure 2. SEM images of (a) pure regenerated cellulose film and (b) cellulose film containing 5wt% of lignophenolate

In Fig. 3 the images of the films prepared using cellulose xanthate (Fig. 3a) and cellulose xanthate blended with lignophenolate (Fig. 3b) are shown.

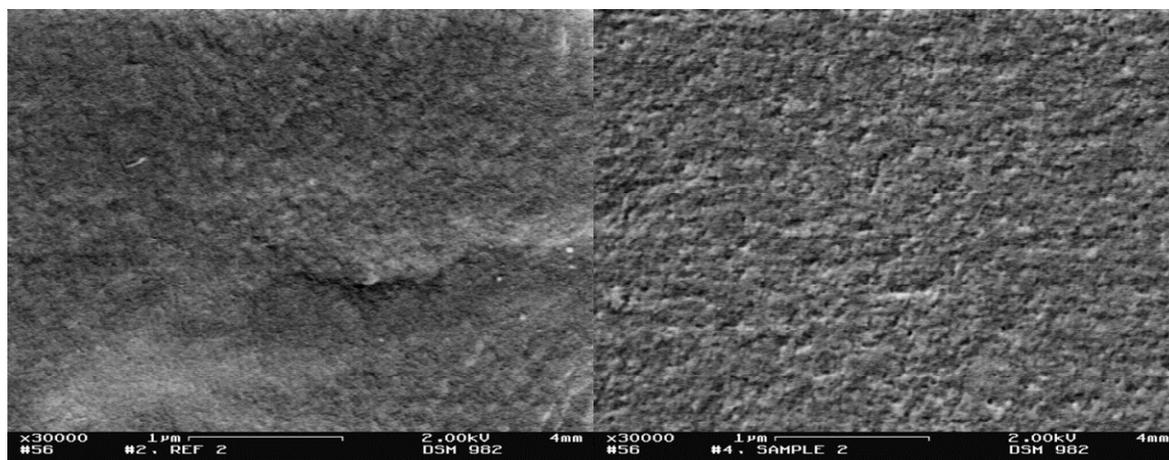


Figure 3. SEM images of (a) pure cellulose xanthate film and (b) cellulose xanthate film containing 5wt% of lignophenolate

The pure cellulose xanthate films were slightly more uneven, compared to the cellulose films, probably due the bubble-forming tendency during coagulation when preparing the films. The air bubbles in the film structure may lead to uncontrolled porosity, and they should be carefully removed prior to, e.g., assessment of the film mechanical properties. However, the lignophenol addition did not impair the film formation, and even structures could be achieved even without further air removal, as can be seen in Fig. 3b.

Figure 4 shows the IR-spectrum of the pure softwood derived lignophenolate, which was prepared according to Funaoka et al. (1995). The spectrum is similar to that reported in Funaoka and Fukatsu (1996): an intensive band is detected around 1509 cm^{-1} that probably arises from aromatic ring stretch, and another characteristic band around 815 cm^{-1} is assigned to C-H deformations of the cresolic structure (out-of plane CH wag, see also the chemical structure of the lignophenol in Fig. 1). These two distinctive bands are used when investigating the chemical homogeneity of the cellulose-lignophenol films.

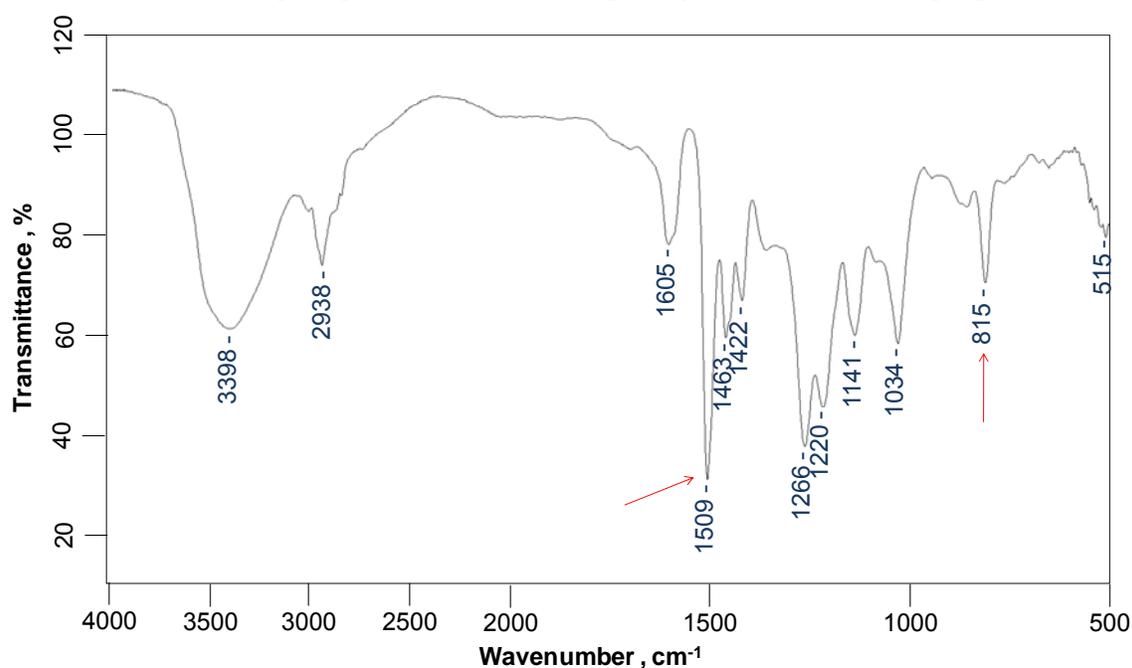


Figure 4. IR spectrum of the softwood derived lignophenol. The arrows emphasize the distinctive bands related to its chemical structure

In general, it is assumed that the IR detection limit for different compounds is 1-5 wt-%. Therefore, only traces of the characteristic lignophenolic bonds can be detected by IR, since the amount of lignophenol in the films was only 5 wt-%. The bands at 1509 cm^{-1} and 815 cm^{-1} , although weak, are observable in the spectra of cellulose/lignophenol film and cellulose xanthate/lignophenol film (see Fig. 5 a and b). Especially the band at 1509 cm^{-1} originating from the aromatic ring stretching can be used as a reliable lignophenol marker, since it is a typical marker for lignin-like materials (Forssskåhl et al. 1995). On the basis of the IR analysis it can be assumed that the lignophenol is evenly

distributed through the cellulose film, since all the recorded spectra showed similar features.

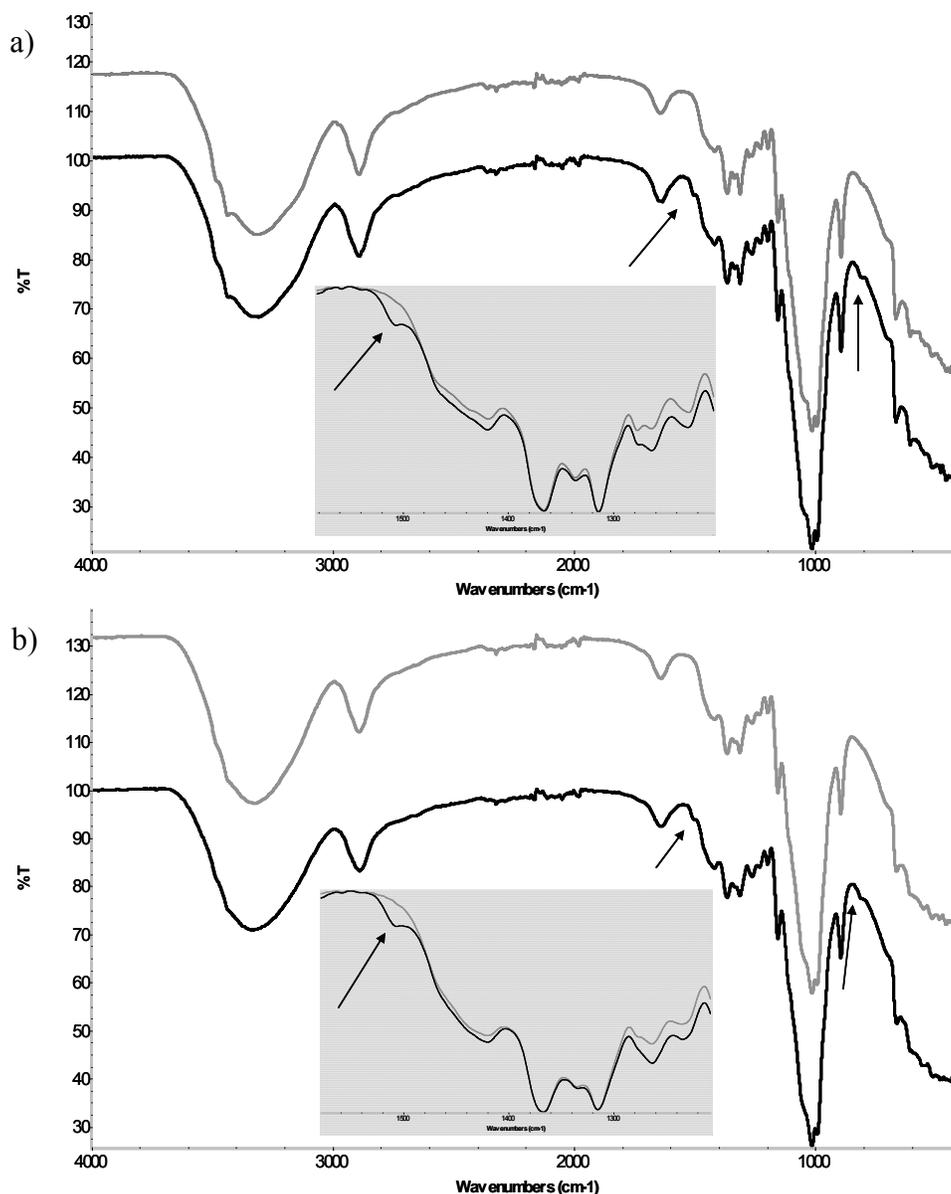


Figure 5. IR spectra of (a) cellulose/lignophenol film and (b) cellulose xanthate/lignophenol film. The grey lines indicate the pure cellulose (a) and pure cellulose xanthate (b). The arrows emphasize the distinctive bands of the softwood derived lignophenol, and the inserts show the enlarged spectral area of the distinctive band of 1509 cm^{-1} . Transmittance scale has been extended to facilitate the comparisons.

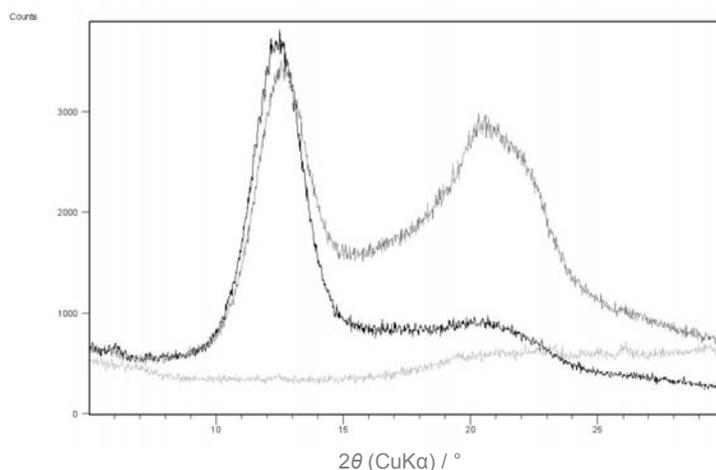
Tentative Discussion on Interactions between Cellulose and Lignophenol

As confirmed by microscopical and FTIR analyses, even-blend films of cellulose and lignophenol can be prepared via the precipitation procedure. In addition, the changes in the organization of organization of the cellulose molecules in the film structure were

investigated with X-ray analysis in order to confirm the evenness of the blend films. The results may also give tentative evidence on the positive attractive interactions between cellulose and lignophenol macromolecules.

Both pure regenerated cellulose and pure cellulose xanthate films generated diffractograms of cellulose II, showing peaks at $2\theta = 12.1^\circ$, 19.8° , and 22.0° , corresponding to the reflections from (1-10), (110), and (020) planes (Langan et al. 1999, 2005). These diffractograms are shown in Fig. 6 a and b as dark grey lines. Black lines in Fig. 6 a and b are diffractograms of cellulose films to which 5 wt-% of amorphous lignophenol is blended.

a)



b)

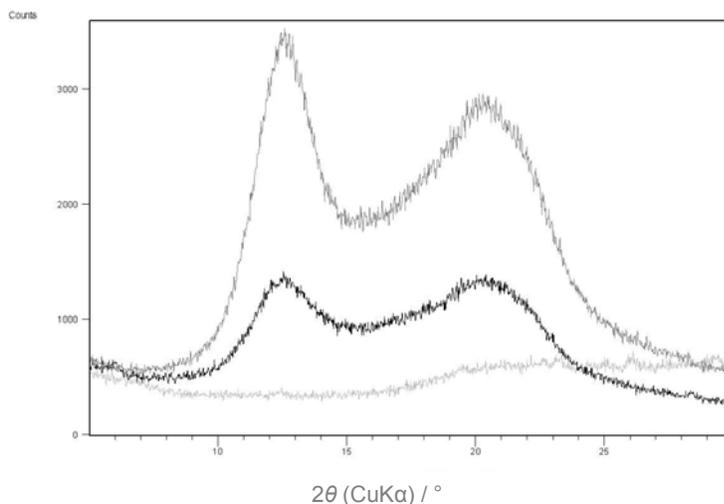


Figure 6. X-ray diffractograms of (a) cellulose/lignophenol film and (b) cellulose xanthate/lignophenol film. The grey lines indicate the pure cellulose (a) and pure cellulose xanthate (b), and the black lines indicate the cellulosic films containing 5 wt-% of lignophenol. Light grey lines indicate the diffraction pattern of highly amorphous cellulose.

It is well known that the (1-10) crystal plane is oriented parallel to the film surface in almost all regenerated cellulose films (Takahashi 1969; Yamane et al. 2006). This phenomenon is called uniplanar orientation, and it is seen as higher peak intensity of the reflection from this particular plane. The intensity of the reflection from the (1-10) plane is pronounced especially in Fig. 6a. Due to the uniplanar orientation observed from film samples, the crystallinity index of cellulose cannot be directly estimated, since it should be calculated using the diffraction patterns of the randomly oriented samples only (Yamane et al. 2006). Therefore, only the changes in reflection intensities and qualitative changes in peak areas can be approximated in order to discuss the changes taking place in film structures upon lignophenol addition.

As shown by Fig. 6 a and b, the crystalline structure of cellulose II is maintained upon lignophenol addition. However, the intensity of the reflections has been changed and the total peak area has been decreased when blending a small amount of lignophenol with cellulose or with cellulose xanthate. Thus, according to the XRD results, clear changes are taking place in the diffraction patterns in the presence of lignophenol. The addition of small amount of lignophenol leads to a more amorphous film structure, since intensities of almost all of the peaks are decreasing with the constant film thickness, and the total peak area is decreasing. This indicates that attractive cellulose-lignophenol interactions may take place, since the changes in the diffractions patterns are so evident (>5%), although the lignophenol content was only 5 wt-%.

The associative behaviour of lignin molecules with cellulose is mainly attributed to the presence of the hemicelluloses, which are covalently linked to lignin (Salmén and Olsson 1998). Atalla (1998) suggested that in the cell wall a dominant organizing influence upon lignin ultrastructure is provided by strong associative interactions between lignin precursors and the polysaccharide matrix. In this way, cellulose provides a key structural pattern for the assembly of lignin. Based on molecular modellings, the strong associative interactions in aqueous media have been reported between lignin precursors (monolignol and trilignol) and the cellulose surface (Houtman and Atalla 1995). The particular system used in this study contains only traces of hemicelluloses, and thus the associative interactions must take place directly within cellulose and lignin derivative.

According to the work conducted by Bezombes and Mazeau (2005a), strong associative interactions occur within small lignin model compounds and cellulose crystal surfaces (Bezombes and Mazeau (2005b)). Evidence for the associative interactions was obtained using both molecular modelling and experimental observations, and the extended lignin molecular models, from β -O-4 dimers up to 20-unit oligomers were considered. The attractive interactions were suggested to take place via hydrophobic interactions between aromatic rings and the more hydrophobic 200 plane of the cellulose crystal (orientation of cellulose molecules such that more hydrophobic C-H groups are available), leading to a parallel orientation of lignin model molecules on the cellulose surface. The other suggested interaction between lignin model compounds and cellulose matrix takes place through H-bonding, where β -O-4 hydroxyl groups act as H-bond donors, and the cellulose oxygen act as an H-bond acceptor. If H-bonding played a significant role in the interactions within lignin-like structures and cellulose, changes in band positions and shape of IR-spectra should have been observed. As shown in Figure 5, there were no changes in band positions observed due to the lignophenol addition.

However, the amount of OH-groups taking part in the lignophenol-cellulose interactions was significantly lower compared to the total amount of available OH-groups. Thus, it probably is not possible to observe clear changes using such resolution what IR method can provide.

Most of lignin model molecules previously used differ in reactivity and size from that of the natural lignin. Until recently it has been difficult to obtain lignin suitable for interactive studies with reasonably high degree of polymerization, truly imitating the influence of its polymeric nature. Soluble lignophenol macromolecules are natural polyethers of coumaryl, coniferyl, and sinapyl alcohols directly extracted from wood meal with cresol compound and hydrolysed with concentrated sulphuric acid. As a result, a linear α -bonded phenolpolymer with high reactivity is obtained. Based on the results it seems that lignophenol tends to interact with cellulose and that even films of regenerated cellulose and lignophenol macromolecules can be achieved. In this paper the aim was to introduce a method to prepare such films and tentatively assess the structure and present interactions. To confirm the findings, more detailed investigations need to be conducted using, e.g. surface sensitive methods such as QCM-D and AFM. We believe that this particular lignophenol derivative will facilitate studying the cellulose-lignin interactions on a molecular level, using these aforementioned sophisticated methods. In addition, more detailed investigations related to, e.g. changes in the water uptake ability and mechanical properties of the films, are worthwhile to continue, since lignophenol addition to cellulose fibre composites have been shown to give interesting properties such as increased water resistance and strength (Funaoka et al. 1996; Aoyagi et al. 2007).

CONCLUSIONS

1. Smooth and even films comprised of cellulose and lignin-modeling polymeric lignophenol can be achieved through a precipitation procedure.
2. The cellulose II crystal structure is maintained, although more amorphous films are achieved when regenerated cellulose or cellulose xanthate is blended with lignophenol. Tentatively it can be concluded that attractive cellulose-lignophenol interactions take place, since changes in the diffractions patterns are so evident.

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