DISTRIBUTION OF OPTICAL BRIGHTENING AGENT (OBA), IN THE FIBRE WALL OF HIGH-YIELD AND KRAFT PULPS

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INTRODUCTION

Optical brightening agents (OBA) are commonly used in the pulp and paper industry, and can be applied to different kinds of pulps, including high-yield pulp (HYP) and Kraft pulps. The purpose of using OBA in the HYP-containing pulp and paper products is to increase their brightness/whiteness and brightness stability [1-4]. Recently, HYP has been used at an increasing rate to replace bleached hardwood Kraft pulp in the manufacturing of higher-quality paper products. This is largely due to their unique properties, including high bulk, good opacity, stiffness and swelling behaviour [5-10].

However, the market HYP still has a lower brightness when compared to hardwood Kraft pulps. There is a commercial interest in improving the optical properties of the HYP. OBA and dyestuff can be used to serve this purpose well [2,3,11-15]. The OBA brightening process has shown to be conveniently incorporated into the alkaline peroxide bleaching process [4]. This approach has several advantages over the conventional method of using OBA in the wet-end of the papermaking process [4].

The OBA brightening efficiency was higher on Kraft pulp than that on HYP [3,16], and there are three possible explanations for this difference:

1) HYP typically has lower brightness than bleached Kraft pulps, which can decrease the OBA efficiency;
2) HYP has a higher light scattering coefficient than bleached Kraft pulps, which decreases the OBA efficiency;
3) The lignin present in HYP competes with OBA for UV, thus, at a given amount of OBA absorbed on fibres, OBA is less effective on HYP than that on Kraft pulp.

HYP is fundamentally different from the bleached Kraft pulp. Unlike bleached Kraft pulp, HYP retains most of the lignin from wood. HYP has more fines, lower average fibre length [14,17], and less porosity in the fibre wall structure [10].

The objective of this study was to determine the fundamental differences between the OBA interaction with HYPs and bleached Kraft pulps, with a concentration on the individual fibres. We adapted the high resolution UV fluorescence image technique for this purpose.
EXPERIMENTAL

Materials and procedures

Two commercial pulps, an aspen HYP (bleached chem-thermo-mechanical pulp or BCTMP) with a 300 mL Canadian Standard Freeness (CSF) and an 85% brightness and a aspen bleached Kraft pulp, were used in this study. These pulps were further fractionated by DDJ (Dynamic Drainage Jar) and the long fibre fractions were used for the fluorescent microscopy image analysis. A disulphonate type of OBA (Tinopal HW) was obtained from Ciba Specialty Chemicals. The detailed procedures on the addition of OBA to pulp have been reported earlier [3].

Latency Removal (Hot Water Disintegration)

The latency of the received pulp was removed following the hot water disintegration. The hot water disintegrator is made of a steel cylinder and equipped with a circulating pump. First, the cylinder was filled with hot water (90°C), which was circulated for three minutes to warm the system. Subsequently, small pieces of the pulp samples were placed in the cylinder, which was filled with hot water. The pulp suspension was then circulated for three minutes to remove the latency. In this study, 40 grams of dry pulp were disintegrated and diluted with 10 litres hot water to a 0.4% pulp suspension, and this suspension was then transferred to a dynamic drainage jar for the fibre fractionation.

Fibre Band Preparation by Dynamic Sheet Former (DSF)

The fibre band was prepared for fibres sectioning by microtome. A total of 3.5 gram OBA-processed long fibres separated by DDJ were diluted in a 10 litres deionized water (DI) water. The DI water was made up to 100 ppm hardness by adding CaCl₂ and MgSO₄ at a weight ratio of 1:1 to the de-ionized water. A total of 10 litres of 0.035% consistency suspensions was then used to form a fibre band in a Dynamic Sheet Former (DSF).

Fibre Cross-sectioning by Microtome

The dried fibre band was cut into small pieces to fit into the embedding moulds, and the Epofix resin was added to the mould. The fibre bands with resin were cured at a room temperature overnight and sectioned with a diamond knife on an ultramicrotome into 1 um thickness sections; some sections were mounted with a cover slip to protect the sample and with immersion oil to increase the optical resolution image.

Fluorescence Microscopic Examination of Fibre Section

Leica digital fluorescence microscopy was used for imaging the sectioned fibres. The object lens used was a oil immersion lens with 63 times magnification. Transmitted images were taken in the Differential Interference Contrast (DIC) mode to visualize the physical sections. Fluorescent images were taken in the DAPI mode (Hg lamp and 4',6-diamidino-2-phenylindole (DAPI) filter cube) with a UV source at wavelength of around 365 nm, and 500 ms UV exposure. The intensity of fluorescence was adjusted to just below saturation of pixel, then the image was recorded by a Peltier-cooled Leica DC 500 charge coupled device (CCD) camera, saved as a tagged image file (TIF) colour image with a size of 1300 x 1030 pixel, and the maximum exposure time of fibres to UV before the image was taken was less than 30 seconds to minimize the photo bleaching.

Fluorescence Image Analysis

The quantitative fluorescence image analysis of fibre cross-section was performed with a commercial software-ImageJ. The fluorescent intensity of the point on fibre cross-section image was measured by taking the blue grey level of the histogram of the fluorescent image. A similar technique has been applied by Liu et al. [18]. The comparison of the fluorescent intensity of fibres under different OBA treatment conditions was made as follows: 1) similar-sized fibres were selected (similar cross-section diameter); 2) the scanning positions were selected in such a manner that the fluorescence distribution of that position could represent the overall fluorescent distribution status of the fibres (extreme cases, e.g. too deep penetration, too shallow penetration and too intense fluorescent positions were excluded); 3) the blue channel grey level of colour histogram of the interesting position on the fluorescent images was recorded by line-scanning the fluorescent image from lumen to the fibre wall outer surface and plotted against the scanning distance; 4) the grey level was reported as the recorded grey level on fibres subtracting the background grey level which was determined from the position far away from the fibres.

RESULTS AND DISCUSSION

Structure Differences between HYP and Kraft Pulp

The cell wall differences between the HYP and the Kraft pulps include the following aspects: i) chemical composition, ii) morphology, and, iii) pore structure. It has been well reported that lignin under ultraviolet irradiation can emit weak blue fluorescence [19,20]; the so-called lignin intrinsic fluorescence. In the present study, the fluorescence micrographs of fibre cross-sections were taken using a high-resolution fluorescence microscopy under UV illumination (365 nm) in the DAPI mode and the results are shown in Figs. 1A and 1B. The fluorescent images clearly show the intrinsic fluorescence of the HYP. The intensity of the fluorescence is higher on the surface of the HYP fibre and diminishes gradually towards the lumen. Under the same microscopy configuration conditions for the HYP (same UV light, source intensity, exposure time, microscopy magnification), the intrinsic fluorescence from Kraft fibres is too weak to be seen. The strong intrinsic fluorescence on the HYP fibre surface and the weak intrinsic fluorescence on the Kraft fibres is consistent with their lignin concentrations. Hua et al. [21], using the electron spectroscopy for chemical analysis (ESCA) technique demonstrate that the surface coverage of lignin on HYP fibres is high, which is supported by the results of others [22,23].

The second difference lies in the morphology between HYP and the Kraft fibre wall. Most of the lignin remains in the HYP fibre, which makes the fibres stiff and resistant to lumen collapse, as shown in Fig. 2A. The Kraft pulp on the other hand, being essentially lignin-free, contains very flexible and collapsed fibres, which is evident in Fig 2B.
Finally, the pore structure of the fibre wall is different between the HYP and the Kraft pulp. Tan and Li [24] analyzed the cross-section of HYP and Kraft fibre wall by using Atomic Force Microscopy (AFM), and found that the Kraft fibres had 10 nm - 60 nm while the HYP pulp fibres had 10 nm - 20 nm granular structure on the wall. This suggests the Kraft fibre wall has bigger pore size than the HYP fibre wall. Berthold and Salmen [25] studied pore size distribution of the mechanical and chemical pulps based on the inverse size-exclusion chromatograph and found that smaller pores are available in the mechanical pulp fibres than the chemical pulp fibres. Hui et al. [10] recently showed that the HYPs generally have a lower fibre saturation point (FSP) than the Kraft pulps, providing direct evidence that HYP has smaller pores than Kraft pulps.

**OBA Penetration and Diffusion in the Fibre Wall**

There are several processes occurring when OBA interacts with fibres: adsorption, penetration/ diffusion. OBA not only adsorbs on the surface of the fibres, but also penetrates and diffuses into the fibre wall due to the fibre's porous structure. Factors such as fibre morphology, chemical composition and porous structure may affect these processes. The fibre cross-section fluorescent image and the same fibre cross-section but with light transmitted images taken in DIC (Differential Interference Contrast) mode are shown in Fig. 3. The thickness of the fibre wall from both images was measured using the line scan feature of the commercial software-ImageJ. The fibre wall was scanned from the lumen to the outer wall surface and the two measurements had similar results. This indicates that when OBA is added in the fibre suspension, OBA does not accumulate solely on the fibre surface; it can penetrate and diffuse into the fibre wall. The OBA adsorption and diffusion on the HYP fibre wall is very different from those of the Kraft fibre due to the difference of the fibre wall structure. One obvious difference is that OBA fluorescence can often be found in the lumen of the HYP, while that is not the case for Kraft pulp. Other factors, such as the OBA concentration, can also have an effect on the OBA adsorption and diffusion. Four different OBA dosages, 0, 0.04, 0.08, 0.15%
were added to the pulp suspension. The fluorescent images of OBA-processed HYPs and Kraft pulps are shown in Figs. 4 and 5, respectively. When the OBA dosage increased, the fluorescent intensity increased correspondingly and this is true for both HYP and Kraft pulp fibres. This indicates that penetration and diffusion play key roles in the interaction of OBA with fibres.

**Quantitative Analysis of the OBA Penetration and Diffusion**

The OBA fluorescent intensity was determined based on the blue fluorescence grey level. This method is based on the consideration that the blue fluorescence from OBA is the interest portion of the light for the pulp brightness measurement, and the blue fluorescence can be filtrated and detected by the Bayer colour filter attached to the Leica CCD camera. The fluorescence distribution of the fibre, treated with four different dosages of OBA, is shown in Fig. 6 (HYP) and Fig. 7 (Kraft pulp). When the OBA dosage increased, the fluorescence grey level on the fibre wall also increased and this is true for both HYP and Kraft pulp. The results further show that when the OBA dosage was high, OBA can be transported into the lumen, resulting in a penetration and diffusion from the lumen towards the fibre surface. More interestingly, one can find that for the HYP, a two-shoulder distribution pattern is evident (Fig. 6) while for the Kraft pulp the outer surface has the highest grey level, which gradually decreases towards the lumen (Fig. 7), indicating that in the case of HYP fibres, the OBA diffusion occurs from both the fibre surface and lumen, while in the case of Kraft fibres, it is from the fibre outer surface. There are two reasons to account for such a difference:

1) The HYP fibres have open ends or fractured fibre walls, by the mechanical pulping process [26]. Their presence allows OBA to be transported to the lumen. Therefore, the OBA diffusion from the lumen outward and from the fibre surface inward can occur at the same time. By contrast, the Kraft pulping process produces pulp fibres with intact fibre structures that allow OBA to penetrate/diffuse into the fibre porous structure only from the fibre outer surface.

2) HYP fibre has a stiff structure due to its high lignin content and less wall collapse. By contrast, Kraft fibre has much less lignin and a more flexible fibre wall structure. It was reported [27,28] that for dried and rewetted Kraft fibres, most of them were collapsed. As a result, one may expect that the OBA diffusion via lumen for Kraft fibre is unlikely.

![Fig. 6 - Typical fluorescence distribution profile of OBA processed HYP fibre wall (HYP-0: 0% OBA, HYP-1: 0.08% OBA, HYP-2: 0.15%OBA).](image1)

![Fig. 7 - Typical fluorescence distribution profile of OBA processed hardwood Kraft fibre wall (Kr-0, 0% OBA, Kr-1: 0.08% OBA, Kr-2, 0.15% OBA).](image2)
The penetration depth and the penetration depth ratio was used to quantify the difference of OBA penetration between the HYP and the Kraft pulp. Since the penetration from the lumen is much less compared with that from the outer surface, the depth of OBA penetration was defined as the distance from the fibre wall surface to the first inflection point of grey level. The penetration depth ratio was defined as the penetration depth divided by the fibre wall thickness. The averaged OBA penetration depth ratios of HYP and Kraft pulp are shown in Table 1. About 72% of Kraft fibres treated with 0.08% OBA had a penetration depth ratio of 30% or higher, while for HYP, only ~8% of the fibres reached such a penetration level. The results are based on a population of 46 and 48 for Kraft and HYP fibres respectively. Clearly, OBA had a deeper penetration into the Kraft fibre wall than into the HYP fibre wall.

The results of the fluorescence grey level of all the fibres processed at OBA charge of 0.08% are included in Table 1. It can be seen that ~93% of the Kraft fibres had a fluorescence grey level of 130 or higher, while for HYP fibres this number was only ~33%. The results support the conclusion that OBA had a higher fluorescent efficiency for Kraft pulp than for HYP. The deeper penetration and higher fluorescence of OBA in the Kraft fibre wall is possibly due to its larger pore size, lower lignin content and to a less extent its smooth surface structure. By contrast, the higher lignin content, lower porosity and rough fibre surface of HYP will retard the penetration of OBA into the fibre wall.

CONCLUSIONS

The OBA interaction difference between an aspen high-yield pulp (HYP) and a hardwood Kraft pulp was investigated. The conditions, the fluorescent intensity of OBA-treated Kraft pulp is stronger than that of the OBA-treated HYP. Further, the quantitative fluorescence microscopy results indicate that for the HYP, the OBA diffusion occurs both from the fibre surface inward and from the lumen outward, resulting in a two-shoulder distribution pattern of OBA across the fibre wall. By contrast, for the bleached Kraft pulp, the OBA diffusion is mostly from the fibre surface inward. Such a difference is caused by the nature of the mechanical and chemical pulping processes and the fact that mechanical pulping leads to the production of open-ended fibres while chemical pulping creates structurally intact fibres.

REFERENCES


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<th>Pulp Sample</th>
<th>Penetration Depth Ratio (%)</th>
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<tr>
<td>HYP</td>
<td>10% 20% 30% 40% &gt;40%</td>
<td>70 90 110 130 &gt;130</td>
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<tr>
<td>Kraft pulp</td>
<td>0 44% 48% 8% 0</td>
<td>6% 33% 26% 13% 20%</td>
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<td></td>
<td>0 0 28% 57% 15%</td>
<td>0 0 7% 37% 56%</td>
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Table 1 - Statistic results of OBA penetration depth ratio and fluorescence grey level of OBA-treated fibres (0.08% OBA charge).


