Available online at www.sciencedirect.com
ScienceDirect
Journal of Photochemistry and Photobiology A: Chemistry 193 (2008) 122–128
Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

An efficient photochemical bleaching of kraft pulps using total halogen-free reducing reagents

Akihiko Ouchi *, Atsushi Saruwatari, Toshiaki Suzuki

National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8565, Japan

Received 23 February 2007; received in revised form 18 May 2007; accepted 15 June 2007
Available online 20 June 2007

Abstract

Total chlorine-free bleaching of kraft pulps was conducted by a reductive photochemical process at room temperature. Reducing reagents were screened, and bleaching conditions were optimized using excimer lasers. The laser used in the best bleaching condition was then substituted by conventional light sources to make the process more easily accessible. The most favorable condition for the bleaching of kraft pulps was irradiation with a low-pressure mercury lamp in the presence of aqueous sodium borohydride solution, which gave bleaching efficiency and the properties of pulps similar to those obtained by a conventional two-stage, elemental chlorine-free process. The photochemical background of the bleaching is discussed.

Keywords: Photochemical decomposition; Decolorization; Lignin; Kraft pulp; Total halogen-free reductive bleaching

1. Introduction

Recently, photochemical decomposition of lignins [1] has received much attention in connection with environmentally benign bleaching of kraft pulps. Bleaching of kraft pulps is considered as delignification and/or decolorization of remaining colored lignin, in which molecular chlorine has been used in conventional processes [2,3]. Conventional processes are now being replaced by elemental chlorine-free (ECF) processes that use chlorine dioxide instead of molecular chlorine [4,5] in an attempt to minimize or avoid the evolution and release of toxic chlorinated organic compounds, adsorbable organic halogens (AOXs), into the environment [2]. However, even after optimization of the ECF processes, significant amounts of halogenated hydrocarbons are still generated [2,6] and released into the environment.

For the complete suppression of the emission of AOXs, the development of efficient total chlorine-free (TCF) processes is an important issue. Photochemical reactions for the TCF bleaching of various pulps have been reported [3] but simple photolysis [7] and photolysis using molecular oxygen [8] or alkaline hydrogen peroxide [9] were found to be insufficient. Recent trends involve photochemical activation of molecular oxygen using photosensitizers [10], photocatalysts [11], or both [12]. Although the reactive species generated by photochemical activation of oxygen is believed to be singlet oxygen, which does not cause damage to the pulp itself, the oxidative processes often result in the generation of reactive species that do cause damage to the pulp. Therefore, further improvement of photochemical TCF processes is still a matter of importance.

We report here an efficient reductive photochemical TCF bleaching of kraft pulps. To the best of our knowledge, photochemical reductive bleaching has not been tested for kraft pulps, probably due to a belief that reductive processes are less effective than oxidative processes. However, our photochemical reductive method showed bleaching efficiency and quality of pulps similar to or better than commercial-grade bleached pulps that are produced by conventional two-stage ECF processes using ClO_2 and H_2O_2.

2. Results

2.1. Screening of reducing reagents for the bleaching of kraft pulps

The efficiency of various reducing reagents for the photochemical bleaching of kraft pulps was tested. A sheet of

* Corresponding author. Tel.: +81 29 861 4550.
E-mail address: ouchi.akihiko@aist.go.jp (A. Ouchi).

1010-6030/$ – see front matter
doi:10.1016/j.jphotochem.2007.06.015

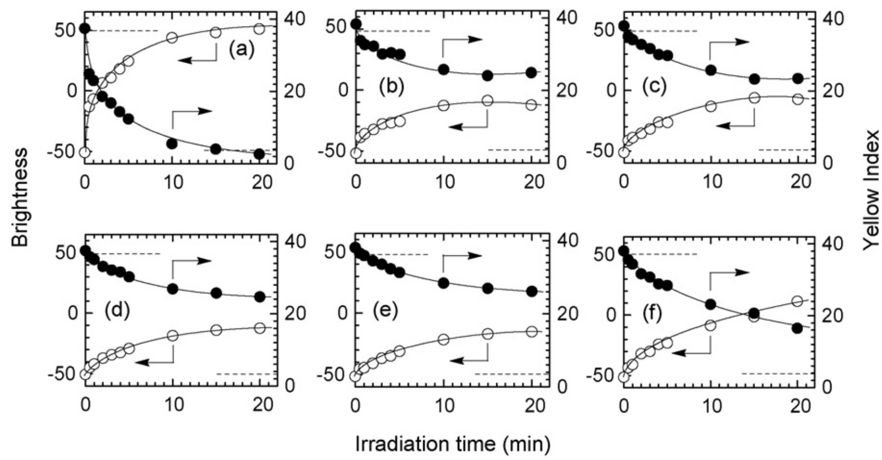


Fig. 1. Brightness and yellow index of XeCl excimer laser bleached NOKP pulp sheets as a function of irradiation time [13]. Reagents: (a) $NaBH_4$, (b) $Na_2S_2O_4$, (c) $NaHSO_3$, (d) Na_2SO_3, (e) $H_2NC(=NH)SO_2H$, and (f) $HOCH_2SO_2Na$. Brightness: white symbols, yellow index: black symbols. Laser bleaching condition: 40 mJ cm^{-2} $pulse^{-1}$, 5 Hz, room temperature. Reagent: 250 mM aqueous solution. Number of pulp sheets: 1 sheet. Brightness and yellow index of a pulp sheet prepared from commercial-grade NBKP are shown in the figures as broken horizontal lines.

softwood kraft pulp (NOKP) was subjected to XeCl excimer laser (308 nm) photolysis using six different halogen-free reducing reagents: sodium borohydride ($NaBH_4$), sodium hydrosulfite ($Na_2S_2O_4$), sodium hydrogensulfite ($NaHSO_3$), sodium sulfite (Na_2SO_3), thiourea dioxide [$H_2NC(=NH)SO_2H$], and formaldehyde sodium sulfoxylate ($HOCH_2SO_2Na$, rongalite).

The degree of bleaching was monitored by measurement of brightness and yellow index of the pulp sheets; a higher degree of bleaching is indicated by a greater brightness and a smaller yellow index [13]. Fig. 1 shows both the brightness and the yellow index of the laser bleached NOKP sheets as a function of laser irradiation time. Fig. 1 shows that $NaBH_4$ gave the best bleaching efficiency among the six reducing reagents; the brightness and the yellow index reached at the levels of conventionally bleached NOKP (NBKP; commercial-grade bleached NOKP by a conventional two-stage ECF process using ClO_2 and H_2O_2) after 15 and 20 min of irradiation, respectively. Sufficient bleaching was not accomplished by any of the six reducing reagents without laser irradiation [14].

2.2. Optimization of the laser bleaching conditions of NOKP using $NaBH_4$

The effect of laser wavelength was investigated by using aqueous $NaBH_4$ solutions. Fig. 2 shows the brightness and the yellow index of the laser bleached NOKP sheets as a function of laser irradiation time, in which KrF (248 nm), XeCl, and XeF (351 nm) excimer lasers were used. For all three lasers, the brightness and the yellow index exceeded at the levels of NBKP. Similar to the previous cases, sufficient bleaching was not accomplished without laser irradiation [14]. The rate of laser bleaching increased with the decrease of the laser wavelength, XeF < XeCl < KrF. It should be noted that KrF laser bleaching required only 2 min irradiation at room temperature to achieve the level of the conventional ECF process.

The effect of laser pulse energy and frequency on the brightness and the yellow index of laser bleached NOKP sheets were studied. The results on the pulse energy indicated that bleaching efficiency is determined mainly by the total dosage of photon energy per unit area [14]. The experiments on the laser pulse frequency showed that the bleaching efficiency is determined mostly by the number of laser shots and is not much affected by the frequency [14].

The effect of the concentration of $NaBH_4$ was tested. A considerable improvement in the brightness and the yellow index was observed by increasing the concentration of this reagent, but they leveled off at approximately 4 wt.% in the cases of KrF and XeCl laser irradiations, and at 8 wt.% for the XeF laser. In the absence of $NaBH_4$, only a slight increase in the brightness and a

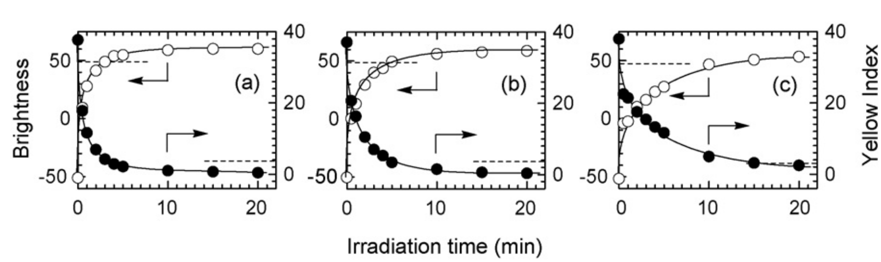


Fig. 2. Wavelength dependence on the brightness and yellow index of excimer laser bleached NOKP sheets by an aqueous $NaBH_4$ solution as a function of irradiation time [13]. Utilized lasers, (a) KrF (248 nm), (b) XeCl (308 nm), and (c) XeF (351 nm) excimer lasers. Brightness: white symbols, yellow index: black symbols. Laser bleaching condition: 40 mJ cm^{-2} $pulse^{-1}$, 5 Hz, 6 wt.% $NaBH_4$ (aq), room temperature. Number of pulp sheets: 1 sheet. Brightness and yellow index of a pulp sheet prepared from commercial-grade NBKP are shown in the figures as broken horizontal lines.

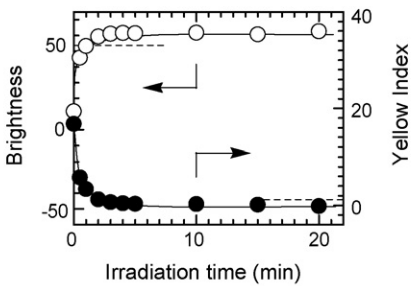


Fig. 3. Brightness and yellow index of KrF excimer laser bleached LOKP/NBKP sheets by an aqueous $NaBH_4$ solution as a function of irradiation time [13]. Brightness: white symbols, yellow index: black symbols. Laser bleaching condition: 40 mJ cm^{-2} $pulse^{-1}$, 5 Hz, 6 wt.% $NaBH_4$ (aq), room temperature. Number of pulp sheets: 1 sheet. Brightness and yellow index of a pulp sheet prepared from a 1:1 mixture of commercial-grade LBKP and NBKP are shown in the figures as broken horizontal lines.

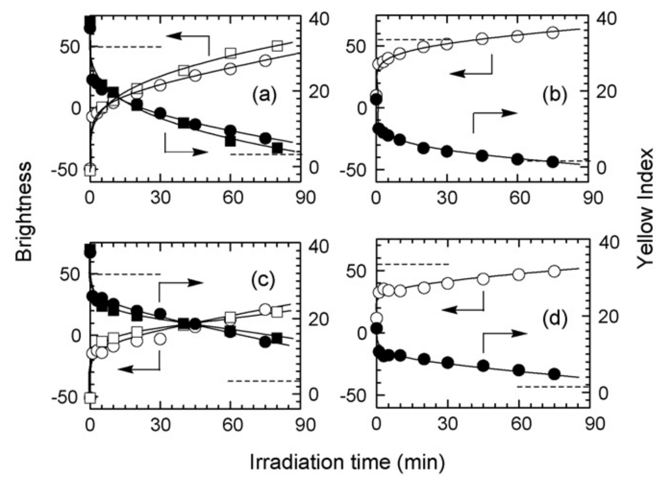


Fig. 4. Brightness and yellow index of photochemically bleached pulp sheets by an aqueous $NaBH_4$ solution as a function of irradiation time [13]. (a and c) NOKP sheets with single (○, ●) and multiple (every 10 mins) (□, ■) padding, and (b and d) LOKP/NBKP sheets with single padding. Brightness: white symbols, yellow index: black symbols. Irradiation condition: (a and b) low-pressure Hg lamp (2.41 mW cm^{-2}) or (c and d) black-light fluorescent lamp (1.53 mW cm^{-2}), 6 wt.% $NaBH_4$ (aq), room temperature. Number of pulp sheets: 1 sheet. Brightness and yellow index of pulp sheets prepared from commercial-grade NBKP and a 1:1 mixture of LBKP and NBKP are shown in the figures as broken horizontal lines.

decrease in the yellow index were observed by laser irradiation [14].

2.3. KrF laser bleaching of hardwood kraft pulp using $NaBH_4$

The best bleaching condition for NOKP was applied to the bleaching of hardwood kraft pulp (LOKP) sheets. The sheets that were made only from LOKP were too fragile to use in experiments, so the bleaching experiments were performed with pulp sheets prepared from a 1:1 mixture of LOKP and NBKP (LOKP/NBKP). Fig. 3 shows the results for KrF laser bleaching of the LOKP/NBKP sheets. The brightness and the yellow index exceeded those of commercial-grade LBKP/NBKP sheets (LBKP: commercial-grade LOKP bleached by a conventional two-stage ECF process using ClO_2 and H_2O_2) within a short irradiation time. In contrast, only a small improvement in either brightness or yellow index was observed without laser irradiation [14].

2.4. Photochemical bleaching of kraft pulps with conventional light sources using $NaBH_4$

The experiments on the laser intensity effect showed that the bleaching efficiency depended mainly on the total dosage of the photon energy per unit area, which suggests that conventional lamps can also be used for the bleaching. Fig. 4 shows both the brightness and the yellow index of photochemically bleached NOKP and LOKP/NBKP sheets using either a low-pressure mercury lamp (major emission: 254 nm) or a black-light fluorescent lamp (emission peak: 352 nm) [14]. The rate of bleaching with the low-pressure mercury lamp was greater than that with the black-light fluorescent lamp, in accord with the results of the wavelength-effect experiments using KrF and XeF lasers (Fig. 2a versus c). In the case of LOKP/NBKP bleaching with a low-pressure mercury lamp (Fig. 4b), the brightness and the yellow index exceeded those of conventional bleaching within 75 min of irradiation. However, in other cases (Fig. 4a, c (single padding) and d), the bleaching efficiency did not reach the level of the conventional ECF bleaching within 90 min of irradiation, although a continuous increase in the brightness and a decrease in the yellow index was observed.

This slow bleaching was attributed to the decomposition of the reducing reagent and/or evaporation of water from the pulp sheets during a long irradiation time. To avoid these two problems, a multiple padding of NOKP sheets to the reducing solution was tested (Fig. 4a and c (multiple padding)), which showed a considerable increase in the rate of bleaching with the low-pressure mercury lamp photolysis (Fig. 4a (multiple padding)); the brightness and the yellow index reached at the level of NBKP after irradiation for 80 and 90 min, respectively. However, a sufficient improvement of the rate was not obtained by the black-light fluorescent lamp photolysis (Fig. 4c (multiple padding)).

2.5. Degree of polymerization and discoloration of photochemically bleached pulp sheets

Table 1 shows the weight loss and the change in the degree of polymerization (DP: number of glucose units) of cellulose in kraft pulps by photochemical bleaching. Although only small weight losses were observed with photochemical bleaching, considerable differences in the DP of the bleached pulps were observed and the difference was highly dependent on the bleaching conditions. In the case of laser bleaching, a larger decrease of DP was observed with shorter wavelength. However, when a low-pressure mercury lamp with the major emission wavelength similar to that of a KrF laser was used, the DP of the pulp sheets was unchanged by the photolysis. This result indicates that the decrease of DP was not dependent on the wavelength of the laser but was dependent on the intensity of the light.

Table 1
Weight loss, viscosity-average degree of polymerization, and discoloration of bleached pulp sheets using sodium borohydride

Bleaching method	Pulp sheets	Weight loss by bleaching[b] (%)	Degree of polymerization[c]	Before test[a]		After test[a]	
				Brightness [b]	Yellow index [b]	Brightness [b]	Yellow index [b]
KrF laser [d]	NOKP	5.3	560	61	0.5	60	0.9
	LOKP[e]	5.4	610	64	0.3	64	0.3
XeCl laser [d]	NOKP	2.6	690	58	1.6	56	2.6
XeF laser[f]	NOKP	7.7	740	57	1.9	43	6.6
Hg lamp [g]	NOKP	2.4	1230 (1160)[h]	38 (50)[h]	8.9 (4.5)[h]	22 (42)[h]	14 (5.5)[h]
	LOKP[e]	5.1	1290	60	1.6	58	2.3
Thermal[i]	NOKP	2.6	1170	5.5	20	−19	28
	LOKP[e]	2.6	1300	41	8.4	32	11
Conventional[j]	NBKP	–	1190	48	3.6	42	6.0
	LBKP[k]	–	1220	55	2.3	51	3.8
None	NOKP	–	1150	−49	38	−44	36
	LOKP[e]	–	1190	11	18	13	17

[a] Test method for color fastness to xenon arc lamp light (lamp irradiation time: 12 h). The irradiation by the xenon arc lamp and the measurements of both brightness and yellow index were performed on the same side as the irradiation of light during bleaching (number of pulp sheets: 1 sheet).
[b] Ref. [13]. Average of three independent runs.
[c] Ref. [17].
[d] Bleaching condition: 40 mJ cm^{-2} $pulse^{-1}$, 5 Hz, 10 min, 6 wt.% $NaBH_4$ (aq), room temperature.
[e] 1:1 mixture of LOKP and NBKP.
[f] Bleaching condition: 40 mJ cm^{-2} $pulse^{-1}$, 5 Hz, 20 min, 6 wt.% $NaBH_4$ (aq), room temperature.
[g] Bleaching condition: low-pressure Hg lamp (2.41 mW cm^{-2}), 60 min, 6 wt.% $NaBH_4$ (aq), room temperature.
[h] Irradiation time: 80 min, pulp sheets were padded in the $NaBH_4$ (aq) solution every 10 mins during irradiation.
[i] Bleaching condition: 60 min, 6 wt.% $NaBH_4$ (aq), room temperature.
[j] Commercial-grade pulps bleached by a conventional ECF process using ClO_2 and H_2O_2 from a paper mill.
[k] 1:1 mixture of LBKP and NBKP.

Discoloration of the photochemically bleached NOKP and LOKP/NBKP sheets was studied by the tests on the color fastness to light. In the case of laser bleaching, as shown in Table 1, the degree of discoloration was less (KrF and XeCl lasers) or comparable (XeF laser) to that of a conventional ECF bleaching.

Table 1 shows also that in the case of 60 min irradiation with a low-pressure mercury lamp, the degree of discoloration of the photochemically bleached LOKP/NBKP pulp sheets was less than that of the conventional ECF bleaching but greater than that of the photochemically bleached NOKP sheets. The same irradiation of the NOKP sheets with multiple padding of aqueous $NaBH_4$ showed the same bleaching efficiency and degree of discoloration as those of the conventional ECF process.

2.6. UV–vis spectra of photochemically bleached pulps

Fig. 5 shows the absorption spectra of NOKP sheets (**OP**), laser bleached, low-pressure mercury lamp bleached, and thermally bleached NOKP sheets (**LP**, **PP**, and **TP**, respectively), and **LP**, **PP**, and **TP** after the test of color fastness to light (**LPT**, **PPT**, and **TPT**, respectively). The efficiency of photochemical bleaching exceeded at the levels of the conventional ECF process (**CP**) when the excimer lasers were used (**LP–CP** in Fig. 5(a–c)) and Fig. 5(A–C) shows that a greater decrease in the absorption, particularly in the UV region, was observed for irradiation with shorter wavelengths. The high-degree of discoloration of the pulps that were bleached by longer wavelength lasers (XeF versus XeCl/KrF lasers) probably originated from remaining chromophores due to insufficient bleaching.

In contrast to the cases of laser bleaching, the efficiency of bleaching using a low-pressure mercury lamp or heat was lower than that of the conventional ECF bleaching (**PP–CP** and **TP–CP** in Fig. 5(d and f)). However, when a multiple padding of the reagent solution was applied to the case of the low-pressure mercury lamp irradiation, the decrease of the absorption (**PP–CP** in Fig. 5e) was comparable to that of the XeCl laser bleaching, which indicates sufficient decomposition of chromophores. This result is consistent with the absence of discoloration in the color fastness test.

The difference absorption spectra, **OP–LP**, **OP–PP**, and **OP–TP**, indicate that colored compounds have broad absorption from UV to visible wavelengths. The decrease of absorption by the bleaching indicates decomposition and/or shortening of the extended π-electron systems of the colored compounds. It should be noted that, in all cases, the absorption spectra of both **LP** and **PP** show an absorption maximum at approximately 280 nm, which is observed also for **OP**. This absorption maximum can be assigned to the substituted benzenes [15], most probably catechol and hydroquinone moieties in the phenolic phenylpropane unit of lignins, and the presence of this absorption maximum in **LP** and **PP** indicates that further photochemical reduction of the substituted benzene moieties is difficult.

3. Discussion

The bleaching of kraft pulps can be considered as degradation and/or decolorization of colored compounds that are adsorbed or chemically bound to cellulosic fibers. The origin of the col-

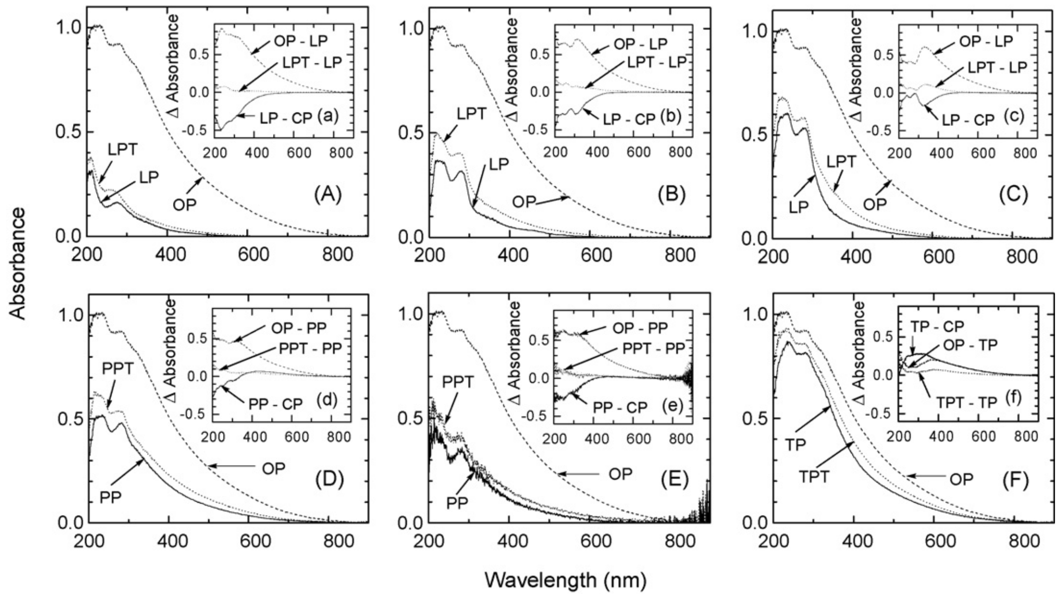


Fig. 5. Absorption (A–F) and absorption difference (a–f) spectra of NOKP sheets. Bleaching condition: (A, a) KrF laser (40 mJ cm^{-2} $pulse^{-1}$, 5 Hz, 10 min, 6 wt.% $NaBH_4$ (aq), room temperature), (B, b) XeCl laser (40 mJ cm^{-2} $pulse^{-1}$, 5 Hz, 10 min, 6 wt.% $NaBH_4$ (aq), room temperature), (C, c) XeF laser (40 mJ cm^{-2} $pulse^{-1}$, 5 Hz, 10 min, 6 wt.% $NaBH_4$ (aq), room temperature), (D, d) low-pressure Hg lamp (2.41 mW cm^{-2}, 60 min, 6 wt.% $NaBH_4$ (aq), room temperature), (E, e) low-pressure Hg lamp (2.41 mW cm^{-2}, 60 min, 6 wt.% $NaBH_4$ (aq), room temperature), multiple padding (every 10 min), (F, f) thermal (60 min, 6 wt.% $NaBH_4$ (aq), room temperature). (A–F) - - -: NOKP sheets (**OP**), —: laser bleached (**LP**) or photochemically bleached (**PP**) or thermally bleached (**TP**) NOKP sheets, · · ·: **LP** or **PP** or TP after the test of color fastness to light (**LPT**, **PPT**, **TPT**, respectively), (a–f) —: **LP–CP** or **PP–CP** or **TP–CP** (**CP**: a pulp sheet prepared from conventionally bleached NBKP), - - -: **OP–LP** or **OP–PP** or **OP–TP**, · · ·: **LPT–LP** or **PPT–PP** or **TPT–TP**. Number of pulp sheets: 3 sheets.

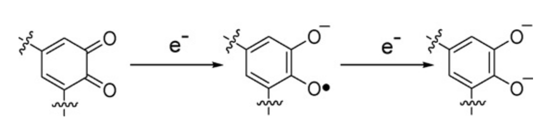
ored compounds is most probably lignin, but lignin itself has only a faint color so that the colored compounds in kraft pulps should be formed by chemical reactions of lignin that occurred during the pulping process. The chromophores in the colored compounds are not well defined but they are reported to have partial structures of quinones, quinone methides, and aromatic rings that are conjugated with olefins [2] having extended π-electron systems. Therefore, decolorization of these compounds can be accomplished by cleaving the extended π-electron systems.

Bleaching of such chromophores has been conducted mainly by oxidative processes, probably due to the belief that oxidative processes are more suitable for removing remaining lignin from the pulps, which prevents discoloration of paper more efficiently. In contrast, reductive processes convert colored compounds mainly to their colorless forms by chemical reactions without sufficient removal of lignin. Therefore, in general, the efficiency of bleaching is lower and the degree of discoloration of the bleached pulps is greater than those of pulps prepared by oxidative processes. However, our photochemical reductive bleaching showed the same or better bleaching efficiency, and discoloration behavior similar to that of pulps produced by a conventional two-stage ECF process using ClO_2.

The reaction mechanism of conventional reductive bleaching is still not known in detail. However, studies on the reductive bleaching of pulps using sodium hydrosulfite, the most widely used reagent in pulp bleaching, showed that *ortho*- and *para*-quinonoid structures can be reduced to *ortho*- and *para*-hydroquinones, probably by two successive one-electron transfers (Scheme 1) [2].

An advantage of the photochemical process over the conventional thermal processes in reductive bleaching is facilitation of electron transfer processes at the initial stage of the bleaching. Redox reactions, which are initiated by electron transfer processes, have an important role in the initial stage of bleaching, and it is well known that electronically excited molecules become more susceptible to redox reactions, so that the chromophores of the colored compounds that cannot react with bleaching (redox) reagents in their ground states (thermal reactions) become able to react with the same reagents in their excited states (photochemical reactions).

For all of the reducing reagents used, the bleaching was largely accelerated by irradiation with light (Fig. 1 versus Fig. S1 [14]). Although the degree of photochemical enhancement of the bleaching was similar for $Na_2S_2O_4$, $NaHSO_3$, Na_2SO_3, $H_2NC(=NH)SO_2H$, and $HOCH_2SO_2Na$, $NaBH_4$ showed remarkable enhancement. This may be due to the different nature of $NaBH_4$ from that of the other five reagents. The mechanism of the photochemical reduction using $NaBH_4$ is still not clear at the moment, but it is explained either as (i) a photoinduced electron transfer and successive proton transfer from $NaBH_4$ to the colored molecules or by (ii) a hydride abstraction from $NaBH_4$ by the excited colored molecules [16]. The hydride abstraction



Scheme 1.

by the excited colored molecules can be considered also as a nucleophilic attack of hydride on the colored compound, in which nucleophilic centers are induced by electronic excitation. The smaller enhancement of the photochemical bleaching with other five reducing reagents may be due to the lack of an effective proton source for radical anions of colored compounds that were formed by the photoinduced electron transfer or to the lack of hydride source for the nucleophilic attack.

A disadvantage, in our present study, is that sufficient bleaching was not obtained at the underside of the pulp sheets by conventional light irradiation. We think that this is not a critical problem, but a matter of processing. This problem can be solved by irradiation of light to the suspension of pulp instead of pulp sheets and this modification of the processing also eliminates the problem of the pulp sheets drying during light irradiation, which decreased the efficiency of the photochemical bleaching.

4. Experimental

The samples used for the photochemical bleaching of kraft pulps were paper sheets of oxygen-bleached softwood kraft pulp (NOKP) ($68\,g\,m^{-2}$) and a 1:1 mixture of oxygen-bleached hardwood kraft pulp (LOKP) and commercial grade bleached softwood kraft pulp (NBKP) (LOKP/NBKP; $62\,g\,m^{-2}$) from a paper mill. A pulp sheet (2 cm × 3 cm) was padded in aqueous solutions of either $NaBH_4$, $Na_2S_2O_4$, $NaHSO_3$, Na_2SO_3, $H_2NC(=NH)SO_2H$, or $HOCH_2SO_2Na$. The solutions were prepared in deionized water. The sheet was then removed from the solution and laid horizontally on a glass plate. The uptake of solutions by the 1 g sheet was approximately 5 g. The sheet was irradiated at room temperature with the light, perpendicular to the surface of the paper sheet, washed with water, and dried.

In the cases of excimer laser irradiation, Lambda Physik LPX210i (KrF (248 nm) and XeF (351 nm)) and Lambda Physik COMPexl02 (XeCl (308 nm)) excimer lasers were used as light sources. The direction of the laser beam that was emitted horizontally from the apparatus was changed to vertical by a dielectric mirror for the high-power laser (TFM-50C08-248 for the KrF laser, TFM-50C08-308 for the XeCl laser, and TFM-50C08-351 for the XeF laser, all from Sigma Koki Co., Ltd.) and the intensity of the laser was controlled by a convex (SLSQ-50-100P or -150P from Sigma Koki Co., Ltd.) or a concave (SLSQ-50-70N or -100N from Sigma Koki Co., Ltd.) synthetic fused silica lens. In the cases of conventional lamp irradiation, a 15 W low-pressure mercury lamp (National Germicidal Lamp GL-15) and a 15 W black-light blue fluorescent lamp (National FL15BL-B) were used as light sources. The pulse energy of the lasers was measured by a Gentec ED-500 joulemeter and a Gentec SOLO PE Monitor. The light intensities of both the low-pressure mercury lamp and the black-light fluorescent lamp were measured by an Ushio UIT-150-A Ultraviolet Radiometer equipped with either an UVD-S254 (for the GL-15 lamp) or an UVD-S365 (for the FL15BL-B lamp) photo detector. The emission spectra of the lamps were measured by an Ushio USR-40D Spectroradiometer. Thermal bleaching at room temperature was conducted similarly without irradiation.

Brightness, yellow index, and absorption spectrum of the paper sheets were measured by a UV–vis spectrophotometer (Shimadzu UV-2400PC), equipped with an integration sphere (Shimadzu ISR-2200) using $BaSO_4$ (Merck, for white standard DIN 5033) as a reference. The brightness (JIS Z 8715; ISO 105-J02) and the yellow index (JIS K 7103) were calculated from measured UV–vis spectra using software for color measurements (Shimadzu P/N 206–65207). Color fastness to light was measured by “test method for color fastness to xenon arc lamp light” using a xenon long-life fade meter (Suga Test Instruments Co., Ltd., FAL-25AX). The viscosity-average degree of polymerization was calculated from limiting viscosity [16] measurements in cupriethylene diamine solutions using a viscometer (LAUDA, Viscosity Measuring System PVS 1).

5. Conclusion

Total chlorine-free bleaching of kraft pulps was conducted at room temperature by a reductive photochemical process. Sodium borohydride was selected as the best reagent out of six commonly used reducing reagents by a screening of reagents using a XeCl excimer laser. Optimization of bleaching conditions (laser wavelength, intensity, and pulse frequency effects, and concentration effect of the reagent) was conducted with KrF, XeCl, and XeF excimer lasers. The best bleaching condition showed bleaching efficiency and quality similar to those of pulps obtained by a conventional two-stage ECF process using ClO_2 and H_2O_2. The KrF laser in the best bleaching condition was substituted by conventional light sources to make the process more accessible. The bleaching of kraft pulps by irradiation with a low-pressure mercury lamp in the presence of aqueous sodium borohydride solutions gave bleaching efficiency and quality similar to those obtained by the conventional ECF process. Although processing problems have to be solved for production, these results indicate that, in principle, an efficient TCF bleaching of kraft pulps can be accomplished by photochemical processes, which is a promising candidate for an efficient environmentally benign TCF bleaching process for kraft pulps.

6. Supplementary data

Brightness and yellow index of thermally bleached NOKP sheets using six different reducing reagents as a function of treatment time. Brightness and yellow index of thermally bleached LOKP/NBKP sheets using $NaBH_4$ (aq) as a function of treatment time. Brightness and yellow index of KrF, XeCl, and XeF excimer laser bleached NOKP sheets using $NaBH_4$ (aq) as a function of laser frequency, laser pulse energy, and $NaBH_4$ concentration. Emission spectra of a low-pressure mercury lamp and a black-light fluorescent lamp. Absorption and absorption difference spectra of LOKP/NBKP sheets with various bleaching conditions. Results on the discoloration test of bleached pulp sheets on the opposite side as the irradiation of light during bleaching.

Acknowledgements

We thank the Ministry of Economy, Trade and Industry, Japan for financial support, Ms. Yoshimi Morita for technical assistance, and Mr. Akihiro Sahashi for conducting the tests of color fastness to light.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2007.06.015.

References

[1] K.-O. Hwang, L.A. Lucia, J. Photochem. Photobiol. A: Chem. 168 (2004) 205–209.
[2] C.W. Dence, D.W. Reeve (Eds.), Pulp Bleaching—Principles and Practice, TAPPI, Atlanta, 1996.
[3] (a) S.M. Shevchenko, Adv. Oxygenated Processes 4 (1995) 131–175;
(b) M. El-Sakhawy, IPPTA 14 (2002) 69–84.
[4] J. Rutkowski, Cellulose Chem. Technol. 31 (1997) 485–497.
[5] U. Hamm, L. Gottsching, Ipw (2003) 42–49.
[6] D.A. Bright, P.V. Hodson, K.-J. Lehtinen, B. McKague, J. Rodgers, K. Solomon, Pulp Pap. Canada 101 (2000) 53–55.
[7] A.L. Andrady, Y. Song, V.R. Parthasarathy, K. Fueki, A. Torikai, Tappi J. 74 (1991) 162–168.
[8] (a) B. Marcoccia, D.A.I. Goring, D.W. Reeve, J. Pulp Pap. Sci. 17 (1991) J34–J39;
(b) B. Marcoccia, D.W. Reeve, D.A.I. Goring, J. Pulp Pap. Sci. 19 (1993) J97–J101.
[9] (a) J. Abbot, Y.-P. Sun, Appita J. 46 (1993) 198–202;
(b) Y.-P. Sun, J. Abbot, C.-L. Chen, Appita J. 47 (1994) 459–462;
(c) E.A. Nascimento, A.E.H. Machado, S.A.L. Morais, L.B. Brasileiro, D. Piló-Veloso, J. Braz. Chem. Soc. 6 (1995) 365–371;
(d) M. Koplík, M. Milichovský, Cellulose Chem. Technol. 32 (1998) 349–363.
[10] (a) J.D. Green, J. Wood Chem. Technol. 6 (1986) 45–71;
(b) A.E.H. Machado, R. Ruggiero, M.G.H. Terrones, A. Nourmamode, S. Grelier, A. Castellan, J. Photochem. Photobiol. A: Chem. 94 (1996) 253–262;
(c) R. Ruggiero, A.E.H. Machado, D. da Silva Perez, S. Grelier, A. Nourmamode, A. Castellan, Holzforschung 52 (1998) 325–332;
(d) L.A. Lucia, K.-O. Hwang, Spectrum, vol. 14, Bowling Green, OH, US, 2001, pp. 8–14.
[11] D. da Silva Perez, A. Castellan, S. Grelier, M.G.H. Terrones, A.E.H. Machado, R. Ruggiero, A.L. Vilarinho, J. Photochem. Photobiol. A: Chem. 115 (1998) 73–80.
[12] (a) A. Castellan, D. da Silva Perez, A. Nourmamode, S. Grelier, M.G.H. Terrones, A.E.H. Machado, R. Ruggiero, J. Braz. Chem. Soc. 10 (1999) 197–202;
(b) D. Da Silva Perez, A. Castellan, A. Nourmamode, S. Grelier, R. Ruggiero, A.E.H. Machado, Holzforschung 56 (2002) 595–600.
[13] The brightness and yellow index obtained in our experiments were calculated from reflectance UV–vis spectra of one paper sheet by a computer program; therefore the values differ from standard ISO measurements.
[14] The original data are provided in the Supplementary data.
[15] H.H. Jaffé, M. Orchin, Theory and Application of Ultraviolet Spectroscopy, John Wiley & Sons, Inc, New York, 1962, chapter 12.
[16] J.A. Barltrop, Pure Appl. Chem. 33 (1973) 179–195.
[17] B.L. Browning, Methods of Wood Chemistry, vol. II, Interscience, 1967, p. 537: DP is calculated as, $DP = [\eta] \times 190$, where $[\eta]$ is limiting viscosity.