Yellowing Inhibition of Bagasse Chemimechanical Pulp

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ABSTRACT

Papers made from unbleached and bleached bagasse chemimechanical pulp were chemically modified by acetylation. The effects of irradiation on unbleached and bleached also reduced papers of bagasse chemimechanical pulp before and after acetylation were investigated in this study. Chemimechanical pulp was prepared from bagasse and then bleached with hydrogen peroxide. Unbleached and hydrogen bleached pulps were reduced by Sodium borohydride in different procedures. Paper sheets were prepared from pulps and then acetylated using a technical grade of acetic anhydride. Accelerated photo-aging was run on the samples using fluorescent lamps to verify photo-stability of paper sheets before and after pretreatments. Brightness reversion (as Post-color number) and other optical properties of the paper sheets were measured. Efficient inhibition of photo-yellowing of papers made from bagasse CMP was achieved by acetylation. The acetylated unbleached CMP was noticeably photo-bleached during irradiation. Sodium borohydride reduction followed by acetylation had the same effect as acetylation alone at the same degree of reaction time and reductive treatment did not affect the yellowing rate to any great extent. The pre-reduced, acetylated unbleached papers were, however, not brightened during irradiation. Calculation done by Kubelka-Munk equation showed that reductive treatment had little effect in reducing the photo-yellowing of paper made from CMP pulp; a small stabilization effect was observed in the case of bleached CMP, while unbleached CMP was slightly more prone to discolor in the later phase of photo-reversion. The improved stability towards light may was closely related to the decrease in the phenolic hydroxyl content as a result of blocking by acetyl groups during treatment with acetic anhydride. The results support the hypothesis that phenolic hydroxyl has an important role in the process of photo-reversion of high-yield pulps. The results obtained in this study demonstrate that the acetylation of paper manufactured from peroxide bleached Bagasse CMP significantly retards light-induced discoloration. The inhibition of yellowing is connected with a decrease in the phenolic hydroxyl content of both unbleached and peroxide bleached papers.

Keywords: acetylation, photo-discoloration, brightness, chemimechanical pulp, sodium borohydride, bagasse.

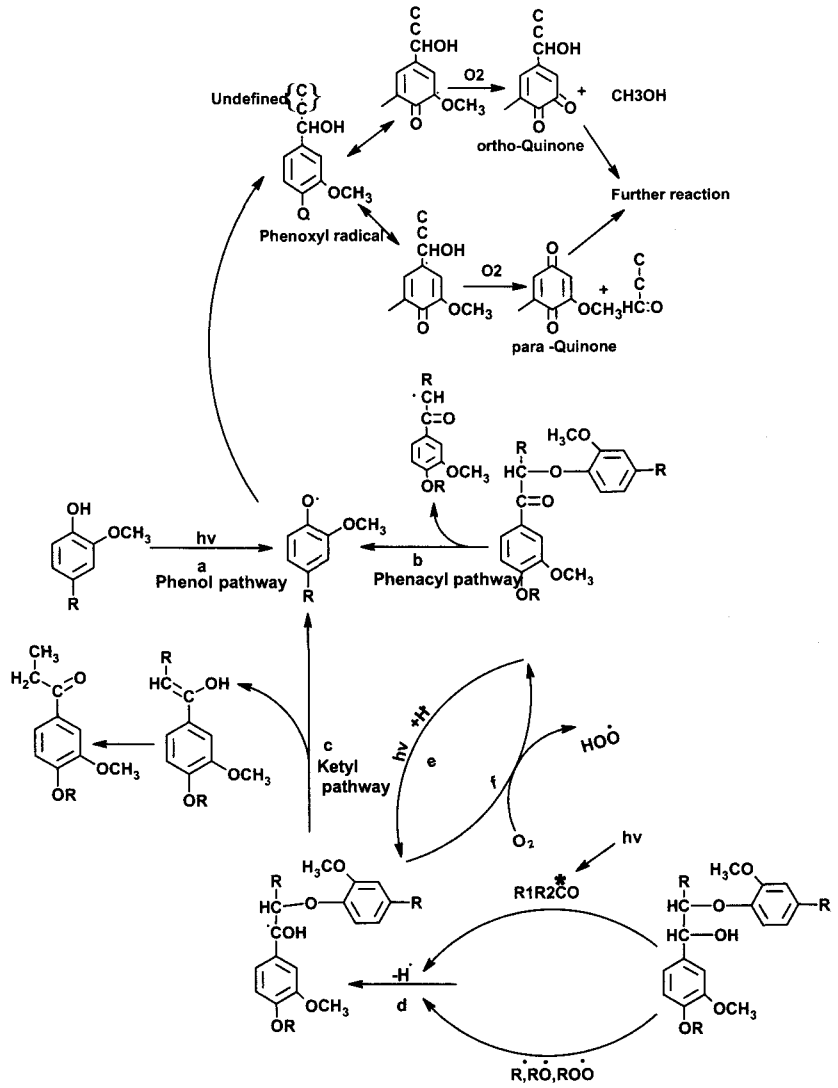
INTRODUCTION

There is a great potential in using mechanical pulps in high value applications. Today, lignin-rich pulps are primarily used in low-value and short-life products such as newsprint, catalogue papers and magazine papers. The major draw back that prevents a more wide spread utilization of high-yield pulps in high quality printing papers is the difficulty in maintaining their bleached brightness over the product lifetime. When exposed to light, lignin containing pulps and papers undergo color reversion (photoyellowing) that is mainly due to the interaction of lignin functional groups with the UV portion of sunlight.1 Photoyellowing has an industrial and environmental relevance and in the last twenty years a considerable effort has been made to understand the mechanistic aspects of this process (1-5)

Schemes 1 shows the proposed reaction pathways for the formation of radicals (phenoxyl, ketyl, *etc.*) and those for the formation of chromophores (initially quinines) (1). Such a knowledge is of fundamental importance for the prevention or reduction of photoyellowing by means of chemical modification of functional groups, use of additives such as antioxidants, reducing agents, or UV screens (2,5-8). Three main reaction pathways have been identified for the photoyellowing process: (1) formation of phenoxyl radicals by direct excitation or hydrogen atom transfer reactions of phenolic groups and further oxidation of phenoxyl radicals to colored products (*phenol pathway*, Scheme 1, path a) (9) (2) â-cleavage of R-aryloxy substituted aromatic ketones to give a pair of phenoxyl and phenacyl radicals which are precursors of colored products (*phenacyl pathway*, Scheme 1, path b) (9) and (3) â-cleavage of ketyl radicals (Scheme 1, path c) formed either by photoreduction of aromatic ketones (path e) or by hydrogen abstraction from arylglycerol â-aryl ethers (path d) with formation of phenoxyl radicals and enols which tautomerize to give aromatic ketones (*ketyl pathway*).

Important intermediates in the photoyellowing process are phenoxy free-radicals, which are oxidized in the presence of ground-state oxygen into chromophoric structures of the quinonoid type (4). The discoloration reactions involve complex and inter-related pathways for the formation of phenoxyl free-radicals. The photo-induced yellowing has also been attributed to the photoreactivity of phenolic chromophores absorbing ultraviolet radiation above 300 nm and giving phenoxl radicals by direct photolysis mechanism without any need to photo-sensitizers (8).

Chemical modification of potential chromophoric groups has been examined (10-15). Derivatization of hydroxyl groups by alkylation or acylation has been more successful. Acetylation of ground wood pulps improved the resistance towards light and, in some cases, also photobleached the pulp (11, 16, 17). Acetylation can also inactivate or remove some chromophores initially present in unbleached or dithionite bleached pulps. The improved photostability observed for acetylated or methylated pulps was, however, accompanied by a substantial decrease in strength. A previous investigation has shown that the acetylation of paper made from spruce TMP and aspen CTMP rapidly removes phenolic hydroxyl groups, and that the paper strength properties are remained almost unaltered in the dry state but considerably increase in the wet state (18). It was therefore of interest to examine how the photo-stabilization of papers made from bagasse (as a non wood resource of fibers) CMP pulp was affected by different degrees of acetylation. The effect of sodium borohydride reduction alone or in combination with acetylation is also reported in the present paper.



Schamel. Proposed reaction pathways in the formation of radicals during photoyellowing

EXPERIMENTAL

Materials

Depithed bagasse, obtained from Pars Pulp and Paper mill. The Chemimechanical pulp was prepared by chemical pre-treatment of bagasse with sodium sulfite (8%) and sodium hydroxide (4%) for 20 minutes in 95°C. CMP pulp was bleached with hydrogen peroxide according to the method proposed by Ni *et al.*(19) under following conditions: Hydrogen peroxide 5%, sodium hydroxide on hydrogen peroxide ratio 0.8, DTPA (*di-ethylene tri amine penta-aceticacid)* charge 0.5%, $MgSO_4$:0.05%,Na_2SiO_3:3%, pulp consistency:18%, time:2 hour, temperature: 65°C.

The procedure applied for sodium borohydride reduction was according the method specified by Ek *et al.* (17), with some modifications. Hydrogen peroxide bleached bagasse CMP pulp (1% consistency) and EDTA (*ethylene di amine tri-aceticacide*) (0.15% consistency) were suspended in water and stirred for one hour at room temperature, after which it was washed and filtered. The pulp was then suspended in water (1% consistency) and sodium borohydride was added (5% on pulp weight basis). The pulp suspension was stirred at room temperature for 3 days, followed by filtering, washing with water and air-drying at room temperature.

Acetylation

The paper sheets were acetylated using a technical grade of acetic anhydride (liquid phase, without any catalyst, 100 °C) for 10, 25, 60 and 120 minutes to obtain different degrees of acetylation. The procedure was as follow:

Conditioned handsheets were placed in a preheated flask with an excess of acetic anhydride. After the reaction time was completed, the handsheets were immersed in water to stop the acetylation reaction. The acetylated paper were then thoroughly washed with water to remove remaining chemicals and thereafter pressed for five minutes at 400 kPa. The sheets were dried on the press plates (24h) and then conditioned at 23 °C and 50% r.h. according to TAPPI T205 om-88 before analysis. In order to study the effect of pulp acetylation and comparing the results with those of acetylated handsheets, CMP pulp was also acetylated using the same procedure.

Accelerated photo-aging

The irradiation procedure was the same as that described by Gellerstedt *et al.* (20). Handsheets were fastened onto a vertical fiberglass cylinder rotating at 2 r.p.m. The cylinder was surrounded by 12 vertical fluorescent tubes (6 Tungsram 20W-F74 and 6 Philips F20W/ 350 BL) placed symmetrically inside an outer cylinder made of fiberglass. The combination of fluorescent tubes was chosen to simulate sunlight, i.e. both UV and visible irradiation. The distance between the paper cylinder and the light-tubes was 6 cm. The temperature was kept close to room temperature with 3 fan placed in top and bottom of the cylinder.

Optical properties

Specific light absorption (k, 557 nm) and light scattering(s, 557 nm) coefficients were calculated using the Kubelka-Munk theory. The degree of brightness reversion during irradiation was expressed as the Post Color (PC) number (at 457nm). The Kubelka-Munk equation was used to calculate $k.s^{-1}$ according to Eq. 1, Giertz (21):

$$(k.s^{-1}) = [(1 - R_\infty)^2 . (2 R_\infty)^{-1}] \qquad (1)$$

Where R_∞= reflectance of an optically thick sheet
And the PC- number was then calculated according to Eq. 2:

$$PC = 100[(k.s^{-1})_t - (k.s^{-1})_{t=0}] \qquad (2)$$

Where t = irradiation time, k = light absorption coefficient and s = light scattering coefficient.

Instruments

Brightness (R_∞, 457 nm) and CIELAB colour scales (L*, a*, b* values) were measured on 60 $g.m^{-2}$ paper sheets using a Technibrite Micro TB-1C spectrophotometer.

RESULTS AND DISCUSSION

Irradiation of unbleached and hydrogen-peroxide bleached CMP pulp

The brightness (R_∞) and change in light absorption coefficient (Δk) of bagasse CMP paper samples after irradiation for up to 100 hours are shown in Fig. 1. The light- induced yellowing is characterized by a rapid initial phase followed by a slower phase, as reported previously (17, 22, 23). It is also evident that the degree of yellowing is more pronounced for the hydrogen peroxide bleached CMP than for the unbleached CMP (7). The brightness values for unbleached and bleached papers were 30% and 40% respectively. Regarding the trend of brightness decrease of unbleached papers, it is expected that by continuing the irradiation, the final brightness of two samples end up to the same values. The yellowing evaluated accordingly to the CIELAB system, was manifested as an increase in b^* and a decrease in L^* that is equivalent to a yellower colour of paper. The changes in H_2O_2 bleached CMP is more evident. This means that applying hydrogen peroxide could lead to formation of some light sensitive structures which can generate colored components during photo aging. In other words, the brightness gain after bleaching is temporary. The brightening effect of hydrogen peroxide has been attributed to reactions with chromophoric structures in the lignin such as coniferaldehyde units and quinonoide structures. Pan *et al.* (1994) reported the major change that occurs on bleaching is a decrease in the content of coniferaldehyde structures present in the lignin (24). It was also shown that the overall structure of the lignin was unaffected by the bleaching conditions. The partial elimination of coniferaldehyde structure by treatment with hydrogen peroxide has also been reported by other investigator (25-29). Because of incomplete accessibility, the elimination of this structure is not possible under commercial bleaching conditions. Model compound studies have, however, shown that coniferaldehde structures are readily cleaved by alkaline hydrogen peroxide yielding aromatic aldehydes (30).

According to Casstelan et al. (1993), methoxyhydroquinones formed during hydrogen peroxide bleaching has a key role in brightness reversion of bleached mechanical pulp (31). Furthermore, it has been shown that diguaiacylstilbenes are to a large extent responsible for the initial fast discoloration of high-yield pulps (32,33). Briefly, stilbene, methoxyhydroquinone and coniferaldehyde units also quinonoid chromophores are present after peroxide bleaching (23).

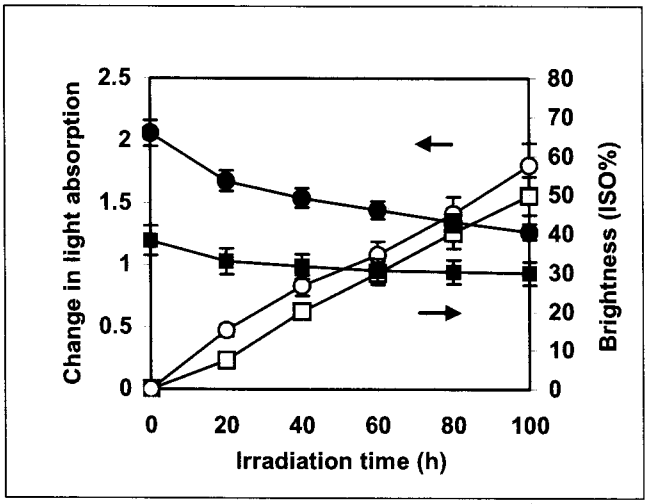


Fig. 1, Brightness (R_{∞}, $_{457}$, filled symbols) and the difference in light absorption coefficient (Δk_{457}, unfilled symbols) after long-term light-induced aging of Bagasse CMP paper samples. (□), Unbleached CMP; (○) Hydrogen- peroxide bleached CMP.

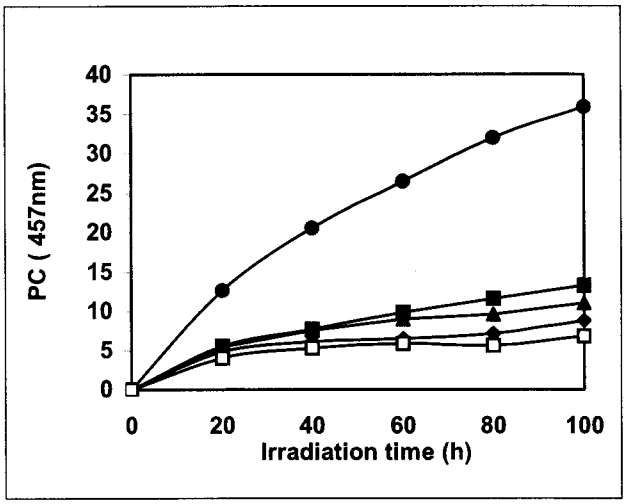


Fig. 2, The effect of acetylation on the post colour (PC) number after accelerated long-term irradiation of unbleached and acetylated (100 °C) unbleached Bagasse CMP paper samples. The numbers in brackets denote the acetylation time (minutes). (●), control; (■), (10); (▲), (25); (♦), (60); (□), (120).

Irradiation of acetylated unbleached Bagasse CMP

The influence of acetylation on the degree of brightness reversion indicated by PC number at 457 nm is shown in Fig. 2.

The acetylation treatment efficiently inhibited light-induced yellowing even after severe irradiation. It is clear that most of the Photostabilization obtained appears after a short period of acetylation (Fig. 3.). Brightness changes due to irradiation have been illustrated in Fig. 4. As it could be seen in the Fig. 4, reduction with sodium borohydride, does not affect the process of yellowing of paper sheets. The brightness level of untreated papers was 33% after 40 hours irradiation, *i.e.* a decrease of only 5 brightness units compared to the non-irradiated control. The corresponding value for the reduced papers was 41 %(a decrease of more than 10 unites). Acetylation efficiently preserves brightness value of the paper even after very intense irradiation. The PC number is less than 5 even after 20 hours irradiation. The corresponding point for unacetylated sodium borohydride reduced paper has been attained after 1-2 hours irradiation. The effect of acetylation could be well evaluated by comparing the brightness changes followed by optical treatments (Fig. 4). The brightness

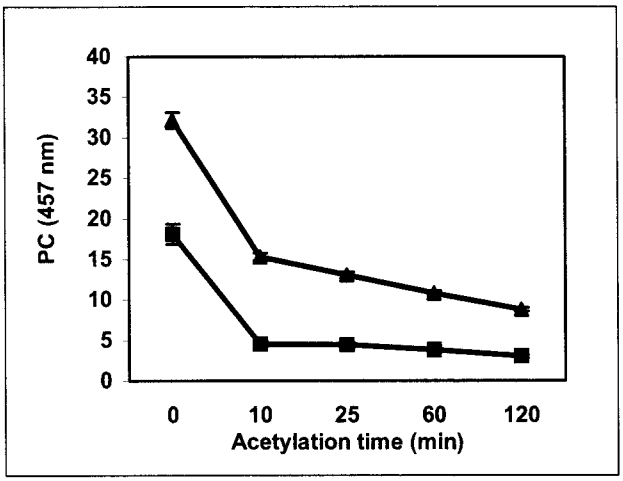


Fig. 3, Relationship between the post colour (PC) number and acetylation time (min) of unbleached CMP paper samples. The relationship is given at two different irradiation times; 20 (■) and 100 (▲) hours.

of acetylated papers after 40 hours irradiation was 50 % which still is 18% more than that unacetylated papers.

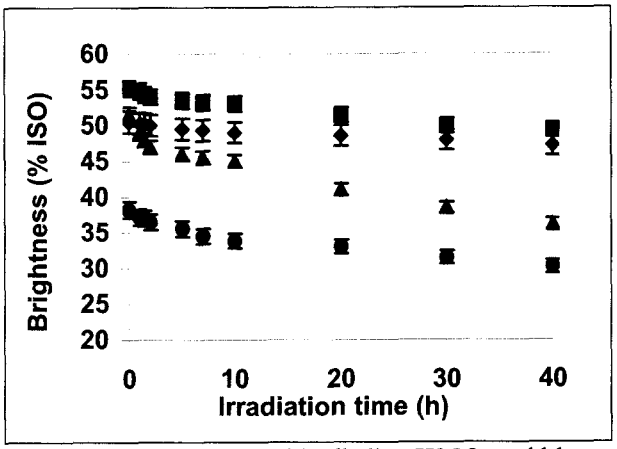


Fig. 4, Effect of irradiation on brightness ($R_{\infty, 457}$) for differently treated unbleached Bagasse CMP papers. Control, (●); Acetylated, (♦);$NaBH_4$-Reduced, (▲);$NaBH_4$-Reduced and acetylated,(■) .

Yellowing of hydrogen peroxide bleached Bagasse CMP papers

The influence of acetylation n the light–induced yellowing of hydrogen-peroxide bleached CMP paper samples is shown in Fig. 5. As in the case of unbleached CMP; acetylation significantly retards the detrimental effect of light exposure. The structures causing discoloration of hydrogen-peroxide bleached CMP are easily derivatized on acetylation. However, the brightness levels after long-term irradiation of acetylated bleached paper samples were almost the same as the values obtained for acetylated unbleached CMP compared at the same degree of acetylation time. The increase in brightness of about 15 units that occurs on bleaching with H_2O_2 could not be preserved by acetylation. As it could be seen the degree of yellowing of acetylated peroxide bleached CMP paper sheets is more pronounced than the yellowing of an acetylated unbleached CMP papers. The removal of most of the coniferaldehyde and quinonoid units in the lignin moiety during treatment with alkaline H2O2 could be one explanation of the lower inhibiting effect observed with acetylated bleached CMP.

The influence of acetylation and reduction on the photoyellowing of hydrogen peroxide bleached papers is shown in Fig. 6. The brightness of peroxide bleached control papers reverted somewhat more than the corresponding unbleached papers throughout the whole investigated irradiation interval. It was further found that the reductive treatment lowered the yellowing rate of the peroxide bleached papers compared with that of the untreated control. Acetylation increased the stability towards light-induced oxidation of both bleached CMP and reduced and bleached CMP papers in a manner analogous to that observed for unbleached papers. Brightness after 20 hours irradiation was 57% for reduced, 61.3% for acetylated and 66.7% for reduced and acetylated bleached CMP papers. The corresponding value for the bleached control was 53.6%.

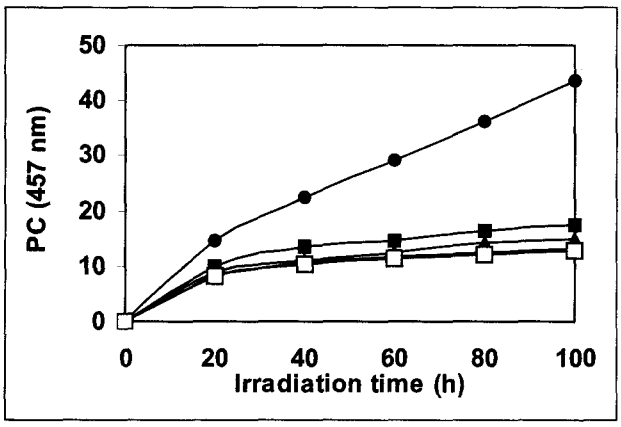


Fig. 5, The effect of acetylation on the post colour (PC) number after accelerated long-term irradiation of hydrogen-peroxide-bleached and acetylated (100 °C) samples. The numbers in brackets denote the acetylation time (minutes). (●), control; (■), (10); (▲), (25); (♦), (60); (□), (120).

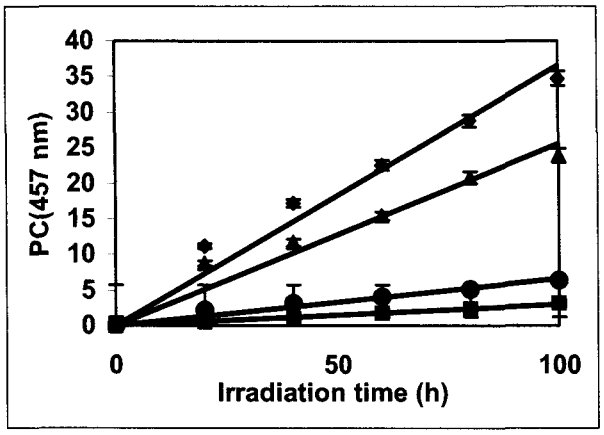


Fig. 6, Effect of irradiation on post colour (PC) number of differently treated hydrogen-peroxide-bleached bagasse CMP papers. Control, (♦); Acetylated, (●);$NaBH_4$-Reduced, (▲); NaBH4-Reduced and acetylated, (■).

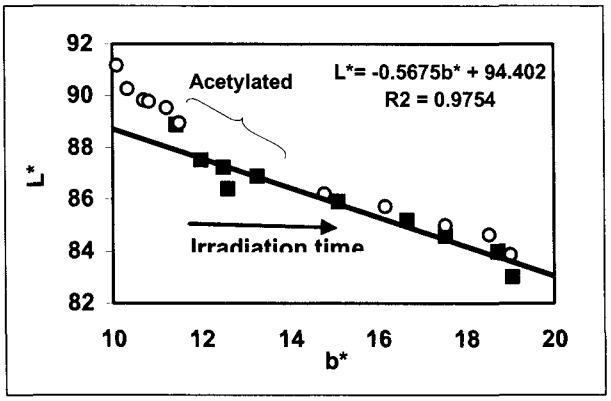


Fig. 7, Lightness (L*) versus yellowness (b*) for hydrogen peroxide bleached bagasse CMP papers subjected to irradiation.

Fig. 7 shows the lightness plotted against the yellowness for the differently treated bleached papers. Borohydride reduction eliminated chromophores responsible for the yellow colour, whereas acetylation generated structures that increased b^*. The lightness was in both cases unaffected by reduction and/or acetylation. Irradiation increased b^* and decreased L^* for all papers, but, the extent of the change was smaller for the acetylated papers. The results obtained from the reductive treatment indicate that the bleached CMP contained some photo reactive structures that could be partly eliminated or inactivated during reduction, whereas the colour-forming structures in unbleached CMP were unreactive towards $NaBH_4$-reduction (Fig. 6). A similar result, for the first phase of yellowing (PC values up to 4), was reported for sodium borohydride stone groundwood pulp from spruce (34). According to these authors, the limited effect of reduction on brightness stabilization indicates that cleavage of phenacyl aryl ether linkages is of minor importance in the initial phase of discoloration. Furthermore, reduction of peroxide bleached CTMP was reported to have no significant effect on chromophore formation (8). Sodium borohydride is able to reduce quinones and carbonyl groups to hydroquinones/catechols and alcohol groups, i.e. structures that may be acetylated. In spite of this, reduction before acetylation did not affect the yellowing rate to any great extent. This is contradictory to earlier reported results for unbleached and bleached groundwood pulps where sodium borohydride reduction before gas phase acetylation greatly diminished the stabilizing effect of acetylation (17).

The acetylation experiments indicate that the brightness reversion can be significantly reduced or eliminated even at low degrees of acetylation. Fig. 8 shows the relationship between PC-number and acetylation time. The inhibiting effect of acetylation seems to proceed more or less in two phases, an initial phase with a rapid decrease in chromophores formation followed by a slower phase. This means that there are some structures that can easily be removed by acetylation and which significantly contribute to brightness reversion. The other leucochromophoric structures demand longer reaction times to be inactivated.

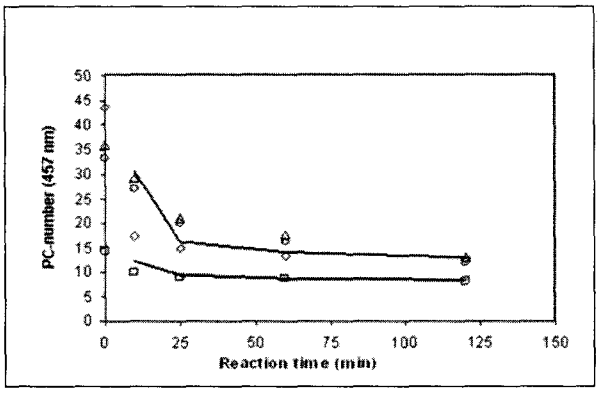


Fig. 8, the effect of acetylation on the PC-number after accelerated light-induced aging (10 hours) for differently treated bagasse CMP papers.acetylation was performed at 100 °C. □, unbleached; ◊, unbleached, NaBH4-reduced; ○, bleached; Δ, bleached, NaBH4-reduce

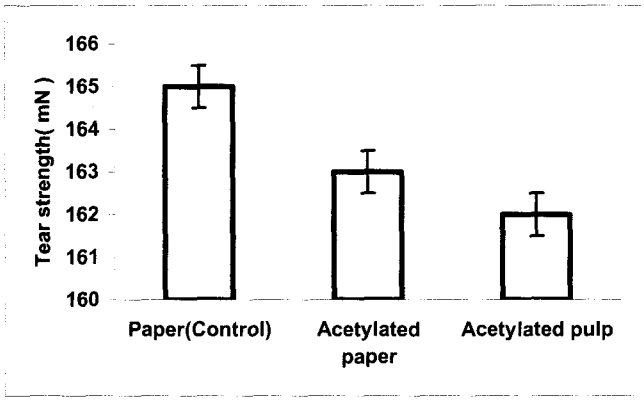
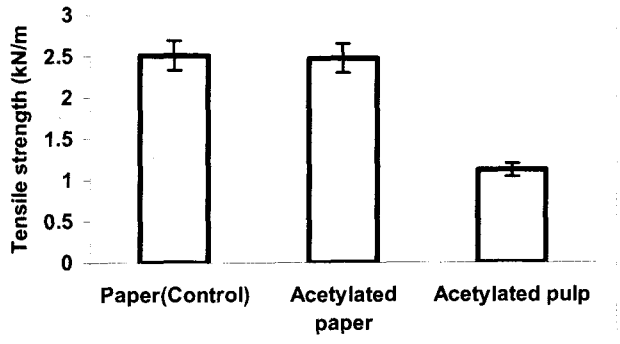


Fig. 10, Effect of acetylation on tensile strengths of pulp and paper sheet.

Mechanical Properties of Acetylated Papers

The reaction was carried out on already formed paper sheets in order to preserve the original strength properties to avoid the reduction in strength that occurs when pulp is drivatized. Fig.s 9 and 10 show the difference between tear and tensile strengths of pulp and paper sheets. It is clear that the strength properties of pulp decreased considerably through acetylation but in those of paper sheets remains constant or has less change during acetylation. Originally, acetylation causes blocking of hydroxyl groups which may contribute to form hydrogen bonds in pulp and this bear to loss of mechanical properties of the acetylated pulp comparing to paper sheets.The effect of acetylation on tensile strength, tear strength of unbleached and hydrogen peroxide bleached CMP paper has been illustrated in Fig.s 11 and 12. Both the tear resistance and the tensile strength were essentially remained unaffected by the acetylation treatment. Since, lignin is the most easily acetylated wood component, it is expected that in low reaction systems (without any catalyzes, low reaction temperature) the mechanical strengths maintained unchanged or diminished to very low extent. The same investigation carried out before showed that the mechanical properties of pulp decreases through pyridine catalyzed acetylation in gaseous phase (15, 16).

Fig. 9, Effect of acetylation on tear strengths of pulp and paper sheet.



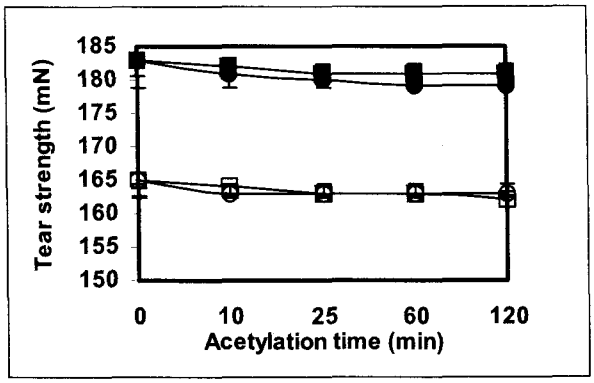


Fig. 11, Tearing strength (mN) versus reaction time for Bagasse CMP. Acetylation temperatures are givenwithin parenthesis. (□), Bleached, 80 °C; (○), bleached 100°C; (■), unbleached 80 °C; (●), unbleached 100°C.

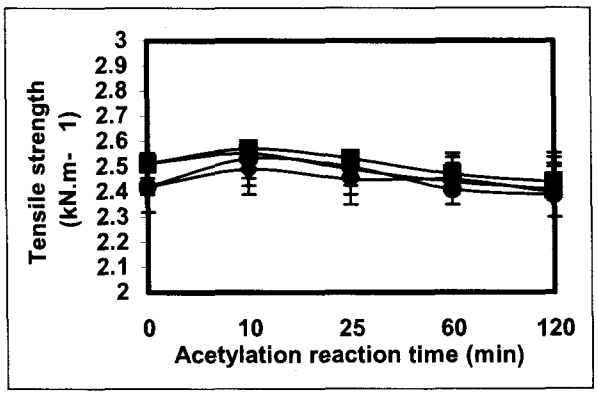


Fig. 12, Tensile strength ($k.Nm^{-1}$) versus reaction time for Bagasse CMP. Acetylation temperatures are given within parenthesis. (▲), Bleached, 80 °C; (■),Bleached, 100°C; (♦), unbleached,80 °C; (●) , unbleached,100°C.

Furthermore, the mechanical properties of the paper samples are affected by the moisture content. The wet strength increased with increasing degree of acetylation, which can be explained by the fact that hydrophilic hydroxyl groups are replaced with more hydrophobic acetyl groups so that the amount of bonded water is reduced. This is in accordance with the results obtained for acetylated fiber boards (23) and for acetylated flake boards (24). Acetylation for short period of times cause up to 4.5% increase in tensile strength. As it is evident in Fig. 11 , tear strength of unbleached and bleached acetylated CMP paper is slightly lower than unacetylated samples. Tensile strength and tearing resistance depend on the number of hydrogen bonding sites and on the strength of individual fibers. Consequently, acetylation of paper seems neither to have diminished the number of hydrogen-bonding between fibers nor to have weakened the fiber structure to any great extent.

CONCLUSION

The results obtained in this study demonstrate that the acetylation of paper manufactured from peroxide bleached Bagasse CMP significantly retards light-induced discoloration. The inhibition of yellowing is connected with a decrease in the phenolic hydroxyl content of both unbleached and peroxide bleached papers. This strongly supports the hypothesis that phenolic hydroxyl groups are involved in the discoloring reactions. The reductive treatment did not affect the yellowing rate to any great extent; a small stabilization effect was observed for unbleached CMP were slightly more prone to discolor after long irradiation times. Borohydride reduction followed by acetylation had the same effect as acetylation alone when the comparison was made at the same degree of acetylation time. Acetylation reaction, even for short period of times, cause to increasing the wet strength of bagasse CMP paper sheets, considerably. On the other hand, acetylation does not affect the strength properties like tensile strength and tear resistance. Tear resistance is slightly decreased while tensile strength is slightly increased due to treatment with acetic anhydride.

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