EFFECT OF BLEACHING PROCEDURE TYPE ON THE AGING RESISTANCE OF CHEMICAL-MECHANICAL PULP

Rumyana Boeva, Greta Radeva

University of Chemical Technology and Metallurgy
8 Kl. Ohridski, 1756 Sofia, Bulgaria
E-mail: grradeva@uctm.edu

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ABSTRACT

Chemical-mechanical pulping methods are for producing pulp from high-yield fiber materials derived from poplar wood. The samples are subjected to a single-stage bleaching with H\textsubscript{2}O\textsubscript{2} and a two-stage procedure combining the effect of H\textsubscript{2}O\textsubscript{2} and Rongalyl C. A kinetic investigation of the bleaching pretreatment effect on the thermal age of chemical–mechanical pulp is presented. Comparative investigations are carried out with pulp chips which were not subjected to preliminary bleaching. The brightness reversion is followed within the interval from 6 to 48 hours at constant temperature. The ageing process is described by an exponential kinetic equation. The initial and the current rates of the process are determined. It is found that they decrease with increase of the extent of the process proceeding. Microscopic images of the samples are taken after preparation, bleaching and ageing, correspondingly.

Keywords: high-yield fiber materials, chemical-mechanical pulp, bleaching, kinetics.

INTRODUCTION

Brightness reversion is a process resulting in changes with time of the properties of fiber materials under the influence of light, air, humidity and heat. In fact the strongest effect is that of the heat and light. Pulp ageing which is largely determined by the lignin content results in further decrease of whiteness and strength of the samples, as well as changes in their chemical composition and optical properties [1 - 3].

The high-yield fiber materials (HYFM) finding a wide application in production of various types of paper and cardboard are not stable to ageing. As their optical and physical-mechanical properties deteriorate rapidly the area of their application is limited. The lignin content in HYFM is high and hence their ageing is faster than that of bleached one. The yellowing starts with the oxidation of the lignin phenolic hydroxyl groups, which in turn leads to subsequent formation of quinones, quinone-methydes and cyclohexadienes [4 - 8].
ing agents during the second stage provides reduction of the residual chromophores or those additionally formed in the course of the oxidation which in turn results in brightness increase. The process is limited to lignin’s transfer, mainly on the fibers’ surface, from an oxidized to a reduced form [10 - 12]. In case of bleaching with hydrogen peroxide, the whiteness of HYFM increases by about 10 units. It provides better stability and besides low cost bleaching agents are used. It is worth noting that the yield of the production is slightly decreased [10 - 12].

Ageing is a complicated process because the rate of changes in the fiber materials depends on the temperature, on the amount of the bleaching reagents, the degree of the delignification, the mass concentration, the bleaching sequence, the process duration, as well as on other factors. The kinetics of the process referring to unbleached wood chips has been successfully described by the exponential kinetic equation valid for processes taking place on uniformly inhomogeneous surfaces [13].

The aim of this work is to proceed further studying the kinetics of thermal ageing of chemical-mechanical pulp obtained from poplar wood. The data obtained may facilitate the elucidation of its mechanism and hence its optimization taking also into consideration the advantages of the methods of treatment and storage.

**EXPERIMENTAL**

**Chemical-mechanical pulp preparation**

The experiments were carried out with chemical-mechanical pulp (CMP) obtained from rapidly growing poplar wood of increased density. The type Populus deltoides cultivar Hunneg was chosen because of its high cellulose content of 50.4 % and relatively low lignin content of 21.2 %. After roots removal the wood was chopped into strips of standard dimensions of 15 mm x20x3 mm.

CMP was obtained under the following conditions: 100 g of absolutely dry strips of a hydromodule of 1:5 were treated with 7 % NaOH and 5 % Na$_2$SO$_3$ for 120 min at 80°C. The mass of the absolutely dry strips used determined the concentration of H$_2$O$_2$. In this case it was 2 %. CMP yield was 88 % (determined by the weight method), while the degree of refining was 14°SR. (the measurements were conducted on a Schopper-Riegler (“SR) equipment in correspondence with the EN ISO 5267 – 1/AC:2004). The application of the weight method required to soak the strips for 24 hours in distilled water, to wash them to a neutral reaction and then to dry them at a temperature of 105°C to a constant weight. Non-treated samples were investigated as well aiming a comparative study of the bleaching effect on the kinetics of CMP thermal ageing.

**CMP bleaching**

CMP prepared under the conditions pointed above was subjected to a two-stage bleaching, i.e. bleaching with an oxidation reagent: H$_2$O$_2$ (I stage) followed by bleaching with the reducing agent Rongalyt C (II stage). The first stage was applied to CMP for 120 min at 80°C. In this case the pH was 10.5, while H$_2$O$_2$ concentration was 2 %. The following additives used: 2 % NaOH, 5 % Na$_2$SiO$_3$, 0.5 % MgSO$_4$ and 0.5 % EDTA (Na$_2$C$_{10}$H$_{14}$O$_8$N$_2$2H$_2$O) as a complexing agent.

All amounts pointed so far were calculated in respect to the absolutely dry fibrous material used. The procedure applied required to place the sample in a polyethylene bag to bring it to the temperature value envisaged and then to introduce the bleaching solution under constant stirring aiming complete homogenization. Then the sample treated had to be transferred to the thermostated reaction vessel where the stirring continued. Upon the first stage completion the fibrous material had to be washed until reaching a neutral reaction. Rongalyt C (NaHSO$_2$.CH$_2$O.2H$_2$O) and EDTA were introduced during the second stage of the bleaching process which was carried out for 60 min at 80°C.

The consumption of Rongalyt C and EDTA was 1.5% and 0.5%, correspondingly. In this case the pH was 5. The bleaching procedure was analogous to that applied during the first stage. The bleached fibrous material obtained was finally washed until a neutral reaction was obtained.

**CMP ageing**

Samples of unbleached, single-step bleached and two-steps bleached CMP were subjected to thermal ageing for 48 hours at a temperature of 105°C. Their brightness and yellowness was determined using “Brightness R$_{457}$, (in correspondence with ISO 2470:2002) prior to and after the ageing. Furthermore, the degree of brightness of the bleached samples was determined at the 6th, 12th, 24th, 36th and the 48th hour of the process aiming to study the kinetics of the ageing process.
Microscopic analysis

Microscopic images were taken of all CMP samples investigated immediately after preparation, bleaching and ageing, respectively. OLYMPUS BX 53 was used. Prior to this a small amount of each sample was treated to produce a fibrous mass, which was then treated with distilled water aiming to obtain a homogeneous suspension of a concentration of 0.05 %. After drying a solution of Cl-Zn-I (Herzberg reagent) was applied in correspondence with ISO 9184-3:1990.

RESULTS AND DISCUSSION

The effect of ageing of CMP is followed on the ground of the comparative investigation of unbleached and bleached samples. The initial brightness value of the unbleached samples ($W_{0,\text{unbleached}}$) is 42.59 %. That of the single-step bleaching is 57.05 %, while the brightness in case of the two step-procedure is 63.15 %. It is seen from Table 1 that the bleached samples have higher degrees of brightness than those of the unbleached one. The comparison carried out shows that the single-step bleaching results in brightness increase of ca 25 %, whereas the two-step process provides brightness increase of ca 32 %. It is worth noting that the difference between the two procedures effects amounts to ca 9.5 %.

The results presented evidence as well that the brightness of the bleached and the unbleached samples shows reversion with time. The final brightness for all three types of samples decreases by 4.5 - 5 units when compared to the initial one as a result of the ageing process. Table 1 shows as well that the yellowness increases with time irrespectively of the type of the samples studied. This increase is about 4 units, i.e. approximately identical for all samples. The smallest value of 3.78 units is obtained for CMP subjected to a two-stage brightening.

The process of thermal ageing is a complex process from chemical point of view. The brightness reversion in this case is attributed to the oxidation of the phenolic hydroxyl groups of lignin which results in increase of the number of chromophore groups. Besides, the bleaching of HYFM is aimed at discoloration of lignin and the other colouring compounds but with the exclusion of their dissolution. This is achieved through modification of the chromophore groups and regrouping of the atoms in those parts of the molecules which absorb electromagnetic energy in the visible spectrum. The bleaching agents affect lignin mainly through some of its functional groups responsible for its colour and that of the fibrous material. The dark shade is due to residual carbonyl groups conjugated to the benzyl nuclei in the lignin molecule and to quinone structures obtained in the oxidation process. The specifics of the process assume in fact the presence of energy and entropy inhomogeneity of the system.

A comparative kinetic investigation is carried out aiming the evaluation of the effect of the brightening consistency on the final product and the elucidation of the mechanism of the process. The consideration of the characteristics of the thermal ageing kinetics is done with the introduction of the kinetic variable, $\alpha$:

$$\alpha = \frac{W_{0} - W}{W_{0}}$$

(1)

where $W_{0}$ is the initial brightness value in % (ISO),

<table>
<thead>
<tr>
<th>Fiber material</th>
<th>0</th>
<th>6</th>
<th>12</th>
<th>24</th>
<th>36</th>
<th>48</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unbleached</td>
<td>42.59</td>
<td>44.95</td>
<td>41.88</td>
<td>45.26</td>
<td>40.70</td>
<td>46.38</td>
</tr>
<tr>
<td>One step bl</td>
<td>57.05</td>
<td>35.61</td>
<td>56.70</td>
<td>36.63</td>
<td>55.86</td>
<td>37.60</td>
</tr>
<tr>
<td>Two steps</td>
<td>63.15</td>
<td>30.56</td>
<td>62.72</td>
<td>30.95</td>
<td>61.95</td>
<td>31.15</td>
</tr>
</tbody>
</table>

Table 1. Values of the degree of brightness, $W / \%$ and yellowness, $Y / \%$ of the fibrous material in the course of the ageing process.
while \( W \) in % (ISO) is the current value connected with the time of the treatment. The variable \( a \) can be also considered as an extent of the thermal ageing proceeding or as a relative decrease of the degree of brightness in the course of the process.

The kinetic curves of the change of \( a \) with time \( t \) (h) obtained for the bleached and unbleached CMP samples are presented in Fig. 1.

As Fig. 1 shows, \( a \) increases with time for all types of samples. This increase of the kinetic variable corresponds to the increase of the extent of the process of thermal ageing, i.e. to the corresponding brightness reversion of CMP. The highest degree of thermal ageing is recorded for the unbleached samples and as it is expected, the lowest effect is recorded for two-steps bleached samples.

The applicability of the exponential kinetic equation is already verified for the process of thermal ageing of different types of fiber materials [13]. The equation is valid for processes taking place on uniformly inhomogeneous surfaces. In accord with the model of the latter [13-15] the active centres on the surface are distributed linearly in correspondence with their energy. Furthermore, the heterogeneous reaction rate decreases exponentially with \( a \) increase.

Taking into consideration the current rate defined by \( v = \frac{da}{dt} \), the exponential kinetic equation becomes:

\[
v = v_0 e^{-a\alpha}
\]

where \( v \) is the current, while \( v_0 \) is the initial rate of the ageing process. The kinetic coefficient of heterogeneity \( \alpha \) in Eq. 2 accounts for the energy and entropy heterogeneity of the system.

All kinetic curves obtained in this study are linearized in coordinates \( a \) vs. \( \ln t \) in correspondence with the approximate integral form of the exponential kinetic equation:

\[
\alpha = \frac{1}{a} \ln \left( v_0 a \right) + \frac{1}{a} \ln t \tag{3}
\]

The linear dependences obtained in correspondence with Eq. 3 are presented in Fig. 2.

The value of the slope of the lines presented (Fig. 2) provides the determination of the kinetic coefficient of heterogeneity \( \alpha \) (Eq. 3). The values of the latter are listed in Table 2. It is seen that the coefficient of heterogeneity increases with the bleaching steps increase.

The integral form of the exponential kinetic equation (Eq. 3) can be used for the determination of the initial rate, \( v_0 / h^{-1} \), of the process of thermal ageing at \( a=0 \). The values of \( v_0 \) are summarized in Table 2. It is seen from the table that the ageing proceeds with the highest initial rate in case of the sample with the highest lignin content.

Table 2. Initial rate and heterogeneity characteristics of the processes studied.

<table>
<thead>
<tr>
<th>CMP</th>
<th>( a )</th>
<th>( v_0 \times 10^3 ), h^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unbleached</td>
<td>21.7</td>
<td>9.75</td>
</tr>
<tr>
<td>One step bl.</td>
<td>22.2</td>
<td>5.5</td>
</tr>
<tr>
<td>Two steps bl.</td>
<td>23.8</td>
<td>4.7</td>
</tr>
</tbody>
</table>
The current rate of the process, $v / h^{-1}$, is estimated on the ground of Eq. 4 at a constant value of the extent of the process proceeding ($a = \text{const}$):

$$v = \frac{1}{at}$$

The values of $v / h^{-1}$ show that the rate of ageing of all samples decreases with increase of the time and the extent of the thermal ageing proceeding. The dependence $v$ vs. $a$ (Eq. 3) is illustrated in the Fig. 3.

Fig. 3 shows that the current rates decrease in the course of the thermal ageing process for all types of samples studied. It is clear that irrespectively of the high initial rates the process starts to slow down. This decrease is better outlined for the unbleached sample because of the higher lignin content. The two-steps bleached samples ageing is the slowest.

Microscopic images of unbleached fibrous materials and those subjected to a single- as well as to two-step bleaching are taken. They are illustrated in Fig. 4.

The microscopic images of the three types of CMP studied show rough and inhomogeneous fibers characteristic for the high-yield fibrous materials. The structural elements of the deciduous wood like wind-pipes, libriformic cells, fibers breakage are also seen. The latter occur most probably in the course of grinding and the subsequent chemical treatment. The two-stage bleaching results in more broken and twisted fibers whose edges are rougher. In fact no essential differences are outlined by the microscopic analysis of the three types of the fibrous materials studied.

**CONCLUSIONS**

The high-yield fibrous materials attain better optical properties depending on the method of bleaching. The combined bleaching is recommended in case a high quality white paper and a cardboard of better printing
properties are required as CMP obtained has better properties. The kinetics of the process is best described by the exponential kinetic equation valid for processes taking place on uniformly inhomogeneous surfaces. The initial and the current rates of the process are determined. It is found that they decrease with increase of the extent of the thermal ageing proceeding.

REFERENCES