KINETIC ANALYSIS OF THE EFFECT OF BLEACHING AND TEMPERATURE INCREASE ON THE AGEING OF A CHEMICAL-MECHANICAL PULP DERIVED FROM POPLAR WOOD

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A comparative kinetic analysis of the effect of bleaching pretreatment and temperature increase on the thermal ageing of high-yield fiber material derived from poplar wood is presented. Comparative investigations have been carried out with pulp chips not subjected to preliminary bleaching. The temperature values studied were the following: 90 °C, 105 °C and 120 °C. Brightness reversion was observed within the interval from 6 to 36 hours. It has been found that the ageing process is best described by an exponential kinetic equation valid for processes taking place on uniformly inhomogeneous surfaces. The values of the activation energy and the preexponential factor in the Arrhenius equation applied increased simultaneously in the course of the process for the bleached and the unbleached samples. The correlation between them indicating a compensation effect leads to the conclusion that the mechanism of the thermal ageing process is identical. It is not affected by the temperature, the treatment duration and the bleaching applied.

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

INTRODUCTION

The scarce natural resources and the increasing demand of fibrous semi-products determine the interest towards pulp processing providing the production of high-yield fiber materials (HYFM). The latter find wide application in the production of various types of paper and cardboard. HYFM are not stable to ageing, their optical and physico-mechanical properties deteriorate rapidly with time and therefore the area of their application is limited.[1-3] The carbohydrate structures of the fibrous materials undergo a number of chemical transformations in the course of ageing. Some of the bonds between hemicelluloses and lignin are cleaved, which leads to the formation of coloured compounds. The lignin content in HYFM is high and hence their ageing is faster than that of bleached ones. The yellowing starts with the oxidation of the phenolic hydroxyl groups in lignin, which in turn leads to the subsequent formation of quinones, quinone-methydes and cyclohexadienes. Various bleaching methods are applied to increase the brightness of HYFM and hence to counteract the quality decrease of the raw materials used. The two-stage method is usually applied for combined bleaching. The oxidizing reagents introduced during the first stage affect strongly the chromophore groups in the lignin macromolecule and the other colouring compounds. The chromophores formation is accompanied by the aromatic nuclei attack and demethoxylation, and this does lead to lignin degradation. The subsequent treatment with reducing agents during the second stage provides reduction of the residual chromophores or of those additionally formed in the course of the oxidation, which in turn results in a brightness increase. The process is limited to the transfer of lignin, mainly on the fiber surface, from an oxidized to a reduced form. Conjugated (double or triple) bonds play an important role in organic substances coloration. Heavy metal ions also form coloured complexes with the pulp and hence decrease the bleaching effectiveness and increase the bleaching reagent consumption. Their effect is

decreased or eliminated by the introduction of complex formation compounds – chelating agents like ethylenediamine tetraacetic acid (EDTA), polysulphates etc.[4-8]

The study of the kinetics of the thermal ageing of HYFM is expected to provide data whose treatment may facilitate the elucidation of its mechanism and hence its optimization, taking into consideration the advantages of the methods of treatment and storage. The problem is that ageing is a complex process, which does not obey formal kinetic principles. The rate of changes in the fiber materials depends on the temperature, bleaching sequence, process duration and other factors. Some authors describe the degradation reactions of the cellulose chains due to the ageing processes as reactions of first or second order.[8-11] However, the equations derived consider the processes discussed as taking place on a homogeneous surface. It is worth noting that in a real heterogeneous system the influence of the physical structure of the surface has to be taken into account.[12] In addition, the correlations between the kinetics of cellulose degradation and the changes in a wide range of macroscopic properties, such as brightness, the relative change of the Kubelka – Munk *k/s* number or tensile strength,[12,13] have also to be taken into account.

The aim of this work has been to carry out a new comparative kinetic analysis of the influence of the bleaching pretreatment and temperature increase on the thermal ageing of non-treated and bleached HYFM derived from poplar wood. The analysis focuses on the complex influence of the heterogeneous nature of the system, with the purpose of explaining the mechanism of the process.

EXPERIMENTAL

The experiments were carried out with chemical mechanical pulp (CMP) obtained from rapidly growing poplar wood of increased density of the type *Populus Trichocarpa Xeuram Populus deltoides cultivar Hunneg* (Italy). After root removal, the wood was chopped into chips of standard dimensions of 15x20x3 mm.

CMP was obtained under the following conditions: 100 g absolutely dry chips, hydromodule of 1:5, treatment temperature of 85 °C, duration of 90 min, addition of 7% NaOH and 5% $Na_2SO_3 \cdot 7H_2O_2$ (the concentrations are evaluated with respect to the mass of the absolutely dry chips used). The same conditions were applied to 10 g of chips, with the aim of yield determination.

The chips, initially weighed, were placed in a thermostated vessel to preserve the temperature applied. Then the solutions of NaOH and Na_2SO_3 were added in the amounts pointed above. The duration of the treatment followed the technological regime. Then the solution left was removed and the chips were washed to a neutral reaction. They were subsequently fibered with the application of a disc fibering device (Spront-Valdron). The extent of fibering reached was 12 °SR. It was determined by the Schoppet-Riegler method (Bulgarian Standart ISO 5267-1). Then the samples were washed and sorted manually using two sieves.

CMP yield was 90%. It was determined by the weight method. The application of the latter required to soak the strips for 24 hours in distilled water, to wash them to a neutral reaction and then to dry them to a constant weight.

Non-treated samples were investigated as well, with the objective of studying the bleaching effect on the kinetics of the thermal ageing of CMP.

Bleaching of CMP

CMP prepared under the conditions pointed above was subjected to a two-stage combined bleaching, i.e. bleaching with H_2O_2 (I stage), followed by bleaching with the reducing agent Rongalyt C (II stage). The first stage was applied to CMP of 10 % at 70 °C within 90 min. In this case, pH ≈10.5, while the amount of H_2O_2 was 2%. The additives used referred to 2% NaOH, 5% Na_2SiO_3, 0.5% $MgSO_4$ and EDTA ($Na_2C_{10}H_{14}O_8N_2.2H_2O$) as a complexing agent. All amounts pointed so far were calculated with 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 ($NaHSO_2.CH_2O.2H_2O$) and EDTA were introduced during the second stage of the bleaching process, which was carried out for 90 min at 70 °C. The concentration of CMP was 5%, while the consumption of Rongalyt C and EDTA was 2% and 0.5%, correspondingly. 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.

Ageing of CMP

After receiving the fiber mass, the casts were made with a diameter of about 6 cm. Then the samples were dried in the absence of light at room temperature. Samples of unbleached and bleached CMP were subjected to thermal ageing for 36 hours at temperatures of 90 °C, 105 °C and 120 °C. The degree

of brightness was determined using ELREPHO – 2000 with a standard light source D 65 and λ = 457 nm. The degree of brightness prior and after the aging was determined following ISO 2470:202. Furthermore, the degree of brightness of the bleached samples was determined at the 6th, 12th, 24th and the 36th hour of the process, with the aim of studying the kinetics of the ageing process. A number of experimental series were conducted. Each value reported was based on three identical ones obtained in the course of the study.

Table 1
Values of the degree of brightness, *W* (%) of CMP – unbleached and bleached, in the course of the process of ageing (h) at the temperature values studied

Temperature / Time, h	Brightness, *W*, %					
	90 °C		105 °C		120 °C	
	Unbleached	Bleached	Unbleached	Bleached	Unbleached	Bleached
6	42.6	59.2	41.9	56.8	40.8	55.6
12	42.4	58.6	41.5	56.2	38.6	52.6
24	42.3	58.0	41.1	54.4	37.4	49.9
36	42.0	57.7	40.6	53.8	36.8	49.3

RESULTS AND DISCUSSION

The effect of ageing of CMP has been observed based on the comparative investigation of bleached and unbleached samples. The initial brightness value of the unbleached samples ($W_{0,unbleached}$) was 43.2%, while that of the bleached ones ($W_{0,bleached}$) was 59.8%, i.e. bleaching brought about a brightness increase of 16.6%. The brightness reversion observed in the course of the thermal ageing of the samples of both types was followed at 90 °C, 105 °C and 120 °C. The values obtained are summarized in Table 1.

It may be noted from Table 1 that the bleached samples have higher degrees of brightness than those of the unbleached ones at all temperature values studied. Furthermore, the temperature increase brings about an increase of the rate of ageing of the samples of both types. The results presented also evidence that the brightness of the bleached samples, although higher than that of the unbleached ones, shows higher reversion with time and temperature. At 90 °C, the brightness reversion is of 2.8% for the unbleached samples, while it is 3.5% for the bleached ones. At 105 °C, it is of 6% and 10%, respectively, while at 120 °C the values found are 14.8% and 18.5%. These observations can be explained with the lower initial brightness of the unbleached samples. It should be noted as well that the brightness reversion of the unbleached samples is higher than that of the bleached ones during the last 12 hours of the process, i.e. within the interval between the 24th and the 36th hour of the experiment. At 90 °C, the brightness reversion is of 0.7% for the unbleached samples, while it is of 0.5% for the bleached ones. At 105 °C, the values found are 12.2% for the unbleached and 11% for the bleached samples. At 120 °C, they are 16% and 12%, correspondingly.

The comparative consideration of the characteristics of the thermal ageing kinetics is done with the introduction of the kinetic variable, α:

$$\alpha = \frac{W_0 - W}{W_0} \quad (1)$$

where W_0 is the initial brightness value in % (ISO), while *W* in % (ISO) is the current value related to the time of the treatment. The variable α 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 α with time (h) obtained for the bleached and unbleached CMP samples at the three temperature values studied are presented in Figure 1.

As Figure 1 shows, α increases with time and temperature for both 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. It is also evident that after the 24th hour the tendency towards ageing of the unbleached samples is better outlined when compared to that of the bleached ones.

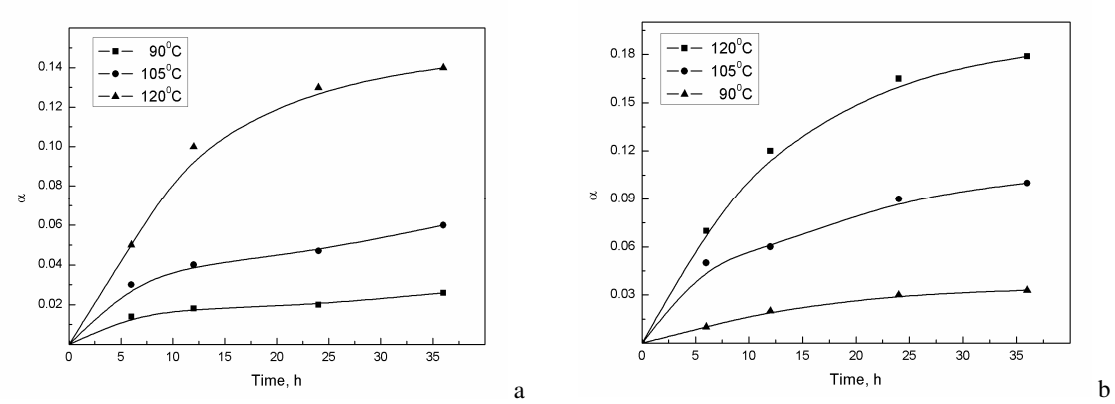
Various kinetic equations describing the kinetics of processes taking place on homogeneous and heterogeneous surfaces[13-16] have been applied, with the objective of elucidating the specifics of the ageing process. The values obtained are presented in Table 2.

Table 2 shows that the process of ageing is best described by the exponential equation (Equation 2) valid for heterogeneous processes taking place on uniformly inhomogeneous surfaces:

$$v = v_0 e^{-a\alpha} \tag{2}$$

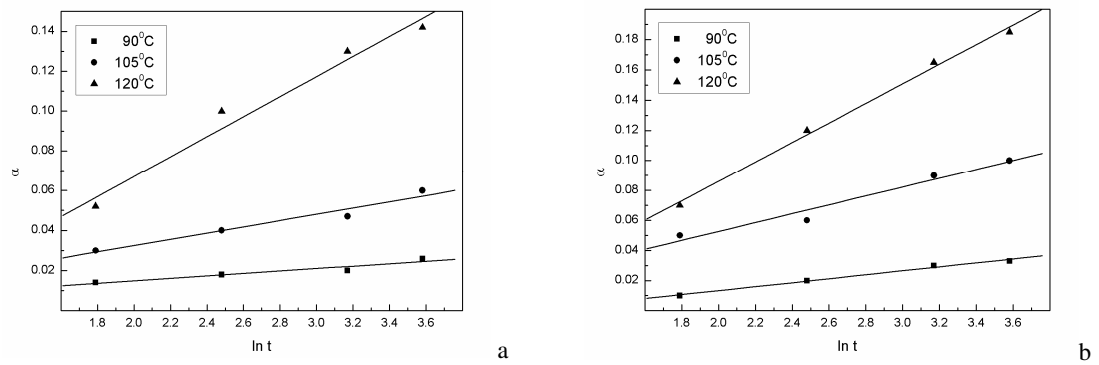
where the current and the initial rate of the ageing process are designated by $v = d\alpha/dt$ and v_0. In accord with the model of uniformly inhomogeneous surfaces,[13-18] the active centres on the fiber surface are distributed linearly in correspondence with their energy.

For a surface of this type, the rate of the heterogeneous reactions decreases exponentially with the α increase.



a b

Figure 1: Kinetic curves of increase of the ageing process extent for: (a) unbleached CMP; (b) bleached CMP



a b

Figure 2: Linearization of the kinetic curves in coordinates α - ln t for: (a) unleached CMP; (b) bleached CMP

Table 2
Equations describing the kinetics of the ageing process taking place on different surfaces

Equations	Correlation coefficient *R*	
	Unbleached	Bleached
First order equation $\ln\alpha = const - kt$	0.81657	0.79682
Exponential equation $\alpha = A + B\ln t$	0.99330	0.99254
Power equation $\ln\alpha = \ln g + \chi\ln t$	0.95610	0.94893
Topochemical equation $\ln(-\ln(\alpha) = n\ln k + n\ln t$	0.95689	0.9470

All kinetic curves are linearized in coordinates α - ln *t* in correspondence with the approximate integral form of the exponential kinetic equation:

$$\alpha = \frac{1}{a}\ln(v_0 a) + \frac{1}{a}\ln t \tag{3}$$

The linear dependences obtained in correspondence with Equation 3 are presented in Figure 2.

The value of the slope of the lines obtained (Figure 2) provides the determination of a (Equation 3). The values of the latter are presented in Table 3. It is seen that the coefficient of inhomogeneity decreases with temperature increase. This tendency is better expressed for the unbleached CMP. The temperature dependence[19] of a can be described by:

$$a = \frac{B}{R}\frac{1}{T} - a_0 \quad (4)$$

The constant B (kJ/mol) in Equation 4 stands for the interval of energy inhomogeneity and takes account of the active centres of different energy, while the coefficient a_0 stands for the interval of entropy inhomogeneity and is connected with the number of the active centres, their disposition and availability. The rest of the symbols have their conventional meaning.

The process of thermal ageing is complex from a 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 the increase of the number of chromophore groups. Besides, the bleaching of HYFM is aimed at discoloration of lignin and of the other colouring compounds, 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 that 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.[20,21] The ratio of a_0 and B found in the present case is a constant with the value of 0.3. It does not depend on the temperature and bleaching, which leads to the conclusion that the inhomogeneity observed is determined only by the type of the system (i.e. it is a constant for the particular system studied).

The integral form of the exponential kinetic equation (Equation 3) can be used for the determination of the initial rate, v_0 (h^{-1}), of the process of thermal ageing at $\alpha \rightarrow 0$. The values of v_0 are presented in Table 4.

The current rate of the process, v (h^{-1}), at different time and temperature values is estimated based on Equation 5 at a constant value of the extent of the process evolution (α=const):

$$v = \frac{1}{at} \quad (5)$$

The values of v are given in Table 4. The latter shows that the rate of ageing of both sample types decreases with the increase of α and increases with the temperature increase.

Table 3
Values of the interval of entropy inhomogeneity, a_0, the interval of energy inhomogeneity, B (kJ/mol) and of kinetic coefficient of inhomogeneity, a

Biomass CMP	a_0	B, kJ/mol	a T = 90 °C	a T = 105 °C	a T = 120 °C
Unbleached	1725	5686	163	66	20
Bleached	1327	4356	124	33	15

Table 4
Values of the initial (v_0, h^{-1}) and current rates (v, h^{-1}) of the process of ageing

	vx10^3, h^{-1}					
	T = 90 °C		T = 105 °C		T = 120 °C	
α	Unbleached	Bleached	Unbleached	Bleached	Unbleached	Bleached
0	v_0=2.73	v_0=16.08	v_0=9.75	v_0=23.00	v_0=33.70	v_0=55.56
0.010	1.20	2.00	5.92	-	30.10	-
0.015	0.72	-	5.05	-	27.70	-
0.020	0.26	1.41	3.52	8.17	20.00	34.40
0.030	-	0.75	2.09	5.25	13.10	24.70
0.040	-	0.22	1.04	3.73	9.85	17.54
0.060	-	-	0.42	1.81	6.92	11.77

The initial rate of ageing of the bleached samples is higher than that of the unbleached ones, but these samples become more stable to temperature increase and their brightness reversion proceeds more slowly with α increase. Thus, for an example, the rate values are very close in the case of α=0.015 for the unbleached CMP and α=0.03 for the bleached one. This tendency is illustrated in Figure 3.

The combined two-stage bleaching process generally results in a decrease in the number of the active centres, but it should be noted that they are more available in the initial time interval. This explains the higher values of the initial rate of the bleached samples. The rate decrease in the case of the unbleached samples is explained with the decrease in the content of the chromophore groups.

The temperature effect on the process parameters can be followed through the investigation of the temperature dependence of the initial and current rates. Based on the Arrhenius equation, it is given by:

$$\ln v_0 = \ln A_0 - \frac{E_0}{R}\frac{1}{T} \quad (6)$$

$$\ln v = \ln A - \frac{E}{R}\frac{1}{T} \quad (7)$$

where E_0 (kJ/mol) and E (kJ/mol) are the activation energies of the process at α→0 and at different constant values of α, while A and A_0 are the corresponding preexponential factors. The values of the activation energy and the preexponential factor and their change at different values of α are summarized in Table 5 and Figure 4.

As Figure 4 shows, the linear dependences obtained have different slopes, i.e. the values of the activation energy and the preexponential factor increase with α increase. That means that the surface is energy and entropy heterogeneous. The activation energy of the unbleached samples is higher at the beginning of the process, α→0. However, in the course of the treatment, the ageing process is hampered with α increase in the case of the bleached CMP, most probably because of the decrease in the number of available active centres on the surface. These findings are in accord with the experimental results concerning the decrease of the current rates of the process for the bleached and the unbleached samples. The values of the preexponental factor increase as well in the course of the process, which indicates that the number of the chromophore groups, responsible for brightness reversion, increases. The total increase of the energy and entropy factors is greater at the bleached samples. Their rate of ageing is lower and hence it can be concluded that bleaching hampers, in fact, the ageing.

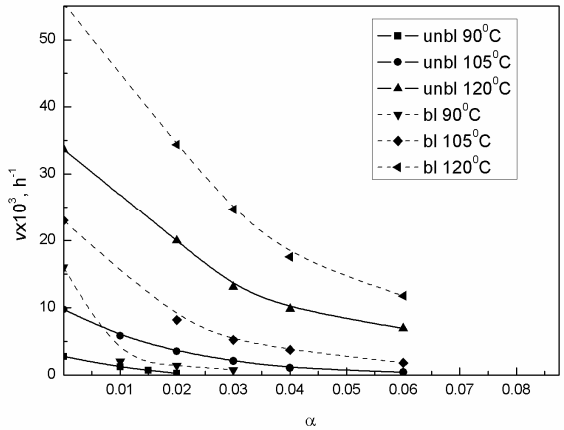


Figure 3: Dependence of the current rate, v (h^{-1}), on the extent of process development, α, at the temperature values studied for bleached (-----) and unbleached (——) CMP

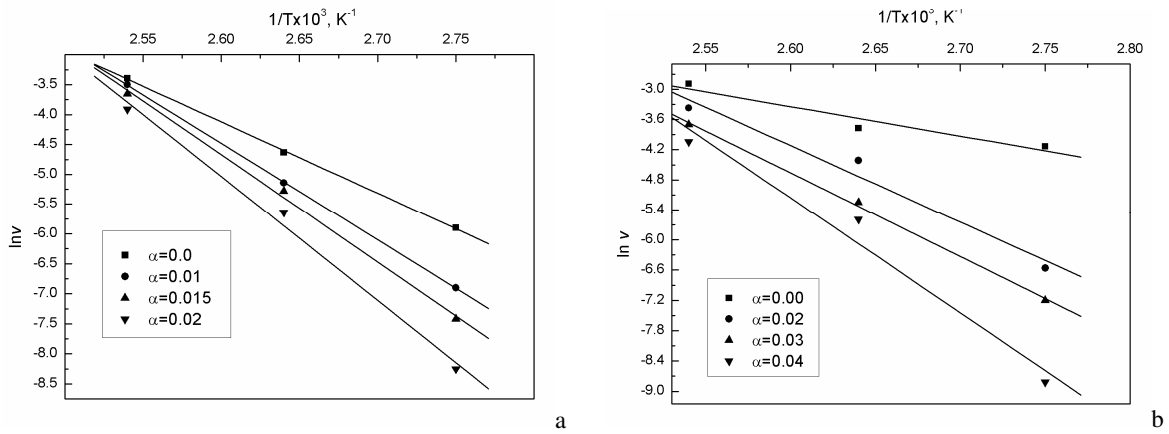


Figure 4: Temperature dependence of the initial and the current rate at α=*const* in case of: (a) unbleached CMP; (b) bleached CMP

Table 5
Values of the activation energy, *E* (kJ/mol) and the logarithm of the preexponential factor, ln *A* at different values of process development, α=const

Biomass	Unbleached				Bleached			
α	0	0.01	0.015	0.02	0	0.02	0.03	0.04
E, kJ/mol	99.26	134.52	144.75	172.18	48.72	126.87	138.67	190.14
ln *A*	26.90	37.60	41.70	48.83	11.89	35.56	38.71	54.30

The dependence of the activation energy and the preexponential factor on α increase is described by:

$$E = E_0 + B\alpha \quad (8)$$

$$\ln A = \ln A_0 + a_0\alpha \quad (9)$$

where E_0 and A_0 are the activation energy and the preexponential factor at $\alpha \to 0$ (Table 5). The values of the range of energy inhomogeneity, B (kJ/mol) (Equation 8) and of the interval of entropy inhomogeneity, a_0 (Equation 9) coincide with those estimated with the application of Equation 4. It is worth noting that their ratio is equal to 0.3. The dependences of the activation energy and the preexponential factor on α are presented in Figure 5.

The increase of the activation energy and the preexponential factor with the α increase can be described by a linear dependence common for both types of samples treatment:

$$\ln A = n + mE \quad (10)$$

The correlation (presented by Equation 10) is well known as a compensation effect.[22-24] It indicates that the mechanism of thermal ageing is identical, i.e. it does not depend on the preliminary treatment of the samples studied. Its illustration is presented in Figure 6. It should be added that constant n is defined through $n = \ln A_0 - \left(\frac{a_0}{B}\right)E_0$, while constant m, which coincides with the slope of the line, has the value of 0.3.

The increase of the activation energy slows down the ageing process, but this cannot compensate for the increase of the number of the chromophore groups responsible for the brightness reversion. Hence, bleaching has a positive, but limited effect on ageing, especially at high temperatures. The correlation obtained indicates a common mechanism of the ageing process of the treated and the non-treated samples. It is characterized by a simultaneous increase of the activation energy and the preexponential factor and is not affected by the increase of temperature, the reaction duration and the degree of bleaching. These results are grounded on the kinetic specifics studied.

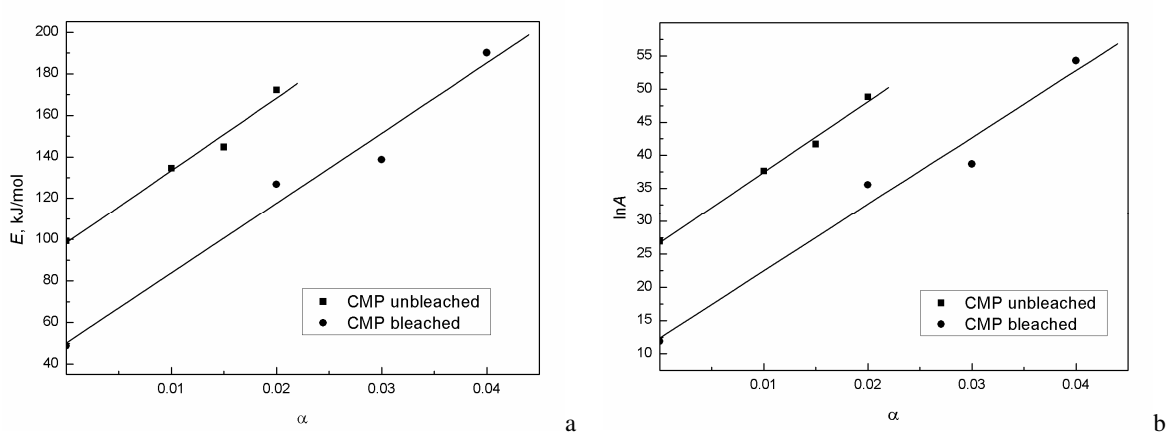


Figure 5: Linear dependences of: (a) the activation energy, E (kJ/mol) and (b) the preexponential factor, ln A, on the extent of process development, α

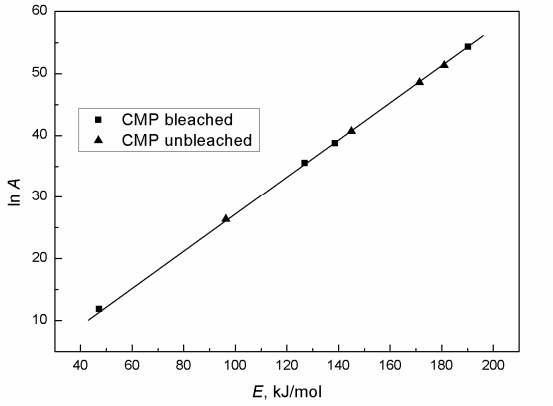


Figure 6: The compensation effect: linear dependence of lnA vs E, kJ/mol

CONCLUSION

A comparative kinetic analysis of the stability to thermal ageing of samples of bleached and unbleached chemical mechanical pulp obtained from a rapidly growing poplar wood is presented. The kinetics of the process is best described by an exponential kinetic equation valid for heterogeneous processes taking place on uniformly inhomogeneous surfaces. The initial and the current rates of the process have been determined. It has been found that they decrease with the increase of the extent of the process proceeding. The temperature dependence of the rate has been followed and the values of the activation energy and the preexponential factor in the Arrhenius equation were estimated. They were found to increase simultaneously with the increase of the extent of the process on the bleached and the unbleached samples. The linear dependence verifying the existence of a compensation effect is common for the samples of both types. It shows that the mechanism of thermal ageing does not depend on the temperature, process duration and degree of bleaching.

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