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Thermochimica Acta 421 (2004) 81–85
thermochimica acta
www.elsevier.com/locate/tca

Mechanical properties of the paper sheets treated with different polymers

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Received 14 October 2003; received in revised form 29 February 2004; accepted 5 March 2004
Available online 20 May 2004

Abstract

The present studies are focused on the effect of different polymer solutions, e.g. chitosan and polyvinyl alcohol (PVA) on the mechanical properties of the paper sheets. The improvement in the mechanical properties of the treated paper sheets with chitosan is higher than that in the other polymer solution. Moreover, the heat resistance of treated paper sheet with chitosan is more improved than with other polymer. The activation energy of the thermal treatment of untreated and treated paper sheets with mixed polymers solution is also calculated.

Keywords: Paper; Aging; Chitosan; Polyvinyl alcohol

1. Introduction

A paper sheet is formed from network structure between cellulose and non cellulose (hemicelluloses and lignin). These materials are held together with hydrogen bonds [1,2]. The improvement of the mechanical properties between these constituents in paper sheet can be achieved by increasing the crossing between the cellulose fibers. A number of polymer materials have been applied, which increase the interfiber bonding between the cellulose chains in the formed paper sheets. These include carboxymethyl cellulose [3], cellulose acetate [4], phenol formaldehyde resin solution [5,6], cationic starch, cationic polyacrylamides [7] and PVA [8]. Each of these polymers must enable the interfiber bonding areas to remain chemically linked in the presence of water. Another way to improve the paper sheet properties is to carry out chemical modification on the cellulose fiber, e.g. acetylation [8], carboxymethylation and grafting [9]. Also, some polymers can be used to improve the resistance of old paper towards brittleness [10]. Moreover, polymer can be used to increase the electrical insulating of paper, e.g. formation of cyanoethylated cellulose [11].

In some studies chitosan (natural polymer) and its blend with some polymers has been used to improve the strength properties of paper sheets [12,13], and also other polymer solution can be used to improve the brightness stability beside the mechanical properties of the paper sheets [10].

The aim of the work is to investigate the effect of the natural polymer, e.g. chitosan and synthetic polymer solution (PVA) on the physical and mechanical properties of the paper sheets (Rakta paper sheets and wood pulp paper sheets). Also the effect of aging on the mechanical properties of the paper sheets is studied. The activation energy of the breaking length of untreated and treated paper sheets at different temperature for different time was also calculated.

2. Experimental

In this study bleached sulfite wood pulp was used to prepare paper sheets according to Swedish standard method (SCA), pulps were beaten to 40° SR in a Jokro mill beater. Handsheets of basis weight of 68 g/m^2 were formed. Besides a paper sheet delivered from Rakta (paper mill—Alexandria). Rakta paper sheets were made from blended bleached rice straw pulp 60%, bleached bagasse pulp 20% and bleached wood pulp 20% beaten at 40° SR. The strength property of hand sheets (breaking length and tear factor) were measured according to Tappi standard.

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0040-6031/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2004.03.005

Paper sheets were dipped in the different concentration of different polymer solution for 30 s. These polymers are chitosan and PVA or mixture of them. After dipping, the paper sheets were pressed between two filter paper sheets to remove the excess polymer, and then dried on drum at 105 °C for 2 h. In another trial, the wood pulp was beated to different °SR and soaked in polymer solution.

Aging was carried out by heating the paper sheets at different temperatures for different time.

3. Results and discussion

3.1. Effect of dipping of paper sheets in different concentration of polymer solutions

Fig. 1(a) and (b) shows that the breaking length and tear factor of the dipped Rakta paper in different concentration of PVA (1–5%) and chitosan solution (0.2–0.75%), respectively. From Fig. 1, it is seen that the breaking length of paper sheet dipped in PVA increases by increasing the concentration of PVA to 1%. This can be attributed to the increase of the interfiber bonding of the paper sheets. By increasing the PVA solution more than 1% the breaking length began to decrease. This can be attributed to the increase of the viscosity of the PVA solution, which decreased its penetration to fiber in paper sheets, and the retained polymer was found on the surface of the paper sheets, which causes a hardness of paper sheet. This causes a brittleness of the paper sheets and consequently, the breaking length decreases. In case of tear factor, it increases by increasing the concentration of the PVA till 2–3% then it began to decrease. In case of chitosan (Fig. 1(b)), the breaking length and tear factor increase by increasing the concentration of chitosan solution. This

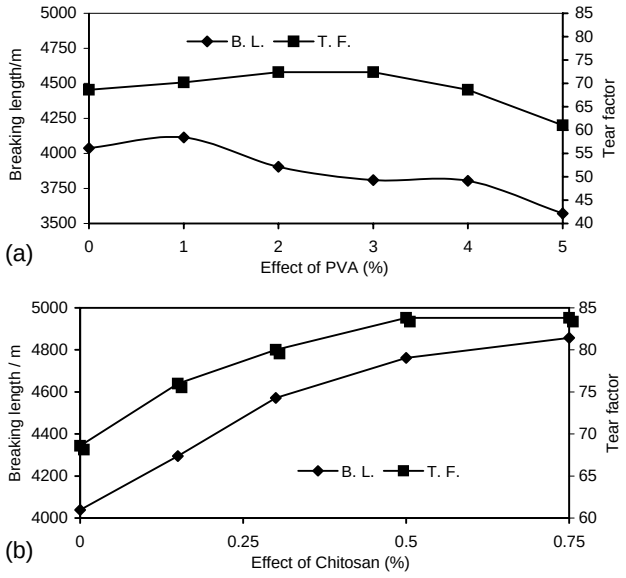

Fig. 1. (a) Effect of PVA percentage on mechanical properties of Rakta paper and (b) effect of chitosan on mechanical properties of Rakta paper.

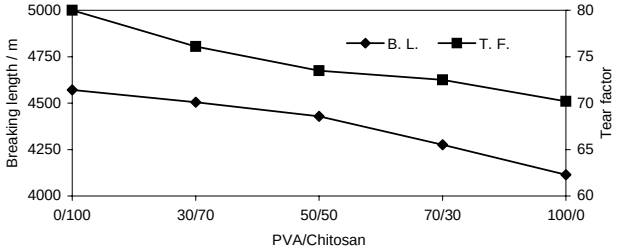

Fig. 2. Effect of a mixture of PVA (1%) and chitosan (0.3%) on mechanical properties of Rakta paper.

is attributed to the increase of the interfiber bonding and compatibility between chitosan and fiber of the paper sheets.

From these mentioned results, it could be seen that treatment with 1% PVA solution or 0.3% chitosan solution gives maximum mechanical properties. So, treating of Rakta paper sheet with a mixture of both two solutions were evaluated. Fig. 2 shows that as the PVA percentage increase (chitosan percentage decrease) breaking length and tear factor slightly decreased. Treatment with PVA and chitosan mixture provided paper with improved mechanical properties in comparison with the blank (untreated) paper.

3.2. Effect of shopper regular (°SR)

Table 1 shows the effect of °SR of beated wood pulp on the retained polymer and mechanical properties of the produced paper sheets. From this table it is clear that the retained polymer on paper sheets increases by increasing the °SR from 30 to 42. This is attributed to the decrease of the crystallinity of the fiber which causes an increase in the absorbed polymer [14]. By increasing the °SR from 42 to 75, the absorbed polymer solution is decreased this is attributed to the increase of the defibrillation of the fiber and consequently this cause an increase in crossing between the fiber in paper sheets causing a decrease in the paper sheet porosity. This decrease in the porosity causes a decrease in the

Table 1
Effect of °SR on retained amount and mechanical properties of wood pulp

°SR	Treatment	Retained (g/m^2)	Breaking length (m)	Tear factor
30	Blank	0.00	2931	360
	Chitosan (0.3%)	0.24	3170	471
	PVA (1%)	0.69	3700	365
42	Blank	0.00	4229	304
	Chitosan (0.3%)	0.30	4489	311
	PVA (1%)	0.80	4484	325
52	Blank	0.00	4520	304
	Chitosan (0.3%)	0.30	5489	311
	PVA (1%)	0.80	5484	325
75	Blank	0.00	5000	178
	Chitosan (0.3%)	0.16	6600	224
	PVA (1%)	0.58	6010	206

polymer solution absorption and consequently, the retained polymer decreases. The breaking length of the paper sheets increases by increasing the degree of beaten of the pulp. These is attributed to that, increase in the degree of beating causes an increase in the defibrillation and interfiber bonding between the fiber in the produced paper sheets increases. The tear factor decreases by increasing °SR from 30 to 75.

Dipping of paper sheets in the different polymer solutions increases the breaking length and the tear factor of the dipped sheets [15]. The increase of the breaking length of the treated paper sheets by different polymeric materials can be due to the increase of interfiber bonding between the fiber and polymer. Also the polymeric material contains functional groups capable of bonding by ionic or covalent bonds with the paper fiber surface.

Generally the polymeric materials increase the breaking length and tear factor of the treated paper sheets. In case of tear factor, the effect of the polymeric material is clear and causes an increase in tear factor due to the increase of the interfiber bonding specially at 30° SR but in case of high °SR, the addition of polymeric materials causes a decrease in the tear factor due to the increase of coated polymeric material on the surface of paper sheets and consequently causes a hardness of the fiber.

3.3. Strength of wetted paper

The conventional paper fibers are held together by hydrogen bond [1], these bonds affect the distance between the separate crosslink fibers. Water molecules play an integral role in the interfiber linkage. The free water causes the paper weakness, which is manifested by wet strength of paper. Table 2 shows that the mechanical strength of the paper sheets is highly affected by the wetting of paper sheets with water. So, it is found that breaking length of the dry paper was 4038, while they decrease to 1310 in case of the wetted paper. Tear factor slightly higher for wetted paper, especially that treated with chitosan. Treated paper sheet with PVA, chitosan and mixture of them improved the strength of the wetted paper. Each of these polymeric materials must enable the interfiber bonding areas to remain chemically linked in the presence of water. On the other hand, the coated paper with chitosan has a higher improvement in the strength of wetted paper than the paper coated with PVA. This is attributed to that chitosan not only increase the fiber bond, and consequently increase the hydrogen bond between fiber, but also is less water absorbent than PVA. The chitosan is more compatible with cellulose fiber and also it contains functional groups capable of ionic or covalent bonding with paper fiber surface.

Table 2
Effect of treatment on wet strength of paper

Treatment	Breaking length (m)	Tear factor
Non	1310	70.48
PVA	1603	70.48
Chitosan	2595	100.95
PVA + chitosan	2635	85.70

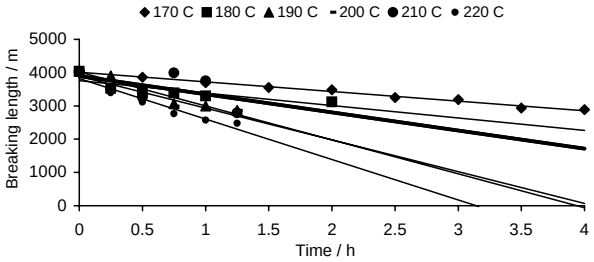

Fig. 3. Effect of aging time on breaking length of untreated Rakta paper.

3.4. Aging of paper sheets

Untreated and treated Rakta paper sheets with mixture of PVA (1%) and chitosan solution (0.3%) were aged at different temperature (100–220 °C) for different time.

From Figs. 3 and 4 it is clear that the breaking length of the untreated paper sheets decreases by increasing the aging temperature for different time. Breaking length of the treated sheet with mixture of PVA solution and chitosan increases by increasing aging temperature 100–150 °C for short time. This can attributed to the increase of adhesion force between polymer and fiber of paper sheets.

3.5. Activation energy of thermally treatment paper sheets

As mentioned, there is a negative relation between breaking length and thermal treatment especially at high temperatures (Fig. 3). This is due to the degradation and oxidation of the cellulose chains. Chemical treatment of paper sheet by PVA, chitosan or mixture of them decreases this degradation and hence decrease the rate of loss of mechanical strength (Fig. 4).

Thermal treatment of paper sheets may be first order [16] that expressed as follows:

$$-\frac{dc}{dt} = kc$$

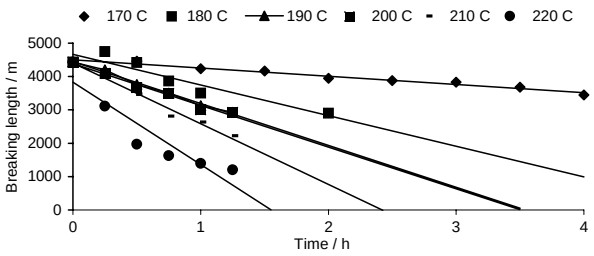

Fig. 4. Effect of aging time on breaking length of treated Rakta paper with a mixture of chitosan (0.3%) and PVA (1%) in ratio of 1:1.

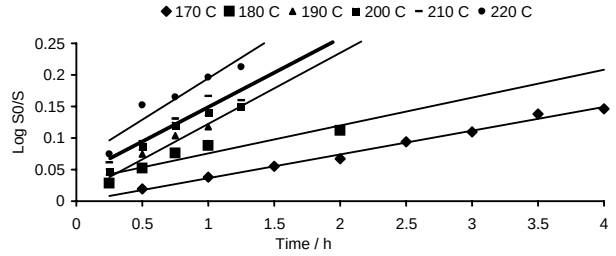

Fig. 5. Relation between $\log S_0/S$ and time for untreated Rakta paper.

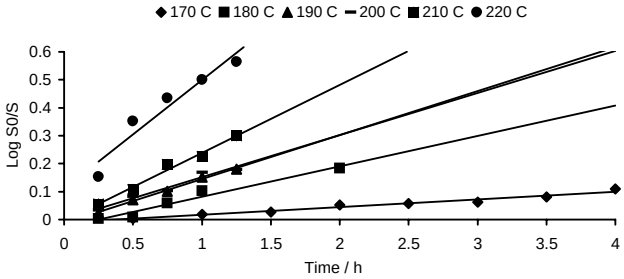

Fig. 6. Relation between $\log S_0/S$ and time for treated Rakta paper.

where c is the concentration of the reactant, t the time and k the rate constant. If c is replaced by the observed breaking length value (S) of the paper sheet, so

$$\frac{d(S_0 - S)}{dt} = k(S_0 - (S_0 - S)) = kS$$

where S_0 is the original breaking length of the untreated paper sheets. Plotting $\log S_0/S$ against t a straight line is obtained (Figs. 5 and 6). Slope of this line determines k (rate constant) at different temperatures. Activation energy was calculated by applying Arhenius equation [17]:

$$\ln k = -\frac{E}{RT} \quad \text{or} \quad \log k = -\frac{E}{2.303RT}$$

A straight line was obtained also (Figs. 7 and 8) by plotting $\log k$ against $1/T$ (T is the absolute temperature). Slope of this line is equal to $-E/2.303R$, where E is the activation energy and R is the gas constant (1.963 cal). Activation energy of the untreated and treated paper sheets with a mixture of chitosan and PVA solution was calculated 52.232 and 107.473 kJ, respectively. The calculated activation energy is resultant of several factors, which include the degradation of cellulose,

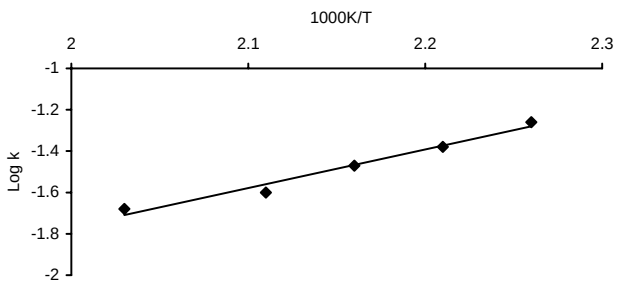

Fig. 7. Relation between $\log k$ and $1/T$ for untreated Rakta paper.

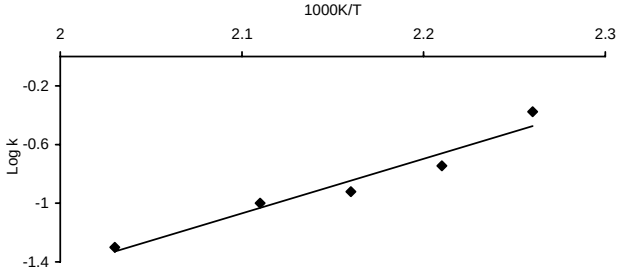

Fig. 8. Relation between $\log k$ and $1/T$ for treated Rakta paper.

the kind of the interfiber bond between the fiber in paper sheets, kind and the retained polymer in the paper sheets.

From the presented results, it is seen that the activation energy of the treated paper sheets with polymer solution has a higher value than untreated one. This can be attributed to the increase of the interfiber bonding between the fiber and fiber as well as between the fiber and polymer in the paper sheets.

4. Conclusions

- Treatment of paper sheet with polymeric solution of chitosan and PVA improves the mechanical properties of the produced paper sheets.
- Chitosan is affecting the properties of paper sheets more than other polymer.
- Wet strength of paper sheet improves by chitosan.
- Activation energy of the loss in the breaking length due to the thermal treatment above 160 °C was calculated for untreated and treated paper sheets with polymer solution. It was 52.23 and 107.47 kJ for untreated and treated paper sheets, respectively.

References

[1] K.J. Ward, Jr., Chemical Modification of Paper Making, Marcel Dekker, New York, 1973.
[2] G.G. Allan, J.R. Fox, G.D. Crosky, K.V. Sarkman, in: Proceedings of the Transaction of the Symposium on Fiber Water Interaction in Paper-making, Oxford, 1977, Fundamental Research Committee, 1978.
[3] A.M.A. Nada, A.A. Ibrahem, M.A. Yousef, S. El-Meadawy, Acta Polym. 34 (1983) 18.
[4] A.A. Ibrahem, A.M.A. Nada, S. El-Meadawy, M.A. Yousef, Acta Polym. 34 (1983) 177.
[5] A.M.A. Nada, A.A. Ibrahem, M.A. Yousef, Indian Pulp Pap. 23636 (2) (1981) 21.
[6] A.M.A. Nada, M.A. Yousef, K.N. Abdel-Nour, Pigment Resin Technol. 26 (1) (1997) 17.
[7] A.A. Ibrahem, A.M.A. Nada, H. El-Said, A.E. El-Ashmay. Angewande, Macromol. Chem. 27 (1984) 89.
[8] A.M.A. Nada, H. Abo Shosha, A.A. Ibrahem, Polym. Plast. Technol. Eng. 35 (3) (1996) 305.
[9] A.M.A. Nada, A.A. Abdel-Hakim, A.S. Badran, Restaurator 20 (1999) 30.
[10] A.M.A. Nada, S. Kamel, M. El-Sakhawy, Restaurator 21 (2000) 238.

[11] A.M.A. Nada, M. Dawy, A.A. Shabaka, Int. J. Polym. Mater. 47 (2000) 195.
[12] M. Mucha, D.J. Miskiewiez, Appl. Polym. Sci. 77 (2000) 3210.
[13] M.H. Stuszczyk, F. Loth, M.G. Peter, Adv. Chitin Sci. 4 (2000) 128.
[14] A.M.A. Nada, M.Z. Sefain, Cellulose Chem. Technol. 20 (1986) 409.
[15] M.A. Yousef, A.A. Shabaka, A.M.A. Nada, K.N. Abd El-Nour, Indian J. Pure Appl. Phys. 29 (1991) 6.
[16] A.M.A. Nada, A.A. Ibrahem, Res. Ind. 31 (1986) 136.
[17] S. Glastone, Textbook of Physical Chemistry, MacMillan, London, 1962, p. 828.