

Chitosan Blends as Fillers for Paper

M. MUCHA, D. MIŚKIEWICZ

Faculty of Process and Environmental Engineering, Technical University of Łódź ul. Wólczajska 213/215, 90–924 Łódź, Poland

Received 12 May 1999; accepted 26 December 1999

ABSTRACT: The presented studies are focused on the dependence of paper sheet strength properties such as tear resistance, burst, and extensibility on the composition of additive [chitosan blends with poly(vinyl alcohol) and gelated starch]. Chitosan acetate (cationic) and its blends caused an improvement of the strength properties of paper sheets by the substantial modification of cellulose (anionic) fibers, probably through the presence of strong ionic interactions. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 3210–3215, 2000

Key words: chitosan; paper additive; mechanical properties

INTRODUCTION

It is now accepted that conventional paper fibers are held together by hydrogen bonds.^{1–4} These bonds affected the distance between the separate crosslinking fibers. One can expect that a few water molecules may play an integral role in the interfiber linkage. A large excess of free water, however, causes the paper weakness, which is manifested by the wet strength of paper.¹ To improve this low strength, a number of polymeric materials have been applied. These include urea, as well as melamine formaldehyde condensates, epoxy-containing polyamides, cationic polyacrylamides, and polyethyleneimines. Each of those must enable the interfiber bonding areas to remain chemically linked in the presence of water; otherwise, they would not be functional. Every additive can be reasonably expected to react either ionically or covalently with the functional groups of cellulose in paper. The surface modification of cellulosic fibers^{2,3} permits the direct formation of hydrogen bonds between the fiber-surface areas. It was clearly proposed⁴ which fea-

tures should possess good strength additive for paper. It should

1. Be soluble in water-based systems for easy application with conventional papermaking systems.
2. Be substantive to cellulose so that retention is efficient.
3. Be compatible with the cellulose surface so that it does not disrupt conventional hydrogen bonding.
4. Be film-forming (of large enough M_w) to offer adhesive resistance to rupture.
5. Contain a functional group capable of ionic or covalent bonding with the paper fiber surface within the papermaking process.
6. Be nontoxic and preferably natural (thus biodegradable) to conform with environmental regulations (no problems in paper recycling).

Such numerous requirements are met by chitosan, a linear high molecular aminopolysaccharide, a major component of many creatures including crustaceans and insects. Obviously, it is biodegradable and environmentally clean, but its close stereochemical similarity to cellulose suggests that a chitosan–cellulose combination

Correspondence to: M. Mucha.

Journal of Applied Polymer Science, Vol. 77, 3210–3215 (2000)
© 2000 John Wiley & Sons, Inc.

should be useful. The presence of basic groups on every ring makes chitosan soluble in dilute aqueous solutions of basic acids. Moreover, the cationic character of the dissolved chitosan should make it substantive to anionic pulp paper.

Chitosan in amounts of 1–3% by weight was been shown⁴ to be an effective mediator of fiber–water interaction in paper, improving both the dry breaking length and the wet strength of treated paper. Additionally, it was been shown^{4,5} that formaldehyde or heat treatments of paper containing chitosan results in further enhancement of the wet strength. Formaldehyde can react with the amino groups in chitosan-forming methylene groups, which subsequently form methylene crosslinks during the curing process. These covalent linkages are more resistant than are ionic linkages to disruption by water. The increase in wet strength of paper sheets containing chitosan in the process of curing or heat is probably due to covalent crosslinking of chitosan molecules, leading to reduced chitosan solubility in water. There has been exploration of the commercial use of chitosan for various industrial applications, particularly in textiles, paper, agriculture, and medicine.^{6–10}

Chitosan forms homogeneous blends in solution and in a limited range of compositions in the solid state with water-soluble polymers such as poly(vinyl alcohol) and poly(ethylene oxide) or within gelated starch by forming strong ionic or hydrogen bonds.^{11–13}

A poly(vinyl alcohol) (PVA) solution was used elsewhere¹⁴ for improving the strength properties of paper sheets. Chitosan and starch have been used as components of clay for paper coating.⁹

The chitosan blends with PVA and gelated starch applied here are new fillers with the purpose to improve paper strength. The presented studies focused on the relationship between the chitosan blend composition and typical paper properties.

EXPERIMENTAL

Materials

The materials used consisted of bleached softwood sulfate unbeaten pulp; chitosan with deacetylation degree (DD) = 78.5% ($M_w = 4.3 \times 10^5$), obtained by deacetylation of chitin from krill shells, supplied by the Fisher Institute (Gdynia, Poland); potato starch (Polish commer-

cial products); weak acetic acid (1% w_f , pH \approx 4); and poly(vinyl alcohol) ($M_w = 70,000$), Polish commercial product.

Blends

Solutions of chitosan and its blends with a weight fraction of PVA ranging from 0 to 100% and gelated starch in the range from 0 to 50% were prepared. Solutions of blends of needed composition were prepared from a 1% (by weight) solution of chitosan in a weak acetic acid and solutions of PVA or gelated starch in water.

Forming of Paper Sheets

After defibering the pulp at an initial rate of 3000 rpm in 20 min, and then at 1000 rpm, paper sheets were formed in a standard manner in a Rapid-type apparatus in conditions similar to industrial ones. The preformed sheets were pressed and initially dried quickly (1 min) to remove excess water. Still-wet sheets on the blotter were sprayed or cast with the solutions of chitosan or chitosan blends of various composition. Then, the sheets were pressed and dried (for 4 min using a hot (90°C) air stream) according to the TAPPI procedure.¹⁵ Additive polymer constituted a 10% weight fraction of the paper dry matter. Prior to testing the paper properties, the samples were conditioned for 4 h at a temperature of $23 \pm 1^\circ\text{C}$ and humidity of $50 \pm 2\%$ according to the Tappi standard.¹⁶

Testing

The following tests on pure paper and paper with fillers were carried out:

Tear Resistance

Tear resistance is the force required to tear a sample of dimensions 50×65 mm. The test was carried out with an Elmendorf tester¹⁷:

$$T_r = \frac{a \times 16 \times 9.81}{n_2}$$

where T_r is the tear resistance (mN); a , the value read from the tester (g); and n_2 , the number of sheets.⁴

Bursting Power

The index of burst strength of a paper product provides a possibility to estimate the product us-

ability and behavior when perpendicular forces act on the surface. Burst is determined by the bursting power which causes breaking of the sample between two rings of specified surface area (MPa). Burst was tested using a Mullen tester:

$$B_p = \frac{\sum P}{n_1}$$

where B is the bursting power; $\sum P$, the sum of read-outs (MPa), and n_1 , the number of measurements.⁴

Breaking Load

The breaking load, B_0 , needed also to calculate breaking length and extensibility of a paper product, was tested by a Schopper tester.

Extensibility

The paper web is extended during breaking. A measure of extensibility, E_x , is the elongation of a testing strap at break. Extensibility is expressed as a ratio of the elongation to the original length (%).

Breaking Length

Breaking length determines the length of a testing strap of an arbitrary, but even, width suspended vertically, which breaks down by gravity at the point of suspension. In practice, 10 testing straps, 180 mm long and 15 mm wide, were used in the measurements:

$$B_l = \frac{\sum nl}{\sum m 9.81}$$

where B_l , is the breaking length (m); $\sum n$, the force needed to break 10 testing straps (sum) (N); $\sum m$, the sum of the weights of 10 testing straps (kg); and l , the clamping length (m).

Errors Analysis

The errors were calculated in the following way:

$$\Delta X = tS(X_a)$$

where $S(X_a)$ is the standard deviation for the average value X_a :

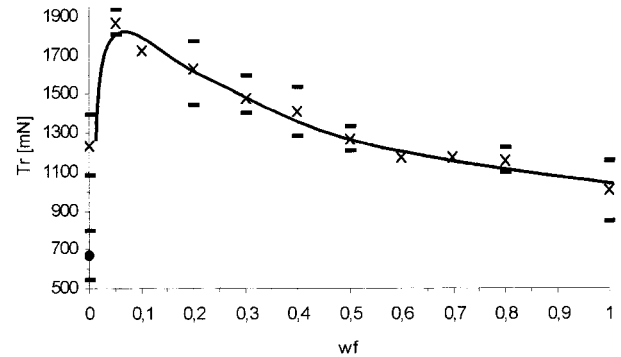


Figure 1 Dependence of tear resistance (T_r) on weight fraction (w_f) of PVA in the blend with chitosan: $w_f = 0$, pure chitosan; (●) pure paper sheet.

$$S(X)_a = \sqrt{\frac{\sum_{i=1}^n (x_i - x_a)^2}{n(n-1)}}$$

where t is the Student's test value for probability equal to 95%, $t = 2.26$ for 10 measurements, and $t = 3.18$ for four measurements.

RESULTS AND DISCUSSION

The results of measuring various properties of paper sheets without additives are shown in the figures as a special point \cdot at weight fraction $w_f = 0$.

Tear Resistance (mN)

Figure 1 shows the tear resistance, T_r , of a paper sheet plotted versus the weight fraction of PVA in the blends with chitosan, and Figure 2 shows the effect of the gelled starch content in the blends on the tear resistance, T_r , of a paper sheet.

In the case of paper filled with chitosan and PVA, the tear resistance is significantly improved when containing chitosan. For unfilled paper, the tear resistance $T_r = 667$ mN, while for paper and the chitosan/PVA blend, it increases, reaching a maximum value ($T_r = 1867$ mN) at $w_f(\text{PVA}) = 0.05$. By increasing the content of PVA further, a decrease in the tear resistance is observed. It is important to notice that the 1% (by weight) solution of chitosan in dilute acetic acid appears to have a much higher viscosity than that of the PVA solution in water of the same concentration.¹¹ It can affect the additive retention on cel-

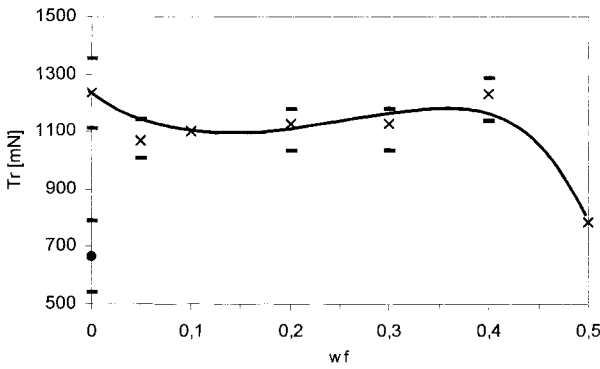


Figure 2 Effect of composition of chitosan/gellated starch blend on tear resistance (T_r). w_f , weight fraction of gellated starch.

lulose fibers in paper. Addition of gellated starch to chitosan causes the tear resistance to be maintained up to 40% starch content. However, starch is not as efficient as is PVA. The application of gellated starch in blends with chitosan allows for a decrease of chitosan content up to 50% without a considerable decrease of the tear resistance of paper sheets.

Bursting Power (MPa)

Figures 3 and 4 shows the effect of PVA and the gellated starch content in the blend with chitosan on the burst values, B_p . The investigation of burst shows that results are much better after filling the paper with the tested blends. In the case of unfilled paper, the value of the bursting power was $B_p = 0.046$ MPa. For paper filled with chitosan and its blends, the burst value increased, with the chitosan/gellated starch blend remaining

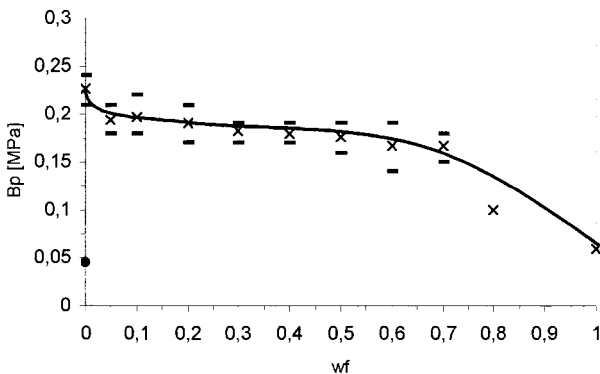


Figure 3 Dependence of burst (B_p) on weight fraction (w_f) of PVA in the blend with chitosan; $w_f = 0$, pure chitosan; (●) pure paper sheet.

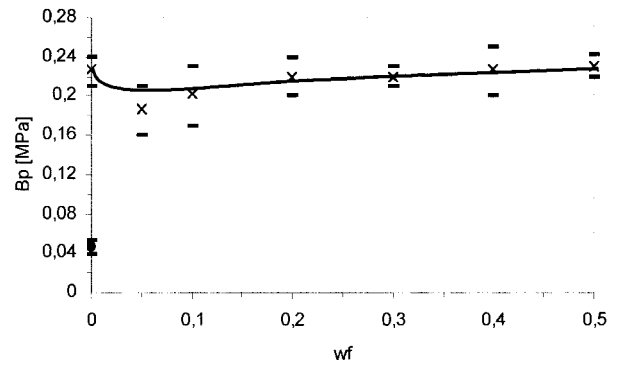


Figure 4 Effect of composition of chitosan/gellated starch blend on burst (B_p); w_f , weight fraction of gellated starch.

very close to about 0.2 MPa. The lowest value of $B_p = 0.178$ MPa was obtained with the gellated starch content being 0.05. The addition of the chitosan/PVA blend caused a stepwise decrease of the burst value from $B_p = 0.228$ (pure chitosan) up to $B_p = 0.06$ MPa obtained for paper filled with pure PVA.

Breaking Load (N)

The effect of PVA and the gellated starch content in the blends with chitosan on the breaking load, B_0 , of paper sheets is shown in Figures 5 and 6. The breaking load, B_0 , is much higher for paper filled with chitosan and its blends with PVA and gellated starch than for unfilled paper. For pure paper, the value of the breaking load is $B_0 = 16.5$ N. The coating of wet paper with the chitosan and its blend with PVA and gellated starch enhances this property. The best result ($B_0 = 37$ N) was

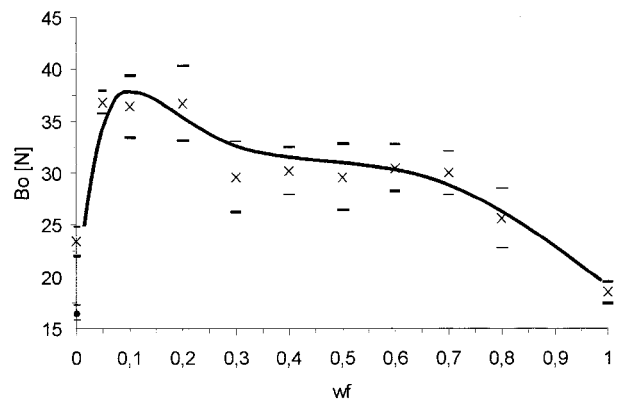


Figure 5 Dependence of breaking load (B_0) on weight fraction (w_f) of PVA in the blend with chitosan; $w_f = 0$, pure chitosan; (●) pure paper sheet.

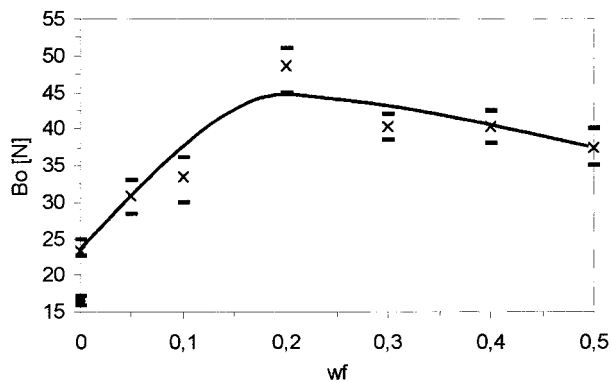


Figure 6 Effect of composition of chitosan/gelated starch blend on breaking load (B_0); $w_f = 0$, pure chitosan; (●) pure paper sheet.

obtained for a low PVA content (up to $w_f = 0.2$) in the chitosan blend.

With an increase of the PVA content in the blend solution, the breaking load decreases; for pure PVA, $B_0 = 18.5$ N. Also, the addition of the chitosan/gelated starch blend clearly enhances this feature. The best result, $B_0 = 48.6$ N, was obtained for a starch content $w_f = 0.2$.

Extensibility (%)

Figure 7 shows the extensibility value, E_x , of paper sheets drawn versus the weight fraction of PVA in the blend and Figure 8 presents the dependence of the extensibility, E_x , of filled paper sheets on the weight fraction of the gelated starch in the blend.

Filling with chitosan causes a 2.5-fold increase in extensibility. The extensibility of treated paper is 1.31%. The content of both PVA and gelated

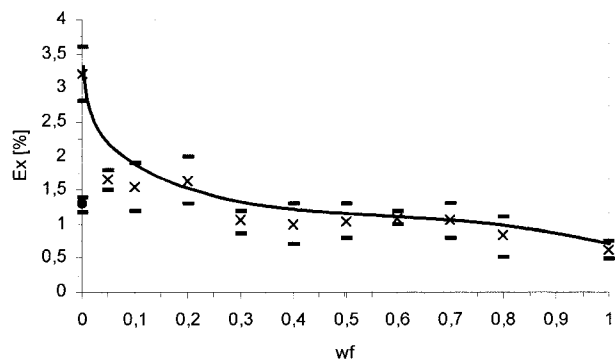


Figure 7 Dependence of extensibility (E_x) on weight fraction (w_f) of PVA in the blend with chitosan; $w_f = 0$, pure chitosan; (●) pure paper sheet.

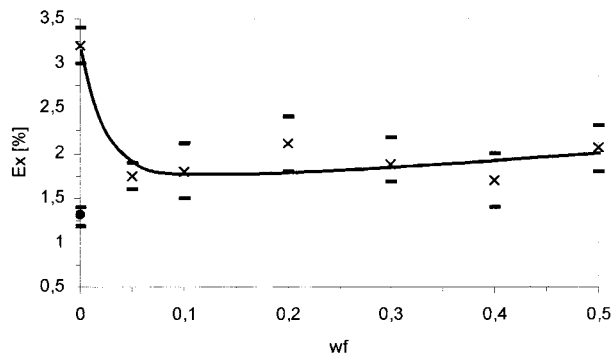


Figure 8 Effect of composition of chitosan/gelated starch blend on extensibility (E_x) of paper sheets; $w_f = 0$, pure chitosan; (●) pure paper sheet.

starch in the blend with chitosan causes a decrease in the extensibility to the values, which does not much exceed the one for untreated paper. In the case of PVA, $E_x = 1.7\%$ for $w_f = 0.2$, but for blends with gelated starch, the value ranges from 1.7 to 2.0%.

Breaking Length (m)

Figures 9 and 10 show the effect of an increasing weight fraction of PVA and gelated starch on the values of the breaking length, B_l , of paper sheets. In the case of paper filled with the chitosan/PVA blend and the chitosan/gelated starch blend, the value of the breaking length, B_l , is higher than for the unfilled paper. The highest values are obtained for the chitosan/gelated starch blend with a starch content $w_f = 0.2$. A higher content of PVA in the blend with chitosan induces a step-wise decrease of the breaking length down to

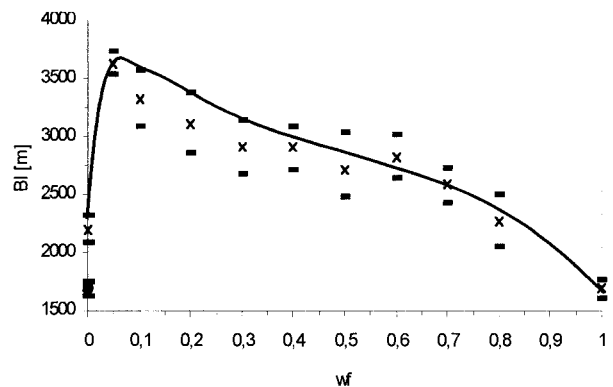


Figure 9 Dependence of breaking length (B_l) on weight fraction (w_f) of PVA in the blend with chitosan; $w_f = 0$, pure chitosan; (●) pure paper sheet.

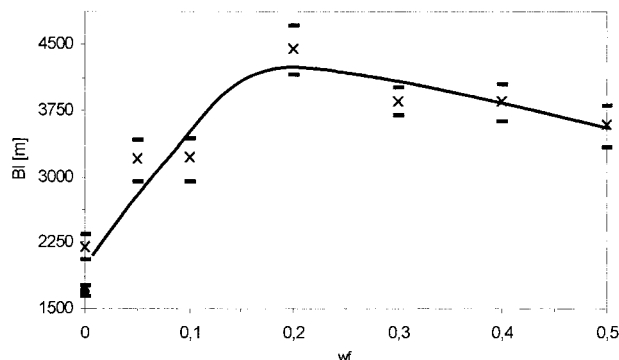


Figure 10 Effect of composition of chitosan/gellated starch blend on breaking length (B_l); $w_f = 0$, pure chitosan; (●) pure paper sheet.

1695 m, which is close to the value obtained for the unfilled paper.

CONCLUSIONS

Homogeneous blends of PVA and gellated starch with chitosan in solution were used as additives to the wet paper sheets. They improve the paper strength properties significantly without any additional treatment or curing process. Cationic chitosan acetate and its blends with PVA and starch cause a substantive modification of anionic cellulose fibers in paper through the expected presence of strong ionic interactions, influencing the original hydrogen bonds. These blends do not inhibit a paper's biodegradability (chitosan blends are biodegradable) and satisfy all requirements which should be met by paper additives presented in the Introduction. As the best results of the tested properties were obtained for low PVA (up to 10% weight fraction) content in the blend with chitosan acetate, future investigations will be limited to this range of PVA and to a lower content of chitosan in reference to the paper weight (1–7%). The studies of the wet strength of paper sheets with chitosan blends as an additive will be done also in the near future. We would like to check how prolonged drying of paper sheets (at 100° or higher), affecting a chemical modification of the filler, can influence the wet-strength properties of paper.

REFERENCES

1. Wet Strength in Paper and Paperboard; Weidner, J. P., Ed.; Tappi Monograph; Tappi: London, England, 1965; p 29.
2. Allan, G. G.; Akagane, K.; Neogi, A. N.; Reif, W. M. The Physics and Chemistry of Wood Pulp Fibers; Page, D. H., Ed.; Tappi Special Technical Association: London, England, 1970; Vol. 8, p. 125.
3. Ward, K., Jr. Chemical Modification of Papermaking Fibers; Marcel Dekker: New York, 1973.
4. Allan, G. G.; Fox, J. R.; Crosby, G. D.; Sarkman, K. V. In Transactions of the Symposium Fibre-water Interactions in Paper-making, Oxford, 1977; Fundamental Research Committee, Ed.; 1978.
5. Mucha, M.; Marszałek, J.; Bratkowska, M.; Woszczański, D. In Proceedings of the Symposium New Aspects on Chemistry and Application of Chitin and Its Derivatives, Poznań, 1999; Struszczyk, H., Ed.; Polish Chitin Society.
6. Muzzarelli, R. A. A.; Pariser, E. R. In Proceedings of 1st Conference on Chitin and Chitosan, MIT, Cambridge, 1978.
7. Kamiński, W.; Eckstein, W.; Modrzejewska, Z.; Sroka, Z. In Chitin World, Proceedings of 6th International Conference on Chitin and Chitosan, Gdynia, 1994; Wirtschftsverlag.
8. Chitin World, Proceedings of 6th International Conference on Chitin and Chitosan, Gdynia, 1994; Wirtschftsverlag.
9. Mucha, M.; Wieczorek, A., In Advances in Chitin Science, Proceedings of 7th International Conference on Chitin and Chitosan, "Euchis" Lyon; Domard, A.; Roberts, G. A. F.; Kjell, K. M.; Varum, M., Eds.; Jacques Andre: Lyon, France, 1997; p 890.
10. Joyce, M. K.; Gilbert, D.; Khan, S. A. Tappi J 1997, 80, 185.
11. Mucha, M. React Func Polym 1998, 38, 19.
12. Mucha, M.; Piekialna, J.; Wieczorek, A. Macromolecular Symposia; Hüthig and Wepf Verlag Zug: Heidelberg, Oxford, CT, 1999; 144, p. 391.
13. Wrzyszczyński, W.; Xia, Qu.; Szosland, L.; Adamczyk, E.; Linden, L.; Rabek, J. F. Polym Bull 1995, 34, 493.
14. Nada, A. M. A.; Abo Shosha, M.; Ibrahim, N. A. Polym Plast Technol Eng 1996, 35, 365.
15. PN-76/P-50060.
16. PN-77/P-50067 (ISO 187: 1977).
17. PN-93/P-50131 (ISO 1974: 1990).