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PLYBOND STRENGTH DEVELOPMENT OF SECONDARY
FIBER USING THE MARINE POLYMER CHITOSAN

By:

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A Thesis submitted
in partial fulfillment of the
course requirements for the
Bachelor of Science Degree

Western Michigan University
Kalamazoo, Michigan

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ABSTRACT

The purpose of this study was to investigate plybond strength development of secondary fiber by the addition of the marine polymer chitosan.

The chitosan was applied to refined, lightly refined and unrefined pulp suspensions. Two-ply handsheets were produced with addition levels of .5, 1, 2, 3, and 4 percent chitosan based on fiber weight.

Results indicate that addition of chitosan to two-ply handsheets significantly increased plybond strength from 30 to 120 percent depending on furnish and degree of refining. It was also determined that maximum strength values of selected tests occurred at approximately the two percent addition level of chitosan.

Chitosan shows considerable promise as a polymeric strength additive for paper of multiply formation and a possible refining substitute.

Keywords: Secondary Fiber, Plybond Strength, Chitosan, Refining

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INTRODUCTION

Prior to sheet formation on the paper or paperboard machine the papermaking fibers are treated to improve the formation process and subsequent finished product. These changes to the fiber are usually done to improve inadequacies in the sheet. One deficiency of utmost importance is sheet strength or, in board manufacture, plybond strength.

The development of this strength is usually done by fiber selection, mechanical or chemical means. The mechanical method is accomplished by beating or refining the fibers. The chemical method involves the addition of polymeric chemicals. These chemicals have an affinity for cellulosic surfaces which improve fiber to fiber bonding which in turn will improve sheet strength and also plybond strength.

Chitosan, a natural marine polymer has shown moderate success in virgin pulp applications as a strength additive.(1,2)

This study will focus on plybond strength development of secondary fibers and a possible accelerated refining process using chitosan as a wet-end strength additive.

THEORETICAL DISCUSSION

In the manufacture of paper or paperboard, a sheet characteristic that is given much consideration is the strength the sheet acquires during forming. The strength of a given sheet will only be as good as its forming process and ultimately the fibers that make up its web. The processing of the fibers before sheet formation, termed stock preparation, will enhance the fibers to a degree which will improve certain features of the dried web. These processes are ones which will create or improve new bonding sites on individual fibers which in turn will increase fiber to fiber bonding, finally leading to a stronger sheet. The methods by which improved bonding takes place can be accomplished by several processes. Two of the more common processes are mechanical and chemical treatments of the pulp suspension.

Mechanical processing of papermaking fibers is done by beating or refining the pulp fibers while in suspension. Refining is one of the most influential processes in controlling the quality of paper and board.(3) For board considerations plybond strength is extremely important. Board that has poor plybond is virtually worthless. It cannot survive the rigors of printing and converting processes. Through mechanical refining, the fiber of paper and board will acquire strength properties that benefit the finished sheet. There are three main results of beating.(4)

1. The fibers are shortened
2. The fibers are abraded and fibrillated on their exterior surface
3. The fibers are crushed, bruised or internally fibrillated which in water makes them more plastic.

There are also other secondary effects of beating but they will not be covered in this study. Therefore, from the three previous statements on

beating, the variables affecting bonding in paper or board are the ones involving fibrillation of the fiber. Bonding in all papermaking fibers is caused by external fibrillation.(5) This, of course, deals with pulps of mechanical treatment. Chemically treated pulps can also operate this way with supplemental help the chemical provides as a bonding agent. Bonding can also occur by the mechanisms of cohesion and adhesion.(6)

For secondary fiber pulps the strength of the formed sheet is somewhat lower than its virgin counterparts. This is due to losses of external fibrils so the cohesiveness of the fibers is reduced and also a compactness of the fiber structure is attained which makes it more difficult to refibrillate without causing extensive damage. However, fibrillation is possible in these pulps.

Chemical addition to fiber pulps is a very well documented area. These chemicals are used primarily to overcome papermaking deficiencies. One such deficiency is in strength development of the sheet.

The additives which are polymeric in nature, also can improve the interfiber bonding process by chemical modification of fiber properties.(2) The chemicals bond well to fiber surfaces and are quite capable of bridging interfiber distances. The bridging mechanisms establishes bonds between fibers and fibrills that would not have normally been formed. The strength of a sheet can, by this bonding phenomena, increase. Refining the pulps in conjunction with polymeric additives can quite often improve sheet strength considerably.

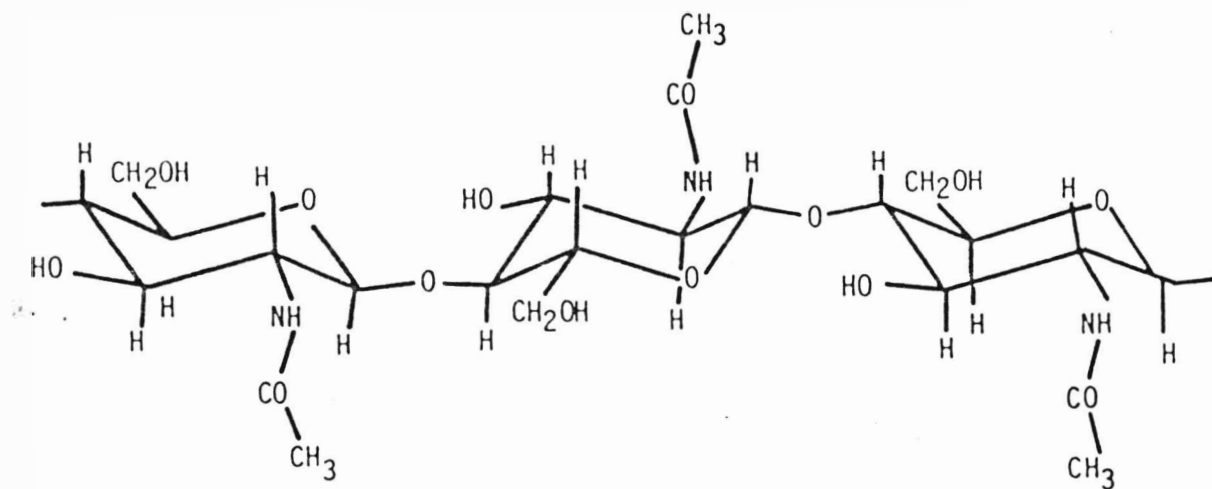
With regards to secondary fiber, this area is of worthy study. The fiber needed for the furnish is, of course, once refined once dried. Repulping the fiber, screening, cleaning and again refining it, weakens is appreciably. Though adequate strength levels are reached, the fact remains that consider-

able energy is used to refine the fibers to induce favorable sheet formation. A possible attempt would be then to enhance or accelerate the beating process using polymeric additives. Polymeric additives have been used in the past as beater additives or adhesives.(7) These additives have also been used to improve other sheet properties such as retention, formation improvement and drainage.

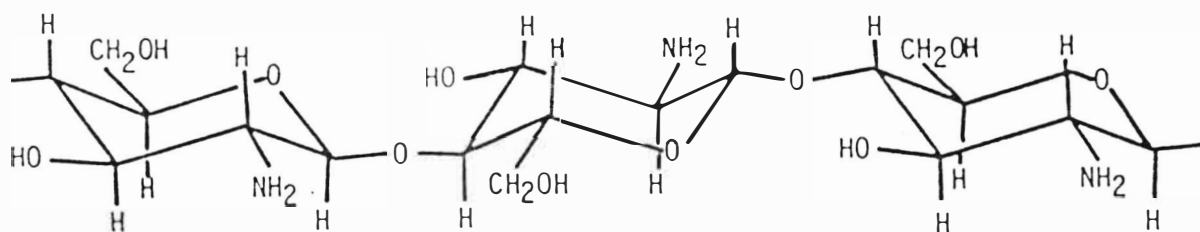
The polymers that are used are of three distinct types: natural polymers, modified natural polymers and synthetic polymers. The first two mentioned are either polysaccharides or modified polysaccharides. The third, synthetic polymers have been used quite extensively as with the case of urea formaldehyde and melamine formaldehyde.(8)

The polymers that function as strength additives base their success on the fact that if better bonding is to occur in the paper web, the need arises to either increase the number of bonds between fibers or improve the bonds already present. The polymer that can achieve these goals must have several features. It must be a linear polymer so as to allow complete accessibility of its functional groups. It must be film forming and of high molecular weight, have cohesive strength and the ability to span interfiber distances, polycationic for ionic bond formation and should have the ability of forming hydrogen bonds with non-ionic areas of the fiber surface.(2) One such chemical is the marine polymer chitosan.

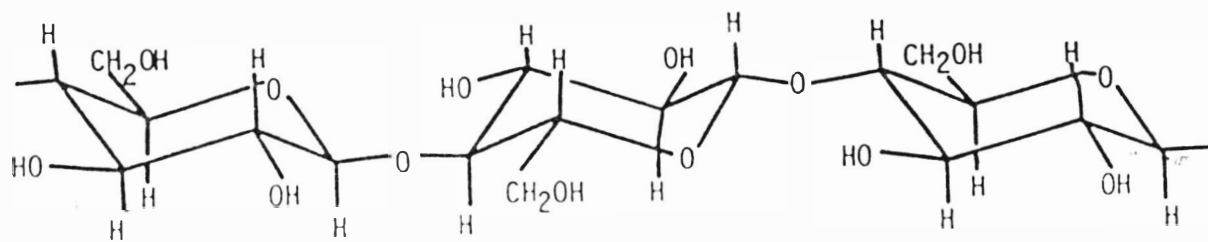
Chitosan is a derivative of chitin. Chitin is a high molecular weight, linear amino-polysaccharide. It is an abundant organic compound that is extracted from shellfish waste such as shrimp, clam, lobster and crab shells. The molecular structure of chitin is quite like that of cellulose. Chitosan, the deacetylation product of chitin, is also quite analogous to cellulose. The structures are shown in Figure 1. As can be seen from Figure 1, the main



(a) CHITIN



(b) CHITOSAN



(c) CELLULOSE

Fig. 1. Molecular structures of chitin (a), chitosan (b), and cellulose (c).

difference in the molecular structures of chitosan and cellulose is in the C₂ position. Cellulose has a hydroxyl group and chitosan, an amino group. In the free amine form chitosan is not soluble in water, but becomes a water soluble salt in acidic conditions. Other than a paper making additive, chitosan has been used as a waste treatment coagulant, a binder in nonwoven fabrics and a fungicide for tree plantations. Graft copolymers of chitosan have also been used in papermaking systems successfully.(9-11)

The mechanism by which chitosan can operate as a papermaking additive is shown in Figure 2. The cationic amino group forms ionic bonds with the acidic functional groups on the fiber, and the hydrogen bonding that exists between cellulose and chitosan.

By this method it will be intended to show plybond strength development using the marine polymer chitosan on secondary fiber with varying degrees of refining.

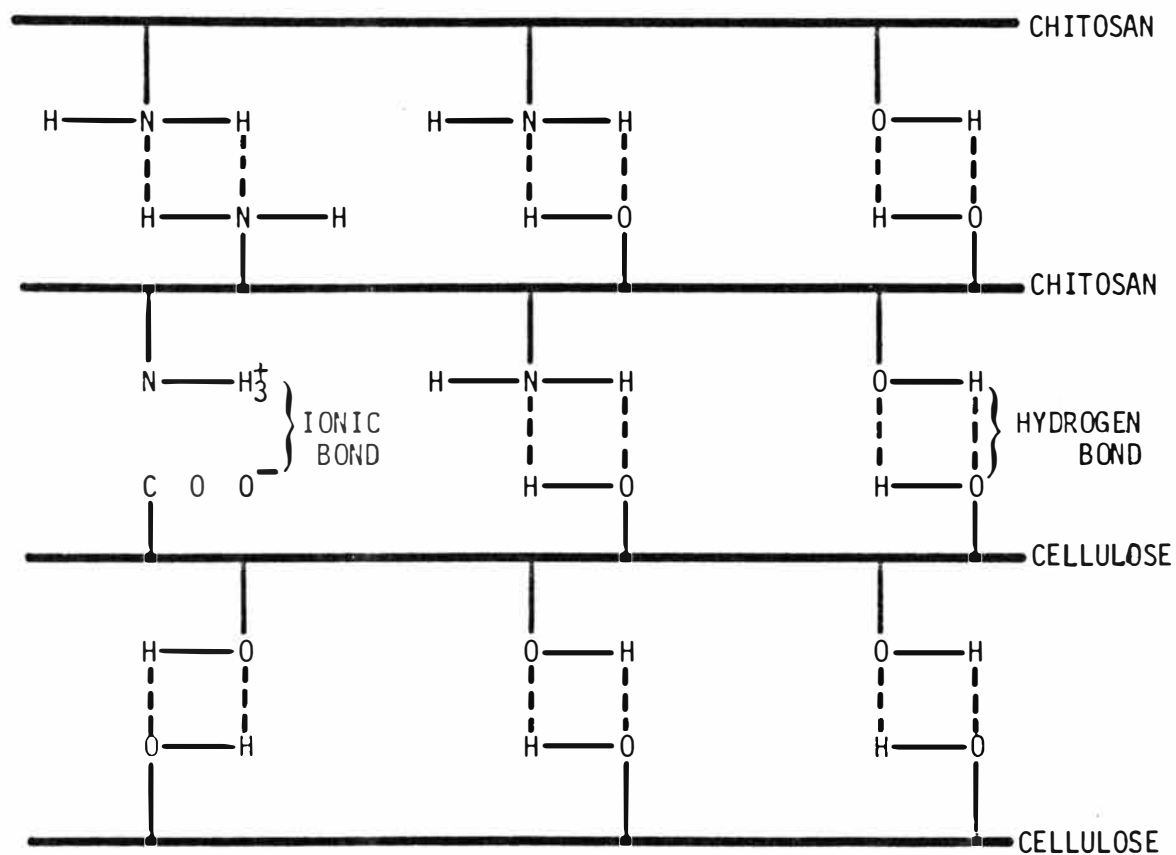


Fig. 2. Cellulosic fiber-chitosan binder system (2)

EXPERIMENTAL PROCEDURE

The experimental portion of this study was broken down into five areas.

1. Furnish Composition
2. Refining Parameters
3. Chitosan preparation and delivery to fiber
4. A procedure for making two-ply handsheets
5. Condition of handsheets and testing

The experimental procedure that was followed was in the general form: establish a furnish of known composition; set refining parameters and refine accordingly; prepare chitosan in a suitable form for use as a wet-end additive; deliver the chitosan to the fiber; produce two-ply handsheets; condition and test the handsheets.

Furnish Composition

The secondary fiber stock that was used was unprinted groundwood newsprint and SBS core waste (solid bleached sulfate) or commonly known as #1 boxshop clippings or cuttings, hereafter known as SBS. The newsprint was a common short fiber pulp and the SBS a long fiber pulp. The furnish composition used was:

	Percent		
Newsprint	0	50	100
SBS	100	50	0

Refining Parameters

The degree of refining was chosen as refined, lightly refined and unrefined. Refining was done by the Valley Beater following TAPPI Standard T200-os70. The fiber was defibered in the Morden Slusher prior to the Valley Beater at 1.60 percent consistency for two minutes at 20°C.

Chitosan Preparation

Raw chitosan was received in dry, flake form and had to be prepared for use as a wet end additive. A one percent solution of chitosan acetate was made by the following method: 50g of dry chitosan was dispersed in 2500ml of distilled water with a high speed stirrer, and while continuing stirring, 2500ml of a two percent acetic acid was added. Dissolution occurred in 45 minutes. The solution was then filtered through a 60 mesh screen to remove any undissolved matter.

Chitosan Delivery to Fiber

The method by which chitosan is delivered to the fiber is the precipitation technique. Other methods exist but were not attempted.(1) A vigorously stirred suspension of fibers (13.2g) in water (844ml) was treated with aqueous solution of chitosan acetate (1.0% solution) for 20 minutes. The pH was then adjusted to pH 10 with .5N NaOH. The chitosan is precipitated onto the fiber at approximately a pH of 6.0 to 7.0. The suspension was stirred for ten additional minutes then diluted to .25 percent consistency then formed into handsheets on the Noble and Wood sheetmold.

Handsheet Procedure

The handsheet formation method used in this study was done by a similar method in an unpublished report by IIT Research Institute.(12) The handsheets were made by forming each ply separately on its own wire, then adjusting the consistency to 10 percent by applying vacuum while still on the sheet mold. One ply was then inverted over the other, then both plies were pressed together between a felt. One wire was couched, the other still attached. This wire with the wet web was then dried on the Noble and Wood drying can. The sheet, therefore, was dried under restraint. The basis weight of the two-ply

handsheet was approximately 32 lbs. per thousand square feet.

In order to obtain handsheet plies that have a known consistency, the wet sheet-mould wire was weighed initially. Ten observations were used. After the sheet was formed in the sheet-mould, the web and wire were weighed, and by returning the web and wire to the sheet-mould and applying four inches mercury vacuum, then reweighing on a trial and error procedure, the web consistency could then be adjusted to ten percent. The separate plys then were pressed together between felt and passed through the Noble and Wood press.

Testing of Handsheets

All handsheets were conditioned under TAPPI Standards and all testing also followed TAPPI Standards. Brightness was measured on the Technidyne Brightness meter at 457nm. ZDT values were measured on the TMI ZDT tester using double sticky tape from 3M Company. Tensile properties were measured on the Instron constant rate of elongation machine and the .03 head was used on the MIT fold tester.

PRESENTATION OF RESULTS

The Effect of Refining on Furnish and Handsheets

The action of refining on the furnishes is quite rapid. The longer fiber SBS furnish generally showed stronger sheet properties, with the 50/50 furnish mix of SBS-newsprint next strongest and the 100% newsprint being the weakest, as expected of the shorter fibered groundwood pulps.

Figure 3 shows this rapid response of the furnishes in relation to refining time and freeness. As expected sheet density increased also as seen in Figure 4. Strength values such as tensile strength, tensile breaking length and ZDT show increasing sheet strength (Figures 5-7). Plybond strength, as measured by ZDT and shown in Figure 7 improves with refining. Porosity, a measure of the degree of bonding supports the polybond strength values by decreasing as seen in Figure 8. The refined sheets showed a tendency towards flexibility as seen in fold, elongation and tensile energy absorption, shown in Figures 9-11. The tearing force dropped as expected with refining as shown in Figure 12. Brightness, the only optical property looked at, showed no change with refining in the 100% newsprint furnish, but dropped slightly with the newsprint mixed furnishes (Figure 13).

The Effect of Chitosan Addition on Handsheets

The addition of chitosan to the furnish showed a modest increase in plybond strength. As seen in Figures 14-16, ZDT values increased quickly, then reached a maximum, then leveled out somewhat. This was true for all three furnishes used. Tensile breaking length also showed these characteristics as shown in Figures 17-19. Folding properties, though showing some data scatter, also followed breaking length and ZDT patterns (Figures 20-22).

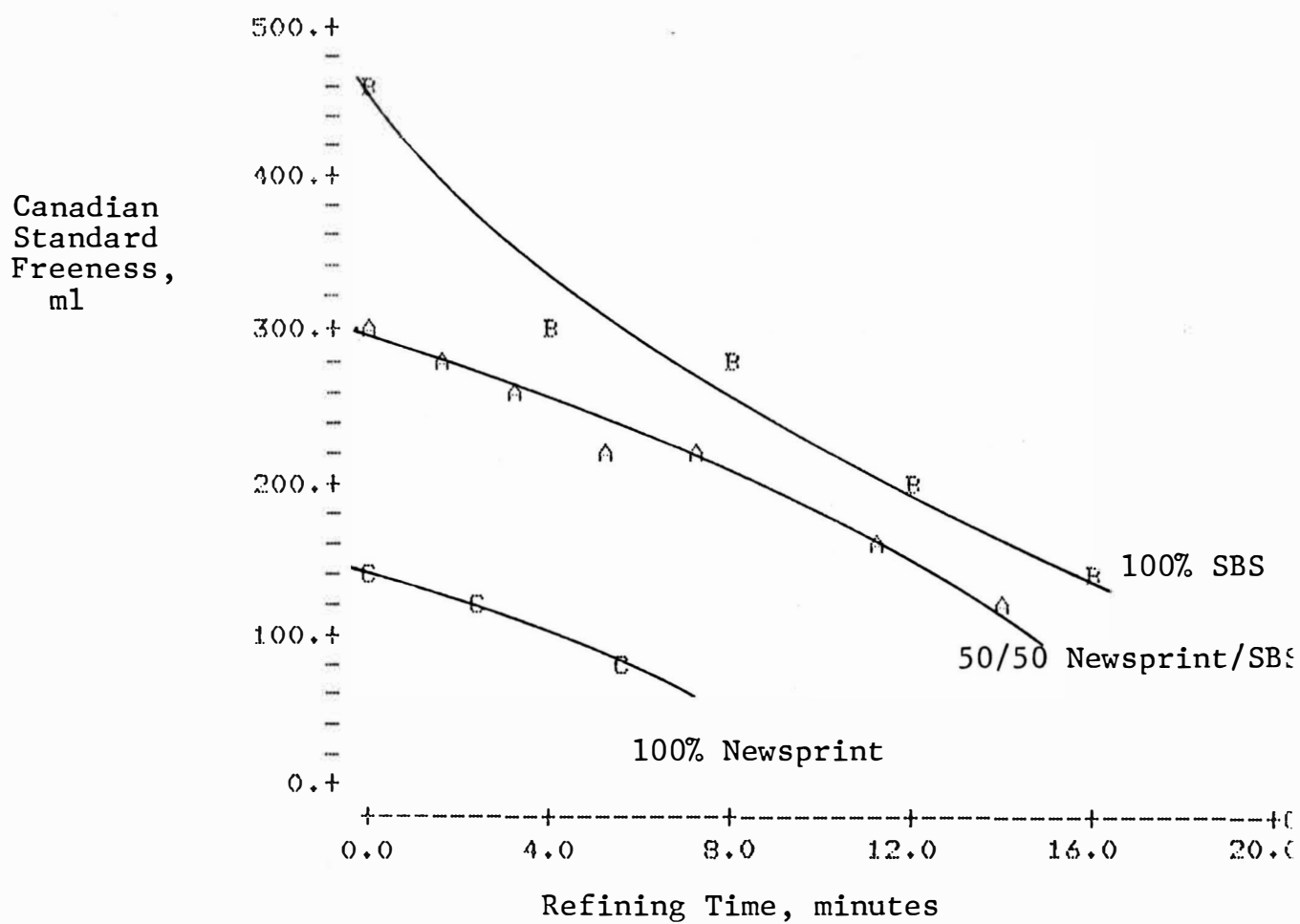


Figure 3. The effect of refining on Canadian Standard Freeness.

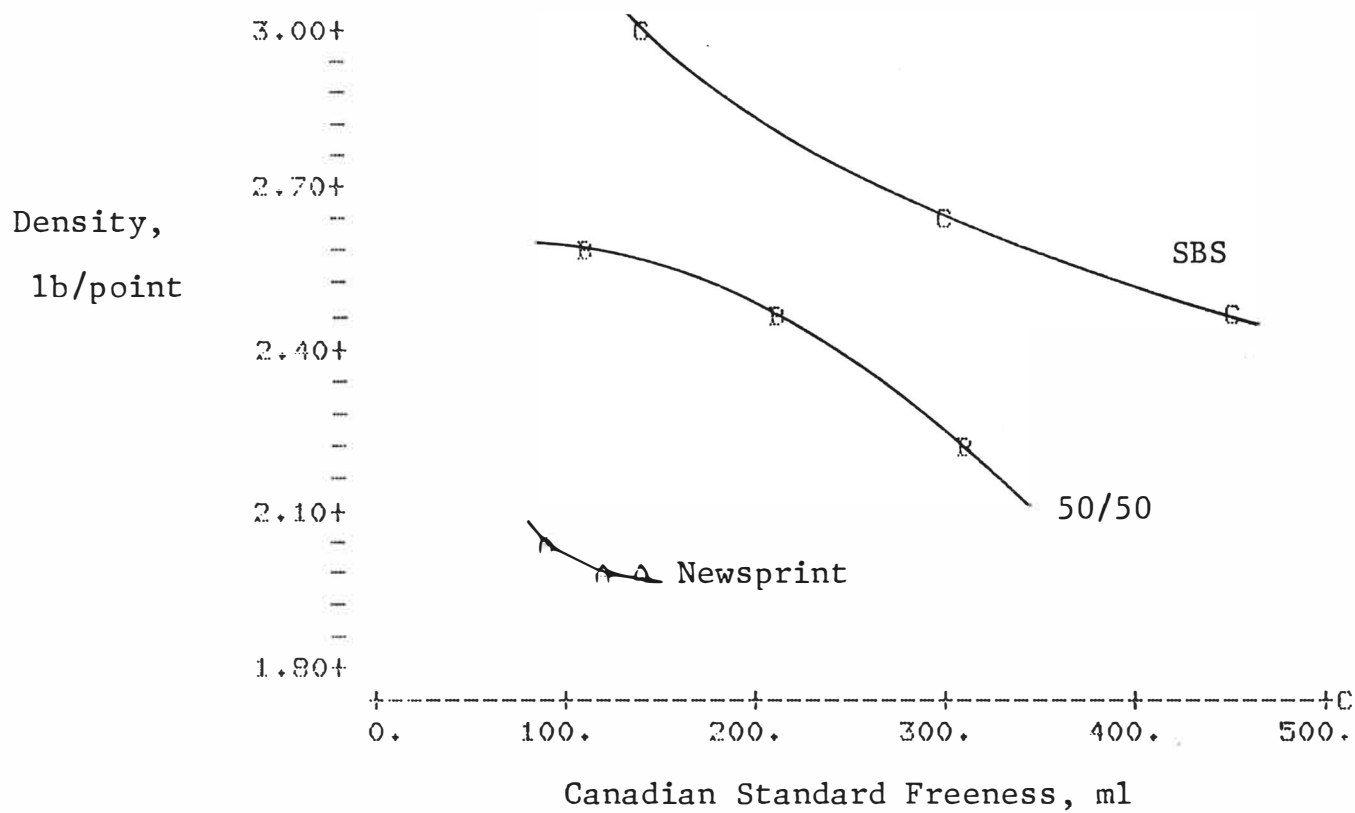


Figure 4. The influence of refining on apparent sheet density.

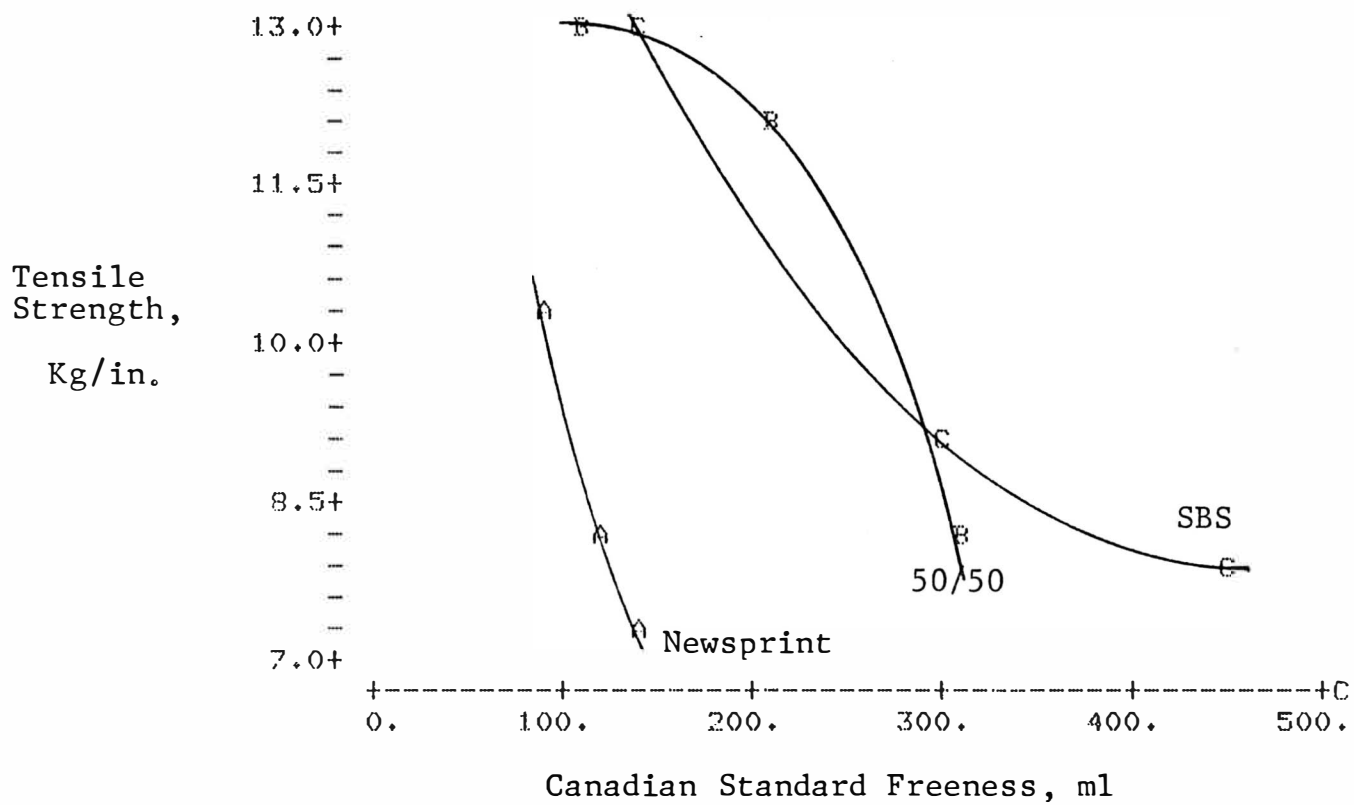


Figure 5. The influence of refining on tensile strength properties of 100% SBS, 50/50 mixture and 100% newsprint

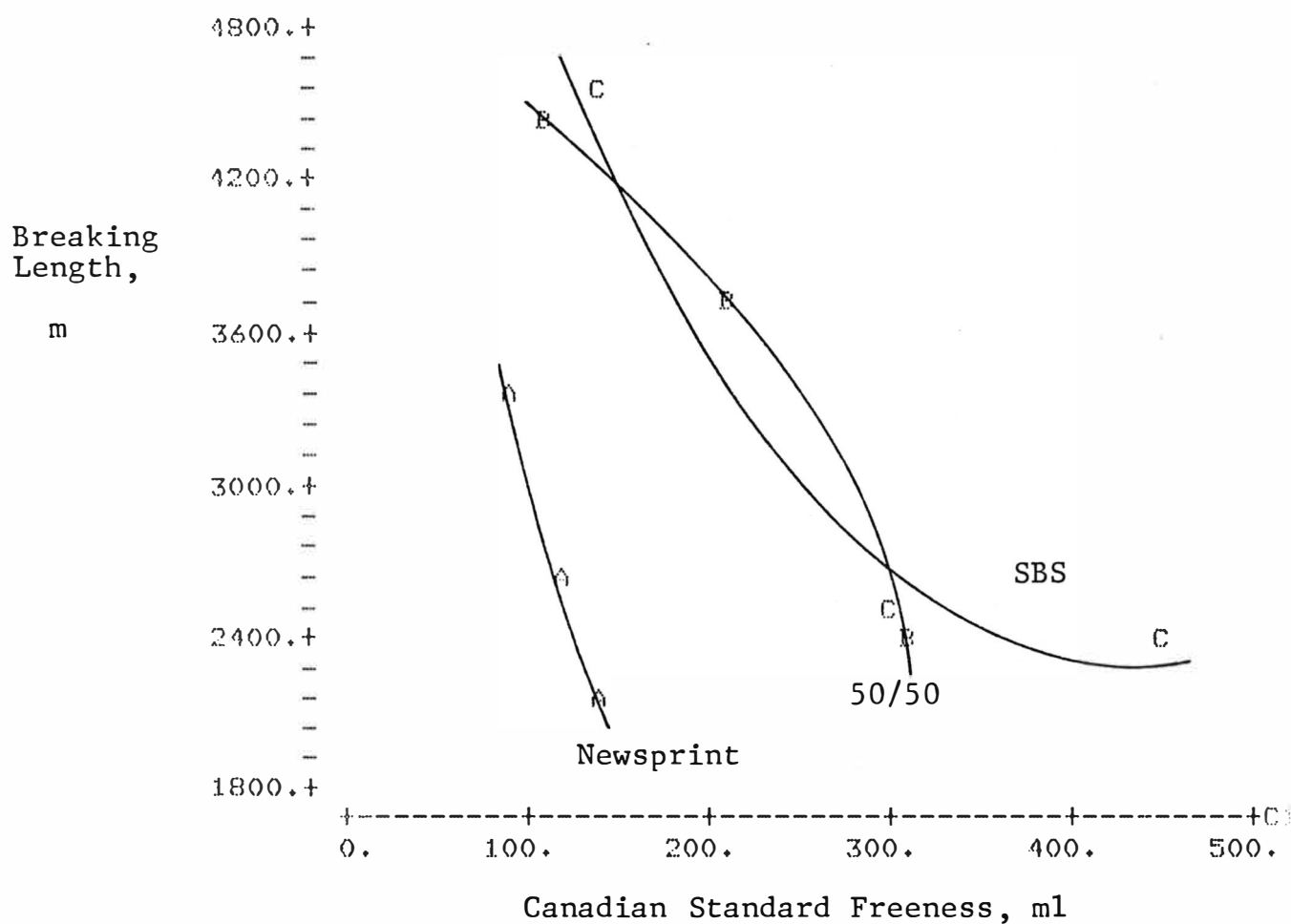


Figure 6. The influence of refining on breaking length properties of 100% SBS, 100% newsprint and 50/50 mixture.

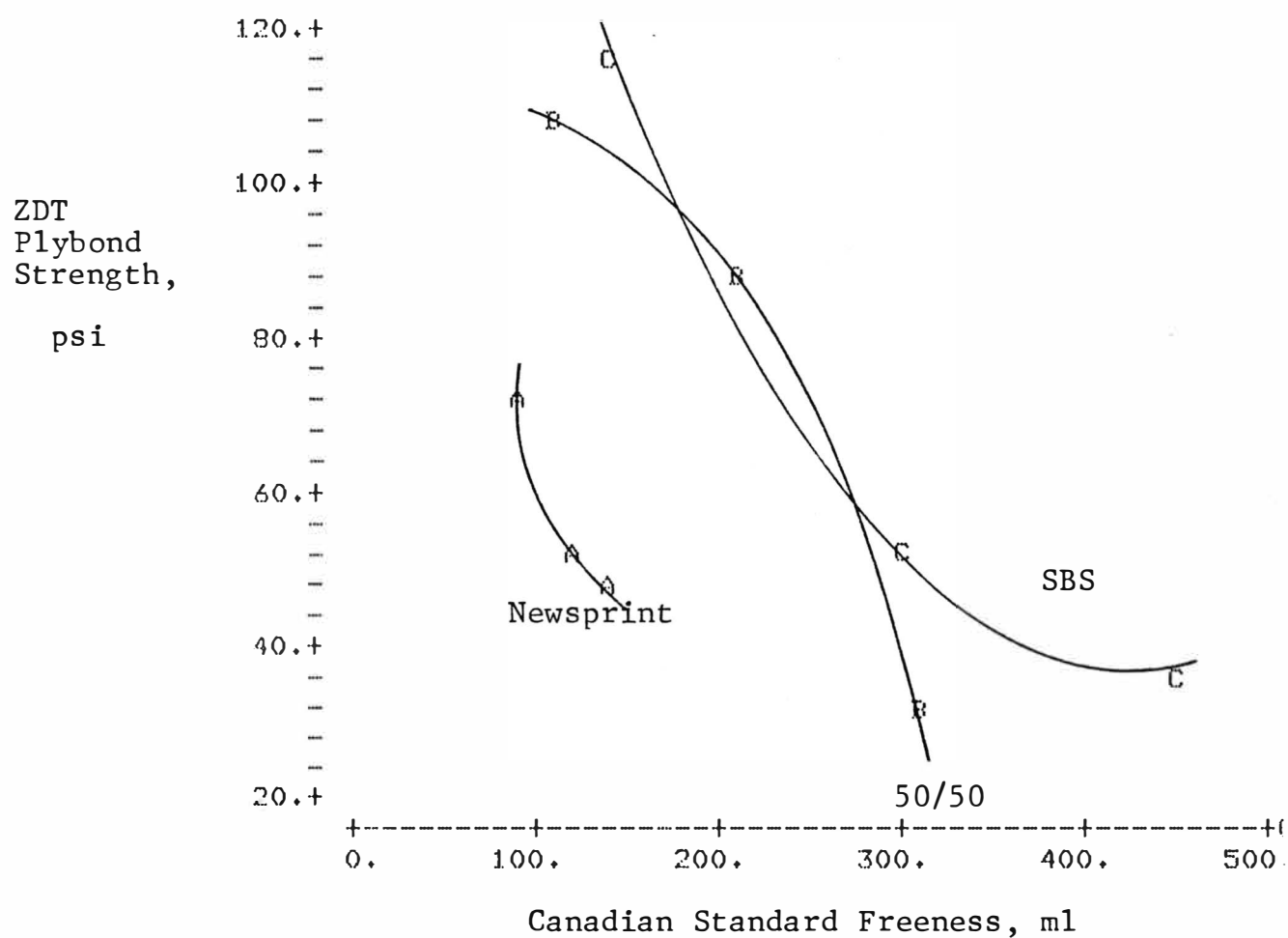


Figure 7. The influence of refining on ZDT plybond strength of 100% SBS, 100% newsprint and 50/50 mixture.

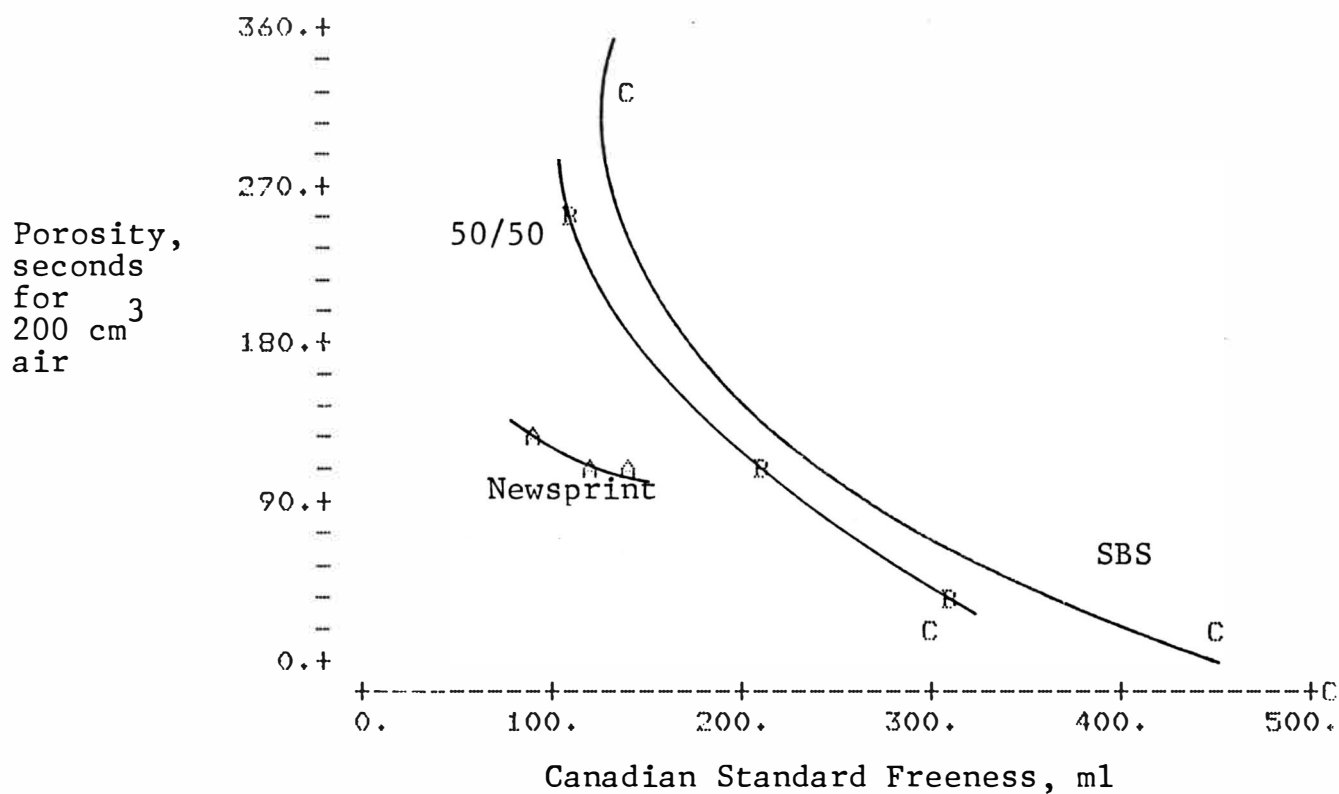


Figure 8. The influence of refining on porosity of 100% SBS, 100% newsprint and 50/50 mixture.

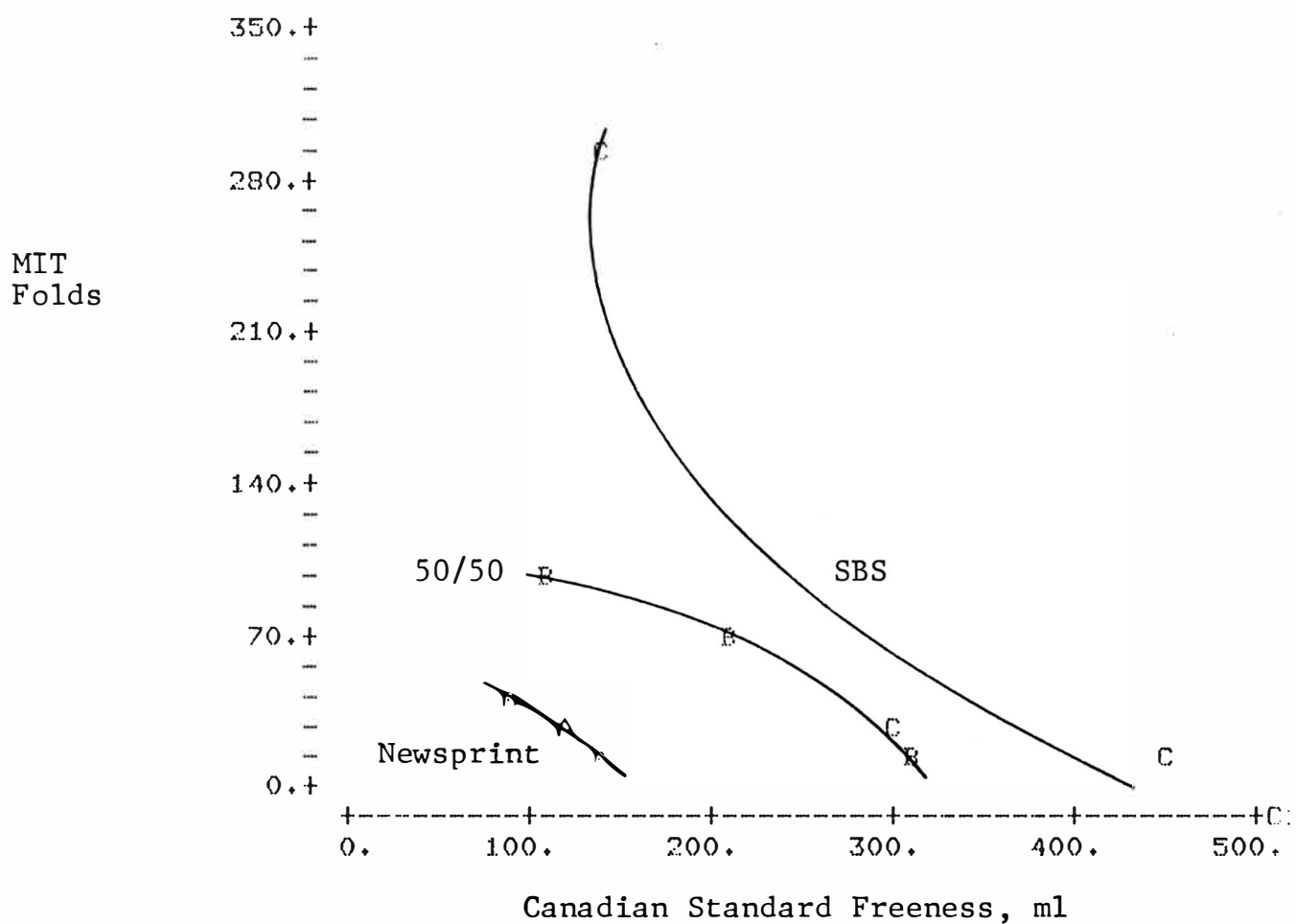


Figure 9. The influence of refining on MIT folding properties of 100% SBS, 100% newsprint and 50/50 mixture.

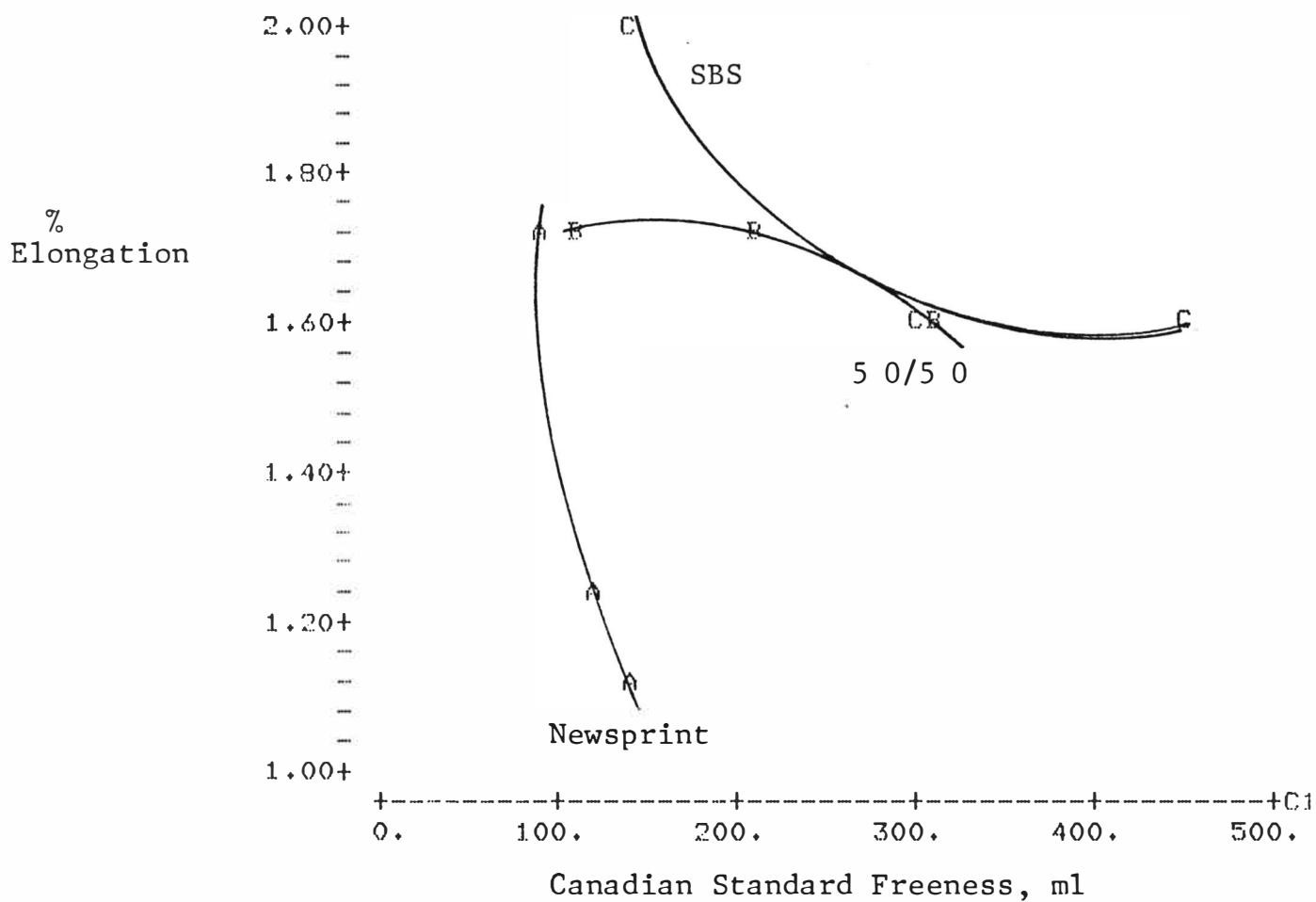


Figure 10. The influence of refining on % elongation of 100% SBS, 100% newsprint and 50/50 mixture.

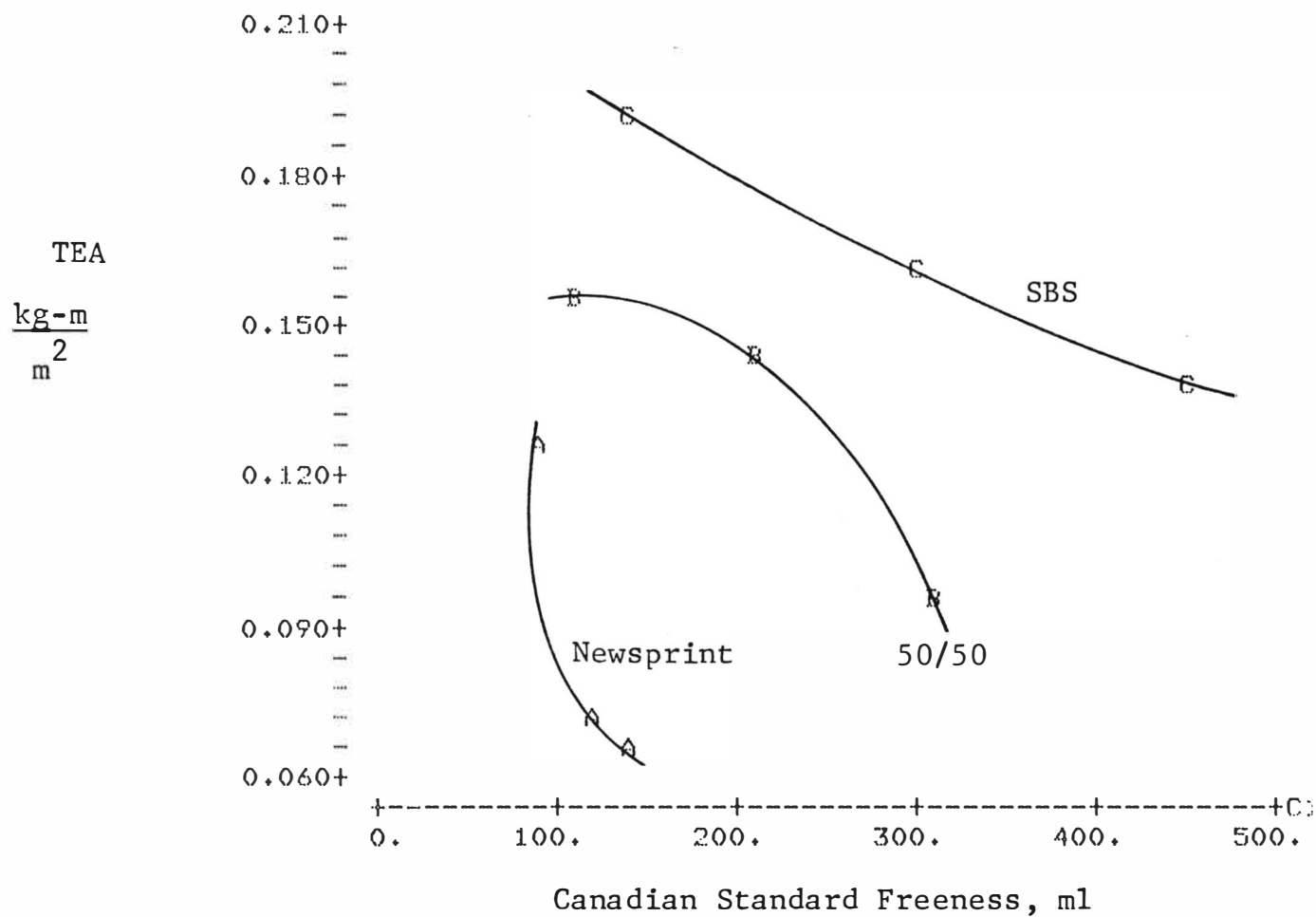


Figure 11. The influence of refining on Tensile Energy Absorption of 100% SBS, 100% newsprint and 50/50 mixture.

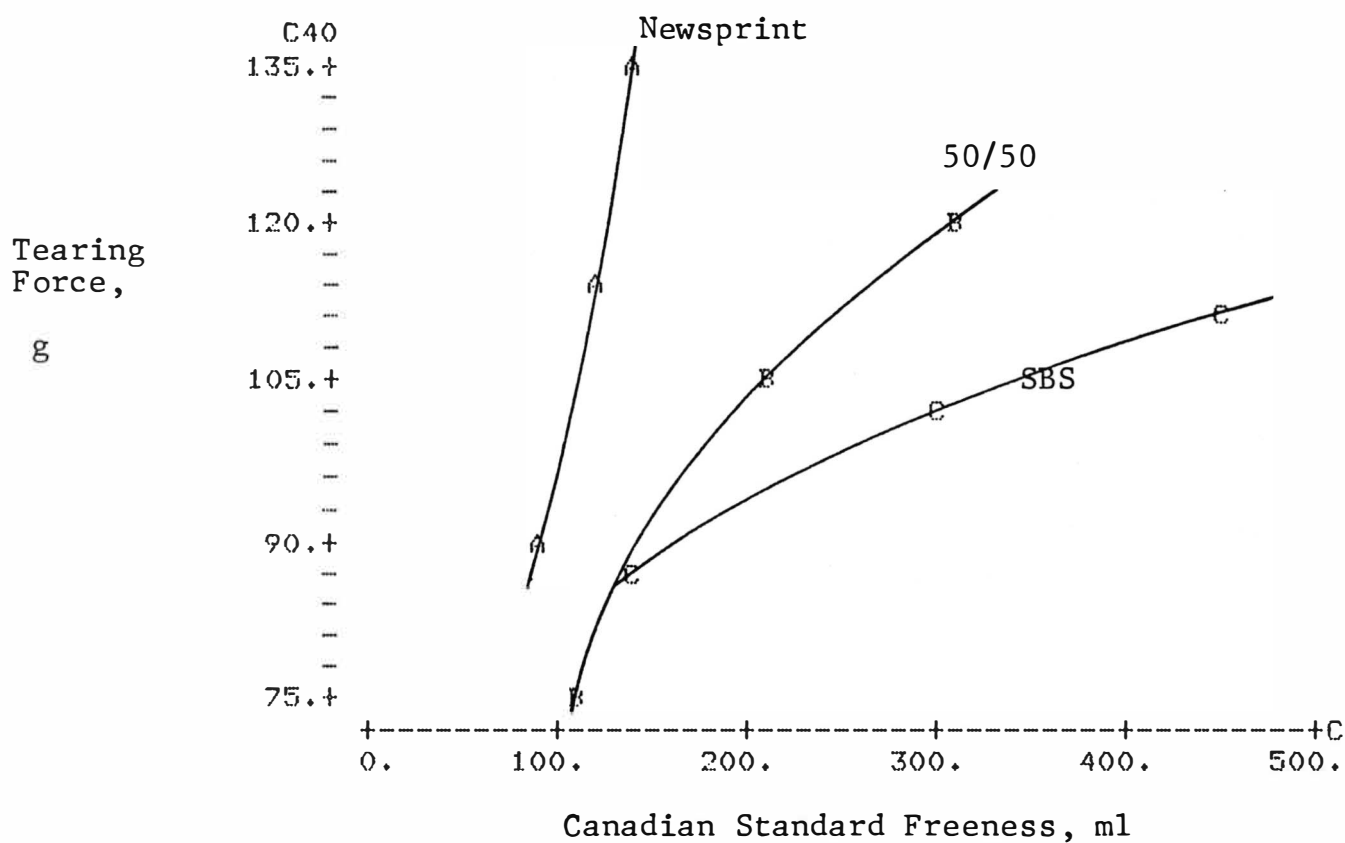


Figure 12. The influence of refining of tearing force of 100% SBS, 100% newsprint and 50/50 mixture.

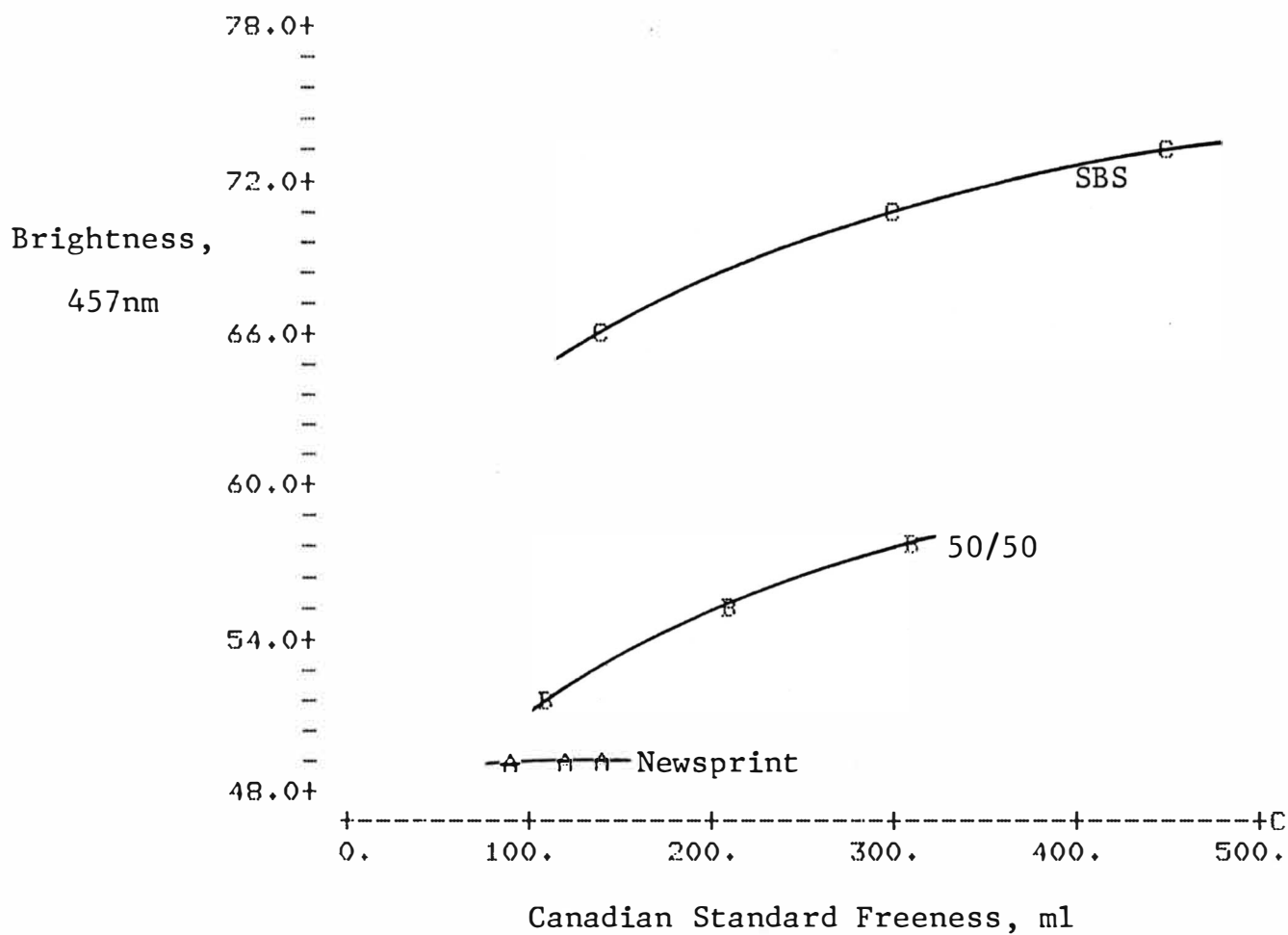


Figure 13. The influence of refining on Brightness of 100% SBS, 100% newsprint and 50/50 mixture.

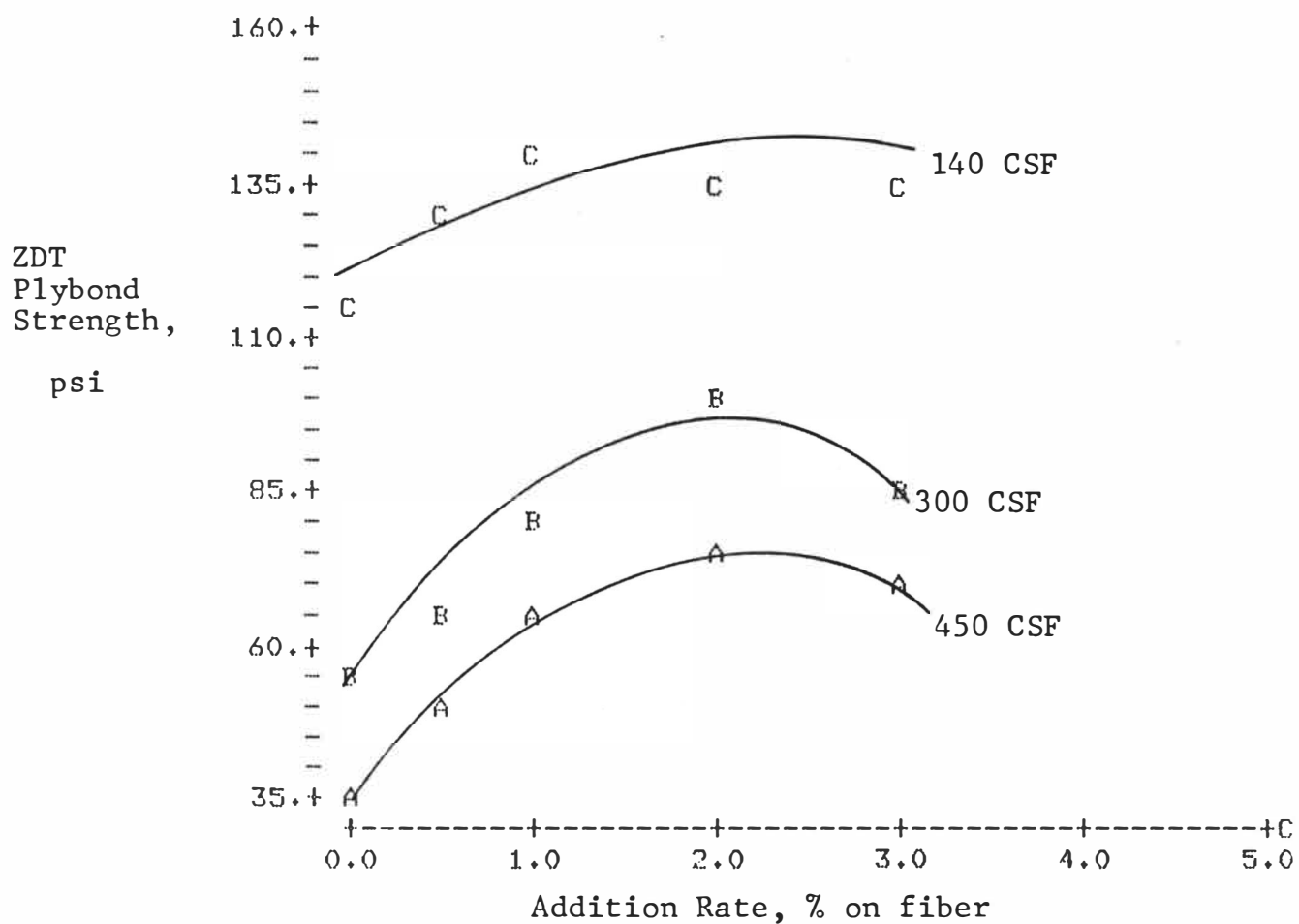


Figure 14. ZDT Plybond Strength properties of 100% SBS handsheets treated with chitosan.

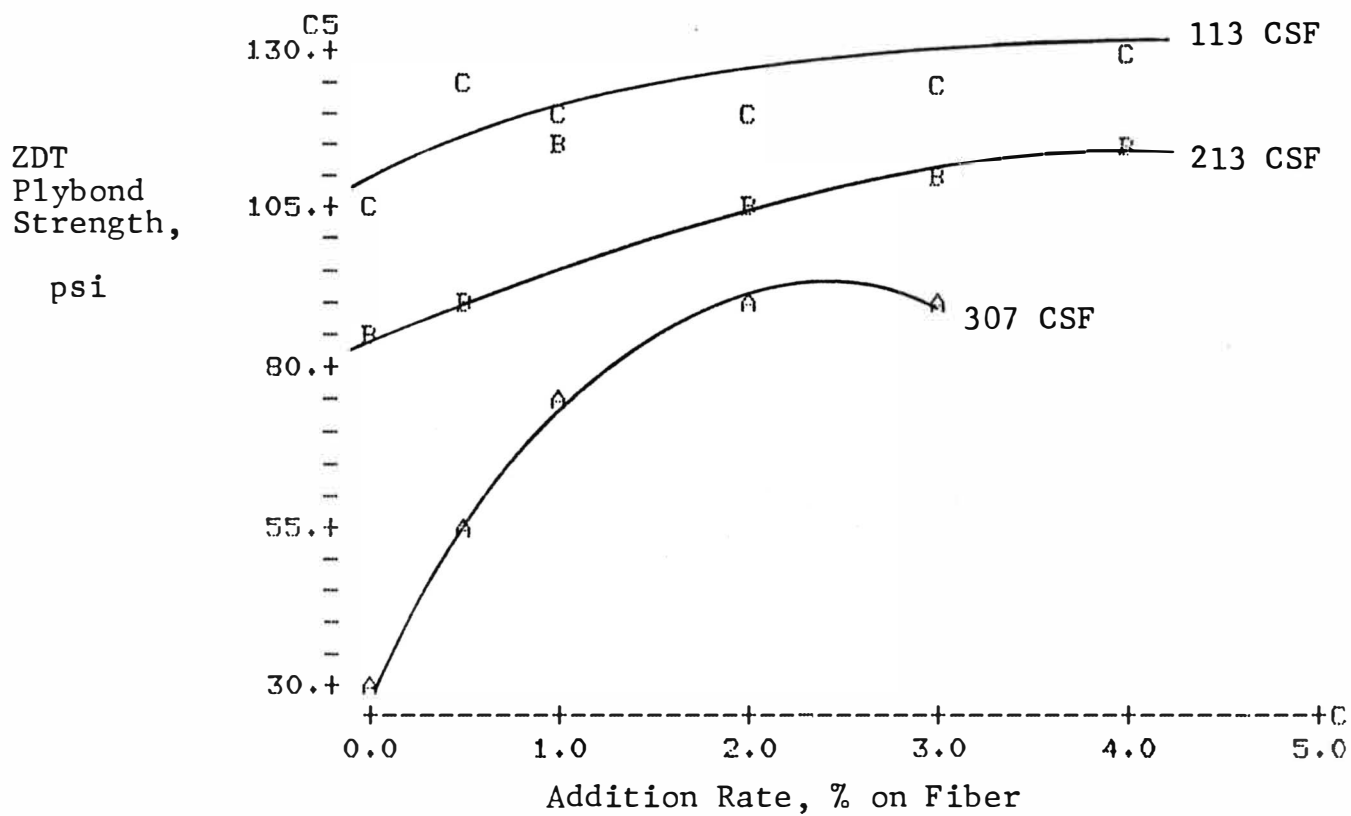


Figure 15. ZDT Plybond Strength properties of 50/50 mixture handsheets treated with chitosan.

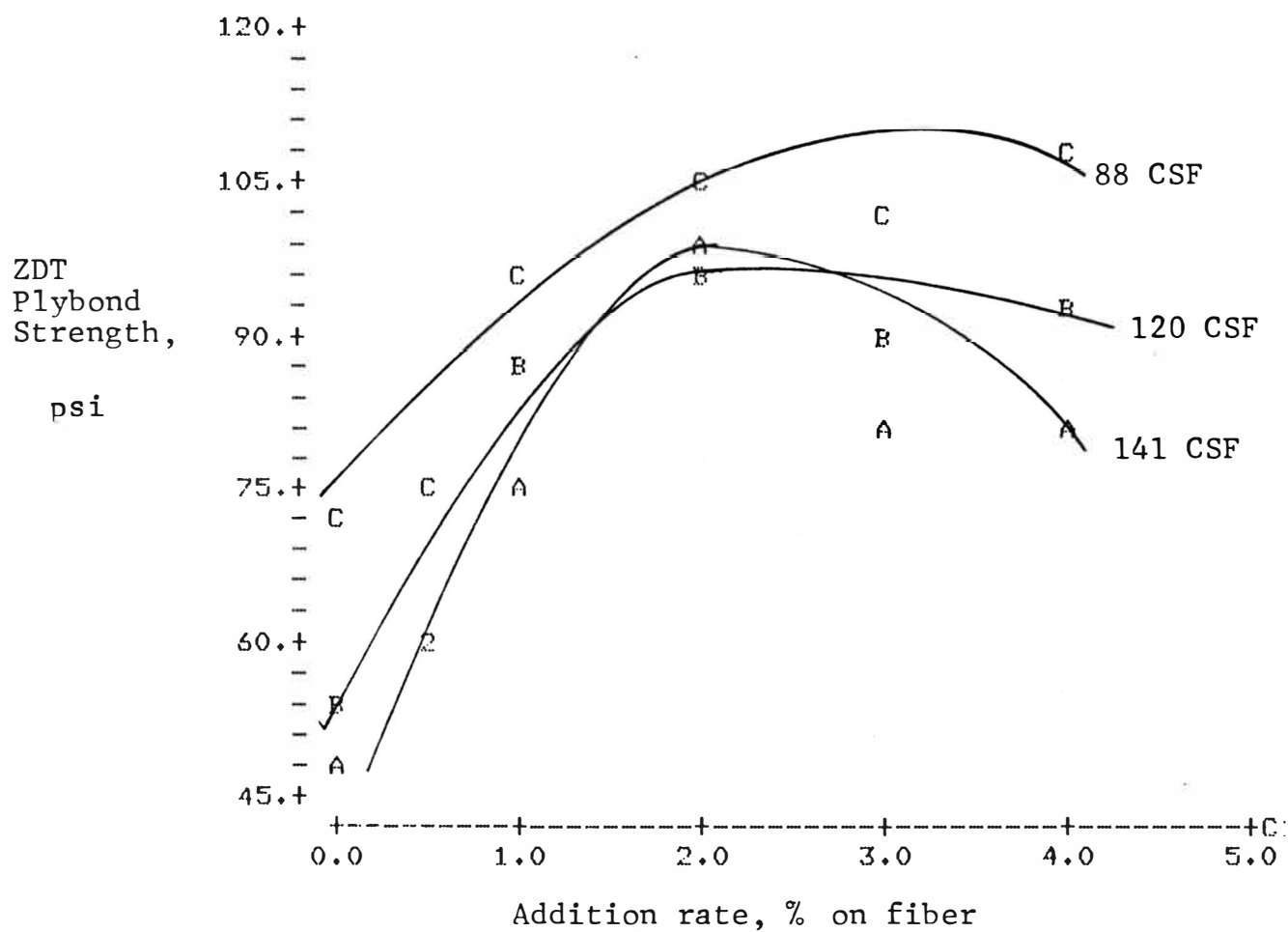


Figure 16. ZDT Plybond Strength properties of 100% newsprint handsheets treated with chitosan.

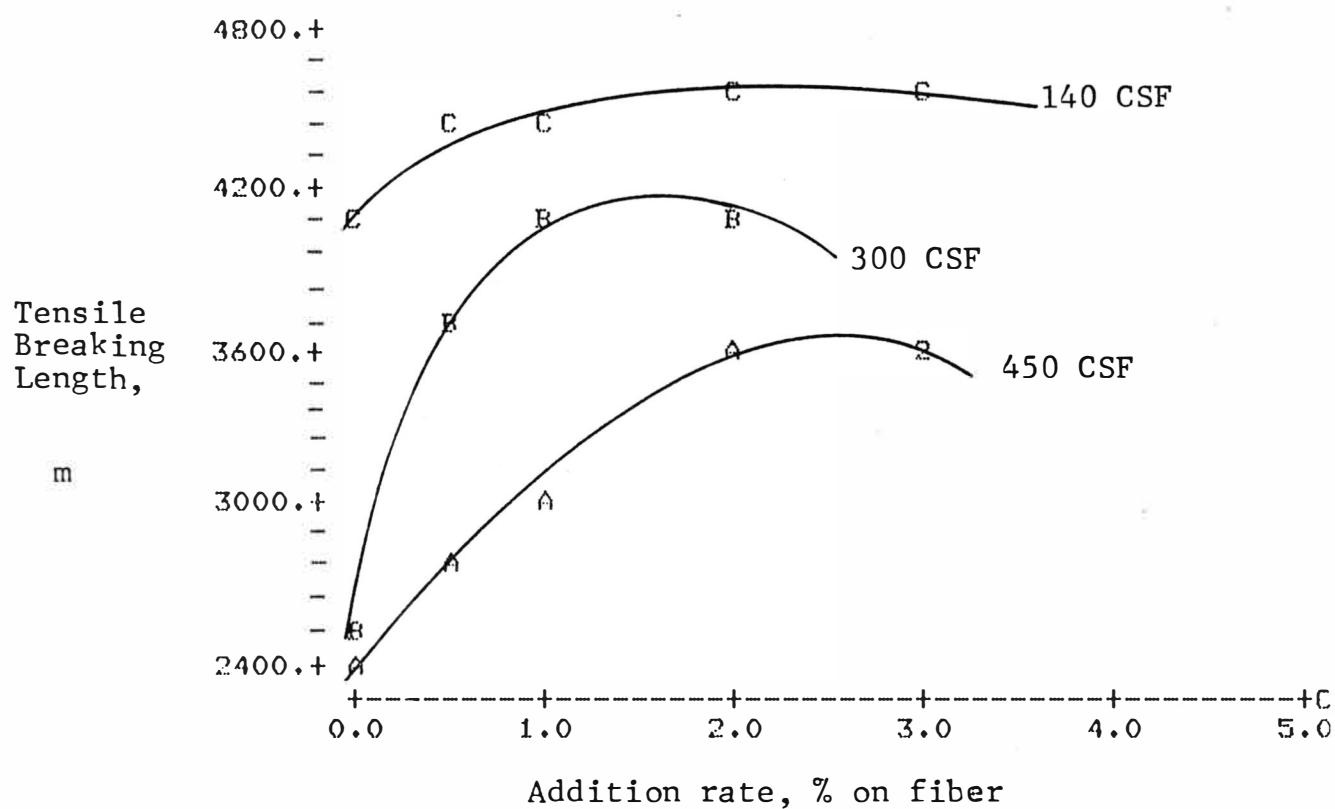


Figure 17. Tensile Breaking Length properties of 100% SBS handsheets treated with chitosan.

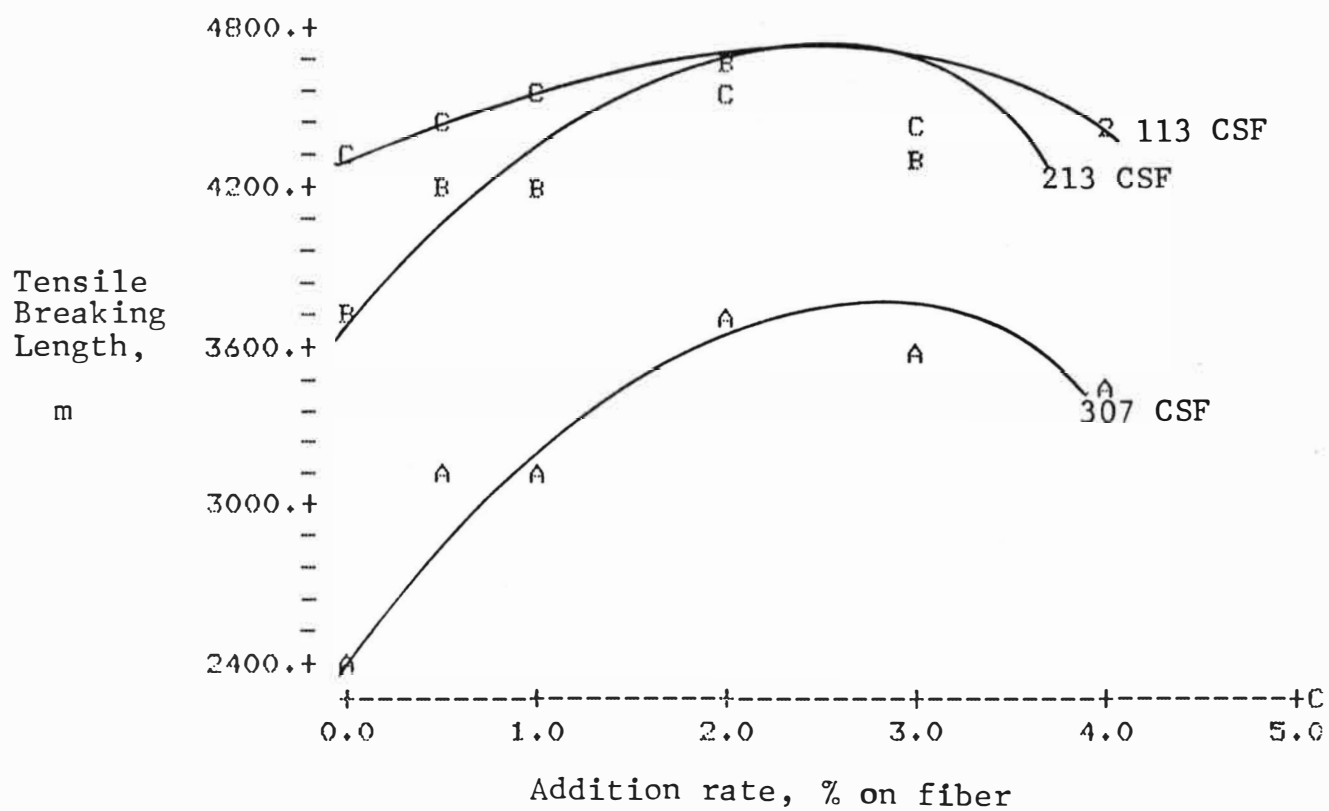


Figure 18. Tensile breaking length of 50/50 mixture handsheets treated with chitosan.

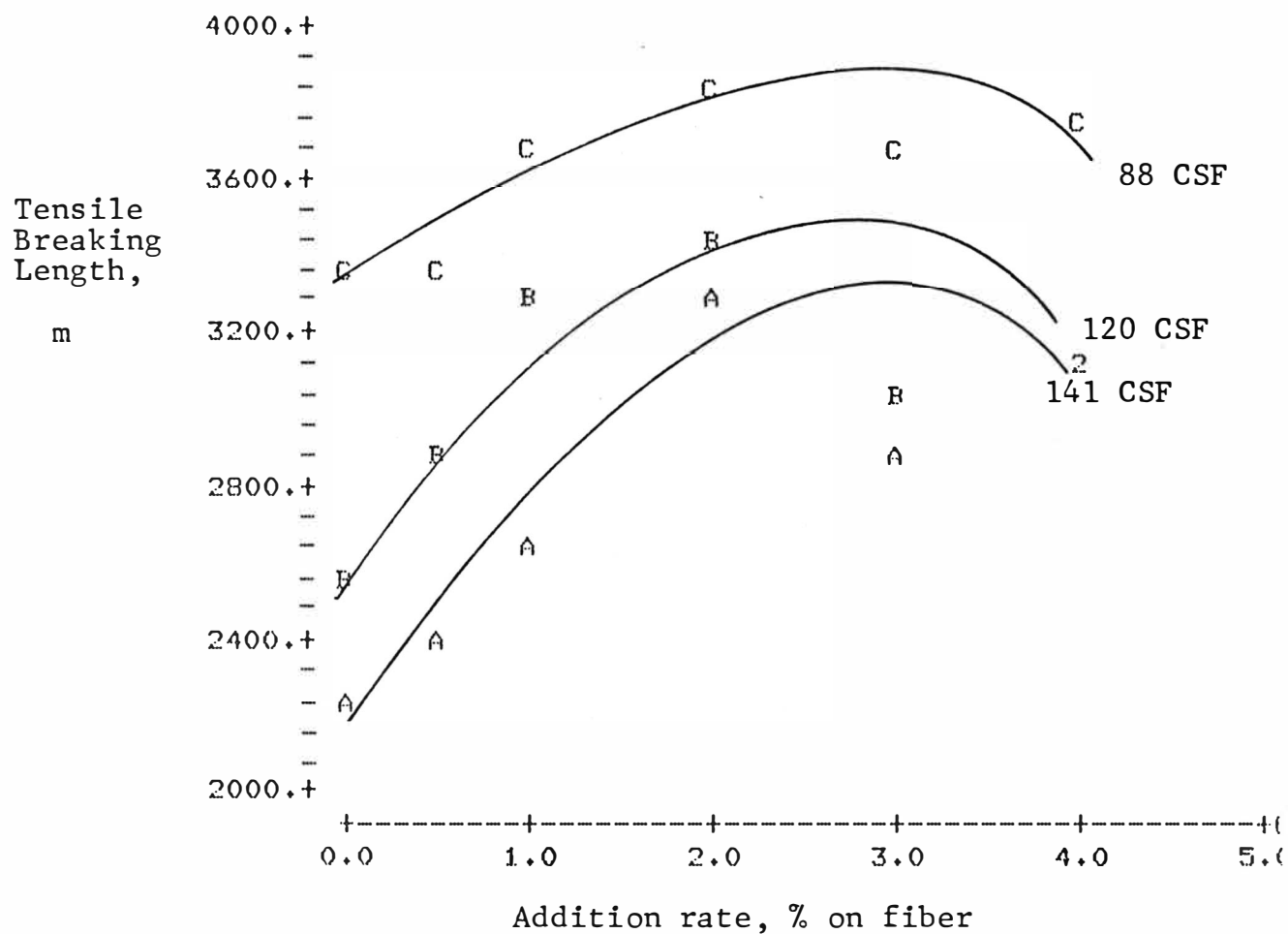


Figure 19. Tensile breaking length properties of 100% newsprint handsheets treated with chitosan.

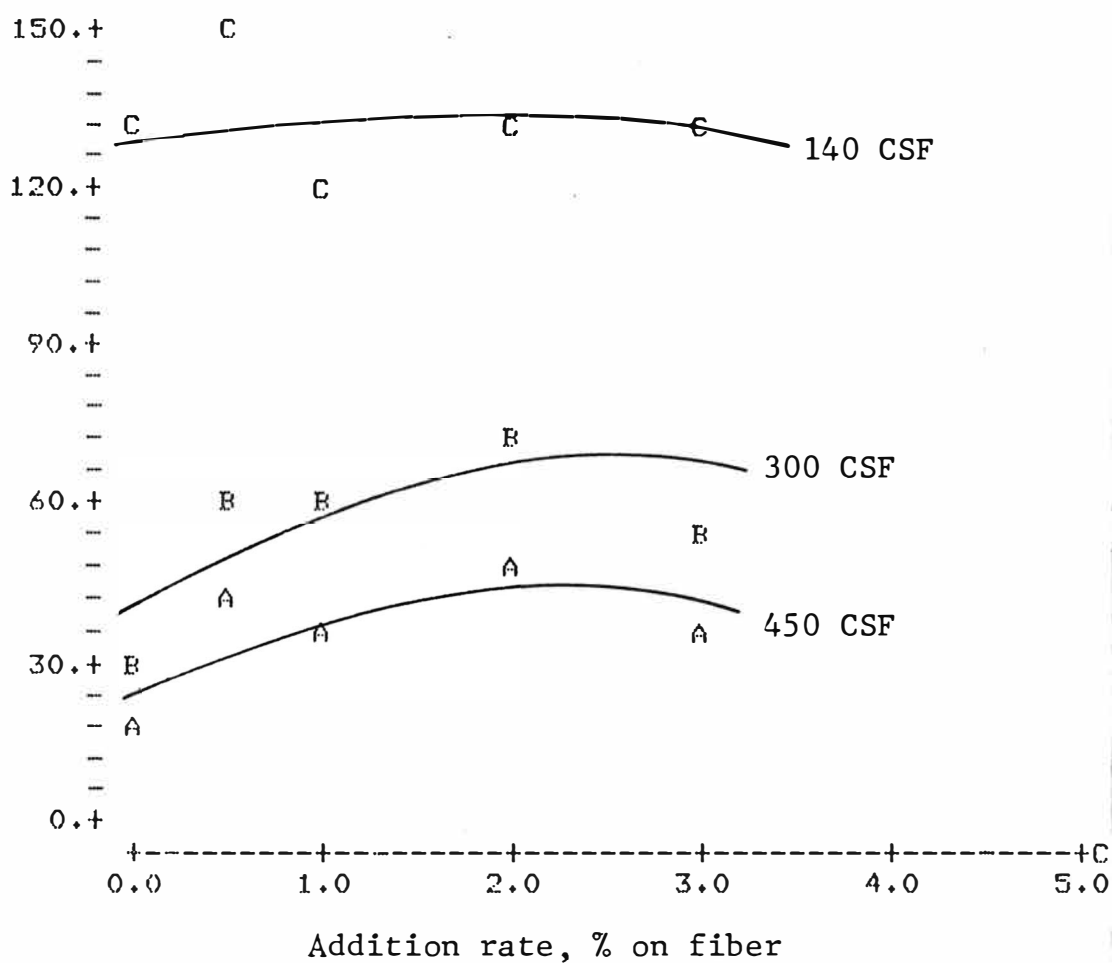
MIT
Folds

Figure 20. Fold properties of 100% SBS handsheets treated with chitosan.

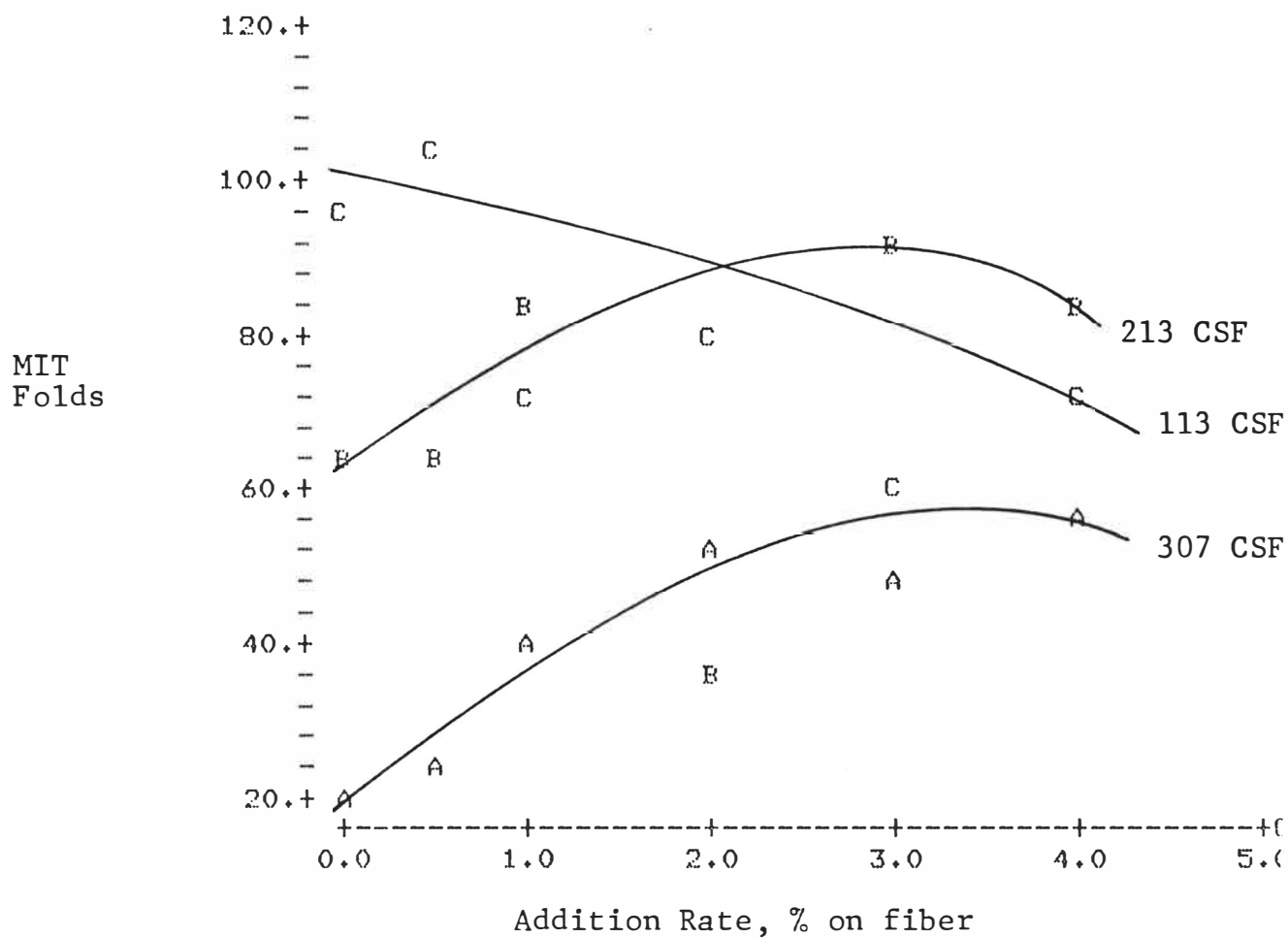


Figure 21. Folding properties of 50/50 mixture handsheets treated with chitosan.

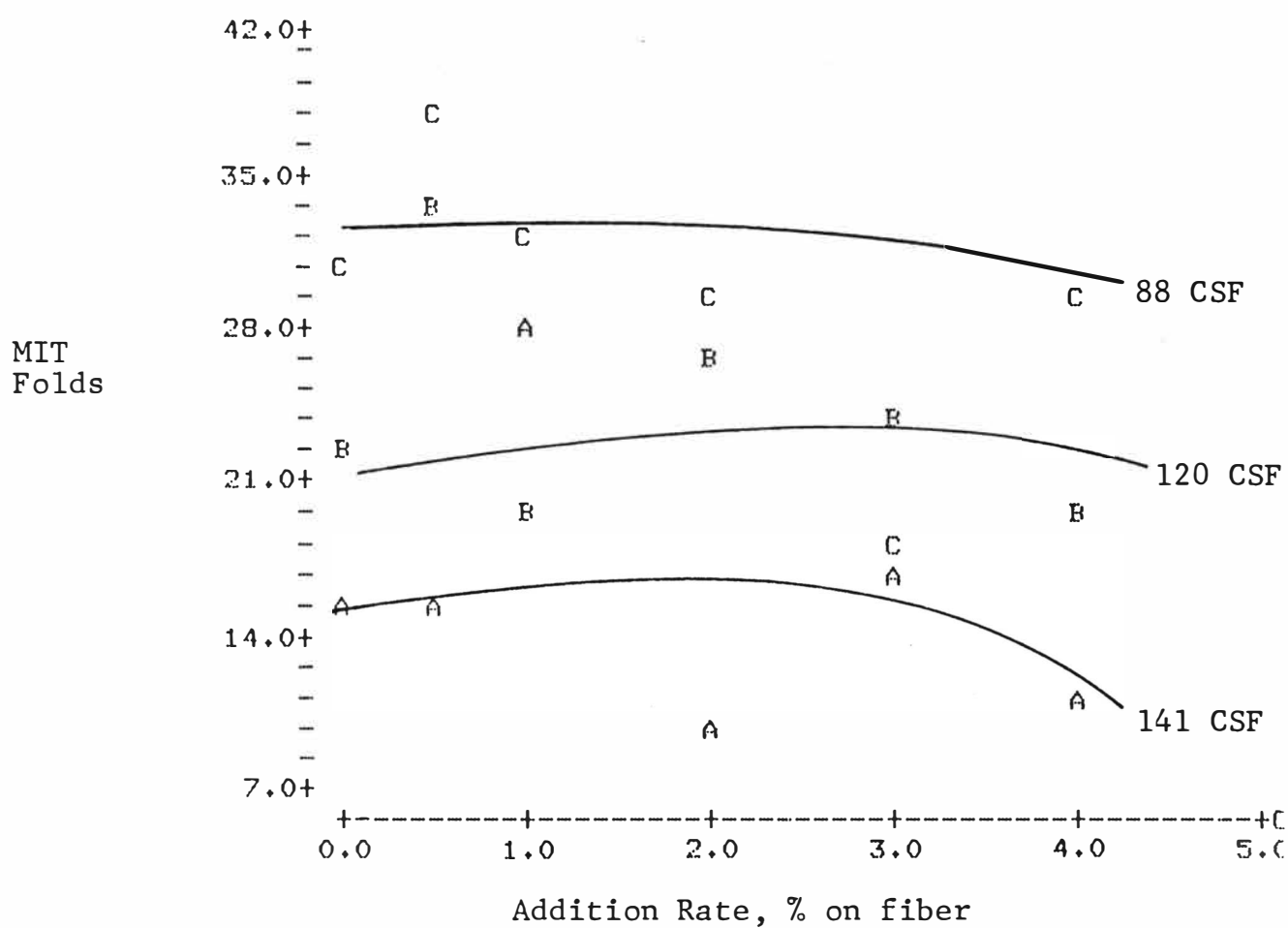


Figure 22. Folding properties of 100% newsprint handsheets treated with chitosan.

Sheet porosity, a bonding measure, also shows the rise to about the two percent addition rate then the leveling out seen in the previous tests. Figures 23-25 show this for all furnishes used. The tearing force was shown as dropping off as addition of chitosan increased. Past one percent, tearing force did not increase nor did it substantially decrease in value (Figure 26-28). As the addition of chitosan in the sheet increases, brightness falls by as much as seven points with as little as three points. All furnishes showed this trend as seen in Figure 29.

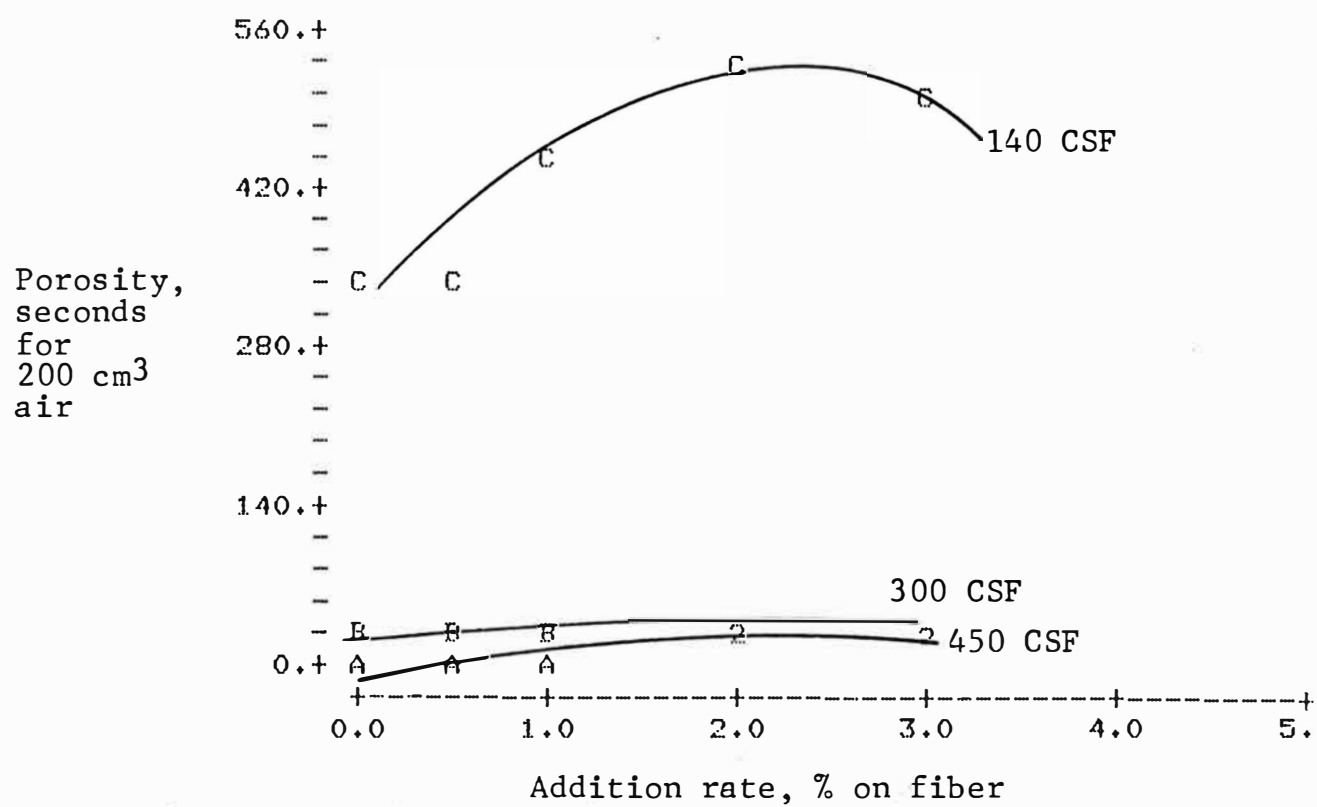


Figure 23. Sheet porosity of 100% SBS handsheets treated with chitosan.

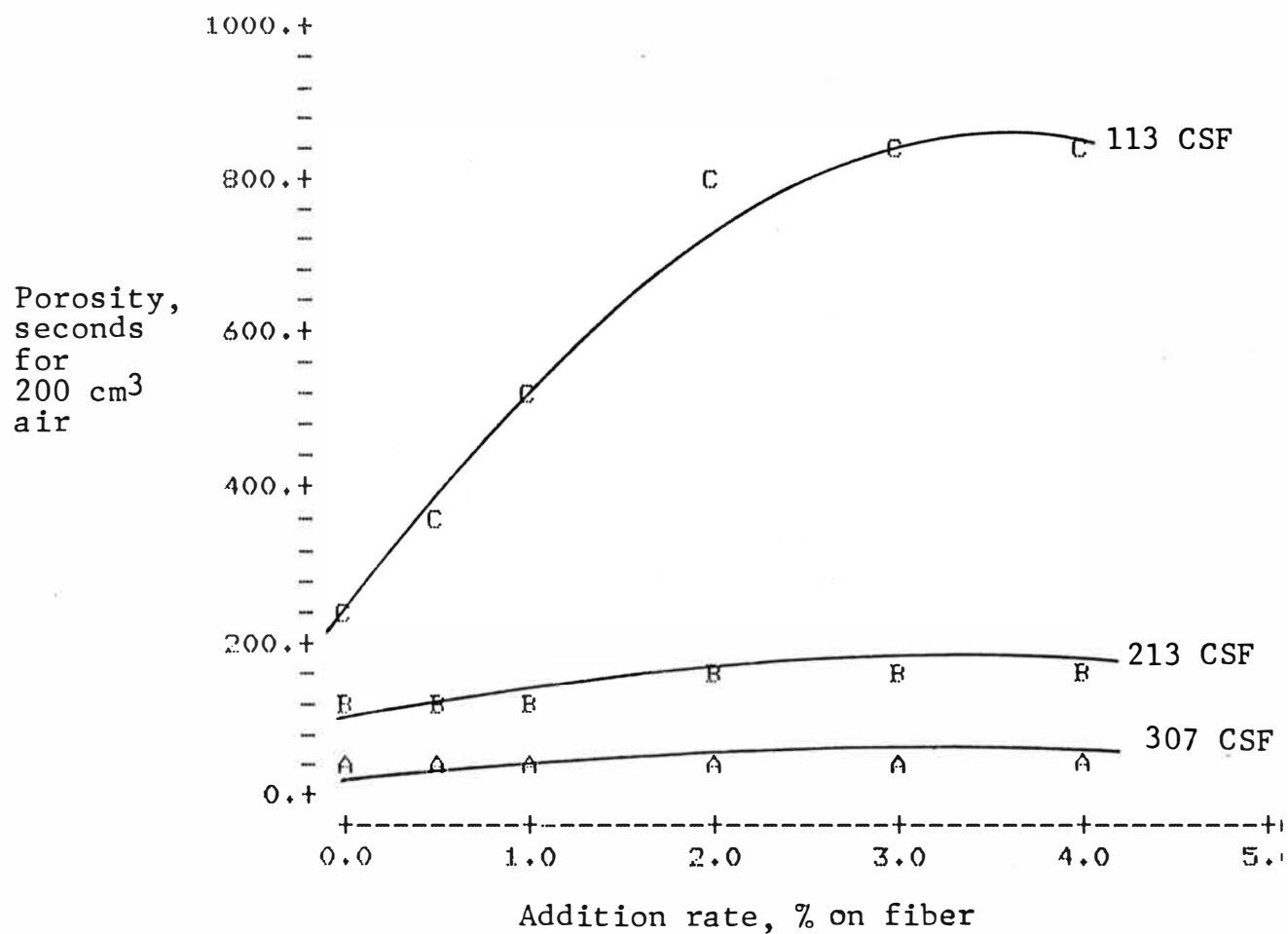


Figure 24. Sheet porosity of 50/50 mixture handsheets treated with chitosan.

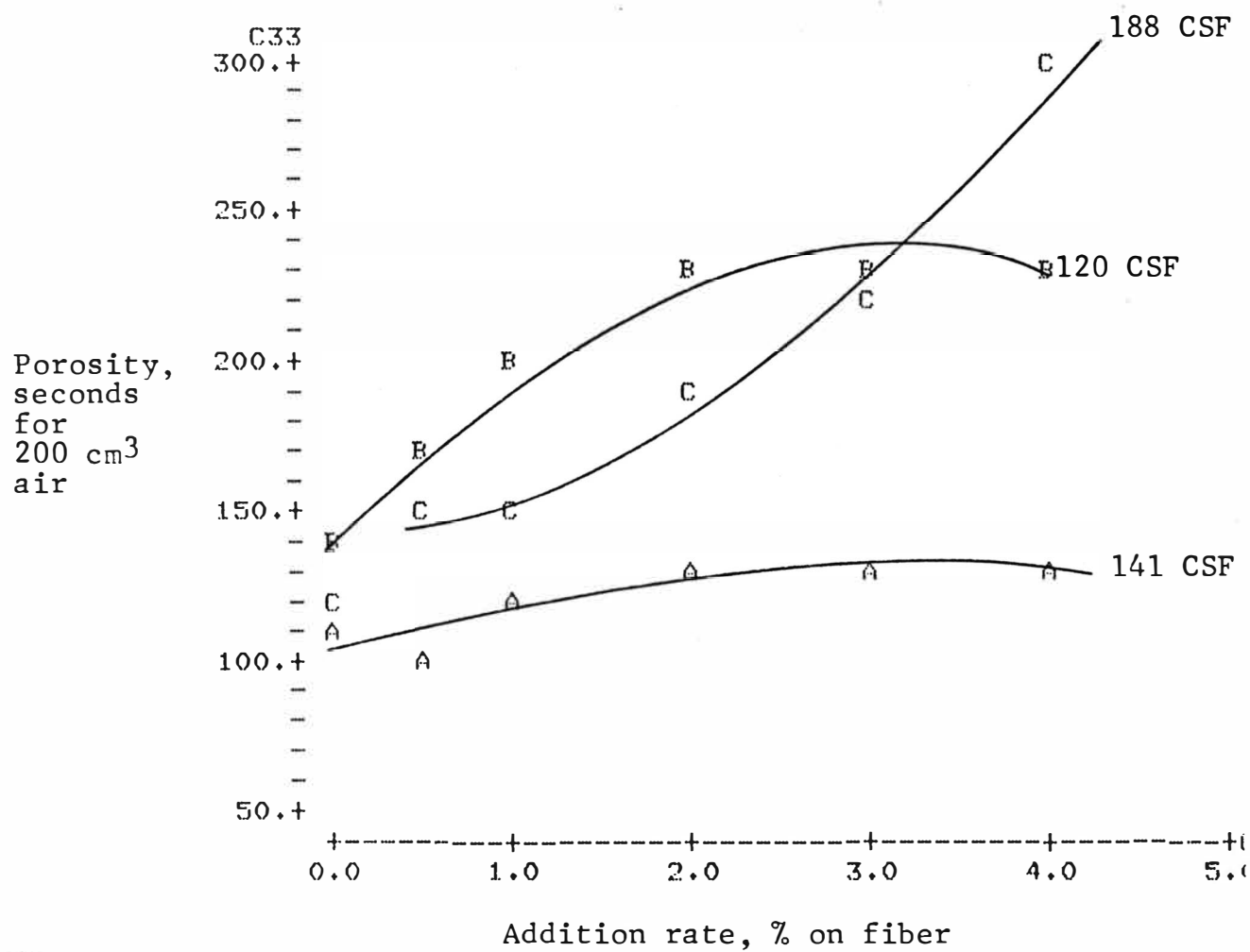


Figure 25. Sheet porosity of 100% newsprint handsheets treated with chitosan.

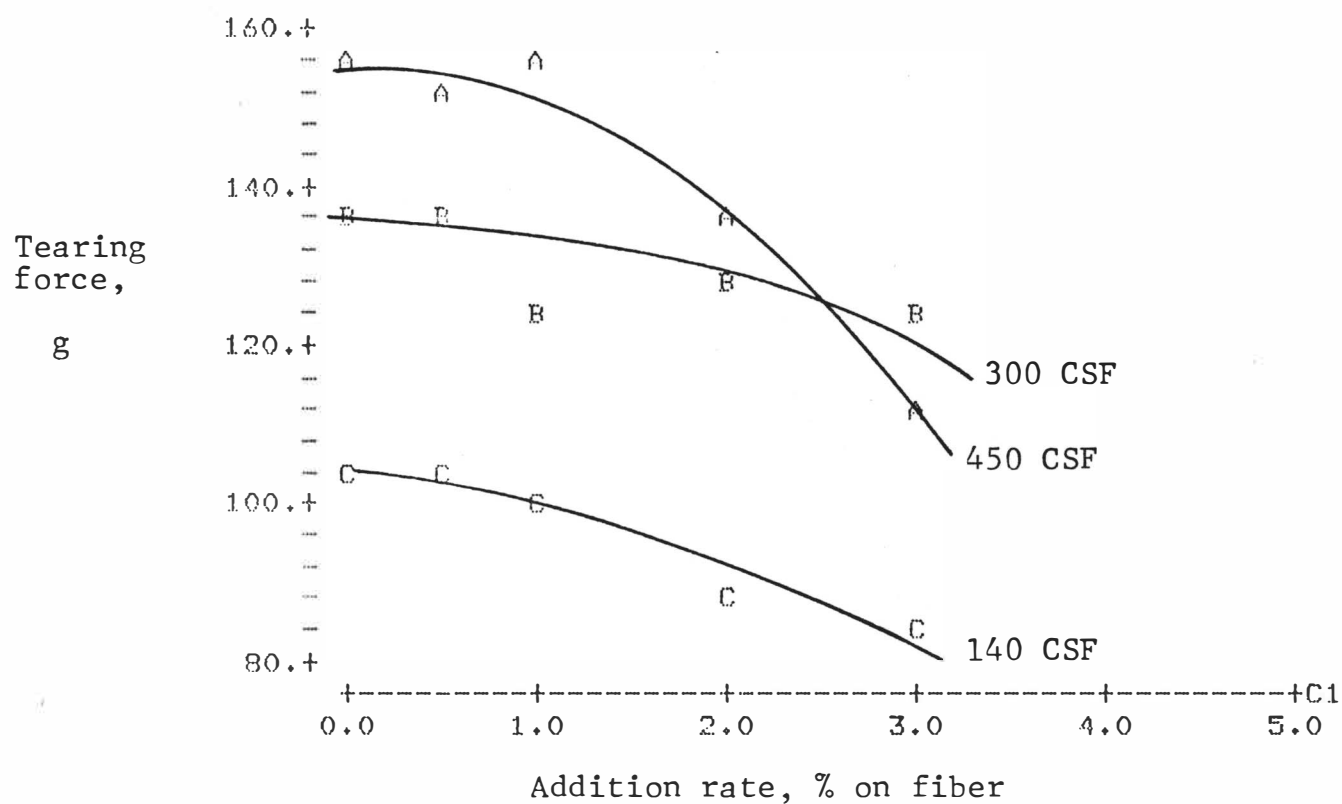


Figure 26. Tearing force properties of 100% SBS handsheets treated with chitosan.

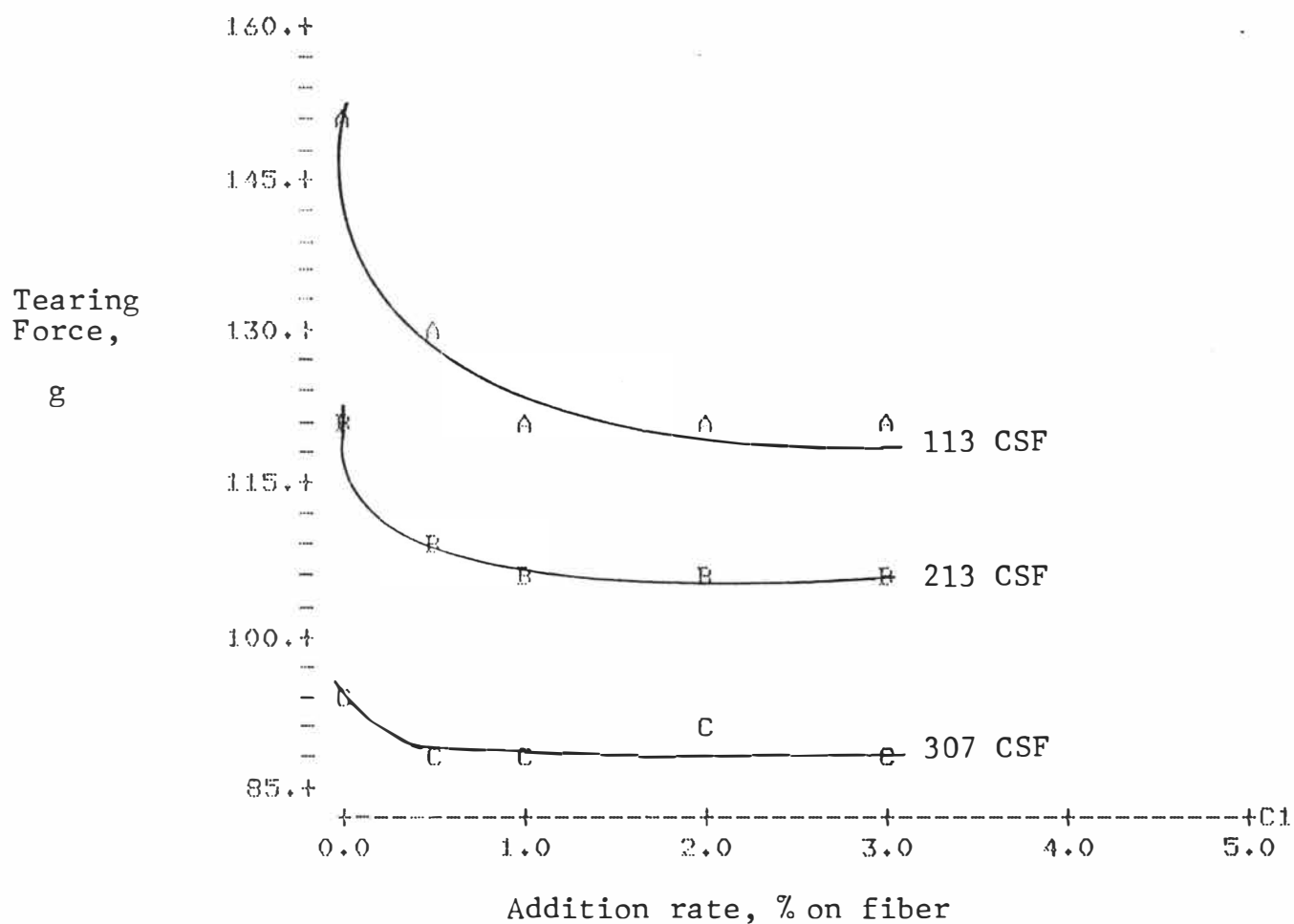


Figure 27. Tearing Force properties on 50/50 mixture handsheets treated with chitosan.

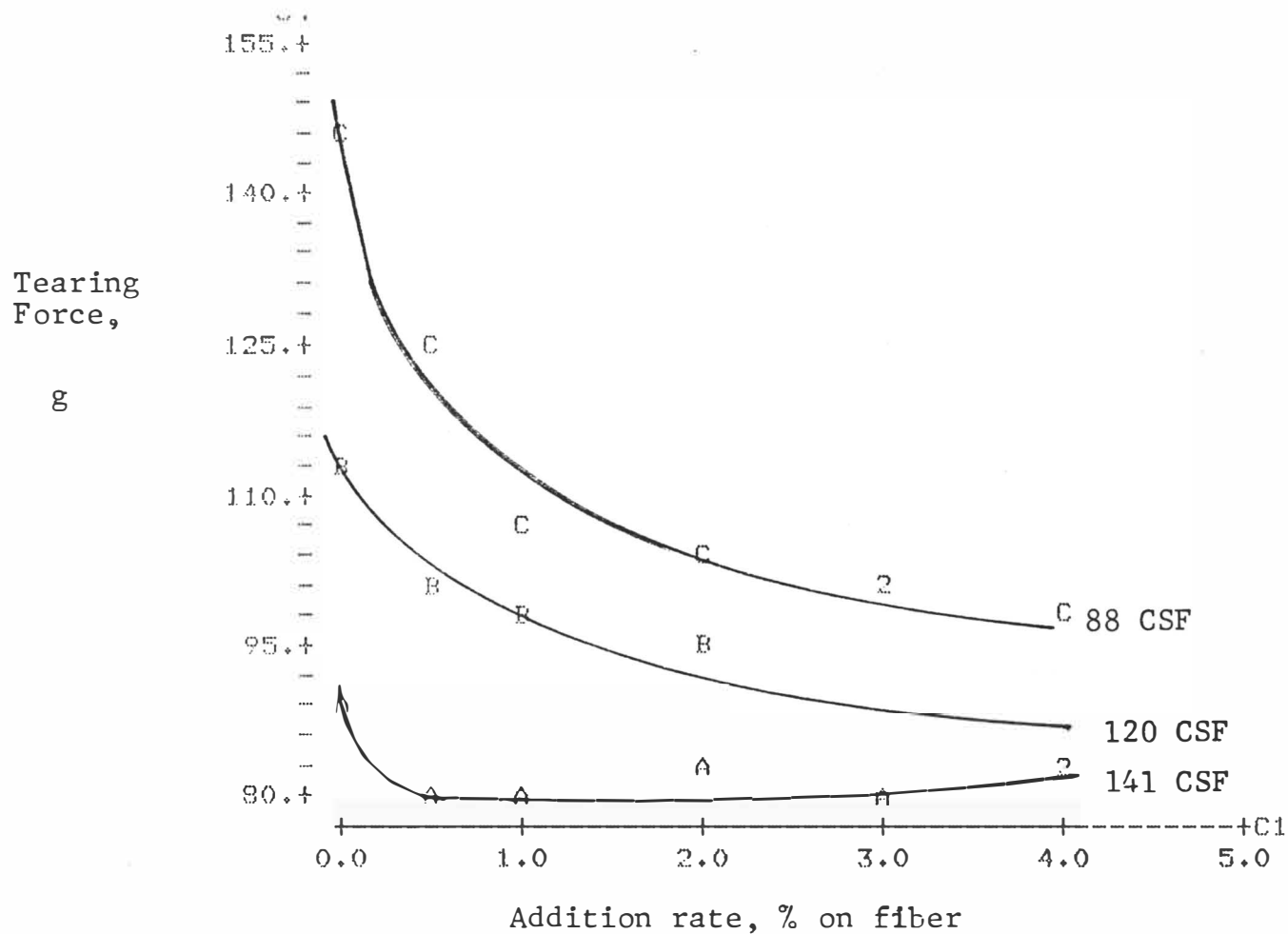


Figure 28. Tearing Force properties of 100% newsprint handsheets treated with chitosan.

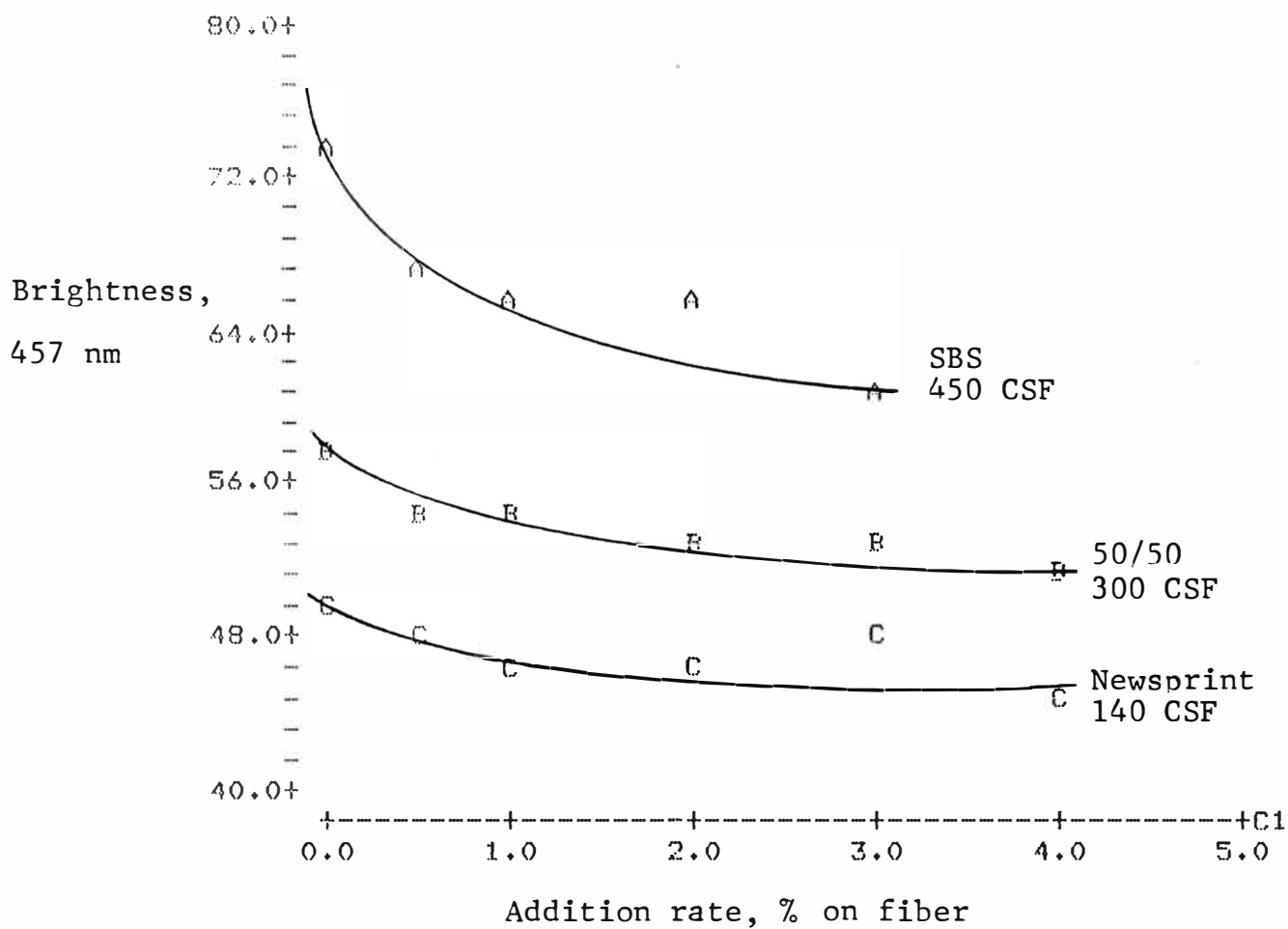


Figure 29. Brightness properties of 100% SBS, 50/50 mixture and 100% newsprint.

DISCUSSION OF RESULTS

Handsheet Forming

The two-ply handsheet procedure was perhaps the most critical part of the experimental portion of the study. Though not a difficult procedure, it must be followed exactly each time a two-ply handsheet is made. Figure 30 shows a graph of sheet consistency plotted against vacuum for a formed sheet on the sheet-mould. The plots are two typical furnishes and freenesses used and shows the extent a sheet must be dewatered to achieve the desired consistency. Ten percent was chosen as a target consistency from unpublished data from a previous study.(13)

The handsheet procedure used here is representative of a cylinder board machine, where one ply is formed with the next ply at approximately ten percent consistency. Though the plies in the handsheet procedure were pressed together between their respective wires, pressing and couching were done at the same time. One wire always couched itself after pressing, with the other wire still attached to the now formed two-ply handsheet. The wire and web were then dried together. If consistency of the plies were less than ten percent, the handsheet formed was in all likelihood "too good". This meaning the handsheet lost its definition of two plies and bonding was such that it appeared to be only one sheet. This could be identifiable by the loss of a definite shear plane upon testing. On the other hand, plies of high consistency had insufficient bonding due to dry plies and delamination would occur quite readily.

It is apparent that strict experimental continuity must be maintained for successful two-ply handsheets forming. Each furnish and freeness was subjected to vacuum in order to reach the ten percent target consistency.

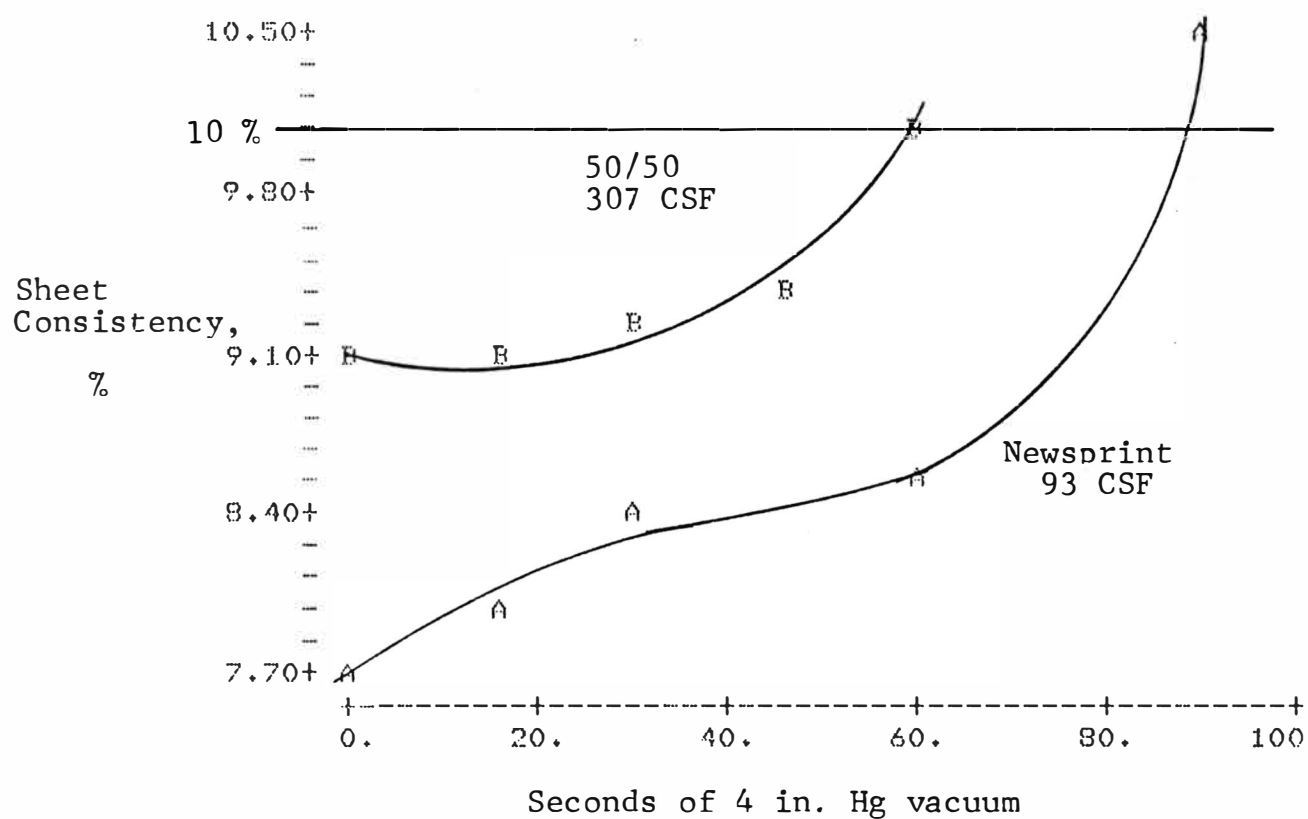


Figure 30. Sheet consistency relative to dewatering vacuum

Polymer Addition and Precipitation

After the chitosan acetate was applied to the pulp suspension, it had to be precipitated on the fibers to satisfy experimental requirements. The chitosan was precipitated from solution by the addition of NaOH. Figure 31 shows titration curves for .5 and 4 percent chitosan acetate solutions. Between the initial pH and up to approximately 6.8, the excess acetic acid is being used up. Precipitation of the chitosan occurs at about pH 6.9 as indicated by the sharp rise in pH relative to addition of NaOH. The latter part of the titration curve is the adjustment of the system to pH 10 which is the pH at which the handsheets were formed.

Chitosan Addition Results

Chitosan appeared to have the greatest affect on plybond strength properties. Increases were shown from 30 to 120 percent depending upon furnish and extent of refining as seen by the ZDT tests. Figures 14-16 again show this well. The longer fiber SBS furnishes showed stronger values with more refining, though the unrefined pulp was weaker initially. This can be accounted for due to the stiffer and stronger fibers characteristic of unrefined SBS pulps.

The groundwood newsprint pulps gave the lowest strength values as expected. The chitosan though did improve sheet strength in these pulps. Tensile breaking length and fold tests, (Figures 19 and 22) help show this to some extent.

Polymeric additives which increase interfiber bonding generally decrease the tear resistance of paper. Chitosan is no exception to this rule as seen in Figures 26-28. Tear values actually drop with chitosan addition but level out past one percent. Chitosan can increase the strength of the inter-fiber

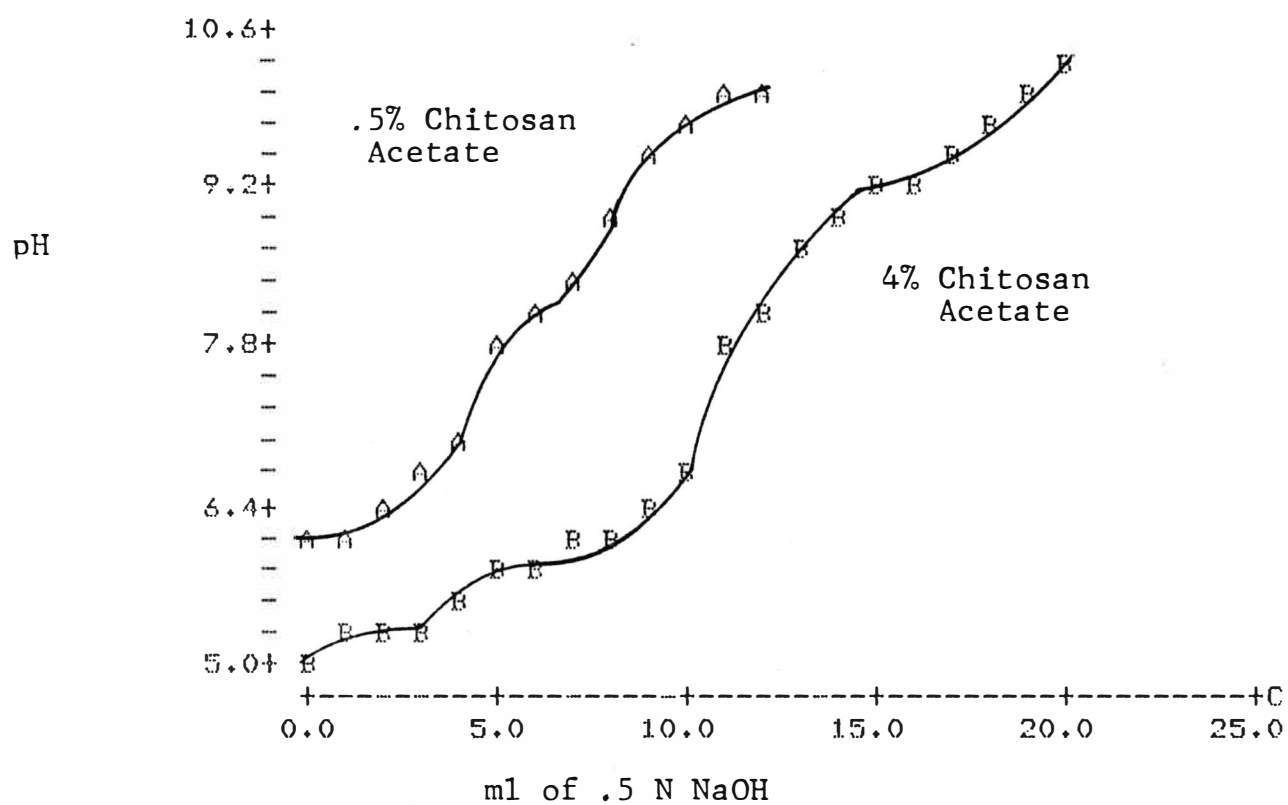


Figure 31. Titration curves for chitosan acetate.

bonding, but will not increase the strength of individual fibers. To some extent fold tests showed this and could possibly explain some of the data scatter. Figures 20-22 help show this theory.

It appears from these results that maximum strength levels of plybond strength and also sheet strength occur at the two percent addition rate of chitosan. This is evident on the graphs mentioned previously. This indicates that increased bonding is occurring due to the addition of the chitosan to the pulps. This is backed up by the porosity levels and tearing resistance. Figures 23-25 show porosity, increasing values indicate decreasing porosity, decreasing with the addition of chitosan to the sheet. Also we see the leveling out of values at the two percent addition rate.

This fact can be explained due to the charge densities that occur between chitosan and the fibers. At low addition levels, the chitosan would adsorb quite readily to the surface of the fiber. At higher addition rates the charge difference is neutralized and additional chitosan is adsorbed weakly and quite possibly not at all. Therefore, this charge neutralization appears to occur at the two percent addition level.

Refining Substitute

The possibility is very good that chitosan can act as a replacement for refining. Though the more heavily refined pulps show excellent strength properties, unrefined and lightly refined pulps also show adequate strength properties when treated with chitosan. Figure 32 and 33 show ZDT and tensile breaking length properties relative to freeness. At any given freeness it is quite apparent that chitosan does indeed impart excellent strength properties. Referring back to Figure 14 and choosing 100 percent SBS furnish, it is possible to achieve a strength value of unrefined pulp using chitosan as a

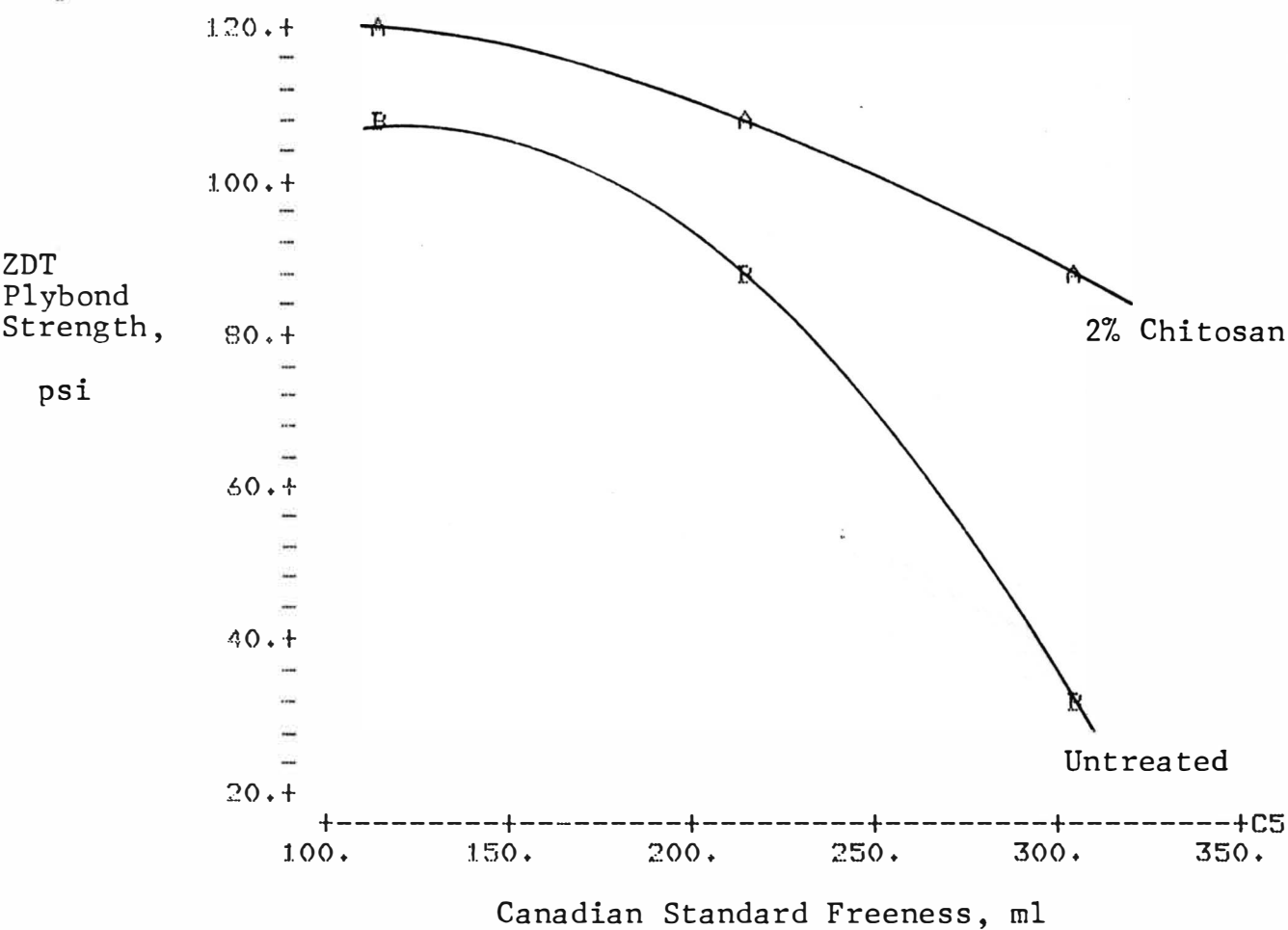


Figure 32. ZDT Plybond Strength Properties for chitosan acetate relative to Canadian Standard Freeness.

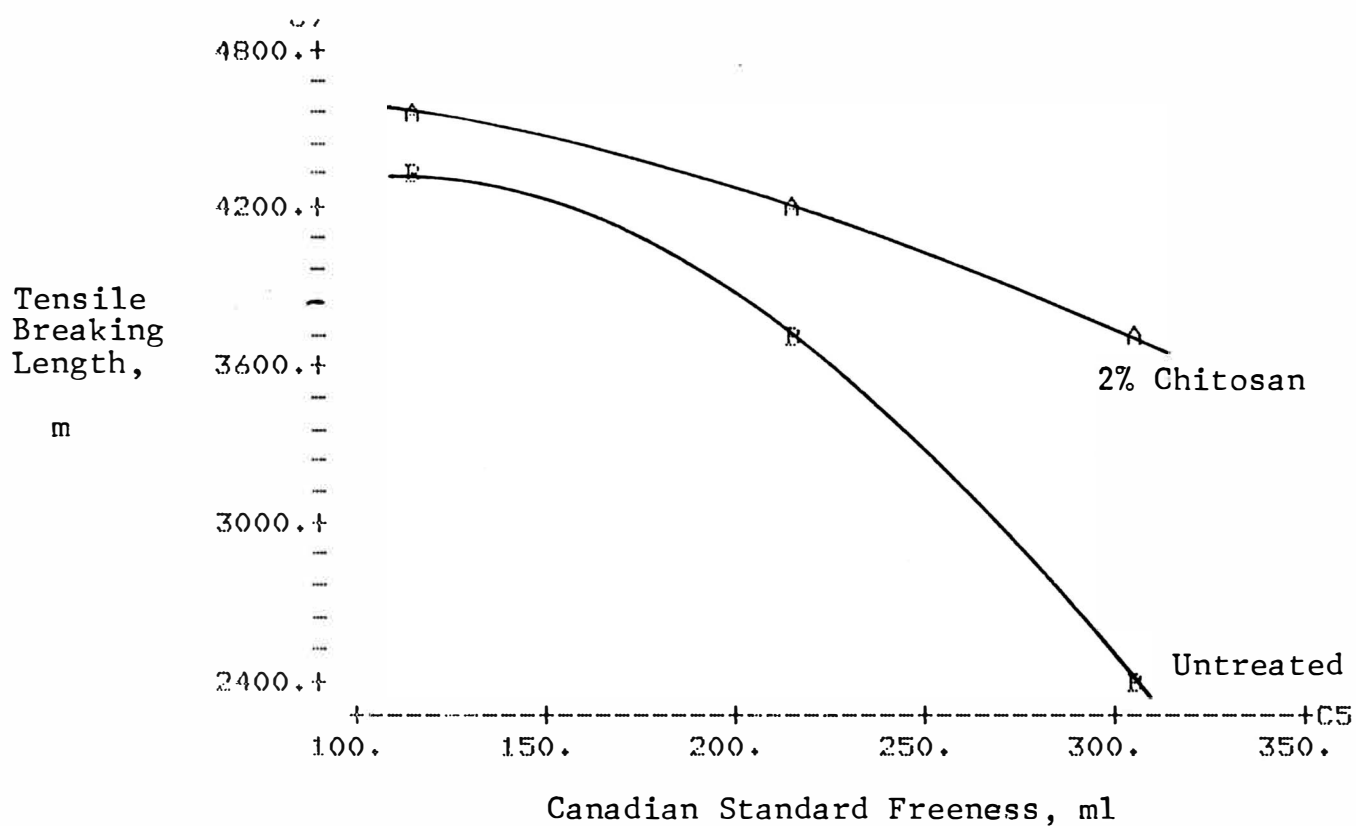


Figure 33. Tensile Breaking Length properties of 100% SBS handsheets relative to Canadian Standard Freeness.

strength increaser that yields values that are all together higher than lightly refined pulp of untreated nature. From the graph, a two percent addition level of chitosan on unrefined pulp (450 CSF) gives a value of 74psi ZDT. The lightly refined (300 CSF) and untreated pulp has an initial ZDT value of 53psi. The difference is 21 points. This would be of most interest to the papermaker. If strength levels could be developed by chemical addition instead of refining, and, if chitosan is available cheaply enough, a cost savings could occur. Even at a one percent addition level to unrefined pulp, it is still 16 points higher than the lightly refined pulp that has not been treated with chitosan.

Lastly, it was noted that brightness dropped with increasing levels of chitosan. The drop is between three to seven points, depending on furnish and freeness. This could possibly be due to the alkali action on the fiber, though this was not studied in detail. The high pH the system adjusted to could possibly "burn" the fibers to some extent and quite possibly create a degraded pulp, this weakening the fibers. Some of the scatter in the fold tests could be explained by this theory.

CONCLUSIONS

To induce strength to the finished sheet, several methods are employed. Fiber selection, mechanical and chemical means are used. Plybond strength, an important parameter in multi-ply sheets, uses the three aforementioned variables to achieve this ply-strength. The chemical method uses polymeric additives to supplement the bonding that exists between fibers and plies. One such polymer that was considered was the marine polymer chitosan.

Chitosan, a linear-amino polysaccharide, has shown a high affinity for cellulosic surfaces. The chitosan was incorporated into two-ply handsheets using a precipitation technique that yielded finished sheet strength properties that are very desirable for the papermaker.

It was found that maximum strength values showed from 30 to 120 percent increases depending on furnish and degree of refining.

Possibilities exist to substitute chitosan in place of refining in unrefined or lightly refined pulps to achieve the strength values attained by refining. This could not be shown in the more refined pulps.

It was also shown that an effective, accurate and reproduceable method of two-ply handsheet forming is possible at the laboratory scale. With careful control of basis weight and ply consistency an accurate method was demonstrated.

This study has shown chitosan to be an effective wet end additive that, given competitive pricing, can be a viable polymer in a papermaking system.

RECOMMENDATIONS

Based on the results and observations of this study several potential research projects could be investigated.

One would be to investigate a de-inked fiber system that characteristically would have ionic "trash" in it that might interfere with chitosan's bonding ability.

Another potential project could be to run a full papermachine trial on the pilot scale. Different techniques on depositing the chitosan to the sheet could be examined.

In regards to this study, changes could be made to more closely resemble an actual boxboard sheet. Instead of using all one fiber or mixes, investigate say a 100 percent SBS-corrugated furnish with the SBS as one ply and corrugated as the other. Newsprint could also be used with corrugated.

Also, instead of adjusting the pH to 10, look at possibilities of using pH as a variable related to plybond or sheet strength. Since precipitation occurs just below neutral, have an endpoint at pH 7, 7.5 or 8, thus preventing pulp degradation that occurs at elevated pH's.

CHITOSAN

Product Description Chitosan (poly-2-deoxy- 2-amino glucose)

General Characteristics:

Appearance	Pale white to slightly pink flakes
Grain size	From less than 3mm to 6mm
Bulk density	0.15 + 0.05 gm/cc (10 lbs/cu.ft.)
Moisture content	Less than 10%
Ash content	Less than 1%
Insolubles	Less than 0.5%
Solution color	Clear
Average MW	100,000 < 2,000,000 gm/mole
-NH ₂ content	7-8%
Viscosity (1% in 1% acetic acid)	From 200 to < 7000 cps
Biodegradable	Yes

Typical Mineral Analysis:

(For 5% ash samples)

Ca	13.8 mg/gm
Mg	.92 mg/gm
Fe	.79 mg/gm
P	5.1 mg/gm
Zn	.0005 mg/gm
Cu	.00023 mg/gm

Solubility:

Usually 1% solutions of Chitosan are prepared in 1% acetic acid. This provides a standard for comparison and viscosities that are readily adaptable to metering by processing equipment. With higher viscosity grades of Chitosan, 0.5% solutions in 0.5% acetic acid become the standard. Other organic acids that can be substituted for acetic acid are adipic, formic, lactic, malic, propionic or succinic acids. Formic acid has proved to be a good solvent over the entire acid concentration range from 0.25 to 50%, although at the extremes of this range, solutions contain gel particles. Stirring normally, will bring solution in 15 minutes to 1.5 hours.

Chitosan is soluble to a limited extent in inorganic acids. It is soluble only within the acid concentration range from 0.15 to 1.1% and is completely insoluble in phosphoric and sulfuric acids. Chitosan must first be dissolved in aqueous solution and a pH of 7 or below maintained or precipitation will occur. It is insoluble in neutral or alkaline media.

Grades:

Premium grade, low viscosity

Ash content	Less than 1%
Viscosity (1% in 1% AcOH)	200-800 centipoise
Insolubles	Less than 0.5%

Premium grade, medium viscosity

Ash content	Less than 1%
Viscosity (1% in 1% AcOH)	800-2000 centipoise

Premium grade, maximum viscosity

Ash content	Less than 1%
Viscosity (1% in 1% AcOH)	< 2000 centipoise

Specialty grades

Specialty grades of chitosan are being developed for medical and other demanding applications. If you have unusual requirements, we would like to supply your needs.

Toxicity:

LD50	> 16 gm per kg body weight (orally, rats)
	> 350 mg/kg body weight (intraperitoneally in mice)

Empirical Formula:



U.S. Environmental Protection Agency Chemical Substance Inventory:

Report (TOSCA) Number — 30930622 8/17/78

Versatile Chemicals With Untapped Uses

Chitin and chitosan have a number of current and potential uses. Established uses include water and waste treatment . . . Precipitation of protein materials from processing wastes . . . Use in animal feeds . . . Sewage treatment . . . Wine and beer clarification. Potential uses that have been studied include formation of ionic bonds and films . . . Casting of coatings resistant to water transpiration . . . Papermaking additives . . . Baby food and stomach anti-acid additives . . . Treatment of wounds . . . Herbicide substrates . . . Textile finishes . . . Water-base paint emulsions . . . Glass fiber modification . . . Food thickeners . . . Biodegradable coatings . . . Specialty adhesives . . . Cold stabilization of fruit juices . . . Retining of nuclear materials . . . Improvement of capacitor tissues. MCRC technical people will be glad to discuss the various applications that have been investigated world-wide for chitin and chitosan with you.

LITERATURE CITED

1. Krumpal, J.D., PhD Thesis, University of Washington, 1980.
2. Crosby, G.D., PhD Thesis, University of Washington, 1973.
3. Highan, Robert R.A., "A Handbook of Paper and Paperboard," Vol. 1, Business Books Limited, London, 1970, p. 137.
4. Clark, James d'A., "Pulp Technology and Treatment for Paper," Miller Freeman Publications, Inc., San Francisco, 1978, p. 205.
5. Ibid., p. 264.
6. Fox, J.R., PhD Thesis, University of Washington, 1979.
7. Swanson, J.W., TAPPI, 44:1424 (1961).
8. "Wet Strength in Paper and Paperboard," (J.P. Weidner, Ed.), TAPPI Monograph Series, No. 29, NY, 1965.
9. Sinkovitz, G.D., Slagel, R.C., U.S. Patent 3,709,780 (1973).
10. Sinkovitz, G.D., Slagel, R.C., U.S. Patent 3,770,763 (1973).
11. Sinkovitz, G.D., Slagel, R.C., U.S. Patent 4,056,432 (1977).
12. Unpublished Report, August 20, 1979, "Plybond Strength Development by Laboratory Simulation Measurement - Phase I", IIT Research Institute, Chicago, Illinois.
13. Unpublished Report, September 30, 1978, "Plybond Survey", IIT Research Institute, Chicago, Illinois.