

CHITOSAN, A MEDIATOR FOR FIBRE–WATER INTERACTIONS IN PAPER

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Synopsis The modes of action of the important commercial wet strength additives for paper are explained in terms of the physics and chemistry of the interfibre bonding areas therein. The theoretical principles expounded are then used to provide the experimentally-verified prediction that the naturally-occurring biodegradable aminopolysaccharide, chitosan, can function effectively to mitigate the adverse effect of water in papers.

It is now well accepted that conventional paper is held together by hydrogen bonds.^(1–4) These bonds must span the distance between the separate segments of crossing fibres which together make up the interfibre bonding area. While a few water molecules may or may not be an integral part of the interfibre linkage it is certain that the presence of larger amounts of water has a disruptive effect on the cohesiveness of paper. A satisfying chemical explanation for this is simply that the existing interfibre linkages are broken by excess water and subsequently the hydrogen bonding sites on the fibre surface are then fully occupied by water molecules which are in turn hydrogen bonded to such a large excess of free water that the fibres can now be regarded as linked by a macroscopic fluid bridge. The weakness of this bridge is manifested by the so-called wet strength of paper.^(5a)

To attempt to improve these low strengths a number of polymeric materials have been developed. These include urea- as well as melamine-formaldehyde condensates, epoxy-containing polyamides, cationic polyacrylamides and polyethyleneimines. Each of those must enable the interfibre bonding areas to remain chemically linked in the presence of water, otherwise they would not be functional. This can be most clearly illustrated by a consideration of polyethyleneimine (PEI), one of the more extensively investigated wet strength

Under the chairmanship of Dr N. K. Bridge

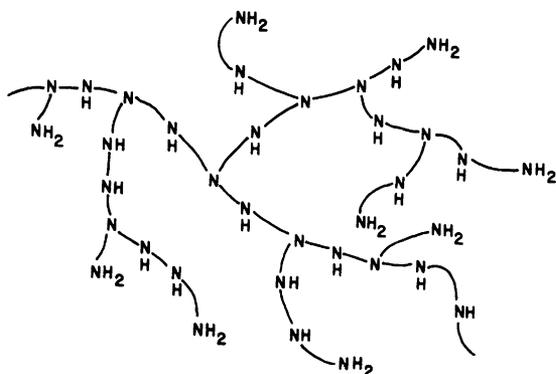
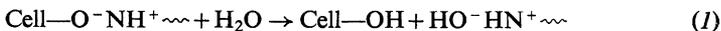


Fig. 1—Idealised structure of polyethyleneimine

agents.^(5b) High molecular weight samples of PEI are globular polyamines (Fig. 1) containing primary, secondary and tertiary centres.⁽⁶⁾ PEI is not a film former and has little tensile strength in bulk. When such a macromolecule ends up between the cellulose surfaces constituting the interfibre bonding area of paper, it can of course form hydrogen-bonds to the cellulose by virtue of its nitrogeneous centres. If these are more numerous than the cellulose-to-cellulose bonds which would normally be in existence at that location then some improvement might be observed in the dry strength of the paper in question.⁽⁷⁾ Of course, on exposure to water these new nitrogen-to-cellulose hydrogen bonds must also be displaced just like the cellulose-to-cellulose bonds in untreated paper. However, pulp normally contains a number of acidic sites originating from oxidation of the cellulose or due to the presence of lignin or hemicellulosic residues. These will be capable of forming ionic bonds with the basic polyethyleneimine. Now, ionic bonds have enthalpies considerably higher than those of hydrogen bonds. Therefore, it can be expected that the energy input to rupture these bonds and separate the fibres will intrinsically be greater. More importantly, the excess water will not be able to so readily rupture these ionic linkages. This can be expressed by equation (1)



Obviously, the more the equilibrium lies to the right the fewer will be the number of interfibre linkages. However, it is important to realise that the ionic polymer-cellulose bonds are in the *solid* phase so that the $[\text{H}_2\text{O}]_f$ term in the equilibrium constant expression depicted in equation (2)

$$K_n = [\text{Cell-OH}]_f [\text{HO}^- \text{NH}^+ \sim]_f / [\text{Cell-O}^- \text{NH}^+ \sim]_f [\text{H}_2\text{O}]_f \quad (2)$$

is the concentration in the fibre. This concentration is small and as such can not exert the massive hydrolytic leverage normal in true solutions.⁽⁸⁾ Furthermore, since cellulose is a polyacid of pK13⁽⁹⁾ ionic linkages can be constructed at many sites other than adventitious carboxylic acid groups on the fibre surfaces.

These arguments have at least three important implications. Firstly, that the introduction of negative sites onto fibre surfaces could be advantageous for bonding in the presence of water; second, that the absolute size of the bonding entity could be important; and third, that a high molecular weight would not be a *sine qua non* for a wet strength additive. The validity of all of these points have been demonstrated using pulp dyed with a fibre reactive dye containing sulphonic acid groups (Fig. 2). The fibres thus are covered with negative sites covalently bonded to the cellulose. The addition of PEI-type polyamines then afforded papers the strengths of which increased with increasing molecular size up to a maximum of about 20 Å (Fig. 3). Furthermore, wet strengths of the order of 40 per cent were observed in comparison to 20 per cent for the same fibre undyed and treated with PEI. Excitingly, the substitution of a low molecular weight polyamine (pentaethylenehexamine) for the high molecular weight PEI still afforded a paper with significant wet strength ($\sim 30\%$).

Of course, it is also possible that by the application of heat the amino

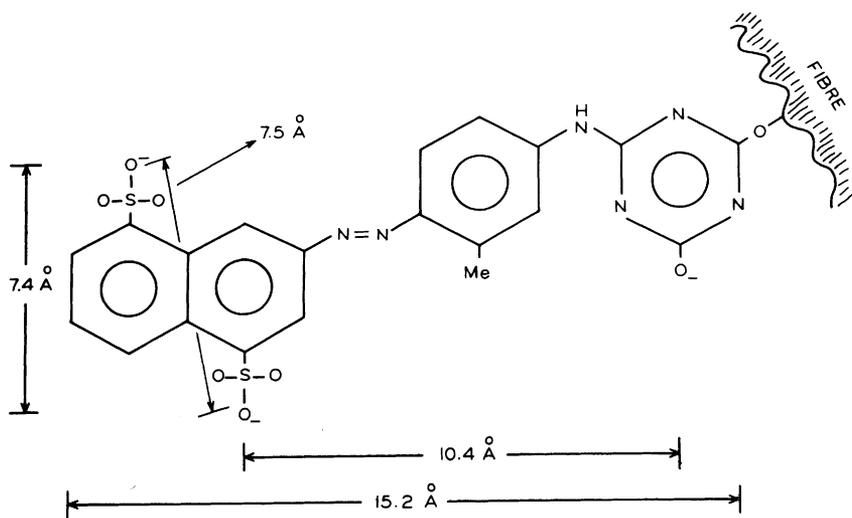


Fig. 2—Fibre surface modified by fibre reactive dye

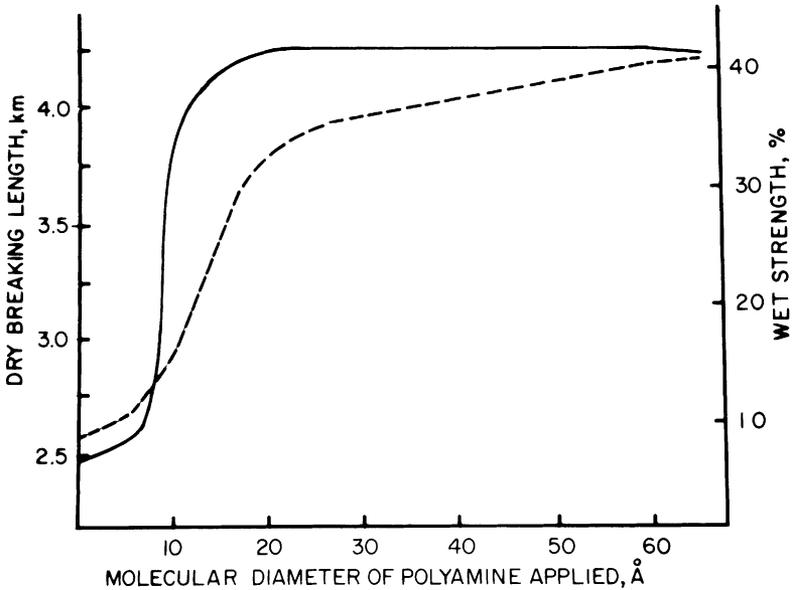


Fig. 3—Effect of molecular size of applied polyamine on the development of dry (—) and wet (---) tensile strengths in dyed handsheets

groups of PEI can form irreversible covalent linkages between fibres in paper. This can either occur by Schiff base formation according to equation (3)



or by the dehydration of an ammonium salt to the corresponding amide as expressed by equation (4),



In fact, covalent bonds to wood fibre surfaces may be created with surprising ease.⁽¹⁰⁾ This is well illustrated by the formation of synthetic wood from the polymerisation of a lignin model precursor, isoeugenol, in the presence of rayon fibres⁽¹¹⁾ and by the covalent bonding of particleboard using lignin and an oxidative coupling mechanism to form wood-lignin-wood bonds.⁽¹²⁾

With these thoughts enunciated the wet strength performance of polymeric additives can be rationalised in basic chemical terms and summarised in Table 1. For example, the ability of the aldehydic materials, formaldehyde, glyoxal and polyacrolein to confer wet strength^(5c) is obviously due to the formation of acetal linkages. The superiority of the small-sized glyoxal to other

TABLE 1—THE CHEMISTRY OF WET STRENGTH TREATMENTS FOR PAPER

Wet strength treatments	Mechanism of additive retention	Nature of crosslinking group	Structure of crosslinking group	Type of chemical crosslink	Structure of crosslinking bond
heat	none	hydroxyl	—CH ₂ OH	ether	—CH ₂ OCH ₂ —
parchmentizing (H ₂ SO ₄)	impregnation	carboxyl	—COOH	ester	—COO—
urea-formaldehyde resin	cationic centre	hydroxyl	—CH ₂ OH	ether	—CH ₂ OCH ₂ —
melamine-formaldehyde resin	cationic centre	carboxyl	—COOH	ester	—COO—
		methylolamide	—NHCH ₂ OH	amidomethylene	—CONHCH ₂ O—
		methylolamine	—NHCH ₂ OH	amidomethylene	—CONHCH ₂ HNCO—
				aminomethylene	—NHCH ₂ O—
				diaminomethylene	—NCH ₂ N—
glycidylated polyaminoamide	cationic centre	glycidylamino	—NCH ₂ CH—CH ₂ O	ether	—C(OH)CO—
polyethyleneimine	cationic centre	<i>p</i> -, <i>s</i> -, <i>t</i> -amino	R ₃ N, R ₂ NH, RNH ₂	amino	—C(OH)CNH—
				ionic	R ₃ NH ⁺ O ⁻ , R ₂ NH ⁺ O ⁻ , RNH ₃ ⁺ O ⁻
				amide	—NHCO—
				imine	—N=C—
				amide	—NHCO—
				imine	—N=C—
				amide	—NHCO—
				ester	—COO—
				ester	—COO—
				acetal	—OCH ₂ O—
				diacetal	—OCHCHO—
				acetal	—CHO—
				acetal	—CHO—
				urethane	—NHCOO—
				ionic	—M ⁺ O—
				inorganic ester	—M—O— O
neoprene latex and zinc oxide	coagulation impregnation	chloro	—CHCl	ether	—CHO—

dicarbonyl compounds can be taken as a reflection of the importance of stereochemistry in the development of interfibre bonds. It also demonstrates convincingly that a small molecule can covalently link macroscopic fibres. This view is further validated by the wet strength values attained using another small difunctional chemical, toluene diisocyanate,^(5c) which is capable of forming carbamate linkages on exposure to the alcoholic hydroxyl groups of the fibre surfaces.

With preformed polymers, the same concepts of discrete interfibre chemical bonds also hold convincingly. Thus, the extensively used glycidylated poly-aminoamides^(5a) are first captured by the fibre surfaces by virtue of their cationic amino centres. Subsequently, the resin-coated fibres in the paper sheet are chemically joined as the epoxy linkages on one fibre are reacted with amine groups on another in conventional epoxy resin curing chemistry.⁽¹³⁾

The urea- and melamine-resins behave similarly. That is, the resin precondensates are again captured by virtue of their cationic centres. Later, after sheet formation, these resins polymerise by methylol group condensation to form interfibre covalent linkages. The correctness of these views can be supported for the two foregoing cases by calculations of distribution of prepolymer on the fibre surfaces. Regardless of the particular assumptions made it transpires that the surfaces of the fibre are probably quite evenly covered with about a single layer of the wet strength additive.^(5a)

The sheet forming process then brings these two layers into chemical juxtaposition so that covalent bonds form between the layers of wet strength additives. There is no actual need to postulate covalent chemical bond formation to the fibre since ionic bond formation is necessary for the initial adsorption in the beater. However, it has certainly been repeatedly demonstrated that fibre surface modification by covalent bond formation can readily occur.⁽¹⁴⁻¹⁶⁾ In this connection it is exceedingly important to appreciate that any reaction of the fibre must occur in the fibre phase and not in the surrounding fluid. Therefore, many reported experiments employing model compounds in solution bear little relation to the real life situation. Failure to recognise that fibre reactions occur in the fibre phase held back the development of the fibre reactive dyes for more than half a century.⁽⁸⁾

Hence, each and every additive in Table 1 can be reasonably expected to react either ionically or covalently with the functional groups of cellulose in paper. With the fibre constraint provided by these definite interfibre chemical linkages the regions of the fibre surfaces immediately adjoining each end of the bond must be in relatively close alignment. This positioning could possibly permit the direct formation of hydrogen bonds between the opposite fibre surface areas which would reinforce the anchoring ionic or covalent inter-

fibre linkage. Certainly the length of this anchor could be spanned by short highly organised bridges of water molecules which already exist in conventional paper.⁽¹⁾ In either event these hydrogen bonds would be rather ordered and resistant to cleavage by bulk water in a wet strength test. The overall wet tensile strength of the paper would thereby be enhanced and of course related to the original dry strength.

With a clear understanding of how existing wet strength additives work it should then be possible to predict the features that a good strength additive for paper should possess. Thus, such a chemical should

1. be soluble in water based systems for easy application within conventional papermaking systems;
2. be substantive to cellulose so that retention is efficient;
3. be compatible regiospecifically with cellulose surfaces so that it does not disrupt conventional hydrogen bonding;
4. be large enough in molecular weight to span more interfibre bonding possibilities;
5. be film-forming to offer cohesive resistance to rupture;
6. contain a functional group capable of ionic or covalent reaction with the pulp fibre surfaces within the papermaking process;
7. be linear to allow accessibility to all its functional groups;
8. not contain any potential chromophoric groups to later impart color to the sheet;
9. be nontoxic and preferably naturally occurring to facilitate compliance with environmental regulations;
10. not present serious problems in the repulping and recycling of paper.

To synthesize *ab initio* a polymer meeting these numerous requirements would be a formidable task but fortunately Nature seems to have provided one ready on the shelf in the form of chitosan,⁽¹⁷⁾ a linear high molecular weight (DP 500) aminopolysaccharide composed of β -1, 4-linked 2-amino-2-deoxy-D-glucose units (Fig. 4).⁽¹⁷⁾ This polymer, as the N-acetate, is a major structural component of many creatures including crustaceans and insects. Obviously it is biodegradable and environmentally and technologically acceptable⁽¹⁸⁾ in repulping and recycling since it is essentially cellulose with replacement of the 2-hydroxyl group by a primary amino function. This close stereochemical similarity suggests that chitosan-cellulose combinations should probably constitute a chemical continuum. Like cellulose, chitosan contains no chromophoric groups although the amino group could be potentially disadvantageous. However, the presence of this basic group on every ring makes chitosan soluble in dilute aqueous solutions of monobasic acids.

Tough films can be cast from these solutions.⁽¹⁹⁾ Moreover, the cationic character of the dissolved chitosan should make it substantive to anionic

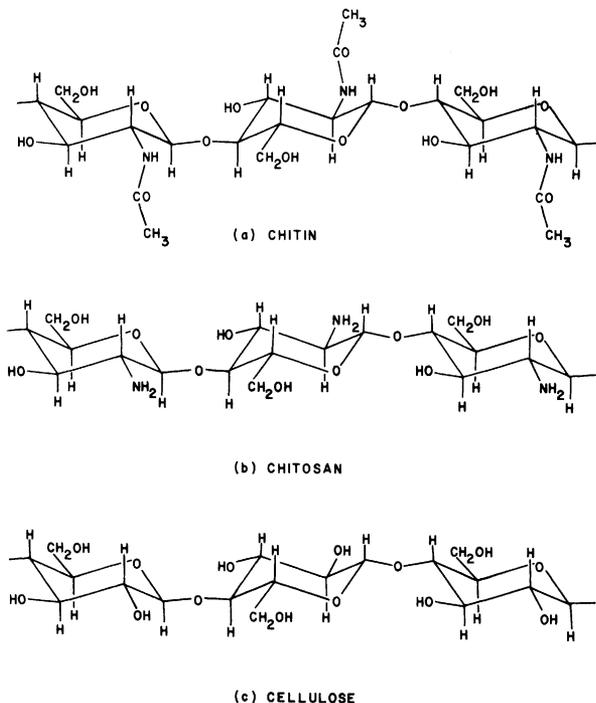


Fig. 4—Molecular structures of chitin (a), chitosan (b) and cellulose (c)

pulp. This substantivity can of course become the bringing interfibre bond which will mediate the adverse effect of water in paper.

Thus, chitosan apparently meets all of the ten theoretical and practical criteria specified above. It can therefore be predicted that chitosan will be an effective mediator of fibre-water interactions in paper. To verify this prediction, chitosan has been applied to papers made from a variety of pulps comprising an α -cellulose, an unbleached sulphite, an unbleached kraft, a softwood groundwood and a newsprint pulp.

In this review, emphasis will be placed only on the effects of chitosan on the wet tensile strength properties, though these cannot be discussed without reference to the corresponding dry tensile strengths. In this connection it is important to always keep in mind that if an additive increases the dry as well as the wet tensile strength then the improvement of the former conceals the augmentation of the latter when the percentage wet strength concept is em-

ployed. Furthermore, in use paper fails because of the limitation of an absolute, not a relative, strength. Nonetheless, the conventional statement of percentage wet tensile values will be retained in this work. However, regardless of the reportorial mode, the effectiveness of any polymer in modifying paper strength is highly dependent upon the method by which it is incorporated into the sheet of fibres.

Three distinct chitosan addition techniques have been previously compared.⁽¹⁹⁾ These were, equilibrium adsorption onto the fibres at pH5 before sheet formation, precipitation onto the fibres at pH10 prior to sheet formation and spray application to preformed sheets. The results in Fig. 5 were obtained using a commercial high α -cellulose dissolving pulp.

Such pulps have some anionic character due to the presence of carboxyl groups originating from hemicellulosic uronic acid residues or from oxidations associated with the bleaching process.

With this pulp the equilibration method, which is equivalent to normal wet-end addition in papermaking, generally gave rise to a modest increase in tensile strength at low chitosan addition, followed by a decrease at the higher chitosan levels. The falloff in tensile strength is principally an effect of increasing fibre flocculation, which causes poor sheet formation and concomitant

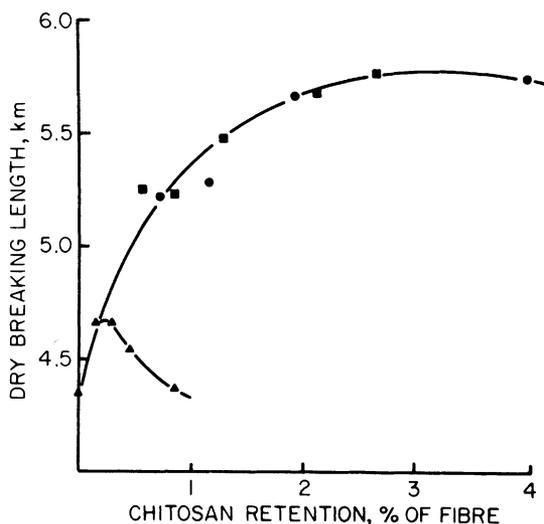


Fig. 5—The tensile strength of α -cellulose handsheets treated with chitosan by the equilibration (▲), precipitation (●) and spray (■) addition techniques

losses in physical properties.⁽²⁰⁾ By analogy with the retention mechanism of polyethyleneimine⁽⁷⁾ ionized chitosan is probably retained mostly by the formation of multiple ionic bonds between the cationic amino groups in chitosan and anionic functional groups present on the fibre surface. When all the negative sites on the fibre surface have reacted with chitosan, adsorption by this mechanism is complete. By virtue of its high charge density and extended linear conformation, chitosan is very efficient in neutralising anionic sites on the fibre. Thus, as Fig. 5 shows, equilibrium adsorption of chitosan gave low retention levels on a weight basis.

Precipitation of chitosan onto the fibres prior to sheet formation obviated the fibre flocculation problem and allowed attainment of a broader range of chitosan retentions. Since chitosan salts revert to the insoluble free amine form under basic conditions, the precipitation was accomplished by straightforward adjustment of the fibre suspension to pH10. Chitosan deposited from solution in this manner is not ionized in the aqueous phase and therefore assumes a much smaller randomly coiled configuration immediately before precipitation. This change in molecular charge and configuration is advantageous in that it minimises fibre flocculation, but was expected to have the associated drawback of reducing the effectiveness of the polymer in improving interfibre bonding. In any event, this expectation could be circumvented by spraying a solution of chitosan acetate (pH5) onto preformed sheets. This approach, which was a most convenient laboratory deposition technique, eliminated sheet formation difficulties and applied the chitosan in the ionised and extended form, optimal for spanning interfibre distances and forming ionic bonds. Moreover, since ionic bonds are much more resistant than hydrogen bonds to disruption by water, differences between this and the deposition-by-precipitation method should show up in their relative abilities to impart wet strength characteristics to paper. The data in Fig. 6 show this to be the case. That is, a less extended, unionised, chitosan macromolecule cannot be expected to develop the same number of interfibre linkages as its fully extended spray-applied counterpart. The identity of the dry tensile strengths resulting from either mode of application only serves to show that with fibres of such low anionicity, the extensive improved hydrogen bonding imparted by the chitosan overshadows the effects of sparse ionic bonding on the tensile properties of the dry sheet.

Similar chitosan addition effects were observed when the α -cellulose substrate was replaced by a typical unbleached sulphite pulp. Such a commercial pulp has a considerable intrinsic anionic character, due not only to the presence of carboxylic acid groups in the unremoved hemicelluloses but also to the sulphonic acids groups of the residual lignin. The sulphite fibres actually

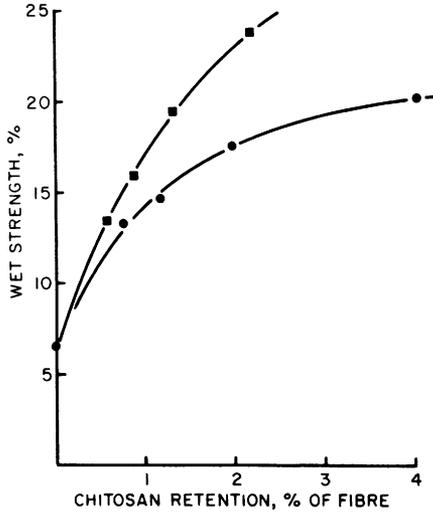


Fig. 6—The wet strength of α -cellulose handsheets treated with chitosan by the precipitation (●) and spray (■) addition techniques

used in this investigation contained a total of 0.1 meq of carboxylate and sulphonate ions per gram and therefore in comparison to the α -cellulose pulp had about thrice the potential for ionic bond formation.

In spite of this, the results in Fig. 7 demonstrate that the direct adsorption of chitosan from aqueous solutions is rather inefficient, especially at the higher addition levels. Here the charge difference between chitosan and the fibres is quickly neutralised and thereafter polymer adsorption is weak or non-existent. Thus, the combination of low retention efficiencies and fibre flocculation tends to eliminate adsorption as a mode of chitosan application. However, chitosan retention efficiencies were considerably improved (Fig. 7) by the use of the other two application techniques even though neither was optimised. The corresponding effects of these three application modes on the dry breaking length are summarised in Fig. 8. It is significant that the maximum strength increase achieved by the direct chitosan adsorption occurred at about 0.5 per cent retention, whereas with the α -cellulose fibre the maximum was 0.3 per cent lower. This difference reflects the threefold difference in anionicity between the two fibres. Obviously, since the unbleached sulphite fibre is more highly charged a greater amount of chitosan is required to bring

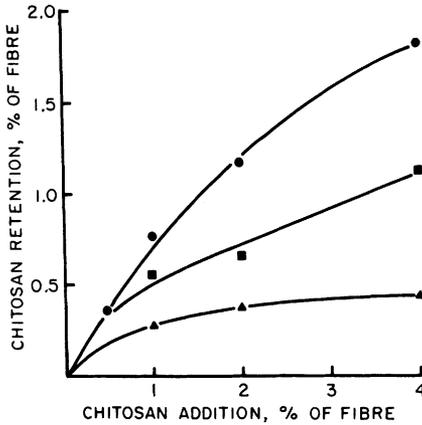


Fig. 7—Chitosan addition *vs.* retention for unbleached sulphite handsheets treated with chitosan by the equilibration (▲), precipitation (●) and spray (■) addition techniques

about charge neutralisation, fibre flocculation and the associated reduction of strength properties.

Among the three techniques discussed, the overall superiority of the spray deposition procedure is manifestly evident from the dry strength data in Fig. 8. This view is confirmed by a recent comparison of the mechanical efficiency of spray and beater addition.⁽²¹⁾ Correspondingly, and as was the case with the α -cellulose sheets, the range of wet tensile properties catalogued in Fig. 9 are substantially a reflection of the extent of the network of ionic interfibre bonds which are less disruptible by water than hydrogen bonds.

Similar effects of chitosan on paper wet strength were noted when the unbleached sulphite pulp was in turn replaced by an unbleached kraft pulp. Such a commercial pulp has a considerable built-in anionic character due to the acidity of the residual lignin contained therein. There are thus excellent opportunities for the construction of interfibre ionic bonds and this is demonstrated by the data in Fig. 10. It is intriguing that comparable wet strengths can be developed in kraft sheets made from well-beaten and very lightly beaten fibres which exhibited dry tensile strengths of 9 700 and 7 100 m respectively in sheet form. This shows that beating contributes little to the ionic action of wet strength additives. Additionally, of course, it is possible to convert these ionic linkages to covalent entities by the action of heat. Thus, the effect of prolonged curing at 105° C on the wet strength of sheets made

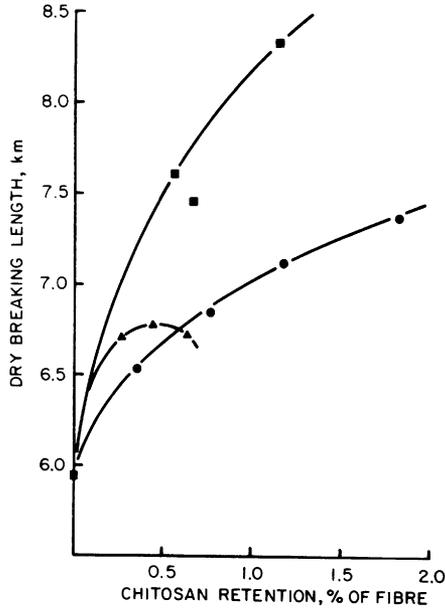


Fig. 8—The tensile strength of sulphite handsheets treated with chitosan by the equilibration (▲), precipitation (●) and spray (■) addition techniques

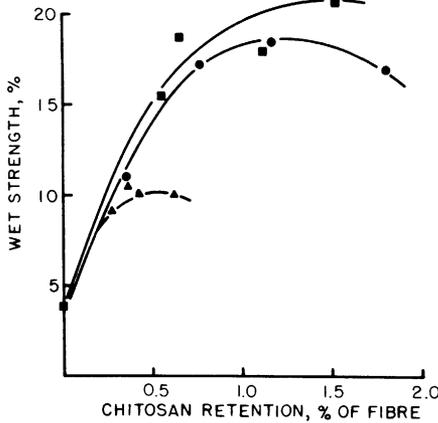


Fig. 9—The wet strength of sulphite handsheets treated with chitosan by the equilibration (▲), precipitation (●) and spray (■) addition techniques

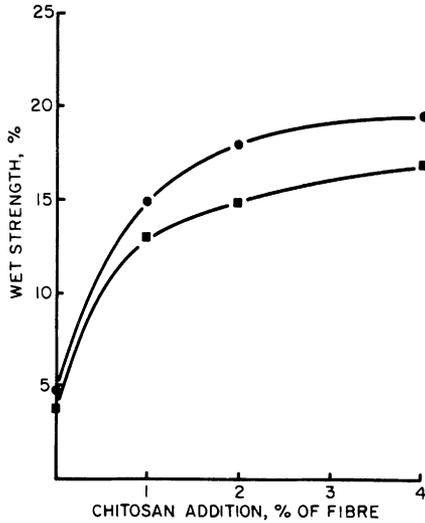


Fig. 10—The wet strength of well beaten (●) and lightly beaten (■) kraft hand-sheets sprayed with chitosan

from unbleached kraft fibres equilibrated with 2 per cent chitosan at pH6.5 is shown in Fig. 11. The initial wet strength of 15 per cent is seen to increase continually for the first 60 minutes of heating until a maximum of 28 per cent is reached.

The effectiveness of this treatment may be attributed to several factors. Firstly, the amino groups in chitosan are capable of reacting with carboxylic acid groups present on the fibre surfaces to form covalent amide linkages. Second, there is some evidence that chitosan is capable of self-condensation, since Merrill⁽²²⁾ reported that by heating dry chitosan for 12 hours at 100° C the viscosity of the product in a 5 per cent neutral solution in acetic acid increased from 5 to 200–300 poise. Third, during prolonged drying, chitosan acetate loses acetic acid⁽²²⁾ and is thereby converted into the insoluble free amine form. Fourth, Rigby⁽²³⁾ noted that when chitosan was used as an adhesive, the water resistance of the bonds could be increased by heating at 100–150° C for a short time. Consequently, the increases in wet strength imparted by curing are probably due to covalent crosslinking and reduced chitosan solubility.

Since all of these changes could lead to an increase in the molecular weight of the chitosan in the sheet it was of interest to explore the effect of increasing the molecular weight of the chitosan prior to application to the fibres. Cer-

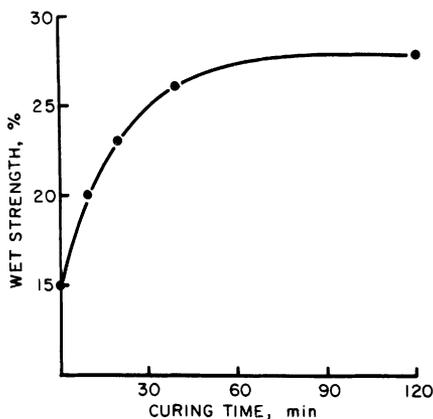


Fig. 11—The influence of curing at 105° on the wet strength of chitosan treated kraft handsheets

tainly longer linear polymers would be able to span larger discontinuities between fibres. On the other hand, if beater addition was the application mode contemplated, augmentation of the chain length would tend to be counterproductive because the bridging and flocculating action leading to poor sheet formation would thereby be intensified.⁽²⁴⁾ Indeed the polymers used as wet strength additives are often identical in chemical structure to those used as water purification aids except in the matter of molecular weight.⁽²⁵⁾

In order to determine the effect of molecular weight on the efficiency of chitosan as a paper strength additive, three fractions with differing molecular weights were prepared by degrading a high viscosity chitosan sample using nitrous acid. This facile procedure for depolymerisation of chitosan has been shown to entail a deamination at the point of cleavage and is stoichiometric with regard to the amount of sodium nitrate consumed, nitrogen evolved and number of new reducing end-groups formed.⁽²⁶⁾ The three fractions prepared had intrinsic viscosities of 4.80, 3.65 and 0.72 in an aqueous solution which was 0.2M in CH₃COOH and 0.1M in NaCl. Using Lee's values⁽²⁷⁾ for the Staudinger constants ($K=8.93 \times 10^{-4}$; $a=0.71$) of chitosan in 0.2M CH₃COOH—0.1M NaCl—4M urea solution, the corresponding average molecular weights of the three fractions are calculated to be 180 000; 122 000; and 12 000; respectively.

The relative effectiveness of these samples in mediating both the wet and dry strength of paper was determined by spray application to preformed softwood groundwood (western hemlock) handsheets. From the data obtained

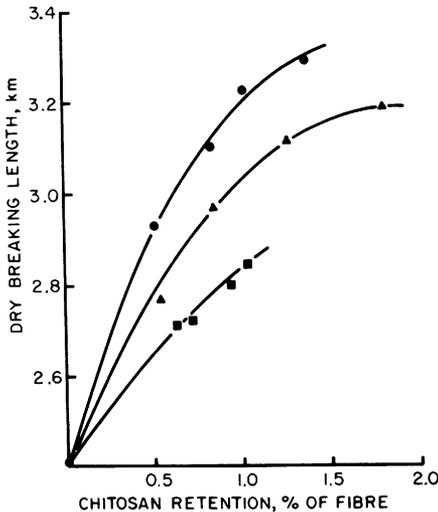


Fig. 12—The breaking length of softwood groundwood handsheets sprayed with chitosan solutions of intrinsic viscosity 0.72 (■), 3.65 (▲) and 4.80 (●)

and presented in Figs. 12 and 13 it is apparent that the greatest effect is provided by the chitosan with the largest molecular weight. This molecular size effect has been observed previously in paper treated with either polyethyleneimine⁽⁷⁾ or cationic polyacrylamide⁽²⁰⁾ and is attributable to the construction of a more extensive interfibre bridging network.

Of course, with any polymer there is a level above which further increases in molecular weight have little beneficial influence on the physical properties of the polymer or on its effectiveness in a composite system. The data in Figs. 12 and 13 indicate that this limit has not been reached and underscores the importance of minimising polymer degradation during the manufacture of chitosan, thereby preserving the high molecular weight of the native chitin. These findings also suggest that future work on chitosan as a paper additive should include quantifying the possible benefits of increasing the molecular weight of chitosan by chemical crosslinking.

The merit of such a research endeavour can be predicted with confidence from some patent literature⁽²⁸⁾ information on the bonding of reconstituted tobacco sheets. In fundamental terms, this process is nothing more than conventional papermaking with tobacco leaf fragments acting as the furnish. Obviously, the phenolic, carboxylic and carbonyl group content of dried

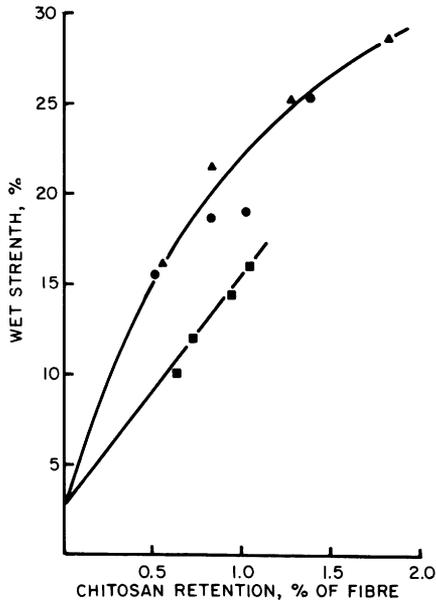


Fig. 13—The wet strength of softwood groundwood handsheets sprayed with chitosan solutions of intrinsic viscosity 0.72 (■), 3.65 (▲) and 4.80 (●)

plant material offers a splendidly reactive surface for ionic and covalent bonding to chitosan and the concomitant development of the high levels of wet strength itemised in Table 2. The further enhancement of this wet strength by heating at 150° C is illustrative of the conversion of ionic to covalent linkages or the formation of imine bonds at the interface between the tobacco leaf debris and the chitosan binder film.

While all of the foregoing results validate the prediction that chitosan should be an effective wet strength additive for paper it was considered desirable to substantiate these handsheet findings by data gathered from paper made on an actual fourdrinier machine.

A paper machine trial was therefore conducted at the facilities of the Crown Zellerbach Corporation, in Camas, Washington. Individual machine runs and subsequent paper testing were carried out by Crown Zellerbach personnel. The paper machine used was a 610 cm trim fourdrinier, running at about 30 m per minute on a newsprint furnish consisting of 80 per cent refiner groundwood and 15 per cent bleached kraft. The initial experimental design called

TABLE 2—COMPOSITION AND PROPERTIES OF RECONSTITUTED TOBACCO SHEETS BONDED WITH CHITOSAN

Patent example number	Furnish composition (%)					Breaking length, m ^b		Wet strength (%)
	tobacco	cellulose	humectant ^a	clay	chitosan	dry	wet	
1 ^{c,e}	82	5	5	4	5	310	210	67
2 ^c	84	6	6	4	5	470	260	57
3 ^d	67	10	10	—	9	280	140	51
4 ^d	71	6	6	4	9	650	230	39
5 ^d	66	11	11	—	12	730	400	55

^a Combination of tetraethyleneglycol and ethylhydroxyethylcellulose.

^b Maximum values selected from either machine or cross direction data.

^c Cured at 105° C. ^d Cured at 150° C. ^e Cross-linked with glyoxal.

for chitosan application by both the spray and precipitation techniques and also at the size press. Unfortunately, the spray deposition was unsuccessful, due to equipment malfunctions which could not be rectified in the limited machine time available. The precipitation was accomplished by addition of the required weight of 1 per cent chitosan acetate solution to the machine chest, followed by adjustment of the pH to 9 using NaOH. At the size press a 1 per cent solution of chitosan acetate was also used. For comparison purposes, several runs were conducted employing a commercially available cationic starch as a wet end strength additive.

During the course of the trial, it became evident that the use of chitosan posed no problems to normal paper machine operation. It was noted, for example, that chitosan did not cause foaming, nor did it slow drainage on the wire. No plugging of the wire or felt was observed, neither was there serious picking at the presses or sticking in the dryers.

A summary of selected physical properties, including tensile, burst, tear and Scott internal bond, is presented in Table 3. Comparison of the data therein shows that, at equivalent addition levels of 1 per cent, precipitated

TABLE 3—SUMMARY OF DATA FROM NEWSPRINT MACHINE TRIAL

Additive	Addition level (%)	Retention level (%)	Breaking length ^a , m		Wet strength (%)	Burst factor	Tear factor	Scott internal bond
			dry	wet				
None	—	—	3 984	365	9.2	15	46	111
Starch ^b	1	—	4 587	442	9.6	15	45	151
Chitosan ^c	0.5	0.27	4 484	770	17.2	16	44	135
Chitosan ^c	1	0.38	4 831	939	19.4	16	43	154
Chitosan ^d	—	0.97	5 301	1 728	32.6	20	41	256

^a Machine direction.

^b Wet-end addition.

^c Precipitated.

^d Size-press application.

chitosan is 40 per cent more effective than the cationic starch in increasing the dry breaking length of the newsprint. The superiority of chitosan is further evidenced by the wet strength of the chitosan treated sheet which is more than twice that of the paper containing the cationic starch.

However, application of chitosan to the paper at the size press proved to be the most successful deposition technique. Not only was the chitosan applied in a fully ionized and extended form, the retention efficiency was 100 per cent. In contrast, the retention efficiencies for precipitated chitosan were in the 40–50 per cent range. The incorporation of 1 per cent chitosan into the sheet at the size press increased the dry breaking length by 33 per cent and augmented the wet breaking length by a factor of almost 5 thus affording a wet strength value also of 33 per cent. The Scott internal bond strength of the size press treated sheet was also more than doubled, indicating that chitosan must have penetrated to the interior of the sheet.

TABLE 4—OPTICAL PROPERTIES OF MACHINE MADE NEWSPRINT

<i>Additive</i>	<i>Addition level (%)</i>	<i>Addition pH</i>	<i>Brightness</i>	<i>Opacity</i>	<i>Scattering coefficient</i>
None	—	5	57.6	92.9	605
Starch ^a	1	5	54.9	94.2	571
Chitosan ^b	0.5	6	54.6	94.6	596
Chitosan ^b	0.5	8.5	51.4	95.4	617
Chitosan ^b	1	9	49.5	95.6	578
Chitosan ^c	—	4.5	55.1	91.7	501

^a Wet-end addition. ^b Precipitated. ^c Size-press application.

The optical properties of selected machine runs are presented in Table 4. The brightness values collected therein superficially suggest that the precipitation of chitosan onto the fibres entails a substantial loss in brightness. Closer examination, however, reveals that the loss in brightness is associated with the increase in pH required to precipitate the chitosan and not with chitosan itself. Such a loss in optical quality could be an important disadvantage inherent in this polymer deposition technique.

In order to further probe the effect of chitosan on paper brightness, samples of both a technical grade and a more highly purified chitosan were sprayed at the 2 per cent addition level onto sheets of Whatman No. 1 filter paper. Brightness readings were taken after drying and also after heat ageing in air for 1 and 20 hours in a 105° C oven. The results, presented in Table 5, show that the purified chitosan did not significantly affect the brightness of the paper. The technical grade product, however, had a light yellow colour in solution, probably due to trace amounts of crustacean carotenoids such as

TABLE 5—INFLUENCE OF CHITOSAN ON PAPER BRIGHTNESS

<i>Treatment</i>	<i>Brightness</i>		
	<i>Original</i>	<i>1 hour heat aged</i>	<i>20 hour heat aged</i>
Control	90.3	90.1	89.7
Purified chitosan	90.1	89.9	89.5
Technical grade chitosan	89.2	88.8	88.0

astaxanthin.⁽²⁹⁾ This colour impurity induced a 1 point drop in initial brightness, which increased to 2 points after heat ageing for 20 hours. For the majority of applications this would probably not be significant but in cases where very high brightness is vital, a purified chitosan would need to be specified.

Chitosan, of course, will also mediate fibre-water interactions in the Z-direction of paper. It can therefore be anticipated that the bonding modes discussed in this article would be reflected in the printing characteristics of a chitosan-bonded sheet. Although many printability testers have been designed and built, the most reliable testing is still done by running the sheet on an actual production press. With this in mind, newsprint samples produced on the papermachine, including a control sheet and sheets containing chitosan or the cationic starch, were taken to a local newspaper for printability tests using offset lithography. Subjective evaluation of the print quality by the printers and other experts in the field led to the general conclusion that the print quality of the chitosan-containing sheets was superior to that of the sheets containing starch and far better than that of the control. These printing improvements were characterized by better print definition, less picking and improved ink holdout. Figs. 14a and 14b are photographs of portions of the printer's proofs for the control and chitosan-treated sheets, respectively. Comparison of the insets which are 4 × magnifications of solid black printed areas from the same sheet discloses that the control has a lighter appearance and shows far more surface picks than does the chitosan-containing sheet. Offset lithography places far more stringent demands on paper properties than does letterpress. The use of tackier inks and rubber blankets, for example, necessitates the use of papers with high surface strength in order to minimise the picking of loosely bonded material from the surface of the sheet. In addition, the use of water as a dampening solution on the plate and blanket requires some resistance to the softening effect of water on paper surfaces. Thus the improved offset printability imparted by chitosan must be due to a fortification of the paper surface with water-resistant interfibre bonds. In addition to enhanced print quality, chitosan-treated paper would no doubt exhibit

improved runnability on the presses since the augmented strength would diminish the frequency of breaks while the reduced picking and dusting would mean longer press runs between washups.

The successful mediation of bonding by chitosan in the machine-made newsprint also provides the opportunity to further test the validity of the concept of the relation between chemical bond energies and interfibre bond strengths⁽³⁰⁾ under the rigours of practical operation. That is, the chitosan-newsprint composite, covalently bonded, should exhibit different strength properties from those ionically bonded provided the structure is bond strength limited.⁽³¹⁾ Thus, heat treatment of the newsprint size press treated with chitosan, with and without the application of a 1 per cent aqueous solution of formaldehyde afforded the data presented in Table 6. The wet strength of the sheet containing 1 per cent chitosan applied at the size press was increased from 34 per cent to 50 per cent by the formaldehyde treatment. Formaldehyde can readily react with the amino groups in chitosan to form methylol groups, which subsequently form methylene crosslinks during the curing process. These covalent linkages are clearly more resistant than ionic linkages to disruption by water and the wet strength of PEI-treated paper can similarly be increased in this manner.⁽³²⁾

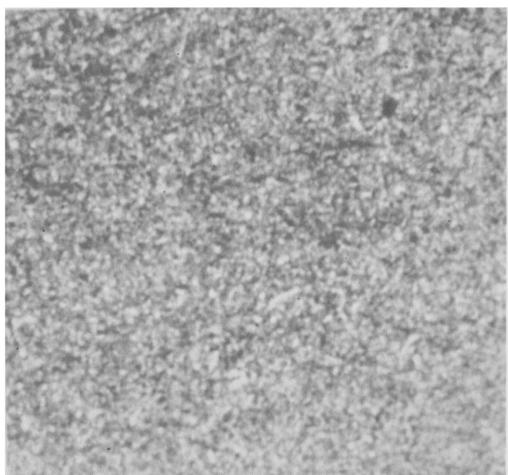
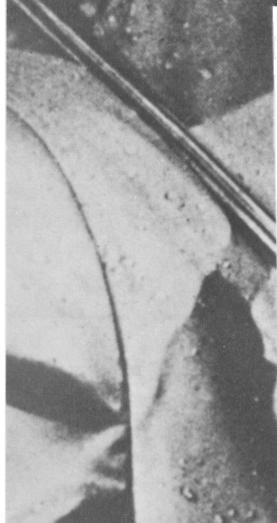
TABLE 6—INFLUENCE OF CURING AND CHEMICAL CROSSLINKING ON THE TENSILE PROPERTIES OF NEWSPRINT CONTAINING CHITOSAN

<i>Treatment</i>	<i>Tensile strength (kg/mm)</i>		<i>Wet strength (%)</i>
	<i>dry</i>	<i>wet</i>	
0% Chitosan, uncured	4.04	0.36	9
1% Chitosan, uncured	5.04	1.73	34
1% Chitosan, cured	5.27	2.00	38
1% Chitosan, CH ₂ O treated	4.64	2.32	50

Although covalent bonds are undoubtedly being formed during these experiments the ionic bonds are still playing a mediating role. This is demonstrated by the information in Fig. 15 where the wet tensile strength of newsprint treated with chitosan or chitosan plus formaldehyde is presented as a function of the pH of the water used in testing. The slopes of these curves demonstrate that the bonding mechanisms are indeed different. The fact that the wet strength of chitosan-treated paper is pH sensitive could facilitate broke recovery and the repulping of paper⁽⁵⁹⁾ containing chitosan. The diminished wet strength in acidic media in all cases is due not only to increased chitosan swelling or solubility, but also to a reduction in the number of ionised



Fig. 14 (a and b)—Photographs of portions of printer's proofs for the control and chitosan-treated sheets, respectively



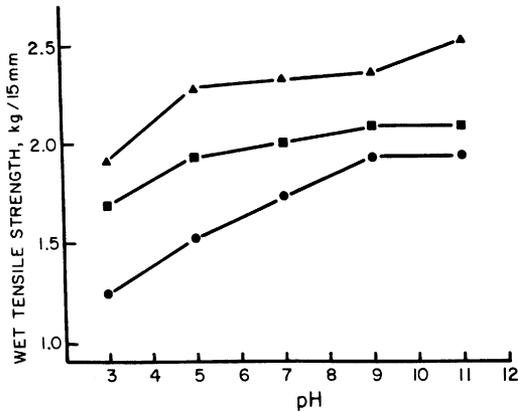


Fig. 15—The influence of different water pH values on the wet tensile strength of chitosan treated newsprint (●), showing the effect of subsequent curing (■) and formaldehyde treatment (▲)

negative bonding sites on the fibres and hence in turn the presence of fewer ionic bonds.

These ionic and covalent bonding characteristics of chitosan can of course be employed to improve the performance of other already commercialised wet strength additives. Modification of the widely-used commercial-type urea-formaldehyde resins is particularly facile. The effects secured by the use of these polymer blends in an unbleached kraft are shown by the data in Table 7. Significant improvements in wet strength resulted at both acidities of application when chitosan was used in conjunction with the synthetic resin. The increase observed at pH 6.5 is due primarily to increased resin retention, since the addition of chitosan resulted in almost 100 per cent retention of the urea-

TABLE 7—THE EFFECT OF CHITOSAN UREA-FORMALDEHYDE RESIN COMBINATIONS ON THE WET STRENGTH OF PAPER

Treatment	pH of application	Breaking length, m		Wet strength (%)
		dry	wet	
Chitosan (0.2%)	6.5	10 830	971	9
U/F	6.5	11 200	1 380	12
U/F and chitosan	6.5	12 670	2 730	22
U/F	3.5	9 740	2 180	22
U/F and chitosan	3.5	11 010	2 840	26

formaldehyde resin. At pH 3.5 the retention was about the same for both the chitosan and non-chitosan treated pulps. Thus, the increase in wet strength is probably the result of formation of covalent bonds between the two polymers under the conditions of cure.

All of the foregoing results establish that chitosan does have a potential for commercialisation as a mediator for fibre-water interactions in paper. Indeed, both chitin and chitosan are now being produced from shellfish wastes by U.S., French and Japanese companies.⁽³³⁾ However, initially chitosan is being marketed in relatively small quantities at prices (\$4.66–11.00/kg) which will prohibit many applications in paper. Nonetheless, larger amounts could be produced because the present availability of chitin from existing shrimp wastes alone is apparently about 20 000 tons/year.⁽³⁴⁾ This volume of material would be significantly augmented if the shrimp heads, now currently discarded at sea, were landed for processing.⁽³⁵⁾ Moreover, there is a population of a small shrimp, which may amount to as much as 5×10^9 tons, available in the Antarctic Ocean,⁽³³⁾ the harvest of which is beginning to be actively investigated by both Japan and the USSR.⁽³⁶⁾ Thus, in the nearterm, chitosan will probably be principally derived from crustacean sources. On the other hand, an increasing use of chitosan by the paper industry will require, over the long haul, the development of new stable sources of supply. As part of the *Sea Grant Program* of the University of Washington an investigation of such alternate sources covering the phyla, *Crustacea*, *Insecta*, *Mollusca* and *Thallophyta*, has been carried out.⁽³⁷⁾ This study indicates that the most promising large volume source for the paper industry would be from filamentous fungi of the order, *Mucorales*.⁽³⁸⁾ These organisms can be grown on a wide variety of waste streams, including pulp and paper mill effluents, processed to yield chitosan and then used directly in the manufacture of paper.

Experimental

Materials

THE chitosan used was isolated from crustacean wastes by Food, Chemical and Research Laboratories, Inc., Seattle, Washington, and made available for research by the Office of Sea Grant, National Oceanic and Atmospheric Administration, U.S. Department of Commerce, Rockville, Maryland. In an aqueous solution of acetic acid (0.2M), sodium acetate (0.1M) and urea (4M), this chitosan had an intrinsic viscosity of 3.0 which from Lee's values for the Staudinger constants ($K = 8.93 \times 10^{-4}$; $a = 0.71$) corresponds to a molecular weight and degree of polymerisation of 93 000 and 581 respectively.⁽²⁷⁾

The cationic starch (Q-TAC #3894) was supplied by CPC International, Inc., Englewood Cliffs, NJ.

The α -cellulose pulp used was an unbeaten commercial dry lap containing approximately 0.02 meq COOH/g made available by ITT-Rayonier of Shelton, Washington. It was beaten to CSF 390 prior to use.

The unbleached sulphite pulp was provided by Publishers Paper Company, Newberg, Oregon and was a commercial grade typically derived from a mixture of (75:20:5) of Western Hemlock (*Tsuga heterophylla*), White fir (*Abies concolor*) and Sitka spruce (*Picea sitchensis*). It was beaten to CSF 400 prior to use.

The unbleached kraft pulp was donated by the Weyerhaeuser Co., Everett, Washington and was a commercial grade made from a mixture (85:15) of Western red cedar (*Thuja plicata*) and Western hemlock (*Tsuga heterophylla*). The softwood groundwood (Western hemlock) pulp was also a commercial product gifted by Boise-Cascade Corp., Steilacoom, Washington.

Methods

Polymer addition and sheet formation procedures Equilibrium Adsorption: A vigorously stirred suspension of fibres (5 g) in water (400 ml) was adjusted to pH5 with acetic acid and treated with an aqueous solution of chitosan acetate (2 per cent solution, pH5). The consistency was adjusted to 1 per cent and stirring was continued for 1 hour at ambient temperatures (25°). The suspension was then diluted to 0.25 per cent consistency, divided into four equal parts, and formed into handsheets in accord with TAPPI Standard T 205 m-58.

Precipitation: The procedure for precipitating chitosan onto the fibre surface was identical to that described above for equilibrium adsorption, except that after stirring for 1 hour the pH of the suspension was adjusted to 10 with 0.5N NaOH. Stirring was continued for an additional 10 min at this elevated pH prior to sheet formation.

Spray Application: Sheets of untreated fibres were formed in the standard manner, couched from the sheetmould and, while still wet and on the blotter, were sprayed with a chitosan solution (1 per cent, pH5) using a chromatography-type laboratory atomiser. The sheets were then pressed and dried in accord with standard TAPPI procedures. Chitosan addition levels were varied by adjustment of the duration of spraying.

Preparation of chitosan solutions Chitosan acetate solutions were typically prepared by treatment of a stirred suspension of dry chitosan (50 g) in water (200 ml), with acetic acid (25 ml) and subsequent dilution with water to afford a 2 per cent (W/V) chitosan solution (250 ml).

Degradation of chitosan Three stirred solutions (2 per cent W/V, 500 ml) of chitosan (10 g, 62 mmol) acetate at 22° were treated with water (47.5 ml) or aqueous solutions (47.5 ml) of sodium nitrite (47.5 mg, 0.69 mmol; 475 mg, 6.9 mmol) added dropwise during 1 hour. After another hour the reaction mixtures were separately adjusted to pH10 using a 0.5N solution of NaOH. In each case the precipitated chitosan was collected by centrifugation, repeatedly washed with water until alkali-free,

and then freeze-dried. The intrinsic viscosities of the products were determined at 25° in 1.0, 0.5 and 0.25 per cent aqueous solutions of acetic acid (0.2M) containing NaCl (0.1M) using an Ostwald Viscometer with an outflow time of 89.7 s.

Testing and analytical procedures The physical testing of handsheets was performed in accord with TAPPI Standard T220 m-60. Wet tensile properties were measured as discussed in TAPPI Standard T456 os-68, using a 10 min immersion. Brightness measurements were made using an Elrepho brightness meter as prescribed by TAPPI Standard T452 m-58. The carboxylic acid content of pulps were determined using the sodium bicarbonate-sodium chloride method contained in TAPPI Standard T237 su-63. Actual chitosan retention levels were determined by analysing paper samples for their nitrogen content using a modified Kjeldahl procedure.⁽³⁹⁾

Conclusions

Since for more than a decade it has been accepted that paper is held together by a distinct type of chemical bond it is past time to extend this acceptance of the existence of chemical bonds between fibres to the phenomenon of bonding under wet conditions. The re-interpretations of published information and the new results presented herein are fully consonant with the concept of interfibre ionic and covalent bond formation, the utility of which has been demonstrated by the fulfilment of a rational prediction of the effectiveness of a novel polymeric mediator for fibre-water interactions in paper.

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Transcription of Discussion

Discussion

Prof. R. H. Marchessault Did I understand you correctly that you hope that the fungi would actually produce chitosan?

Mr G. G. Allan There are fungi which produce a mixture of chitosan and chitin. They seem to be also associated with other polysaccharides, so we are not going to be dealing with the pure entity that would be produced by *Cyrtocrypta cryptica* or from crabs but I think that it ought to have enough of the characteristics that we have defined to make this material functional as a paper additive. We have already shown this to be the case with one fungus and we are now attempting to extend this finding to other fungi.

Mr Brudell Two questions please. Was the newsprint you used in the experiment sized? I think that could be important in regard to the vast improvement in Scott bond. Performance functions of wet strength in paper often relate to its alkali resistance, i.e. 2 per cent caustic solutions. Do you have any data as to the wet strength retained after treatment by caustic?

Allan In answer to your first question, the paper was not sized. I don't believe I can recall any data with 2 per cent caustic, I would guess that the wet strength would fall off under these conditions. There is the complication, however, that the ionisation of the cellulose would be increased and it might be that you would be generating enough cellulose ions to compensate for the drop-off in concentration of amine carboxylates.

Dr G. Hunger How does this material compare to cationic starch in regard to effect and price?

Allan If you look at Table 3 you will see a comparison with cationic starch under machine conditions. As regards price, cationic starch is cheaper but less effective. So that unless you had a very special paper in mind I couldn't recommend chitosan in preference to cationic starch from a cost point of view.

Under the chairmanship of Dr N. K. Bridge