

A NEW INTERFIBRE SYSTEM FOR PAPER INVOLVING ZWITTERIONS

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ABSTRACT

This paper examines the effects of the natural ability of the fibres to bond and the introduction of moieties able to provide balanced ionic interactions, on the dry and wet mechanical properties of paper. Thus, the effects of the introduction of zwitterionic moieties (*i.e.* amino acids coupled with *s*-triazines) onto the surface of the fibers and their interaction are interpreted in the light of accepted theories of dry and wet paper strength and the topology of the location of the zwitterionic sites. The tensile strength and other mechanical properties of paper made with the zwitterionic fibers are reported. Paper made from zwitterionic fibers retain more than 35% of their dry strength after being immersed in water for weeks. The importance of these results is considerable when it is realized that no wet strength resins are being used. The benefits of zwitterionic bonding in papermaking are briefly discussed.

INTRODUCTION

Cellulose surfaces show the ability to bond naturally in the presence of liquid water which provides the needed forces during its departure as to bring the surfaces into contact as it is illustrated in the papermaking process. It is now widely accepted that the nature and extent of bonding, as well as the intrinsic strength of the fibres play a definite role in holding together the fibres and subsequently in the development of mechanical strength of fibre assemblages. One of the ways in which these properties, in particular the tensile strength can be improved would be through a better and increased interfibre bonding.

Thus, the now widely accepted postulate that interfibre bonding in paper occurs by means of a kind of chemical bond, hydrogen bonding (1, 2) together with the consolidation of the corresponding theories on the tensile strength of paper (3) has led to the idea of modifying the surface chemistry of lignocellulosic and cellulosic papermaking fibres. The purpose of such work has been to change the nature of the physicochemical interaction between the surfaces of the fibres and thus the ways in which they bond with each other. Many approaches have been taken in the chemical modification of papermaking fibres for various purposes with different degrees of success in improving interfibre bonding (4). One of these approaches, the use of surface modification to achieve zwitterionic interactions, is the subject of this work.

Stereotopochemistry of cellulose fibres

One factor worth taking into consideration in the developing of a better bonding system is the stereotopochemistry of cellulosic pulp fibres. One simplified physical representation in harmony with the experimental results of Stone and Scallan (5) visualizes the fibre cell wall as a composite of several hundred concentric lamellae of cellulosic microfibrils. In the swollen state, these lamellae are separated by relatively large water-filled spaces (25-100 Å, with the larger being

located nearer the periphery of the cell wall). Molecules in solution can diffuse through these macrospace to reach the water-filled micropores within the disordered areas of the lamellae themselves. These micropores were found to range in width from 25 Å down to the size of a single water molecule.

This fibre cell wall model suggests that improvements in interfibre bonding may not necessarily increase the strength of paper because as interfibre junctions are reinforced by new higher energy bonds, the site of the bond rupture may be transferred from this interface to the discrete lamellar arrangement lying just below, which may in effect comprise planes of weakness. Thus, it should not be surprising that the shear strength of the cell wall becomes the limiting factor in paper strength, because the pulping and bleaching processes have been shown to effect discontinuities in the structure of the fibre cell wall (6).

Dry and wet strength in paper

Paper is usually characterized by its ability to resist stresses and the primary requirements depend on the particular application for which the product is intended. Most of the strength properties are increased by additional bonding between the fibres in a sheet i.e. tensile strength, burst strength abrasion and pick resistance, etc. Accordingly, this paper is concerned primarily with the mechanisms for development of dry and wet strength in paper by the use of zwitterionic interactions.

Dry strength is an inherent structural property of a paper sheet which is due primarily to the development of fibre to fibre bonds during consolidation and drying of the fibre network. There are several ways in papermaking practice to increase sheet strength (Z), which may include changes in the furnish (higher proportion of long fibres, less inert filler, or use of strength additives) or process modification (alkaline pH, beating, increased wet pressing, etc.). In regards to the use of strength additives, most materials merely provide extra adhesive for fibre-fibre bonding, which increase the degree of bonded area at each contact point and/or the frequency of bonding per unit fibre length (g).

Also a good wet strength is also the determinant for various end-use requirements of a number of cellulosic fibre paper, paperboard and related products. While many of these have ample dry strength, they lose most of their strength properties when wetted, and this is primarily attributed to the loss of bond strength. This has been explained by the fact that water interacts with the cellulose fibres and this destroys the interfibre hydrogen bonding, which in combination with the strength of the fibre is responsible for the dry strength of the assemblage (g). Hence, any approach to improving the wet strength properties of a cellulose fibre assemblage would require either a means of retaining the hydrogen bonding established in the dried web or the introduction of new bonds that would be less affected by water.

Ionic Bonding of Paper

Electrostatic forces are, in fact, already utilized in the manufacture of paper, notably in the areas of sizing, dyeing, and in the retention of resins and fillers. A bonding system based on electrostatic linkages offers the following practical advantages (10): (a) ionic bonds are instantaneously formed in aqueous media and need no subsequent curing period, (b) ionic bond formation is reversible, *i.e.* if such linkages are ruptured, bond reformation only requires realignment of the formally charged atoms, (c) electrostatic attractions can occur over greater intermolecular distances than those necessary for covalent or hydrogen bond formation and (d) the resulting linkages are of a higher energy ($\Delta H=10-20$ kcal/mol).

In addition to influencing the dry tensile properties of handsheets, it can be anticipated that ionic bonding could be of greater importance in its effect on wet strength. Allan (10) demonstrated the concept of using ionic and/or covalent for improving dry and particularly wet strengths of fibre networks, by increasing the normally existing anionic charges (cellulose fibres normally possess negative charges in amounts 1-10 mM/g) in the fibres by reaction with a reactive dye or reactive dye intermediate and bridging the modified fibres with cationic polyelectrolytes. In particular, polyethyleneimine (PEI), a well known wet strength additive, has been used as the positively charged entity that would be sandwiched in between negatively charged lignocellulosic and/or cellulosic fibres or lamellae (9, 10). This work showed that the development of wet strength in paper by PEI depends on the formation of water-insensitive ionic bonds and that the decrease in the dry tensile strength observed could be a result of hydrogen bond obliteration rather than interference in the formation of ionic bonds. The considerable amount of wet strength obtained (>30%) with the relatively small molecule, pentaethylenhexamine could not be attributed to the formation of any protective sheath around pre-existing hydrogen bonds. The wet strength observed, most plausibly resulted from the creation of interfibre ionic linkages.

The validity of this view is supported by the long-term durability of the wet strength of paper. Furthermore, dyed handsheets treated with pentaethylenhexamine, retained their original wet strength throughout continuous immersion in water for 30 days when the test was discontinued (10).

It is also important to mention that when negatively and positively charged fibres were prepared separately and then mixed in an aqueous suspension, severe flocculation occurred, which could prove that ionic interactions indeed can take effect (6). Furthermore, three important implications were derived. First that the introduction of negative sites (which create potential ionic bonding loci) onto fibres is 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 for the polycation is not indispensable for a wet strength additive (11).

In another investigation ionic bonding using polyethyleneimine as the multication and the normal existing negative sites in cellulose pulp plus 5% carboxymethylcellulose fibres (CMC, 0.7 DS) as the anionic counterparts, also produced an encouraging outcome (9). It resulted in up to a sixfold increase in wet tensile strength. When no CMC was used, the increase in the wet strength was only threefold (Table 1). Although ionic bonding increased wet strength considerably, dry strength remained virtually unaffected. This was explained as being due to the fact that a high degree of bonding is already achieved in the dry state and any additional bonding in this state does not contribute further to the strength.

Table 1. Wet strength of ionically bonded fiber webs (9).

Pulp	Basis weight, g/m ²	Wet-web treatment	Tensile strength, KN/m		Wet strength retention %
			Dry	Wet	
Unbleached kraft	290	None	14.7	0.42	2.9
Unbleached kraft	290	PEI ¹	15.1	1.27	8.4
Unbleached kraft +5% CMC fibers	290	PEI	15.3	2.54	16.6

¹ Polyethyleneimine

The Zwitterionic Bonding Concept

It was shown by Allan and Reif (6) that when both positively and negatively charged fibres were prepared and mixed it was very difficult to form homogeneous suspensions because of electrostatic effects. To overcome this difficulty, webs of totally negatively charged fibres were prepared and then sprayed with solutions of polycationic substances (PEI and chitosan). Although strong structures were indeed formed, considerable practical difficulties in attaining the critical ionic balance between positive and negative sites remained. Nonetheless, it was clear from these studies that the optimum situation would be to modify pulp surfaces with exactly equal numbers of accessible positive and negative sites.

Under the light of these results, a different approach is here contrived, *i.e.* the chemical modification of the pulp fibres to introduce zwitterionic sites capable of forming inter- and perhaps intra-fibre bonds, and greater in strength than the pervasive hydrogen bond. Because a zwitterion ('hermaphrodite' ion) has by definition an equality of positive

and negative charges, it is, for this work, a logical choice (Figure 1). The stereochemical fact that two ionic bonds should be formed as a result of any single interaction between modified surfaces supports this choice. Furthermore, a zwitterion carries its own counterion, a fact that already allows for a way to conveniently get rid of the simple salts (usually NaCl) formed by the combination of the positive and negative gegenions (12). The utilization of a zwitterion circumvents then one of the most serious drawbacks of ionic bonding.

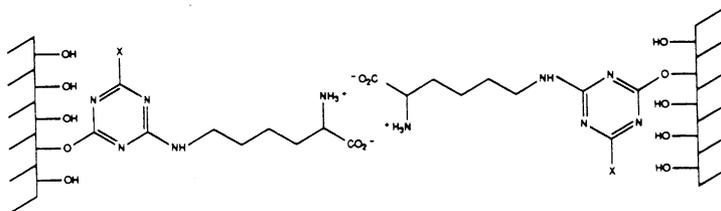


Figure 1. Simplified visualization of the interfibre zwitterionic interactions.

In order to test the validity of the zwitterionic bonding of lignocellulosic fibre assemblages, the chemical synthesis of such fibres was undertaken. Based on previous remarks, the reactive dye chemistry was the method chosen to achieve the desired modified fibres. Some of the common amino acids were selected as the zwitterions, specially the trifunctional amino acids tyrosine, cysteine and lysine, since the third functional group would permit the condensation of the amino acid with cyanuric chloride to produce reactive dye-like amino acid-dichloro-s-triazines.

The merits of the reactive dye chemistry for modifying the surface of cellulosic fibres have been already discussed elsewhere (13, 14) and it was remarked that the most important and relevant characteristics of these dyes are that they are applied in aqueous media, usually at room temperature, under moderately alkaline conditions and that the covalent bonds formed to the cellulose molecule are relatively stable. Thus the application of these sorts of reactive substances is relatively simple and could be adapted very well to the papermaking process.

Thus, our idea of improving the dry and/or wet strength of a paper sheet is based in the modification of the fibre surface by the attachment of zwitterionic entities such as α -amino acids, to provide a stoichiometric balance of negative and positive charges under stereochemically favorable conditions. To evaluate this approach, the following concrete objectives were established: (a) to synthesize reactive dye-like compounds containing an α -amino acid moiety, based on cyanuric chloride chemistry; (b) to study the reaction of these compounds with wood pulp fibres and characterize the fibres modified in this manner; (c) to prepare handsheets with the modified pulp and perform some standard tests to evaluate the effect of the surface modification on its mechanical properties.

MATERIALS AND METHODS

Materials

L-Tyrosine (Degussa AG, Frankfurt FRG or Aldrich Chemical Co., Milwaukee, WI), L-lysine monohydrochloride and L-cysteine hydrochloride (Aldrich) were reagent grade and used without further purification. All solvents were also reagent grade. Cyanuric chloride (2,4,6-trichloro-1,3,5-triazine) (American Cyanamid Co., Wayne, NJ) was recrystallized from CCl_4 and kept in tightly capped glass bottles under dry nitrogen inside a desiccator for up to a month. Triton X100 (Rohm & Haas, Philadelphia, PA) was used as such. The lignocellulosic pulps

were an air dry bleached unbeaten kraft Douglas fir (*Pseudotsuga menziesii* (Mirb.) Franco), air dried, containing approximately 0.04 meq COOH/g, made available through the courtesy of the Weyerhaeuser Co. Tacoma, WA, and a never dried unbleached kraft Loblolly pine (*Pinus taeda* L.) (prepared in the laboratory, courtesy of Dr. Qiusheng Pu, College of Forest Resources, University of Washington). All other materials, chemicals and solvents were standard stock items.

Methods

A. Synthesis of reactive alpha-amino acids

Synthesis of (VI) N^ε-(4,6-dichloro-1,3,5-triazin-2-yl)-L-lysine copper complex: a thin stream of cyanuric chloride (6.64 g, 36 mmol) solution in 1,4-dioxane (30 mL) was slowly added with vigorous magnetic agitation to a slushy ice-water (120 mL)-acetone (40 mL) mixture in an appropriate vessel, immersed in a NaCl-ice bath, keeping the temperature at -5 °C at all times. Then a chilled (0 °C) solution (100 mL) of (L-lysine)₂Cu(II) complex (12 meq) was slowly added, and the mixture stirred at between -5 and 0 °C while aqueous NaOH 1.0 N (72 mL, 72 mmol) was added at such a rate that the pH stayed between 6.5 and 7.0 (about 2 h). At the end of this addition, the pH remained stable (between 6 and 7) and the solution was divided in portions as needed and was ready for further immediate reactions or frozen right away in solid CO₂. The compound was not isolated at this stage, but the whole reaction mixture used for the reaction with pulp.

The preparation of the above and following zwitterionic compounds is described somewhere else (15): (I) O-(4,6-dichloro-1,3,5-triazin-2-yl)-L-tyrosine, (XVI) 2-chloro-4,6-bis((5-amino-5-carboxypentyl)amino)-1,3,5-triazine and (V) N^ε-(4,6-dichloro-1,3,5-triazin-2-yl)-L-lysine.

B. Reaction of cellulosic fibres with triazinyl reactive zwitterions

Pulp (10 g oven dry basis or ~ 62 mmol based on anhydroglucose) were suspended in ~ 400 mL of distilled water at 20 °C, and wholly disintegrated by mechanical stirring. Then the dichloro-*s*-triazinyl-L-lysine reaction preparation was admixed and the necessary amount of distilled water added to complete 500 mL total of aqueous phase. The suspension was stirred (15 min) and then over the next 15 minutes solid NaCl (15 g) divided into two portions were added. Then an aqueous saturated solution of Na₂CO₃ (equivalent to 5 g or the amount necessary to reach a pH of 10.5) was added over 10 min. The mixture was then stirred for different lengths of time, adding sat. Na₂CO₃ (aq.) as needed to keep the pH at 12. After the desired time had elapsed, the suspension was filtered on the foraminous plate of a Büchner funnel and washed extensively in running tap water. Then if the pulp had been reacted with a dichloro-*s*-triazinyl-L-lysine copper complex, the blue pulp was suspended in 400 mL of distilled water containing Na₂EDTA.2H₂O (2 g, 5.4 mmol) and stirred for 10 min. Then the now white pulp was filtered again and washed extensively with running tap water. After this the pulp was resuspended in 400 mL of an aqueous solution of Na₂EDTA.2H₂O (1 g) and Triton X100 (0.1%), and boiled for 5 minutes. The pulp was then filtered, washed and treated with a N 0.05 AcOH solution (400 mL), washed again in running water, then with distilled water and finally air dried.

C. Treatment of pulp and preparation of handsheets for testing of mechanical properties

1). *Pulp treatments*: Three zwitterionic pulps were prepared with amino acid target contents of ~ 0.01, ~ 0.04 and ~ 0.10 mM/g as has been described in part B, using 40 g (oven dry basis, ODB) of pulp and 0.1 mM/g, 0.4 mM/g and 1.3 mM/g (based on L-lysine) of the dichloro-*s*-triazinyl-L-lysine copper complex preparation. A fourth sample of pulp (40 g ODB) was treated similarly, but without the dichloro-*s*-triazinyl-L-lysine copper complex reaction mixture, and was used as the control material.

2). *Handsheet preparation and testing*: Handsheets were prepared in a British sheetmold in accordance with the procedures specified by Tappi standard T-205 om-81. The caliper measurement, grammage and the tear, burst and tensile tests were performed as specified by Tappi standard T-220 om-83 and related methods. The wet strength was determined according to Tappi standard T-456 with 1 h immersion time in distilled H₂O.

3). *Hot pressing*. Some of the Tappi conditioned handsheets were sprayed with distilled water until saturated, placed in between two Tappi standard 15.9 cm in diameter stainless steel press plates and pressed at 4.5 Kg/cm² at 110 °C (plate temperature) during 5 min in a 30 ton hydraulic bench press (model 0-2300, Pasadena Hydraulics Inc., La Brea CA), and then conditioned in Tappi drying rings under standard Tappi conditions (50% relative humidity, 23°C).

4). *Integrity experiments*: Square (2 x 2 cm) samples were cut from both the control handsheets and the 0.1 mmol/g α -amino acid handsheets and then immersed at room temperature, in 60 mL of different aqueous solutions (distilled H₂O; Na₂CO₃, pH 10; Na₂CO₃-NaOH, pH 12; phosphate pH 4 buffer; saturated NaOAc/AcOH pH 5 buffer; 0.1 M CuSO₄), contained in 100 mL beakers together with a 2 cm magnetic fluorocarbon coated stirring bar. Subsequently the specimens were rapidly stirred for 12 h, and then left in the solutions without stirring for 60 days. The observed results with respect to the integrity of the specimens and the apparent continuance of their mechanical strength were recorded.

D. Spectroscopy.

UV-visible spectrophotometry was performed on a Perkin-Elmer (Norwalk, CT) Lambda Array 3840 UV/VIS spectrophotometer.

E. ESCA surface analyses

They were performed using a Surface Science Instruments (SSI) X-Probe ESCA instrument. This instrument permits analysis of the outermost 50-100 Å of a sample in an elliptical area whose short axis can be adjusted from 150 μm to 1000 μm. An aluminum $K\alpha_{1,2}$ monochromatized X-ray source was used to stimulate photoemission. The energy of the emitted electrons was measured with a hemispherical energy analyzer at pass energies ranging from 25 eV (resolution 1) to 150 eV (resolution 4). Lower pass energies provide higher spectral resolution. Higher pass energies permit more rapid data acquisition and more accurate quantitative analysis. SSI data analysis software was used to calculate the elemental compositions from the peak areas and to peak fit the high resolution spectra. An electron flood gun set at 5 eV was used to minimize surface charging of the samples. The binding energy (BE) scale was referenced by setting the CH_x peak maximum in the C 1s spectrum to 285.0 eV. Typical pressures in the analysis chamber during spectral acquisition were 10^{-9} torr. This equipment was made available thanks to NESAC/BIO and the Division of Research Resources (N.I.H. Grant RR01296).

F. SEM microscopy

Scanning electron microscopy was performed with a JSM-5200 scanning microscope (JEOL Ltd, Tokyo JPN) at magnifications of 200x to 500x.

G. Nitrogen analyses

A modified Kjeldahl procedure was used (16, 17).

H. Amino acid determination in zwitterionic pulps by the ninhydrin method

Pulp (either 0.025 or 0.050 g) is suspended and disintegrated in a 20 mL test tube containing 2 mL of distilled water and 1 mL of an aqueous 0.1%(w/v) solution of Triton X100. Then 1 mL of the ninhydrin reagent (Appendix A) is added, and the test tube capped. The mixture is shaken five times and then placed in a boiling water bath for 18 min then immediately cooled to room temperature, and diluted to 10 mL with ethanol-water 7:3 (v/v). The results were either qualitatively evaluated by noting the intensity or the lack of color produced or by the light absorption of the resulting filtered solution read in a spectrophotometer at 570 nm. A strong purple-blue color develops if an α -amino acid moiety is present in amounts greater than about 0.001 mmol/g pulp.

I. Conductometric titrations (20, 21)

Approximately 4 g ODB of pulp was dispersed in 546 mL of 0.001 M NaCl prepared in freshly boiled deionized water. Then 4 mL of 0.1 N HCl were added. The titration was carried out with 0.1 N NaOH dispensed from a microburette while the suspension was stirred under a nitrogen atmosphere. The alkali was added at a rate of 0.5 mL every 5 min so as to allow sufficient time for equilibrium to be reached between readings. The instrument used was a YSI model 35 conductance meter employing a dip-type glass cell YSI model 3401 with a constant of 1.0 cm^{-1} (Yellow Springs Instrument Co., Yellow Springs, OH). Tappi method T 237 om-83 for the carboxyl content of pulp was used as a standard to compare with conductometric analysis for weak acids in pulp.

RESULTS AND DISCUSSION

Preparation of zwitterionic compounds

The preparation of reactive α -amino acids was based on the chemistry of cyanuric chloride, which is also the basis of the *s*-triazinyl reactive dyes. The acylation of the trifunctional amino acids tyrosine, cysteine and lysine presents the specific problem that two different groups on the molecule can react, the α -amino and the ω -functional group. In the particular case of the present work, the group that was of interest to react was not the α -amino group, but the ω -functional group ($-\text{SH}$ for cysteine, $\text{Ar}-\text{OH}$ for tyrosine and $-\text{NH}_2$ for lysine) (Figure 2), which would be attached to the *s*-triazine ring of cyanuric chloride. In order to achieve the regioselectivity of the reaction to the ω -group, the usual way is to block or protect the α -amino group by various means (20), all but one of which involve chemistry done in organic solvents, which for the purposes of this work are totally impractical since a system that works in an aqueous medium is what is desired. Thus, the protective group that seems to be the best fitted for aqueous media is the copper (II) complex as has been described (21). The removal of the copper has been achieved by the formation of insoluble cupric sulfide, through the action of hydrogen sulfide or thioacetamide, by acidification with strong acids such as HCl, by the use of ion exchange resins or by the use of strong sequestering agents, such as ethylenediaminetetraacetic acid (EDTA) (22).

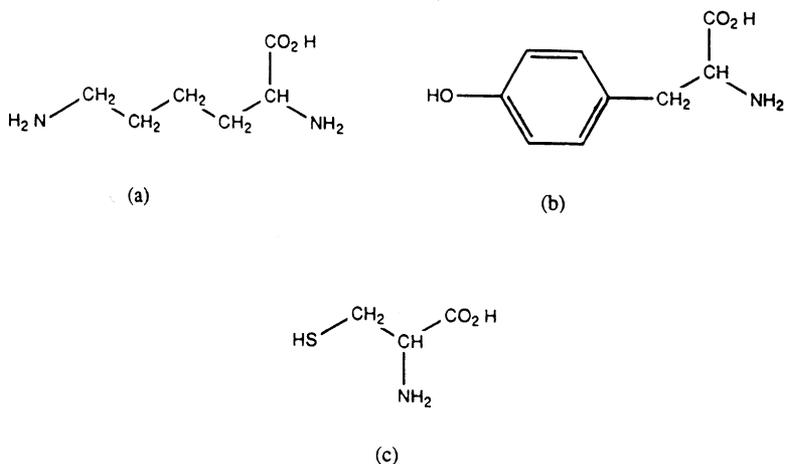


Figure 2. The structure of lysine (a), tyrosine (b) and cysteine(c).

It has been shown that lysine complexed with copper (to protect the α -amino group) reacts with cyanuric chloride to form an amino-chloro-*s*-triazine compound (15). The inspection of the mass, NMR and IR spectra confirmed that the reaction proceeded through the ϵ -amino group of lysine and that two chlorine atoms remained on the triazine ring. It was also found that tyrosine and cysteine complex with copper but their products were unstable and produced poor yields of the desired amino-dichloro-*s*-triazine compound after reaction with cyanuric chloride (15).

Fixation of some dichloro-N^ε-(L-lysiny)-s-triazine preparations on lignocellulosic fibres.

Once it became possible to synthesize reactive amino acid-s-triazines with the desired chemical structure, the next step was to react these compounds (without isolating them from the reaction mixture) with lignocellulosic pulps under a series of varying conditions. Reactants ratio, temperature, and pH, were varied in order to realize an understanding of the receptivity of the cellulosic fibre to the dichloro-s-triazine.

Dichloro-s-triazinyl compounds react with cellulose through the formation of covalent bonds with the hydroxyl groups, since it is essentially a polyalcohol. However the reaction with water should be reduced sufficiently to avoid too low levels of substitution. In addition the dichloro-s-triazine—fibre reaction should proceed with relative irreversibility, because in the overall equilibrium the end-product should be strongly favored. The covalent bond between the hydroxyl group and the reactive component must be sufficiently stable to resist subsequent aftertreatments (23).

In the reaction of a dichloro-s-triazinyl compound with unbleached kraft fibres, two distinct types of groups within the fibre structure can participate; the phenolic hydroxyl groups of the lignin macromolecule and the various alcoholic hydroxyl functions of the cellulose and hemicellulose polymers, Allan *et al.* (24). The lignin reaction proceeds by means of the phenolate anion, the structural environment of which may have a significant effect on the extent of reaction. The mechanism of the reaction can be considered as an SN₂ type.

The plot of the amount of amino acid fixated to the pulp (receptivity) obtained by increasing the amount of reactive L-lysine/g of pulp (Figure 3) shows that first receptivity increases rather rapidly with incremental additions of reactive dye and then levels off. No definite maximum is reached. The quasi-maximum observed probably represents near saturation reaction at the most reactive and accessible cellulose hydroxyl groups, which most likely are those at the exterior surface.

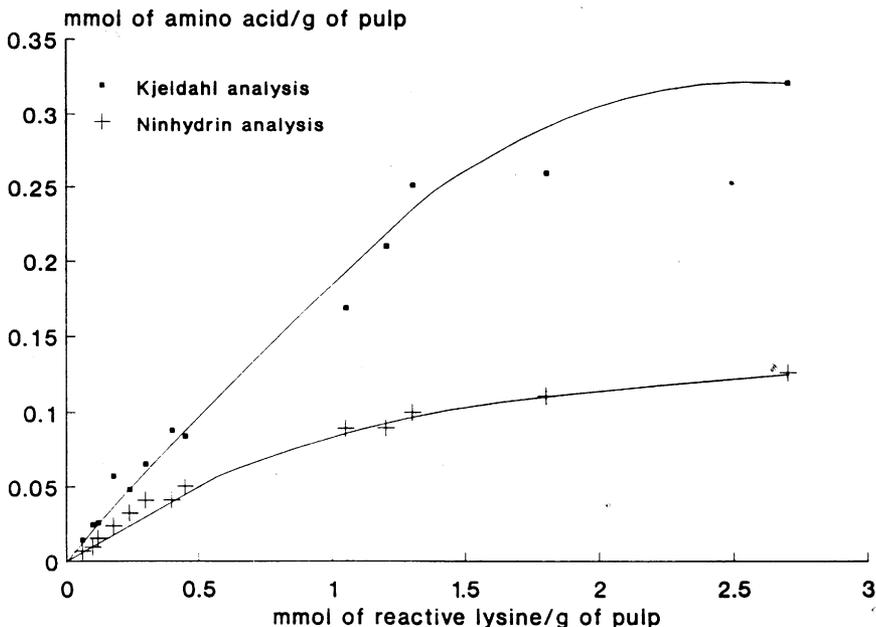


Figure 3. Amino acid content of zwitterionic pulps as a function of the amount of reactive lysine used.

The untreated and treated pulps were characterized by conductometric titrations in order to investigate the expected increase in carboxyl groups brought about by the attachment of the amino acid molecules to the pulp. This technique has proven to be of high value in the determination of weak acidic groups in cellulosic pulps (18, 19). The

weak acidic content of the bleached kraft pulp was calculated to be ~ 0.04 meq/g by both conductometric titration and acid-base titration (Tappi method 237 om-83). Examples of the titration results for untreated and treated pulps are shown in Table 2 and in Figure 4.

Table 2. Content of amino acid in zwitterionic pulps determined by conductimetry, nitrogen analysis and ninhydrin analysis.

Pulp	Treatment	Conductometric titration, meq CO ₂ H/g	Nitrogen analysis, mmol amino acid/g	Ninhydrin analysis, mmol amino acid/g
Untreated	none	0.04	blank	blank
Zwitterionic	lysine	0.01 ¹	0.004	0.001
Zwitterionic	lysine-Cu (II)	0.16 ¹	0.321	0.127

¹after subtracting blank (0.04).

The results together with the content of amino acid moieties determined by the ninhydrin method, permit us to confirm that at least for the most part, the L-lysine fraction is in fact attached to the *s*-triazine ring by means of its ϵ -amino group, leaving thus free the α -amino group to form the desired zwitterionic moiety.

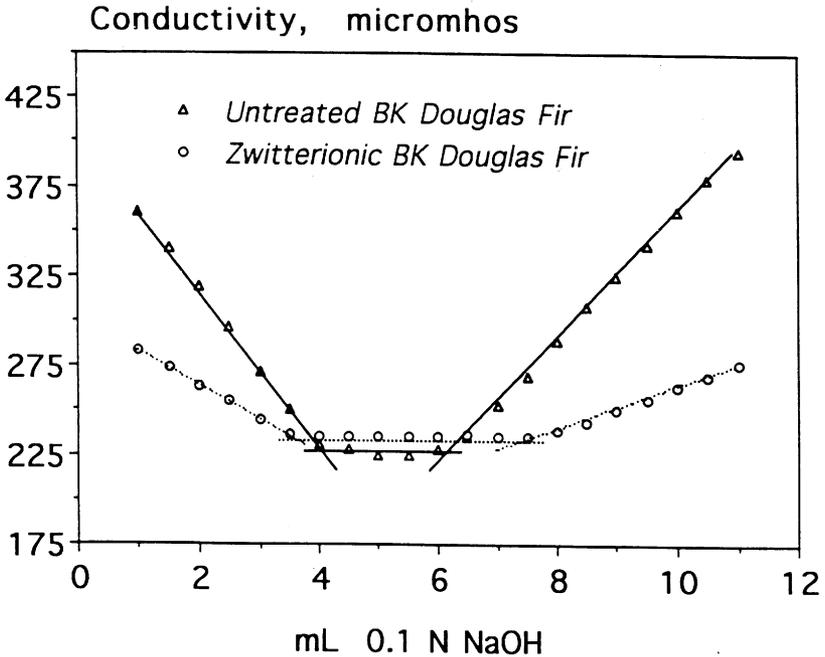


Figure 4. Conductometric titration curves of untreated and zwitterionic pulps.

The untreated bleached kraft pulp and a lysine-zwitterionic pulp were examined by ESCA surface analysis (spectra in Figure 5) and the results are summarized in Table 3. The results show that at or near the outer surface (up to a depth of $\sim 100 \text{ \AA}$) of the pulp fibres the nitrogen content corresponds to about one *s*-triazine-L-lysine group in between 5 and 15 anhydroglucose units, depending on whether the nitrogen analysis results or the ninhydrin results were used as basis for the calculation. The carbon atom count is high both for the untreated and the treated pulp (O/C ratios of 0.47 and 0.54) (the theoretical O/C ratio for pure cellulose is 0.83), which can be explained by the existence of surface hydrocarbon contamination, which is a common phenomenon or perhaps by residual lignin in the fibre. The reported values for bleached

kraft pulps vary widely, for example Dorris (24, 25) reports O/C ratios of 0.72, 1.14 and 0.62. The slightly higher value for the chlorine in the treated pulp means that not all of the residual chlorine atoms were hydrolyzed. The chlorine content for the untreated pulp can be explained by the occurrence of some chlorination during the bleaching stages of the pulp.

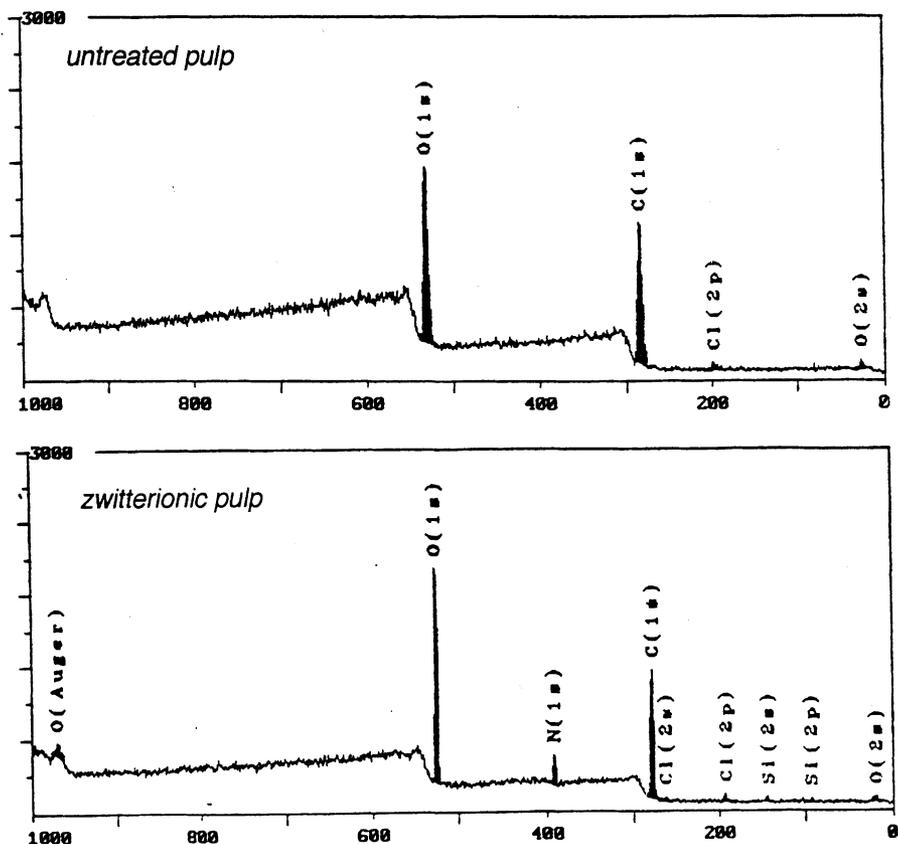


Figure 5. ESCA spectra of untreated and zwitterionic pulps.

Table 3. Results of ESCA analysis of untreated and zwitterionic pulps

Pulp	Element	O(1s)	N(1s)	C(1s)	Cl(2p)	Si(2s)
Untreated		31.70%	none	66.97%	1.33%	none
Treated		31.24	6.56%	58.54	1.58	1.91%
Cellulose composition		45.45	—	54.55	—	—
Calculated ¹		38.89 or 37.50	6.94	54.17	0.00 or 1.39	none

¹ for a 1:5 *s*-triazine-lysine:anhydroglucose ratio, the two values for O(1s) and Cl(2p) are for either no chlorine or one chlorine atom remaining in the *s*-triazine ring

Finally, the overall efficiencies for the reaction are of only between 10 and 20% of the added dichloro-*s*-triazinyl-L-lysine copper complex. Of course it can be argued that because such a complex contains two molecules of the reactive L-lysine, automatically half of the reactant is probably wasted, so the efficiency could be thought of being from 20 to 40% which is still rather low. As a conclusion, it can be remarked that the target amount of amino acid substitution of 0.1 mM/g in the fibres, was effectively achieved. Also it can be argued that the conductometric analysis together with the ninhydrin analysis proves the existence of α -amino acid groups in the fibres and hence zwitterions (at the appropriate pH range). The ESCA results prove that the modification has occurred mainly at the surface of the fibre, since the concentration at the outer surface is ~ 10 times that of the bulk according to calculations based on the O/N ratios obtained from the ESCA (in the surface, the O/N ratio is 4.8) data and ninhydrin analysis (in the bulk, the O/N ratio is 48).

STEREOTOPOCHEMISTRY OF THE ZWITTERIONIC FIBERS

In the previous section, it has been described that it was possible to derivatize lignocellulosic pulp with a dichloro-*s*-triazinyl-L-lysine copper complex preparation. The bulk maximum degree of substitution achieved was ~ 0.12-0.13 mmol of α -amino acid/g of pulp, according to the ninhydrin and conductometric methods of analysis. These numbers fit very well with those published by other authors for similar reactions of other dichloro-*s*-triazines with cellulosic fibres (14). Also with the ESCA technique for probing chemical composition of surfaces, it may be concluded that a good part of the chemical modification, in proportion of between 6:1 to 10:1, depending on the calculation method, occurred at the surface of the fibres. It has also been published elsewhere that these reactions indeed do occur preferentially at the fibre surface. In one example, the reaction of 2-diallylamino-4,6-dichloro-*s*-triazine with paper sheets made out of bleached kraft softwood pulp, surface to bulk ratios of 32:1 were found using ESCA surface analysis (26).

The amount of α -amino acid attached to cellulose by covalent bonding at the substitution level of 0.10 mmol/g observed, corresponds to approximately 10^{20} amino-acid-triazinyl molecules per gram of fibre. Thus it was calculated that one α -amino acid molecule had been introduced for about each sixty anhydroglucose units, if all the glucose units are assumed to be equally accessible. Furthermore, the ESCA results demonstrated that on the surface of the fibre, the frequency of amino acid presence is in the neighborhood of 1 in 10 anhydroglucose units for the pulp containing 0.1 mmol/g of amino acid. All this means that in this case, the number of zwitterions available on the fibre's surface and stereotopochemically capable of interfibre interaction should suffice to produce a measurable and significant effect.

Of course, one might think that there is not likely to be a one-to-one, stoichiometric, topochemical coincidence of zwitterionic moieties of the two surfaces belonging to the fibres being bonded. But surely the length of the 'leash' from the ether oxygen linking the cellulose to the *s*-triazine

ring, up to the carbon atom supporting the zwitterionic group of the lysine residue and its flexibility and freedom to rotate around single bonds, should allow for an improved likelihood of encountering similar groups on the opposing surface.

Putting that in semiquantitative terms, if there is one zwitterionic group every ten anhydroglucose units, in terms of area, the distance between the point of attachment to cellulose of the two zwitterionic sidechains is hence on average about 16.3 \AA , taking as the size of an anhydroglucose unit as a $5.15 \times 5.15 \text{ \AA}$ square. On the other hand the maximum length of the 'leash' is estimated to be about 11 \AA from the ether oxygen to the α -carbon (Figure 6), using Cochrane's molecular models. Thus when two surfaces containing such groups are juxtaposed, the average distance between the points of attachment of the sidechains will be $16.3/\sqrt{2} \text{ \AA}$ because the number of zwitterionic groups per unit of juxtaposed area will be effectively doubled, hence the distance would be now about 11.5 \AA .

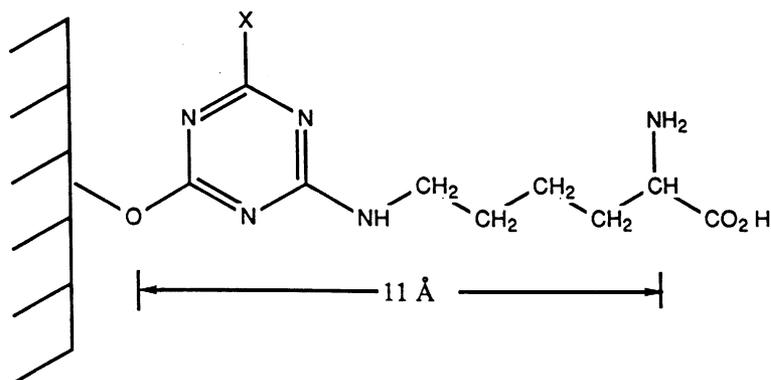


Figure 6. Dimensions of the zwitterionic sidechain.

This means that the 11 Å length of the leash is close to twice as much as would be needed to allow it to breach the gap between zwitterionic groups on the opposing surfaces. However, this also brings to light the likely problem of having two such vicinal groups on the same surface interacting with each other. Nevertheless, one might think that in view of the reversibility of ionic bonds in aqueous media, these intrasurface bonds could be disassembled and perhaps be available again to form intersurface zwitterionic bonds (Figure 7).

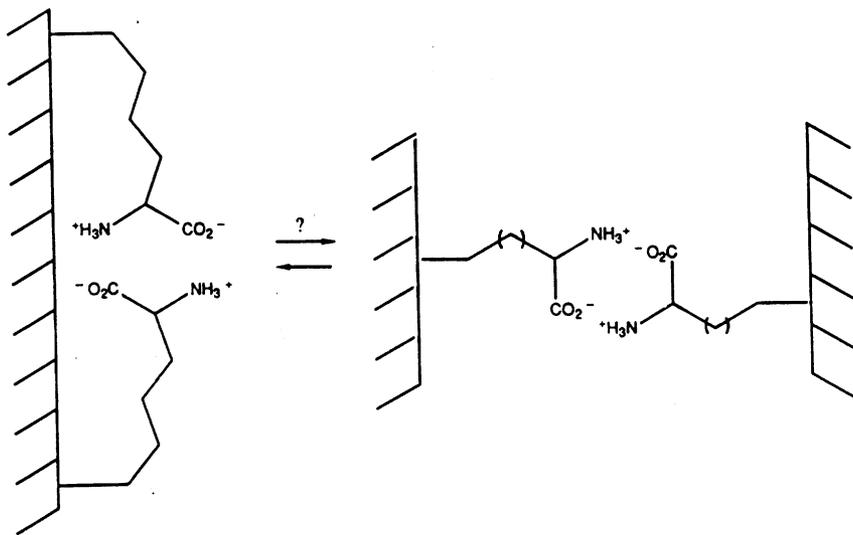


Figure 7. Possible interactions between zwitterionic sidechains and their interconversion.

There is of course, the question of which bond would be the thermodynamically preferred one, the intersurface or the intrasurface one, and the answer is not clear, since both bonds are essentially the same. On the other hand, the probability of interaction between zwitterionic groups on different surfaces is larger, since they do not have fixed, unchangeable distances between them.

These considerations should suffice to convince us without the need of formal calculations, that there is a better chance for interfacial zwitterionic bonding than for the intrafacial phenomenon when the level of surface substitution is such that the latter might occur. When the distances between the sites of attachment of the zwitterions are such that the intrafacial ionic linkages are no longer possible (*i.e.* longer than about 25 Å), then the situation is reduced to only the interfacial interaction. A high content of zwitterionic groups on the fibre surface would lead to a situation in which the intrafacial interaction might occur, with a consequent reduction of the interfibre hydrogen bonding because of stereotopochemical hindrance, making the interaction of hydroxyl groups of cellulose on the two opposing surfaces difficult. As the abundance of zwitterionic substituents is diminished, the possibility for hydrogen bonding should likely increase, therefore producing a mixed type of interfibre bonding, *i.e.* both zwitterionic and H-bonding.

MECHANICAL PROPERTIES OF ZWITTERIONIC HANDSHEETS

Thus the last part of this work focused at preparing paper sheets with the α -amino acid (and consequentially zwitterionic) modified pulp followed by the measurement of their mechanical strength against similar sheets prepared from the non-zwitterionic control pulp. The results of the strength tests are summarized in Table 4. The results for the air-dried standard Tappi handsheets show clearly that tensile strength first drop rapidly, in comparison with the non-zwitterionic pulp (the first point of the curve at 0.00 mmol amino acid/g pulp), as is depicted in the corresponding plot (Figure 8 for the Tappi handsheets). At higher levels

of substitution, *i.e.* 0.04 and 0.10 mM amino acid/g of pulp, the negative effects have bottomed out, and there is even a hint, at the larger α -amino acid content level, of a possible improvement of the tensile strength, although statistically it is arguably not significant. Bursting strength and tearing resistance behaved following a similar pattern. This is congruent with the fact that the apparent density of the sheets also diminishes first markedly and then plateaus, as may be observed in the plot of α -amino acid content vs. apparent density (Figure 9).

Table 4. Mechanical properties of zwitterionic and non-zwitterionic pulps.

Pulp		Zwitter- ionic 0.01 mM/g	Zwitter- ionic 0.04 mM/g	Zwitter- ionic 0.10 mM/g	Reference (control)
Property					
Grammage g/m ²		62	63	64	62
Apparent density g/cm ³	Tappi	0.39	0.32	0.31	0.48
	HP	0.67	0.65	0.66	0.65
Burst index KPa·m ² /g	Tappi	2.39	1.94	1.96	2.79
	HP	2.47	2.18	2.00	2.66
Tear index mN·m ² /g	Tappi	14.6	9.34	8.10	21.36
	HP	15.86	13.13	12.35	18.36
Breaking length meters (% Strength retention)	Tappi	1.322	984	1.011	2.382
	wet Tappi	280(21%)	~200(~20%)	362(36%)	very low
	HP	1.986	1.552	1.922	2.343
	wet HP	292(15%)	304(20%)	586(30%)	very low

Thus, it was observed that there was a direct relationship between the apparent density of the handsheets and their strength properties, and it should be noted that this relationship is both recognized and documented in the literature (27), and is widely known in the paper trade.

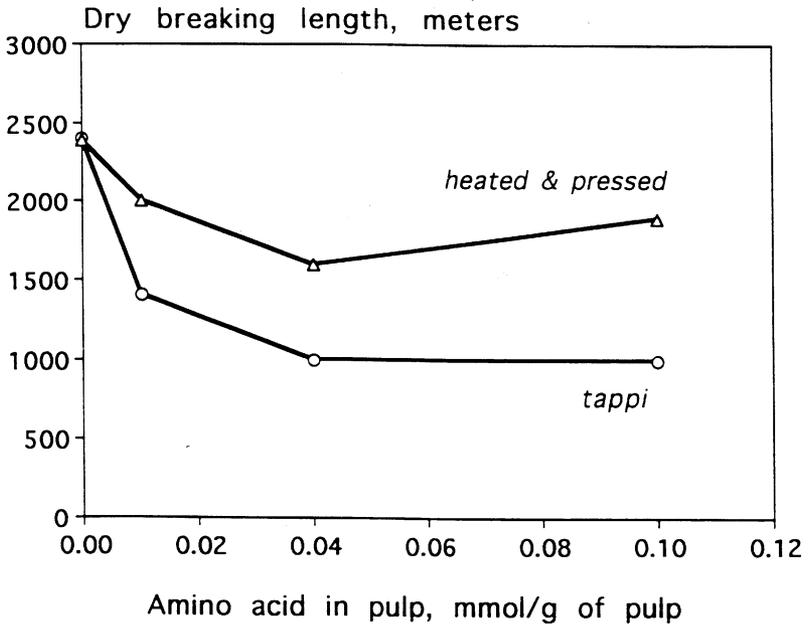


Figure 8. Dry breaking length of conventional Tappi and heated and pressed handsheets (HP) as a function of their amino acid content.

In trying to remove the effect of apparent density and consequently also improve the amount of relative bonded area between fibres, a set of Tappi handsheets of the pulps in question were completely wetted with distilled water. This treatment helped plasticize the fibres, improving their conformability and provided the opportunity for the zwitterionic groups to rearrange. This was then followed by pressing the sheets at 4.5 Kg/cm² and 110 °C (plate temperature) for 5 min, with the idea to even out the apparent density.

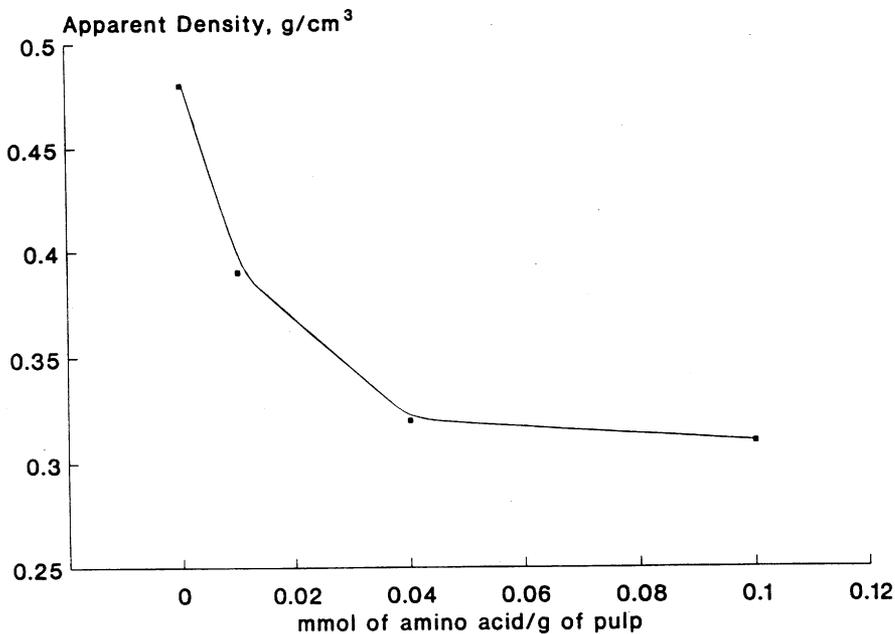


Figure 9. Apparent density of Tappi standard handsheets as a function of their amino acid content.

The results in Table 4 show that the aim of equalizing the apparent density at 0.65 g/cm³ was achieved. According to published data, such density usually provides a more or less well bonded sheet (of course, some other factors, like beating, will affect the bonding).

The data for the hot-pressed sheets (HP) also show that although the tensile strength (Figure 8) improve significantly for the treated pulps they remained essentially the same for the control pulp. The data and plots demonstrate that even with the same apparent density, the treated sheets had significantly lower mechanical properties.

But, when the tensile strength tests were performed on wet sample strips, the results were reversed as can be seen in Table 4 and the plot amino acid content vs. wet tensile strength (as breaking length) (Figure 10). The wet control handsheet had such a low tensile strength that it could not be measured with the available equipment. On the other hand the wet strength increased significantly with zwitterionic level, up to about 30-35% of the corresponding dry strength of both the Tappi and hot-pressed sheets.

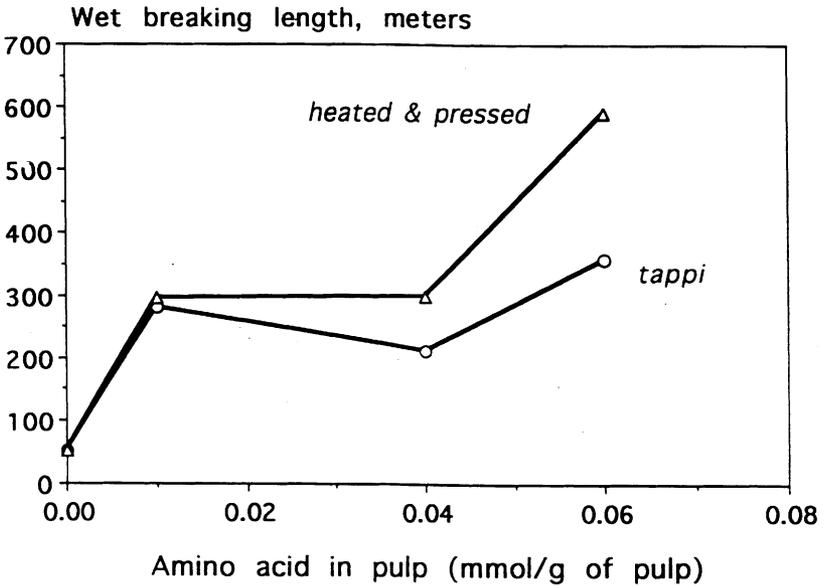


Figure 10 Breaking length of wet conventional Tappi and heated and pressed handsheets (HP).

In another set of experiments, squares of 2 cm per side were cut from both the Tappi and hot-pressed sheets containing 0.1 mmol/g of zwitterions and the control sheet also both Tappi and hot-pressed and placed in different solutions and stirred rapidly with a magnetic bar for 12 h. The specimens from the control sheets broke into pieces within 10 min and later into individual fibres in 30 min time. The zwitterionic handsheet samples did not breakup and kept their integrity for 12 h of stirring, and when inspected after 60 days of immersion in the different solutions, they still preserved their integrity. This is summarized in Table 5.

Table 5. Qualitative assessment of bonding strength of zwitterionic and control paper samples in contact with diverse solutions.

Test solution	Control handsheet		Zwitterionic handsheets 0.1 mM/g	
	Tappi	HP	Tappi	HP
pH 4 (phosphate)	(-)	(-)	(+)	(+)
pH 10 (Na ₂ CO ₃)	(-)	(-)	(+)	(+)
pH 12 (Na ₂ CO ₃ -NaOH)	(-)	(-)	(+)	(+)
pH 5 (saturated NaOAc-AcOH)	(-)	(-)	(+)	(+)
0.1 M CuSO ₄	(-)	(-)	(+)	(+)

(-) means that the paper disintegrated within 30 min of stirring

(+) means that the paper kept its integrity after 30 min of stirring

When handling the wet strips, the zwitterionic handsheets had a 'plastic' feeling and did not bend completely under their own weight as the control strips did. Furthermore, the results showed that the zwitterionic pulp sheets did not disintegrate. In comparison, the control sheets disintegrated within minutes. This attests to the existence of a type of bonding that is stronger than H-bonding and that withstands the aggression of M 1.0 acetic acid, pH 4, pH 10, pH 12, M 0.1 CuSO₄

solutions and saturated sodium acetate-acetic acid pH 5 buffer solution. All this means that most likely, in view of the double nature of the presumed zwitterionic bond and the ~ 30 kcal/mole associated with it, that once formed, it would take an aggressive chemical or physical treatment to disengage them and obviously none of the immersion solutions sufficed under the conditions described.

Two additional observations were made, the first was noticed particularly when the Tappi zwitterionic handsheets (*i.e.* not hot-pressed) were torn, whereby free fibres were scattered in the air, and second, the fluffy appearance of the handsheets. This led to question of whether or not the poor bonding in the dry sheets and lower apparent density had its origins in some morphological changes in the individual fibres themselves. SEM photomicrographs were taken at two different magnifications (200x and 500x) of both the Tappi control and 0.1 mM/g zwitterionic sheets in an attempt to see how the fibres looked in respect to the degree of collapse, kink, curl or some other visible characteristic.

When comparing the SEM images at 500x it was observed that more tubular fibres seemed more collapsed in the control than in the zwitterionic pulp, where the latter look rounder and smoother, particularly toward the edges. This observation supports the idea that one important reason for the zwitterionic sheets to be generally weaker in the dry state is the relative lack of interfibre contact. In other words, because of the uncollapsed state of the fibres and the lack of fibrils, the opportunity for the needed close contact of large surfaces to produce effective bonding is diminished, be it ionic or H-bonding. Hence the bonded area of paper is decreased, which in turn is reflected in the lower apparent density of the sheets.

This is in part proven by the fact that when the treated fibres were forced together by hot pressing, the apparent density increased together with the tensile strength, the latter becoming close (~ 80%) to the value of the control handsheets. This was probably due to the increase in the bonded area. The fact that heating and pressing improved the tensile

strength of the zwitterionic handsheets but did not produce tensile strengths higher than the control handsheet, seems to suggest that, in essence, a well "zwitterionically" bonded sheet would not present a significantly different strength from a well hydrogen-bonded sheet in the dry state.

However, the most important observation was that of wet tensile strength, in which clearly, when the interfibre hydrogen bonding has been greatly obliterated by the action of water, the effect of the ionic bonding comes out strikingly and almost undoubtedly, since the differences between treated and untreated pulp in respect to tensile strength are completely the opposite of the dry strength. Moreover, they cannot be attributed in the case of the hot-pressed sheets to some kind of covalent bonding facilitated by the process, since a similar wet strength tendency is seen with the Tappi, non-hot-pressed sheets. It may be proposed that a better and easier contact between the fibre surfaces can be achieved by means of beating the pulp to enhance fibrillation, pliability and other well established consequences, which are known to improve the amount of bonding in addition to, and perhaps also hot-press treatment.

CONCLUSIONS

It was possible to prepare a reactive *s*-triazinyl lysine compound useful in the surface modification of lignocellulosic fibres. It was verified that this modification occurs mainly on the surface of the fibres by ESCA analysis, and was found to reach levels which seem to be at least if not more than adequate. Moreover, it was found that the modified pulp in fact contained α -amino acid moieties by ninhydrin nondestructive analysis and conductometric titrations. Thus, under the right pH conditions (around neutrality), which are easy to achieve, fibres with zwitterionic surfaces were available.

When handsheets were prepared with these zwitterionic fibres, a difference in bonding of the sheets was observed, which was particularly evident when wet. The zwitterionic content had a clear positive effect upon the tensile strength of the wet paper strips. The negative effects upon the dry strength of the handsheets prepared from zwitterionic pulp are attributed to a reduced relative bonded area and not to the actual poor quality of the bonding. It is suggested that this might be overcome, particularly by beating the pulp, in order to increase the ability to develop pliable, fibrillated fibres easier to collapse when pressed and dried and with improved RBA when formed into sheets. This was partially demonstrated by hot-pressing otherwise normal Tappi sheets.

Finally, it may be concluded that the merits of ionic interfibre bonding through directly attaching zwitterions on fibre surfaces to provide stoichiometric amounts of positive and negative charges and a favorable stereochemical environment, have been at least partially substantiated.

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Transcription of Discussion

A NEW INTERFIBRE SYSTEM FOR PAPER INVOLVING ZWITTERIONS

E Delgado, F Lopez-Dellamary & G G Allan

Dr D Priest, UMIST, UK

I was wondering about the effect of pH on the state of the zwitterions. When you did your pressing experiment, if you altered the pH of the water that you used to soak the handsheet, before you pressed it, would you find any differences in the result?

E Delgado

Yes, when you have a zwitterionic fibre you see that they reach a pH where you have a pre-selected point, ie the point in which you can have a right number of positive and negative charges. In the case of the zwitterionic fibres our studies have shown that the pH ranges are fairly wide, from 5-8.

Dr K Ebeling, Kymmene Corp, Finland

You have studied both bleached and unbleached pulp., Could you please comment as to the importance of the residual lignin in the cell wall. Was the effect more pronounced with the unbleached pulp?

E Delgado

Yes. Normally the coupling agent we are using reacts easily with cellulose fibres and it reacts with lignin as well. Actually we expected to see a larger number of zwitterionic units when we have more lignin in the fibres but as I recall our results didn't show that very clearly. We do not have an explanation for this as yet. We expect that this system works well with lignocellulosic fibres as there are more possibilities for reaction, ie all the hydroxyl groups of cellulose, phenolic groups of lignin which we can react cyanuric chloride to get an effect. You can also see from the results that we accounted for 0.1 mmole of these zwitterions per gramme of fibre and that was enough to show the wet strength.

K Ebeling

What are the commercial possibilities of utilising this technology?

E Delgado

I think the concept of zwitterionic bonding is a very interesting one. We used this procedure just to demonstrate the concept, to see if the theoretical basis would have a correlation or expression in the practice. I am sure that there must be simpler, more efficient ways which are more compatible with papermaking conditions, but as you saw in this paper this is a procedure that worked well for the purpose that we wanted, which was to demonstrate the concept.

Dr W Sampson, UMIST, UK

I know you didn't measure formation but as you could pull out fibres from the dry sheet and you obtained this very low apparent density, it would be very interesting to know what effect the zwitterions were having on formation.

E Delgado

It is really difficult to judge from the results that we have because we have not done any formal study on that. On one hand we can think that the hydroxyl groups in the amino acid are hydrophilic and they can drain or pull water to the fibres and in that sense that will make the fibres more flexible but on the other hand, as I mentioned, the interactions of the zwitterions may work in the ideal way and you can have one in one fibre and one in another and just establish the linkage. What also may happen is that two of these arms may be in the same body and they cross link which would make the cell wall a bit stiffer and perhaps that will pose difficulties in the formation of the fibre, how well they will collapse.

Dr L Wagberg, SCA Research, Sweden

A somewhat detailed question about your conductometric titrations in figure 4. Titrating these fibres conductometrically is not easy since you have zwitterions in the fibres. One thing that bothers me is when we have an excess of sodium hydroxide you get different slopes for the different pulps. Do you have any suggestions as to why this is so?

E Delgado

Perhaps no, not now. I did this not only with lysine but with other zwitterions that might have a different isoelectric range. It seems to me that even though you may find different variations and slightly

different pH at which you can get the balance of these charges. Even in the case where you don't have the right isoelectric point these ionic interactions can still express themselves.

Prof J Roberts, UMIST, UK

Do you think there is any possibility that the wet strength arises through cross linking through covalent amide formation between the NH_2 groups and the carboxylic acid groups?

E Delgado

It is a possibility since we applied heat to the handsheets, even though the temperature was not very high about 105° . But if we take that explanation then we cannot explain what happens with the fibres in the handsheets that were neither pressed, nor heated.

Dr W Hewertson, CSIRO, Australia

I was interested that the formation was poorer with the triazine derivatives rather than with the pulp alone. I wonder if what has happened is that you may have got the concentration of the triazine derivative too high. As you say in your paper the reaction takes place mainly on the surface. This type of compound is used by ICI and Ciba Geigy to fix reactive dyes onto cotton and wool. They only use very small concentrations per OH or NH_2 . I wonder if you have got the concentration too high and then you have only one of the options you put up, ie an internal bridging, so you virtually isolated the material or the fibre from forming bonds between fibres.

E Delgado

I think this is a very interesting point of view but when you increase the number of zwitterions on the fibre you are also increasing the chances for them to interact in the same chain; at the same time you

have more available groups on different fibres and there is a chance for them to interact when the fibres come close together. I think it is likely that the ones on different fibres will connect better because they can move freely to reform and interact when the fibres surfaces reconfirm upon wetting rather than the ones in the same chain especially if they are too separated from each other then you can have the first state as you mentioned when there are very few of them. In this case any group here perhaps will have more chances to interact with this one; as you put more and more you are increasing this chance but you are also increasing the chances for the other one and I think this latter could have a better effect just because of the possibility of these two points meeting when the surfaces have a chance to re-accommodate. This is just a speculation.

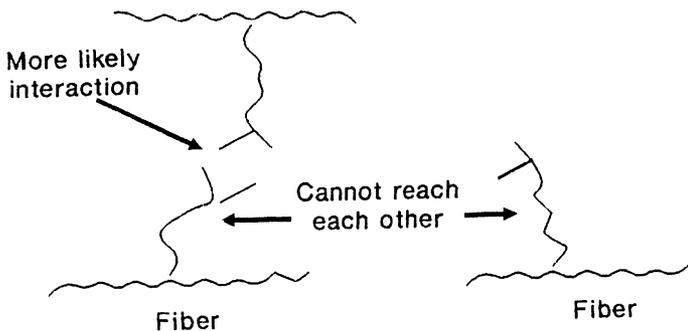


Figure 1

Dr R Shet, Kimberly Clark Corp, USA

One comment regarding the effect of the salt. You showed it did not have any negative effect. This is probably because of the low concentration. Normally in the presence of the salt the shielding

effect between carboxylate and ammonium ions the wet strength should have decreased. You showed that there was a large decrease in density is it because of the interfibre bonding. Any explanation for that?

E Delgado

Again, there is no clear or definitive answer for that, but it seems to me that once you dry the fibres this meeting cannot occur if the number of the molecules is low. When you treat these zwitterionic fibres remember you are rewetting the web already formed so they can come in close contact, so it is a matter of re-arrangement of these groups to a more stable configuration. There is also a point that we tend to forget and this is that when you have these type of hydrophilic groups all over the surface and you have water around, these groups raise up as they look for the water molecules. When you dry them they may stick back into the polymeric matrix. As you remember in the zwitterion molecule we have a triazine ring here and a hydrophobic part there and also a hydrophilic part; so, even though these considerations are very difficult to prove they actually exist. I was talking to the person who did the ESCA analysis about this and she has been trying now to use ESCA on frozen samples and she said she might be able to eliminate the response from the water layer and then use the signal to see the groups that are now raising up and being exposed to that medium. Those questions are still open for us.

