

Anion Control of Wet Strengthening Reactions Catalysed by Thermal Treatment

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INTRODUCTION

Wet strength and related properties, such as wet stiffness and wet rub resistance, are generally imparted by the use of synthetic resins. However, other methods can be used to achieve a similar result, most notably the use of thermal treatment (1-3). Previous research has shown the effect of such treatment is enhanced by the presence of acids (4-7); indeed the presence of such materials reduces the treatment temperature and duration required to achieve acceptable wet paper properties.

Work reported in this article describes model experiments performed to understand the nature of reactions that occur during thermal treatment. Though the work was performed in the area of paper conservation, it compliments that performed by previous researchers on processes that have commercial application in the area of wet property enhancement.

EXPERIMENTAL

Whatman chromatography paper was impregnated with analytical-grade aluminium chloride or nitrate solution, air dried without restraint, then thermally treated in an oven at 105°C. The degree of wet strength was assessed by tensile testing using an Instron 1122 Universal Tester, after the sample had been saturated fully with de-ionised water. Degradation was assessed by use of a Pulmac Zero-Spann.

In some experiments analytical-grade sodium salts were added to the aluminium solutions prior to impregnation of the paper. These provided a source of different anions for the investigation.

RESULTS AND DISCUSSION

Data in Figure 1 show the change in wet tensile index of papers impregnated with aluminium chloride solutions of three different strengths (2.5, 5 and 10mM), and heated for up to 90 minutes. A samples treated with water is

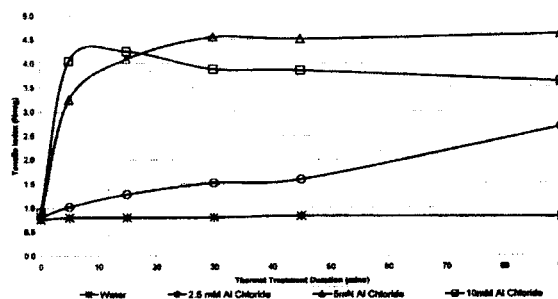


Figure 1. Wet Finite-Span Tensile index Effect of Aluminium Solution Concentration

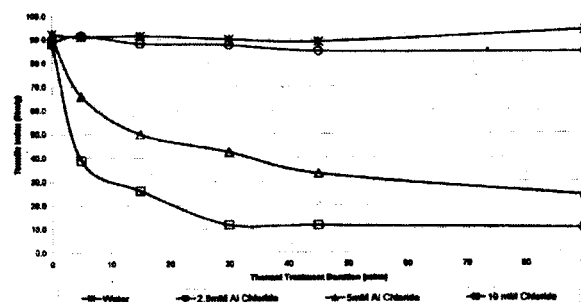


Figure 2. Wet Zero-Span Tensile Index Effect of Aluminium Solution Concentration

included as a control. As anticipated for a reaction that is known to be acid catalysed, the more concentrated aluminium solutions result in a greater degree and faster rate of wet property development. Changes in wet stretch, wet modulus and wet tensile energy absorption increased similarly. However, note that for the most concentrated solution, the high initial wet strength decreased as thermal treatment progressed.

Dry paper properties (not illustrated) showed no change for paper impregnated with the low and middle concentration solutions, and a decrease in tensile strength of roughly 25% after 90 minutes heat treatment for paper impregnated with the 10mM solution. Data in Figure 2

show the corresponding acid-catalysed degradation that accompanies the wet strengthening reaction. The degree of degradation, assessed indirectly by wet zero-span tensile index, quickly becomes highly significant for paper impregnated with the more concentrated aluminium solutions. This is an unwanted side reaction to that of wet property development.

This time dry paper properties (not illustrated) mirrored those for the wet sheets, though the absolute numbers were higher due to the influence of inter-fibre bonding on dry zero-span strength.

Since both reactions occur concurrently, the challenge is to prevent degradation becoming too severe, whilst optimising wet strength formation. Data in Table 1 show one possible route to this outcome. It highlights the effect on the wet strengthening and degradation reactions of adding various sodium salts to the aluminium chloride impregnation solution. (The original aluminium solution was 5mM: sodium salts were added such that the ratio of aluminium cations to added anions was 1:2, except in the

Table 1. Effect of small amounts of added sodium salts on the wet finite-span and zero-span indices of paper, heated at 105°C for up to 10 minutes.

| Thermal Treatment Time (Minutes) | Wet Finite-Span Tensile Index (Nm/g) | | | | Wet Zero-Span Tensile Index (Nm/g) | | | |
|----------------------------------|--------------------------------------|-------------------|---------|----------|------------------------------------|-------------------|---------|----------|
| | (Nothing) | Added Sodium Salt | | | (Nothing) | Added Sodium Salt | | |
| | | Sulphate | Citrate | Chloride | | Sulphate | Citrate | Chloride |
| 0 | 1.0 | 0.9 | 1.0 | 1.1 | 96.3 | 93.7 | 97.8 | 96.9 |
| 5 | 3.9 | 1.4 | 1.1 | 3.9 | 46.5 | 95.4 | 96.2 | 69.4 |
| 10 | 4.1 | 1.7 | 1.2 | 4.1 | 36.0 | 91.7 | 99.6 | 52.0 |

case of citrate, where it was 1:1.3. These ratios were chosen so as keep the impregnation solution pH reasonably constant, at between 3.7-3.9)

We find that the original solution, and that with added sodium chloride, behave almost identically as regards wet strengthening, whereas the solutions with added sodium sulphate or sodium citrate show a reduction in this property. However, the corresponding effect of the added salts on acid-catalysed degradation, again assessed by zero-span tensile index, shows that all papers with added sodium salts experience decreased degradation, though the sample with added sodium chloride was still degraded severely.

Data in figure 3 and 4 show the effect of increasing the ratio of added anions to aluminium cations, on both wet

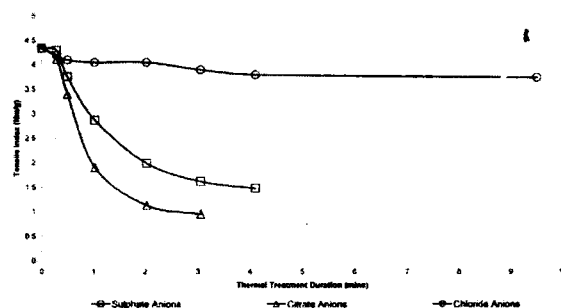


Figure 3. Wet Finite-Span Tensile Index Effect of Added Anions

strength and degradation. Again, sulphate, citrate and chloride sodium salts were used, but the base solution this time was 5mM aluminium nitrate. In this experiment no attempt was made to keep solution pH constant: the original solution pH was 3.9; that of the solutions with added chloride varied between 3.4-3.7; the sulphate solutions stayed reasonably constant at 3.8-3.9; whilst the citrate solutions varied most, measuring between 3.0-5.7.

Increasing levels of the two multivalent anions (sulphate

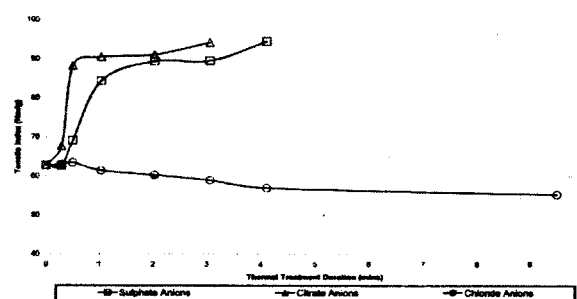


Figure 4. Wet Zero-Span Tensile Index Effect of Added Anions

and citrate) caused a significant decrease in the rate and extent of both reactions, whereas increasing the chloride content caused a small decrease in the wet strengthening behaviour, but a large increase in the degree of

degradation.

DISCUSSION

The acid that catalyses both reactions comes from three sources :

1. Sorption by paper of acid released by aluminium cations in solution, caused by the hydrolysis reactions they undergo.
2. Acid released by the aluminium cations as they undergo further hydrolysis, in situ, once sorbed into the paper.
3. By products of the acid-hydrolysis of cellulose.

Aluminium solution chemistry is highly complicated. It is affected by temperature, concentration, and most particularly, by the presence of anions that can coordinate with the aluminium cation, so suppressing or altering hydrolysis (8). The first two sources noted above can be modified by the presence of different anions being dissolved in solution with the aluminium cations. Data reported above indicate that altering the anion mix of the impregnation solution has some potential merit in controlling reactions with cellulose.

Further examination of the data indicates the relative importance of in-situ hydrolysis over that caused by acid sorbed at the time of impregnation from the original solution. Data for the paper impregnated with added citrate anions (figure 5 and 6) are most important in this respect. Small levels of added citrate (up to around 1 citrate anion added per two aluminium cations) result in a significant decrease in solution pH, of around 1 unit. However, even though the impregnation solution contains nominally ten times the amount of acid as the original solution, paper impregnated with this solution showed decreased wet-strengthening and degradation.

From this we can say that addition of anions that coordinate with aluminium, so reducing the degree of in-situ hydrolysis, help prevent degradation, admittedly at the expense of reduced wet strengthening. Optimising the cation-anion mix of the impregnation solution therefore offers one potential route to controlling the rate of the two reactions.

Another interesting facet of the work is the slightly increased degradation that occurs when non-coordinating anions are added to aluminium solutions prior to impregnation into the paper. Whereas coordinating anions reduce acidity by hindering hydrolysis; non-coordinating anions such as chloride or nitrate (not shown) should in theory have little effect on the degree of hydrolysis the

aluminium cation undergoes. However, the reason added sodium salts containing non-coordinating anions are so detrimental is believed to be due to the effect they exert on the ionic strength of the medium, which previous researchers have shown tends to increase the rate of carbohydrate hydrolysis by acid salts (9).

Finally, as noted in a previous publication, the acid catalysed wet strengthening described here is believed to occur due to the formation of formal crosslinks between cellulose chains in the paper fibres. The permanence of this wet property improvement, and the stability when faced with attack by oxidising or reducing agents, as well as by acids and alkalis, suggests these crosslinks are ether linkages(10), formed by a dehydration reaction. Since dehydration reactions of this sort can occur in other carbohydrates, it is suggested that the method may be applicable to hardening and crosslinking of starches and other papermaking additives having large numbers of free hydroxyl groupings.

CONCLUSIONS

Overall, the work shows that the selection and addition level of counter anions added to solutions of aluminium salts prior to impregnation into paper, can be used to control both the degree of wet strengthening achieved, and the associated cellulose degradation that occurs in parallel, during thermal treatment. It is suggested this offers a route to controlling both reactions, so making industrialisation of the process, as proposed by Ernst Back, more of a possibility.

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