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Research Note

Effect of Treatment with Very Dilute Acids on the Short-span Tensile Strength of Paper

INTRODUCTION

It has been shown by Nevell and Nugawela (1987) that the wet strength of paper made from pure cellulose is increased by heating it with very dilute aqueous acids. The effect was attributed to the formation of ether linkages between adjacent fibres in the paper web. Such linkages are stable to water, whereas the hydrogen bonds that keep the dry paper sheet intact are broken by it. The strength measurements were made mainly on strips 2·54 cm wide, the effective test length being 15 cm. Some zero-span measurements were also made to obtain an estimate of the intrinsic strength of the cellulose fibres. We have made more extensive short-span measurements of wet strength and supplemented them with similar measurements of dry strength. We used the same paper and experimental methods as in the previous work except that no strength measurements with the Instron were made. The readings of the Pulmac tester were converted into breaking lengths in accordance with the manufacturer's instructions; all quoted results are averages of at least 10 measurements.

EFFECT OF MINERAL ACIDS

Figures 1 and 2 show the effect on wet and dry strength, respectively, of heating for 1 h with 0.001 M sulphuric, hydrochloric, phosphoric and boric acids. It is evident that boric acid is so weak that its action is indistinguishable from that of water. In agreement with the previous work, as the test length approaches 1.3 mm the wet strength of the water-treated sample approaches zero because the only forces holding the paper together are inter-fibre hydrogen bonds and these are destroyed by water. As the test length is decreased, the wet strength increases because more of the individual fibres span the gap between the jaws of the tester

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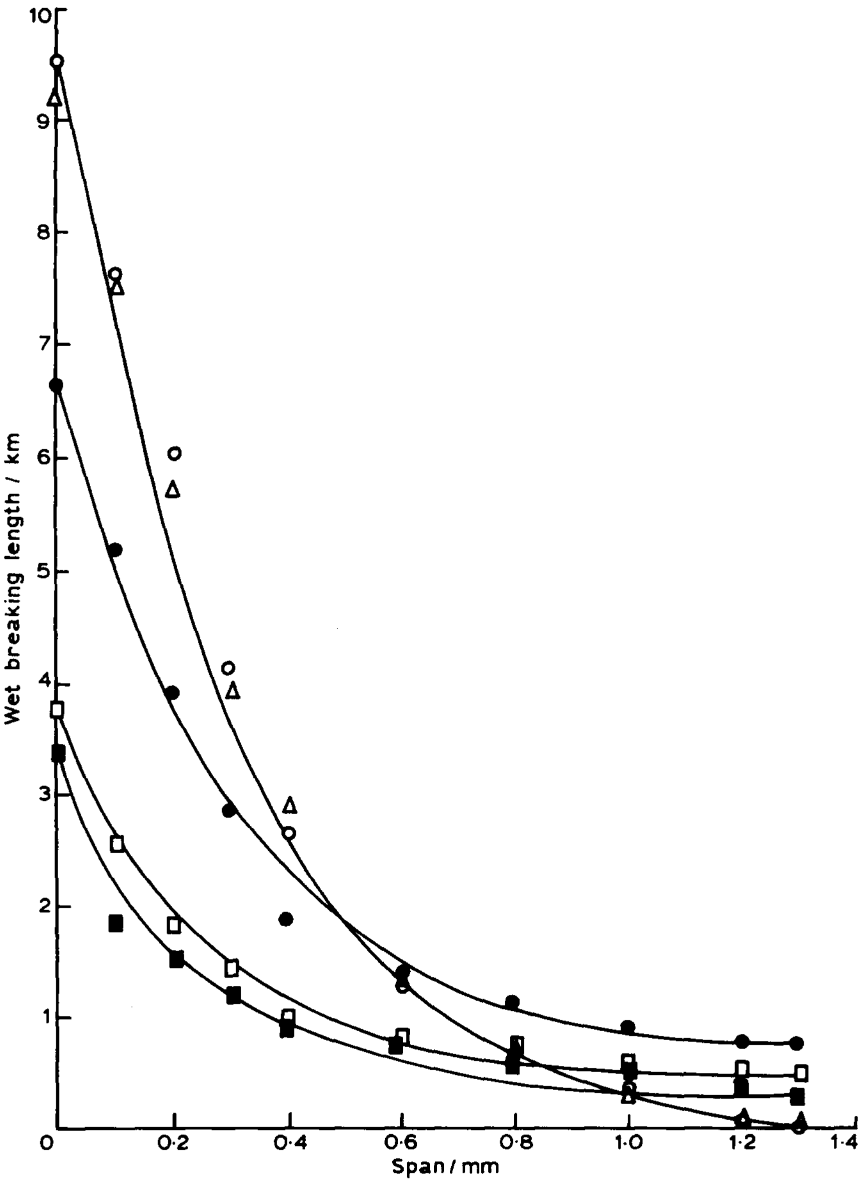

Fig. 1. Variation of measured wet breaking length with jaw span for paper treated with water or 0·001 M mineral acids and heated for 1 h at 140°C. (○, water; △ boric acid; ●, phosphoric acid; □, hydrochloric acid; ■, sulphuric acid.)

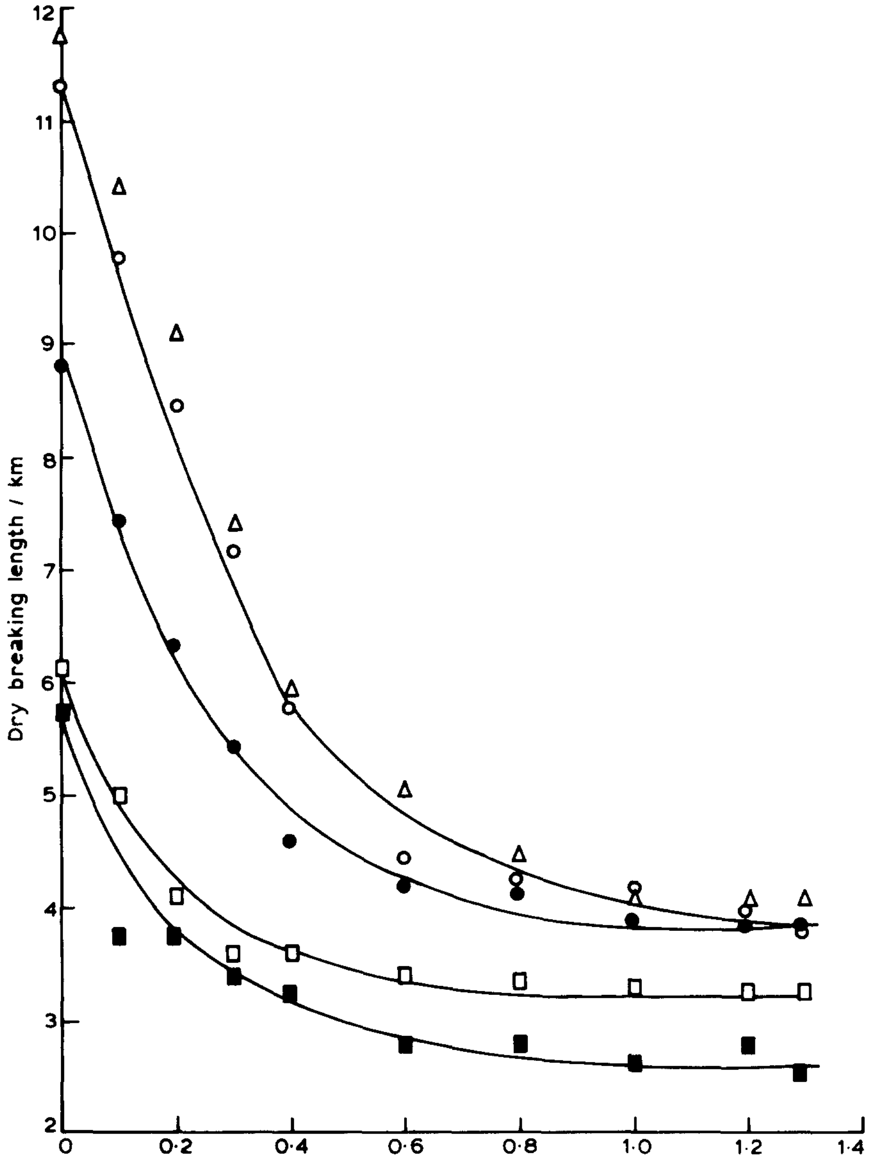

Fig. 2. Variation of measured dry breaking length with jaw span for paper treated with water or 0·001 M mineral acids and heated for 1 h at 140°C. (○, water; △ boric acid; ●, phosphoric acid; □, hydrochloric acid; ■, sulphuric acid.)

until, at zero span, the result represents the intrinsic fibre strength. The zero-span dry strength should also represent fibre strength alone and should therefore be the same as the wet strength. In fact, it is slightly higher (see Fig. 2), but the discrepancy is small. It is probably due to the impossibility of achieving a genuine zero span. The slope of the dry-strength curve is less than that of the wet so that, if both were extrapolated backwards, their point of intersection (nominally negative on the scale of abscissae) would represent the true zero span and intrinsic fibre strength. Because of the low degree of accuracy of the results and the consequent scatter of the plotted points, it has not been considered worthwhile to make this extrapolation, and the measured zero-span strength has been taken as representing the fibre strength in each case.

The stronger mineral acids bring about a fall in both wet- and dry-measured zero-span strength, the relative effectiveness of the acids being $H_2SO_4 > HCl > H_3PO_4$. This is the same order as the hydrogen-ion concentration in the three solutions. The falls in strength are clearly due to the hydrolysis of glycosidic bonds in the fibres. As the jaw span is increased, the wet strengths of the acid-treated papers decrease more slowly than that of the water-treated paper and eventually level out at values well above zero. The magnitudes of these finite-span strengths decrease in the same order as those at zero span. They are determined by a combination of the effects of hydrolytic degradation and ether cross-linking. It seems likely that the amount of cross-linking is less with phosphoric acid than with hydrochloric and sulphuric acids. The extent of degradation is less and the overall result is a paper of higher finite-span wet strength.

The dry strengths of the acid-treated papers also level out to constant values as the jaw span increases, but the values are lower than (or, with H_3PO_4, approximately equal to) that of the water-treated paper. They are determined by a combination of hydrogen bonding (the predominating effect), covalent cross-linking and fibre degradation, and are between five and nine times the corresponding wet strengths. The final dry strength of the paper heated with phosphoric acid is the same as that of the water-treated paper. This suggests that the loss of strength due to degradation is approximately equal to the gain due to cross-linking under the particular conditions of acid treatment used. Such equivalence would not necessarily arise from other phosphoric acid treatments.

EFFECTS OF ALIPHATIC DICARBOXYLIC ACIDS

Figures 3 and 4 show the effect on wet and dry strength, respectively, of oxalic (ethanedioic), malonic (propanedioic) and succinic (butanedioic)

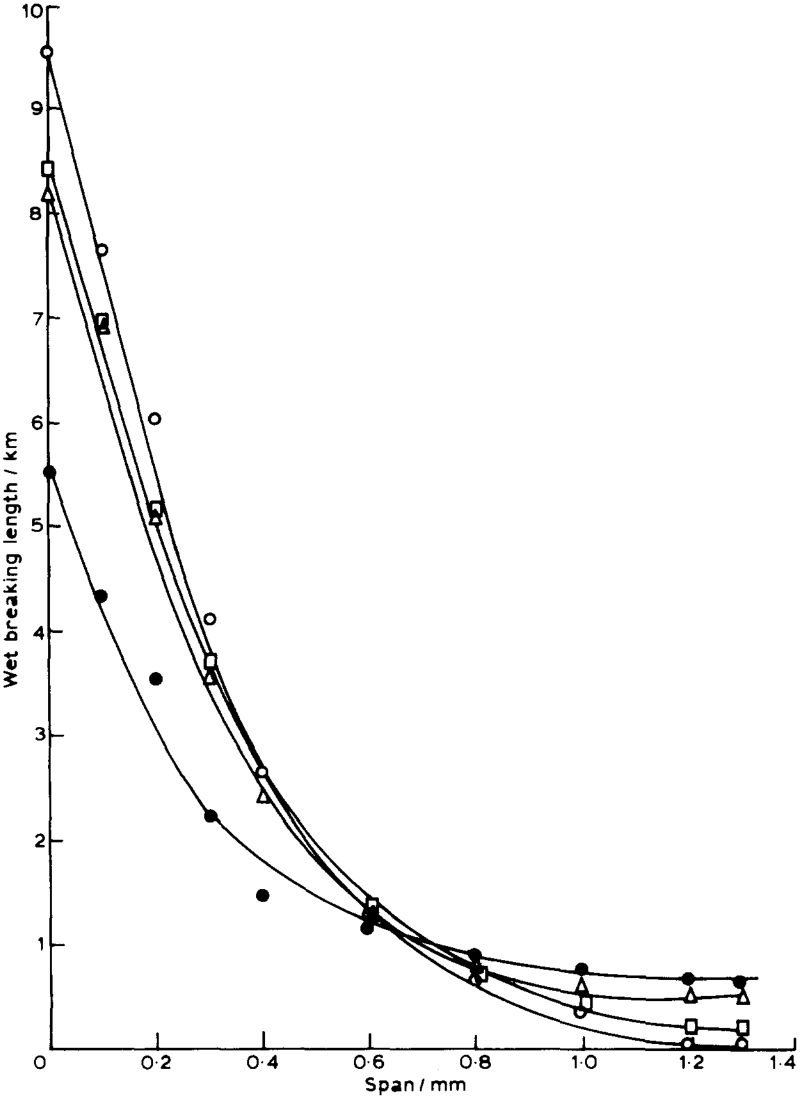

Fig. 3. Variation of measured wet breaking length with jaw span for paper treated with water or 0·001 M aliphatic dicarboxylic acids and heated for 1 h at 140°C. (○, water; ● oxalic acid; △, malonic acid; □, succinic acid.)

acids. The results are similar to those for the mineral acids. Only oxalic acid appears to cause both appreciable hydrolytic degradation and covalent cross-linking. Its effect on wet and dry strength at both zero and 1.3-mm spans is intermediate between that of phosphoric and hydrochloric acids, as would be expected from its intermediate strength

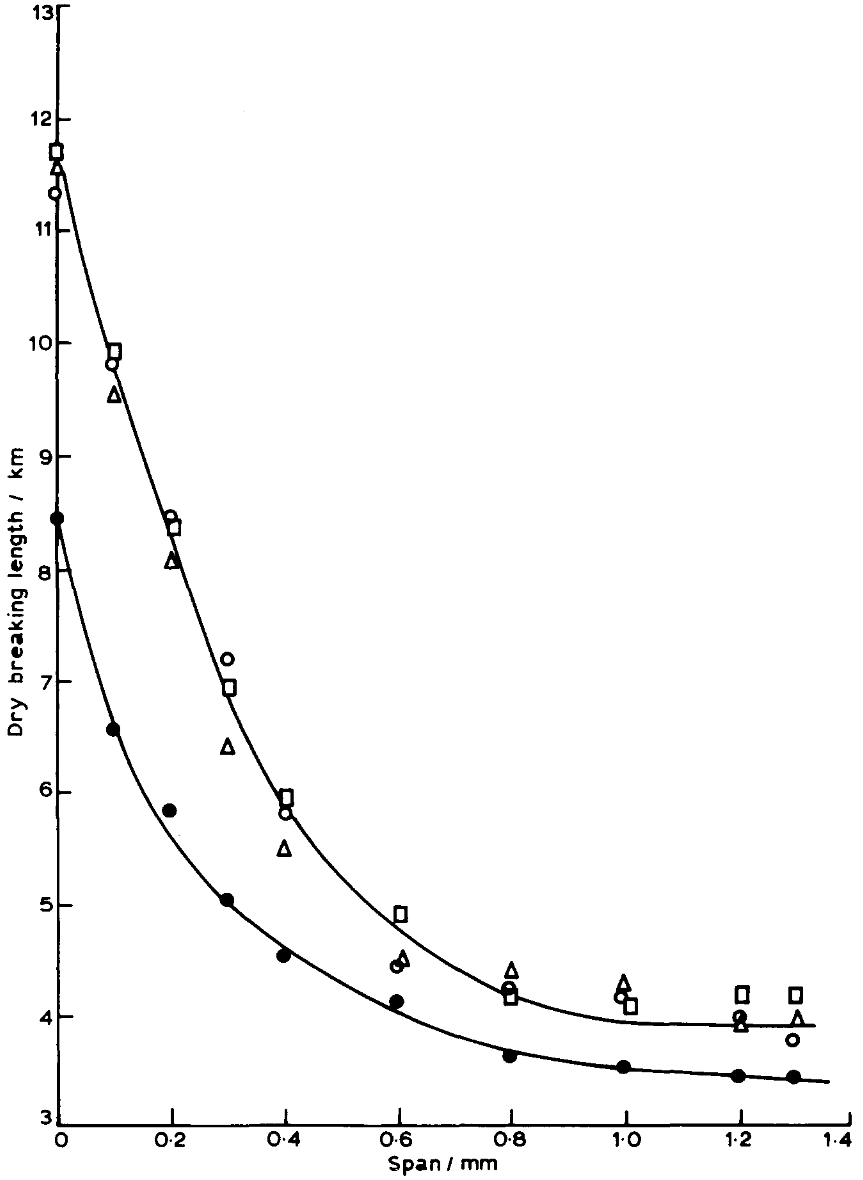

Fig. 4. Variation of measured dry breaking length with jaw span for paper treated with water or 0·001 M aliphatic dicarboxylic acids and heated for 1 h at 140°C. (○, Water; ●, oxalic acid; △, malonic acid; □, succinic acid.)

($pK_1 = 1{\cdot}19$ compared with 2·16 for phosphoric acid). Malonic acid ($pK_1 = 2{\cdot}77$) has little degradative effect, but seems to cause a very small amount of cross-linking. Succinic (butanedioic) ($pK_1 = 4{\cdot}17$), and glutaric (pentanedioic), adipic (hexanedioic) and suberic (octanedioic) acids (all of which have $pK_1 \simeq 4{\cdot}4$) were all indistinguishable from pure water in their effect on the relation of tensile strength to test length. This is in agreement with the long-span strength tests reported in the previous work.

APPLICATION OF PAGE'S THEORY OF THE TENSILE STRENGTH OF PAPER

Page (1969) has shown that the finite-span tensile strength (T) of paper can be represented by eqn (1):

$$\frac{1}{T} = \frac{1}{F} + \frac{1}{B} \tag{1}$$

where F = an index that describes only the resistance of the fibres to breakage and B = an index that describes only the resistance of inter-fibre bonds to breakage.

We have used this formula to compare the fibre and inter-fibre bond strengths in four samples of wet acid-treated paper. The index F has been taken as the zero-span strength and T as the mean of the last two strength measurements (i.e. at 1·2 mm and 1·3 mm) in each series. The results of these calculations are given in Table 1. Thus, while the wet strength of the untreated paper is negligible, the strength of covalent cross bonding in treated paper is about 13% of intrinsic fibre strength.

TABLE 1

Finite-span Breaking Lengths, Fibre-strength Indices, and Cross-bonding Strength Indices of Wet Paper that has been Treated with 0·001 M Acid for 1 h at 140°C

Acid	*F/km*	*T/km*	*B/km*		*100 B/F*
Phosphoric	6·65	0·76	0·86		13
Oxalic	5·52	0·67	0·76		14
Hydrochloric	3·78	0·49	0·56		15
Sulphuric	3·42	0·31	0·34		10
				Mean	13

For dry water-treated paper, $F = 11{\cdot}32$ km and $T = 3{\cdot}74$ km. Hence $B = 5{\cdot}585$ km and $100\ B/F = 49$. In this case, B is an index of inter-fibre hydrogen bonding.

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