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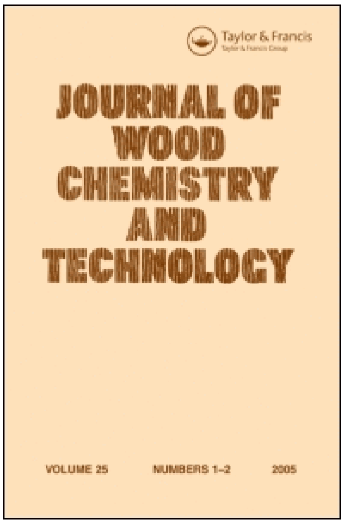

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THE VISCOSITIES OF UNBLEACHED ALKALINE PULPS

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ABSTRACT

The viscosities of unbleached kraft, kraft-AQ, soda, and soda-AQ pulps were determined over a wide range of additive concentrations and sulphidities, but at constant effective alkali and H-factor. There was no significant effect of AQ or sulphide ion on viscosity. As expected, effective alkali had a large effect on viscosity, while H-factor had a lesser influence. Viscosity is not a reliable indicator of the strengths of unbleached pulps made by reductive alkaline processes.

INTRODUCTION

We have recently expanded the concept of reductive alkaline delignification to show that it applies to all alkaline pulping processes, including kraft [1-4]. Our mechanism considers the pulping additive, be it sodium sulphide or a reduced quinone, to be a reservoir of reducing power which accelerates delignification. In this article, we relate the viscosities of bleachable-grade pulps from different alkaline processes to two variables, alkali and cooking time. The strong effect of alkali charge on viscosity is known for kraft pulping [5], but it is now generalized to include other alkaline processes. Reducing additives appear to have no effect on pulp viscosities. The previous observation that the viscosities of unbleached kraft pulps do not correlate with their strengths [5] is also extended to pulps from different alkaline processes.

EFFECT OF ADDITIVES ON PULP VISCOSITY

In our earlier publications, the viscosities of various soda-additive pulps were plotted in the conventional way against either the pulp yield or degree of delignification (usually expressed as Kappa number), and appeared to show that different additives like ethylenediamine (EDA) [1], anthraquinone (AQ) [6,7] or even Na_2S itself, had an important effect on pulp viscosity. Figure 1 shows viscosity-kappa number plots for black spruce pulps prepared by alkaline processes, and confirms this earlier impression about viscosity differences.

When the cooking conditions (effective alkali charge and cooking time) were kept constant, however, pulp viscosity was found to be independent of the dose of additive (Figure 2). Indications of this phenomenon in kraft-anthraquinone-2-sulphonate pulping of pine have been published [8]. Although there were large differences in kappa numbers between the pulps represented by the right- and left-hand data points in Figure 2 (showing the impact of AQ or sulphide ion on the delignification rate), the additives had no effect on pulp viscosity in the concentration ranges investigated. Data from soda and soda- AQ pulping of spruce wood meal corroborate this conclusion [9-11]. The viscosity differences apparent in Figure 1 result from the variety of alkalinities and cooking time levels needed to reach a given kappa number - a consequence of the differing delignification rates of the processes.

Figure 3 shows that it was the alkali charge that had a profound effect on pulp viscosity. At constant temperature and cooking time, and independent of the pulping process, pulp viscosity declined rapidly as the effective alkali (EA) charge was raised. This relationship was observed despite large differences in the

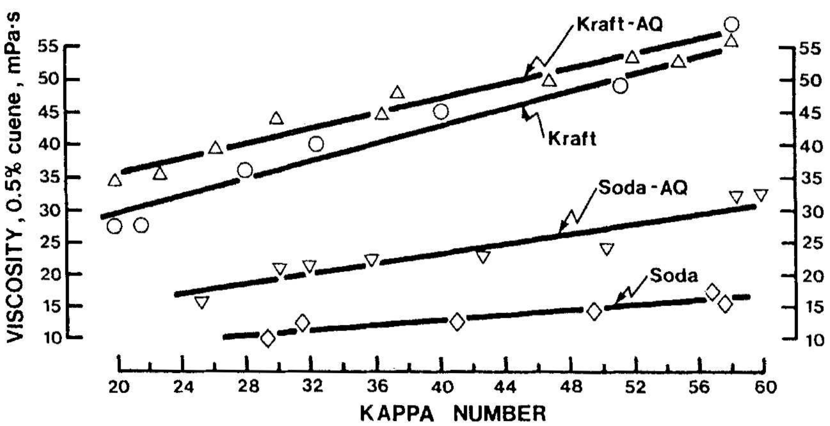

FIGURE 1. Viscosity-kappa number relationships of pulps prepared in kraft, soda, soda-AQ, and kraft-AQ liquors. The unbleached pulps were completely delignified in mild acid chlorite solutions[17] before viscosities were measured.

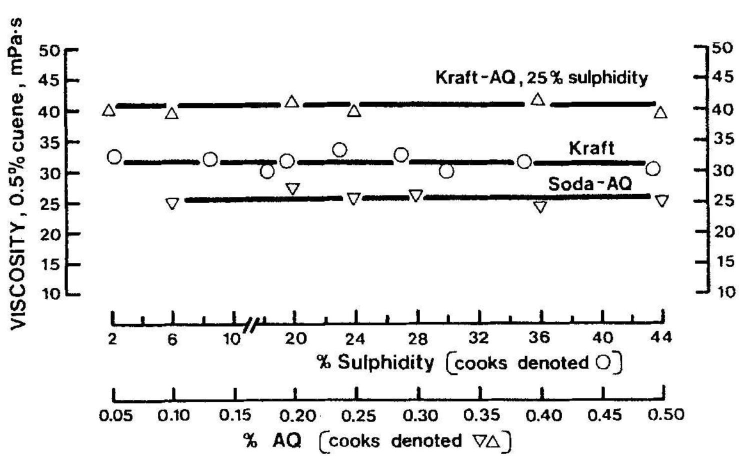

FIGURE 2. Relationship of viscosity to additive charge. Kraft-AQ: 14% effective alkali on o.d. wood, 25% sulphidity, 95 minutes cooking time at 170°C; conventional kraft: 18% effective alkali, 80 minutes cooking time at 170°C; soda-AQ: 15.3% effective alkali and 95 minutes cooking time at 170°C. AQ is reported as % on o.d. wood.

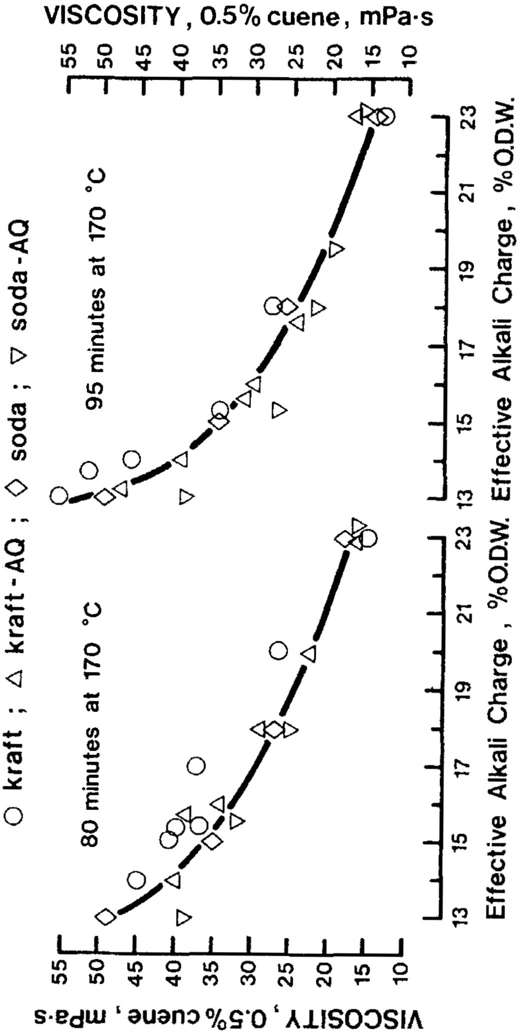

FIGURE 3. Dependence of viscosity on the charge of effective alkali at two levels of cooking time at 170°C. Kraft liquor sulphidity was 27%, and the concentration of anthraquinone in pulping liquor was 0.1% (kraft-AQ) or 0.25% (soda-AQ) on o.d. wood.

kappa numbers of the pulps at given EA charges. For example, at 23% EA, all four processes yielded pulps with viscosities of 15 ± 2 mPa.s, while the Kappa numbers varied from 16 for kraft-AQ to 65 for soda pulp.

As can be seen from the small slope of the lines in Figure 4, cooking time had a lesser effect on pulp viscosity. Once again, close coincidence of the data points of all four processes is evident. Over the entire cooking time range of 70-120 minutes, pulps produced with a charge of 15.3% EA had higher viscosities than those at 18% EA.

The conventional method of comparing pulp viscosities at a given yield or lignin content relates two dependent variables. While this is useful for comparing the selectivities of processes, it can be misleading if one is looking for the effect of an additive on cellulose stability in alkaline media. The problem has usually been that in order to compare pulps at the same lignin content, when made with and without an accelerating additive, the pulping conditions had to be different: the accelerated cook had to have less alkali or less pulping time, and thus two parameters (either additive plus cooking time or, additive plus alkali) had to be altered simultaneously. Algar _et al._[12] made such a comparison, and concluded that because _P. radiata_ soda-AQ pulp had a higher viscosity than soda pulp at the same lignin content, the quinone was protecting the carbohydrates from alkaline attack. In fact, soda-AQ pulps have higher viscosities _only because cooking time is much shorter when the accelerator is present_. It is well established that AQ protects polysaccharide end-groups from hydroxide ion attack[13,14]; however, this should not be confused with viscosity preservation. Quinone additives which oxidize end-groups and stop the peeling reaction would not necessarily inhibit hydroxide ion attack on the cellulose chain linkages - the major factor in decreasing the degree of polymerization of the polysaccharides.

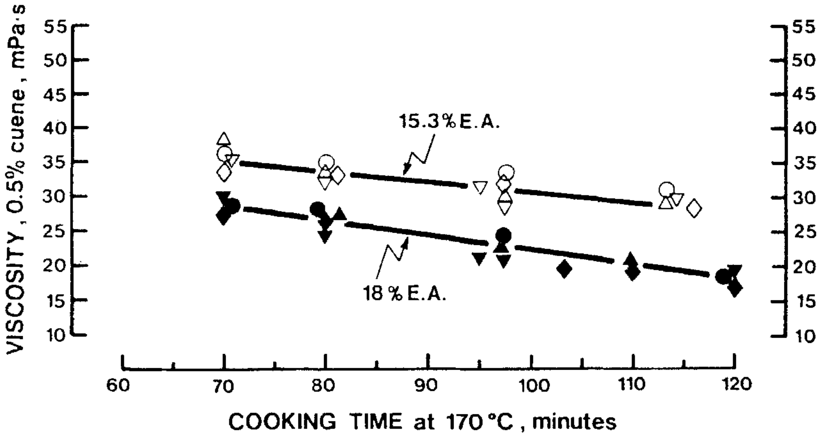

FIGURE 4. Relationship of viscosity to cooking time at 170°C for the soda◇, kraft○, kraft-AQ Δ, and soda-AQ Δ processes. AQ charge varied from 0.1 to 0.25% on o.d. wood; sulphidity of the liquor in all kraft pulping was 30%.

VISCOSITY AS A MEASURE OF UNBLEACHED PULP STRENGTH

Viscosity is often used as an indicator of pulp strength, especially of bleached pulps. Among unbleached pulps, the relationship is not obvious. For example, we have observed [1] that the viscosities of high-tear-strength soda-EDA pulps were somewhat lower than those of kraft pulps. Kraft-AQ softwood pulps, however, usually had higher viscosities than kraft pulps at similar kappa numbers, while viscosities of soda-AQ pulps were typically lower than those of kraft (Fig. 1). It was unclear whether any correlation existed between the viscosities and the mechanical strengths of various alkaline pulps.

Tear-*vs*-breaking length data were plotted for unbleached soda-EDA, kraft, kraft-AQ, soda-AQ, and soda pulps spanning a wide range of kappa numbers (and hence, viscosity values). Tear values at a constant breaking length (viz., 10 km) were determined from these plots, thereby putting all the pulps on the same comparative strength basis. These tear values were then plotted against the corresponding pulp viscosities, as shown in Figure 5. This plot clearly shows that when making strength comparisons among alkali-additive pulps, a particular viscosity value may bear no relationship whatsoever to pulp strength. For example, a viscosity of 30 mPa.s corresponds to five different tear strengths (in mN.m^2/g) for these five different kinds of pulp: soda-EDA, 22; kraft, 19; kraft-AQ, 16; soda-AQ, 14; and soda, 11.

In other words, the relative strengths of pulps made by different alkaline processes cannot be deduced from the viscosities of the pulps. Rather, it is necessary to build up a reliable collection of viscosity and pulp strength data for each process, and make

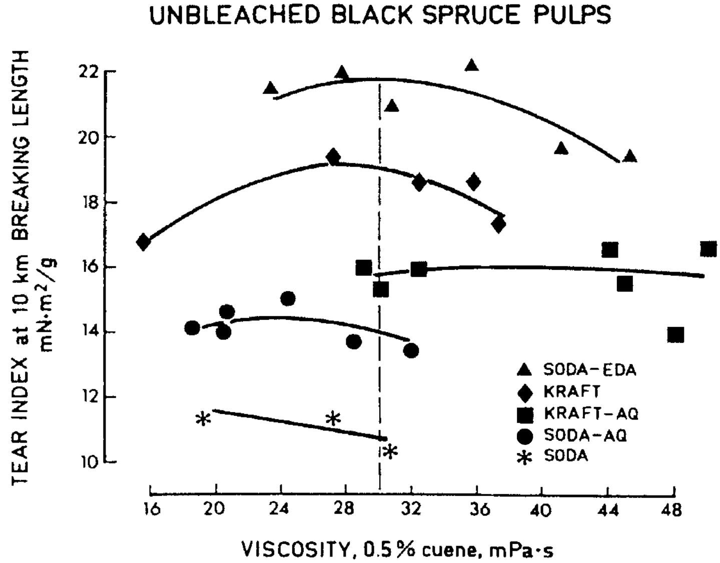

FIGURE 5. The relationship between strength and viscosity of various soda-additive pulps. The tear values at 10 km breaking length were obtained from tear-tensile graphs of each pulp. The same relationships were observed for tear values at 13 km breaking length. EDA is ethylenediamine. The pulps were delignified by acid chlorite bleaching before the viscosities were determined.

inferences from the former to the latter only within one process. Even then, tear strength at constant breaking length may peak at a particular viscosity level (e.g., 28 mPa.s for kraft), or may remain relatively unchanged over a wide range of viscosities (e.g., soda-AQ or kraft-AQ). Thus, viscosity may be a satisfactory rough indicator of optimum unbleached pulp strength within the kraft process, but not within either the soda-AQ or kraft-AQ processes.

CONCLUSIONS

The conventional method of comparing viscosities at a given yield or lignin content relates two dependent variables, and can be misleading if one is looking for the effect of an additive on cellulose stability in alkaline media. Under conditions of constant alkalinity and cooking time at maximum temperature, four alkaline pulping processes yielded pulps of closely similar viscosities; thus, while profoundly changing the yield and lignin content, the additives AQ and sodium sulphide had no effect on unbleached pulp viscosity. Only the effective alkali charge strongly affected pulp viscosity, which is in agreement with a recent report on kraft-AQ pulping [15]. Cooking time had a lesser influence.

Viscosity proved not to be a useful indicator of the strengths of unbleached pulps made by alkaline processes such as soda, soda-AQ, soda-EDA, kraft and kraft-AQ. Neither was it of any value for predicting unbleached pulp strengths within one of the above processes, with the possible exception of kraft.

EXPERIMENTAL

Black spruce mill chips (250 g o.d. and 1 kg o.d. respectively) were pulped in 2-L bombs or a 20-L digester; the equipment and conditions were described in earlier work[1], except:

effective alkali charge (as Na_2O), % on o.d. wood	13 - 23
g/L of liquor	32.5 - 57.5
sulphidity, (% Na_2S based on active alkali charge)	2 - 24
anthraquinone, % on o.d. wood	0.05 - 0.50

The 2-L bombs contained air equivalent to only 1.6 mmol O_2/100 g dry wood[16].

Cooking time to temperature was 90 minutes for all cooks, and time at maximum temperature (170°C) was in the range 70-120 minutes, which corresponds in the kraft process to "H" factors in the range 1000-2200. Liquor-to-wood ratio was 4 L/kg.

Pulp properties were measured according to the CPPA and PPRIC standard methods described in Reference 1. Before the viscosities were determined (Tappi T-230), the unbleached pulps were delignified by acid chlorite bleaching[17].

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