

# KRAFT PULP VISCOSITY AS A PREDICTOR OF PAPER STRENGTH: ITS USES AND ABUSES

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## ABSTRACT

For bleached kraft pulps, two factors - the individual fiber strength and the bond strength that adhere the individual fibers together in the paper matrix - governed paper strength. Inherent fiber strength is related to the length of the carbohydrate polymers, also known as the degree of polymerization (DP). Average DP ( $\overline{DP}$ ) is inferred by performing pulp viscosity measurements. Under certain circumstances during kraft pulping and bleaching, the average polymer lengths can be shortened, which results in lower pulp viscosity and may indicate fiber damage. Fiber damage typically manifests itself as a reduction in tear strength for well-bonded handsheets.

This paper will review the literature on how pulp viscosity can predict paper/fiber strength and how it can be used as a diagnostic tool. It can be a means to monitor pulp quality during pulping and bleaching, and to alert when such operations approach a critical threshold. However, viscosity losses must be carefully and judiciously analyzed. Like most diagnostic tools, viscosity measurements can be misused and abused, which can lead to incorrect inferences about intrinsic fiber strength. This review will also cover these misuses. The overall goal is to provide the papermaker a better understanding of what pulp viscosity is, how it correlates to potential sheet strength, and what are its limitations.

## INTRODUCTION

The paper industry has used pulp viscosity measurements to characterize chemical pulps since about the 1940s [1-11]. Such measurements are reported in the pulping and bleaching literature. It quantifies how much cellulose degradation has occurred to the fibers as the wood is converted to pulp. Viscosity data are often coupled with kappa number or brightness data. Analysis of these data sets can quantify how selective unit operations are at delignification or brightening versus damaging the carbohydrates.

Mills have routinely conducted viscosity tests to monitor pulping and bleaching operations. Pulp samples are taken at several points, particularly where appreciable strength losses can occur. Such points can include after the digester and the bleach plant. Additional sampling may be required following certain bleaching stages. Historically, this included hypochlorite (H) and extraction ( $E_1$ ) stages for bleach plants that used chlorination (C) stages [1-7]. Nowadays, viscosity test may be done on pulps after oxygen (O) and ozone (Z) stage. In these cases, the viscosity test is used as a surrogate for pulp strength tests. Although this test takes a few hours to conduct, it is considerably quicker to perform than physical handsheet testing. Substantial time is required to convert the unbeaten samples into conditioned handsheets, which are then subjected to the appropriate mechanical tests (*e.g.*, burst, tensile, and tear).

The viscosity test has been mistrusted by scientists as how it relates to pulp strength [8,9,11-14]. Oglesby and co-workers [11] reported that there were no discernible relationships between handsheet strength properties of bleach plant pulps and their cupriethylenediamine (CED) viscosities as measured by TAPPI Standard Method T230. Seth and Chan [12] stalwartly stated that pulp viscosity is a very poor predictor fiber strength based on their work on bleached market kraft pulps. Gurnagul *et al.* [13] concluded that there was no correlation between the dry or wet zero-span tensile strength of softwood kraft pulps and their SCAN intrinsic viscosities over the 690 to 1180 mL/g range. Earlier, Gurnagul and Page [14] examined the tensile strength, as well as dry and wet zero-span tensile, of several

unbleached and bleached kraft pulps; these authors did not note any apparent relationships between tensile measurements and SCAN intrinsic viscosity.

On the other hand, there are several investigators who have reported a linear or curvilinear relationships between a pulp's wet zero-span tensile or other strength properties and its TAPPI viscosity over the 8 to 24 mPa·s gamut [1,3,5-7,15-22]. Rydholm [1] examined the 1940s to 1960s literature for softwood kraft pulps. He noted that tensile indices have a somewhat positive correlation with its cuprammoniumhydroxide (cuoxam) falling-ball viscosities below 30 mPa·s; tear indices have a stronger positive correlation with cuoxam viscosities below 50 mPa·s. (*ca.* 12 and 19 mPa·s TAPPI T230, respectively [10]). Rydholm advised that pulp viscosities greater than these levels exhibit no relationships to pulp strength. In 1951, Valeur [16] examined the tensile, burst and tear of bleached softwood pulps versus cuoxam viscosity. Examination of the raw data from this study (Fig. 1A), when converted [10] to TAPPI T230 viscosity, showed correlations between pulp strength and viscosity, particularly for values below 15 mPa·s. Otero D'Almeida [17] observed similar trends with a bleached eucalypt pulp (Fig. 1B), mostly for values lower than 9 mPa·s. Still, many others [5-7,19-22] have seen nonlinear between pulp viscosity measurements and tear for well-bonded sheets (at constant tensile).

This cursory overview suggests that there are inconsistent interpretations of pulp viscosity data. A better holistic comprehension is needed of what this test exactly communicates. Many papermills and market pulp customers stipulate a floor-level (*e.g.*,  $\geq 16$  mPa·s for bleached softwood kraft) expecting that this parameter accurately reflect pulp strength [23]. The objective of this study is to re-analyze some of the historical data to provide a clearer understanding of how the viscosity relates to pulp strength, and what are some of inherent weaknesses and limitations of this test. It is hoped that this review will dispel some of the mythology surrounding the pulp viscosity test, as well as point out how the test may be misapplied.

## OVERVIEW OF VISCOSITY, MOLECULAR WEIGHT, AND DEGREE OF POLYMERIZATION

The degree of polymerization (DP) or the molecular weight (M) of a pulp sample can be ascertained from the intrinsic viscosity,  $[\eta]$  (mL/g), of the sample when dissolved in a solvent [8,9,24-31]. Cellulose solvents used include CED, cuprammonium hydroxide (cuam), cadmium ethylenediamine (cadoxen), and iron sodium tartaric acid (EWNN) solutions. The most commonly used solvent is CED. A series of pulp solutions are made at low concentrations and the viscosity ( $\eta$ ) of these individual solutions is measured. These values are then ratio to that of the pure cellulose solvent ( $\eta_0$ ). The  $[\eta]$  is calculated from  $\eta/\eta_0$  values by taking the limit as the pulp concentration  $c$  (g/mL) approaches zero:

$$[\eta] = \lim_{c \rightarrow 0} \left( \frac{\frac{\eta}{\eta_0} - 1}{c} \right) \quad \text{Eq. 1}$$

The average molecular weight of the sample,  $\bar{M}$  (g/mol), is related to  $[\eta]$  by the Mark-Houwink expression [1,7,24-29]:

$$[\eta] = K\bar{M}^a = K'\bar{DP}^a \quad \text{Eq. 2}$$

Empirical parameters  $K$  and  $a$  vary depending on what pulp solvent is used and how  $\bar{M}$  is determined by other external test with appropriate cellulose or Pulman standards [7-10,13,24-30]. The average DP ( $\bar{DP}$ ) calculated from Eq. 2 can be determined by using the appropriate  $K'$  value. Historically, the SCAN intrinsic viscosity procedure [32] simplifies the above process. It measures  $\eta$  for a single solute concentration  $c$  such that the value of the  $c \cdot [\eta]$  product is near 3.0. The cellulose solvent used is 1 M CED.

Alternative methods for measuring pulp viscosity [3,4,10],  $\eta$  (mPa·s), include the TAPPI Test Methods T230 om-13 (capillary viscometer) [33], T254-cm10 (falling ball) [34] and T206-os62. TAPPI T230 measures the viscosity of 0.5% pulp solution in 0.5 M CED using an Ostwald viscometer. Viscosity is calculated from the time it takes the cellulose solution to pass through a capillary at a fixed distance. TAPPI T254 measures the viscosity of a 1% pulp solution in a 1 M CED solution that is saturated with cupric hydroxide. Viscosity is determined by how long it takes

for an aluminum sphere to drop through the solution over a fixed distance. TAPPI T206, which was withdrawn in 1972, is similar to TAPPI T253 but used cuoxam instead of CED as the cellulose solvent.

Sihtola *et al.* [10] compared various viscosity tests with one another. The authors established equations that could convert the TAPPI T230 viscosity  $\eta$  to  $[\eta]$  and *vice versa*. This provided a means to approximate  $\overline{DP}$  and  $\overline{M}$  if the SCAN protocol was not employed. The SCAN method uses  $K'$  of 1.33 and  $a$  of 0.905 in the Mark-Houwink equation (Eq. 2) to approximate a number-average DP ( $\overline{DP}_n$ ). Technically, the  $\overline{DP}_n$  values derived from  $[\eta]$  are viscosity-average ( $\overline{DP}_v$ ) values [27,28].

Measurements of viscosity yield limited information about the average chain length of the carbohydrates. It is just a parameter. It cannot provide any information about the size distribution of the carbohydrate chains in the pulp. Chemical pulps can have the same intrinsic or TAPPI viscosity, but have entirely different molecular weight distributions. **Figure 2** illustrates this with data from Montet's study [35], which subjected a hardwood pulp from a bleach plant to additional carbohydrate degradation. The initial bleached pulp had an  $[\eta]$  of *ca.* 895 mL/g ( $\overline{DP}_v$  of 1370). Montet treated the pulp with ozone (O<sub>3</sub>), hypochlorous acid (HOCl), or cellulase enzyme to induce carbohydrate damage. Montet manipulated each treatment to bring about an  $[\eta]$  of *ca.* 582 mL/g ( $\overline{DP}_v$  *ca.* 850). Despite the similarity in  $[\eta]$ , the various molecular weight distributions ( $M$ ) of the pulps are dissimilar. Overall  $\log(M)$  distributions are commonly bimodal. For the initial pulp, the lesser than 5  $\log(M)$  peak is assigned to hemicelluloses, whereas the greater than 5  $\log(M)$  peak is attributed to cellulose. The O<sub>3</sub> treatment results in a distribution analogous to the starting pulp, albeit uniformly displaced to lower values. The cellulase treatment has the most pronounced effect on the distribution. It appreciably diminished its bimodality when compared to the control and shifts the main peak to lower levels. Finally, the HOCl degradation results in an intermediate distribution that is between the others. **Table I** displays the various  $\overline{DP}$  and  $\overline{M}$  values from Montet's investigation [35].

## RELATIONSHIP OF PULP VISCOSITY TO PULP AND INHERANT FIBER STRENGTH

Paper strength made from chemical pulps is governed by two global factors. These fundamental aspects are inherent fiber strength and fiber-fiber adhesion [5,7,36-39]. For tensile strength, the simplified Page equation [36] illustrates this for tensile strength ( $T$ ):

$$\frac{1}{T} = \frac{9}{8Z} + \frac{1}{B} \quad \text{Eq. 3}$$

where  $Z$  is the zero-span tensile strength and  $B$  is the fiber-fiber bonding index, which incorporates relative bonding area (RBA), shear bonding strength ( $b$ ), and fiber morphology and conformability. The  $9/8Z$  term accounts for the contribution of inherent fiber strength to the overall sheet tensile strength, whereas the  $1/B$  term represents the contribution of inter-fiber bonds to hold. Usually, the first term is the one most affected by pulping and bleaching operations [5]. The fibers are chemically attacked, which causes cellulose chains to shorten, and/or the fibers experience excessive mechanical treatment, which leads to fiber wall defects. To a lesser extent, pulping and bleaching can alter inter-fiber bonding by modifying the hemicellulose content, coarseness, and conformability of the fibers. Fiber morphology, which is set by wood species used to produce the pulp, affects the  $1/B$  term. Several of these issues are covered in more details in other literature reviews [5,7,38].

In most cases, the adhesion of the fibers ( $B$  term) rather than fiber strength ( $Z$  term) dominates tensile strength ( $T$ ). It is only where  $B$  becomes very large in the Page equation that the effects of  $Z$  become noticeable. This is illustrated with McKenzie's data [38] of pine kraft pulps (**Fig. 3**). McKenzie degraded fiber strength with cold hydrochloric acid treatment of the pulp at two levels. The fiber bonding index was manipulated by increasing wet fiber conformability by PFI beating. Increases in apparent sheet density improve RBA, which magnifies  $B$ .  $T$  is enhanced as sheet density increases. However,  $T$  is invariant for fixed density levels as  $Z$  declines. It is only at high sheet densification, hence high  $B$ , where lower  $Z$  becomes perceptible on  $T$ .

Likewise, data from the Oglesby *et al.* [11] bleached hardwood study shows a similar phenomenon (**Fig. 4A**). Although the wet zero-span tensile ( $Z$ ) varies, the  $T$  value remains constant at given levels of pulp freeness. Lower freeness leads to higher RBA which in turns leads to larger  $B$ . However, the changes in  $B$  are not appreciably high

enough to observe how lower  $Z$  affects  $T$ . The corresponding viscosity data (**Fig. 5**) shows a strong linear correlation with  $Z$  but no relationship to  $T$  (**Fig. 4B**). Both the viscosity and wet zero-span data suggest that the lower values show lower inherent fiber strength, but this lower strength is a minor contributor to overall tensile strength when compared to the fiber bonding index in the Page equation. Here, the carbohydrate chemical damage is not severe enough to affect tensile strength. In fact, the wet zero-span tensile strength would have to decrease to below 62 N·m/g (9 mPa·s TAPPI T230 viscosity) before it began to affect the tensile index for the 330 mL CSF pulp. This value is similar to the Otero D'Almeida study [17] for bleached eucalypt pulps.

**Figure 6** compares wet zero-span tensile data from several softwood studies where the investigators also reported pulp viscosity values. In these cases, there is a curvilinear relationship between pulp viscosity and wet zero span tensile when a broader range is examined. Typically, a small decrease in TAPPI viscosity (*ca.*  $\Delta 1$  mPa·s) in the 5 to 15 mPa·s range results in large reductions of wet zero-span tensile, whereas above 15 mPa·s results in small to negligible changes to wet zero-span. This transition occurs at *ca.*  $885 \overline{DP}_r$  ( $\overline{M}_v$ , *ca.* 143,000). This nonlinear behavior is not unusual when compared to other polymeric materials.

Correlations of intrinsic polymer viscosity,  $\overline{DP}$ , or  $\overline{M}$  values to various polymer strength properties, such as tensile or affect strength, are frequently nonlinear [40-45]. Often, these empirical trends take the form:

$$y = \alpha - \frac{\beta}{x} \quad \text{Eq. 4}$$

where  $y$  is the strength property of interest;  $\alpha$  is the plateau value of the property;  $\beta$  is some positive constant; and  $x$  is the polymer's intrinsic viscosity in an organic solvent (or  $\overline{DP}$  or  $\overline{M}$  values). In the 1940s, Flory [41,42] arrived at this expression for the tensile strength versus the  $\overline{M}_n$  of the polymer. He showed that the unfractionated polymer tensile strength could be deduced from the individual tensile strengths of fractionated polymers as long as the molecular weight distribution of the unfractionated sample is known. Similar findings were reported by Sookne and Harris [1,40] for cast films made from cellulose acetate (**Fig. 7**).

The shapes of wet or dry  $Z$  versus a pulp viscosity curves follow similar tendencies when examining a wide viscosity range (**Fig. 6**). The broader trends probably explain why there are so many disparate observations in the literature regarding pulp viscosity. For example, Seth and Chan [12] stated that pulp viscosity does not predict zero-span tensile, whether wet or dry. However, the viscosity range examined, *ca.* 12 to 25 mPa·s, is at or past the transition zone where wet zero-span value plateaus. In other examples [5,7,15,39,45-47] investigators examined the 9 to 14 mPa·s range where wet zero-span incrementally grows as viscosity increases.

As mentioned earlier, pulp viscosity only provides information about the molecular weight or DP distribution. For example, the treated pulps [35] shown in **Figure 2** and **Table I** have nearly identical pulp viscosity. However, the distributions are distinct. The wet zero-span values for the treated pulps are not the same. The O<sub>3</sub> and HOCl treatments afford pulps with similar wet zero-span, whereas the cellulase treatment results in a wet  $Z$  that is 33% lower. These viscosity values of the treated pulps, at first glance, would have implied that they should all have the same wet zero-span tensile. The  $\log(M)$  distributions of the cellulase-treated pulp show it has more cellulose of lower  $M$ , 25,000 to 63,000 g/mol, than the other pulps. The greater proportion of these weaker and smaller chains results in the pulp having a reduced wet zero-span tensile. Pulps treated with O<sub>3</sub> or HOCl have a greater fraction of  $M$  in the 100,000 to 250,000 g/mol range that are stronger. Hence, caution should be exercised when making inferences about fiber strength strictly based on viscosity data. This proviso has been stated in numerous studies, particularly regarding the effects of oxygen and ozone in pulp bleaching [35,47-49]. Knowledge of  $M$  or  $\log(M)$  distributions are needed to draw valid conclusions from viscosity data, particularly if the pulp process conditions are vastly different, such as comparing elemental chlorine free (ECF) and totally chlorine-free (TCF) bleached pulps.

The above examples have focused on how pulp viscosity related to a pulp's tensile strength. In most cases, during pulping and/or bleaching, a reduction in tear resistance manifests itself as a result of fiber damage [5,38]. Tear failure of well-bonded softwood sheets involves fiber breakage, and is therefore dominated by fiber strength and fiber length [5,50,51]. Tensile failure, on the other hand, usually involves fiber pullout, and typically dominated by fiber-to-fiber bond strength. Tear can be thought of as how brittle the paper sheet is, and tensile can be thought of as how much a

force it can support before failure. Page and MacLeod have shown that the work of tear ( $W$ ) for softwood kraft pulps is related to both tensile and zero-span tensile:

$$W \propto \frac{Z^n}{T} \quad \text{Eq. 5}$$

where  $n$  is an exponent value that is typically between 2.5 and 3.0. For a given  $T$  level for well-bonded sheets, tear is expected to vary in accordance to zero-span tensile to the  $n^{\text{th}}$  power. This means that if the  $Z$  value drops a small amount, for instance 5%, then the tear strength could be reduced by 12% to 15%.

**Figure 8** shows the relationships of pulp viscosity to tear index and wet zero-span tensile for bleach softwood kraft pulps using data from Flink and Norborg [7,15]. Pulp viscosity varies linearly with wet zero-span over the 9 to 27 mPa·s (600 to 1000 mL/g) range. Tear strength seems relatively stable for viscosity levels above 13 mPa·s (750 mL/g) or wet zero-span values above 125 N·m/g. However, tear precipitously decreases below these threshold levels. Similar nonlinear correlations of tear index versus pulp viscosity are given in **Figure 9** for softwood pulps treated with different bleaching sequences. In these cases, this threshold occurs *ca.* 13 to 16 mPa·s.

Oglesby *et al.* [11] did not see any relationships between tear and pulp viscosity for hardwood kraft pulps. However, Otero D'Almeida [17] study of bleached eucalypt pulps shows a correlation for viscosities for values below 9 mPa·s (**Fig. 1B**). Re-examination of Oglesby *et al.* [11] study also revealed there were no discernible relationships between tear index and wet zero-span tensile (not shown). All of these hardwood observations at first glance seem inconsistent with softwood pulps. It should be noted that tear is also a function of fiber length [38,50]. Tear mechanics differ for short fibers than for long fibers. In the former, the work to pull the short fiber out is much less than it is to break the fiber, whereas the opposite is true for long fibers. It is only when there is substantial damage to the short fiber strength that its tear resistance is affected. This probably explains why tear strength for hardwoods does not depend as strongly on inherent fiber strength as softwoods, unless the carbohydrate damage is excessively severe.

## FINAL REMARKS

The previous sections have examined the connections between pulp viscosity measurements and pulp strength properties determined from physical handsheet testing. Pulp viscosity relates to  $\overline{DP}$  (or  $\overline{M}$ ) of the carbohydrates, and specifically to the long cellulose chains. The pulp's  $\overline{DP}$  (or  $\overline{M}$ ) is associated with inherent fiber strength. The correlation of pulp viscosity with fiber strength is nonlinear over a broad range of viscosity values. This nonlinear trend is in line with the strength-viscosity relationship of other polymeric materials. Depending on what part of the range examined, pulp viscosity values will either have strong positive correlations, or little correlations to zero-span tensile strength. This limit, where pulp viscosity becomes relevant, occurs around 10 to 15 mPa·s TAPPI T230 viscosity, or about 630 to 800 mL/g SCAN intrinsic viscosity; this corresponds to a relative SCAN  $\overline{DP}_v$  value between 720 and 890.

The  $\overline{DP}_v$  derived from viscosity provides partial information regarding the  $DP$  or molecular weight distributions of the carbohydrates in the pulp. Pulps can have nearly identical viscosity values but have distinct  $DP$  or molecular weight distributions. It is the higher  $DP$  chains that have the greatest effect on zero-span tensile strength. Pulps that have a greater fraction of high  $DP$  cellulose chains will exhibit higher zero-span tensile values when compared to pulps with identical pulp viscosity but lower fraction of these chains. Therefore, caution should be exercised when drawing fiber strength inferences when comparing viscosity values for pulps from different chemical treatments. Prior knowledge of the carbohydrate molecular weight distribution is needed in order to draw conclusions from viscosity comparisons.

Tensile indices of kraft pulps are determined by two factors as generalized in the Page equation: inherent fiber strength and degree of fiber-fiber bonding. Most times, the amount of inter-fiber adhesion dominates the tensile index versus inherent fiber strength. It is only when the fiber strength, and hence pulp viscosity, has been reduced below a critical level that this factor becomes relevant to tensile failure.

Tear resistances of kraft pulps are more sensitive to changes in inherent fiber strength and fiber length. For softwood kraft pulps, there is a nonlinear relationship between the tear index (at a fix tensile index) and pulp viscosity, similar

to wet zero-span tensile. The threshold level when softwood pulp viscosity transition from strongly correlated to weakly correlated occurs around 15 to 20 mPa·s TAPPI T230 viscosity, or 800 to 915 mL/g SCAN intrinsic viscosity. The viscosity-tear relationship for hardwood kraft pulp differs from that of softwoods. For hardwoods, the shorter fiber of the pulp makes fiber pull out the overriding factor in tear failure rather than fiber breakage, which is predominant for softwoods. It is only when hardwood fiber damage, and consequently pulp viscosity, drops below a critical value ( $\leq 9$  mPa·s) that this factor becomes germane to tear failure.

Overall, it is emphasized that low pulp viscosity values ( $<10$  mPa·s TAPPI T230) denote lower inherent fiber strengths. High pulp viscosity values ( $>20$  mPa·s TAPPI T230) do not imply higher pulp strengths. It is only when viscosity drops below a threshold value where any further reductions will cause considerable declines in fiber strength, which affects tear and tensile. Any viscosity reductions above the critical value will not affect pulp strength.

In this context, pulp viscosity should be used to monitor pulp mill operations. It should not be used as a set-point value, such as a kappa number or brightness level, to control pulp mill operations. Instead, it should be used as a warning gauge to alert when extensive cellulose damage is so severe that it negatively affects fiber strength.

An example of this can be seen in the 1950s data presented by Dahm [18] who investigated the chlorine-hypochlorite bleaching of a softwood pulp at a Norwegian kraft mill. Dahm examined the tensile, tear and cuoxam falling ball viscosity of the pulp after the sodium hypochlorite (H) stage. It well known hypochlorite bleaching can cause severe drops in viscosity and fiber strength if the bleach conditions are not carefully monitored. Dahm compared the mill data to the laboratory data where the brownstock was bleached and subsequently beaten. The graphical data from the study are shown in **Figure 10**, which is updated into equivalent TAPPI T230 viscosity [10].

Dahm [18] looked at both the individual tensile and tear strengths, as well as the tensile-tear product, versus pulp viscosity. The tear of the bleach plant pulps after the H stage uniformly decreased as the pulp viscosity decreased below 22 mPa·s (TAPPI T230). A similar trend is observed for tensile when the pulp viscosity dipped below 14 mPa·s (TAPPI T230). This is more compactly shown in **Figure 10**, along with the laboratory data to show the individual effects of fiber strength and fiber-fiber bonding. The tear-tensile product helps to normalize differences in the two strength parameters for the bleach plant pulps. Including the laboratory data helps to estimate the effects of fiber-fiber bonding level. Data analysis showed that the papermaking strength of the pulps with viscosities above 14 mPa·s are similar, whereas pulps with viscosities below 14 mPa·s became weaker as viscosity decreased.

The Dahm study with the chlorine-hypochlorite bleach plant represents an extreme when compared to today's bleacheries. Modern ECF sequences use more selective bleaching agents than sodium hypochlorite, such as chlorine dioxide, which minimally attacks the carbohydrates. Marcoccia and co-workers [52] conducted softwood fiberline audits on six North American bleach plants in order to determine how bleaching affected pulp strength delivery. The authors collected samples after brownstock washing (BS), oxygen delignification (O), extraction after chlorine dioxide delignification ( $D_0E_1$ ), and the final chlorine dioxide ( $D_2$ ) stage. The samples were tested for viscosity and zero span tensile, as well as beaten and made into handsheets for physical testing. **Figure 11** is a plot of the viscosity or relative zero-span against the relative tear index to the brownstock (BS) pulp. Viscosity values did not correlate to the relative tear index (at fixed tensile 90 N·m/g). Likewise, there was no relationship between relative zero-span tensile to relative tear (not shown). Pulp viscosity shows a somewhat linear relationship to the relative zero-span tensile over the 18 to 36 mPa·s range (not shown). The above data analysis suggests that losses in inherent fiber strength, as measured by drops in pulp viscosity or zero-span tensile, are not great enough to contribute to overall pulp strength delivery.

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## REFERENCES

1. Rydholm, S. A., *Pulping Processes*, Interscience Publishers, New York, NY, pp. 1118–1120, and 1152–1166 (1965).
2. Seymour, G.W., “Bleach plant testing, control and instrumentation,” In: *The Bleaching of Pulp*, 2nd Ed. (W.H. Rapson, Ed.), Technical Association of the Pulp and Paper Industry, New York, NY, pp. 360–378 (1963).
3. Reeve, D.W., “Bleaching technology,” In: *Pulp and Paper Manufacture, Vol. 5 Alkaline Pulping* (T.M. Grace, B. Leopold, and E.W. Malcolm, Tech. Eds.), 3rd edn., Joint Textbook Committee of the Paper Industry, TAPPI PRESS, Atlanta, GA, pp. 391–424 (1989).
4. Tasman, J.E., “Evaluation of raw materials and product quality,” In: *Pulp and Paper Manufacture, Vol. 9 Mill Control & Control Systems: Quality & Testing, Environmental, Corrosion, Electrical* (M. Kouris, Tech. Ed.), 3rd edn., Joint Textbook Committee of the Paper Industry, TAPPI PRESS, Atlanta, GA, pp. 48–84 (1992).
5. Fahey, M.D., “How bleaching can change pulp strength,” In: *1992 Bleach Plant Operations Short Course*, TAPPI PRESS, Atlanta, GA, pp. 55–68 (1992).
6. Annergren, G.E., “Strength properties and characteristics of bleached chemical and (chemi)mechanical pulps,” In: *Pulp Bleaching: Principles and Practice* (C.W. Dence and D.W. Reeve, Eds.), TAPPI PRESS, Atlanta, GA, pp. 719–748 (1996).
7. Sjoström, J. and Brodin, A., “Bleached pulp composition and its determination,” In: *Pulp Bleaching: Principles and Practice* (C.W. Dence and D.W. Reeve, Eds.), TAPPI PRESS, Atlanta, GA, pp. 677–693 (1996).
8. Lapiere, L., Bouchard, J. and Berry, R., “On the relationship between fibre length, cellulose chain length and pulp viscosity of a softwood sulfite pulp,” *Holzforschung* 60(4):372–377 (2006). DOI: 10.1515/HF.2006.058
9. Lapiere, L., Bouchard, J. and Berry, R., “The relationship found between fibre length and viscosity of three different commercial kraft pulps,” *Holzforschung* 63(4):402–407 (2009). DOI: 10.1515/HF.2009.072
10. Sihtola, H., Kyrklund, B., Laamanen, L., Palenius, I., “Comparison and conversion of viscosity and DP-values determined by different methods,” *Paperi ja Puu* 45(4a): 225–232 (1963).
11. Oglesby, R. J., Moynihan, H.J., Santos, R. B., Ghosh, A. and Hart, P.W., “Does kraft hardwood and softwood pulp viscosity correlate to paper properties?,” *TAPPI JOURNAL* 15(10):643–651 (2016). DOI: 10.32964/tj15.10.643
12. Seth, R. S. and Chan, B. K., “Measuring fiber strength of papermaking pulps,” *TAPPI Journal* 82(11):115–120 (1999).
13. Gurnagul, N., Page, D. and Paice, M., “The effect of cellulose degradation on the strength of wood pulp fibers,” *Nordic Pulp and Paper Research Journal* 7(3):152–154 (1992). DOI: 10.3183/NPPRJ-1992-07-03-p152-154
14. Gurnagul, N. and Page, D., “The difference between dry and rewetted zero-span tensile strength of paper,” *TAPPI Journal* 72(12):164–167 (1989).
15. Flink, J. and Norborg, K., “Bleaching—Quality and environmental aspects,” In: *3rd European Workshop on Lignocellulosics and Pulp (EWLP)*, Stockholm, Sweden, pp. 125–129 (1994).
16. Valeur, C., “Cooking of bleachable kraft pulp” (in Swedish), *Svensk Papperstidning* 54(18):613–620 (1951).
17. Otero D’Almeida, M. L., “Pulp viscosity and paper strength” (In Portuguese), *O Papel* 47(8):39–42 (1986).
18. Dahm, H. P., “On the relation between pulp viscosity and paper strength of sulfate pulp degraded by chlorine-hypochlorite bleaching,” *Norsk Skogindustri* 13(6):188–192 (1959).
19. Fossum, G. and Marklund, A., “Pretreatment of kraft pulp is the key to easy final bleaching,” *Tappi Journal* 75(11):79–84 (1988).
20. Lindholm, C.-A., “Effect of pulp consistency and pH in ozone bleaching: Part 6. Strength properties,” *Nordic Pulp & Paper Research Journal* 5(1):22–27 (1990). DOI: 10.3183/npprj-1990-05-01-p022-027
21. Liebergott, N., van Lierop, B., Teodorescu, G. and Kubes, G.J., “Oxygen delignification of kraft pulps—Effect of variables on pulp quality,” In: *International Oxygen Delignification Conference*, TAPPI PRESS, Atlanta, GA, pp.231–244 (1987).
22. Liebergott, N., van Lierop, B., and Skothos, A., “A survey of the use of ozone in bleaching pulps, Part 2,” *Tappi Journal* 75(2):117–124 (1992).
23. Nanko, H., Button, A. and Hillman, D., “Market pulp atlas,” In: *The World of Market Pulp* (C.E. Swann, Ed.), 3rd edn., WOMP, LLC, Appleton, WI, 2005, pp. 137–262 (2005).

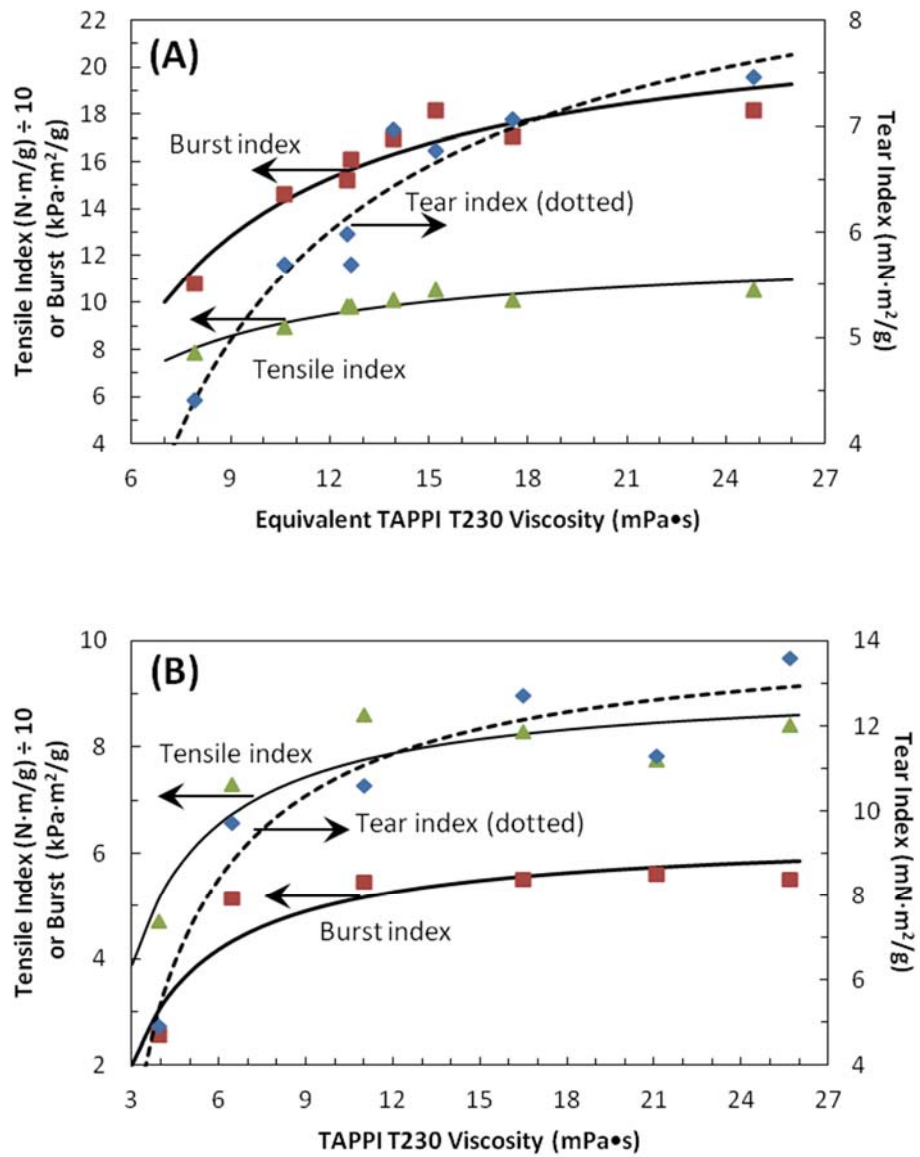
24. Staudinger, H. and Schweitzer, O., "About high-polymer compounds, Part 48: About the molecular size of cellulose" (in German), *Berichte der deutschen chemischen Gesellschaft (A and B Series)* 63(11):3132–3154 (1930). DOI: 10.1002/cber.19300631129
25. Immergut, E. H., Ranby, B. G. and Mark, H.R., "Recent work on molecular weight of cellulose," *Industrial and Engineering Chemistry* 45(11):2483–2490 (1953). DOI: 10.1021/ie50527a036
26. Immergut, E.H., Schurz, J. & Mark, H., "Viscosity number-molecular weight relationship for cellulose and studies of nitrocellulose in various solvents" (in German), *Monatshefte für Chemie* 84:219–249 (1953). DOI:10.1007/BF00899186
27. Evans, R. and Wallis, A. F. "Cellulose molecular weights determined by viscometry," *Journal of Applied Polymer Science* 37(8):2331–2340 (1989). DOI: 10.1002/app.1989.070370822
28. Evans, R., Wearne, R.H., Wallis, A.F.A., "Molecular weight distribution of cellulose as its tricarbonyl by high performance size exclusion chromatography," *Journal of Applied Polymer Science* 37(12):3291–3303 (1989). DOI: 10.1002/app.1989.070371202
29. Swenson, H. A., "Viscosity-strength relation in bleached pulps. I," *Svensk Papperstidning* 78(2): 61–65 (1975).
30. Swenson, H. A., "Viscosity-strength relation in bleached pulps. II," *Svensk Papperstidning* 78(2):103–104 (1975).
31. da Silva Perez, D. and van Heiningen, A. R. P., "Determination of cellulose degree of polymerization in chemical pulps by viscometry," *7th European Workshop on Lignocellulosics and Pulp (EWLP)*, Turku, Finland, pp. 393–396 (2002).
32. SCAN Standard C15:62, "Viscosity of cellulose in cupriethylenediamine solution (CED)," Secretariat Scandinavian Pulp, Paper and Board Testing Committee, SCAN Testing Standards, Stockholm, Sweden (1962).
33. TAPPI Method T230 om-99, "Viscosity of pulp (capillary viscometer method)," *TAPPI Test Methods*, TAPPI Press, Atlanta, GA (2012).
34. TAPPI Method T254 cm-10, "Cupriethylenediamine disperse viscosity of pulp (falling ball method)," *TAPPI Test Methods*, TAPPI Press, Atlanta, GA (2012).
35. Montet, E., *Investigation of the Consequences of the Use of Ozone in the Bleaching of Cellulosic Fibers*, Ph.D. Dissertation, Université Grenoble Alpes, Grenoble, France (2021).
36. Page, D.H., "A theory for the tensile strength of paper," *Tappi* 52(4):674–681 (1969).
37. Jones, A.J., "Strength evaluation of unbleached kraft pulps," *Tappi* 55(10):1522–1527(1972).
38. McKenzie, A.W., "Interpretation of pulp evaluation results," *Appita Journal* 38(4):284–290 (1985).
39. Mohlin, U.-B., Molin, U. and De Puiseau, M.W., "Some aspects of using zero-span tensile index as a measure of fiber strength," In: *2003 International Paper Physics Conference Preprints*, PAPTAC, Montreal, PQ, pp. 107–113 (2003).
40. Sookne, A. M., and Harris, M., "Polymolecularity and mechanical properties of cellulose acetate," *Industrial and Engineering Chemistry* 37(5):478–482 (1945). DOI: 10.1021/ie50425a026
41. Flory, P. J., "Tensile strength in relation to molecular weight of high polymers," *Journal of the American Chemical Society* 67(11):2048–2050 (1945). DOI: 10.1021/ja01227a506
42. Flory, P. J., "Effects of molecular structure on physical properties of butyl rubber," *Industrial and Engineering Chemistry* 38(4):417–436 (1946). DOI: 0.1021/ie50436a023
43. Nunes, R. W., Martin, J. R., and Johnson, J. F., "Influence of molecular weight and molecular weight distribution on mechanical properties of polymers," *Polymer Engineering and Science* 22(4):205–228 (1982). DOI: 10.1002/pen.760220402
44. Martin, J. R., Johnson, J. F. and Cooper, A. R., "Mechanical Properties of Polymers: The Influence of Molecular Weight and Molecular Weight Distribution," *Journal of Macromolecular Science, Part C* 8(1):57–199 (1972), DOI: 10.1080/15321797208068169
45. Nguyen, T.Q. and Kausch, H.H., "Molecular weight distribution and mechanical properties," In: *Mechanical Properties and Testing of Polymers: An A-Z Reference* (Swallowe, G.M., Ed.), Kluwer Academic Publishers, Norwell, MA, pp. 143–150 (1999). DOI: 10.1007/978-94-015-9231-4\_32
46. Iribarne, J. and Schroeder, L. R., "High-pressure oxygen delignification of kraft pulps," *Tappi Journal* 80(10):241–250 (1997).
47. Berggren, R. *et al.*, "Fiber strength in relation to molecular mass distribution of hardwood kraft pulp," *Nordic Pulp & Paper Research Journal* 16(4):333–338 (2001). DOI: 10.3183/npprj-2001-16-04-p333-338



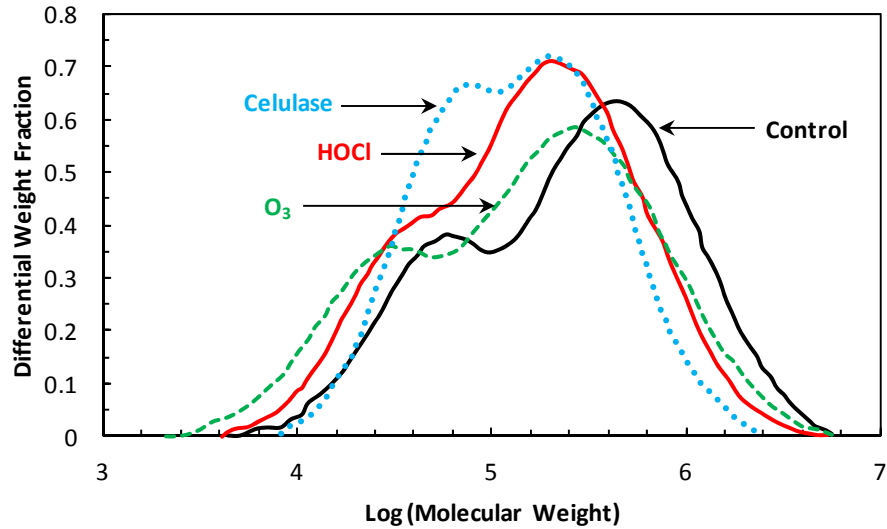
48. Sjöholm, E., Gustafsson, K. et al. "Fibre strength in relation to molecular weight distribution of hardwood kraft pulp. Degradation by gamma irradiation, oxygen/alkali or alkali," *Nordic Pulp & Paper Research Journal* 15(4):326–332 (2000). DOI: 10.3183/npprj-2000-15-04-p326-332
49. Godsay, M. P. and Pearce, E. "Physico-chemical properties of ozone oxidized kraft pulps," In: *TAPPI Oxygen Delignification Symposium Notes*, TAPPI PRESS, Atlanta, GA, pp. 55–70 (1984).
50. Seth, R.S. and Page, D.H., "Fiber properties and tearing resistance," *Tappi Journal* 71(2):103–107 (1988).
51. Page, D.H. and MacLeod, J.M. "Fiber strength and its impact on tear strength," *Tappi Journal* 75(10):172–174 (1992).
52. Marcoccia, B., Sweeney, B., and Lowe, R., "On the use of laboratory references for predicting and measuring the performance of bleach plant operations. Part I: The effects of bleaching on pulp strength," In: *1996 International Pulp Bleaching Conference*, TAPPI PRESS, Atlanta, GA, pp. 53–62 (1996).

**Table I.** Average molecular weight ( $\bar{M}$ ) and degree of polymerization ( $\bar{DP}$ ) of the carbohydrates from a bleached hardwood kraft pulp (control) treated with O<sub>3</sub>, HOCl or cellulase enzyme [10]. Data from Montet's Ph.D. dissertation [35]. Treatments conducted to result in yield intrinsic viscosity value of *ca.* 582 mL/g. The molecular weight distributions for these pulps are given in Fig. 2.

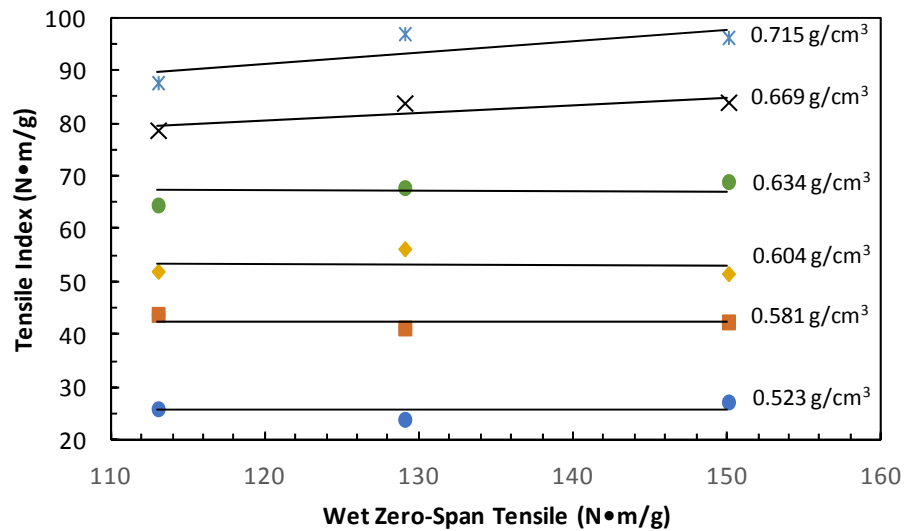
Treatment	Intrinsic viscosity (mL/g)	Estimated T230 viscosity (mPa·s)	Average Molecular Weight (g/mole)			Average DP			Wet Zero-Span Tensile (N·m/g)
			$M_r$	$M_n$	$M_w$	$DP_v$	$DP_n$	$DP_w$	
Control (none)	895	19.0	222,000	90,700	536,000	1370	560	3310	34.9
O <sub>3</sub>	587	9.0	139,000	50,200	410,000	860	310	2530	31.4
HOCl	570	8.6	134,000	81,000	290,000	830	500	1790	32.0
Cellulase	593	9.2	141,000	89,100	277,000	870	550	1710	21.3



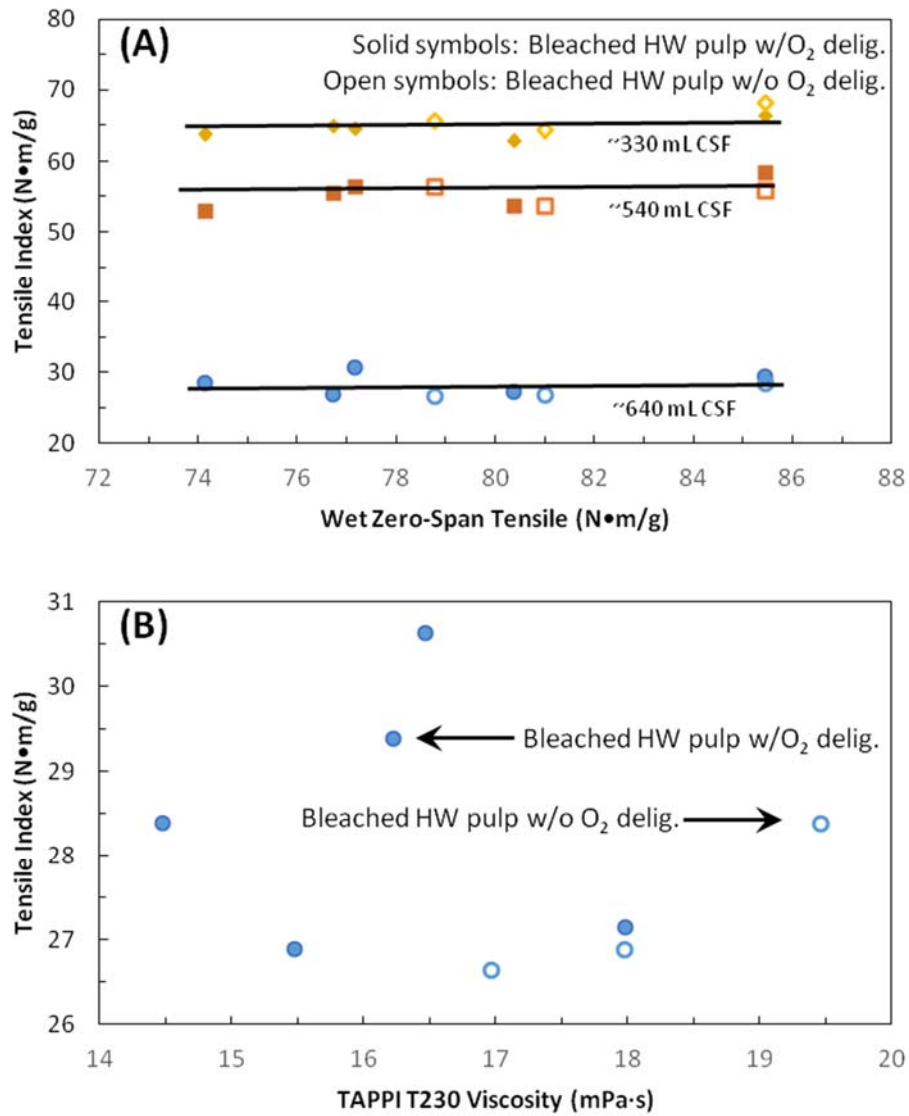
**Figure 1.** Correlations of physical handsheet strength properties to pulp viscosity: (A) data from Valeur [16] that examined a bleached softwood kraft pulp with CEHD sequence; and (B) data from Otero D'Almeida study [17] that examined a eucalypt pulp bleached with CEHD sequence. Data from Valeur was converted to equivalent TAPPI T230 viscosity using Sihtola *et al.* procedure [10].



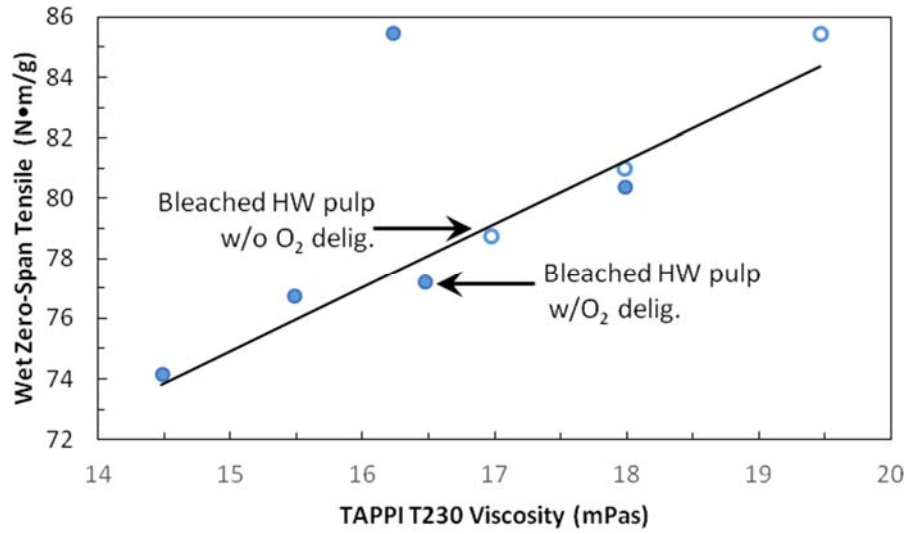
**Figure 2.** Logarithmic molecular weight distributions of the carbohydrates from a bleached hardwood kraft pulp (control) treated with  $O_3$ , HOCl or cellulase enzyme [10]. Data from Montet's Ph.D. dissertation [35]. Treatments conducted to result in yield intrinsic viscosity value of *ca.* 582 mL/g. Data on various average  $DP$  and  $M$  values are listed in Table I.



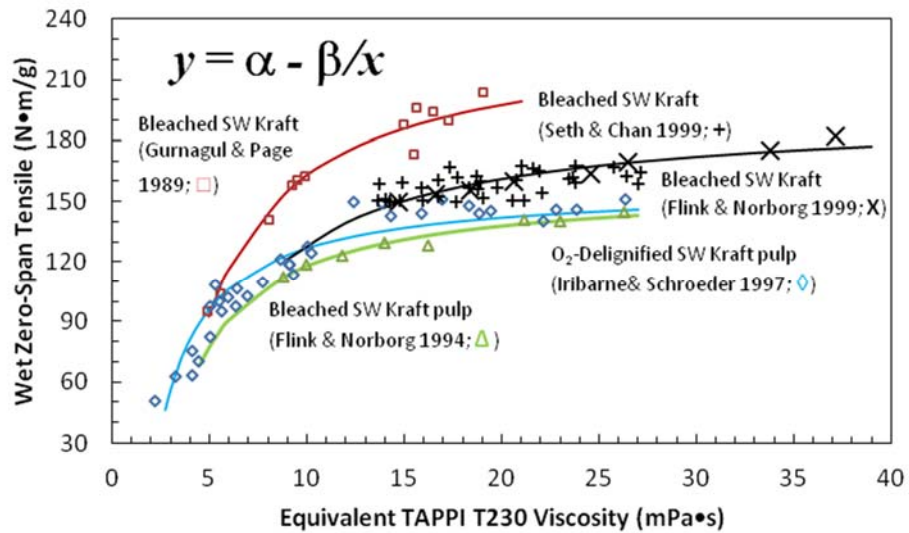
**Figure 3.** Wet zero-span tensile ( $N\cdot m/g$ ) versus tensile index ( $N\cdot m/g$ ) for MacKenzie softwood kraft pulp data [38] at different fiber bonding levels as denoted by apparent sheet density ( $g/cm^3$ ). Untreated control had wet zero-span of 150  $N\cdot m/g$ . Controls treated with cold liquid HCl at two levels to obtain weakened fibers with wet zero-spans of 129 and 113  $N\cdot m/g$ . Lower fiber strength did not affect the tensile index. It was only the most severe acid treatment and highest sheet densification (*i.e.* 0.715  $g/cm^3$ ) that fiber strength becomes apparent.



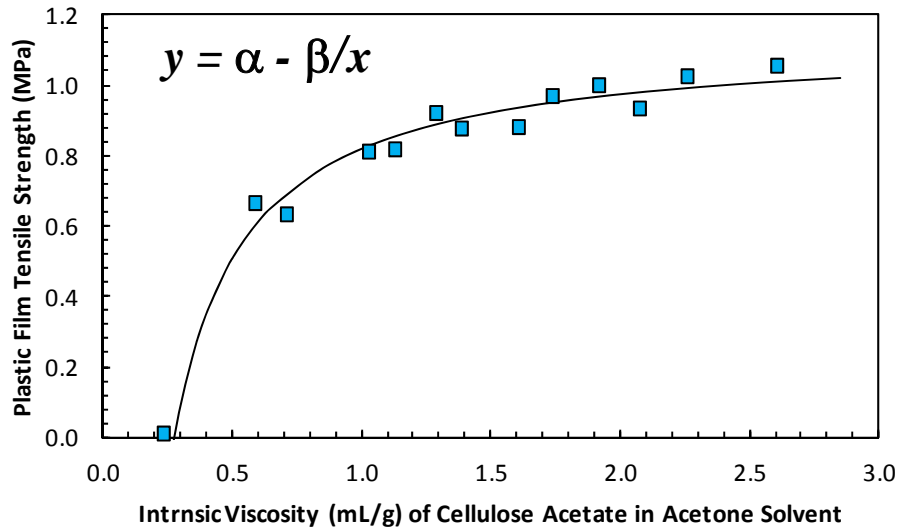
**Figure 4.** Wet zero-span tensile (A) or pulp viscosity (B) versus tensile index for Oglesby *et al.* bleached hardwood kraft pulp data [11] at different fiber bonding levels (denoted by Canadian standard freeness (CSF)). Tensile index unaffected by intrinsic fiber strength measured by wet zero-span or pulp viscosity.



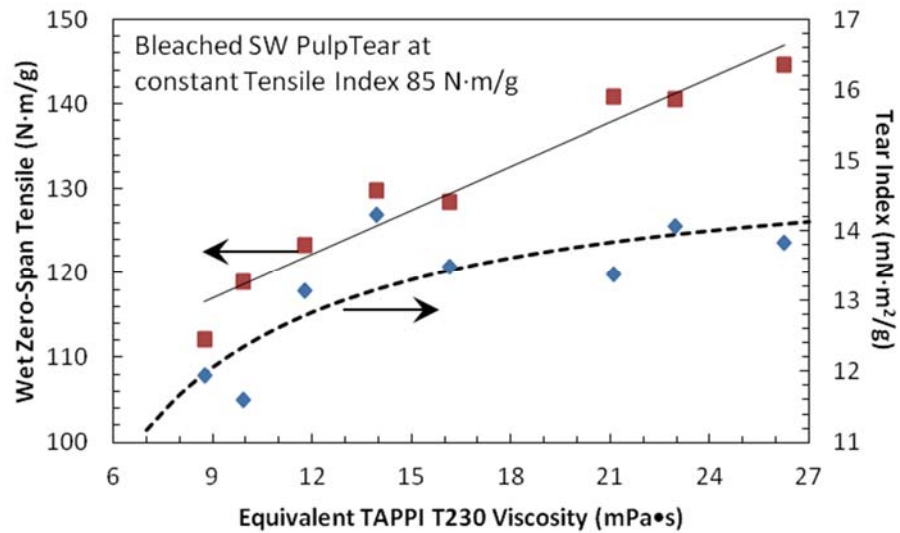
**Figure 5.** Pulp viscosity versus wet zero-span tensile for Oglesby *et al.* bleached hardwood kraft pulp data [11].



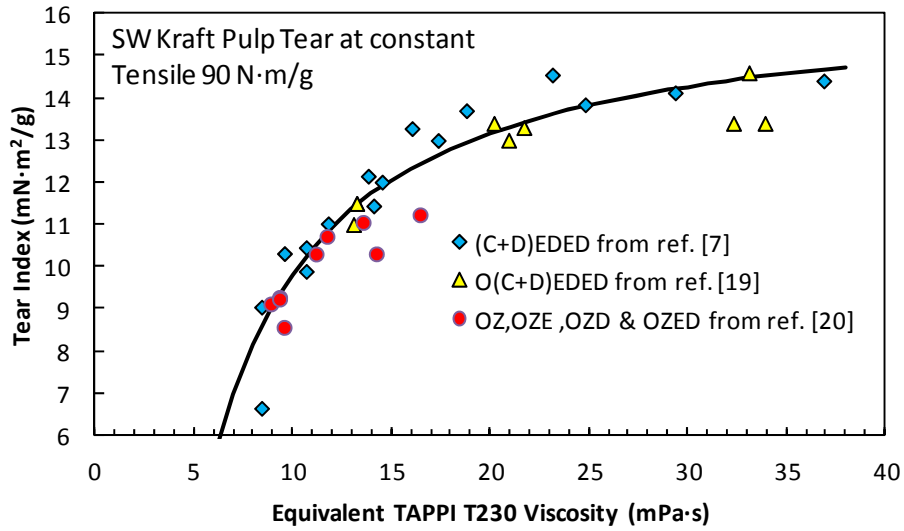
**Figure 6.** Pulp viscosities over a wider range versus wet zero-span tensile indices for oxygen delignified or bleached softwood kraft pulps. The relationship between viscosity and wet zero-span follows Eq. 4, which is a similar nonlinear behavior observed for intrinsic viscosity-tensile strength for polymeric materials.



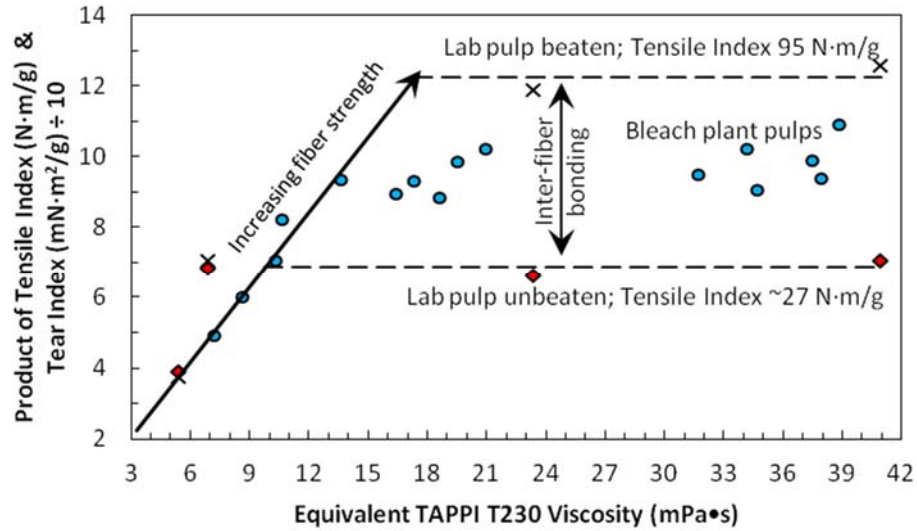
**Figure 7.** Intrinsic viscosity versus tensile for polymeric cellulose acetate films. Data from Sookne and Harris study [40]. Nonlinear trend line follows Eq. 4.



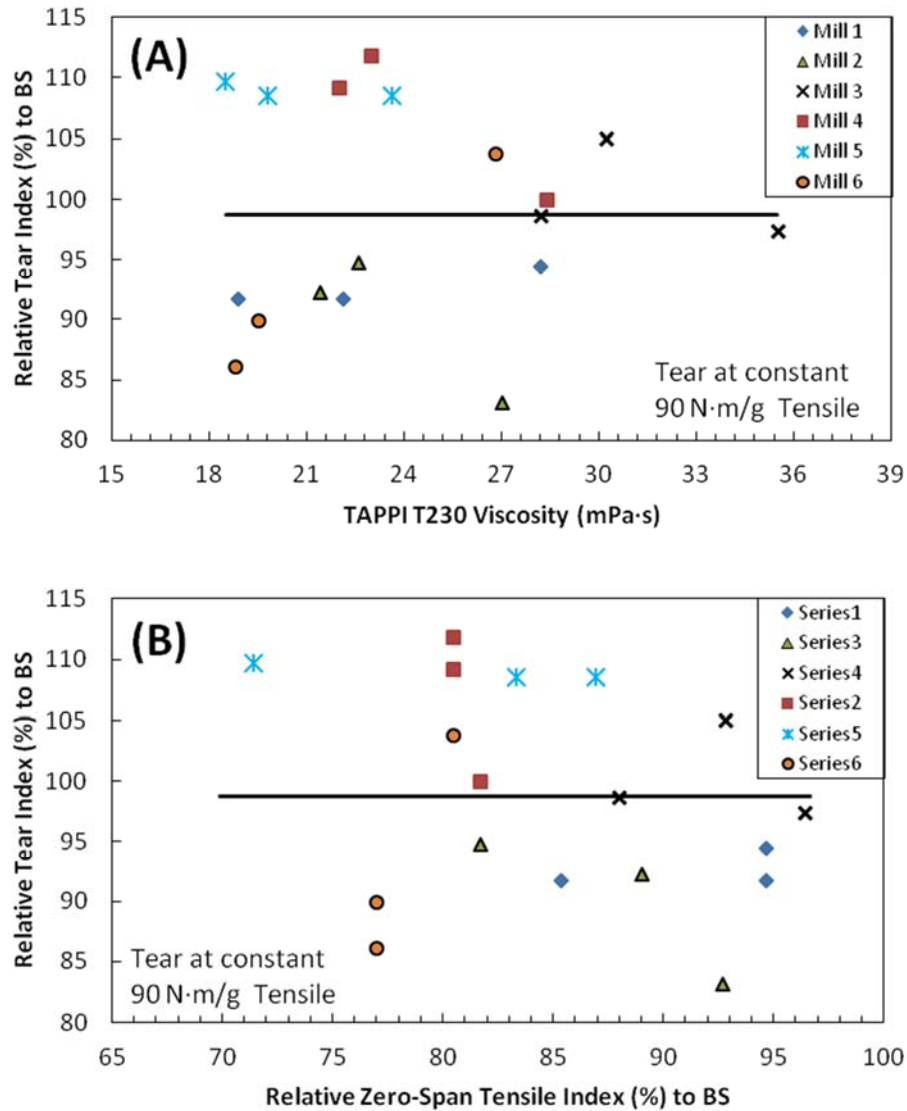
**Figure 8.** Relationships of pulp viscosity versus tear index and wet zero-span tensile for softwood kraft pulp bleached with different sequences. Data from Flink and Norborg study [40] where reported SCAN intrinsic viscosities converted to equivalent TAPPI T230 viscosities [10].



**Figure 9.** Relationships of pulp viscosity over a wide range versus wet zero-span tensile for softwood kraft pulp bleached with different sequences. Data from Sjostrom and Brodin [7], Fossum and Marklund [19], and Lindholm [20] studies where reported SCAN intrinsic viscosities converted to equivalent TAPPI T230 viscosities [10].



**Figure 10.** Relationship of pulp viscosity to tensile-tear product for bleach plant softwood kraft pulp. Data from Dahm [18] who examined pulp viscosities of pulps after the CEH bleach sequence and compared handsheet strength data to laboratory data. Data was converted to SI units and to equivalent TAPPI T230 viscosity using Sihtola *et al.* procedure [10].



**Figure 11.** Mill audit data from Marcoccia *et al.* study [53] who examined six different North American fiber lines using generic O(C+D)E<sub>1</sub>D<sub>1</sub>E<sub>1</sub>D<sub>2</sub> sequence to bleach softwood kraft pulps to full brightness. Authors examined samples after brownstock washing (BS), oxygen delignification (O), first extraction stage (E<sub>1</sub>) and final chlorine dioxide stage (D<sub>2</sub>). Relative tear index is the tear index value relative to BS. As the BS goes through the bleach plant (right to left), the pulp viscosity decreases. In most cases, the decrease in viscosity does not correspond to changes in relative tear index. Viscosity values in the above cases are >15 mPa·s, the critical threshold where softwood fiber strength become noticeable. Similar trends with relative zero-span tensile.