**Preferred citation:** R. Wathén, O. Joutsimo and T. Tamminen. Effect of different degradation mechanisms on axial and z-directional fiber strength. In **Advances in Paper Science and Technology**, *Trans. of the XIIIth Fund. Res. Symp. Cambridge, 2005*, (S.J. I'Anson, ed.), pp 631–647, FRC, Manchester, 2018. DOI: 10.15376/frc.2005.1.631.

# EFFECT OF DIFFERENT DEGRADATION MECHANISMS ON AXIAL AND Z-DIRECTIONAL FIBER STRENGTH

*Rolf Wathén, Olli Joutsimo and Tarja Tamminen*

KCL Science and Consulting, P.O.Box 70, FIN-02151 ESPOO, FINLAND

## ABSTRACT

We have exposed pulp handsheets to two different degradative treatments, and compared their effects on strength properties. In accordance with earlier research, tensile stiffness and the shape of the stress-strain curve were independent of cellulose chain length and the fiber defects caused by the degradative treatments. When evaluated at the same viscosity, we found acid vapor treatment to be more detrimental to axial fiber strength than ageing treatment at elevated temperature and humidity. At the same mean fiber strength, acid vapor-treated handsheets show higher tensile strength. This is because acid vapor treatment is more heterogeneous than ageing treatment. The fiber network is able to compensate for the local defects, but not for the general degradation in fiber strength. In both treatments the mechanism for cellulose cleavage is assumed to be acid hydrolysis, the difference in the effect on fibers coming from the treatment conditions. Acid vapor treatment induces a fast reaction at defect sites and discontinuities in a fiber, while ageing treatment induces a slow, more homogeneous hydrolysis in fibers. Unlike axial strength, the Z-directional strength of softwood decreases only after harsh degradation when viscosity has dropped below 400 ml/g. The Z-directional strength of hardwood is already compromised at a viscosity of around 700 ml/g. The differences probably arise from differences in fiber ultrastructure.

## 1 INTRODUCTION

Cellulose chains are the smallest building blocks of the load-carrying fiber elements. Cellulose chains form microfibrils, which further form fibrils (or fibril aggregates). Hemicelluloses and lignin act as a stress transfer matrix between these, and together they form the fiber ultrastructure. In industrial pulping processes, delignification and bleaching chemicals attack cellulose to some extent. This leads to lower average cellulose chain length, typically detected as viscosity loss. Viscosity alone does not define the strength properties of fibers [1]. Different types of fiber defects have a strong influence on fiber strength [2], dominating over cellulose chain length. Joutsimo has recently shown that actually the main reason for strength losses on kraft pulp lines is the fibers' exposure to mechanical stress [3].

According to Berggren [4–6], the cellulose degradation pattern depends on the conditions inducing the degradation. Thus, the same average cellulose chain length may result from, say, acidic or oxidative alkaline pulp treatment. However, in the case of acidic degradation, cellulose damage is localized at certain points, whereas alkaline degradation is homogeneous throughout the cellulose fibrils [4–6]. As a result of these different degradation patterns, acidic degradation is far more detrimental to fiber strength when evaluated at the same average cellulose chain length. The effect of acid depends on the acid species, acid concentration, exposure time and temperature [7].

Gurnagul et al. [8] have studied the effect of different cellulose degradation methods on fiber strength. They used kraft cooking, vapor and liquid-based acid hydrolysis and enzyme treatment to degrade chemical pulp fibers. Their results indicate that enzyme treatment and liquid-based acid hydrolysis degrade fibers more heterogeneously than kraft cooking and vapor-based acid hydrolysis. The latter two treatments are said to cause homogeneous degradation of fibers.

Ander and Daniel [9] used liquid based HCl treatment to induce fiber cleavage. Depending on the HCl concentration and treatment time, the number of cleavages per fiber at 80°C varied from 0 with 0.1M HCl and 4h treatment time to 6.34 with 2M HCl and 4h treatment time. The number of cleavages was used to characterize the number of dislocations and other weak points since HCl cleaves fibers at these locations.

Seth and Page [10] used vapor-based acid hydrolysis in degrading fibers.

This procedure is particularly interesting for this kind of study because it is performed on handsheets and not pulps. Network structure, drying stresses, level of bonding and fiber activation all depend on fiber properties. Altering fiber properties before sheeting thus influences the structure and type of sheets formed. This introduces a speculation factor into the analysis of measurements – for example, has fiber tensile stiffness decreased or are the fibers simply less activated? During pulp treatments hemicelluloses dissolve, thus changing the chemical composition of the fibers. This does not occur when handsheets are treated. Treating handsheets with hydrochloric acid vapor has been shown not to affect fiber tensile stiffness [10, 11] based on the fact that the tensile stiffness of handsheets did not change. After very harsh treatment, however, a decrease in tensile stiffness has been observed [11]. According to [10], inter-fiber bonding is unaffected by acid vapor treatment if evaluated using the Page equation [12].

In the field of paper conservation it is very popular to study the effect of ageing on paper by accelerating the assumed reactions by exposing papers to warm and humid conditions for certain periods of time. Strlič has demonstrated with pullulans, which have a structure comparable to cellulose, that this leads to homogeneous degradation [13]. Zou et al. [14, 15] have studied the phenomenon and given a formula for the change in the degree of polymerization as a function of paper moisture content, temperature and activation energy. Barański [16] has applied the formula to various papers.

As mentioned above, if pulp properties are changed before sheeting, the properties affecting network formation are also likely to change. In addition to acid vapor and ageing treatments, gamma-irradiation has been used to degrade handsheets by Sjöholm et al. [17], who also applied alkali and oxygen/alkali degradations to pulps. Gamma-irradiation led to homogeneous degradation of the pulps.

In this study, we used two cellulose degradation methods for spruce fibers and one for birch. The idea was to investigate the effect of the cellulose degradation methods and patterns on fiber strength properties. We used acid vapor hydrolysis as well as thermal ageing treatment. Since network structure affects measured handsheet properties, degradation treatments were performed with handsheets instead of pulps in order to ensure a constant network structure. Based on our measurement results, we discuss the effect of the different degradation mechanisms on axial and Z-directional fiber strength. We also discuss acid-labile fiber strengthening interactions between hemicelluloses and cellulose, confirming an earlier finding by Zou et al. [14, 15] that they do not exist in fibers.

## 2 EXPERIMENTAL

We prepared standard handsheets from spruce and birch pulps according to ISO 5269–1. The pulps were produced in the laboratory from sawmill chips and bleached at low consistency with a DED sequence to ca. ISO 80% brightness. Before sheeting the fibers were refined in a PFI refiner to ensure adequate bonding (3000 revolutions for spruce and 2000 for birch).

The handsheets were subjected to two different degradation methods:

1. Spruce and birch pulp handsheets were exposed to hydrochloric acid vapor in a desiccator.
2. Spruce handsheets were placed in a temperature and humidity controlled oven.

Acid vapor treatment was performed by placing a container with 200 ml of concentrated HCl in the bottom of a desiccator. Handsheets were hung on a rack from small holes punched in their corners, and the rack was placed inside the desiccator for a specified time. After removal from the desiccator the sheets were aerated and conditioned at 23°C and 50% RH. Treatment times in minutes were 3:45 (spruce only), 7:30, 15 (spruce only), 120, 240, 480 and 960 minutes. A further test point was obtained for birch handsheets exposed to HCl for a very short undetermined time.

Thermal treatment was performed only for spruce handsheets. The handsheets were placed in an oven at 80°C and 65% RH for 5 and 10 days and at 90°C and 80% for 1, 2, 5 and 6 days. After treatment the handsheets were aerated and conditioned.

The following tests were performed on the handsheets at 23°C and 50% RH:

- Wet and dry zero-span strengths according to ISO15361 for fiber strength.
- Tensile strength, breaking strain, tensile stiffness and fitted stress-strain curves were measured according to SCAN-P 67:93 using an L&W fracture toughness tester.
- Modified Scott-Bond measurement TAPPI T 833 to characterize Z-directional fiber strength and bonding.
- Pulp viscosities were determined according to ISO 5351–1 to evaluate the extent of the degradation.

## 3 RESULTS AND DISCUSSIONS

Fibers in the handsheets were degraded using two different methods, 1) by ageing at elevated temperature and humidity and 2) by exposure to acid vapor in a desiccator. According to Strlič [13], the ageing treatment leads to homogeneous degradation. Gurnagul et al. [8] say that acid vapor treatment of handsheets also leads to homogeneous degradation of fibers, but that acid treatment in the liquid phase results in heterogeneous degradation. The latter finding is attributed to acid hydrolysis occurring at kinks and nodes. Nyholm et al. conclude in a review article that dislocations may contain cracks that facilitate the penetration of cell wall degrading chemicals and enzymes [18]. Our fibers were quite carefully prepared, but some irregularities and discontinuities certainly exist in the fiber structure. We consider it possible that acid vapor treatment would, at least initially, also prefer these locations, while the ageing treatment would be more homogeneous. Acid vapor induced hydrolysis is a very fast reaction compared to ageing, which also contributes to its heterogeneity.

In addition to axial strength, the Z-directional strength of fibers is important. Assuming that degradation creates defects in fibers that trigger failure in axial testing, it can also be expected that these defects will weaken the fibers in the Z-direction.

### 3.1 Fiber degradation pattern and axial fiber strength

Figure 1 shows how zero-span measurements react to decreasing viscosity. When dry zero-spans are compared at the same viscosity, acid treatment weakens the fibers more. This suggests that acid vapor accesses defects and other discontinuities, creating and enhancing local defects that cause fiber failure at lower stress than with thermal treatment. We have added two data points from [19], which fall nicely on the same line as the acid vapor-treated sheets. These data points are a gently cooked and bleached laboratory softwood pulp handsheet reference and a handsheet exposed to HCl vapor for 4 minutes.

Mohlin attributed the difference between wet and dry zero-span measurements to fiber defects [20], wet zero-span being more susceptible to fiber defects than dry zero-span. In our experiments for spruce, both treatments decreased wet zero-span strength more than dry, though with the ageing treatment the difference was larger. We hypothesize that hydrogen bonds reinforce aged fibers more effectively than they do acid vapor-treated fibers, and their removal during wetting causes the greater decrease in wet zero-span. Mohlin [20] showed wet zero-span to differ more from the dry measurement the larger the *number* of defects per fiber. This would imply that

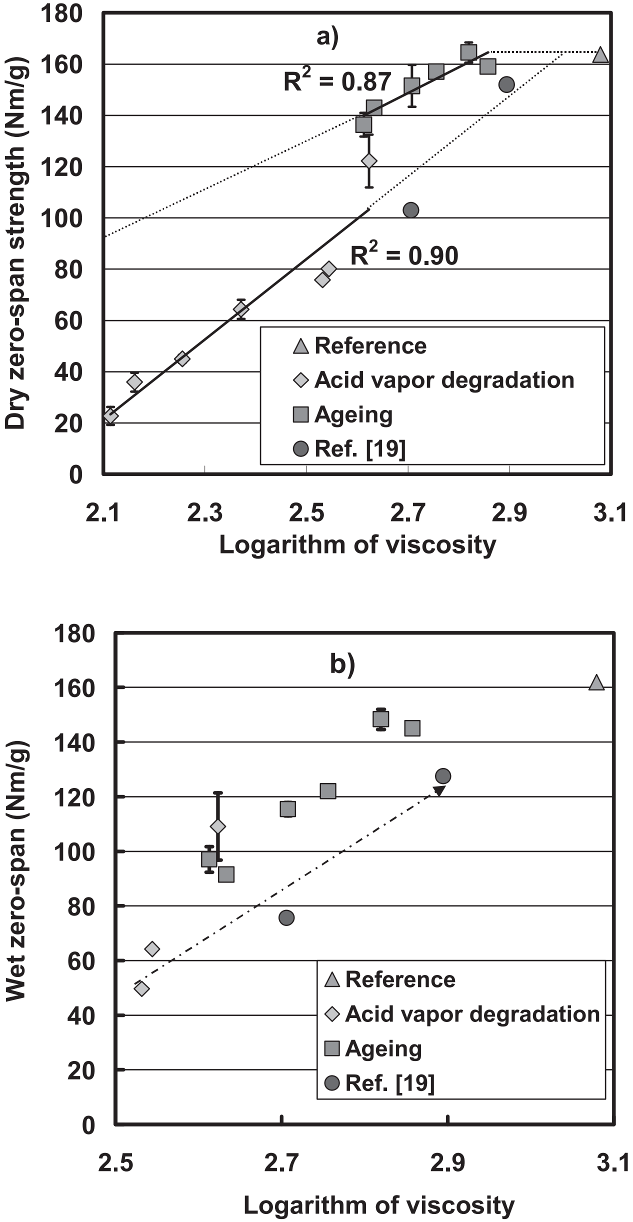


**Figure 1** Dry zero-span strength a) and wet zero-span strength b) as a function of viscosity for acid vapor-treated and aged spruce handsheets (The line in b) is not a fitted trend line but presents the assumed effect of acid vapor degradation).

there are more defects in the aged fibers than in the acid vapor-treated fibers, even though the defects measured by Mohlin are probably very different from those in our fibers. The analogy here is as follows: the more heterogeneous acid vapor treatment produces fewer but more serious fiber defects than the more homogeneous ageing treatment, which produces a larger number of smaller fiber defects.

According to Gurnagul [19], the difference between wet and dry zero-span measurements can be attributed to degradation of the hemicellulose-lignin matrix, which allows the fibrils to slide against each other in the wet state. They state that the weaker the supporting matrix, the larger the reduction in zero-span strength on wetting. With chemical pulps, this matrix has been removed to a large extent in cooking. We thus think that the contribution from the above mentioned fiber defects is larger.

For our acid degradation series of birch handsheets, the situation is very interesting indeed. Dry zero-span actually drops more than wet. We have no explanation why wet zero-span actually gives larger values than dry zero-span at initial degradation points. Figure 2 plots the two zero-span measurements against each other.

The relationship between zero-span strength and tensile strength is plotted in Figure 3. It seems that initially the ageing treatment decreases tensile index but has little impact on zero-span results, while with acid vapor the effect appears to be the opposite. When evaluated at the same fiber strength, acid vapor-treated handsheets have higher tensile strength. Both of these findings can be attributed to the different degrees of homogeneity/heterogeneity between treatments. Acid vapor produces fewer but more significant defects in the fibers, which cause the mean fiber strength to drop – although the fiber network can actually compensate for this. On the other hand, ageing treatment weakens the fibers homogeneously, which has a smaller but more uniform effect on fiber strength, but also weakens the fiber locations which in acid vapor treatment would have been left unharmed and able to help distribute the load. Data points from [11] have been added to further illustrate the relationship between fiber strength and tensile index.

To sum up, there exist three indicators that acid vapor treatment is more heterogeneous than ageing treatment:

1. Dry zero-span strength at the same viscosity is higher for aged handsheets.
2. At the same dry zero-span strength, acid vapor treatment yields higher wet zero-span strength. We hypothesize that hydrogen bonds reinforce aged fibers more effectively than they do acid vapor treated fibers, and their removal during wetting causes the larger drop in wet zero-span.

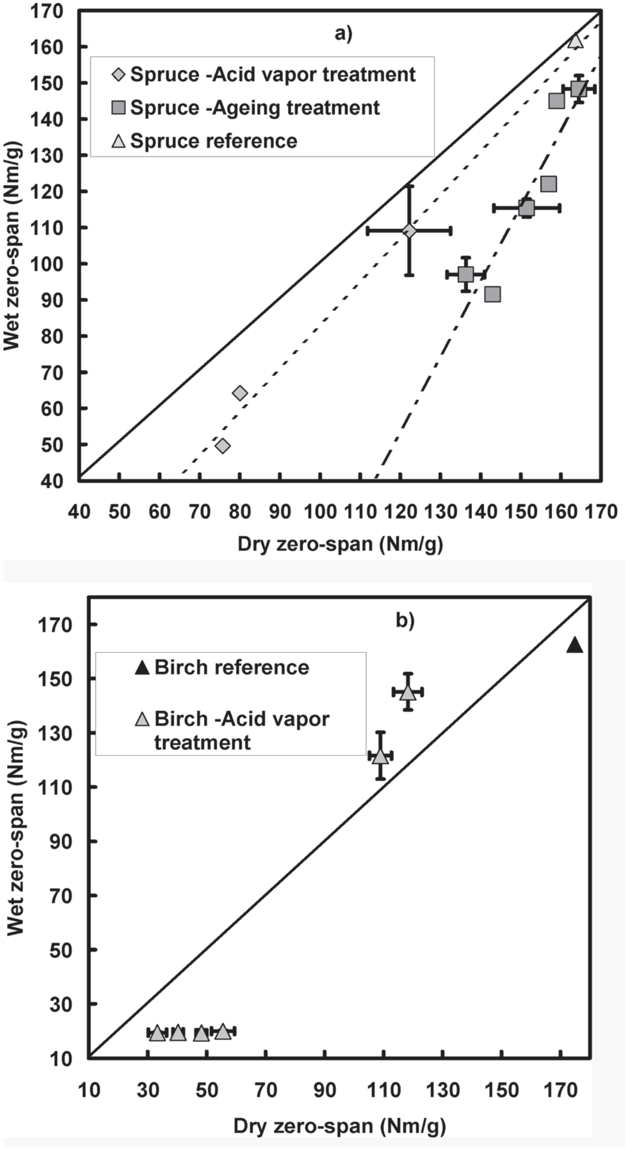


**Figure 2** Dry zero-span vs. wet zero-span measurements for spruce a) and birch b).

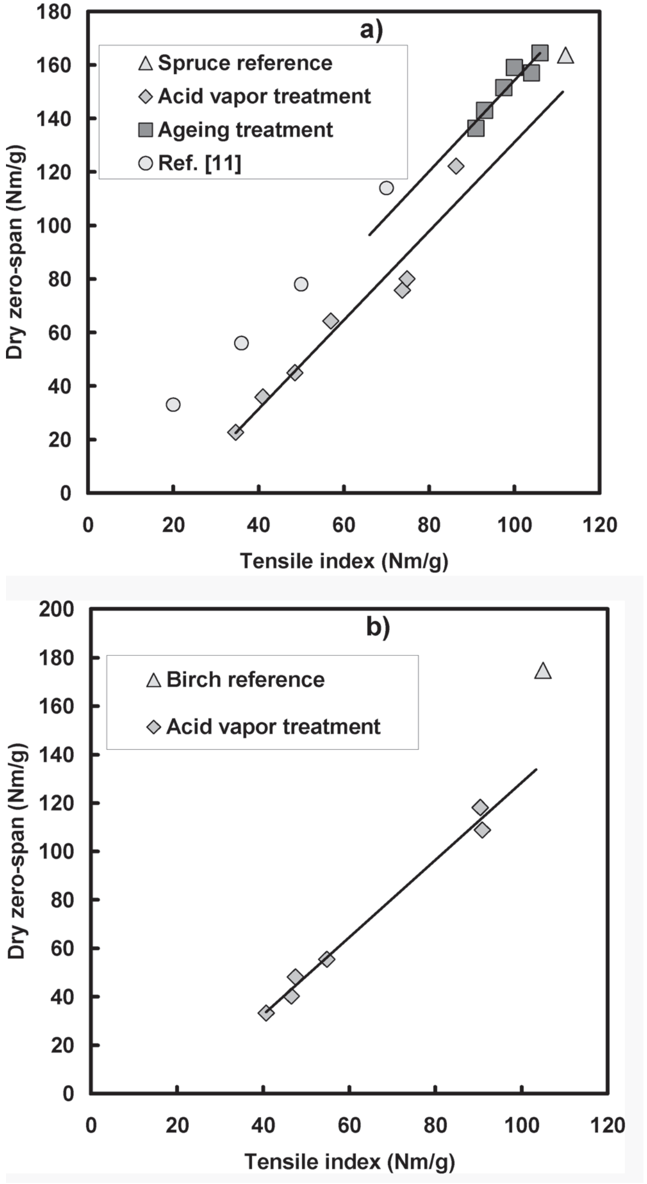


**Figure 3** Tensile index of spruce a) and birch b) handsheets vs. dry zero-span measurements. Acid vapor degraded data from [11] added for further illustration of the relationship.

3. When evaluated at the same fiber strength, dry zero-span vs. ordinary tensile strength reveals that acid vapor treated handsheets have higher tensile strength. The fiber network is able to compensate for the few larger local fiber defects, but not for the numerous smaller defects, which in combination cause network failure at lower tensions.

## 3.2 Tension-strain curves

Tension-strain (stress-strain) curves characterize fiber properties and bonding. The shape of these curves is defined by fiber properties [21]. Bonding may extend the curve, but it does not define its shape. Figure 4 shows fitted tension-strain curves for handsheets after exposure to degradative treatments.

Degradation does not change tensile stiffness, so the fibers on average do not lose their initial elastic load-bearing capability. Because all stress-strain curves overlap, fibers yield similarly independent of the degradation treatment. The break point, tensile strength and breaking strain move to a lower strength area as treatment time is increased. Since tensile stiffness was

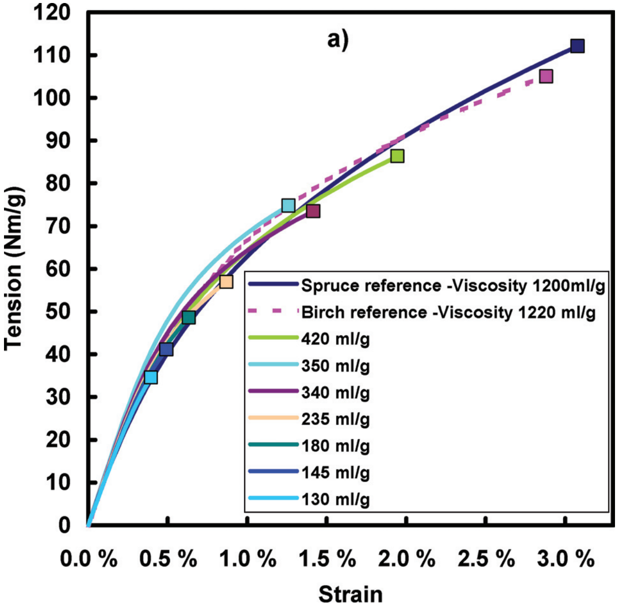


**Figure 4** Tension-strain curves and/or break points of degraded handsheets: acid vapor treated spruce a), aged spruce b) and acid vapor treated birch c).

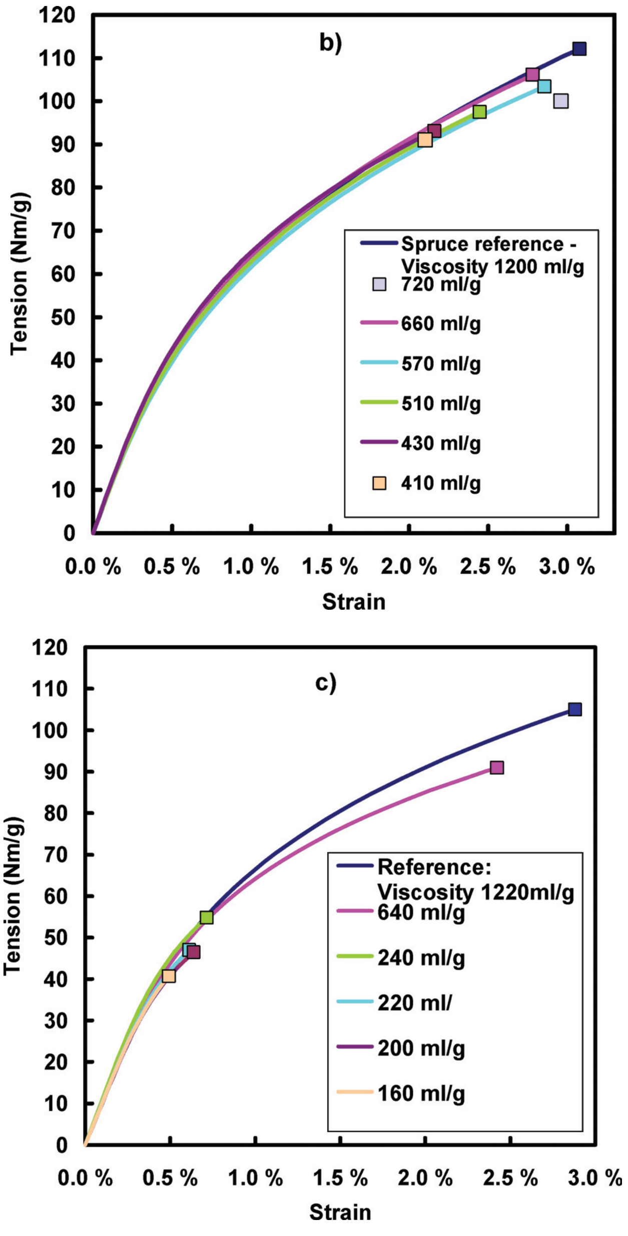


**Figure 4** Continued.

decreased in neither treatment, fiber ultrastructure must contribute decisively to fiber stiffness, while cellulose chain length and chain length distribution contribute more to strength due to the emergence of stress-concentration points (=defects) of different magnitudes.

### 3.3 Degradation pattern and Z-directional strength

Scott-Bond measures fiber bonding and Z-directional strength. According to Seth and Page [10], acid vapor degradation affects only fiber strength and not inter-fiber bonding. They base the claim on the Page equation [12]. If the Page equation is applied to our data, assuming that only fiber strength, bonding and tensile index can change, the claim that acid vapor treatment has no effect on bonding is not valid. However, Figure 5a below indicates that no change in inter-fiber bonding or Z-directional fiber strength occurred above viscosities of 400 ml/g for spruce and 700 ml/g for birch. Therefore either the Page equation is not applicable here, or else one of its parameters changes, probably fiber length (or rather *effective* fiber length). Figure 3 above showed a linear relationship between tensile index and dry zero-span strength. The effect of bonding for zero-span strength is next to non-existent [22]. It can therefore be concluded that the degradation treatments do not influence bonding above the viscosity (degradation) levels mentioned. Furthermore, if the degradation treatments do influence bonding below the level mentioned, the effect on tensile index cannot be observed because the fibers are already so weak that inter-fiber bond-related failure does not occur.

Figure 5b shows how axial fiber strength is compromised much earlier than Z-directional fiber strength or bonding as depolymerization advances. Spruce fibers require viscosity to drop below 400 ml/g before any difference can be detected in the Scott-Bond values. At this level of degradation, the fibers are probably critically weakened in the Z-direction. For birch fibers the same happens at a viscosity of 700 ml/g. If fiber bonding is not affected by the degradation treatments, these differences can probably be attributed to differences in fiber ultrastructure.

### 3.4 Strength contribution from hemicelluloses

Cellulose is the main strength-delivering component in fiber. Interactions have been found between cellulose and glucomannan in softwood fibers, and xylan in hardwood fibers [23]. However, the contribution of hemicelluloses to fiber strength is not well known. Despite the short chain length of hemicelluloses compared to cellulose, they may reinforce the cellulose fibrils *via* the mechanism depicted in Figure 6.

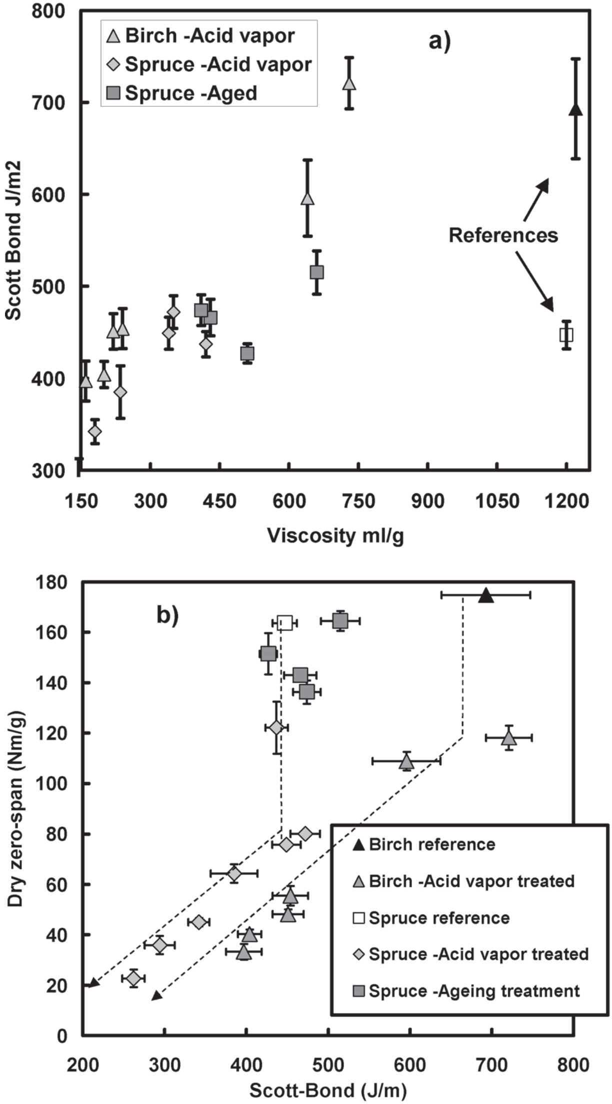


**Figure 5** Scott-Bond vs. viscosity a) and Scott-Bond vs. dry zero-span measurement b) for degraded handsheets.

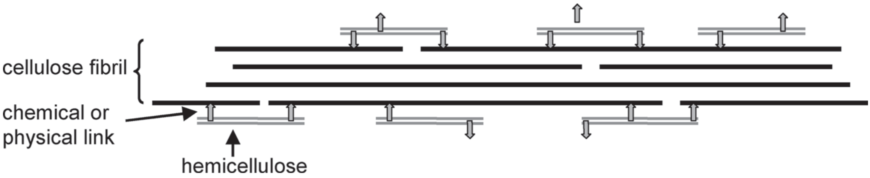


**Figure 6** Possible reinforcement of cellulose fibrils by hemicelluloses.

Viscosity reflects the average length of the fiber polymer chains, particularly cellulose. Thus, a viscosity drop indicates depolymerization of cellulose and thus correlates with fiber strength. Under acidic conditions, certain hemicellulose components are particularly susceptible to hydrolysis. These reactions thus coincide with cellulose depolymerization and may contribute to fiber strength indirectly. Typical acid-labile hemicellulose components are the arabinose substituents of softwood xylan [24].

Figure 7 shows plots of dry zero-span vs. viscosity for both spruce and

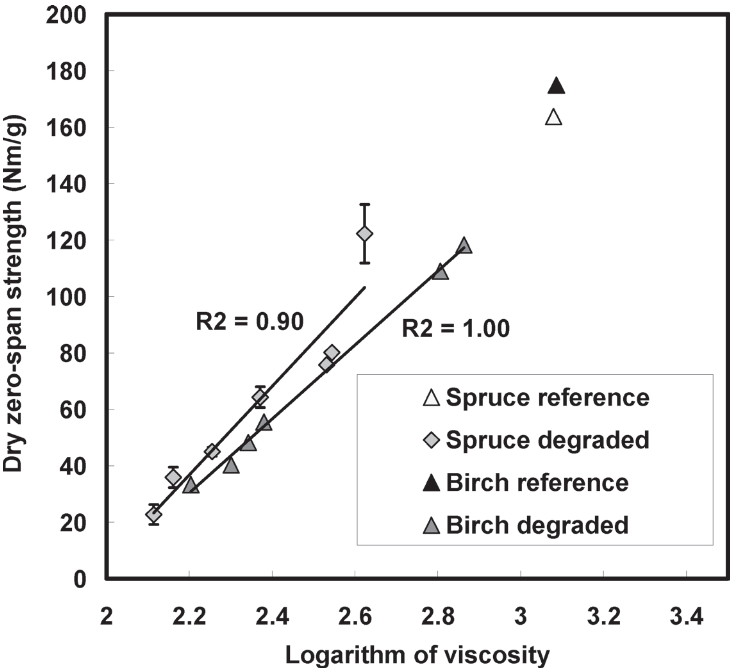


**Figure 7** Dry zero-span strengths vs. logarithm of viscosity for spruce and birch.

birch handsheets. It can be concluded from this figure that the correlation between viscosity and zero-span strength is practically the same for the two wood species. No clear initial fast strength loss is observed in either case, which would indicate the existence of acid-labile reinforcing components in one of the wood species. Thus we conclude that even acid-induced fiber strength loss is primarily due to cellulose degradation, as concluded also by Zao [14, 15].

## 4 CONCLUSIONS

We tested the effects of two cellulose degradation methods on fiber and handsheet strength. We found acid vapor-induced degradation of cellulose to be more detrimental to axial fiber strength than ageing treatment when evaluated at the same viscosity. This is explained by the heterogeneous formation of detrimental local weak points in cellulose fibrils in acid vapor treatment. These weak points are also formed in ageing treatment, but they are probably more numerous, smaller and more evenly distributed. Reaction kinetics plays a large role in determining the homo- and heterogeneity of degradation. It may be that the key words in these types of studies are *more* and *less* in relation to homo-/heterogeneity.

The behavior of Z-directional strength was not analogous to that of axial strength. At the same viscosity there may be a great difference in the axial strength of the fibers but the same Z-directional strength. Modest degradation does not affect Z-directional strength measured with Scott-Bond. Only when the viscosity falls below 400 ml/g for spruce and below 700 ml/g for birch does there appear any effect on Z-directional strength (or bonding). A potential explanation for the difference lies in fiber ultrastructure.

Arabinose side chains of xylan are released from spruce fibers during acid treatment, whereas in the case of birch, this reaction does not take place due to the lack of arabinose substituents. Based on our measurements it is likely that these side chains do not reinforce fibers.

We showed that fiber ultrastructure, not cellulose chain length, is the main factor affecting tensile stiffness. Thus it seems that even in degraded fibers the internal load distribution is very effective. Furthermore, the tension-strain behavior of all degraded samples follows the same curve, indicating little change in fiber properties other than strength.

## ACKNOWLEDGEMENTS

We are grateful for financial support from TEKES via the Wood Material Science Research Programme (BUNDLE, Fibre wall modelling). The Finnish Cultural Foundation and The Jenny and Antti Wihuri Fund are thanked for financing Rolf Wathén's graduate studies.

## REFERENCES

1. R.S. Seth and B.K. Chan. Measuring fiber strength of papermaking pulps. *Tappi J.* **82**(11):115–120, 1999.
2. T.A. Clark and M.J. Ellis. Softwood kraft pulp strength – its measurement and the effect of fiber deformations. In proc. *51st Appita Annual General Conference*, pp573–580, Melbourne, Australia, 1997.
3. O. Joutsimo. Effect of mechanical treatment on softwood kraft fiber properties. Doctoral thesis, Department of Forest Products Technology, Laboratory of Pulp Technology, HUT, Espoo, Finland, 2004.
4. R. Berggren. Cellulose degradation in pulp fibers studied as changes in molar mass distributions. Doctoral thesis, Department of Fibre and Polymer Technology, KTH, Stockholm 2003.
5. R. Berggren, U. Molin, F. Berthold, H. Lennholm and M. Lindström. Alkaline degradation of birch and spruce: influence of degradation conditions on molecular mass distributions and fibre strength. *Carbohydrate Polymers* **51**(3):255–264, 2003.
6. R. Berggren, F. Berthold, E. Sjöholm and M. Lindström. Fiber strength in relation to molecular mass distribution of hardwood kraft pulp. *Nordic Pulp Pap Res.J* **16**(4):333–338, 2001.
7. M.M. de Souza Lima and R. Borsali. Rodlike Cellulose Microcrystals: Structure, Properties, and Applications. *Macromolecular Rapid Communications* **25**(7):771–787, 2004.
8. N. Gurnagul, D.H. Page and M.G. Paice. The effect of cellulose degradation on the strength of wood pulp fibers. *Nordic Pulp Pap Res.J* **7**(3):152–154, 1992.
9. P. Ander and G. Daniel. A novel method to compare industrial and laboratory pulp fibres using hydrochloric acid treatment and fibremaster analyses. In proc. *Eight European Workshop on Lignocellulosics and Pulp*, pp49–52, Riga, Latvia, 2004.
10. R.S. Seth and D.H. Page. Fiber properties and tearing resistance. *Tappi J.* **71**(2):103–107, 1988.
11. P. Kärenlampi and Y. Yu. Fiber Properties and Paper Fracture – Fiber Length and Fiber Strength. In **The Fundamentals of Papermaking Materials**, Trans. 11th Fund. Res. Symp., (ed. C.F. Baker), pp512–545, Pira International, Surrey, UK, 1997.
12. D.H. Page. A Theory for the Tensile Strength of Paper. *Tappi J.* **52**(4):674–681, 1969.

13. M. Strlič, D. Kocar, J. Kolar, Rychly and B. Pihlar. Degradation of pullulans of narrow molecular weight distribution – the role of aldehydes in the oxidation of polysaccharides. *Carboh. Polymers* **54**(2):221–228, 2003.
14. X. Zou, T. Uesaka and N. Gurnagul. Prediction of paper permanence by accelerated ageing I. Kinetic analysis of the ageing process. *Cellulose* **3**(4):243–267, 1996.
15. X. Zou, T. Uesaka and N. Gurnagul. Prediction of paper permanence by accelerated ageing II. Comparison of the predictions with natural aging results. *Cellulose* **3**(4):269–279, 1996.
16. A. Barański, J.M. Łagan, T. Łojewski and T. Sawoszczuk. Experimental Verification of Zou, Uesaka and Gurnagul Formalism, Based on Kinetic Data Obtained for Various Kinds of Paper. In proc. *Durability of Paper and Writing*, pp76–77, Ljubljana, Slovenia, 2004.
17. E. Sjöholm, K. Gustafsson, E. Norman, T. Reitberger and A. Colmsjö. Fibre strength in relation to molecular weight distribution of hardwood kraft pulp. *Nordic Pulp Pap Res.J* **15**(4):326–332, 2000.
18. K. Nyholm, P. Ander, S. Bardage and G. Daniel. Dislocations in pulp fibres – their origin, characteristics and importance – a review. *Nordic Pulp Pap Res.J* **16**(4):376–384, 2001.
19. N. Gurnagul and D.H. Page. The difference between dry and rewetted zero-span tensile strength of paper. *Tappi J.* **82**(12):164–167, 1989.
20. U-B. Mohlin, U. Molin and M.W. de Puiseau. Some aspects of using zero-span tensile index as a measure of fiber strength. In proc. 2003 *International Paper Physics Conference*, pp107–114 Victoria, BC, Canada, 2003.
21. K. Niskanen and P. Kärenlampi. In-plane tensile properties. Ch. 5 in **Paper Physics** (ed. Kaarlo Niskanen), Fapet Oy, Jyväskylä, Finland, 1998.
22. R.S. Seth. Zero-span tensile strength of papermaking fibres. *Paperi ja Puu – Paper and Timber* **83**(8)597:604, 2001.
23. T. Liitiä, S-L. Maunu, B. Hortling, T. Tamminen, O. Pekkala and A. Varhimo. Cellulose crystallinity and ordering of hemicelluloses in pine and birch pulps as revealed by solid-state NMR spectroscopic methods, *Cellulose* 10(4):307–316, 2003.
24. E. Sjöström. **Wood chemistry, Fundamentals and applications**, 2$^{nd}$ Ed., Academic Press, San Diego, 1993.

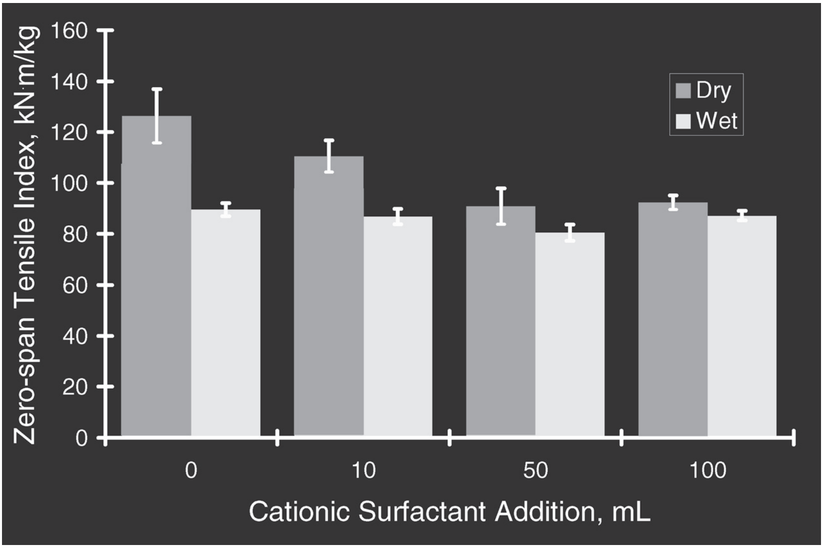
**Transcription of Discussion**

# EFFECT OF DIFFERENT DEGRADATION MECHANISMS ON AXIAL AND Z-DIRECTIONAL FIBER STRENGTH

*Rolf Wathén, Olli Joutsimo and Tarja Tamminen*

KCL Science and Consulting, P.O.Box 70, FIN-02151 ESPOO, FINLAND

*Jose Iribarne* Solvay Paperboard
*(prepared contribution summarised by the editor)*



Jose showed the above graph, which indicates that dry zero-span tensile strength changed with varying addition level of a debonding agent, whereas wet zero-span strength remained constant. He suggested that this made the wet test more appropriate for studying the fibre strength in paper.

*Rolf Wathén* (*in reply to the prepared contribution by J. Iribarne*)

Our treatments did not change bonding. Thus bonding cannot be causing the difference between wet and dry zero-span strengths. I do not know how these debonding agents work, so I really cannot comment on them.

*Jean-Claude Roux*

So this is still an open problem.

*Tom Lindström* STFI-Packforsk AB

There are several interesting issues here. Ignoring, for a moment, the inherent complications of measuring short span strength, I do not think you have to be worried about that the wet short span strength is larger than the dry short span strength. It is well known that wet single fibre strength is larger than dry single fibre strength for undamaged fibres because the load is more even across the fibre cross-section when the fibre is wet. It can also easily be imagined that the birch pulp has been less damaged than your spruce fibres in the cooker as they are shorter than spruce fibres.

*Rolf Wathén*

That comment helps me out a great deal.

*John Roberts* University of Manchester

I have some concerns with the conclusions that the acid vapour treatment is causing heterogeneous degradation and the thermal aging is causing homogeneous degradation. You say in your paper that both of these are due to cleavage of glycosidic linkages in the cellulose polymer and, if that is the case, the reaction is essentially with water and would be extremely highly catalyzed by acidity. However, the distribution of the degradation would be expected to be in the non-crystalline amorphous regions of the fibres and microfibrils. Therefore the only distinction you would really expect would be a difference in the rate of the processes not in the distribution of where the degradation took place. I just wonder if you would like to comment on that?

*Rolf Wathén*

Fibre level defects are regions where non-crystalline or non-ordered cellulose are in a sense concentrated. We think these are the regions attacked initially by the acid vapour treatment. Aging treatment on the other hand probably affects other disordered regions without similar initial preference.

*Øyvind Gregersen* NTNU

In Figure 4 you show the stress strain curve of papers where the fibres have been weakened by a gas phase reaction with HCl. The tensile strength is decreasing with the gas treatment, whereas the tensile stiffness is constant. In Figure 5 you showed us that the Scott-bond strength is also almost constant and you would need a really severe gas treatment to see reduction in Scott-bond. Is this not directly contradictory of the nice tensile strength model that Kaarlo Niskanen presented a few papers ago?

*Rolf Wathén*

Kaarlo's model does not yet include the effect of fibre strength.

*Doug Coffin* Miami University

I was just trying to size up the difference between your tensile strength and your zero-spans. If you look at the ratio, for each of your sheets, how close is your tensile strength to zero-span?

*Rolf Wathén*

I have not looked at the ratio.

*Doug Coffin*

I am just trying to assess it. It is a pretty well developed sheet and you have lot of bonding

*Rolf Wathén*

Yes, the pulps were refined in a PFI mill and were well bonded.

*Discussion*

*Warren Batchelor* Australian Pulp and Paper Institute

I have just one comment to make about the zero-span. Dr. Raj Seth wrote a paper a few years ago in which he looked at the effect of wet pressing on the dry zero-span strength and showed that as you increased the bonding that there was no effect on the dry zero-span.

*Rolf Wathén*

Thank you for your comment.

*Jose Iribarne* Solvay Paperboard LLC

I just want to respond to that. It is very fitting that we are talking about Raj Seth when he just passed away. The data that he presented in the paper to which you refer[1] can also be interpreted as indicating that bond strength was originally high enough so wet pressing did not contribute any more. He actually also included an experiment in the same paper in which he cut fibres and did not find any impact of shorter fibres on dry zero-span. He should have done because the zero-span test, as the standard tensile test, is biased towards longer fibres. In any test in which you can put a reference line, the likelihood of fibres to be crossing that line is proportional to their length. So there should have been a difference and yet he did not see it, which suggests that the bond strength was high enough to mask the effect. I think this is another point that should be discussed further.

[1] Seth, R.S. "Zero-span tensile strength of papermaking fibres", in 85th Annual Meeting, PAPTAC, Montreal, pp. A161–A173, 1999.

*Heinrich Baumgarten*

I understand that you check the long lifetime ageing for your paper with high temperature treatment which is a normal way to do it. I cannot understand why you want to treat this long life paper with acid when there is an easy solution which is to put some calcium carbonate (with large particle size) into the paper.