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Carboxylic Acid Groups and Fibre Bonding

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ABSTRACT

It has been known for a long time that carboxylic acid groups in cellulosic fibres increase swelling in fibres and hence this impacts flexibility, bonded area, and strength. In a few recent publications, attention has been drawn to the possibility that carboxyl groups may serve another function. Those located at the fibre surface have an effect on specific fibre-fibre bond strength. The evidence for this possibility is at present indirect. Using a technique developed for this work, pulps were prepared with uniform distribution of carboxyl groups across the fibre cell wall, and with carboxyl groups located primarily at the fibre surface. Using values of light scattering coefficient, tensile strength, and z-bond strength, it was possible to determine the relative importance of increased bonded area caused by swelling. and increased bond strength caused by localized surface effects. It was found that specific bond strength could be enhanced roughly 50% by surface enrichment, and this could exceed the strength increase attributable to enhanced bonded area. Previous work on the effect of carboxyl groups on strength needs reevaluation to determine the extent of the two effects. The mechanism of strength increase by

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surface carboxylic acid groups is not understood. It may be an ionic effect, but it is possible that the increased localized surface swelling allows more molecular flexibility and more intimate molecular contact and interdiffusion as found in other polymers. In practice, there are opportunities, especially in bleaching or other pulp treatments, for enhancing fibre surface carboxyl group concentration, and these may have practical value. The field looks ripe for exciting developments.

INTRODUCTION

Chemical pulps contain carboxylic acid groups from hemicellulose retained through the pulping and bleaching processes. Certain bleaching agents, such as ozone, oxygen, and peroxide, can increase the carboxylic content through direct oxidation of cellulose. Carboxyl groups can have a large impact on final sheet strength. The effect of these weakly acidic groups on a fibre's ability to swell is well-known (1). Acid groups can cause fibre swelling, resulting in increased fibre plasticity, bonded area, and strength in the sheet. Recently, however, the literature has indicated that the introduction of acid groups onto the surface of pulp fibres might be affecting sheet strength by increasing the specific strength of the fibre-fibre bonds. This has been suggested by several authors working with mechanical pulps modified by oxidation or sulfonation (3-5) as well as by two studies concerning oxygen delignification of kraft pulps (6,7). In none of these experiments, however, was the concentration of surface acid groups deliberately changed in a controlled manner. The purpose of this study was to carry this out to examine the contribution of acid groups on fibre surfaces to paper strength. Pulps were prepared with different acid group distributions across the cell wall, but the same total acid content. In this way, the contribution of surface acid groups was decoupled from the contribution of uniformly distributed acid groups.

APPROACH

In designing the procedure for the introduction of acid groups, several constraints were considered. It was essential that the overall fibre characteristics should be retained, and the cellulose should not be degraded. For these reasons, oxidation was ruled out, as was the use of lignin-containing pulps. A partially bleached kraft pulp was chosen, and additional carboxylic acid groups were introduced using a halo-

acetic acid reaction to form carboxymethyl cellulose (8). Chloroacetic acid itself was used, or converted, in-situ, to the more reactive iodoacetic acid.

The methodology to produce surface or bulk substitution of carboxyls was based upon a reevaluation of previous work, which is published elsewhere (9). The key to producing a desired acid group topochemistry with halo-acetic acid is to control the fibre history prior to the reaction. To produce surface substitution, the fibres were first dried from water. This caused the cell wall to become impervious (10), so that in a non swelling medium, the reaction occurred primarily with fibre surfaces. To produce bulk substitution, solvent exchange dried fibres were used as a starting material. Solvent exchange drying retains some of the wet fibre structure (11), allowing penetration of reactants into the cell wall. Control (blank) fibres were prepared using the surface substitution procedure and omitting the halo-acetic acid reagent. The bulk substituted pulp was subjected to a restrained drying cycle from water prior to testing. In this way, all three pulps experienced one restrained drying cycle from water prior to production of sheets for strength testing, giving all pulps a similar drying history.

The substitution topochemistries were confirmed using a scanning electron microscopy - energy dispersive spectrometry (SEM-EDS) technique developed for this study. The carboxylic acid groups in the pulps were deprotonated and ion exchanged to the calcium form. The treated fibres were freeze-dried, imbedded in Epox 812, and sectioned on an ultramicrotome with a diamond knife to 400 nm. The calcium ions acted as tracers by tagging the carboxyl groups and allowing for detection with EDS. Cation tagging of carboxylic groups has been used previously to increase contrast in transmission electron microscopy (12), but has not been used in the SEM to determine spatial distribution of functional groups. The calcium peak/background ratio of x-ray counts was taken to be proportional to carboxylic The electron beam was scanned across fibre cell walls, and concentration. peak/background ratios for calcium were determined at five relative positions. Five line scans per fibre were taken, and three fibres from each treatment were examined. The carboxyl group topochemistry was also investigated using a cationic polyelectrolyte titration technique (13).

RESULTS AND DISCUSSION

The results of an SEM-EDS study are shown in Figure 1, which is the peak/background ratios for the relative positions across the fibre cell walls. Position 1 is adjacent to the lumen, and Position 5 is adjacent to the cell outer wall. The distribution of carboxylic groups is uniform across the cell wall for the blank and bulk substituted fibres. Surface substituted fibres show carboxylic enrichment of the lumen and outer cell wall surfaces. Presumably, the enrichment of the cell wall adjacent to the lumen occurred by reactant penetration through fibre pores. The carboxylic distributions determined by SEM-EDS were also evaluated with analysis of variance (AOV). At the 95% confidence level, there was no difference from position to position across the cell walls for the blank and bulk treatments, but there was for the surface treatment. The polyelectrolyte titration determined that 35% of the carboxyl groups were accessible for the surface substituted fibres, 5% for the bulk fibres, and 3% for the control fibres.



Figure 1. Carboxylic acid content across the fibre cell walls indicates the change in reaction topochemistry with fibre treatment.

The modulus of elasticity of the handsheets was measured to determine if pulp preparation affected the stress transfer in the sheets. The modulus was calculated using the method of Page (14), resulting in units of kilometers analogous to breaking length. Modulus was plotted against soft platen apparent density as shown in Figure 2. There was no effect of fibre treatment in the plot, indicating that the various treatments did not introduce fibre deformations that would alter stress transfer in the sheets. With this knowledge, tensile strength can be used as an indication of fibre-fibre bond strength. Tensile strength is plotted against light scattering coefficient as shown in Figure 3. At the same scattering coefficient, the surface substituted sheets are 45% stronger. The clear implication of this observation is that surface enrichment of carboxylic groups results in an increase in specific bond strength. This result was confirmed using the Scott-Bond test. Scott-Bond strength is dependent on specific bond strength, among other factors, and has been used to measure increases in specific bond strength caused by addition of Scott-Bond strength can be used to compare the effects of fibre starch (15). treatments on bonding if a single type of pulp is used and the treatments do not change fibre properties (16). Figure 4 contains the plot of Scott-Bond strength against light scattering coefficient. Here, again, the surface enriched pulp has the highest strength at any level of scattering coefficient, the strength being about 50% higher.



Figure 2. Elastic modulus of handsheets plotted against density. No change in stress transfer in the sheets occurred with treatment.



Figure 3. Tensile breaking length plotted against light scattering coefficient. Surface treated fibres produce sheets with increased strength at any level of bonded area.



Figure 4. Scott-Bond strength plotted against light scattering coefficient. Surface treated fibres have the highest internal bond strength at any level of bonded area.

It is known that increased acid group content can result in increased strength in the sheet (8, 17-19). The previous work was performed at a constant wet pressing pressure and used beating/refining. Consequently, although strength increases have been attributed to fibre flexibility, there is no justification for this explanation. It is necessary to change bonded area while maintaining specific bond strength constant (as in changing wet pressing) to separate the effects of flexibility and bond strength. The work on the effects of acid groups on sheet strength should be repeated using this experimental technique. Figure 5 is a plot of RBA versus wet pressing pressure for the handsheets in this study. No clear differences emerge in this plot, possibly due to the pulp being unrefined. The increase in sheet strength from the change in specific bond strength far outweighs the contribution from bonded area. The mechanism of this effect is not yet understood, but could well involve intermolecular diffusion (20). We speculate that the anionic charged sites on the fibres could be enhancing the localized swelling on the fibre surfaces and causing increased fibre-fibre intermolecular entanglement. The results displayed in Figure 4 are very similar to those obtained by Gaspar with the addition of cationic starch (15). Portions of Gaspar's work have been replotted in Figure 6. We suggest that the same mechanism can account for both sets of results. In the case with starch, the starch polymers could be involved in molecular entanglements with two adjacent fibres, thereby producing the same effects as surface enrichment of carboxvls.



Figure 5. Relative bonded area (RBA) and wet pressing pressure. There is no discernible difference with fibre treatment.



Figure 6. Scott-Bond strength of handsheets treated with starch from Gaspar (15).

This work demonstrates that the topochemistry of halo-acetic acid substitution of kraft pulp fibres can be influenced by the degree of swelling of the fibres at the time of reaction. If the fibre cell wall is in a dry collapsed state, the substitution occurs primarily at the fibre surface. If the fibre is in a more expanded state, then the substitution occurs uniformly across the cell wall. Carboxylic enrichment of fibre surfaces results in improved paper strength properties when compared to bulk carboxylation or no treatment at all.

We were aware of one instance in the recent literature where commercial treatment of a fully bleached deinked fibre with oxygen and peroxide appeared to increase the specific fibre-fibre bond strength (21). We investigated this treatment with a laboratory-scale simulation of the process using a fully bleached softwood dry lap market pulp. Oxygen and peroxide reinforced oxygen bleaching increased the carboxyl content by approximately 50%. The Scott-Bond strength results appear in Figure 7. The same result is obtained as with the surface enriched pulp, that being an increase in specific fibre-fibre bond strength.



Figure 7. Scott-Bond strength with bleaching treatment. Both treated pulps have a higher internal bond strength when compared to the control.

The results obtained in this study concerning specific bond strength are unique only in that the introduction of acid groups was rigidly controlled. Several previous studies used mechanical pulps and oxidative treatments to increase pulp acid contents, and all reached the conclusion that acid groups on fibre surfaces were important to sheet strength (3-5). Ampulski (5) developed good empirical relations of sheet tensile strength to both surface and bulk acid group contents. In the work involving the bleaching of kraft fibres (6), Page's Equation (22) was used to determine specific bond strength. The inclusion of oxygen delignification in the bleaching process increased specific bond strength by 20-30%. The more recent work with oxygen delignification (7) also demonstrated an increase in specific bond strength.

CONCLUSIONS

While the presence of carboxylic acid groups in fibres is known to affect fibre swelling and hence sheet density and strength, little attention has been given to their possible effect on specific fibre-fibre bond strength. By locating carboxyl groups uniformly throughout the fibre or by locating them specifically at the fibre surface, we have been able to show that specific bond strength can be enhanced considerably if the carboxyl groups lie preferentially near the fibre outer surfaces.

The possibility exists in pulping, bleaching, or other pulp post treatments for enhancing specific bond strength in this way and hence producing stronger, bulkier sheets than by conventional processes.

EXPERIMENTAL

Materials

The solvents were anhydrous, and all reactants were ACS reagent grade and used without further purification.

Pulp

The long fibre fraction (>35 mesh) of an unbeaten, never-dried OZE bleached commercial kraft pine was the starting material for this study. The pulp was converted into the sodium form according to the procedure described by Scallan (1). The pulp was then dried using either a six-step solvent exchange process (water/methanol/toluene % volume: 75/25/0, 25/75/0, 0/100/0, 0/100/0, 0/100/0, 0/0/100) or formed into sheets (couched, not pressed) and dried under restraint in rings.

Halo-Acetic Acid Substitution

Blank, bulk, and surface reactions occurred at 1.5% consistency in a reaction medium consisting of 87% isopropanol and 13% methanol with an amount of KOH stoichiometrically equivalent to the amount of added chloroacetic acid with an additional 0.15 excess weight percent KOH. The surface substituted pulp was prepared by heating under reflux for 1 hour a mixture of restraint dried pulp in the reaction medium containing 0.6 weight percent chloroacetic acid and 1.2 weight percent KI. The bulk substituted pulp was prepared by first immersing solvent exchanged dried fibres in isopropanol containing 0.13 weight percent chloroacetic acid. These fibres were then heated under reflux for 1 hour in the reaction medium. The blank (control) pulp was prepared by heating under reflux for 1 hour a mixture of restraint dried pulp in the reaction medium. Final carboxylic acid contents were determined with conductometric titration (23) to be 72 meq/kg for the blank pulp and 144 meq/kg for both substituted pulps.

Scanning Electron Microscopy

The samples were analyzed on a JEOL JSM-6400 SEM with a Link exL EDS. The EDS detector had a 40° incline and was operated in beryllium window mode. The accelerating voltage was 15 kV, sample tilt was 20°, and the working distance was 39 mm. A mount for viewing thin sections in the SEM was prepared by attaching a machined carbon grid holder over a 4-mm hole in an aluminum stub. The hole was coated with carbon paint and trapped electrons passing through the sample in the mount.

Bleaching

Bleaches were performed on slurried dry lap market pulp at 10% consistency, 80 °C, with 1% sodium hydroxide and 60 psig oxygen. Bleaches were performed with and without 1% hydrogen peroxide.

Handsheets

The three pulps produced (blank, bulk, surface) were dispersed with a British disintegrator and converted to the calcium form. TAPPI standard handsheets were produced (T 205), with the exception that wet pressing pressures of 173, 345, 690, 1380, and 2760 kPa were used to change bonded area. The sheets were dried under restraint in rings. The handsheets were evaluated with TAPPI standard methods (T 494, T 231). Four measurements were performed per test condition for tensile and elastic modulus, 10 measurements for Scott-Bond strength, 12 measurements for light scattering coefficient.

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Transcription of Discussion

Carboxylic Acid Groups and Fibre Bonding

Dr David Barzyk, Process Engineer, Weyerhaeuser Paper Company, USA

Bruce Lyne, Senior Manager, International Paper, USA

In the light of this paper I would like to go back and ask two questions of Prof Stenius. First, you added xylan and changed bonded area (lowered the scattering coefficient) without changing tensile while Dr Barzyk added starch and created stronger bonds. Secondly, are the stronger bonds between the fibres due to surface charge or is it due to swelling of the fibre wall. In other words does the added charge have to be in the fibre wall to increase bonding?

Professor Per Stenius, Helsinki University of Technology, Finland

We did not see a weakening of bonds when adding xylan, the sheet strength increased when adding more xylan. We varied the amount of xylan by absorption from solution and then we see changes in the tensile strength without changing the bonding area, ie when the amount of xylan increases the bond strength increases. So it is quite clear there is no discrepancy with Barzyk's work.

About surface charge - our results indicate that with increasing total charge the swelling increases, which results in increased flexibility and increased bonding area. This is the dominating effect.

Janne Laine, Research Scientist, STFI, Sweden

We did not see the type of effect that Dr Barzyk observed. We analysed a ratio of surface charge to total charge and found it was the same . We calculated specific bond strength using the Page equation and found no big differences between different pulps.

I have a question for David. You could perhaps change light scattering vs tensile curves by adding salt or by converting the carboxylic group to acid form.

David Barzyk

I agree with you it would be very interesting to see what would happen. Please call me when you have done it.

Peter Wrist, Consultant, Peter E Wrist, USA

Figure 1 in your paper shows that the surface concentration of carboxylic acid content in the case of the bulk treated sample was approximately midway between that for the surface treated and the blank. The strength of the bulk treated samples was however equal to that of the blank. I would have expected the bulk sample strengths to be midway between the blank and the surface treated samples if the surface concentration of carboxylic acid content has a primary influence on bond strength. Does this suggest some other parameter is more important?

David Barzyk

This was an unrefined pulp. It was a long fibre fraction and we did not see any of this increased swelling and bonding so there was no change in the bonded area. The polyelectrolyte titration showed that there was not much difference between the amount of acid groups on the surface for the bulk treated fibres and the control fibres. It could be a matter of degree.

The surface treated fibres produced sheets that were stronger. But we will have to discuss the SEM results in more detail later.

Professor Borge Steenberg, KTH PMT, Sweden

I think the reply to Peter Wrist is that the difference in carboxyl content between the original pulp and substituted is very small. It is 70 on the basic pulp and 140 roughly, then the tensile strength of these papers are between 1000m or 3000m - I guess there are no papers anywhere that have such a low strength. Is this a study of paper or rather pulp?

David Barzyk

We wanted to stay in the bond strength limited regime - we did not want to get up into the fibre strength regime. That is why we used unrefined pulp and our strengths were so low.

Lars Wågberg, Research Manager, SCA Research, Sweden

We have to get a way from looking at molecular bonding mechanisms with the relative bonded area concept. As I see it you are increasing the charge on the surface and if you think about Prof Wahren's picture, even though it might be an artefact, we naturally have fibrils in the fibre wall and as they start to become very charged they actually repel each other to such an extent that the surface starts to look more like a surface gel. So what we have here is a surface gel coming together with another surface gel (when two fibres meet). Maybe we could model the interaction between fibres as surface gels coming together and maybe we could even start to calculate this by using the polymer brush theory, as an example.

David Barzyk

Yes that would be nice to see something like that.

Dr Theo van de Ven, Director, Paprican/McGill, Canada

Regarding you speculation about macro-molecules extending from the surface, which is related to Lars Wågberg's question, do you see this in terms of entanglements or simply because these large flexible molecules have more chance of forming hydrogen bonds that way?

David Barzyk

I do not have data to address that question. Our speculation is that it is actually entanglement of molecular chains. I would like to see some data to prove it one way or the other.

Per Stenius

I think Lars Wågberg is quite right. The nature of the bond between fibres is obviously much too complex to be monitored just by measuring RBA from light scattering. The fact that we see strong swelling of the cellulose surface in humid air which is accompanied by increased adhesion is quite a good example of the problems we are facing.

Dr Derek Page, IPST, USA

I would like to respond to the question related to not using relative bonded area. That is nonsense. You have got to use relative bonded area - the whole point is that you have to use specific bond strength as well. Because we do not have any knowledge about the details of the interaction between fibres we divide it up into bonded area where we know there is optical contact, and then we ask how good is the bonding within that contact area, because within that contact area is where the important bonds are. Now I think there is a discrepancy between the work that David has presented here and your (Janne Laine) work. You used the Page Equation and did a beating run and extrapolated back down to zero to get relative bonded area. Wrong! It does not work. You have got to change wet pressing pressure which is what we did. Changing beating or swelling changes too many other things, like specific bond strength and fibre straightness. Changing wet pressing pressure keeps specific bond strength and fibre straightness constant, so the extrapolation to zero tensile strength gives the correct RBA. So I think you didn't do the right experiments and your conclusions are incorrect. But I think your results are probably consistent with Dave's results if you look at them from the right point of view.

Dr Kari Ebeling, Director, UPM Kymmene Group, Finland

I would like to compliment you on a very good piece of work and for the hypothesis put forward. Still I need to emphasise you should not describe the paper structure with Scott Bond or tensile alone. The most valuable work that the long fibre can do is as a reinforcement fibre and the papermakers make their profit or loss with how little long fibre they can put into the sheet and how much mechanical fibre they can put in. The important bonds are not tensile type of bonds; they are ductile bonds they can take a load and extend and extend and still carry the load as they bond to the mechanical pulp fibres. So if you test bonding between cellulosic pulp fibres in tensile strength you are getting the wrong picture.

Lars Wågberg, Research Manager, SCA Research, Sweden

I just want to comment on Derek Page's comment. Of course the concept of relative bonded area is correct, there is nothing wrong with it, but you have to determine it with the right measurement. You cannot determine a relative bonded area on a molecular level with optical measurements using white light. We have shown that the interactions start around 3-30nm and I definitely doubt that you can measure this interaction with optical contact measurements.

Derek Page

I have said this so many times at different meetings but I guess nobody was listening! Optical contact between two surfaces occurs when they are separated by less than 100-150 Å or 10-15 nm!! I refer you to Sir Isaac Newton's treatise on 'Optichs' written in the 18th Century. If you look at the work that was done by Hazleton many years ago he showed that for paper sheets there was a one-to-one correspondence between the value of scattering coefficient and the magnitude of the surface area that is available for nitrogen absorption. The interface function of this result is that the nitrogen molecule cannot get in to these optical contact regions. This means their separation can be no greater than 4Å. But having said that it really does not matter because if you make an error by assuming that the optical contact area is too big you will find that the bond strength is too low. The two compensate out for each other but as long as you do it that way nothing can go wrong.

Lars Wågberg

You have to separate what you are looking for - are you looking for a bonding mechanism on a molecular level or are you looking for an engineering approach. I think Prof Stenius and his co-workers could definitely tell you more about what they start to find in their studies of interactions between pure cellulosic surfaces.

Derek Page

The procedure for determining bonded area and specific bond strength has not failed yet when operated properly. It fails when you do not do the right things. One example of not doing the right thing is to measure tensile strength and scattering coefficient for a beating run, and extrapolate to zero strength to obtain the RBA. This gives a meaningless result. Beating changes many properties of the fibre. If you change wet pressing pressure to change scattering coefficient you do get a true value of RBA and you can then get specific bond strength. The challenge for physical chemists then becomes 'How do you explain why the specific bond strength changes with different chemical treatments?' That is where we need an explanation at the molecular level. But, you've got to do the physics right first before embarking on the physical chemistry.

Lars Wågberg

I have several examples where the model has its shortcomings but we should ask ourselves why are we debating this if everything is already solved?

Professor Robert Pelton, Senior Scientist, McMaster University, Canada

I propose that somebody does a neutron scattering experiment, the wavelengths are lower and we should be able to put this whole issue to bed.