SWELLING OF RECYCLED WOOD PULP FIBERS: EFFECT ON HYDROXYL AVAILABILITY AND SURFACE CHEMISTRY

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ABSTRACT

The objective of this research was to examine how swelling treatments affect the hydroxyl availability and surface chemistry of recycled fibers. It also assessed the use of organic liquids in mitigating fiber hornification, the loss of hydrogen-bonding ability in recycled fibers. Hardwood bleached kraft pulp fibers were recycled, swollen, and subsequently analyzed for water retention value (WRV), dynamic contact angle, and hydroxyl number. Results show that the relative swelling powers of the liquids were: 12% NaOH > formamide > dimethyl sulfoxide = 2% NaOH = ethylene glycol. These liquids resulted in WRVs that were 23–72% higher than the control, i.e. the water-swollen recycled fibers (WRV 1.10). Swelling increased the hydroxyl number of the fibers except for those treated with 12% NaOH. Fibers that were swollen to a greater extent had a higher total surface-free energy and a lower water contact angle. By swelling the fibers in organic liquids, polar surface-free energy increased with an increase in hydroxyl numbers. Such a relationship was obscured for the alkaline treatments, which presumably altered the chemical composition of the fibers. These findings promote understanding for a more effective formulation of treatment methods for recycled fibers. An immediate implication from this study is the strong fiber swelling power of formamide whose concentration and cost efficiency should be optimized in future studies.

Keywords: Recycled fiber, swelling, surface chemistry, hydroxyl group, fiber hornification.

INTRODUCTION

Swelling of fibers has been a common approach to enhance the bonding of recycled pulp fibers. Recycled fibers, especially those of chemical pulp, lose their swelling ability and hence conformability. This phenomenon is termed fiber hornification. Fiber hornification is known to associate with fiber cell-wall collapse during fiber web consolidation (Katz et al. 1981). It is thought to result in the loss of fiber bonding capacity in the subsequent papermaking process. To recover the bonding capacity of recycled fibers, much emphasis has been placed on reversing the hornification process: restoring the swelling ability of the fibers. Swelling treatments are known to result in promoting internal stresses in the fiber cell wall, thereby breaking the hydrogen bonds between the cellulose chains, re-exposing hydroxyl groups, and allowing subsequent bonding in paper recycling (Katz et al. 1981).

Although alkaline swelling is the most common treatment for recycled fibers, other unconventional chemicals can possibly be useful for mitigating fiber hornification. The alkaline treatments are commonly carried out in a sodium hydroxide solution at a dosage of less...
than 1.0% based on the oven-dry weight of fibers (Howard 1990). This minimal dosage leads to only a limited fiber swelling. A higher dosage, however, is restricted by alkaline degradation of cellulose, an undesirable effect that weakens the fibers. A possible alternative to promote swelling of recycled fibers is by using organic liquids. Some of the liquids that swell pulp fibers more than water are dimethyl sulfoxide (DMSO), formamide, and ethylene glycol (Mantanis et al. 1995). These liquids are comprised of small molecules (molar volumes < 100 cubic centimeters), and are high in both hydrogen-bonding capacities and cohesive energy density (CED). They do not disrupt the structure of cellulose crystallinity (Mantanis et al. 1995), the highly ordered regions that provide stiffness and strength to individual fibers.

Besides the swelling-reduction attribute, the strength degradation of recycled paper may also be due to changes that occur on fiber surfaces. McKenzie and Higgins (1955) concluded that interfiber bonding is affected mainly by the hydrogen-bonding capacity of the fiber surface, instead of the degree of swelling. They investigated the effects of hydroxyl substitution, which was performed using the acetylation method, on two categories of parameters: (1) sheet thickness, which is related to the degree of fiber swelling (fibers that were swollen more would conform better to produce a denser or thinner sheet of paper), and (2) rheological properties, i.e. tensile breaking load, extensibility, rupture energy, and Young’s modulus, which are a manifestation of the extent of interfiber bonding. McKenzie and Higgins (1955) found that the response of sheet thickness to the hydroxyl availability was not similar to the rheological response. Therefore, they argued that the degree of fiber swelling was not a primary factor that influenced interfiber bonding; instead, the hydrogen-bonding capacity, which varied with the degree of hydroxyl substitution (or availability), was the controlling factor. Surface phenomena may also play an important role in causing the strength degradation of recycled paper. Fiber surfaces require exposed hydroxyl groups to allow for hydrogen bonding. Surface wettability of fibers has been reported to decrease (Klungness and Caulfield 1982) upon drying, the same phenomenon that causes fiber hornification. Conventional wisdom acknowledges that substrates that have a low wettability or surface free energy are generally not reactive in bonding.

To improve the efficiency of mitigating fiber hornification, the relationships between swelling, hydroxyl availability, and surface chemistry should be examined. Swelling has been related to the breakage of intrafiber bonds between the opposite inner cell walls within a fiber (Katz et al. 1981); the restored cell-wall flexibility increases bonded areas during the subsequent sheet formation. Hydrogen-bonding sites, though only consumed as little as 0.5 to 2% for interfiber bonding (Corte et al. 1957), are so important that no other factors can restore the strength of the resulting paper once these bonding sites are lost (Robinson 1980). Surface-free energy, on the other hand, predicts how well a substrate will interact and bond with another substrate. Therefore, the interplay between swelling, hydroxyl availability, and surface chemistry needs to be understood better to effectively formulate treatment methods for recycled fibers. Such a possibility is difficult to realize by merely using the bulk mechanical property data which do not directly reflect the mechanism of fiber treatments.

Little information is available concerning the effects of swelling on the hydroxyl availability and surface chemistry of recycled fibers. For lignocellulosics, most studies that evaluate such a relationship aimed at examining the effect of initial surface chemistry on final swelling—an objective opposite to the present study. For example, Nayer and Hossfeld (1949) found that the degree of swelling is directly related to the intensity of hydrogen bonding between the constituents of wood and the swelling agent. Another study discovered that the ultimate tangential swelling of wood in various organic liquids is independent of the specific wettability of the surfaces (Mantanis
and Young 1997). For cellulose fibers, the swelling study of Mantanis et al. (1995) examined the relationship between ultimate swelling and the hydrogen bonding capability (and other physical properties) of the solvent.

**OBJECTIVES**

The objective of this research was to examine how swelling treatments affect the hydroxyl availability and surface chemistry of recycled fibers. This study also assessed the possible use of organic liquids in mitigating fiber hornitication. For reference purposes, it also investigated alkaline swelling, an industrial practice, although data interpretation is potentially complicated by alteration of chemical composition because of the fact that alkaline solution extracts hemicelluloses from pulp fibers.

**MATERIALS AND METHODS**

Hardwood bleached kraft pulp was obtained from Mead Paper Co., Escanaba, Michigan. The pulp slurry was collected after the final washing stage of a chlorine-dioxide bleaching sequence. These pulps, consisting of mainly maple, birch, and beech wood fibers, had a residual lignin level of about 0.7 permanganate number. The collected pulp became the material source for this study.

A pulp slurry containing 1.2 g oven-dry weight (o.d.w.) was adjusted to a consistency of 0.5%, i.e., 0.5 g o.d.w. for every 100 ml of pulp slurry. The dispersed pulp was decanted from water using a funnel and an aspirator to produce fiber mats each of 15 cm in diameter. The fiber mats were dried in an oven at 105°C to 2% moisture content. The resulting paper was slushed at a consistency of 0.3% in a blender whose blade had been blunted. The pulp slurries were then thickened, using a centrifuge, to 30% consistency for further processing.

Fiber swelling was carried out using formamide, ethylene glycol, dimethyl sulfoxide (DMSO), aqueous sodium hydroxide (2% based on oven-dry weight of pulp), and concentrated sodium hydroxide solutions (12% based on the weight of water). Some properties of these solvents or swelling liquids are presented in Table 1. Depending on the swelling media, water or organic liquid was added to the pulp slurries to attain a consistency of 5% for the swelling experiment. The swelling treatments, adapted from Freeland and Hrutfiord (1994), were performed at ambient temperature for 2 h at a consistency of 5%. At the end of the treatment time, the residual caustic (in the case of alkaline swelling) was titrated to neutral pH with 50% hydrochloric acid. The salts of neutralization products (for alkaline swelling) or the residual organic liquids (for swelling in organic liquids) were removed from the pulp by washing in distilled water for five cycles at 3% consistency.

The swelling degree of fibers was determined according to TAPPI Useful Method UM 256 (TAPPI 1991). About one gram (oven-dry weight basis) of these fibers were decanted. These fibers were subsequently centrifuged for 30 min at a temperature of 21 ± 3°C and an acceleration of 900 G. The swelling degree was expressed in water retention value (WRV), which is the weight of water (in grams) retained by one gram (o.d.w.) of the swollen pulp after centrifuging.

Surface analysis was carried out on fibers that were freeze-dried after the swelling treatments. The analysis was conducted using a CAHN model DCA-322 Dynamic Contact Angle Analyzer. This analysis, as described by Liu et al. (1994), involved immersing single fibers at a rate 12 μm/s into different probe liquids: methylene iodide, ethylene glycol.

**Table 1. Some properties of the solvents or organic liquids used for fiber swelling.**

<table>
<thead>
<tr>
<th>Solvent or organic liquid for fiber swelling</th>
<th>Molar volume (cm³)</th>
<th>Solubility parameter (J/cm)³</th>
<th>Hydrogen bonding index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>18.07</td>
<td>48.1</td>
<td>16.2</td>
</tr>
<tr>
<td>Formamide</td>
<td>39.75</td>
<td>39.3</td>
<td>16.2</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>55.77</td>
<td>29.2</td>
<td>9.6</td>
</tr>
<tr>
<td>Dimethyl sulfoxide</td>
<td>71.29</td>
<td>26.6</td>
<td>5.0</td>
</tr>
</tbody>
</table>

* Data were adopted from Rodriguez (1982); parameters are for 25°C.  
  1 (J/cm)³ = 0.489 Hildebrand = 0.489 (cc/cm³).
formamide, and water, all of which meet the American Chemical Society (A.C.S.) grade of over 99% purity. The force exerted on the fibers was recorded using a microbalance so that contact angles can be calculated using the Wilhelmy equation (Wilhelmy 1863) as described by Hodgson and Berg (1988). The resulting contact angle data were used to calculate various components of surface-free energy as performed by Gardner et al. (1999) based on the Good-van Oss-Chaudhury (GvOC) model (van Oss et al. 1988) and the Chang model (Qin and Chang 1995). These independent models express the surface-free energy, a material property of a solid, as a sum of the physical (dispersion) and chemical (polar or acid-base) interactions. In the GvOC model, the chemical component is further broken up into Lewis acidic (electron accepting) and basic (electron donating) characteristics.

The hydroxyl number determination was performed on freeze-dried fibers that were further dried in an oven at 60°C to insure complete moisture removal. Dry fibers of 2.5 g were analyzed according to Method A of the ASTM D4274-94 Standard (ASTM 1996). The standard method, primarily used for determining hydroxyl contents of polyols in the formulation of polyurethane systems, was adopted with a slight modification: instead of the specified 20 ml, 50 ml of the acetylation reagent (a solution of acetic anhydride in pyridine) was used. The modification was made because the bulky, unbonded freeze-dried fibers absorbed liquid reagent to a considerable extent, and hence a sufficient quantity of the liquid was required to ensure that the fiber samples had an even chemical coverage. The acetylation reaction was carried out at 98 ± 2°C for two hours after which the amount of hydroxyl groups reacted were quantified from the concentration of acetic acid, a side product of the reaction. The hydroxyl groups available for acetyl substitution were quantified in terms of hydroxyl number, which is expressed in milligram of KOH per gram of sample. For example, a hydroxyl number of 200 would mean for every gram (o.d.w.) of fiber sample, the hydroxyl groups available is as much as the amount of hydroxyl groups contained in 200 mg of potassium hydroxide.

Statistical analyses were carried out on the swelling, surface-energetic, and hydroxyl data. The Tukey test was used to determine the rankings of the swelling degrees (WRV) of fibers treated with different liquids. The t-tests were performed to compare the hydroxyl numbers between two fiber samples that were swollen differently. Regression analyses were carried out to quantify the relationships between surface-free energy components and the fiber swelling ability.

**RESULTS AND DISCUSSION**

**Swelling of recycled fibers by chemical treatments**

The swelling powers of the different liquids were statistically analyzed and are categorized in Table 2. The results show that all the liquids swelled recycled pulp fibers to an appreciable extent, resulting in water retention values that

<table>
<thead>
<tr>
<th>Fiber history</th>
<th>Swelling agent</th>
<th>Water retention value*</th>
<th>Hydroxyl number*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin</td>
<td>Water</td>
<td>1.92 (0.031) A</td>
<td>261 (1.5)</td>
</tr>
<tr>
<td>Recycled</td>
<td>12% NaOH</td>
<td>1.89 (0.009) A</td>
<td>157 (6.0)</td>
</tr>
<tr>
<td>Recycled</td>
<td>Formamide</td>
<td>1.56 (0.014) B</td>
<td>212 (2.0)</td>
</tr>
<tr>
<td>Recycled</td>
<td>Dimethyl sulfoxide</td>
<td>1.42 (0.027) C</td>
<td>226 (0.5)</td>
</tr>
<tr>
<td>Recycled</td>
<td>2% NaOH</td>
<td>1.40 (0.013) C</td>
<td>201 (1.5)</td>
</tr>
<tr>
<td>Recycled</td>
<td>Ethylene glycol</td>
<td>1.35 (0.020) C</td>
<td>188 (2.5)</td>
</tr>
<tr>
<td>Recycled</td>
<td>Water</td>
<td>1.10 (0.033) D</td>
<td>177 (3.0)</td>
</tr>
</tbody>
</table>

*Average water retention values (with standard errors in parentheses) that are designated the same alphabet are not different from one another as indicated by Tukey test.

*b Values are average hydroxyl numbers with standard errors in parentheses.
were 23–72% higher than the untreated, water-swollen recycled fibers (WRV 1.10).

Recycled pulp fibers had water retention values approaching that of the virgin fibers (WRV 1.9 for both fibers) if the hornified fibers were swollen in a concentrated alkaline solution of 12%. A concentration of 12% NaOH is the marginal alkaline strength for de-crystallizing cellulose, the major component in bleached kraft fibers. Decrystallization modifies the native cellulose into sodium cellulose (Fengel and Wegener 1984). In this sodium-cellulose lattice, relatively large distances occur between the cellulose molecules, and the interspaces are large enough to allow water molecules to penetrate and stay trapped (Fengel and Wegener 1984). Therefore, the water retention value was high, approaching that of virgin fibers. Although excessive alkali will adversely degrade cellulose and dissolve hemicelluloses, findings of this experiment demonstrate an extreme case where swelling ability of hornified fibers is restored to that of virgin fibers through intracrystalline swelling by disrupting the crystalline structure of cellulose.

Table 2 also indicates that formamide was the best swelling agent among the organic liquids used in the study. This swelling liquid resulted in a water retention value of 1.56, a 42%-increase compared to the WRV of the control (hornified) fibers. Formamide also swelled recycled fibers better than the conventional diluted alkaline solution, which only increased the WRV of the hornified fibers by 27%. Notable is the moderate swelling power of DMSO (WRV 1.42), which was found earlier to be a better swelling agent than formamide and ethylene glycol on spruce kraft fibers (Mantanis et al. 1995). However, in that study, the fibers were oven-dried before swelling treatments, and the swollen fibers were un-rinsed when analyzed for swelling, hence yielding the centrifuged retention values of the organic liquid instead of water.

The better swelling capacity of formamide can be attributed to the greater compatibility between the organic liquid and water. Because swelling was carried out under aqueous conditions, the existing water in the fibers should be displaced before the organic liquids can penetrate the fibers to cause swelling (Stamm 1964). To displace water, the organic liquids should be compatible with water. This compatibility is expressed by how close the solubility parameters (square root of CED) are between the two liquids (Rodriguez 1982). Compared to the other two organic liquids, formamide has a solubility parameter that is closest to water (Table 1), indicating a larger affinity to water. Formamide, therefore, should displace water more efficiently than DMSO or ethylene glycol. As more organic liquid molecules enter the fibers, the work required to displace water molecules becomes so large that it is easier to swell the fiber rather than displace the water (Stamm 1964). Therefore, an additional swelling occurs, making the fibers swell more than the original swelling in water. The additional swelling depends on the efficiency of the water displacement, thereby making formamide a better swelling liquid than DMSO or ethylene glycol under aqueous conditions.

The attribute of water/liquid compatibility to the effectiveness of swelling liquids can possibly be complicated by other properties such as liquid polarity. Compared to DMSO (Table 1), ethylene glycol has a slightly larger solubility parameter, a considerably smaller molecular size (molar volume), and twice as large hydrogen-bonding index, all of which indicate a favorable attribute for swelling cellulose fibers. However, ethylene glycol swelled fibers only as much as DMSO. Robertson (1964) commented that the effectiveness of a liquid to swell cellulose fibers is dependent on a number of liquid properties (some of which are listed in Table 1), but the swelling power cannot be assessed by using just one or two parameters. The hydrogen-bonding capacity of swelling liquids has been summarized as the most important factor in the fiber swelling process (Mantanis et al. 1995). We postulated that once this prerequisite is met, as in the case of this study where
Effect of swelling on the hydroxyl numbers of recycled fibers

The hydroxyl numbers of swollen fibers were determined by acetylation using acetic anhydride with pyridine as the solvent. Pyridine has been found to swell cellulose (McKenzie and Higgins 1955), hence possibly inducing an unintended increase of hydroxyl sites. However, the results can still serve as a relative measure of how easily pyridine penetrates the swollen structure of differently treated fibers to allow hydroxyl substitution by acetyl groups. Therefore, the hydroxyl numbers discussed in this study are a relative indicator of hydroxyl availability but not a true measure of hydroxyl contents.

The hydroxyl numbers of the swollen fibers are also presented in Table 2. Several useful comparisons were selected to assess the relationship between swelling and hydrogen-bonding site availability. The first comparison aims at elucidating the influence of fiber treatment history on hydroxyl number (Table 3). Virgin pulp fibers have a higher hydroxyl availability than recycled fibers (hydroxyl numbers 261 versus 177). Virgin fibers in the

Table 3. Some comparisons of hydroxyl numbers.

<table>
<thead>
<tr>
<th>Fiber history</th>
<th>Swelling agent</th>
<th>Mean difference</th>
<th>P-value</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin versus recycled</td>
<td>Water</td>
<td>84</td>
<td>0.02</td>
<td>Significantly different</td>
</tr>
<tr>
<td>Recycled</td>
<td>Water versus 2% NaOH</td>
<td>24</td>
<td>0.09</td>
<td>Significantly different</td>
</tr>
<tr>
<td>Recycled</td>
<td>Water versus 12% NaOH</td>
<td>20</td>
<td>0.21</td>
<td>Not significantly different</td>
</tr>
<tr>
<td>Virgin versus recycled</td>
<td>Water (virgin) versus 12% NaOH (recycled)</td>
<td>104</td>
<td>0.04</td>
<td>Significantly different</td>
</tr>
</tbody>
</table>

* A comparison yields a significant difference when the P-value is not larger than 10%.

* P-value represents the probability of being wrong in concluding that there is a significant difference between two means.
swollen state, as represented by freeze-dried fibers, have many hydrogen-bonding sites. In pulp slurries, most hydrogen bonding occurs with water. When the fibers are dried during papermaking, not only interfiber bonding occurs but the structural units of the cellulose fibers also are hydrogen-bonded to one another to form intrafiber bonding. These intrafiber bonds cannot be completely broken upon recycling (Atalla 1992). Therefore, the hydrogen-bonding sites in recycled fibers are decreased.

The second comparison verifies the basis of dilute alkaline treatments in increasing the hydroxyl availability of the fibers (Table 3). The hydroxyl number of 2% NaOH-swollen recycled fibers was 14% higher than that of water-swollen recycled fibers (201 versus 177). Hydroxyl ions from the NaOH solution hydrolyze hemicelluloses to yield acidic groups that cause water uptake in the interior of the fibers (Katz et al. 1981). The penetrating water molecules break the intrafiber bonds and form hydrogen bonds with the hydroxyl sites. When the fibers are freeze-dried, many of the bonding sites will remain exposed after the removal of water molecules. These exposed bonding sites react with the acetylation reagent to allow detection of available hydroxyl groups, hence yielding a higher hydroxyl number. Likewise, the exposed hydroxyl groups, if in a normal recycling process, would provide additional bonding sites for enhanced fiber bonding.

The next two comparisons indicate that excessive alkali did not contribute to the increment of hydroxyl availability. As discussed earlier, a concentrated solution of 12% NaOH was able to swell recycled fibers to a large extent, but comparison 3 (Table 3) shows that the hydroxyl numbers (157) of the mercerized fibers were not significantly greater than the untreated recycled fibers (hydroxyl numbers 177). A related argument is depicted by the final comparison in Table 3: the degraded hydroxyl availability could not be restored even though recycled fibers could be swollen as much as virgin fibers. Indeed, mercerized fibers swelled as much as virgin fibers (WRV 1.90), but their hydroxyl numbers were 40% smaller than that of virgin fibers (157 versus 261). The results of these comparisons, accompanied by the detrimental effects of strong alkaline solution in degrading cellulose and dissolving hemicelluloses (Fengel and Wegener 1984), once again confirm that concentrated alkaline solutions should not be used for remedying fiber hornification.

The observation of a low hydroxyl number in the 12% NaOH-treated fibers can be attributed to several phenomena. The first of these is the dissolution of xylans and glucomannans, the two components of hardwood hemicelluloses. The dissolution of hemicelluloses in strong alkaline solution is commonly known and has been utilized to obtain samples of high cellulose content from holocellulose (Fengel and Wegener 1984). If we can assume that bleached kraft pulp fibers consist of mainly holocellulose, a collective term for cellulose and hemicelluloses, their reaction with sodium hydroxide can be simplified as illustrated in Fig. 2. The backbones of the hemicellulose components are comprised of pyranose sugar chains that contain hydroxyl molecules (Fengel and Wegener 1984). The depletion of hemicelluloses of the pulp fibers, therefore, resulted in the loss of hydroxyl availability.

Another attribute to the depleting hydroxyl availability is possibly the transformation of OH groups to ONa groups as a result of mercerization. Kim et al. (1993) discovered that cellulose I (natural cellulose fibers), after treated with 3.5 M NaOH for 2 h, was transformed into different lattices, depending on the temperature of the water used for post-treatment washing. For washing at 20°C, as done in the present study, the sodium-cellulose I formed after alkaline reaction was hydrated to sodium-cellulose IV, with some cellulose I and cellulose I coexisting in the washed sample. Kim et al. (1993) also reported that washed fiber samples had all their sodium-cellulose I converted to sodium-cellulose IV at very low temperature (0°C). Therefore, fibers washed at 20°C with subsequent freeze drying may also contain a significant amount of sodium-cellu-
In sodium-cellulose lattices, the OH groups of the cellulose molecules are transformed to ONa groups (Fengel and Wegener 1984). This transformation results in a lower hydroxyl accessibility for acetylation, thereby yielding a low hydroxyl number even though the recycled fibers were swollen as much as virgin fibers in water.

In short, the comparisons involving concentrated alkaline solutions suggest that the effects of exposing hydroxyl sites in the opening up of crystalline structure are perturbed by the loss of hemicelluloses and the transformation of the increased hydroxyl sites to ONa groups. Investigating mercerized fibers, though problematic as it is, helps in elucidating the pitfalls of overemphasizing swelling in remedying fiber hornification. On the other hand, the comparisons involving fiber drying and re-swelling in dilute alkaline solution indicate that hydroxyl numbers reflect the physical occurrence of hornification and its reversal. This indication further suggests that hydroxyl numbers can be used to reflect the relative hydroxyl group availability in recycled fibers. Once the validity of the hydroxyl number is established, further discussions can be made regarding the hydroxyl availability and surface chemistry of the swollen fiber samples.

**Effect of swelling on the surface-free energy of recycled fibers**

To explore the possible effect of swelling treatments on surface chemistry, the surface-
free energy of recycled fibers was determined from the contact angles (Table 4) formed with a series of probe liquids. In the endeavor to evaluate whether and how surface chemistry was altered by swelling treatments, fibers treated with ethylene glycol (EG) were not analyzed for surface-free energy. This omission was made to avoid redundancy because the EG-swollen fibers exhibited water retention values and hydroxyl numbers that were comparable to those of NaOH-treated fibers (Table 2).

The total surface-free energy of recycled fibers was increased by all swelling treatments. This total free energy, whether calculated using the GvOC or Chang model, was linearly related to the degree of swelling (Fig. 3). In both calculations, an outlier was observed for the fibers treated with 12% NaOH. This exception indicates that the increase in total surface-free energy is associated with the intercrystalline swelling of cellulose fibers; the intracrystalline swelling, which occurred in fibers treated with 12% NaOH, is accompanied by a different incremental behavior of total surface-free energy. This behavior is analogous to the findings of Thode and Guide (1959) where amines, which are known to penetrate the crystalline regions of cellulose, did not follow the linear relationship that other organic liquids exhibited when their solubility parameters were correlated to the resulting volumetric swelling of cellulose fibers. Nevertheless, the present study suggests that swelling treatments result in higher surface energetics to provide a more reactive surface for fiber bonding.

The postulation that fiber surface chemistry changes favorably during swelling treatments is further strengthened by the data depicted in Fig. 4, which shows a lower water contact angle for fibers that are swollen to a greater extent. Because swelling treatments were found to increase the affinity of fibers to water (lower contact angles), more hydroxyl groups of the swollen fibers are expected to orient toward water. This tendency of hydroxyl group orientation suggests that more hydroxyl groups should be available for fiber bonding once the interfiber water is removed in the drying process. Swelling treatments improve the surface chemistry of recycled fibers and the effect should be favorable for fiber bonding. An additional point to note is the outlying data point of mercerized fibers in Fig. 4; this observation is also noted in Fig. 3, hence sug-

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**Table 4. Average and standard errors (in parentheses) of the contact angles formed at fiber/liquid interface.**

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Swelling agent</th>
<th>Contact-angle probe liquid</th>
<th>Methylene iodide</th>
<th>Ethylene glycol</th>
<th>Formamide</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin</td>
<td>Water</td>
<td></td>
<td>54.9 (1.3)</td>
<td>43.9 (2.5)</td>
<td>33.8 (3.7)</td>
<td>30.6 (2.6)</td>
</tr>
<tr>
<td>Recycled</td>
<td>Water</td>
<td></td>
<td>53.0 (0.9)</td>
<td>32.0 (3.4)</td>
<td>45.0 (4.3)</td>
<td>46.3 (3.1)</td>
</tr>
<tr>
<td>Recycled</td>
<td>2% NaOH</td>
<td></td>
<td>34.9 (2.2)</td>
<td>31.3 (1.9)</td>
<td>33.9 (4.7)</td>
<td>31.8 (2.1)</td>
</tr>
<tr>
<td>Recycled</td>
<td>12% NaOH</td>
<td></td>
<td>51.4 (3.5)</td>
<td>27.9 (2.9)</td>
<td>42.0 (4.9)</td>
<td>32.3 (2.5)</td>
</tr>
<tr>
<td>Recycled</td>
<td>Dimethyl sulfoxide</td>
<td></td>
<td>53.2 (0.9)</td>
<td>30.7 (1.0)</td>
<td>38.1 (4.7)</td>
<td>37.1 (1.9)</td>
</tr>
<tr>
<td>Recycled</td>
<td>Formamide</td>
<td></td>
<td>42.1 (2.1)</td>
<td>31.5 (1.6)</td>
<td>26.2 (0.9)</td>
<td>25.2 (2.4)</td>
</tr>
</tbody>
</table>

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**Fig. 3.** The relationship between the total surface free energy of swollen fibers and the extent to which the recycled fibers were swollen. Note: Error bars indicate the standard errors of the respective treatment means. Regression analysis does not include data point for 12% NaOH.
suggesting the consistency of the experimental results.

The basic (electron donating) character of the swollen fibers was closely related to the degree of swelling. Figure 5 shows the basic parameters of the fibers swollen to different degrees. Regardless of the swelling agent used, the basic parameter increased as fiber swelling increased until it exceeded the water retention value of about 1.7. The limiting factor for the basicity increase, is therefore, most likely the intracrystalline swelling. If this inference is true, a water retention value of 1.7 is the maximum amount that the recycled pulp fibers can be swollen without disrupting the crystalline structure of the cellulose. Although the surface basicity was observed to be related to fiber swelling, no specific pattern was observed for the correlation between acidic parameters and water retention values.

Relationship between surface chemistry and hydroxyl availability

To allow the optimization of both surface-free energy and hydroxyl availability in enhancing fiber bonding, the relationship between these two parameters needs to be evaluated. Figure 6 presents the relationship between polar surface-free energy and hydroxyl numbers. To demonstrate the independence of fiber history or hornification level, the data for virgin fibers are also included in the plot. Figure 6 indicates that as the hydroxyl number increases, the polar surface-free energy also increases regardless of chemical treatment. This observation can be explained by the highly electronegativity of oxygen atom in hemicellulose hydroxyl molecules; the oxygen atoms contain lone-paired electrons having no attached atoms to neutralize the negative charges. Fibers treated with 2% and 12% NaOH, however, did not follow the correlation...
trend. These outliers were commonly observed when the polar surface-free energy was calculated using both the GvOC and Chang model.

To confirm the anomalous behavior of alkaline-treated fibers, an attempt was made to indicate surface polarity without using the surface-free energy models. This involved calculating the acid-base contribution to the work of adhesion for the fiber/liquid interface using the contact angle and the total surface tension of a non-polar liquid and a polar liquid as described by Berg (1993). Because bleached kraft pulp fibers have been reported to have more acidic than basic functional groups (Jacob and Berg 1993), formamide, a basic probe liquid, was chosen for determination of the work of adhesion \( W_A \). This work of adhesion was then subtracted from the work of adhesion between fibers and methylene iodide, a non-polar liquid. The resulting acid-base work of adhesion \( W_A^{AB} \), when correlated to the hydroxyl numbers, showed similar patterns as discussed in the previous paragraph: a linear relationship with outlying data points corresponding to the alkaline-treated fibers (Fig. 7).

Assuming that 2% NaOH treatment was able to dissolve some xylans that contain polar functional groups such as acetyl (-OCH\(_3\)) and carboxyl (-COO) groups (Fig. 2), the treatment is expected to result in a lower polarity of the insoluble reaction products (the swollen fibers). Although alkaline treatments disrupt the hydrogen bonds of holocellulose (fiber) units through swelling, and the free OH groups should increase the polarity of the treated fibers, such a slight increase (from hydroxyl number 177 to 201) may not be sufficient to compensate for the loss of polar functional groups resulting from alkaline degradation. This postulation possibly explains why the 2% NaOH treatment reduced the polarity of the fiber surfaces, although the treated fibers had increased hydroxyl sites. The loss of polar functional sites such as acetyl and carboxyl groups, though led to the decrease in fiber surface polarity, was not accounted for in hydroxyl number determination. As a consequence, the 2% NaOH-treated fibers had a polar surface-free energy that was lower than predicted at a given hydroxyl number. Therefore, an outlying data point exists below the correlation trend in Fig. 6.

On the other hand, fibers treated with 12% NaOH behave towards the other extreme because their polar surface-free energy was found to be higher than the untreated fibers (Fig. 6). This different behavior can possibly be attributed to the formation of cellulose-\( \text{ONa} \) during intracrystalline swelling as explained earlier. Oxygen-containing functional groups, such as \( \text{ONa} \), contribute to polarity of the fiber surfaces (Liu et al. 1998). Although the hydroxyl availability is low in the 12% NaOH-treated fibers, it is only because the increased hydroxyl sites formed \( \text{ONa} \) complexes upon mercerization. Although mercerized fibers had fewer OH groups, these fibers had more polar sites (summative of OH and \( \text{ONa} \) groups) compared to the untreated fibers. These abundant polar sites also rendered the fiber surfaces more polar than fibers that depended on intercrystalline swelling to increase their free hydroxyl groups. Therefore, a relatively higher polar surface-free energy was observed in the 12% NaOH-treated fibers although the hydroxyl groups were not abun-
dant, giving a data point above the correlation trend (Fig. 6).

No specific correlation was obtained between either the acidic or basic parameter and the hydroxyl number. This observation did not agree with the molecule structure of a hydroxyl group that contains a proton-donating hydrogen atom (Lewis acid) and a lone-paired oxygen atoms (Lewis base); such a structure should exhibit a close relationship with Lewis acid-base. The lack of correlation can be explained by (1) the unselective detection of electron accepting or donating sites of functional groups other than the hydroxyl groups or (2) the possible flaw of the GvOC model in defining acid-base parameters (Berg 1993), causing the parameters to not relate to hydroxyl availability on a one-to-one basis. Further details for the second explanation were discussed in Tze and Gardner (2001).

From the relationship between surface chemistry and hydroxyl availability, several postulations can be made for further verification in future studies. These postulations are: (1) In the alkaline treatment of recycled fibers, the effects of re-exposing hydrogen bonding sites (e.g., the increased conformability during sheet formation) plays a more important role than surface polarity in improving the strength properties of recycled paper. (2) In treatments with organic liquids, where no chemical changes occur, the increase of polar surface free energy possibly further enhances the favorable effects of increased hydroxyl sites for improving recycled-paper strength.

CONCLUSIONS

This paper examined the swelling ability, hydroxyl availability, and surface chemistry of recycled fibers that were treated with alkaline solutions or organic liquids. Swelling was found to increase the hydroxyl availability of the fibers, except for those treated with 12% NaOH, which presumably caused the dissolution of hemicelluloses and formation of ONa groups in many hydroxyl sites of the cellulose. With the exception of mercerized fibers, swelling also increased the water wettability and total surface free energy of the fibers regardless of what swelling agents were used. Fibers swollen in organic liquids have polar surface-free energies that increased with an increase of hydroxyl numbers. Such a relationship was obscured for the alkaline treatments which presumably altered the chemical structure of the fibers.

Future studies should evaluate the strength properties of paper made of fibers swollen with organic liquids such as formamide, which is a stronger swelling agent than the 2% NaOH solution. In parallel to such an effort, the concentration of formamide in pulp slurries should be optimized bearing in mind that a large amount of formamide ($1.96/kg; Anon. 2000) was used in this study to dilute a 30% pulp consistency to 5%. The cost efficiency currently favors swelling with sodium hydroxide ($3.75/kg; Anon. 2000) whose dosage, as little as 1–2% of the fiber content, is minimal in 5% pulp consistency.

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