Improving the wet tensile strength of recycled paper by increasing its bond capacity

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ABSTRACT

This research relates to the cellulosic fibres of treated deinked Mixed Office Waste (MOW) paper and is directed particularly to a method for improving the wet strength of recycled paper. The effect of chemical treatment of fibre was investigated. Fibres were treated with 6 and 10% Succinic Acid (SA), with 3% and 5% catalysts (based on the total weight of fibres). The catalysts used for this research were Sodium di-hydrogen Phosphate (SDHP) and Sodium hypophosphite (SHP).

INTRODUCTION

The object of this study is to provide a method for adding wet strength to recycled paper, principal to which is fibre charge. Cellulosic fibres contain various ionisable groups (carboxyl, sulfonic acid, phenolic and hydroxyl groups) and are therefore negatively charged at all pH values – specifically in the surface and bulk charge. Surface charges are important for fibre and paper strength (Fors and Norman 2003). It was shown that curing is necessary for a reaction between the amino groups of PAE (wet strength resin) and the carboxyl groups of the fibres (Nordel 2006). Several researchers have recently reported the use of specific oxidative treatments (Kitaoka et al. 1999) and grafting treatments that increase fibre charge and fibre-fibre bonding (Gellerstedt et al. 2000; Johansson et al. 2006).

The tensile or sheet strength of fibrous products derived from cellulose fibres is due in large part to attractive fibre-fibre interactions. These inter fibre interactions include hydrogen-bonding interactions between fibres that have hydrogen-bonding sites. For cellulosic, hydrogen-bonding sites primarily include the hydroxyl groups of the individual cellulose chains. Treating cellulose fibres with polycarboxylic acids is not uncommon: polycarboxylic acids, for example, have been used as crosslinking agents for cellulose, while Phthalic, Maleic, and Succinic anhydrides have been used to form diester crosslinks in cellulose. Generally, the catalyst promotes ester bond formation between the carboxylating agent and the cellulose fibres and is effective in increasing bond formation at a given cure temperature. Particularly preferred catalysts include alkali metal polyphosphates, such as sodium hexametaphosphate, and alkali metal hypophosphites, such as sodium hypophosphite (Richard, 2003). Previous research (Richard, 2003) further shows that treating fibres with Succinic Acid (6% based on the total weight of fibres) and Sodium hypophosphite (3% based on the total weight of fibres) and heating at the indicated temperature for 20 minutes, improves the Water Retention Value (WRV) of fibrous composites. Sheet strength can be increased by enhancing the bonding of recycled fibres with a highly carboxylated fibre addition, increasing cationic starch retention or by increased retention of other cationic polymer dry and wet strength additives (Richard et al. 1999). Succinic Acid (SA) changes the structure of fibres, and these changes can increase the carboxyl group, anionic charge and bonding capacity of fibres - thereby improving the wet strength of paper.

Wet end disturbances have a chemical nature usually related to dissolved and colloidal substances, which are called “DisCo’s”. The main DisCo’s in mechanical and recycled pulp suspensions are: hemicelluloses, pectins and wood resin (pitch). Today water systems are relatively closed, leading to the accumulation of DisCo’s in the circulation waters. The dissolved and colloidal substances even contaminate the fibres and paper by sorption or deposition. It is very important to know the chemistry of the molecules and particles present in the wet end, as well as how they interact with each other and with the added chemicals, fibres and fillers (Holmstrom and sundberg 2003).

The present research studied the effect of Succinic Acid (SA) with two catalysts and two pH on the crystallinity index of cellulose and the chemical properties of fibres. Crystallinity and chemical changes to fibres were assessed as a function of SA treatment and pH changes, using x-ray diffraction (XRD) and Fourier transform infra-red spectroscopy (FT-IR).

MATERIALS

Recycled deinked Mixed Office Waste (MOW) pulp was prepared from Latf paper mill in Iran. Also obtained from this mill were PAE (produced by BASF, Germany) and ATC (DICON FC, produced by GIG Chemie, Germany). Succinic Acid (SA) with a purity of 99.5% (Merk, Germany), Sodium dihydrogen Phosphate (NAH2PO4) with a purity of 99% (Merk, Germany), Sodium hypophosphite or Sodium Phosphate (NAH2PO4.H2O) with a purity of 99% (Merk, Germany), Sulfuric acid (H2SO4) with purity of 97% (Merk, Germany) and Sodium hydroxide with a purity of 98% (Merk, Germany) were supplied from Laboratory of Science and Research branch, Islamic Azad University, Tehran, Iran.

METHODS

Treatment

In this research, the experimental treatments conducted were based on those used in Richard, 2003. For fibres treated with Succinic Acid (SA), prepared pulp was dewatered to about 30% consistency, then treated with 10% SA and 5% Sodium dihydrogen Phosphate (SDHP) catalyst. After 60 minutes, the fibres were heated to 140°C for 20 minutes. Thereafter, fibres were treated with 6% SA and 3% SDHP catalyst, 10% SA and 5% Sodium hypophosphite (SHP) catalyst, and 6% SA and 3% SHP catalyst.

After treating fibres with the carboxylating agent, fibres were then treated with cationic polymeric resin ATC in two different batches: 0 and 1%. Finally, after 10 minutes, 2% PAE was used as a wet strength resin. All of the handsheets, including the control handsheet, were treated with 2% PAE.

The pH of those fibres treated only with SA was neutralised by sodium hydroxide (NAOH). Additionally, the pH of the fibre was changed to about 3.5 by Sulfuric acid (H2SO4). Then, the chemical structure of the fibres was investigated with FTIR and XRD analyses.

Measurement of pH

The pH of the samples was measured with a pH meter (Metrohm, Switzerland).

Hansheets

Handsheets were made for the evaluation of wet tensile strength (by Lab Tech Semi-Automatic sheet machine) according to TAPPI Test Method 205 om-88.

Wet tensile strength test

The wet tensile strength properties of hansheets were tested according with TAPPI Method T4560 om-03.

XRD analysis

The measurement of crystallinity in cellulose fibres was carried out by powder X-Ray Diffactometry as described by Segal et al. (1959). Intensities were recorded between 0° and 80° (2θ –angle range). Crystallinity (%) was defined as (I002 – Iam) /I002 × 100, where I002 is the crystalline peak of the maximum intensity at 2θ between 22° and 23° for cellulose I, and Iam is the minimum intensity at 2θ between 18° and 19° for cellulose I.

The average size of crystallites was calculated by the Scherrer equation, Eq. 1. This is a method based on the width of the diffraction patterns in the X-ray reflected crystalline region. In this study, the crystallites size were determined by using the diffraction pattern obtained from 002 lattice planes of pulp samples,
Dhkl = kλ / (Bhkl cosθ)  (1)

where Dhkl is the size of crystallite, k is the Scherrer constant (0.84), λ is the X-ray wavelength, and Bhkl is the FW1/1M (full width half maximum) of the reflection hkl measured at 2θ, the corresponding Bragg angle (Mwaikambo and Ansell 1999).

**FTIR analysis**

To determine the content of carboxyl groups in carboxylated fibres and carboxyl, methyl groups in carboxymethylated cellulose fibres, the dried powder of samples was analysed by Fourier Transform Infrared (FTIR, Thermo Nicolet, USA) spectroscopy. A KBr disc technique was used. The IR spectra of pulp were obtained over a wavelength range of 400 to 4000 cm⁻¹.

**RESULTS AND DISCUSSION**

**FTIR Results**

FTIR spectra of pulp treated with Succinic Acid (SA) and two catalysts with two pH (3.5 and neutral pH) were compared with an untreated sample. Figure 1 through 5 show spectra of untreated pulp and pulp treated with SA. According to Heydarzadeh et al. (2009), carboxyl, methyl, and hydroxyl functional groups yield bands at wavelengths of 1618, 1426 and 1300 cm⁻¹. The absorbance peaks in the 3300- 3400 cm⁻¹ region were attributed to the stretching of O-H groups, whereas those around 2800-2900 cm⁻¹ were due to the stretching of C-H (Khall et al. 2001).

Carboxylation of cotton linters was investigated relative to its use in ion exchange, and the effect of these treatments in cotton-linter fibres was considered in relation to the FTIR spectrum (Nada et al. 2009). Stensted et al. (2008) reported that for each GMA (Glycidil methacrylate) monomer added to the polymer chain a new ester group is introduced. The peak at 1722 cm⁻¹ in FTIR spectrum shows that a large a mount of ester groups were introduced, indicated that polymer chains of GMA were grafted on microfibrillated cellulose. The peaks at 2916 and 2847 cm⁻¹ were assigned to the asymmetric and symmetric C-H stretch modes of the –CH3 and –CH2 groups (Rowell 2005). According to reported data, the peaks at wavelength around 1611 to 1642 cm⁻¹ and 1730 to 1739 cm⁻¹ was attributed to the presence of carboxyl group (-COO) and absorption band around 1323 to 1377 cm⁻¹ and 3414 to 3587 cm⁻¹ confirmed the presence of the hydroxyl group (-OH) (Mohkami and Talaeipour 2011).

In a study characterising carboxymethyl cellulose and polyacrylamide graft copolymer, a peak at 1603 cm⁻¹ was attributed to the presence of carboxyl group and peaks of 1325 and 1423 cm⁻¹ were allocated to methyl and hydroxyl groups (Biswal et al. 2004). The peak occurring at 1740 cm⁻¹ can be assigned to the acid function, while the peak occurring at 1434 cm⁻¹ is in the fingerprint region, and thereof cannot be assigned unambiguously (Gilli et al. 2009). The peak 1632 cm⁻¹ in Blank sample showed the carboxyl group in fibres. The OH groups have a higher value in the pulp treated with sodium hydroxide than in the untreated one. This is due to the sodium hydroxide decreasing the hydrogen bonds between the OH groups of pulp. This can be confirmed by the shift of OH groups to the higher wave length (Adel et al. 2010).

The treated samples (carboxylated) and untreated sample (blank sample) were analysed by FTIR. As shown in Figs. 1 to 5, there were distinct increases in both the carboxyl groups in pulp samples treated with SA. Table (1) shows the different infrared data of untreated and carboxylated fibres.

It is obvious that the broad absorption band around 3400 cm⁻¹ is due to the stretching frequency of the hydroxyl group (-OH). From table 3 it is clear that the crystallinity index of treated fibres was decreased. This can be confirmed by the shift that occurred for OH group at 3409 cm⁻¹ to 3418 cm⁻¹ in carboxylated fibres with neutral pH due to the decrease in hydrogen bonds by breakage of hydrogen bonds in the crystalline part of cellulose chains. Also, from the table, the crystallinity index of SA treated fibres without neutral pH was decreased. This may mean that the wave number of OH groups at 3409 cm⁻¹ was decreased by increasing SA, due to the decrease in the amorphous region. The bands around 1300 cm⁻¹ are assigned to hydroxyl group (-OH) bending vibration. The presence of a strong absorption band around 1500 to 1700 cm⁻¹ confirmed the presence of the carboxyl group (-COO).

**Table 1. Infrared Spectra of Blank Sample and Treated (Carboxylated) Fibres**

<table>
<thead>
<tr>
<th>Material</th>
<th>Wavenumber (cm⁻¹) (-COOH)</th>
<th>Wavenumber (cm⁻¹) (-OH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank sample</td>
<td>1623</td>
<td>1374</td>
</tr>
<tr>
<td>sample treated by SA with SDHP in pH=3.5</td>
<td>1625</td>
<td>1376</td>
</tr>
<tr>
<td>sample treated by SA with SDHP in pH=7</td>
<td>1623</td>
<td>1372</td>
</tr>
<tr>
<td>sample treated by SA with SHP in pH=3.5</td>
<td>1642</td>
<td>1327</td>
</tr>
<tr>
<td>sample treated by SA with SHP in pH=7</td>
<td>1641</td>
<td>1327</td>
</tr>
</tbody>
</table>

**Table 2 show the relative absorbance** (ratio of intensity of any band to intensity of band at 1325 cm⁻¹; Nada et al. 2009) of COOH at 1720 cm⁻¹ and OH 3439 cm⁻¹. This table shows that treated fibres with SHP catalysts had higher relative absorbance of COOH and OH than fibres treated by SDHP catalysts. Also, this table shows that neutral fibres had higher relative absorbance of COOH and...
Relative absorbance of OH

Blank sample  0.72

Sample treated by SA with SHP in pH=3.5  0.74

Sample treated by SA with SDHP in pH=3.5  0.74

Sample treated by SA with SHP in pH=7  0.87

Sample treated by SA with SHP in pH=7  0.86

Table 2. Relative Absorbance of Infrared Spectra from Treated (Carboxylated) Fibres

% Crystallinity index

Blank sample  49

Sample treated by SA with SHP in pH=3.5  47

Sample treated by SA with SHP in pH=7  39

Sample treated by SA with SHP in pH=7  27

Sample treated by SA with SHP in pH=7  21

Table 3. Effect of carboxylation on the Crystallinity Index and Crystallinity Size of Cellulose in Treated and Untreated Fibres

OH. This is attributed to the increase of swelling of cellulose chains. This result showed the penetration of chemicals through cellulose chains and consequently the increased incorporation of carboxylic groups onto cellulose. The result of the FTIR analysis showed that the fibre treated with SHP catalysts was better carboxylated during SA treatment than fibres treated with SDHP catalysts.

XRD analysis

X-ray diffraction was used to investigate the samples’ cellulose crystallinity. Table (3) shows the crystallinity index and crystallinity size of Blank and treated samples.

The result of XRD analysis showed that crystallinity decreased in fibres after being treated by SA. There was a breakage of hydrogen bonds in the crystalline part of cellulose chains of the carboxylated fibres. Crystallinity of cellulose treated with SDHP and in pH 3.5 was higher than fibres treated with SHP and in neutral pH. This result might be attributed to the removal of extractive lignin and other compounds with an amorphous nature, or more degradation of hydrogen bonds in the amorphous part of cellulose chains than the others. In samples without neutral pH (pH=3.5), fibres were treated with acid due to the increase in the hydrogen bonds by degradation of amorphous parts in the cellulose fibres, according to Nada et al. (2009).

Otherwise, NaOH used for neutralisation can cause a cleavage of the hydrogen bonds in the crystalline part of cellulose chains and reduce the crystallinity (Mohkami and Talaiepour, 2011). This can be confirmed by the shift that occurred for OH group at 3409 cm⁻¹ to high wave number of treated fibres in neutral pH (pH=7).

The crystallinity of cellulose fibres has been investigated in several studies. X-ray diffraction has been used for evaluation of crystallinity index in carboxylated cellulose and explains that treating fibres with acid causes an increase in the hydrogen bonds by degradation of hydrogen bonds in the amorphous part of cellulose (Nada et al. 2009). X-ray diffraction has been used for investigation of the percentage crystallinity in carboxymethylated and carboxylated fibres from waste paper (Mohkami and Talaiepour 2011). According to Joonobi et al. (2009), an increase in the crystallinity index was expected after chemical treatment by the removal of lignin and hemicelluloses, because of their amorphous nature. Kumar et al. (2010) determined the crystalline content of nanoparticles increased from 37% (deglinified raw materials) to 48% (nanoparticles). The crystallinity was found to increase owing to the smaller particle size and removal of amorphous substances such as lignin, hemicelluloses, and extractives.

Measurement Wet Tensile of Treated Fibres

According to Fig. 1, the treated handsheets with SA and two catalysts only and treated handsheets with a combination of SA and ATC showed higher wet tensile strength compared with the control handsheet. It seems that applying SA in fibres leads to increase bonds and carboxyl groups into fibres, so the strength increased, especially at 10% SA (except the handsheet treated with 10% SA and SHP catalyst, and 1% ATC). Also, consumption of ATC causes a dramatic rise in strength in handsheets made from treated SA and particularly with SDHP catalyst.

According to investigations made for statistical results, it was observed that there was no meaningful difference between the wet strength of handsheet made from fibres treated with 6% SA and SHP catalyst only. Regarding the higher wet tensile strength of treated handsheets with combination of SA and ATC compared with the control handsheet, it can be pointed out that SA treatment would cause the formation of ester bonds, and the catalyst promotes ester bond formation between it and the cellulose fibres. Results showed that SDHP promotes ester bond formation better than an SHP catalyst.

Treated fibres with ATC would cause the Dissolved and Colloidal Substances (DCS) that have anionic charge to be taken off and omitted from the fibres. Therefore, wet strength resin (caticonic charge) can be more effective and improved the wet tensile strength of handsheets. As shown in Fig. 1, the highest strength of the handsheets was 4.26 Nm/g for the treated fibres with 10% SA and SDHP catalyst, and 1% ATC. 1.27 and 1.66 Nm/g were wet tensile strength index for 0% and 1% ATC control handsheet, respectively. In contrast, the lowest strength of treated handsheets was 1.48 for the handsheets made from SA with SHP catalyst, and 1% ATC treated fibres. It seems that for treated fibres, ATC had a positive effect on wet tensile strength (except at 10% SA with SHP catalyst). The results from the ATC treatment showed that wet tensile strength decreased at 10% SA with SHP catalyst compared to the control handsheet treated with ATC, presumably due to reduced anionic sites of fibres, thus reducing the effectiveness of the wet strength resin and the wet tensile strength of handsheet.

Fibre-to-Fibre interactions increased by SA treatments (Richard 2003). The tensile or sheet strength of fibrous products derived from cellulose fibres is due largely to attractive fibre-to-fibre interaction (Westland 1998). The more charged groups are attached to the fibres, the more they swell, thus increasing the flexibility and conformability of the fibres. An increased amount of xylan on the surface strengthens the paper, whereas kraft lignin and lipophilic extractives are known to impair the strength properties of paper (Koljonen 2004). Depending on the grafting agent employed, it was possible to increase the negative fibre charge by 50-100%, or alternatively, generate a fibre with a net positive charge. Physical testing of these biografted pulps demonstrated that these changes in fibre charge could yield distinct changes in physical strength properties including enhancements in burst, tensile, tear index and, most notably, a 30-60% increase in wet-strength values (Johansson 2006).

According to Table 3, the crystallinity index of treated fibres decreased as confirmed by the increase in wet tensile strength in samples. As seen in the figure 11, samples treated with SDHP catalyst have a higher wet tensile strength compared with the sample treated with SHP catalyst, but this unusual behaviour could be brought about by other phenomena, such as the curling of the fibres and the deposition of solids onto the fibres (Sheikhi et al. 2010). The decrease in the crystallinity index is attributed to the degradation of the cellulose materials in the primary wall, whereas an increase in the tensile strength indicates the improvement in the packing order of the crystalline materials, particularly in the S1 layer. The tensile strength is directly related to the crystallinity index (Mwaikambo 2009).

CONCLUSIONS

1. FTIR analysis indicated that functional groups of carboxyl had slightly increased. The presence of a strong absorption band around 1500 to 1700 cm⁻¹ was confirmed the presence of carboxyl group (-COO).

2. X-ray diffraction demonstrated that crystallinity
index and crystallinity size of fibres decreased during treatment. This is due to the cleavage of the hydrogen bonds in pulp during treatment.

3. Results indicated that wet tensile strength of paper improved by SA treatment and highest wet tensile strength was shown in the sample treated by 10% SA, 5% SDHP and 1% ATC.

REFERENCES


