The Investigation of Carboxyl Groups of Pulp Fibers during Kraft Pulping, Alkaline Peroxide Bleaching, and TEMPO-mediated Oxidation (2007)

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Over the past 10 years, growing concerns over the modification of fibers have led researchers to focus on enriching the carboxyl group content of fibers by chemical oxidation and topochemical grafting. The current series of experiments continues this line of research by investigating the carboxyl group content of fibers during kraft pulping, alkaline peroxide bleaching, and 2,2,6,6-tetrametyl-1-piperidinyloxy radical (TEMPO)-KBr-NaClO oxidation system.

The first study characterizes changes in the carboxyl group content of fibers for two sets of kraft pulps: 1) conventional laboratory cooked loblolly pine kraft pulps, and 2) conventional pulping (CK) versus Lo-Solids pulping (LS) pulps. The results indicate that effective alkali (EA), temperature, and H-factor are the primary factors controlling fiber charge during kraft pulping. This result is supported by the following findings. When pulping to the same H-factor, low EA charge and low pulping temperature were favorable for increasing bulk carboxylic acid group content of fibers. Sulfidity did not have an obvious effect on bulk or surface carboxylic acid group content of fibers. Bulk fiber charge had a linear relationship with water retention value. Another set of kraft pulps distinguished by conventional pulping and Lo-Solids pulping were investigated to determine the effect of H-factor and pulping protocol on fiber charge. When bulk fiber charge was plotted against kappa number, pulps from Lo-Solids pulping had a higher slope value than the conventional pulping pulps. The charge on holocellulose fibers approaches a constant value as pulping advances for both types of pulping processes.

The second study examines the influence of alkaline peroxide treatment on elementally chlorine-free (ECF) bleached softwood kraft pulp. Alkaline peroxide treatment on fully bleached pulp was carried out because it is known that peroxide can increase fiber charge, but there's no detailed study explored on it. The results indicate that fiber charge increases with the increase of peroxide charge. These increases were demonstrated in the following way: a maximum fiber charge increment of 16.6% was obtained with 8.0% more peroxide charge on oven dried (o.d.) pulp at 60.0°C. Copper number decreased when peroxide charges were 0.5% and 1.0% at 60.0°C and 90.0°C treatments, respectively, and then increased with the increment of peroxide charge. Both fiber charge and copper number approached constant values when a 4.0% or higher peroxide charge was applied. Fiber charge and copper number were compared after the peroxide treatment of ECF bleached kraft pulp versus sodium borohydride reduced ECF bleached kraft pulp. The results indicate that carbonyl group content of fibers is favorable for improving fiber charge after peroxide treatment. The effect of increased fiber charge on refining, cationic starch adsorption, and hornification was examined. Two pulps were investigated: (1) an ECF bleached softwood kraft pulp served as control and (2) the control pulp treated with alkaline peroxide which had a higher fiber charge. It was shown that the increased fiber charge can improve the efficiency of the refining treatment as indicated by differences in tensile index when pulps were refined from 0 to 1000 revolutions. Upon the addition of 2% cationic starch to both pulps, the tensile index of the control pulp increased by 13.7% and that of high fiber charge pulp by 23.7%. Enhanced fiber charge was beneficial for reducing hornification when pulp was dried at 105°C.

The final study investigates the effect of TEMPO-mediated oxidation of an ECF bleached softwood kraft pulp on carboxyl group content, carbonyl group contents, degree of polymerization, and water retention value of fibers. The results show that TEMPO-mediated oxidation is useful in enriching the carboxyl and carbonyl groups to fibers, as well as enhancing the property of water adsorption of fibers. This result is supported by the findings that the carboxyl group content of the fibers was improved with increasing NaClO charge whereas, the carbonyl group content of fibers approached a maximum when a charge of 0.85 mmol NaClO/g o.d. fibers or higher was employed. The degree of polymerization of fibers drastically decreased from 2416 to 688 depending on the NaClO charge during the TEMPO-mediated oxidation. Oxidized fibers were shown to exhibit 62.9% higher water retention values (WRV) than the original fibers. Due to the enhanced carboxyl group content after oxidation, a measurement of the physical strength of the paper revealed that the tensile index of the oxidized fibers was 13.8% greater than that of the original fibers. The individual fiber strength of the oxidized fibers was lower than that of the original fibers as determined by a zero-span strength measurement showing a 17.0% decrease.

These findings suggest that: (1) kraft pulping process can be modified to obtain the target carboxyl group content, (2) terminal peroxide bleaching provides higher fiber charge which can save energy and chemical charge of subsequent refining and wet-end processes, respectively, as well as reduce hornification during drying, (3) TEMPO-mediated oxidation of fibers is capable of improving the properties of fibers, including fiber charge and water adsorption, and enhancing final paper strength.