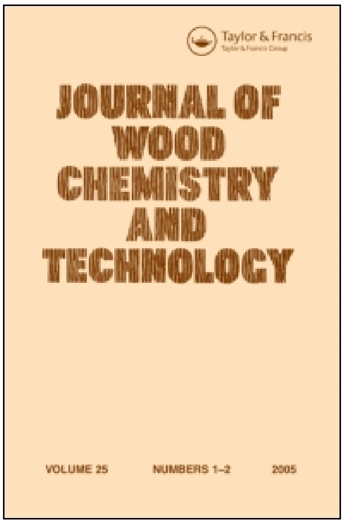

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DISTRIBUTION OF ANIONIC GROUPS IN TMP SUSPENSIONS

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ABSTRACT

The distribution of anionic groups in fibres, fines, the colloidal fraction, and the dissolved fraction of thermomechanical pulp (TMP) suspensions was determined. The influence of extraction, alkaline treatment, and peroxide bleaching of spruce TMP were also studied.

Spruce TMP was extracted with hexane, treated with alkali, or bleached with peroxide. Suspensions were made at pH 5.5 or 8, and fractionated into long fibres, large fines, small fines, a colloidal fraction, and a dissolved fraction. The surface and total charge of the fractions were determined separately by polyelectrolyte titration. To determine the origin of the charges, the contents of fatty acids, resin acids, and acidic units in polysaccharides in the different fractions were determined by gas chromatography.

Extraction of TMP with hexane prior to fractionation increased the measured total and surface charge of the fibres. The removal of wood resin probably uncovered some anionic groups on the fibre surface, or improved the penetration of the polymers into the pores of the fibres. The total charge, determined with polybrene titration, of the fines and the colloidal fraction was lower when the resin had been removed, while the surface charge, determined with poly-DADMAC, was not greatly affected.

Alkaline treatment of the TMP increased both the total charge and the surface charge of the fibres and fines, mainly because of demethylation of pectins. Alkaline treatment also increased the total and surface charge of the dissolved substances, due to the release of pectic acids into the water phase. Alkaline peroxide bleaching further increased the total and surface charge of fibres and dissolved substances, most likely due to oxidation of lignin. The total charge and the surface charge of the colloidal substances, consisting mainly of wood resin, were only slightly affected by alkaline treatment and peroxide bleaching.

The anionic charge in TMP suspensions originated mainly from free uronic acids in the xylans, arabinogalactans, and pectic acids. The contribution from the fatty and resin acids was substantial only for the colloidal fraction.

INTRODUCTION

Wood substances are released from wood and fibres during the production and further treatment of mechanical pulp. The pulp is seldom washed, therefore, the major part of the dissolved and colloidal substances is carried over to the paper machine.

Most charged groups in wood and mechanical pulp are carboxyl groups of uronic acids which are units of mainly xylans and also pectins.[1,2] Wood resin components, i.e. fatty and resin acids, also contain carboxyl groups. Carboxyl groups in uronic acids have acid constants of 3.5-4, whereas the carboxyl groups in oxidised lignin and in fatty acids and resin acids have constants in the range of 5-6.5 (Table 1).[3,4]

Mechanical pulping is usually conducted without pH adjustment, resulting in a pH of around 5. At this pH only small chemical changes take place in the fibres. However, it is known that the charge, i.e. the amount of carboxyl groups, is increased during alkaline treatment or peroxide bleaching.[1,5-7] This increase mainly arises from the demethylation of galacturonic acid methyl ester groups in pectins[8,9] and, in the case of peroxide bleaching, also from oxidation of lignin.[10]

The carboxyl group content of the pulp used in papermaking is important for paper strength through fibre swelling and increased specific bond strength.[11-13] Furthermore, fines retention, sizing, and adsorption of wet end additives, such as cationic starches and fixation aids, are affected by the amount of carboxyl groups. The carboxyl groups can be both beneficial and detrimental in the papermaking

TABLE 1

Charged Groups in Wood and Mechanical Pulps.

Chemical group	(Structure)	Acid constant, pK_A
Carboxyl, uronic acid	R-COOH	3.5 - 4
oxidised lignin		ca. 5
fatty and resin acids		5.5 - 6.4
Phenolic	Ar-OH	ca. 10
Hydroxyl	R-OH	> 12
Sulphonic	$R\text{-}SO_3H$	ca. 1
Protein: both carboxyl and amino groups		

process. Carboxyl groups situated in or on the surface of fibres and fines can be considered beneficial since, in addition to the swelling effect, these groups can interact with added cationic process chemicals, and thereby retain fillers and fines in the papersheet. The carboxyl groups located in the dissolved or colloidal fractions will give an anionic charge to the dissolved and colloidal substances. These substances are sometimes referred to as anionic trash and are normally detrimental in papermaking, since they consume added process chemicals without increasing the retention of fillers or fines. Aggregates of dissolved and colloidal substances can also be formed and may be deposited on the paper machine equipment, consequently leading to runnability problems and poor paper quality.

The total amount of acid groups in pulp samples can be determined, for example, by polyelectrolyte or potentiometric titrations.[7,14-16] Acid methanolysis, followed by gas chromatographic analysis of the formed methylated sugar units, has been found to give good yields of hemicellulose sugars, including uronic acids, for both wood and mechanical pulp samples.[17] The amount of fatty and resin acids can be determined by gas chromatography.[18]

The aim of this study was to determine the distribution of anionic groups between different fractions of unbleached, resin-free, alkali-treated, and peroxide-

TABLE 2

Amount of Metal Ions in TMP.

	Unbleached TMP µmol/g	Extracted TMP µmol/g	Alkali-treated TMP µmol/g	Peroxide-bleached TMP µmol/g
Calcium	20.0	25.0	27.4	25.0
Sodium	780	1200	1600	1300
Iron	0.4	1.6	0.5	0.5
Copper	0.2	0.3	0.1	0.5
Manganese	1.5	1.8	2.2	1.5
Magnesium	4.1	4.5	9.9	9.1

bleached TMP at pH 5 and 8. The contribution to the charge given by uronic acids, free fatty acids, and resin acids was also determined.

RESULTS AND DISCUSSION

The original pulp was not washed with acid to remove metal ions, since acid treatment may induce chemical changes, and washing will remove the dissolved and colloidal substances from the pulp. The amounts of different metal salts in the treated pulps were determined (Table 2). The amounts of sodium varied a little due to differences in the conductivity adjustment where sodium chloride was used. The amounts of magnesium were a little higher in alkali-treated and peroxide-bleached TMP due to the addition of magnesium sulphate as a bleaching chemical. The metal contents were otherwise on the same level for the different pulps. The charge, determined with polyelectrolyte titration, may not exactly correspond to the amount of carboxyl groups, since some of the carboxyl groups in the fibres and fines can be bound to metal ions.

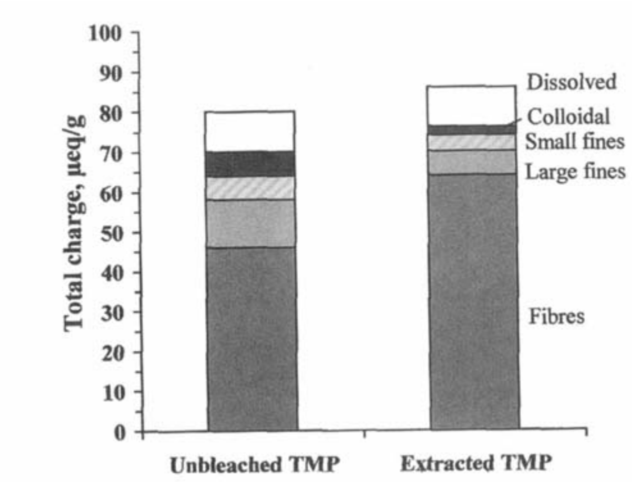

FIGURE 1. The total charge, extrapolated from the adsorption values of polybrene, was highest for the fibres. The contribution of the dissolved and colloidal substances to the total charge was 20%, although these fractions comprised of only 3.3% of the suspension dry matter. The total charge of the fibres was higher when the TMP had been hexane-extracted prior to fractionation.

"Total Charge" in Unbleached and Extracted TMP

The total charge, extrapolated from adsorption data using polybrene, was about 80 µeq/g for unbleached TMP (Fig. 1). The fibres contributed to about 60% of the total charge, the fines to about 20% and the substances released from the TMP fibres, i.e. the dissolved and colloidal fractions, to about 20% of the total charge. According to total organic carbon, TOC, measurements, about 3.3% of the original fibre material was released from the fibres, while the amount of fines separated by this fractionation method was about 13%. The amount of fines was most probably somewhat low, since not all fines passed the wire in the first dynamic drainage jar, DDJ, fractionation step. The specific total charge, calculated per gram of each fraction, was higher for fines, and much higher for the dissolved and colloidal fractions, compared to fibres.

The carboxyl groups in the fibres may not be completely accessible to polybrene adsorption, due to a lower specific surface area[7] or a slow adsorption process.[19] The surface of the fibres can also be different in chemical character from the surface of the fines. Hardell et al.[20] found that TMP fines mainly consist of material from the middle lamella region and the primary wall. It has also been reported that lignin and the hemicellulose monomers arabinose and galactose are abundant in the fines and middle lamella.[21,22] This suggests that the amount of arabinogalactans, containing uronic acids, is higher in the fines than in the fibres. Pectins are located especially in the middle lamella and the primary wall.[23] However, pectins are to a large extent methylesterified in native wood and unbleached TMP, and will hence not adsorb polybrene. The substances released from TMP are to a large extent wood resin and polysaccharides.[24-26] The wood resin can be dispersed as negatively charged colloidal droplets.[27,28] The dissolved polysaccharides contain uronic acids,[17,24] but the small amounts of pectic substances dissolved from unbleached pulp consists primarily of methylesterified pectins.[29]

Extraction of TMP with hexane prior to fractionation removed about 85% of the wood resin (Fig. 2). Small amounts of resin were found in the fibres and fines, and in the dissolved fraction, but little resin was left in the colloidal fraction. The total charge of the fibres from extracted TMP was clearly higher compared to unextracted TMP (Fig. 1). Most probably, removal of the resin uncovers some carboxyl groups. Allen[28] found that wood resin could be smeared onto tracheid and parenchyma cell surfaces in patches. This could prevent polybrene from interacting with carboxyl groups covered by wood resin, but also prevent polybrene from penetrating into some of the pores in fibre wall. The total charge of extracted TMP was lower for the large fines, the small fines, and the colloidal fraction (Fig. 1). The resin, which was removed by hexane extraction, adsorbed some of the polybrene. Removal of the resin from the fines did not uncover new

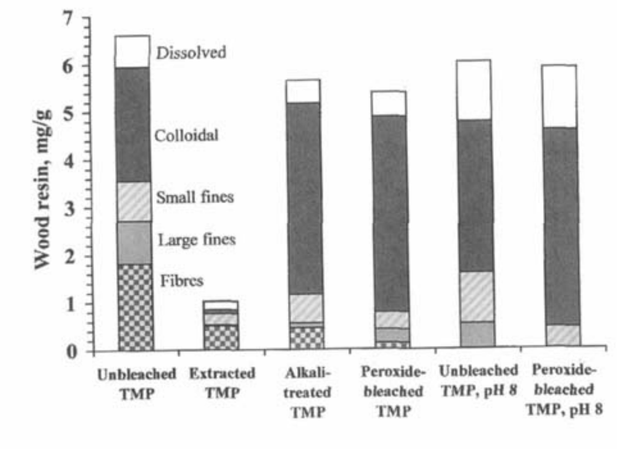

FIGURE 2. Extraction of the TMP with hexane removed most of the wood resin. More resin was dispersed in the colloidal fraction when the TMP had been alkali-treated or peroxide-bleached. The amount of dissolved resin was higher when TMP was fractionated at pH 8 compared to pH 5. No resin were found in the large fines from extracted TMP, fibres in unbleached TMP at pH 8, and in the fibres and large fines from peroxide-bleached TMP at pH 8.

carboxyl groups, as it did for the fibres, probably because the resin did not block carboxyl groups in the pores due to the larger surface area of the fines. The total charge of the dissolved fraction was not affected by the resin removal (Fig. 1), since the amount of resin in the dissolved fraction was small (Fig. 2).

"Surface Charge" in Unbleached and Extracted TMP

The surface charge, extrapolated from adsorption data using poly-DADMAC, was considerably lower for the fibres of unbleached TMP, about 14 μeq/g (Fig. 3), compared to the total charge, 46 μeq/g (Fig. 1). The surface charge was lower also for the fines (Fig. 1 and 3). Carboxyl groups located in the fibre pores or in the

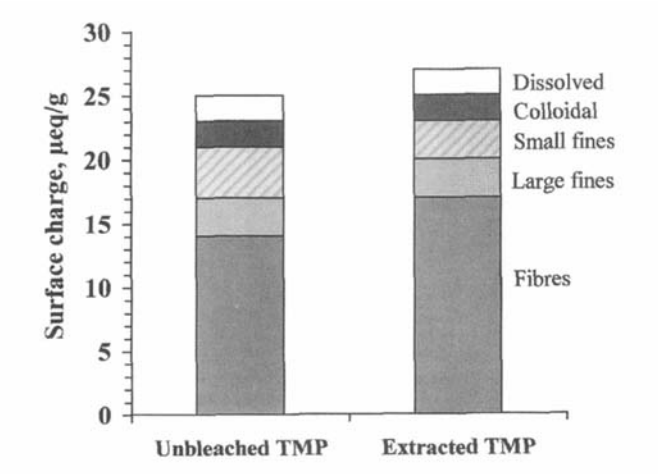

FIGURE 3. The surface charge, extrapolated from the adsorption values of poly-DADMAC, was lower than the total charge. Extraction of the TMP prior to fractionation uncovered new carboxyl groups on the surface.

fibre wall are not accessible to a polymer of higher molecular weight.[30] The surface charge for the colloidal fraction and the dissolved fraction was also lower than the total charge (Fig. 1 and 3). In the colloidal and dissolved fractions, all carboxyl groups should be accessible to both polymers, but still more polybrene was adsorbed than poly-DADMAC. The polymer adsorption for a dispersion of model resin was about 75 µeq/g resin using polybrene but only 25 µeq/g using poly-DADMAC. Obviously, more polybrene than poly-DADMAC will interact with resin, and perhaps also other substances released from unbleached TMP fibres.

When the TMP was extracted prior to fractionation, the surface charge of the fibres was higher compared to unextracted TMP (Fig. 3). As already concluded for the total charge, the wood resin located on the fibres probably covered some carboxyl groups. The fines, colloidal fraction and dissolved fraction were not much affected by extraction (Fig. 3), probably because poly-DADMAC was not adsorbed to any higher degree onto wood resin.

Dispersion of Wood Resin after Alkaline Treatment and Peroxide Bleaching

The total amount of wood resin in the pulp was slightly lower for the TMP that had been alkali-treated or peroxide-bleached compared to unbleached TMP (Fig. 2). Ekman and Holmbom[25] demonstrated that most of the resin components remain unaltered during alkaline peroxide bleaching, except for resin acids with conjugated double bonds, which are oxidised and degraded. However, the distribution of resin between the different fractions changed considerably. Much more resin was found in colloidal form after alkaline treatment and peroxide bleaching (Fig. 2). The fatty acids and resin acids dissociate at alkaline pH and dissolve as soaps in the water phase. The neutral resin components will then apparently be "washed" out from the fibres and fines, and be dispersed in the water phase, even at the relatively mild mixing conditions during the treatments. When the suspension was acidified after the bleaching, a major part of the fatty and resin acid soaps were again converted into their undissociated acid form. Most of the fatty and resin acids and the neutral resin components then formed colloidal droplets.

The amount of colloidal resin was higher when unbleached TMP was suspended and fractionated at pH 8 (Fig. 2). The resin in the fibres and fines was obviously "washed" out already at pH 8. The amount of dissolved resin was higher in suspensions of unbleached and peroxide-bleached TMP at pH 8 compared to pH 5, due to the dissolution of fatty and resin acid soaps (Fig. 2).

"Total Charge" in Unbleached, Alkali-Treated, and Peroxide-Bleached TMP

The total charge of a TMP suspension was doubled when the TMP was

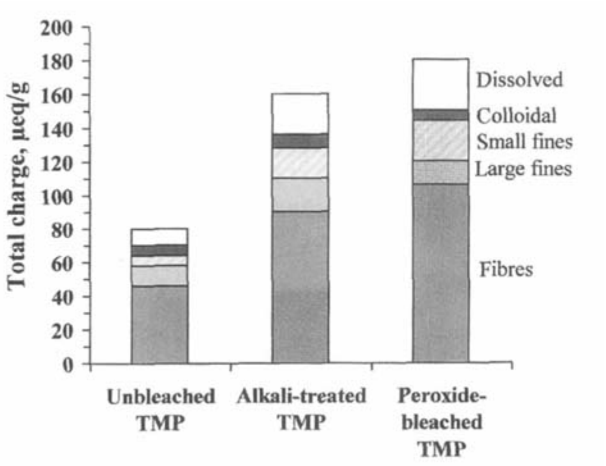

FIGURE 4. The total charge, extrapolated from the adsorption values of polybrene, was doubled when the TMP was alkali-treated, and peroxide bleaching further increased the total charge. The total charge of the dissolved fraction increased the most.

alkali-treated prior to disintegration and fractionation (Fig. 4). The total charge was twofold for the fibres and the large fines, while the total charge was 2.5-fold for the small fines and about threefold for the dissolved fraction (Fig. 4). This increase can, to a large extent, be attributed to demethylation of pectins. It has been found that TMP fines contain ray cells and flake-like material originating from the primary wall and middle lamella where the pectins are located.[20,23,31] Holmbom and Pranovich[9] demonstrated that methanol was released during alkaline treatment of TMP, indicating that pectins were demethylated during alkaline treatment. Part of the pectic acids was released from the fibres into the dissolved fraction, but the major part remained in the fibres or fines[17], thereby increasing the charge of these fractions.

The total charge of the colloidal fraction increased slightly when the TMP was alkali-treated (Fig. 4). The amount of colloidal resin was significantly higher in alkali-treated TMP compared to unbleached TMP (Fig. 2). However, the total charge was not greatly affected, since a major part of the resin is neutral components, such as triglycerides and sterylesters.

The total charge increased further when TMP was peroxide-bleached compared to alkaline-treated. This was the case for the fibres, the small fines, and the dissolved fraction, whereas the total charge decreased slightly for the large fines and colloidal fraction. Lignin is oxidised during peroxide bleaching, and new carboxyl groups are formed.[10,26] Peroxide bleaching of TMP has been shown to increase the charge on the fibres[5-7] and the increase was larger when the amount of peroxide, the initial pH or the pulp consistency was increased. The total charge of the large fines was somewhat lower in peroxide-bleached TMP compared to alkali-treated TMP, but this may be due to inconsistent separation of large and small fines. The total charge of the colloidal fraction from peroxide-bleached TMP was slightly lower than the colloidal fraction from alkali-treated TMP. Peroxide bleaching causes oxidation of resin acids with conjugated double bonds,[25] but otherwise the wood resin is little affected by peroxide bleaching.

The total charge increase during alkaline treatment or peroxide bleaching was very sensitive to the initial pH. Small variations in initial pH caused variations in the titration values.

"Surface Charge" in Unbleached, Alkali-Treated, and Peroxide-Bleached TMP

The surface charge was also increased for all fractions when the TMP was alkali-treated compared to unbleached TMP (Fig. 5). The surface charge was about two to threefold for all fractions, except for the dissolved fraction, where the surface charge increased from 2 μeq/g to 23 μeq/g, i.e. more than eleven-fold (Fig. 5). The surface charge for the fibres and the fines was lower than the total charge for the same pulps, due to the reduced penetration of poly-DADMAC in the fibres and fines. The values for the total charge and surface charges were on the same

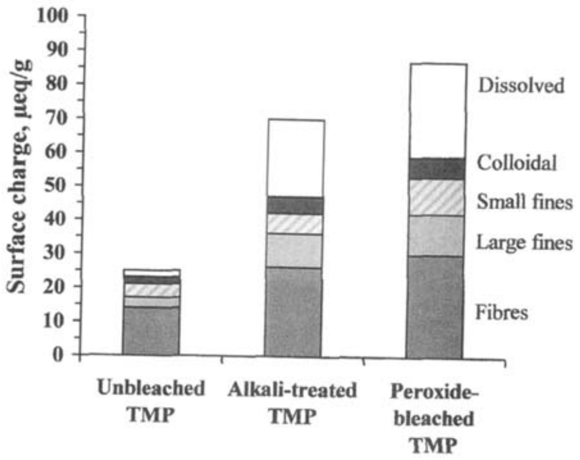

FIGURE 5. The surface charge, extrapolated from the adsorption values of poly-DADMAC, increased almost threefold when the TMP was alkali-treated prior to fractionation. The increase in surface charge was highest for the dissolved fraction, more than tenfold. Addition of peroxide further increased the surface charge.

level for the colloidal and dissolved fractions from alkali-treated TMP (Fig. 4 and 5). This indicates that polybrene interacts with other substances dissolved from unbleached TMP, since more polybrene than poly-DADMAC was adsorbed on the dissolved fraction from unbleached TMP. The amount of hemicelluloses is lower in the dissolved and colloidal fractions after alkaline peroxide bleaching, since glucomannans are deacetylated and resorbed onto the fibres.[17,24]

The surface charge further increased for the fibres, the fines and the dissolved fraction from peroxide-bleached TMP compared to alkali-treated TMP, probably due to the oxidation of lignin.

"Total Charge" in Unbleached and Peroxide-Bleached TMP at pH 8

The total charge was only slightly higher for unbleached and peroxide-

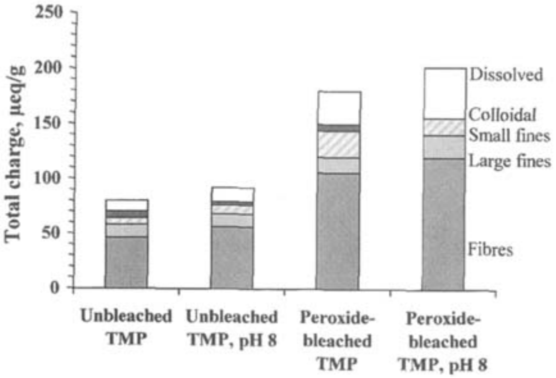

FIGURE 6. The total charge was slightly higher when unbleached or peroxide-bleached TMP was fractionated and titrated at pH 8 compared to pH 5. The total charge for the colloidal fraction was lower at pH 8, since the resin and free fatty acids were dissolved as soaps at pH 8.

bleached TMP suspensions agitated and fractionated at pH 8 compared to pH 5 (Fig. 6). Some of the carboxyl groups in the fibres may not have been dissociated at pH 5. It has been shown that the maximum adsorbed amount of polybrene is reached when the pH is higher than 7.[15] The swelling of the fibres will also be somewhat higher at pH 8 compared to pH 5,[11] which may increase the accessibility of some of the carboxyl groups in the fibres. The total charge was notably lower in the colloidal fraction at pH 8 both from unbleached and peroxide-bleached TMP, but higher for the dissolved fraction (Fig. 6). This can be attributed to the dissociation and dissolution of fatty and resin acids soaps. The amount of resin was higher in the dissolved fraction at pH 8 (Fig. 2).

Origin of Carboxyl Groups

The amounts of uronic acids, fatty acids, and resin acids were determined by GC and recalculated to µmol/g. Most galacturonic acid units in wood and untreated pulp are methylesterified.[23] It was therefore assumed that the degree of methylation of galacturonic acid was 80% in unbleached and extracted TMP and 0% in alkali-treated and peroxide-bleached TMP (Table 3).

In all fractions, except the colloidal fraction, most carboxyl groups were located in the uronic acids in the hemicelluloses and the pectic acids (Table 3). The contribution from the fatty and resin acids was substantial only for the colloidal fraction, where most of the resin was located (Fig. 2). When the TMP was suspended and fractionated at pH 8, most of the fatty and resin acids were located in the dissolved fraction, since the fatty and resin acids were dissociated at this pH and formed soluble soaps (Table 3).

Fibres. The total amount of carboxyl groups determined by GC in the fibres of unbleached TMP was somewhat higher than the amount determined with polyelectrolyte titration using polybrene (Table 3). However, in the fibres from extracted TMP, the amount of carboxyl groups determined with polybrene titration and GC analyses, were very similar. This suggests that wood resin covered some carboxyl groups and prevented polybrene adsorption. The titration value for alkali-treated fibres was higher than the amount of carboxyl groups determined by GC analysis. Chelating agents were added in the alkaline treatment and peroxide bleaching. These form complexes with the metal ions, which may result in an increased titration value, since some of the metal ions may have been blocking carboxyl groups. In peroxide-bleached TMP, the titration value for the fibres was substantially higher compared to the amount of carboxyl groups from GC analyses (Table 3). Obviously, alkaline peroxide bleaching also generated other carboxyl groups than those in hemicelluloses, pectic acids, and wood resin. Analysis of bleached mechanical pulps has demonstrated that carboxyl groups are formed in lignin during peroxide bleaching.[10,26] The carboxyl groups determined by GC analysis for unbleached TMP at pH 5 and pH 8 were similar (Table 3). The amount of carboxyl groups for fibres from peroxide-bleached TMP fibres was somewhat higher at pH 8 than at pH 5, probably due to variations in the bleaching process.

TABLE 3

Amounts of Free Uronic Acids, Free Fatty Acids, and Resin Acids and their Calculated Charge Contribution, Compared to the Charge Obtained by Polyelectrolyte Titration with Polybrene and Poly-DADMAC.

		GlcA μmol/g	GalA μmol/g	MeGlcA μmol/g	Fatty and resin acids μmol/g	Total amount of carboxyl groups μmol/g	Titration with polybrene μmol/g	Titration with poly-DADMAC μmol/g
Unbleached TMP								
	Fibres	17.5	9.0*	41.8	1.4	70	46	14
	Large fines	1.2	2.9*	5.0	0.5	9.7	12	3
	Small fines	0.8	3.4*	3.4	1.5	9.1	6	4
	Colloidal	0.8	0.1*	0.0	1.8	2.8	6	2
	Dissolved	0.3	0.5*	0.2	0.5	1.5	10	2
Extracted TMP								
	Fibres	13.6	8.5*	43.1	0.0	65	64	17
	Large fines	0.8	3.6*	2.4	0.0	6.8	6	3
	Small fines	0.3	2.7*	1.5	0.8	5.3	4	3
	Colloidal	0.3	0.1*	0.0	0.3	0.7	2	2
	Dissolved	0.5	0.6*	0.1	0.1	1.3	10	2
Alkali-treated TMP								
	Fibres	13.6	19.1	32.8	1.0	63	90	26
	Large fines	1.0	13.9	5.5	0.1	20.5	20	10
	Small fines	0.8	14.5	4.0	0.6	20	18	6
	Colloidal	0.0	3.8	0.3	2.0	6.1	8	5
	Dissolved	1.0	10.5	0.7	0.6	12.8	24	23
Peroxide-bleached TMP	Fibres	12.9	27.8	34.6	0.1	73	106	30
	Large fines	2.3	10.3	5.3	0.3	18.2	14	12
	Small fines	0.3	14.8	3.6	0.6	19.3	24	11
	Colloidal	0.1	3.2	0.1	2.0	5.4	6	6
	Dissolved	1.4	10.8	0.7	0.6	13.5	30	28
Unbleached TMP, pH 8	Fibres	20.3	6.4	41.7	0.0	68	56	-
	Large fines	1.2	3.8	5.9	0.4	11.3	12	-
	Small fines	0.6	3.8	4.1	0.8	9.3	8	-
	Colloidal	0.5	0.2	0.0	1.6	2.3	3	-
	Dissolved	0.5	0.7	0.2	3.2	4.6	13	-
Peroxide-bleached TMP, pH 8	Fibres	20.2	23.2	39.9	0.0	83	120	-
	Large fines	1.0	17.6	6.0	0.0	24.6	21	-
	Small fines	0.9	15.7	3.4	0.1	20.1	15	-
	Colloidal	0.0	0.7	0.3	1.3	2.3	0	-
	Dissolved	1.3	9.8	0.5	3.6	15.2	46	-

* 20% of the total amount due to the high degree of methylation of pectins

The amount of carboxyl groups, determined with poly-DADMAC titration, in the fibres was substantially lower than the amount determined with GC. The carboxyl groups in the smaller pores in the fibres were not accessible to poly-DADMAC, due to the higher molecular weight and larger radius of gyration of this polymer.

Fines. For the fines from the different treatments at both pH 5 and 8, the amount of carboxyl groups obtained by titration with polybrene was at the same level as the amount of uronic, fatty, and resin acids determined by GC (Table 3). Polybrene was probably adsorbed on most of the carboxyl groups in the fines due to the smaller size and higher surface area of the fines. The titration values of poly-DADMAC were again lower than the amounts determined with GC, due to the lower penetration of this polymer.

Colloidal fraction. The polybrene titration value for the colloidal fraction from unbleached TMP was somewhat higher than the amount of carboxyl groups determined with GC, while the titration value using poly-DADMAC was quite similar to the amount of carboxyl groups. Polybrene may be adsorbed on other neutral substances to a higher extent than poly-DADMAC. For the colloidal fraction from the other treatments, the titration values using polybrene or poly-DADMAC, and the amounts of carboxyl groups determined with GC were quite similar.

Dissolved fraction. For the dissolved fraction from unbleached, extracted, alkali-treated and peroxide-bleached TMP, the polybrene titration value was higher than the amount of carboxyl groups determined by GC (Table 3). Polybrene was probably also adsorbed on other substances and lignin, giving too high a titration value. The titration value for the carboxyl groups using poly-DADMAC was substantially lower than the value obtained with polybrene for the dissolved fraction from unbleached and extracted TMP (Table 3), and was well covered with the amount of carboxyl groups determined by GC. For the dissolved fractions from alkali-treated and peroxide-bleached TMP, the titration values were similar using polybrene and poly-DADMAC, and substantially higher than the amount of carboxyl groups determined by GC. Both polymers obviously interacted with other substances in the dissolved fraction from alkali-treated and peroxide-bleached TMP. Low molecular mass lignin is dissolved during alkaline peroxide bleaching,[26] and could adsorb some polybrene.

EXPERIMENTAL

Materials

TMP was obtained from a mill in Finland using two-stage refining of Norway spruce. The pulp consistency was about 40%. The pulp was stored at -24°C.

The cationic polymers used were "polybrene" (1,5-dimethyl-1,5-diazaundecamethylene polymethobromide) from Sigma chemicals Co. (St. Louis, MO, USA) and "poly-DADMAC" (polydiallyldimethylammonium chloride) from Allied Colloids Ltd. (Yorkshire, England). The polybrene had a molecular weight $M_w \approx 8*10^3$ Daltons and a charge density ≈ 5.3 meq/g, and was used without further purification. Poly-DADMAC was ultrafiltered with an Amicon Inc. instrument (Beverly, MA, USA) according to Laine et al.,[16] and had a molecular weight $100\,000 < M_w < 300\,000$ and a charge density ≈ 4.5 meq/g.

Model resin was isolated according to Sundberg, K. and his co-workers.[27]

Methods

Extraction. Unbleached TMP was freeze-dried and extracted in a large Soxhlet apparatus with n-hexane for 20 h. The pulp was air-dried overnight, and stored in a cold room until needed.

Peroxide bleaching. Portions of TMP were placed in polyethylene bags and mixed with bleaching chemicals at 10% consistency.[24] The chemicals used were diethylenetriaminepentaacetic acid, Titriplex V, (2 mg/g), magnesium sulphate (0.5 mg/g), sodium silicate (30 mg/g), and hydrogen peroxide (30 mg/g). The initial pH was adjusted to about 11.5 with NaOH. The bags were held at 60°C for 90 min. After this treatment, the samples were acidified to pH about 5.5 or 8 with SO_2-water.

Alkaline treatment. This treatment was carried out as peroxide bleaching although no peroxide was added. The TMP was treated at pH about 11.5 and 60°C for 90 min. The pulp was then acidified with SO_2-water.

Fractionation. The pulps were diluted to 0.5% consistency with distilled water, and the suspensions were agitated at 150 min^{-1} and 60°C. The conductivity was adjusted with 1 M NaCl to about 1 mS/cm, corresponding to 0.01 M NaCl. The pH was adjusted to about 5.5 or 8 using SO_2-water or NaOH. After stirring for 3 h, the suspension was disintegrated with a household mixer for 2 min. The consistency was again adjusted to 0.5% to make up for evaporated water. The fibres were separated from the rest of the suspension by filtration in a DDJ equipped with a 100-mesh wire (150 μm). One litre of the suspension was added to the DDJ, the stirring speed being 900 min^{-1}. The bottom valve was opened after 10 s, and about 300 mL of the filtrate was collected. The DDJ was washed and the procedure was repeated. The large fines were removed by filtration in a DDJ equipped with a 400-mesh wire (45 μm). About 750-1000 mL was filtered and 300-500 mL was collected. The DDJ was washed and the filtration repeated when necessary. The small fines were removed from the dissolved and colloidal fractions by centrifugation at 500 g for 30 min. The supernatant, containing the dissolved and colloidal fractions, was pipetted off. The colloidal fraction was separated from the dissolved fraction by filtration with a 0.1-μm filter. The different fractions were stored in a cold room until the next day.

Analyses

The charge was determined with polyelectrolyte titration according to Wågberg et al.[14,15] Adsorption isotherms were determined for all fractions and the polyelectrolyte adsorption was determined by extrapolating the plateau level of adsorption to zero polymer concentration. Portions of 50 g of the fractions containing fibres or fines, were weighed into bottles, and 20 mL of the polymer solution (polybrene or poly-DADMAC) and distilled water was added. The suspension was agitated for 2 h to ensure equilibrium adsorption of the cationic polymers. The suspension was then centrifuged at 500 g for 30 min and the supernatant was collected. The supernatant was titrated with a Mütek particle charge detector 03 (Herrsching, Germany) using potassium polyvinyl sulfate (KPVS) as anionic polymer. The colloidal and dissolved fractions were added directly to the measuring cell, an excess of the cationic polymers (polybrene or poly-DADMAC) was added and the samples were titrated with KPVS.

Wood resin. The TMP suspension was freeze-dried and Soxhlet-extracted with acetone:water:acetic acid 90:9:1 vol.-%. Water, acetic acid, and a small volume of acetone were added directly onto the sample. After 1 h, the sample was Soxhlet-extracted for about 3 h. The amount of resin was determined after silylation by gas chromatography (GC) as previously described.[18] The fines, the colloidal fraction, and the dissolved fraction were extracted with methyl *tert*-butyl ether, and after silylation the amounts of wood resin were analysed by GC.

Polysaccharides in pulps and waters were determined using acid methanolysis to obtain monomeric methyl glycosides of neutral sugars and methyl ester methyl glycosides of uronic acids. After silylation, the amounts of the monomers were determined by GC.[17]

TOC was measured with a TOC 5050 instrument (Shimadzu Corp., Japan).

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REFERENCES

1. E. Sjöström, J. Janson, P. Haglund and B. Enström, J. Polym. Sci. 5, 221 (1965).
2. E. Sjöström, Nord. Pulp Paper Res. J. 4, 90 (1989).
3. J. Laine, L. Lövgren, P. Stenius and S. Sjöberg, Colloids Surf. 88, 277 (1994).
4. V. Nyrén and E. Back, Acta Chem. Scand. 12, 1516 (1958).
5. J.A. Lloyd and C.W. Horne, Nord. Pulp Paper Res. J. 8, 48 (1993).
6. J. Thornton, R. Ekman, B. Holmbom and C. Eckerman, Pap. Puu 75, 426 (1993).
7. Y. Zhang, B. Sjögren, P. Engstrand and M. Htun, J. Wood Chem. Technol. 14, 83 (1994).
8. B. Holmbom, Proc. 9th Intern. Symp. Wood and Pulping Chem., CPPA, Montreal 1997, pp. PL3-1 (1997).
9. B. Holmbom and A.V. Pranovich, Proc. Fifth European Workshop on Lignocellulosics and Pulp, Univ. of Aveiro, Aveiro, pp. 559 (1998).

10. G. Gellerstedt, H.-L. Hardell and E.-L. Lindfors, Acta Chem. Scand. B 34, 669 (1980).

11. T. Lindström and G. Carlsson, Svensk Papperstidn. 85, R14 (1982).

12. A.M. Scallan, Tappi J. 66, 73 (1983).

13. R.S. Ampulski, Tappi Papermakers Conf. Proc. 1985, 9 (1985).

14. L. Wågberg, L. Winter and T. Lindström, In "Papermaking raw materials", Vol. 2, V. Punton (ed.), Mechanical engineering Publ. Ltd., London, pp. 917-923 (1985).

15. L. Wågberg, L. Ödberg and G. Glad-Nordmark, Nord. Pulp. Paper Res. J. 4, 71 (1989).

16. J. Laine, J. Buchert, L. Viikari and P. Stenius, Holzforschung 50, 208 (1996).

17. A. Sundberg, K. Sundberg, C. Lillandt and B. Holmbom, Nord. Pulp Paper Res. J. 11, 216 (1996).

18. F. Örså and B. Holmbom, J. Pulp Pap. Sci. 20, J361 (1994).

19. L. Wågberg, L. Winter, L. Ödberg and T. Lindström, Colloids Surfaces 27, 163 (1987).

20. H.-L. Hardell, G. Leary, M. Stoll and U. Westermark, Svensk Papperstidn. 83, 44 (1980).

21. H. Chang, J. Sinkey and J. Yan, Tappi 62, 103 (1979).

22. J. Sorvari, V. Pietarila, A. Nygren-Konttinen, A. Klemola, J.E. Laine and E. Sjöström, Pap. Puu 65, 117 (1983).

23. U. Westermark and F. Vennigerholz, Proc. 8th Intern. Symp. Wood and Pulping Chem., Vol I, KCL, Espoo 1995, p. 101 (1995).

24. J. Thornton, C. Eckerman and R. Ekman, Proc. 6th Int. Symp. Wood and Pulping Chem. Proc., Vol 1, Appita, pp. 571 (1991).

25. R. Ekman and B. Holmbom, Nord. Pulp Paper Res. J. 4, 188 (1989).

26. B. Holmbom, R. Ekman, R. Sjöholm, C. Eckerman and J. Thornton, Papier 45, V16 (1991).

27. K. Sundberg, C. Pettersson, C. Eckerman and B. Holmbom, J. Pulp Pap. Sci. 22, 226 (1996).

28. L.H. Allen, Pulp Pap. Can. 76, T139 (1975).

29. K. Sundberg, A. Sundberg, J. Thornton and B. Holmbom, Tappi J. 81, 131 (1998).

30. L. Winter, L. Wågberg, L. Ödberg and T. Lindström, J. Colloid Interface Sci. 111, 537 (1986).

31. J. Boutelje and I. Eriksson, Holzforschung 38, 249 (1984).