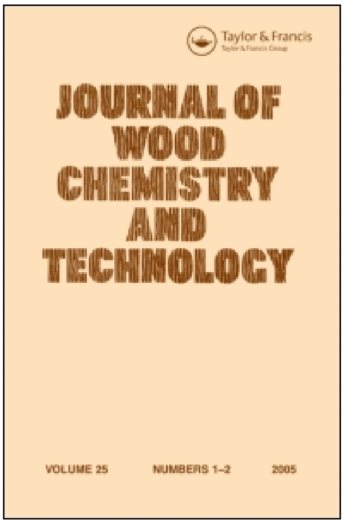

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DETERMINATION OF CHARGED GROUPS IN MECHANICAL PULP FIBRES AND THEIR INFLUENCE ON PULP PROPERTIES

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ABSTRACT

The content of charged groups, i.e carboxylic and sulfonic acid groups in various kinds of mechanical pulp fibres has been investigated. Special emphasis has been given to the determination of the charged groups located at the fibre surfaces using a polyelectrolyte titration technique. The significance of these charged groups for some physical properties of the pulps has also been evaluated.

The results suggest that it is feasible to determine the surface charges of the various kinds of mechanical pulp fibres by applying the polyelectrolyte titration technique. This study also indicates that fibre surface charges can

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serve as one of the basic chemical parameters to characterise fibre surface properties, and that both total charged groups and surface charged groups are important for the physical properties of the pulps.

INTRODUCTION

The use of thermomechanical and chemimechanical pulps in different paper grades has increased significantly in recent years. The driving forces for this development are lower cost and higher yield and some specific properties which these TMP and CTMP fibres possess. To further improve pulp quality and to be able to design an appropriate pulp quality profile by proper control or modification of the pulping process, a basic understanding of the chemical properties of the pulp fibres is of great importance.

It is known that the acidic groups present in cellulosic fibres are important for pulp swelling and thus for pulp strength properties and beatability in general[1-7]. It has also been suggested that pulp strength properties can be related to the acidic groups specifically located on the surfaces of pulp fibres[8].

Table 1 gives a comparison of typical contents of acidic groups in different type of pulps. It can be seen that the content of acidic groups in mechanical pulps is much higher than that in bleached sulfate pulps. The same is also true of unbleached sulfate pulps with kappa numbers less than 32. It is therefore expected that the acidic groups in TMP and CTMP fibres may exert a strong influence on pulp properties.

A number of methods are available to analyse the content of acidic groups in wood materials[9]. One of the most used methods is the conductometric titration method[10]. However, this method cannot determine selectively the charged groups located at fibre surfaces.

TABLE 1

Acidic Groups in Mechanical and Chemical Pulps.

Pulp	Sulfonic groups [mmol/kg]	Total acidic groups (Carboxylic + sulfonic groups) [mmol/kg]
Unbleached TMP	–	80 – 110
Bleached TMP	–	150 – 250
Unbleached CTMP	40 – 70	120 – 180
Bleached CTMP	40 – 70	190 – 320
Unbleached sulfate (Kappa Number < 32)	–	< 60 – 80
Unbleached sulfite (Kappa Number < 32)	< 100 –120	< 150 – 180
Bleached sulfate	–	10 – 25

A method which is suggested for the determination of charged groups on the fibre surface is the polyelectrolyte titration technique. The basic idea for this technique was first suggested by Terayama in 1952[11]. Later, Horn developed this technique by constructing an automatic device to detect the end point during polyelectrolyte titration[12]. Recently, this technique was applied successfully by Wågberg et al to study polyelectrolyte adsorption on cellulosic fibres[13-16]. Based on studies of polyelectrolyte adsorption on carboxymethylated, bleached softwood kraft pulps, they suggested that the acidic groups at different structural levels in this type of fibres can be

estimated by determining the adsorbed amount of polyelectrolyte[16].
The aim of the present work has been twofold. Firstly, the feasibility of determining surface-charged groups in various kinds of TMP and CTMP fibres by applying the polyelectrolyte titration technique was evaluated. Secondly, the significance of these surface charged groups and total charged groups for some physical properties of hydrogen peroxide bleached CTMP pulps was investigated.

EXPERIMENTAL

Preparation of Pulp Materials

In order fully to evaluate the feasibility of the polyelectrolyte titration technique, various types of mechanical pulp fibres have been studied.

One industrial CTMP from Norwegian spruce (Picea abies) was used. This CTMP was first treated with 0.5% DTPA at 5% pulp consistency and 70°C for 10 minutes and then washed thoroughly with warm water (80-100°C) to reach a COD level of 16.1 kg/ADMT in the pulp. This DTPA-treated CTMP was then bleached with hydrogen peroxide in this laboratory. Both the DTPA-treated and the hydrogen peroxide bleached CTMP were used for polyelectrolyte adsorption studies.

The hydrogen peroxide bleaching was carried out at 60°C for different periods of times (30, 60 and 120 minutes). The bleaching chemicals used were 4% hydrogen peroxide, 4% sodium silicate (technical quality) and 0.1% $MgSO_4$ (based on o.d pulp). Two different initial pH levels, pH 12 and pH 13, were employed. The initial pH is defined as the pH of the total bleaching liquor at 25°C and was adjusted by addition of sodium hydroxide solution. For the bleaching at 15% pulp consistency, the conventional bleaching method using a plastic bag was used. For hydrogen peroxide bleaching at 40% pulp consistency, the pulps were first air-dried at room temperature to about 90% dryness and the pulp was then mixed with appropriate bleaching chemicals using a laboratory mixer to reach a pulp consistency of 40%. The mixing time was 10 minutes. Finally the ready mixed pulp was placed in a warm water bath for a predetermined period of time.

One industrial TMP from Norwegian spruce (Picea abies) was also used to represent another important type of mechanical pulp. Some of this TMP was first post -sulfonated in the laboratory according to Table 2 and was then used for polyelectrolyte adsorption studies.

In one case, only the long fibre fraction of the TMP was used in order to separate the effect of fine materials. This fibre fraction was prepared by removing the fines in a Celleco laboratory filter (300 μm filter). Bauer McNett fraction analysis on the retained fibre fraction showed that the content of the fines left was negligible. In some other cases, several hydrogen peroxide treatments were carried out on this long fibre fraction and the treated long fibre fractions were then used for polyelectrolyte adsorption studies. Before the hydrogen peroxide treatment, the pulps was first pretreated with 0.1% DTPA and hot-disintegrated. The hydrogen peroxide treatments were performed in a manner similar to that described for hydrogen peroxide bleaching of the CTMP.

Determination of Surface Charge by Polyelectrolyte Titration Technique

It has been shown that the adsorption of certain cationic polymers on cellulosic fibres can be regarded as an ion-exchange reaction[15]. It is therefore possible to determine the charges on cellulosic fibres by measuring the amount of the cationic polymers adsorbed on cellulosic fibres.

TABLE 2

The TMP and post-sulfonated TMP.

Sample	Sulfonation conditions*			Bound sulphur *** g S/kg	Freeness (CSF) ml
	Temp. °C	Time Min.	Sulfite charge**		
TMP	-----	-----	-----	0,10	135
Sulfonated TMP - 1	90 - 150 150	30 5	12,6	5,77	-----
Sulfonated TMP - 2	90 - 150 150	30 5	31,5	8,07	-----

* The sulfonation was carried out in an autoclave and the reaction was terminated by washing in cold water after a predetermined reaction time. Liquor- to- pulp ratio was 5:1 calculated on o.d. pulp.

** Percentage Na_2SO_3 on o.d. pulp.

*** The bound sulphur content was measured on handsheets by the Schöniger method[17], except that the sulfate ion content was determined by ion chromatography.

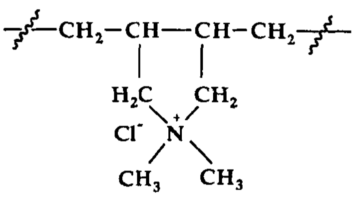

FIGURE 1 The chemical structure of the cationic polyelectrolyte used in the adsorption studies.

A cationic polyelectrolyte, polydimethyldiallylammonium chloride (p-DMDAAC) (Allied Colloids, England) was used in the adsorption studies. The chemical structures of the polymer is given in Figure 1.

Before use, this commercially available p -DMDAAC was first washed with 0.2 M NaBr solution and thereafter with deionized water in an ultrafiltration cell in order to remove low molecular mass material. The ultrafiltration cell used was a Mini-Pellicon from Millipore Corp. (Bedford, MA, USA) fitted with a Millipore polysulfone membrane PTHKOLCP 2 with a molecular mass cut -off of 10^5. During the ultrafiltration process, the counter ions to the polymer were also changed from chloride to bromide. The molecular mass distribution of the polymer after filtration was characterised by size exclusion chromatography (SEC) using an eluent consisting of 0.3 M sodium acetate and 0.3 M acetic acid. Polyethylene oxides, PEO (Toyo Soda Manufact. Co., Tokyo, Japan) and polyethylene glycols, PEG (Polysciences Inc., PA, USA), were used as molecular mass stardards. The relative molecular mass of the p-DMDAABr, calculated as weighted average from the PEO/PEG calibration curve, was $2.2 \cdot 10^5$, which gives a radius of gyration of approximately 33 nm[18]. The charge density of p-DMDAABr is $4.86 \cdot 10^{-3}$ eq/g.

The pore size distribution in cellulosic fibres has been studied extensively by Stone and Scallan who have shown that the average pore width of cellulosic fibres is far less than 33 nm[19]. It is therefore reasonable to assume that p–DMDAABr adsorbs only at the surface of the pulp fibres. The charge determined by p-DMDAABr adsorption is thus considered to be a measure of surface charges in pulp fibres.

Sample Preparation

Prior to the adsorption experiments, the pulps were washed with 0.01 M HCl to remove most of the metal ions and then with deionised water to pH 5. The

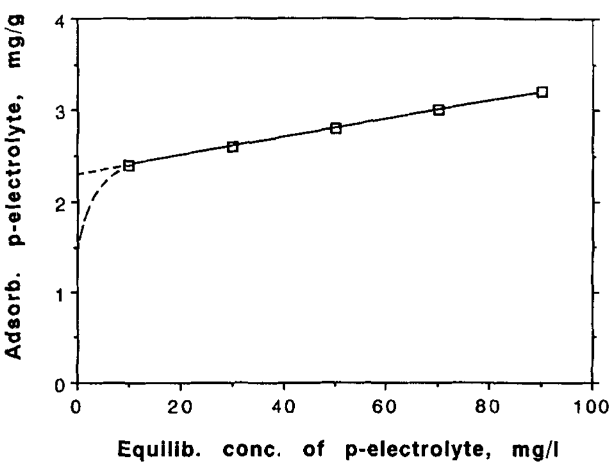

FIGURE 2 The adsorbed amount of polyelectrolyte, in mg/g, as a function of equilibrium concentration of the polymer in solution.

sulfonic and carboxyl groups were then converted to their Na^+-form by treatment with 1 mM Na_2CO_3 and addition of NaOH to pH 9. To remove excess electrolyte, the pulps were washed with deionised water until the conductivity of the filtrate was less than 5 µS/cm. In order to avoid loss of fines, a displacement washing device fitted with a 300 mesh wire cloth was used.

Adsorption Measurements

The fibres in Na^+ form were suspended in deionised water to give a pulp suspension with a fibre concentration of 5g/l. The pH in the pulp suspension was adjusted with 0.1 M NaOH to pH 8. To a series of at least five 100 ml samples, different amounts of p-DMDAABr were added. This mixture was then stirred for 30 minutes in order to reach adsorption equilibrium. The pulp suspension was then filtered on a Buchner funnel and the filtrate collected.

The concentration of p-DMDAABr in the filtrate is called the equilibrium concentration and is determined by titrating with an anionic polymer, potassium polyvinyl sulfate (KPVS, from Wako Pure Chem. Ltd., Japan) together with a cationic indicator, orthotoluidine blue (OTB)[11]. The end point during the titration is detected by a colour shift of OTB using an automatic device similar to that described by Horn [12].

Knowing the total amount of charged polymers and the equilibrium concentration of the polymers in solution, the adsorbed amount of the polymers can be easily calculated. This gives adsorption isotherms of the type shown in Figure 2. By extrapolating the plateau level to zero equilibrium concentration, the adsorbed amount of polyelectrolyte at zero concentration can be obtained. The amount of polymer charge adsorbed at this point (in μeq/g) is then taken to be the surface charges of the fibres[16].

The assumption that the adsorption of cationic polymers on cellulosic fibres can be regarded as an ion-exchange reaction between the negatively charged groups in the cellulosic fibres and the positively charged groups in the polyelectrolyte is further verified by stoichiometric studies (The stoichiometry is defined as the ratio of the number of bromide ions released upon polyelectrolyte adsorption to the total number of polymer charges adsorbed). It has been shown that over 90% of the polymer charges are combined with charges in cellulosic fibres when the plateau level is reached in the adsorption isotherm[16]. This means that there is almost 1:1 stoichiometry. However, further adsorption along the plateau level leads to a decrease in the stoichiometry[16]. By extrapolating the plateau level to zero concentration, the stoichiometry requirement is guaranteed.

Evaluation of Other Pulp Properties

The content of total charged groups in the pulps was determined by conductometric titration according to Katz et al[10].

For assessment of papermaking properties, handsheets were made from the hydrogen peroxide bleached CTMP according to SCAN-M 8:76 (with recycling of white water) and their mechanical properties were determined according to appropriate SCAN-standards.

RESULTS AND DISCUSSIONS

Application of the Polyelectrolyte Titration Technique to Mechanical Pulp Fibres

The adsorption isotherms for CTMP pulp and several hydrogen peroxide-bleached CTMP pulps are shown in Figure 3 and Figure 4. It can be seen that these isotherms are of the high affinity type with a pronounced plateau level. This enables the charge to be easily determined as indicated in Figure 2.

As shown in Figure 3, the hydrogen peroxide-bleached CTMP gave higher adsorption levels than unbleached CTMP, due to the increased carboxylic acid content introduced by hydrogen peroxide bleaching. Moreover, bleaching carried out at an initial pH of 13 has a higher content of carboxylic acid groups than that at an initial pH of 12 shown by the differences in the adsorption levels. The mechanism of this pH effect on the carboxylic acid group content is not yet fully elucidated, but it is believed that the higher concentration of peroxide anions at a higher initial pH value may contribute to the effect. The decomposition products of hydrogen peroxide, such as hydroxyl radicals and superoxide anion radicals, may also play an important role.

Figure 4 shows that hydrogen peroxide bleaching at a pulp consistency of 40% gave a higher adsorption level than that at 15% pulp consistency under otherwise similar bleaching conditions. The higher hydrogen peroxide concentration in the bleaching liquor in the former case results in a more

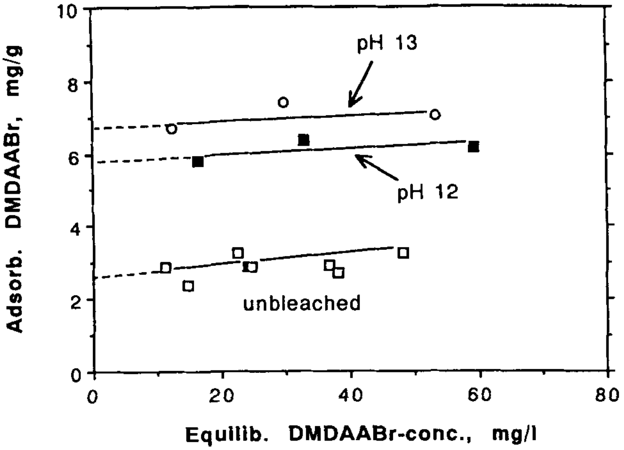

FIGURE 3 The adsorbed amount of p-DMDAABr (mg/g) as a function of equilibrium concentration of the polymer (mg/l). Unbleached and hydrogen peroxide-bleached CTMP. Bleaching conditions: 4% H_2O_2, 15% pulp consistency, 60 minutes, initial pH 12 and 13, respectively.

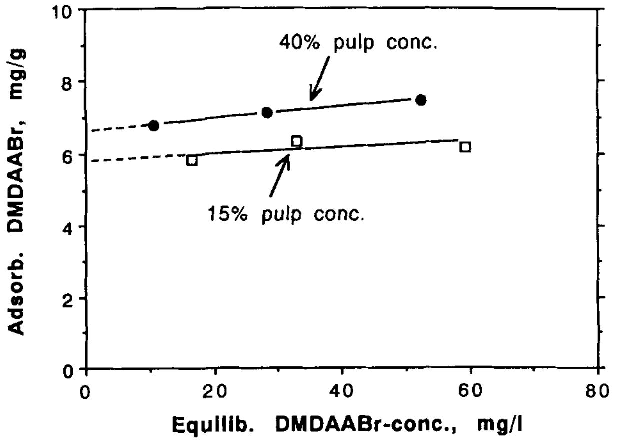

FIGURE 4 The adsorbed amount of p-DMDAABr (mg/g) as a function of equilibrium concentration of the polymer (mg/l). CTMP bleached with hydrogen peroxide at 15% and 40% pulp consistency, respectively. Other bleaching conditions: 4% H_2O_2, 60 minutes, initial pH 12.

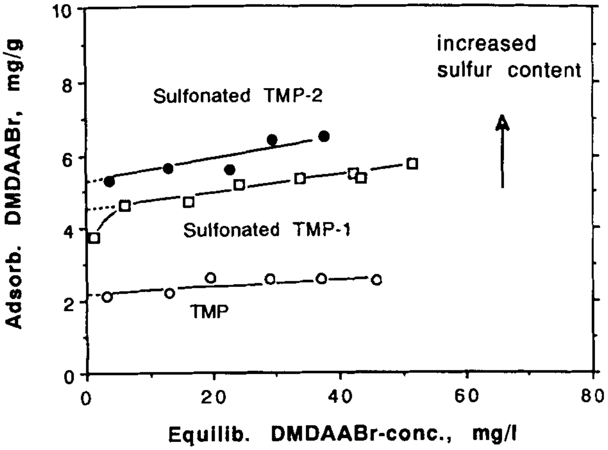

FIGURE 5 The adsorbed amount of poly -DMDAABr (mg/g) as a function of the equilibrium concentration of the polymer (mg/l). TMP and sulfonated TMP. Sulfonation conditions according to table 2.

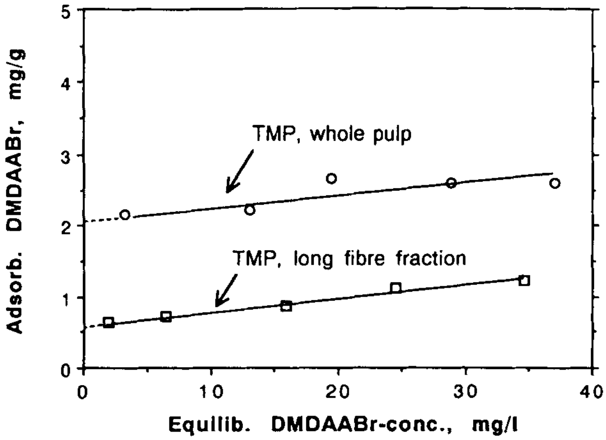

FIGURE 6 The adsorbed amount of poly -DMDAABr (mg/g) as a function of the equilibrium concentration of the polymer (mg/l). Long fibre fraction of the TMP and the unfractionated TMP.

intense bleaching reaction which gives a higher content of carboxylic groups and thus a higher adsorption level.

The adsorption isotherms on TMP and post-sulfonated TMP fibres are shown in Figure 5. These isotherms are also of the high affinity type, giving an easy determination of surface charges. The surface charge is increased by the post-sulfonation and the pulps with a higher degree of sulfonation exhibit a higher adsorption level.

The difference in surface adsorption isotherms between a long fibre fraction and the whole pulp for an industrial TMP pulp is shown in Figure 6. The fibre fraction gave a much lower surface adsorption due to its lower specific surface area. The fine material in the whole pulp had a much larger surface area and gave rise to a higher adsorption level. Using the poly-DMDAABr adsorption method it is thus possible to follow the relative changes in surface area caused by extra refining or beating.

Adsorption isotherms were also obtained for TMP long fibre fractions treated with hydrogen peroxide (Figure 7). As in the case of hydrogen peroxide bleached CTMP, these isotherms showed a good plateau level which gave a fairly easy charge determination.

Significance of Charged Groups for Some Physical Properties of Mechanical Pulp Fibres

Two strongly limiting factors for the increased utilisation of mechanical pulps in many paper qualities are their relatively low brightness and low strength. Hydrogen peroxide bleaching has proved to be an good alternative to enhance both their brightness and their strength properties. In addition to the chromophore eliminating effect of hydrogen peroxide, carboxylic acid groups are also introduced into the pulps mainly through the following mechanisms:

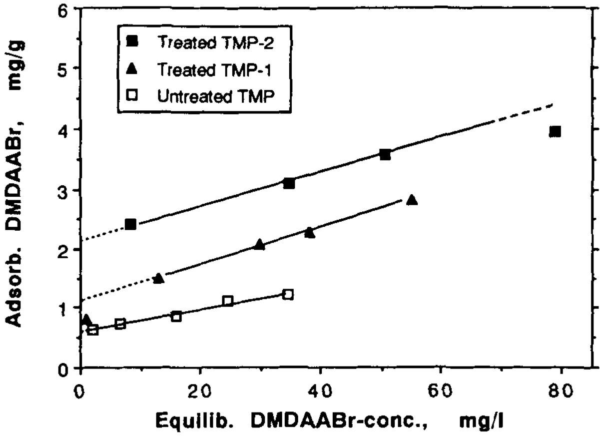

FIGURE 7 The adsorbed amount of poly -DMDAABr (mg/g) as a function of the equilibrium concentration of the polymer (mg/l). Long fibre fractions of TMP treated with hydrogen peroxide at 30% pulp consistency and at 60°C. Other treatment conditions: Treated TMP -1: 2 % H_2O_2 charge, initial pH 12.5, 10 minutes treatment time. Treated TMP -2: 10% H_2O_2 charge, initial pH 12.5, 5 minutes treatment time.

1. Hydroperoxide anions react with quinonoid and other enone structures of the lignin, leading to the formation of carboxylic type end groups[20,21].

2. Other reactive species, i.e hydroxyl radicals, superoxide anion radical and oxygen, arising from the transition-metal-ion-catalysed decomposition of hydrogen peroxide, are involved in the reactions leading to the formation of carboxylic acid groups in the lignin structures[20, 22, 23]. Besides introducing carboxylic acid groups, this type of reaction can also cause changes in the cross-link structure of the polymeric lignin matrix.

3. Under the alkaline conditions prevailing during hydrogen peroxide bleaching, carboxylic acid esters and lactones in the hemicellulose constituent of the pulp are hydrolysed, yielding free carboxylic acid groups[9].

In order to verify the importance of these carboxylic acid groups for pulp properties, handsheets were made from the hydrogen peroxide bleached CTMP and their mechanical properties were studied in relation to the contents of total charged groups and surface charged groups. The fibre surface charge was measured by the polyelectrolyte titration technique as described above .

Figure 8 shows the correlation between tensile index and the total amount of charged groups and Figure 9 the correlation between tensile index and surface charged groups. Although no simple relationship exists between the studied parameters, both total charged groups and surface charged groups are important for the tensile strength.

The importance of these acidic groups can be interpreted in terms of increased fibre hydrophilicity or increased fibre swelling. An increase in fibre swelling makes fibres more flexible by plasticization of the fibre wall and thus facilitates the formation of bonds between fibres. Since fibre-fibre bonding occurs at fibre surfaces, the importance of fibre surface charge is also easily understood. This is to some extent even reflected in the correlation between surface charges and Scott-bond strength of the paper sheets (Figure 10).

At high levels of charged groups, however, the effects of total charged groups and surface charged groups on tensile strength development is more complicated, indicating that factors other than charged groups have to be considered. The increase in fibre flexibility and conformability by cleavage of cross-links in the polymeric lignin and/or hemicellulose structures and the removal of small amounts of lignin from fibre surfaces may also contribute to the observed strength improvement. The dissolution of lignin during alkaline hydrogen peroxide bleaching has recently been confirmed by Holmbom et al[24]. The role of hemicellulose is also important considering the large amount of hydrophilic hydroxyl and carboxylic groups present in the hemicellulose constituent of the pulp fibres. It is known, for instance, that the alkaline

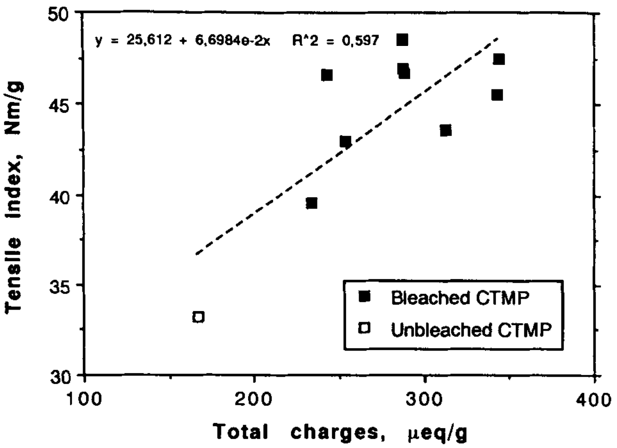

FIGURE 8 Tensile index as a function of total charge. Unbleached CTMP and CTMP bleached with hydrogen peroxide under different conditions.

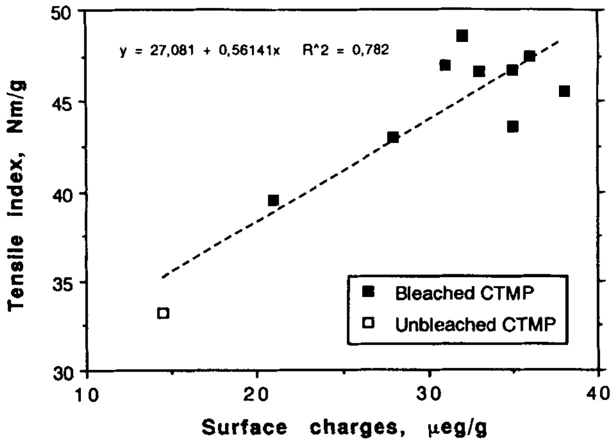

FIGURE 9 Tensile index as a function of surface charge. Unbleached CTMP and CTMP bleached with hydrogen peroxide under different conditions.

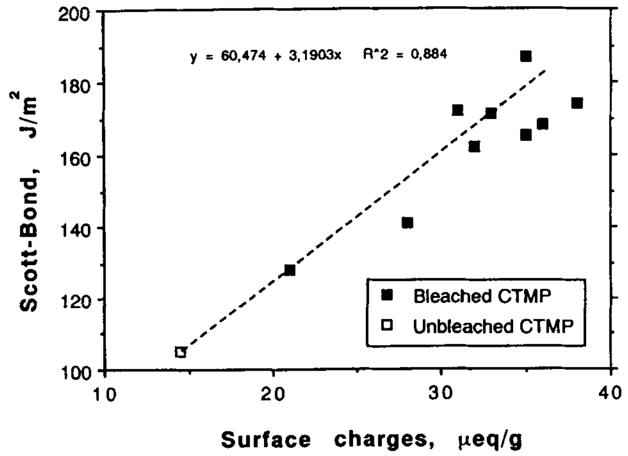

FIGURE 10 Scott-bond as a function of surface charge. Unbleached CTMP and CTMP bleached with hydrogen peroxide under different conditions.

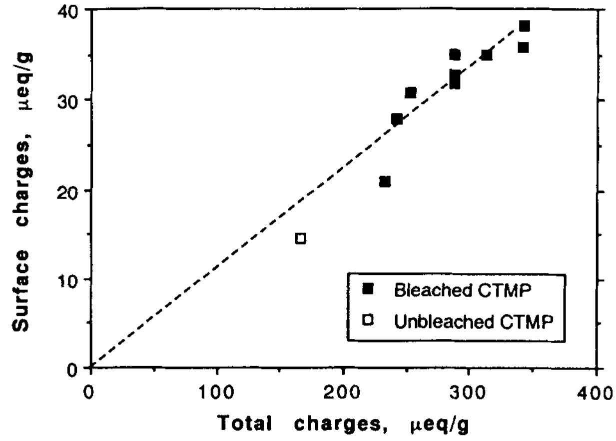

FIGURE 11 Surface charge as a function of total charge. Unbleached CTMP and CTMP bleached with hydrogen peroxide under different conditions.

conditions prevailing during hydrogen peroxide bleaching can cause a complete deacetylation of galactoglucomannans[24]. The release of the bulky acetyl groups may increase the accessibility of the hydrophilic hydroxyl and carboxyl acid groups for eventual fibre-fibre bonding. The effects of hydrogen peroxide treatment on these factors, other than the charged groups content, remain to be evaluated.

The relationship between surface charges and total charges of the CTMP fibres treated with hydrogen peroxide is shown in Figure 11. It can be seen that the amount of charges increases almost proportionately with the amount of total charges. The ratio of surface charges to the total charges of these CTMP fibres lies between 9 and 13%, regardless of the amount of total charges. This result shows that no selective surface modification of the fibres has occurred. A selective surface treatment would introduce charged groups selectively at fibre surfaces without greatly changing the content of bulk charged groups and the cross-link structures of the polymeric lignin and/or hemicellulose network. The importance of surface charged groups for pulp properties could then be evaluated unambiguously. However, such a method has not been found in the case of hydrogen peroxide treatment.

FINAL COMMENTS

The adsorption isotherms of p-DMDAABr on various kinds of mechanical pulp fibres are of the high affinity type with pronounced plateau level which enables a fairly easy charge determination. It is therefore feasible to determine the surface charges of the various kinds of mechanical pulp fibres by applying the polyelectrolyte titration technique. Together with other analytical methods, this technique contributes to a better understanding of important fibre properties.

As a basic chemical parameter to characterise fibre surface properties, the fibre surface charge is important for the physical properties of the pulps. However, the rather complicated relationship between content of charged groups and the physical properties of the pulps indicate that factors, other than the charged groups content must be investigated before a complete understanding can be obtained.

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