SURFACE CHARGE DETERMINATION FOR BALANCING CHARGE QUANTITIES AND MODELLING THE REACTIVITY OF FURNISH FOR THE EFFICIENT APPLICATION OF WET STRENGTH AGENTS

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Abstract. Papers used in the label, decor, filter and tissue paper sectors require high wet strength. Optimizing the use of wet strength agents (WSA) is difficult. Large dosages can cause a cationic charge reversal in the paper machine circuit. Plant operators are forced to find a compromise between the action of the wet strength agent and charge reversal. Knowledge of charges along the stock preparation process, especially in the approach system of the paper machine, is essential for optimizing the use of WSA. Charge measurements - cationic demand and zeta potential - are widely used in the PM circuit and on pulps to investigate the impact of WSA. The informative value of these methods must be viewed critically, however.

A modified surface charge measuring procedure makes it possible to characterize charge relationships and to balance charge quantities. The original method was primarily intended to characterize pure cellulosic fibres. In order to characterize mill pulps efficiently, the sample preparation was modified and lab work was considerably reduced. The modified method has been tested on model pulps. It was employed on a fine paper machine and two paper machines producing wet strength papers. Based on surface charge measurements, the material balance and additive dosages, it was possible to calculate charge balances for single process steps as well as for the entire production process. The differences between measured values and the charge calculated indicated performance-reducing side reactions of WSA, for example with fines not retained. This paper emphasizes how the new measuring method can be usefully employed to optimize WSA and as a basis for modelling the reactivity of paper furnish.

Keywords: Surface charge, balancing, wet strength agents
1 Introduction

Suboptimal application of wet strength agents (WSA) in the production of wet strength paper grades leads to production failures and product quality defects due to deposits and specks, and to additional costs due to increased additive consumption as well as increased amounts of broke. Evaluating the reactivity of pulp suspensions and the adsorption of WSA on suspension components within a given stock system is a prerequisite for tracing adsorption and identifying optimization potentials. Only the share of WSA adsorbing on fibres is fully effective for paper wet strength.

It is common practice to apply zeta potential measurements to scan the evolvement of fibre stock charge along the process chain. But zeta potential does not lend itself for determining additive adsorption in a quantitative way.

The aim of our investigations was to refine a fibre surface charge measuring method and to determine WSA adsorption on pulp suspensions on a production scale. The method opens up the possibility of charge balancing and modelling the polyelectrolyte adsorption on paper furnishes along the production process.

2 Surface charge determination

Surface charge measurement of cellulosic fibres was introduced by Winter, Ödberg and Wågberg [5, 7], and developed further by Erhard and Frohberg [2]. The potential of this method to give evidence of additive efficiency has been proven on lab scale. The method has not been used for process evaluation on a production scale beforehand.

To determine the surface charge of an anionic sample, a cationic polyelectrolyte is added in excess. The polymer adsorbs on the anionic sites of the sample (e.g. carboxylic or sulphonate groups). Afterwards the non-adsorbed Poly-DADMAC is determined by polyelectrolyte back titration with an anionic polyelectrolyte (Figure 1).

An adsorption isotherm can be set up. An extended Langmuir isotherm was used in our studies, as the curve deviates from a standard Langmuir isotherm due to the following effects:

- Polydispersity in the adsorbing polyelectrolyte causes a deviation. High molecular mass material is preferentially adsorbed on accessible fibre surfaces, displacing low molecular mass material [1].
A low molecular mass polyelectrolyte has higher accessibility to charges inside the fibre wall than a high molecular mass polyelectrolyte [6].

Polyelectrolyte adsorbs hyper-stoichiometrically, most probably due to increased interactions between the polyelectrolyte molecules on the surface, visible as a swelling of the adsorbed polyelectrolyte layer on the surface [5].

The molecular weight of the polyelectrolyte used and the reaction medium have major impacts on surface charge determination. The molecular weight of the polyelectrolyte determines the extent of penetration into the pores of the pulp components. Anionic charge sites inside the fibre walls are not accessible for polyelectrolyte chains above 100,000 to 200,000 g/mol [5]. Typical epichlorohydrin type WSA has a higher molecular weight. Own preliminary investigations have shown that surface charges of pure pulp and of pulp mixtures are easier to distinguish between in a NaHCO₃ solution than in a NaCl solution. The slightly alkaline NaHCO₃ solution causes deprotonation of the carboxylic groups in the fibrous material. These findings confirmed earlier results [3].

3 Experimental

3.1 Materials

The lab investigations were carried out with hardwood (eucalyptus) kraft pulp (Aracruz) and softwood (spruce) kraft pulp (Rosenthal) as model pulps, refined to different freeness levels. Commercial-grade titanium dioxide was used as filler. WSA on the basis of epichlorohydrin resins was used.

For charge balancing, furnish samples were taken from different sampling points along the process chain in a fine paper machine and in two paper machines producing wet strength papers.

Polydiallyldimethyl ammonium chloride (Poly-DADMAC) of Mₙ 255,000 and a polydispersity index of 5.3 was used as cationic polyelectrolyte, sodium polyethylene sulphate (PES-Na) as anionic polyelectrolyte.

3.2 Methods

For the model pulps, dry fibre samples were pulped and drained over a 200 mesh sieve to dry contents of 25-30%. Mill pulp samples were directly drained to dry contents of 25-30%.

To determine the surface charge, samples were suspended in 0.001 M NaHCO₃ solution. Defined amounts of Poly-DADMAC were added to suspension aliquots. The prepared samples were stirred for 60 min. The actual solids content of the suspension was checked. The solid phase was separated by means of centrifugation. With filtrate aliquots, surplus Poly-DADMAC was back titrated with PES-Na using a PCD04 from BTG Instruments. From the resulting isotherm the surface charge was calculated by means of a linear regression method.

Modifications of this procedure were tested during method development to find optimum settings and reduce the lab work. In contrast to earlier lab studies with up to
ten measuring points per isotherm, two measuring points showed to be sufficient to characterize mill samples within an expected range. Thus lab work was considerably reduced. To prove the validity of the method for clarifying WSA adsorption, the determination was comparatively performed with WSA instead of Poly-DADMAC. Furthermore pulp pre-treated with WSA was examined.

4 Results

4.1 Validity of the surface charge determination

Using Poly-DADMAC adsorption as an indicator for the adsorption potential of WSA, the adsorption characteristics of these cationic polyelectrolytes should be similar. Figure 2 shows the results of trials where Poly-DADMAC or WSA was added to softwood kraft pulp, traced by zeta potential measurement. The surface charges of the softwood kraft pulp determined beforehand with Poly-DADMAC and with WSA as cationic polyelectrolytes amounted to 43 μeq/g and 39 μeq/g, respectively. The slightly smaller value determined with WSA corresponds to its typically higher molecular weight reducing its access to fibre pores.

The bold vertical lines represent the dosages at which the positive charges added equal the negative pulp surface charges determined beforehand. At higher dosages the zeta potential scarcely increases further, indicating that virtually no additional cationic polymer is adsorbed on fibre surfaces. Measuring the zeta potential of treated pulps again after one hour showed no significant changes. This indicates that there had been no significant conformation changes of the polymers. These findings suggest similar adsorption behaviours of Poly-DADMAC and the WSA.

![Figure 2: Comparison of adsorption behaviour of Poly-DADMAC and WSA on softwood kraft pulp. Bold vertical line: Added cationic charge equals initial anionic surface charge of the pulp.](image)

To detect disturbing side reactions affecting the surface charge determination when both WSA and Poly-DADMAC are present, a decor paper model pulp treated with various amounts of WSA was analyzed. As shown in Figure 3, the measured surface charges of the treated pulp suspension correspond with the calculated surface charges...
within the measurement accuracy. Side reactions between WSA and Poly-DADMAC either do not take place or do not affect the measurements.

Figure 3: Monitoring of WSA adsorption on decor paper model pulp

4.2 Surface charge determination and charge balancing in paper mills

A paper machine producing fine paper and specialty paper from chemical pulp was chosen for a first mill test of the modified surface charge method. A balance for the mixing chest was determined. No additives were added here. The mass flows and surface charges of all inputs were determined. Based on these inputs, a surface charge of 48 μeq/g was calculated for the output; the measured value was 44 μeq/g (Figure 4). The deviation lies within the determination accuracy.

Figure 4: Charge flows and charge balance of the mixing chest of a fine paper machine

In a second test case, the surface charge profile and balances were set up for a decor paper machine. The focus was on balancing the cationic additives, WSA and poly aluminium chloride (PAC). Pulp samples were collected along the production process,
and the surface charge of samples was determined. Balances were set up for the additive dosage points – mixing chest and cleaner approach pipe (Figure 5). Mass flows were calculated on the basis of production rate and consistencies (Figure 6).

![Surface charge determination in the stock preparation and approach flow system of a decor paper machine](image)

**Figure 5:** Surface charge determination in the stock preparation and approach flow system of a decor paper machine

![Mass flows (suspended solids) of the decor paper production](image)

**Figure 6:** Mass flows (suspended solids) of the decor paper production (STA: head box approach system)

To calculate the charge balances, the mass flows and surface charges of stock components as well as the dosages and charge densities of additives were used (Figure 7). As observed earlier in lab investigations, refining increases the surface charge by exposing anionic groups inside the fibres, thus making them detectable on the surface. Added cationic additives neutralize the anionic surface charge.

The output surface charge calculated from the charge inputs of the mixing chest amounts to 22.7 μeq/g. The measured value of 23.0 μeq/g is in good agreement with this, indicating that additives have been adsorbed almost completely on the surface of solids. When comparing the calculated and measured output surface charges (24 μeq/g and 34 μeq/g, respectively) at the dosing point before the cleaners, a nominal loss of approx. 30% is observed. This loss may be explained by the adsorption of additives on filler and fine particles, which are not covered by the determination method. A second investigation confirmed these findings, which finally indicate wet strength losses.
In a third case, charge balancing was performed for a specialty paper machine (Figure 8). The focus was on WSA balancing, and a global charge balance was set up. Figure 9 and Figure 10 show Sankey diagrams of the mass flows and surface charge flows. The balances investigated in detail - mixing chest and forming section - showed a balancing deviation of approx. 5%, which lies within the limits of measuring accuracy.
Figure 9: Mass flows (suspended solids) of the specialty paper mill

Figure 10: Charge flows of the specialty paper mill

5 Conclusions and outlook

The improved surface charge measuring method lends itself to calculating the surface charge flows in paper production stock systems and balancing charges with satisfying accuracy. This makes it possible to address typical questions which could not be answered so far with reasonable effort:

- To what extent does an electrostatically reacting chemical additive adsorb on furnish components?
- At which point in the process does adsorption take place?
- Is the additive used suited for this furnish?

An optimization strategy can be derived from charge balances for the additive application concerned, particularly for applications of WSA in specialty paper production. If the additive adsorbs weakly, adsorption can be improved by changing the dosage point or increasing the reaction time. If the fibrous material used has a low surface charge causing low adsorption, adsorption can be improved by choosing an additive with lower charge density. Alternatively, the surface charge of the fibrous
material can be increased by refining or by adding hydrocolloids, e.g. carboxymethyl cellulose.

The balancing of charges opens up the possibility of integrating charge as a stream characteristic in process simulation models. Furthermore, future research work will comprise the balancing of colloidal charges and an online-measuring method for surface charge.

6 References


