

Interaction of Spherical Polyelectrolyte Brushes with Calcium Carbonate and Cellulose Fibers: Mechanistic Studies and Their Application in Papermaking

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ABSTRACT: We present a comprehensive study of the interaction of spherical polyelectrolyte brushes (SPBs) with cationically modified polyacrylamide (CPAM), calcium carbonate (CaCO_3) particles, and cellulose fibers. A link to the use of this system as a model for retention aids in the papermaking process is elaborated. Anionically functionalized SPBs with a high cation exchange capacity (CEC) are used together with CPAM as a model system for fiber flocculation and deposition of CaCO_3 , which are integral steps in the papermaking process. The flocculation efficiency is tested by means of a dynamic drainage jar. Field emission scanning electron microscopy (FESEM) and atomic force

microscopy (AFM) are used to analyze the system, the structure of the agglomerated flocs, and the mechanism of floc formation. The data suggest that the flocculation efficiency can be attributed to the high CEC of SPB in combination with the flexibility of grafted polyelectrolyte chains. FESEM images and AFM support the model of anionic SPBs acting as a particle bridge between fibers and CaCO_3 . © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 233–241, 2006

Key words: spherical polyelectrolyte brush; dual-component flocculation; retention aid; flocculation mechanism; papermaking

INTRODUCTION

Polyelectrolyte brushes are systems in which polyelectrolyte chains are densely attached to a planar or curved surface. Since the first seminal papers of Pincus¹ and Borisov et al.² in 1991, these systems have been the subject of numerous theoretical studies. Up to now, it has been shown that polyelectrolyte brushes can dramatically affect the surface properties of a surface such as the adhesion,³ lubrication,⁴ wettability,⁵ friction,⁶ biocompatibility,⁷ and so forth. Furthermore, colloidal particles with attached polyelectrolyte brushes may greatly enhance their stability against flocculation.⁸ In contrast, spherical polyelectrolyte brushes (SPBs) can be considered as a flocculation agent of potentially high efficiency, provided that the charged brushes interact with an appropriate counterpart in a multicomponent flocculation system. In the present article we focus on the use of SPBs in such a multicomponent system in which charged particles are flocculated in an aqueous environment. The reten-

tion of calcium carbonate (CaCO_3) and cellulose fibers is the main purpose in the papermaking process. Controlling electrostatic interactions and their dynamics in fiber and filler flocculation is one of the keys to modern papermaking.

Simply speaking, papermaking can be viewed as a dewatering process of a dilute pulp suspension on a sieve. The average mesh size of a dewatering sieve is about the same dimension as the cellulose fibers. However, large amounts of particles that are much smaller than the average mesh size are present in industrial pulp slurry, such as fiber fragments (fines) and fillers, mostly ground CaCO_3 (GCC). Precipitated CaCO_3 (PCC) and kaolin are also very common fillers and PCC is actually taking over from GCC. A typical GCC slurry contains particles of about 1–5 μm average diameter. In order to retain fines and fillers during the dewatering process on the coarse sieve, so-called retention aids are used. These retention aids induce flocculation of fibers, fillers, and fines in a complex slurry in which further components such as dyes, sizing agents, or impurities from recycled (deinked) paper and so forth may be present.⁹ In the search for more efficient flocculants, dual-component retention systems have proven to be particularly interesting. All dual systems consist of two strongly interacting polymers or colloidal particles, which are subsequently

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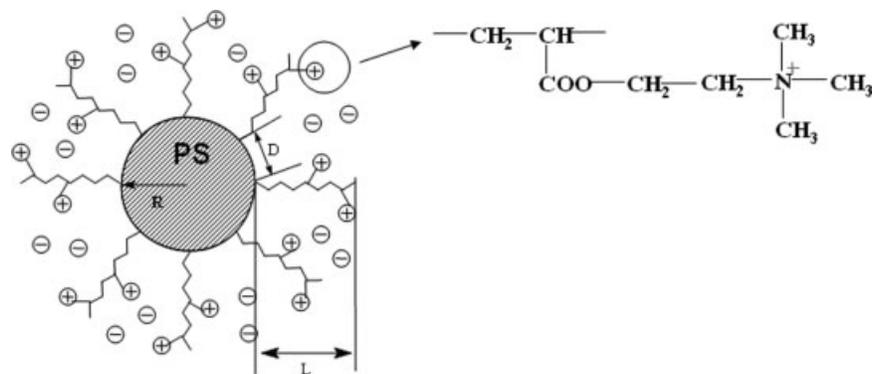


Figure 1 The schematic structure of cationic SPBs with a poly(2-(acryloyloxy)ethyltrimethylammonium chloride) brush.

added to the stock. In many cases dual-component flocculation systems exhibit stronger flocculating ability than the corresponding single-component retention systems.^{10–13} The mechanism explaining this high efficiency is not fully understood. The primary interaction between the two components in the dual system may either be based upon strong hydrogen bonding¹⁴ or electrostatic interaction.^{12,13,15} Another important motivation for the papermaker to use dual- rather than single-component systems is that they tend to cause flocculation into much finer and denser flocs, thus creating paper sheets of better optical appearance that is due to high homogeneity (so-called formation).

Currently, the most popular dual flocculation system is the so-called microparticle system, consisting of a high molecular weight primary retention aid in combination with a colloidal particle that usually carries the opposite charge. Typical primary flocculants are copolymers of acrylamide and cationically charged comonomers or cationically modified starches. Colloidal silica^{16,17} or montmorillonite (bentonite) types of layered silica are frequently used as the second component. Compared with conventional single- and other dual-component retention systems, the microparticle retention system shows many significant advantages,^{18–20} including increased retention and drainage, with no sacrifice in formation and better performance, even in the presence of high concentrations of interfering substances. Most of the advantages can be attributed to compact flocs, resulting in an open and uniform sheet formation.²¹

In order to obtain deeper insight into dual flocculation systems, it is necessary to use model systems that show well-defined surface characteristics. Here we present a comprehensive study of the interaction of SPBs with CaCO_3 particles and model cellulose fibers. Anionically functionalized SPBs and cationically modified polyacrylamide (CPAM) are used as efficient model compounds to achieve fiber flocculation and deposition of CaCO_3 . Field emission scanning electron microscopy (FESEM) and atomic force microscopy (AFM) are used to analyze the final floc structure.

EXPERIMENTAL

Materials

GCC (Hydrocarb OG) obtained from OMYA GmbH was used without further treatment; 60 wt % of the particles were less than 2 μm in diameter. This material was wet ground in the presence of a polyacrylic dispersing agent and then spray dried.²² Bentonite for water-based systems (Fluka) was used as received. The cation exchange capacity (CEC) of this material given by the supplier is 0.80 meq/g. CPAM was used as the primary flocculation agent; Polymin KP 2515 provided by BASF Aktiengesellschaft had a charge density of 1.7 meq/g.

Cationic and anionic spherical brushes were synthesized and characterized as described recently.^{23,24} Figures 1 and 2 show the chemical structures of poly(2-(acryloyloxy)ethyltrimethylammonium chloride) and poly(styrene sulfonate) brushes, respectively. All pertinent parameters, namely, the core radius of polystyrene (R), the contour length (L_c) of the attached chains, as well as the grafting density (σ ; number of chains per unit area), are known from the analysis,²³ Table I gathers these data for SPBs LA2, LB1, and LB2. Detailed studies of the SPB systems were performed by

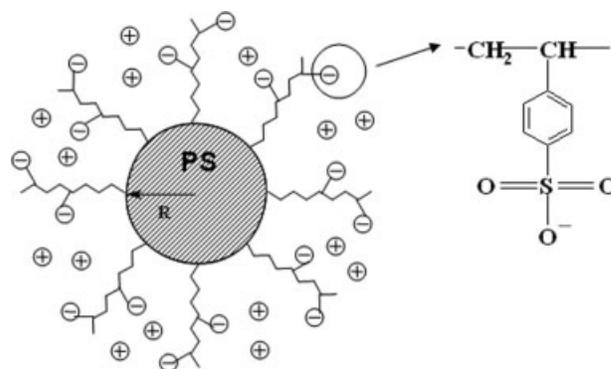


Figure 2 The schematic structure of anionic SPBs with a poly(styrene sulfonate) brush.

TABLE I
Characterization of SPBs LA2, LB1, and LB2

Label	Charge	Brush	R [nm]	L_c [nm]	M_{η} [g/mol]	σ [nm ⁻²]	D [nm]	L_c/R	CEC [meq/g]
LA2	positive	PATAC	45	116	89700	0.049	5.1	2.57	–
LB1	negative	PSS	58	103	84300	0.065	4.4	1.78	1.50
LB2	negative	PSS	25	141	115800	0.040	5.6	5.64	2.27

R , core radius of polystyrene; M_{η} , molecular weight of grafted chains as determined by viscosimetry; L_c contour length of grafted chains determined from M_{η} ; σ , graft density on surface of core particles; D , the average distance between two neighboring graft points; CEC, cation exchange capacity.

AFM,²³ rheology,²⁵ dynamic light scattering,²⁶ and small angle X-ray scattering.²⁷

The model system of pulp slurry selected for the retention experiments was composed of 30% GCC and 70% bleached chemical fibers, which consisted of 70% birch sulfate (SR 33°) and 30% pine sulfate (SR 70°). The final concentration of the pulp slurry was adjusted to 0.8 wt %, and the pH was set at 8.1. The pulp slurry was prepared at BASF AG and used within 24 h.

Methods

Dynamic drainage jar (DDJ)

The DDJ is a common and reliable tool to evaluate retention and drainage of single or multicomponent flocculation systems under conditions that are quite similar to large-scale papermaking processes. Of importance, the DDJ can simulate the impact of shear as induced, for example, by screens in paper machines.²⁸ In the present work a DDJ with a 200-mesh bottom screen and an impeller speed of 400 or 900 rpm was used.

The retention efficiency of each flocculation system is quantified using the so-called first-pass retention (FPR) and the corresponding ash retention (AR), which are defined as follows^{29–31}:

$$FPR = \frac{C_i - C_0}{C_i} \times 100\% \quad (1)$$

$$AR = \frac{A_i - A_0}{A_i} \times 100\% \quad (2)$$

where C_0 and C_i are the concentrations of colloidal particles in the stock before drainage and in the filtrate, respectively, which are obtained by filtering the respective suspension using a filter paper and weighing the fully dried filtrate; and A_0 and A_i are the total inorganic (ash) content of the stock before drainage and in the filtrate, respectively. The latter is determined by incineration of the filtrated material at 500°C for 5 h.

In a typical flocculation sequence 0.04% CPAM (wt % with respect to solid pulp) was added into the 0.8 wt % paper suspension in order to induce agglomeration of fibers and fillers. Subsequently, a shear of 900 rpm was applied for 20 s, inducing partial breakdown of the primary flocs. Then, between 0 and 3.2×10^{-2} g/L (0–0.40 wt % with respect to the solid contents in the primary pulp suspension) bentonite or SPB was added. During the addition of the SPB (or bentonite) the mixture was stirred at 400 rpm for 15 s, at which point the formation of flocs in the pulp suspension occurred. Stirring was continued during the drainage.

FESEM

FESEM is a powerful tool for topographic analysis. It produces clearer, less electrostatically distorted images with a generous depth of field and ultrahigh spatial resolution down to a few nanometers. Topographic information and compositional information can be obtained with special detectors. FESEM is suitable for the observation of the surface of fibril aggregates.³²

In order to get clearer images from FESEM, the retention test was repeated on a smaller scale, namely, 0.2% fibers and 0.1% CaCO₃ fillers. CPAM, SPB, and bentonite were kept in the same weight concentrations in relation to the solid contents of the pulp slurry. Floc samples collected from each stage of the retention test were dried in air and coated with a very thin layer (circa 1 nm) of platinum to attain electrical conductivity and captured by an FESEM Leo1530. All measurements were performed in the Bayreuther Institut für Makromolekülforschung of Bayreuth University.

AFM

AFM measurements were performed using a NanoScope IIIa (Digital Instruments Inc.) to investigate the morphology of the fiber surfaces. The images were scanned in tapping mode in air using commercial Si cantilevers (Digital Instruments Inc.) with a resonance frequency of 320 kHz. Images of at least four different areas were scanned for each sample. The images show

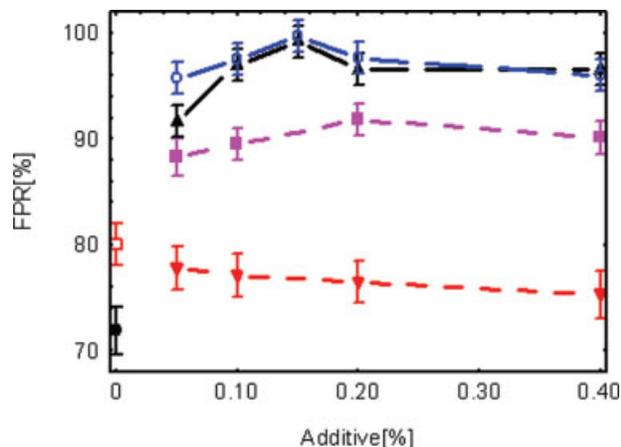


Figure 3 The first-pass retention in the presence of different retention aids. The dashed lines are guides to the eye. (●) blank experiment, without any additive; (□) 0.04% CPAM; (○) 0.04% CPAM with varying amounts of LB2; (▲) 0.04% CPAM with varying amounts of LB1; (■) 0.04% CPAM with varying amounts of bentonite; (▼) 0.04% CPAM with varying amounts of LA2. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

unfiltered original data. All the AFM data in this article show typical morphology that is representative for the corresponding sample.

The samples used for AFM were prepared as for the FESEM except of coating with platinum. A 40 μL droplet of pulp slurry containing the respective SPB particles, CaCO_3 filler, and fibers was placed on a freshly cleaved mica surface (muscovite white mica, Plano GmbH) and dried in air. All measurements were performed in the Lehrstuhl für Physikalische Chemie II of Bayreuth University.

RESULTS AND DISCUSSION

Cationic and anionic SPBs as dual-component retention system

Figures 3 and 4 show FPR and AR with different retention aids. Without any additive, the FPR and AR are at a very low level. The FESEM image in Figure 5(a) shows the distribution of negatively charged fibers and CaCO_3 without any additive. The micrograph reflects the fact that in the dilute pulp slurry the fibers and CaCO_3 are well dispersed without large agglomerates of pigments and fines. The lack of agglomeration as observed on the mica surface is in agreement with the very low retention value as shown in Figure 3 at low additive concentration.

High molecular weight CPAM is an effective flocculation agent and it can be used as a single-component retention aid.^{33,34} The Polymin 2515 CPAM used here showed strong flocculating ability in the retention experiments. With only 0.04% dosage, the AR was

evidently improved from 19.4 to 43.3% (see Fig. 4). The increase in FPR and AR due to the addition of CPAM must be due to an agglomeration process in which mainly CaCO_3 is involved, either by forming CaCO_3 agglomerates or by binding onto the fiber surface. Figure 5(b) clearly shows the formation of large CaCO_3 agglomerates. Note that the size of an entire agglomerate with a three-dimensional network structure is so big that only a minor part is shown in the FESEM image in Figure 5(b).

The effect of shear on the agglomerate effect can be clearly seen by comparing Figure 5(b,c). A large number of CaCO_3 aggregates that have been attached to fibers appear as separate agglomerates on the mica surface in Figure 5(c), indicating that they have been detached via shear forces.

The classical microparticle system consisting of bentonite and CPAM shows high performance in both retention and drainage. As shown in Figures 3 and 4, the FPR and AR reach maxima of 91.8 and 79.8%, respectively. Hence, the obtained retention criteria are much better than that of CPAM used alone. Although a few free CaCO_3 particles are still seen in Figure 5(d), most of them are now linked to fibers.

In analogy to the bentonite-based microparticle system, CPAM was combined with anionic SPB (LB1 or LB2) to give excellent drainage and retention, as shown in Figures 3 and 4. Note that similar to bentonite, LB1 and LB2 exhibit a significant excess of anionic charges at their surface. In the case of SPB LB2 as a dual system in combination with CPAM, the FPR and AR were increased to 99.7 and 99.2%, respectively,

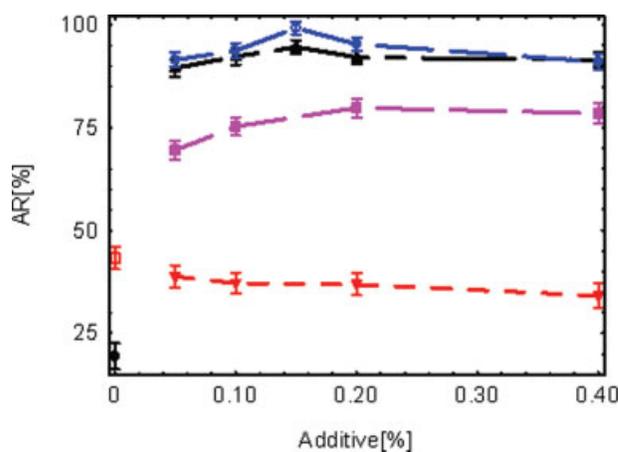


Figure 4 The ash retention in the presence of different retention aids. The dashed lines are guides to the eye. (●) blank experiment, without any additive; (□) 0.04% CPAM; (○) 0.04% CPAM with varying amounts of LB2; (▲) 0.04% CPAM with varying amounts of LB1; (■) 0.04% CPAM with varying amounts of bentonite; (▼) 0.04% CPAM with varying amounts of LA2. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

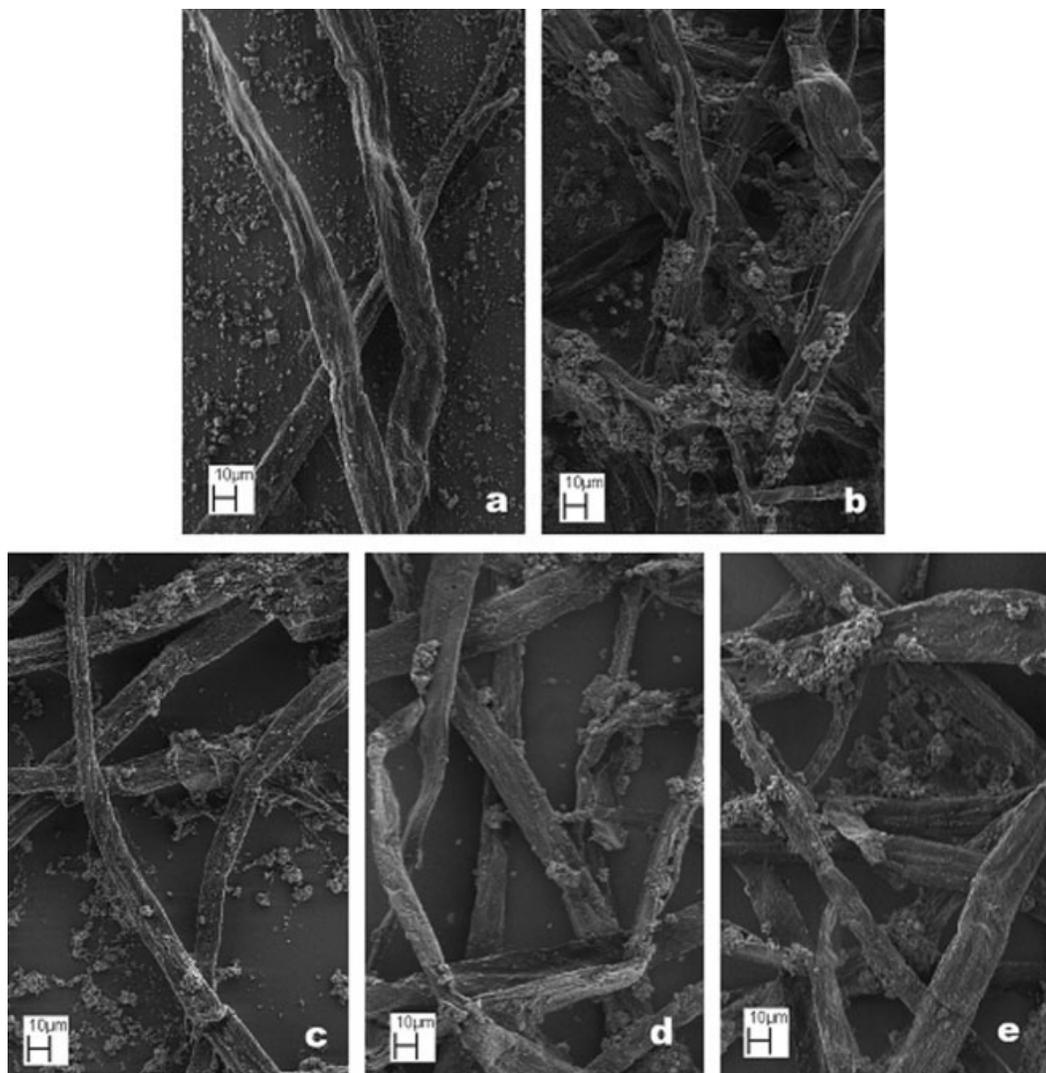


Figure 5 FESEM images of fibers and CaCO_3 particles at different stages of the retention test. (a) Fibers and CaCO_3 without any additive, (b) an agglomerate caused by CPAM, (c) the influence of shear after (b), (d) an agglomerate caused by the addition of bentonite after shear, and (e) the agglomerate caused by the addition of SPB LB2 after shear.

which means nearly all the raw materials remain in the paper sheets. A comparison of the FESEM micrographs shown in Figure 5(d,e) indicates that the re-agglomeration process by both layered silica (bentonite) and SPBs gives rise to a rather uniform attachment of CaCO_3 particles onto the fibers. Apparently, anionic SPBs act as efficient coflocculants in a way similar to the layered silica. Both SPBs and bentonite exhibit a high surface area such that negative surface charges can interact with CPAM moieties. However, it can be assumed that the hydrodynamic corona of SPBs is very distinct from that of bentonite platelets.

The CEC is a value given on a clay material (or similar material) to indicate its capacity to hold positively charged ions (cations). From the molecular weight of the grafted polymer brushes and grafting density, the theoretical CEC of SPB can be calculated. As shown in Table I, the CECs of LB1 and LB2 are 1.50

and 2.27 meq/g, respectively, whereas that of bentonite is only 0.80 meq/g. Obviously, the high CECs of anionic SPBs due to polyelectrolyte chains in the corona favors strong interaction with other colloidal particles such as CaCO_3 via the CPAM. Similarly, modified SPBs can also be used as a nanoreactor, high performance catalyst, or protein adsorbent because of the evidently enlarged specific surface area and charges in polymer brushes, which was recently proved by Sharma and Ballauff³⁵ and Wittemann et al.³⁶

In contrast, if a cationic SPB (as LA2) is chosen in combination with cationic polyacrylamide, the flocculation efficiency is not improved compared to the single-component flocculation as shown by the FPR and AR values in Figures 3 and 4, respectively. This suggests that the cationic LA2 hardly interacts with the sheared macroflocs, indicating that, indeed, the macroflocs show positive surface charge after shearing

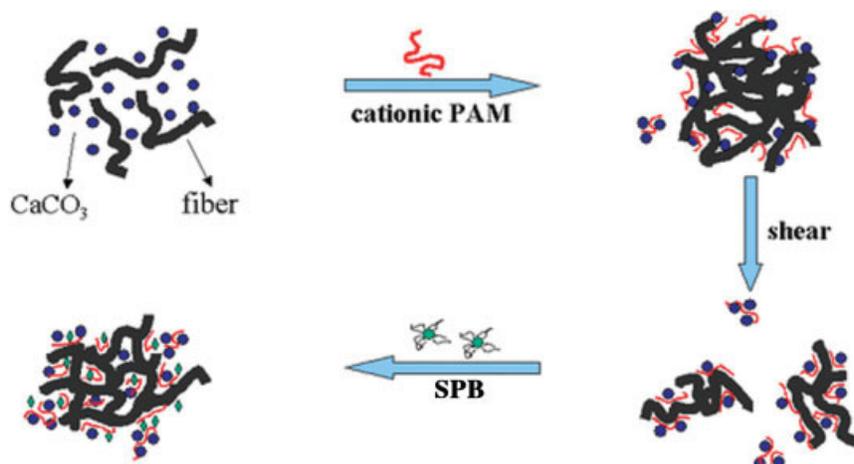


Figure 6 The suggested flocculation mechanism with anionic SPBs as the dual retention aid. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

that is due to excess cationic flocculant (CPAM). Consequently, the sheared flocs cannot be flocculated by a second cationic additive. The repulsion induced by redundant charges even reduces the retention of fibers and CaCO_3 fillers. Therefore, both the FPR and AR decrease slightly with increasing amounts of LA2 (see Figs. 3, 4).

Flocculation mechanism of anionic SPB as dual retention aid

The flocculation mechanism in papermaking due to retention aids was studied by many authors.^{16,20,37–43} According to the interactions between retention aids and paper raw materials, they can be summarized in three fundamental mechanisms: charge neutralization, bridging, and patch flocculation.^{44,45} In practice, modern retention-aid systems used in the papermaking industry consist of several components and usually combine more than one mechanism. According to the retention tests and the FESEM images, the flocculation mechanism of anionic SPBs as dual retention aids can be summarized in four steps, which is similar to that of microparticle retention aid.⁴⁶ As shown in Figure 6, at first, fibers, fines, and fillers in the pulp slurry are homogeneously dispersed because of vigorous stirring; upon the addition of cationic flocculant the negative surface charges of the paper suspension are largely neutralized, and a macrofloc is obtained. During this step, a rather nonuniform distribution of cationic polymeric flocculant between fibers, fines, and fillers occurs. During the subsequent shearing macroflocs are partially redispersed into finer flocs. Of importance, these flocs now exhibit mainly a cationic surface charge due to the flocculant. Note that the specific surface area of the given GCC particles is only about $12 \text{ m}^2/\text{g}$ ⁴² hence the amount of cationic flocculation that is necessary to give rise to excess cationic surface

charge after the shear is very small. During the last step, negatively charged SPBs are added to the pulp slurry. They neutralize the excess positive charges on the microflocs and build a consistent tight network due to the high specific surface area and CEC. During the latter agglomeration step most CaCO_3 particles are incorporated into the flocs or patched on larger fibers because of the anionic SPBs.

Deposition mechanism of CaCO_3 on fibers

According to Alince et al.,⁴³ the deposition of CaCO_3 on fibers can be summarized as follows: in the presence of CPAM, CaCO_3 fillers deposit with an intermediate bond on the fibers [see Fig. 7(a)]; in the presence of CPAM and bentonite at optimum dosages, a much stronger bond is provided by bentonite particles [Fig. 7(b)]. Alince et al.⁴³ suggested that bentonite may further delaminate upon dilution, thus causing the CaCO_3 to partially detach from the fiber, and may further coagulate [see Fig. 7(b)].³⁶ Some of the released particles can be observed, for example, in Figure 5(d).

It is important to note that the theoretical surface area of the bentonite (montmorillonite) is about $800 \text{ m}^2/\text{g}$,^{47,48} whereas for the polystyrene core of LB1 and LB2 the theoretical specific surface areas are only about 49 and $114 \text{ m}^2/\text{g}$, respectively. By contrast, spherical particles do not show delamination [see Fig. 7(c)]. The key question then is why the dual flocculation system using anionic SPBs works so efficiently despite their minor specific surface area compared to bentonite. The data suggest that bentonite does not delaminate completely in practice, so it cannot reach the theoretical surface area; in contrast, the high CEC (see Table I) along with the particle character of the SPBs are responsible for their flocculation efficiency in

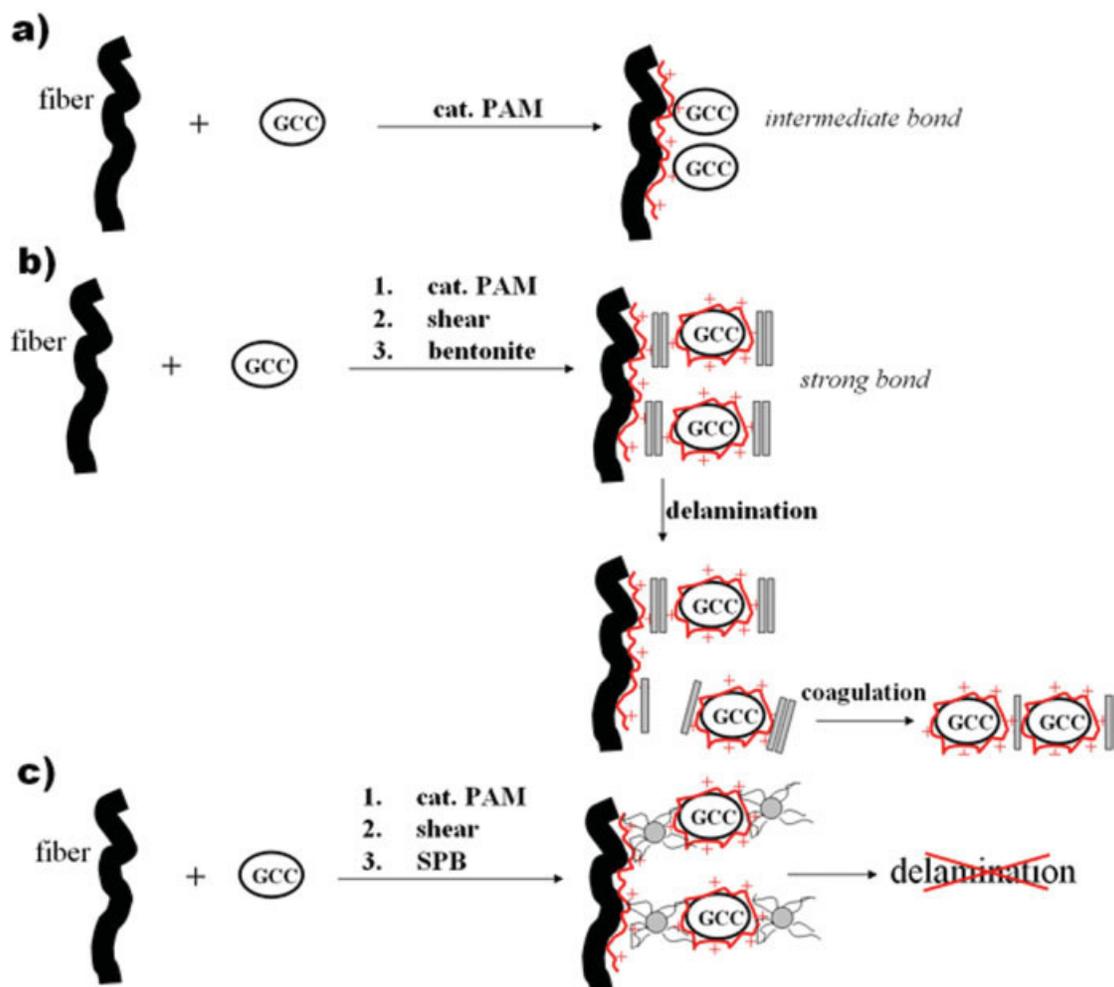


Figure 7 The deposition of CaCO_3 on fibers caused by the presence of different retention aids: CPAM,⁴³ (b) CPAM and bentonite,⁴³ and (c) CPAM and anionic SPB. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

the present model system, rather than their apparent specific surface area (theoretical CEC = 1.50 and 2.27 meq/g for LB1 and LB2, respectively, compared to 0.8 meq/g for bentonite). In addition, one can argue that the SPB's flexible anionic polymer brushes grafted on polystyrene cores give rise to a whole corona of anionic charges rather than just a surface charge as in the case of a montmorillonite. The flexible polymer brushes may adopt a more appropriate conformation in order to fit the rugged surface of fibers and CaCO_3 particles compared to a flat layer silica surface.

Figure 8 shows FESEM images of flocs as a result of different flocculation systems. Using only CPAM, CaCO_3 particles are observed on the fibers, but they are only loosely bound by polymer composite bridges [Fig. 8(a)]. In the case of the microparticle system, in which bentonite is added after shear, a quite different micrograph was obtained. Figure 8(b) shows bentonite platelets on both the fiber and the CaCO_3 particle, thus acting as glue between the latter. Figure 8(c) shows

SPBs on both the cellulose and the CaCO_3 particles. These images strongly support the mechanism suggested by Alince et al.⁴³

The surface roughness of the cellulose could be confirmed by AFM. In Figure 9(a,b) the morphology of the pure paper fiber on mica is observed, showing the rugged surface seen in Figure 9(c,d); the rugged surface of the fibers was smoothed upon the addition of the dual flocculation system of CPAM and SPB (LB1). In addition, because of the incorporation of CaCO_3 , micron-scale agglomerates can be observed in Figure 9(c,d). It can be clearly seen that SPBs are preferentially adsorbed on the filler particles rather than on the cellulose.

CONCLUSIONS

We synthesized anionic and cationic SPBs. They were tested as a dual flocculation system in combination with CPAM and compared with a traditional micro-

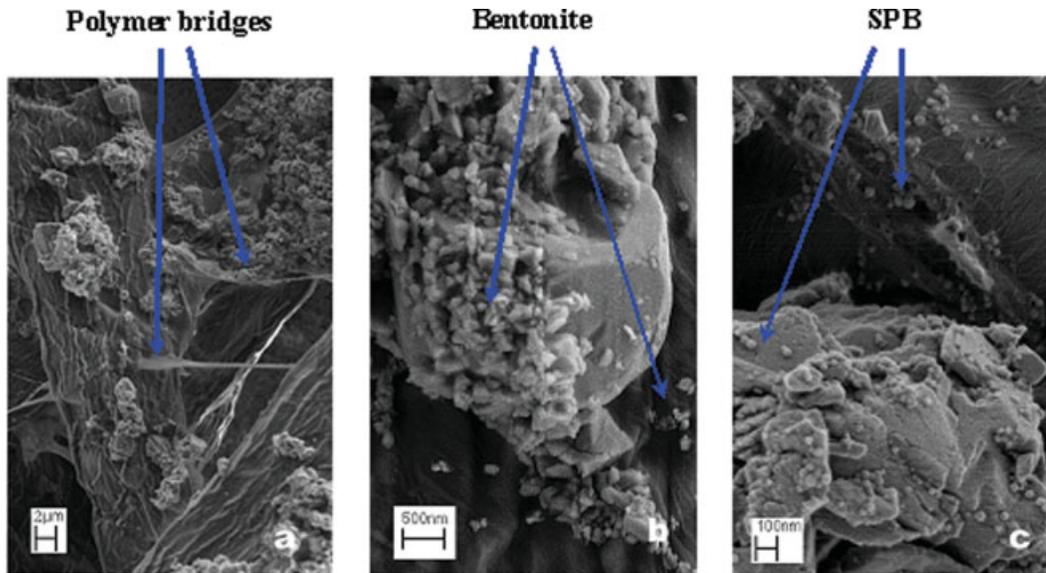


Figure 8 FESEM images of flocs caused by different retention aids. (a) Deposition of CaCO_3 in the presence of CPAM, showing polymer composite bridges; (b) deposition of CaCO_3 in the presence of bentonite and CPAM, showing bentonite and CaCO_3 ; and (c) deposition of CaCO_3 in the presence of LB2 and CPAM, showing SPB and CaCO_3 . [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

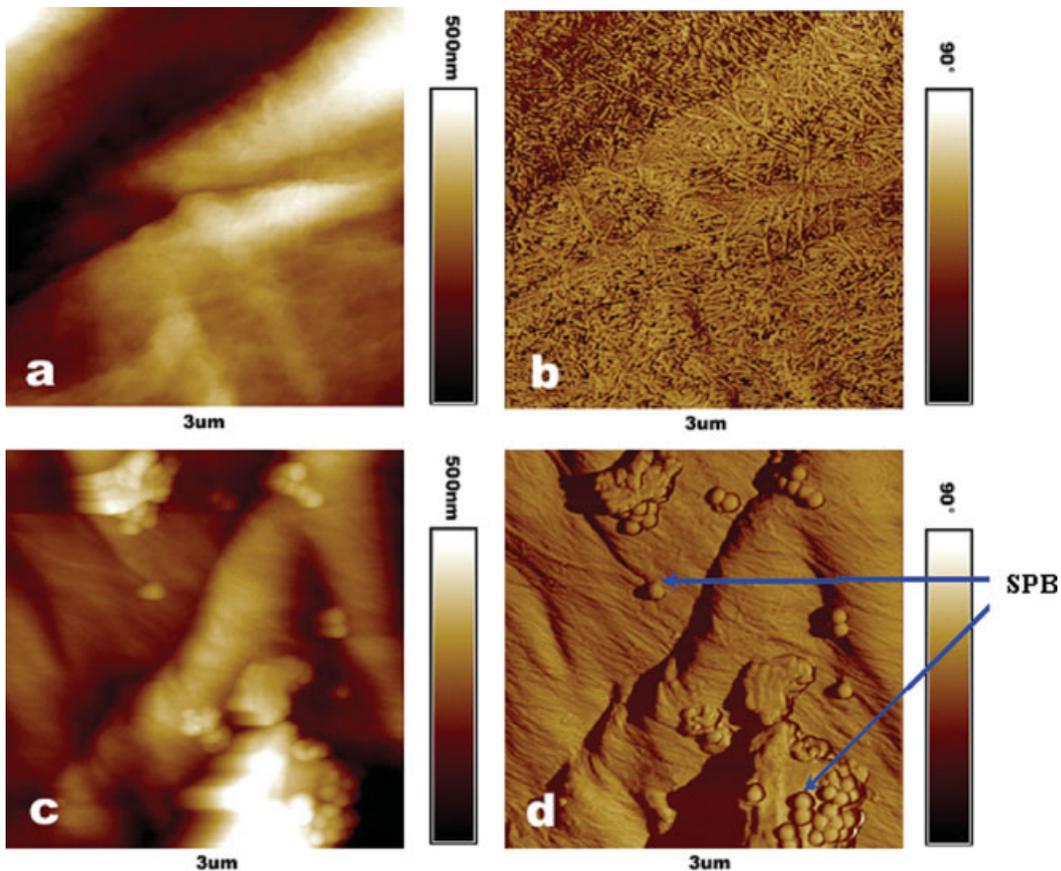


Figure 9 An AFM comparison of the morphology of the fiber and floc caused by the dual-component retention-aid system. The topography and phase images of (a,b) fiber on mica and (c,d) floc caused by LB1 and CPAM. The deposited CaCO_3 and SPB particles are shown. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

particle system in which bentonite acts as a secondary flocculant. The anionic CPAM/SPB system shows high flocculation efficiency as tested under sheared conditions using a DDJ. The high retention level of the SPB dual system contrasts with the apparent low specific surface area that is about an order of magnitude lower than conventional bentonite. The data suggested that the flocculation efficiency could be attributed to the high CEC of SPB in combination with the flexibility of grafted polyelectrolyte chains. FESEM images and AFM supported the model of anionic SPBs acting as a particle bridge in between fibers and CaCO₃ fillers.

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