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Biobased polymers and cationic microfibrillated cellulose as retention and drainage aids in papermaking: Comparison between softwood and bagasse pulps

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Water soluble cationic chitosan (C-Ch) and surface-modified microfibrillated cellulose (C-MFC) were prepared and characterized. C-MFC was prepared by reaction of MFC (microfibrillated cellulose) with β-chloroethyldiethylamine followed by quaternization using methyl iodide while C-Ch was prepared by reaction of a commercial chitosan (Ch) with 2,3-epoxypropyltrimethyl ammonium chloride. C-Ch and C-MFC were characterized by elemental analysis (nitrogen content), Fourier transform infrared spectroscopy (FTIR) and surface charge determination. The prepared C-Ch and C-MFC were used with bentonite in order to improve drainage and filler retention in paper handsheets made from softwood and bagasse pulps. Dosage rates were 0.05–0.2% (w/w, weight of additive by weight of fibres) and 0.05–1% (w/w) for C-Ch and C-MFC, respectively. When used alone, these polymers did not induce any noticeable effect on drainage but they improved the retention of ground calcium carbonate (GCC). The effect of C-MFC/bentonite and C-Ch/bentonite systems on filler retention was more pronounced in case of bagasse pulp than for softwood pulp. The use of C-Ch improved filler retention more than C-MFC did. Comparisons with a commercially available cationic polyacrylamide (CPAM) showed that CPAM was the most efficient additive regarding both drainage and GCC retention, followed by Ch, C-Ch, and finally C-MFC.

1. Introduction

In papermaking, various additives are introduced into the fibrous suspension to improve end-use properties of produced papers (functional additives) as well as the pulp dewatering and retention of fine elements during the wet web formation (process additives). Retention and dewatering aids act as flocculants and promote the aggregation of fillers, cellulosic fines particles and fibers by electrostatic interactions, mainly. The resulting flocs impart better drainability to the pulp suspension which allows increasing the paper machine speed. The use of retention aids is particularly required when mineral fillers are added into the pulp suspension due to their small size. Indeed, mineral fillers (calcium carbonate, kaolin clay, talc, dioxide titanium ...) improve optical properties of the paper sheet, increase dimensional stability and lower the production costs to name but a few of their effects. Among these fillers, ground calcium carbonate is the most commonly used because of its brightness, availability and low cost and a lot of works focus on its retention during papermaking (Vanerek et al., 2000a,b,b; Solberg and Wägberg, 2002).

Classical retention aids are single- or multi-components systems involving natural or synthetic polymers (Swerin and Ödberg, 1997; Cadotte et al., 2007; Hubbe et al., 2009). Synthetic polymers (e.g., cationic or anionic polyacrylamide, polyethylene imine...) exhibit well controlled properties which can be adapted to specific conditions in papermaking (high closure level and high contamination of the circuit water, recycled pulps...).

Among natural polysaccharides, cationic or anionic starch is by far the most used polymer due to its availability and low price (Wägberg and Lindström, 1987; Björklund and Wägberg, 1995; Zakrajsek et al., 2009). But considering the present growing interest for the renewable carbohydrate polymers and their derivatives and

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the current tendency toward the replacement of synthetic products by bio-based ones, it is important to study other polysaccharides (Kuutti et al., 2011; Shen and Fatehi, 2013). In this context, chitosan appears to be a good candidate. This is a linear polymer obtained by partial deacetylation of chitin, the second must abundant polysaccharide in nature after cellulose, which is found in the exoskeleton of crustaceans and insects, mainly. Chitosan is a heteropolymer composed of *N*-acetyl-2-amino-2-deoxy-D-glucose and 2-amino-2-deoxy-D-glucose units, the latter being predominant (Peniche et al., 2008; Cunha and Gandini, 2010). These units are linked through β-(1 → 4) bonds. Chitosan exhibits very interesting physicochemical properties some of which being related to the presence of the primary amines: it is soluble in diluted aqueous acid solutions (polyelectrolyte character), biocompatible, biodegradable, non-toxic and has antimicrobial activity. Consequently, numerous potential applications of chitosan have already been investigated: in food industry, for pharmaceutics, water treatment.. . . (Peniche et al., 2008; Cai et al., 2010; Sun et al., 2010; Zhang et al., 2010; Gu et al., 2011 Kuutti et al., 2011; Miranda-Castro et al., 2013). In papermaking, chitosan has been studied as an additive in order to enhance paper properties such as dry strength (Fatehi et al., 2010; Nicu et al., 2011; Ashori et al., 2013; Salam et al., 2013a,b), wet strength (Hamzeh et al., 2013; Chen et al., 2013), to improve retention and dewatering (Li et al., 2004a,b,b; Chi et al., 2007; Kuutti et al., 2011; Nicu et al., 2013) and to control the water-circuit contamination (Liu et al., 2010, 2012). Its film-forming ability makes it a good candidate for enhancing mechanical and barrier properties in packaging applications (Gällstedt and Hedenqvist, 2006; Khwaldia et al., 2014). Considering the fact that chitosan is insoluble at pH above 6.5, cationization of this polymer is a way to extend the range of its potential applications (Prado and Matulewicz, 2014). Indeed, a lot of the above cited papers investigate the use of cationized chitosan with this objective (Li et al., 2004a,b,b; Chi et al., 2007; Cai et al., 2010; Fatehi et al., 2010; Zhang et al., 2010; Miranda-Castro et al. 2013).

When polymers used as retention aids are added alone into the fibrous suspension, they are positively charged in such a way that they adsorb onto the anionic particles (cellulosic fibers and fines, fillers) and induce flocculation by bridging mechanisms, generally. But they are most often used in combination: sequential addition of cationic and anionic polymers contributes significantly to the increase of the retention (Swerin and Ödberg, 1997). Nevertheless, these dual systems may induce high level of flocculation and negatively impact the sheet formation; in certain cases, they may decrease the dry-solid content of the wet web before it enters the press section. Microparticles retention and drainage aids have thus been developed to counteract these drawbacks. The use of anionic microparticles in conjunction with a cationic polymer offers an interesting alternative: these retention aids yield a better balance between sheet formation and retention than the traditional retention systems (Wägberg and Lindström, 1987; Cho et al., 2006). The major difference between these systems relies on the kind of microparticle used, such as anionic colloidal silica, bentonite, colloidal aluminium hydroxide and micropolymers (Andersson et al., 1986; Lindström et al., 1989; Andersson and Lindgren, 1996; Swerin et al., 1993; Swerin and Ödberg, 1996; Honig et al., 1993, 2000; Khosravani and Rhamaninia, 2013). System based on the use of colloidal silica is considered as the most effective but its price is high and this is the main reason for the increasing use of bentonites which are less expensive. Bentonite consists mainly of montmorillonites (up to 90%) with traces of silica, quartz. . . In the dry state, bentonite is made of stacked octahedral aluminum-oxygen and tetrahedral silicon-oxygen layers and its general chemical formula is $Al_2Si_4O_{10}(OH)_2$. These layers are organized in platelets and larger aggregates. Because of the existence of isomorphous substitution, a fraction of the Al ions is replaced by cations of lower valence. In water, the resulting negative net charge is compensated by the presence of exchangeable cations on the surface of the plates which are responsible for the penetration of water in the interlayer space and the huge swelling ability of the bentonites. After swelling and delamination, the surface area of montmorillonite can reach 800 $m^2\,g^{-1}$ and the cation exchange capacity, depending on the substituting cations, is usually close to 1 meq g^{-1}, which corresponds to a high surface charge density of about 0.2 C/m^2 (Hessen and Smit, 2002; Vanerek et al., 2006). In papermaking, bentonites are used with two objectives: for adsorbing contaminants such as wood colloids which can interact with process additives (Asselman and Garnier, 2000) and, as already mentioned, for improving the drainage and retention. Flocculation and retention mechanisms of bentonite-based microparticle systems have been investigated even if they are not still fully understood. Interactions between bentonites and cationic polymers or colloids result from electrostatic forces and the high surface charge density of the bentonite plays a major role and explains the efficiency of these systems. These interactions are probably affected by the swelling extent of the bentonite and the resulting surface area (Asselman and Garnier, 2001; Burgess et al., 2000; Alince et al., 2001; Cho et al., 2006; Vanerek et al., 2006). More specifically, bentonite based-microparticle systems could improve drainage and retention for non-wood pulps which are often characterized by a poor dewatering but this subject has not been extensively studied (Rainey et al., 2010; Vishtal et al., 2011).

Besides, microfibrillated cellulose (MFC) is a new material exhibiting very interesting properties. It can be produced from different lignocellulosic materials by variety of methods: mechanical treatments either high-pressure homogenization or grinding combined or not with prior enzymatic or chemical treatments of the fibres (Siró and Plackett 2010; Klemm et al., 2011; Hassan et al., 2012; Lavoine et al., 2012; Alila et al., 2013; Missoum et al., 2013). There is a recent interest in using MFC in papermaking although their small size makes them difficult to retain during the web formation and negatively impacts the pulp dewatering: additions of MFC into softwood or hardwood pulps, and kraft thermomechanical pulps were thus investigated, mainly for improving the dry strength properties of the produced papers (Taipale et al., 2010; Chauhan and Chakrabarti 2012; González et al., 2012; Hii et al., 2012), but also for imparting wet strength when MCF are used in conjunction with polyamine-amide-epichlorohydrin (Ahola et al., 2008). Positive effects of MFC on the properties of papers produced from bagasse pulps have also been reported (Hassan et al., 2011; Djafari Petroudy et al., 2014). Nevertheless, to the best of our knowledge, MFC, at very low dosages, were never tested for improving the retention and drainage of pulps.

In this context, the aim of this work is to study the use of bio-based additives, namely cationic MFC, chitosan and water soluble cationic chitosan in combination with Egyptian bentonite in order to increase the retention of ground calcium carbonate in the produced handsheets and improve the dewatering of fibrous suspensions made from bagasse pulps. For comparison purpose, a softwood pulp was also tested in this study and the performance of these bio-based microparticle systems was compared to that of a commercial cationic polyacrylamide.

2. Methods & materials

2.1. Materials

2.1.1. Pulps

Two bleached kraft pulps were studied in this work: a bagasse pulp (BP) which was kindly supplied by Quena Company for Pulp and Paper, Quena, Egypt and a bleached kraft softwood pulp (SW)