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Preparation and application of cationic cellulose fibers modified by in situ grafting of cationic PVA

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ABSTRACT

Rendering the cellulose fiber cationic via in situ graft copolymerization has been regarded as one of the effective approaches to improve the filler retention and distribution. In this work, cationic cellulose fibers were prepared by in situ copolymerization of vinyl acetate (VAc) and diallyldimethyl ammonium chloride (DADMAC) onto softwood sulphite pulp fibers using ceric ammonium nitrate (CAN) as a free radical initiator, followed by alkaline hydrolysis. Effects of various process parameters were systematically investigated, such as temperature, reaction time, initiator concentration, etc. Fourier transform infrared spectroscopy (FT-IR) was performed to confirm the existence of the grafted copolymers on the surface of sulphite pulps. The charge density of modified fibers was determined via back titration using a Particle Charge Detector MÜtek PCD 03. The difference between grafted fibers and virgin fibers was also revealed by the SEM observation. The resulting cationic pulps led to significant improvement of filler retention and distribution. Further improvement in filler retention was achieved by the synergy between cationic pulps and a conventional cationic polymer. In addition, the improved distribution of filler along fiber surfaces achieved by the addition of cationic pulp was demonstrated by both optical microscope and SEM observation.

1. Introduction

Papermaking nowadays is a large, capital-intensive industry, which is characterized by high-speed machines and complex systems of control for manufacturing. Cellulose fiber, as the most abundant, inexpensive, renewable, fully biodegradable natural resource in the world, has been widely used in papermaking industry. To further reduce paper cost, enhance the printability and provide desired functional end-use properties of paper products, mineral fillers have been extensively used in papermaking processes. Nevertheless, the surface charge of wood pulp fibers generally used in papermaking, is anionically oriented, which repels other anionic species in the papermaking process, such as inorganic fillers, sizes, fines, etc. This reduces the mechanical properties of the sheet and causes some retention problem. It is common practice to add polymer at the wet end to improve the filler retention [1–7]. However, such soluble polymers also exhibit some drawbacks. The main drawback is the performance of the polymer tends to be sensitive the pH and salt concentration in the papermaking environment and causes the accumulation of the unadsorbed polymer in the white water. The performance of polymeric aids also relies on the proper dosage. Over dosage tends to result in another repelling interaction. Also, large filler aggregates are often formed with the addition of the polymeric polymer. This induces the non-uniform filler distribution, resulting poor optical and printing properties of paper [8].

It is known that a more favourable self retention of the primary filler particles should result from the natural attraction between opposite charges instead of the using of water soluble cationic polymer. In order to achieve high filler retention and uniform filler distribution, it is natural to consider developing fillers or cellulose fibers with predominantly cationic charge based on above arguments.

Filler engineering technology was therefore introduced to the papermaking industry back to 1970s in order to improve the strength properties and the filler retention efficiency for high filler-filled papers. Nguyen et al. [9] employed a free-radical graft polymerization to introduce vinyl acetate (VAc) onto nonporous silica particles. A new technique of coating starch on the clay surface was developed to improve the paper mechanical properties [5,10–15]. Over the past years, cationic-modified fillers have been attempted to increase filler loading in paper while maintaining sheet strength, improved runnability and filler retention, and to

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reduce cationic additive demand and more uniform filler distribution. However, there were still drawbacks to this process, such as slurry instability, formation of agglomerates and more proneness to sedimentation. Papers made with such fillers were liable to cause increased dusting.

Based on the above discussion, fiber engineering technology still has some room for improvement for papermaking industry. As summarized by Baum in IPST, current chemical and mechanical processes are not enough to unlock fiber's true potential. In order to produce superior results, there are at least four ways fibers can be engineered, namely genetic modification, chemical modification, enzymatic modification and mechanical modification [16]. Some researchers made enormous efforts to graft functional polymer or monomer onto fiber to enhance its properties, including conductivity [17], hydrophobicity [18], water absorbance [19], antimicrobial activity [20], temperature-responsive [21–24], pH-sensitive [25], etc. Carlmark and Malmstrom [18] successfully rendered the paper hydrophobic by grafting with methyl acrylate (MA). But for the purpose of improving filler retention and improved paper physical properties, Zheng et al. [26] rendered the fibers cationic via in situ polymerization to introduce AAm, cationic monomer [2-(methacryloyloxy)ethyl]trimethyl ammonium chloride (MAETMAC) to the fiber backbone using cerium (IV) ammonium nitrate (CAN) as initiator and also studied the resulting cationic fiber in the papermaking process. The drawback here is that the cationic polymer grafted on the fiber surface was not tolerant towards the alkaline condition of the papermaking process due to the hydrolysis reaction.

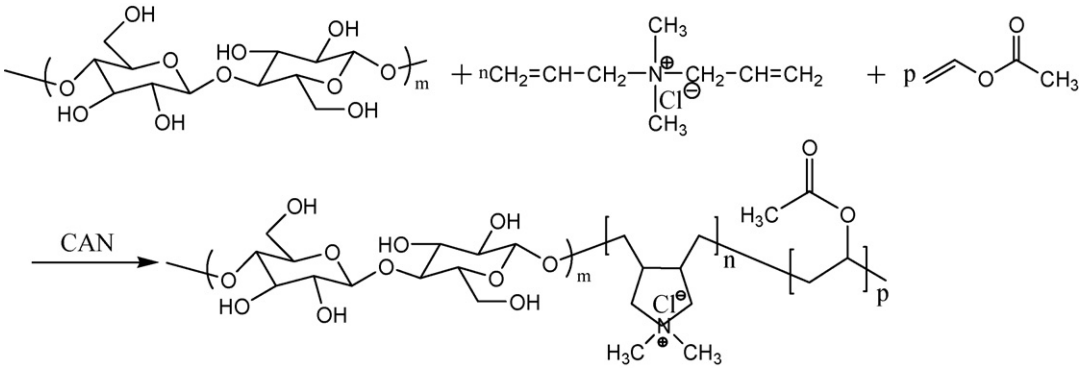
Of great interest in this paper is a higher cationic charge was introduced into the fiber independent of pH, providing the potential anchoring site for the negatively charged filler. Such engineered fibers could offer some benefits over soluble polymer for the improving filler retention, and be less accumulated in the white and waste water.

In this paper, we reported the graft of DADMAC and vinyl acetate following by alkaline hydrolysis without damage the cationic group containing in the DADMAC, and at the same time to generate more –OH groups (contributed from polyvinyl alcohol (PVA) segments) for potential bonding ability. Moreover, due to the high compatibility of PVA, the pended polymer chains tend to be biodegradable as well. We also adopted the DDJ to simulate the papermaking process (especially turbulent flow and the shear force) to test the cationic fibers performance in improving the filler retention and distribution. The key objectives of our work were to develop an appropriate approach to graft cationic monomer onto fiber surface; and to verify whether the cationic-modified fibers via in situ copolymerization could achieve satisfactory filler retention and improve filler distribution. In addition, the synergy between the modified fibers and conventional cationic polymer in improving filler retentions was also identified.

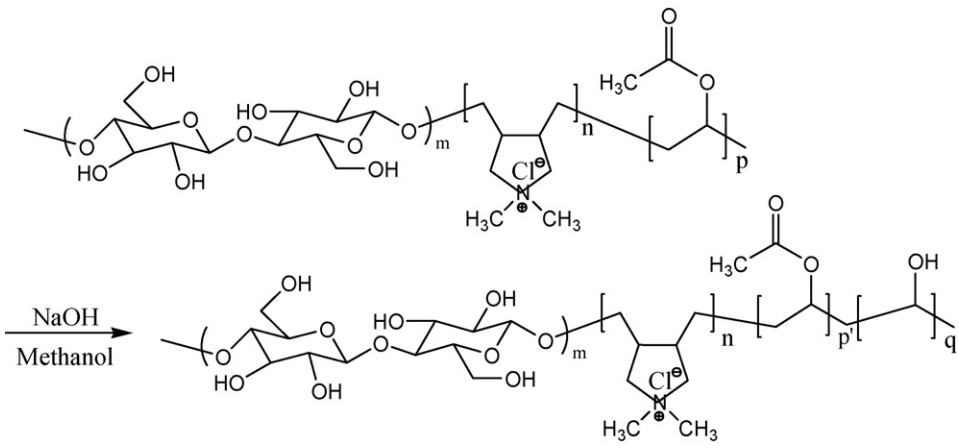
2. Experimental

2.1. Materials

The bleached sulphite pulps were supplied by Fraser Papers, Edmundston, New Brunswick, Canada. The pulp was purified with distilled water for three times. Ceric ammonium nitrate (CAN, $Ce(NH_4)_2(NO_3)_6$, 99.99%), an initiator for the graft copolymerization on fiber surfaces, was purchased from Sigma–Aldrich and



Scheme 1. In situ graft copolymerization.



Scheme 2. Hydrolysis reaction.