POLYMERIC COATINGS OF PCC FILLERS FOR PRINTING AND WRITING PAPERS

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ABSTRACT

This study deals with the process of coating paper fillers with polymeric materials in order to increase fibre-to-filler bonding and, therefore, to enable the use of high filler contents in printing and writing papers, without detrimental effects in the mechanical resistances and, if possible, with remarkable gains in terms of the optical and printing properties. PCC particles were coated with several polymeric materials (starch, cellulose acetate, poly(acrylic acid) and carboxymethylcellulose) and using distinct methodologies. The results obtained so far showed that, for each polymer, the coating process and the selection of the retention aids should be further optimized for better controlling particles size, shape and retention. Although preliminary, the results are promising with regard to the resistance and optical paper properties.

INTRODUCTION

Mineral fillers are the most important non-fibrous component of printing and writing papers, adding positively to sheet formation and improving opacity and brightness. The use of fillers also leads to dramatically lower furnish cost since fibre cost is usually much higher. However, fillers decrease fibre bonding and therefore reduce paper strength. Additionally, they increase the demand of internal sizing agents and the phenomena of abrasion, dusting and bad filler retention. As a consequence, filler content in paper has to be limited. In general, for a fine paper grade with 60 g/m^2 basis weight, values superior to 20-25% are uncommon. These limiting figures reflect the compromise of the papermakers in developing the optical properties while maintaining an acceptable level of mechanical paper resistance, as well as the effort of the filler suppliers in manipulating some mineral particle properties (e.g., shape and size).Thus, it is not surprising that active research has been lately developed in this area, aiming at improving the filler content in order to obtain better end-use paper properties without sacrificing paper strength, with an obvious positive impact in terms of product differentiation.

Studies developed up to now include fillers prefloculation and modification, synthesis of new fillers (fibrillated fillers), polymers incorporation in the sheet and fillers incorporation into the fibres lumen. More recently, novel filler modification approaches based on filler coating by a swollen starch gel, originating shell structure fillers, have been proposed [Deng 2005, Zhao *et al.* 2005]. Good results have been achieved regarding handsheet strength properties when compared to handsheets made with unmodified fillers, for the same fillers level, and also acceptable results were obtained regarding the optical properties, even though it is questionable the true adhesion of the polymer over the all mineral surface. In fact, fillers coating is a recent and promising research area of papermaking, with many topics to be addressed such as polymers efficiency, polymers and coating costs, influence on paper internal sizing and recycling and environmental impacts.

Preliminary results are presented concerning the study of different polymeric coating methodologies for bonding fillers and fibres together. PCC was used since it is the most common filler for fine papers produced in alkaline conditions. The selection of polymers was based on the fact that they must possess hydrophilic substitute groups, in order to favour chemical bonds with fibres, exhibit good optical properties and be available at competitive prices.

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MATERIAL AND METHODS

Different polymers were tested in this study: cationic starch, cellulose acetate, poly(acrylic acid) (PAA) and carboxymethylcellulose (CMC). The PCC was supplied by a paper mill.

The PCC coating with starch was performed by four distinct methods reported in the open literature: M_1) low water content cooking mixture [Deng 2005, Zhao *et al.* 2005]; M_2) precipitation of cooked starch over PCC with ammonium sulphate [Yoon and Deng 2006a]; M_3) precipitation of cooked starch over PCC through the formation of a starch-fatty acid complex [Yoon and Deng 2006b]; M_4) spray-drying of a PCC and starch mixture [Deng 2005]. As for the coating of PCC particles with cellulose acetate, a water-in-oil-in-water (w/o/w) double emulsion technique was used. In this case, an aqueous PCC suspension was added to the coating solution (organic phase consisting of cellulose acetate dissolved in acetone) which was in turn added to water. For the coating process with PAA, a free radical polymerisation in solution was used. After adding PCC powder into a potassium persulphate solution (1%), the suspension was filtered, ressuspended in water and finally added to an acrylic acid solution (1%) at 40-45°C to polymerize for 2-3h. The CMC coating was performed by adsorption of the polymer on PCC particles, as described by Xu, *et al.* [2005].

Both the original and the coated PCC particles were characterized in terms of particle size, by laser diffraction (Coulter LS130 – Coulter Electronics); particles shape, by scanning electron microscopy (JSM 5310 – JEOL); zeta potential, by electrophoresis (Zetasizer nano ZS – Malvern Instruments). The chemical analysis of the coated particles surface was performed by FT-IR (Magna-IR 750 FT-IR Spectrometer – Nicolet). Thermal degradation studies were performed by thermogravimetric analysis (SDT Q600).

The effect of the coating processes on the papermaking properties was evaluated by comparing the properties of handsheets produced with uncoated PCC and the properties of handsheets produced with some of the coated particles (those coated with starch, method M1, and cellulose acetate). The handsheets (80 g/m^2 basis weight) were made with a commercial Eucalyptus globulus based kraft pulp, bleached in an ECF sequence. In each case, PCC, starch, AKD, commercial acrylamide (Percol) and bentonite were added to the pulp furnish. The amount of each additive, as well as the sequence of addition, are specified in Table 1. Finally, the handsheets were tested in terms of bulk, air resistance, tensile index, brightness and light scattering, in accordance with the corresponding ISO standards.

Table 1 – Amounts and sequence of addition of each additive

	PCC	Starch	AKD	Percol	Bentonite
Amount (% w/w)*	20	1,1-1,3	0,1	0,02	0,25
Time sequence (s)	0	120	290	300	315

* relative to the total paper weight (od).

RESULTS AND DISCUSSION

The scanning electron microscopy photographs of Figure 1 reveal the differences in shape between the original and the coated PCC particles. As can be seen, the scalenohedral shape of the original particles was only preserved in the cases of the starch coating by the low water content cooking mixture (method M_1, image b_1), when the spray dryer was used (method M_4, image b_4) and with the CMC coating (image e). The other coatings show distinct morphological differences and some of them seems to be inadequate for paper filling, namely b_2 and b_3 starch coatings. The chemical identification of the polymeric materials at the surface of the modified PCC samples was performed by FT-IR (not shown). However, for the samples treated with starch and CMC, no identification was possible, may due to the small quantities of polymer that were used. Nonetheless, starch was detected in samples b_1 and b_4 by using an iodine solution. In addition, the thermogravimetric tests confirmed the presence of the coating polymers in all samples.

In all situations, the control of particle size after coating, grinding and sieving was very difficult and therefore, comparing to the original PCC particles, boarder distributions, with larger mean sizes, were generally obtained, as can be seen in Table 2. The size distribution results of samples b_2 and b_3 are closer to those of the original PCC, but, as Figure 1 reveals, the particle shape is not adequate. The coating process slightly increases the value of the particles zeta potential.

Up to the moment, only the PCC coated with starch by the low water content cooking mixture method (M1) and the PCC coated with cellulose acetate were used to study the papermaking potential of these novel fillers. The preliminary results shown in Table 3 reveal that the retention of the coated fillers was inferior to that of the uncoated PCC. Therefore, it is not surprising that handsheets with smaller bulk and light scattering and higher air resistance and tensile resistance were obtained with the coated fillers. In addition it is visible that starch is detrimental to brightness, whereas cellulose acetate has no significance influence. The results of retention indicate that different chemicals, respective amounts and sequences of addition are necessary for optimizing the retention of the same filler particles coated with distinct polymers. Supplementary tests have demonstrated that, without retention aids, the retention of the PCC particles coated with starch (by the method M1) was of 45%. This value is practically the same that was obtained when the handsheets were produced with AKD and Percol (47%, Table 3), which confirms the positive effect of the coating process with starch in bonding fillers and fibres, thus reducing their loss through the sheet former wire.

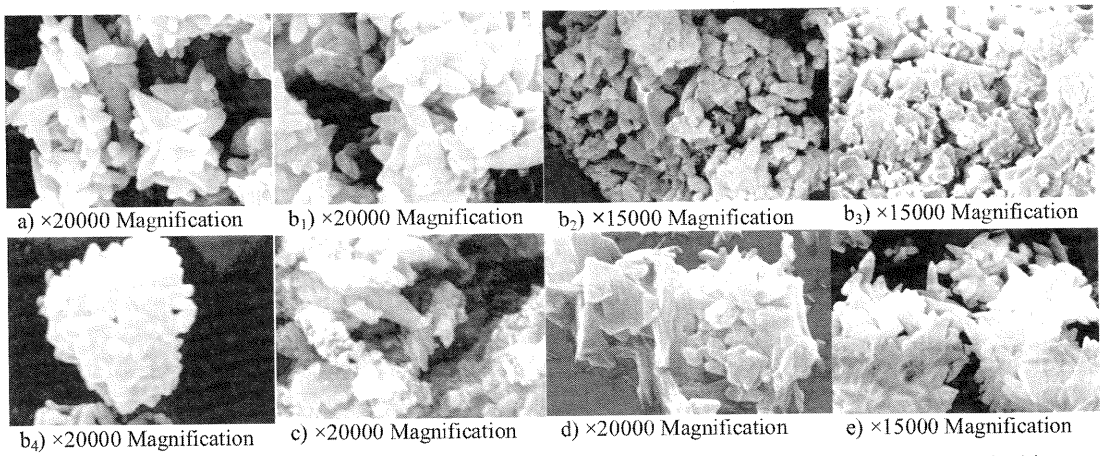

Figure 1 – Scanning electron microscope photographs: a) original PCC filler; b_1-b_4): filler coated with starch (methods M_1-M_4, respectively); c), d) e): filler coated with cellulose acetate, PAA and CMC, respectively.

Table 2 – Properties of the original and coated PCC particles

	Original PCC	Starch coating b_1)	Starch coating b_2)	Starch coating b_3)	Starch coating b_4)	Cellulose acetate coating	PAA coating	CMC coating
d_{10} (μm)	2,14	1,51	0,75	0,74	0,77	0,78	2,70	0,77
d_{50} (μm)	3,94	7,25	2,83	4,00	7,86	6,57	6,89	2,56
d_{90} (μm)	7,30	50,67	8,30	13,00	15,52	662,40	32,50	5,68
Zeta Potential (mV)	-24,0	-16,9				-19,3	-18,6	

Table 3 – Most relevant papermaking properties of paper sheets prepared without filler and with uncoated and coated PCC (starch and cellulose acetate coatings)

PCC	Retention (%)	Bulk (cm^3/g)	Air resistance (s/100ml)	Tensile Index (Nm/g)	Brightness (%)	CEDL (m^2/kg)
---	---	1,42	4,10	74,10	86,6	29,1
uncoated	65,7	1,61	2,30	42,10	89,2	51,0
Starch coated	47,0	1,48	3,70	55,90	87,7	41,0
Cellulose acetate coated	33,7	1,47	4,90	52,60	89,3	46,4

CONCLUSIONS

Despite being preliminary, the results are promising concerning the papermaking potential of coated fillers. Nevertheless some more studies have to be done in order to better control the polymeric filler coatings and the size and shape of the resulting particles. Furthermore, it is necessary to optimize the retention mechanisms of the coated fillers, based on their surface properties and reactivity. From the results, it is possible to conclude that the use of the spray-dryer after any coating process seems promising for controlling the size and shape of the final product.

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