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Understanding Interactions between Cellulose and Phosphate Esters in Papermaking

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Abstract Linting is a major problem affecting printing processes. It is characterised by the detachment of fibres from paper surface and their accumulation on press blankets. Recently, the addition of blends of phosphate esters to the pulp suspension prior to sheet formation has been identified as an effective way of reducing the linting propensity of paper. The objective of this study was to understand how phosphate esters are retained on cellulosic substrates and how they can contribute to the potential reduction of the linting of paper. Techniques like XPS, MS and conductometric titration were used to give an explanation of this phenomenon. The results tend to confirm the presence of phosphorus on cellulosic substrates and provide evidence of phosphate ester-cellulose linkages. This study allows us to elucidate part of the retention mechanism of phosphate esters in paper and explain their lint reduction ability.

Keywords Cellulose, Phosphate Esters, Linting, Papermaking

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1. Introduction

Nowadays, chemical products are commonly added to the wet pulp to improve paper properties[1-5]. Among these many chemicals, phosphate esters have been shown to reduce the linting propensity of paper during the printing process.However, this effect was mainly demonstrated by industrial experience[2-4]. The exact mechanism by which phosphate esters prevents linting is still under investigation. It has been proposed that the surfactant nature of phosphate esters made then act as "internal" release agents preventing the partial detachment of fibres during sheet pressing and drying thus reducing the complete detachment of fibres in the printing process (linting)[5].

This paper is an attempt to determine if phosphate esters are retained in the sheet during formation on the papermachine and, if it is the case, by what kind of interaction with the fibres. However, it was shown that the efficiency of these molecules depend greatly on variables such as product solubility, alkyl chain length and type, physicochemical parameters of the pulp suspension (pH, calcium ion concentration) and adsorption on fibres. Therefore, the aim of this study was to investigate the occurrence of phosphate esters action in lint reduction applications by trying to find interactions between cellulose fibres and phosphate esters.

2. Experimental

In this investigation, cellulose powder (CP, 20 µm, Aldrich) and bleached kraft pulp (KP, Kruger Wayagamack Inc., Trois-Rivières Canada) were suspended in solutions of phosphate esters in standard papermaking conditions.

Phosphate esters consisted in a commercial blend of C8 to C12 mono- and di- esters. Its exact component was already determined[6].

2.1. Methods

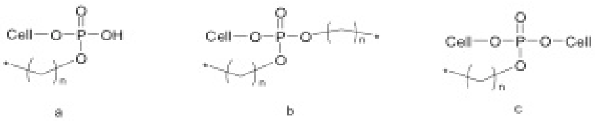

Figure 1. Possible cellulose-Phosphate ester reaction products

KP fibres or CP were added to solutions of phosphate esters (6, 12 and 24 g/L). Cellulosic substrate suspensions (5% w/w) were kept under stirring for 6h at room temperature. After the reaction, KP fibres and CP were isolated by centrifugation at 2 500 rpm for 10 min, then dried for 24h at 105°C and stored under a dry atmosphere. CP samples identified as A061, A121 and A241 are samples treated with 6, 12 and 24g/L of phosphate esters respectively. The same nomenclature was used for KP fibres (K061, K121 and K241). Recovered solutions after centrifugation are identified A062 (for fibre suspension A061) and so on. The initial phosphate esters solution is identified as Z. Possible reaction products that are obtained after this treatment are

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presented in Figure 1.

2.2. Physicochemical Characterisation

Several analytical techniques like mass spectrometry (MS), conductometric analysis and X-ray photoelectron spectroscopy (XPS) were used to characterise treated fibres and recovered solutions.

The composition of recovered solutions was determined by MICROMASS spectrometer (QUATROMICRO model). Samples were injected by syringe and ionized by the electrospray method (ESI).

Conductometric titrations were performed with a THERMO ORION conductometer (model 150). The titration of acidic groups required a pre-treatment of dried fibres. Therefore, 6g of dried fibres were treated with 200 mL of 0.1N HCl for 45 min, filtered and washed 5 times with 100 mL of demineralised water. This step was repeated once again. The titration was performed by suspending, 3g of pre-treated fibres in 400 mL of 0.001N NaCl and 5 ml of 0.100N HCl. The suspension was held at room temperature and stirred under nitrogen gas flow to minimise carbon dioxide interference. A 0.0100N NaOH solution was added at a rate of 0.1 mL/min with continuous stirring[7-9].

XPS experiments were recorded on a KRATOS ULTRA ELECTRON SPECTROMETER (Kratos Analytical) using a monochromatic Al KÎ± X-ray source (15 kV, 5 mA). The samples were previously dried for a week and then placed in an ultrahigh vacuum chamber (10^{-8} mbar) and collected data were analysed by CASA XPS software. The C-H signal was used as a reference peak at 284.9 eV. A complete description of the XPS characterisation method can be found in the literature[10].

3. Results and Discussion

3.1. Recovered Solution Analysis

In agreement with Daemen results[6], the presence of different hydrogeno-phosphate (mono- and di-ester) was observed in the original ester blend (Z) (Table 1). After 6h of contact with cellulosic substrates and filtration, monohydrogen phosphates, identified mC_8 and mC_{10}, were not detected in the recovered solution indicating a reaction with cellulose fibres or an adsorption on their surface (Table 1). Moreover, MS results also showed that all phosphate esters in the mixture did not react equally with fibres. This is quite normal, because monohydrogen phosphates are supposed to have a higher reactivity than dihydrogen.

In the original ester mixture, the relative amounts of mC_8 and mC_{10} are 9.3% and 6.3% respectively. After 6h of reaction with cellulose, at least 76% and 100% of monohydrogen phosphate reacted with 6g/L and 12g/L of mixture solution. We can also observe in Table 1 that the proportion of monohydrogen phosphate decreased with increasing concentration of ester solution. Similar results were obtained for the two studied cellulosic substrates. After 6h of treatment, two phases were obtained. The reduction of the quantity of monohydrogen phosphate in recovered solutions tends to indicate that hydrogen phosphates are adsorbed onto cellulose substrates.

The LC-MS results show that there are hydrogen phosphates adsorbed onto cellulosic substrates.After6 hours of treatment,two phases were obtained (liquid and solid).Since hydrogen phosphates were not found in the liquid phase, they should all be in the solid phase (fibres). But in light of these results, some reflections must be taken into account. Probably some dihydrogen phosphate may be adsorbed on the fibres without chemical bonds.

Table 1. Quantitative analysis of LC-MS spectra

	M	Z	A061	K061	A121	K121
		%R				
mC_8	209	9.3	1.8	2.2	0	0
mC_{10}	237	6.3	0.7	1.1	0	0
diC_8	321	25.2	28.1	27.4	33.2	28.9
diC_9[a]	349	22.3	22.8	23.5	25.3	29.2
diC_{10}	377	13.2	14.9	13.6	15.1	16.3
diC_{11}[a]	401	11.9	16.0	20.1	13.9	15.1
diC_{12}	429	5.0	9.9	9.6	5.6	5.1
diC_{13}[a]	457	4.2	4.4	2.6	5.1	3.3
	485	2.6	1.4	0.0	1.8	2.1

3.2. Fibres Characterization

Results of conductometric titration of acidic groups for CP and KP fibres are presented in Table 2. Titration curves of treated fibres exhibit a plateau and a shift of the equivalence point (Figure 2).

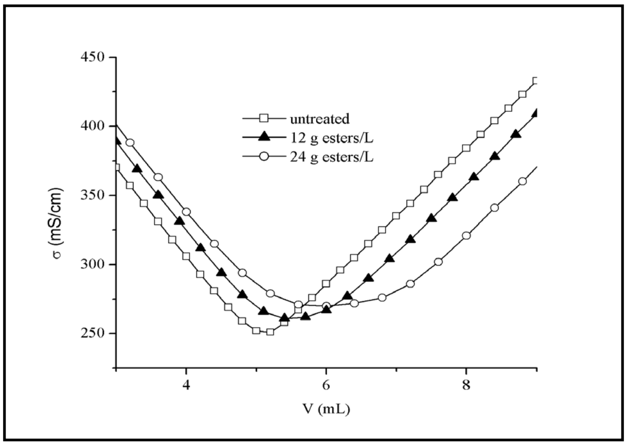

Figure 2. Conductometric curves of unmodified and modified fibres

These are evidence of the presence of new acid functions in fibres. Since adsorbed phosphates are removed by the pre-treatment, the reactivity of monohydrogen phosphates, which was showed by MS analysis, is confirmed. The increased acidity can only be caused by the reaction of monohydrogen phosphates with a single cellulose hydroxyl group (see Figure 1.a). Compounds (b) and (c) in Figure 1 do not contribute to the acidity.

Fibre titration analyses (Table 2) also show an increase in acid function concentration. This fibres acidity increases with esters concentration, which is consistent with MS results on ester adsorption. But for the same ester concentration, CP is more reactive than KP fibres.

Table 2. Titration of acidic group of untreated and treated fibres

Cellulosic substrates	Samples	[Ester] g/L	Acidity mmol/kg*
Cellulosepowder (CP)	A	0	15.4
	A061	6	25.9
	A121	12	38
	A241	24	68.3
Kraft pulp (KP)	K	0	28.3
	K061	6	33.4
	K121	12	48
	K241	24s	52

* millimol of acid per kg of fibres

These results tend to confirm the presence of phosphate esters in cellulose fibres. The lint reduction in papermaking is probably related to their presence. Since phosphate esters are retained in the sheet, they can still have a release effect on the printing press. However, it was not possible to measure the quantity actually adsorbed on cellulosic substrates.

XPS spectroscopy was also used to characterise cellulosic substrate surfaces (Figure 3, Figure 4, and Table 3). Full XPS (Figure 3) spectra of CP (a) and KP (b) fibres before treatment show only the presence of carbon C_{1s}(285 eV) and oxygen O_{1s} (532 eV) peaks[10-16]. After treatment, two new peaks at 132 eV and 191 eV are observed corresponding to P_{2p} and P_{2s} respectively[10, 17-19].

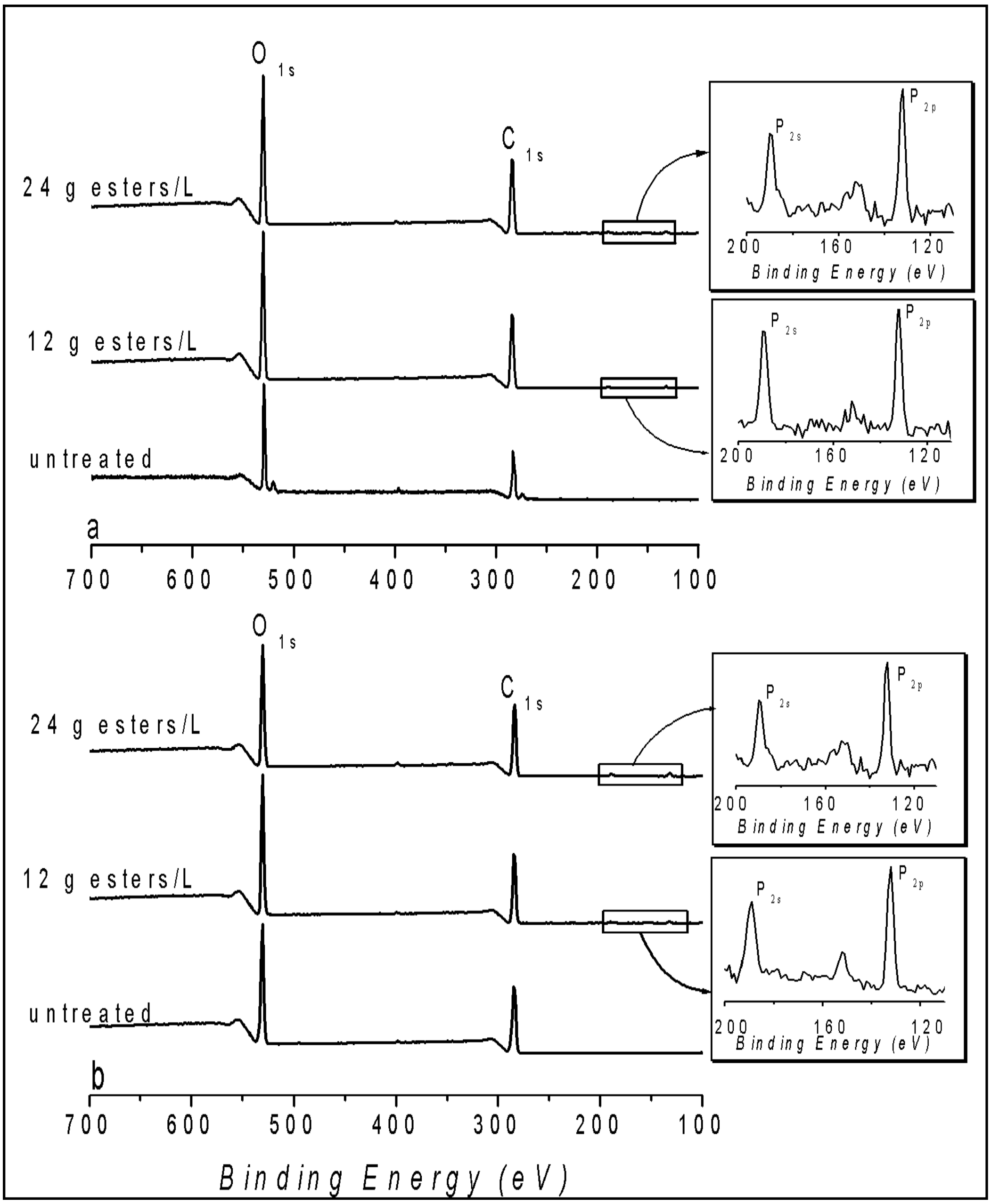

Figure 3. Full XPS of cellulose (CP and KP) before and after treatment

Table 3 presents the XPS results for the surface composition of treated and untreated fibres. It can also be noted from Table 2 that samples treated with the 12g/L ester solution (A121 and K121) have more phosphorus than those treated with the 24g/L solution. This may seem ambiguous in comparison with conductometric results, but it is due to the fact that XPS results take into account only the contribution of surface atoms. Moreover the treatment of fibres was done in water which is a swelling medium, it cannot be excluded that diffusion of ester and reaction with internal hydroxyl groups occurred.

Table 3. Fibre surface composition (%) by XPS

	P_{2p}/P_{2s}	C_{1s}	O_{1s}
Energy (eV)	132/191 eV	285 eV	532 eV
A	0	58.14	41.86
A121	1.22	63.38	35.40
A241	1.10	63.47	35.43
K	0	67.73	32.27
K121	2.61	64.94	32.45
K241	1.43	64.49	34.08

The oxygen spectra have been deconvoluted by using CASA XPS Software (multi Gaussian fit) calibrated at 532eV. The deconvoluted O_{1s} peak of untreated cellulose fibres show peaks assigned to O-C/O-H (O2) and O=C (O1) bonds at 532 and 530.9 eV respectively[10, 20-23]. After treatment of fibres, XPS analysis of fibres reveals a new oxygen peak (O3) at 533.6 assigned to O-P[16, 22] was observed (Figure 4).

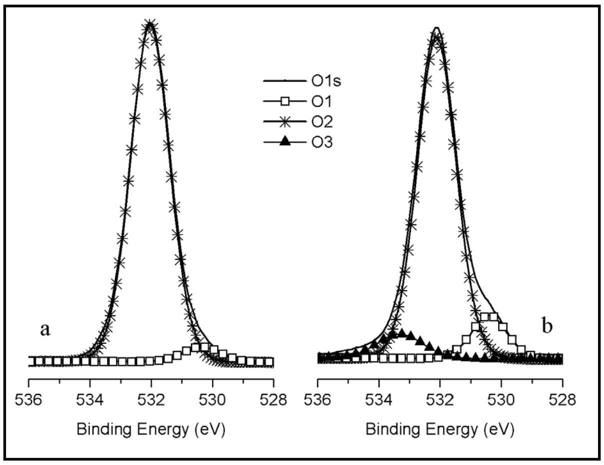

Figure 4. O_{1s} deconvolution of unmodified (a) and modified (b) fibres

Concerning O=P bond, many suggestions are proposed. Some authors[20-22] positioned it at lower energies than the O-P bond, between 530.9 and 531.5 eV, and identified it with O=C bond in the same zone. Others[24, 25] suggest that the O=P binding energy is greater than the O-P bond energy and assigned it beyond 533eV. In a recent publication, Rupper and co-workers[18]reporteda lower energy for O=P than for O-P by 1.5eV. In our case (Figure 4.b), an increase of O1 bonds at the surface was observed, which can only come from O=P bonds. Moreover, it seems to be well agreed among scientists[18, 20-22]that O=P binding energy is lower than O-P.

These different results (MS, XPS and conductometric) show the presence of phosphorus in cellulosic substrates. The phosphorus content that was obtained was not high enough to determine the degree of substitution of cellulose. According to MS analysis, the linkage between fibres and phosphate is done only through cellulose hydroxyl groups and ester function without alcohol liberation. We propose that phosphate esters are adsorbed on the cellulose fibres by hydrogen linkage. After washing and drying at 105°C, water molecules are released and a small number of CellO-P linkages are formed.

4. Conclusions

Results presented above show the presence of phosphate esters on the two studied cellulosic substrates. The preference for monoester overdiester was also noted. This study makes it possible to confirm interactions between cellulose fibres and phosphate esters. Itwas demonstrated that phosphorus could be introduced on fibre surfaces by adding phosphate esters to a fibre suspension. Itwas also revealedthatchemical bonds were formed between fibres and the anti-lint compound. O-P bonds were observed on the fibre surface after multiple washing of the treated fibres. So we can conclude that phosphate esters are linked by chemical bonding and the CellO-P bond is a part of O-P bonds.

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