

# Alkylated Phosphorylated Fibers: A New Substitute for Silicone in Release Paper Manufacturing

Lahbib Abenghal, Hamid Lamoudan, and François Brouillette \*

The production of release coatings has been increasing in recent years because of their use in various fields. However, commercially available release coatings are regarded as non-recyclable. As a consequence, the repulping of these residues is difficult, and their presence in the recycling stream represents an important source of contamination. One solution to this problem is to use new coating materials that can replace the siliconized backing, provided that these new materials are recyclable. As a solution to this problem, the authors propose the use of alkylated phosphorylated fibers to produce an environmentally friendly and inexpensive release paper. The results show that a surface application of hydrophobic phosphorylated fibers reduces the surface free energy of the paper support, as well as the peel strength, which facilitates the separation of the adhesive tape.

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Contact information: Innovations Institute in Ecomaterials, Ecoproducts and Ecoenergies (I2E3), Department of Chemistry, Biochemistry and Physics, Université du Québec à Trois-Rivières (UQTR), Trois-Rivières, Quebec, Canada; \*Corresponding author: francois.brouillette@uqtr.ca

## INTRODUCTION

Release liners are paper or plastic film substrates that are coated on one or both sides with a release material. They are essential to protect the adhesive during transportation and storage without the risk of degradation or contamination. Currently, release liners are used in a variety of self-adhesive applications such as labels, fiber composites, tapes, graphic arts, medical, and hygiene products, *etc.* However, about half of them are used to make self-adhesive labels for product identification (name, price, or composition) and to improve visual appearance (von Gradowski *et al.* 2019; Vasilev *et al.* 2020; Tučeková *et al.* 2020). Commercial release liners are generally based on clay-coated kraft paper with a smooth closed surface. The porous structure of the paper is closed with pigments to prevent liquids from penetrating the paper (Bollström *et al.* 2013).

Silicones (or polysiloxanes) synthetic polymers are most widely used for the industrial production of release coatings. They have unique properties such as biocompatibility, good chemical and thermal stability, hydrophobicity, low surface energy, and high gas permeability. Linear polydimethylsiloxane (PDMS) is the most common commercially available polysiloxane (Gordon *et al.* 1998; Ba *et al.* 2018). In terms of physicochemical properties, silicones mainly differ from organic polymers with respect to their weak intermolecular attractive forces. In terms of chemical structure, the Si-O-Si bond length and angle are greater than those of C-O-C or C-C bonds. In addition, the dissociation energy of Si-O-Si bonds reaches 460 kJ/mol, which is greater than that of C-O-C bonds, which does not exceed 345 kJ/mol (Somasundaran *et al.* 2006; Eduok *et al.* 2017). This

high energy confers chemical and thermal stability to PDMS, while the flexibility of its polymer backbone is enhanced by its low glass transition temperature. However, the high chemical stability of the (-Si-O-) silicone bonds makes the release liners non-recyclable with standard paper recycling technology. Consequently, it generates wastes that persist for many years in the environment (Venditti *et al.* 2000; Oku *et al.* 2002). In addition, these contaminants are a serious problem when they reach the recycling and papermaking process (Belosinschi *et al.* 2012). Manufacturers are looking for new and convenient ways to reuse liner materials to make labels and tapes, while eliminating wastes and reducing the cost associated with release liner manufacturing. Therefore, there is a strong need for the development of new biodegradable, biocompatible, reusable, and recyclable release coating agents. Early works with chromatogeny attempted the direct grafting of alkyl chains onto the paper surface at high temperatures (150 to 180 °C). Even though the final release paper had a peel force that did not exceed 6 N/25 mm, it was found that only 15 to 28% of alkyl groups were actually grafted onto paper surface (von Gradowski 2019). Another approach was to introduce a polyvinyl alcohol alkylation step prior to coating, by reacting polyvinyl alcohol with stearic acid chloride. The resulting product showed low adhesion to a pressure-sensitive adhesive (PSA) adhesive, but the release coating was not stable above the melting temperature of the adhesive (Kinning 1997).

Phosphate esters have also been considered as a potential coating material to replace siliconized backing. Indeed, ester alkyl chains provide a hydrophobic and low surface energy, down to 17.7 mJ/m<sup>2</sup>, which is a mandatory condition for the paper to be antiadhesive. Nevertheless, an undesirable mass transfer of the esters to the adhesive tape was observed, due to the weak bonds with cellulose, causing a reduction of the residual adhesion of the tape (Belosinschi *et al.* 2012). To reduce mass transfer, another approach was investigated in which kraft fibers were treated with two long-chain phosphate esters in the presence of urea at elevated temperatures (150 °C) to chemically graft the phosphate esters by covalent bonds. However, analyses confirmed only the grafting of the phosphate group. The alkyl chain was hydrolyzed before the esterification reaction occurred (Shi *et al.* 2014; Nourry *et al.* 2016). In contrast, phosphorylated fibers have a flame-retardant character, making them good materials for thermal insulation or composite materials (Mouandhoime and Brouillette 2021). In addition, the phosphate groups are negatively charged, which gives the phosphorylated fibers the ability to exchange ions for certain transition metals. These functionalities could be exploited in the treatment of wastewater (elimination of metal ions and color) (Shi *et al.* 2015).

In this study, a durable and low-cost route for the production of a release paper is described. The presence of alkylated phosphorylated fibers will make it possible, because of their alkyl chain and their modulable viscosity, to easily adjust the surface properties of the unmodified base paper. Unlike silicone, which has stable silicon-oxygen bonds, alkylated phosphorylated fibers used in this work are single molecules that have carbon-carbon, carbon-oxygen, and phosphate-oxygen bonds, making their repulping easy and less expensive. In addition, the fibers recovered after recycling have a high value with respect to their use for thermal insulation in buildings or as ion exchangers. As an additional way to reduce the manufacturing costs of the release paper, a lower grade old corrugated cardboard was used instead of a glossy kraft paper.

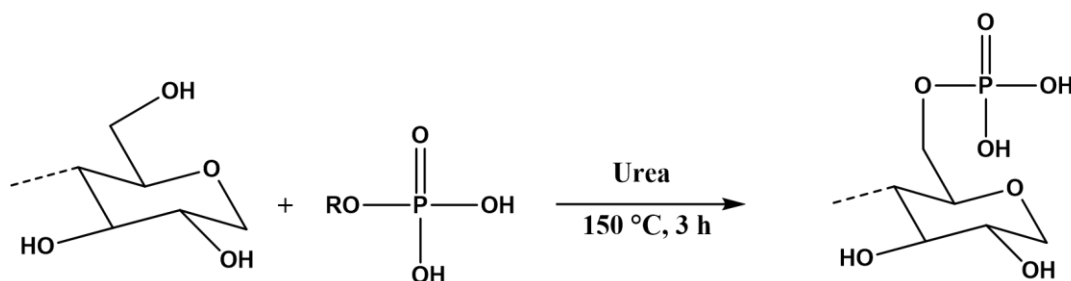
## EXPERIMENTAL

### Materials

The old corrugated cardboard (OCC) fibers used in this work were received from Kruger Inc. (Trois-Rivières, Canada) in two different forms: a 100% OCC calendered paper and OCC fibers. The sheet samples have a basis weight of  $56.4 \pm 2.4$  g/m<sup>2</sup> and a thickness of  $100 \pm 5$  μm. The siliconized commercial paper used as a reference was the release liner retrieved from an AIEX (Shenzhen, China) self-adhesive label roll number A13043. All reagents were purchased from Sigma-Aldrich (Oakville, Canada) and were used as received without further purification: polyvinyl alcohol (PVOH, 99% hydrolyzed, molecular weight 85,000 to 124,000 Da), carboxymethylcellulose sodium salt (molecular weight ~90,000 Da), latex polymer (Acronal NX4787X, BASF, Mississauga, Canada), 1-decanol, phosphorous pentoxide, and butyryl, octanoyl, decanoyl, and dodecanoyl chlorides (99%).

### Phosphorylation of Cellulosic Fibers

The phosphorylation of OCC fibers was performed in molten urea using a phosphate ester according to the work of Shi *et al.* (2014). The phosphorylation is realized using 17 equivalents of urea and 3 equivalents of mono-decylphosphate (PE-C10), which is a phosphate ester that was synthesized from the reaction of phosphorous pentoxide P<sub>2</sub>O<sub>5</sub> and 1-decanol, for one equivalent of anhydroglucose units. The urea and phosphate ester were placed in a crystallizer maintained at 150 °C in an oven equipped with a gas evacuation and trapping system. Once a white foam had formed, OCC fibers were added to the crystallizer and left to react in the oven for 3 h (Fig. 1). Then, the fibers were thoroughly washed with deionized water and with 0.1 M aqueous HCl solution to ensure complete protonation of the phosphate groups. The washed fibers were filtered through a Buchner funnel and dried in an oven at 40 °C for 24 h. After the phosphorylation of the OCC pulp, only the phosphate group is grafted to the fibers, giving negatively charged fibers. Another reaction step is required to alkylate phosphorylated fibers.

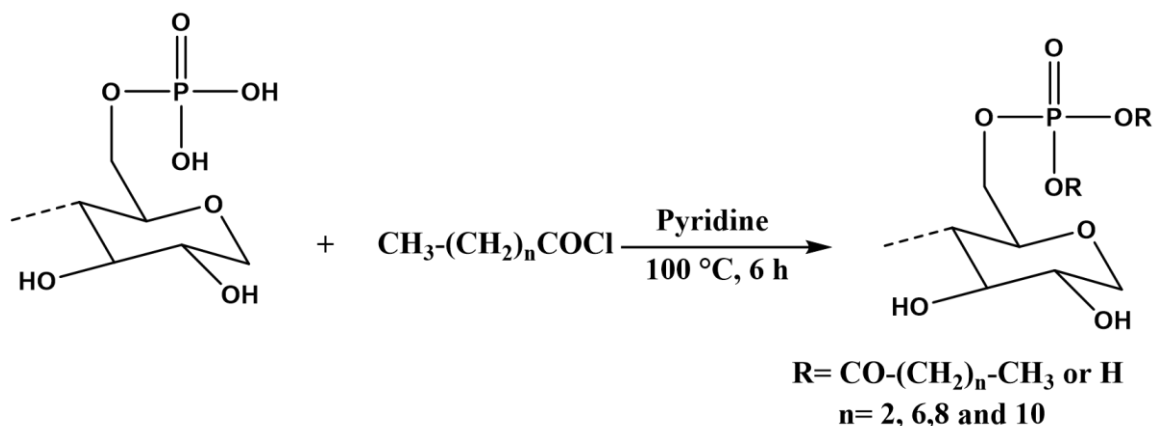


**Fig. 1.** Phosphorylation of OCC fibers with phosphate esters and urea (fibers are shown in their protonated form)

### Alkylation of Phosphorylated Fibers

The simplest method to alkylate phosphorylated fibers is to use acid chlorides with a weak base. For this purpose, the alkylation was completed according to a procedure adapted from Willberg-Keyriläinen *et al.* (2017) (Fig. 2). The heterogeneous esterification was completed using 1 equivalent of fibers previously treated with 0.1 M HCl and dispersed in toluene (solvent). Then, 2 equivalents of anhydrous pyridine were slowly added to the reaction medium. Finally, 2 equivalents of fatty acid chlorides (C<sub>4</sub>, C<sub>8</sub>, C<sub>10</sub>,

or C12) were added. The mixture was then heated at 100 °C for 6 h. The resulting product was washed several times with deionized water and finally with acetone.



**Fig. 2.** Alkylation of phosphorylated fibers with acid chlorides in the presence of pyridine

### Characterization of Alkylated Phosphorylated Fibers

#### *Fourier transform infrared spectroscopy (FTIR)*

The FTIR spectra of fibers were examined for changes in various bands reflecting the presence of alkyl groups. Absorption spectra of fibers were directly recorded in attenuated total reflectance (ATR) on a Thermo is10 FTIR (Thermo Fisher Scientific, Waltham, MA, USA). The bands were expressed in  $\text{cm}^{-1}$ , and the acquisition range was from 600 to 4000  $\text{cm}^{-1}$ .

#### *Scanning electron microscopy with energy-dispersive X-ray analysis (SEM-EDX)*

Scanning electron microscopy (15 kV, variable pressure) coupled to energy dispersive X-ray spectroscopy (SEM/EDX, Hitachi SU1510 with Oxford X-max 20  $\text{mm}^2$ ) was used to evaluate the chemical composition of the surface of alkylated phosphorylated fibers. Fiber samples were directly mounted on a conductive double-sided tape, without metallization.

The surface degree of substitution for the phosphorylation reaction per anhydroglucose unit ( $DS_P$ ) was calculated with Eq. 1 using the phosphorus contents previously measured by EDX. Then, the surface degree of substitution for the alkylation reaction ( $DS_A$ ), to determine the amount of carbon chains grafted onto the phosphorylated fibers after the alkylation reaction, was calculated with Eq. 2 according to a previously described method (Nourry *et al.* 2016). Finally, the degree of alkylation was calculated as a ratio of  $DS_A$  and  $DS_P$ ,

$$DS_P = \frac{162 \times \%P}{3092 - 79.98\%P} \quad (1)$$

$$DS_A = \frac{\% \Delta C \times (M_{\text{OCCP}})^2}{(1201 \times M_{\text{OCCP}} - 14.03 \times \% \Delta C \times M_{\text{OCCP}} - 101100,18) \times L} \quad (2)$$

where  $\% \Delta C$  is the variation of the carbon content after alkylation,  $M_{\text{OCCP}}$  is the molar mass of the phosphorylated anhydroglucose units, and  $L$  is the carbon length of the grafted alkyl chain.

### Total charge

The total charge of phosphorylated fibers was determined by conductimetric titration according to the SCAN-CM 65:02 (2004) method. First, the fibers were treated with 0.1 M aqueous HCl for 30 min to ensure total protonation of the phosphates. Then, 0.5 to 1 g of fibers was dispersed in a 1 mM sodium chloride solution and titrated with sodium hydroxide (0.1 M). The titration was performed using a Thermo Orion (model 150; Thermo Fisher Scientific, Waltham, MA, USA) conductivity meter and an automatic titrator (Dosimat 765; Metrohm Brinkmann, Camden, NJ, USA).

### Water retention value measurement

The measurement of the water retention value (WRV) is the simplest method to evaluate the interaction between modified fibers and water (Gu *et al.* 2018). The procedure was performed with 1 g of fibers saturated with 30 mL of deionized water for 24 h at room temperature according to the TAPPI UM 256 (2015) method. Then, the wetted fibers were centrifuged at a relative force of 3000 g for 15 min. Finally, the weight of the wet sample was determined, and the sample was weighted again after drying at 105 °C for 12 h. The WRV was calculated using the Eq. 3,

$$\text{WRV} = \frac{m_w - m_d}{m_d} \quad (3)$$

where  $m_w$  and  $m_d$  are, respectively, the wet and dry substrate masses (g).

### Fiber Length Distribution

The fiber length distribution after phosphorylation and alkylation was measured with an L&W Fiber Tester Plus (ABB, Kista, Sweden) fiber quality analyzer (FQA). The arithmetic mean length was reported. These results are helpful to determine optimal conditions to complete phosphorylation with minimum fiber degradation ensuring a high mass yield.

### Preparation of Coating Solutions

The preparation of coating solutions containing alkylated phosphorylated fibers was completed by dispersing 10 g of fibers in 100 mL of water. To improve fiber dispersion in water, a mechanical treatment was applied with a grinder to reduce their average length. The treatment consisted of drying fibers in an oven at 120 °C for 12 h and dispersing for 5 min in a grinder (model CBG110SC; Black & Decker, Middleton, WI, USA). Then, 0.20 to 0.25 g of carboxymethyl cellulose (CMC) was added as a dispersing agent and the solution was homogenized for 10 min at 3500 rpm at room temperature. Finally, the suspension was mixed with 5 mL of a latex polymer (solids content ~ 50%) used as a binder to ensure adhesion of fibers to the paper surface. Two strategies were evaluated to improve the release properties of paper coated with alkylated phosphorylated fibers. The first was to precoat the OCC paper with a 2 g/m<sup>2</sup> layer of PVOH to create a physical barrier to prevent the penetration of the coating solutions inside the paper structures. The second strategy was to add 0.5 g of phosphate esters in the coating solutions (Table 1) to increase their hydrophobicity.

The obtained coating solutions were applied to the surface of OCC sheets. A variable speed drawdown coater (model EC-200; ChemInstruments, OH, USA) was used to apply the coating at room temperature and atmospheric pressure, at a speed of 10 m/min with a #24 wire-wound metering rod.

**Table 1.** Composition of the Coating Solution

Component	Amount Added
Alkylated Phosphorylated Fibers	10 g
Carboxymethyl Cellulose	0.20-0.25 g
Latex Polymer	5 mL
Phosphate Esters (PE-C10)	0 or 0.5 g
Deionized Water	100 mL

## Characterization of Coated Papers

### *Coat weight and sheet thickness*

To determine the coat weight, paper samples cut to a size of 10 cm × 10 cm were stored in a controlled room for 24 h (23 °C, 50% relative humidity) and weighed before and after coating. The basis weight was determined according to ISO 536 (2019) standard method. Three replicates were performed on each sample to determine the coating weight.

The thickness of the samples was determined with a TMI model 549 E thickness tester (Testing Machines Inc., New Castle, DE, USA), with an accuracy of 1/10000 m according to the ISO 534 (2011) standard method. Measurements were made in triplicates at 10 random locations on each sample.

### *Air permeability and water absorptiveness*

Air permeability was determined with the TAPPI/ANSI T555 om-22 (2022) standard method, using a Labtech PPS (Parker Print Surf; (Testing Machines Inc., New Castle, DE, USA) at a maximum air pressure of 1960 kPa. Three replicates were made on each sample.

The water absorptiveness was evaluated by the Cobb method according to TAPPI T441 om-20 (2020). This method determines the amount of water that can be absorbed per unit area of paper during a specified time (60 s). The purpose of this test is not to determine the actual water absorption of the samples, but to provide a comparative value between coated samples.

### *Surface free energy*

The measurement of the surface free energy is required to evaluate the release properties that can explain or predict the release behavior of the adhesive tape. In general, release materials must have a low surface energy to allow easy separation of adhesive tapes.

The surface free energy ( $\gamma$ ) was calculated according to the three-component model of Van Oss, Chaudhury, and Good known as VOEG. This method calculates the polar  $\gamma^p$  and dispersive  $\gamma^d$  components of the surface energy by describing the polar component using the Lewis acid-base model. Formamide, ultrapure water, and  $\alpha$ -bromonaphthalene were used as liquid probes. Five contact angle measurements were made for each sample with a FTA4000 Microdrop analyzer (First Ten Angstroms, Portsmouth, VA, USA).

## Peel Strength and Residual Adhesion

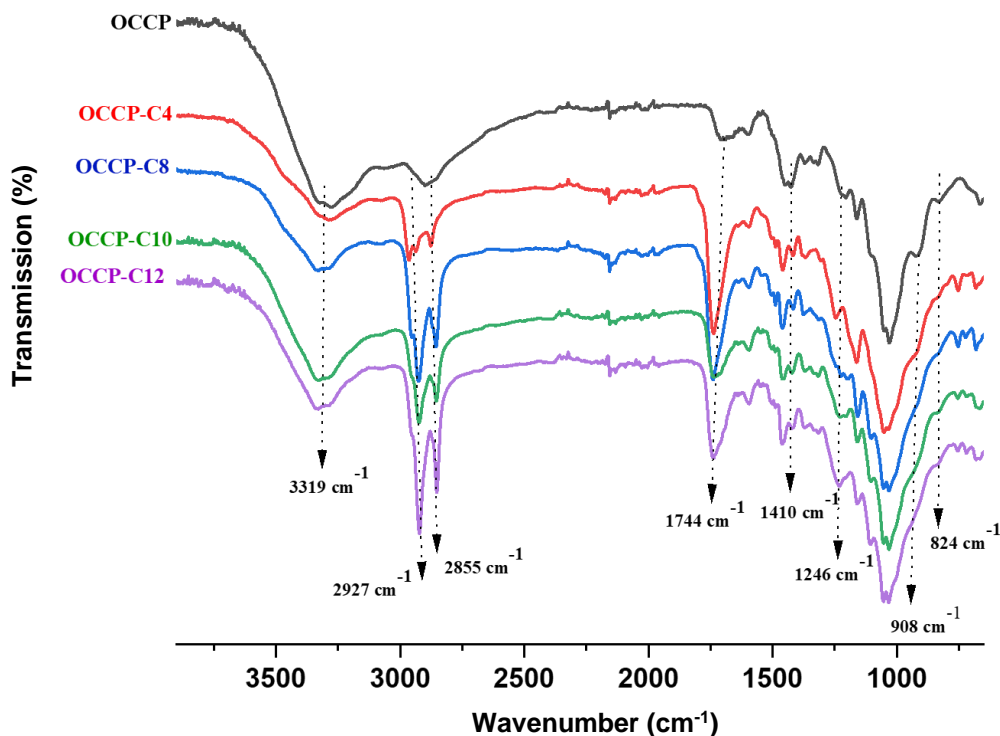
The peel test is used to evaluate the release performance of release liners. The test measures the strength required to peel a standard adhesive tape from a coated paper sample surface at a given angle and speed after it has been applied under specified conditions.

The peel force of coated papers was measured with an acrylic tape (Tesa 7475; Tesa Tape Inc., Charlotte, NC, USA) according to FINAT FTM 10 (2019) standard method at a 180° angle. Representative samples were cut into five strips (25 mm wide and a minimum 175 mm long). The acrylic tape was applied to the strips using a 13 kg standard roller and then attached to a metal plate using a double-sided tape. Peel forces were measured with an Instron Tester model 4201 tensile tester coupled to the Bluehill software (Instron, Norwood, MA, USA). The instrument is able to realize the peeling of an adhesive material at a 180° angle with a separation speed of 300 mm/min. After the test, the tape was collected and reapplied to a stainless-steel plate. The plate was placed on the measuring device in the same way as previously described and the peeling test is performed according to the conditions indicated in FINAT FTM 11 (2019) to obtain the residual adhesion.

## RESULTS AND DISCUSSION

### Characterization of Modified Fibers

Infrared spectra recorded before and after the alkylation of phosphorylated fibers are given in Fig. 3. All spectra show characteristic absorption bands of the cellulose glycosidic unit: stretching vibrations of O-H ( $3319\text{ cm}^{-1}$ ), stretching vibrations of C-H and C-O-C ( $2855$  and  $1053\text{ cm}^{-1}$ ), bending vibrations of C-H ( $1410\text{ cm}^{-1}$ ), and adsorbed water O-H bond ( $1688\text{ cm}^{-1}$ ). Moreover, the phosphate group is characterized by an elongation band around  $1246\text{ cm}^{-1}$  (P=O bond), two bands around  $1020$  and  $824\text{ cm}^{-1}$  (P-O-C bonds), and a shoulder around  $908\text{ cm}^{-1}$  (P-O-H bonds) (Inagaki *et al.* 1976).



**Fig. 3.** FTIR spectra of phosphorylated fibers (OCCP) before and after the alkylation reaction, where C4, C8, C10, and C12 are the length of the alkyl chain attached to the phosphorylated fibers

The alkylation of phosphorylated fibers was confirmed by the appearance of a new band around  $1740\text{ cm}^{-1}$ , associated with the carbonyl stretching vibration of the alkyl chain attached to the phosphorylated fibers (Duchatel-Crépy *et al.* 2020). The new peak around  $1286\text{ cm}^{-1}$  was attributed to the C-O elongation band. In addition, the substituted alkyl groups are mainly characterized by the presence of two peaks at  $2855$  and  $2927\text{ cm}^{-1}$ , corresponding to the C-H stretching vibrations. These changes in different regions clearly confirm that the alkylation reaction was successfully completed.

The length of the carbon chain affects the profile of the bands in the  $2850$  to  $2950\text{ cm}^{-1}$  range. In fact, the addition of carbon chains to already phosphorylated cellulose noticeably increases the intensity of the C-H elongation bands in this region.

The chemical composition of the surface of phosphorylated fibers was determined by elemental analysis, in which the comparison of the percentages of the different elements present on the surface of fibers, before and after the alkylation reaction of phosphorylated fibers, allows for the degree of substitution  $DS_P$  of phosphorylated fibers and  $DS_A$  of alkylated phosphorylated fibers to be determined. Generally, the reaction occurred at the fiber surface where cellulose hydroxyls are more accessible. In addition, the phosphorus content of the modified fibers decreased with increasing phosphate ester chain length. Even for the same  $DS_P$ , an increase in alkyl chain length contributes to a decrease in phosphorous percentage (Shi *et al.* 2014).

The phosphorus content found on the surface of fibers phosphorylated with PE-C10 was  $9.2 \pm 0.1\%$ , and the degree of substitution  $DS_P$  was  $0.63 \pm 0.01$ . This high phosphorus content is probably attributable to a different arrangement of phosphate groups on the fiber surface. As shown in Table 1, an increase in carbon content was observed after the alkylation reaction, which shows that the alkylation of phosphorylated fibers using acid chloride (C4 to C12) was well achieved. In addition, alkylation levels ranged between 36.5 and 90.5% and they decreased with the increase of the carbon chain length, as explained above.

**Table 2.** Carbon Content, Degree of Substitution for the Alkylation Reaction and Degree of Alkylation

Sample	Carbon Content (%C)	$DS_A$	Degree of Alkylation (%)
OCCP	$56 \pm 5$	N/A	N/A
OCCP-C4	$63 \pm 1$	0.57	90.5
OCCP-C8	$63 \pm 4$	0.31	49.2
OCCP-C10	$63 \pm 1$	0.23	36.5
OCCP-C12	$67 \pm 1$	0.32	50.8

Table 3 gives the average fiber length, water retention value, and total charge, measured before and after the alkylation of phosphorylated fibers. These measurements reflect the effect of the grafted alkyl chains on fiber properties. The alkylation reaction decreased the WRV of phosphorylated fibers from 1.92 to 0.2 g water/g fibers. The presence of alkyl chains on the hydroxyls of the phosphorylated fibers prevents the penetration of water inside the fiber structure due to their high hydrophobicity, thus the water remains on the surface, which explains the low WRV values found.



As expected, the phosphorylation remarkably increased the total charge of the fibers, from 415 to 3673 mmol/kg. The alkylation reduced this charge by approximately 50% (except for OCCP-C8), which confirms that the alkylation reaction takes place on the more acidic hydroxyl of the phosphate group. However, the fiber length reveals that there was a degradation of fibers up to 50% after the alkylation due to the release of HCl by acid chlorides.

**Table 3.** Water Retention Value, Total Charge Contents, and Mean Fiber Length

Sample	WRV ( $\pm 0.01$ g Water/g Fibers)	Total Charge (mmol/kg)	Mean Fiber Length ( $\pm 0.003$ mm)
OCC	1.23	415	1.157
OCCP	1.92	3673	1.069
OCCP-C4	0.20	1869	0.498
OCCP-C8	0.20	2723	0.483
OCCP-C10	0.40	1857	0.478
OCCP-C12	0.31	2007	0.476

## Characterization of Coated Papers

### *Basic properties*

The variation in size, shape, and length of the alkyl chains grafted onto the phosphate groups of phosphorylated fibers can affect the rheological behavior of the coating color as well as base paper barrier properties. The heat treatment after the coating step also positively influences the barrier properties, as it gives a quick drying that prevents the cellulose from swelling, leading to good adhesion and anchoring of the coating.

Based on the average basis weight of the reference paper, the barrier properties of the modified fiber coated papers were calculated, and they are presented in Table 4. The results clearly show that the coating of an alkylated phosphorylated fiber dispersion on the surface of an unmodified base paper resulted in excellent barrier properties. These dispersions filled paper pores and formed a dense layer on the surface of the paper, building an excellent barrier to water and air. Table 4 also shows that the barrier properties (water absorptiveness and air permeability) improved with increasing weight of the alkylated phosphorylated fiber layer. However, an excess of these fibers on the paper surface is undesirable because it leads to a mass transfer from the paper surface to the adhesive tape during the peel test.

**Table 4.** Properties of OCC Sheets Coated with Alkylated Phosphorylated Fibers

Coating Material	Coating Weight (g/m <sup>2</sup> )	Coating Thickness ( $\mu$ m)	Water Absorptiveness (g/m <sup>2</sup> )	Air Permeability - PPS Porosity (mL/min)
OCC (uncoated, as received)	-	-	58 $\pm$ 5	340 $\pm$ 10
OCCP-C4	13 $\pm$ 5	25 $\pm$ 3	8 $\pm$ 1	4 $\pm$ 1
OCCP-C8	12 $\pm$ 1	20 $\pm$ 3	12 $\pm$ 3	2 $\pm$ 1
OCCP-C10	12 $\pm$ 1	10 $\pm$ 3	33 $\pm$ 4	2.6 $\pm$ 0.5
OCCP-C12	6 $\pm$ 1	10 $\pm$ 3	27 $\pm$ 2	51 $\pm$ 4

The measurement of the surface free energy of the dried coated paper is essential to evaluate the release properties of the coated paper. A low surface free energy is required to obtain an easy separation from the adhesive tape, as measured by the peel test. Table 6 shows the surface free energy obtained for OCC sheets as received from the mill (OCC), OCC sheets coated with alkylated phosphorylated fibers (OCCP-C4, OCCP-C8, OCCP-C10, and OCCP-C12), and siliconized commercial paper (silicone) considered in this study as a reference.

The dispersion of alkylated phosphorylated fibers lowers the surface energy and makes the paper surface hydrophobic and anti-adhesive (water contact angles exceeding  $90^\circ$  as shown in Table 5) because of the alkyl chains present on the paper surface. In fact, the coated papers show surface free energy values that range between 24.7 and 29.9 mJ/m<sup>2</sup> with a polar component close to zero. These surface energies are low enough to perform peel tests. In addition, the values found are close to those of commercial siliconized paper.

**Table 5.** Contact Angle of Different Liquid Probes with Sheets

Coating Material	Contact angle (°)		
	Water	$\alpha$ -Bromonaphthalene	Formamide
OCC (uncoated, as received)	86±4	28±8	47±7
OCCP-C4	99±3	50±8	76±1
OCCP-C8	114±3	59±10	86±7
OCCP-C10	106±6	55±11	84±5
OCCP-C12	103±2	55±11	79±4

**Table 6.** Surface Energy of Coated OCC Sheets Measured by the VOGG Method

Coating Material	Surface Energy (mJ/m <sup>2</sup> )					
	Total ( $\gamma$ )	Dispersive ( $\gamma^d$ )	Polar ( $\gamma^p$ )	Acid ( $\gamma^+$ )	Base ( $\gamma^-$ )	R <sup>2</sup>
<b>OCC (uncoated, as received)</b>	40.51	39.26	1.247	2.096	0.1856	0.99
<b>OCCP-C4</b>	29.88	29.73	0.1526	0.0069	0.84	0.99
<b>OCCP-C8</b>	24.74	24.74	n.d.*	0.0833	n.d.	0.86
<b>OCCP-C10</b>	25.83	25.83	n.d.	n.d.	0.3581	0.99
<b>OCCP-C12</b>	27.69	27.54	0.1513	0.0175	0.3267	0.99
<b>Silicone (reference)</b>	23.26	23.26	n.d.	0.4898	n.d.	0.99

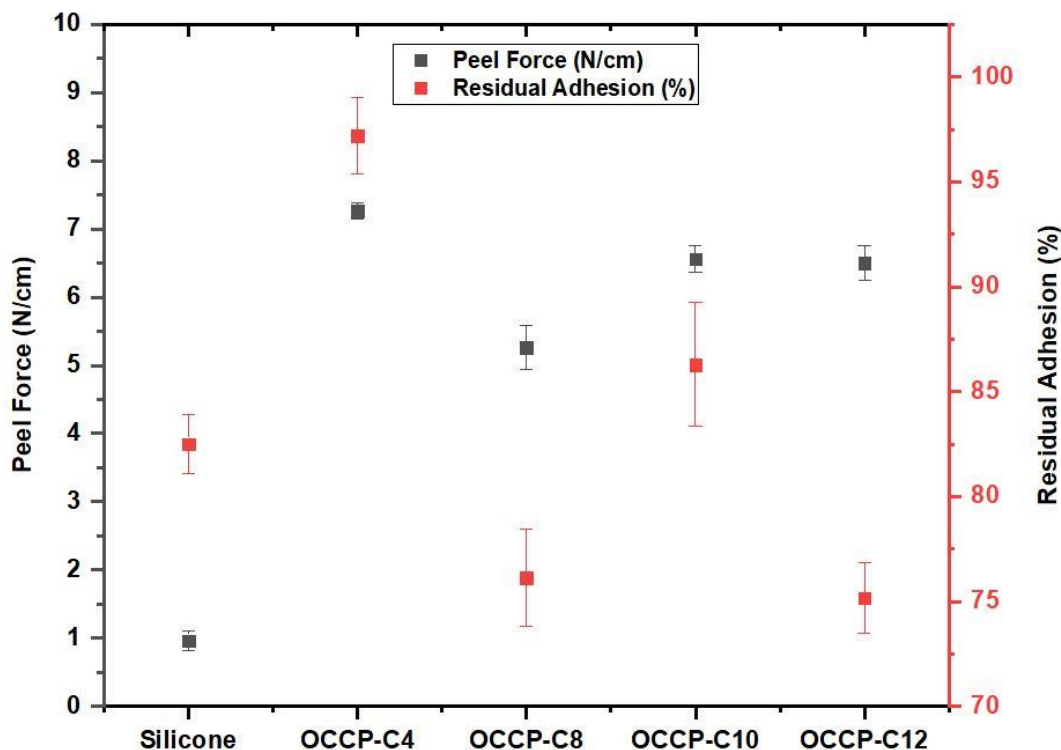
\*n.d. = not detectable

### Release Properties

The simplest methods to evaluate the interactions existing between the coated surface and the PSA adhesive at macroscopic scale are the peel strength test (FINAT FTM 10 (2019)) and the residual adhesion test (FINAT FTM 11 (2019)). In addition, one of the

most essential requirements for release coatings is to have an easy peeling of the adhesive tape without mass transfer. Therefore, a stable anchoring of the coating to the paper surface is important for the adhesive to avoid fiber contamination after the tape has been removed.

The peel force and residual adhesion of papers that had been coated with alkylated phosphorylated fibers were determined. Figure 4 reveals that the peeling forces found in the paper coated with the modified fibers were in the 5.26 to 7.26 N/cm range. These values are much higher compared to those of the reference paper (silicone). This effect could be explained by physicochemical interactions between the adhesive and the coating due to the porosity and roughness of the paper. Contrastingly, the residual adhesion values exceeded 76%, which confirms that there is few mass transfer and the adhesive tape retains its adhesive character.



**Fig. 4.** Peeling force of different papers coated with alkylated phosphorylated fibers

Two strategies were evaluated to improve the hydrophobic properties and homogeneity of the coating. The first option was to apply PVOH before fiber coating. The PVOH is a barrier coating commonly used to close the pores and prevent the penetration of the coating sauce into the base paper. The second option was to use a mixture of modified fibers and phosphate ester (PE-C10) as a coating mixture to reduce the peel force without mass transfer.

The results found with the pre-coated application of the PVOH are shown in Fig. 5. As expected, closing the base paper pores slightly decreases the peel force. Values found were in the 5.11 to 6.76 N/cm range. However, these peel forces were still higher than that of a silicone-based release coating (approximately 1 N/cm according to Fig. 4).

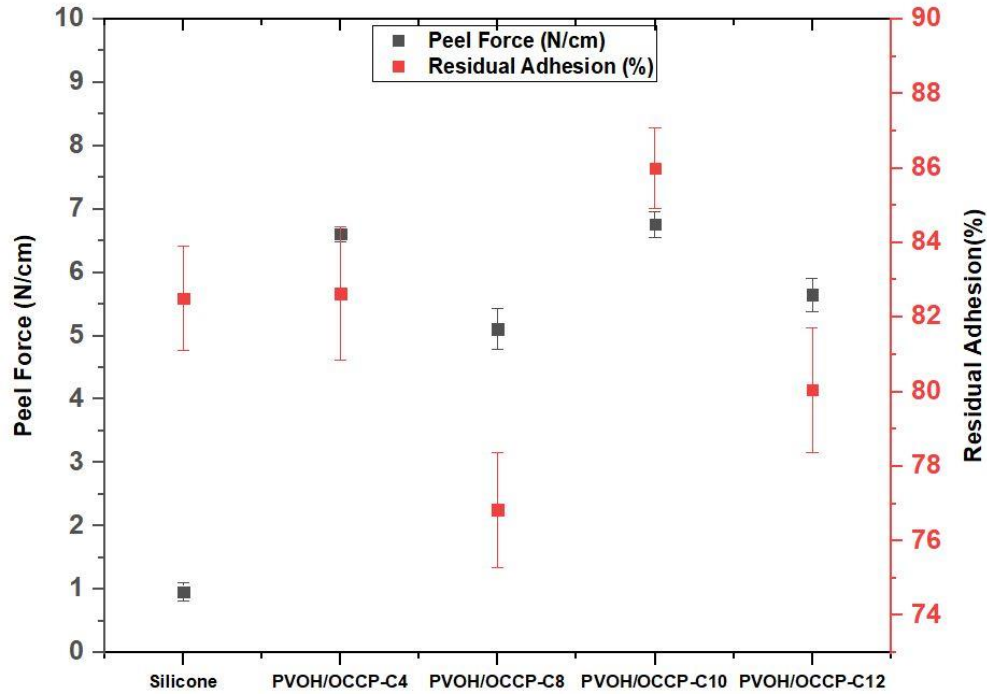


Fig. 5. Effect of a PVOH pre-layer on the peeling force and residual adhesion

Figure 6 shows the peel forces obtained when adding 0.5 g of PE-C10 to the coating solution. In this case, peel forces were markedly reduced from 7.26 N/cm to almost 2 N/cm (2.02 N/cm was achieved when using OCCP-C4), which is close to the silicone reference paper.

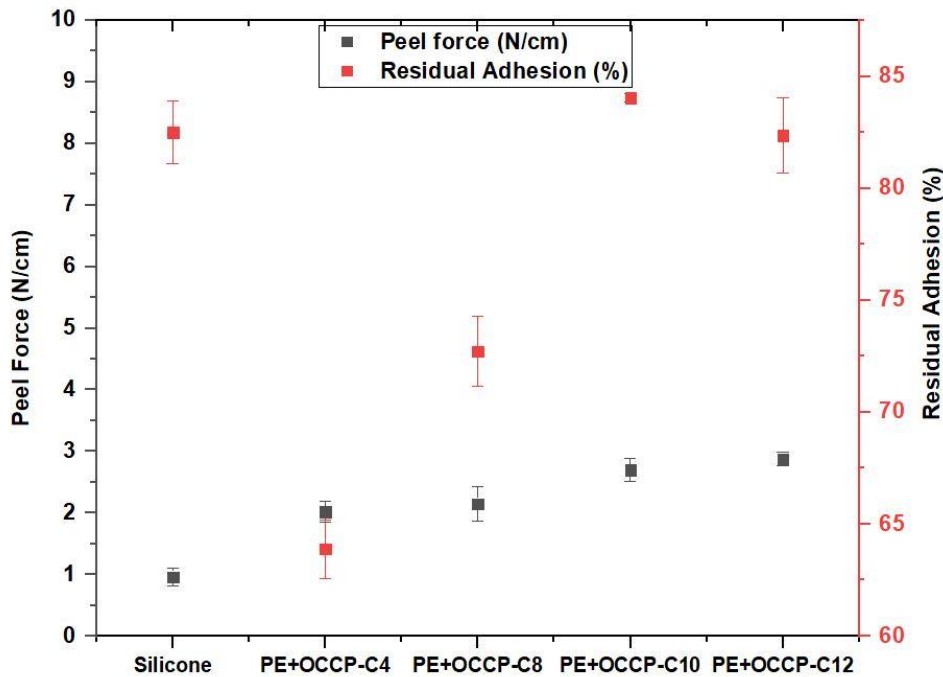


Fig. 6. Effect of phosphate esters (PE-C10) addition on peeling force and residual adhesion

Furthermore, the residual adhesion of coated paper is still in the appropriate range, the tape peel is completed without mass transfer, and the surface remains intact. In contrast, there is an excellent chemical compatibility between phosphorylated fibers and phosphate esters that makes their anchoring to the paper surface almost permanent (less mass transfer). However, it is difficult to predict what kind of interactions, chemical or physical, are established between phosphorylated fibers and phosphate esters. More work needs to be done to resolve this issue.

## CONCLUSIONS

1. Old corrugated container pulp (OCC) sheets coated with alkylated phosphorylated fibers were found to be hydrophobic (water contact angles larger than  $90^\circ$ ), and their surface free energy (23 to  $30 \text{ mJ/m}^2$ ) was much closer to a standard silicone paper than uncoated OCC ( $40 \text{ mJ/m}^2$ ). These coated sheets showed the required characteristics of an antiadhesive release paper.
2. Adding only 0.43% of phosphate ester (PE-C10) to the coating solution reduced the peeling force from 7.26 to 2.02 N/cm for sheets coated with OCCP-C4, but it also reduced residual adhesion to 65%.
3. The hydrolysis of phosphate ester's alkyl chain during the phosphorylation reaction using urea limits the use of this procedure on an industrial scale. The alkylation step would always be required after phosphorylation. In a future work, it is planned to evaluate other approaches, not involving the use of urea, allowing simultaneous phosphorylation and alkylation of fibers without the use of alkylating agents.

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