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Adsorption of a lignosulphonate polymer onto PVC and PET surfaces: Evaluation by XPS

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As part of the separation by froth flotation of PVC and PET from waste bottles before recycling, the adsorption mechanism of a lignosulphonate used to selectively render one of the plastics hydrophilic has been studied. As the 'rest' method is not sufficiently sensitive for this purpose, X-ray Photoelectron Spectroscopy analysis was conducted. A method of calculating the surface coverage of both plastics by the reagent is proposed based on the fact that the lignosulphonate contains sulphur whereas PVC and PET do not. The results show that a greater quantity of lignosulphonate adsorbs on PET than PVC, leading to a higher surface coverage of LS on PET. The surface coverage values are a function of the lignosulphonate macromolecular configuration. For the sphere and film configurations hypothetised, the surface coverage values remain less than 1, which is consistent with the patchy adsorption assumed in the calculations.

1. Introduction

As part of the separation by froth flotation of plastics (PolyVinyl Chloride [PVC]—PolyEthylene Terephthalate [PET]) from beverage bottles before recycling, a lignosulphonate is applied to render the surface of one of the plastics hydrophilic [1]. Although this depressant action of lignosulphonate has been known since the 1970s [2], the mechanism of action is not fully understood. More specifically, although the adsorption of lignosulphonate on plastics was suspected [3], it has not been demonstrated.

As froth-flotation of plastics uses rather coarse particles (1 cm in our case), and the fine grinding ($<100\ \mu$m) of plastics is problematic, the study of adsorption of the reagent is difficult due to the low specific surface area of the particles. An illustration of this is the lack of sensitivity of the 'rest' method, as experienced by Fraunholcz *et al*. [3] who tried to construct isotherms for Acrylonitrile Butadiene Styrene (ABS) treated with lignosulphonate.

In the case of PVC and PET treated with lignosulphonate, the purpose of this investigation was to analyse the surface chemistry of the plastics to detect any modification caused by treatment with lignosulphonate. The problem caused by the similar nature of both the reagent and materials, which are all organic polymers, is overcome by paying particular attention to sulphur; the lignosulphonate contains sulphur, whereas PVC and PET do not.

Of the two spectroscopic techniques used, Fourier Transform Infra-Red (FTIR) spectroscopy (attenuated total reflection mode on plates) did not provide interesting results, probably due to the depth of analysis being too large. On the other hand, interesting results have been obtained with X-ray Photoelectron Spectroscopy (XPS), and are described hereafter.

2. Materials and methods

Experiments were conducted on the thermoplastics PolyVinyl Chloride (PVC) and PolyEthylene Terephthalate (PET), the bulk chemical compositions of which are given in Fig. 1.

The reagent used to modify the surface wettability of the plastics belongs to the lignosulphonate family. More specifically, it is classified (by the producer)

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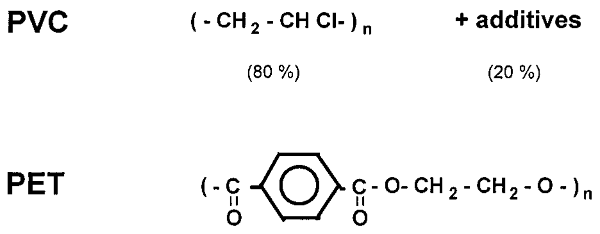

Figure 1 Bulk chemical composition of PVC and PET.

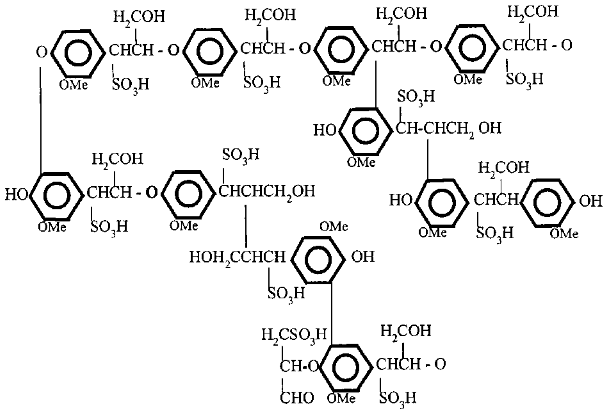

Figure 2 Theoretical composition of lignosulphonate family [5].

as a sodium and ammonium lignosulphonate (LS). In the literature, lignosulphonates are described as macromolecules composed of bridged hydrophobic hydrocarbons having hydrophilic sulphonated groups on their surface [4]. A theoretical composition of LS, presented in Fig. 2 [5], shows the complexity of this reagent. Dissociation of -OH groups is believed to occur in solution [6].

The understanding of the mechanism of lignosulphonate adsorption forms part of a study on plastics behaviour during froth-flotation with a view to industrial separation. Tap water (TW) was used in these experiments as it is used in the industrial separation process. The pH of TW was equivalent to 7.5. Its ionic content, analysed by a combination of ICP/MS, ionic chromatography, and free carbon analytical techniques, is shown in Table I. Demineralised (DW) and bidistilled (bDW) water were also used in these experiments.

Plastic plates (10 × 3 mm) were cut directly from new water and soda bottles, washed with distilled water and dried, and then treated in 100 ml of 0.02 to 1 g/l lignosulphonate solution for 10 minutes with strong magnetic stiring (1000 rpm). The plates were then left in the LS solution for a further 5 minutes without any stiring. Finally, the plates were left to air-dry on absorbent paper before being analysed.

An AEI ES 200B photoelectron spectrometer equipped with an Mg anode was used for the chemical surface analysis. Large scans of C_{1s}, O_{1s}, N_{1s}, S_{2p}, Ca_{2p} and Na_{2s} photoelectron peaks were performed. Binding energies (E_b) were referenced to adventitious and aliphatic carbon with $E_b(C_{1s}) = 284.6$ eV. Peak intensities were corrected with photoelectron cross-section and kinetic energy-dependent parameters. All quantitative measurements were expressed as atomic ratios equivalent to element to carbon peak intensity ratios. These ratios allowed us to obtain the relative abundance of the various elements present. Carbon was used as the reference because of its predominance in both lignosulphonate and in the plastics. In this respect, adventitious carbon was assumed to be present in negligible amounts in comparison to the amount of carbon contained in the substrates.

TABLE I Ionic content of tap water

	Cations				Anions			
Content	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	HCO_3^-	Cl^-	SO_4^{2-}	NO_3^-
mg/l	40	6	20	4	126	21	41	3
meq	2	0.5	0.87	0.10	2.07	0.59	0.85	0.05

3. Results and discussion

3.1. Individual materials and reagent characterisation

In order to further interpret the XPS results obtained for the plastics treated with the LS, each substrate was characterised individually.

3.1.1. Analysis of lignosulphonate

Because lignosulphonates have no established structure and therefore no strict formula [7], we characterised the powdered LS used in these experiments. Three samples were analysed. The calculations of element to carbon peak intensity ratios indicated that the lignosulphonate used throughout this study contained a large amount of oxygen, as is expected from the theoretical macromolecular formula presented in Fig. 2 : $O/C = 0.57 +/- 0.03$. The ratios for sulphur, nitrogen and sodium were very low in comparison to oxygen : $S/C = 0.074 +/- 0.02$, $N/C = 0.049 +/- 0.004$, $Na/C = 0.066 +/- 0.025$. Some calcium was also detected : $Ca/C = 0.010 +/- 0.001$. Although low, these ratios were well above the detection limit, which was equivalent to 0.001 for S/C and Ca/C. From these ratios, we calculated a unit chemical formula (H was estimated from theoretical formula) for the lignosulphonate used in our experiments: $C_1\ O_{0.57}\ S_{0.074}\ N_{0.049}\ Na_{0.066}\ Ca_{0.010}\ [H_{0.7}]$.

3.1.2. Analysis of PVC and PET

The analysis of PVC and PET surfaces demonstrated that neither sulphur nor sodium was detectable on these plastics. In addition, both plastics had lower O/C ratios than the lignosulphonate.

Lignosulphonate adsorption was therefore expected to render S detectable on the plastics' surfaces. It was also expected to render Na detectable, and to increase the O/C ratios of the plastics.

It is interesting to note that calcium was not detected on PET, and was detected only once on PVC. The presence of calcium in this one instance may reflect the migration of a bulk additive, such as calcium stearate.

3.2. Evidence of lignosulphonate adsorption on PVC and PET

The XPS analysis of PVC and PET treated in a solution of lignosulphonate dissolved in tap water (1 g/l) is presented in Table II. These results are compared to the analysis of the untreated PVC and PET samples. The results of analysis of samples treated in tap water are also presented, to determine the effect of tap water. The results presented in Table II correspond to mean values and standard deviations calculated on series of 4 to 8 samples.

These results demonstrate that exposure of the plastic samples to tap water alone does not lead to sulphur deposition on the surface of either plastic. However, some calcium is deposited on both PVC and PET surfaces upon exposure of the samples to tap water. The Ca/C ratios reached 0.002 for both PVC and PET, and showed little standard deviation. These ratios indicate that a similar amount of calcium was adsorbed on the surfaces of both plastics. Further, this result is in agreement with the fact that PVC and PET have the same magnitude of negative charge in water (see [9] for more details). It is interesting to note the slight decrease of the O/C ratio of both plastics, and the decrease of PVC Cl/C ratio, upon exposure to tap water. The PET O/C ratio decreased from an initial value of 0.39 + /− 0.02 before exposure to tap water to a value of 0.33 + /− 0.02 when treated in tap water. A similar percentage decrease was seen for PVC, in which the O/C ratio decreased from 0.13 + /− 0.02 to 0.11 + /− 0.00. These variations reflect slight modification (partial dissolution) of the platics' surfaces.

Following treatment with lignosulphonate solution, sulphur appears on the treated plastics' surfaces, as demonstrated by the S/C ratio increasing from below the limit of detection for untreated surfaces to a value of 0.004 and 0.006 for PVC and PET, respectively, after treatment. As the absorption peak widths were equivalent for PVC and PET, we conclude that while lignosulphonate was adsorbed onto both plastics, a higher quantity of lignosulphonate was adsorbed on PET. This is in good agreement with flotation experiments and wettability measurements, both of which showed a higher depression/hydrophilization of PET compared to PVC after LS treatment [8].

It is also interesting to note that no Na was detected on the plastics after treatment with LS solution. This suggests that Na was dissociated from the lignosulphonate when it was dissolved in water.

The O/C ratio for both PVC and PET was observed to increase between immersion in tap water and treatment in a lignosulphonate solution: from 0.11 + /− 0.01 to 0.17 + /− 0.01 for PVC and from 0.33 + /− 0.02 to 0.35 + /− 0.02 for PET respectively. This evolution was consistent with an adsorption of lignosulphonate, which has a higher oxygen content than the plastics.

There was also a slight decrease in the Cl/C content of PVC from 0.11 after immersion in tap water to 0.09 after immersion in LS solution. This slight decrease could be due to the masking of chloride by the lignosulphonate.

Finally, we noted the appearance of a significant amount of calcium on the surfaces of both PET and PVC after immersion in lignosulphonate solution, as evidenced by a Ca/C ratio of 0.006–0.007, much higher than the Ca/C ratio of 0.002 for the substrates when immersed in tap water alone. As lignosulphonate itself has a very low Ca content, the data indicates that there was co-adsorption of calcium. This suggests that calcium plays a role in the mechanism of adsorption of the lignosulphonate.

This is consistent with the results obtained from flotation and wettability experiments [8, 9], which show that bivalent cations (such as Ca^{++} and Mg^{++}) play a significant role in the depressant/hydrophylisating action of LS, whereas monovalent cations (e.g.: Na^{+} and K^{+}) and anions do not.

Based on these results, we then focused on the S/C and Ca/C ratios to understand the role of calcium in the mechanism of adsorption of lignosulphonate.

3.3. Role of calcium ions in the mechanism of adsorption of lignosulphonate

In order to study the role of calcium ions in the mechanism of adsorption of the lignosulphonate, the influence of several parameters was studied using a combination of experimental methods, *viz*: floatability tests, wettability and electrokinetic measurements and surface chemical analysis. We report only the surface chemistry results (XPS) here. Details of the other experiments can be found in [8] and [9].

TABLE II Comparison between XPS analysis of plastics without immersion, after immersion into tap water, and after immersion into a solution containing 1 g/l of lignosulphonate prepared with tap water: Mean values (4 to 8 samples analysed) and standard deviation

Plastic	Treatment	S/C	O/C	Cl/C	Ca/C	Na/C
PVC	None	<0.001	0.13 (+/−0.02)	0.14 (+/−0.03)	<0.001-0.003	<0.001
	TW alone	<0.001	0.11 (+/−0.005)	0.11 (+/−0.01)	0.002 (+/−0.0005)	nd
	LS (1 g/l) in TW	0.004 (+/−0.001)	0.17 (+/−0.01)	0.09 (+/−0.01)	0.007 (+/−002)	<0.001
PET	None	<0.001	0.39 (+/−0.02)	nd	<0.001	<0.001
	TW alone	<0.001	0.33 (+/−0.02)	nd	0.002 (+/−0.001)	nd
	LS (1 g/l) in TW	0.006 (+/−0.002)	0.35 (+/−0.02)	nd	0.006 (+/−0.002)	<0.001

TW: tap water, LS: Lignosulphonate, nd: not determined.

3.3.1. Influence of water ionic content

In order to verify that Ca plays a role in the adsorption of lignosulphonate, we studied the influence of the calcium content of the water used to prepare the treatment solution, on the amount of lignosulphonate adsorbed. For this, we used water samples with different ionic content: tap water (TW), demineralized water (DW) and bi-distilled water (bDW). In tap water, calcium is the main bivalent cation (40 mg/l). The calcium content of DW is several orders of magnitude lower than in TW; whereas bDW contains no calcium. The XPS results are presented in Table III.

For both plastics, the lower the ionic content of the water, the lower the S/C ratio. The ratio decreased from 0.004 to 0.002 for PVC and from 0.006 to 0.004 for PET when the treatment solution was prepared with DW rather than TW. When bDW was used, the S/C ratio decreased to 0.002 for PET, and S was no longer detectable on PVC.

The results indicate that the less calcium present in solution, the less reagent was adsorbed on both plastics. On the basis of electrokinetic results showing an increase of the plastics' surface charges due to the presence of calcium in solution [8, 9], and taking into account additional flotation tests indicating the reversibility of the adsorption, we conclude that calcium interferes in electrostatic interactions. That is, Ca^{++} acts as a bridging agent between the plastic surface and the lignosulphonate molecule, both of which are negatively charged at the pH of the experiments (neutral).

3.3.2. Influence of lignosulphonate concentration

From Table IV, it appears that the Ca/S ((Ca/C)/(S/C)) ratios were different for PVC and PET treated in a 1 g/l lignosulphonate solution prepared with tap water. Complementary analysis was therefore performed, examining the influence of a lower lignosulphonate concentration of 0.02 g/l on these Ca/S ratios. The results are presented in Table IV. The 0.02 g/l solution corresponded to the optimized concentration of reagent for efficient separation of the platics by flotation.

For both LS concentrations (Table IV), PVC showed a larger amount of Ca linked to LS adsorption than was seen on PET. The Ca/S ratios were equivalent to 1.75 and 3 for PVC and 1 for PET.

Because more LS adsorbs on PET than PVC although both plastics have a similar negative charge [9], the lower Ca/S ratio of PET indicated the presence of another type of interaction. We therefore assume that LS adsorption on PET is partly governed by

TABLE III Influence of the ionic content of water on the quantity of sulphur detected on PVC and PET surfaces treated with lignosulphonate (1 g/l): Mean values (4 to 8 samples analysed) and standard deviation

Plastic	Treatment	O/C	S/C	Ca/C	Cl/C
PVC	None	0.13 (+/−0.02)	<0.001	<0.001-0.003	0.14 (+/−0.03)
	LS (l g/l) in DW	0.16 (+/−0.02)	0.002 (+/−0.001)	nd	nd
	LS (1 g/l) in TW	0.17 (+/−0.01)	0.004 (+/−0.001)	0.007 (+/−0.002)	0.09 (+/−0.01)
PET	None	0.39 (+/−0.02)	<0.001	<0.001	
	LS (1 g/l) in bDW	0.31 (+/−0.02)	0.002 (+/−0.001)	<0.001	
	LS (1 g/l) in DW	0.31 (+/−0.01)	0.004 (+/−0.002)	nd	
	LS (1 g/l) in TW	0.35 (+/−0.02)	0.006 (+/−0.002)	0.006 (+/−0.002)	

DW: demineralized water, TW: tap water, bDW: bi-distilled water, LS: Lignosulphonate, nd: not determined.

TABLE IV Influence of lignosulphonate concentration on the adsorbed quantities of sulphur and calcium on the surfaces of treated PVC and PET: Mean values (4 to 8 samples analysed) and standard deviation

Plastic	Treatment	O/C	S/C	Ca/C	Cl/C	Ca/S
PVC	TW alone	0.11 (+/−0.00)	< 0.001	0.002 (+/−0.000)	0.11 (+/−0.01)	—
	LS (1 g/l) in TW	0.17 (+/−0.01)	0.004 (+/−0.001)	0.007 (+/−0.002)	0.09 (+/−0.01)	1.75
	LS (0.02 g/l) in TW	0.16 (+/−0.01)	0.002 (+/−0.000)	0.006 (+/−0.001)	0.11 (+/−0.04)	3
PET	TW alone	0.33 (+/−0.02)	< 0.001	0.002 (+/−0.001)	nd	—
	LS (1 g/l) in TW	0.35 (+/−0.02)	0.006 (+/−0.002)	0.006 (+/−0.002)	nd	1
	LS (0.02 g/l) in TW	0.36 (+/−0.04)	0.003 (+/−0.001)	0.003 (+/−0.001)	nd	1

TW: tap water, LS: Lignosulphonate, nd: not determined.

non-electrostatic interactions in which Ca plays no role. This assumption is supported by flotation tests [9] that, as previously noted, demonstrated the reversibility of LS adsorption on plastics. Nevertheless, while LS adsorption appeared completely reversible for PVC, it was not completely reversible for PET (85% reversibility). The partial irreversibility of LS adsorption on PET indicates that interactions stronger than purely electrostatic ones influence LS adsorption onto PET. It has been demonstrated [10] that PET is more polar than PVC and can therefore develop more acid-base interactions than PVC. We therefore suggest that acid-base interactions are responsible for the stronger LS adsorption on PET. The surface sites involved in such interactions on the plastic substrates would be carbonyl groups and aromatic carbon cycles, which are of a basic nature and are present in larger quantities on the surface of PET than on the surface of PVC. Carboxyl and phenol moieties, which are of an acidic nature at neutral pH, would be involved in the LS.

It is reasonable for the Ca/S ratio for PVC to be more than 1, as Ca^{++} can enter the LS structure between negatively charged groups (such as SO_3^- [6]). Indeed, Ca^{++} may play a cohesive function within the LS macromolecule.

The difference in the nature of the interactions between LS and the two plastics probably leads to a different spreading of the macromolecule on the plastics' surfaces. We expect a larger spreading of LS molecules on PET than on PVC due to the stronger acid-base interactions present in the PET-LS case. We will now discuss the calculation of the surface coverage of LS on PVC and PET for different macromolecular configurations.

3.4. Estimation of surface coverage of LS on PVC and PET

Based on the experimental results, the surface coverage of LS on plastics can be estimated using peak intensity ratios.

3.4.1. Algebraic expression of surface coverage θ

3.4.1.1. Peak intensity definition. In the field of XPS, the elementary photoelectron peak intensity dI for electrons from a layer of thickness dz at depth z in the sample is defined as [11]:

$$dI = aF\sigma K C(z) e^{-z/\lambda}\, dz \tag{1}$$

where, a: roughness factor of the surface, F: X-ray flux, σ: photoionization cross-section, K: transmission factor of the analyser, $C(z)$: atomic concentration at depth z per nm^3, λ: inelastic mean free path of photoelectrons in the sample in nm.

The material is assumed to be homogeneous along the x and y directions, K and λ are dependent on the kinetic energy of the photoelectron, and parameters a and F are unknown.

3.4.1.2. Calculation of S/C ratio on plastics surfaces. It is possible to obtain an algebraic expression of the S/C ratio determined experimentally on plastics surface, by first integrating Equation 1 for S and C, so as to express the peak intensities on the plastics' surfaces (Is and Ic); followed by dividing the equation Is by Ic.

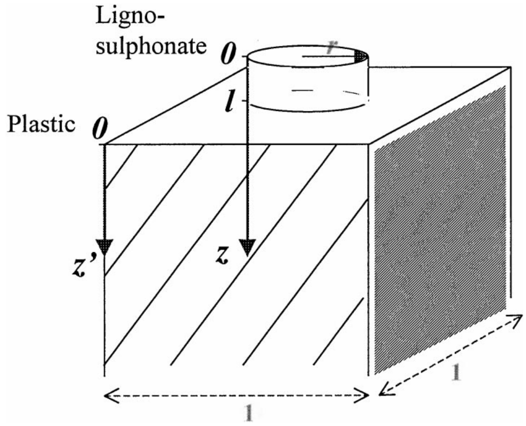

Figure 3 Assumptions on LS surface coverage calculations: patchy adsorption, lignosulphonate equivalent thickness ℓ, plastics unit surface.

To calculate the S and C peak intensities, we assumed that the lignosulphonate coverage on plastics was partial (patchy), and called θ the part of plastics covered by lignosulphonate (the surface coverage) and ℓ the equivalent thickness of the LS adsorbed on the plastic's surface (Fig. 3).

Sulphur electrons are derived from the lignosulphonate alone. The S_{2p} peak intensity can thus be written as (assuming $C(z) = \text{cte}$):

$$I_S \approx \theta \int_0^{\ell} aF\sigma_S K_S C_S^{LS} e^{-z/\lambda_S^{LS}}\, dz \tag{2}$$

And after integration:

$$I_S \approx \theta aF\sigma_S K_S C_S^{LS} \lambda_S^{LS} \left(1 - e^{-\ell/\lambda_S^{LS}}\right) \tag{3}$$

where, σ_S: photoionization cross-section of S_{2p} photoelectron, K_S: transmission factor for S_{2p}, C_S^{LS}: sulphur concentration in LS, λ_S^{LS}: inelastic mean free path of S_{2p} photoelectron in LS.

Unlike the case of sulphur, the carbon detected on the plastics' surfaces originates both from the plastic as well as from the adsorbed LS (see Fig. 3). Carbon electrons are derived from : (i) the lignosulphonate (weighted by θ), (ii) the plastic beneath the lignosulphonate (weighted by θ), and (iii) the plastic not covered by any lignosulphonate (weighted by $1 - \theta$). Thus, the carbon peak intensity is the sum of these three components, which can be written as:

$$\begin{aligned} I_C \approx{}& \theta \int_0^{\ell} aF\sigma_C K_C C_C^{LS} e^{-z/\lambda_C^{LS}}\, dz \\ &+ \theta \int_{\ell}^{\infty} aF\sigma_C K_C C_C^{PET} e^{-z/\lambda_C^{PET}}\, dz \\ &+ (1-\theta) \int_0^{\infty} aF\sigma_C K_C C_C^{PET} e^{-z'/\lambda_C^{PET}}\, dz' \end{aligned} \tag{4}$$

And after integration:

$$\begin{aligned} I_C \approx{}& aF\sigma_C K_C \big\{\theta C_C^{LS} \lambda_C^{LS} \left(1 - e^{-\ell/\lambda_C^{LS}}\right) \\ &+ \theta C_C^{PET} \lambda_C^{PET} e^{-\ell/\lambda_C^{PET}} + (1-\theta) C_C^{PET} \lambda_C^{PET} \end{aligned} \tag{5}$$

where, σ_C: photoionization cross section of C_{1s} photoelectron, K_C: transmission factor for C_{1s} photoelectron, C_C^{LS}: carbon concentration in LS, C_C^{PET}: carbon concentration in PET, λ_C^{LS}: inelastic mean free path of C_{1s} photoelectron in LS, λ_C^{PET}: inelastic mean free path of C_{1s} photoelectron in PET.

From Equations 3 and 5, we can write the sulphur to carbon peak intensity ratio, S/C, called R, as:

$$R = \frac{I_S}{I_C} = \frac{K_S \sigma_S \lambda_S^{LS} C_S^{LS}}{K_C \sigma_C \lambda_C^{LS} C_C^{LS}} \times \frac{\theta\left(1 - e^{-\ell/\lambda_S^{LS}}\right)}{\theta(1 - e^{-\ell/\lambda_C^{LS}}) + \theta \frac{C_C^{PET}\lambda_C^{PET}}{C_C^{LS}\lambda_C^{LS}} e^{-\ell/\lambda_C^{PET}} + (1-\theta)\frac{C_C^{PET}\lambda_C^{PET}}{C_C^{LS}\lambda_C^{LS}}} \tag{6}$$

As the kinetic energies of the C_{1s} (965 eV) and S_{2p} (1082 eV) peaks are similar, we assume that: $\lambda_S^{LS} \cong \lambda_C^{LS} \cong \lambda_C^{PET}$

To simplify Equation 6, we write:

$$A = e^{-\ell/\lambda_S^{LS}} = e^{-\ell/\lambda_C^{LS}} = e^{-\ell/\lambda_C^{PET}}$$

$$B = \frac{\lambda_C^{PET}}{\lambda_C^{LS}} \frac{C_C^{PET}}{C_C^{LS}}$$

$$D = \frac{R_{LS}}{R}$$

With these simplifications Equation 6 becomes:

$$\frac{1}{D} = \frac{(1-A)\theta}{(1-A)\theta + BA\theta + B(1-\theta)} \tag{7}$$

where R_{LS} refers to the S/C ratio of lignosulphonate. Indeed, lignosulphonate spread as powder onto adhesive conducting tape is assumed as a homogeneous sample ($C(z) = \text{cte}$) with $z \gg \lambda$. For sulphur, the intensity of the photoelectron peak is:

$$I_S \approx aF\sigma_S K_S C_S^{LS} \lambda_S^{LS} \tag{8}$$

And for carbon:

$$I_C \approx aF\sigma_C K_C C_C^{LS} \lambda_C^{LS} \tag{9}$$

The sulphur to carbon peak intensity ratio in LS (called R_{LS}) can be expressed using Equations 8 and 9:

$$R_{LS} = \frac{I_S}{I_C} = \frac{\sigma_S K_S \lambda_S^{LS}}{\sigma_C K_C \lambda_C^{LS}} \frac{C_S^{LS}}{C_C^{LS}} \tag{10}$$

3.4.1.3. Algebraic expression of θ. From Equation 7 we deduce an expression of θ

$$\theta = \frac{B}{(B - 1 + D)(1 - A)} \tag{11}$$

3.4.2. Numerical calculation of θ

In order to calculate θ from experimental values of R_{LS} and R, it is first necessary to determine the parameters included in terms A, B and D, that is to say: ℓ, λ_S^{LS}, λ_C^{LS}, λ_C^{PET}, λ_C^{PVC}, C_C^{LS}, C_C^{PET}, and C_C^{PVC}.

3.4.2.1. Estimation of the equivalent thickness of lignosulphonate: ℓ. After Le Bell [12], the lignosulphonate molecule resembles a sphere of diameter 3 nm, average molar mass of 10,000 g, and contains about twenty SO_3 groups.

The equivalent thickness of such a molecule, which is assumed to be the height of a cylinder of similar diameter and same volume, is given by the following relationship:

$$\ell \pi r^2 = \frac{4}{3}\pi r^3 \Leftrightarrow \ell = \frac{4}{3} r \tag{12}$$

Leading to $\ell = 2$ nm

Lignosulphonate, however, may change its shape from a sphere to a film of less thickness during adsorption. In the calculations presented hereafter, we consider two other possible thicknesses for the lignosulphonate layer, *viz*: 1 nm and 0.5 nm.

3.4.2.2. Estimation of the inelastic mean free path of electrons in the polymers: λ_S^{LS}, λ_C^{LS}, λ_C^{PET}, λ_C^{PVC}. The estimation of the inelastic mean free path is based on the work of Ashley [13]. The author proposes, for the organic material poly(butene-1-sulphone), the following equation:

$$\lambda = \frac{0.0159E}{\ln(E) - 1.88 - 116/E} \tag{13}$$

where λ represents the inelastic mean free path of the electron (in nm) and E the kinetic energy of the electron (in eV).

Because the densities of the polymers differ slightly (1.35 for plastics and 1.2 for LS [7]), we calculated λ using the same parameters for C_{1s} ($E = 965$ eV) and S_{2p} ($E = 1082$ eV). We find:

$$\lambda_C^{LS} = \lambda_C^{PET} = \lambda_C^{PVC} = 3.2 \text{ nm}; \quad \lambda_S^{LS} = 3.4 \text{ nm}$$

The mean free paths of electrons from sulphur and carbon in the lignosulphonate and from carbon in the plastics are very similar due to the slight difference in kinetic energy.

3.4.2.3. Atomic concentration of carbon in the plastics and in the lignosulphonate: C_C^{LS}, C_C^{PET}, C_C^{PVC} $\mathbf{C_C^{PET}}$. The PET monomer has a formula of $C_{10}O_4H_8$ and a density of 1.35 g/cm^3. Its molecular mass is thus:

$$\text{M} = 120 + 64 + 8 = 192 \text{ g}.$$

Accordingly, there is one mole of C for each 14.22 cm^3 of PET. Thus, the atomic concentration of carbon in

PET is:

$$C_{\mathrm{C}}^{\mathrm{PET}} = 42.3\,\text{atoms of C/nm}^3\text{of PET}$$

$\boldsymbol{C_{\mathrm{C}}^{\mathrm{PVC}}}$. The PVC monomer has a formula of $C_2Cl_1H_3$ and a density of 1.35 g/cm^3. Its molecular mass is thus:

$$\mathrm{M} = 24 + 35.4 + 3 = 62.4\,\mathrm{g}.$$

Accordingly, there is one mole of C for each 23.1 cm^3 of PVC. Thus, the atomic concentration of carbon in PVC is:

$$C_{\mathrm{C}}^{\mathrm{PVC}} = 26.1\,\text{atoms of C/nm}^3\text{of monomer of PVC}$$

The actual resin used for PVC bottles contains 80% of monomer and 20% additives. As FTIR spectra indicated that the additives present in the subsurface of PVC contain similar functionalities to PET [9], we consider that the carbon atomic concentration of the additives is equivalent to that of PET, i.e. 42 atoms/nm^3.

Taking into account the presence of organic additives in the PVC subsurface, we obtain the following corrected value for the atomic concentration of carbon in PVC: $0.8 * 26.1 + 0.2 * 42 = 29.3$

$$C_{\mathrm{C}}^{\mathrm{PVC}} = 29.3\,\text{atoms of C/nm}^3\text{of PVC}$$

$\boldsymbol{C_{\mathrm{C}}^{\mathrm{LS}}}$. As established in 3.1, the unit formula of the lignosulphonate used is:

$$C_1O_{0.57}S_{0.074}N_{0.049}Na_{0.066}Ca_{0.010}[H_{0.7}].$$

From this, we deduce the molar mass of the lignosulphonate corresponding to one mole of C:

$$\mathrm{M} = 19.09\,\mathrm{g}$$

Based on the data of Nedosvitii *et al.* [7], the lignosulphonate density is assessed as 1.2 g/cm^3, from which we deduce (as before) the density of C in lignosulphonate:

$$C_{\mathrm{C}}^{\mathrm{LS}} = 37.8\,\text{atoms of C/nm}^3\text{of lignosulphonate}$$

3.4.2.4. S/C ratios for lignosulphonate and on plastics surfaces: R_{LS} and R. The ratio R_{LS} has an average value of 0.074 for the lignosulphonate used in these experiments.

The ratio R varies depending on the conditions of treatment of the plastics. Values as per Table IV are used in the calculations. These values correspond to treatment of the substrates with two different lignosulphonate concentrations: 1 g/l and 0.02 g/l.

3.4.2.5. Calculation of surface coverage. The results of the calculations integrating the values of the various parameters in Equation 11 are presented in Table V.

Whatever the configuration assumed for the lignosulphonate (sphere or film), the calculations give surface coverages less than 1, thus indicating that the assumption of 'patchy' adsorption was reasonable. In order to determine whether adsorption was continuous or discontinuous, it would be necessary to determine the whole adsorption isotherm, which was not possible for the reasons mentioned in the introduction.

TABLE V Calculated surface coverage for PET and PVC using two lignosulphonate concentrations during immersion and three possible configurations of the adsorbed macromolecule

Configuration of LS	Plastic	[LS] (g/l)	S/C (measured, see Table IV)	θ (calculated from Eq. 11)
Sphere	PET	1	0.006	0.19
		0.02	0.003	0.10
	PVC	1	0.004	0.09
		0.02	0.002	0.05
Film 1 nm	PET	1	0.006	0.33
		0.02	0.003	0.17
	PVC	1	0.004	0.16
		0.02	0.002	0.08
Film 0.5 nm	PET	1	0.006	0.62
		0.02	0.003	0.31
	PVC	1	0.004	0.29
		0.02	0.002	0.15

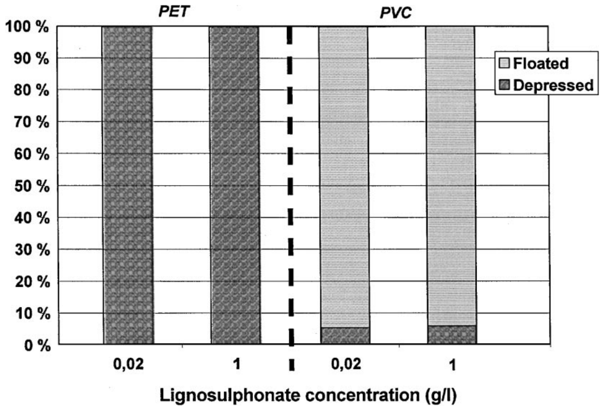

Figure 4 Comparison of flotation behaviour of PVC and PET at two concentrations of lignosulphonate.

For a given concentration of lignosulphonate with a given macromolecular configuration, the surface coverage of LS on PET was always higher than that on PVC. However, when the different reagent concentrations are considered for a given macromolecular configuration, the surface coverage on PVC could be equivalent to the surface coverage on PET. This result is not in good agreement with the flotation results, which, for the two concentrations tested, demonstrated that PET flotation was depressed whereas PVC flotation was not depressed (Fig. 4). From this, we assume that the difference in behaviour between PVC and PET during flotation is not only due to a greater adsorption of lignosulphonate on PET, but probably also due to different configurations of the macromolecule on the surfaces. According to the surface coverage calculation, the adsorbed LS molecules should spread more on PET than on PVC. This is in good agreement with the assumptions made in 2b, *viz*: a greater spreading of the LS molecule adsorbed on PET due to the greater force of acid-base interactions that occur in addition to electrostatic interactions between LS and PET.

4. Conclusions

As part of the modification of the wettability of PVC and PET particles from plastic beverage bottles for separation by froth flotation before recycling, XPS was used to study the adsorption phenomena of a lignosulphonate used to selectively render one of the plastics hydrophilic. XPS is shown to be a suitable technique for studying adsorption phenomena on particles with low specific surface areas. The nature of the reagent used and the plastics to be separated are very similar, i.e. organic macromolecules, with the main difference being the sulphur content of the reagent. A method of calculating the surface coverage of lignosulphonate on PVC and PET surfaces is proposed based on this difference in sulphur content.

The results demonstrate that while lignosulphonate adsorbs on both PVC and PET, it more adsorbs onto PET. Because LS adsorption is linked to the co-adsorption of Ca, and both plastics surfaces and lignosulphonate are negatively charged at the pH of the experiments ($\mathrm{pH} = 7.5$), we conclude that the adsorption of lignosulphonate is mainly due to electrostatic interactions, in which Ca^{++} plays the role of a bridging ion.

As more LS is adsorbed on PET, despite that there is less bridging Ca^{++} adsorption and that both PET and PVC have similar negative surface charges, indicates the presence of additional, non-electrostatic, interactions influencing LS adsorption on PET. Given the partial irreversibility of LS adsorption on PET and that PET has a larger capacity to develop acid-base interaction than PVC, we conclude that the adsorption of LS is also partly linked to acid-base interactions. These stronger interactions would lead to a larger degree of spreading of the LS molecule on the PET surface.

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