



### KeyWords

XPS, Superabsorbent Polymers, Water, Solid-liquid and Solid-gas Interfaces, Environmental Charge Compensation

## Investigation of a Superabsorbent Polymer (SAP) with EnviroESCA

This application note describes how EnviroESCA can be used to analyze the surface of superabsorbent polymers under different environmental conditions. EnviroESCA's ability to perform X-ray Photoelectron Spectroscopy (XPS) under ambient conditions shows its main advantage when being applied to insulating material that change their surface (chemistry) when they come in contact with different liquids and gases - in this case water. Specimens that tend to charge up under vacuum conditions can be measured with ease.

### Motivation

Superabsorbent polymers (SAP) are slightly crosslinked hydrophilic polymers with three-dimensional structures that are able to absorb and retain huge quantities of water or other biological fluids [1].

Nowadays SAPs are made from lightly cross-linked and partially neutralized, poly(acrylic acid) **PAA** based on the outstanding performance versus cost ratio of that polymer. Typically SAPs appear as sugar-like white granular solids.

Water exposure of SAPs results in an immediate water uptake through hydrogen bonding caused by osmosis (concentration of water inside and outside of the polymers differs significantly). This water absorption continues until identical concentrations of water are reached in the polymers inside and on the outside. As a result a rubbery polymeric hydrogel is formed which is many times larger in size than the original powder in some cases with up to 99 weight percent of water.

SAPS are mainly used in disposable diapers (74% of SAP global market in 2014) but other applications include personal disposable hygiene products, medical treatment, sanitation, water treatment, horticulture, agriculture, and forestry.



Fig. 1. Superabsorbent polymer (SAP) taken from a disposable baby diaper. The upper photo shows the polymer in dry condition and the lower photo after adding water.

## Method

EnviroESCA utilizes X-ray Photoelectron Spectroscopy (XPS) as its main analytical technique. Hereby an electron beam is generated inside the X-ray source and focused onto an X-ray anode made of aluminum. The deceleration of the electrons on the anode leads to the production of X-rays. This X-ray beam is monochromated and focused onto the sample. X-ray photons impinging the sample excite electrons in the material which are subsequently emitted with specific kinetic energy determined by their binding energy and the photon energy of the X-rays.

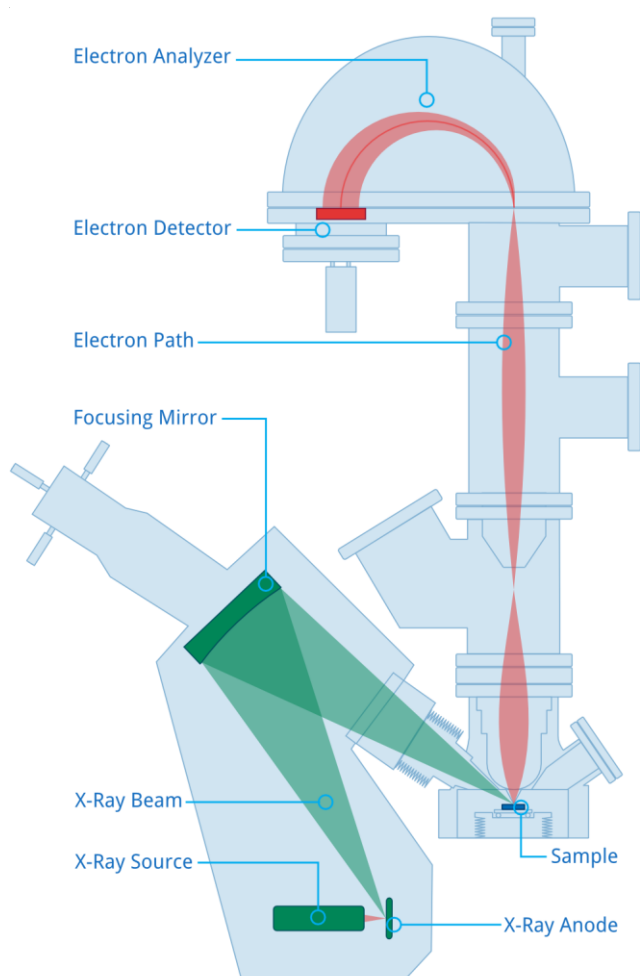


Fig. .2 XPS with EnviroESCA.

Photoelectrons with a specific kinetic energy are released due to the interaction between the photons and the atoms and molecules on the surface. Thereby only electrons from atoms up to a depth of approx. 10nm are able to leave the surface.

These electrons travel through the lens system of the Electron Analyzer into the hemisphere which acts as a spherical capacitor forcing the electrons onto circular paths with radii depending on their kinetic energy. The electron paths end at an electron sensitive detector where the electrons are amplified and measured as an intensity in counts / second. Sweeping the voltage of the spherical capacitor while measuring the number of electrons per second on the detector results in a photoelectron spectrum. From these spectra a quantitative analysis of the atomic composition of the sample surface can be done.

## Experimental Section

The superabsorbent polymer (SAP) sample used in this study was taken from the inner layers of a disposable baby diaper after opening the overlaying fabric covers. In the dry state *as received* the SAP appears as fine granular powder as shown in Fig. 1.

The majority of commercially used SAPs is based on the sodium salt **PAA-Na** of poly(acrylic acid) **PAA**. Copolymers with poly(acrylamide) **PAM** are also used, e.g., in disposable personal hygiene products.

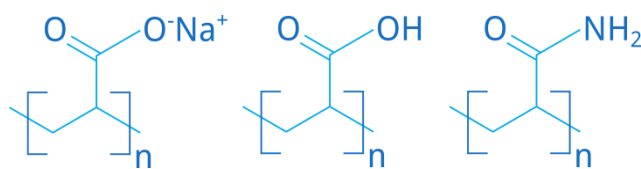


Fig. 3. Typical examples of polymers used in superabsorbent polymers (SAP). Sodium salt PAA-Na (left) of poly(acrylic acid) PAA (middle) and poly(acrylamide) PAM (right).

The SAP powder was mounted onto a polymer block with double sided carbon tape. Then the SAP sample was introduced directly from ambient air atmosphere on a standard sample plate without any pre-treatment, e.g., masking, contacting, etc.

EnviroESCA can work in pressures up to several dozens of mbar and therefore does not necessarily require vacuum conditions which overcome the problem of outgassing of almost all samples. In classical XPS systems non-conducting organic materials especially polymers tend to quickly charge up under X-ray illumination which makes charge compensation inevitable. In classical XPS low energy electron and ion sources are being used in addition to the X-ray source to compensate the surface charge of the surface.

In EnviroESCA an intrinsic charge compensation method which we call Environmental Charge Compensation makes additional electron or ion sources unnecessary. The gas atmosphere that is surrounding the sample delivers all the free charges, when illuminated with the soft X-rays, that is needed to compensate for surface charging as illustrated in Fig. 4.

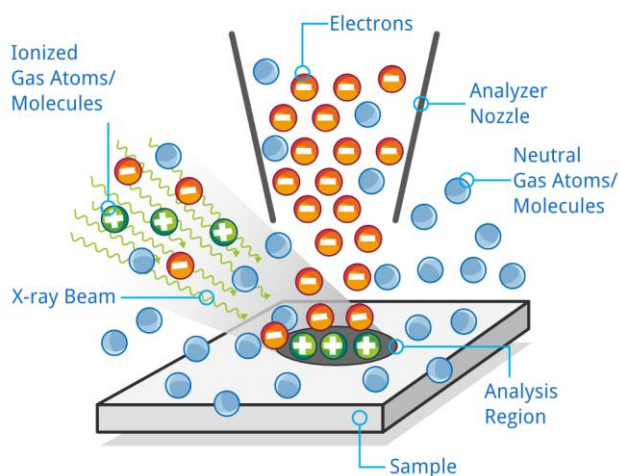


Fig. 4. Illustration of Environmental Charge Compensation.

In this study the surface of a superabsorbent polymer used in baby diapers was investigated with the EnviroESCA in the presence of different amounts of absorbed water.

## Results

In the following section we present original data taken on a commercial SAP with EnviroESCA. All detail spectra were referenced using the maximum of the C 1s core-level region at 285 eV.

Fig. 5 shows the polymer about 10mm in front of the analyzer nozzle. After sample introduction into the Sample Environment of EnviroESCA the automated pressure controlled pumping system was started with a set point of 2 mbar. The survey spectrum recorded on the dry polymer obtained under these conditions is shown in Fig. 6.



Fig. 5. Dry SAP close to the analysis position.

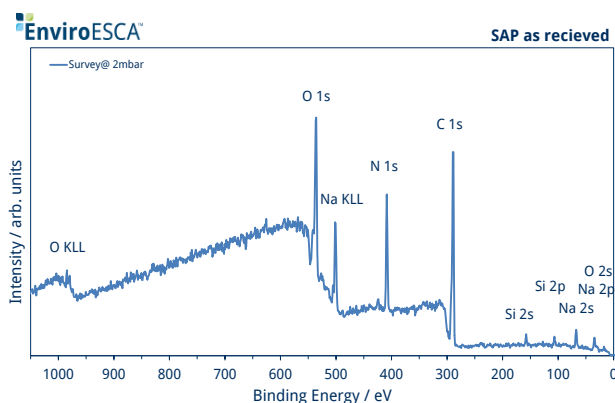


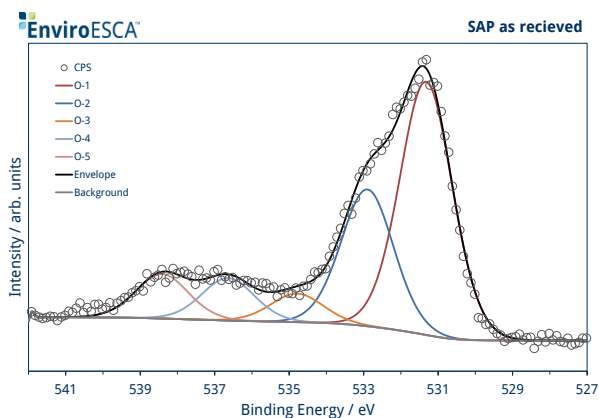
Fig. 6. Survey spectrum of the SAP as received taken at 2 mbar.

It reveals emission lines originating from oxygen, nitrogen, carbon, sodium and silicon. An overall shift of about 4 eV to higher binding energies is concluded when comparing the measured peak position to literature values of other polyacrylates.[2]

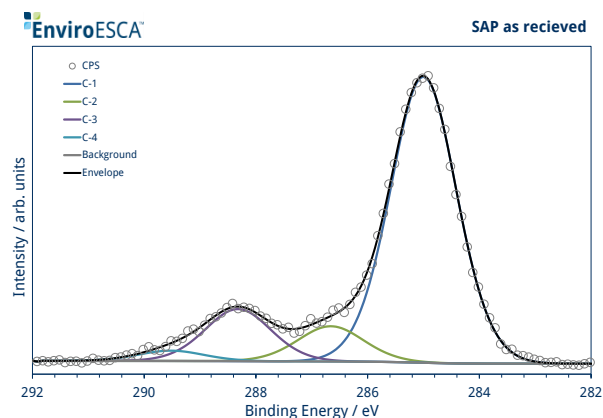
Potentially all of these elements can be part of the polymers composition since the exact formulation (incl. monomers, additives, cross-linker) of that specific SAP taken from a commercial diaper is confidential and not known to us.

Also additional elemental contributions arising from ambient air (oxygen, nitrogen), adventitious hydrocarbons (carbon), production processes (carbon, oxygen, silicon) have to be considered.

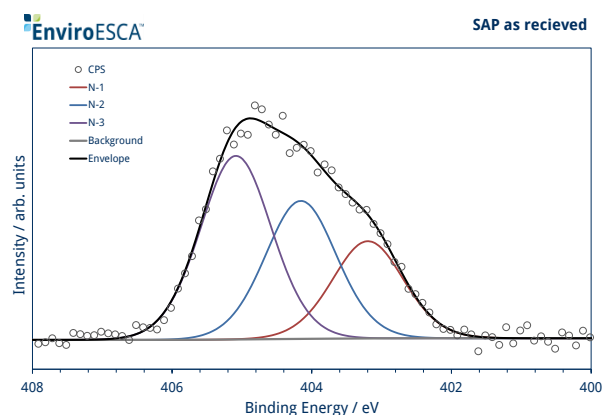
In the next step detail scans of the O 1s, C 1s, and N 1s regions were acquired, which are presented in Figs. 7-9. From these detail spectra typical chemical functionalities related to acrylate-based polymers namely  $\underline{C}C / \underline{C}H$ ,  $\underline{C}O / \underline{C}N$ ,  $\underline{C}O$ , and  $HN-\underline{C}O / O-\underline{C}O$  can be identified. Further contributions in the O 1s and N 1s core-level spectra could be caused by ambient air, water, and overlapping Auger lines, respectively.



**Fig. 7. O 1s core-level spectra of SAP as received @2 mbar. Colored lines correspond to oxygen atoms located in  $O=C$  (O-1),  $O-C / H_2O_{ads}$  (O-2),  $H_2O_{gas}$  (O-3 / O-4) moieties. Additional contributions may arise from an overlapping  $Na\ KL_1L_{23}$  Auger line.**



**Fig. 8. C 1s core-level spectra of SAP as received @2 mbar. Colored lines correspond to carbon atoms located in  $\underline{C}C / \underline{C}H$  (C-1),  $\underline{C}O / \underline{C}N$  (C-2),  $\underline{C}O$  (C-3), and  $\underline{C}OO$  (C-4) moieties.**



**Fig. 9. N 1s core-level spectra of SAP as received @2 mbar. Colored lines correspond to nitrogen atoms located in  $\underline{N}C / \underline{N}H$ ,  $\underline{N}C=O$ ,  $\underline{C}N^+$ , and  $N_2$  moieties.**

As EnviroESCA is capable of performing XPS measurements in near ambient pressure conditions the polymer was now studied after the uptake of water (outside of the EnviroESCA) at different pressures to follow the spectral changes during the drying process. Fig 10 shows the wet polymer about 3 mm in front of the analyzer nozzle



Fig. 10. Wet SAP close to the analysis position.

The drying process is illustrated in Fig. 11. The sample powder was placed on a polymer block and that block was standing in a Petri dish filled with water (Fig. 11a). Then the analysis compartment is differentially pumped through the analyzer nozzle with a distance of 0.3 mm above the sample. Therefore the water vapor (continuously evaporating from the Petri dish due to pumping) must pass over the sample surface, ensuring saturation with water-derived adsorbates (Fig. 11b).

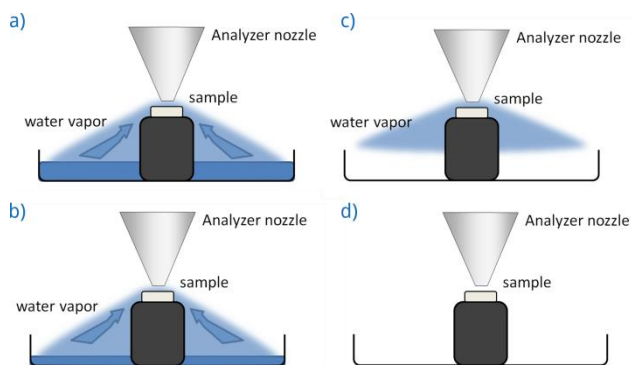


Fig. 11. Illustration of the used measurement set-up inside the EnviroESCA for studying the drying of a wet SAP.

As the water continuously evaporates and is removed, the liquid water slowly depletes. Once the liquid water is depleted (Fig. 11c), the remaining water vapor is pumped away, and then the adsorbates will slowly desorb from the surface (Fig. 11d). In this state, the surface can be measured while „drying“.

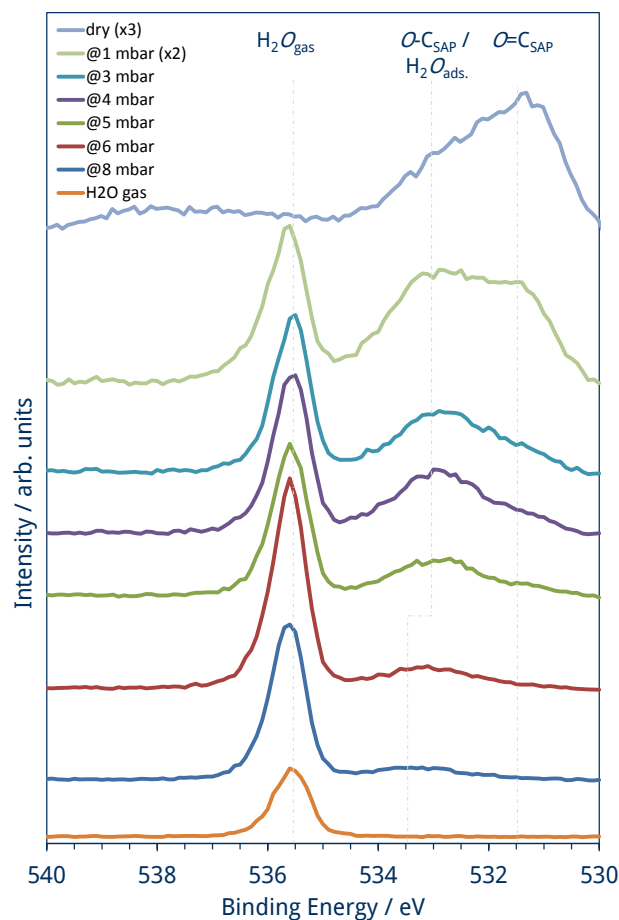
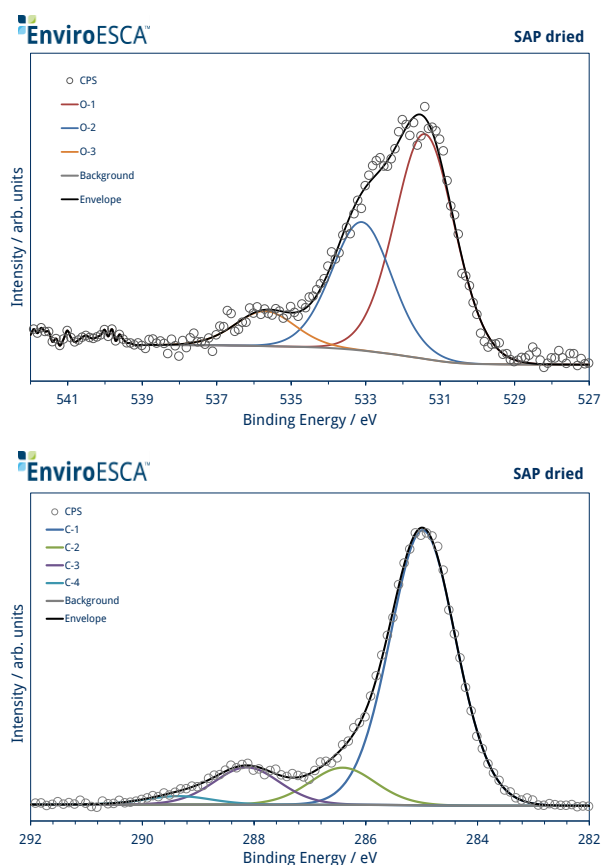


Fig. 12. O 1s core-level spectra of the SAP in different states during drying @8 mbar, @6 mbar, @5 mbar, @4 mbar, @3 mbar, @1 mbar. Also the spectra of the dry polymer (as received) @2 mbar and the H<sub>2</sub>O gas phase without a sample in front of the nozzle are shown for comparison.

The evolution of the O 1s core-level region during that drying is shown in Fig. 12. The most obvious effect during pump down is the decreasing O 1s peak at ~535.5 eV related to water vapor (H<sub>2</sub>O<sub>gas</sub>) evaporating from the petri dish and the SAP surface, respectively. In the pressure region between 1–5 mbar a second O 1s peak around 533.5 eV becomes more and more prominent which originates from adsorbed water molecules (H<sub>2</sub>O<sub>ads</sub>).

In parallel the O 1s peak components  $O-C_{SAP}$  (~533 eV) and  $O=C_{SAP}$  (~531.5 eV) that can be assigned to the SAP are increasing in intensity with the ongoing drying process. Finally in dry SAP these two components are dominating the O 1s region.

An additional survey spectrum (not shown here), and C 1s and O 1s core-level spectra were acquired after drying the SAP overnight at 0.5 mbar. These spectra shown in Fig. 13 resemble very much the initially obtained spectra of the *as received* SAP, see Figs. 7-9. One main difference is found in the O 1s region, here the peak components located at binding energies over 536 eV are absent after drying.



**Fig. 13. O 1s (top) and C 1s (bottom) core-level spectra of a wetted and then dried (overnight at 0.5 mbar) SAP sample.**

## Conclusion

EnviroESCA's ability to work with liquids, gases, and in pressures much higher than ultra-high vacuum conditions opens new routes to study functional materials under application relevant conditions.

Here we demonstrated the possibility to study a super-absorbent polymer (SAP) in three states with different amounts of adsorbed water i) dry, ii) wet, and iii) during drying. EnviroESCA's new and much easier to use method of charge compensation prevents surface charging of otherwise problematic specimens.

[1] F.L. Buchholz and A. T. Graham (Eds.), *Modern Superabsorbent Polymer Technology*, John Wiley & Sons, 1997, ISBN 0471194115

[2] G. Beamson and D. Briggs, *High resolution XPS of organic polymers*, John Wiley & Sons Ltd, West Sussex, England, 1992, ISBN 0471935921