Publ. V Reunió Espanyola del Buit i les seves Aplicacions (Barcelona 1979)

Surface and Interface Analysis in the Polymer Field

R. Holm and S. Storp
Bayer AG, Dept. of Applied Physics
D-5090 Leverkusen

Abstract

Surface analysis methods like ESCA, AES, SIMS and ISS can provide valuable information on the structure and composition of polymer surfaces. Examples of application are the investigation of surface changes, such as the effects of weathering, etching and corona treatments, and the detection of surface deposits consisting of materials like antistatic agents, lubricants and exuded constituents. Because of their high surface sensitivity and ability to differentiate between surface and bulk phenomena, surface analysis methods are particularly suitable for the investigation of interfaces between polymers and metals, glass fibres etc., e.g. in radial tires, cable insulations and capacitor foils.

1. Introduction

High polymers are encountered in many forms, e.g. as fibres, foams, engineering plastics, and coatings. The problems that can be investigated by the methods of surface analysis are correspondingly diverse. They include, not merely such typical surface changes as the effects of etching, weathering and corona discharge, but also the contamination of polymer surfaces and the detection of migration by such polymer additives as lubricants, antioxidants, and antistatic agents, the identification of which is important, because they may prevent bonding, printing or other treatments. Interface problems also arise where there is contact between polymers and pigments, fillers, glass fibres or metals. Examples of polymer-metal bonds are found in galvanized plastics, radial tires, cable insulations, and capacitor foils.

2. Methods

The principal methods for surface analysis of solids [1] are ESCA (XPS), AES, SIMS and ISS. All have their advantages and disadvantages. ESCA is in general non-destructive, permits more reliable detection of compounds and more reliable quantitative measurement and is normally free from charging problems in measurements on insulators.

In AES difficulties arise in the measurement of organic compounds because these are easily decomposed by the electron beam. The great advantage of AES appears in microanalysis: the electrons, unlike the X-rays of ESCA, can be focussed. SIMS is the most sensitive method for surface analysis. Unlike AES and ESCA it enables even hydrogen, together with its compounds, and isotopes, to be detected. The information depths are $\leq$ 10 nm with ESCA, $\leq$ 5 nm with low energy-AES, and $\leq$ 1 nm with SIMS. ISS offers the least information depth, only elements in the uppermost layer being detected. If these methods are combined with continuous sputtering of the surface, information on greater depths and depth profiles can be obtained. These general remarks are of course valid for polymers too. But the surface analysis of polymers requires some special precautions. Polymers are generally non-conducting materials and, in comparison with metals and oxides, highly sensitive to electron or ion bombardment.

For example, the satellite of the ESCA C1s line, which is characteristic of aromatic rings, enables one to observe how easily polystyrene is destroyed by ion bombardment (Fig. 1) [2]. After ion bombardment for only 100 seconds with 1 μA cm^{-2} Ar^{+} ions (5 kV, 90 $^{\circ}$C) the satellite completely disappears: an aromatic ring is no longer detectable in the uppermost monolayers of the specimen. With ISS and SIMS one must therefore expect the composition of the surface to be altered by ion induced reactions and selective sputtering unless the primary ion energy and ion dose are restricted to a very low level, i.e. to establish quasistatic SIMS and ISS conditions. As technical high polymers are unsuitable for baking it may be impossible to establish static conditions.

SIMS, and especially ISS, having a higher surface sensitivity (smaller information depth) than ESCA, require sputter removal of at least parts of the layer to detect the elements and compounds underneath. Furthermore, where high polymers are concerned, practically every mass number may be obscured by a fragment ion, with the result that unequivocal interpretation of the SIMS spectra becomes more difficult. For example, Figure 2 shows a positive secondary spectrum of pure PTFE [3]. To compensate for the positive charge, induced by the primary ions, the sample was simultaneously bombarded with low energy electrons. The high intensity and great number of the fragment ions of a polymer matrix limit the sensitivity for the detection of any other component, e.g. additives. Higher mass resolution is normally not applicable because it reduces the intensity too far for trace analysis. In some cases elemental ions can be discriminated against molecular ions by suitable secondary ion optics or by destroying the molecular ion, e.g. by using a DC accelerator. On the other hand, if one succeeds in interpreting the SIMS spectra unambiguously, one can

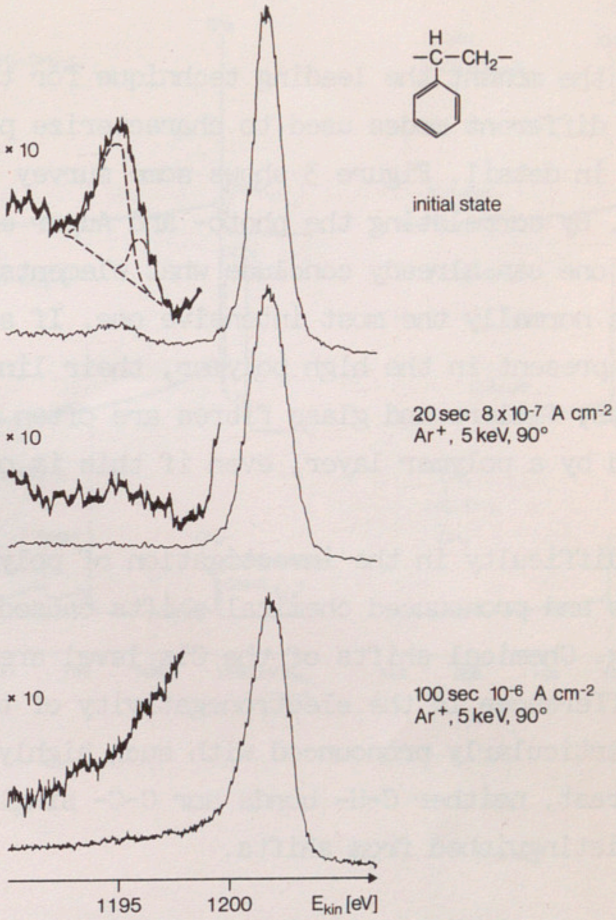
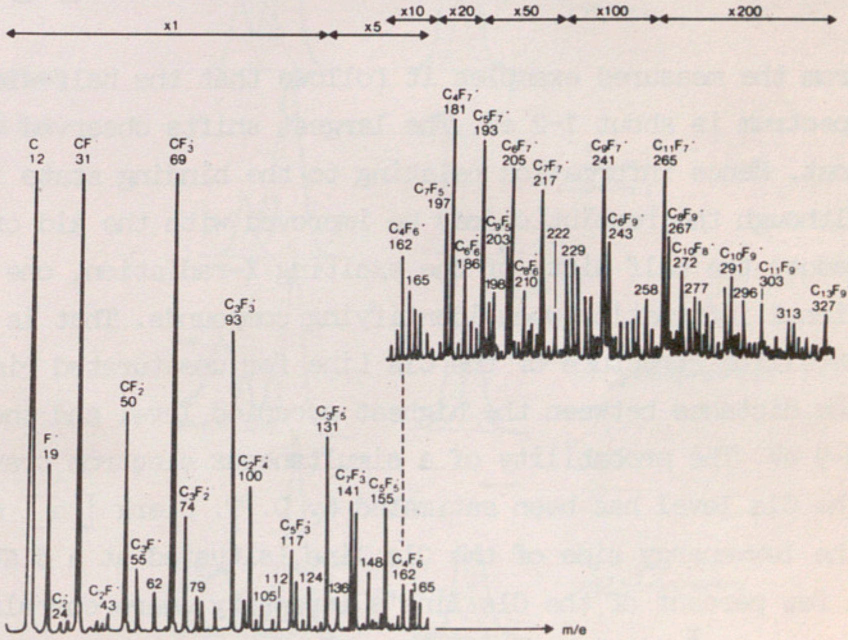


Fig. 1 ESCA-C1s-line of polystyrene before and after ion bombardment

Fig. 2 Secondary ion mass spectrum of pure PTFE [3]



derive very detailed information about the system under study.

ESCA is at the moment the leading technique for the investigation of polymer surfaces. The different modes used to characterize polymers by ESCA will therefore be dealt with in detail. Figure 3 shows some survey spectra of frequently used polymers [4]. By correlating the photo- and Auger electron lines from the spectra to the tables one can already conclude what elements are present at the surface. The C1s line is normally the most intensive one. If additional elements (e.g. O, Cl, F, Si, N) are present in the high polymer, their lines too are found in the spectrum. But pigments, fillers and glass fibres are often not detected by ESCA because they are covered by a polymer layer, even if this is only a few monolayers thick.

A special difficulty in the investigation of polymers is that the carbon is always tetravalent and pronounced chemical shifts caused by changes in the oxidation state are lacking. Chemical shifts of the C1s level are therefore observed only as a result of differences in the electronegativity of the binding partners of the carbon. They are particularly pronounced with such highly electronegative elements as F and O. In contrast, neither C-H- bonds nor C-C- single or C-C- multiple bonds can normally be distinguished from shifts.

Chemical shifts in the C1s and O1s ranges, as frequently observed in high polymers, are shown in Fig. 4. In carbonyl groups not only C, but also O, are not bound in the same way as in ether type groups. When F is the binding partner instead of O, the shifts of the C1s line are still more pronounced [5].

From the measured examples it follows that the half-width of the lines in the ESCA spectrum is about 1-2 eV. The largest shifts observed were ten times greater at the most. Hence information relating to the binding state is not always unequivocal. Although the resolution may be improved with the aid of an X-ray monochrometer to reduce the half width of the exciting X-radiation, one is often dependent on additional information when identifying compounds. That is provided by, for example, the satellite structure of the C1s Line for unsaturated ring systems. For π-electrons the distance between the highest occupied level and the lowest unoccupied level is 5-9 eV. The probability of a simultaneous electron transition in the ionization of the C1s level has been estimated by D. T. Clark [6] et al. as 1-8 %. Weak lines on the low-energy side of the C1s line, situated at a distance of about 7 eV and having a few percent of the C1s line's intensity, were correlated by these authors to $\pi \longrightarrow \pi^*$ shake-up transitions.

Fig. 3 ESCA survey spectra of some polymers:
left: polyethylene, polyvinylchloride, polytetrafluorethylene
right: polyacrylonitrile, polymethyleneoxide, polydimethylsiloxane

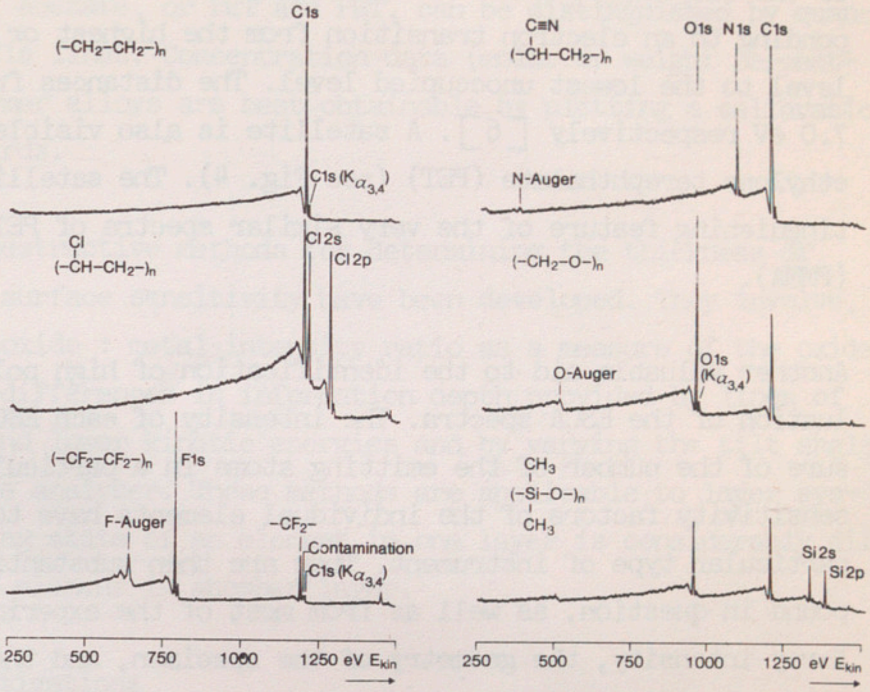


Fig. 4 ESCA Cls and Ols spectra of
a) polyvinylacetate,
b) polymethylmethacrylate,
c) polyethylene terephthalate,
d) polybutylene terephthalate

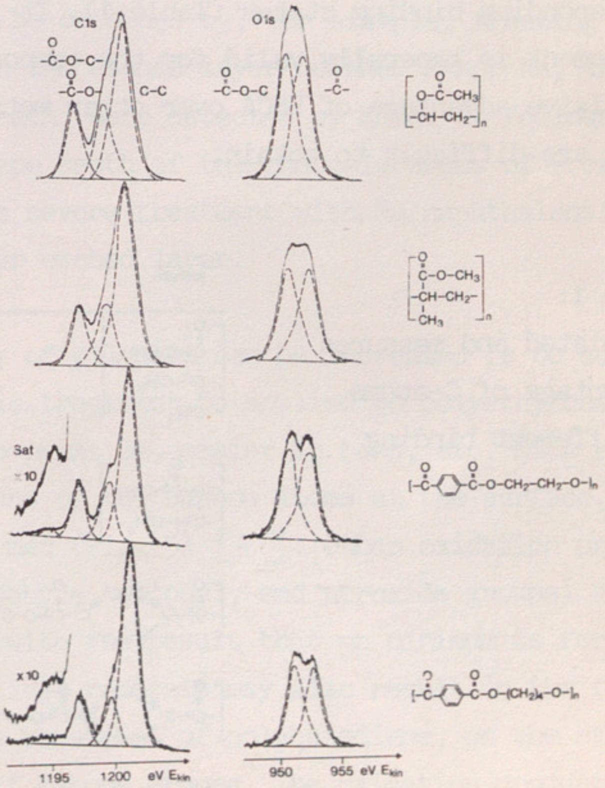
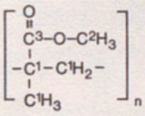
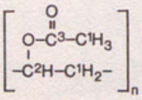
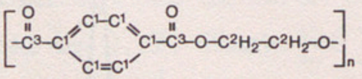
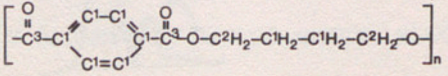


Fig. 1 (top) shows the satellite for polystyrene. It has about 8 % of the intensity of the Cls line. The line shape suggests a deconvolution into two components corresponding to an electron transition from the highest or second highest occupied energy level to the lowest unoccupied level. The distances from the Cls line are 6.2 and 7.0 eV respectively [6]. A satellite is also visible in the Cls spectrum of polyethylene terephthalate (PET) (see Fig. 4). The satellite is the most reliable distinguishing feature of the very similar spectra of PET and polymethyl methacrylate (PMMA).

Another valuable aid to the identification of high polymers is the quantitative evaluation of the ESCA spectra. The intensity of each ESCA line can be used as a measure of the number of the emitting atoms in a particular binding state. The relative sensitivity factors of the individual elements have to be measured only once for a particular type of instrument. They are then substantially independent of the compound in question, as well as from most of the experimental parameters, such as the X-ray intensity, the geometry of the specimen, and the vacuum conditions. The sensitivity factors published for various electron spectrometers and modes of operation of the analyser are within a factor of 10 for the most intensive lines of most elements.

Where there are chemical shifts in the spectrum of an element (as in Fig. 4) the intensity ratios (e.g. Cls_{C-C}: $\mathrm{Cls}_{C=O}$) reflect accurately the quantity ratios for the corresponding binding states (Table 1). It follows that a calibration performed for an element is generally valid for the compounds of that element too. This represents a decisive advantage of ESCA over other methods, for calibration standards for surfaces are difficult to obtain.

Table 1:
Calculated and measured percentage of C-atoms in different binding types

sample	percentage of C-atoms bound in					
	$-C^1-C^1-$		$-\overset{O}{\overset{\|}{C}}-O-C^2-$		$-\overset{O}{\overset{\|}{C^3}}-O-$	
	calc.	meas.	calc.	meas.	calc.	meas.
	60	63	20	19	20	18
	50	52	25	24	25	24
	60	60	20	20	20	20
	66.7	67	16.6	16	16.7	17

From Table 1 it can be seen that polymers having the same shifts in their Cls spectra, e.g. PMMA and polyvinyl acetate, or PET and PBT, can be distinguished by quantitative evaluation of the Cls lines. Concentration data (molar or weight percentages) for copolymers or polymer alloys are best obtainable by plotting a calibration curve with the aid of standards.

In the case of metals, non-destructive methods for determining the thickness of oxide layers by varying the surface sensitivity have been developed. They involve, for example, the use of the oxide : metal intensity ratio as a measure of the oxide layer thickness, and the differences in information depth provided by lines of the same element at higher and lower kinetic energies and by varying the tilt angle of the sample relative to the analyser. These methods are applicable to layer systems in general if the binding state of an element in one layer is considerably different from that of the same element in another layer.

3. Examples of surface investigations

Some investigations will now be described to illustrate the points made in the discussion of ESCA, ISS, SIMS and AES at the beginning of this paper.

Several publications describe investigations concerned with the etching of polytetrafluoroethylene (PTFE) as a means of facilitating the bonding of this material [7,8]. Satisfactory sticking of adhesives can be obtained by, for example, treating the surface with Na in liquid ammonia [8]. In the etched layer neither N nor Na, and no F, but only C and O in one binding state each, were detected by ESCA. It follows that a layer of the PTFE thicker than the escape depth of the photoelectrons of F or of C in C-F_2 groups was decomposed. The less severe treatment with Na/naphthalene/tetrahydrofurane gives a considerably thinner etched layer.

Another way in which the surface energy of polymers can be increased is to subject them to corona discharge treatment. This treatment is applied to polyethylene, for example, to make the material easier to print on, easier to bond, etc. ESCA reveals that this treatment results in oxidations of the carbon atoms at the surface, even acid or acid anhydride groups being formed (Fig. 5) [4]. Other oxidation products with smaller chemical shifts (keto, aldehyde, alcohol, and peroxide groups) are represented by almost equal intensities, with the result that no minimum is formed in the region of 1,196 to 1,201 eV. Long-lived radicals may also result in the formation of lines within this shift range. Ozone treatment of polybutadiene, on the other hand, results mainly in the formation of ketone groups. The oxidation products can

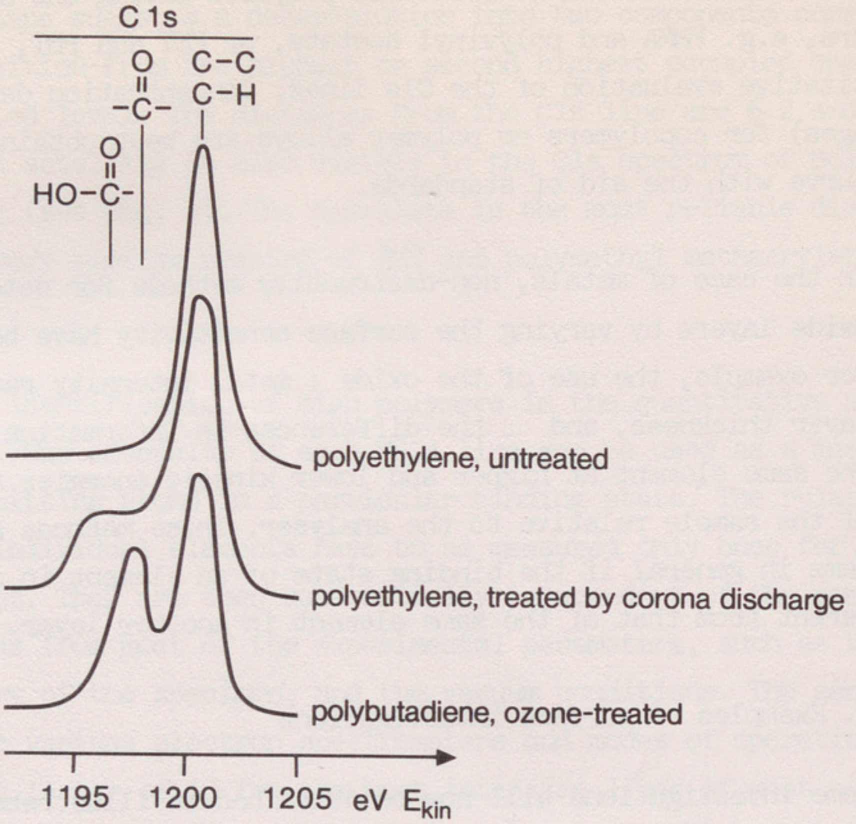


Fig. 5 ESCA C1s spectra of polyethylene, oxidized polyethylene and oxidized polybutadiene

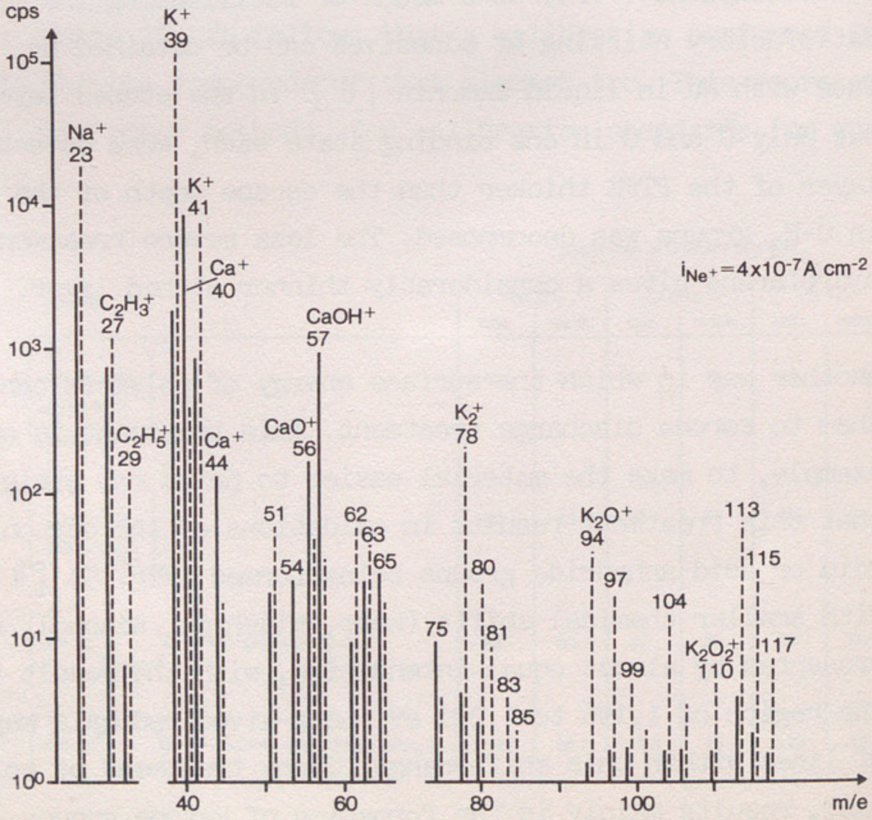


Fig. 6 Determination of calcium stearate on polyethylene by SIMS [13]

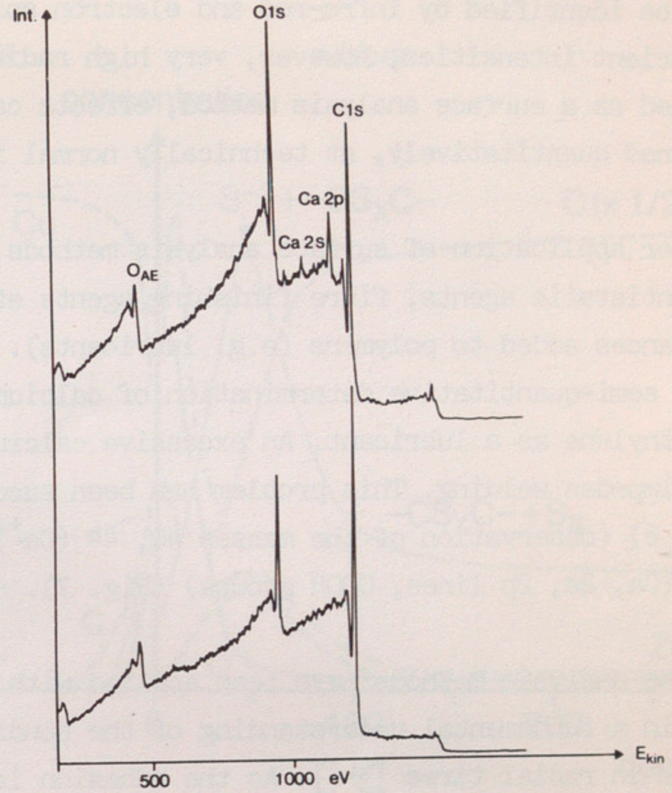


Fig. 7 Determination of calcium stearate on polyethylene by ESCA

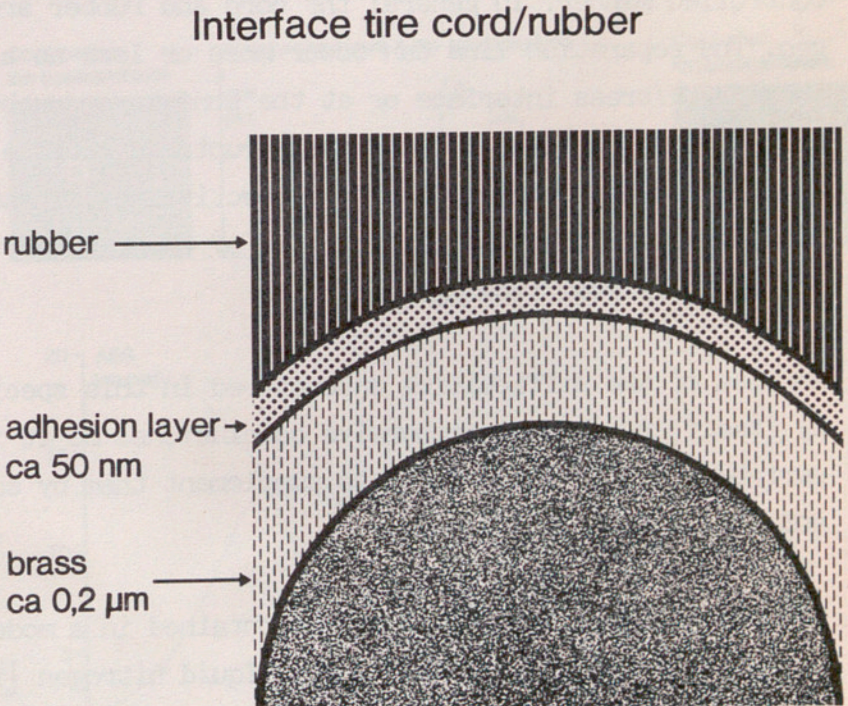


Fig. 8 Schematic drawing of the rubber/tire coat interface

also be identified by infra-red and electron spin resonance spectroscopy; to obtain sufficient intensities, however, very high radiation doses are necessary. When ESCA is used as a surface analysis method, effects can not only be detected, but also determined quantitatively, at technically normal irradiation doses.

Another application of surface analysis methods is the detection of surface deposits (of antistatic agents, fibre finishing agents etc.) and of surface exudations by substances added to polymers (e.g. lubricants). An example is the detection and at least semi-quantitative determination of calcium stearate, which is often added to polyethylene as a lubricant. An excessive calcium stearate concentration at the surface impedes welding. This problem has been successfully studied both by SIMS (Fig. 6) (observation of the masses 40, 44 (Ca^+), 56 ($Ca\ O^+$), 57 ($CaOH^+$)) and by ESCA (Ca, 2s, 2p lines, COOH groups) (Fig. 7).

Surface analysis methods have been applied with great success in model experiments to gain a fundamental understanding of the bonding of brass-coated steel cords to rubber in radial tires [9]. As the adhesion is brought about by a very thin interfacial zone (Fig. 8) it is reasonable to study this zone by surface analysis methods. For this purpose, however, preparation techniques are needed which enable the interface to be uncovered. In this way a problem of interface analysis becomes one of surface analysis. Unfortunately no existing technique allows that to be done in a controlled manner. In general the cord and rubber are separated under liquid nitrogen. The separation line can occur more or less as a matter of chance either at the bond layer/brass interface or at the bond layer/rubber interface, or it may be in the adjacent rubber. As the freshly ruptured surface reacts in ambient air the sample must be prepared under a protective gas. These preparative difficulties, considerably more than the inadequacies of the methods themselves, may reduce the value of the analytical findings.

In view of the difficulties encountered in this specific case, none of the methods by itself permits comprehensive conclusions. So it is necessary to combine several surface analysis methods and to supplement them by such other methods as SEM, TEM and the electron microprobe.

Figure 9 shows ESCA depth profiles obtained in a model experiment with brass plate after separation of the bond under liquid nitrogen [17]. Starting from the surface of the break, depth profiles were obtained both in the direction of the brass and in that of the rubber; they were then put together at zero depth in Fig. 9. This gives the concentration profile of a number of elements in the interface between the brass

Fig. 9 ESCA in-depth profile of a rubber-to-brass sample broken at liquid nitrogen temperature (adhesion system: hexamethylene tetramine/resorcinol/SiO_2)

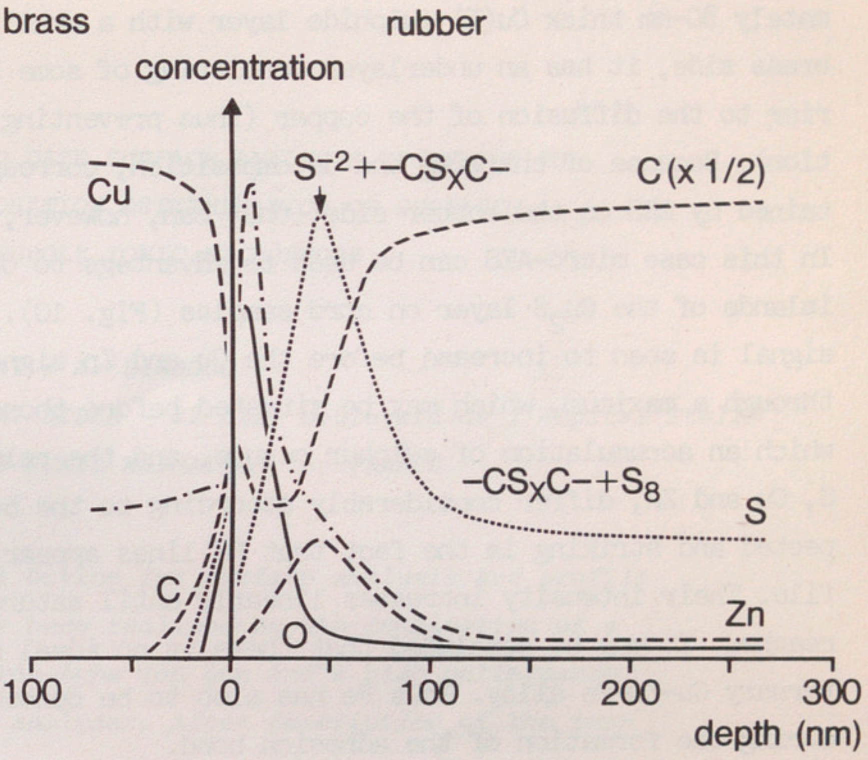
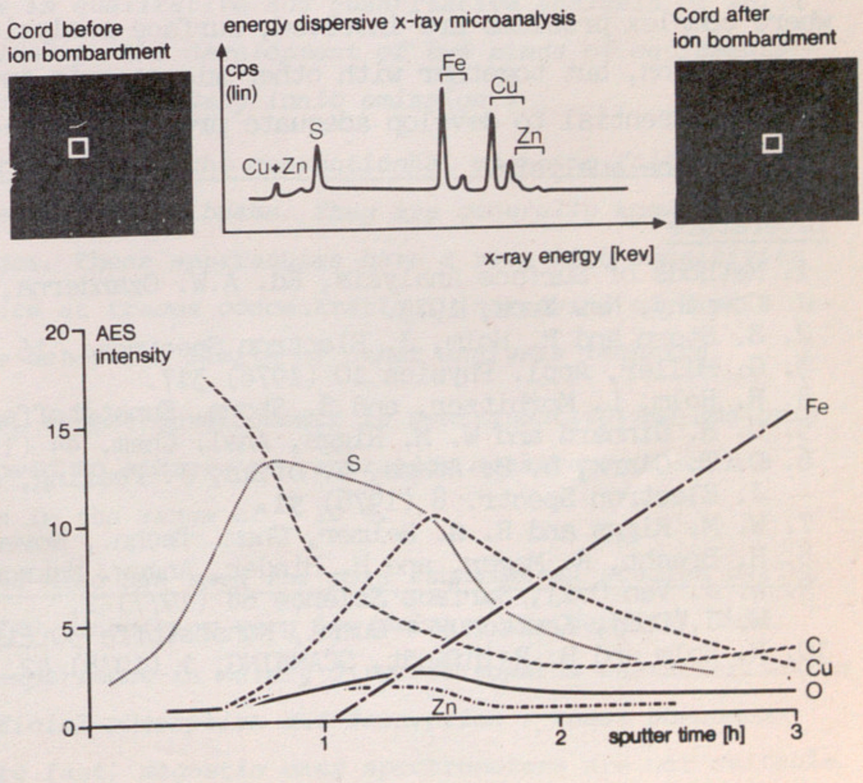


Fig. 10 AES in-depth profile of a tire cord surface taken with a combined SEM/AES apparatus [10]. The tire was broken at liquid nitrogen temperature. The analyzed area was selected by energy dispersive X-ray microanalysis.



and rubber. As can be seen, the adhesion layer consists essentially of an approximately 80-nm thick Cu(I) sulphide layer with a small excess of sulphur and, on the brass side, it has an underlayer consisting of some ZnS + Zn O, which acts as a barrier to the diffusion of the copper (thus preventing excessive copper sulphide formation). Because of charging and decomposition, corresponding profiles cannot be obtained by AES on the rubber side; they can, however, be obtained on the brass side. In this case micro-AES can be used to advantage to obtain depth profiles of residual islands of the Cu_2S layer on cord samples (Fig. 10). As the C signal declines, the S signal is seen to increase before the Cu and Zn signals. The S intensity passes through a maximum, which may be situated before those of Cu and Zn. The depth to which an accumulation of sulphur occurs, and the relative positions of the maxima of S, Cu and Zn, differ considerably according to the bonding system employed. Unexpected and striking is the fact that FE lines appear rather early in the depth profile. Their intensity increases linearly until saturation in the steel core is reached. It may be concluded that there is no ideal brass layer on the cord but a ternary Cu-Zn-Fe alloy. Thus Fe has also to be considered as a reaction partner during the formation of the adhesion bond.

The use of surface analysis methods in the study of high polymer problems is still in its infancy. The examples discussed should have demonstrated, though, that polymer surfaces and - if suitable preparation techniques are used, interfaces, too - can be characterized. The last example, in particular, was intended to show that, where complex problems are involved, surface analysis methods should be used, not in isolation, but together with other microscopic and spectroscopic techniques. It is also essential to develop adequate preparation techniques, especially in the case of interface analysis.

Literature

1. Methods of Surface Analysis, Ed. A.W. Czanderna, Elsevier Scientific Publ. Company, New York, 1975.
2. S. Storp and R. Holm, J. Electron Spectrosc. 16 (1979) 183.
3. G. Müller, Appl. Physics 10 (1976) 317.
4. R. Holm, L. Morbitzer, and S. Storp, Kunststoffe 67, 11 (1977) 717.
5. C. R. Ginnard and W. M. Riggs, Anal. Chem. 44 (1972) 1310.
6. D. T. Clark, D. B. Adams, A. Dilks, J. Peeling, and H. R. Thomas, J. Electron Spectr. 8 (1976) 51.
7. W. M. Riggs and R. G. Beimer, Chem. Techn., November 1975 p. 652.
8. H. Brecht, F. Mayer, and H. Binder, Angew. Makromol. Chem. 33 (1973) 89.
9. W. J. Van Ooij, Surface Science 68 (1977) 1,
   W. J.V.Ooij, Kautschuk + Gummi, Kunststoffe 30 (1977) 739.
10. R. Holm and B. Reinfandt, SCANNING, 1 (1978) 42.