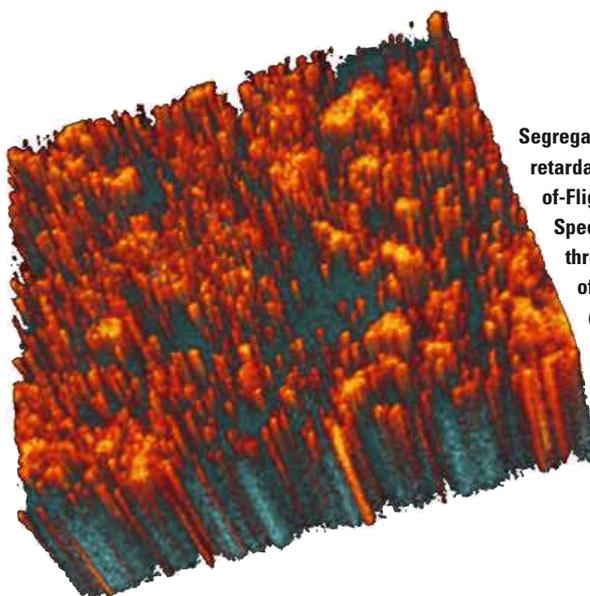


Polymers Under the Chemical Magnifying Glass

Surface Analysis. To obtain a detailed look at and into the chemical composition of polymers, it is essential to select the most appropriate analytical method. With the aid of X-ray Photoelectron Spectroscopy (XPS) and Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) properties can be selectively identified, localized and quantified.



Segregation of an organic flame retardant can be revealed by Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) in a three-dimensional plot (field of view: 30 x 30 x 1 μm^3) (figures: Tascon)

BIRGIT HAGENHOFF

Many important properties, such as adhesion, friction, oxidation and optical behavior, are determined by a polymer's chemical composition. Furthermore, these properties are determined by compositional differences that originate from different depths. For example, wettability, which influences bonding and adhesion, is determined almost exclusively by the composition of the outermost atomic layers (1/1000 micrometers). In contrast, oxidation processes are governed by compositional differences within the top 2 to 20 nm while appearance and color are governed by compositional differences extending to a depth of 100 nm (Fig. 1). Analytical techniques that are used optimize composition – performance relationships should therefore target these depths precisely, i.e. the analytical information must come from the depth that is relevant to the property of interest. Matching the an-

alytical technique to the appropriate information and sampling depth is analogous to selecting the depth of field in a camera. Almost all analytical measurements focus on the following questions: what elements or molecules are present (identification), where are the elements or molecules located (localization) and how much is present (quantification)?

The Analytical Toolbox

In order to select the most suitable analytical technique, the analyst must consider both the sampling depth (information depth) and the lateral resolution. The lateral (or spatial) resolution is defined as the ability to distinguish two points as separate in space. It is comparable to the smallest pixel size of an image that can be detected by the sensor of a digital camera. The lateral resolution determines how crisply the chemical maps of a surface can be shown.

No technique can analyze a surface at all depths. It must therefore be matched to the problem. Another factor to consider in the case of polymers is that not only is the elemental composition relevant

(e.g. the ratio of oxygen to carbon), but also the molecular composition, such as the nature of the polymer or the additives.

Figure 2 illustrates the most common analytical techniques. High lateral resolution (techniques shown in red) is achieved only by those techniques that yield virtually no information about chemical composition. No one technique can analyze a surface at all depths; therefore, the technique must match the problem. For polymers, both elemental composition (e.g. the ratio of oxygen to carbon) and molecular composition (e.g. presence of additives) are important. Therefore, the analyst will typically select one of the analytical techniques shown in light brown, whose lateral resolution for practical applications is limited to

Contact

Tascon GmbH
D-48149 Münster
Germany
TEL +49 251-625622-100
→ www.tascon.eu

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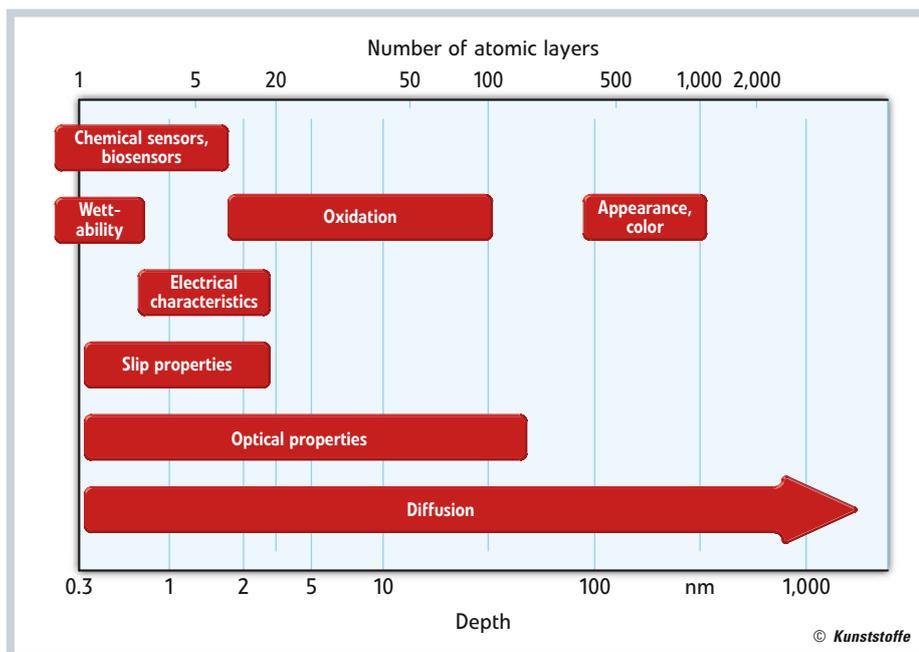


Fig. 1. Different surface regions of a material are responsible for different material properties (based on [1])

about 100 nm. Among the most suitable for polymer analysis are X-ray Photoelectron Spectroscopy (XPS) and Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) because of their depth of information. These will be presented in more detail below, along with their applications.

X-Ray Photoelectron Spectroscopy

XPS, which is based on the photoelectric effect, employs X-rays to eject electrons from the shells of the atoms in the sample. This kinetic energy of the ejected electrons is characteristic of the chemical element from which they were released. Furthermore, accurate determination of the electron kinetic energy allows the bonding state of each atom to be determined. For example, electrons ejected from a carbon atom in a C-C bond differ substantially in energy from those ejected from the carbon in a C=O bond. This means that, in addition to the atomic composition, molecular groups can be quantified. In Figure 3, this is illustrated by the example of polyethylene terephthalate (PET).

XPS is suitable for detecting all elements except hydrogen. The detection limit is about 0.1 (atomic) percent. Detection is quantitative, i.e. concentrations can be recorded to within an accuracy of 5%. The maximum information depth is about 10 nm and a lateral resolution of about 3 μm is routinely achieved. Values

energy introduced into the sample is transported through collisions between the atoms and molecules back to the surface, where particles characteristic of the surface's chemical composition are emitted. Their masses, which can be used to accurately identify the particles, are then determined. This technique can detect both elements and molecules, including intact molecules having atomic masses up to about 10,000 u, i.e. the majority of polymer additives, along with oligomers. Larger molecules, such as polymers, are fragmented by the ion bombardment, but the fragments are characteristic and can be used for identification.

ToF-SIMS spectra are highly sensitive to changes in molecular structure. As an example, Figure 4 shows the spectra for the oxidation-inhibiting additive tris(2,4-di-tert-butylphenyl) phosphite (grade: Irgafos 168; manufacturer: Ciba AG, Basel, Switzerland), both in its starting form

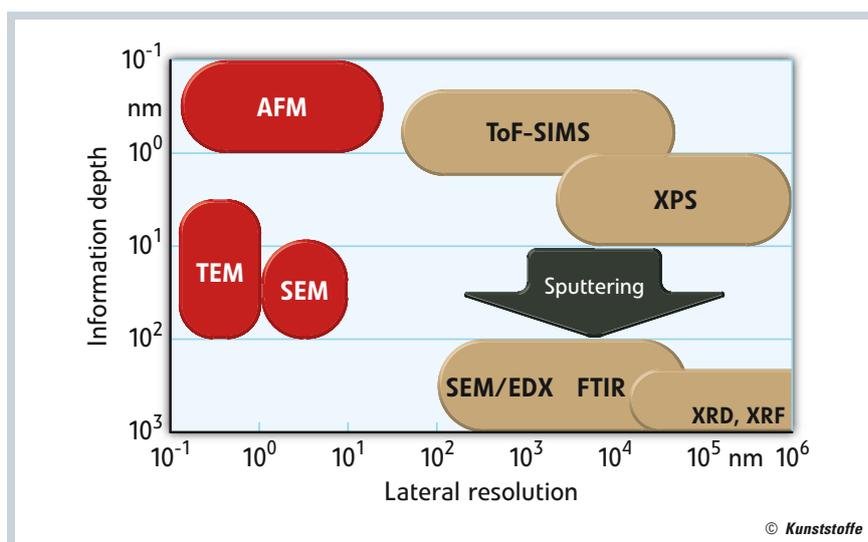


Fig. 2. Analytical techniques can be classified by their lateral resolution and information depth. The techniques highlighted in red do not provide chemical information, unlike the light-brown techniques. Sputtering can remove sample material (AFM: Atomic Force Microscopy; TEM: Transmission Electron Microscopy; SEM: Scanning Electron Microscopy; ToF-SIMS: Time-of-Flight Secondary Ion Mass Spectrometry; XPS: X-ray Photoelectron Spectroscopy; EDX: Energy-dispersive X-ray Detection; FTIR: Fourier Transform Infrared Spectroscopy; XRD: X-ray Diffraction; XRF: X-ray Fluorescence Analysis)

below 1 μm can be achieved by prolonging the measurement time. XPS requires vacuum conditions which most plastic materials, however, can withstand.

Time-of-Flight Secondary Ion Mass Spectrometry

In Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) the surface is analyzed by bombarding it with ions. The

and after oxidation. The two forms of the additive can be distinguished analytically.

This detection limit of this technique is a few ppb for elements and fmol for molecules. With an information depth of 1-3 nm, ToF-SIMS ranks among the most surface-sensitive analytical techniques. It is now possible to achieve lateral resolutions of less than 100 nm, with 300 nm to 3 μm being routine, the exact figure de- →

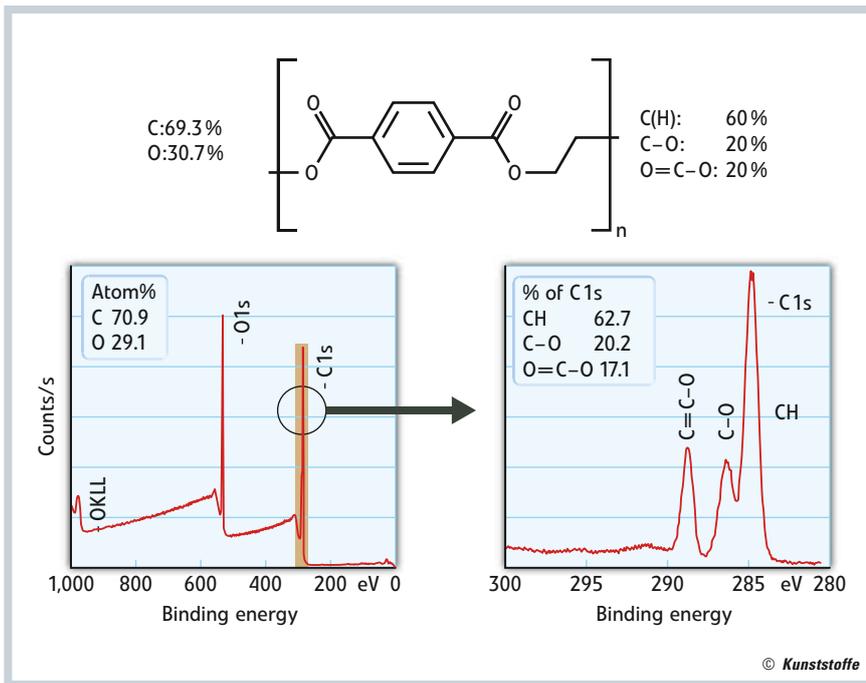


Fig. 3. XPS quantitatively reveals the structural formula of a polyethylene terephthalate (PET, above). The survey spectrum on the left reveals the atomic composition while the detailed spectrum on the right shows the bonding states of the carbon in PET

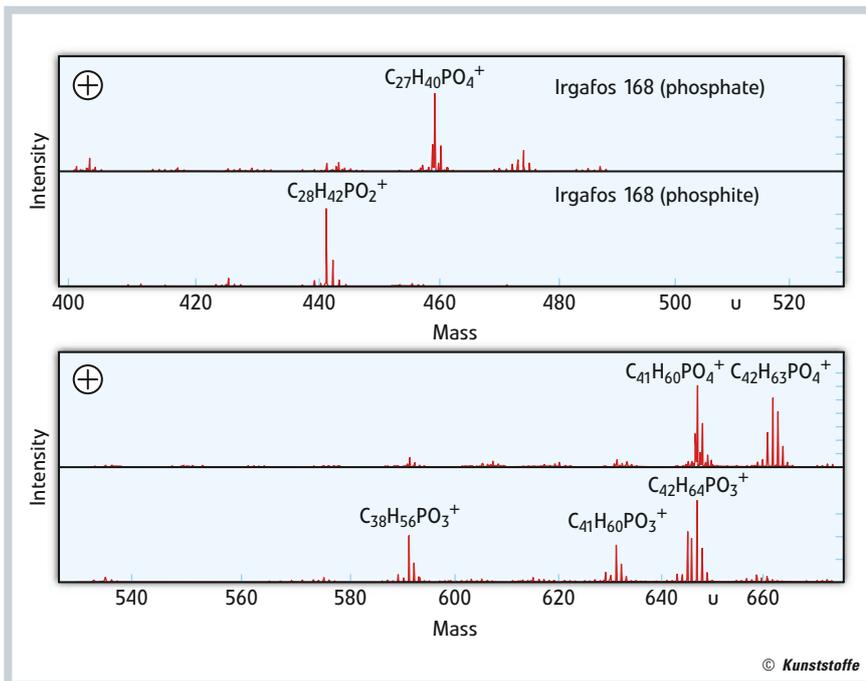


Fig. 4. The ToF-SIMS spectra of the antioxidant Irgafos 168 in polyethylene (LDPE) vary according to whether an oxygen atom has been scavenged (oxidation, above) or not (below)

pending on the application. ToF-SIMS is only semi-quantitative, i.e. differences in concentration in samples of similar composition can be detected to within an accuracy of 5 %, but not their absolute amounts. ToF-SIMS, too, requires vacuum conditions. Table 1 lists the most important performance data for the two techniques.

Identifying and Avoiding Coating Defects

Figure 5 shows an optical image of a coating defect in the form of a crater on a polymer coating. Organic contaminants aside, cratering is often caused by inhomogeneous mixing of the various coating components. Since the adhesion is im-

parted in the outermost monolayers of a material (see Fig. 1), the pertinent analytical technique must deliver detailed molecular information from this depth. After optical analyses have ruled out other causes, ToF-SIMS is the technique of choice. Figure 6 shows the result of this analysis (different, yet comparable point on Fig. 5; bright: high intensities; dark: low intensities). While polysiloxanes, which are added to the coating as a leveling agent, are relatively homogeneously distributed inside and outside the defect (left picture), a perfluorinated polyether which cannot be detected outside the defect is found in the center of the crater

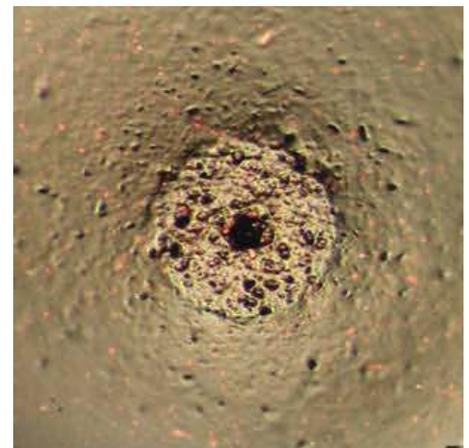


Fig. 5. Wetting defects in coatings can give rise to visible craters

(right picture). Such heat-resistant perfluorinated polyethers serve, for example, as lubricants for production robots and conveyors. An inspection of the production area, accompanied by sampling and ToF-SIMS analysis, enabled the substance that caused the crater to be identified and eliminated from production.

Understanding Surface Modifications Specifically

Flame treatments and plasma treatments are often used to customize the surface properties of a polymer. For example, oxygen or nitrogen can be incorporated into near-surface regions to influence wettability as well as electrical characteristics. XPS is ideal for quantifying the accompanying molecular changes. The left side of Figure 7 shows a detailed XPS spectrum of the carbon signal for an untreated polyethylene surface. The signal is a single peak that is characteristic of the C-C bonds of polyethylene. After plasma treatment, O=C-O-, C=O-, CO, and CN-bonds are found to have formed (Figure 7, right side) within the XPS information

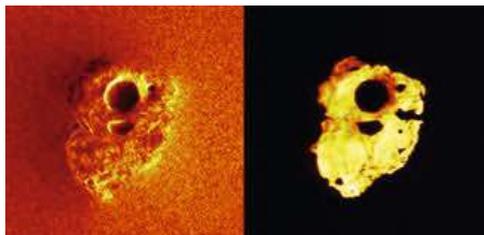


Fig. 6. The constituents of the material (left). The cause of the crater, perfluorinated polyether, is detected only in the center of the wetting defect (right). (Both images: ToF-SIMS; field of view: $500 \times 500 \mu\text{m}^2$; bright: high intensities; dark: low intensities)

depth (10 nm). In a subsequent step, the fractions of the modified carbon atoms were correlated with the macroscopic properties of the surface (e.g. adhesive strength).

Segregation of Additives

Segregation of additives in polymers can be both desirable and undesirable. In the first case, the surface or interface is specifically modified (e.g. by leveling agents) while, in the second, the surfaces have unwanted optical efflorescence, undesirable

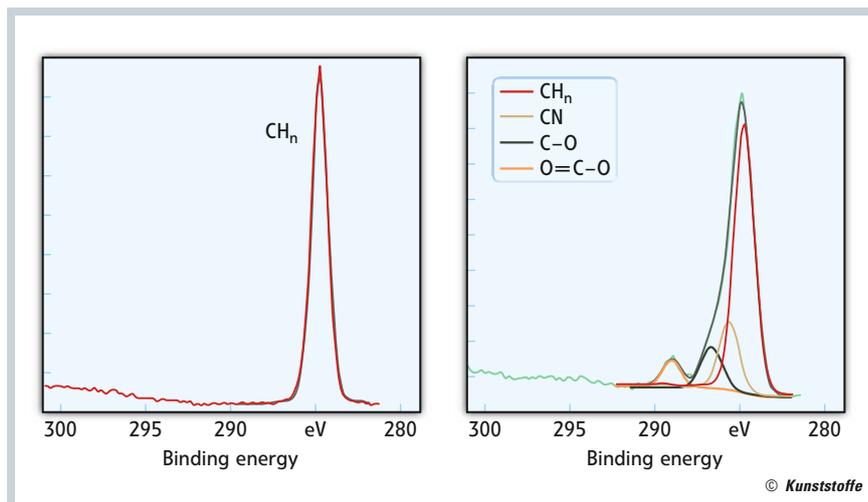


Fig. 7. Plasma treatment of polyethylene (XPS detailed spectrum of the carbon, left) leads to formation of O=C-O-, C-O-, and CN-bonds (right)

electrical characteristics or coating problems. The **Title figure** shows a three-dimensional distribution plot for an organic flame retardant in a polyamide. ToF-SIMS was chosen because it can identify and distinguish between these different organic additives, even when various additives are simultaneously present in a material. As it was already known in this

case that the electrical characteristics of the sample had been influenced too, analysis of the outermost monolayers of the sample alone, and the information depth returned by the ToF-SIMS proved insufficient (see **Figs. 1 and 2**). Deeper layers therefore were included by successively sputtering the sample with Ar cluster ions (AR_{1000}^+) and capturing a ToF-SIMS im- →

| | XPS | ToF-SIMS |
|------------------------------|---|--|
| Measurement principle | Excitation of surface with X rays; determination of energy of ejected photoelectrons (photoelectric effect) | Excitation of surface with high-energy ions; determination of mass of sputtered charged atoms and molecules (secondary ions) |
| Type of information | Atomic composition; information on the binding states of the elements detected | Chemical composition of surface; detection of all elements, stable isotopes, molecules |
| Information depth | Topmost 10 nm | Topmost monolayer |
| Operating modes | Spectroscopy, microscopy, depth profiling | Spectrometry, microscopy, depth profiling |
| - Maximum field of view | Approx. 500 x 300 µm ² | Approx. 9 x 9 cm ² |
| - Lateral resolution | 300 nm; in routine operation: 3 µm | 100 nm; in routine operation: 300 nm |
| - Maximum depth | 10 µm (through sputtering), 20 nm (non-destructive, angle-resolved XPS (ARXPS)) | 10 µm (through sputtering), 500 µm (slice image) |
| -Depth resolution | Several 10 nm (sputtering); dependent on model assumptions (ARXPS) | Several nm (sputtering), 100 nm (slice image) |
| Quantitative | Yes | Semi-quantitative |
| Detection limit | 1000 ppm | Several 10 ppb (elements), fmol (molecules) |
| Identification of components | Possible, with restrictions | Possible (screening of unknown substances, as well) |
| Requirements on sample | Must tolerate vacuum | Must tolerate vacuum |

Table 1. Characteristics of the analytical techniques discussed

age after each sputtering step. The result was a three-dimensional image of the molecular structure of the sample. Segregation of the flame retardant toward the surface is clearly visible. The cause in this case was a non-optimally configured injection molding process.

Conclusion

Surface analytical methods such as XPS and ToF-SIMS yield a comprehensive picture of the chemical composition of polymer surfaces. Modern instruments can even plot the three-dimensional distribution of additives in the polymer. This enables development processes to be shadowed, production processes optimized and errors uncovered. ■

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THE AUTHORESS

DR. BIRGIT HAGENHOFF (DIPL.-PHYS.), born in 1962, has been CEO of Tascon Gesellschaft für Oberflächen- und Materialcharakterisierung mbH, Münster, Germany, since 1997.