tascon GmbH
Analytical Services & Consulting

Characterisation of Polymer Additives

The properties of polymer materials are not only influenced by the nature of the matrix polymers but also by the additive composition specifically tailored for the respective application. Usually up to 10 different additives with concentrations ranging from some 100 ppm to several weight percent are used in order to adjust properties like viscosity, brittleness, as well as light and thermal stability. Additives are also used to influence the optical appearance (like glossiness) or to improve the handling during production (e.g. release from matrices). If the additive composition is not exactly administered as designed it is possible that the originally intended polymer properties change. In many of these cases this modification is restricted to the surface near regions. As a result adhesion problems can occur or physical phenomena like diffusion and segregation can find their optical counterpart in blooming, different colouring and blistering. A successful failure analysis in these cases requires analytical techniques which are able to detect both, the matrix polymers as well as the various additives.

In polymer analysis many techniques are applied for the development of new additive compositions, the ongoing production control or the composition elucidation of competitor's products. Besides wet chemical techniques mainly GCMS, HPLC, IR, XPS and MALDI are used. None of these techniques, however, is able to detect the detailed molecular composition of a surface with high sensitivity and sub-µm lateral resolution.

For this purpose, Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) has proved to be most valuable. This analysis technique offers information on the elemental as well as molecular composition of a surface.

Intact molecules can be detected up to several thousand mass units which allows to identify most commercial polymer additives. The information is exclusively coming from the uppermost 1-3 monolayers. Therefore, surface phenomena can be studied easily. As many compounds can be detected in parallel, no pre-separation is required. The technique therefore is also well suited for screening purposes using "real samples" as received. By cutting the sample e.g. using microtomes it is also possible to access deeper layers or the bulk material. In this case the data are generated by an imaging experiment of the sections.

The examples presented below show a selection of ToF-SIMS analyses performed to characterise the respective additive composition. All examples are taken from our daily routine tasks.

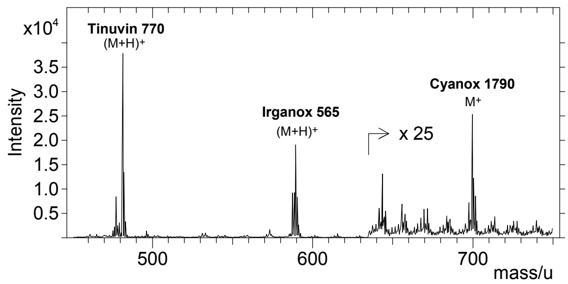

Figure 1: ToF-SIMS spectrum of a technical LDPE surface (detail). Three different additives can be identified.

Figure 1 shows the ToF-SIMS spectrum of a low density polyethylene (LDPE) surface. The sample consisted of small granules which are used for injection moulding. The analysis was performed directly at the granule surface. As can be seen, three different additives, Tinuvin 770 (a light stabiliser), Irganox 565 (a thermal stabiliser), and Cyanox 1790 (an antioxidant) are identified. By the way, at Tascon a data base system has been developed which makes the additive identification fast and reliable. Currently, more than 150 additives are filed including information on application areas and host polymers.

The second example is taken from failure analysis. After prolonged storage periods whitish crystals appeared at the surface of an otherwise black polypropylene ("blooming"). Apart from this optical deviation no coating of the stored material was possible. Figure 2 shows microscope images of the crystals at the sample surface.

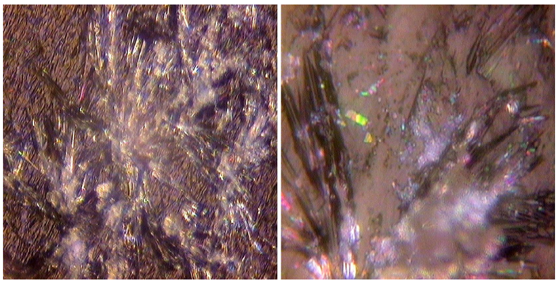

Figure 2: Optical images of blooming on a polypropylene (PP) surface.

In order to characterise the chemical composition of the polymer surface first TOF-SIMS survey spectra were taken from large fields of view. Besides peaks originating from the polypropylene (PP) matrix polymer several polymer additives could be identified including the phosphate antioxidant Ultranox 626 and the release agent Li-Stearate. However, in order to elucidate the source of the crystals information on the lateral distribution of the respective additives is required.

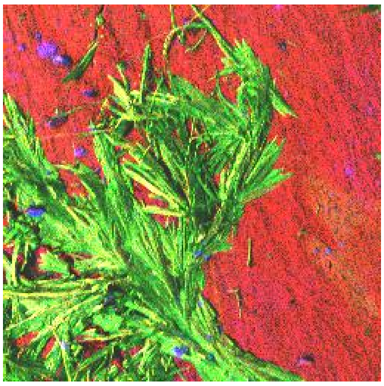

Figure 3: RGB colour overlay of the PP matrix (red), the phosphate antioxidant Ultranox 626 (green) and the release agent Li-Stearate, blue).
Field of View: 500 x 500 µm ².

Figure 3 shows the results of the corresponding TOF-SIMS imaging experiment. Here, the surface is probed using a finely focussed ion beam being rastered across the area of interest. Thus the lateral distribution can be visualised for any ion of interest. In figure 3, the PP distribution is given in red, the Ultranox 626 distribution is given in green and the Li-Stearate distribution is given in blue. Areas where 2 or 3 of the compounds are present appear in the respective mixed colour (RGB colour addition).

It clearly can be seen that the crystalline material consists of Ultranox 626 whereas the Li-Stearate is only present in small spots.

Related Applications:

- Characterisation of end groups (ToF-SIMS)
- Effect of plasma, flame or corona treatments on polymers studied by XPS
- Cross sections of layered polymer systems anylsed by means of ToF-SIMS
- Surface roughness of polymer films (interferometry)
- Organic depth profiling (ToF-SIMS)