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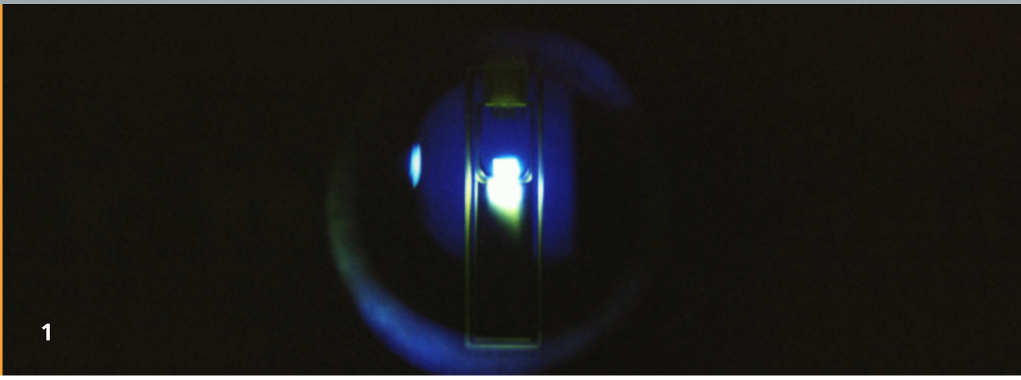

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FUNCTIONAL GROUP ANALYSIS ON POLYMER SURFACES

The wetting, the adhesion to other objects, or the adhesion of paints is determined by the chemical and physical structure of a surface layer which is less than 1 nm thick. An analysis of chemically complex surfaces in that dimension is very challenging for modern analytical technology. Chemical functionalities have to be analyzed in a concentration in the order of 10^{-10° mol/cm^2 before a background of the bulk material which is usually at least 10^4 times higher. Therefore, traditional methods for the structural analysis in organic chemistry which are based on difference measurements between the actual sample and a reference fail and others lack sensitivity. On the other hand, surface sensitive techniques like x-ray photoelectron spectroscopy (XPS) or secondary ion mass spectroscopy (SIMS) have difficulties in dealing with chemically complex and heterogeneous surfaces.

Labelling techniques

The combination of surface chemistry with instrumental methods creates powerful tools for the determination of functional groups on polymer surfaces. The idea behind this so called labelling or derivatization is that a certain functional group or a class of functional groups is reacted specifically with an agent that can be easily analyzed by an instrumental method. This basic scheme has been used for a number of instrumental methods successfully (Fig. 1).

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Fig. 1 xxx.

Chemical derivatization XPS

The power of XPS is the quantification of the surface’s elemental composition. In many cases it also helps to determine structural features from the binding states of the elements. But if the chemical structures are more complex this task is more difficult. With a so called chemical derivatization the problem of functional group analysis can be transformed into the determination of element concentrations. Selected functional groups are labelled with molecules which contain an element that has not been present on the surface before. Elements like fluorine or iodine are most useful because they can be determined with a very high sensitivity. But other elements as nitrogen, bromine, or sulfur have been used too.

Fluorescence labelling

In contrast to XPS, fluorescence spectroscopy is not surface sensitive. But the sensitivity is extremely high because it measures an absolute signal without the need of relating it to a reference. Using a state of the art equipment, the fluorescence spectrum of a femtomolar solution of fluoresceine can be recorded. This volume concentration translates into a detection limit at a surface concentration of 10^{-16} mol/cm^2. With real polymer samples where fluorescence dyes are coupled to selected functional groups this value is reduced (mainly due to defraction and to the fluorescence of additives) to $10^{-12°}$ mol/cm^2 which is about one functional group per 1000 carbon atoms of the outermost surface layer.

In our laboratory we use routinely fluorescence labelling techniques for the determination of hydroxyl, carboxyl, carbonyl, and amino group concentrations.

Other labelling techniques

With infrared reflection absorption spectroscopy of thin layers (100° nm or less) alterations in the surface region become accessible. Derivatization reactions can help to identify functional groups more precisely and they can gain information about secondary structures.

Contact angle goniometry probes a less than 1 nm thick surface region which is exactly the part of a material which determines the interaction with other phases and, therefore, is responsible for effects like wetting or adhesion. With derivatization reactions, the presence of a certain functional group can be detected by coupling long alkyl chains which cover a polar surface and effect a drop in the dispersive (Lifshitz -van der Waals) part of the surface free energy.

Examples

It is not only the concentration of a number of functional groups which can be measured by labelling techniques. In some cases it is also possible to determine the concentration of radicals and double bonds and to obtain additional information about the environment of a particular group. Some examples will demonstrate the power of this approach.

Hydroxyl groups and amines

The derivatization with trifluoroacetic anhydride (TFAA) is used for the quantification of hydroxyl groups. The concentration of this functional group can be calculated from the fluorine elemental concentration and from the fraction of the CF_3 carbon in the C1s spectrum. The carbon spectrum can reveal even more information. The binding energy of CF_3 carbon depends on the environment of the carbon atom the trifluoroacetate group is bonded to. Furthermore, if amines are reacted with TFAA, the CF_3 binding energy of the trifluoroacetamide is well separated from that of the corresponding ester.
This situation can be used to quantify hydroxyl groups and amines side by side.

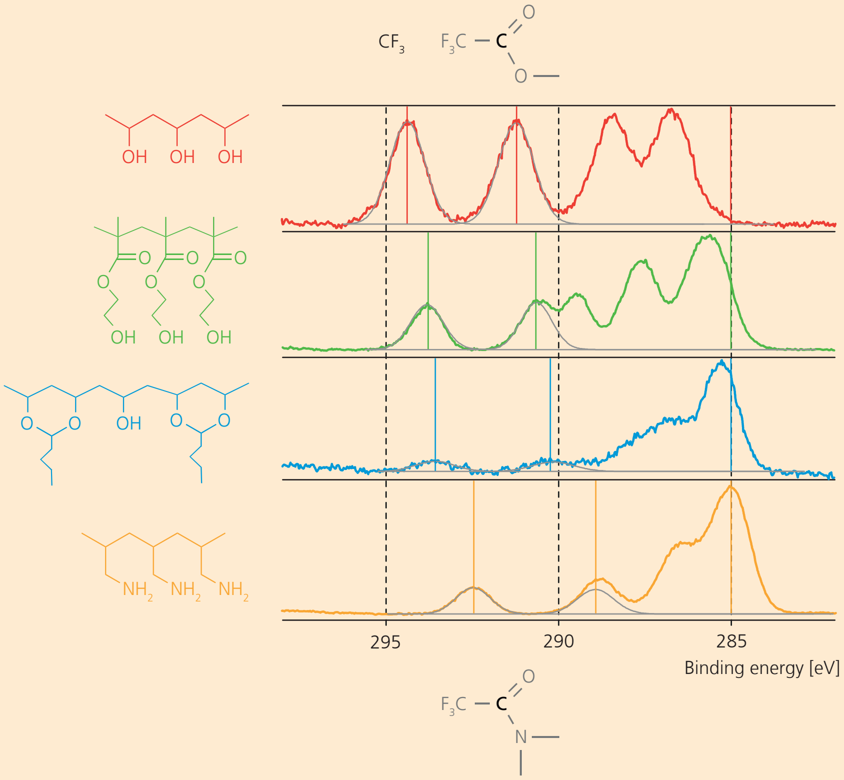

Fig. 2 C1s XPS of various OH polymers (poly(vinyl alcohol), poly(hydroxyethyl methacrylate, poly(vinyl butyral) and an NH polymer (poly(allylamin) which were derivatized with TFAA showing variations in the binding energy of similar structures. left: structure of original polymers.

Plasma treated polyethylene

The carbonyl groups at the surface were reacted with diaminoethane (DAE) and the XPS nitrogen concentration could be used to calculate the concentration of this functional group. Dansyl hydrazine (DHy) can be coupled in a very similar way. Its fluorescence represents the carbonyl groups concentration. The fluorescence dye fluram reacts selectively and quantitatively with primary amines. The determination of the DAE primary amino groups allows the direct comparison of the XPS and the fluorescence data. XPS has a detection limit in the order of tenths of atomic percents. The great advantage of fluorescence labelling comes into the play at very low concentrations.

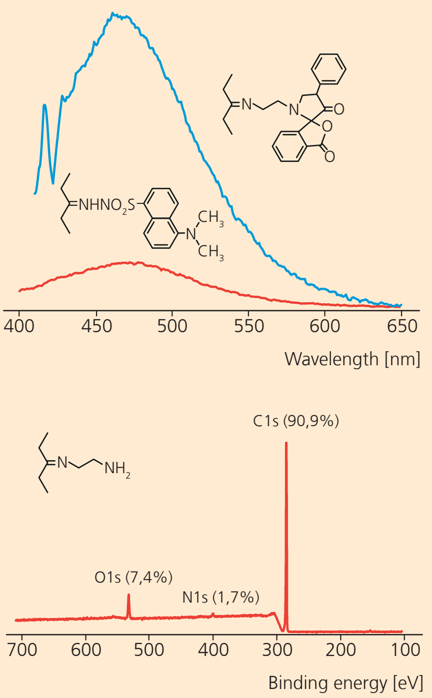

Fig. 3 Polyethylene treated with oxygen plasma. XPS after derivatization of carbonyls with DAE (below) and fluorescence spectra after labelling the carbonyls with DHy (green) and with DAE and fluram (red), respectively.

Stacked fluorescence labelling

On the surface of a hydrogen/ nitrogen plasma treated polyethylene one can find beside others amino groups and carbonyl groups. DHy couples to carbonyl groups while Fluram binds to primary amines. While the emission peaks of both dyes are at about the same wavelength (470 nm) they are excited at 350 nm (DHy) and 420 nm (Fluram), respectively, and can be distinguished clearly. The coupling and the fluorescence of both dyes is completely independent.

Reaction with	**Fluorescence intensity**	
	[-NH_2], kcps	[>C=O], kcps
Fluram	155 +/- 7	–
DHy	–	205 +/- 9
Fluram & DHy	159	212
DHy & Fluram	151	198

Double bond analysis

In the absence of oxygen functional groups, carbon-carbon double bonds react with bromine without side reactions. The chemical state imaging displays the lateral distribution of electrons with a selected binding energy. A copper grid as it is used for electron microscopy can be visualized by its Cu2p electrons. Such a grid was used as a mask during the irradiation of a poly¬ethylene film with vacuum-ultraviolet photons. The dark parts of the first picture (low copper concen¬tration) are light in the second picture where they stand for a higher bromine concentration.

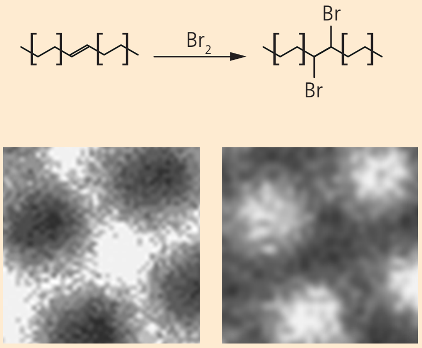

Fig. 4 Chemical state image of a copper grid (left, Cu2p at 932.6° eV) and a polyethylene film which was irradiated with vacuum-ultraviolet photons and then derivatized with bromine (right, Br3d at 67.1° eV). The lighter a pixel the higher the emission intensity of photoelectrons.