INELASTIC MEAN FREE PATHS OF PHOTOELECTRONS FROM POLYMER SURFACES DETERMINED BY THE XPS METHOD

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Dedicated to Academician O. Wichterle on the occasion of his 70th birthday.

Inelastic mean free paths were determined for a number of polymeric materials by using the X-ray photoelectron spectroscopy method. Some of the results obtained are confronted with other reported data; the majority have not been published yet.

A quantitative investigation of the surface of solids (surface composition, layer thickness, depth profiles) by the XPS method requires, among other things, also the knowledge of electron inelastic mean free paths (IMFP or λ) for the electron levels of elements which appear in the respective material. IMFP's provide information on the escape depth of electrons from the surface layer of the sample from which the signals of XPS spectra are recorded. For many materials the IMFP values have not yet been described; on the other hand, values reported for the same materials are often at considerable variance with each other[1-3].

In the field of polymeric materials, IMFP values have been reported only for a small number of polymers[4-9]. Moreover, the results differ greatly between themselves and are a subject of polemics between various teams. Papers published by Clark and coworkers[7-9] report IMFP values comparable with the IMFP's of metals and other inorganic materials which are measured more often. On the contrary, IMFP's of polymers reported by Cadman and coworkers[4-6] are much higher.

Several methods exist for the determination of IMFP of photoelectrons by means of XPS spectra. The commonest of them is the so-called overlayer method when the intensities of XPS signals from the surface layer of known thickness are compared with weakened signals from the support[7,10]. Another method for the determination of IMFP which avoids some experimental difficulties involved in the overlayer method consists in the determination of the intensities of XPS signals of sample and of the standard under identical experimental conditions[4,5,11,12]. The intensities thus determined are proportional to the concentration of emitted atoms, photoionization effective cross-sections and IMFP's of photoelectrons of these materials[4,5].

In this study which is a contribution to the investigation of polymer surfaces the IMFP values were determined for a number of polymers by employing the latter method[4,5].

EXPERIMENTAL

The XPS spectra were recorded with an ESCA 3 Mark II electron spectrometer manufactured by VG Scientific, using AlKα X-rays in vacuum in the range between 10^{-6} and 10^{-7} Pa. Films of polymers, purified and dried in a vacuum drying-box in advance, were fixed to the holder by means of a double-stick Scotch tape.

The same experimental conditions for recording the XPS spectra were provided by placing the sample and standard next to each other on a holder situated in the direction of the axis of the probe and by merely shifting the probe in this direction. A smooth gold plate, chemically purified and sputtered with argon ions, was the standard. The intensities of the XPS signals were determined by measuring the Au_{4f} doublet of the gold samples, and the levels of C_{1s}, F_{1s}, O_{1s}, N_{1s} of the other samples depending on their composition. The peak areas were estimated by planimetering. The intensities of the XPS signals were corrected for the transmission function of an electron analyzer $T(E)$ for which an approximate dependence $T(E) \sim E^{-1}$ was taken, where E is the kinetic energy of phootelectrons. The reference IMFP value of gold (Au_{4f}) $\lambda = 1{\cdot}5$ nm for the excitation with AlKα X-rays was determined by recalculating the value 1·4 nm used[4,11,12] in the excitation with MgKα by means of the dependence $\lambda \sim E^{1/2}$.

The real concentrations of atoms in the surface layer of the samples were used in the relation for IMFP calculations. These concentrations were calculated from the density of the materials determined pycnometrically and from the surface stoichiometry determined from XPS spectra (with the exception of polyethylene and polypropylene). Photoionization cross-sections according to Scofield[13] were used.

RESULTS AND DISCUSSION

Table I gives average IMFP values determined for the individual materials from several measurements. IMFP's reported for these materials and recalculated to the same electron kinetic energy values are used for comparison. In addition to the main results, some auxiliary values (ϱ, n) are given which had to be determined for the final calculation of IMFP, and values of the kinetic energy of electrons (E) to which the resulting λ values are to be attributed.

The surface stoichiometry of the individual polymers was found to differ from their theoretical composition (mainly for fluorinated polymers). These differences may be attributed to the surface contamination of the samples and to degradation likely to take place in the X-ray irradiation.

No marked processes of photoelectron energy losses were observed in the determination of the intensity of XPS signals, and it is assumed, therefore, that the effect of these losses may be neglected. Only in the case of polystyrene was the shake-up satellite typical of the aromatic carbon atom added to the intensity of the main C_{1s} peak.

The main problem met in the measurement of the intensities of XPS signals consists in the contamination of sample surfaces and in their topography (roughness). These unfavourable effects were minimized by measurements performed with an almost vertical direction of photoelectron emission from the sample surface. The surface contamination of gold with carbon and oxygen was investigated from the XPS spectra. Corrections of IMFP with respect to the contamination of the gold surface were calculated using the ratio of the intensity of C_{1s} contamination peaks to the intensity of Au_{4f} peaks on gold samples at various detection angles. Since the contaminating carbon is difficult to distinguish in polymers with the exception of teflon, one should be satisfied by assuming that the distortion of results due to contamination does not exceed 8%. The oxygen peaks in samples not containing oxygen were negligible.

TABLE I

IMFP (λ) values and other parameters of the investigated polymers: ϱ density, n concentration of atoms of the given element, E. L. electron level of the given element, E kinetic energy of photoelectrons of elements for the given electron levels

Polymer	ϱ g/cm³	$n \cdot 10^{21}$ cm⁻³	E.L.	E eV	λ nm
hd-Polyethylene	0·97	—	C_{1s}	1 197	[a]
ld-Polyethylene (PE)	0·92	39·5	C_{1s}	1 197	4·0[b]
Poly(vinyl fluoride) (PVF)	1·70	56·0	C_{1s}	1 194	2·2
		14·0	F_{1s}	793	1·8
Poly(vinylidene fluoride) (PVDF)	1·51	46·2	C_{1s}	1 191	2·4
		16·2	F_{1s}	792	1·9
Polytetrafluoroethylene (PTFE)	2·25	31·5	C_{1s}	1 190	2·7[c]
		51·4	F_{1s}	792	2·2
Polypropylene (PP)	0·90	38·6	C_{1s}	1 197	3·7
Polyamide 6 (PA)	1·15	40·0	C_{1s}	1 197	3·2
		4·1	N_{1s}	1 086	3·1
		6·8	O_{1s}	952	2·9
Poly(methyl methacrylate) (PMMA)	1·17	38·3	C_{1s}	1 197	3·0[d]
		11·4	O_{1s}	954	2·7
Polystyrene (PS)	1·03	47·4	C_{1s}	1 197	3·1[e]
Polyurethane[f] (PU)	1·13	36·0	C_{1s}	1 197	3·5
		2·6	N_{1s}	1 086	3·2
		11·0	O_{1s}	954	3·1
Polycarbonate[g] (PKB)	1·22	42·7	C_{1s}	1 197	3·2
		9·8	O_{1s}	954	2·9
Poly(ethylene terephthalate) (PET)	1·37	48·1	C_{1s}	1 197	2·5
		12·4	O_{1s}	952	2·2

[a–e] Values λ (nm): [a] 7·8 (ref.[4]), 1·2 (ref.[9]), 10·0 (ref.[14]); [b] 6·7, 7·9 (ref.[4]); [c] 1·0, 5·5, 6·7 (ref.[4]); [d] 2·9 (ref.[15]); [e] 6·9 (ref.[4]); [f] Adduct of 4,4'-methylenebis(phenyl isocyanate) with 1,3-trimethylenediol. [g] Poly[3-oxapentamethylene-1,5-bis(allyl carbonate)].

Fluctuation of the measured intensities of XPS signals was investigated by repeated measurement of XPS spectra of the same sample and of various samples of the same material. The estimated maximal error in the intensity measurement of XPS signals amounted to some 10%.

Substitution into the propagation of errors formula after an analysis of the maximal possible errors in the individual partial quantities led to a conclusion that the IMFP values thus determined might be subjected to a maximal total error up to 30%. The source of the greatest errors may consist in the use of theoretical values of the photoionization cross-sections (up to 20%) instead of the experimental ones[16], determination of the intensities of XPS signals (up to 10%) and determination of the surface concentrations of atoms (up to 10%). Basing on the reproducibility of measurements we assume, however, that the resulting error in the determined IMFP values is much lower than 30%.

The results summarized in Table I show that the λ values determined by us are much lower than those given by Cadman and coworkers[4]; on the other hand, Roberts and coworkers[14] obtained an almost identical result for $\lambda_{C_{1s}}$ of methyl methacrylate. If the polymer densities are compared with the λ values for electron levels of the individual elements, one can see that λ decreases with increasing polymer density. This finding is more distinctly illustrated in Fig. 1 which shows the dependence of λ for the C_{1s} electron levels of the individual polymers on their density. This dependence is a logical consequence of the fact that the density values contain both the supermolecular structure of polymers and the total concentration of all atoms, *i.e.* quantities which affect considerably the magnitude of IMFP. As can be seen in Fig. 1, the only essential deviation from this dependence is the $\lambda_{C_{1s}}$ value determined by us for PTFE. The cause of such a high value may consist in the considerably rough surface of our PTFE samples which generally characterizes these polymers. On the other hand, the $\lambda_{C_{1s}}$ value for PTFE determined by D. T. Clark and H. R. Tho-

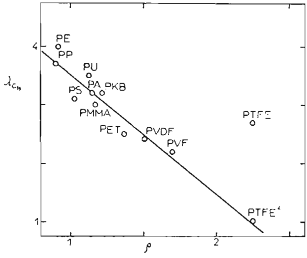

FIG. 1

The dependence of $\lambda_{C_{1s}}$ (nm) on polymer densities (gcm^{-3}). Symbols of polymers *cf.* Table I mas (taken from the Table given by Cadman and coworkers[4]) fits the dependence very well. Using the determined $\lambda_{C_{1s}}$ value (with a reported[4] $\lambda_{C_{1s}} = 1{\cdot}0$ nm substituted for PTFE), polymer densities and the method of linear regression, an empirical equation

$$\lambda_{C_{1s}} = -2{\cdot}043\varrho + 5{\cdot}556\,,$$

was calculated, with the correlation factor being 0·969. This equation allows us to obtain the first estimate of IMFP for the C_{1s} electron levels, if the polymer density is known. A similar λ *vs* ϱ dependence is also observed with the O_{1s} and F_{1s} electron levels, but general empirical equations cannot be derived for these elements because of the small number of data.

The results of our measurements show that the IMFP's of polymers determined by the method of comparison of the intensities of XPS signals of the samples and of the standard are comparable with the IMFP's determined by the overlayer method.

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