Hydrogen detection and quantification at polymer surfaces investigated by elastic peak electron spectroscopy (EPES)

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ARTICLE INFO

ABSTRACT

The elastic peak electron spectroscopy (EPES) combined with the electron single scattering model calculations is applied for detecting and quantifying hydrogen at a surface region of selected polymers: polyethylenes (low, high densities and ultra high molecular weight – PELD, PEHD, PEUHMW), polypropylene – PP, polystyrene – PS, and poly[methyl(phenyl)silylene] – PMPSi. The physics under the procedure is based on an electron quasi-elastic scattering on a target atom (a recoil effect). The photoelectron C 1s and Auger electron C KLL spectra induced by Mg Kα radiation (1253.6 eV) are used for characterization of the polymer surfaces' damage produced by incident electron irradiation when applying the EPES method. The polymer surfaces irradiated with low electron dose revealed hydrogen content and C sp^2/sp^3 ratio close to the nominal values. Ongoing electron irradiation led to the hydrogen content decrease and the C sp^2 percentage growth. The effect of surface charging on the recoil effect is also discussed.

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1. Introduction

In the present days, it has become highly desirable to develop an alternative energy sources. As a promising route, the hydrogen storage in convenient solid materials is considered [1,2]. Consequently, there is a need for reliable experimental methods for quantitative determination of the hydrogen content in different solids. There are several methods applied for this purpose, i.e. the elastic recoil detection analysis (ERDA), the nuclear reaction analysis (NRA), the nuclear magnetic resonance (NMR), the infrared spectroscopy (IR), the secondary ion mass spectroscopy and the thermal desorption. It has been recently shown that the surface sensitive electron spectroscopy can be also used for detecting and quantifying the hydrogen in a surface region of a solid. Particularly, the electron energy loss spectroscopy in a high-resolution mode (HREELS) [3,4] or the near edge X-ray absorption spectroscopy [5] is able to identify the hydrogen content at solid surfaces. The elastic peak electron spectroscopy (EPES), currently applied for the inelastic mean free path determination [6], seems to be also the promising method for surface hydrogen detection and quantification in selected solids [7–15]. In EPES spectroscopy the primary electron undergoes the quasi-elastic scattering called a recoil effect, where its quasi-elastic energy loss depends on the atomic mass of the scattering atom. Due to the difference in recoil effects on

hydrogen and, for example, on carbon atoms, the recorded elastic peak is splitted up to several electron volts, depending on the primary electron kinetic energy and the scattering angle. Orosz et al. [7] and Varga et al. [8] have found experimental conditions for successful detection of hydrogen in polyethylene. For electron energy of 2000 eV and the scattering angle of 105°, the recoil shift between carbon and hydrogen elastic peaks reached about 3 eV. The two elastic peaks can be easily measured and resolved by electron spectrometers. A phenomenological sensitivity factor approach for elastic electron backscattering was applied by Yubero et al. [9] and Rico et al. [10].

However, the majority of polymers and materials containing hydrogen are sensitive to electron beam [16]. In such materials, the electron beam results in bond scission, hydrogen depletion from the sample analyzed region and carbonization [16]. These effects can be minimized by optimizing the primary electron beam conditions, such as electron kinetic energy, the beam current and the beam current density. The characterization of C atom bond hybridization in carbon containing materials may proceed by X-ray photoelectron spectroscopy (XPS), X-ray induced Auger electron spectroscopy (XAES) or Auger electron spectroscopy (AES). The methods include resolving of the C 1s spectra into component referring to sp^2 and sp^3 C bonds, and estimating the parameter D from the C KLL first derivative spectra, which allow to estimate the ratio of C atom sp^2/sp^3 hybridizations. As reported elsewhere, the binding energy shift between C sp^2/sp^3 components in C 1s photoelectron line is 0.9 eV [17]. The parameter D, defined as the kinetic energy difference between the maximum and the minimum

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of the Auger C KLL first derivative spectra, has been already measured for amorphous carbon structures containing hydrogen [18,19], diamond films prepared under different deposition conditions (CH_4 pressure and temperature) [20,21], graphite [20,21] and a mixture of co-polymer polyethylene–polystyrene [22]. Considering the values of parameter D for extreme cases, i.e. sp^3 bonded diamond and sp^2 bonded graphite, the linear interpolation of D values allows to determine the fraction of sp^2/sp^3 C bonds [18–21]. The values of parameter D reported in the literature for diamond and graphite varied between 13.0 eV–14.5 eV and 22.6 eV–22.8 eV, respectively [18,20,21]. For polymers, the linear interpolation between 100% sp^3 bonded polyethylene and 25% sp^3 bonded polystyrene, where values of parameter D were 13.4 eV and 16.0 eV, respectively, was found more convenient [22]. However, the information depth of XPS, XAES/AES and EPES methods in polymers defers since it depends on the applied experimental technique and the investigated electron kinetic energy [23].

The present study is part of ongoing effort to understand the recoil effects in hydrogen containing materials and the hydrogen evolution at their surfaces due to electron beam induced effects. We present XPS, XAES and EPES analyses on mechanically cleaned polyethylene (low density, high density and ultra high molecular weight), polypropylene, polystyrene and poly[methyl(phenyl)-silylene] surfaces. The experimental data are compared to the theoretical results applying in calculations a model of a large angle single elastic backscattering of electron.

2. Model calculations

2.1. Hydrogen content from electron recoil effect in EPES

The evaluation of hydrogen content at the surface from the EPES spectra is based on the phenomena called the electron recoil from an atom, in which electron scattering from atoms of different atomic number, Z, undergoes the recoil energy loss broadening [24]. The electron energy loss depends on the atomic number, Z, of the recoiled atom, the mass of the scattered particle, its kinetic energy, the geometry of analysis and the temperature [24]. The recorded elastic peak splits into components of different recoil energy shift and broadening. Within the classical model of electron elastic scattering on an atom, the energy transferred to an atom, i.e. the recoil energy shift, E_r, is expressed as:

$$E_r = \frac{4m}{M} E_k \sin^2\left(\frac{\theta}{2}\right), \tag{1a}$$

and a full width at half maximum (FWHM), ΔE_r, as:

$$\Delta E_r = 8\sin\left(\frac{\theta}{2}\right)\sqrt{\frac{m}{M}E_k kT \ln 2}, \tag{1b}$$

where m is the mass of electron, M is the mass of the scattering atom, θ is the scattering angle (the angle between the direction of the primary beam and the direction towards the analyzer), E_k is the electron primary kinetic energy, k is the Boltzmann constant and T is the temperature [24]. It was shown that for selected number of elemental solids, the classical model of quasi-elastic scattering based on electron single scattering remains in agreement with a model of electron multiple scattering [25,26].

The simple theoretical model of elastic backscattering is based on the assumption that an electron undergoes only one large angle elastic scattering event occurring along the trajectories and then enters the analyzer. Other elastic collisions are not significant. If the large angle elastic collision occurs at a depth, z, then the probability that an electron reaches the analyzer without energy loss is proportional to:

$$\xi(z, \alpha_{out}, \alpha_{in}) \propto \exp\left[-\frac{z}{\lambda_{in}}\left(\frac{1}{\cos\alpha_{in}} + \frac{1}{\cos\alpha_{out}}\right)\right], \tag{2}$$

where $\xi(z, \alpha_{out}, \alpha_{in})$ is the penetration depth distribution function, λ_{in} is the electron inelastic mean free path (IMFP) [6,27], α_{in} is the primary electron incidence angle with respect to the surface normal and α_{out} is the backscattered electron emission angle with respect to the surface normal [23]. If the solid acceptance angle of the analyzer, $\Delta\Omega$, is small, then Eq. (2) can be generalized to:

$$\eta(\Delta\Omega) = M_a \lambda_{in} \Delta\Omega \frac{d\sigma_e}{d\Omega} \frac{\cos\alpha_{in}\cos\alpha_{out}}{\cos\alpha_{in} + \cos\alpha_{out}}, \tag{3}$$

where η, is the electron backscattering probability [6], M_a is the atomic density, i.e. the number of atoms per unit volume, and $d\sigma_e/d\Omega$ is the differential backscattering cross-section taken from the NIST database [28].

For a given geometry of the measurement and the primary energy of electron, considering the differential backscattering cross-sections [28] for constituents of the sample, the ratios of backscattering probabilities of different contributions in the investigated samples, i.e. C and H atoms, (η_C and η_H), as a function of hydrogen percentage, x, can be estimated from the equation:

$$\frac{\eta_H}{\eta_C} = \frac{(d\sigma_e/d\Omega)_H x}{(d\sigma_e/d\Omega)_C (100 - x)}, \quad \text{where } 0 \le x < 100. \tag{4}$$

2.2. Information depth in XPS and EPES

The information depth (ID) for XPS and AES is defined as the maximum depth, normal to the surface, from which a specified percentage (e.g. 95% or 99%) of detected signal originates, whereas the respective mean escape depth (MED) of electron is defined as the average depth normal to the surface from which the specified particle escapes [29]. The value of MED is evaluated from the emission depth distribution function, which defines the probability that the particle leaving the surface in a given direction originates from the specified depth measured normally from the surface. For a single scattering event, if elastic scattering is neglected, the value of MED can be estimated from simplified equation [30]:

$$\text{MED} = \lambda_{in}\cos\alpha_{out}, \tag{5}$$

where λ_{in} is the electron IMFP in a considered material taken from the NIST database of IMFPs [27].

In the EPES spectroscopy, the information depth is defined as a maximum depth from which a specified percentage (e.g. 95% or 99%) of the detected signal originates [30]. These depths are distributed with a probability density function called the penetration depth distribution function, defined as the probability that an electron incident on the surface at an angle α_{in} will be elastically backscattered from a maximum depth, z, and emitted in a direction of the analyzer at an angle, α_{out}, and not to be inelastically scattered [30]. The mean penetration depth (MPD) of elastically backscattered electron can be estimated from a simplified equation:

$$\text{MPD} = \lambda_{in}\cos\alpha_{out}\frac{\cos\alpha_{in}}{\cos\alpha_{in} + \cos\alpha_{out}}. \tag{6}$$

3. Experimental

3.1. Materials

Low density, high density, and ultra high molecular weight polyethylene (PELD, PEHD, PEUHMW), polypropylene (PP), and

polystyrene (PS) samples purchased from GoodFellow (UK) were investigated as "ex situ" mechanically cleaned by a finishing cutter surfaces.

Poly[methyl(phenyl)silylene] was prepared by Wurtz coupling polymerization, as described by Zhang and West [31]. The low-molecular weight fractions were extracted with boiling diethyl ether. Thin films were prepared from a toluene solution by casting on silicon and Au covered silicon substrates under protecting He atmosphere in a small preparation chamber attached to a photo-electron spectrometer. Thickness of films reached about 20 nm.

3.2. Measurement

The EPES and XPS spectra were recorded with an angle-resolved photoelectron spectrometer ADES 400 (VG Scientific, UK) equipped with an electron gun (Varian, model 981-2455), Mg Kα and Al Kα excitation sources and a rotatable hemispherical electron energy analyzer. During EPES measurements, the electron-beam incidence angle was normal to the sample surface. The emission angle was set to 35° from the surface normal. The EPES spectra were recorded using a defocused electron beam of energy of 1500 eV and 2000 eV, the beam current of 1×10^{-6} A, and a spot diameter at the sample surface of 3 mm. The elastically backscattered electrons were collected at pass energy of 20 eV within a small conical analyzer acceptance angle of $\pm 4°$. Typical width of the elastic peak was about 0.5 eV (FWHM).

Before and after measurements of EPES spectra, the C 1s photoelectron and C KLL Auger spectra were recorded using Mg Kα radiation.

4. Results

4.1. Hydrogen content from EPES

The EPES experiments were performed on clean polymer surfaces. No oxygen contaminations were found from the XPS measurements. The geometry of EPES measurement is shown in Fig. 1.

To evaluate the surface hydrogen content, the EPES spectra were fitted to Gaussian peaks assuming the peak separation and full width at half maximum (FWHM) for H and C (Si in case of PMPSi sample) contributions, as resulting from the classical model of the electron recoil (Eq. (1)). Exemplary illustration of fitting of the EPES spectrum recorded from PELD surface at electron kinetic energy of 2000 eV and electron dose of 2.8 Cm^{-2} is shown in Fig. 2. The atomic percent of surface hydrogen measured using the EPES
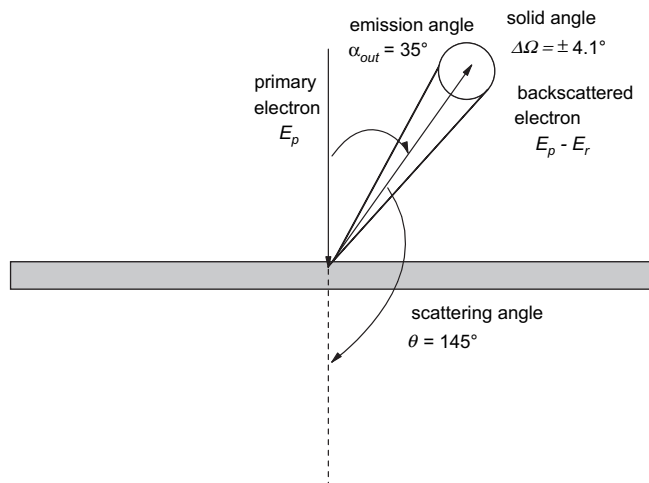

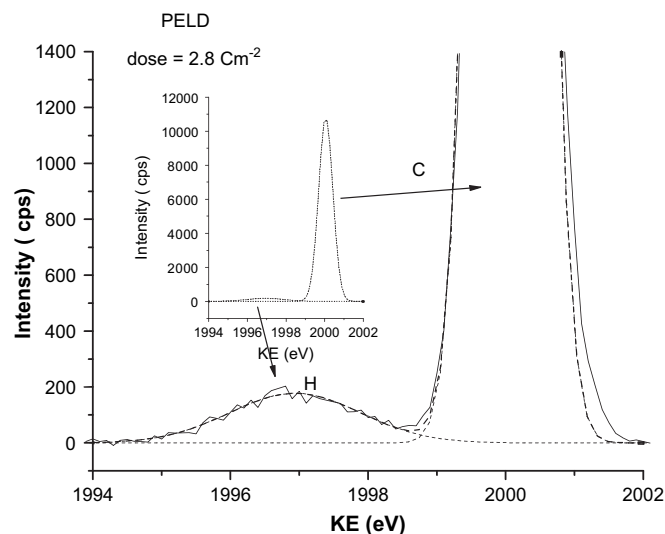Fig. 1. The electron scattering geometry in the EPES experiment.

Fig. 2. The exemplary fitting of Gaussian peaks to elastic peak contributions due to the electron recoil effect on H and C atoms recorded from low density polyethylene (PELD) at the electron kinetic energy of 2000 eV and the scattering angle of 145°.
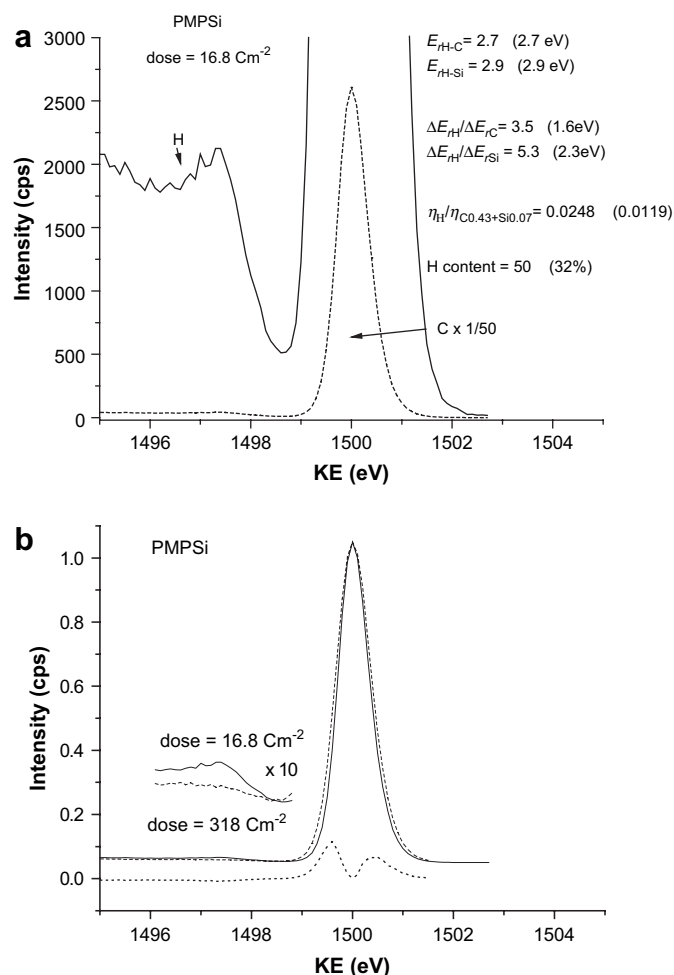

Fig. 3. The EPES spectra recorded from poly[methyl(phenyl)silylene] (PMPSi) at the electron kinetic energy of 1500 eV and the scattering angle of 145°. The elastic peak contributions due to the electron recoil effect on H and C atoms are indicated. (a) The irradiated surface at an electron dose of 16.8 Cm^{-2} (spectra acquisition), the theoretical and the experimental (in the bracket) values of the electron recoil shifts, the ratio of FWHMs, the ratio of intensity contributions and the atomic content of H are compared. (b) Comparison of spectra recorded from surfaces electron irradiated at different doses. Solid line: electron dose of 16.8 Cm^{-2}; dashed line: electron dose of 318.0 Cm^{-2}; dotted line: subtracted spectra.

Table 1
Comparison of theoretical and experimental parameters resulting from the electron recoil effect on H and C atoms

Sample/E_k (eV)/ dose (Cm^{-2})	Theory				Experiment			
	$E_{r\ H-C(Si)}$ (eV)	$\Delta E_{r\ H}/\Delta E_{r\ C(Si)}$	$\eta_H/\eta_{C(+Si)}$	H (Si) (at.%)	$E_{r\ H-C(Si)}$ (eV)	$\Delta E_{r\ H}/\Delta E_{r\ C(Si)}$	$\eta_H/\eta_{C(+Si)}$	H (Si) (at.%)
PELD 2000								
2.8	3.6	3.5	0.0487	67	3.1 ± 0.1	2.6 ± 0.2	0.0427 ± 0.0045	64
42.4					2.3 ± 0.1	2.0 ± 0.2	0.0290 ± 0.0051	55
527.3					1.5 ± 0.1	0.9 ± 0.2	0.0099 ± 0.0035	32
PEHD 2000								
3.2	3.6	3.5	0.0487	67	2.9 ± 0.1	2.5 ± 0.2	0.0428 ± 0.0045	64
32.4					2.2 ± 0.1	1.9 ± 0.2	0.0273 ± 0.0050	53
77.3					2.0 ± 0.1	1.7 ± 0.2	0.0242 ± 0.0039	50
101.6					2.0 ± 0.1	1.6 ± 0.2	0.0244 ± 0.0045	50
PEUHMW 2000								
2.0	3.6	3.5	0.0487	67	2.9 ± 0.1	2.7 ± 0.2	0.0480 ± 0.0041	67
36.0					2.2 ± 0.1	1.9 ± 0.2	0.0278 ± 0.0047	54
112.8					1.8 ± 0.1	1.3 ± 0.2	0.0176 ± 0.0042	42
PP 1500								
1.6	2.7	3.5	0.0470	67	1.7 ± 0.1	1.4 ± 0.2	0.0176 ± 0.0050	43
3.2					1.3 ± 0.1	0.8 ± 0.2	0.0064 ± 0.0048	22
PS 1500								
0.4	2.7	3.5	0.0231	50	1.6 ± 0.1	1.2 ± 0.2	0.0150 ± 0.0043	40
2.0					1.4 ± 0.1	0.7 ± 0.2	0.0063 ± 0.0045	21
PMPSi 1500								
16.8	2.7 (2.9)	3.5 (5.3)	0.0248	43 (7)	2.7 ± 0.1 (2.9 ± 0.1)	1.6 ± 0.2 (2.3 ± 0.2)	0.0119 ± 0.0010	32 (7)
318.0					2.7 ± 0.1 (2.9 ± 0.1)	1.6 ± 0.2 (2.3 ± 0.2)	0.0035 ± 0.0006	13 (7)

The EPES spectra are recorded at the kinetic energy, $E_k = 1500$ eV and 2000 eV, and the scattering angle, $\theta = 145°$. The values in the bracket refer to Si in PMPSi.

method was estimated from the experimental intensity ratios of H and C (Si) elastic peak contributions and evaluated dependencies assuming a classical model of large angle electron single scattering (Eq. (4)). Exemplary comparison of predicted theoretical and experimental values of the energy recoil loss, the ratio of broadening, the ratio of H, C (Si) intensity contributions and the hydrogen atomic percentage for PMPSi polymer is shown in Fig. 3(a). Comparison of the EPES spectra recorded from PMPSi polymer at electron doses of 16.8 Cm^{-2} and 318 Cm^{-2} is shown in Fig. 3(b). Comparison of elastic peak parameters due to electron recoil effect, resulting from calculation and experiment, for unirradiated and electron irradiated at various doses surfaces of polyethylenes, PP, PS and PMPSi is shown in Table 1.

4.2. C atom sp^2/sp^3 hybridizations from XPS/XAES

Comparison of C atom sp^2/sp^3 hybridization fractions at the surface of polymers unirradiated and submitted to different electron doses is shown in Table 2. These fractions were obtained by applying XAES C KLL first derivative and XPS C 1s spectra. For evaluating the value of parameter D and sp^2 content the linear interpolation for mixture of polyethylene–polystyrene co-polymer was applied, where the value of D for 100% of sp^3 hybridization polyethylene was 13.4 eV and for 75% of sp^2 hybridization polystyrene was 16.0 eV [22]. The additional results of C sp^2 and sp^3 hybridization fractions obtained from fitting C 1s XPS spectra to two Gaussian–Lorentzian peaks are also listed in Table 2. The values in bracket refer to FWHMs of fitted Gaussian–Lorentzian contributions, assuming C 1s sp^2 and sp^3 C bond separation to be equal to 0.9 eV [17,19].

4.3. Information depth of EPES and XPS/XAES

Comparison of IMFP values, mean escape depths for XPS/XAES and mean penetration depths for EPES at electron kinetic energy of 1500 eV and 2000 eV is shown in Table 3. The values of the IMFP were evaluated from the NIST database [27] using the TPP-2M predictive formula by Tanuma et al. The values of MED and MPD

were evaluated by assuming a large angle electron single scattering from Eqs. (5) and (6), respectively.

5. Discussion

The experimental results of EPES method for PMPSi polymer remain in a reasonable agreement, indicating predicted theoretically recoil energy shift between H–C and H–Si contributions (Fig. 3(a)). However, the experimentally measured ratio of energy broadening is smaller. Also, the evaluated hydrogen atomic percentage indicates its deficiency, although the EPES spectra were recorded for low electron dose.

Table 2
Comparison of the parameter D (from the XAES C KLL first derivative spectra) and the fraction of C atom sp^2/sp^3 hybridizations (from fitting of C 1s spectra) in polymers at various electron doses

Sample	Dose (Cm^{-2})	C KLL		C 1s	
		Parameter D (eV)	sp^2 (%)	284.2 (eV) sp^2 (%)	285.1 (eV) sp^3 (%)
PELD	0	13.2	0	0	100 (2.6)
	42.4	16.4	87	78 (2.3)	22 (2.7)
	527.3	16.8	98	81 (2.3)	19 (2.7)
PEHD	0	12.8	0	0	100 (2.6)
	32.2	15.2	52	61 (2.2)	39 (2.7)
	101.6	16.0	75	81 (2.3)	19 (2.7)
PEUHMW	0	13.6	6	0	100 (2.6)
	36.0	15.6	63	52 (2.1)	48 (2.5)
	112.8	16.4	87	81 (2.3)	29 (2.7)
PP	0	13.6	6	5 (2.3)	95 (2.5)
	100	15.2	52	53 (2.3)	47 (2.7)
	200	16.0	75	78 (2.5)	22 (2.8)
	300	16.0	75	76 (2.4)	24 (2.6)
PS	0	15.7	66	77 (2.6)	23 (2.6)
	100	16.0	75	75 (2.4)	25 (2.5)
	200	16.0	75	77 (2.4)	23 (2.9)
	300	16.7	95	85 (2.5)	16 (2.9)

The values in the bracket refer to the full width at half maximum (FWHM) of C 1s spectra.

Table 3
Comparison of the electron inelastic mean free path (IMFP), the mean escape depth (MED) in XPS/XAES analyses and the mean penetration depth (MPD) in the EPES analysis of polyethylene, assuming a large solid angle single electron scattering and the electron backscattering cross-sections from the NIST database

Analysis	Spectra	E_k (eV)	IMFP (Å)	MED (Å)	MPD (Å)
XAES	C KLL	272	13.3	13.3	
XPS	C 1s	980	33.7	33.7	
EPES	EPES	1500	47.3		21.3
		2000	59.8		26.9

For polyethylenes (PELD, PEHD and PEUHMW), PS and PP, the predicted values of the recoil energy shift between elastic peak contribution C–H are larger than the measured (Table 1). This also refers to the values of width ratios for all polymers (Fig. 3(a), Table 1). With increasing electron dose, the decrease of the recoil energy shift between C–H contributions and the width ratios are observed (Table 1).

At small electron dose, for polyethylene samples, atomic percent content of surface hydrogen is nearly approaching the nominal composition (Table 1). With increasing electron dose, the hydrogen content decreases (Fig. 3(b), Table 1). For PP, PS and PMPSi at low electron dose hydrogen deficiency is observed, what may be related with easier polymer degradation under electron irradiation during the EPES spectra acquisition. Then, for all samples the hydrogen deficiency increases under electron irradiation. Polyethylenes seem to be more stable under electron irradiation than PP, PS and PMPSi.

The values of parameter D, allowing for estimating percentage of C atom sp^2/sp^3 hybridizations from the Auger C KLL first derivative spectra, indicate that for unirradiated polymers nominal content of sp^2/sp^3 bonds is observed (Table 2). At this stage, polyethylenes and PP, show mainly sp^3 C hybridizations and parameter $D = 13.2$ eV, whereas PS about 77% of sp^2 and parameter $D = 15.7$ eV. The nominal percentage of sp^2 C bonds in undamaged PS is 75%, whereas the value of parameter D reported in the literature is 16.0 eV [22]. With increasing electron dose the values of parameter D increase, indicating the increasing content of C sp^2 hybridizations, and then the polymer degradation, graphitization and carbonization.

The results of C 1s spectra fitting to two Gaussian–Lorenzian components, referring to sp^2 and sp^3 C hybridizations defer slightly quantitatively from results obtained using D parameter (Table 1). At unirradiated surfaces of polyethylenes and PP polymer mainly sp^3 hybridizations are observed. For unirradiated PS polymer fitting results indicate the percentage of sp^2 and sp^3 bonds close to the nominal stoichiometry. Under irradiation, sp^2 C hybridization content increases, more rapidly for polyethylenes and PP than for PS. For PS no large changes are observed under electron dose (both, in D parameter and C 1s contributions). The increase of sp^2 C bond fraction under electron irradiation indicating degradation, graphitization and carbonization (Table 2) is correlated with decrease of hydrogen content (Table 1). However, the percentage of hydrogen in polymers exhibiting fraction of sp^2 C bonds between 75% and 98% is not negligible.

The presented results are not quantitatively consistent due to several reasons. The theoretically predicted values of the electron recoil energy shift and broadening are obtained using a classical approach applying an electron large angle single scattering model. The EPES and XAES/XPS experimental data and the fitting procedure applied to all the spectra contain statistical and systematic errors. The experiments are recorded from different information depths, depending on the considered transition and electron kinetic energy (Table 3). The most surface information is obtained from C KLL spectra using D parameter, whereas the information obtained from C 1s spectra and EPES spectra at 2000 eV is closer to each other and nearly three times larger (Table 3).

However, the main reason of discrepancies between EPES experimental and theoretical results is caused by surface charging of polymer samples (Table 1). This is especially valid for polyethylenes, PP and PS, whereas it is not a case of thin layer of PMPSi on Si. Electron irradiation induces the charging effect of the surface. This influences the binding energy shift of the XPS C 1s transitions and the EPES spectra recoil energy shift and broadening. For PMPSi the theoretical values of the recoil energy shift for H, C and Si elastic peak components obtained from Eq. (1a) approach the respective experimental values and equal to 2.7 eV and 2.9 eV, respectively. The ratios of widths obtained experimentally are smaller than the values predicted by Eq. (1b), however, they remain constant with an electron dose. For polyethylenes, PP and PS the values of the electron recoil shift and the width ratio decrease with an electron dose what is related with the insulating properties of samples (Table 1). Similar case, where the experimentally obtained energy separation and the width ratio were smaller than the predicted, was observed for the EPES measurements at polyethylene surface at electron kinetic energy of 15 keV and 40 keV [15]. This effect was attributed to the charging effect of the sample surfaces caused by an incident electron beam, resulting in deaccelerating the incident electrons which then scattered quasi-elastically at smaller kinetic energy.

6. Conclusions

The methods applied for investigating the polymer unirradiated and electron irradiated surfaces applying EPES, XAES/XPS spectra were found to be convenient for evaluating the surface sp^2/sp^3 C bond hybridization fraction and hydrogen percentage. The results obtained using different methods were found qualitatively consistent. Quantitative discrepancies result from different information depths of applied methods. The surfaces of unirradiated polymers exhibited C sp^3 hybridization content and hydrogen percentage close to the nominal stoichiometry. Under electron irradiation increasing C sp^2 content and decreasing hydrogen content were observed. The graphitization of polymers, which is obtained in the sample containing about 100% of sp^2 C bonds, does not exclude existence of surface hydrogen. Differences between predicted and experimental values of the electron recoil shift and broadening in the EPES spectra of polyethylenes, PP and PS occur due to charging properties of insulating surfaces, resulting in deaccelerating of incident electrons, what may be applied for evaluating the surface potential. Better agreement between predicted and experimental values of the electron recoil shift is observed for the PMPSi thin overlayer grown on the semi-conducting silicon substrate.

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