in order to clarify the mechanism of WC formation. The present study shows that the free carbon which accumulates on the WO_x ($x \leqq 3$) surface by the disproportionation of CO contributes to the carburization of WO_3. The carburization process seems to be based on a direct reaction of WO_x with the free carbon. It can also be concluded that WC is formed according to processes (a)–(e). The processes are summarized as follows: (a) the disproportionation of CO and the onset of the deposition of free carbon, (b) the initial stage of WC formation, (c) the formation of free carbon layer, (d) the maximum rate of WC formation, and (e) the deposition of graphite-like carbon on WC.

Acknowledgements

We would like to thank Drs. S. Yamamoto, T. Kudo and G. Kawamura for their useful discussions. We further acknowledge Drs. M. Ogirima and F. Nagata for their encouragement and helpful suggestions during this work.

References

[1] L.E. Toth, Transition Metal Carbides and Nitrides (Academic Press, New York, 1971).
[2] R.B. Levy and M. Boudart, Science 181 (1973) 547.
[3] L. Ramqvist, K. Hamrin, G. Johansson, A. Fahlman and C. Nordling, J. Phys. Chem. Solids 30 (1969) 1835.
[4] L.H. Bennet, J.R. Cuthill, A.J. McAlister, N.E. Erickson and R.E. Watoson, Science 184 (1974) 563; 187 (1975) 858.
[5] J.E. Houston, G.H. Laramore and R.L. Park, Science 185 (1974) 258.
[6] R.J. Colton, J.J. Huang and J.W. Rabalais, Chem. Phys. Letters 34 (1975) 337.
[7] P.N. Ross and P. Stonehart, J. Catalysis 39 (1975) 298; 48 (1977) 42.
[8] G. Schulz-Eleloff, D. Baresel and W. Sarholz, J. Catalysis 43 (1976) 353.
[9] V.SH. Palanker, R.A. Gajev and D.V. Sokolsky, Electrochim. Acta 22 (1977) 133.
[10] R. Miles, J. Chem. Tech. Biotechnol. 30 (1980) 35.
[11] J.T. Yates, Jr., T.E. Madey and N.E. Erickson, Surface Sci. 43 (1974) 257.
[12] P.M. Stefan, C.R. Helms, S.C. Perino and W.E. Spicer, J. Vacuum Sci. Technol. 16 (1977) 577.
[13] E.I. Ko, J.B. Benziger and R.J. Madix, J. Catalysis 62 (1980) 264.
[14] M. Nakazawa and H. Okamoto, Appl. Surface Sci. 24 (1985) 75.
[15] K.J. Carter, G.K. Schweitzer and T.A. Carlson, J. Electron Spectrosc. Related Phenomena 5 (1974) 827.

Applied Surface Science 27 (1986) 93–105
North-Holland, Amsterdam

SURFACE ANALYSIS OF POLYMERS END-CAPPED WITH METAL CARBOXYLATES USING X-RAY PHOTOELECTRON SPECTROSCOPY

R. JEROME, Ph. TEYSSIE

Laboratory of Macromolecular Chemistry and Organic Catalysis, University of Liège, Sart Tilman, 4000 Liège, Belgium

J.J. PIREAUX * and J.J. VERBIST

Laboratoire de Spectroscopie Electronique, Facultés Universitaires de Namur, 5000 Namur, Belgium

Received 20 March 1986; accepted for publication 10 June 1986

X-ray photoelectron spectroscopy is an efficient tool to determine how the metal carboxylate groups of halato-telechelic polymers are distributed in moving from the surface to the bulk of the host polymer. Depending on the nature and structure of both the polymeric matrix and the metal carboxylate end-groups, the surface layer of bulk halato-telechelic polymers can exhibit a continuum of situations going from a high depletion to an enrichment in metal carboxylates compared to the theoretical composition. When an excess of metal atoms is observed in the surface region, these atoms are present at a depth of a few tens of Å below the very surface. Finally, when an excess of Zr or Ti alkoxide is used to neutralize α,ω-dicarboxylic acid polymers, the hydrolysis of the unreacted alkoxide groups do promote the formation of carboxylato metal oxohydroxide aggregates.

1. Introduction

The surface structure and properties of polymers are of prime importance in determining their suitability for applications such as coatings, adhesives, films and fibers. Hydrophilic modifications of nonpolar polymers is required to impart them adhesion, wetting, coating, printability and antistatic properties. Conversely, hydrophobic modification of polar polymers is the best way to improve water repellency, and frictional properties. Block and graft copolymers provide an efficient means of controlling the surface properties by the preferential surface accumulation of one segment. For instance, the surfaces of poly(styrene-b-dimethylsiloxane) generally resemble pure polydimethylsiloxane [1]. Similarly, a short perfluorinated segment (C_8F_{17}–) attached at one end of a polyester concentrates at the air/solid interface, giving an fluorocarbon-like surface [2]. In the same way, the surface of polymers containing

---

* Research Associate of the Belgian National Fund for Scientific Research.

0169-4332/86/$03.50 © Elsevier Science Publishers B.V.
(North-Holland Physics Publishing Division)

small amounts of suitable block or graft copolymers can be modified by the accumulation of either hydrophilic or hydrophobic segments depending on the processing conditions [3].

Ion containing polymers, or ionomers, deserve now an increasing attention. The introduction of a few percent ions into traditional low-polarity polymeric materials is responsible for dramatic changes in the properties of the base polymer and for new ranges of applications [4]. A few years ago, du Pont de Nemours and Co commercialized an ion-containing polyethylene, or Surlyn, which enjoys improved stiffness, toughness, oil and abrasion resistance, while being still processable. That behavior results from the thermoreversible aggregation of the metal (Na or Zn) carboxylates attached to the polyethylene backbone. In ionomers, the ion aggregation process is however expected to be hindered to some extent by the entanglements of the polymeric segments onto which the ion pairs are randomly attached. This situation could be improved by selectively attaching the ion pairs (metal carboxylates) at both ends of linear chains resulting in a greater freedom to associate and possibly to migrate in the materials (especially above the glass transition temperature) [5–7]. Polymers carrying a metal carboxylate at each chain-end have been purposely synthesized and dubbed "halato-telechelic polymers" (HTP's). For sake of clarity, the Greek word "halato" means salt-like, whereas the word "telechelic" derives from the Greek "tele", far off, and "chele", claw, and commonly designates linear polymers having two reactive terminal groups. It is of great interest to evaluate to which extent HTP's can modify the surface properties of polymeric materials. Needless to say that the accumulation of ionic species at the surface of hydrophobic polymers would improve the adhesion to a large range of polar and metallic substrates. The question to be addressed is thus how the ionic groups of HTP's and their aggregates are distributed in moving from the surface to the bulk of the host polymer.

This paper deals with the investigation of metal carboxylate telechelic polymers by X-ray photoelectron spectroscopy (XPS or ESCA). Soft chains of polyisobutene (PIB), polybutadiene (PBD) and poly(propylene oxide) (PPO) have been selected in order to provide the ionic groups or aggregates with a sufficient mobility at room temperature. As the investigated polymers generally contain a small percentage of metallic ions (13 mol% in PPO, 5 mol% in PIB and 2.35 mol% in PBD), attention will be paid to the ESCA capability in deriving both the oxidation state of the metal cations embedded in the polymers and the atomic stoichiometry (i.e. the mean number of metal cations per chain) in the surface region. Of still greater interest, this investigation will focus on the trend in the composition profile ("in depth analysis") of HTP's. Finally, as halato-telechelic polymers result from the neutralization of polymers terminated with carboxylic acids, the structure of the ion aggregates will be investigated especially when an excess of metal IVB (Ti or Zr) alkoxide is used in the neutralization step and the unreacted alkoxy groups hydrolyzed.

2. Experimental

2.1. Materials

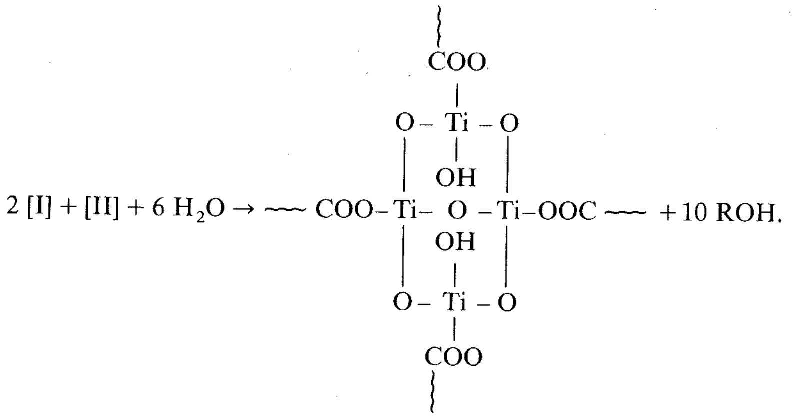
α,ω-dihydroxyl poly(propylene oxide) ($\overline{M}_n$: 1000 and functionality: 2.0) was obtained from Hoechst AG and converted to dicarboxylic acid terminated polymer by reaction with a twofold molar excess succinic anhydride in toluene. After refluxing for 16 h, the polymer was precipitated in hexane and purified by three reprecipitations from benzene in hexane. Its functionality was higher than 1.95. α,ω-dicarboxylic acid polybutadiene – or carboxy-telechelic polybutadiene – (Hycar CTB 2000 × 156) was commercially available from BF Goodrich ($\overline{M}_n$: 4600 and functionality: 2.01). Carboxy-telechelic polyisobutene was supplied by Exxon ($\overline{M}_n$: 2200 and functionality: 1.8). As described elsewhere, carboxy-telechelic polymers were neutralized with stoichiometric amounts of alkaline and alkaline-earth alkoxides under anhydrous conditions [5] (eq. (1)):

$$n\mathrm{HOOC{-}P{-}COOH} + (2n/v)\mathrm{Me(OR)}_v \rightleftharpoons \left[\mathrm{-OOC{-}P{-}COO{-}Me}_{2/v}\mathrm{-}\right]_n + 2\,\mathrm{ROH}, \qquad (1)$$

where P is the polymeric backbone, Me the metal of v valence and R an alkyl group (e.g. methyl, isopropyl). Eq. (1) does not reflect the association of the metal carboxylate ion pairs. Metal alkoxides are very convenient agents in terms of solubility, reactivity and formation of a volatile alcohol byproduct (ROH). Stoichiometric amounts of alkoxides can thus be used and the reaction equilibrium easily displaced towards the HTP's formation by distilling off the formed alcohol. Removing this byproduct is also required to eliminate a powerful solvating agent of the ion pairs. Finally, the reaction must proceed under strictly anhydrous conditions in order to prevent the metal alkoxide from a partial hydrolysis.

Contrary to alkaline and alkalino-earth alkoxides, using a stoichiometric amount of alkoxide groups derived from Ti or Zr alcoholates results in only a partial neutralization. This drawback is easily overcome when a metal (IV B) alkoxide excess is used, the further hydrolysis of which is expected to promote the formation of metal–oxygen–metal intermolecular bridges, and ultimately of carboxylato metal oxohydroxide aggregates [7] (eqs. (2) and (3)):

$$2\ \underbrace{\sim\!\sim\ \mathrm{COO{-}Ti{-}(OR)_3}}_{[\mathrm{I}]} + \mathrm{H_2O} \rightarrow \underbrace{\sim\!\sim\ \mathrm{COO{-}}\overset{|}{\underset{|}{\mathrm{Ti}}}\mathrm{{-}O{-}}\overset{|}{\underset{|}{\mathrm{Ti}}}\mathrm{{-}OOC}\ \sim\!\sim}_{[\mathrm{II}]} + 2\,\mathrm{ROH}, \qquad (2)$$



$$2\,[\mathrm{I}] + [\mathrm{II}] + 6\,H_2O \rightarrow \begin{array}{ccccc} & & \mathrm{COO} & & \\ & & | & & \\ & \mathrm{O}- & \mathrm{Ti} & -\mathrm{O} & \\ & | & | & | & \\ & | & \mathrm{OH} & | & \\ \sim\mathrm{COO}- & \mathrm{Ti}- & \mathrm{O} & -\mathrm{Ti} & -\mathrm{OOC}\sim \\ & | & \mathrm{OH} & | & \\ & | & | & | & \\ & \mathrm{O}- & \mathrm{Ti} & -\mathrm{O} & \\ & & | & & \\ & & \mathrm{COO} & & \end{array} + 10\,\mathrm{ROH}. \qquad (3)$$

In order to investigate the effect of the excess in the metal (IVB) alkoxide used, the carboxy-telechelic polyisobutene was neutralized with as well stoichiometric amount (i.e. half a $Zr(OR)_4$ molecule per PIB chain: PIB–0.5Zr) as three- and sixfold molar excess of zirconium tetra n-propoxide (PIB–1.5Zr and PIB–3.0Zr, respectively).

Caprylic or octanoic acid was similarly neutralized with the same Zr alkoxide used in stoichiometric amount (Cap –0.25Zr) and increasing molar excess (Cap–0.5Zr, Cap–1.0Zr and Cap–1.5Zr, respectively); potassium, magnesium and zirconium acetates were also used as reference compounds. They were prepared by end-neutralizing glacial acetic acid with potassium methoxide, magnesium methoxide and zirconium tetra n-propoxide, respectively, according to the same procedure as the one applied for carboxy-telechelic polymers [5,7].

Halato-telechelic polymers were analyzed as thin films prepared by melt compression (~ 90°C) between a gold plate and a tetrafluoroethylene sheet. The latter was easily removed leaving a thin layer of polymer at the surface of the gold plate. All the samples were kept for at least one month at room temperature before being characterized by ESCA.

2.2. X-ray photoelectron spectroscopy

The X-ray photoelectron spectra were recorded using a HP 5950-A ESCA spectrometer, equipped with a monochromatized Al Kα X-ray source (800 W, nominal resolution measured as full width at half maximum (FWHM): 0.7 eV). The base pressure in the analysis chamber was kept in the 10^{-9} Torr range (~ 10^{-7} Pa) by cooling the sample at 230 K with a controlled liquid nitrogen flow. No evidence of water contamination on the sample surfaces could be found.

Spectra of the insulating polymers were recorded with the "electron flood gun technique", to neutralize spurious charging effects. The photoelectron spectra binding energy scale was calibrated with the C 1s (hydrocarbon "CH_n" component) peak fixed at 285.0 eV as an internal reference [8]. Other related reference compounds were also studied in the same way (see below) to ascertain particular features found in the recorded ESCA spectra.

Table 1
Elemental sensitivity factor σ^* and electron mean free path value (λ) expressed relative to the C 1s line

	C 1s	Mg 2p/Mg 2s	K 2p	Ti 2p	Zr 3d$_{5/2}$	Ba 3d/Ba 4d
Binding energy	284	52/90	294	455	180	780/90
σ^* [a]	1.00	0.26/0.54	2.40	5.38	3.58	36.19/2.95
λ [b]	1.00	1.141/1.120	0.994	0.892	1.064	0.671/1.119

[a] Values are from ref. [9].
[b] Calculated from eq. (5), as from ref. [10].

For further analysis, peak intensities (I) were measured simply as peak heights, after subtraction of a linear background adjusted on both sides of the peak. Semi-quantitative information on the polymer composition was derived according to the relation

$$\frac{[\mathrm{A}]}{[\mathrm{B}]} = \frac{I_{\mathrm{A}}}{I_{\mathrm{B}}} \frac{\sigma_{\mathrm{B}}^*}{\sigma_{\mathrm{A}}^*} \frac{\lambda_{\mathrm{B}}}{\lambda_{\mathrm{A}}}, \qquad (4)$$

where A and B refer to different chemical elements (B being the reference one), [ ] is the calculated atomic concentration, σ^* is the elemental sensitivity factor determined for the HP spectrometer [9], λ is the electron mean free path evaluated from the formula

$$\lambda = \text{constant} \times E^{0.75}, \qquad (5)$$

where E is the kinetic energy of the photoelectron [10]. The σ^* and λ parameters used in this work are reported in table 1.

3. Results

As the metallic ions to be detected by ESCA are selectively attached to the two ends of linear chains, their concentration is relatively low. That is the reason why low-molecular weight polymers – still compatible with ultrahigh-vacuum measurements – were analyzed, and metals of sufficiently high cross-section for Al Kα photoemission selected. Under such conditions, it is quite feasible to record significant signals from the metallic species embedded in the polymers, as assessed by the wide scan photoelectron spectrum for α,ω-Zr-dicarboxylato oxohydroxide polyisobutene (fig. 1). The only system for which the ESCA measurements failed to detect the metallic species was the

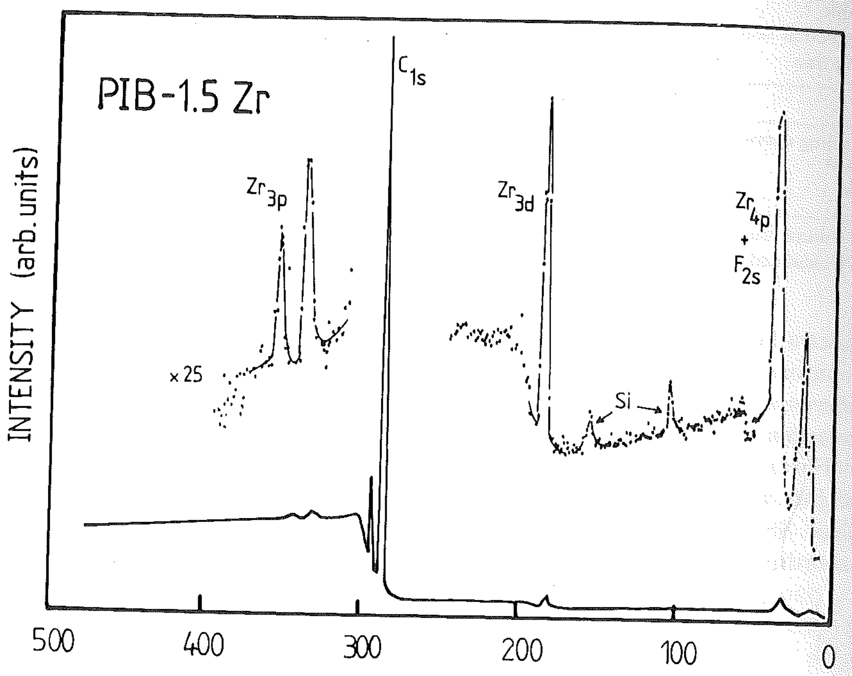


Fig. 1. Wide scan ESCA spectrum of α,ω-Zr-dicarboxylato oxohydroxide polyisobutene (PIB–1.5Zr).

Ti-carboxylate containing polybutadiene. Furthermore, the analysis of α,ω-K-dicarboxylato polyisobutene was less direct due to the superposition of low intense K 2p peaks (at about 290 eV) on the inelastic tail of the C 1s core level line.

3.1. Binding energy measurements

Table 2 reports calibrated binding energies measured for the investigated polymers. In order to get an estimate of the oxidation state of the metal cation, literature data relative to some metal compounds are included in the last column of table 2. Spectra of purposely synthesized reference compounds were also recorded. Metal acetates and barium sulfate are indeed chemical compounds mimicking very closely the corresponding metal carboxylate groups attached at the chain-ends. This is asserted by the agreement in the experimental values of the binding energies for each halato-telechelic polymer-reference metal salt pair. Furthermore, the metal chemical shift exhibited by all these pairs of compounds agrees with an oxidation state higher than the one observed for the related metal, metal oxide or less ionic derivatives. From table 2, it is obvious that the metal is really in a carboxylate-like environment inside the polymeric material.

Table 2
Calibrated binding energies [a] in eV measured on the metal core level photoelectron peaks, for the halato-telechelic polymers and for reference compounds

ESCA peak	Binding energy for the polymers	Binding energy for reference compounds	Reference
Mg 2p	PIB: 50.7 PPO: 50.4	Mg: 49.50 MgO: 50.45 Mg acetate: 50.55	This work This work This work
K $2p_{3/2}$	PIB: 293.2	K_2UF_6: 291.9 KF: 292.6 K acetate: 292.9	[11] [11] This work
Ti $2p_{3/2}$	PIB: 459.1	Ti: 453.8 TiO: 454.7 TiO_2: 458.5	[12] [12] [12]
Zr $3d_{5/2}$	PIB: 182.9	Zr: 178.7 ZrO_2: 182.5 Zr acetate: 182.8	[12] This work This work
Ba $3d_{5/2}$	PIB: 780.5 PBD: 780.1	BaO: 779.6 BaF_2: 779.5 $BaSO_4$: 780.6	[12] [12] [12]

[a] Accuracy for data from this work is better than ±0.15 eV.

3.2. Semi-quantitative analysis

Eq. (4), data from table 1 and the experimental area ratio of the C 1s peak (hydrocarbon type at 285.0 eV) and of the metal peak provide a semi-quantitative analysis of the surface composition of the investigated polymers (table 3). The uncertainties reported in the third column correspond to the maximum scattering of the experimental data for repeated analyses on different samples.

Referring to the series of PIB neutralized with Zr n-propoxide (table 3), the experimental and theoretical carbon-to-metal ratios are in a good agreement as long as a Zr n-propoxide excess is used to neutralize the carboxy-telechelic PIB. An anomaly is however observed under conditions corresponding to stoichiometry: a 50% defect in Zr atoms is reported.

According to the results summarized in table 3, the polymers all investigated under the same experimental conditions, may be classified into three categories:

- polymers neutralized with Mg methoxide and excess of Zr n-propoxide, for

Table 3
Relative areas of the core level photoelectron peaks and predicted atomic ratios

Polymer [a]	C/metal measured area ratio [b]	C/metal ESCA measured atomic ratio	C/metal atomic ratio from the chemical formula
PPO–Mg	(Mg 2s) 98.4	59	58
PIB–Mg	(Mg 2p) 202	60 ± 10	80
PIB–K	(K 2p) 45.2	108 ± 20	160
PIB–1.5Ti	(Ti 2p) 72	350 ± 20	107
PIB–0.5Zr	126	482 ± 15	320
PIB–1.5Zr	(Zr 3d) 27	105 ± 20	107
PIB–3.0Zr	16	60	53
PIB–Ba	(Ba 3d) 2.58	63	150
PBD–Ba	(Ba 4d) 40.6	106	340

[a] Halato-telechelic polymers are designated by the nature of the polymeric backbone, the metal alkoxide over α,ω-dicarboxylic acid polymer chain molar ratio (if unstated, this ratio corresponds to the stoichiometry) and the nature of the metal.

[b] The metal core level peak used for this calculation is indicated in parentheses.

which a good correspondence is noted between the measured and the expected metal concentrations,

– polymers containing K and Ba carboxylate end-groups which display 1.5 and 2.5 to 3 times more metal atoms than expected respectively,

– polymers neutralized with the stoichiometric amount of Zr alkoxide, and mainly with excess of Ti alkoxide, which are characterized by a defect of metal atoms in the surface region compared with the expected concentration.

3.3. Depth profile information

A depth profile analysis of a specimen can be performed without destruction of its surface (no Ar^+ ion bombardment) by recording angularly resolved spectra or by using different photon sources. As such experimental procedures are not compatible with our spectrometer, depth profile information was searched from the analysis of relative intensities of different core level lines of the same element, i.e. the metallic ion hosted in the polymeric matrix. Photoelectrons of different binding energies have indeed different kinetic energies when escaping from the solid and have therefore a different mean free path in the studied material. Comparing these relative intensities measured from standard homogeneous compounds, it is theoretically possible to infer some qualitative information about the concentration of the metallic ions within the first 0–100 Å depth of the polymeric material surface.

Table 4
Information on the distribution of the metallic ion in the polymeric film depth as measured from the apparent relative intensities of metallic ESCA core level lines

Polymers	ESCA measurements	Reference data
PIB–Ti (Ti 2p/Ti 3p ratio)	1/0.82	σ *: 1/0.13 TiO_2 [a]: 1/0.15
PIB–1.5Zr (Zr 3p/Zr 3d/Zr 4p ratio)	1/1.6/2.0 [b]	σ *: 1/0.71/0.18 ZrO_2 [a]: 1/1.5/0.24
PIB–3.0Zr (Zr 3p/Zr 3d/Zr 4p ratio)	1/1.7/0.29	σ * 1/0.71/0.18 ZrO_2 [a]: 1/1.5/0.24
PIB–Ba (Ba 3d/Ba 4d ratio)	1/0.29	σ *: 1/0.14 BaO [a]: 1/0.21
PDB–Ba (Ba 3d/Ba 4d ratio)	1/0.84	σ *: 1/0.14 BaO [a]: 1/0.21

* Cross section values are corrected for the instrument sensitivity factors [9].

[a] Spectra for reference compounds were recorded for this work.

[c] See in the text the remark relative to the Zr 4p peak intensity.

In order to undertake this study, two core level lines from the same metallic element have to be recorded. Unfortunately, this is impossible for polymers containing magnesium (the 1s core level is out of range of the spectrometer, and the 2s and 2p levels are too close to each other), and potassium atoms (too weak core level lines). Moreover, some of the data of the Zr-polymers might be influenced by the sample preparation: Fig. 1 shows some fluorine content (from the PTFE sheet) whose F 2s level might obscure the Zr 4p peak, therefore, information relative to this Zr 4p peak intensity must be interpreted with caution.

Table 4 reports the relative intensities of the ESCA signals for the Ti, Zr and Ba neutralized polymers. As the last column of table 4 shows a good agreement between the data calculated from tabulated cross-sections [9] and measured from reference compounds, it might be inferred that, in the studied polymers, the population of photoelectrons of low binding energy (i.e. of higher kinetic energy) is greatly enhanced (~ 4 times), meaning that the metal cations are *preferentially located below the very surface* of the polymers. Indeed, the higher the kinetic energy, the greater the electron escape depth from the solid. From table 4, a departure from this behaviour is obvious for PIB–3.0Zr and PIB–Ba, which rather display a homogeneous profile.

4. Discussion

The semi-qualitative analysis of the experimental results shows that the location of the metal carboxylates in the polymeric matrix corresponds to three different situations (table 3). Before embarking on any discussion, it is worth recalling that the polymer surface as analyzed by ESCA was in contact with a polytetrafluoroethylene (PTFE) sheet during the sample preparation. It could be anticipated that the highly hydrophobic character of PTFE would trigger the migration of the polar metal carboxylate groups away from the surface. Nevertheless, all the investigated polymers are soft materials at room temperature (glass transition temperatures $\ll 25\,^\circ\mathrm{C}$), which allows the system to tend to its equilibrium, especially at the air/polymer interface. On average, the samples were investigated one month after molding and release of the PTFE sheet.

From table 3, it is thus obvious that the host polymer, and the nature and structure of the metal carboxylate control the metal distribution in the surface layer probed by ESCA. In the series of α,ω-alkaline and alkalino-earth dicarboxylato polydienes, it is well-known that the bigger the cation is, the weaker the ion pair interactions are, and the more extensive the ion aggregation is [5,6]. K and Ba carboxylate end-groups would therefore enjoy a sufficient mobility to migrate towards the surface layer and to form there large-size aggregates, accounting for the reported surface accumulation of the metal. Due to a decrease in the cation radius ($r_{\mathrm{Mg}} = 0.66$ Å; $r_{\mathrm{Ba}} = 1.34$ Å; $r_{\mathrm{K}} = 1.33$ Å), Mg carboxylates form stronger dipoles than Ba and K carboxylates when located in a low dielectric constant medium such as a PIB matrix. Of course a more polar PPO environment favours the charge separation in the Mg carboxylate ion pairs. The increase in the strength of the metal carboxylate dipole (going from PIB–Ba to PIB–Mg in table 3) or in the ionicity of the ion pair (going from PIB–Mg to PPO–Mg in table 3) strongly reduces, and even suppresses, the tendency of the metal carboxylates to preferably migrate towards the surface layer. A random distribution is then observed between the bulk and the surface of the polymeric host.

The behaviour of the tetravalent metal (Ti, Zr) carboxylates is puzzling. Indeed, when an excess of Ti alkoxide is used to neutralize the carboxylic acid telechelic PIB and PBD, an important defect in Ti is observed in the surface layer of PIB (PIB–1.5Ti in table 3), while no Ti is detected in the PBD matrix. This means that the carboxylato Ti oxohydroxide aggregates are likely to push away from the surface during molding and have no spontaneous tendency to migrate towards the air/polyhydrocarbon interface. Using the Zr alkoxide in stoichiometric amounts, this metal exhibits the same but less pronounced behaviour as Ti (PIB–0.5Zr and PIB–1.5Ti in table 3). Quite surprisingly, an excess of Zr alkoxide in the neutralization of α,ω-dicarboxylic acid PIB is responsible for the randomization of the metal distribution in the PIB matrix. So far sufficient information is lacking to rationalize the discrepancy in the Ti and Zr carboxylates distribution in PIB.

Except for PBD–Ti, metal cations are detected in the surface layer probed by the ESCA technique. The so-called depth analysis however shows a particular distribution of these cations in the surface region: Table 5 reports the metal/carbon ratio as calculated from the intensities of the different metal core level peaks. The intensity of the less energetic (kinetic energy) metal peak (i.e. the most sensitive to the surface of the material) is taken as unity. These data must be considered cautiously, but the calculated trends are consistent with a model wherein the metal cations are present at a depth of a few tens of Å below the very surface. This means that on the microscopic scale of the ESCA measurements, the metal carboxylate end-groups of HTP's (or their aggregates) are not homogeneously distributed. For PIB–Ti, the metal concentration gradient towards the bulk is quite large (table 5) a fact already suggested by the anomalous C/metal ratio of table 3. By comparison, the PIB–1.5Zr and PIB–3.0Zr are much more homogeneous (see also table 3); note however the surprisingly high metal content found below the surface for PIB–1.5Zr! For the same Ba carboxylate ion pairs, the molecular structure of the host hydrogenated polymer has an obvious effect as supported by the

Table 5
Metal/carbon relative ratios as calculated from the different metal core level peaks ("in depth" analysis); the kinetic energy of the photoelectrons is increasing from the left to the right of the table

Sample	Me/C surface	Me/C →	Me/C bulk
PIB–Ti	1		7.5
PIB–1.5Zr	1	2.1	~ 10 (?)
PIB–3.0Zr	1	2.2	1.4
PIB–Ba	1		2.1
PBD–Ba	1		6.2

(?) See in the text the remark relative to the Zr 4p peak intensity.

Table 6
Computer analysis of the core level lines of octanoic acid neutralized with various amounts of Zr alkoxide

x [a]	C 1s peak binding energy			O 1s peak binding energy		Zr $3d_{5/2}$ peak binding energy
	CH_n	C–O	$\mathrm{C}\begin{smallmatrix}/\!\!/\mathrm{O}\\ \diagdown\mathrm{O}\end{smallmatrix}$	I	II	
1.5	285.0	285.6	288.9	529.9	531.6	182.7
1.0	285.0	286.3	288.7	529.9	531.6	182.7
0.5	285.0	285.9	288.2	529.9	531.7	182.9
0.25	285.0	285.9	288.6	–	531.6	182.8

[a] x is the Zr alkoxide / octanoic acid molar ratio.

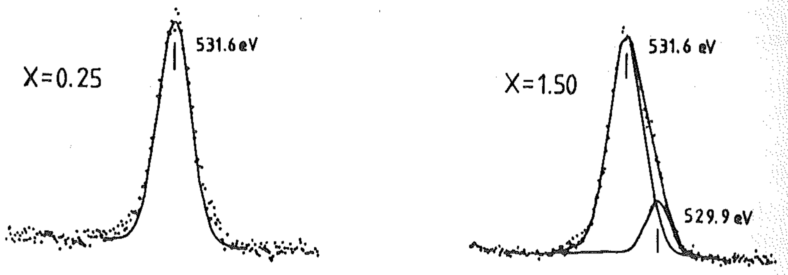


Fig. 2. Deconvoluted O 1s core level spectra of octanoic acid neutralized with two different amounts of Zr alkoxide.

comparison of PIB–Ba ($\overline{M}_n$: 2200) and PBD–BA ($\overline{M}_n$: 4600) (table 5). Tables 3 and 5 highlight the dependence of the location of the metal carboxylates aggregates on the nature of the ion pair, and the nature and molecular weight of the polymeric matrix. Accordingly, these molecular parameters are key-factors in the control of the surface properties of organic materials based on HTP's.

In order to support the evidence for formation of carboxylato Ti or Zr oxohydroxide aggregates when an excess of Ti or Zr alkoxide is used, the series of Zr octanoates was analyzed in detail. The shape of the O 1s peak (fig. 2) revealed to be dependent upon the Zr alkoxide/octanoic acid molar ratio (x). As reported in table 6, this core level line consists of one or two components depending on the value of the ratio x: when x amounts to 0.5, 1.0, and 1.5, two oxygen components are clearly observed, whereas peak I is not detected for $x = 0.25$. The O 1s binding energy at 531.6 eV should be assigned to metal carboxylate end-groups in comparison with the O 1s peak measured at 531.7 eV for the metal acetates studied earlier in this work as reference compounds. As peak I is only observed when a Zr alkoxide excess is used and hydrolyzed into expected oxohydroxides, the O 1s binding energy of 529.9 eV is assigned to the oxygen of the metal oxide bonds and should therefore be experimental evidence for the existence of carboxylato Zr oxohydroxide aggregates, as suggested by eq. (3).

Acknowledgements

RJ and PT are indebted to the "Services de la Programmation de la Politique Scientifique" (Brussels) for support of this work. JJP thanks the National Fund for Scientific Research (Belgium) for financial support.

References

[1] J.J. O'Malley and H.R. Thomas, in: Contemporary Topics in Polymer Sciences, Vol. 3, Ed. M. Shen (Plenum, New York, 1979) pp. 215–228.
[2] B. Albert, R. Jerome, Ph. Teyssie, J.J. Pireaux and J.J. Verbist, Makromol. Chem. 185 (1984) 579.
[3] Y. Yamashita and Y. Tsukahara, in: Modification of Polymers, Eds. C.E. Carraher, Jr. and J.A. Moore (Plenum, New York, 1983) pp. 131–140.
[4] A. Eisenberg and M. King, Ion-Containing Polymers, Physical Properties and Structure, in: Polymer Physics, Vol. 2, Ed. R.S. Stein (Academic Press, New York, 1977).
[5] G. Broze, R. Jerome and Ph. Teyssie, Macromolecules 15 (1982) 920.
[6] G. Broze, R. Jerome, Ph. Teyssie and C. Marco, Macromolecules 16 (1983) 996, 1771; J. Polymer Sci., Polymer Phys. Ed. 21 (1983) 2205.
[7] G. Broze, R. Jerome and Ph. Teyssie, J. Polymer Sci., Polymer Letters Ed. 21 (1983) 237.
[8] J.J. Pireaux, J. Riga, R. Caudano, J.J. Verbist, J. Delhalle, S. Delhalle, J.M. Andre and Y. Gobillon, Phys. Scripta 16 (1977) 329.
[9] I. Elliott, C. Doyle and J.D. Andrade, J. Electron. Spectrosc. 28 (1983) 303.
[10] C.D. Wagner, L.E. Davis and W.M. Riggs, Surface Interface Anal. 2 (1980) 53; C.D. Wagner, private communication.
[11] J.J. Pireaux, N. Mårtensson, R. Didriksson, K. Siegbahn, J. Riga and J. Verbist, Chem. Phys. Letters 46 (1977) 215.
[12] C.D. Wagner, W.M. Riggs, L.E. Davis, J.F. Moulder and G.D. Muilenberg, in: Handbook of X-Ray Photoelectron Spectroscopy (Perkin–Elmer, Physical Electronics Division, Eden Prairie, MN, 1978).