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Processing and interpretation of core-electron XPS spectra of complex plasma-treated polyethylene-based surfaces using a theoretical peak model

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Interpretation of X-ray photoelectron spectroscopy (XPS) spectra of complex material surfaces, such as those obtained after surface plasma treatment of polymers, is confined by the available references. The limited understanding of the chemical surface composition may impact the ability to determine suitable coupling chemistries used for surface decoration or assess surface-related properties like biocompatibility. In this work, XPS is used to investigate the chemical composition of various ultra-high-molecular-weight polyethylene (UHMWPE) surfaces. UHMWPE doped with α-tocopherol or functionalised by active screen plasma nitriding (ASPN) was investigated as a model system. Subsequently, a more complex combined system obtained by ASPN treatment of α-tocopherol doped UHMWPE was investigated. Through ab initio orbital calculations and by employing Koopmans' theorem, the core-electron binding energies (CEBEs) were evaluated for a substantial number of possible chemical functionalities positioned on PE-based model structures. The calculated ΔCEBEs showed to be in reasonable agreement with experimental reference data. The calculated ΔCEBEs were used to develop a material-specific peak model suitable for the interpretation of merged high-resolution C 1 s, N 1 s and O 1 s XPS spectra of PE-based materials. In contrast to conventional peak fitting, the presented approach allowed the distinction of functionality positioning (i.e. centred or end-chain) and evaluation of the long-range effects of the chemical functionalities on the PE carbon backbone. Altogether, a more detailed interpretation of the modified UHMWPE surfaces was achieved whilst reducing the need for manual input and personal bias introduced by the spectral analyst.

KEYWORDS
ASPN, plasma nitriding, polyethylene, UHMWPE, XPS, α-tocopherol

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1 | INTRODUCTION

Polyethylene (PE) remains the second most widely used polymer in the past century.[1] Ultra-high-molecular-weight polyethylene (UHMWPE) is predominantly the material of choice for biomedical applications, such as total joint replacements.[2] Over the past decades, various attempts have been made to improve or expand the use of UHMWPE biomaterials including surface modifications.[3–7] Such modifications aim to enhance the mechanical properties and biocompatibility, subsequently improving implant longevity and patient compliance by reducing the chance of implant failure. Plasma treatments are a popular route to alter surface-related properties. Once plasma-treated, the surface often has a complex chemical composition. X-ray photoelectron spectroscopy (XPS) has been shown to be invaluable for the analysis of such surfaces, allowing quantitative chemical characterisation in the upper few nanometres of the material surface.[8]

When investigating materials with few and/or distinct chemical states, XPS spectra interpretation can be relatively straightforward. However, with an increasing number of chemical functionalities present on the surface, peak fitting becomes more complex and potentially prone to personal bias. Generally, when investigating polymeric materials with unknown functionalities, reference data such as provided by Beamson and Briggs and the NIST database are used for comparison.[9,10] However, the subsequent peak fitting applied is limited by the available references and therefore does not always reflect the range of possible functionalities that may form during the surface treatment. Additionally, specifically in the case of the NIST XPS database, a spread in binding energies (BEs) is noted, and this can result in arbitrary spectral interpretation.[11] This is of particular concern in cases where potentially overlapping or unknown chemical functionalities, such as those obtained after surface plasma treatment of polymers, are present.

Using conventional reference databases, the BE assignments used to construct a peak model will originate from various materials. Although some existing reference data can provide a reasonable initial indication for peak assignments, chemical shifts in XPS are dependent on the electronic structure of the investigated molecule(s), and reference data alone can be insufficient for accurate and detailed XPS peak assignment. Specifically, in complex systems where biomolecules are incorporated within the plasma-treated polymer matrices, no suitable literature reference exists. The inability to establish a detailed interpretation of the spectra limits the understanding of the chemical nature of the surface, which may impact the suitability of coupling chemistries used for surface decoration or evaluation of the relation between the chemical surface composition and biomaterial properties like biocompatibility. In such cases, alternative reference sources are desirable to allow a more in-depth interpretation of the experimental XPS spectra.

An extensively applied tool to provide additional reference data for core-electron BE (CEBE) assignments are ab initio orbital calculations, which can be performed in various ways using the Hartree–Fock (HF) molecular orbital (MO) theory and density

functional theory (DFT).[12] Although both theories are used to describe the quantum states of many-electron systems, HF MO theory neglects the electron correlation and therefore results in higher energies compared with DFT, which implicitly includes exchange and electron correlation effects.[13,14] A hybrid approach between the two theories also exists, where the exact exchange from the HF theory is 'hybridised' with DFT to improve the description of various molecular properties that tend to be poorly described by ab initio density functionals.[15,16] The main limitations encountered in such calculations are the required computational effort and the complexity in the subsequent data evaluation. The latter is especially true for those who are not frequent users of computational methods, as in the case of many surface analysts and material scientists. However, due to the development of new and/or more complex material surfaces, the need for CEBE estimation for the interpretation of unidentified spectral features/chemical functionalities increases drastically.

Most literature that utilises calculated CEBEs to interpret experimental XPS spectra make use of simplified model structures, as calculations of solids using periodic conditions as seen in the projected augmented wave (PAW) can be costly and result in the formation of artefacts arising from the periodic unit cells.[12,17] The unrestricted generalised transition-state (uGTS) method was one of the earlier methods to provide accurate absolute BEs for small gas molecules, displaying a mean error of 0.2 eV compared with experimental BEs.[18] Later, it was found that this accuracy was achieved as a result of consistent error cancellation, but it is occasionally still used in the estimation of BEs.[19,20] Other approaches, for example, those employing correlation-consistent basis sets or configuration interaction calculations, display a mean error of around 0.15 eV.[21,22] However, the high computational cost limits their applicability for larger structures and use on 'average' PCs.

A more forthright approach for the estimation of CEBEs is using Koopmans' theorem (KT), where the negative orbital energy ($-\varepsilon_i$) is equated to the ionisation potential and thereby provides an estimate for the respective CEBE.[23] KT allows the estimation of CEBEs without calculating the work function, but these CEBEs only include initial state effects as the structure remains in its neutral ground state. KT neglects the electronic relaxation in response to the formed electron core-hole and the CEBEs estimated with KT are therefore also referred to as frozen orbital (FO) CEBEs. Corrections can be applied to absolute CEBEs to account for the relativistic effects and the zero-point energy contribution, but such corrections typically do not influence the CEBE shifts (ΔCEBEs) significantly as the errors are small due to error cancellation effects.[12] No differentiation was made between HF orbital energies (ε_{HF}) and Kohn–Sham (KS) orbital energies (i.e. the DFT analogues of HF orbital energies, ε_{KS}), as in both cases, KT is validated in regard to the calculated initial state ΔCEBEs.[24] However, contrary to $\Delta\varepsilon_{HF}$, $\Delta\varepsilon_{KS}$ may not solely be a result of initial state effects due to the exchange and electron correlation effects included with the use of DFT.

The ΔCEBEs obtained through KT are shown to allow satisfying spectral interpretation if the energy offset of the calculated CEBEs, relative to the experimental CEBEs, are constant throughout a set of

structures.[25–28] Depending on the method and basis set used for the calculations, the mean error of calculated KT ΔCEBEs are typically between 0.2 and 0.7 eV for atoms in the second row of the periodic table when compared with experimental ΔCEBEs. This approach is utilised extensively in the literature to aid in the interpretation of various elemental regions, but often focussing on one region at a time and with materials of known chemical composition. However, when working on potentially overlapping and/or unknown functionalities, a single region does not allow for accurate interpretation of the spectra. Instead, it would be desirable to constrain the peak areas of each functionality with all its corresponding components to uphold its theoretical composition during peak fitting to guide the component identification.

As with any XPS peak fitting routine, care has to be taken to avoid data over- and misinterpretation. Recent publications provide a succinct overview of common errors in XPS peak fitting[29,30] and guidance on peak fitting for plasma-treated samples.[31] The theoretical peak model in our approach takes these issues into account and is consistent with all but one of the six points raised in Grecsynski and Hultman's guidelines on XPS data interpretation; namely, (#5) the number of component peaks is not kept to a minimum, although each component in our peak model does have a physical interpretation.[32] Next to that, regarding the other guidelines, (#1) the purpose of the model is formulated, (#2) the model is comprehensive, the model is both (#3) qualitatively and (#4) quantitatively self-consistent, and (#6) uses physically meaningful constraints.[32] However, the very nature of the sample, a complex composition of functionalities with unknown type and quantity of chemical functionalities for which no reference material exists inherently precludes a priory minimisation of the number of component peaks used as would normally be the case in XPS peak fitting. The purpose of this work is to reduce bias in peak assignment of (nitrogen) plasma-treated polymers where conventional approaches relying on reference materials or established reaction pathways of surface modifications are unavailable or fail. For the current system, to be as unbiased as possible with regard to the qualitative assessment of functional groups, we propose that all potential functionalities that may form during the plasma-treatment of PE and subsequent oxidation/ageing of the plasma-treated surface when in contact with air should be considered. It is important to note that we do not propose general use of this unbiased peak fitting approach, but we suggest that its application should only be considered for complex samples that display a large number of different, unpredictable chemical functionalities such as some (not necessarily all) plasma-treated samples.

The present work proposes a self-consistent theoretical peak model suitable for multi-region peak fitting of complex PE-based surfaces that lack suitable reference materials. A ΔCEBE database of varying C/N/O functionalities positioned on a PE model structure was generated by ab initio orbital calculations and by employing KT. The calculated ΔCEBE database was converted into a multi-region peak model, providing a material-specific solution for the spectral interpretation of merged high-resolution C 1s, N 1s and O 1s XPS spectra. UHMWPE doped with α-tocopherol or functionalised by active screen plasma nitriding (ASPN) was investigated as a model system. Subsequently, the use of the KT-based peak model for processing and interpretation of XPS spectra of the more complex, combined system, obtained by ASPN treatment of α-tocopherol doped UHMWPE was assessed by comparison to conventional peak fitting procedures.

2 | MATERIALS AND METHODS

2.1 | Computational details

The investigated model structures were based on a 7-mer PE chain (i.e. $[CH_2–CH_2]_7$), where functionalities were positioned in the centre (C7 or C8) or at the end of the chain (C1 or C14). Next to the model structures, α-tocopherol (vitamin E, aT) and two by-products that may form during its antioxidative activity [α-tocopherylquinone (aTQ) and α-tocopherylhydroquinone (aTHQ)] were also evaluated (25). All structures were drawn in 'Avogadro' and pre-optimised using the 'Merck Molecular Force Field' (MMFF94) energy minimisation; the coordinates of the pre-optimised structures were used to prepare the input files for the quantum chemistry package 'GAMESS' (v2019.R1.P1.pgiblas).[33,34] Calculations in 'GAMESS' were performed using the 6-311++G(d,p) Pople basis set and the HF method alone or including the long-range and dispersion-corrected hybrid DF wB97X-D.[35,36] The wB97X-D hybrid DF was chosen as it is shown to provide reduced errors in covalent systems compared with more commonly used DFs such as B3LYP-D.[36] It was also demonstrated that self-interaction errors (i.e. the interaction of an electron with itself that results when exchange–correlation contributions to the total energy are approximated, also referred to as delocalisation error) can be greatly reduced by long-range corrected hybrid DFs.[36] This is of importance as self-interacting electrons are observed in core orbitals and the non-bonding regions of valence 1s orbitals (e.g. in hydrogen).[37] The inclusion of a dispersion correction was also found to be beneficial for geometry optimisations, because intramolecular dispersion interactions already affect medium-sized organic molecules.[38] Cartesian basis functions were used to construct the symmetry-adapted linear combination (SALC) of the basis functions, with a linear dependence threshold of 1.0E-6. Second-order SCF orbital optimisation was used for the pure HF calculations, and Pulay's DIIS interpolation was used for the hybrid DFT calculations. The molecular geometries were optimised until they reached a convergence limit of 1.0E-5 with the use of Jacobi diagonalisation. Once completed, the model structures were visualised in 'wxMacMolPlt' to inspect and assign the HF/KS orbital energies to the atoms within the model structures. The orbital energies were assigned to the atom with the highest occupant in the atomic orbital coefficient, that is, the orbital predominantly localised at the atom of interest—for simplicity, from here forth referred to as CEBE. The unrestricted HF (UHF) calculations on the evaluated doublet systems were susceptible to spin contamination; the spin contamination in organic molecules is generally deemed negligible if the total spin ($<S^2>$) deviates less than 10% from $s(s + 1)$, where 's' refers to half of the unpaired electrons.[39]

The spin contamination for the carboxylate model structure was shown to be negligible, showing a <S^2> value of 0.760 and 0.755 as calculated by UHF and wB97X-D, respectively. The spin contamination for the centred and end-chain ammonium ion model structures was also negligible, showing a <S^2> value of 0.751 as calculated by both methods. Examples of the GAMESS input files are available in the Supporting Information.

2.2 | Sample preparation

UHMWPE sheets were purchased at Direct Plastics Ltd (Sheffield, UK) with a thickness of 5 mm. For preparation, the sheets were waterjet cut into squares of 10 × 10 mm and polished. The polishing was performed using silicon carbide grinding papers of 400, 800, 1200 and 2000 grit consecutively for 2 min each, after which finished with a 6-μm diamond polishing paste for an additional 2 min—resulting in undoped and untreated UHMWPE (UHMWPE UD/UT). Prior to any treatment, the samples were washed with ethanol and subsequently left to dry in air at room temperature. α-Tocopherol was purchased at Sigma-Aldrich Ltd (Dorset, UK) with a purity of 96%. Doping of the polished UHMWPE samples was carried out with fresh α-tocopherol in a round-bottom flask at 90°C for 4 h under stirring and blanketed with nitrogen—resulting in doped and untreated UHMWPE (UHMWPE D/UT). Plasma nitriding on the undoped and doped UHMWPE surfaces was performed with a 40-kW DC nitriding unit (Klöckner Ionon, Köln, Germany) in combination with an active screen set-up.[40] The active screen mesh cylinder was made of 0.7-mm-thick perforated sheet steel, with an average height of 130 mm and a diameter of 120 mm. The distance between the sample surface and the active screen was set at 20 mm. A gas mixture of 80% N_2 and 20% H_2 was used with an initial flow rate of 4 NL/h, after which the vacuum pump was adjusted to balance the pressure at 75 Pa. All treatments were performed at 90°C for a duration of 60 min once the desired temperature was achieved. When completed, the power and inlet gas were switched off so that the plasma chamber was cooled down in the presence of the remaining working gas whilst maintaining the pressure of 75 Pa. When the plasma chamber was cooled down to about 50°C, the vacuum was slowly released, and the samples were removed from the plasma chamber—resulting in undoped plasma-treated and doped plasma-treated UHMWPE (UHMWPE UD/PT and D/PT). The samples were stored in polystyrene Petri dishes and kept in a desiccator for about 2 weeks prior to XPS analysis.

2.3 | XPS analysis

XPS spectra were taken at the EPSRC Harwell XPS facility using a Kratos AXIS Supra (Didcot, UK) using a monochromatic Al K_α X-ray source (12 mA × 12 kV = 144 W). The samples were mounted using a double-sided scotch tape placed on a glass slide and attached using copper clips to the sample bar. The glass slide ensured the samples were floated from the spectrometer. To prevent surface charge build-up, charge neutralisation was used with a filament current, filament bias voltage, and charge balance voltage of 0.3 A, 4 V, and 4 V, respectively. The base pressure of the spectrometer was 5×10^{-10} Torr, rising to ca. 1×10^{-9} Torr during analysis. Survey spectra were collected in a single sweep at a pass energy of 160 eV, with a dwell time of 100 ms and sweep time of 120 s, using a step size of 1 eV over the energy range of −5–1200 eV. High-resolution spectra were recorded at a pass energy of 20 eV, with a dwell time of 260 ms and sweep time of 60 s, using a step size of 0.1 eV over an energy window of 23–26 eV, depending on the element. The observed spectral quality and number of sweeps for each of the high-resolution spectra are presented in Table S1. All data was collected at the 'magic angle' (i.e. 54.74°) in the hybrid mode using a slot aperture, resulting in an analysis area of 700 × 300 μm.

2.4 | Peak fitting

All peak fitting was performed using CasaXPS (v2.3.24rev1.1B). The high-resolution XPS spectra were corrected manually using the relative transmission function as obtained from the respective VAMAS files of the high-resolution spectra. The relative transmission function needed to be applied manually, as the default transmission correction in CasaXPS is otherwise applied after the user's set area constraints—resulting in the erroneous conversion of peak area between elemental regions. The Kratos RSF library was used to define the area constraints between the respective functionality-related components that were present in the different elemental regions. The peak fitting of the survey spectra was performed using both the 'Shirley' and 'Tougaard' backgrounds in separate data processing procedures, whereas the high-resolution spectra were fitted using the 'Shirley' or 'Polymer U Tougaard'. Both background types were used to investigate the influence of the background type on the observed atomic composition. However, as the survey spectra also contained non-polymeric elements, the choice was made to use the regular 'Tougaard' background instead of the 'Polymer U Tougaard' to allow all elements to be fitted with the same background. Unless stated otherwise, all component peaks were described by the symmetric Voight-type lineshape LA(1.53,243), the default lineshape in the version of CasaXPS used to perform the presented peak fits. To account for its vibrational structure, the main [CH_{PE}] component representing the [CH_2]$_n$ of the unmodified UHMWPE was described by the asymmetric Voight-type lineshape LA(4.2,9,4)—this lineshape was established by M. C. Biesinger through peak fitting PE and a C18 alkane.[41] The higher-order [CH_2]$_n$ carbon shifts, [CH_x], are fitted using the symmetric LA(1.53,243) lineshape, unless stated otherwise. During the high-resolution spectra peak fitting, the component peaks were referenced in position and constrained in FWHM (initial guess: 1 eV; constraint: 0.8–1.8 eV) to a single component per respective elemental region—these may be referred to as 'peak model reference components'. The peak model reference components consist out of [CH_{PE}] within the C 1s region, [CNH_2] within the N 1s region and [$C=O^*$] within the O 1s region. The initial position of [CH_{PE}] in the C

1s region, [CNH$_2$] in the N 1s region and [C=O*] in the O 1s region was set to 284.8, 399 and 532 eV, respectively, and were constrained between 282 and 286 eV, 397 and 401 eV and 530 and 534 eV, respectively. Apart from the area% of the contaminants predetermined by the survey spectra, the initial area of all the component peaks in the C 1s region was set to 10E2 and constrained between 0 and 10E6. The area of the component peaks in the other elemental regions was constrained by the respective RSFs and theoretical composition associated with the evaluated functionalities. The peak fits presented in this work were optimised using the 'Levenberg–Marquardt' algorithm as available in CasaXPS. The developed peak models (excluding the sample-specific contaminants) are available upon request; inquiries can be directed to the corresponding authors.

3 | RESULTS AND DISCUSSION

3.1 | Peak model

3.1.1 | Functionality evaluation

The functionalities considered during peak fitting of nitrogen and/or oxygen plasma-treated polymers vary in the literature but typically include hydroxyl, ether/epoxide, carbonyl, acid/ester, amine, imine, nitrile, amide, and imide functional groups.[5,42–46] However, this is not an exhaustive list of all the possible functionalities because the peak identification, as mentioned previously, is based on comparison with the available reference materials and cannot always provide conclusive results. Furthermore, functionalities showing overlapping/closely positioned BEs are often grouped in the C 1s spectrum (e.g. assigning a single peak between 1 and 1.6 eV above the main hydrocarbon peak to all [C–O/N]-based functionalities) and are most often not further investigated by peak fitting the areas of their corresponding elemental regions. Unfortunately, plasma–polymer surface reactions are not as well understood as pure plasma gas chemistries. Especially in the case of ASPN, where plasma is formed on the active screen instead of directly on the sample, the sample surfaces are mainly subjected to ion bombardment. Consequently, the ion bombardment of the surface can lead to electron-induced fragmentation and low-energy (i.e. ≤50 eV) electron-induced surface reactions.[47] As ASPN was originally introduced as a treatment for metals, there is also little literature available on ASPN of polymers.[40] Additionally, the available literature focusses on changing surface-related physical/biological properties rather than determining the surface-related chemical changes that have occurred during the ASPN treatment.[5,48] Therefore, a range of additional functionalities were evaluated to encompass more possible functionalities that may have formed during the plasma-chemical reactions—considering the presence of the polymer ([CH$_2$]$_n$), at least three different gases (oxygen diffused within the polymer and the nitrogen–hydrogen working gas) and two transition metals (Fe and Cr, from the active screen set-up positioned near the sample surface). The complete list

of functionalities, their IDs and additional visual structural information is available in Table S2.

3.1.2 | Peak model assembly

To assemble the calculated peak model that was used during the high-resolution peak fitting, the calculated CEBEs were calibrated over the lowest observed CEBE per model structure, which showed an average of 304.97 ± 0.08 eV as calculated by HF and 279.45 ± 0.07 eV as calculated by wB97X-D ($\alpha = 0.0001$; $n = 50$). From here on, considering UHMWPE chains contain an average of 125,000 to 263,000 [CH$_2$] repeating units, all carbon shifts will be considered relative to the averaged [CH$_2$] of the PE model structure ΔCEBE (i.e. [CH$_{PE}$]) as it is expected to be the most abundant functionality.[49] Examples of various centred and end-chain model structures and their corresponding carbon ΔCEBEs are displayed in Figure 1, showing the structural differences in the model structures with an increasing number of non-carbon atoms included. The calculated primary carbon shifts, nitrogen and oxygen shifts and higher-order carbon shifts covering the full PE-based model structures are presented in Tables S3–S5, respectively. On occasion, asymmetry in the estimated ΔCEBEs of the PE backbone in model structures with centred functionalities can be observed; this effect is due to long-range effects of the evaluated functionalities and is further discussed in Section 3.1.4. The simplified chemical structures and corresponding ΔCEBEs of the tocopherol-like components ([aT], [aTQ] and [aTHQ]) are shown in Table S6.

3.1.3 | Effect of functional group positioning

The effect of the functionality positioning on the calculated ΔCEBEs was investigated by taking the difference between the ΔCEBEs of end-chain and centred model structures. Within the literature, the effect of functionality positioning is rarely investigated during XPS analysis of modified polymers, and these structural differences are most often grouped during conventional peak fitting despite the clear differences in theoretical composition. Within the Beamson and Briggs reference database, a few experimentally observed ΔCEBE deviations due to a difference in functionality positioning were observed. As presented in Table 1, a comparison between the calculated (this work, as available in Table S3) and experimental (Beamson and Briggs reference database) ΔCEBEs of esters and carboxylic acids, as well as primary and secondary amides, shows clear differences in the ΔCEBEs due to the functionality positioning. Both the calculated and experimental primary carbon ΔCEBEs were found to increase when the functionalities were in the end-chain positioning (i.e. carboxylic acid and primary amide) when compared with centred positioning (i.e. ester and secondary amide), showing a ΔCEBE increase of roughly 0.30 eV regardless of the functionality. The experimental ΔCEBEs showed a slightly higher deviation between the primary and secondary amide positioning when compared with

ID	3D Model structure	Carbon ΔCEBEs
CH_2 & CH_3*		
COH		
COH*		
O=COC		
O=COH*		
COC(=O)NHC		
COC(=O)NH_2*		
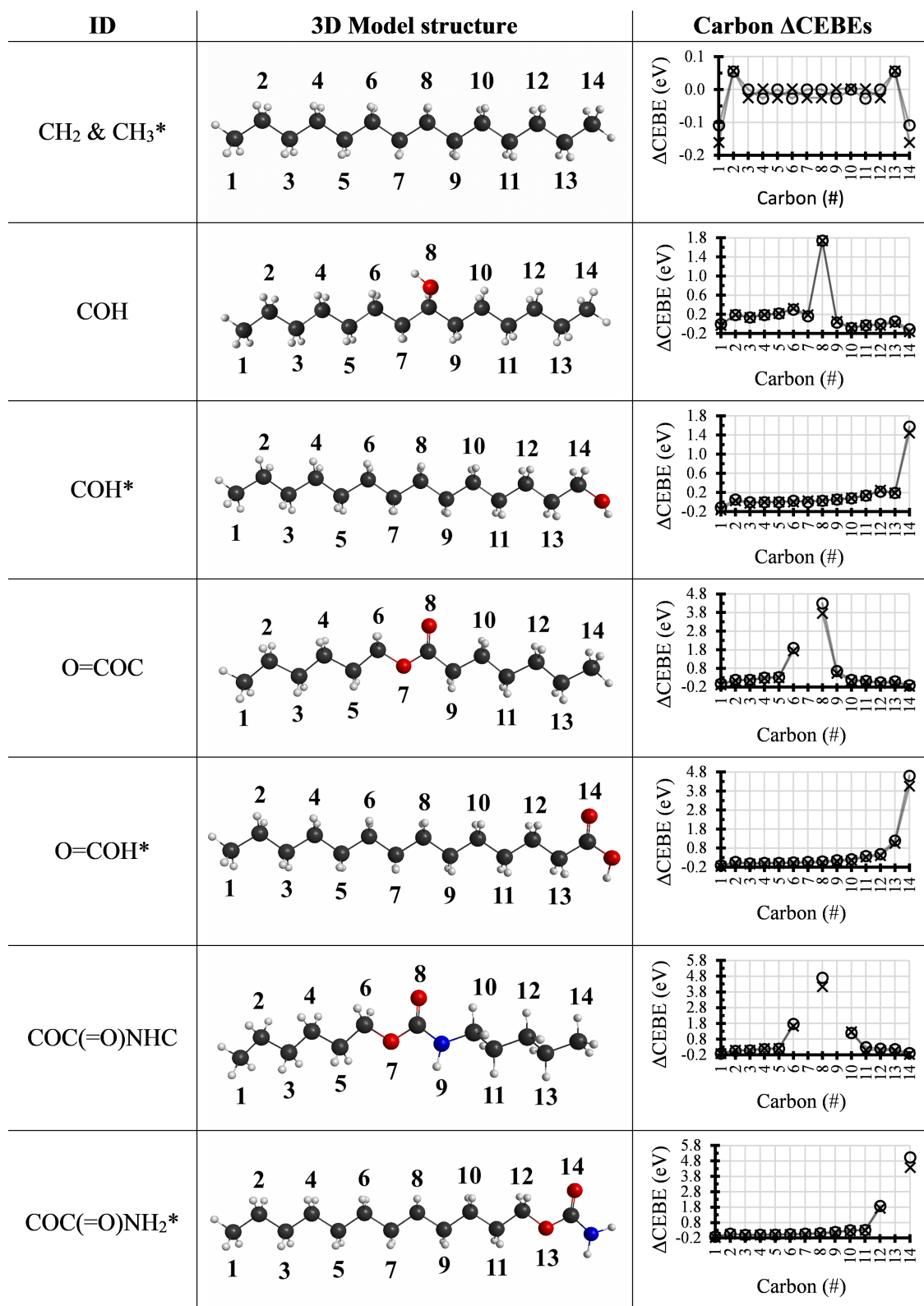
FIGURE 1 Examples of 3D model structures, showing carbon (**black**), oxygen (**red**), nitrogen (**blue**) and hydrogen (light grey) atoms. The numbers refer to the plotted carbon ΔCEBEs relative to [CH$_{PE}$], as calculated by HF (circles) and wB97X-D (crosses).

the calculated ΔCEBEs. However, the calculated deviation for this functionality was still within the experimentally observed ΔCEBE range. At least one of the calculated ΔCEBEs involved in each functionality exceeds the resolution of state-of-the-art XPS instruments (i.e. >0.1 eV) as shown in Table S7. Therefore, the calculated ΔCEBE differences are expected to be significant enough to allow

	HF (eV)		wB97X-D (eV)		Experimental[9] (eV)	
	O=COR	O=CNHR	O=COR	O=CNHR	O=COR	O=CNHR
Centred	4.30	3.41	3.76	2.91	3.99 ± 0.30	3.00 ± 0.02
End-chain	4.60	3.70	4.06	3.21	4.26 ± 0.10	3.45 ± 0.15
$\Delta_{end\text{-}centred}$	0.30	0.29	0.30	0.30	0.27	0.45
$\Delta_{calc\text{-}exp}$	0.03	0.16	0.03	0.15		

TABLE 1 Comparison between the calculated and mean experimental primary carbon CEBE deviations observed in esters/acids and primary/secondary amides

Note: 'R' represents the different atom present in the centred or end-chain functionality, C or H, respectively.
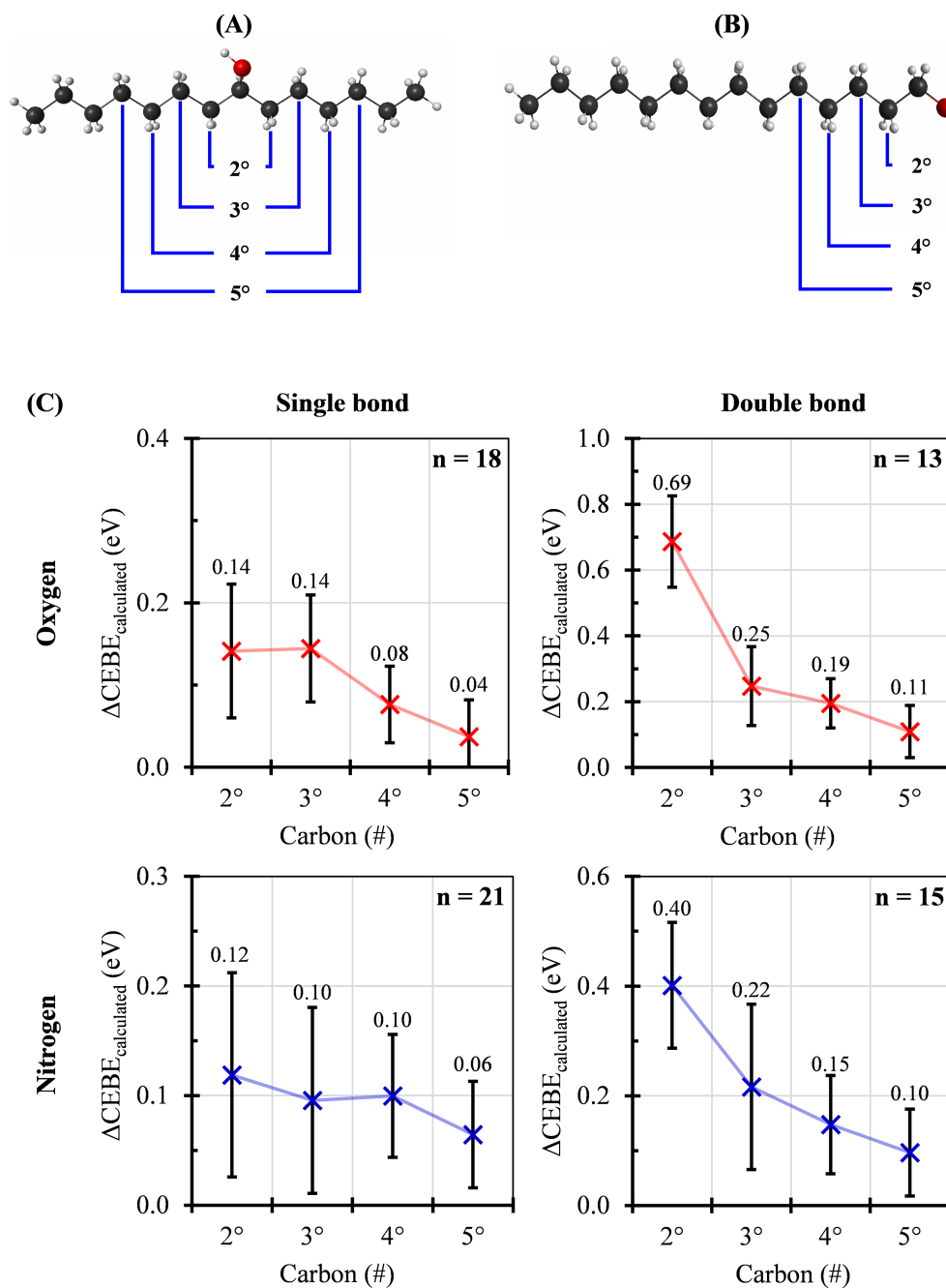
FIGURE 2 Assignment of higher-order carbon shifts (i.e. [CH$_x$]) in the centred (A) and end-chain (B) model structures, with the [COH] model structure serving as an example. The graphs (C) depict the mean secondary (2°, x = 1), tertiary (3°, x = 2), quaternary (4°, x = 3) and quinary (5°, x = 4) ΔCEBEs for [CH$_2$] groups in the vicinity of carbon–oxygen and carbon–nitrogen functionalities, calculated with 'wB97X-D' relative to [CH$_{PE}$]. Values are separated by atom type (i.e. oxygen or nitrogen) and bond type (i.e. single or double bond), confidence interval of α = 0.01 with n as shown per group within the respective graphs.

differentiation between the positioning of functionalities during the high-resolution spectra peak fitting—especially in the case of functionalities with more than one non-carbon atom.

3.1.4 | Long-range effects of functional groups

The PE model structures also allowed investigation into the ΔCEBEs of neighbouring carbon atoms present in the model structures, which are susceptible to so-called 'long-range' effects (i.e. chemical shifts in the XPS spectra due to the presence of a functionality that is not the first nearest neighbour of the functional group under consideration). These long-range effects have been investigated and observed for other polymers, such as TFAA and PVTFA.[28,50] However, to the best of our knowledge, there is a lack of literature on the secondary and higher-order carbon shifts (i.e. BE shifts exerted on carbons that are positioned two or more carbons away from the functionality) as seen in functionalised PE-based material surfaces.

In this work, higher-order carbon shifts are expected to be of importance for several reasons. Excluding this fine structure can result in the erroneous estimation of functionalities, especially those close to the main hydrocarbon peak, such as single-bonded oxygen/ nitrogen functionalities. Additionally, by including the higher-order carbon shifts, the theoretical composition of an otherwise unknown chemical surface composition can be estimated during peak fitting (i.e. by constraining the component peak areas by the expected C/N/O ratios of the evaluated functionalities) and component stability (i.e. the observed change in component presence with the inclusion of its associated higher-order carbon shifts) can be evaluated. As ASPN is known for its homogeneous treatment of materials, even in the case of complex geometries/morphologies, an even spatial distribution of the functionalities on the polymer surface was assumed.[5] Using this assumption, increasingly higher-order carbon shifts can be introduced to the peak model until the introduced theoretical composition results in [CH_x] overestimation in the C 1s region or underestimation of the components within the N 1s and O 1s regions.

The assignment of the higher-order carbon shifts and the mean influence of carbon–oxygen and carbon–nitrogen functionalities on the ΔCEBEs of the PE carbon backbone are shown in Figure 2— separated by atom type and bond type, as calculated by wB97X-D. The mean values calculated by HF are shown in Figure S1, and graphs showing the individual carbon shifts as calculated by HF and wB97X-D per functionality are displayed in Figures S2 and S3, respectively. As the calculated database in this work only contained two model structures containing a carbonyl group, all model structures with double-bonded oxygen are grouped (i.e. carbonyls, esters, and acids). As seen in Figure 2, the secondary carbon shift for single-bonded oxygen is ~0.14 eV, for double-bonded oxygen ~0.69 eV, for single-bonded nitrogen ~0.12 eV and for double-bonded nitrogen ~0.40 eV. Typically, the average deviation between the functionalities was roughly ± 0.11 eV and continuously decreased towards higher-order carbon shifts. It can be clearly observed that double-bonded functionalities influenced the ΔCEBEs of [CH_2] more than single-bonded functionalities. Additionally, the difference

between the primary and secondary carbon shift was most prominent; this difference decreases considerably when the functional group is situated further away from the primary carbon. Around the quinary carbon shift, most functionalities showed no significant (≤0.1 eV) long-range effects on the ΔCEBEs of the PE carbon backbone. Within the reference database of Beamson and Briggs, only four mean secondary carbon shifts were reported that relate to oxygen-based functionalities.[9] The reported secondary carbon shift for single-bonded oxygen was ~0.2 eV, for carbonyl oxygen ~0.4 eV and for ester/acid-like functionalities ~0.4 to ~0.7 eV. The mean calculated and experimental oxygen-based secondary carbon ΔCEBEs are similar although not identical. Differences in the ΔCEBEs were also most likely affected by energy referencing/material-specific differences. It is worth to note the higher-order carbon shifts can be small (as shown in Figure 2, for 3° or above typically <0.30 eV) and within the range of experimental errors of around 0.20–0.30 eV, but only through their inclusion the self-consistency of the peak model can be maintained. The inclusion of the higher-order carbon shifts should reduce the erroneous estimation of functionalities close to the hydrocarbon peak during high-resolution peak fitting.

In the present work, the higher-order carbon shifts were introduced as individual component peaks per respective functionality during peak fitting. This was done to maintain the stoichiometry of the present elements and to account for the occasional asymmetry observed in the carbon ΔCEBEs of the PE backbone in the model structures with centred functionalities as was observed in Figure 1. The observed charge distribution in the model structures, which are clearly asymmetrically affected by the orientation of the centred functional groups in cases such as [COH] but symmetric in cases such as [COC$_α$] and [C=O], gives rise to inequivalent or equivalent carbon sites, respectively. The origin of the asymmetry in the ΔCEBEs of the PE backbone can be illustrated by the 2D molecular electrostatic potential contour maps of the model structures; examples of [COH], [COC$_α$] and [C=O] are depicted in Figure S4. This shows that despite the alkyl segments on both sides of the centred functionality are chemically equivalent, electrostatic effects introduced by the functionalities impact the observed ΔCEBEs in the carbon backbone and are dependent on the orientation of the functionality. The influence of electrostatic effects arising from chemical functionalities positioned in hydrocarbon backbones was reported in the literature for molecules in a self-assembled monolayer theoretically and experimentally.[51,52] In this work, it was shown that functional groups exert long-range effects on the alkyl segments regardless of chain length, which resulted in asymmetry in the CEBEs of the carbons in the alkyl segments.[51,52] This work highlighted that electrostatic effects significantly contribute to the shifts observed in CEBEs, which is in agreement with our observations.[51]

### 3.1.5 | Comparison and validation of peak models

To assess the peak model quality, the calculated ΔCEBEs and experimental ΔCEBEs from the Beamson and Briggs database are compared

by linear correlation.[9] A difficulty in the comparison of calculated ΔCEBEs versus experimental ΔCEBEs is introduced by energy referencing. When comparing the same material of a known composition that displays a XPS spectrum with a clear separation of components, energy referencing the C1s region has little to no impact on the relative shifts. However, this is not valid when the aliphatic hydrocarbon peak cannot be clearly identified, as is the case with complex samples where introduced functionalities have peak positions near the aliphatic hydrocarbon peak (e.g. C−O/N) as is frequently observed in the literature of plasma-treated polymers.[5,42–46] Within the reference database, the XPS spectra for aliphatic polymers are calibrated to 285 eV, but this neglects the fact that different polymers may have a difference in their C 1s region

maximum. Because of this, energy referencing can result in data misinterpretation and has received substantiated criticism over the past decades.[11] Furthermore, averaged experimental ΔCEBEs are used for the assignment of functional groups, most of which originate from various materials and occasionally show relatively large material-specific deviations in their ΔCEBE.

To allow one-to-one comparison, the ΔCEBEs in the linear correlations are compared from the lowest experimental CEBE available per respective region—the hydrocarbon in the C 1s region, the secondary amine in the N 1s region and the secondary amide in the O 1s region. The linear correlation graphs and corresponding statistical analysis are displayed in Figure 3 and Table 2, respectively. The origin of the experimental reference data within the Beamson
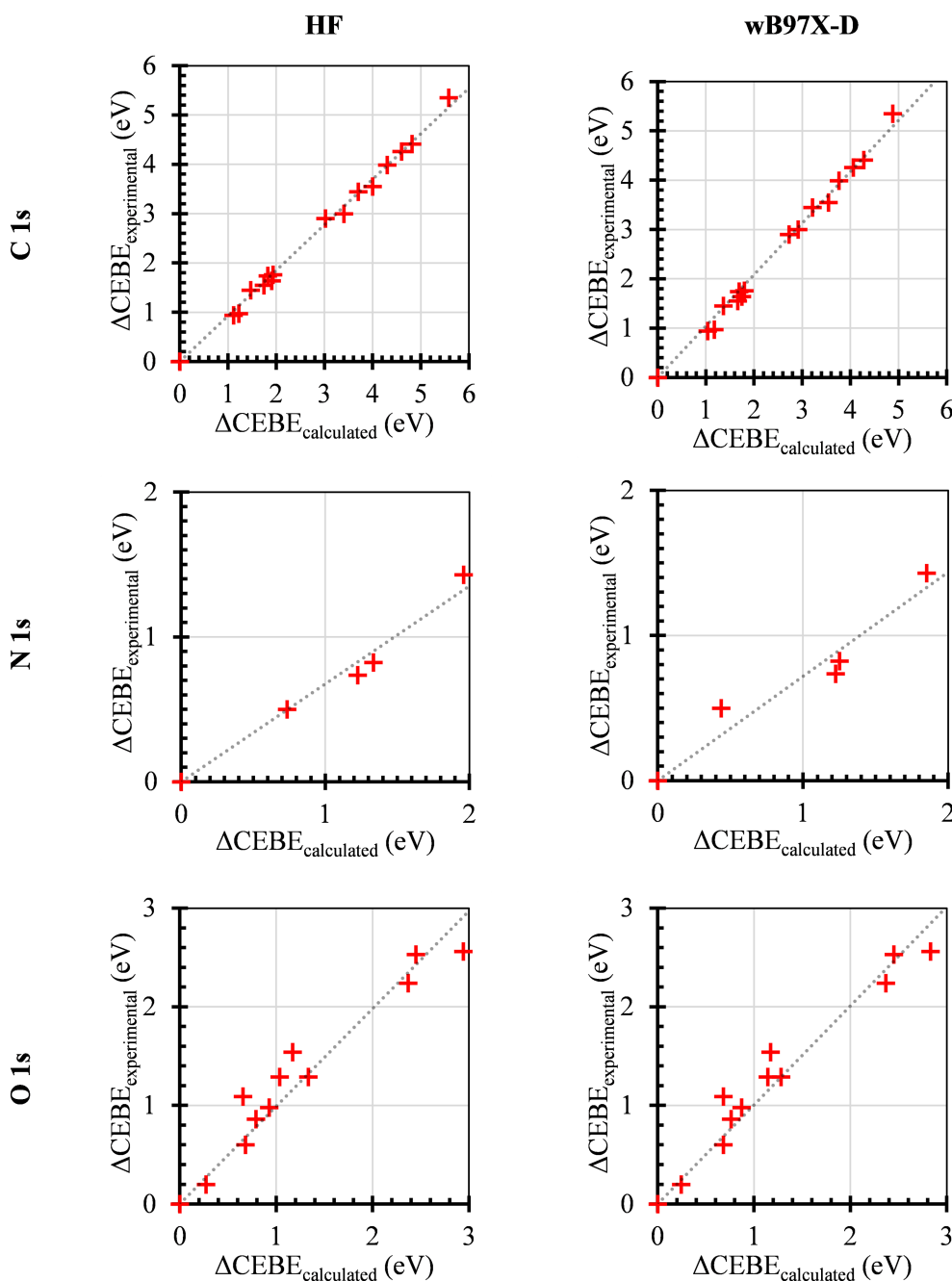
FIGURE 3 Linear correlation fits of the HF (left) and wB97X-D (right) calculated ΔCEBEs versus the experimental ΔCEBEs, relative to the lowest experimental CEBE per elemental region. The C 1s values are relative to the hydrocarbon, the N 1s shifts are relative to the centred secondary amine, and the O 1s shifts are relative to the centred secondary amide

TABLE 2 Statistical analysis showing the slope (a), offset (b) and regression coefficient (R^2) of the linear fits, as well as the Pearson correlation coefficient (r_p), the mean absolute error (MAE), and the maximum absolute deviation (MAX) between the experimental and calculated ΔCEBE datasets

		Slope (a)	Offset (b; eV)	R^2	r_p	MAE (eV)	MAX (eV)
HF	C 1s	0.92	20.07	1.00	1.00	0.22	0.45
	N 1s	0.68	23.53	0.99	0.99	0.36	0.53
	O 1s	0.99	26.28	0.98	0.97	0.16	0.44
wB97X-D	C 1s	1.04	−5.39	1.00	1.00	0.14	0.48
	N 1s	0.72	−6.86	0.97	0.97	0.30	0.49
	O 1s	1.01	−9.11	0.98	0.98	0.15	0.41

and Briggs database is shown in Table S8. The individual (Δ)CEBEs per functionality as used in the linear correlation fits are shown in Tables S9–S11.

The C 1s ΔCEBEs are reasonably well estimated by HF, but the linear correlation is notably improved after the introduction of wB97X-D with a reduction of the mean absolute error from 0.22 to 0.14 eV. The observed mean absolute error and maximum absolute error when involving DFT in this work (0.14 and 0.48 eV, respectively) showed to be smaller than those observed in the simulated C 1s spectra of organic monolayers by Giesbers et al (0.30 and 0.67 eV, respectively; compared with the average error based on the methods that used a Pople basis set).[25] A direct comparison with the C 1s simulated spectra of Giesbers et al was also performed; the observed differences in the estimated ΔCEBEs compared with this work are shown in Table S12.[25] The mean absolute difference of the C 1s ΔCEBEs between this work and the work of Giesbers et al is 0.2 and 0.1 eV for HF and wB97X-D, respectively.[25] There are methodological and structural differences between this work and the work of Giesbers et al (Giesbers et al used a smaller basis set, different DF and silicon clusters, whereas this work made use of a PE backbone), and the values provided by Giesbers et al were only available up to the first decimal place, limiting the extent to which conclusions can be drawn. The calculated N 1s ΔCEBEs are overestimated by both HF and wB97X-D when compared with the experimental N 1s ΔCEBEs and showed an increased mean absolute error of 0.36 and 0.30 eV, respectively. Compared with our results, almost identical errors in calculated N 1s CEBEs are reported in the literature, where organic monolayers on silicon and metal-based model structures were investigated, although the literature values show a linear correlation that is closer to unity when compared to our work.[25,53] The N 1s CEBEs estimated by Zuilhof et al (using B3LYP/6-311+G(d,p)) showed a mean absolute error of 0.40 eV and a maximum absolute error of 0.54 eV, whereas Zhao et al (also using B3LYP/6-311+G(d,p)) showed a mean absolute error of 0.27 eV and maximum absolute error of 0.67 eV. Both above-mentioned articles made use of the commercially available package 'natural bond orbital (NBO) analysis' to estimate CEBEs. This was not included in this work with the intent to keep our method free of charge. The similarity of the mean absolute errors between the estimated and experimental CEBEs in our work and that reported in the literature shows the quality of estimation to be comparable. Zuilhof et al and Zhao et al compared their estimated CEBEs to experimental data acquired at various laboratories including their own for their small-molecule-based monolayers. This work solely

compared the calculated CEBEs with the Beamson and Briggs polymer database, as this database is built from data acquired from polymer-based samples, which is more appropriate for our PE-based surfaces. Lastly, the observed mean absolute error in the O 1s region is relatively small, showing an error of 0.16 eV with HF and 0.15 eV with wB97X-D.

Altogether, a comparison of the calculated ΔCEBEs to the mean experimental ΔCEBEs indicated a strong correlation. Both methods demonstrated a regression coefficient (R^2) and a Pearson correlation coefficient (r_p) of 0.97 or higher for all the investigated regions, indicating that the experimental and calculated values linearly correlate with each other. The overestimation of the ΔCEBEs in the N 1s region as observed by the linear correlation slope is noted as a concern. However, this error may be (partially) introduced by energy referencing/material-specific differences. Despite that, the calculated ΔCEBEs are in reasonable agreement to the experimental ΔCEBEs, with those obtained by wB97X-D consistently exhibiting a lower error compared with those obtained by HF. Therefore, the wB97X-D-based peak model was used during the high-resolution peak fitting.

3.2 | XPS analysis

3.2.1 | Survey XPS spectra

The XPS survey spectra of the various UHMWPE samples are available in Figure S5, showing the polymer undoped and untreated (A; UD/UT), undoped and plasma-treated (B; UD/PT), doped and untreated (C; D/UT) and doped and plasma-treated (D; D/PT). The region maxima after energy referencing the C 1s region maximum to 284.8 eV (to allow comparison with the literature) are presented in Table S13. To quantify the elemental regions, both the 'Shirley' and the 'Tougaard' background were used, in separate data processing procedures, to inspect the change in the atomic composition due to the choice of background, as shown in Table 3. Generally, the deviations in the observed atomic composition due to the change in the background are small apart from iron (more specifically, Fe 2p). The results from the survey spectra needed to perform the high-resolution peak fitting are discussed below; a more in-depth discussion on the survey spectra peak fits and the rational on contaminant assignments is available in the Supporting Information.

For the identification of the contaminants and their contributions to the C 1s and O 1s peak fits into account, reference BE tables were

TABLE 3 Atomic composition of UHMWPE UD/UT (A1-3), UD/PT (B1-3), D/UT (C1-3) and D/PT (D1-3), determined by the survey spectra fitted with a Shirley/(Tougaard) background

	Atomic concentration ± St. dev. (%)			
	C 1s	N 1s	O 1s	Contaminants	
A1	91.46 ± 0.07 (91.59 ± 0.08)	0.64 ± 0.05 (0.50 ± 0.07)	5.92 ± 0.04 (5.94 ± 0.03)	Si 2p	1.72 ± 0.02 (1.67 ± 0.02)
				F 1s	0.27 ± 0.03 (0.31 ± 0.04)
A2	98.24 ± 0.05 (98.33 ± 0.07)	–	1.76 ± 0.05 (1.67 ± 0.07)	–	
A3	89.20 ± 0.05 (89.14 ± 0.11)	0.83 ± 0.03 (0.88 ± 0.11)	7.74 ± 0.04 (7.72 ± 0.04)	Si 2p	2.23 ± 0.03 (2.25 ± 0.02)
B1	64.28 ± 0.10 (61.56 ± 0.09)	15.55 ± 0.09 (16.15 ± 0.08)	16.42 ± 0.07 (16.86 ± 0.07)	Fe 2p	2.10 ± 0.05 (3.63 ± 0.03)
				Cr 2p	0.98 ± 0.03 (1.40 ± 0.03)
				Mo 3d	0.08 ± 0.01 (0.06 ± 0.01)
				Na 1s	0.32 ± 0.03 (0.18 ± 0.02)
				Cl 2p	0.27 ± 0.01 (0.16 ± 0.01)
B2	64.50 ± 0.09 (61.98 ± 0.07)	16.37 ± 0.08 (16.39 ± 0.07)	16.28 ± 0.05 (16.34 ± 0.06)	Fe 2p	1.34 ± 0.06 (3.50 ± 0.03)
				Cr 2p	1.03 ± 0.03 (1.37 ± 0.03)
				Mo 3d	0.07 ± 0.01 (0.06 ± 0.01)
				Na 1s	0.23 ± 0.02 (0.22 ± 0.02)
				Cl 2p	0.19 ± 0.01 (0.15 ± 0.01)
B3	84.39 ± 0.07 (83.88 ± 0.07)	5.47 ± 0.06 (5.79 ± 0.07)	9.66 ± 0.04 (9.86 ± 0.05)	Si 2p	0.49 ± 0.02 (0.47 ± 0.02)
C1	90.55 ± 0.05 (90.61 ± 0.05)	–	6.03 ± 0.04 (6.09 ± 0.04)	F 1s	2.75 ± 0.03 (2.61 ± 0.04)
				Si 2p	0.66 ± 0.02 (0.69 ± 0.02)
C2	90.91 ± 0.06 (90.83 ± 0.06)	–	6.50 ± 0.05 (6.64 ± 0.05)	Si 2p	2.18 ± 0.03 (2.11 ± 0.03)
				Al 2p	0.41 ± 0.01 (0.42 ± 0.02)
C3	95.38 ± 0.08 (95.27 ± 0.08)	–	4.11 ± 0.08 (4.40 ± 0.07)	Si 2p	0.51 ± 0.02 (0.34 ± 0.02)
D1	77.59 ± 0.09 (77.01 ± 0.09)	11.00 ± 0.08 (11.36 ± 0.08)	11.41 ± 0.06 (11.63 ± 0.06)	D1-3[a]	
D2	79.90 ± 0.08 (79.45 ± 0.07)	10.42 ± 0.08 (10.88 ± 0.06)	9.68 ± 0.04 (9.67 ± 0.04)	Fe 2p	0.32 ± 0.02 (0.34 ± 0.02)
D3	81.55 ± 0.08 (81.20 ± 0.08)	8.95 ± 0.07 (9.06 ± 0.07)	9.50 ± 0.05 (9.73 ± 0.05)	Cr 2p	0.33 ± 0.01 (0.36 ± 0.01)

[a]Averaged presence as determined in the summed spectrum; intensity too low in individual spectra to determine component area.

prepared based on the data available in the NIST database.[10] The BEs used to identify the minor contaminants (i.e. fluoride, chloride, sodium and aluminium) are shown in Table S14. The major contaminants (i.e. silicon, chromium and iron) were evaluated using more extensive BE tables, as shown in Tables S15–S17, respectively. Lastly, where applicable, the corresponding oxygen and nitrogen BEs of the contaminants are presented separately in Table S18. Next to assigning the most likely components based on the observed region maxima, the major contaminants are also investigated by means of peak fitting. The survey spectra peak fits of the Si 2p, Cr $2p_{(3/2)}$ and Fe $2p_{(3/2)}$ regions are presented in Figures S6–S8, respectively. The observed component concentrations of the fits are depicted in Figures S9–S11, respectively; these are also tabulated per peak fit individually in Tables S19 and S20.

In preparation for the high-resolution peak fitting, a conversion table was prepared to account for the expected presence of the silicon- and metal-based contaminants in the high-resolution spectra as determined by the survey peak fits, available in Tables S21 and S22, respectively. To allow conversion, the components are assumed to uphold their assigned theoretical composition. As it was uncertain

if the constrained or unconstrained survey peak fits were more accurate, an average of the respective peak fits was used to estimate the contaminant species present within each region. It was expected that this would introduce the least amount of error, considering the different survey peak fits identified the same components, albeit in somewhat different quantities. The conversion tables contain those that will be included in the high-resolution fits, apart from an unidentified fluoride-based component in 'C1' and aluminium identified as Al_2O_3 in 'C2'—which is expected to make up ([0.41 At $\%_{Al2p}$ * $\frac{3}{2}$]/6.50 At$\%_{O1s}$ =) 9.46 area% of the 'C2' its O 1s region.

3.2.2 | High-resolution XPS spectra

The high-resolution XPS spectra of UHMWPE UD/UT (A1-3), UD/PT (B13), D/UT (C1-3) and D/PT (D1-3) are available in Figure S12. The C 1s region maximum was referenced to 284.8 eV to allow comparison of the peak positions to the literature. Both the 'Shirley' and the 'Universal Polymer Tougaard' background were used, in separate data processing procedures, to fit the high-resolution spectra to inspect

the difference in the atomic composition due to the background change as shown in Table S23. After introducing the peaks associated with the contaminants, constraining their position as determined by the BE reference tables and constraining their area% as was established by the survey spectra peak fits, the high-resolution spectra were fitted using the peak model as calculated by wB97X-D. One of the UHMWPE-based high-resolution spectra fitted using the 'Shirley' background was selected from each of the sample series, namely, 'A2' (as it was the least oxidised/contaminated UHMWPE reference sample), 'B1', 'C3' (as it indicated the presence of α-tocopheryl quinone, [aTQ], similarly to 'D1-3') and 'D1'.

The tables depicting the component concentrations (pre-determined contaminants established with the survey spectra were omitted) as obtained from the individual high-resolution peak fits of UHMWPE UD/UT (A1-3), UD/PT (B1-3), D/UT (C1-3) and D/PT (D1-3) using a 'Shirley' background and the wB97X-D-based peak model including the respective higher-order carbon shifts are presented in Tables S24–S27. When comparing the component tables, it can be observed that the introduction of the higher-order carbon shifts had minimal effect on the type of functionalities identified by the peak model, but it does influence the estimated presence or positioning (i.e. centred or end-chain). This is due to the positional constraints set for the peak model reference components (see Section 2.4), as the peak models could move freely within the set BE ranges per elemental region, the influence of energy referencing in terms of component identification is prevented (as the ΔCEBEs relative to the peak model reference component remain constrained). As shown in Figure S13, energy referencing still introduced a deviation in the observed absolute CEBEs between sample series (A, B, etc.). It was observed that the untreated samples (A and C) showed the [CH$_{PE}$] component at about 284.7 eV, whereas the plasma-treated samples (B and D) showed the [CH$_{PE}$] component at about 284.5 eV—this may be caused by the C1s region maximum shifting upwards as the newly introduced functionalities form photoelectron peaks close to the main hydrocarbon peak. Apart from samples series 'B1-3', the peak model reference components in the showed a similar positioning between the samples of the same series (D1, D2, etc.).

The high-resolution peak fits of the UHMWPE UD/UT and D/UT samples ('A2' and 'C3') allowed a reasonable fit of the C 1s region using the LA(4.2,9,4) lineshape for the [CH$_{PE}$] peak model reference component, as presented in Figures S14 and S15, respectively. The introduction of the higher-order carbon shifts had negligible influence on the peak fits of 'A2'; only a small improvement in the residual standard deviation (STD) was noted from 1.747 to 1.634—which was expected considering the low degree of oxidation components that are associated with the higher-order carbon shifts. A minor [π − π*] presence was observed in the C 1s region of 'A2', likely due to some contamination originating from the polystyrene Petri dishes used for sample storage—which was accounted for by introducing an additional position-constrained component to the peak model between 291 and 292 eV. Based on ATR-FTIR peak fits of UHMWPE D/UT, the expected presence of the tocopherol-like components is between 9% and 22%

as shown in Figure S16. It is worth to note that the sampling depth of ATR-FTIR (several microns) is much higher than for XPS (several nanometres), making it difficult to compare the observed chemical composition between these two techniques. However, the estimation of the tocopherol-like components present in the polymer matrix is necessary to guide the model when overestimation of the tocopherol-like components is expected. The introduction of the higher-order carbon shifts to 'C3' only slightly increased the presence of [aTQ]; when comparing the composition observed with the 1° and 4° carbon peak model, it increased from 14.9%$_{[aTQ]}$ to about 17.7%$_{[aTQ]}$, respectively; the estimated presence of the tocopherol-like components matches closely to that observed by ATR-FTIR (ranging from 9% to 22%). Further addition of the higher order carbon shifts had a negligible impact on the composition as seen in Table S26, indicating the peak model reached a 'stable' component estimation.

From the peak fits of UHMWPE UD/PT (B1-3), it was established that the wB97X-D-based peak model including the 3° carbon shifts was most suitable for fitting the high-resolution XPS spectra of the plasma-treated UHMWPE surfaces evaluated in this work. As can be observed in the fitted spectra of 'B1' shown in Figure S17, the introduction of the higher-order carbon shifts improved the residual STD of the spectra fits from 1.671 to 1.492 until the introduction of the 4° carbon shifts (residual STD = 3.311); Following the incorporation of the 4° carbon shifts, the peak model suffered from [CH$_x$] overestimation in the C 1s region and underestimation of the components within the N 1s and O 1s regions. This also indicates that, although lineshapes designed from unmodified polymers are suitable to fit their reference spectra, a single unconstrained asymmetric peak is not sufficient to estimate the hydrocarbon presence in the modified PE-based surfaces due to the long-range effects arising from the newly introduced functional groups affecting the [CH$_2$] ΔCEBEs of the polymer backbone. It is thought that the increase of the C 1s region FWHM, as observed in Figure S12, forced the [CH$_{PE}$] peak to broaden (average FWHM$_{[CH]}$ in A13 was 1.07 eV; average FWHM$_{C1s}$ in B1-3 was 1.17 eV) and resulted in increased tailing towards higher BEs with the asymmetric lineshape used for the [CH$_{PE}$] component peak.

The high-resolution peak fits of the combined system, UHMWPE D/PT (D1), using the higher-order carbon shift models are presented in Figure 4 and its corresponding component graph in Figure 5. Using the ATR-FTIR peak fits discussed previously (showing 9%–22% tocopherol-like products) and the UHMWPE D/UT (C3) model system (showing ~78% [CH$_{PE/x}$] and ~16% tocopherol-like products), the presence of the tocopherol-like components in the high-resolution peak fits of 'D1' using the 1° carbon peak model appeared drastically overestimated (showing ~19% [CH$_{PE/x}$] and ~44% tocopherol-like products). When comparing the high-resolution spectra of sample series 'C' and 'D' in Figure S12, this overestimation was expected to be the result of spectral broadening introduced after plasma-treatment of doped UHMWPE. The broadened spectra made it more complicated for the 1° and 2° carbon peak models to distinguish between the [CH$_{PE/x}$] associated with the UHMWPE carbon backbone or the tocopherol-like components. The inclusion of the
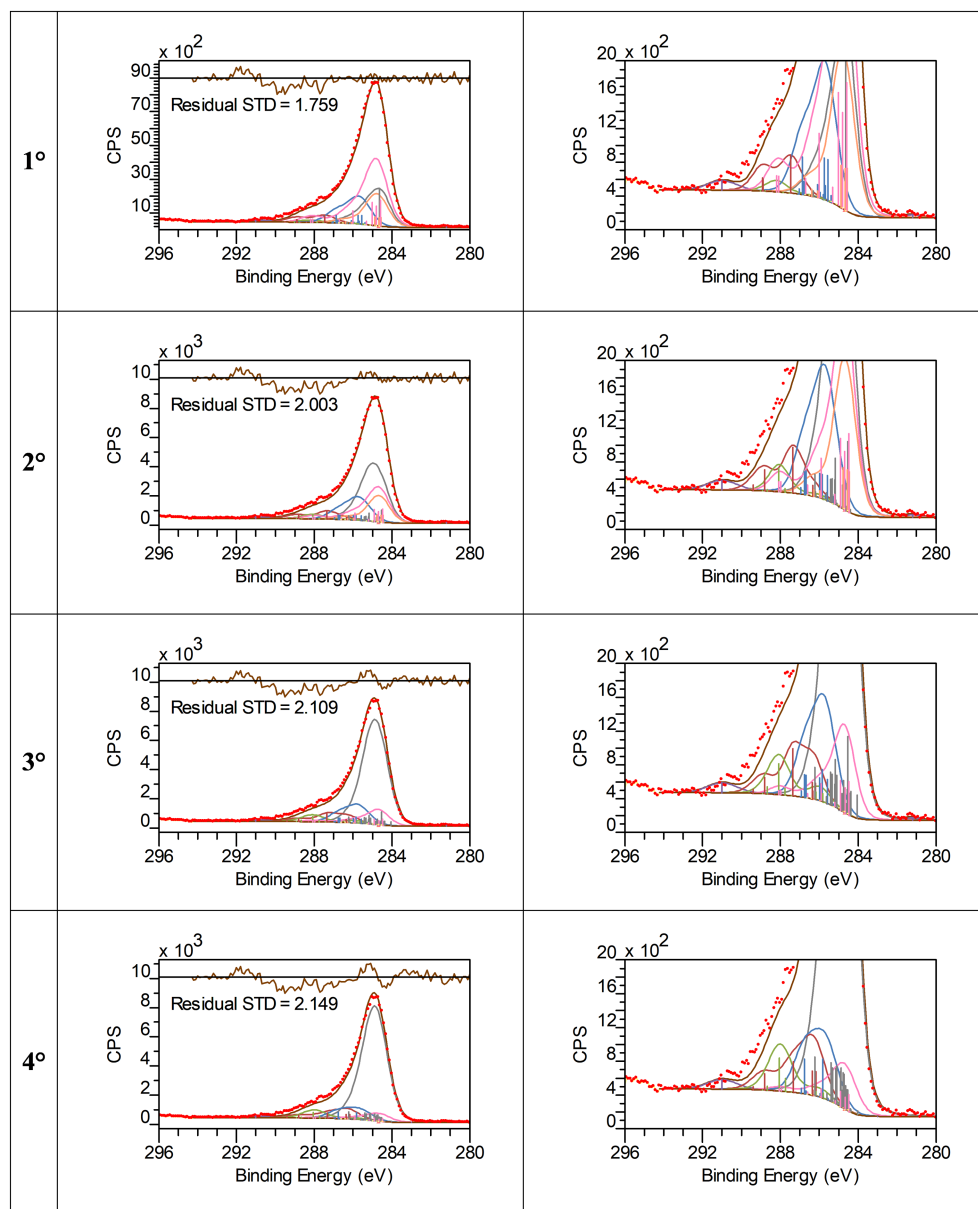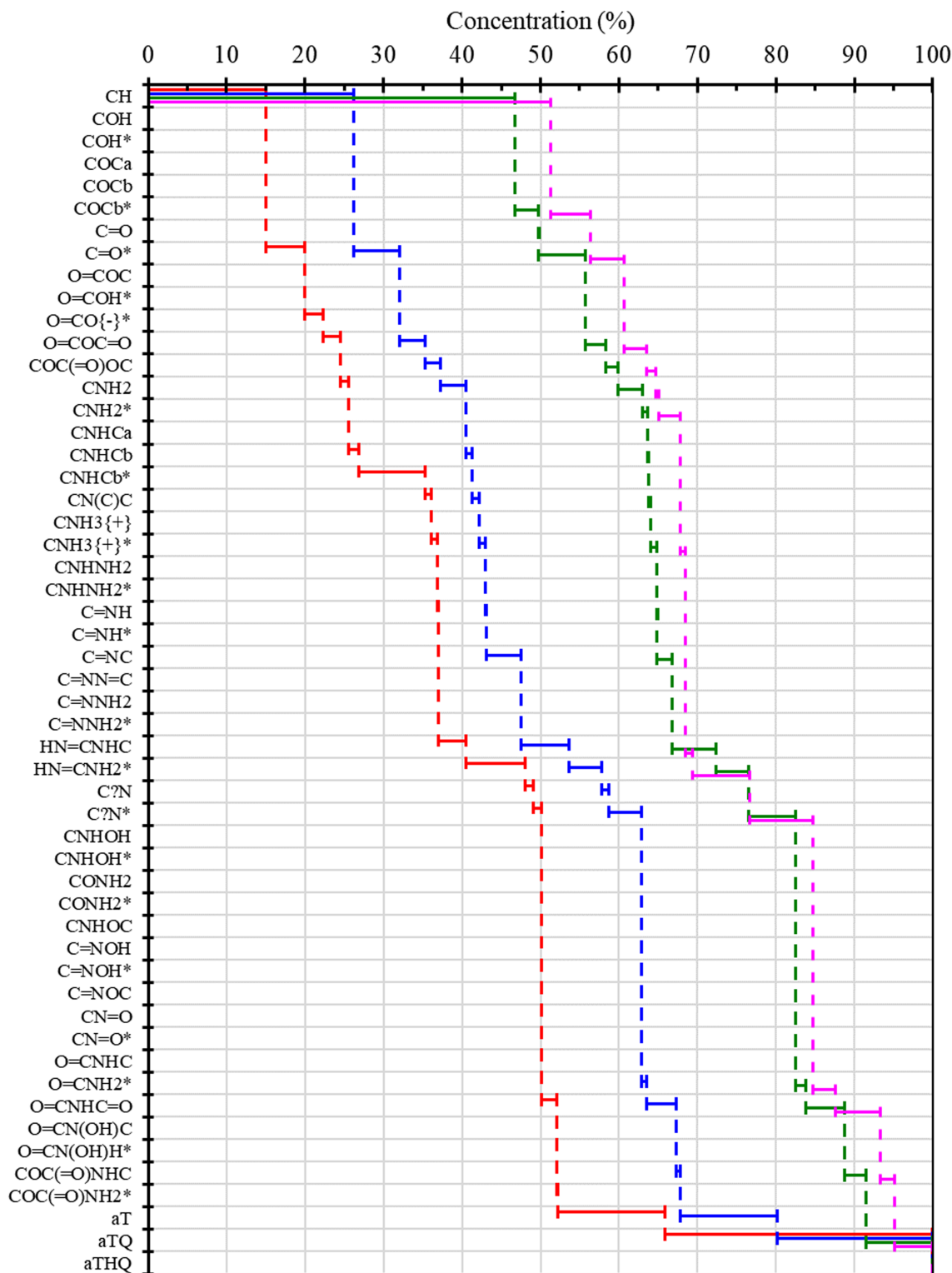
FIGURE 4 High-resolution C 1s spectra peak fits of UHMWPE D/PT (D1) using a 'Shirley' background and the wB97X-D-based peak model including the respective higher-order carbon shifts. The spectra display the recorded experimental data (**red**, dotted) and the summed peak model envelope (**brown**, solid). The colours represent the various component groups: [CH] (**grey**), [CO] (**dark red**), [CN] (**blue**), [CNO] (**green**), [aT] (**orange**), [aTQ] (**pink**), [aTHQ] (**yellow**) and contaminants (**purple**)

higher-order carbon shifts forced the reduction of the tocopherol-like components, but the peak model consistently identified [aTQ] throughout the peak fits. Similarly, as it was established during the peak fitting of UHMWPE UD/PT (B1), the 3° carbon peak model seemed most suitable for fitting the high-resolution XPS spectra of the UHMWPE D/PT surfaces evaluated in this work. As it can be observed in Figure 4, most of the residual area is situated at the higher BEs (288–291 eV) in the C 1s region and may be a result of unresolved loss events, neglected peak asymmetry or a minor error in the RSFs used as peak area constraints between the elemental regions—as Kratos RSFs are related to homogeneous materials, which excludes homogeneous materials with surface contamination. The high-resolution peak fit of 'D1' using the 3° carbon peak model is presented in more detail with labelling in Figure 6. The peak fits indicated that the inclusion of the higher-order carbon shifts prevented

the overestimation of the tocopherol-like components incorporated within the polymer matrix.

The component graph of the high-resolution peak fits, displaying the observed component concentrations of the above-discussed samples' high-resolution peak fits (i.e. 'A2', 'B1', 'C3' and 'D1') using the 3° carbon peak model, is shown in Figure 7. As it can be observed in the component graph, the components identified by the peak model in the combined system (UHMWPE D/PT) generally agree to those identified from the respective model systems (UHMWPE UD/UT, UD/PT and D/UT). The high-resolution peak fits of the untreated reference samples, UHMWPE UD/UT (A2) and D/UT (C3), both showed the presence of [C=O*]. However, only the peak fit of UHMWPE UD/UT (A2) showed some minor additional oxidation products (i.e. [O=COH*] and [O=COC=O]), and UHMWPE D/UT (C3) showed the presence of [aTQ]. When comparing the high-resolution peak fits

FIGURE 5 Composition of UHMWPE D/PT (D1) determined by the high-resolution spectra peak fits using a 'Shirley' background and the wB97X-D-based peak model including the 1° (**red**), 2° (**blue**), 3° (**green**) and 4° (**pink**) higher-order carbon shifts. The bars depict the component presence, stacking up to a total of 100%

of the functionality-rich samples obtained after ASPN treatment of the reference samples, UHMWPE UD/PT (B1) and D/PT (D1), the presence of [C=O*], [O=COC=O], [CNH₂⁽*⁾], [O=CNH₂*] [O=CNHC=O] and [HN=CNHR] were observed in both plasma-

treated sample series – where 'R' represents the atom present in the centred or end-chain functionality, C or H, respectively. However, only the peak fit of UHMWPE UD/PT (B1) showed the presence of [CNHNH2*] and [C=NH*], and only with UHMWPE D/PT (D1) the
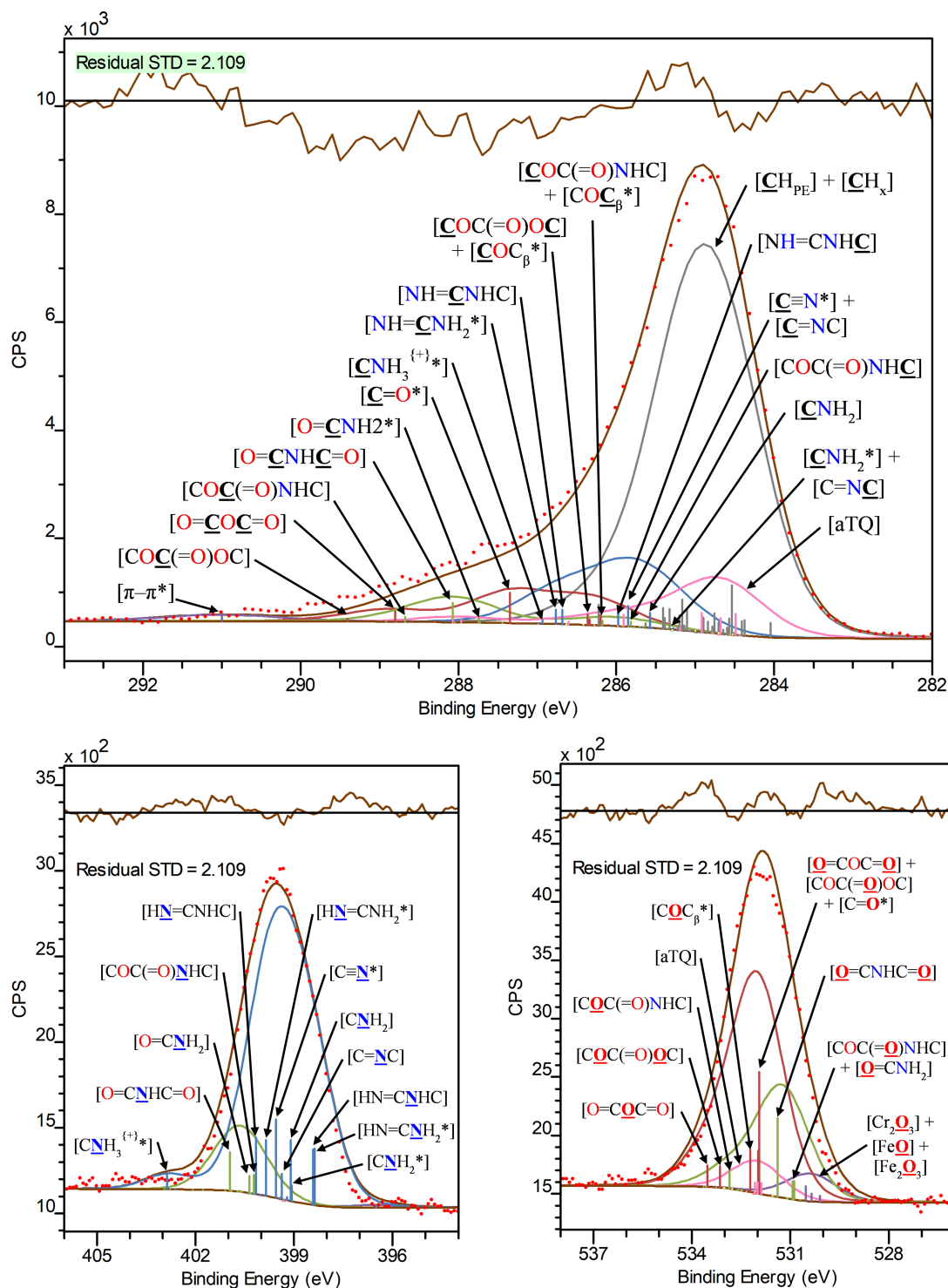
FIGURE 6 High-resolution C 1s, N 1s and O 1s spectra peak fit of UHMWPE D/PT (D1) using a 'Shirley' background and the wB97X-D peak model with the 3° higher-order carbon shifts. The spectra display the experimental data (**red**, dotted) and the summed peak model envelope (**brown**, solid). The colours represent the various component groups: [CH] (**grey**), [CO] (**dark red**), [CN] (**blue**), [CNO] (**green**), [aTQ] (**pink**) and contaminants (**purple**). The labels denote the component IDs, with the evaluated atom **bold** and underlined

presence of [C≡N$^{(*)}$] was noted. As it can be observed in Tables S23–S26, the components identified in the 'B' sample series correspond more often to functionalities in their end-chain positioning when the samples also showed metal contamination (i.e. Fe and Cr) in their corresponding survey spectra (i.e. 'B1' and 'B2'; see Section 3.2.1). But the samples showing little to no sign of metal contamination (i.e. 'B3' and 'D1-3') predominantly showed the presence of functionalities in their centred positioning.
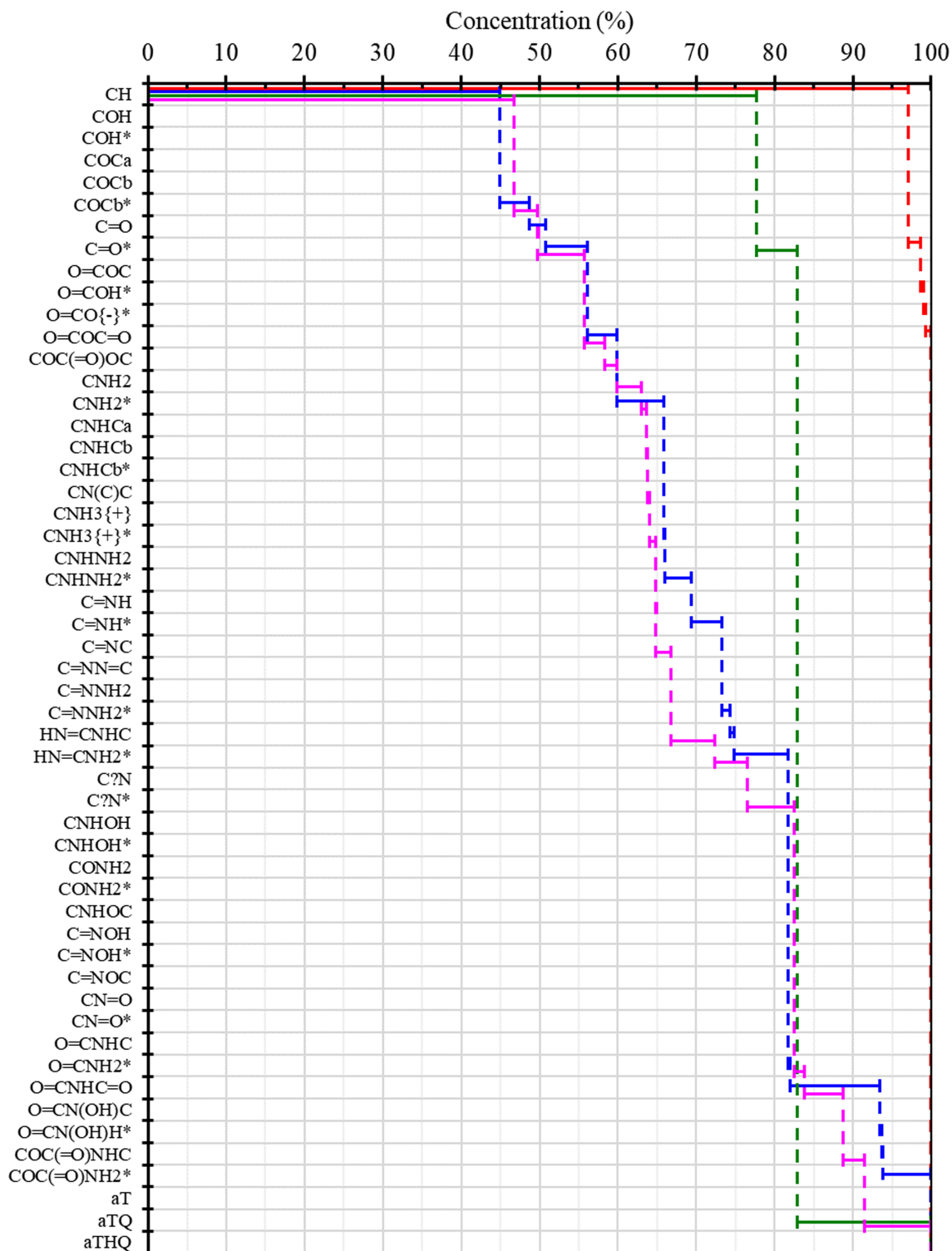
FIGURE 7 Composition of UHMWPE UD/UT (A2, **red**), UD/PT (B1, **blue**), D/UT (C3, **green**) and D/PT (D1, **pink**), determined by the high-resolution spectra peak fits using a 'Shirley' background and the wB97X-D-based peak model including the 3° higher-order carbon shifts. The bars depict the component presence, stacking up to a total of 100%

The high-resolution spectra of selected samples (i.e. 'B1' and 'D1') were also further investigated by using the 'Universal Polymer Tougaard' background during peak fitting with the 3° carbon peak model to observe the difference in peak model response due to a change in background. In addition to that, the use of the asymmetric lineshape LA(4.2,9,4) was also tested for all [CH$_x$] components instead of solely for the [CH$_{PE}$] component to investigate the influence of increased peak asymmetry on the peak model response. As presented

in Figure S19, the change in the background and peak asymmetry had a negligible impact on most component with the peak fits of 'B1' and 'D1' when using the 3° carbon peak model. When using the asymmetric lineshape for the higher-order [CH$_x$] components, only minor variation is observed in the presence of some components. The peak fits involving 'B1' showed a maximum average deviation of 2.55 At% for [COC(=O)NH$_2$*]. The peak fits involving 'D1' showed a maximum average deviation of 4.98 At% for [αT] and 4.58 At% for [CH]; the [aT] component was only present in the fits including the asymmetric higher-order [CH$_x$] components. The minimal changes observed when changing the background type or introducing peak asymmetry indicate that the peak model is robust, especially in terms of component identification.

3.2.3 | Comparison with reference-based peak fitting

To demonstrate the improved detail that was achieved when using the developed multi-region peak model for the interpretation of the complex system (UHMWPE D/PT, D1), a comparison was made with (i) conventional reference-based peak fitting (i.e. area-unconstrained peak fitting of the C 1s region; informed but not computationally connected to the N 1s and O 1s regions) and (ii) advanced reference-based peak fitting (i.e. area-constrained multi-region peak fitting of the C 1s, N 1s and O 1s regions). The C 1s spectra peak fits of the comparison between the various peak fitting approaches are presented in Figure 8. The corresponding N 1s and O 1s spectra peak
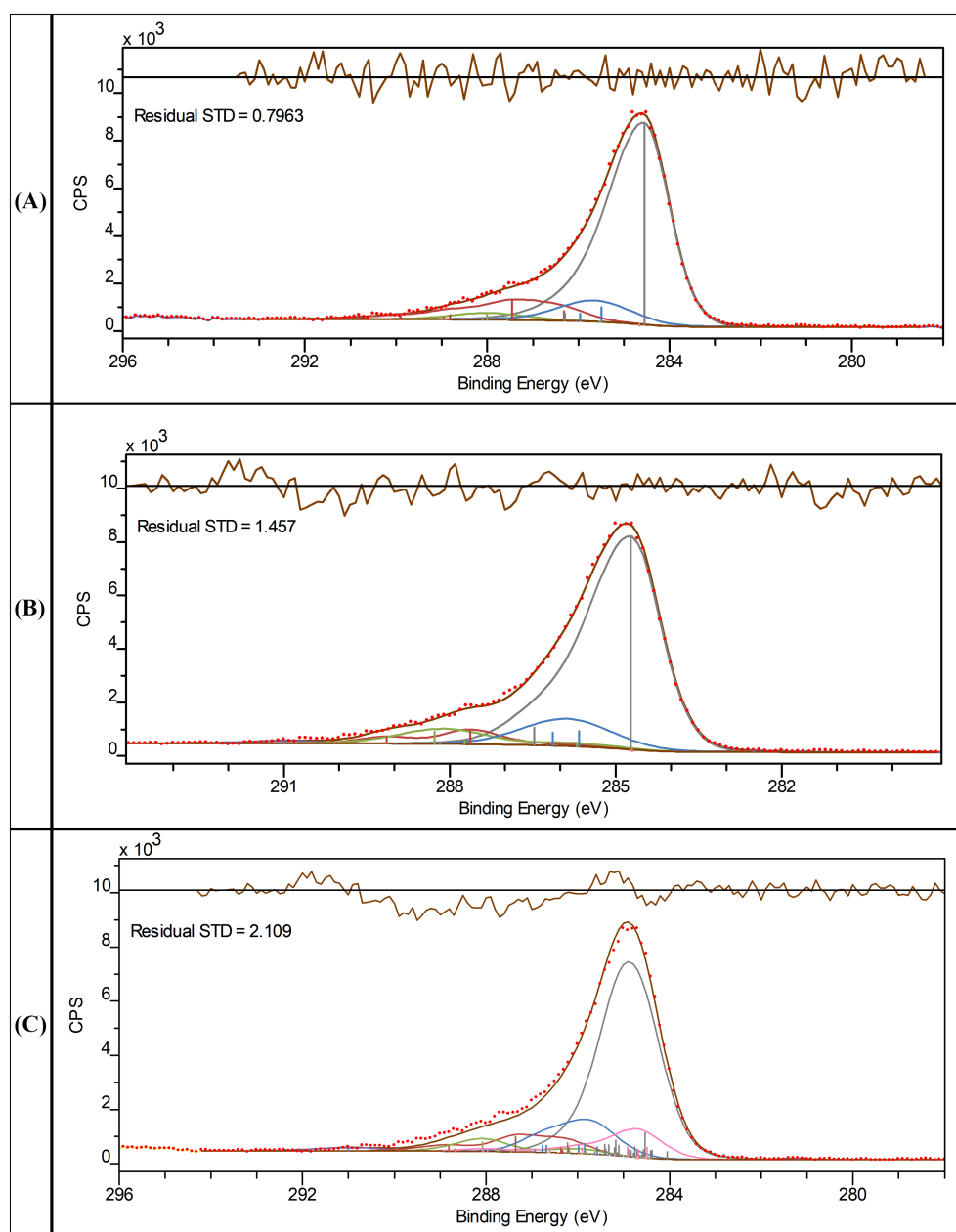
FIGURE 8 High-resolution C 1s spectra peak fits of UHMWPE D/PT (D1) using a 'Shirley' background following conventional reference-based peak fitting (A), advanced reference-based peak fitting (B) and the wB97X-D-based peak fitting using the 3° higher-order carbon shifts (C). The spectra display the experimental data (**red**, dotted) and the summed peak model envelope (**brown**, solid). The colours represent the various component groups: [CH] (**grey**), [CO] (**dark red**), [CN] (**blue**), [CNO] (**green**), [aTQ] (**pink**) and contaminants (**purple**)

fits are shown in Figure S20. Positional constraints were based on the mean ΔCEBEs from the Beamson and Briggs database as used in the linear correlations, available in Tables S9–S11. With the reference-based peak fitting (i and ii), the considered functionalities were those typically seen with the XPS spectral interpretation of plasma-treated polymeric surfaces.[5,42–46] The evaluated functionalities and chemical compositions as obtained after peak fitting are tabulated in Table 4; the components that showed no presence after peak fitting using the wB97X-D-based peak model were omitted for readability but are depicted in Table S27.

With the conventional reference-based peak fitting, a C 1s region peak model was used to identify the present components. The observed presence of the components was informed by the observed peak shifts and magnitude of the peak ratios of the corresponding peak fits of the N 1s and O 1s regions. However, as the peak areas of the components within each elemental region are unconstrained, the peak fits are individual least-square solutions and therefore hard to control—often resulting in subjective interpretation due to manual influence from the spectral analyst. Nonetheless, as it can be observed in the N 1s and O 1s peak fits of the conventional reference-based peak fits in Figure S20, both regions were fitted with three components. The N 1s region is fitted with a component to reflect carbon single-bonded nitrogen ([C–NX]), carbon triple-bonded nitrogen ([C≡N]) and oxygen double-bonded to a carbon single-bonded nitrogen ([O=C–N]), whereas the corresponding O 1s region was fitted with components presenting carbon single-bonded oxygen ([C–OX]), carbon double-bonded oxygen ([C=O]) and oxygen double-bonded to a carbon single-bonded nitrogen ([O=C–N]). Altogether, this minimal

TABLE 4 Composition of the high-resolution spectra peak fits of UHMWPE D/PT (D1) using a 'Shirley' background following (a) conventional peak fitting, (b) reference-based advanced peak fitting and (c) wB97X-D-based peak fitting using the 3° higher-order carbon shifts

ID	A (At%)	B (At%)	ID	C (At%)
CH	57.5	59.9	CH	46.7
C–OX	0.00	0.91	COC_β*	3.06
C=O	8.97	5.59	C=O	0.04
			C=O*	5.95
O=COC	2.85	0.02	O=COC	0.00
O=COH*	1.16	0.00	O=COH*	0.00
O=COC=O	0.95	3.15	O=COC=O	2.60
COC(=O)OC	7.06	0.22	COC(=O)OC	1.57
C–NX	9.56	9.31	CNH_2	3.04
			CNH_2*	1.57
			$CNHC_\beta$	0.04
			CN(C)C	0.34
			$CNH_3^{[+]}$*	0.69
C=NX or HN=C–NX	Not evaluated		C=NC	1.93
			HN=CNHC	5.66
			$HN=CNH_2$*	4.19
C≡N	5.07	7.95	C≡N*	5.96
O=CNHC	1.15	3.66	O=CNHC	0.00
$O=CNH_2$*	5.26	0.00	$O=CNH_2$*	1.31
O=CNHC=O	0.50	9.28	O=CNHC=O	4.84
COC(=O)NHC	Not evaluated.		COC(=O)NHC	2.75
aTQ	Not evaluated.		aTQ	8.55
ID	**A (At%)**	**B (At%)**	**C (At%)**	
CH	57.5	59.9	55.2	
CO	21.0	9.90	13.2	
CN	14.6	17.3	22.6	
CNO	6.91	12.9	8.90	

Notes: Presenting the individual component presence (based on the combined presence of all corresponding atoms related to the respective IDs) and the summed presence of the various component groups as grouped in the peak fits: [CH], [CO], [CN] and [CNO]. For ease of comparison, the atomic composition determined with the conventional reference-based peak fitting of the C 1s region (a), was adjusted to reflect the inclusion of the corresponding [N and O] atoms. Additionally, as the reference-based peak fitting did not include the tocopherol-like components, the summed [CH] presence in 'C' represents the combined presence of [CH] and [aTQ].

interpretation of the N 1s and O 1s provides sufficient rationale to consider the major functionalities that are typically peak fitted with plasma-treated polymeric surfaces to the C 1s region peak model.[5,42–46] The subsequent peak fit of the C 1s region, where effort was made for the peak fit to reflect the peak ratios of the above-discussed components fitted within the N 1s and O 1s regions, showed a major presence (>5%) of [C=O], [COC(=O)OC], [C–NX], [C≡N] and [O=CNH$_2$].

Despite that the conventional reference-based peak fitting provided strong indications of the present component groups (i.e. [C–OX], [C–NX], [O=C–N], etc.), the area-unconstrained peak fits do not provide a detailed interpretation, remain hard to control and are prone to arbitrary interpretation. Therefore, advanced reference-based peak fitting was also explored, where a reference-based multi-region peak model was used to interpret the merged high-resolution spectra. Similarly, as with the high-resolution peak fitting performed using the developed peak model in Section 3.2.2, the areas of the component peaks in the N 1s and O 1s regions were constrained to the C 1s region components with the respective RSFs and theoretical composition associated with the evaluated functionalities. In contrast to the area-unconstrained reference-based peak fit, a significantly larger presence of [O=CNHC=O] is noted instead of [O=CNH$_2$*]. The presence of the [CO] components showed a decrease from 21.0% to 9.90%, the [CN] components showed an increase from 14.6% to 17.3%, and the [CNO] components showed an increase from 6.91% to 12.9% between the reference-based area-unconstrained and multi-region peak fits, respectively.

Altogether, little change was observed in the [CH] presence, and the main interplay of the component's presence was noted between the other component groups: [CO], [CN] and [CNO]. The main difference observed when switching from the reference-based multi-region peak model (Model B) to the developed multi-region peak model (Model C) was an increase in [CO] and [CN], most likely because significantly more nitrogen-based functionalities were evaluated, which were not included within the Beamson and Briggs database. However, despite the inclusion of the additional functionalities in the developed peak model, various similarities between the reference-based and developed multi-region peak fits were also recognised. For example, both multi-region peak fits showed a notable presence of [C=O], [C≡N] and [O=CNHC=O]. However, where the reference-based peak fit showed a major presence of [C-NX], this seemed to have shifted in the wB97X-D-based peak fit to the newly introduced [HN=CNHR] components—where 'R' represents the atom present in the centred or end-chain functionality, C or H, respectively. The inclusion of the carbon double-bonded nitrogen functionalities with the developed peak model increased the presence of nitrogen and reduced that of [O=CNHC=O] compared with the reference-based multi-region peak fit.

The residual STD increased when comparing the conventional reference-based peak fitting with the advanced reference-based peak fitting and with the wB97X-D-based peak fitting (0.7963, 1.457 and 2.109, respectively), which was to be expected as the peak model became increasingly more constrained. Most of the residual in both

the reference-based and developed multi-region peak models was noted at the higher BEs in the C 1s region (i.e. 288–291 eV) and likely a result of unresolved loss events, neglected peak asymmetry or a minor error in the RSFs used as peak area constraints between the elemental regions (as RSFs are related to homogeneous materials, which excludes homogeneous materials with surface contamination). However, as was observed with the reference-based peak fits, it was difficult to identify functionalities that extend outside the reference database. More specifically, various functionalities that contain more than one ΔCEBE within an elemental region (i.e. amidine, carbamate, etc.) were seldomly evaluated within the reference database—limiting the ability of detailed spectral interpretation. This is where conventional peak fitting becomes more subjective when involving other references or prone to personal experience or bias in terms of component identification.

Another difficulty of using the conventional reference database to construct a peak model for the interpretation of complex, high-resolution XPS spectra arises from the fact that the observed ΔCEBEs will originate from a variety of materials. As a result of the latter, common evaluated component groups such as [C–NX] display broad BE ranges (>0.8 eV) in the reference database. Additionally, as discussed in Section 3.2.2, there are indications that energy referencing the C 1s region maximum to 284.8 eV is not suitable when comparing the XPS spectra of the unmodified and modified UHMWPE surfaces—as the functionalities closely positioned to the main hydrocarbon peak influence the C 1s region maximum. However, contrary to reference-based peak fitting, this issue was resolved by using the developed multi-region peak model and with positional constraints for the peak model reference components (see Section 2.4) that are flexible enough to overcome the influence of the functionalities near the main hydrocarbon peak.

Using conventional peak fitting, the typical generalisations observed to improve peak fitting convenience (e.g. assigning a single peak to describe all [C–O]/[C–N]-based functionalities, or grouping differences in functionality positioning despite the variation in the theoretical composition of, e.g. centred and end-chain functionalities) limit the ability to establish a detailed spectral interpretation. As was shown previously in Section 3.1.3, a comparison of the calculated ΔCEBE database to the experimental ΔCEBEs showed that the deviation introduced by the change in functionality positioning is significant enough to allow differentiation during the high-resolution XPS spectra peak fitting. Ultimately, the developed approach allowed the identification of a small number of functional groups (out of a larger number of possible functionalities) whose presence could not readily be predicted or 'guessed' otherwise using conventional XPS peak fitting. Biomolecules incorporated within the polymer matrix were able to be distinguished by the peak model—which was not possible with reference-based peak fitting due to a lack of available references in the literature.

Furthermore, as the long-range effects of the evaluated functionalities on the carbon backbone are not considered with reference-based peak fitting, component stability (i.e. the observed change in component presence with the inclusion of its associated higher-order

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