X-ray Photoelectron Spectroscopic Studies of Poly(ether ketone ketone): Core Level and Valence Band Studies and Valence Band Interpretation by Xα Calculations

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X-ray photoelectron spectroscopy was employed to characterize the surface chemistry of poly(ether ketone ketone) (PEKK) resin. Four types of carbon and two types of oxygen were identified from the core-level spectra with a stoichiometry that is correlated with the chemical structure of PEKK. In the valence band spectra, two types of oxygen were also identified with a larger chemical shift than that in the core level spectra. The results reveal that valence band spectral studies can be understood by comparison of the spectra with spectra calculated using multiple-scattered wave Xα calculations.

Introduction

A rapidly developing aerospace industry has always been seeking advanced lightweight composite materials, with excellent mechanical strength, to replace traditional metals. A novel semicrystalline polymer, poly(ether ketone ketone) (PEKK) has been developed by du Pont[1-4] as the latest member of the matrix resin family for high-performance, advanced composites. PEKK is a thermoplastic resin with excellent performance. As compared with poly(ether ether ketone) (PEEK), PEKK has comparable tensile strength and tensile modulus, density, and flammability. Preliminary assessment has shown[1,2] that PEKK has a higher glass-transition temperature T_g, a lower melting temperature, and lower melt viscosity than PEEK. This implies that PEKK has a better thermal stability and better processibility than PEEK. Performance of composites based on PEKK as matrix resin and carbon fiber as reinforcement has shown[1-4] excellent mechanical properties with high flexural, shear, and compressive strength equivalent or superior to composites using PEEK resin as matrix. Tests also show[1-4] that carbon fiber/PEKK composites have good damage tolerance, excellent environmental durability, and hot-wet stability. The excellent performance has made PEKK a good candidate for aerospace application.

Application of PEKK in carbon fiber reinforced composites has shown that PEKK is an excellent matrix resin for high performance composites with specific properties. It is well-known that the overall composite properties are controlled by the reinforcing carbon fibers, matrix, and fiber-matrix interactions. As a result of this multiphase nature many physical properties of advanced composites based on PEKK will be greatly influenced by the fiber-matrix interface. A clear understanding of surface chemistry of PEKK is important in controlling the interfacial behavior of composites using PEKK as matrix. The objective of this study is to characterize the surface of PEKK by X-ray photoelectron spectroscopy (XPS), to use theoretical calculations to interpret the valence band spectrum, and to distinguish spectral features in the valence region which may be important in identifying the characteristic features of the spectrum that can be used in the application of PEKK in advanced composites.

Experimental Section

The PEKK resin used in this study was kindly provided by du Pont (P11923-15501). The resin is additives-free with a number average molecular weight of 8220 (GPC) and a weight average molecular weight of 28 500 (GPC). The glass transition temperature is 156 °C (DSC) and the melting temperature is 305 °C (DSC).

The as-received resin was in the form of pellets with an average diameter of about 2 mm. Two methods were employed to prepare XPS samples: (1) Grinding: The as-received resin pellets were ground into a fine powder in a glass mortar. A double-sided adhesive type was used to fix the finely ground resin powder on a copper plate. (2) Solution casting thin film: 1 g of as-received resin was dissolved in 50 mL of a mixture of 1:1 phenol and 1,2,4-trichlorobenzene at 100-120 °C under stirring. The solution was cast on a copper sheet and dried in a convection oven for 24 h at 50 °C and then vacuum dried for 24 h at 80 °C to remove the solvent.

XPS analysis was conducted on an AEI (Kratos) ES200B X-ray photoelectron spectrometer using Mg Kα X-rays. A fixed retardation ratio (FRR) mode with a ratio of 1:23 was used to run all core level spectra and valence band spectra. The base pressure in the sample chamber was in the range 10^{-8}–10^{-9} Torr. The XPS spectrometer was calibrated using the Cu 2p region of an etched Cu sheet. In this spectrum, the separation between the Cu $2p_{1/2}$ peak (952.33 eV) and the Cu $2p_{3/2}$ peak (932.71 eV) is 19.62 eV. The separation between the Cu $2p_{3/2}$ peak and the Cu L_3MM Auger peak (335.03 eV) is 597.68 eV. Data analysis was performed using the same methods as previously described.[5] The nonlinear background of the experimental valence band spectra was removed according to the method described elsewhere,[6,7] so that the spectra can be compared with the calculated spectra. The binding energy of the experimental spectra was calibrated on the basis of the most intense peak of C 1s region as 284.6 eV.

The multiple-scattered wave Xα calculation was performed on an IBM RISC System/6000 computer.

Results and Discussion

Core Level. The repeating unit of the macromolecular chain for PEKK is seen in Figure 1,[1] in which three types

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(1) Chang, I. Y. *SAMPE Q.* **1988,** *19,* 29.

(2) Pratte, J. F.; Krueger, W. H.; Chang, I. Y. *34th Int. SAMPE Symp.* **1989,** 2229.

(3) Khan, S.; Pratte, J. F.; Chang, I. Y.; Krueger, W. H. *35th Int. SAMPE Symp.* **1990,** 1579.

(4) Chang, I. Y.; Hsiao, B. S. *36th Int. SAMPE Symp.* **1991,** 1587.

(5) Xie, Y.; Sherwood, P. M. A. *Chem. Mater.* **1991,** *3,* 164.

(6) Proctor, A.; Sherwood, P. M. A. *Anal. Chem.* **1982,** *54,* 13.

(7) Tougaard, S.; Sigmund, P. *Phys. Rev. B* **1982,** *25,* 4452.

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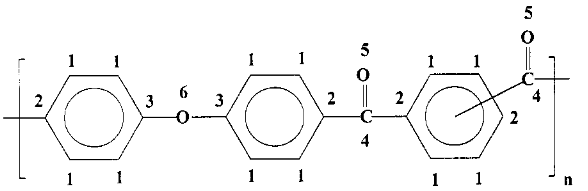

Figure 1. Molecular structure of poly(ether ketone ketone).

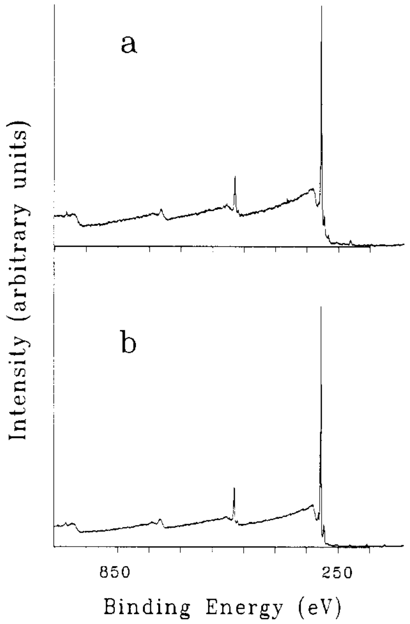

Figure 2. XPS survey scan for poly(ether ketone ketone): (a) ground powder sample; (b) solution-cast thin film sample.

of unit, phenyl ether, terephthalaldehyde, and isophthalaldehyde, are incorporated. Assuming the surface and the bulk to have the same chemical structure, it is expected that four types of carbon and two types of oxygen would be identified from the spectrum. For carbon, they are labeled as 1 (*C*—H and *C*—C), 2 (*C*—C=O), 3 (*C*—O), and 4 (*C*=O), and for oxygen 5 (C=*O*) and 6 (C—*O*). From this structure, an O/C ratio of 0.150 is expected.

The survey scan is shown in Figure 2. Only carbon and oxygen are found on the PEKK surface. No other heteroatoms, such as chlorine, have been detected. This indicated that the solution-cast thin film sample was solvent free. C 1s and O 1s spectra were obtained from the ground powder sample and the solution-cast thin film sample. The C 1s and O 1s peak areas were measured and an O/C ratio was calculated using sensitivity factors of 1.00 and 2.85 for carbon and oxygen, respectively. The O/C ratios were 0.137 in both cases. The experimental O/C ratio is slightly less than expected (0.150) from stoichiometry for both as-received powder sample and solution-cast thin film sample.

The C 1s core level spectra are shown in Figure 3. According to the molecular structure in Figure 1, the C 1s envelope was fitted using five component peaks. The five peaks are *C*—H and *C*—C (type 1), *C*—C=O (type 2), *C*—O (type 3), *C*=O (type 4), and $\pi \rightarrow \pi^*$ shakeup. There may be shakeup features associated with the five component peaks, but we use the $\pi \rightarrow \pi^*$ features to represent the most notable shakeup feature in the spectrum. The expected relative peak area is type 1:type 2:type 3:type 4 = 6:2:1:1. All the fitting parameters are given in Table I.

The last column in Table I shows the relative peak area. It can be seen that the experimental value is basically in an agreement with that expected. The chemical shifts of the five component peaks are seen in Table I. The main peak (type 1) in both powder sample and film sample was set as zero chemical shift. β-type carbon (type 2) has a chemical shift of 0.67 eV for powder sample and 0.50 eV for thin-film sample. In determining the chemical shift for carbonyl carbon (type 4), the conjugation effect[8] was taken into account. The expected value would be about 0.7 eV lower than that without the effect of conjugation. In our work, this conjugation effect was 0.34 eV for the powder sample (chemical shift 2.66 eV) and 0.51 eV for the thin film sample (chemical shift 2.49 eV). Pawson et al. also reported[9] a conjugation effect of 0.7 eV for poly(ether ether ketone) (PEEK).

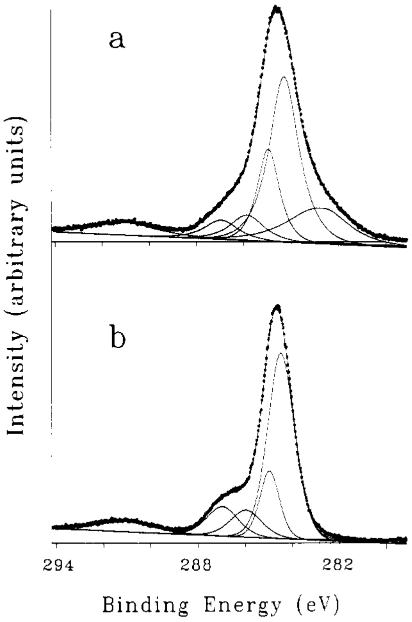

Figure 3. C 1s core level XPS spectra for poly(ether ketone ketone): (a) ground powder sample; (b) solution-cast thin film sample.

Table I. Nonlinear Least-Squares Curving-Fitting Results for PEKK

sample	peak type	assignment	chem shift from the main peak (eV)	fwhm (eV)	Gaussian/Lorentzian mixing ratio	rel peak area
C 1s Region						
			-1.63	2.51	0.80	2.52
powder PEKK[a]	1	*C*—H, *C*—C	0	1.46	0.85	6.00
	2	*C*—C=O	0.67	1.08	0.80	2.43
	3	*C*—O	1.58	1.67	0.80	1.01
	4	*C*=O	2.66	1.67	0.80	0.77
		$\pi \rightarrow \pi^*$ shakeup	6.71	3.06	0.80	0.94
thin-film PEKK[a]	1	*C*—H, *C*—C	0	1.33	0.50	6.00
	2	*C*—C=O	0.50	0.95	0.50	1.56
	3	*C*—O	1.50	1.56	0.50	1.01
	4	*C*=O	2.49	1.56	0.50	1.10
		$\pi \rightarrow \pi^*$ shakeup	6.62	2.68	0.50	0.67
O 1s Region						
powder PEKK[b]	5	C=*O*	0	2.03	0.85	2.00
	6	C—*O*	2.07	1.56	0.80	0.98
thin-film PEKK[b]	5	C=*O*	0	1.32	0.50	2.00
	6	C—*O*	1.96	1.22	0.50	1.18

[a] Most intense peak is no. 1. [b] Most intense peak is no. 5.

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(8) Briggs, D. *Practical Surface Analysis, Vol. 1: Auger and X-ray Photoelectron Spectroscopy*, 2nd ed.; Briggs, D., Seah, M. P., Eds.; Wiley; Chichester, 1990; p 447.

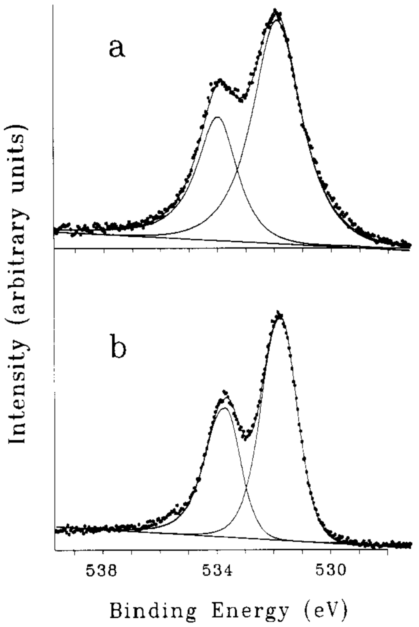

Figure 4. O 1s core level XPS spectra for poly(ether ketone ketone): (a) ground powder sample; (b) solution-cast thin film sample.

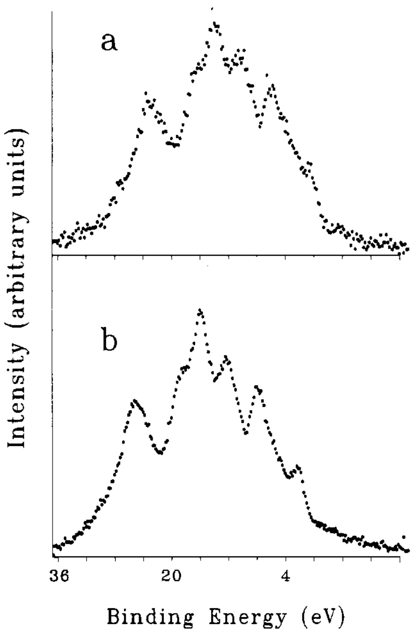

Figure 5. Valence band XPS spectra for poly(ether ketone ketone): (a) ground powder sample; (b) solution-cast thin film sample.

In fitting the C 1s core level spectrum of the gound powder sample, an extra peak was found at 1.63 eV of the low binding energy side of the main peak with a relative area of 2.52 if the main peak area was fixed as 6. The shape of the low binding energy side of the spectrum indicates the presence of this sixth peak. The inclusion of the sixth peak at low binding energy side improves the fits greatly. Figure 3 shows the profile of the powder sample to be broader than that of the thin-film sample. The low binding energy side of the powder sample has a shoulder, and the peak envelop shows more Lorentzian character than the film sample. This broadening effect was observed on all different powder samples (as-received powder sample without grinding and powder samples ground to different extent). We believe that the difference between the powder and thin-film samples arises from differential sample charging[10–12] in the powder and that both samples have the same composition. We have accounted for this by using different peak shapes to fit the powder and thin film samples, together with a sixth peak on the low binding energy side of the C 1s spectrum arising from the reduced charging shift of surface-adsorbed hydrocarbon. The best fits could be achieved for the powder sample if a Gaussian/Lorentzian mixing ratio of 0.85 (85% Lorentzian character) was used for the main peak and a value of 0.80 for other component peaks, and for the thin film sample if a ratio of 0.50 (50% Lorentzian character) was used for all the component peaks.

The broadening effect was observed in O 1s region as well. Figure 4 shows the O 1s core level spectra. The O 1s profile was fitted to two component peaks, as expected from the structure in Figure 1, C═*O* (type 5) and C—*O* (type 6) with type 5 on low binding energy side and type 6 on high binding energy side. Theoretically, the relative peak area is type 5:type 6 = 2:1. In curve fitting the O 1s region, it was found that the same Gaussian/Lorentzian mixing ratio that had been satisfactorily used for C 1s region could be applied to O 1s region to achieve the best fits. Using these Gaussian/Lorentzian mixing ratios, a relative peak area of type 5:type 6 = 2:0.98 was obtained for the powder sample and type 5:type 6 = 2:1.18 for the thin-film sample. This fitting result is in fairly good agreement with that expected. The peak separation for the two types of oxygen is 2.07 eV for the powder sample and 1.96 eV for the thin-film sample, as shown in Table I. In Pawson et al.'s work on PEEK,[9] a separation of 2.0 eV was used for these two types of oxygen.

Stoichiometry calculation and curve-fitting results showed that all the C 1s and O 1s components are correlated with the functional groups in chemical shift and relative peak area. The agreement between the stoichiometric O/C ratio and the component peak information obtained from curve fitting, and the results expected from the structure in Figure 1 indicates that macromolecular structure is the same on the surface and in the bulk for both powder PEKK and thin-film PEKK.

Peak assignments can be correlated with the molecular structure shown in Figure 1. The differences in the C 1s region of the powder sample shown in Figure 3 arises from differential sample charging in the powder.

Valence Band. Figure 5 shows nonlinear background removed (by Tougaard method[7]) valence band XPS spectra of PEKK. Both powder sample and thin-film sample have the same profile pattern, and all the features can be seen from both samples. The O 2s region lies in the range 22–30 eV. Two overlapping features can be assigned to this region, they are attributed to oxygen type 5 (C═*O*) and type 6 (C—*O*), respectively. The feature at about 24 eV originated from type 5 and the feature at about 28 eV was assigned to type 6. This valence region is often more sensitive to chemical environment than the core region and is a valuable tool to investigate chemical difference in polymeric materials. We have also found[13]

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(9) Pawson, D. J.; Ameen, A. P.; Short, R. D.; Denison, P.; Jones, F. R. *Surf. Interface Anal.* **1992**, *18*, 13.

(10) Dickinson, T.; Povey, A. F.; Sherwood, P. M. A. *J. Electron Spectrosc.* **1973**, *2*, 441.

(11) Citrin, P. H.; Thomas, T. D. *J. Chem. Phys.* **1972**, *57*, 4446.

(12) Hagenhoff, B.; Leyen, D. van; Niehuis, E.; Benninghoven, A. *J. Vac. Sci. Technol.* **1989**, *A7*, 3056.

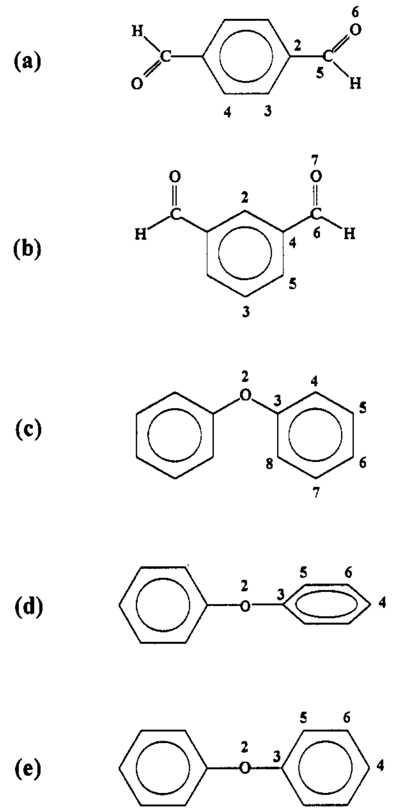

Figure 6. Five component units used in calculation of valence band spectra of PEKK: (a) terephthalaldehyde (C_{2v}); (b) isophthalaldehyde (C_{2h}); (c) phenyl ether (C_{2v}); (d) phenyl ether (D_{2d}); (e) phenyl ether (D_{2h}).

in both metallic and nonmetallic systems[5] that the O 2s region is more sensitive to chemical environment than the O 1s region. In the 10–22-eV region, a triplet pattern is seen clearly. This is characteristic of C2s feature for aromatic structure and has been confirmed on other aromatic structures.[5]

Xα Calculations. The ground-state multiple-scattering Xα method was used to calculate the valence band spectra of the PEKK molecule. The repeat unit structure in Figure 1 was used as a model to represent the PEKK molecule. The repeat unit was divided into three component units, phenyl ether, terephthalaldehyde, and isophthalaldehyde, and the calculations performed separately. Energy levels from the three parts were then combined stoichiometrically to obtain the ground-state energy levels of the PEKK molecule.

On the basis of the molecular structure in Figure 1, one part of the repeat unit is assumed to come from phenyl ether. We have taken the other part of the repeat unit to be made up of one-half terephthalaldehyde and one-half isophthalaldehyde. In fact the calculated spectrum of these two units is very similar, and thus the proportion used to mix these two calculated spectra together has little effect on the final calculated spectrum. The actual proportion of terephthalaldehyde to isophthalaldehyde in the polymer is a proprietary property of the Du Pont Co. For the phenyl ether part, three types of conformation with different symmetry were taken into account. All the five component units for calculation of the valence band spectra of the PEKK molecule are shown in Figure 6. The PEKK molecule is represented by the following three models:

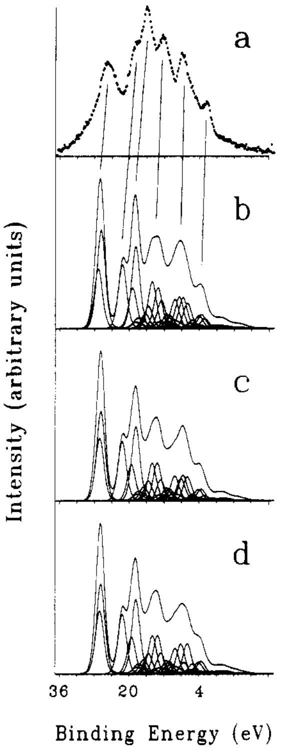

Figure 7. Comparison between experimental and calculated valence band XPS spectra for PEKK: (a) experimental (solution-cast thin-film sample); (b) model 1: $^1/_2$terephthalaldehyde + $^1/_2$isophthalaldehyde + phenyl ether (C_{2v}); (c) model 2: $^1/_2$terephthalaldehyde + $^1/_2$isophthalaldehyde + phenyl ether (D_{2d}); (d) model 3: $^1/_2$terephthalaldehyde + $^1/_2$isophthalaldehyde + phenyl ether (D_{2h}).

Model 1: $^1/_2$terephthalaldehyde +
$^1/_2$isophthalaldehyde + phenyl ether (C_{2v})

Model 2: $^1/_2$terephthalaldehyde +
$^1/_2$isophthalaldehyde + phenyl ether (D_{2d})

Model 3: $^1/_2$terephthaldehyde +
$^1/_2$isophthalaldehyde + phenyl ether (D_{2h})

Multiple-scattering Xα calculations and construction of the calculated spectra were carried out based on the three models. Table II shows parameters used in the calculation for the five component units. The calculated spectra were constructed by weighing the atomic contributions to the molecular orbitals with the Scofield cross sections.[14] The component energy levels were represented by a 50% mixed Gaussian–Lorentzian product function with equal width (1.18 eV). X-ray satellite features from the Mg X-ray radiation were included, all of these being combined together to obtain the calculated spectra.

All the five component models used in the calculation have benzene rings in their structures. In calculated valence region spectra, all five component units show the distinct triplet "fingerprint" in the 10–20-eV region. In construction of the valence band spectra for the whole PEKK repeat unit, this triplet feature, present in all the components, was used as a basis for aligning the calculated spectra of the relevant component units.

Figure 7 shows the calculated valence band spectra using

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(13) Welsh, I. D.; Sherwood, Peter M. A. *Phys. Rev. B* **1989**, *40*, 6386.

(14) Scofield, J. H. *J. Electron Spectrosc.* **1976**, *8*, 129.

Table II. Parameters Used and Features of the Xα Calculation

α value:	carbon, 0.759 28; oxygen, 0.744 47; hydrogen, 0.776 54
max l value:	carbon, 1; oxygen, 1; hydrogen, 0

Cluster:	C_6H_4-1,4-$(CHO)_2$ terephthalaldehyde	C_6H_4-1,3-$(CHO)_2$ isophthalaldehyde	C_6H_5-O-C_6H_5 phenyl ether	C_6H_5–O–C_6H_5 phenyl ether	C_6H_5–O–C_6H_5 phenyl ether
symmetry	C_{2h}	C_{2v}	C_{2v}	D_{2d}	D_{2h}
outer sphere α value	0.7639013	0.7639013	0.7661404	0.7661404	0.7661404
C—C═O bond length (Å)	1.47	1.47			
$\overline{\text{C—C}}$ (aryl) bond length (Å)	1.37	1.37	1.37	1.37	1.37
O═C—R bond length (Å)	1.22	1.22			
$\overline{\text{O═C}}$—H bond length (Å)	1.10	1.10			
Ar $\overline{\text{C—H}}$ bond length (Å)	1.09	1.09	1.09	1.09	1.09
Ar C—O bond length (Å)			1.34	1.34	1.34
carbon sphere radius (Å)					
no. 2	0.820	0.820			
no. 3	0.832	0.822	0.820	0.820	0.820
no. 4	0.832	0.810	0.862	0.860	0.860
no. 5	0.794	0.822	0.862	0.860	0.860
no. 6		0.784	0.862	0.860	0.860
no. 7			0.862		
no. 8			0.850		
oxygen sphere radius (Å)	0.841	0.830	0.822	0.820	0.820
hydrogen sphere radius (Å)	0.423	0.423	0.423	0.423	0.423
outer sphere radius (Å)	4.449	4.438	5.593	5.593	5.593
virial ratio (−2 T/V)	1.018 01	1.020 08	1.024 53	1.019 89	1.019 91
convergence[a]					
calculated O 2s area (counts/eV)	30 190	34 216	19 161	21 725	21 479
calculated O 2s relative area	2 (av of terephthalaldehyde and isophthalaldehyde)		1.19	1.35	1.33

[a] The convergence was reached when energy levels differed by less than 10^{-6} Ry between the last two iterations. This was fulfilled when the difference in potentials between the beginning and the end of the iteration was less than 10^{-5} of the potential at the start of the iteration.

the three models for PEKK with the experimental spectrum for comparative purpose. Spectral addition of the appropriate component units was performed to construct the spectra in a manner consistent with the assumed PEKK stoichiometry. A good agreement between theory and experiment is obtained for all the features in valence region for all the three models. It can be seen that the O 2s region of all three models show two types of O 2s peaks with the one on the high binding energy side being assigned to type 5 oxygen and the one on the low binding energy side assigned to type 6 oxygen. This explains the shoulders on the high binding energy side of the O 2s region in the experimental valence band spectra. In the O 2s region of calculated spectra of the five component units (Figure 6), the O 2s relative peak area between terephthalaldehyde/isophthalaldehyde (average of these two units) and phenyl ether, as shown in Table II, is approximately 2 to 1. For the PEKK model 1, the O 2s relative peak area between terephthalaldehyde/isophthalaldehyde and phenyl ether (C_{2v} symmetry) is 2:1.19, which is very close to curve-fitting results of the experimental spectrum of the thin film sample, 2:1.18. While there is small difference between the models, it is not possible to conclusively distinguish one model from another on the basis of comparison with the experimental data.

The separation between the two types of oxygen in model 1 is 0.64 eV, while the separations in model 2 and 3 are 0.26 and 0.19 eV, respectively. A large separation would be consistent with the experimental data as well as with our results on other compounds.[5] The peak separations, together with the calculated O 2s relative area, might imply that PEKK has a phenyl ether part that has a significant amount of the C_v symmetry component. In the 12–24 eV region, the triplet pattern associated with the aromatic structure is precisely predicted by the calculations for all three models. The relative peak position and peak height of the two other features in the experimental spectra in the low binding energy side of the spectra (0–10 eV) are also predicted by the calculation.

Conclusions

XPS studies of PEKK show that four types of carbon and two types of oxygen can be identified. The stoichiometry and chemical shift are consistent with the macromolecular structure of PEKK. In the valence band spectra two types of oxygen and characteristic features of the aromatic structure can be identified. The spectroscopic results indicate that the surface of PEKK has the same chemical structure as the bulk. The multiple-scattering Xα calculation provides a good explanation of the valence band spectra, and explains the features the valence band region. The valence band spectrum of PEKK is distinctive and allows PEKK to be distinguished from other polymeric materials.[15–17]

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(15) Sherwood, P. M. A. *J. Vac. Sci. Technol. A*, **1992**, *10*, 2783.
(16) Hamilton, L. E.; Sherwood, P. M. A.; Reagan, B. M. *Appl. Spectros.* **1993**, *47*, 139.
(17) Briggs, D.; Beamson, G. *High Resolution XPS of Organic Polymers: The Scienta ESCA300 Database*; Wiley: Chichester, 1992.