RESEARCH ARTICLE

Revisiting degradation in the XPS analysis of polymers

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A study on the degradation of both halogenated and non-halogenated polymers has been made by x-ray photoelectron spectroscopy on two different types of common place photoelectron spectrometer. The degradation results herein are compared with the degradation index of Beamson and Briggs, and a notable difference was observed. The effects of neutraliser and spot size on the degradation kinetics are explored and lead to simple recommendations for the successful analysis of damage-susceptible polymers.

KEYWORDS
damage, degradation index, polymer, XPS, X-ray

1 | INTRODUCTION

X-ray photoelectron spectroscopy (XPS) has a long and established role in the surface analysis of polymeric materials,[1–10] with angle-resolved XPS especially useful in the determination of surface modification and concentration gradients.[11–14] Such ubiquitous use in polymer analysis led to the seminal resource 'High resolution XPS of organic polymers: The Scienta ESCA300 Database', by Beamson and Briggs.[1]

In their work, Beamson and Briggs presented the high-resolution spectra of over 100 homopolymers, drawing attention to the analysis-induced damage, generating the so-called *degradation index,* which allows researchers a means to acquire data from similar polymer classes with minimal degradation or to assess potential damage from previous analysis. This index is reported as a change in the atom ratio, for example, F/C for a fluoropolymer, with respect to the ratio at time zero and denoted as $(X_t/X_0) \times 100$, where X is the atom ratio, the corresponding percentage is then rounded to the nearest 5% for reporting; an example plot is given in Figure 1 for fluoropolymers taken from Beamson and Briggs.[1] In simple terms, the higher the value for the degradation index, the more susceptible the polymer is to damage.

Of course, x-ray-induced damage is not unknown in XPS analysis, and many studies have been initiated on an array of polymeric materials,[15–22] including a VAMAS interlaboratory study.[23] The importance of appreciating and understanding such damage is exemplified by ISO standard 18554, which provides a simple procedure for the identification, estimation and correction degradation in the elemental composition of a material during analysis by XPS.

However, damage is not limited to the x-rays alone. The effect of dual-neutralisation (combination of low energy argon ions and electrons) has been shown to accelerate the reduction of some inorganic materials,[24] whilst for some organic materials, the reduction effects from the neutraliser are comparable with the reduction by the x-rays alone.[15]

These observations led us to continue our work into sample degradation and begin a preliminary re-investigation of the work by Beamson and Briggs, utilising modern XPS systems. Given that manufacturers are giving us as end users high-quality instruments for rapid and accessible use by a broad church of research disciplines and combined with the erosion of knowledge by no-longer having dedicated and experienced XPS instrument operators, the misinterpretation of sample damage is highly probable, and such issues have been highlighted in recent series of guides focussing on reproducibility Challenges in XPS analysis, see for example, other studies.[25–27]

2 | EXPERIMENTAL

Two systems were employed in this study. The first is a Thermo Scientific K-Alpha[+] system that utilises micro-focussed Al kα radiation operating at a power of 72 W (6 mA x 12 kV). The system uses a combined low energy electron-low energy ion source for charge
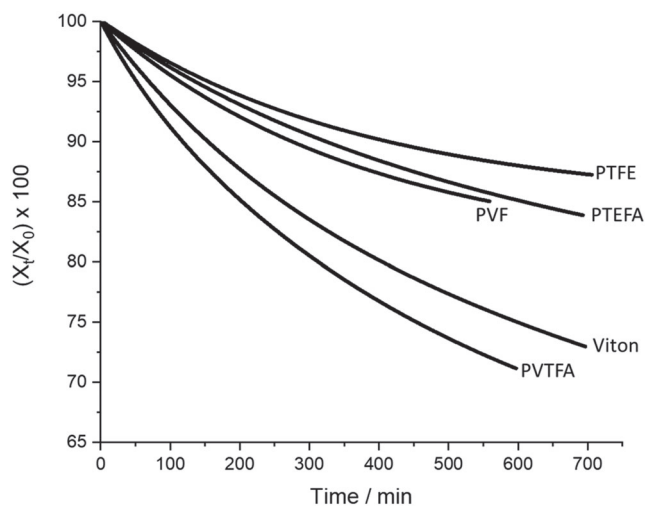
FIGURE 1   Digitised plot of the data used for the determination of the degradation index of selected fluoropolymers as reported by Beamson and Briggs.[1] $X = $ F/C atom ratio.

compensation. Unless otherwise specified, all data were collected at a pass energy of 50 eV with a 0.1-eV step size, using the 400-μm spot mode, which is an elliptical area of approximately 400×600 μm and defines the analysis area. For all spectral regions collected, the time per region was kept to approximately 1 min and acquisitions totalled a maximum of approximately 530 min for degradation studies.

The second system is a Kratos Axis Ultra DLD, which utilises electron-only charge compensation and a lens-defined analysis area of approximately 700×300 μm as defined by the slot mode. As the x-ray source illuminates an area larger than the analysis area, the source was operated at 144 W (12 mA × 12 kV) in an attempt to offset the effect of the x-ray micro-focussing in the Thermo system. Data were collected at a pass energy of 40 eV and a step size of 0.1 eV and under similar iterative conditions to that described previously.

Bulk polymer sheets (25×25 cm^2) of polyvinylidene difluoride (PVdF), polyvinylidene chloride (PVdC), polyvinyl chloride (PVC) and polyvinyl fluoride (PVF) were purchased from Goodfellow, from which sections were cut and then mounted using stainless-steel tweezers on to sections of UV cleaned glass microscope slides to ensure the samples were floated from the spectrometer, only the corners of the samples were touched with tweezers and the samples cut sufficiently large so that analysis could take place in areas away from the edges. The polymer surface was scraped using a clean surgical blade in the spectrometer load lock and then the system pumped down to vacuum. PTFE was studied as both a section cut from a PTFE rod (Goodfellow), and plumbers' tape, no discernible difference was found between them so are treated as one herein. Where applicable, polymer films were prepared in accordance with the method and solvents described in Beamson and Briggs.[1]

Data were analysed using CasaXPS v2.3.25.[28] Where required data were calibrated to the C 1s peak for aliphatic C—C/C—H bonds, taken to be 285 eV, and quantified after subtraction of a Shirley type background.

For the K-alpha$^+$ system, atomic ratios were calculated using Scofield sensitivity factors[29] with an electron escape depth correction according to the TPP-2M formula of Tanuma et al.[30] as recommended by the instrument manufacture, whereas for the Kratos Axis Ultra system, modified Wagner sensitivity factors were used as supplied by the instrument manufacturer.

Where fitting was required, a Voigt type function was used according to the LA line shape in CasaXPS and described by LA(1.53,243).

3 | RESULTS AND DISCUSSION

Sample degradation arises from changes in the bonding induced by the interaction of the incident x-rays with the analysed volume and the secondary electron cascade emitted from the sample. It follows that sample damage from monochromatic x-ray sources is typically perceived as less damaging than older achromatic sources, which would typically be operating around 100°C within a few millimetres of the sample surface. Degradation is not limited to effects from the x-rays alone but also to the nature of the charge compensation source employed.[15,24,31] Although sample degradation cannot be avoided for certain classes of material, it can be minimised and examples of ways of minimising and correcting for degradation can be found in the literature and ISO standard 18554.[32] Our analysis of a small but pertinent subset of polymers studied by Beamson and Briggs are presented below.

3.1 | Fluorinated polymers

The application of fluorinated polymers is widespread, with uses as insulation, lubrication, and hydrophobic surfaces (PTFE); photovoltaics and clothing (PVF); and as chemically inert binder in Li-ion batteries (PVdF) among their many uses. An understanding the surface chemistry of these materials is critical in their application, and hence, appreciation of analysis-induced degradation is important.

Beamson and Briggs studied seven fluorine-containing polymers, which they reported to have degradation indexes between 10% and 30%; here we study a small set of the polymers to investigate the reduction rates.

Figure 2 shows the degradation data plotted the same way as that in Beamson and Briggs, for (A) Kratos Axis Ultra and (B) Thermo K-alpha$^+$ systems. Clearly the K-alpha data have a pronounced exponential decay profile leading to higher degrees of damage than noted in Beamson and Briggs.[1] It is of note that even for the Kratos system, there is a disagreement in the level of damage with the data presented by Beamson and Briggs, but this may be expected given the differences in spectrometer design, x-ray power, and so forth as noted in previous studies and possibly the quality of the polymers used.[23] Nevertheless, there is a general trend that relative to PTFE, the other fluorinated polymers degrade in a similar fashion. However, the reduction on the Thermo system is inherently greater, with approximately 2–2.5 times greater reduction levels at similar time intervals.
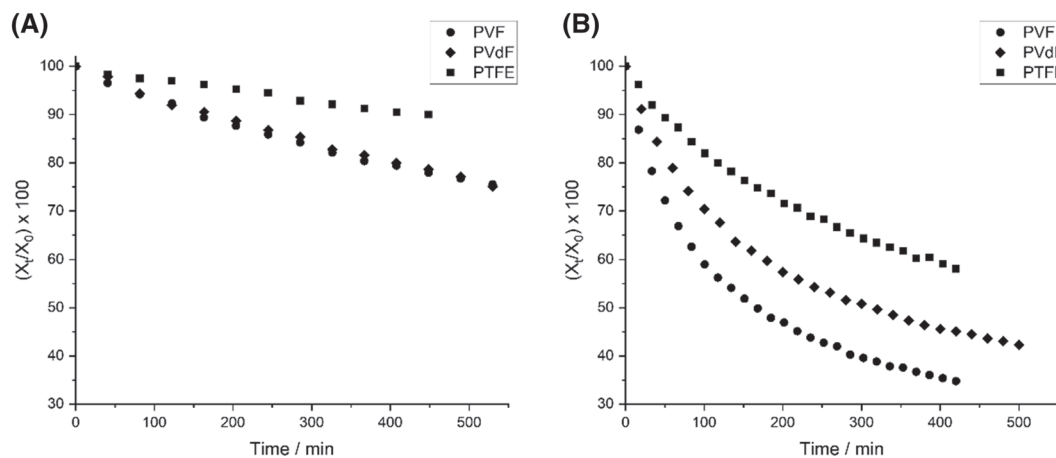
FIGURE 2 Degradation plots for three fluorinated polymers, where: (A) broad-spot analysis on Kratos Axis Ultra, and (B) micro-focussed analysis on Thermo K-alpha[+]. Note the y-axis scales are different.
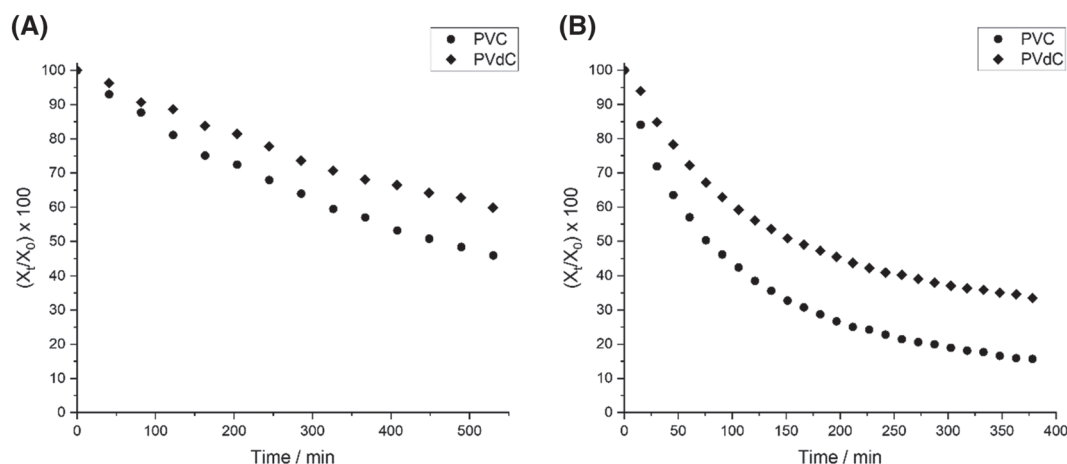
FIGURE 3 Degradation plots for two chlorinated polymers: (A) analysis from Kratos Axis Ultra, and (B) on Thermo K-alpha[+].

3.2 | Chlorinated polymers

Beamson and Briggs studied nine chlorine-containing polymers, of which three were chlorinated styrene's where the position of Cl substitution differs but exhibits near-identical degradation. By far, the most widely studied chlorinated polymer is PVC, and its degradation has been extensively reported.[17,20,23,33–37] All studies indicate a degradation pathway following first-order kinetics through loss of HCl.[23,38] Baer et al. suggested that PVC could be used as a degradation reference, allowing the generation of a 'Photon threshold index (PTI)', to reference the rate of degradation of different polymers for a given XPS system[16]; however, a cursory view of the literature does not seem to suggest its mainstream adoption.

Figure 3 shows a comparison of the behaviour of PVC and PVdC on the two XPS systems employed in this study, and again, two significantly different trends and degrees of degradation are observed.

It is of note that the degradation of the PVC used in this study was evident in the K-Alpha system, within approximately 1 min of analysis, with a feint golden-brown colouration visible on the internal camera system of the spectrometer, characteristic of polyene formation. As observed for PVF and PVdF, the degradation of PVC is greater than PVdC, which is in variance with Chaney and Barth who postulated that the degradation rate of PVC should be less than that of PVdC based on a derived 'molar photoelectric cross-section',[39] but in agreements with the expected degradation order from Beamson and Briggs.[1]

3.3 | Non-halogenated polymers

For non-halogenated polymers, the degradation is expected to be slower than their halogenated counterparts, with the data of Beamson and Briggs indicating most degradation indexes for C—O and C—N containing polymers are in the range of 5%–10%. Spin-coated films of polyvinyl alcohol (PVA), polyethylene glycol (PEG), polypropylene glycol (PPG) and N-vinyl-2-pyrrolidone (PVP, referred to as PVnP in Beamson and Briggs [1]) were analysed solely on the K-Alpha instrument, the results of which are shown in Figure 4.
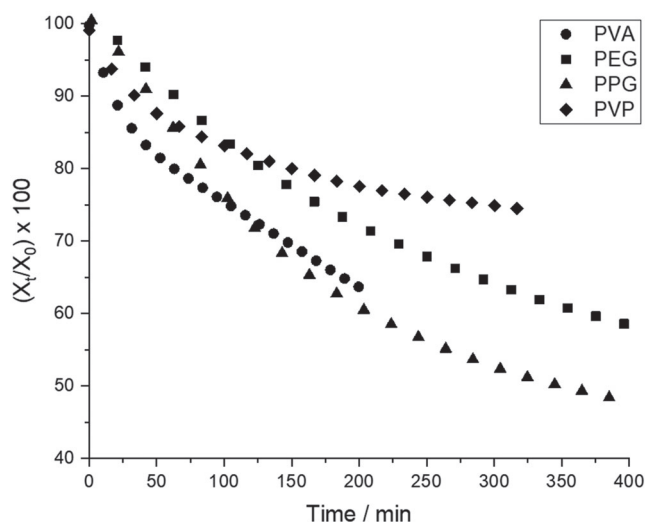
FIGURE 4 Degradation index plot of polyvinylalcohol (PVA), polyethylene glycol (PEG), polypropylene glycol (PPG) and polyvinyl pyrrolidone (PVP)
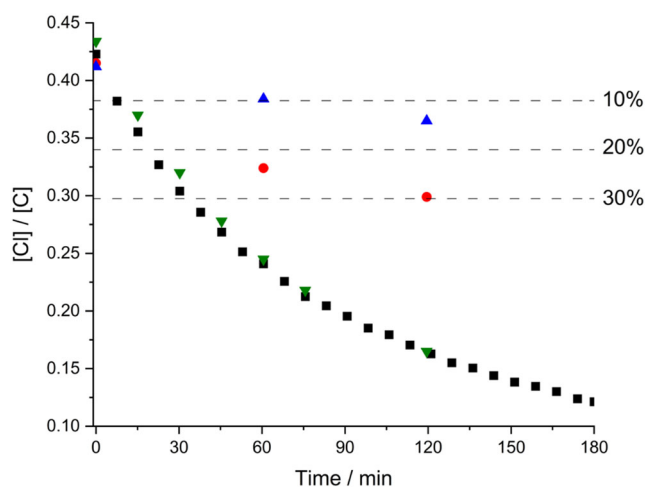

FIGURE 5 Polyvinyl chloride (PVC) degradation recorded on thermo K-Alpha$^+$ system in the 400-μm spot mode, with levels of 10%, 20% and 30% degradation of the polymer based on the original atom ratio highlighted. Key: (■) = x-rays and neutraliser standard operating conditions, (▼) = x-rays and 30-V neutraliser settings, (●) = neutraliser only (40 V) and (▲) = neutraliser only (30 V)

In stark contrast to the degradation indexes noted, we observe degradation levels in the range of 25%–50%. If we follow the Beamson and Briggs index, then PEG and PPG should have identical degradation as should PVA and PVP; clearly this not the case here. At present, we do not have an explanation for the differences and although we have made no characterisation of film quality or thickness, there is no indication of Si from the support detected in the survey spectra recorded at the start and end of degradation experiments, suggesting the films are of sufficient thickness to avoid any substrate-induced effects.

4 | THE EFFECT OF THE DUAL NEUTRALISER AND ANALYSIS AREA

Although it is known that electrons and ions from charge compensation systems within the spectrometer can play a part in sample degradation,[15,24,31] little delineation of their effect on degradation has been extensively presented, especially for dual sources, to the best knowledge of the authors. Taking PVC as the archetypal degradation polymer, we can follow the effect of x-rays and neutraliser alone for a dual neutraliser system in comparison to the standard analysis.

In Figure 5 we show the plot for PVC over a 180-min period plotted for simplicity as the Cl/C atom ratio, together with markers for 10%, 20% and 30% damage of the original atom ratio, which correspond to values for the percentage decrease levels reported in Baer et al. and ISO 18554.[16,32]

The data clearly indicate that the majority of degradation comes from the x-ray irradiation (black squares, Figure 5); however, the role of the neutraliser over a 120-min time frame (red circles) is significant. Although this is a longer time frame than would commonly be used for analysis of polymers, it does highlight the damaging nature of the neutraliser and care that should be taken in setting up an area for analysis. By simply reducing the extract voltage of the dual-charge compensation system used here, the rate of degradation alone from the neutraliser can be halved, as indicated by the blue triangles. It should be noted that the irradiated area of the neutraliser is greater than the x-ray spot and hence damage from the neutraliser will be spread over a greater distance on the surface; hence, the degradation may be more pronounced in, for example, line-scan analysis.[24,40]

Given the overriding influence of the x-rays alone, the influence of spot size is naturally of importance, especially for micro-focussed systems, where to maintain the signal intensity and sensitivity, a high photon flux is maintained, but delivered into a smaller area. The results of such analysis are shown in Figure 6, utilising the 400- and 200-μm spot modes of the K-Alpha$^+$ system.

From both plots, the rates are clearly different, with the rate of the 200-μm mode being twice than that of the 400-μm mode as shown in the accompanying table. Although other spot sizes are as yet untested, it is reasonable to assume a similar relationship.

5 | DEGRADATION KINETICS AND DEGRADATION INDEX

As already noted, photodegradation in XPS typically follows first-order kinetics.[20,23,33,37,38,41] Indeed, of all the bulk polymers studied herein can be modelled in this way, but over different time frames.

Using PVC as the exemplar of the degradation, Figure 7A shows the plots for the degradation profiles for both systems, whilst the first-order kinetic plots (Figure 7B) show that although the Axis Ultra system can be modelled linearly over the entire degradation period, the K-Alpha system deviates from this behaviour. This deviation is attributed to the increased damage rate, with first-order degradation
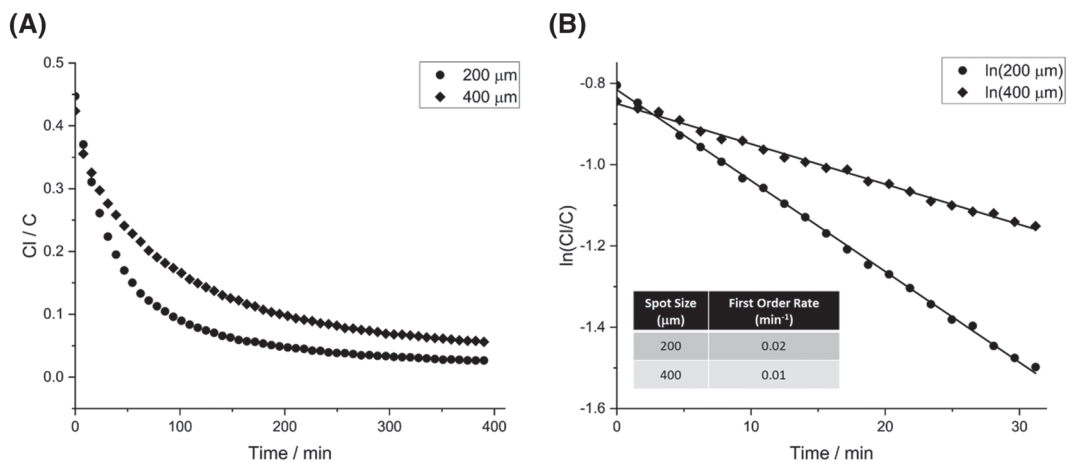
(A)

(B)

FIGURE 6 Influence on spot size on the degradation of polyvinyl chloride. (A) Plot of Cl/C for 200- and 400-μm spot modes and (B) first-order plot over the first 30 min of analysis
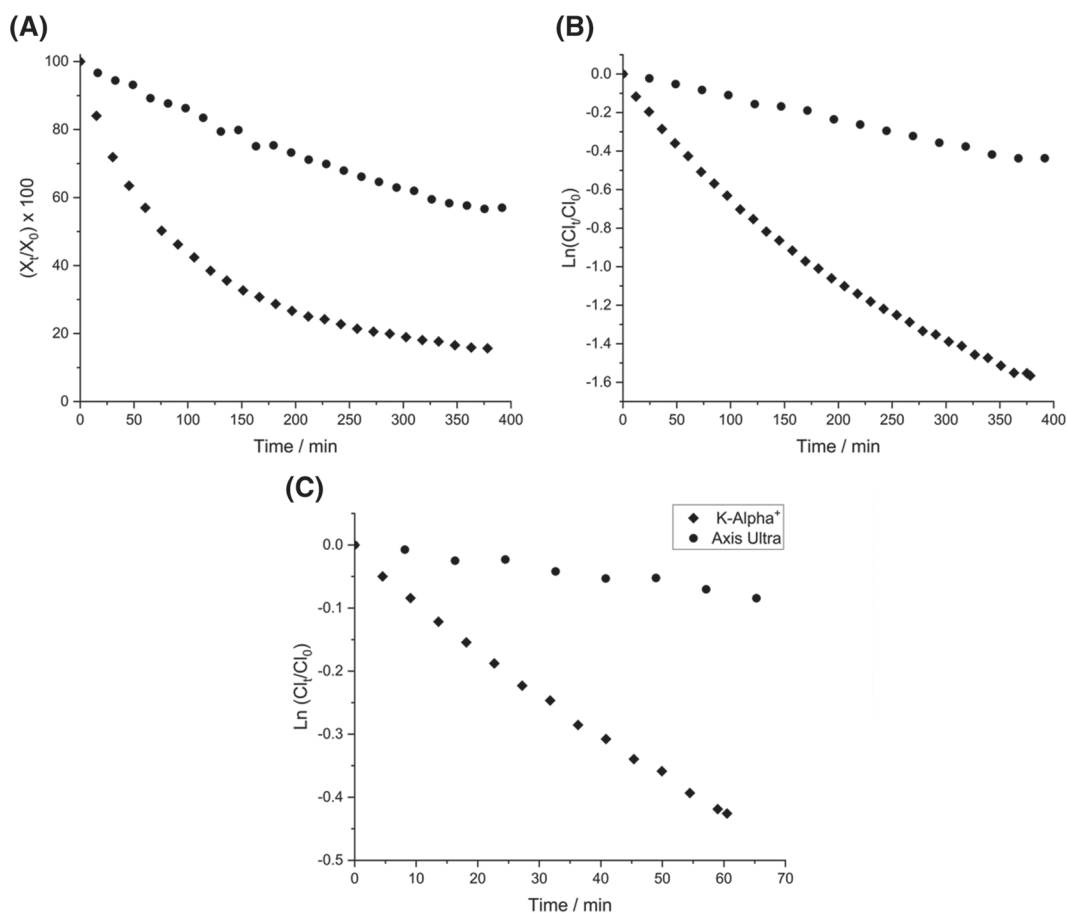
(A)

(B)

(C)

FIGURE 7 Degradation plots for polyvinyl chloride on the Axis Ultra and K-Alpha systems: (A) degradation index plot, (B) first-order rate plot of data and (C) first-order plot over first 60 mins

kinetics exhibited for the first 60 min for the 400-μm spot mode as shown in Figure 7C.

For the K-Alpha system, it is logical to assume there are at least two kinetic regions in the degradation profile. The first follows the expected degradation route with, in the case of PVC, the loss of HCl, but then given the more rapid depletion of chlorine from the polymer, the kinetics are likely to be influenced by that of the damaged polymeric material and hence more evident with increased levels of damage.

Table 1 shows the measured degradation index for different polymers for both Axis Ultra and K-Alpha$^+$ systems, and a graphical plot

TABLE 1 Degradation index and calculated values of the degradation constant (k) from first-order plots for maximum analysis areas quoted in experimental.

Polymer	B&B index[1]	Current data degradation index (total time)		Current data degradation index (60 min)		Calculated rate constant, k ($\times 10^{-3}$) /min^{-1} for 60 min	
		Axis Ultra	K-Alpha	Axis Ultra	K-Alpha	Axis Ultra	K-Alpha
PVC	25	55	85	10	45	1.30	7.30
PVdC	20	40	70	10	30	0.77	4.10
PVF	15	25	65	5	30	0.59	4.50
PVdF	15	25	60	5	25	0.28	2.50
PTFE	10	10	40	5	10	0.13	0.36
PEG	5	—	60	—	10	1.80	13.0
P4CS	15	—	65	—	35	—	8.70
PPG	5	—	55	—	15	—	2.00
PVP	10	—	30	—	15	—	2.20
PVA	10	—	40	—	20	—	4.85

Note: The total time refers to equivalent time frames to Beamson and Briggs (B&B).

TABLE 2 Photon threshold index (PTI) for the polymers in this study (higher value is better)

Polymer	PTI value	
	Axis Ultra	K-Alpha
PVC	60	8
PVdC	75	10
PVF	100	13
PVdF	100	13
PTFE	150	20

Abbreviations: PTFE, polytetrafluoroethylene; PVdC, polyvinylidene chloride; PVdF, polyvinylidene difluoride; PVC, polyvinyl chloride; PVF, polyvinyl fluoride.

FIGURE 8 Plot of the photon threshold index (PTI) for chlorinated and fluorinated polymers for both x-ray photoelectron spectroscopy systems. PTFE, polytetrafluoroethylene; PVdC, polyvinylidene chloride; PVdF, polyvinylidene difluoride; PVC, polyvinyl chloride; PVF, polyvinyl fluoride

of the differences are shown in Figure S1. There is typically a higher degradation rate for the two systems compared with the Beamson and Briggs index, but the K-Alpha is consistently much higher. As expected, this is true for the initial 60 min also, but here the Axis Ultra system has a much lower degradation index by a factor of between approximately two and five times, depending on the polymer and are exemplified by the calculated first-order rate constants for both systems.

The difference in the B&B (Beamson & Briggs) values and those recorded are significant and clearly rates and behaviours differ between different instruments. Of the bulk polymers used, little is known about their manufacture such as the molecular weight of the precursors and the presence of stabilisers; however, significant variations in polymer quality have been observed previously with PVC films[16,37] and have generally been shown to have little effect. However, this argument is somewhat immaterial as we are looking at the differences between two classes of spectrometer and neutraliser whilst using the same polymer batch. Neglecting any influence of polymer quality, the differences observed may be down to

instrumental features such as the type and operating power of the x-ray source and angle of incidence and analysis and the area illuminated by the source.

Although the rates and extent of damage are clearly greater, the general trend in which polymers degrade faster compared with others is similar; therefore, a more self-consistent model for a given system is to use the photon threshold index (PTI), which is measured relative to a 10% degradation of PVC, which has been shown to be a useful reference material.[16] The values for both systems are shown in Table 2, whilst Figure 8 shows a plot of the data.

The use of the PTI succinctly illustrates the difference in degradation between the systems, highlighting a difference of approximately

×7.5. The small spread of the PTI index for the K-Alpha instrument that damage susceptible polymers should be recorded as quickly as possible. Such understanding of these significant differences will undoubtedly improve analysis, especially for supported thin film polymers, where the influence of the substrate can lead to significant enhancement of the degradation rates.[42–44]

The PTI method allows a much greater understanding in analysis requirements for an end-users system, but serves as a self-consistent, in-house check for those involved in the analysis of polymers, requiring only the user to analyse a fresh sample of PVC should there be any significant change to the system, for example, installation of a new x-ray anode.

6 | CONCLUSIONS

Driven by previous degradation studies, we have performed a partial reinvestigation of the Beamson and Briggs polymer degradation index on two classes of instruments from leading manufacturers, which are commonplace in academic and industrial research environments across the world.

Although the study presented is far from exhaustive, it does demonstrate the care and consideration that should be taken in analysing polymers and related materials and not relying on published data. It has been shown that although the Beamson and Briggs index mostly holds true in this study, we have highlighted potential differences between the degradation index and those measured herein for non-halogenated polymers. Furthermore, we have shown the importance of the neutraliser on potential pre-analysis damage and to the spot size on the degradation rate, showing that successful analysis can only be made in many cases in times less than 60 min. In illustrating these points, we have also shown the importance of the PTI on a per-system basis for a greater understanding of how a particular polymer class may behave during analysis. It is worthy to recall that we have only studied homopolymers herein, and the effects on co-polymers or those materials with compositional gradients may differ significantly.

For meaningful analysis, regardless of XPS system used, the following points should be considered as part of a standard operating procedure when working with polymers and related materials.

1. Derive a PTI under your standard operating conditions for your XPS system. The PTI will need to be remeasured for different analysis modes.
2. Work at the largest spot size possible to minimise degradation rate.
3. Set-up your neutraliser on an area a significant distance away from your intended analysis area to minimise potential degradation from a combined ion/electron source.
4. Keep analysis time at a minimum. For micro-focussed systems, the analysis time should be kept below 30 min, especially for small-spot analysis.

DATA AVAILABILITY STATEMENT

Data can now be downloaded from https://doi.org/10.5281/zenodo.7074887.

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SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.