Electron and X-ray Damage Susceptibility Tables

Many research groups have observed electron and x-ray damage on a variety of materials. It is, of course, highly desirable to take advantage of the considerable experience gained by others in observing the presence of damage. Several compilations of x-ray damage rates are available in the literature[1, 2], or from Companies[3]. In most cases the data from these potentially useful data sets are not likely to directly relate to the damage rates that might be observed for other instruments. There are two related reasons for this. First there is over an order of magnitude difference between x-ray damage rates observed on instruments in current use, as reported by Yoshihara and Tanaka.[4] In addition, many new instruments have higher x-ray fluxes than many older instruments.

Various protocols for using a reference material with reproducible damage rates to compare instruments and specimens have been offered in the literature. [1,4,5] In the tables below the approach of Pantano and Madey[6] for ranking electron beam damage has been used to obtain *relative damage susceptibility indices* for both electron and x-ray damage that can be relevant to specific instruments or conditions. The resulting electron threshold and x-ray threshold damage indices provide very approximate guides to the ease of damaging particular types of specimens.

The damage index tables that follow assume that 1) the damage threshold is usefully identified as the time or dose for which a 10 % change in signal can be observed, as suggested by Pantano and Madey,[6] 2) that damage processes are sufficiently linear in time and dose that linear extension of existing data can be used to determine expected damage at other exposure conditions, 3) that x-ray induced damage rates for a common material (relatively pure PVC in this example[7,8]) can be used to normalize different sets of XPS damage measurements.

The four tables that follow contain the damage threshold indices derived (and in a few cases expanded) from data contained in three collections of damage information available,[1,2,3] and data from a PHI Quantum 2000 located in EMSL at PNNL. In a few cases, data from the different data sets can be compared to provide an indication of the accuracy of the process. The electron threshold index (ETI) uses existing data to indicate an approximate time for which a 1mA cm^{-2} electron beam would cause a 10 % change in the Auger spectrum from a specimen. The x-ray or photon threshold index (PTI) uses different data sets to approximate the time for which a 10 % change would be induced by the x-ray beam in the PNNL PHI Quantum 2000 operating in the high power mode. The methods used to compare damage measurements are described more fully in references 7 and 8.

Electron Beam Based Damage Table

An expanded version of the electron beam damage threshold table of Pantano et al.[2] is used for Table 1. The table contains values of the electron threshold as an indication of the electron energy for which the electron beam damage data was collected, the basis assumed for the measurement of the 10 % effect, the critical electron damage dose in Coulomb cm^{-2} and the reported time for a 10 % effect at a current density of 1 mA/cm^2. Several additions have been made to this table based on measurements made on the PNNL PHI 680 AES instrument as well as some made by other researchers. It is useful to remember that electron damage rates are highly energy dependent. This makes comparison of damage for different electron energies much less accurate.

X-ray Damage of Polymers

Beamson and Briggs[1], and Crist[3] have each assembled data on the damage rates for polymers. Although the damage information was collected or reported in very different ways a comparison method[7, 8] has been used x-ray damage observed for the high power mode of the PNNL PHI Quantum. The Beamson and Briggs data set is the most comprehensive and Table 2 is organized by type of polymer. Tables 2 and 3 contain the Photon Threshold Indices described above and information about the damage rates as reported in the original references. As will be noted later in summary Table 5, much of the data in common are relatively consistent in spite of the different data collection methods and the simple comparison process.

Damage rate data collected on the PNNL Quantum 2000 is included in Table 4. Since PVC was used as the common material on which to base the system and for data set comparison. This has provided fairly consistent data for the damage rates reported here, but there are indications that PVC of different molecular weights and purity can have significantly varying damage rates.

Table 5 compares PTI values where the same materials (other than PVC) have been measured on different systems. The values for PCEMA, Teflon, PMMA and PVAc are quite consistent, given the varying nature of the data sources. The values for commercial materials (Nylon 6 and Kapton) are less consistent with the Kapton values, differing by more than an order of magnitude.

1 G. Beamson and D. Briggs "*High Resolution XPS of Organic Polymers: The Scienta ESCA300 Database*" John Wiley, Chichester, 1992.

2 C. G. Pantano, A. S. D'Souza and A. M. Then, "Electron Beam Damage at Solid Surfaces", in *Beam Effects, Surface Topography and Depth Profiling in Surface Analysis*, Ed by A.W. Czanderna, T.E. Madey and C.J. Powell, Plenum Press 1998, p39.

3 V. Crist, XPS-International Data Tables, LLC, 754 Leona Lane, Mountain View CA 94040, USA.

4 K. Yoshihara and A. Tanaka, *Surf. Interface Anal*. **33**, 252 (2002).

5 B.D. Ratner and D.G. Castner, *Colloids and Surfaces B* **2**, 333 (1994).

6 C. G. Pantano and T. E. Madey, *Appl. Surf. Sci*. **7**, 115 (1981).

7 D. R. Baer, D. J. Gaspar, M. H. Engelhard, and A. S. Lea. "Beam Effects During AES and XPS Analysis." in *Surface Analysis by Auger and X-ray Photoelectron Spectroscopy* (D. Briggs and J. T. Grant Eds.), Chapter 9 and Appendix C, IM Publications and Surface Spectra LTD, Chichester, United Kingdom (2003).

8 D. R. Baer, M. H. Engelhard, A. S. Lea, L. Saraf. "Simple Method for Approximate Comparison of X-ray Damage Data." *Journal of Vacuum Science and Technology A* 23(6):1740-1745(2005).

Table 1

Electron Beam Damage Table [Expanded from Pantano et. al. Reference 2]

electron threshold Index	Electron Beam Energy [keV]	Material	basis	Critical Electron Dose	time @ 1 mA cm^{-2} for 10% effect [s]	from Ref 2 Unless noted
>15000	2.0	Si_3N_4	at% assumed	stable		
10800.0	5.0	Al_2O_3	at% assumed	10	10800	
900.0	1.0	Cu, Fe pthalocyanines	at% assumed	1	900	
600.0	2.0	SiO_2	%SiO2	0.6	600	
3600.0	10.0	SiO_2	%Si in SiO2	5	4500	PHI 680
480.0	1.0	Li_2WO_4	at% assumed	0.5	480	
80.0	3.0	TiO_2	surface amorphous	0.08	80	Joyce
10.0	3.0	TiO_2	10% loss Bridging O	0.01	10	Joyce
60.0	0.1	NaF, LiF	at% assumed	0.06	60	
50.0	1.0	$LiNO_3$, $LiSO_4$	at% assumed	0.05	50	
30.0	1.5	KCl	at% assumed	0.03	30	
20.0	2.0	TeO_2	at% assumed	0.02	20	
20.0	10.0	$NaNO_3$	at%	0.02	20	Ref 7
10.0	1.5	H_2O Film	at% assumed	0.01	10	
2.0	5.0	Native oxides	at% assumed	0.002	2	
1.0	75.0	Formvar	at% assumed	0.001	1	
1.0	10.0	PAN	N/C	0.001	1	PHI 680
0.5	0.6	SAM (chain damage) - $Cl_3Si(CH_2)_{17}CH_3$ on SiO_2	C/Si	0.0005	0.5	
2.0	10.0	SAM (chain damage) - $Cl_3Si(CH_2)_{17}CH_3$ on SiO_2	C/Si	0.002	2	
0.3	0.1	CycloHexane film [C_6H_{12}]	at% assumed	0.0003	0.3	
0.3	1.5	Methanol film [CH_3OH]	at% assumed	0.0003	0.3	
0.1	10.0	PVC (10 μm thick layer)	Cl/C	0.0001	0.1	PHI 680

Table 2

X-ray Polymer Damage Table - [derived from G. Beamson and D. Briggs Reference 1]

photon threshold index	Polymer Abreviation	Polymer	Indicator	Beamson & Briggs Degregation Index	change after 200 min	Time for 10% [min]
		C-H Polymers				
100	HDPE	Poly(ethylene), High Density	C 1s FWHM	10		
200	PP	Poly(propylene)	C 1s FWHM	5		
>1000	PMP	Poly(4methyl-1-pentene)	C 1s FWHM	0		
>1000	PS	Poly(styrene)	shape-up/C 1s	0		
33	PcI	Poly(*cis* -isoprene)	shape-up/C 1s	30		
33	PtI	Poly(*trans* -isoprene)	shape-up/C 1s	30		
		CHO Polymers				
200	PEG	Poly(ethylene glycol)	O/C	5	1%	1500
200	PPG	Poly(propylene glycol)	O/C	5	1%	1500
200	PTMG	Poly(tetramethylene glycol)	O/C	5	1%	1500
100	PViBE	Poly(vinyl isobutyl ether)	O/C	10	2%	500
100	PVEE	Poly(vinly ethyl ether)	O/C	10	3%	400
100	PVME	Poly(vinyl methyl ether)	O/C	10	3%	300
100	PVAc	Poly(vinyl acetate)	O/C	10		
100	PMMA	Poly(methyl methacrylate)	O/C	10		
50	PMG	Poly(methylene glycol)	O/C	20	8%	125
		Cl-Containing Polymers				
67	P2CS	Poly(2-chlorostyrene)	Cl/C	15	3%	440
67	P3CS	Poly(3-chlorostyrene)	Cl/C	15	3%	440
67	P4CS	Poly(4-chlorostyrene)	Cl/C	15	3%	440
50	PVdC	Poly(vinylidene chloride)	Cl/C	20	5%	320
40	PVC [film]	Poly(vinyl chloride)	Cl/C	25	10%	190
29	PCEMA	Poly(2-chloroethyl methacrylate)	Cl/C	35	18%	110
		F-Containing Polymers				
40	VIT	Viton A	F/C	25	13%	160
33	PVTFA	(vinyl trifluoroacetate)	F/C	30	15%	120
100	PTFE	Poly(tetrafluoroethylene)	F/C	10	6%	420
67	PTFEA	Poly(trifluoroethyl acrylate)	F/C	15	6%	330
67	PVF	Poly (vinyl fluoride)	F/C	15	7%	270
		N-Contining Polymers				
>1000	PAN	Poly(acrylonitrile)	N/C	0		
100	PEI	Poly(ethyleneimine)	N/C	10		
100	PAM	Poly(acrylamide)	N/C	10		
15	CTN	Cellulose trinitrate	N/C	65		
200	PU	Poly(urethane)	N/C	5		
200	Nylon 6		O/C	5		
100	Kapton		O/C	10		

Table 3

X-ray Polymer Damage Table - [derived from XPS International Reference 3]

photon threshold index	Polymer Abreviation	Polymer	Indicator	Mono 14 hr change	achromatic 14 hr change
>2400	PAN	Poly Achrylonitrile (PAN)	N/C	0%	28%
1960	Kapton	Poly Imide (Kapton)	O/C	1%	20%
653	PET	Poly Ethylene terephthalate (PET)	O/C	3%	13%
653	PPS	Poly Phenylene sulfide	S/C	3%	
280	PC	Poly Carbonate (PC)	O/C	7%	
245		Poly Sulfone	O/C	8%	
131	PMMA	Poly Methyl methacrylate (PMMA)	O/C	15%	
115	PVA	Poly Vinyl acetate (PVA)	O/C	17%	
109		Poly Acetal	O/C	18%	
98	Nylon6	Poly Caprolatam (Nylon 6)	N/C	20%	55%
78	PAA	Poly Acrylidc Acid (PAA)	O/C	25%	
70	PTFE	Poly Tetrafluoro Ethylene (Teflon)	F/C	28%	
40	PVC	Poly Vinyl Chloride (PVC)	Cl/C	49%	

Table 4

X-ray Polymer and Self Assembled Monolayer Damage (including temperature effects)

based on measurements from PHI Quantum 2000 operated in High Power mode, typically 100 watts, 1.5 mm x 0.2 mm area

photon threshold index	Material form or condition	Material	Indicator	change after 200 min	Time for 10% [Min]
		PVC - Different forms and temperatures			
70	143 K	Poly(vinyl chloride)	Cl/C	15%	70
40	303 K	Poly(vinyl chloride)	Cl/C	35%	40
30	373 K	Poly(vinyl chloride)	Cl/C	40%	30
40	Film	Poly(vinyl chloride) 10 μm thick film	Cl/C	35%	40
40	Bulk	Poly(vinyl chloride) data for Ref. 11	Cl/C	33%	40
		PCEMA - Different temperatures and components			
50	143 K	PCEMA (143K)	%Cl	40%	50
35	303 K	PCEMA (300K)	%Cl	45%	35
25	373 K	PCEMA (373K)	%Cl	65%	25
250	143 K	PCEMA (143K)	%O	7%	250
250	300 K	PCEMA (300K)	%O	7%	250
250	373 K	PCEMA (373K)	%O	7%	250
		Self Assembled Monolayers - chain and terminal group			
15	terminal group	SAM - $HS(CH_2)_{15}COOH$ on Au	O/C-H	80%	15
50	chain	SAM - $HS(CH_2)_{15}COOH$ on Au	C-H/Au	30%	50
50	chain	SAM - $HS(CH_2)_{15}CH_3$ on Au	C-H/Au	30%	50
50	chain	SAM - $HS(CH_2)_{15}COH$ on Au	C-H/Au	25%	50
		PAN			
500		PAN - Poly (acrylonitrile)	N/C	4%	500

The PTI index is approximately the time in minutes for which data can be collected on the PNNL Quantum 2000 operating in the high power mode before the surface composition is altered by 10%.

Table 5
Camparison of Damage Parameters Determined on From Different Data Sets

PTI = Photon Threshold Index

Material	Beamson & Briggs	XPS International	EMSL Quantum 2000*	
	PTI	PTI	PTI	
PCEMA	30		35	
PTFE Teflon	100	70		
PV Ac	100	80		
PMMA	100	130		
Nylon 6	200	100		
Kapton	100	2000		
PAN			500	

* based on X-ray induced damage in PHI Quantum normalized to PVC data