Evaluating the Photo degradation of polymer nano coating systems using slow positron beam

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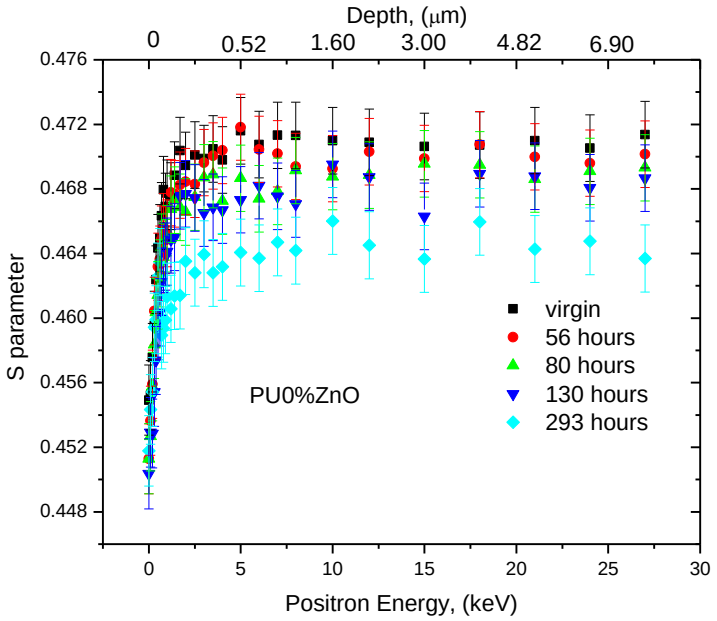
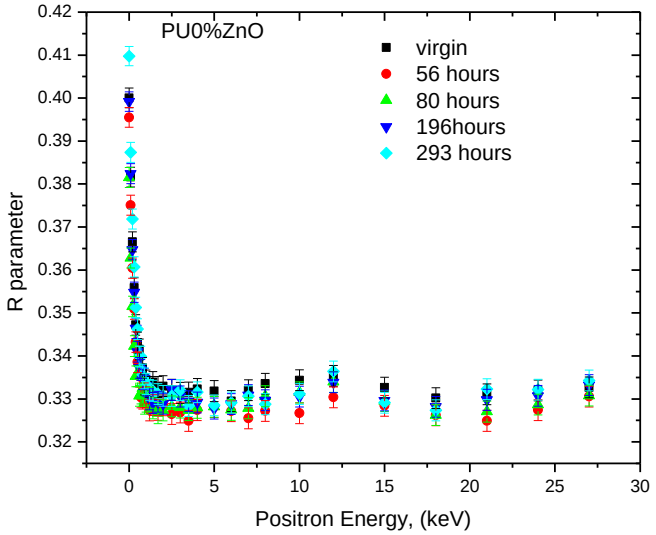
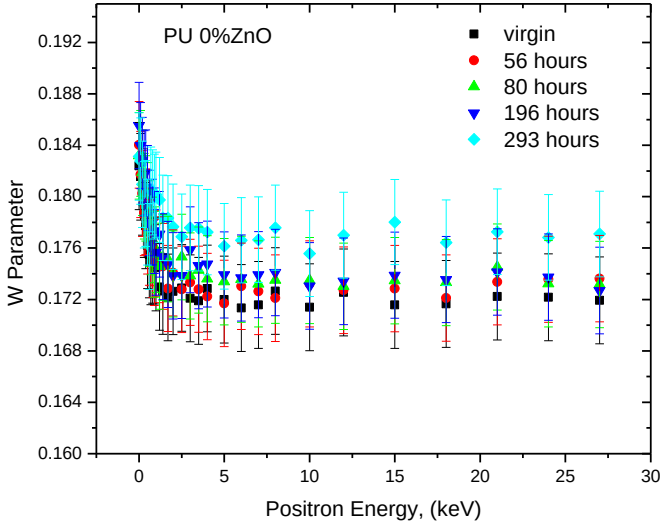
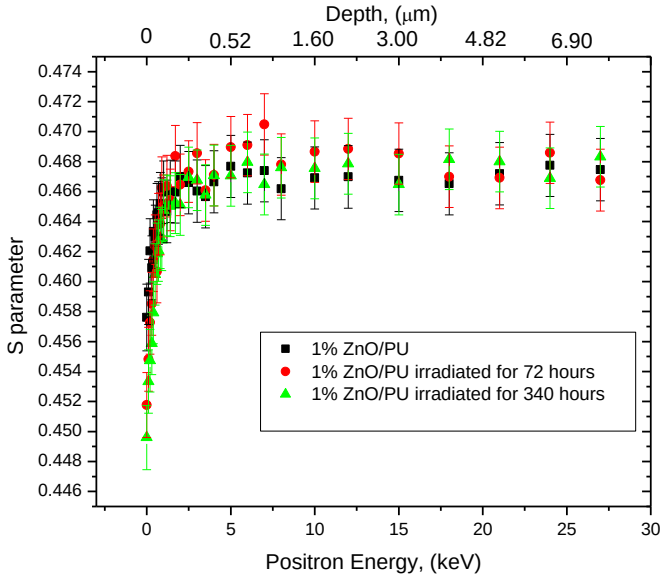
The degradation of polymer nano coating systems due to UV irradiation is investigated using positron annihilation spectroscopy. Doppler broadened spectra of positron annihilation are measured as a function of slow positron implantation energy from 0 to 30 keV and irradiation time up to 293 hours in a series of waterborne polyurethane zinc oxide nanocomposites(WBPU/ZnO) coating systems. The photodegradation of the nano coating is characterized in terms of sub nanometer defect changes. Significant change of The S parameter from the Doppler broadened energy spectra vs positron energy is observed. From the S parameter results, Increasing the loading of the zinc oxide nanoparticles into the WBPU coating system leads to accelerate the photodegradation process of the nanocoating. The results are presented and discussed in the frame of the variation of the free volume percentage in the nanocoating systems.

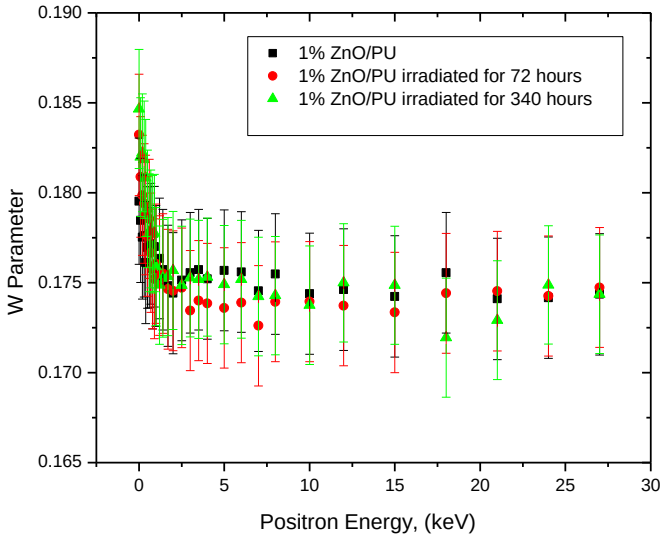
Effect of UVB in 0%ZnO/WBPU nanocomposite membrane

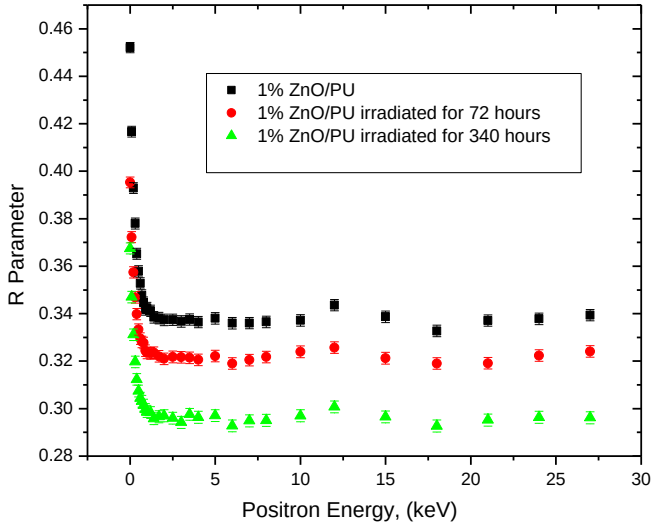


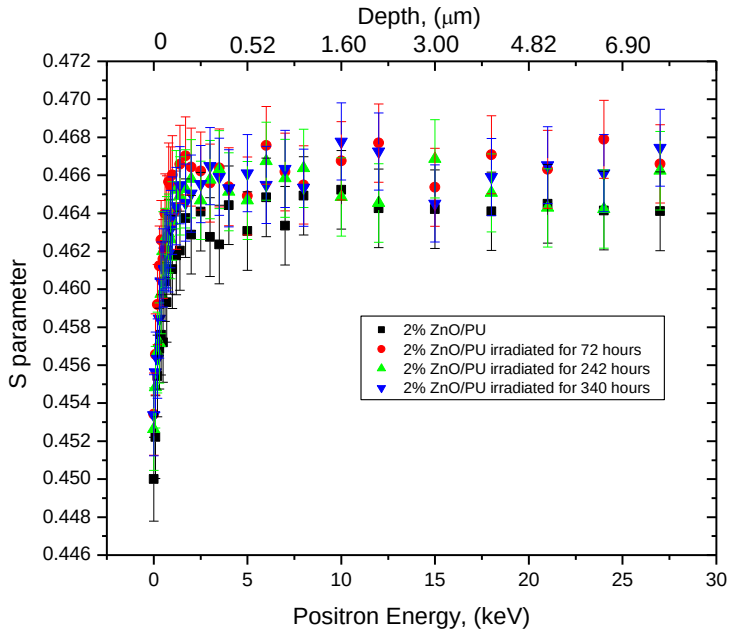


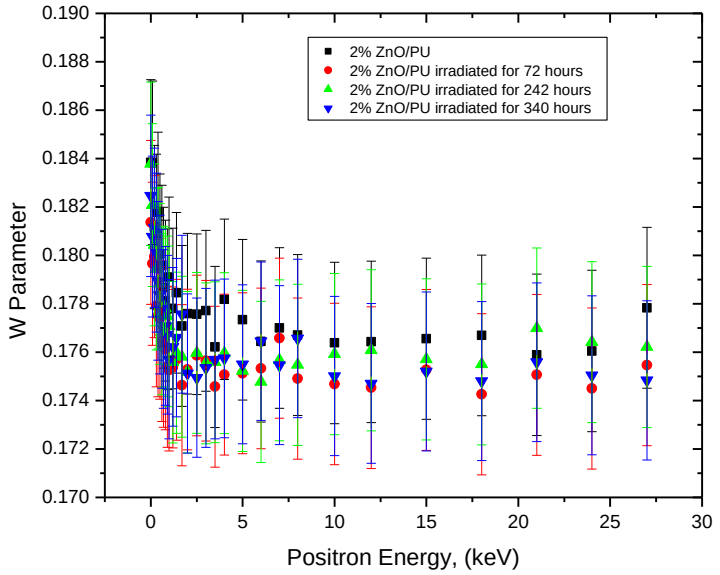


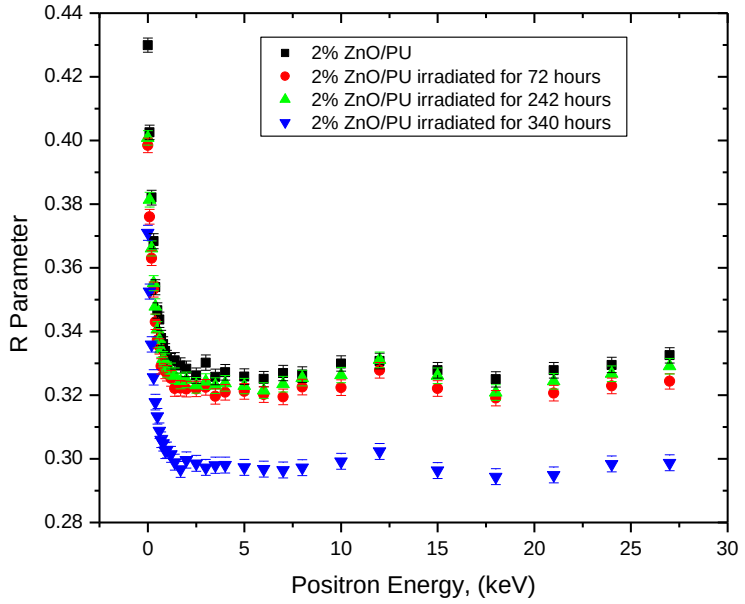

Depth, (μm)
0
0.52
1.60
3.00
4.82
6.90
S parameter
Positron Energy, (keV)
1% ZnO/PU
1% ZnO/PU irradiated for 72 hours
1% ZnO/PU irradiated for 340 hours

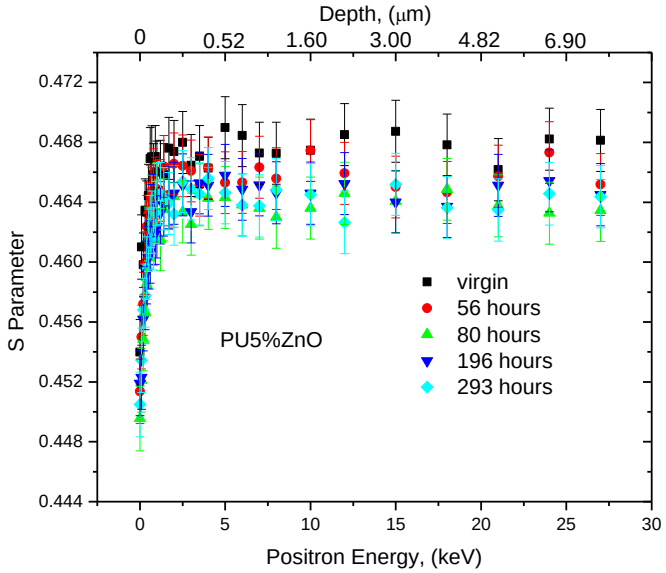

W Parameter
Positron Energy, (keV)
1% ZnO/PU
1% ZnO/PU irradiated for 72 hours
1% ZnO/PU irradiated for 340 hours

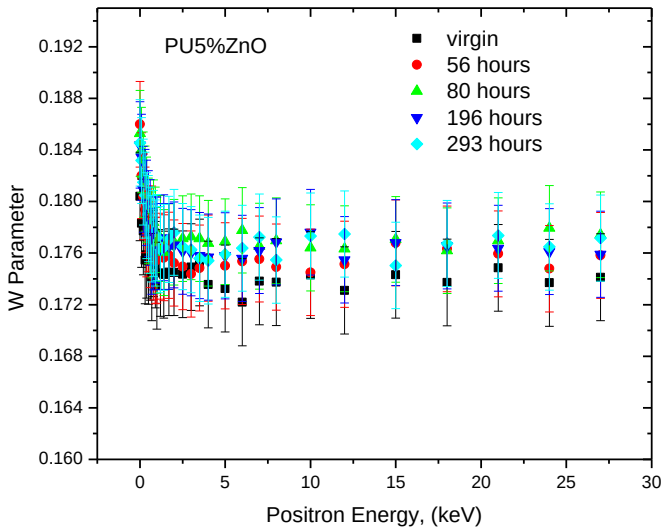

R Parameter
Positron Energy, (keV)
1% ZnO/PU
1% ZnO/PU irradiated for 72 hours
1% ZnO/PU irradiated for 340 hours

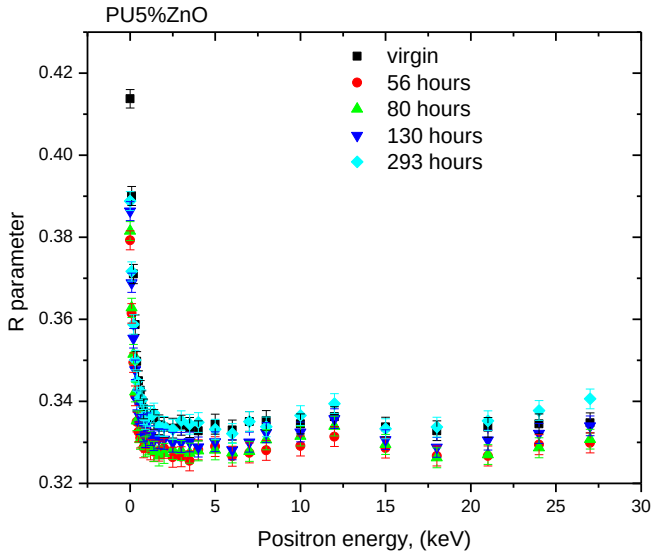

Depth, (μm)
0
0.52
1.60
3.00
4.82
6.90
S parameter
Positron Energy, (keV)
2% ZnO/PU
2% ZnO/PU irradiated for 72 hours
2% ZnO/PU irradiated for 242 hours
2% ZnO/PU irradiated for 340 hours

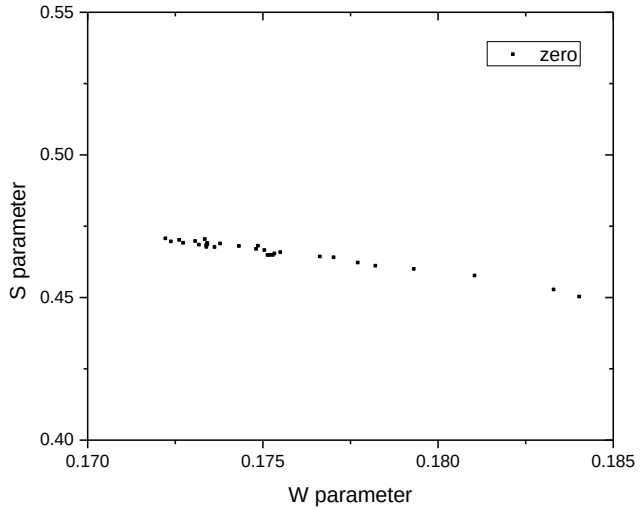

W Parameter
Positron Energy, (keV)
2% ZnO/PU
2% ZnO/PU irradiated for 72 hours
2% ZnO/PU irradiated for 242 hours
2% ZnO/PU irradiated for 340 hours

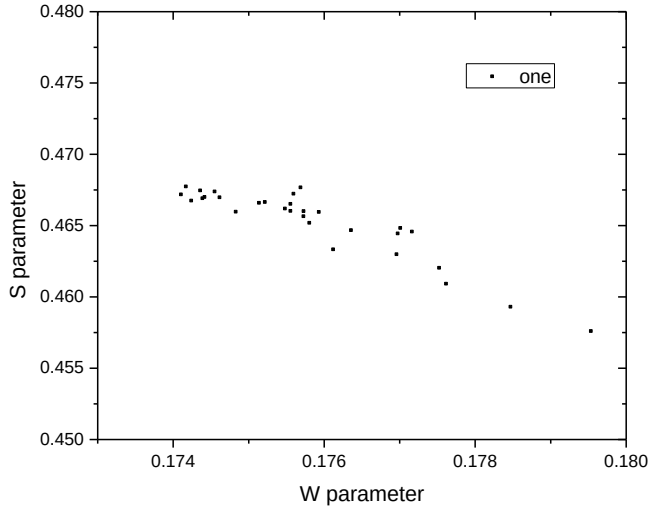

R Parameter
Positron Energy, (keV)
2% ZnO/PU
2% ZnO/PU irradiated for 72 hours
2% ZnO/PU irradiated for 242 hours
2% ZnO/PU irradiated for 340 hours

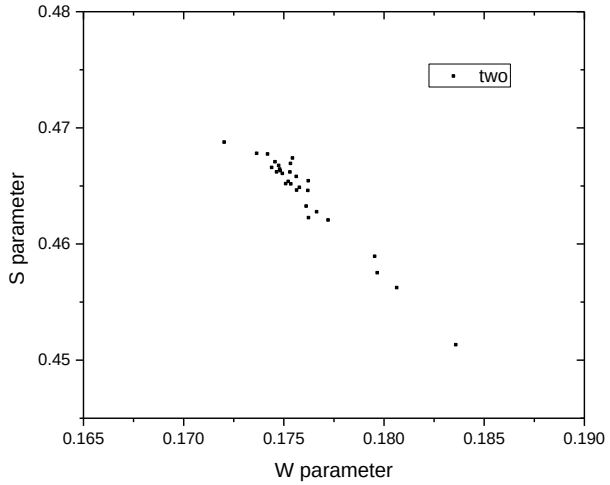

Depth, (μm)
0
0.52
1.60
3.00
4.82
6.90
S Parameter
Positron Energy, (keV)
PU5%ZnO
virgin
56 hours
80 hours
196 hours
293 hours

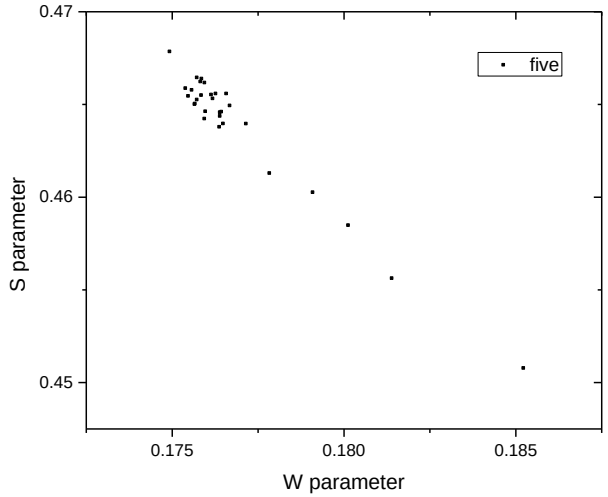

W Parameter
Positron Energy, (keV)
PU5%ZnO
virgin
56 hours
80 hours
196 hours
293 hours


PU5%ZnO
R parameter
Positron energy, (keV)
virgin
56 hours
80 hours
130 hours
293 hours

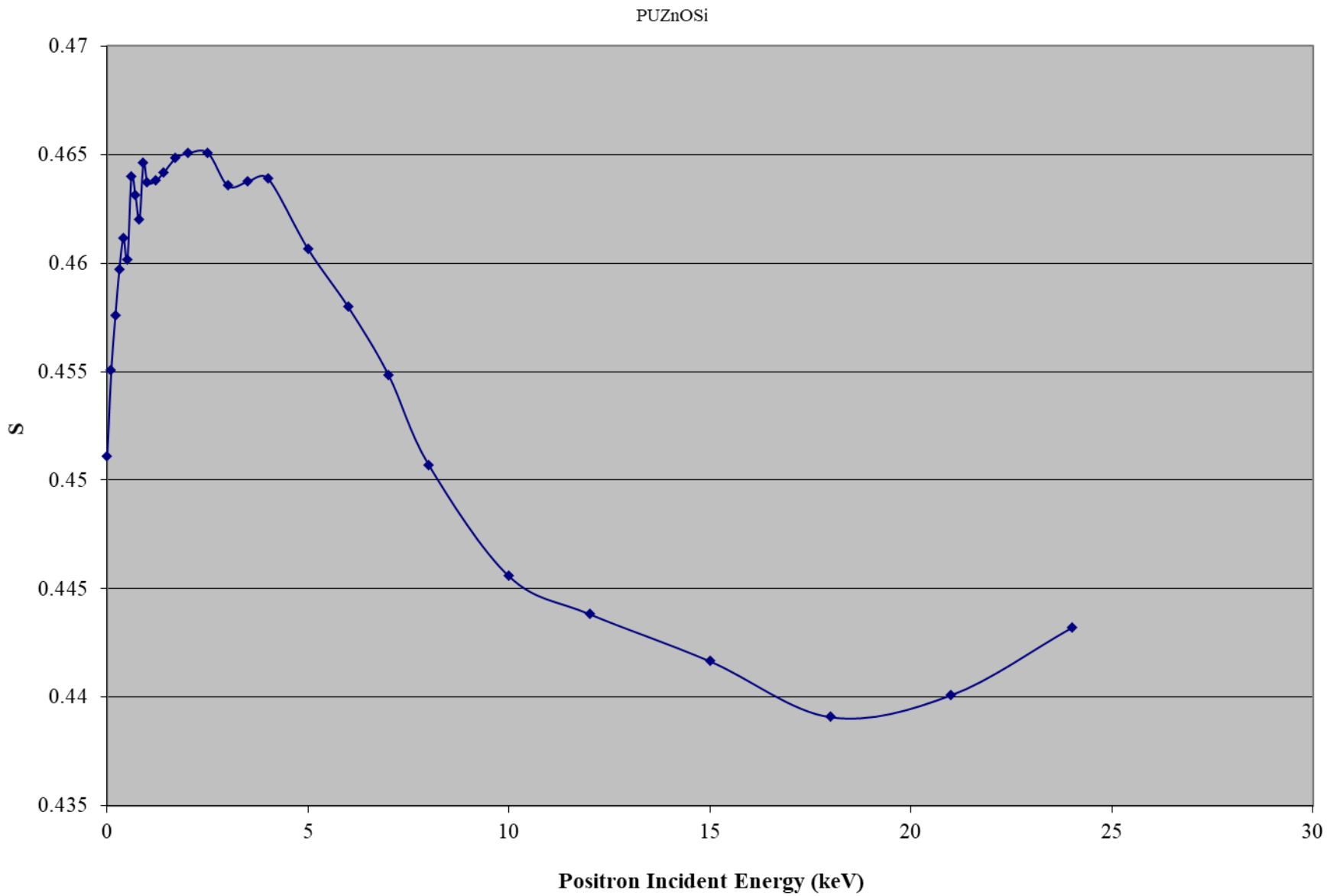

zero
S parameter
W parameter
0.55
0.50
0.45
0.40
0.170
0.175
0.180
0.185

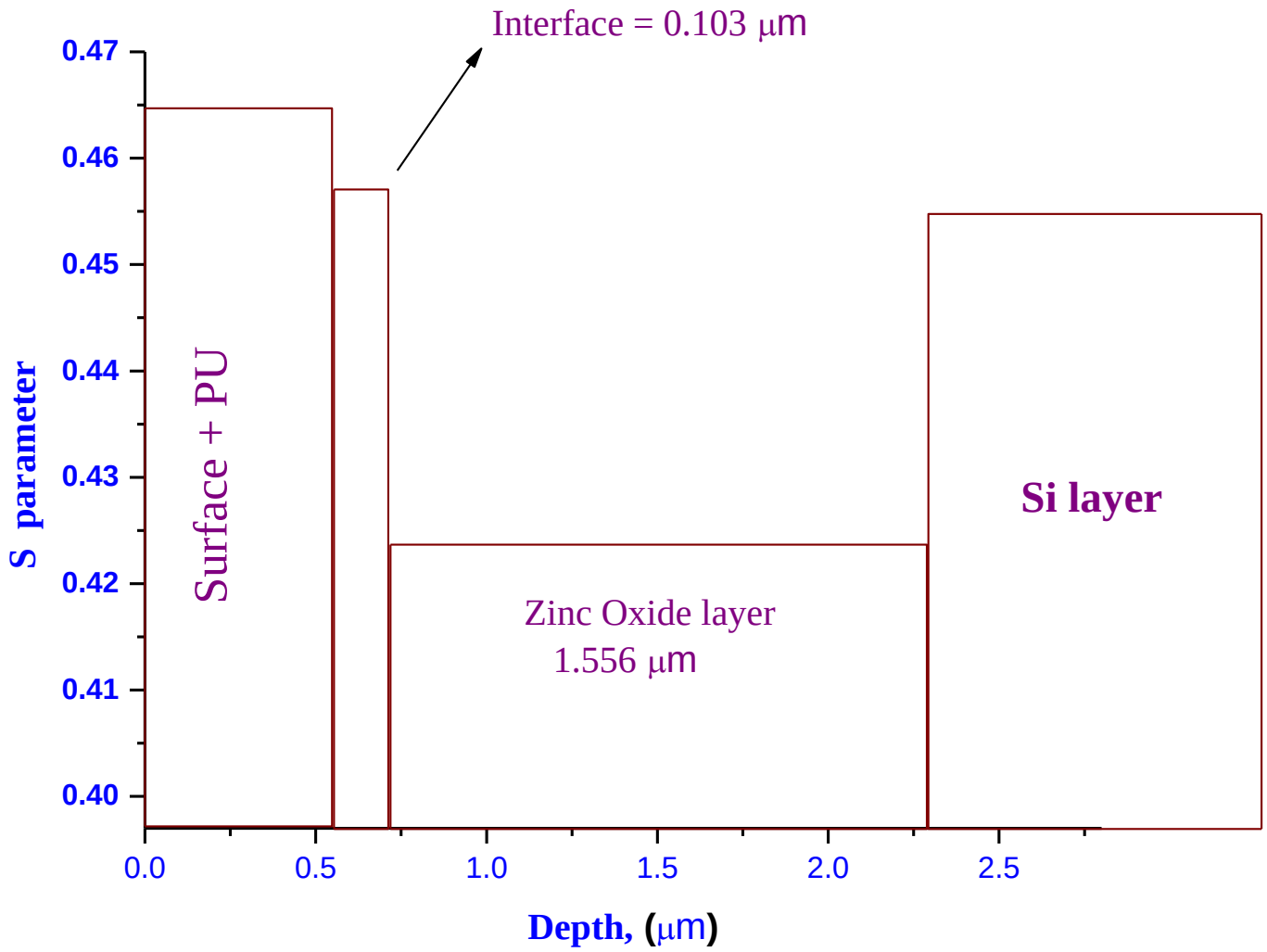

one
S parameter
W parameter
0.480
0.475
0.470
0.465
0.460
0.455
0.450
0.174
0.176
0.178
0.180

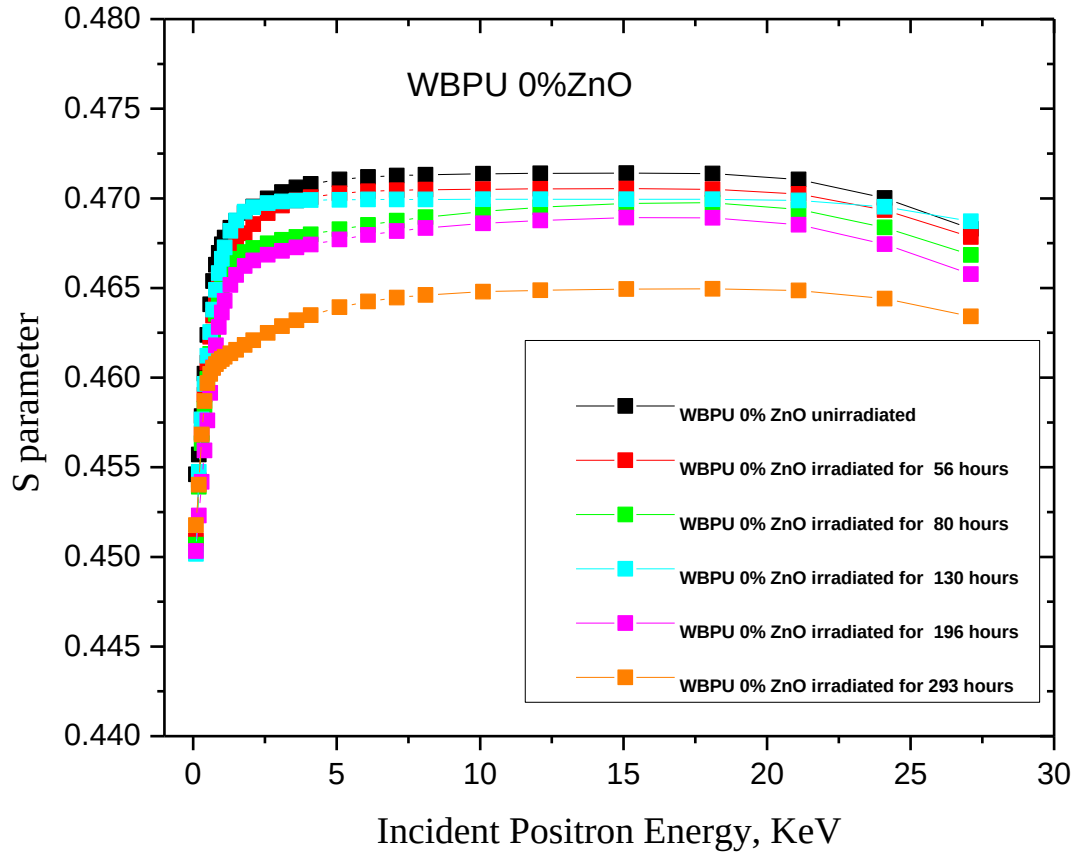

two
S parameter
W parameter
0.48
0.47
0.46
0.45
0.165
0.170
0.175
0.180
0.185
0.190

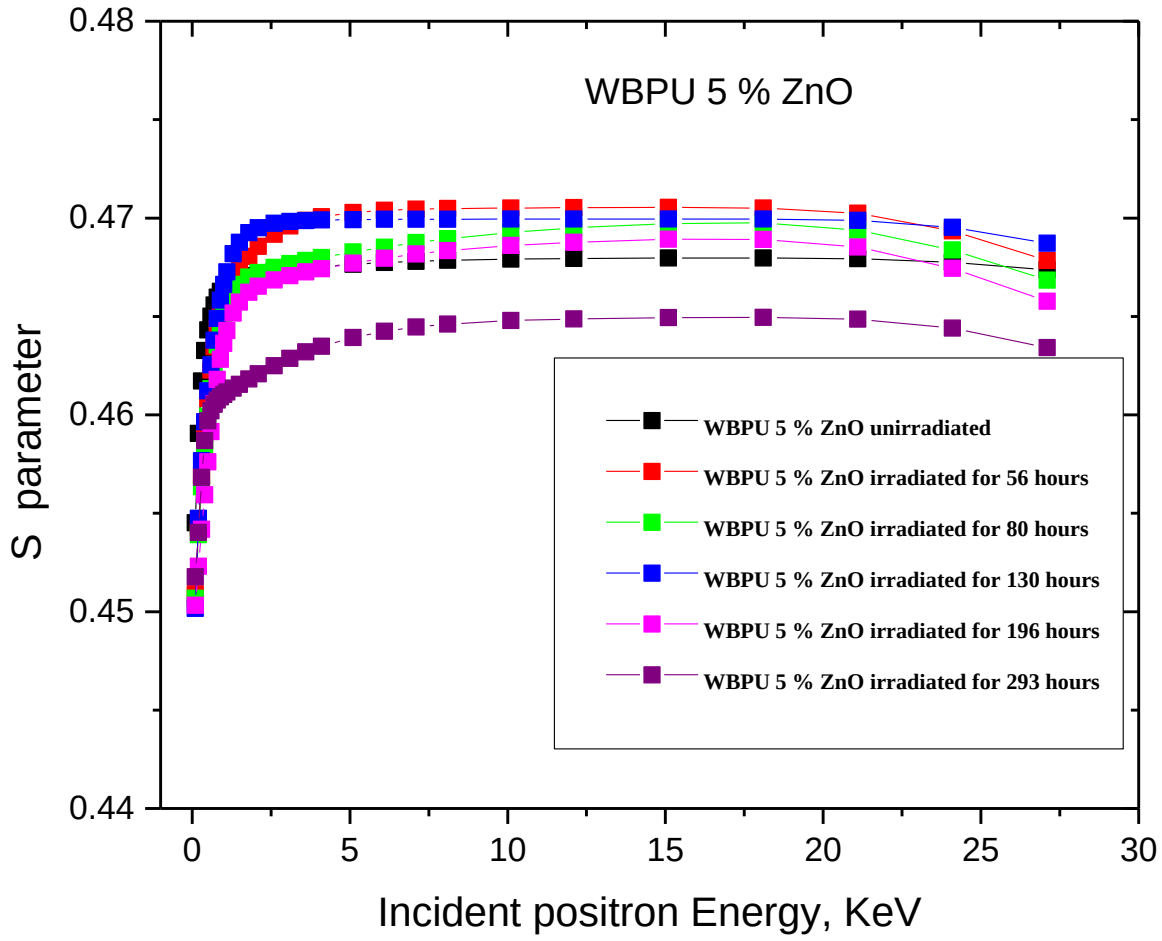

five
S parameter
W parameter
0.47
0.46
0.45
0.175
0.180
0.185

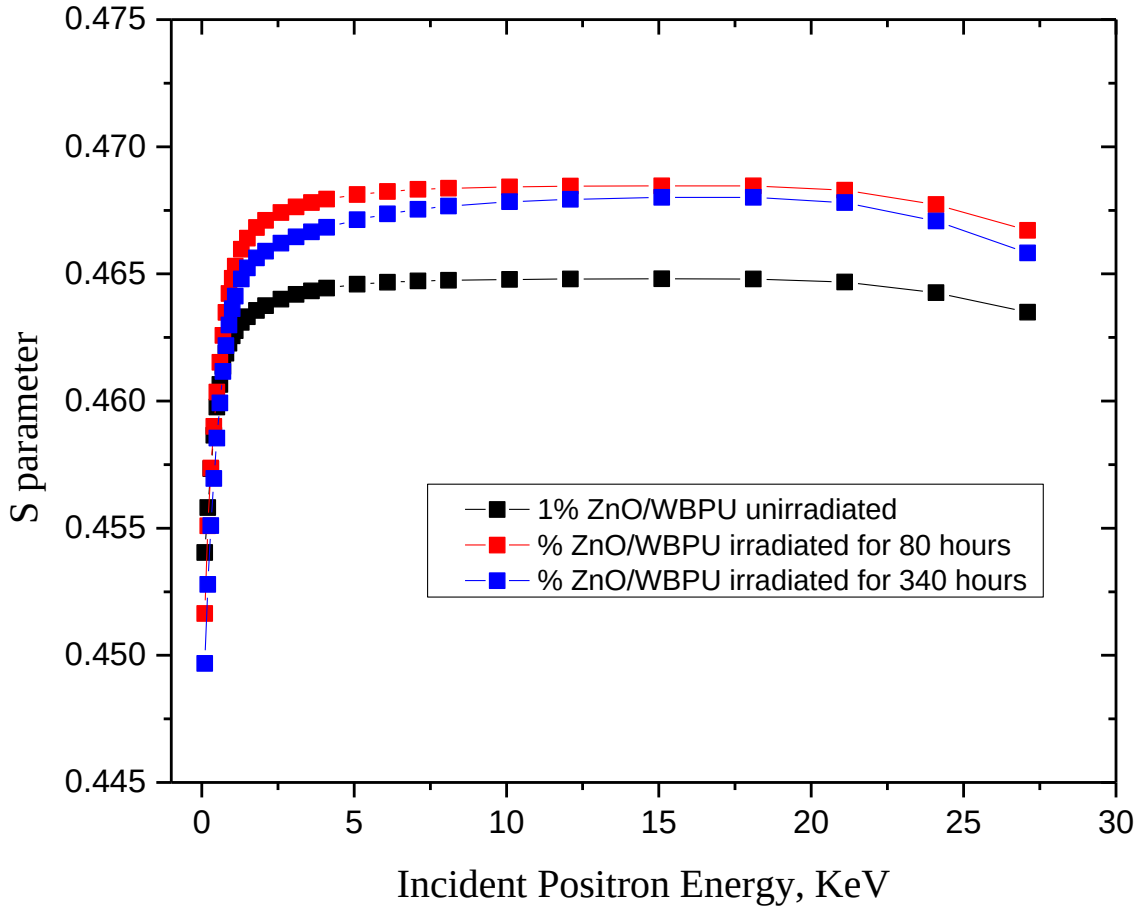
Determine the ZnO-WBPU interface value using Slow Positron Beam

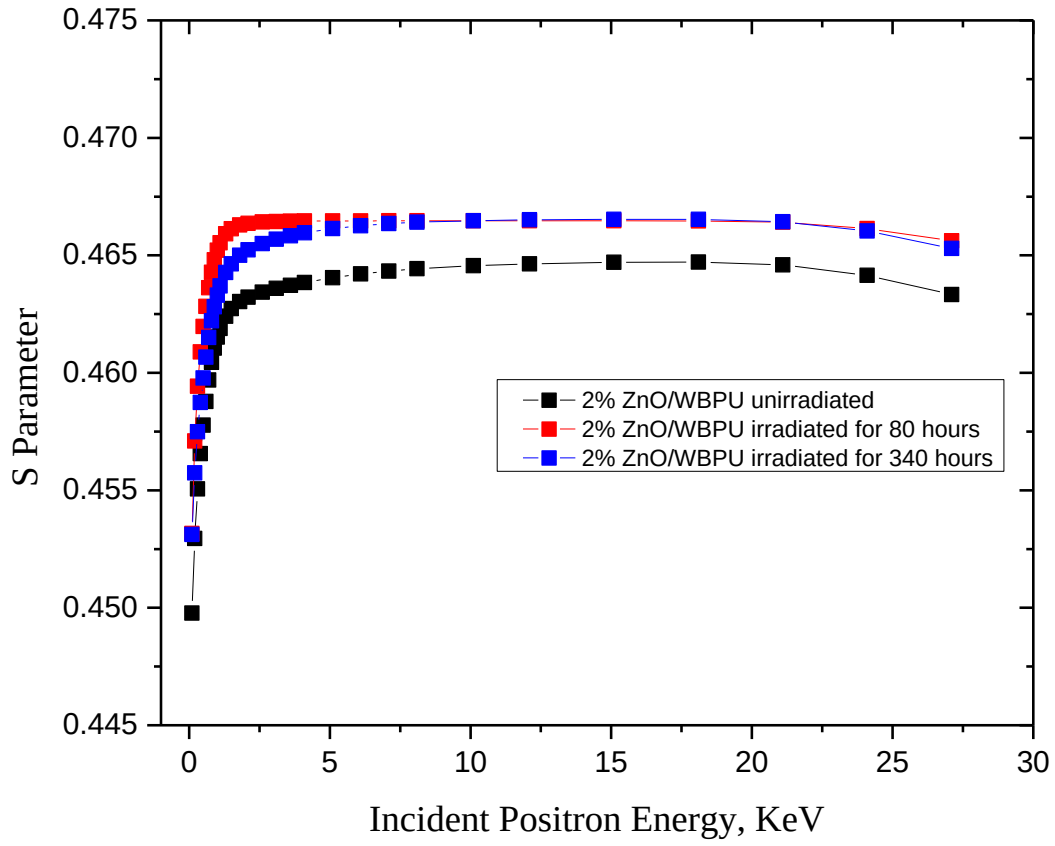

PUZnOSi
0.47
0.465
0.46
0.455
0.45
0.445
0.44
0.435
S
0
5
10
15
20
25
30
Positron Incident Energy (keV)


Interface = 0.103 μm
0.47
0.46
0.45
0.44
0.43
0.42
0.41
0.40
S parameter
Surface + PU
Zinc Oxide layer
1.556 μm
Si layer
0.0
0.5
1.0
1.5
2.0
2.5
Depth, (μm)


WBPU 0%ZnO
S parameter
Incident Positron Energy, KeV
0.480
0.475
0.470
0.465
0.460
0.455
0.450
0.445
0.440
0
5
10
15
20
25
30
WBPU 0% ZnO unirradiated
WBPU 0% ZnO irradiated for 56 hours
WBPU 0% ZnO irradiated for 80 hours
WBPU 0% ZnO irradiated for 130 hours
WBPU 0% ZnO irradiated for 196 hours
WBPU 0% ZnO irradiated for 293 hours


WBPU 5 % ZnO
S parameter
Incident positron Energy, KeV
0.48
0.47
0.46
0.45
0.44
0
5
10
15
20
25
30
WBPU 5 % ZnO unirradiated
WBPU 5 % ZnO irradiated for 56 hours
WBPU 5 % ZnO irradiated for 80 hours
WBPU 5 % ZnO irradiated for 130 hours
WBPU 5 % ZnO irradiated for 196 hours
WBPU 5 % ZnO irradiated for 293 hours

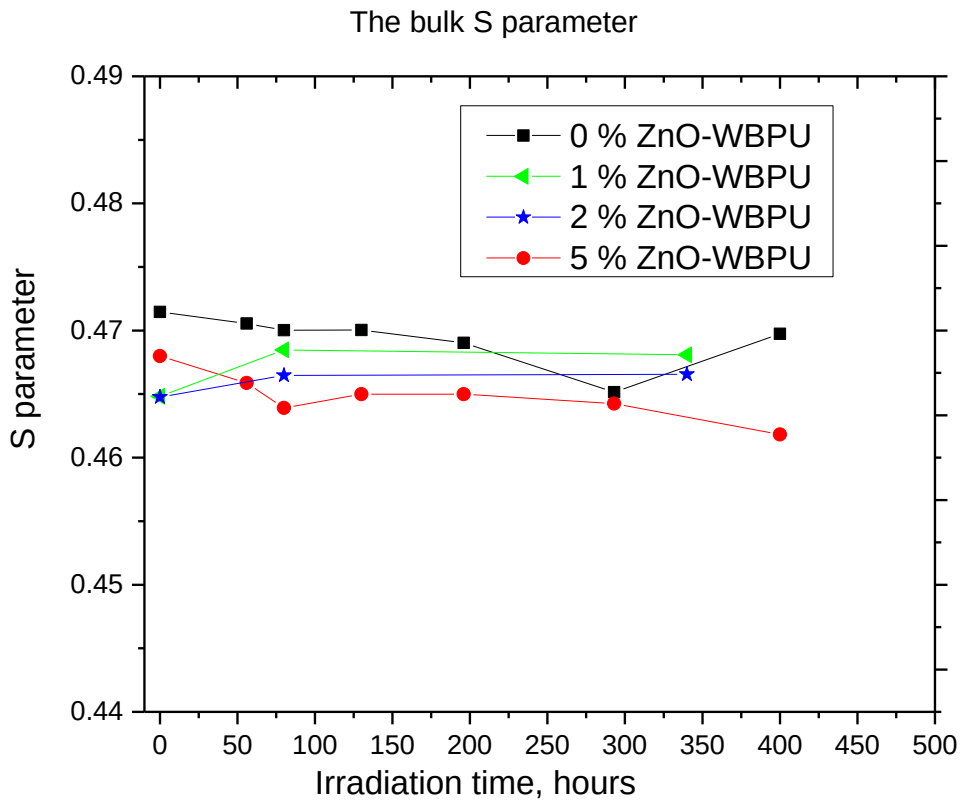

0.475
0.470
0.465
0.460
0.455
0.450
0.445
S parameter
0
5
10
15
20
25
30
Incident Positron Energy, KeV
1% ZnO/WBPU unirradiated
% ZnO/WBPU irradiated for 80 hours
% ZnO/WBPU irradiated for 340 hours

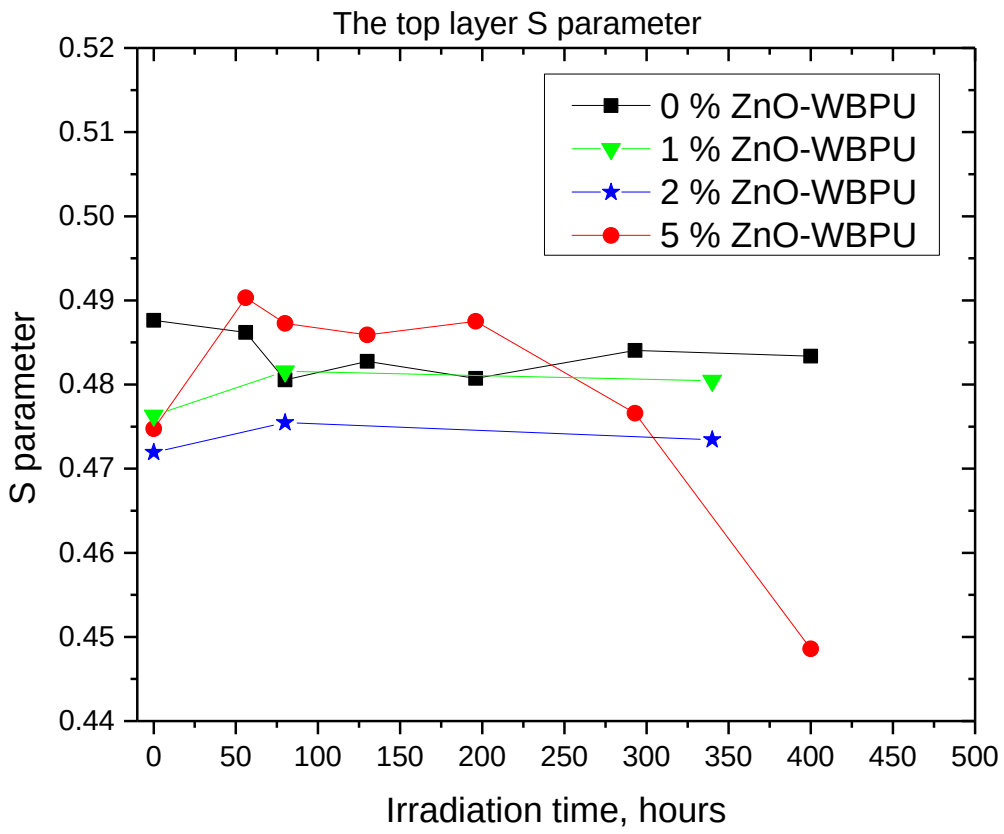

0.475
0.470
0.465
0.460
0.455
0.450
0.445
S Parameter
0
5
10
15
20
25
30
Incident Positron Energy, KeV
2% ZnO/WBPU unirradiated
2% ZnO/WBPU irradiated for 80 hours
2% ZnO/WBPU irradiated for 340 hours

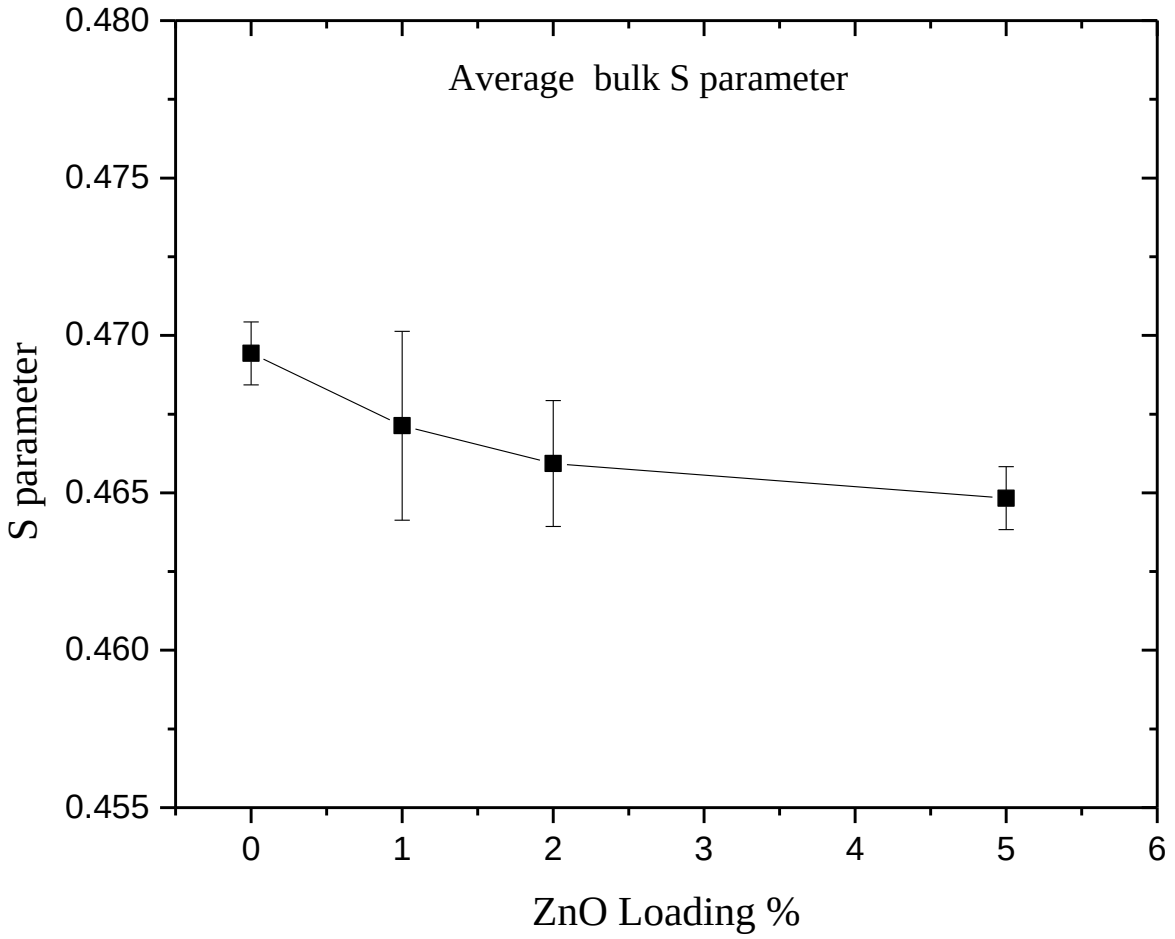
Vepfit Results

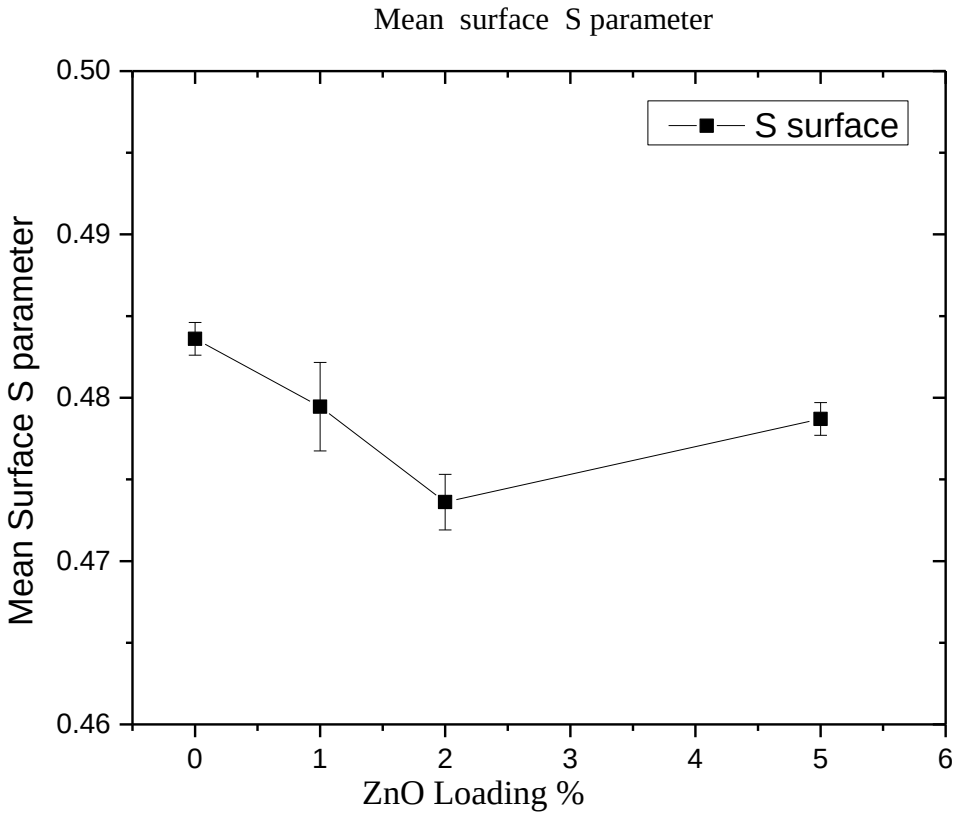
sample	Irradiation time hours	ρ	S 1 surface	S2 bulk	Upper boundary layer (nm)	D1 surface (nm)	D2 bulk (nm)
WBPU 0 % ZnO	0	1.1	0.487620	0.471466	31.81	27.50	197.15
	56		0.486193	0.470547	29.40	30.12	82.93
	80		0.480548	0.740026	44.35	34.49	870.99
	130		0.482745	0.470035	68.04	47.90	2.26
	196		0.480737	0.469026	50.33	38.08	575.51
	293		0.484057	0.465151	11.32	14.24	287.34
WBPU 5 %ZnO	0	1.15	0.474748	0.467993	28.51	27.11	306.0
	56		0.490305	0.465879	26.47	24.28	0.100
	80		0.487259	0.463912	31.31	25.16	0.310
	130		0.480503	0.485903	39.44	27.62	0.520
	196		0.487516	0.464989	18.82	21.20	46.40
	293		0.476581	0.464258	35.83	31.34	340.41
WBPU 1 % ZnO	0	1.19	0.476303	0.464816	28.33	28.48	138.80
	80		0.481570	0.468483	46.38	71.6	198.17
	340		0.480462	0.468092	42.14	35.12	383.21
WBPU 2 % ZnO	0	1.25	0.471935	0.464772	43.11	32.99	428.82
	80		0.475467	0.466467	60.35	38.80	0.186
	340		0.473440	0.466555		37.85	244.38

All the following data obtained from fitting the results using Vepfit program

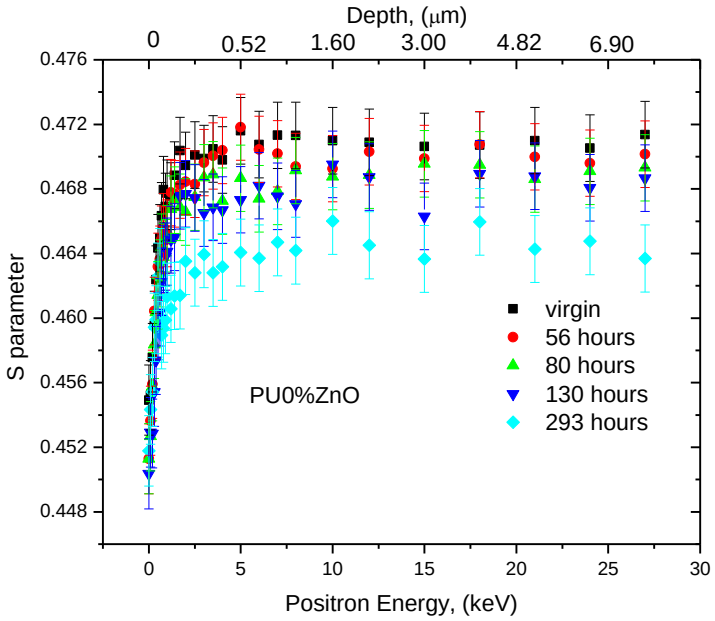


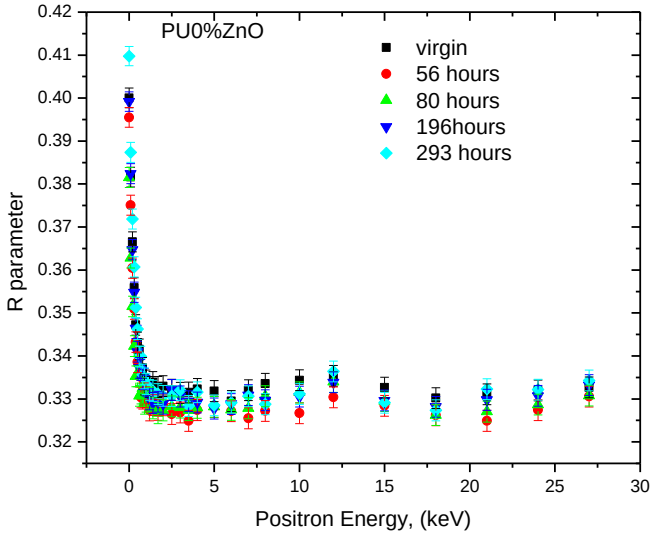

The top layer S parameter
S parameter
Irradiation time, hours
0.52
0.51
0.50
0.49
0.48
0.47
0.46
0.45
0.44
0
50
100
150
200
250
300
350
400
450
500
0 % ZnO-WBPU
1 % ZnO-WBPU
2 % ZnO-WBPU
5 % ZnO-WBPU

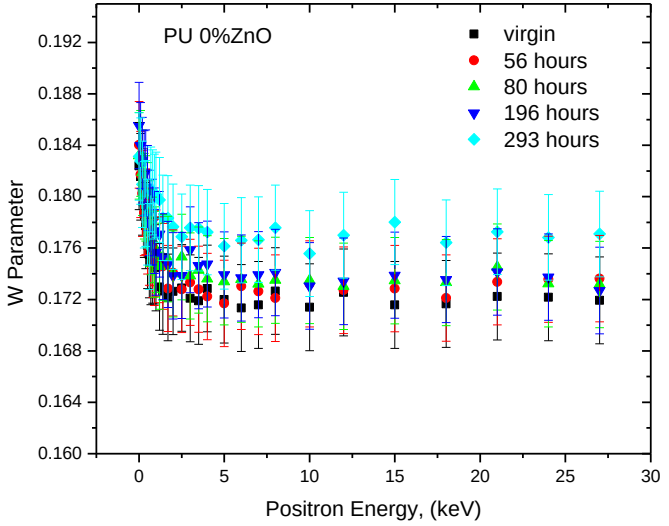

Average bulk S parameter
S parameter
ZnO Loading %
0.480
0.475
0.470
0.465
0.460
0.455
0
1
2
3
4
5
6


Mean surface S parameter
S surface
Mean Surface S parameter
0.50
0.49
0.48
0.47
0.46
0
1
2
3
4
5
6
ZnO Loading %

0%ZnO/WBPU

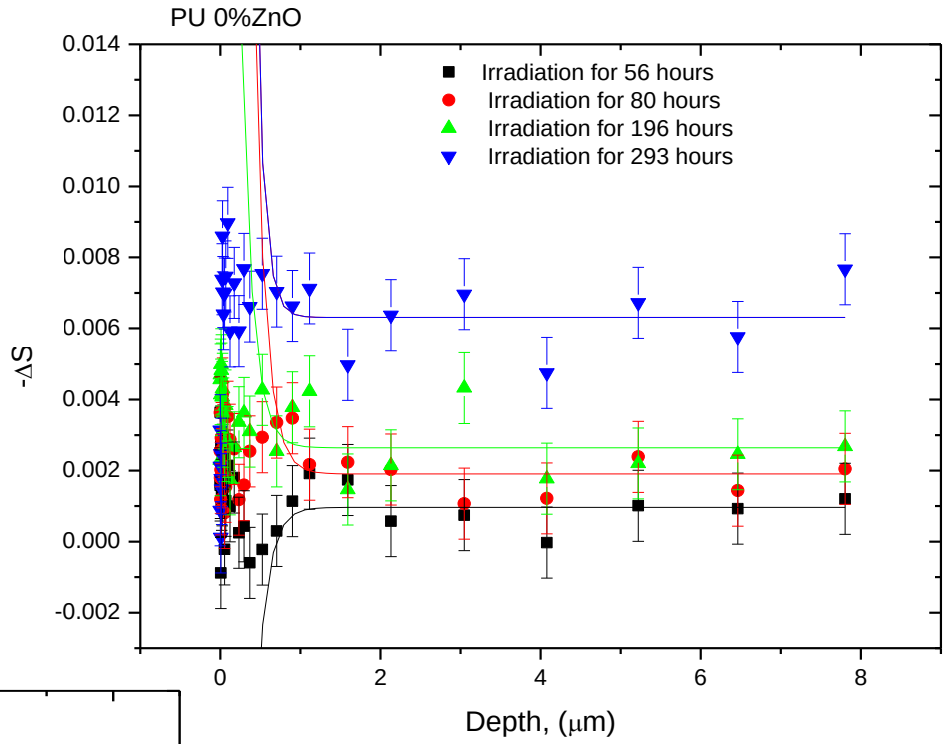

Depth, (μm)
0
0.52
1.60
3.00
4.82
6.90
S parameter
Positron Energy, (keV)
PU0%ZnO
virgin
56 hours
80 hours
130 hours
293 hours

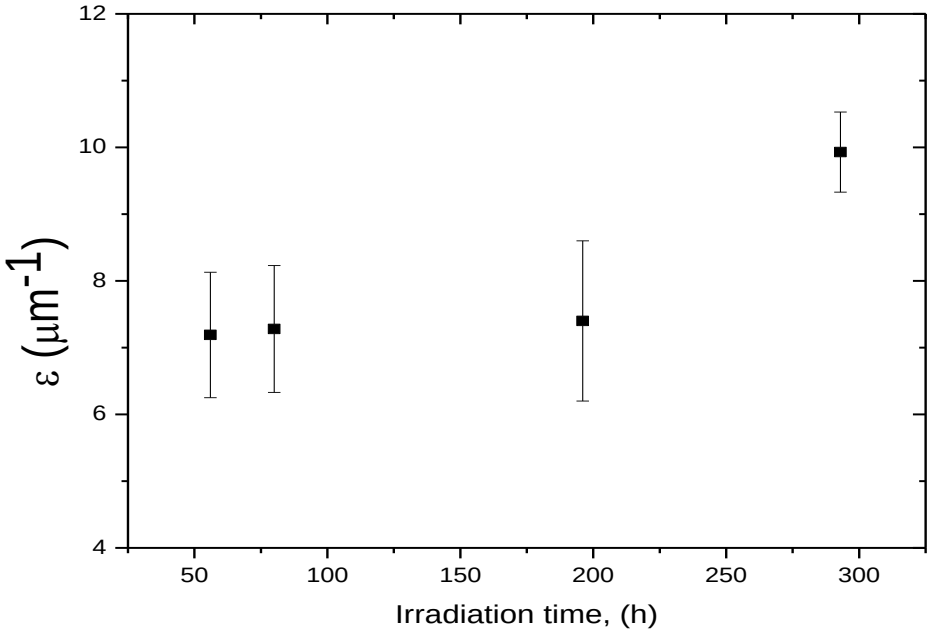

PU0%ZnO
R parameter
Positron Energy, (keV)
virgin
56 hours
80 hours
196hours
293 hours


PU 0%ZnO
W Parameter
Positron Energy, (keV)
virgin
56 hours
80 hours
196 hours
293 hours

$$-\Delta S = -\Delta S_0 \times 10^{-\varepsilon d},$$

where $-\Delta S_0$ is the fitted ΔS at d =0 and ε represents a parameter with a property similar to the extinction coefficient for UV absorption.





It has been demonstrated that there is a direct relationship between the decrease in the S parameter (loss of free volume) and an increase in the cross-linking density due to degradation for PU coatings. We can postulate that the ΔS is a measure of the product concentration of the degradation process (which appears reasonable in light of the relationship between Δ S and cross-linking density). The ΔS vs. time plots can be fitted to an exponential function for polymer coatings:

$$-\Delta S = -\Delta S_{\max}(1 - e^{-kt}),$$

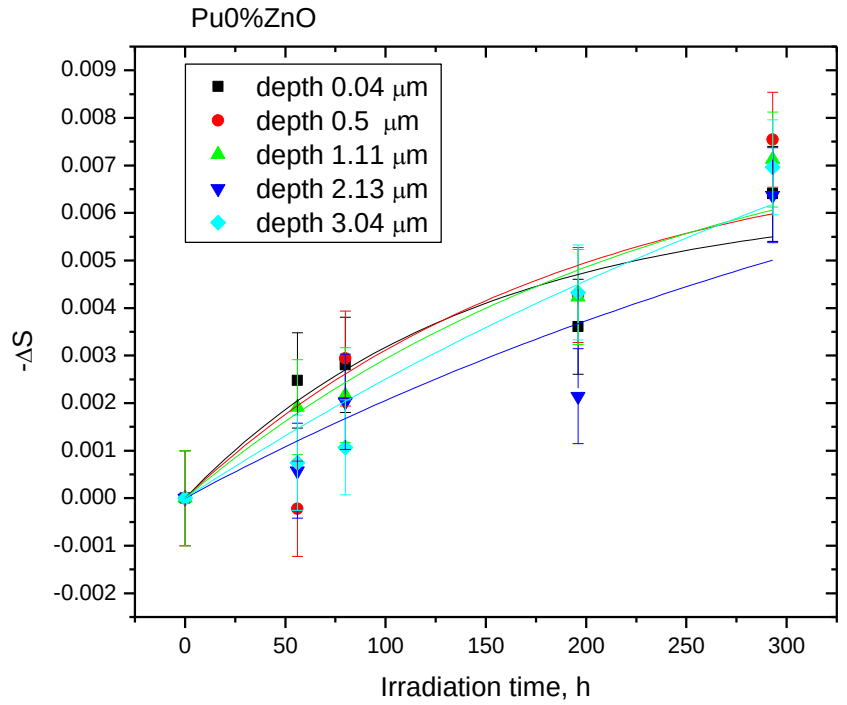
where t is the time of exposure and k is a rate constant. A good fit of this exponential function indicates a first order kinetics of the degradation process, at least near the surface. The half-life of the degradation can also be determined from the first-order kinetics using the relationship:

$$t_{1/2} = \ln \frac{2}{k}.$$

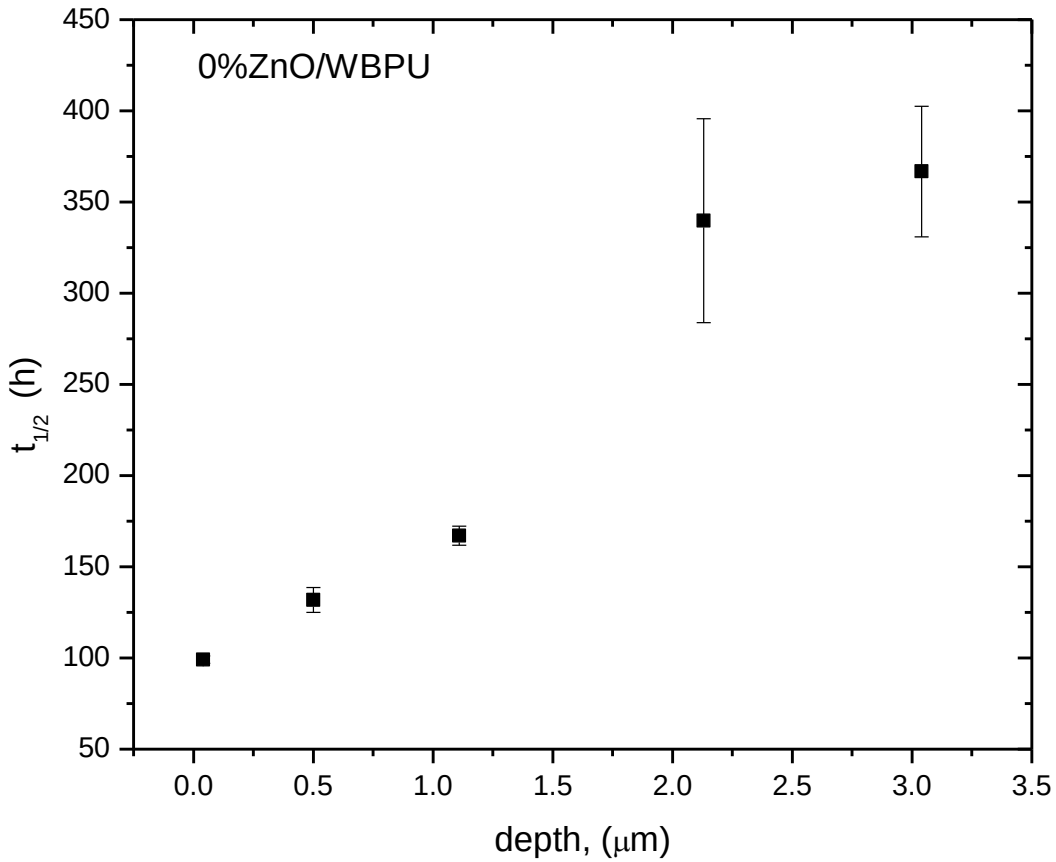
This t1/2 value is a characteristic parameter representing the durability of the coating with respect to UVB photodegradation.

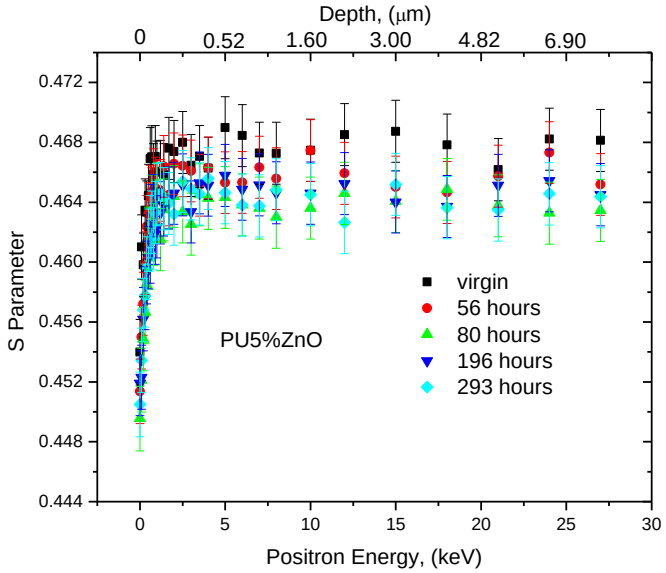
y = a*(1 - exp(-b*x))

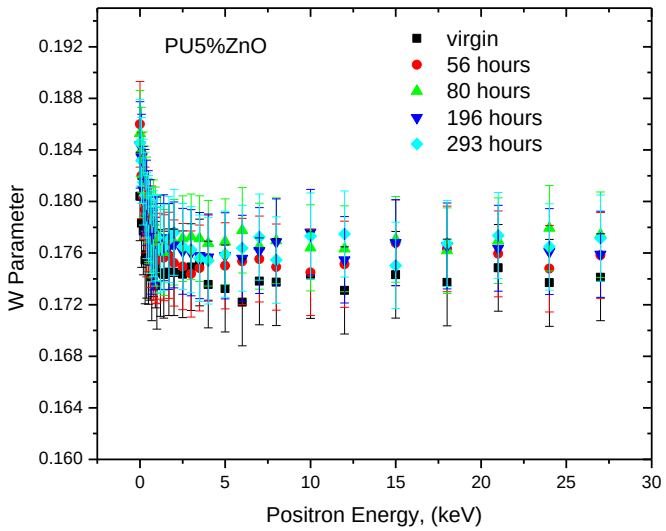
$$-\Delta S = -\Delta S_{max}(1 - e^{-kt}),$$

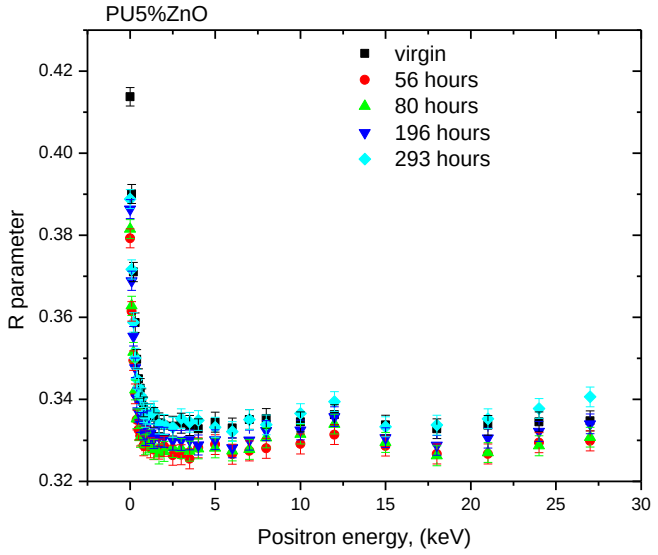


				a*(1-Exp-b*x)					
a	err a	b	err b	τ	dev τ	t1/2	err t1/2	R^2	Depth μm
0.00631	0.00189	0.00699	0.00441	143.0615165	2.999531	99.16269	2.079116	0.89517	0.04
0.00761	0.00562	0.00526	0.00706	190.1140684	9.827973	131.777	6.812232	0.81709	0.5
0.00862	0.00386	0.00415	0.00304	240.9638554	7.553183	167.0234	5.235467	0.94773	1.11
0.01113	0.02618	0.00204	0.00617	490.1960784	80.71279	339.778	55.94584	0.81159	2.13
0.01452	0.02025	0.00189	0.00333	529.1005291	51.65289	366.7445	35.80306	0.9394	3.04


0%ZnO/WBPU
$t_{1/2}$ (h)
depth, (μm)
450
400
350
300
250
200
150
100
50
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5

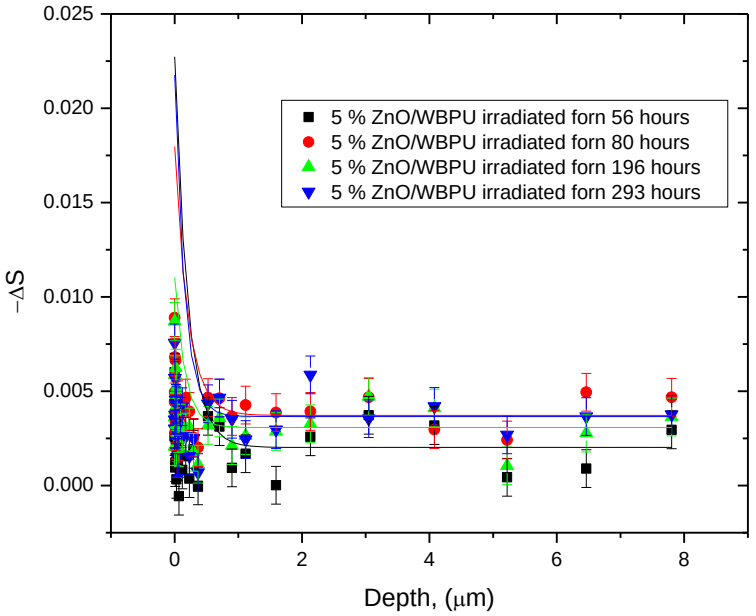

Depth, (μm)
0
0.52
1.60
3.00
4.82
6.90
S Parameter
Positron Energy, (keV)
PU5%ZnO
virgin
56 hours
80 hours
196 hours
293 hours

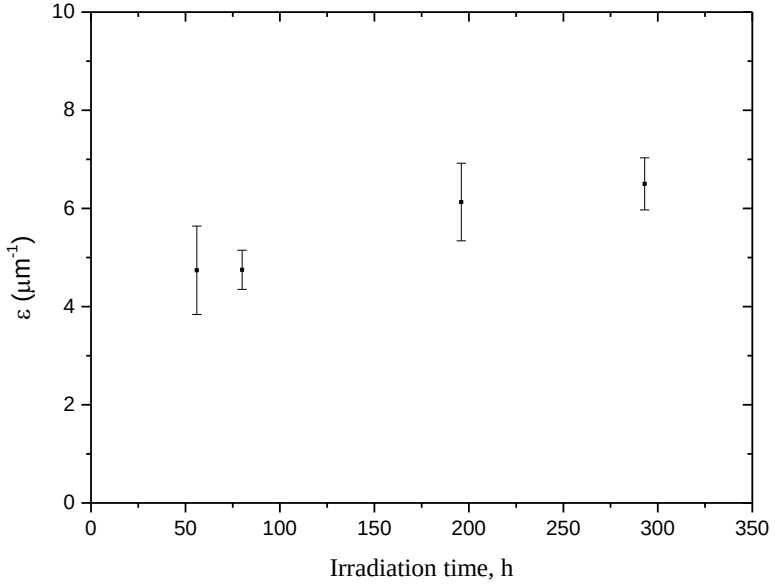

W Parameter
Positron Energy, (keV)
PU5%ZnO
virgin
56 hours
80 hours
196 hours
293 hours


PU5%ZnO
R parameter
Positron energy, (keV)
virgin
56 hours
80 hours
196 hours
293 hours

$$-\Delta S = -\Delta S_0 \times 10^{-\varepsilon d},$$

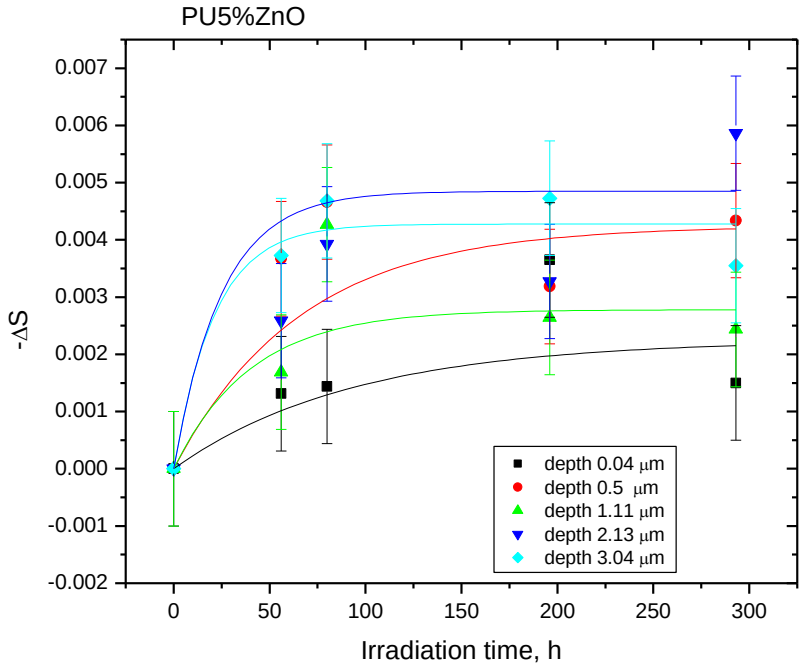
where $-\Delta S_0$ is the fitted ΔS at d =0 and Ɛ represents a parameter with a property similar to the extinction coefficient for UV absorption.



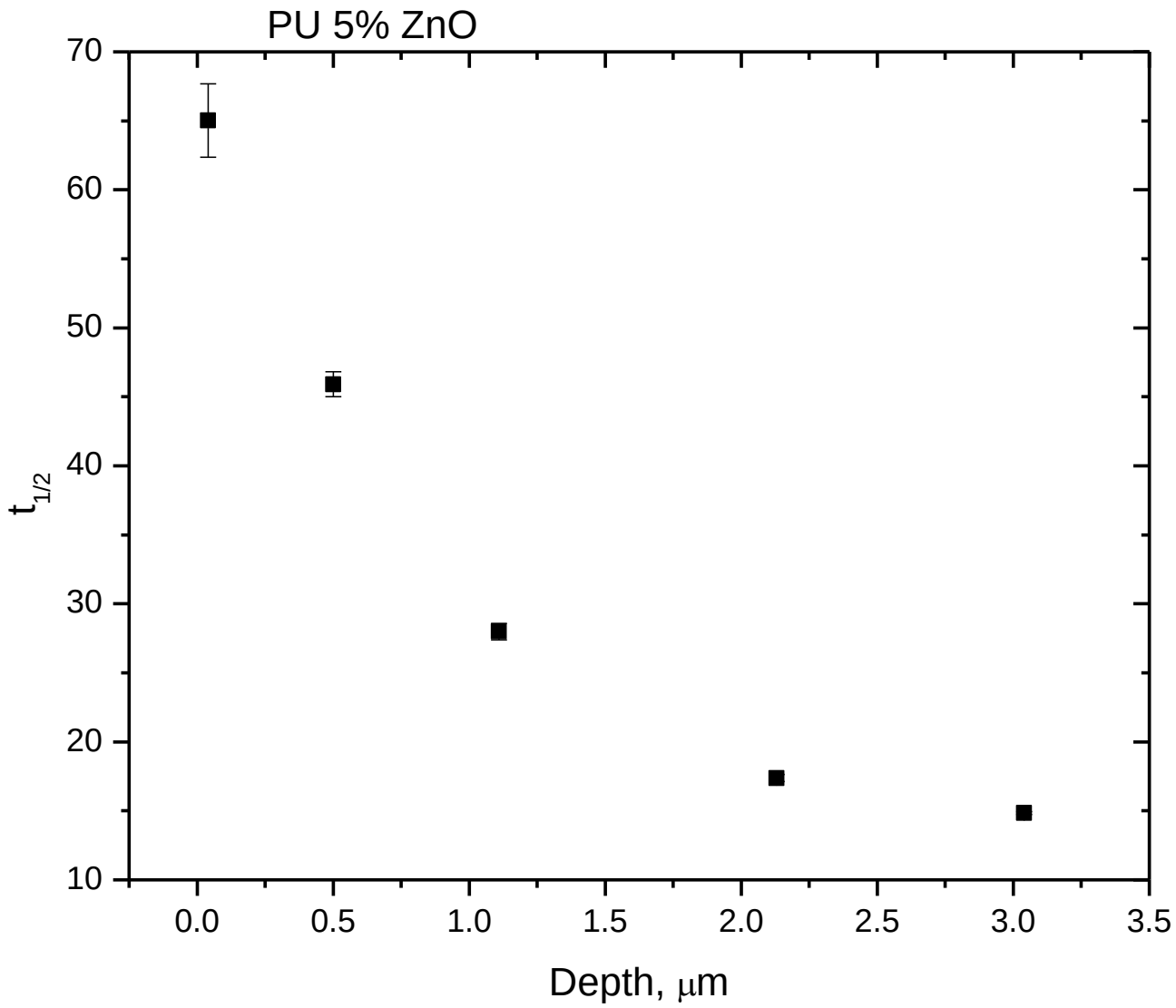


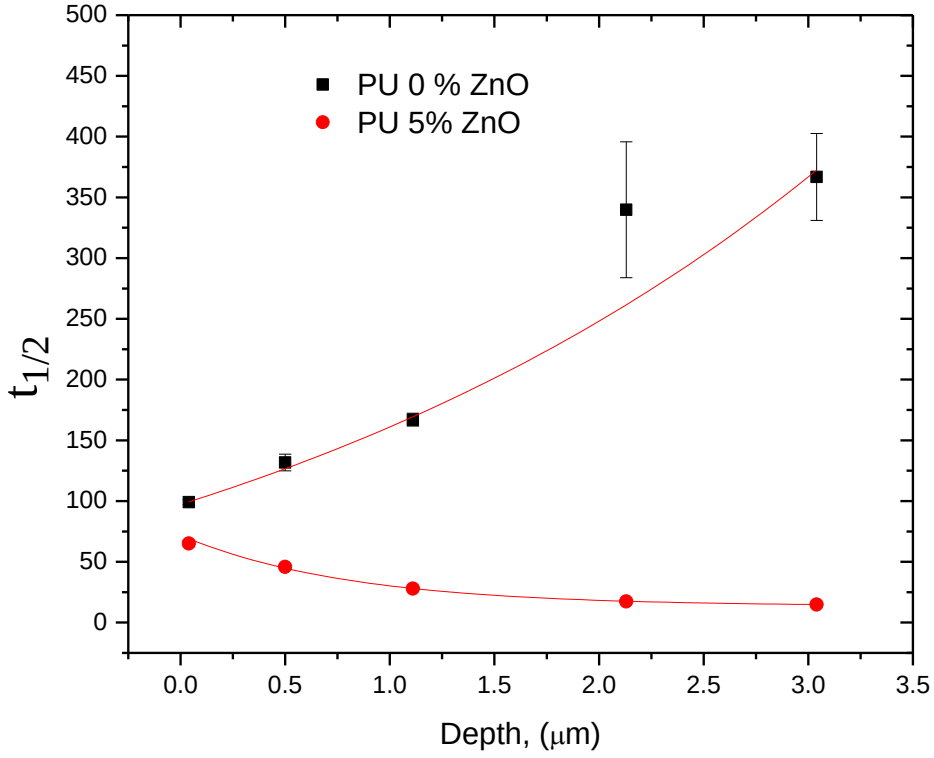
y = a*(1 - exp(-b*x))

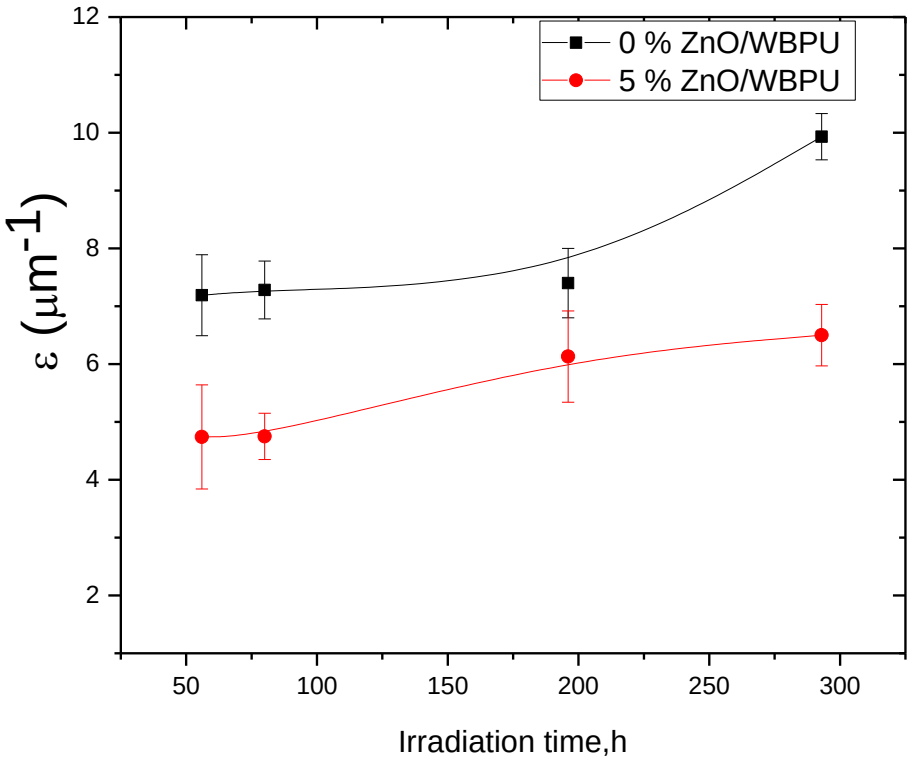
$$-\Delta S = -\Delta S_{max}(1 - e^{-kt}),$$



				a*(1-Exp-b*x)					
a	err a	b	err b	τ	dev τ	t1/2	err t1/2	R^2	Depth μm
0.00225	0.00131	0.01066	0.0162	93.80863039	3.823223	65.02319	2.650056	0.51295	0.04
0.00424	0.0012	0.0151	0.01305	66.22516556	1.312008	45.90379	0.909415	0.63081	0.5
0.00278	0.00083	0.02477	0.03057	40.37141704	0.843734	27.98333	0.584832	0.60644	1.11
0.00485	0.00105	0.0399	0.06137	25.06265664	0.379816	17.37211	0.263268	0.61218	2.13
0.00428	0.0004	0.0467	0.04018	21.41327623	0.140087	14.84255	0.097101	0.93065	3.04


PU 5% ZnO
70
60
50
40
30
20
10
$t_{1/2}$
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
Depth, μm


PU 0 % ZnO
PU 5% ZnO
$t_{1/2}$
Depth, (μm)
500
450
400
350
300
250
200
150
100
50
0
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5


0 % ZnO/WBPU
5 % ZnO/WBPU
ε (μm-1)
Irradiation time,h
12
10
8
6
4
2
50
100
150
200
250
300

Conclusion

- The effect of ZnO nanoparticles on the performance of a waterborne polyurethane coating under UV exposure has been investigated using slow positron beam. The S parameter results as function of UVB exposure indicated that the ZnO nanoparticles behaved as photo-catalysts, accelerating the photodegradation of the PU.

- The photo-catalytic effect of ZnO nanoparticles was enhanced at a higher nanoparticle loading and elevated time of UVB exposure.

- Based on the results of this study, one should be cautious when predicting long term performance of a polymer containing a nanosized inorganic UV absorber.


thank
you