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Use of Atomic Oxygen for Increased Water Contact Angles of Various Polymers for Biomedical Applications

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ABSTRACT

In the low Earth orbit (LEO) space environment, spacecraft surfaces can be altered during atomic oxygen exposure through oxidation and erosion. There can be terrestrial benefits of such interactions, such as the modification of hydrophobic or hydrophilic properties of polymers due to chemical modification and texturing. Such modification of the surface may be useful for biomedical applications. For example, atomic oxygen texturing may increase the hydrophilicity of polymers, such as chlorotrifluoroethylene (Aclar), thus allowing increased adhesion and spreading of cells on textured Petri dishes. The purpose of this study was to determine the effect of atomic oxygen exposure on the hydrophilicity of nine different polymers. To determine whether hydrophilicity remains static after atomic oxygen exposure or changes with exposure, the contact angles between the polymer and a water droplet placed on the polymer's surface were measured. The polymers were exposed to atomic oxygen in a radio frequency (RF) plasma asher. Atomic oxygen plasma treatment was found to significantly alter the hydrophilicity of non-fluorinated polymers. Significant decreases in the water contact angle occurred with atomic oxygen exposure. Fluorinated polymers were found to be less sensitive to changes in hydrophilicity for equivalent atomic oxygen exposures, and two of the fluorinated polymers became more hydrophobic. The majority of change in water contact angle of the non-fluorinated polymers was found to occur with very low fluence exposures, indicating potential cell culturing benefit with short treatment time.

INTRODUCTION

In low Earth orbit (LEO), chemical and mechanical properties of spacecraft materials can change significantly from exposure to various space environmental effects, such as ultraviolet radiation, ionizing radiation, thermal cycling and atomic oxygen. The naturally occurring form of oxygen in Earth's atmosphere is diatomic, but in LEO, diatomic oxygen is photodissociated by short wavelength ultraviolet radiation from the Sun and becomes monatomic. When the resulting monatomic particle collides with materials with gaseous oxidation products, the resulting gas dissipates, and the surface of the material is eroded away. Polymers used on the exterior of spacecraft are chosen for certain favorable attributes, such as high flexibility, low density, electrical and optical properties (such as a low solar absorptance to thermal emittance ratio (α_s/ε)). For most polymers, the oxidation products are gaseous species, and therefore polymers are textured and eroded away in the LEO space environment due to atomic oxygen exposure.

There can be terrestrial benefits of such atomic oxygen interaction. For example, the modification of hydrophobic or hydrophilic properties of polymers through chemical modification and texturing may be useful for biomedical applications. For certain biomedical applications cellular attachment to polymer surfaces is desired. By altering the surfaces of polymers, increased cell attachment can be achieved for cell culturing applications [1]. Atomic oxygen texturing may increase the hydrophilicity of plastic containers thus allowing increased adhesion and spreading of cells on textured Petri dishes. NASA Glenn Research Center and the Cleveland Clinic Foundation have studied increased adhesion and spreading of osteosarcoma cells on atomic oxygen textured Aclar [2,3] .

Previous studies have been conducted at NASA Glenn Research Center investigating texturing of polymer surfaces, using techniques such as ion beam and atomic oxygen texturing and grit-blasting, for various industrial, art restoration and biomedical applications. Various materials' properties have been investigated as a function of texturing duration. For example, the effect of atomic oxygen exposure on the coefficient of static friction and morphology of polymer surfaces has been investigated; specifically to determine a decrease as a function of fluence [1]. Studies were also conducted using abrasive grit blasting for examining RMS roughness growth of glass microscope slides, 300 series stainless steel, and polymethylmethacrylate [2]. Also, the effect of atomic oxygen exposure on the hydrophilicity of polyimide Kapton, polystyrene, and natural rubber at an atomic oxygen fluence of 10^{20} atoms/cm^2 has been investigated [1].

The purpose of this study was to determine the effect of atomic oxygen exposure as a function of fluence on the hydrophilicity of nine chemically different polymers. The polymers were exposed to nine different atomic oxygen fluences, or exposure levels. To determine whether hydrophilicity remains static after atomic oxygen exposure or changes with exposure, the contact angle between the polymer and a water droplet placed on the polymer's surface were measured in relation to fluence. The greater the contact angle the more hydrophobic the substance. Details on the polymers tested, the experimental procedures, and the water contact angle versus fluence data are provided.

MATERIALS AND EXPERIMENTAL PROCEDURES

Polymers

Nine different thin film polymers, of varying chemistries, were tested. These polymers along with their chemical abbreviations and film thicknesses are provided in Table 1. These polymers were chosen because they are commonly used for polymer characteristics testing. In addition, some are used for storing liquids, such as PMMA (beverage containers) and Polystyrene (Petri-dishes). Both fluorinated and non-fluorinated polymers were evaluated.

Table 1. Polymers Tested for Atomic Oxygen Altered Hydrophilicity.

Abbreviation	Polymer Name	Trade Name	Thickness
PE	Polyethylene	Alathon; Lupolen	2 mil
PET	Polyethylene terephthalate	Mylar A	2 mil
POM	Polyoxymethylene	Delrin; Celcon	4 mil
PS	Polystyrene	Lustrex; Polystyrol	2 mil
PP	Polypropylene	Profax; Propathene	20 mil
PMMA	Polymethylmethacrylate	Plexiglas; Lucite	2 mil
FEP	Fluorinated ethylene propylene	Teflon FEP	2 mil
PTFE	Polytetrafluoroethylene	Fluon; Teflon	2 mil
PCTFE	Polychlorotrifluoroethylene	Neoflon CTFE M-300	5 mil

Atomic Oxygen Exposure

Polymer samples were treated with atomic oxygen using a 100-watt, 13.56 MHz RF plasma asher operated on air. The plasma was adjusted by sight to the brightest level in order to decrease the amount of time a sample would be exposed to reach the desired fluence level. For this experiment the effective atomic oxygen fluence (F) was found by determining the mass loss of a Kapton H witness coupon. The vacuum desiccated witness coupons were weighed before and after ashing using a Mettler Balance Model 3M.

The equation used for finding the LEO effective fluence is provided in equation 1. Polyimide Kapton H is used as the specified witness coupon because the erosion yield (E_y) is well characterized in the LEO space environment (3.0×10^{-24} cm^3/atom) [4]. Erosion yield is a measurement of the volume of the material that will erode for each atom of atomic oxygen that impacts the surface. Effective fluence is defined as the total number of particles (in this experiment, oxygen atoms) that interact with the sample per area (cm^2). The atomic oxygen flux (f), used to determine the necessary exposure time for a desired fluence, is the number of oxygen atoms to which the material was exposed (per cm^2) per second ($F = f \times t$).

$$F = \frac{\Delta M}{\rho A E_y} \tag{1}$$

F = Fluence (atoms/cm^2)
ΔM = Change in mass (g)
ρ = Density of Kapton (1.42 g/cm^3)
A = Surface area (cm^2)
E_y = erosion yield of Kapton H (3.0×10^{-24}cm^3/atom)

Pristine samples were compared with samples that had been exposed to atomic oxygen at various fluence levels. Minimum and maximum fluences for the ashing trials were set based on the effective AO erosion of the witness coupon in the asher. The time intervals for ashing were determined by finding the logarithmic values of the minimum and maximum fluences. The difference of these two values was divided by the desired number of intervals (8). The initial desired fluence was then multiplied by this result (2.371374), as was each subsequent desired fluence. The flux in the asher was determined to be approximately 3.0×10^{15} cm^3/atom sec. The desired fluences and thus the planned exposure times are provided in Table 2.

Table 2. Atomic Oxygen Fluence, Flux and Exposures Durations.

Fluence (atoms/cm^2)	**Flux (atoms/cm^{2}sec)**	**Time in Asher (hours)**
1.00E+18	3.00E+15	0.1
2.37E+18	3.00E+15	0.2
5.62E+18	3.00E+15	0.5
1.33E+19	3.00E+15	1.2
3.16E+19	3.00E+15	2.9
7.50E+19	3.00E+15	6.9
1.78E+20	3.00E+15	16.5
4.22E+20	3.00E+15	39
1.00E+21	3.00E+15	92.6

Water Contact Angle Procedures

The water contact angle for each sample was measured using a Contact Angle Measuring System Model G1, manufactured by Kernco Instruments. Droplets of deionized water were placed upon each sample using a 20 μl micropipette and the tangent was found using adjustable crosshairs. For each exposed polymer three measurements were obtained at three different locations of the polymer. The water contact angle for each exposure was based on an average of the three values.

RESULTS AND DISCUSSION

The average water contact angles and standard deviations for each polymer at each exposure level are provided in Table 3 along with the pristine sample data (fluence = 0 atoms/cm^2). The water contact angle versus fluence is graphed for each of the polymers and is provided in Figures 1 through 9. Testing at a fluence level of 1.0×10^{21} atoms/cm^2 was not conducted as planned because the majority of polymers were too severely eroded at this fluence level. For comparison purposes, the non-fluorinated polymers have been plotted together in Figure 10 and the fluorinated polymers have been plotted together in Figure 11.

It was determined that after even the shortest atomic oxygen exposure, non-fluorinated polymer samples became more hydrophilic than their pristine counterparts. This may be due to either surface texture changes or oxidation functionality surface changes. Despite long-term exposure (fluence of 5.16×10^{20} atoms/cm^2), the water contact angles remained relatively unchanged after initial exposure (seen in Figure 10). This implies that increasing the atomic oxygen fluence did not affect the hydrophilicity of the polymers. Rather, polymers were affected similarly by a very short exposure ($<1\times10^{19}$ atoms/cm^2). This implies that oxidation functionality is more likely the contributor to increased hydrophilicity rather than texture, as texture would continue to develop with fluence.

The water contact angles of fluorinated polymers did not exhibit the same trend as the non-fluorinated polymers. For example, PCTFE and PTFE became slightly more hydrophobic after atomic oxygen exposure (as seen in Figures 1 and 6, respectively). Although Teflon FEP did become more hydrophilic, its water contact angles did not decrease as much as those of the non-fluorinated polymers, as shown in Figure 10. Therefore, two trends occurred based on the fluorination of the polymer. In the first trend, non-fluorinated polymers saw a decrease in water contact angle and a significant increase in hydrophilicity with atomic oxygen plasma exposure. In the second, fluorinated polymers had either a small increase in hydrophilicity or became more hydrophobic with atomic oxygen plasma exposure.

As mentioned, the majority of change in water contact angle of the non-fluorinated polymers was found to occur with very low fluence exposures. This indicates potential cell culturing benefit with very short treatment time.

Table 3. Average Water Contact Angles.

Polymer	Fluence (atoms/cm^2)	Average Contact Angle	Std Dev	Polymer	Fluence (atoms/cm^2)	Average Contact Angle	Std Dev
PE	0	94.1	1.5	PP	0	81.5	0.9
	2.07E+18	37.9	1.0		8.16E+18	55.3	0.1
	2.83E+18	31.4	0.1		1.64E+19	43.1	0.1
	8.16E+18	30.7	0.3		1.79E+19	54.8	0.7
	1.79E+19	32.4	0.8		4.85E+19	43.1	0.1
	2.22E+19	23.9	0.1		6.20E+19	35.3	0.3
	4.85E+19	32.2	0.2		9.57E+19	47.2	0.9
	6.20E+19	23.1	0.2		1.00E+20	40.2	0.2
	1.00E+20	28.1	0.2		1.37E+20	25.8	0.4
	5.16E+20	27.3	0.1		5.16E+20	0	0.0
PET	0	67.5	2.4	PMMA	0	75.3	1.5
	2.07E+18	18.8	0.6		2.07E+18	45.7	0.6
	8.16E+18	16.7	0.1		1.79E+19	35.8	0.3
	1.79E+19	16.8	0.2		2.22E+19	20.4	0.3
	2.22E+19	3.52	0.7		5.35E+19	35.2	0.2
	4.85E+19	8.52	4.4		6.20E+19	12.5	0.2
	5.02E+19	16.1	0.1		7.26E+19	12.3	0.3
	6.20E+19	9.82	0.2		8.16E+19	38.5	1.2
	7.26E+19	8.33	0.1		9.57E+19	46.4	0.5
	9.57E+19	17.6	0.5		1.00E+20	39.7	0.2
	5.16E+20	16.5	0.2		5.16E+20	0	0.0
POM	0	68.3	0.8	FEP	0	95.7	1.6
	2.83E+18	48	0.1		8.16E+18	76.1	0.6
	8.16E+18	39.6	0.4		1.79E+19	83.1	0.4
	1.79E+19	26	0.4		2.22E+19	90.4	0.9
	2.22E+19	30.7	8.7		4.85E+19	83.8	0.1
	4.85E+19	35.6	0.1		6.20E+19	75.2	0.3
	6.20E+19	28	0.1		9.57E+19	80.6	0.8
	1.00E+20	35.6	0.2		1.00E+20	82.2	0.2
	1.37E+20	35	0.2		1.37E+20	65.4	0.3
	5.16E+20	45.7	0.1		5.16E+20	75.1	0.1
PS	0	72.5	1.9	PTFE	0	72	1.0
	2.07E+18	11	0.5		8.16E+18	81.1	0.4
	2.83E+18	10.9	0.1		1.40E+19	81.9	0.1
	7.17E+18	6.65	0.1		2.22E+19	81.2	0.8
	1.79E+19	5	0.4		5.02E+19	78.6	0.3
	2.22E+19	11	0.9		5.35E+19	80.6	0.4
	4.85E+19	9.68	0.0		6.20E+19	81.6	0.6
	6.20E+19	5.37	0.2		9.57E+19	76.3	0.8
	1.00E+20	4.18	0.2		1.37E+20	81.4	0.0
	5.16E+20	8.03	0.2		5.16E+20	82.4	0.2
				PCTFE	0	34.3	2.9
					8.16E+18	74.6	0.6
					1.79E+19	68	0.9
					2.22E+19	56.6	0.4
					4.85E+19	54.7	0.3
					6.20E+19	42.7	0.2
					9.57E+19	65.3	0.8
					1.00E+20	51.2	0.1
					5.16E+20	82.4	0.1

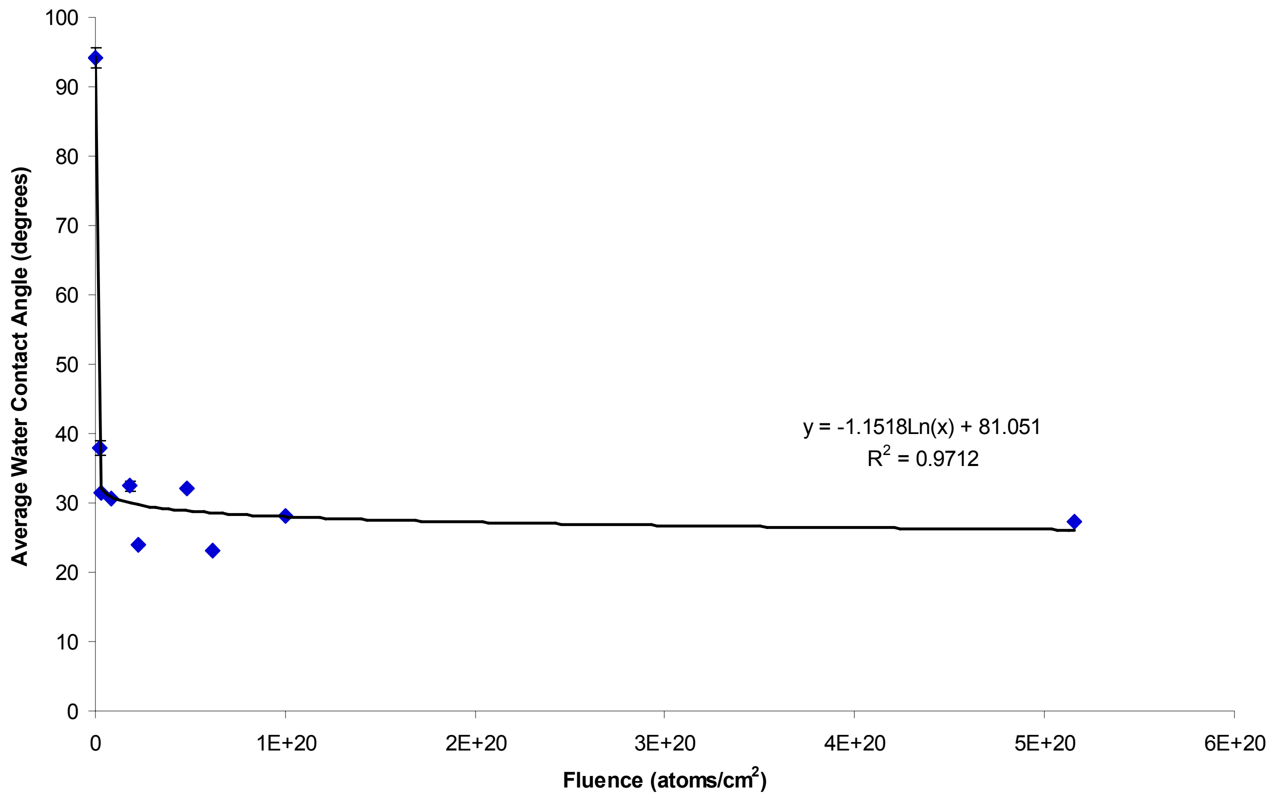

Fig. 1. Water contact angle versus atomic oxygen fluence of PE

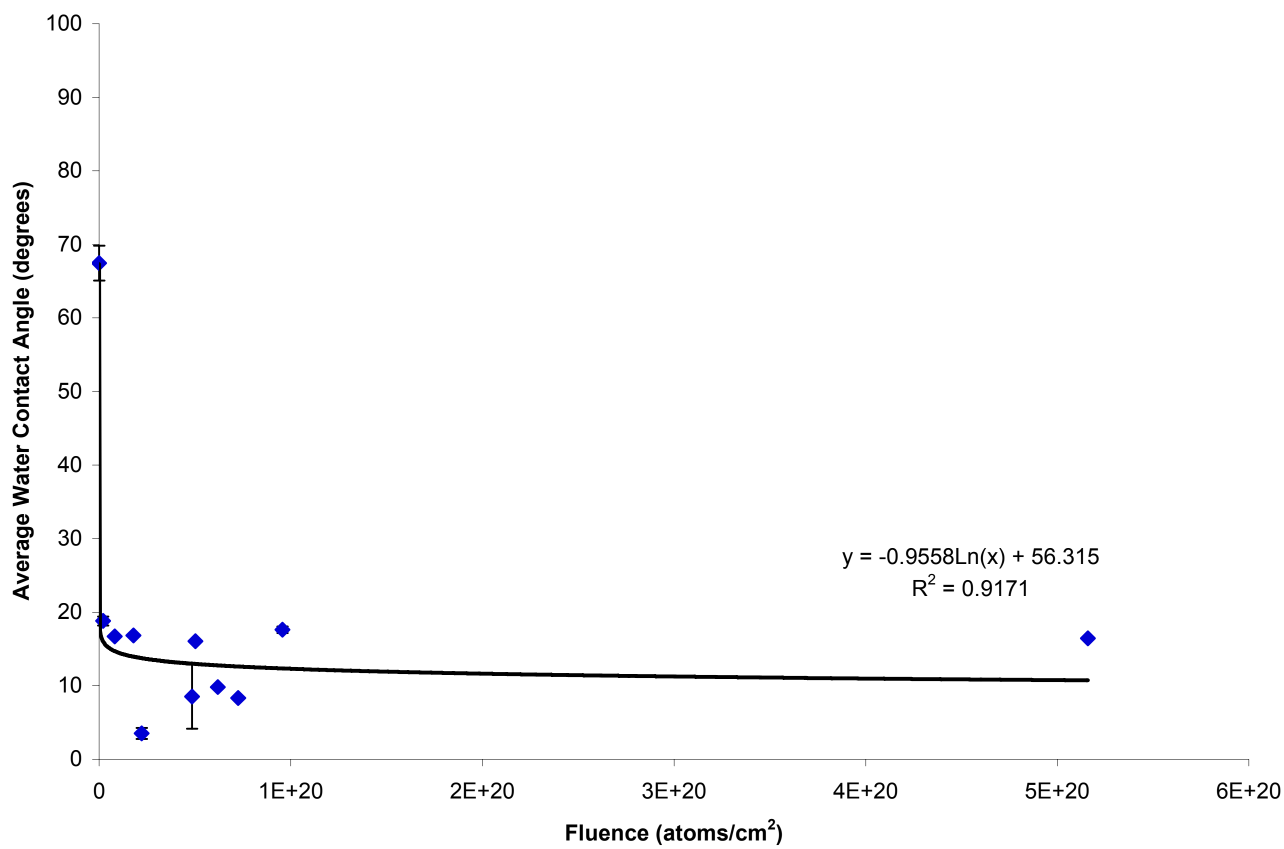

Fig. 2. Water contact angle versus atomic oxygen fluence of PET

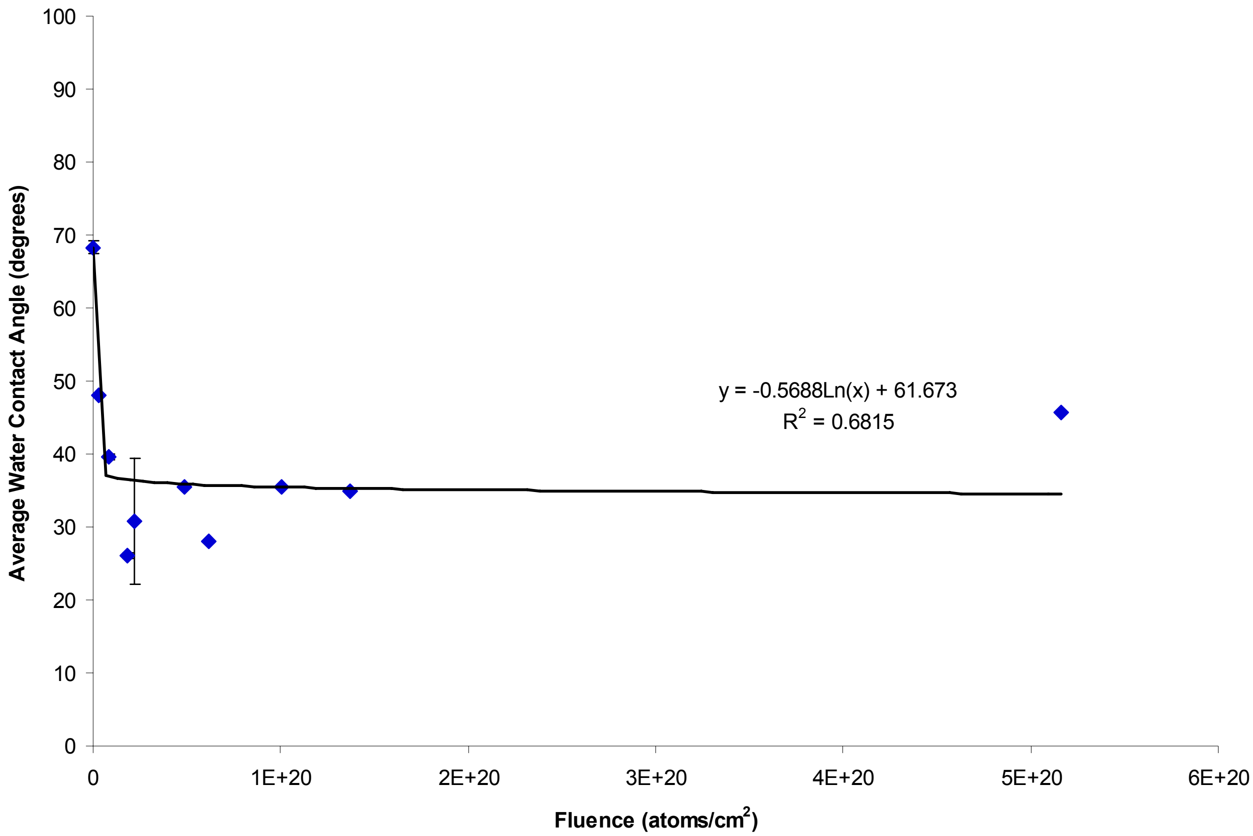

Fig. 3. Water contact angles versus atomic oxygen fluence of POM

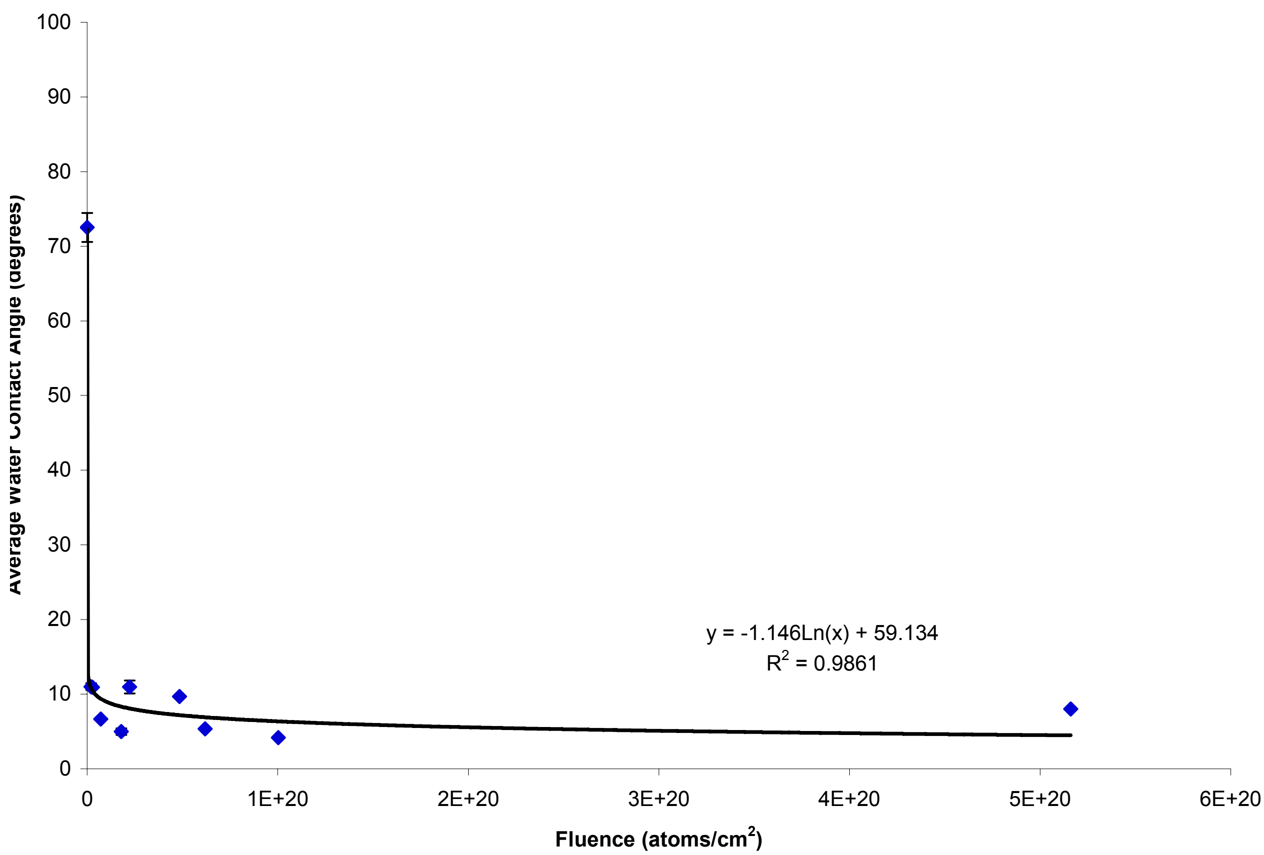

Fig. 4. Water contact angles versus atomic oxygen fluence for PS

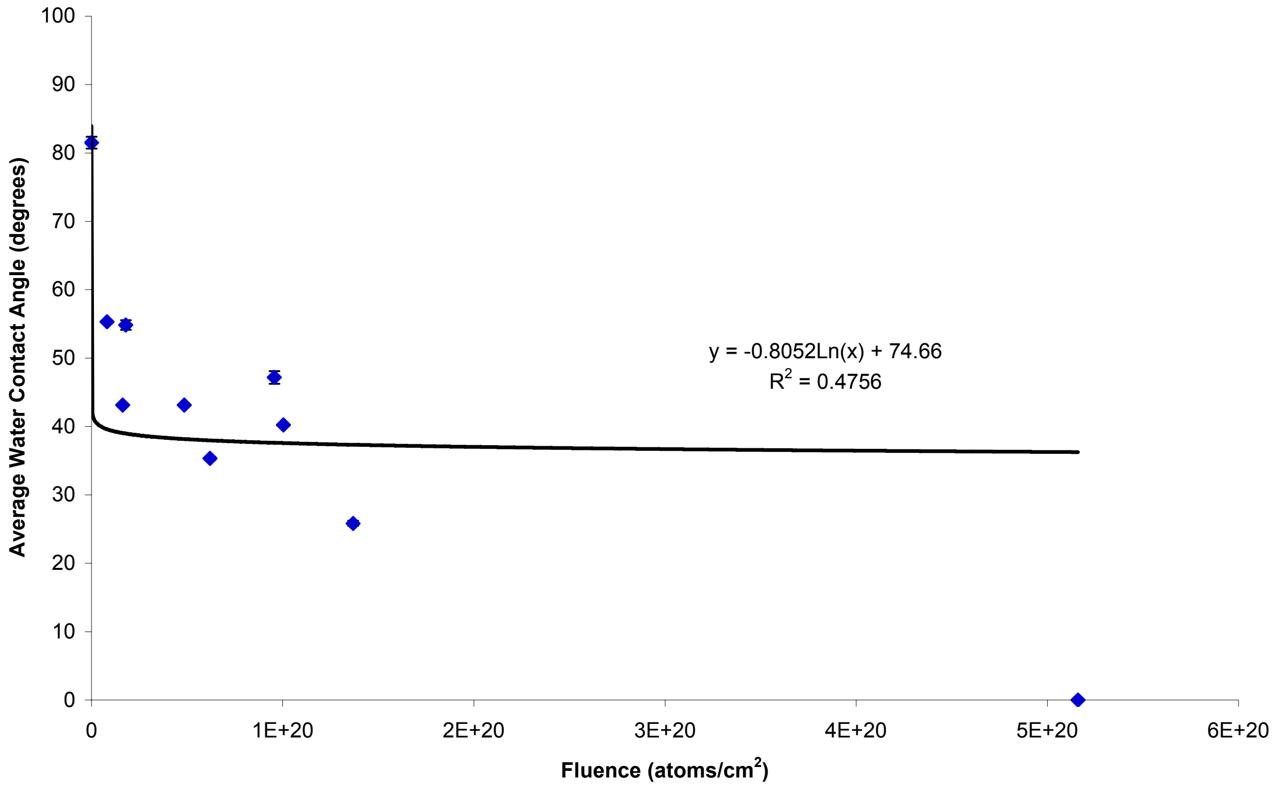

Fig. 5. Water contact angle versus atomic oxygen fluence of PP

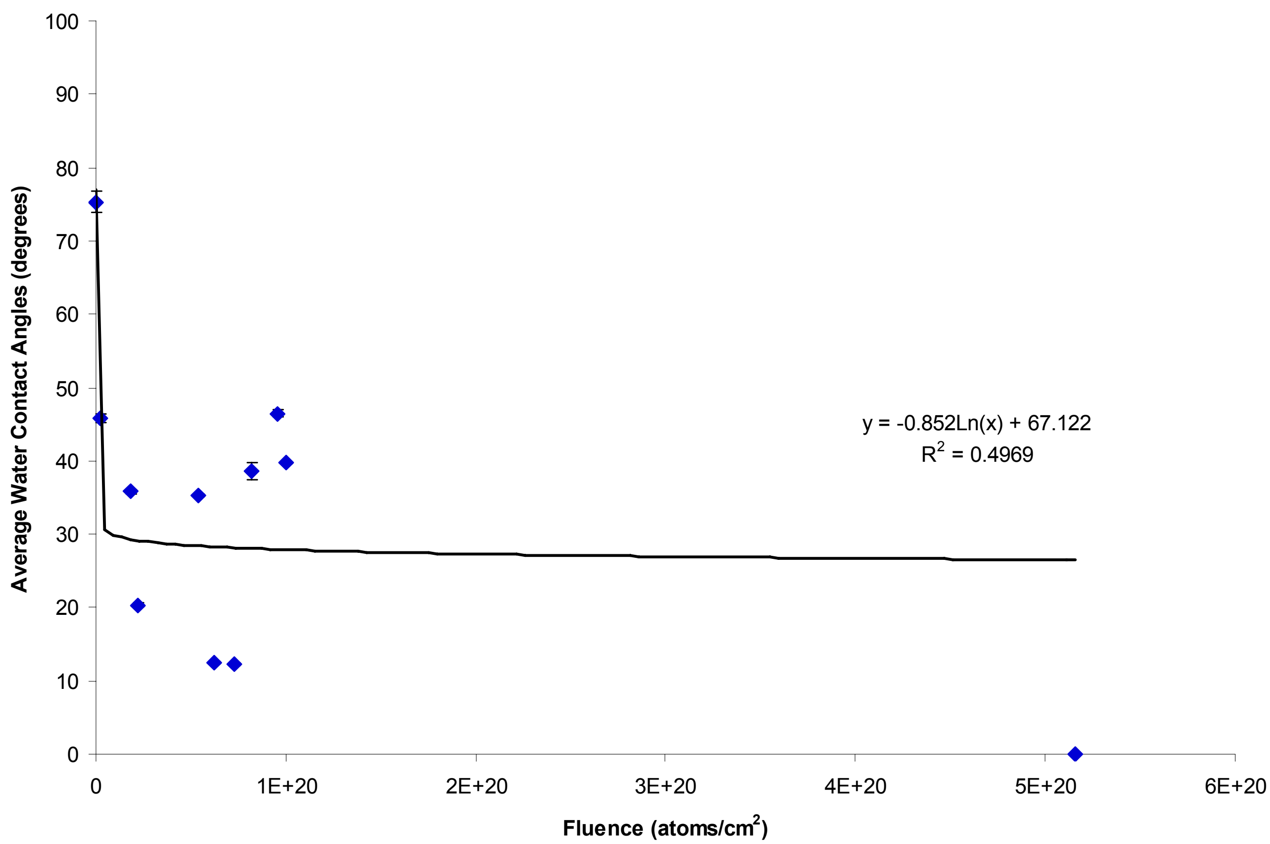

Fig. 6. Water contact angles versus atomic oxygen fluence of PMMA

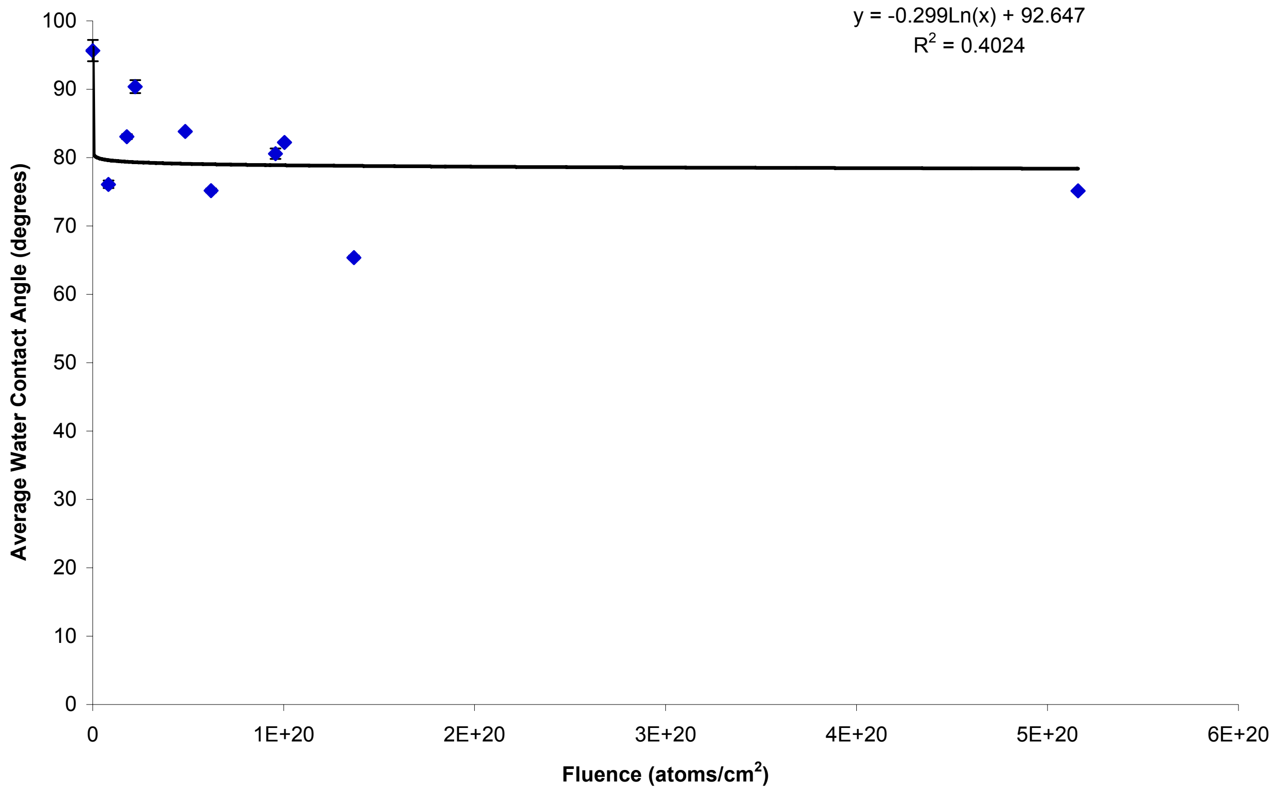

Fig. 7. Water contact angle versus atomic oxygen fluence for FEP

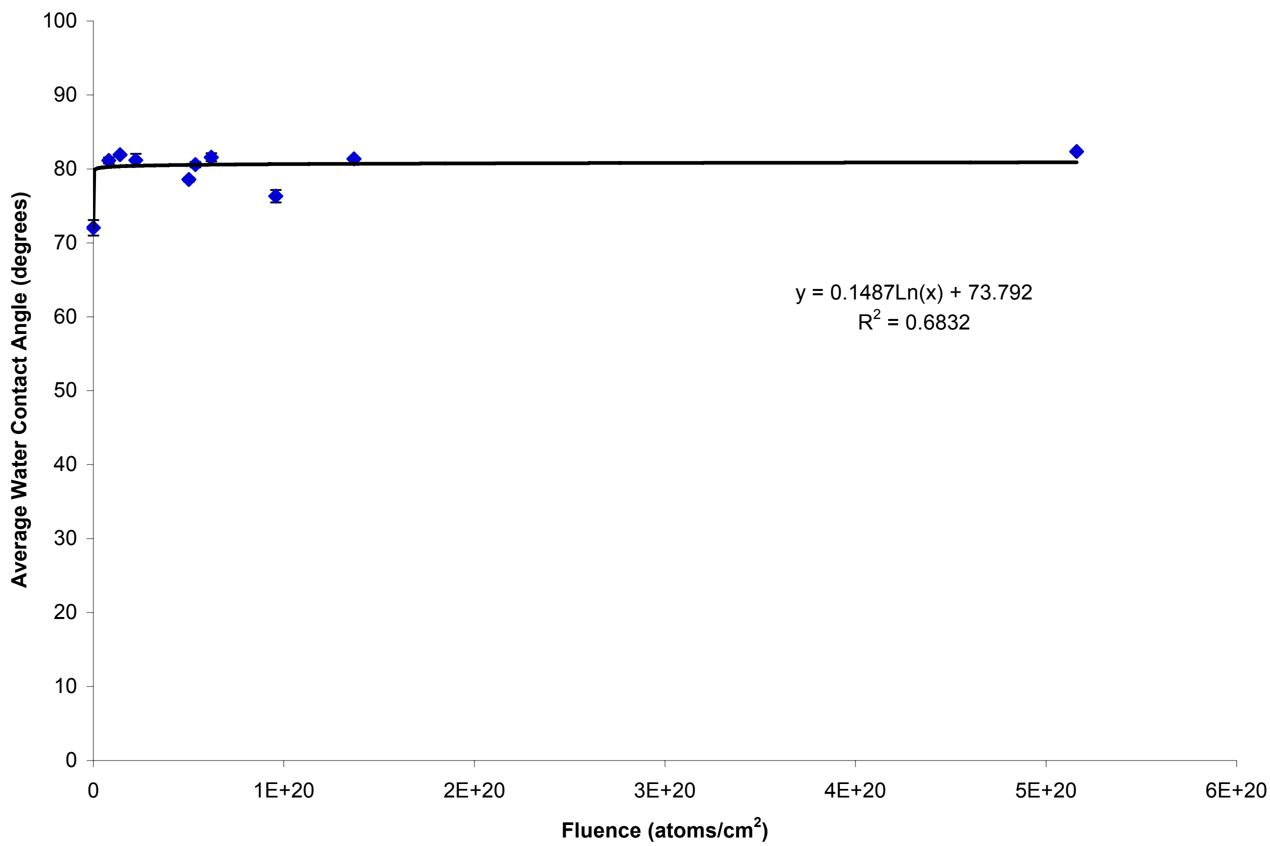

Fig. 8. Water contact angles versus atomic oxygen fluence of PTFE

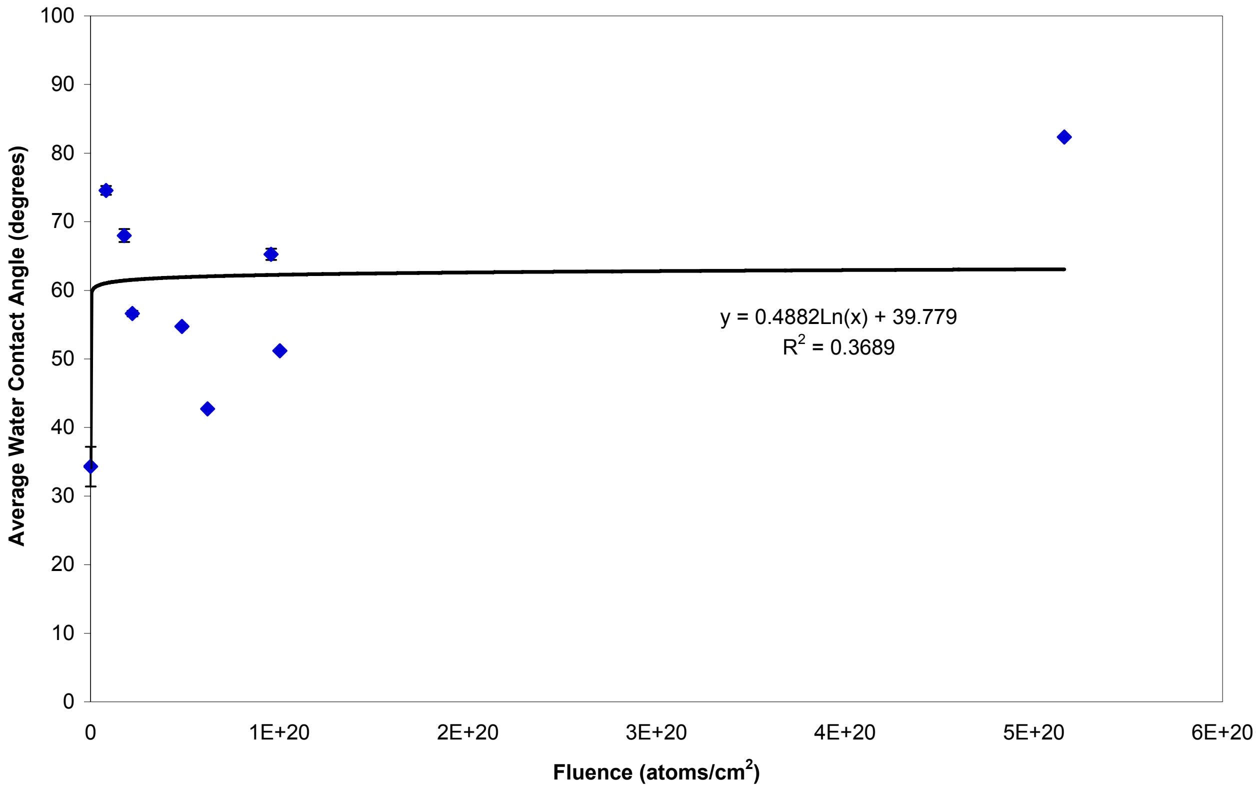

Fig. 9. Water contact angle versus atomic oxygen fluence of PCTFE

SUMMARY & CONCLUSIONS

The purpose of this study was to determine the effect of atomic oxygen exposure, measured as a function of effective Kapton fluence, on the hydrophilicity of nine different polymers. Modification of hydrophobic or hydrophilic properties of polymers due to chemical modification and texturing through atomic oxygen exposure can be useful for biomedical applications. The polymers were exposed to atomic oxygen in a RF plasma asher operated in air. Samples were exposed to nine fluences ranging from 2.07×10^{18} to 5.16×10^{20} atoms/cm^2. Atomic oxygen plasma treatment was found to significantly alter the hydrophilicity of non-fluorinated polymers. Significant decreases in the water contact angle occurred rapidly with atomic oxygen exposure. Fluorinated polymers were found to be less sensitive to changes in hydrophilicity for equivalent fluence exposures, and two of the fluorinated polymers became more hydrophobic. The majority of change in water contact angle of the non-fluorinated polymers was found to occur with very low fluence exposures, indicating potential cell culturing benefit with very short treatment time.

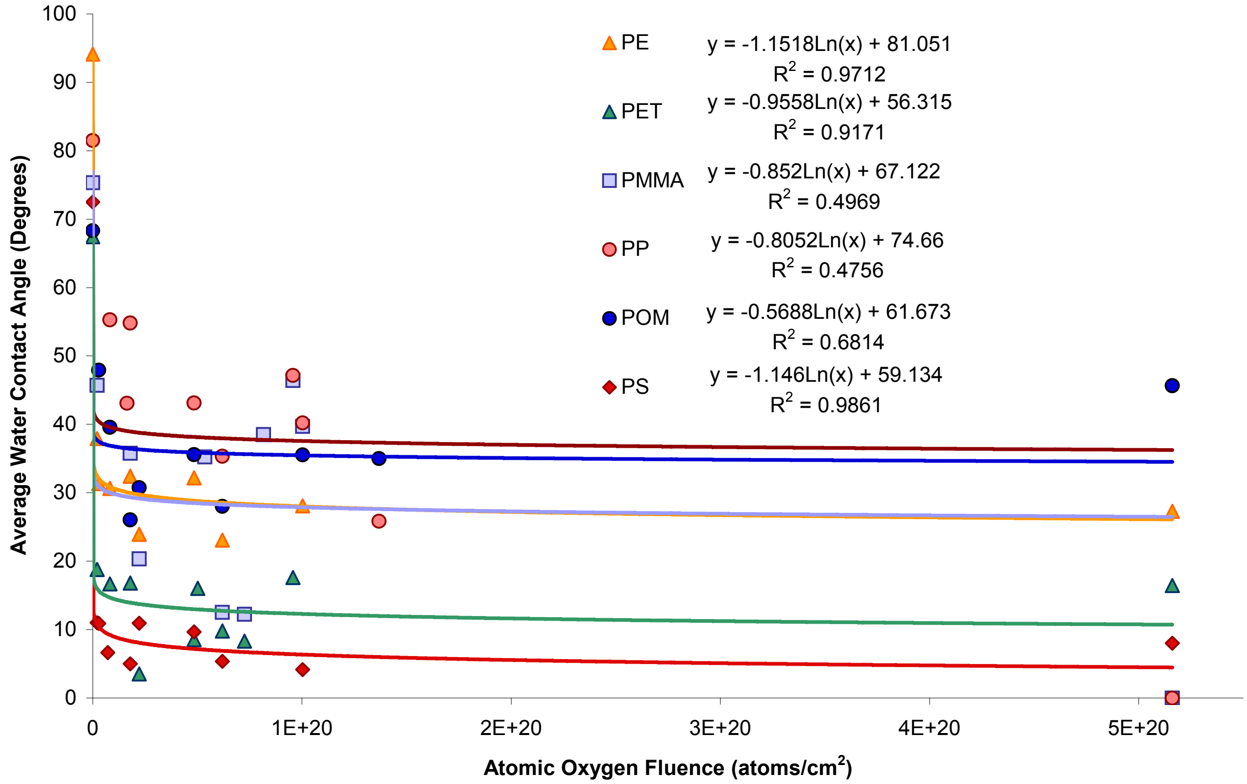

Fig. 10. Water contact angles versus atomic oxygen fluence for non-fluorinated polymers

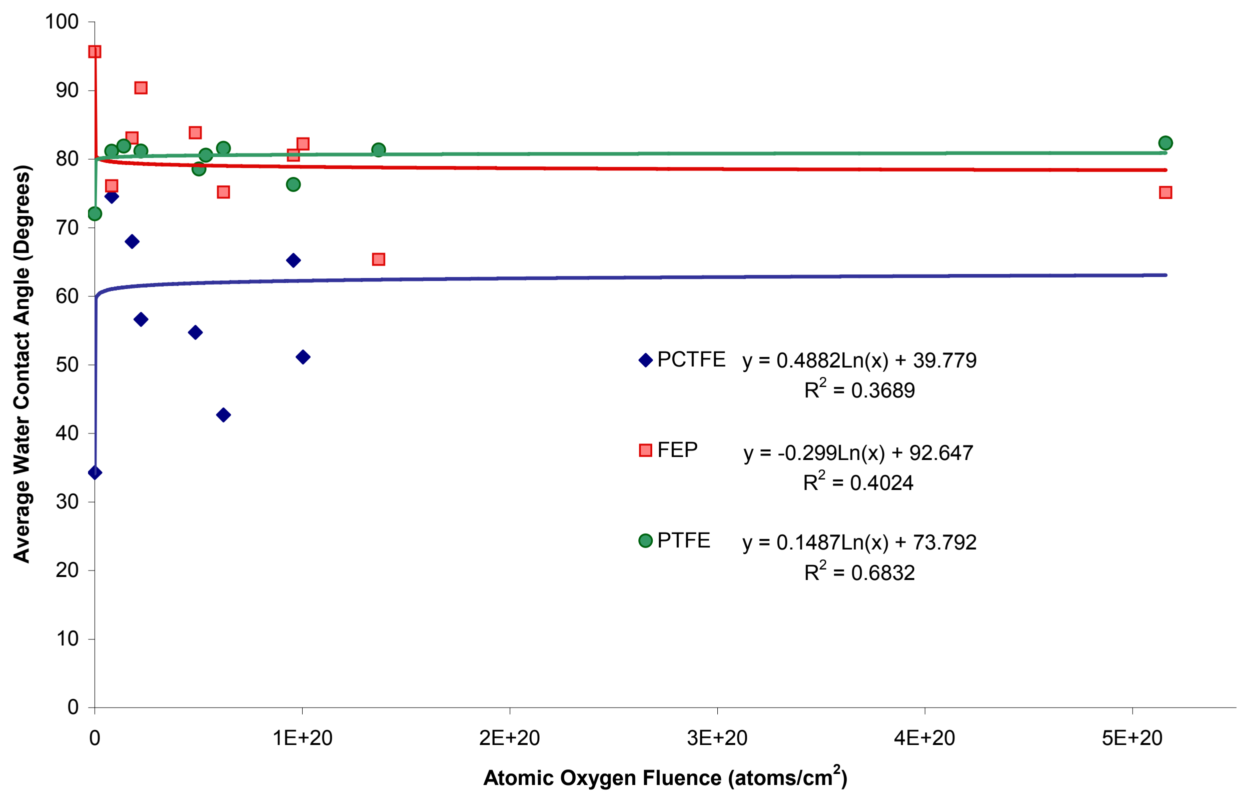

Fig. 11. Water contact angles versus atomic oxygen fluence for fluorinated polymers

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13. SUPPLEMENTARY NOTES

14. ABSTRACT
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