UV-resistant amorphous fluorinated coating for anodized titanium surfaces

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INRODUCTION

Thanks to the photocatalytic activity of anodized titanium, TiO_2 is widely studied in a variety of technologies including photocatalysis[1], environmental cleanup [2], solar energy convertion[3], electrochromic devices[4], and antimicrobial coating[5]. One of the major drawbacks of applications for anodized titanium with photochemical activity is the degradation of the protective hydrogenated polymeric coatings under the UV exposure on the titanium oxide surface [6].

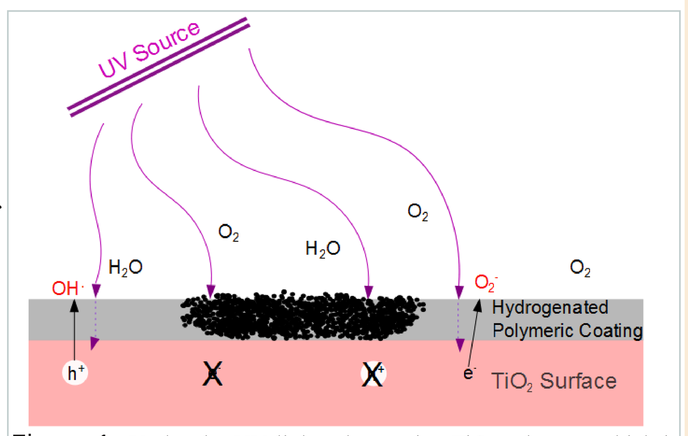


Figure 1. Under the UV light, photoactive TiO_2 substrate which is coated with the hydrogenated protective layer undergoing the photocatalytic reaction in presence of water and oxygen. With the increase of the UV irradiation time, degradation of the UV unstable hydrogenated coatings can form substances which will block the UV light and deactivate the photoproduced electrons and holes on TiO_2 surface.

Perfluoropolymers are characterized by very high thermal and chemical stability, low surface energies and low wettability [7]. These properties are useful to improve both the dirt resistance and the washability of the anodized surface. Moreover, amorphous perfluoropolymers are highly transparent materials in a very wide electromagnetic wavelength region and are characterized by a very low refractive index [8].

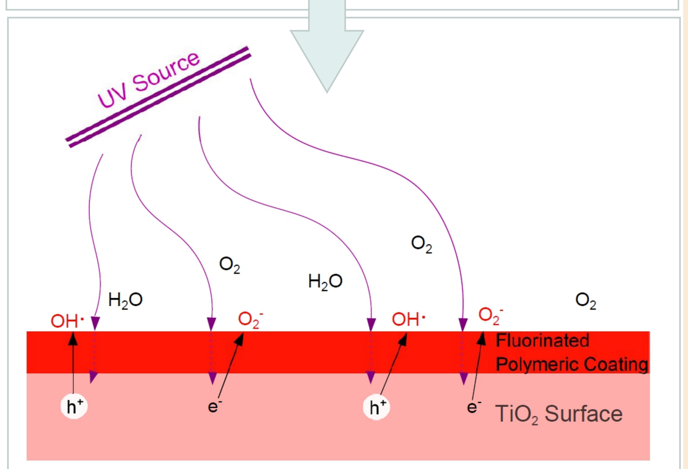
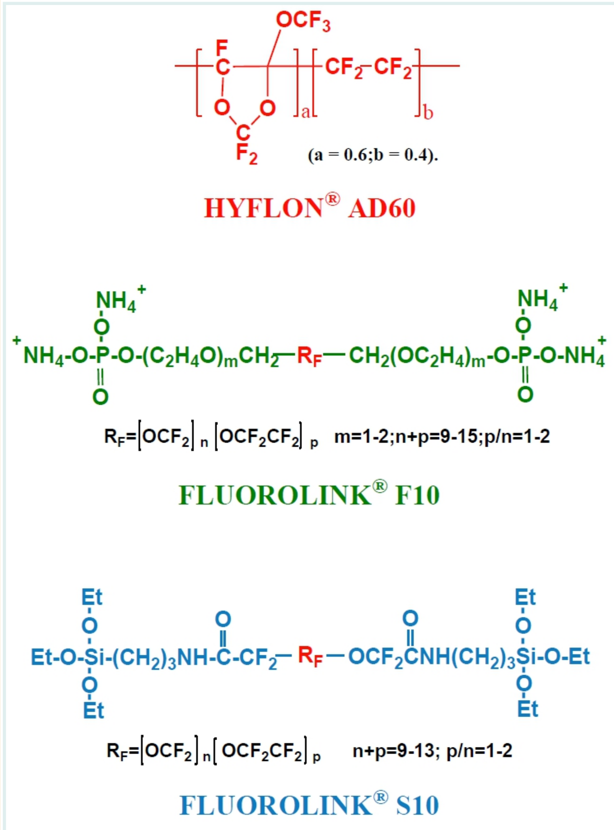


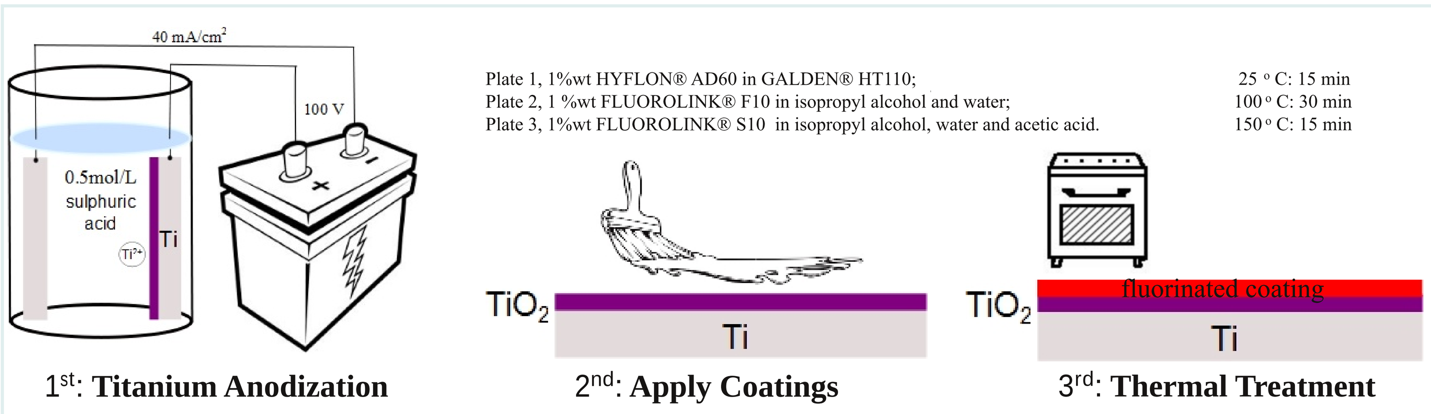
Figure 2. Fluorinated polymer can be applied as UV stable protective coating for photocatalytic TiO_2 surface.

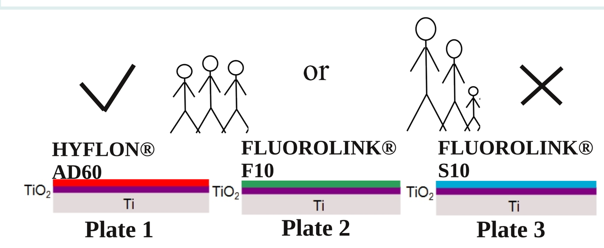
Chemically inert and highly transparent amorphous perfluoropolymers with low refractive index are successfully used to produce polymeric waveguides [9], and UV transparent thin films [10]; therefore highly fluorinated polymers can be the perfect candidate for the creation of transparent and chemically stable coatings for optical application on anodized titanium.

METHODS

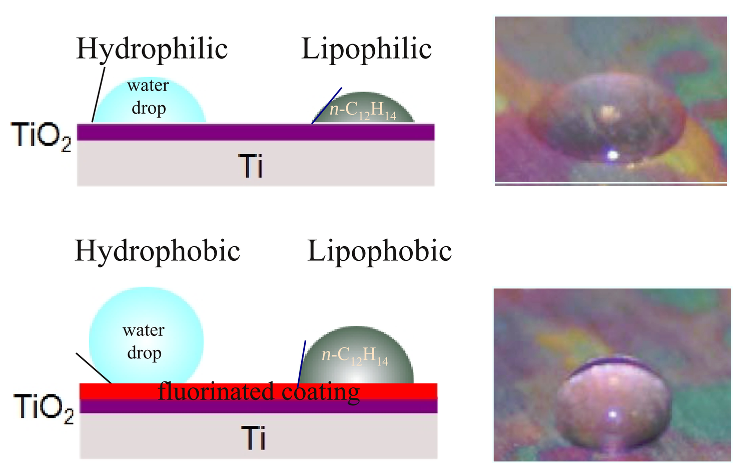


Amorphous fluorinated Polymeroc Coatings





Ellipsometry & Ponderal evaluation to check the thickness of 3 coated films.

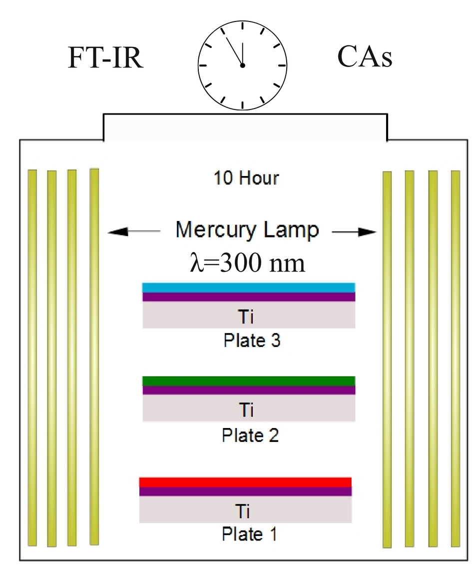


Contact Angle (CA) Measurement

Offering a direct indication that the hydrophobic fluorinated polymers wether or not coated on the oxide substrates.

Mechanical Resistance Test

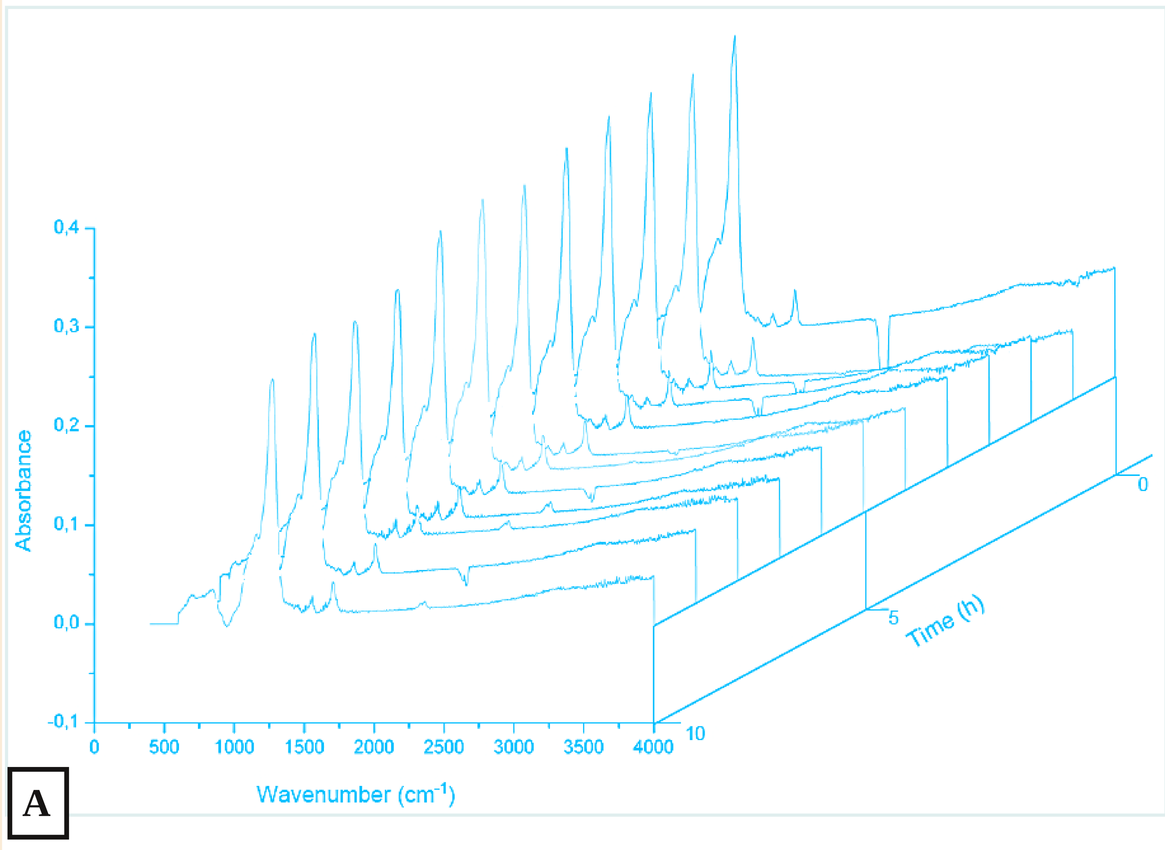
The plates were rubbed by blotting paper under a pressure of 63 kPa. The decrease in CAs as a function of the number of rubbing cycles was measured.



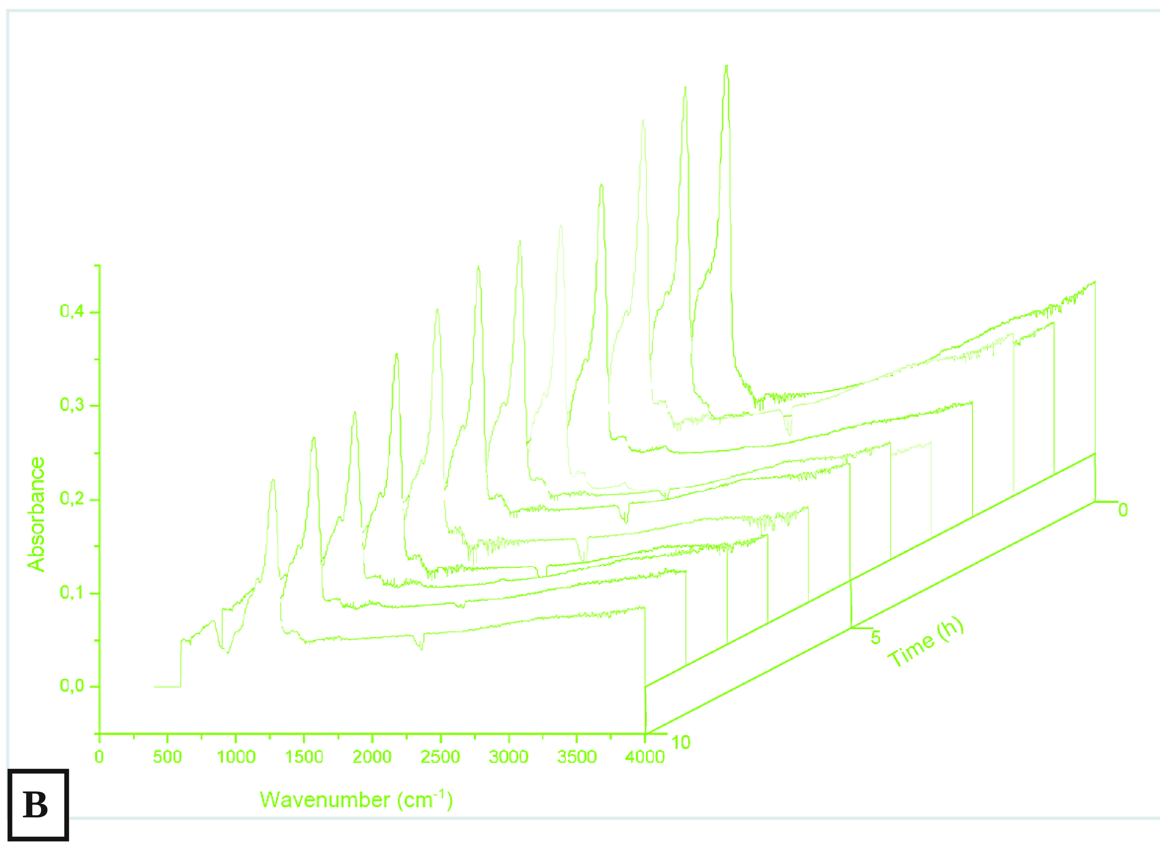
Exposure Under UV Irradiation

The 3 plates were placed inside the Rayonet photoreactor which equipped with 8 mercury lamps for 10 hours.

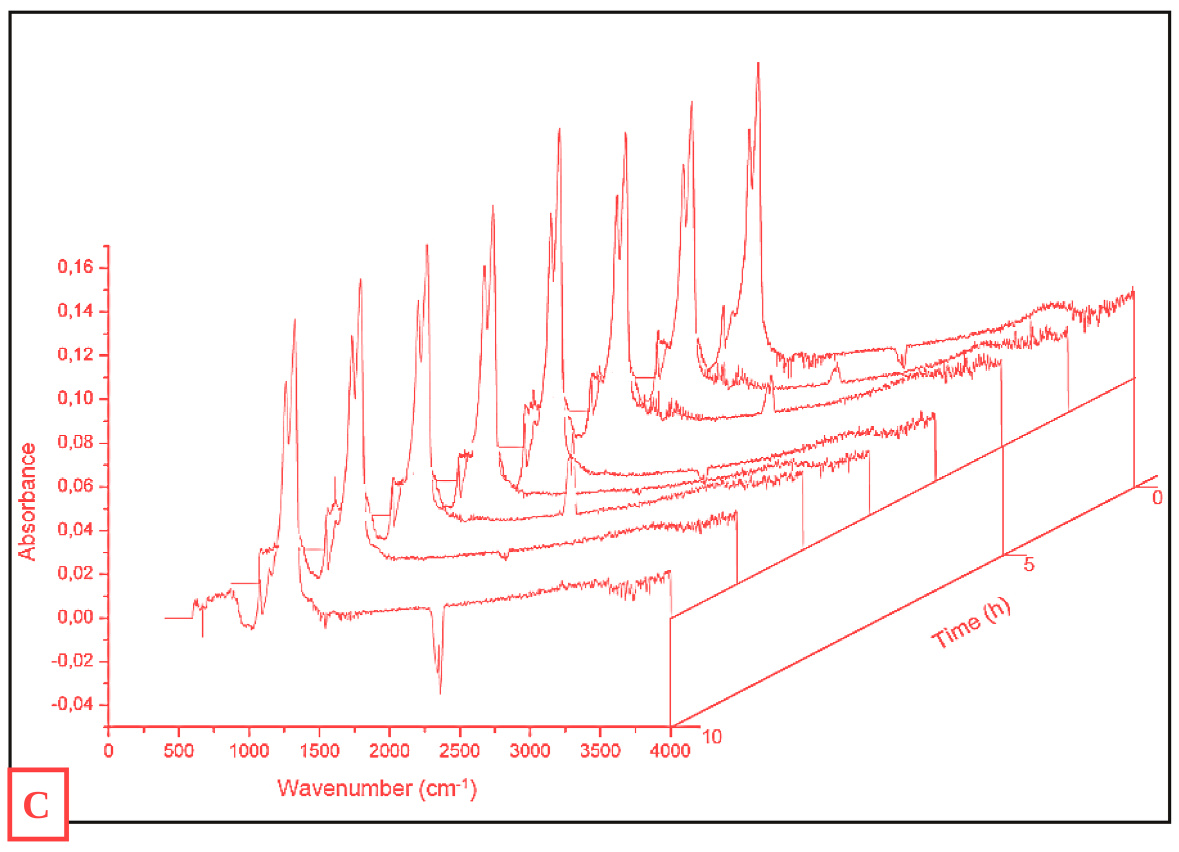
RESULTS



FT-IR spectra of FLUOROLINK® S10 coated anodized titanium during UV exposure.



FT-IR spectra of FLUOROLINK® F10 coated anodized titanium during UV exposure.



FT-IR spectra of Hyflon® AD60 coated anodized titanium during UV exposure.

By monitoring the variation of the absorption bands in FT-IR spectra, obtained from the samples coated with FLUOROLINK® F10 and FLUOROLINK® S10, we noticed that the IR bands in the spectra region from 1250 cm^{-1} to 1000 cm^{-1} significantly decreased with increasing UV exposure time; these bands are in the typical spectra region corresponding with the stretching of C–F, C–C and C–O–C bonds from the polymer backbone.

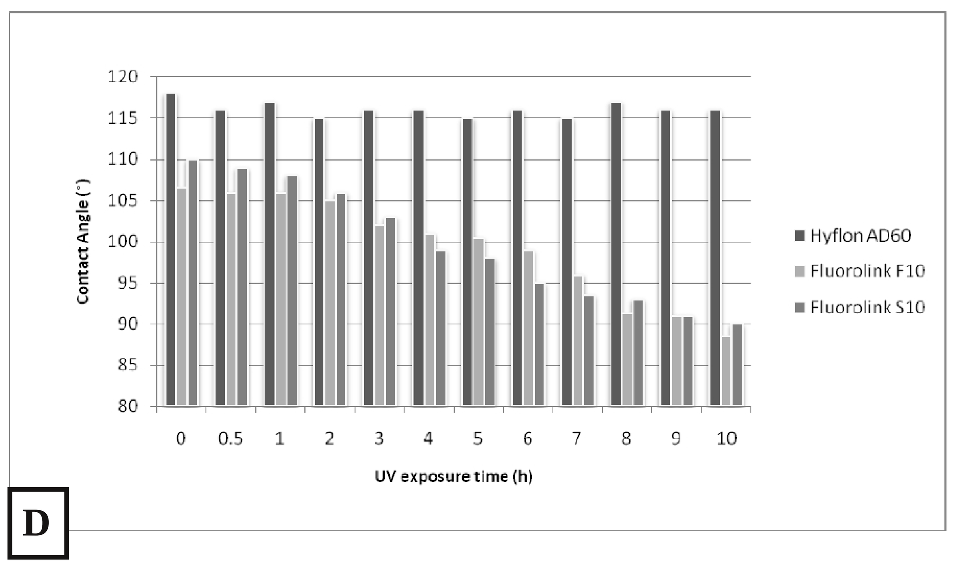
In contrast, the corresponding IR bands in the same spectra region of sample coated by HYFLON® AD60 which was exposed under the same frequency UV irradiation showed no significant change with the time increasing, this confirmed the photocatalytic stability of HYFLON® AD60 fluoropolymer in presence of activated TiO_2 under the UV irradiation.

The photo-induced decomposition of FLUOROLINK® F10 and FLUOROLINK® S10 coatings was supposed to undergo a stepwise oxidation, through the formation of fluorinated alcohols, aldehydes and acids. A rapid oxidation occurred, rather than a stepwise oxidation, leading to the formation of perfluorinated acids subsequently decomposed into carbon dioxide and volatile low-molecular hydrofluorocarbon.

RESULTS

Table 1: Water and *n*-dodecane contact angle and apparent surface energy of uncoated and fluoropolymer-coated samples

Sample	Contact Angle		Apparent Surface Energy (mN/m)
	Water	*n*-$C_{12}H_{14}$	
Plate 0	49.12°	5°	46.16
Plate 1	119.53± 0.22°	64.84 ± 3.32°	24.77
Plate 2	90.53± 3.69°	66.67 ± 4.56°	25.89
Plate 3	121.78± 1.32°	65.33 ± 4.27°	24.80



Water CA values measured on anodized titanium samples coated with FLUOROLINK® F10, FLUOROLINK® S10 and HYFLON® AD60 at different exposure time to UV light.

RESULTS

Table 2: Ellipsometry data and coating thicknesses

Sample	Fluropolymer-coating	Ψ_{sp}	Δ_{sp}	Ψ_{calc}	Δ_{calc}	Thickness (nm)
Plate 1	HYFLON® AD60	29.46	80.32	30.07	82.35	200
Plate 2	FLUOROLINK® F10	33.38	74.64	32.35	74.22	200
Plate 3	FLUOROLINK® S10	23.35	96.00	23.51	95.81	170

Table 3: Ponderal evaluation of the coating thicknesses and comparison with ellipsometry data.

Sample	Coating			Thickness	
	m (mg)	d (mg/mm^3)	V (mm^3)	Ponderal (nm)	Ellipsometry (nm)
Plate 1	0.8	1.68	0.476	176.4	200
Plate 2	0.9	1.73	0.52	192.7	200
Plate 3	0.7	1.51	0.464	171.7	170

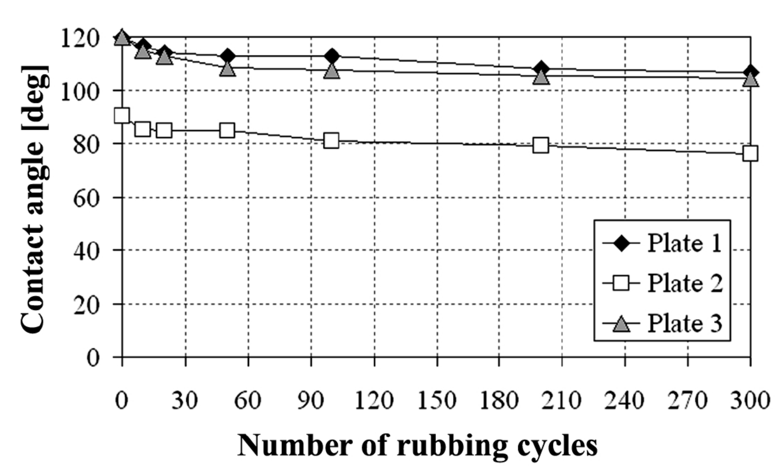


Plate 1: HYFLON® AD60, Plate 2: FLUOROLINK® F10, and Plate 3: FLUOROLINK® S10.

CONCLUSIONS

Among the above three fluorinated polymers, we observed that the high T_g amorphous transparent Hyflon® AD60 revealed a good adhesion on the anodized titanium substrate and in addition it conferred both hydrophobicity and oleophobicity to the substrate; moreover, it resulted in a good UV stability which has been evaluated by monitoring the decreasing of absorption intensity from FT-IR spectra and corroborated by the CAs measurements.

In addition, a straightforward methodology to decompose perflurinated carboxylic acids into carbon dioxide and hydrofluorocarbons in presence of photocatalytic TiO_2 has been hypothesized. Further studies in this direction are under progress.

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