

SUPPORTING INFORMATION

Hydrophobic carbonaceous materials obtained by covalent bonding of perfluorocarbon and perfluoropolyether chains

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1. Physioadsorption of PFPE fluid on carbon black.

In a glass reactor 500 mg of carbon black and 5 ml of solution, obtained dissolving 80 mg of PFPE fluid (FOMBLIN® M03 by Solvay Solexis Inc.; average molecular weight around 4000 uma, linear structure with (CF₂CF₂O) and (CF₂O) as monomeric units in molar ratio around 1, no peroxidic units along the polymer chain) in 5 ml of inert fluorinated solvent (CF₃OCFCICF₂Cl) were introduced. The carbon black suspension was heated at 40 °C until the complete evaporation of the solvent. The solid residue was finally dried under vacuum (0,01 mmHg) at 40 °C for 24 hours. The effects of the physioadsorption of the not peroxidic PFPE fluid were evaluated by BET analysis and contact angle measurement. After these characterizations, the sample was washed three times with 50 ml of pure fluorinated solvent (CF₃OCFCICF₂Cl) and finally three times with 50 ml of deionized water. Thus the BET and contact angle characterizations were repeated and furthermore the elemental composition was determined by XPS analysis. For an additional comparison, a portion of sample **IVa** was washed continuously for 24 h with pure fluorinated solvent (CF₃OCFCICF₂Cl) by means of a Soxhlet extractor and then characterized as described before.

2. Experimental data corresponding to carbon black comparative sample.

Table 2.1. Surface composition (at%) by XPS analysis referred to the carbon black comparative sample.

Samples	Amount (at%)					
	F	O	C	S	Cl	Si
VULCAN [®] XC72R	-	1.2	98.4	0.4	-	-
VULCAN [®] XC72R with physioadsorbed PFPE fluid (after washings)	-	0.8	98.6	0.2	-	0.4
IV-0.14	8.3	3.5	88.0	0.2	-	-
IV-0.14 (after Soxhlet washings)	8.2	5.0	86.5	0.3	-	-

Table 2.2. BET surface area and contact angle with water measurements referred to the carbon black comparative sample.

Samples	Contact Angle	Surface Area (m ² /g)
VULCAN [®] XC72R	n.s. ^a	262
VULCAN [®] XC72R with physioadsorbed PFPE fluid (before washings)	136°	58
VULCAN [®] XC72R with physioadsorbed PFPE fluid (after washings)	n.s. ^a	149
IVa	140°	110
IVa (after Soxhlet washings)	138°	103

^a the droplet is not stable and is adsorbed in few seconds into the pellet.

3. Physical deposition of PFPE fluid on DLC.

The a-C:H DLC thin film was dip coated with a proper volume of solution, obtained dissolving 100 mg of PFPE fluid (FOMBLIN[®] M30 by Solvay Solexis Inc.; average molecular weight around 14000 uma, linear structure with (CF₂CF₂O) and (CF₂O) as monomeric units in molar ratio around 1, no peroxidic units along the polymer chain) in 6.2 ml of inert fluorinated solvent (CF₃OCFCICF₂Cl). The solvent was evaporated at room temperature and then the sample was completely dried under vacuum (10⁻³ mmHg) at 60 °C for 2 hours. The effects of the deposition of the not peroxidic PFPE fluid were evaluated by contact angle measurement. Then the sample was washed three times with 50 ml of pure fluorinated solvent (CF₃OCFCICF₂Cl) and finally three times with 50 ml of deionized water. Thus the contact angle characterizations were repeated and in addition the elemental composition was determined again by XPS analysis.

4. Experimental data corresponding to DLC comparative sample.

Table 4.1. Experimental conditions of the physical deposition of PFPE coatings on DLC thin films – comparative example.

Coating	PFPE	DLC surface (mm ²)	PFPE Weight (mg)	Solution Volume ^a (ml)	Temp. (°C)	Reaction Time (h)	PFPE Surface Density (g m ⁻²)
PFPE	Fomblin [®] M30	254.5	2.4	0.15 ^b	60	2	1

^a the solvent used for these solutions is CF₃OCFCICF₂Cl.

^b volume of a 1% solution.

Table 4.2. Contact angle measurements and surface composition (at%) by XPS analysis referred to the comparative example.

Coating	Contact Angle with water	Amount (at%)					
		F	O	C	Cl	N	Impurities
DLC	76°	-	9.9	87.3	-	1.5	Na 0.7; Si 0.6
DLC with physically deposited PFPE fluid	99°				n.d. ^a		
DLC with physically deposited PFPE fluid (after washings)	76°	-	9.8	87.5	-	1.6	Na 0.6; Si 0.5

^a not determinable because of the vapour pressure of the deposited PFPE fluid under the high vacuum conditions of XPS analysis.

5. Experimental conditions and yields for the synthesis of PFDA peroxides.

Table 5.1. Experimental conditions and yields for the preparation of PFDA peroxides.

Peroxide	Acyl-X (mmol)	NaOH (mmol)	H ₂ O ₂ (mmol)	Temp. (°C)	Reaction time (min)	Yield (%)
PFDP (1)	50	65	100	2	2	29
PFDnB (2)	26	39	60	2	2	46
PFDiB (3)	47	49	94	2	10	70

6. Expanded views of C_{1s} high resolution spectra of PFE and PFiP coatings on DLC.

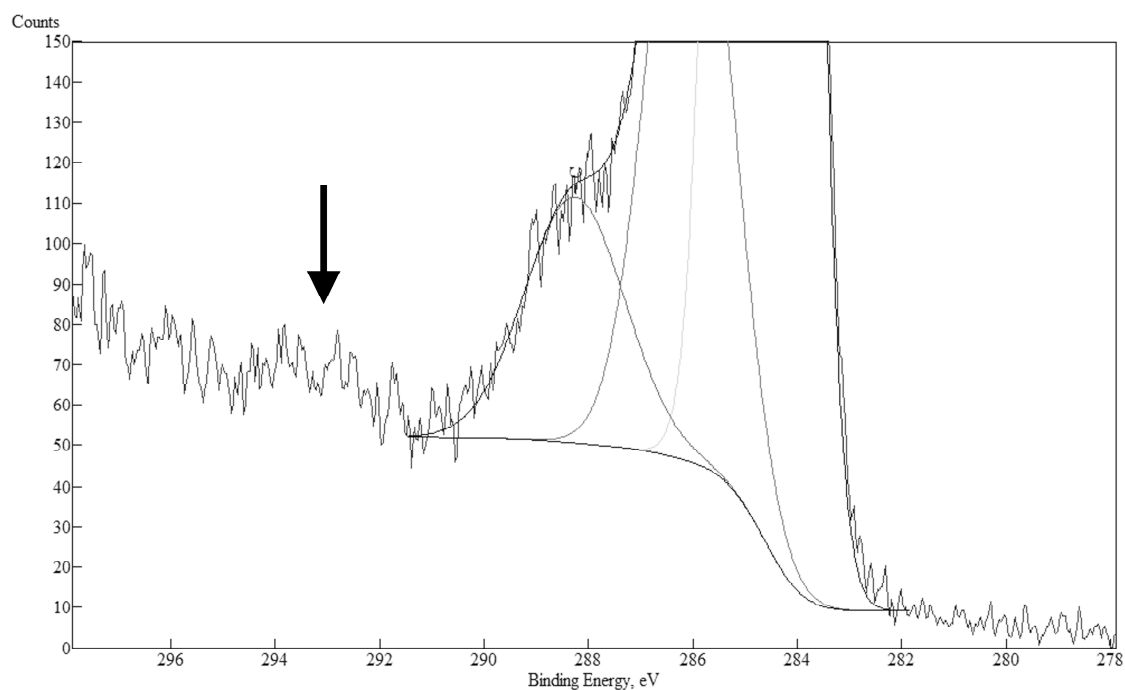


Fig. 6.1. Expansion of the C_{1s} region of XPS spectrum of a PFE coating (V) on DLC film: the signal of C-F bonds (arrow indicated) slightly rises from the background noise.

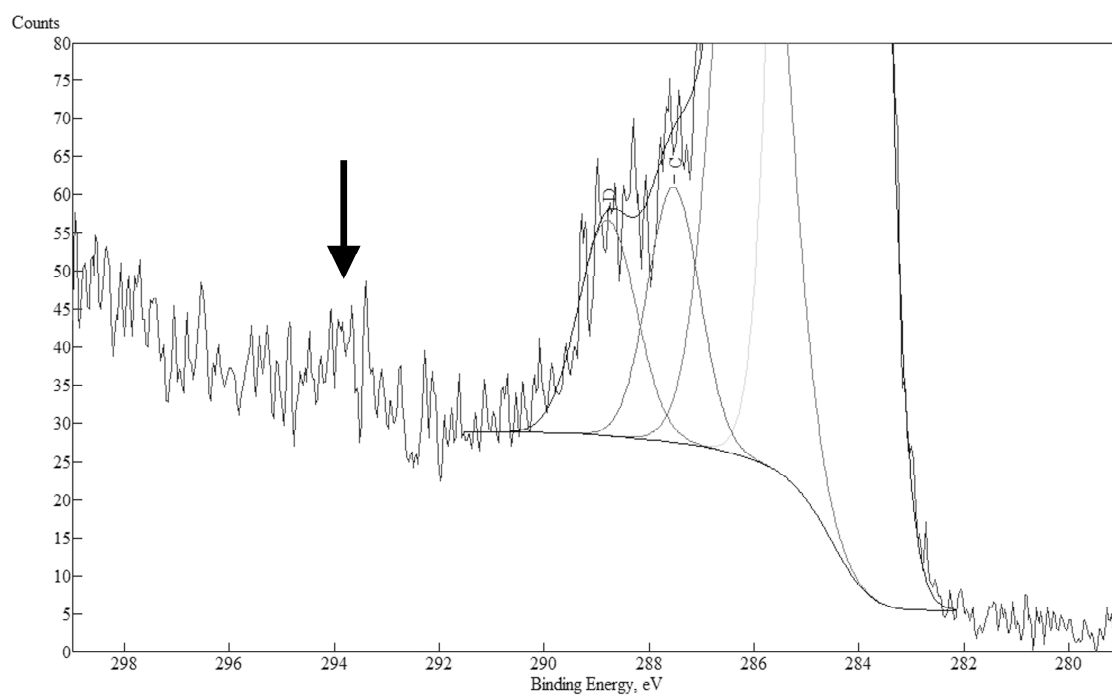


Fig. 6.2. Expansion of the C_{1s} region of XPS spectrum of a PF₆B coating (**VII**) on DLC film: the signal of C–F bonds (arrow indicated) slightly rises from the background noise.