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Highly Hydrophobic Carbon Black Obtained by Covalent Linkage of Perfluorocarbon and Perfluoropolyether Chains on the Carbon Surface

Maurizio Sansotera,*,† Claudia L. Bianchi,‡ Giorgio Lecardi,† Giuseppe Marchionni,§
Pierangelo Metrangolo,† Giuseppe Resnati,† and Walter Navarrini†

†*Dipartimento di Chimica, Materiali ed Ingegneria Chimica "Giulio Natta", Politecnico di Milano, via Mancinelli 7, 20131 Milano, Italy,* ‡*Dipartimento di Chimica Fisica ed Elettrochimica, Università degli Studi di Milano, via Golgi 19, 20133 Milano, Italy, and* §*Solvay Solexis, R&D center, viale Lonbardia 20, 20021 Bollate (MI), Italy*

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Perfluorocarbon chains, that is, perfluoroethyl, CF_3CF_2-, perfluoro-*n*-propyl, $CF_3CF_2CF_2-$, perfluoro-*iso*-propyl, $(CF_3)_2CF-$, and perfluoropolyether (PFPE) residues, were covalently bonded on the surface of a carbon black using perfluorodiacyl and PFPE peroxides. Thermal decomposition of the fluorinated peroxides allows the covalent linkage of fluorinated radicals to the polycyclic aromatic structure of the carbon black. Contact angle measurements in agreement with XPS data revealed a gradual enhancement of the water repellence with increasing fluorine content on the surface. When perfluoroalkyl chains were bonded to the carbon black the morphology and the surface areas of the modified carbonaceous materials were mostly retained as shown by BET and SEM analyses.

Introduction

Carbonaceous materials are commonly used as additives and fillers and exhibit interesting structural, mechanical, electrical, catalytic, and electromechanical properties. These materials have found application in a wide variety of fields, such as in the reinforcement of plastics to form advanced, lightweight composite materials, as filler in rubbers, and in the development of electrochemical devices.[1]

Nevertheless, their application has been limited in some cases by the difficulty of dispersion and compatibility with different media, especially in fluorinated phases.[2] The instability of the dispersion is due to the low surface fluorophilicity of carbonaceous materials.[3,4]

Carbon black treatments with fluorinated peroxides are particularly suitable to decrease the carbonaceous material surface energy, therefore enhancing the hydrorepellence and the affinity to fluorinated substrates.[5] For these reasons, a great attention has been recently devoted to surface modification of carbonaceous materials by means of functionalization through the introduction of fluorinated groups on their surface[6,7] and the use of surface agent modifiers.[8,9]

It is known that graphitic carbon black is constituted by polycyclic aromatic structured aggregates with several functional groups bonded at the edge of the polycyclic structure.[10] Consequently the introduction of perfluorinated groups into such carbonaceous substrates with carbon−carbon bond formation can be approached as homologous reaction of the aromatic perfluoroalkylation.[11−13] Perfluorodiacyl peroxides are typical perfluoroalkylating agents[14] and Zhao et al. proposed in 1983 a single electron-transfer mechanism for this reaction with electron rich aromatic substrates.[15] More recently evidence of a free chain radical mechanism for this reaction has been observed also on electron poor substrates.[12] Similarly to perfluorodiacyl peroxides, PFPE peroxides thermally decompose through the homolytic cleavage of the peroxidic units present along their polymeric backbone, generating reactive carbon-centered PFPE radicals obtained by rapid β-scission of the early formed PFPE alkoxy radicals.[16]

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*To whom correspondence should be addressed. Tel: +39-02-2399-3035. Fax: +39-02-2399-3180. E-mail: maurizio.sansotera@polimi.it.

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In this work the covalent linkage of fluorinated radicals to the polycyclic aromatic structure of a graphitic carbon black by chemical treatment with fluorinated peroxides was studied, and the structural and chemical features of the products were analyzed. Perfluorodipropionyl **1**, perfluorodi-*n*-butyryl **2**, and perfluorodi-*iso*-butyryl **3** peroxides were used for the perfluoroalkylation of carbon black. A linear high molecular weight PFPE peroxide **4** (see Materials for details) was thermally decomposed in the presence of carbon black to covalently link PFPE chains on its surface. The perfluorinated moieties were directly bonded without any hydrogenated spacer, which usually decreases both thermal and chemical stabilities of the resulting fluorinated materials.[16−18]

The modified carbonaceous materials were investigated by X-ray photoelectron spectroscopy (XPS) analysis to study the influence of the chemical treatment with perfluorodiacyl and PFPE peroxides on the surface elemental composition of carbon blacks. Measurements of contact angles of carbon black molded pellets demonstrated the modifications of surface hydrophilicity for the treated carbonaceous materials. Scanning electron microscopy (SEM) and BET analysis were used to monitor the morphology changes and the surface area variations of the substrates.

Experimental Section

Safety Precaution. Perfluorodiacyl peroxides may decompose very quickly through auto induced decomposition; solutions having peroxide concentrations as high as 15% have been prepared and stored at the appropriate temperature for days.[19] Only diluted peroxidic solution were prepared for safety reasons. The PFPE peroxides with content of peroxidic oxygen (PO) up to about 4 wt % are stable at room conditions, while they become extremely unstable when the PO content exceeded values of about 6 wt %.[16] The PO content of the examined PFPE peroxide was 2.3 wt % and, therefore, in the safety range stated above.

Materials. The carbon used for this work was a highly conductive, commercially available graphitic carbon black with high surface area: the CABOT VULCAN XC72R.

The solutions of perfluorodiacyl peroxides **1**−**3** were prepared in good to medium yields from the perfluoroacyl halides with H_2O_2 in alkaline conditions, according to methods described in the literature.[19] The inert fluorinated solvent was $CF_3OCFClCF_2Cl$. The yields in perfluorodiacyl peroxide with respect to perfluoroacyl halides, $R_FC(O)$-X, the amounts of the reagents, and the operative conditions are reported in the Supporting Information.

The high molecular weight PFPE peroxide **4** was a FOMBLIN Z PFPE peroxide with linear structure where the monomeric units $(CF_2CF_2O)_m$ and $(CF_2O)_n$ and peroxidic units $(O)_v$ were randomly distributed along the polymer chain: $TO(CF_2CF_2O)_m(CF_2O)_n(O)_vT'$. The chemical characteristics of this peroxide are here resumed: average molecular weight around 39 000 uma, ratio of 1.15 between perfluoroethylene oxide, C_2, and perfluoromethylene oxide, C_1, units, peroxidic content of 2.3 wt %, equivalent molecular weight around 900 g/equiv, and CF_3, COF, and CF_2COF as terminals (T, T′). The PFPE peroxide **4** was industrially prepared by light-assisted oxidation of TFE, that is, oxidative photopolymerization.[16,20] PFPE peroxides are characterized by higher thermal decomposition temperatures as compared to perfluorodiacyl peroxides. In fact, they decompose generating radical species, with half-life of 30 min at temperatures in the range between 140 and 250 °C.[20]

Treatment of Carbon Black with Perfluorinated Peroxides. *a. Perfluorodiacyl Peroxides*. In a glass reactor the carbon black (250 mg) and the correct volume (from 3 to 50 mL) of solution containing the perfluorodiacyl peroxide were introduced. Low peroxide concentrations solutions (2−8 wt %) and multiple additions were adopted to minimize the homocoupling side-reaction. The exact volume of perfluorodiacyl peroxide solution was calculated to reach the ratios of millimoles of added peroxide to surface area of virgin carbon black ($[\text{Peroxide}]_{\text{SUP}}$) reported in Table 1. For this appraisal the surface area of the CABOT VULCAN XC72R carbon black evaluated by BET analysis was considered. The overall peroxide solution volume was divided in four fractions that were added at different reaction times. The reaction time between each addition was threefold the half-life time of peroxide decomposition, $t_{1/2}$, to ensure the complete peroxide decomposition. Modifying the temperature conditions, it was possible to choose appropriate $t_{1/2}$ so that the reaction time was on the order of a few hours. In particular, the temperatures for peroxides **1** and **3** were 25 and 55 °C, respectively, to obtain a $t_{1/2}$ of 8 h and consequently a reaction time of 24 h. The $t_{1/2}$ at 25 °C for peroxide **2** was 4 h, and the reaction time chosen was 12 h. After every addition, the reactor was brought at 0 °C in a water-ice bath and then bubbled for 5 min with nitrogen to ensure an oxygen-free environment. The reaction mixture was heated at the selected temperature and left for the corresponding reaction time. At the end of the treatment the solvent was evaporated, and the solid residue was washed with pure fluorinated solvent, with an aqueous solution of $NaHCO_3$ (2%) and thereafter with deionized water. The sample was finally dried under vacuum (10^{-3} mmHg) at 180 °C for 24 h. The amount of the recovered carbon black was usually above 90−95 wt % of the starting carbon black. This was due to physical powder lost. Following this general procedure, three series of carbonaceous samples were prepared: series **I**, **II**, and **III**, obtained with peroxide **1**, **2**, and **3**, respectively.

b. Perfluoropolyether Peroxides. A different procedure for the chemical treatment with peroxide **4** was applied. In a glass reactor, 500 mg of carbon black and a solution, obtained dissolving 0.16 g of PFPE peroxide **4** in 10 mL of inert fluorinated solvent, were introduced. At first the so-prepared reaction mixture was heated at 40 °C until the complete evaporation of the solvent. Thereafter the peroxide **4** was thermally decomposed from 150 to 195 °C, by increasing the temperature stepwise at the rate of 15 °C/h, and then heated at 200 °C for 4 h. At the end of the thermal treatment, the solid residue was washed with pure fluorinated solvent and finally with deionized water. The sample was finally dried under vacuum (0.01 mmHg) at 200 °C for 6 h. The acyl fluoride end-groups generated during the thermal decomposition of the PFPE peroxide (Scheme 2B) were hydrolyzed to carboxylic acid during the washings with water and then decarboxylated during the final heating under vacuum. In the case of peroxide **4**, the ratio of milliequivalents of

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Table 1. Experimental Conditions of the Chemical Treatment of Carbon Black with Perfluorodiacyl and PFPE Peroxides

series	sample	peroxide	$[\text{peroxide}]_{\text{SUP}}$[a] (mmol/m^2)	m_C[b] (g)	m_P[c] (g)	V[d] (mL)	T[e] (°C)	t[f] (h)
I	**I-1.6**	**1**	0.016	0.25	0.340	7.6[g]	25	48
	I-3.2	**1**	0.032	0.25	0.679	15.3[g]	25	48
	I-8.0	**1**	0.080	0.25	1.678	38.1[g]	25	48
II	**II-1.6**	**2**	0.016	0.25	0.444	3.3[h]	25	24
	II-3.2	**2**	0.032	0.25	0.888	6.6[h]	25	24
	III-1.6	**3**	0.016	0.25	0.444	10.0[i]	55	48
III	**III-3.2**	**3**	0.032	0.25	0.888	20.1[i]	55	48
	III-8.0	**3**	0.080	0.25	2.219	50.2[i]	55	48
IV	**IV-0.14**	**4**	0.0014	0.50	0.16	10.0[j]	200	24

[a] Ratio of millimoles of added peroxide to square meter of virgin carbon black surface area; in the case of PFPE peroxide **4** it is expressed as milliequivalents of peroxidic units to square meter of virgin carbon black surface area. [b] Carbon black weight. [c] Peroxide weight. [d] Volume of the peroxidic solution (the solvent used for these solutions is $CF_3OCFClCF_2Cl$). [e] Reaction temperature. [f] Reaction time. [g] Volume of 2.78 wt % solution of **1**. [h] Volume of 8.4 wt % solution of **2**. [i] Volume of 2.49 wt % solution of **3**. [j] Volume of solvent, i.e., $CF_3OCFClCF_2Cl$, in which pure PFPE peroxide **4** was dissolved.

peroxidic units (i.e., $(O)_\nu$) to surface area of virgin carbon black corresponded to the value of $[\text{Peroxide}]_{\text{SUP}}$ reported in Table 1. The experimental conditions of the chemical treatments with both perfluorodiacyl and PFPE peroxides are reported in Table 1. A comparative sample was also prepared by adsorption of a PFPE fluid (with no peroxidic units along the polymer chain) onto the carbon black, as described in the Supporting Information.

Characterizations. X-ray photoelectron spectroscopy spectra were obtained using an M-probe apparatus (Surface Science Instruments). The source was monochromatic Al Kα radiation (1486.6 eV). A spot size of 200 μm × 750 μm and pass energy of 25 eV were used. 1s level hydrocarbon-contaminant carbon was taken as the internal reference at 284.6 eV. For each sample, survey analyses in the whole range of X-ray spectra and high resolution analyses in the typical zone of C-bonds and F-bonds have been performed. Fittings were performed using pure Gaussian peaks, Shirley's baseline, and without any constraints.

The contact angle instrument was Data Physics OCA 150, and the software was SCA20 version 2.3.9. build 46. Contact angle measurements have been done to analyze wetting and adhesion properties. Pellets were prepared with carbon samples, and water droplets were deposited on their surface to analyze the surface differences. Each pellet was obtained by press molding at room temperature a small amount (5−20 mg) of modified carbonaceous material under a load of 7000 kg/cm^2 for a few minutes (3−5 min). The reference pellet made of untreated native carbon was prepared using an amount of carbon previously washed with perfluorinated solvent at room temperature and dried under vacuum. This choice of reference allowed us to evaluate the effect due to perfluoroalkylation rather than wetting effects of solvent.

The specific surface areas of the samples were measured by N_2 adsorption utilizing the Brunauer−Emmett−Teller (BET) method. Prior to surface area determination, the samples were outgassed under vacuum (0.1 mmHg) at 80 °C overnight. The instrument used for BET analyses was a Costech Instruments Sorptometer Kelvin 1042, managed by the software Kelvin 1042 v.3.05.

The SEM observation of the carbon black samples was made by using a ZEISS EVO50 EP scanning electron microscope. The samples were analyzed without applying surface etching or conductive layer coating techniques. The SEM parameters were as follows: working distance of 7.0 mm, beam current of 20 pA, acceleration voltage of 17.0−17.5 kV, and magnification of 100 000× with respect to a 1024·768 pixel image.

Table 2. Surface Composition (atom %) by XPS Analysis of Carbon Black Surface before and after Treatments with Perfluorodiacyl and PFPE Peroxides

	amount (atom %)					
sample	F	O	C	S	Cl	N
VULCAN XC72R		1.2	98.4	0.4		
I-1.6	4.5	4.2	91.2	0.2		
I-3.2	8.0	4.7	87.1	0.3		
I-8.0	7.9	4.1	87.7	0.3		
II-1.6	6.0	3.2	90.7	0.2		
II-3.2	6.1	5.0	88.6	0.2		
III-1.6	4.3	6.0	88.7	0.2		0.8
III-3.2	8.0	3.5	85.0	0.2	0.3	
III-8.0	8.6	4.6	86.0	0.3	0.2	
IV-0.14	8.3	3.5	88.0	0.2		

Results and Discussion

The covalent linkage of perfluoroalkyl and perfluoropolyether residuals for the surface modification of carbon black consists of a straightforward thermal decomposition of peroxides **1**−**4** in the presence of the carbonaceous material. The effects of the chemical treatments and the properties of the carbon black surfaces were studied by means of XPS, BET, SEM analyses, and contact angle measurements. XPS survey analyses measured the elemental composition of the modified carbonaceous surfaces (Table 2).

The thermolysis of perfluorodiacyl and perfluoropolyether peroxides generates carbon centered perfluorinated free radicals,[19,20] which attack the aromatic moieties acting as radical scavengers on the carbon black surface.[10,12] Competitively, these radicals can combine forming perfluoroalkanes[21] or nonperoxidic PFPE;[16] we detected a reliable presence of these compounds in the reaction mixture at the end of the reaction. The presence of the perfluorinated coupling products is an experimental evidence of the presence of free radicals in the reaction environment; since is known that perfluorinated radicals react with aromatic compounds,[22] the presence of perfluorinated coupling products is an indirect evidence that the reaction follows a free radical mechanism. The main side-products of the chemical treatment with

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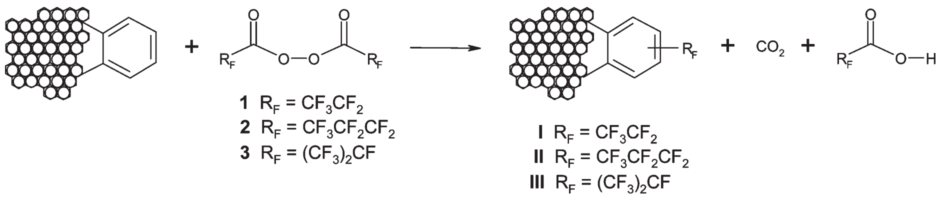
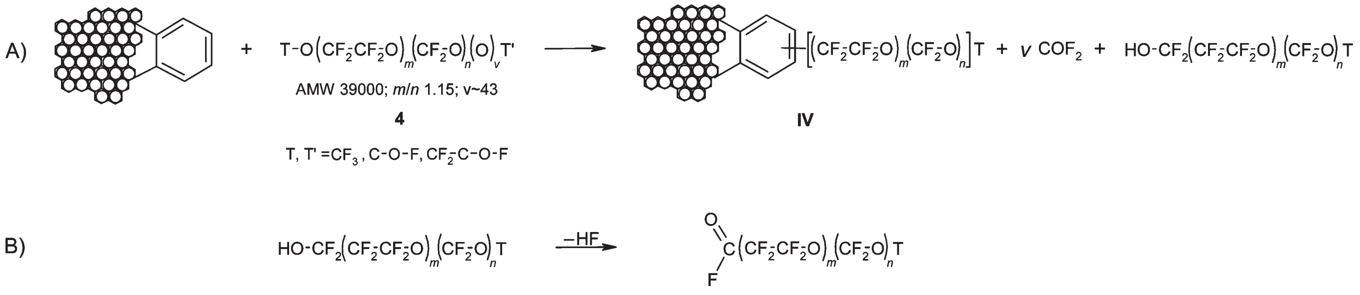
Scheme 1. Reaction of Carbon Black with Perfluorodiacyl Peroxide



Scheme 2. Reaction of Carbon Black with Linear PFPE Peroxide (A) and Decomposition of Primary Perfluorinated Alcohol (B)



perfluorodiacyl peroxides were carbon dioxide and the perfluorinated carboxylic acids (Scheme 1);[15] with PFPE peroxides, carbonyl fluoride and primary perfluorinated alcohols were formed (Scheme 2A).[16] These latter are thermodynamically unstable and instantaneously rearrange to acyl fluorides by eliminating HF (Scheme 2B).[23] An appropriate post treatment procedure was settled to remove these side products (see Treatment of Carbon Black with Perfluorinated Peroxides for details). The perfluorinated radicals react preferentially on the aromatic rings but, when benzylic positions are available, low to medium amounts of byproduct deriving from the hydrogen abstraction from the methyl group can be detected.[12]

In our previous works[20,24] we observed by EPR analyses that perfluoroethyl, perfluoro-*n*-propyl, perfluoro-*iso*-propyl, and PFPE radicals are respectively generated during the decomposition of peroxides **1**−**4**. Thus depending on the peroxide involved, the chemical treatment of carbonaceous materials allowed the introduction of the corresponding perfluorinated chains: respectively perfluoroethyl, CF_3CF_2-, perfluoro-*n*-propyl, $CF_3CF_2CF_2-$, perfluoro-*iso*-propyl, $(CF_3)_2CF-$, and PFPE residual. An experimental evidence of the chemical bonding of fluorinated chains was also observed by the comparison of the carbon black treated with PFPE peroxide **4** with a sample of carbon black on which a PFPE fluid was adsorbed.

XPS data reported in Table 2 show that the amount of fluorine on the surface raised with the increase of the amount of added peroxide. The data analyzed indicated that there was a fluorine content threshold that was difficult to exceed. This behavior can be explained supposing that the perfluoroalkylation reaction was achieved uniquely on the active sites of the carbon black surface, and once they were all occupied with perfluorochains, the reaction did not proceed any further. The substantial absence of the XPS peak due to chlorine atoms was an experimental evidence for the complete removal of the solvent $CF_3OCFClCF_2Cl$ by means of washing and vacuum treatments. Thus the fluorine content was due to the reaction of perfluorinated peroxides on carbon black surface and it could not be attributed to the presence of adsorbed solvent. In sample **IV-0.14**, despite the few milliequivalents of added peroxide **4**, the resulting fluorine content was in the range of the more fluorinated samples **III-8.0** and **I-8.0**. This behavior can be explained by the high equivalent weight of **4** and by the macromolecular structure of the PFPE chains linked on the carbon black surface.

The oxygen content on the virgin carbon black surface (1.2 atom %) revealed the presence of several oxygenated functions, such as alcohols (286.3−287.0 eV), carbonyls (287.5−288.1 eV), and carboxyls (289.3−290.0 eV).[25] Hydroxylic moieties hydrolyze the perfluorodiacyl peroxides, generating perfluorinated esters. The finishing washings with water described in the experimental procedure were settled to remove these perfluorinated esters, because they are easily hydrolyzable.[21] After chemical treatments with perfluorinated peroxides, a general increase of oxygen content on the carbon black surface was observed. The oxygen content in sample **IV-0.14** was around 3.5 atom %, equating what was stoichiometrically expected on the basis of the fluorine content due to the linkage of PFPE chain. In the series **I**, **II**, and **III** the oxygen increased independently from the amount of reagents and from bonded fluorine, as shown in Table 2. In our opinion it could be ascribed to free radical side reactions, activated by traces of adsorbed water and atmospheric oxygen from the reaction environment, particularly from the fluorinated solvent.

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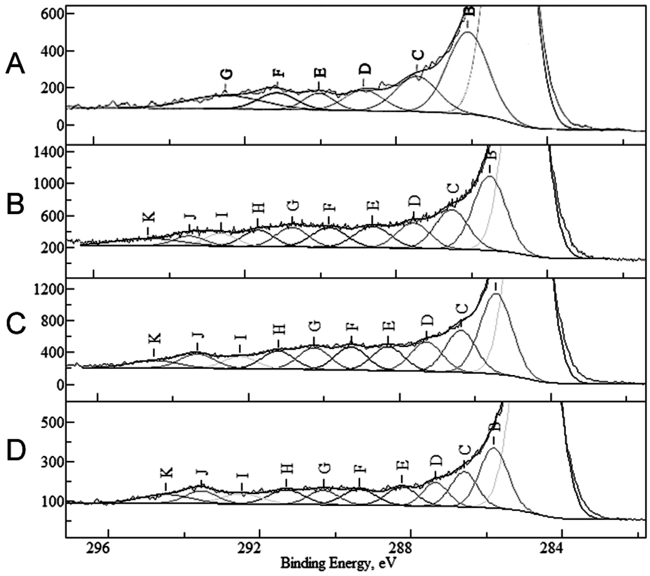

Figure 1. C 1s region of XPS spectra for different samples: (A) VULCAN XC72R; (B) **I-8.0**; (C) **III-8.0**; and (D) **IV-0.14**.

The high resolution XPS spectrum was recorded for pure carbon black and in the typical zone of C-bonds the tailed peak 1s of carbon covered a region from 284 to 292 eV (Figure 1A). After the chemical treatments, tailed peaks over a broader region between 284 to 294 eV were observed (Figure 1B,C,D). The zone between 292 and 294 eV can be associated with the presence of perfluoroalkyl (292.3−293.6 eV) and perfluoropolyether (293.4−294.8 eV) chains on the carbon black surface.[26,27] Samples with high percentage of fluorine showed an evident second peak approximately at 293.4 eV (Figure 1C,D, peak J), but it was not possible to discriminate the different CF$_x$ (x = 1, 2, 3) groups of the perfluorinated chains. As expected, the fitting of the C 1s carbon peaks into different contributions allowed us to observe that the percent area of the zone of the tail between 292 and 294 eV followed the same course of fluorine content on the carbon black surface (Table 3). In series **III**, the sample **III-1.6** with 4.3% fluorine content had a 293.1 eV peak with an area of 2.1%; accordingly, the sample **III-8.0** with a fluorine content approximately double the previous one had the 293.4 eV peak size that followed the same course with a 4.7% area. Also for series **I** it was possible to observe that the values of fluorine content and peak areas showed a consistent behavior. High resolution XPS analyses in the typical zone of F-bonds showed a sharp 1s peak at 690 ± 0.3 eV, associated to the presence of organic F−C bonds. Clearly the spectrum of pure carbon black did not have any peaks in this region.

Table 3. XPS Data Referenced to the C−F Peaks

sample	fluorine content (atom %, XPS data)	C−F peak (eV)	C−F peak area (%)[a]
I-1.6	4.5	293.2	2.0
I-8.0	7.9	293.5	2.9
III-1.6	4.3	293.1	2.1
III-8.0	8.6	293.4	4.7

[a] The peak area is calculated for each sample as percent ratio between the area of the C−F peak at 293.4 eV (±0.2 eV) and area of C−C peak at 284.6 eV (±0.1 eV).

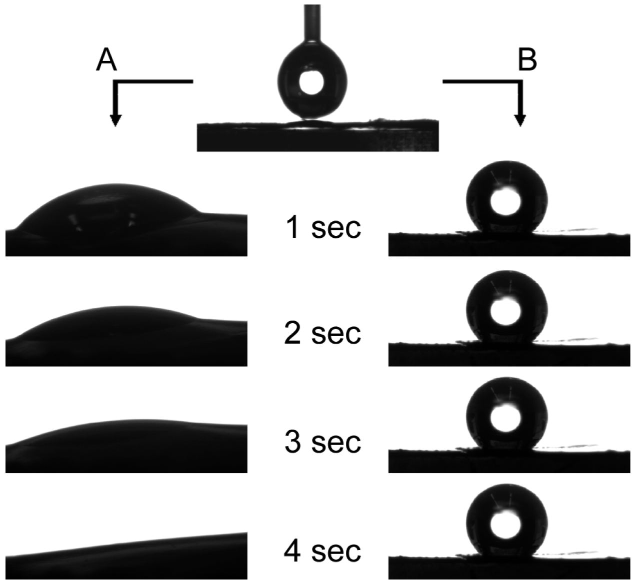

Figure 2. Spreading and permeating behavior of a water droplet on a pellet of native carbon black (A) and enduring stability of the droplets of water on the pellets made with treated carbon blacks (B).

Perfluorinated chains exhibit low surface energy and therefore the chemical treatment with perfluorinated peroxides was expected to transfer this property to the carbon black surface. Indeed this treatment modified the surface properties of the carbon black, particularly increasing its hydrophobicity. The contact angle measurement on a molded pellet of untreated carbon black revealed that the water droplets were adsorbed in a few seconds (2−4 s) by the carbonaceous matrix (Figure 2A). This phenomenon is due to the porous structure of the surface of pure carbon black. On the contrary droplets of water carefully placed on the molded pellets made with treated carbon blacks were enduringly stable (Figure 2B), and thus an accurate measurement of the contact angle with water for each sample was easily determined. One of the main results of the covalent bonding of perfluoroalkyl and PFPE chains on the carbon black surface was the modification of the hydrophilic surface properties (Figure 3). In series **I**, the hydrorepellence raised coherently with the amount of added peroxide (Figure 4A). Also in series **II**, the greater the amount of added peroxide, the higher the increase of hydrorepellence. However, a smaller amount of peroxide was enough to obtain a higher hydrophobic effect and particularly for the sample **II-3.6** the threshold of superhydrophobicity (i.e., 150°)[28] was exceeded (Figure 4-B). This behavior can be attributed to the long linear perfluoroalkyl chain of perfluoro-*n*-propyl radicals. In contrast, all the samples of series **III** showed contact angle values around 130°,

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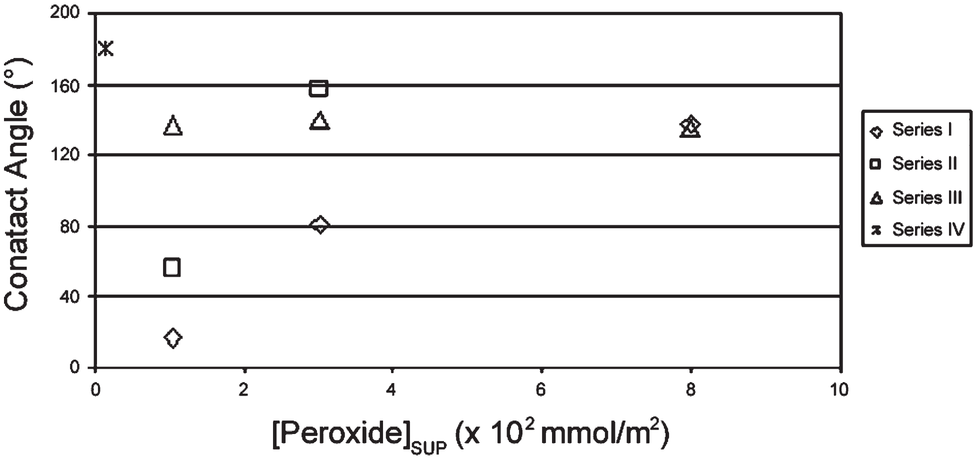

Figure 3. Course of the contact angle properties with increasing surface concentrations of perfluorodiacyl and PFPE peroxides.

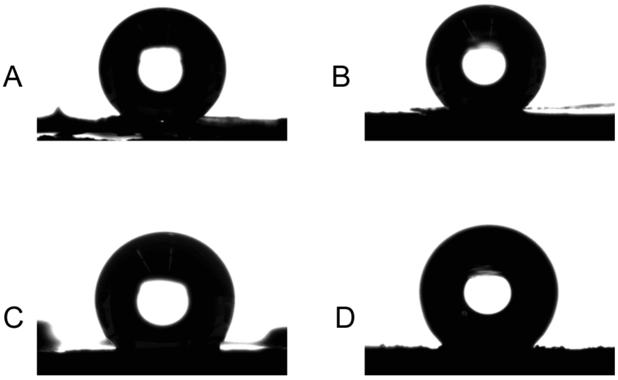

Figure 4. Contact angle measurements on different pellets of carbon black: (A) **I-8.0**; (B) **II-3.2**; (C) **III-8.0**; and (D) **IV-0.14**.

independently of the amount of added peroxide (Figure 4C). This difference in performance could be due to the higher steric effect of perfluoro-*iso*-propyl radicals as compared to perfluoroethyl or perfluoro-*n*-propyl radicals. In sample **IV-0.14**, the much longer length of the fluorinated polymeric chains determined a deep variation of the surface properties of the carbon black, even though few milliequivalents of fluoropolymer were used (Figure 4D). Contact angles values are a combination of physical and chemical characteristics of a surface: in accordance with the Cassie–Baxter model, for samples with the same chemical composition, the higher the roughness, the higher the contact angle values.[29] BET analyses showed that the morphology of carbon black was only moderately influenced by the chemical treatment with perfluorodiacyl peroxides and surface area was decreased with PFPE peroxide **4** (Figure 5). Native CABOT VULCAN XC72R carbon black had a surface area of 262 m^2/g and the more intense the treatment with perfluorodiacyl peroxides, the higher the surface area decrease. The surface properties of the carbon black after the treatments changed remarkably, but the values of surface area remained high, with values around 150 m^2/g. The case of sample **IV-0.14** was different, because the treatment with the polymeric PFPE peroxide **4** generated a significant decrease of the surface area to a value of 110 m^2/g. In our opinion the polymeric properties of the liquid PFPE peroxide, as well as its poly functionality, had a fundamental part in these results. The linkage of macromolecular PFPE linear chains to the carbonaceous matrix during the treatments with peroxide **4** deeply influenced the native carbon black morphology where multilinked PFPE–carbon surface structures are likely expected. Also the physical adsorption of a PFPE fluid onto the carbon black generated a variation of its surface properties (see Supporting Information). The surface area decreased to 58 m^2/g, and a contact angle of 136° was measured, revealing the typical hydrophobic properties of fluorinated samples. However, simple washings with fluorinated solvent increased back the surface area and removed the hydrophobic properties, because no chemical linkage of the fluorinated chains occurred in this case. In fact, after washings, no fluorine content on the carbon black surface was detected by XPS analysis, as demonstrated by the removal of physioadsorbed PFPE fluid. Conversely the surface properties of sample **IV-0.14** were permanently stable, even after it was washed continuously for 24 h with pure fluorinated solvent by means of a Soxhlet extractor.

The granular morphology of carbon black powders after treatments with fluorinated peroxides was resolved at high magnification. The high resolution images of specks of the two most hydrophobic samples, **II-3.2** and **IV-0.14**, are reported in Figure 6A,B, respectively. In both the images it was possible to detect a homogeneous distribution of pores with diameters larger than 50 nm. Nevertheless, a more marked decrease of surface area in **IV-0.14** than in **II-3.2** can be observed. In **II-3.2** perfluoro-*n*-propyl chains with a length of 0.4 nm were covalently linked to the carbonaceous surface; in **IV-0.14** high molecular weight PFPE radicals with lengths of at least 3 nm were linked to the carbon black surface. The length of 3 nm corresponds to the uncoiled average distance between two peroxidic moieties in PFPE peroxide **4**. The size of perfluoro-*n*-propyl chains in **II-3.2** suggested that the majority of the micropores ($d_p < 2$ nm) could be preserved during the chemical treatment,

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[29] Lafuma, A.; Quèrè, D. *Nat. Mater.* **2003**, *2*, 457.

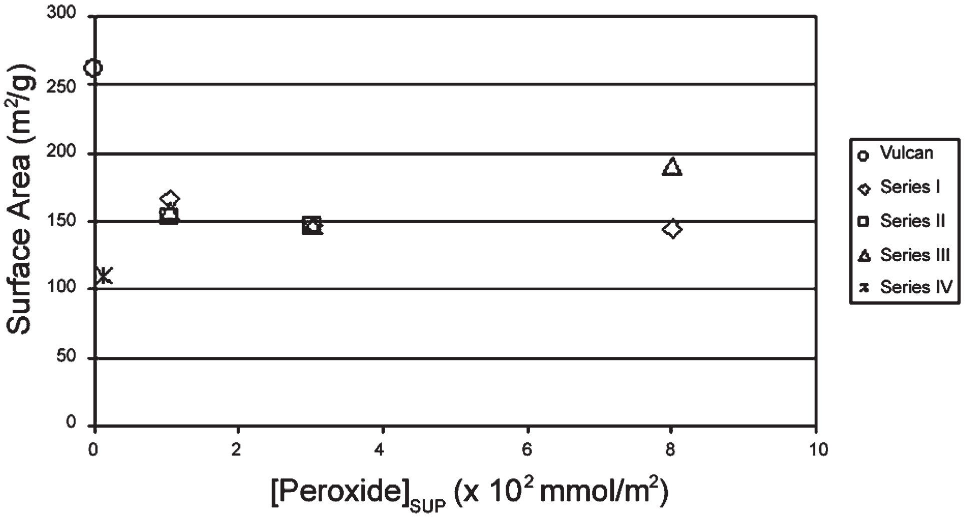

Figure 5. BET surface area measurements on carbon blacks before and after treatments with perfluorodiacyl and PFPE peroxides.

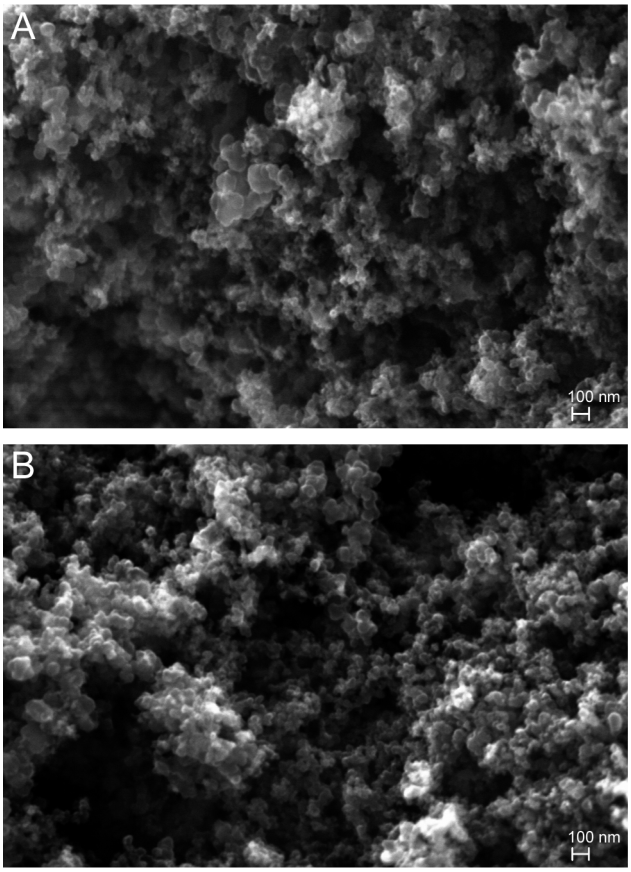

Figure 6. High resolution SEM images of specks of carbon black powder after treatments with perfluorodiacyl (A, **II-3.2**) and PFPE (B, **IV-0.14**) peroxides. The macroporous structure (d_p > 50 nm) was not modified by the chemical treatment with fluorinated peroxides, and the macromorphology was preserved.

assuring the retention of the high surface area. On the other hand the PFPE chains in **IV-0.14** were long enough to cover micropores and the smallest mesopores ($2 < d_p <$ 50 nm). Thus it is reasonable to assume that the macroporous structure (d_p > 50 nm) was not modified by the chemical treatment with fluorinated peroxides and the macromorphology was preserved. In the case of treatments with perfluorodiacyl peroxides the differences in surface area can be due to variations in micromorphology; whereas treatment with PFPE peroxide can modify both micro- and mesomorphology of the carbon black. Thus the hydrophobic properties can be attributed to the variation of the surface composition and to the rough morphology, which minimally underwent physical change.

Conclusions

Carbonaceous samples treated with either perfluorodiacyl or PFPE peroxides were permanently modified, and the atomic fluorine content detected on their surface was around 10%. The presence of fluorine was due to the covalent linkage of fluorinated chains obtained by the thermal decomposition of peroxides **1**−**4**. The perfluorinated chains bonded on the surface of the carbonaceous materials modified permanently their surface properties, enhancing the hydrorepellence. Conversely, the physioadsorption of a PFPE fluid was easily removable by means of washings with fluorinated solvent. Morphology and surface areas of the carbon black were mostly retained when perfluorodiacyl peroxides **1**−**3** were the modifying reagents; on the contrary, important reduction of the surface area were observed when PFPE peroxide **4** was used.

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Supporting Information Available: The comparative example (physioadsorption of PFPE fluid on carbon black, surface composition, surface area, and contact angle), synthetic scheme of the synthesis of perfluorodiacyl peroxides, table of the experimental conditions of the synthesis of perfluorodiacyl peroxides, table of the contact angle measurements with water, and table of the BET surface area measurements. This information is available free of charge via the Internet at http://pubs.acs.org.