Surface Functionalization with Phosphazenes. V. Surface Modification of Plasma-Treated Polyamide 6 with Fluorinated Alcohols and Azobenzene Derivatives Through Chlorinated Phosphazene Intermediates

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ABSTRACT: In this article, we describe the synthesis and characterization of surface-modified polyamide-6, using polydichlorophosphazene and hexachlorocyclophosphazene as coupling agents. The solid surface of this polymer was modified first by the introduction of polar functions (C=O, OH, OR, COOH, COOR, etc.) with a cold plasma technique, then by the treatment of the alcoholic groups on the surface with $(NPCl_2)_n$ and $(NPCl_2)_3$ to graft these substrates through the formation of strong covalent P—O—C bonds, and eventually by the substitution of the residual chlorines on the polyamide-6 surface with different types of fluorinated alcohols (2,2,2-trifluoroethanol and heptadecafluorononanol) and with 4-hydroxyazobenzene. Contact-angle measurements, together with X-ray photoelectron spectroscopy and ultraviolet–visible spectroscopy techniques, support the occurrence of these surface-functionalization reactions. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 3191–3199, 2008

Key words: cold plasma; ESCA/XPS; polyamides; polyphosphazenes; UV–vis spectroscopy

INTRODUCTION

The modification of the surface properties of materials, such as wettability, roughness, biocompatibility, and adhesion, is a fundamental area in polymer chemistry and materials chemistry because of the impressive industrial and technological implications of this process.[1–5]

In previous articles of this series,[6–9] we developed three different strategies to modify the surface of solid samples. The first method was based on the utilization of cyclophosphazenes partially substituted with γ-aminopropyltriethoxy silane and also containing various types of different nucleophiles [e.g., fluorinated alcohols, 4-cyanophenol, 4-hydroxyazobenzene, and poly(ethylene glycol) monomethyl ether groups] to functionalize the surface of silica beads in a predictable way.[6,8] In the second one, we used chlorophosphazenes, typically hexachlorocyclophosphazene (HCCP), to modify the surface of free-hydroxy-group-containing materials based on silicon [i.e., silica, crystalline (100) silicon wafers, and soda lime glass slides] in different ways.[7,10–13] In the third approach, we could eventually achieve the modification of polymer surfaces by reacting previously oxidized high-density polyethylene (HDPE) samples via a cold plasma technique with polydichlorophosphazene (PDCP) and HCCP and substituting the residual chlorines in these substrates successively with different fluorinated alcohols.[9] In this last series of investigations, HDPE was selected as a suitable polymer for surface-functionalization processes because of its scientific and technologic relevance and because of the nonpolar nature of its surface.[14]

In this article, we present the results of our investigations on plasma-modified polyamide-6 (PA6) solid samples containing free hydroxyl groups on the surface. These groups could be treated with PDCP and HCCP, leaving a certain number of their original chlorines unreacted. The successive step implies the reaction of these chlorines with suitable

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For part IV of this article series, see ref. 8.
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nucleophiles (e.g., different fluorinated alcohols and 4-hydroxyazobenzene) to graft these products onto the surface of the PA6 sample.

PA6 was selected because of the polar nature of its surface, at variance with the nonpolar structure of the previously investigated HDPE material,[9] to assess the general feasibility of this surface-functionalization method, whereas fluorinated alcohols and 4-hydroxyazobenzene substituents were chosen because of the possibility of modifying the surface wettability of the virgin PA6 material and granting its surface photochromic characteristics, respectively.

EXPERIMENTAL

Solvents

Tetrahydrofuran (THF), chloroform, ethanol, triethylamine, toluene, and *n*-heptane were Aldrich products (Saint Quentin Fallavier, France). THF was dried by distillation from sodium/benzophenone, whereas dry *n*-heptane and triethylamine were purified by distillation from CaH_2 according to standard methods.[15,16] All anhydrous solvents were freshly distilled before use.

Reagents

HCCP ($N_3P_3Cl_6$, 95–98%) was purchased from Shin Nissho Kako (Japan) and purified by vacuum sublimation followed by crystallization from *n*-hexane.[17] PDCP was prepared by the thermally induced polycondensation reaction of dichlorophosphinoyliminotrichlorophosphorane [$Cl_3PNP(O)Cl_2$] at 563 K in accordance with the literature.[18–21] This polymer, with an intrinsic viscosity of 44 mL/g, was stored as a 37% (w/w) solution in 1,2,4-trichlorobenzene. It was also stabilized with 1% (w/w) $SOCl_2$.[22]

Before utilization, PDCP was first precipitated in anhydrous *n*-heptane and then redissolved in anhydrous toluene with a concentration of 0.110 g/mL. Sodium, tetrabutylammonium bromide, 2,2,2-trifluoroethanol (TFE), 1,1-*H*-heptadecafluoro-1-nonanol (HDFN), 4-phenylazophenol (AzB), benzophenone, and calcium hydride were Aldrich products and used as received.

Polymeric substrates

PA6 was purchased from Goodfellow (Goodfellow Cambridge Ltd., Huntingdon, England) as 0.5-mm-thick films with a density of 1.13 g/cm^3. The substrate was previously cut into squares or rectangles with dimensions ranging from 10 × 10 to 25 × 35 mm^2, depending on characterization needs, and was cleaned by sonication in an ethanol bath for 18 min. The samples were then dried overnight in an oven at 333 K before use.

Equipment

Plasma equipment

All plasma treatments were performed in a Europlasma 300PC-GHZ apparatus (Europlasma, Oudenaarde, Belgium) with a microwave generator power supply of up to 600 W operating at 2.46 GHz and an aluminum treatment chamber of 30-L capacity connected to an Edwards rotative vacuum pump (BocEdwards, Paris, France).

Ultraviolet–visible (UV–vis)

Spectra were taken with a Cary Varian 100 double-beam spectrometer (Varian France, les Ulis) equipped with an apparatus for reflectance measurements. Irradiation of the samples for photochromism experiments was performed using a UV lamp for thin layer chromatography having an excitation wavelength of 365 nm.

Contact angle

Measurements were carried out with a GBX Digidrop instrument (Digidrop, GBX, France) at a controlled substrate temperature of 300 K and with solvent droplets of 5 μL. The reported findings are the averages of five measurements taken in different parts of the PA6 plate surfaces. Surface energy calculations were performed with WindroP++ software with the Owens–Wendt model and with contact-angle values with water, formamide, and diiodomethane.

X-ray photoelectron spectroscopy (XPS)

XPS analyses were performed with the VG Escalab 220XL spectrometer (VG Scientific, East Grinstead, West Sussex, England). The Mg Kα line (1253.6 eV) was used for excitation with 300 W of applied power. The spectrometer was operated in a constant pass energy mode (40 eV) for the recording of high-resolution spectra. Binding energies were referenced to the C_{1s} core level energy at the hydrocarbon species. During the experiment, the vacuum level was less than 10^{-7} Pa. The sample film was stuck to the sample holder with double-faced conducting adhesive tape. Experimental quantification and spectral simulation were obtained with Eclipse software provided by VG Scientific (East Grinstead, West Sussex, England).

Procedures

The functionalization process took place in three steps: (1) PA6 plate plasma activation, (2) grafting of HCCP or PDCP, and (3) residual chlorine substitution with TFE, HDFN, or AzB. All manipulations were performed under a nitrogen atmosphere, with the only exception of the plasma treatment and sample washing after substitution step 3.

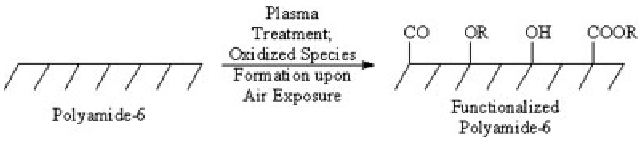

Figure 1 Schematic representation of the formation of surface-oxidized species on PA6 plates through plasma treatment (step 1).

Plasma activation of polymeric substrates

The typical plasma activation procedure was as follows. A PA6 sample was put into the plasma reactor, and the pressure inside the chamber was brought down to 17.3 Pa. Then, Ar was let inside with a controlled flux of 0.30 dm^3/min while the pumping was kept going, and 2 min passed to allow the system to reach a steady state. The microwave generator was turned on with a power of 300 W, and the plasma treatment was carried on for 3 min, after which the generator was turned off, the Ar flux was interrupted, and the chamber was finally brought back to atmospheric pressure by air being let inside. Treated samples were used for phosphazene grafting immediately after the plasma treatment.

Grafting of PDCP

Plasma-treated PA6 samples were dipped into 20 mL of a PDCP solution in anhydrous toluene (concentration = 0.110 g/mL) and kept at room temperature for 7.5 h. Then, they were extracted and washed with 20 mL of anhydrous THF under stirring for 10 min before utilization for the substitution step.

Grafting of HCCP

Samples were dipped into a solution of 0.35 g (1.0 mmol) of HCCP and 0.9 mL (0.66 g, 6.5 mmol) of anhydrous triethylamine in 10 mL of anhydrous THF and were kept at 323 K for 24 h. Precipitation of a white solid was observed, and the solution turned brown. Then, the samples were extracted and washed with 20 mL of anhydrous THF under stirring for 10 min before utilization in the substitution step.

Substitution with TFE

Finely divided sodium (0.35 g, 15.2 mmol) was put into 10 mL of anhydrous THF, and 2 mL (2.75 g, 27.4 mmol) of TFE was cautiously added, causing hydrogen evolution. After consumption of all the sodium, PDCP- and HCCP-functionalized PA6 samples were dipped into the solution, which was stirred at room temperature for 16 h. PDCP-grafted PA6 samples were successively washed with 10 mL of THF, whereas 10 mL of chloroform was used in the case of HCCP-grafted plates. Successive washings were the same for both kinds of samples: 10 mL of THF, 10 mL of distilled water, and finally 10 mL more of THF. Drying was performed in an oven at 323 K before characterization.

Substitution with HDFN

Finely divided sodium (0.09 g, 3.9 mmol) was put into 10 mL of anhydrous THF, and 2.25 g (5.0 mmol) of HDFN was cautiously added, causing hydrogen evolution. After 7 h of stirring at room temperature, the remaining sodium was removed, 0.02 g (0.06 mmol) of tetrabutylammonium bromide was added, and a phosphazene-functionalized sample was dipped into the solution, which was stirred at room temperature for 16 h. PDCP-grafted PA6 samples were then washed with 10 mL of THF, whereas 10 mL of chloroform was used in the case of HCCP-grafted plates. Successive washings were the same for both kinds of samples: washing with 10 mL of THF, sonication for 30 min in a mixture of 15 mL of THF and 6 mL of distilled water, and washing with 10 mL of distilled water and then with 10 mL more of THF. Finally, all HDFN-functionalized samples were Soxhlet-extracted with THF for 8 h and then dried in an oven at 323 K before characterization.

Substitution with AzB

Finely divided sodium (0.09 g, 3.9 mmol) was put into 10 mL of anhydrous THF, and 0.99 g (5.0 mmol) of AzB was cautiously added, causing hydrogen evolution. After consumption of all the sodium, 0.02 g (0.06 mmol) of tetrabutylammonium bromide was added, and the phosphazene-functionalized sample was dipped into the solution, which was stirred at room temperature for 16 h.

PDCP-grafted PA6 samples were washed with 10 mL of THF, whereas 10 mL of chloroform was used in the case of HCCP-grafted plates. Successive washings were the same for both kinds of samples: 10 mL of THF, 10 mL of distilled water, and finally 10 mL more of THF. Drying was carried out in an oven at 323 K before characterization.

RESULTS AND DISCUSSION

Experimental approach to the surface functionalization of PA6

The general strategy adopted to functionalize the surface of solid PA6 samples was based on three successive steps in the following order:

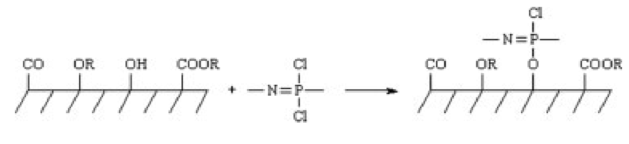

Figure 2 Grafting of chlorophosphazenes onto the surface of Ar-plasma-treated PA6 plates (step 2).

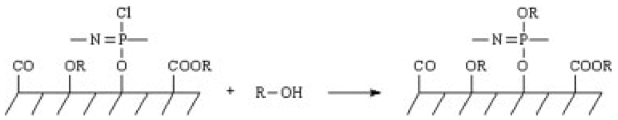

Figure 3 Substitution of the residual chlorine atoms in the phosphazene substrates with different nucleophilic groups (step 3).

1. Plasma treatment of the PA6 polymeric support to introduce hydroxyl groups onto the polymer surface (Fig. 1).
2. Grafting of the chlorinated phosphazene trimer $(NPCl_2)_3$ and polymer $(NPCl_2)_n$ onto the surface of PA6 by the reaction of C—OH groups with the P—Cl linkages of the phosphazenes (Fig. 2).
3. Substitution of the residual reactive chlorines with selected nucleophiles (Fig. 3).

The first step was performed by PA6 samples being exposed to cold, low-pressure argon plasma and allowed to get into contact successively with atmospheric air. The experimental conditions used for this surface-functionalization process, as a result of an extensive study reported in detail elsewhere,[9] were as follows: microwave generator power of 300 W, argon flux of 0.30 dm^3/min, and exposure time of 3 min. This treatment brought about several effects on the sample surfaces, such as cleaning, chain scission, volatilization of smaller polymer fragments, and formation of radicals.[23–26] The last effect was responsible for the superficial reticulation of the polymer samples and for the formation of oxidized species as soon as the samples were exposed to atmospheric oxygen and moisture.[25,27] These species can vary greatly in nature and polarity, ranging from alcoholic and ethereal moieties to carbonyl, carboxyl, and ester functions.

The hydroxyl groups, introduced onto the surface of PA6 samples as described previously, were able to react with the P—Cl functions of chlorinated phosphazenes, forming strong covalent P—O—C bonds through the elimination of an HCl molecule according to the literature.[17] In the second step of this work, therefore, PDCP and HCCP were grafted onto the surface of the substrates by the simple immersion of plasma-treated PA6 samples into a solution of these phosphazenes in the presence of bases. Only some of the original chlorine was consumed in the process of anchoring the phosphazene onto the surface of PA6 samples, the residual P—Cl groups being susceptible to undergoing successive substitution reactions with a large variety of different nucleophiles (e.g., alcohols, phenols, and primary amines), as well established in the phosphazene literature.[28]

In principle, therefore, in the third step of the overall functionalization reaction, a large number of different organic molecules can be attached to the surface of the PA6 substrate to modify its properties. This could be simply obtained by the immersion of the polymer in THF solutions of selected alcoholates or phenates in the presence of bases.

In this work, we selected three different nucleophiles for the surface functionalization of PA6 samples: (1) TFE because of its known and well-explored reactivity toward chlorophosphazenes,[29] because it can be considered a good marker in XPS analysis on account of its high fluorine content, and because of the potential biomedical applications of the corresponding poly[bis(2,2,2-trifluoroethoxy)phosphazene] as biocompatible and antithrombogenic coatings;[30–42] (2) HDFN, which may be considered a good example for the introduction of longer fluorinated chains onto the PA6 surface, which may lead to major modifications of the surface energy and hydrophilicity of the PA6 substrates; and (3) 4-hydroxyazobenzene, a compound with known photochromic properties[43–45] and a possible prototype for the surface functionalization of polymeric substrates with push–pull azobenzene systems of similar chemical structures for non-linear optics applications.

Characterization of the functionalized PA6 samples

As far as the characterization of surface-functionalized PA6 samples is concerned, we attempted first to use attenuated total reflectance/Fourier transform infrared spectroscopy for the determination of both

TABLE I
Contact-Angle Results for Virgin, Plasma-Treated, and Functionalized PA6 Samples

		Free surface energy (mJ/m^2)			
Sample	Contact angle with H_2O (°)	Total	Polar component	Dispersive component	Polar/dispersive
1. Virgin PA6	76.5	39.6	5.2	34.4	0.15
2. PA6 + Ar plasma	43.3	60.9	21.0	40.0	0.53
3. PA6, Ar + PDCP + TFE	103.1	15.3	3.0	12.3	0.24
4. PA6, Ar + PDCP + HDFN	123.2	7.1	1.0	6.2	0.16
5. PA6, Ar + PDCP + AzB	92.3	45.6	0.3	45.3	0.01
6. PA6, Ar + HCCP + TFE	99.0	36.4	0.2	36.2	0.01
7. PA6, Ar + HCCP + HDFN	99.7	23.8	0.8	23.0	0.03
8. PA6, Ar + HCCP + AzB	81.6	45.1	2.4	42.8	0.06

TABLE II
Atomic Percentages as Revealed from XPS Analysis for Virgin, Plasma-Treated, and Functionalized PA6 Samples

	C	O	N	P	F	N/P	F/P
1. Virgin PA6	77.1	12.4	10.4	—	—	—	—
2. PA6 + Ar plasma	70.6	16.9	11.1	—	—	—	—
3. PA6, Ar + PDCP + TFE	58.6	14.6	10.3	2.2	14.3	4.68	6.50
4. PA6, Ar + PDCP + HDFN	49.6	8.2	6.0	1.3	34.8	4.61	26.76
5. PA6, Ar + PDCP + AzB	73.7	13.3	11.7	1.3	—	9.0	—
6. PA6, Ar + HCCP + TFE	67.5	14.0	11.1	1.5	5.8	7.40	3.86
7. PA6, Ar + HCCP + HDFN	59.6	14.3	8.9	2.1	15.1	4.23	7.19
8. PA6, Ar + HCCP + AzB	68.4	15.8	12.2	3.3	—	3.69	—

grafted phosphazene and attached substituent groups, but this technique failed because the deposited phosphazene layer appeared to be extremely thin, whereas the infrared spectrum of PA6 is rather complicated and presents strong peaks in the diagnostic regions. We decided therefore to take into consideration other analytical techniques, such as contact-angle measurements, XPS characterization, and UV–vis absorption spectroscopy.

Contact-angle characterization

The values of the contact angle measured with distilled water and the results of surface energy measurements for virgin, plasma-treated, and phosphazene-functionalized PA6 samples are reported in Table I.

In this table, the measurements of contact angles for substrates that underwent only plasma functionalization reactions were performed immediately after plasma treatment because of the high mobility of plasma-modified surface polymer chains that turn the introduced polar chemical functions inside the polymer bulk over time to minimize surface energy.[46] Moreover, contact-angle characterization of samples containing surface-grafted PDCP and HCCP only is not reported, as these substrates are extremely sensitive toward water and atmospheric moisture exposure[17] and may undergo hydrolysis phenomena during measurements.[7,10]

According to Table I, the plasma treatment of PA6 samples brought about a decrease in the contact angle of the virgin polyamide from 76 to 43° as an effect of the creation of new polar moieties on the polymer surface. This was confirmed also by the higher value of the surface energy, with a marked increase in the polar component over the dispersive component.

After phosphazene grafting and substitution with fluorinated alcohols, the contact angle with water grew back and reached values significantly higher than that of virgin PA6, whereas the ratio of the polar and dispersive components decreased, clearly indicating that the functionalization process was successful. As expected, this effect was particularly striking in the case of HDFN, which presents a longer fluorinated chain. Substitution with this molecule allowed contact angles with water to reach as high as 123° and values of the energy surface to be as low as 7.1 mJ/m^2.

Similar considerations were made for azobenzene-functionalized PA6 samples, the modifications in the contact angle and surface energy being lower as the azobenzene groups have a weaker hydrophobic character than perfluorinated alkyl chains. All these findings strongly supported the success of the surface-functionalization reaction of PA6.

By comparing contact-angle measurements with water for PDCP- and HCCP-grafted PA6 samples, we found that the introduction of the substituent molecules during the third functionalization step seemed to be more effective when PDCP was used. This was not unexpected both because the phosphazene polymer is more reactive than its trimeric homologue[17] and because a relatively small number of P—Cl groups are probably required to graft this polymer onto the PA6 surface, thus leaving a greater quantity of reactive chlorine available for further substitution reactions with selected nucleophiles.

XPS characterization

The results of XPS characterization of functionalized PA6 substrates are presented in Table II, in which the atomic percentages of different elements are reported for virgin PA6, a plasma-treated PA6 sample, and the

TABLE III
Results for the Curve Fitting of XPS C_{1s} Spectra of Virgin and Plasma-Treated PA6

Sample 1			Sample 2		
Position (eV)	Area	fwhm (eV)	Position (eV)	Area	fwhm (eV)
285.0	1.00	1.4	284.9	1.00	1.5
285.9	0.22	1.4	285.9	0.23	1.5
			286.9	0.06	1.5
287.9	0.22	1.4	287.9	0.22	1.5
			288.6	0.04	1.5

fwhm = full width at half-maximum.

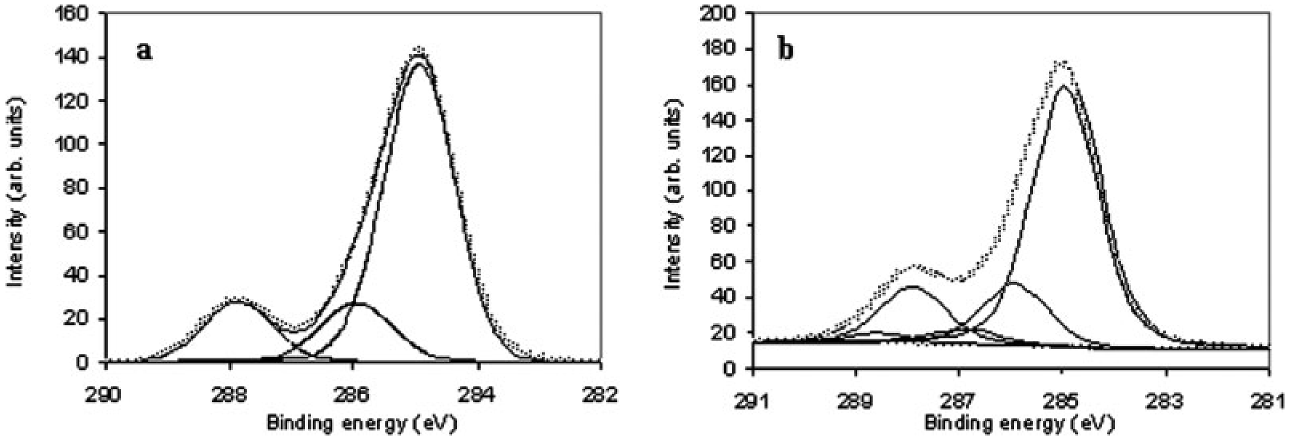

Figure 4 Curve fitting of XPS C_{1s} spectra of (a) virgin PA6 and (b) plasma-treated PA6.

whole series of functionalized samples, together with N/P and F/P atomic percentages ratios.

The oxidizing effect of the plasma treatment was revealed by the increase in the oxygen content, as the O/C ratio changed from 0.16 in sample 1 to 0.24 in sample 2.

Further information could be inferred by curve fitting of the C_{1s} and O_{1s} spectra of these two samples as illustrated in Table III and in Figure 4.

C_{1s} spectra of both samples present one major component at about 285.0 eV due to aliphatic CH_2 groups bonded only to another CH_2 and two other components located at 285.9 and 287.9 eV coming from nitrogen-bonded CH_2 and from amide groups, respectively. In the spectrum of sample 2, however, two minor components arose at 286.9 and 288.6 eV, the first of which could be assigned to alcoholic and/or ethereal moieties,[47] whereas the second was probably due to carboxylic groups.[48]

The spectral simulation of the O_{1s} spectrum of the same two samples yielded the results reported in Table IV and in Figure 5.

The components at about 531 and 533 eV were common to the two samples and were assigned to carbonyl oxygen free and engaged in hydrogen bonds, respectively.[49] In the plasma-treated sample, a new component appeared at 532.2 eV, attributed to the sum of different oxidized carbon species, such as oxygen double-bonded to carbon in carboxylic groups and CH-bonded hydroxyl groups,[50–52] confirming the observations already made for C_{1s} spectral simulations. The minor component at 534.1 eV could be assigned to carboxyl OH groups.[53]

Observing the results for functionalized samples 3–8, we found that the presence of phosphorus at 134 ± 0.3 eV and the clear appearance of a new component in the spectrum of N_{1s} around 398.1 eV, both assignable to the N—P bonds of phosphazenes,[54–56] accounted for the success of the grafting reaction of the phosphazene substrates. The spectra of N_{1s} for samples 2 and 3 are reported as an example in Figure 6.

The relatively low values of the phosphorous atomic percentages indicated that the grafted layer was extremely thin, possibly monomolecular. Such values were essentially similar for HCCP- and PDCP-containing samples. This is striking if one considers the dimensions of the two compounds and the fact that the linear phosphazene polymer is supposed to be more reactive than the trimer,[17] which could lead to a higher phosphorous content when PDCP is employed. This could be due to steric reasons or to the different experimental conditions used in the grafting step, as the reaction with HCCP was performed for a longer time, at a higher temperature, and in the presence of triethylamine acting as a catalyst. Another possible explanation is that the incomplete substitution of the chlorine atoms during

TABLE IV
Results for the Curve Fitting of XPS O_{1s} Spectra of Virgin and Plasma-Treated PA6

Sample 1			Sample 2		
Position (eV)	Area (au)	fwhm (eV)	Position (eV)	Area (au)	fwhm (eV)
531.3	1.00	1.6	531.3	1.00	1.7
			532.2	0.42	1.7
533.1	0.14	1.6	533.1	0.26	1.7
			534.1	0.05	1.7

fwhm = full width at half-maximum.

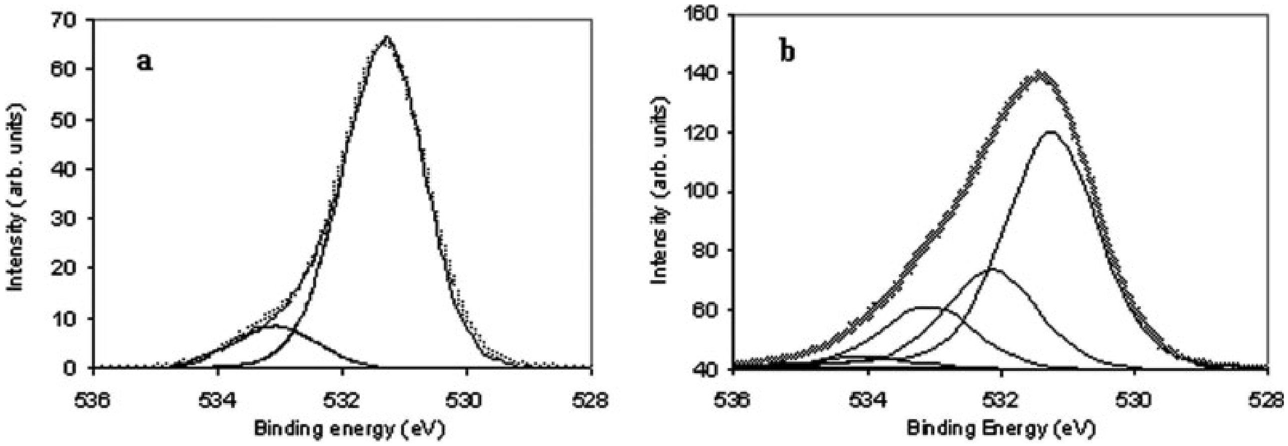

Figure 5 Curve fitting of XPS O_{1s} spectra of (a) virgin PA6 and (b) plasma-treated PA6.

the third step may lead to hydrolysis phenomena, causing chain degradation during the final washing of the samples and thus lowering the phosphazene content on the surface.

The presence of fluorine in samples 3, 4, 6, and 7 indicated that the substitution of chlorine atoms with the fluorinated alcohols actually occurred. Moreover, spectral simulation studies carried out on C_{1s} spectra of these samples revealed the appearance of new components around 293.1 (CF_3 groups) and 291.9 eV (CF_2 groups, present in HDFN-containing samples). Furthermore, in the case of samples 5 and 8, for which substitution was performed with AzB, higher contents of carbon and nitrogen with respect to the other functionalized samples were detected, together with new bands in the UV–vis spectra, thus accounting for the grafting of azobenzene groups on the PA6 surface (as discussed later).

UV–vis characterization

Reflectance UV–vis spectra were collected in the case of azobenzene-functionalized PA6 samples to verify both the functionalization with the optically active molecule and the photochromic properties of the obtained materials. This was achieved through exposure of the samples to 365-nm radiation and collection of spectra at different irradiation times. After illumination, moreover, a thermal relaxation treatment in an oven at 333 K was performed to thermally reverse the photochemically induced isomerization process. The spectrum of the sample functionalized with PDCP and AzB is reported in Figure 7.

The neat azobenzene molecule can exist in trans and cis forms characterized by two different absorptions in the UV (330 nm) and visible (430 nm) ranges of the spectrum. Interconversion between the two isomers can occur both photochemically (trans → cis and cis → trans) and thermally (cis → trans).[43–45]

The reported spectrum does present both these bands, as expected. When the sample was irradiated with 365-nm light, the trans band became less intense, and the cis band grew, although in a less remarkable way, because of spectral noise and a lower absorption cross section of the corresponding isomer; this accounted for the isomerization of the azobenzene moieties from the trans form to the cis form.

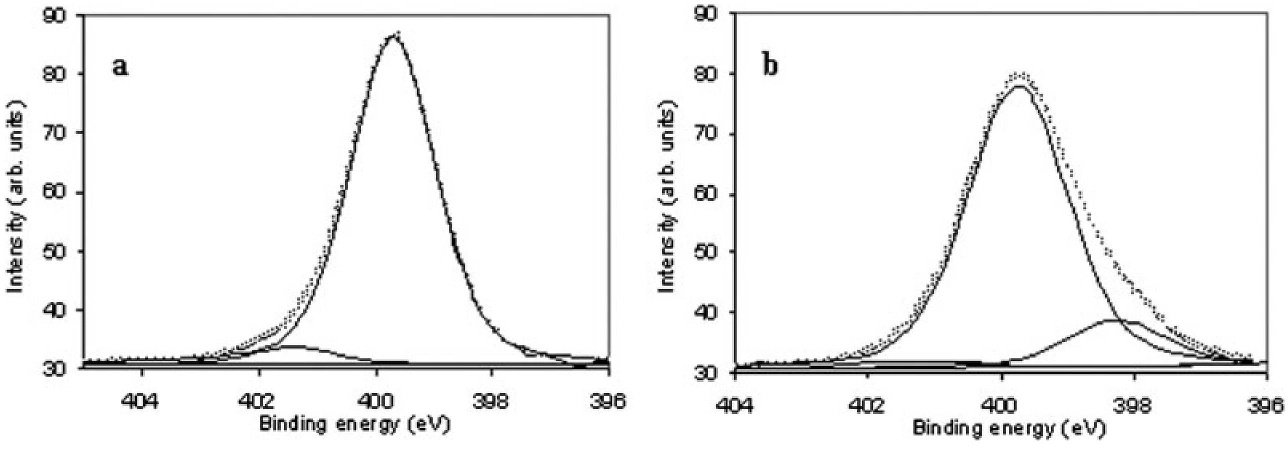

Figure 6 Curve fitting of XPS N_{1s} spectra of (a) plasma-treated PA6 and (b) PA6 functionalized with PDCP and TFE.

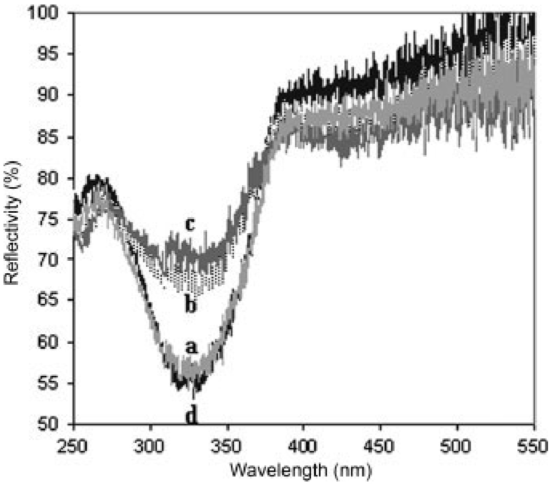

Figure 7 UV–vis reflectance spectra of PA6 functionalized with PDCP and AzB: (a) as prepared, (b) after 1 h of 365-nm irradiation, (c) after 23 h of 365-nm irradiation, and (d) after 23 h of 365-nm irradiation and 20 h of relaxation at 50°C.

The reversibility of the process was explored by exposure of the irradiated sample to a thermal relaxation treatment in an oven at 333 K for several hours. The curve representing the reflectance spectrum of the sample after 23 h of UV-light irradiation followed by thermal relaxation for 24 h shows that the photochromic effect in this system is almost completely reversible.

CONCLUSIONS

In this article, we have described the surface modification induced on solid PA6 samples as a particular application of a general method for surface-functionalization processes. Solid PA6 samples were treated with low-pressure, cold argon plasma to introduce free hydroxyl groups onto the PA6 surface. The oxidized samples were then reacted with PDCP and/or HCCP under a nitrogen blanket and in dry solvents to graft these materials onto the surface of the polymer through strong P—O—C covalent bonds. The grafted phosphazene derivatives, furthermore, still maintained free unreacted chlorines in their chemical structure, which were successively substituted with a variety of nucleophiles during a second functionalization process. In this way, the surface of PA6 samples could be functionalized with fluorinated alcohols of different lengths, which changed the surface polarity, as revealed by contact-angle measurements, and with 4-hydroxyazobenzene, which thus introduced into the PA6 surface photochromic features, as determined by UV–vis spectroscopy.

It is worthwhile to stress that the illustrated functionalization procedure has a general character and can in principle allow the surface modification of a great number of substrates,[9] with the introduction of a wide range of nucleophiles able to grant very different physical and/or chemical features thanks to the versatility of phosphazene chemistry.[17,28]

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