Chem. Mater. **2007,** *19,* 4975−4981

Surface Functionalization with Phosphazenes, Part 3: Surface Modification of Plasma-Treated Polyethylene with Fluorinated Alcohols Using Chlorinated Phosphazenes as Coupling Agents

Roberto Milani,[†] Mario Gleria,[*,‡] Alessandro Sassi,[‡] Roger De Jaeger,[§] Ahmed Mazzah,[§]
Leon Gengembre,[||] Martine Frere,[||] and Charafeddine Jama[#]

Dipartimento di Scienze Chimiche, Universitá di Padova, via F. Marzolo 1, 35131 Padova, Italy, Istituto di Scienze e Tecnologie Molecolari (ISTM) del Consiglio Nazionale delle Ricerche, Sezione di Padova, c/o Dipartimento di Scienze Chimiche dell'Universitá, via F. Marzolo 1, 35131 Padova, Italy, Laboratoire de Spectrochimie Infrarouge et Raman (LASIR), UMR-CNRS 8516, and Unité de Catalyse et Chimie du Solide (UCCS), CNRS UMR 8181, Université des Sciences et Technologies de Lille, 59655 Villeneuve d'Ascq, France, and Laboratoire des Procédés d'Elaboration de Revêtements Fonctionnels (PERF), LSPES UMR 8008, Ecole Nationale Supérieure de Chimie de Lille, BP 90108, 59652 Villeneuve d'Ascq, France

Received April 12, 2007. Revised Manuscript Received June 28, 2007

In this paper, we present a new strategy to functionalize the surface of high-density polyethylene plates using a cold plasma technique and chlorinated phosphazenes as coupling agents. The clean surface of polyethylene samples was modified by argon plasma treatments to introduce polar groups (e.g., $C{=}O$, COOR, OR, OH, etc.); the free hydroxylic functions thus introduced were successively reacted with $(NPCl_2)_3$ and $(NPCl_2)_n$ to graft these substrates onto the surface of the polymer samples through the formation of strong covalent Cl−P−O−HDPE bonds. The residual unreacted chlorines, still present in the phosphazenes, were eventually substituted with alkoxy substituents (e.g., trifluoroethanol and heptadecafluorononanol) according to the classical nucleophilic substitution reaction of both cyclic and polymeric phosphazene materials. In this way, surface features of polyethylene samples could be deeply modified in a rather general and easy way.

Introduction

Surface properties of poly(organophosphazenes), POPs, such as hydrophilicity or hydrophobicity, adhesion, permeability, biocompatibility, roughness, and the possibility of determining composite formation, are important characteristics of these materials that strongly depend on their practical utilization in different applicative domains.[1] Therefore, the possibility of tailoring these features is of primary importance in phosphazene chemistry.

Surface problems of phosphazene materials have been faced over time according to two main strategies:

(1) modification of the surface of solid poly(organophosphazene) films through a variety of experimental techniques, and

(2) modification of the surface of conventional, carbon-backboned macromolecules by exploiting polyphosphazene derivatives.

As far as the first point is concerned, the surface modification of polyphosphazene films has been obtained by UV[2] or laser[3] irradiation; plasma treatment;[3] nitration[4] or sulfonation[5] reactions; bromomethylation[6] or oxidation[7,8] of 4-methylphenoxy substituents; hydrolysis of propyl-4-carboxylatephenoxy moieties;[8] surface hydrosilylation processes;[9] metathetical exchange of trifluoroalkoxy substituents in poly[bis(trifluoroethoxy)phosphazene] with diethyleneglycol monomethylether,[10,11] different fluorine-containing alkoxides,[12] or with other alkoxides containing OH,[13] NH_2,[13−16] CN[13] functions, or hydroxylic groups;[17] metalation reactions;[18−20] and by thermally and/or photochemically induced grafting reactions of organic conventional macromolecules onto the surface of polyphosphazene films.[21,22]

---

[*] Corresponding author. E-mail: gleria@chin.unipd.it.

[†] Universitá di Padova.

[‡] Istituto di Scienze e Tecnologie Molecolari del Consiglio Nazionale delle Ricerche.

[§] Laboratoire de Spectrochimie Infrarouge et Raman, Université des Sciences et Technologies de Lille.

[||] Unite de Catalyse et Chimie du Solide, Université des Sciences et Technologies de Lille.

[#] Ecole Nationale Supérieure de Chimie de Lille.

(1) Allcock, H. R. *Appl. Organomet. Chem.* **1998**, *12*, 659.
(2) Minto, F.; Gleria, M.; Bortolus, P.; Daolio, S.; Facchin, B.; Pagura, C.; Bolognesi, A. *Eur. Polym. J.* **1989**, *25*, 49.
(3) Exarhos, G. J. *NTIS Spec. Publ.* **1990**, *801*, 324.
(4) Allcock, H. R.; Kwon, S. *Macromolecules* **1986**, *19*, 1502.
(5) Allcock, H. R.; Fitzpatrick, R. J.; Salvati, L. *Chem. Mater.* **1991**, *3*, 1120.
(6) Neenan, T. X.; Allcock, H. R. *Biomaterials* **1982**, *3*, 78.
(7) Allcock, H. R.; Fitzpatrick, R. J.; Salvati, L. *Chem. Mater.* **1992**, *4*, 769.
(8) Allcock, H. R.; Morrissey, C. T.; Way, W. K.; Winograd, N. *Chem. Mater.* **1996**, *8*, 2730.
(9) Allcock, H. R.; Smith, D. E. *Chem. Mater.* **1995**, *7*, 1469.
(10) Ohkawa, K.; Matsuki, T.; Saiki, N. U.S. Patent 4 959 442, 1990; *Chem. Abstr.* **1991**, *114*, 83683y; assigned to Teijin Ltd.
(11) Lora, S.; Palma, G.; Bozio, R.; Caliceti, P.; Pezzin, G. *Biomaterials* **1993**, *14*, 430.
(12) Kolich, C. H.; Klobucar, W. D.; Books, J. T. U.S. Patent 4 945 139, 1990; *Chem. Abstr.* **1990**, *113*, 154152q; assigned to Ethyl Corp.
(13) Allcock, H. R.; Fitzpatrick, R. J.; Salvati, L. *Chem. Mater.* **1991**, *3*, 450.
(14) Matsuki, T.; Saiki, N.; Emi, S. U.S. Patent 5 380 658, 1995; *Chem. Abstr.* **1991**, *115*, 227837; assigned to Teijin Ltd.
(15) Matsuki, T.; Saiki, N.; Emi, S. Eur. Pat. Appl. 425 268, 1991; *Chem. Abstr.* **1991**, *115*, 227837v; assigned to Teijin Limited.
(16) Matsuki, T.; Saiki, N.; Emi, S. U.S. Patent 5 268 287, 1993; *Chem. Abstr.* **1991**, *115*, 227837; assigned to Teijin Ltd.

10.1021/cm071002m CCC: $37.00

On the contrary, surface modification of conventional organic polymeric materials using poly(organophosphazenes) has been achieved basically by two different synthetic approaches, i.e., surface coating[23,24] and surface grafting reactions of different phosphazene macromolecules on poly(ethylene),[25] poly(propylene),[26] poly(vinyl chloride),[26] poly(ethylene terephthalate),[26] poly(bisphenol A carbonate),[26] poly(methylmethacrylates),[26] poly(vinyl alcohol),[27−29] poly(ethylene-co-vinyl alcohol),[29] and on carbon black.[30]

All these functionalization reactions brought about the modification of the surface properties of the different polymeric materials, both organic and inorganic in nature, thus significantly widening the possibility of their practical utilization. In this domain, a few years ago, we started a long-range research project aimed at designing general strategies to attain surface functionalization of solid materials using cyclic and polymeric phosphazene derivatives as coupling agents.[31] Preliminary work in this area was carried out by Grunze,[32−38] who succeeded in grafting polydichlorophosphazene, PDCP, onto oxidized human tissues, successively reacting the residual chlorines with trifluoroethoxy groups.

In this project, our attention was first devoted to substrates already containing free hydroxylic groups, such as silica gel beads, crystalline (100) silicon wafers, and sodalime glasses, and we synthesized a series of cyclophosphazenes containing about 50% of 4-cyanophenol,[39] 2,2,3,3-tetrafluoropropanol,[40] poly(ethylene oxide)-750 monomethylether,[40] or 4-hydroxyazobenzene,[40] the residual sites in the cyclophosphazenes being substituted by γ-aminopropyltriethoxysilane (APTES) groups. In these compounds, the trialkoxysilane residues have been used to graft the selected substituents on the surface of silicon-based materials.

We considered successively the possibility of functionalizing the surface of crystalline (100) silicon wafers directly with hexachlorocyclophosphazene (HCCP)[41] and undertook a series of theoretical calculations to ascertain the feasibility of this process.[42]

In the present paper, we address surface functionalization of solid samples of conventional organic macromolecules by developing a rather innovative strategy on the basis of the preliminary surface functionalization of solid organic polymers using a cold argon plasma technique to introduce free hydroxylic groups on the surface of these materials and successively using HCCP and PDCP as suitable coupling agents to be grafted on the surface of these polymeric films via the formation of strong P−O−C covalent bonds. The residual chlorines, still present in the exploited chlorophosphazenes, are prone to react successively with a large variety of nucleophilic reagents, according to the classical substitutive approach usually exploited in phosphazene chemistry.[43−45] In this way, grafting of an almost infinite number of compounds on the polymer surface is possible. The organic polymer selected for this work was high-density polyethylene (HDPE) because of the well-known scientific and industrial importance of this material;[46] the organic groups grafted on its surface were 2,2,2-trifloroethanol and 1,1-*H*-heptadecafluoro-1-nonanol.

Experimental Section

Solvents. Tetrahydrofuran, chloroform, ethanol, triethylamine, toluene, and *n*-heptane were Aldrich products. Tetrahydrofuran was dried by distillation from sodium/benzophenone, whereas *n*-heptane and triethylamine were anhydrified by distillation from CaH_2, according to standard methods.[47,48] All anhydrous solvents were freshly distilled before use.

Reagents. Hexachlorocyclotriphosphazene, $N_3P_3Cl_6$ (HCCP; 95−98%), was purchased from Shin Nissho Kako, and purified by vacuum sublimation followed by crystallization from *n*-hexane.[43] Polydichlorophosphazene (PDCP) has been prepared by a thermally induced polycondensation reaction of dichlorophosphinoyliminotrichlorophosphorane, $Cl_3PNP(O)Cl_2$, at 290 °C, according to literature procedures.[49−52] This polymer, with an intrinsic viscosity

---

(17) Allcock, H. R.; Rutt, J. S.; Fitzpatrick, R. J. *Chem. Mater.* **1991**, *3*, 442.
(18) Allcock, H. R.; Silverberg, E. N.; Nelson, C. J.; Coggio, W. D. *Chem. Mater.* **1993**, *5*, 1307.
(19) Spitaleri, A.; Pertici, P.; Scalera, N.; Vitulli, G.; Hoang, M.; Turney, T. W.; Gleria, M. *Inorg. Chim. Acta* **2003**, *352*, 61.
(20) Pertici, P.; Vitulli, G.; Salvatori, P.; Pitzalis, E.; Gleria, M. In *Phosphazenes A Worldwide Insight*; Gleria, M., De Jaeger, R., Eds.; Nova Science Publishers: Hauppauge, NY, 2004; Chapter 26, p 621.
(21) Minto, F.; Scoponi, M.; Gleria, M.; Pradella, F.; Bortolus, P. *Eur. Polym. J.* **1994**, *30*, 375.
(22) Fambri, L.; Minto, F.; Gleria, M. *J. Inorg. Organomet. Polym.* **1996**, *6*, 195.
(23) Adams, B. E.; Hansel, R. D.; Quinn, E. J. U.S. Patent 4 145 479, 1979; *Chem. Abstr.* **1979**, *90*, 206024c; assigned to Armstrong Cork Co.
(24) Adams, E. B.; Quinn, E. J.; Rodger, W. R. Brit. U.K. Pat. Appl. 2 046 627, 1980; assigned to Armstrong Cork Co.
(25) Dez, I.; De Jaeger, R. *J. Appl. Polym. Sci.* **2003**, *89*, 1925.
(26) Allcock, H. R.; Fitzpatrick, R. J.; Visscher, K.; Salvati, L. *Chem. Mater.* **1992**, *4*, 775.
(27) Pemberton, L.; De Jaeger, R. *Chem. Mater.* **1996**, *8*, 1391.
(28) Dez, I.; De Jaeger, R. *Macromolecules* **1997**, *30*, 8262.
(29) Pemberton, L.; De Jaeger, R.; Gengembre, L. *J. Appl. Polym. Sci.* **1998**, *69*, 1965.
(30) Tsubokawa, N.; Tsuchida, H. *J. Macromol. Sci. Chem.* **1992**, *A29*, 311.
(31) Milani, R. Master's Thesis, University of Padova, Padova, Italy, 2003.
(32) Grunze, M.; Welle, A. PCT Int. Appl. WO, 99 16 477, 1999; *Chem. Abstr.* **1999**, *130*, 272061h; assigned to Universität Heidelberg.
(33) Grunze, M. PCT Int. Appl. WO 01 70 296, 2001; *Chem. Abstr.* **2001**, *135*, 262311; assigned to Polyzenix GmbH, Germany.
(34) Grunze, M.; Gries, C. PTC Int. Appl. WO, 01 80 919, 2001; assigned to Universität Heidelberg.
(35) Grunze, M.; Welle, A. U.S. Patent, 2002 54851, 2002.
(36) Grunze, M. PTC Int. Appl. WO, 02 64 666, 2002.
(37) Grunze, M.; Tur, D. R.; Pertsin, A. Ger. Offen. D. E. 10 113 971. 2002.
(38) Grunze, M.; Tur, D.; Pertsin, A. PCT Int. Appl. WO, 2002 77 073, 2002; *Chem. Abstr.* **2002**, *137*, 264178; assigned to Polyzenix Gmbh, Germany.
(39) Sassi, A.; Milani, R.; Venzo, A.; Gleria, M. *Des. Monomers Polym.* **2006**, *9*, 627.
(40) Milani, R.; Sassi, A.; Venzo, A.; Bertani, R.; Gleria, M. *Des. Monomers Polym.* **2007**, submitted.
(41) Sassi, A.; Maggioni, G.; Milani, R.; Carturan, S.; Gleria, M.; Della, Mea, G. *Surf. Coat. Technol.* **2007**, *201*, 5829.
(42) Silvestrelli, P.; Gleria, M.; Milani, R.; Boscolo-Boscoletto, A. *J. Inorg. Organomet. Polym. Mater.* **2006**, *16*, 327.
(43) Allcock, H. R. *Phosphorus-Nitrogen Compounds. Cyclic, Linear, and High Polymeric Systems*; Academic Press: New York, 1972.
(44) Allcock, H. R. *Chemistry and Applications of Polyphosphazenes*; John Wiley & Sons: New York, 2003.
(45) *Phosphazenes. A Worldwide Insight*; Gleria, M., De Jaeger, R., Eds.; NOVA Science Publishers: Hauppauge, NY, 2004.
(46) Allcock, H. R.; Lampe, F. W. *Contemporary Polymer Chemistry*; Prentice Hall: Englewood Cliffs, NJ, 1981.
(47) Vogel, A. J. *A Textbook of Practical Organic Chemistry*; Longman: London, 1970.
(48) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon Press: Oxford, U.K., 1980.
(49) Helioui, M.; De Jaeger, R.; Puskaric, E.; Heubel, J. *Makromol. Chem.* **1982**, *183*, 1137.

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 $SOCl_2$[53].

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

Polymeric Substrates. High-density polyethylene (HDPE) was purchased from Goodfellow as 0.5 mm thick films, with a density of 0.95 g/cm^3. The substrate was previously cut in squares or rectangles with dimensions ranging from 10 × 10 mm^2 to 25 × 35 mm^2 depending on characterization needs and cleaned by sonication in ethanol bath for 18 min. The samples were then dried overnight in an oven at 60 °C before use.

Equipment. *Plasma Equipment.* All plasma treatments were performed with a Europlasma 300PC-GHz apparatus, with a microwave generator power supply of up to 600 W operating at 2.45 GHz, and an aluminum treatment chamber of a 30 L capacity connected to an Edwards rotative vacuum pump.

FTIR-ATR. Infrared absorption spectra were collected with a Perkin-Elmer Spectrum One spectrometer, equipped for measurements in attenuated total reflection (ATR) conditions on a diamond crystal. Subtraction of the spectrum of virgin HDPE from that of functionalized samples was always performed.

Contact Angle. Measurements (±2°) were carried out with a GBX Digidrop instrument at a controlled substrate temperature of 37 °C, using solvent droplets of 5 μL, as an average of 5 measurements in different zones of the sample. Surface-energy calculations were performed with the Windrop++ software utilizing the Owens-Wendt model and contact angle values with water, formamide, and diiodomethane.

XPS. XPS analyses were performed using the ESCALAB 220XL spectrometer. The $Mg_{k\alpha}$ line (1253.6 eV) was used for excitation with a 300W applied power. The spectrometer was operated in a constant pass energy mode (E_{pass}= 40 eV) for high-resolution spectra recording. Binding energies were referenced to the C_{1s} core level energy at 285 eV for the hydrocarbon species. During the experiment, the vacuum level was less than 1×10^{-7} Pa. The sample film was sticked on the sample holder using a double-face conducting adhesive tape. Experimental quantification and spectral simulation were obtained using the Eclipse software provided by VG Scientific.

Experimental Procedures. Functionalization processes were carried out using a three-step procedure implying first a plasma activation of the polymer surface, followed by grafting of HCCP or PDCP, and concluding by saturation of the residual chlorines with TFE or HDFN. Manipulations were all performed under a nitrogen atmosphere, with the only exceptions of plasma treatment and sample washing after the final substitutional step.

Plasma Activation of Polymeric Substrates. The typical plasma activation procedure is as follows. An HDPE sample was put into the plasma reactor, and the pressure inside the chamber was brought to 130 mTorr. Plasma gas was then let inside with a controlled flux (0.30 dm^3/min of Ar for the argon-only procedure, or 0.26 dm^3/min of Ar and 0.04 dm^3/min of O_2 for the mixed gases procedure) while the pumping was kept going, and we waited 2 min to allow the system to reach a steady state. The microwave generator was turned on at a selected power and the plasma treatment was carried on for the selected time, after which the generator was turned off, the gas flux interrupted, and the chamber finally brought back to atmospheric pressure by allowing air to get inside. Treated samples were utilized for phosphazene grafting within 5 min from plasma treatment.

Standard conditions for these functionalization experiments, selected after a preliminary study on HDPE plasma activation (vide infra), are as follows: Ar-only procedure, gas flux of 0.30 dm^3/min, microwave generator power of 300 W, treatment duration of 3 min. These conditions were applied to all functionalized samples presented in this work.

Grafting of PDCP. Plasma-treated HDPE samples were dipped into 20 mL of a PDCP solution in anhydrous toluene (concentration = 0.110 g/mL), kept at room temperature for 7.5 h. They were then extracted and washed with 20 mL of anhydrous THF under stirring for 10 min before utilization in 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 kept at 50 °C for 24 h. Precipitation of a white solid was observed, and the solution turned brown. Then samples were extracted and washed with 20 mL of anhydrous THF under stirring for 10 min before utilization for 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* were cautiously added, causing hydrogen evolution. After metal sodium consumption, phosphazene-functionalized samples were dipped into the solution, which was stirred at room temperature for 16 h. When PDCP was previously grafted onto the sample, the first washing step was performed with 10 mL of THF, whereas in the case of HCCP-grafted samples, 10 mL of chloroform were utilized to remove precipitated triethylammonium chloride. Successive washings were the same for both kinds of samples, in sequence with 10 mL of THF, 10 mL of distilled water, and finally with more 10 mL of THF. Drying was performed in an oven at 50 °C 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 were cautiously added, causing hydrogen evolution. After 7 h of being stirred at room temperature, the remaining sodium was removed, 0.02 g (0.06 mmol) of tetrabutylammonium bromide were added, and a phosphazene-functionalized sample was dipped into the solution, which was stirred at room temperature for 16 h. When PDCP was previously grafted onto the sample, the first washing was performed with 10 mL of THF, whereas 10 mL of chloroform were utilized in the case of HCCP-grafted samples to remove precipitated triethylammonium chloride. Successive washings were the same for both kinds of samples, in sequence with 10 mL of THF, sonication for 30 min in a mixture of 15 mL of THF and 6 mL of distilled water, washing with 10 mL of distilled water, and then with another 10 mL of THF. Finally, all HDFN-functionalized samples were washed for 8 h in a THF Soxhlet and then dried in an oven at 50 °C before characterization.

Results and Discussion

General Strategy for Surface Functionalization of HDPE Plates. The general strategy adopted to functionalize the surface of solid HDPE samples was based on three successive steps that are described in the reaction scheme of Figure 1.These processes will be described in detail below.

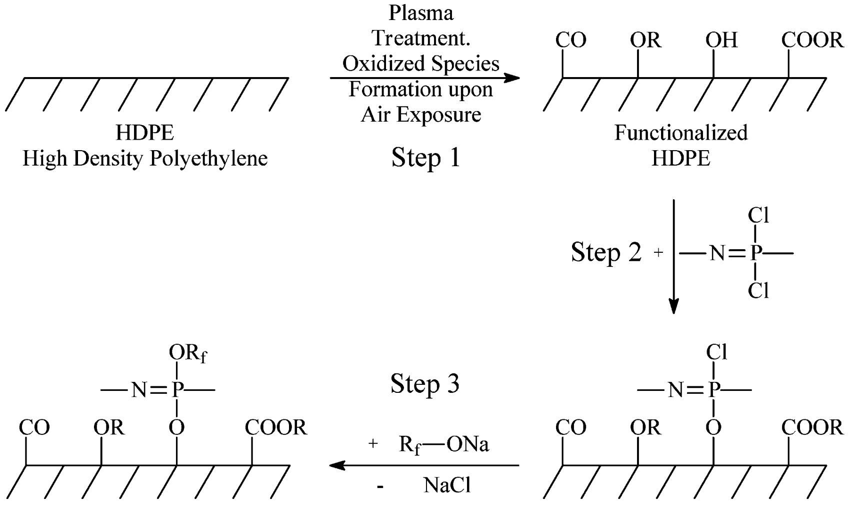
---

(50) D'Halluin, G.; De Jaeger, R.; Chambrette, J. P.; Potin, P. *Macromolecules* **1992**, *25*, 1254.

(51) De Jaeger, R.; Gleria, M. *Prog. Polym. Sci.* **1998**, *23*, 179.

(52) De Jaeger, R.; Potin, P. In *Phosphazenes: A Worldwide Insight*; Gleria, M., De Jaeger, R., Eds.; NOVA Science Publishers: Hauppage, NY, 2004; Chapter 2, p 25.

(53) De Jaeger, R.; Potin, P. Fr. Demande FR, 2 697 008, 1994; assigned to Elf-Atochem, France.



where OR_f stands for OCH_2CF_3 or $OCH_2(CF_2)_7CF_3$

Figure 1. Schematic representation of the surface functionalization strategy of high-density polyethylene plates through plasma treatment and phosphazene coupling agents.

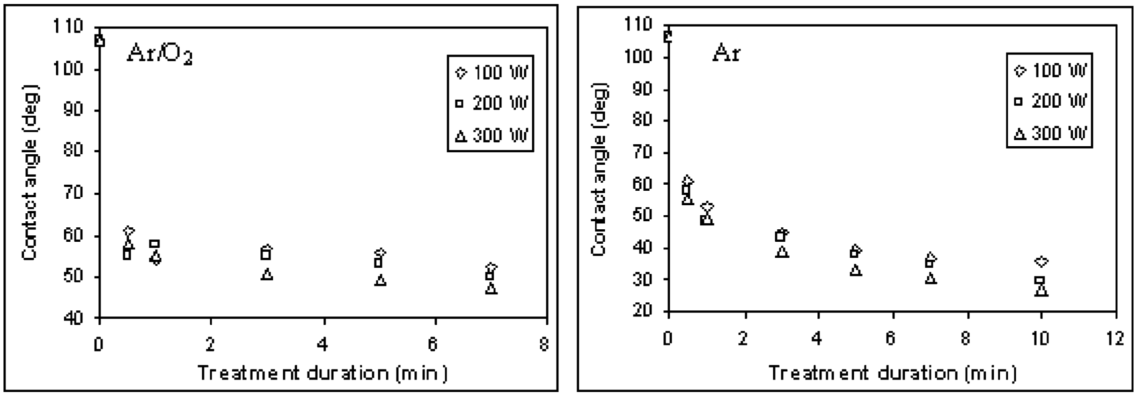


Figure 2. Contact-angle measurements with water of HDPE surfaces treated with mixed Ar/O_2 plasma and with neat Ar plasma as a function of treatment duration.

Step 1: Surface Modification of HDPE Plates. High-density Polyethylene (HDPE) is a well-known, apolar, inert material totally unable to undergo surface functionalization reactions unless a previous modification of the surface features could be carried out with a variety of different techniques.[54] In our case, in order to induce the surface modification of HDPE plates, we decided to utilize a cold plasma technique and start preliminary investigations to determine the best experimental conditions to form the highest quantity of reactive hydroxyl functions on the surface of this material.

Thus HDPE samples were first exposed to different cold low-pressure plasmas, allowing them to successively come into contact with atmospheric air. According to literature, this treatment brought about the cleaning of the polymer surface, the scission of HDPE chains, the volatilization of small polymer fragments, and the formation of surface radicals.[55−58] This last effect was responsible for the superficial reticulation of the polymer substrates and for the surface formation of polar species (e.g., carbonyl, carboxyl, ether groups, and hydroxylic functions) as soon as the samples were exposed to oxygen and moisture.[57,59]

Water contact-angle measurements for plasma-treated HDPE plates allowed us to select appropriate experimental conditions for surface modification of HDPE plates. As suitable gases for plasmas, we exploited an argon/oxygen mixture and neat argon, using different generator powers and exposure times. The corresponding results are reported in Figure 2.

As can be seen from this Figure, the water contact angle of clean untreated HDPE surfaces is about 106°. As an effect of the plasma treatment followed by air exposure, this value drops dramatically to 47.2° (Ar/O_2 mixture) and to 26.7° (neat Ar), using the highest generator powers (300 W) and longest treatment times (7 and 10 min, respectively). On the basis of these results, we decided to choose the following standard experimental conditions for the surface functionalization of HDPE plates carried out in this work: argon plasma, power of 300 W, plasma duration of 3 min, and gas flux of 0.30 dm^3/min. This was estimated to be the best compromise between the formation of reactive functions on the surface of HDPE plates and the reduced damage of the

---

(54) Desai, S. M.; Singh, R. P. *Adv. Polym. Sci.* **2004**, *169*, 231.

(55) Nitschke, M.; Hollander, A.; Mehdorn, F.; Behnisch, J.; Meichsner, J. *J. Appl. Polym. Sci.* **1996**, *59*, 119.

(56) Hegemann, D.; Brunner, H.; Oehr, C. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2003**, *208*, 281.

(57) Guruvenket, S.; Mohan Rao, G.; Komath, M.; Raichur, A. M. *Appl. Surf. Sci.* **2004**, *236*, 278.

(58) Tajima, S.; Komvopoulos, K. *J. Phys. Chem. B* **2005**, *109*, 17623.

(59) France, R. M.; Short, R. D. *Langmuir* **1998**, *14*, 4827.

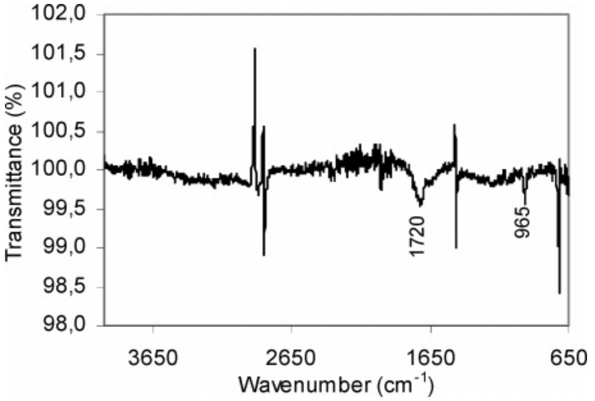


Figure 3. FTIR-ATR difference spectrum of HDPE treated with Ar plasma according to standard conditions with respect to untreated HDPE sample.

Table 1. XPS Atomic Percentages for a Virgin HDPE Plate and for a Sample Treated According to Standard Plasma Activation Procedure

sample	C	O	N	Si	O/C
1, virgin HDPE	93.38	4.40		2.22	0.047
2, Ar plasma-treated HDPE	83.35	16.09	0.56		0.193

polymer surface that would probably occur with more drastic experimental conditions.[57]

The samples obtained were characterized by FTIR-ATR and XPS spectroscopy. All measurements were carried out immediately after 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.[60]

The HDPE infrared spectrum, as a difference between samples treated with plasma according to the above-described standard conditions and neat polymer, is reported in Figure 3.

This figure shows bands located at about 1720 cm^{-1}, assignable to C═O moieties (possibly also forming hydrogen bonds, as indicated by the presence of a shoulder at lower wavenumbers), at 965 cm^{-1}, assigned to C−O bonds,[55] together with signals at about 2890, 1460, and 730 cm^{-1} that are attributed to imperfect subtractions of the polyethylene peaks. It is worth noting that no significant differences could be detected between the infrared spectra of samples analyzed 5 min, 1 h, or 3 h after plasma treatment, to suggest that the formation of polar functional groups on the surface took place immediately as soon as the treated HDPE plates were put into contact with atmospheric air.

XPS analysis, also performed on samples prepared according to the standard procedure, gave the results reported in Table 1.

Although the virgin sample seems to already contain some oxygen, perhaps because of the slight oxidation of the starting material, these data clearly evidenced the effect of the activation procedure, as the O/C atomic percentages ratio grew from 0.047 to 0.193 as a result of the plasma treatment. The introduction of a small quantity of nitrogen onto the sample surface seems to be a side effect, possibly coming from molecular nitrogen present as an impurity in the utilized argon gas.

Curve fitting of the C_{1s} spectrum of sample 2 (plasma treated) is illustrated in Figure 4 and shows the presence of components assignable to carboxyl or ester (289.4 eV) functions and carbonyl (287.6 eV) groups as well as carbon single-bonded to one oxygen atom that may come from alcoholic or ethereal moieties (286.5 eV).[58,61,62] All these features are substantially absent in the spectrum of untreated HDPE.

All these findings support the idea that cold argon plasma-treated HDPE samples have their surface deeply modified under these conditions, with surface formation of free hydroxylic groups.

Step 2: Surface Grafting of Chlorinated Phosphazenes onto Functionalized HDPE Plates. Once functionalized by plasma treatments, HDPE plates containing free hydroxylic groups on the surface were dipped in anhydrous THF or toluene solutions of chlorophosphazenes to graft these substrates onto the surface of HDPE. In the case of HCCP, anhydrous triethylamine (TEA) was added to facilitate grafting.

As chlorophosphazenes suitable for these reactions we selected hexachlorocyclophosphazene $(NPCl_2)_3$ and polydichlorophosphazene $(NPCl_2)_n$, which are very well-known precursors for the preparation of cyclo(organophosphazenes) and of poly(organophosphazenes), respectively.[43,45,46]

The overall reaction, reported in Step 2 of Figure 1, makes it possible to attach both cyclic and polymeric phosphazenes onto the surface of HDPE plates, leaving in these substrates a number of unreacted P−Cl groups potentially susceptible to undergoing further functionalization reactions.

No characterization was attempted for polyethylene samples functionalized with chlorophosphazene substrates because of the extremely high hydrolytic instability of chlorophosphazenes grafted onto the surface of solid materials.[31,42]

Step 3: Surface Functionalization of HDPE Plates by Nucleophilic Replacement of the Residual Chlorines in the Phosphazene Coupling Agents. The nucleophilic substitution of the residual chlorines present in the chlorophosphazenes grafted onto the surface of HDPE plates with suitable nucleophiles brought about the final functionalization of the polyethylene material. This process was carried out by dipping HDPE samples, functionalized with chlorophosphazene derivatives, into THF solutions of sodium trifluoroethoxide and heptadecafluorononoxide (as obtained by treating the corresponding alcohols with metallic sodium) at room temperature for several hours.

The substitution reaction that takes place in the phosphazene coupling agents is reported as Step 3 in Figure 1.

The polyethylene plates functionalized with phosphazenes and fluorinated alcohols were characterized by FTIR-ATR and XPS spectroscopy and contact-angle measurements.

FTIR-ATR Characterization. The polyethylene plates functionalized with phosphazenes and fluorinated alcohols were characterized first by attenuated total reflectance (ATR) FTIR spectroscopy, as a difference spectrum between functionalized samples and virgin HDPE.

---

(60) Atkins, P. W. *Physical Chemistry*; Oxford University Press: Oxford, U.K., 1998.

(61) Martin, A. R.; Manolache, S.; Denes, F. S.; Mattoso, L. H. C. *J. Appl. Polym. Sci.* **2002**, *85*, 2145.

(62) Wickson, B. M.; Brash, J. L. *Colloid Surf., A* **1999**, *156*, 201.

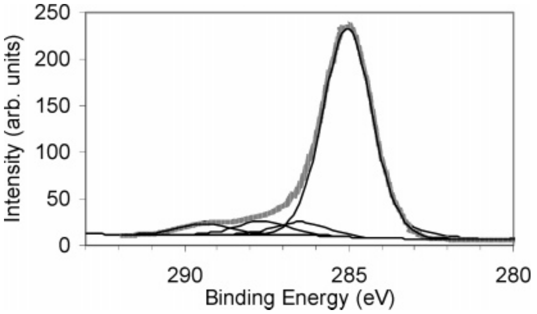


Figure 4. Curve fitting of XPS C_{1s} spectrum of sample 2 (plasma-treated HDPE).

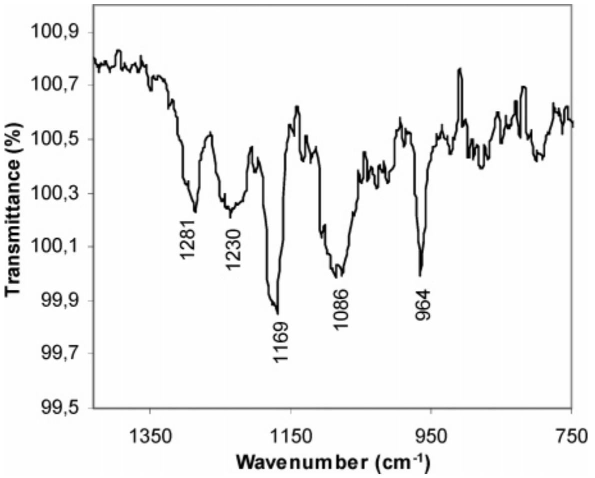


Figure 5. FTIR-ATR spectrum of HDPE functionalized with HCCP and TFE.

Table 2. Contact Angle Values (±2°) and Surface Energy for Virgin, Plasma-Treated, and Functionalized HDPE Samples

sample	contact angle w/H_2O (deg)	surface energy (mJ/m) total	polar	dispersive	pol/disp
1, virgin HDPE	106.7	33.2	0.0	33.2	0.00
2, Ar plasma-treated HDPE	38.8	61.2	23.3	37.9	0.61
3, HDPE+PDCP+TFE	73.1	43.6	6.6	37.0	0.18
4, HDPE+PDCP+HDFN	118.9	10.8	0.3	10.5	0.03
5, HDPE+HCCP+TFE	91.9	25.5	3.2	22.3	0.14
6, HDPE+HCCP+HDFN	103.5	19.5	0.7	18.7	0.04

As reported in Figure 5, the FTIR-ATR spectrum of a HDPE sample with surface-grafted HCCP and TFE shows a first series of bands located at 1230 and 1085 cm^{-1} that are assignable to the asymmetric stretching of the P═N bond and to the P−O−C absorption of the phosphazene substrate, respectively. The presence of the TFE is proved by a signal at 1281 cm^{-1} assignable to the asymmetric C−F stretching of the fluorinated alcohol.

Similar IR pattern could be obtained for HDPE with grafted HCCP and HDFN, the C−F symmetric stretch of this compound being at about 1150 cm^{-1}. The narrow signal at 964 cm^{-1} present in the spectrum of Figure 5 has already been assigned in the preliminary study on HDPE surface activated by plasma (vide supra).

Contact-Angle Characterization. In Table 2 are reported the values of water contact angle and the results of surface-energy measurements for virgin, plasma-treated, and functionalized HDPE samples.

Table 3. Atomic Percentages as Revealed from XPS Analysis for Virgin, Plasma-Treated, and Functionalized HDPE Samples

sample	C	O	N	P	Cl	F	N/P	F/P
1, virgin HDPE[a]	93.4	4.4						
2, Ar plasma treated HDPE	83.3	16.1	0.6					
3, HDPE+PDCP+TFE	84.1	12.5	0.9	0.7		1.8	1.32	2.59
4, HDPE+PDCP+HDFN	71.1	9.8	0.9	0.7		17.5	1.31	26.20
5, HDPE+HCCP+TFE[b]	69.5	13.0	2.6	2.3	0.6	7.8	1.14	3.41
6, HDPE+HCCP+HDFN	66.0	10.5	1.9	1.6		20.0	1.24	12.90

[a] Si contamination 2.2%. [b] Si (2.6%) and Na (1.6%) contaminations.

Plasma treatment of HDPE samples brings about a decrease in contact angle of the substrate from 106.7 to 38.8°. This is also confirmed by the higher value of surface energy, with the appearance of polar components that are originally absent in the virgin polymer.

After phosphazene grafting and substitution with fluorinated alcohols, the contact angle with water grows back and in one case even reaches a value (118.9°) higher than that of virgin HDPE. At the same time, the ratio between polar and dispersive components drops significantly, thus indicating that the grafting of the fluorinated alcohols took place. As expected, these effects are particularly evident with HDFN, which presents a longer fluorinated chain and gives evidence of an enhanced hydrophobic character of the fluorinated surfaces having water contact angles higher than 100°.

XPS Characterization. The results of XPS characterization of functionalized HDPE substrates are presented in Table 3, where the atomic percentages of different elements are reported for virgin HDPE, a plasma-treated HDPE sample, and the whole series of functionalized samples, together with two interesting atomic percentage ratios.

The presence of nitrogen and phosphorus in functionalized samples 3−6 in a N/P ratio slightly higher than 1, accounting for the success of phosphazene grafting, and the relatively low values of the atomic percentages revealed for this element indicate that the grafted layer is extremely thin, possibly monomolecular. Such percentages are higher in HCCP-containing samples than in those where PDCP has been grafted, which is striking, considering the dimensions of the two compounds and the fact that the linear phosphazene polymer is supposed to be more reactive than the corresponding trimer,[43] a fact that could lead to expectation of a higher phosphorus and nitrogen content when PDCP is exploited. This fact could be accounted on the basis of different hypotheses, such as differences in steric hindrance between these two compounds, different experimental conditions during the surface substitution, as the reaction with HCCP is performed for a longer time, at higher temperature, and in the presence of triethylamine as a catalyst, or incomplete substitution of the chlorine atoms during reactions with the fluorinated alcohols that may lead to hydrolysis phenomena and chain degradation during the final washing of the samples.

Further information can be inferred by curve fitting of the N_{1s} spectra of the samples, whose results are reported in Table 4. The N_{1s} spectrum of sample 5 is reported in Figure 6 as an example.

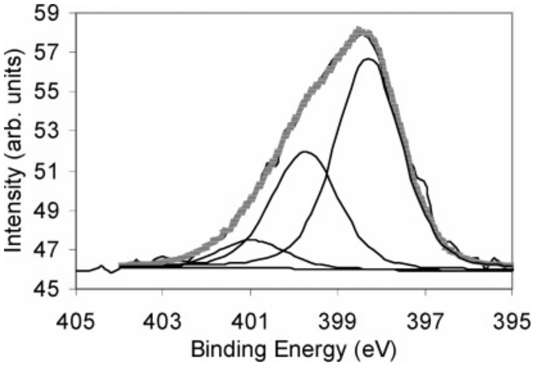


Figure 6. Curve fitting of XPS N_{1s} spectrum of sample 5 (HDPE functionalized with HCCP and TFE).

Table 4. Results for Curve Fitting of XPS N_{1s} Spectra of Functionalized HDPE Samples; Peak Areas of Each Sample are Normalized against the Component Assigned to Phosphazene Backbone Nitrogen

sample	peak position (eV)	area ratio	assignment
3, HDPE+PDCP+TFE	398.40	1.00	PDCP chain
	399.84	1.02	second comp. (see text)
	401.50	0.14	protonated N
4, HDPE+PDCP+HDFN	398.75	1.00	PDCP chain
	400.12	0.84	second comp. (see text)
	401.50	0.24	protonated N
5, HDPE+HCCP+TFE	398.30	1.00	HCCP ring
	399.75	0.56	second comp. (see text)
	400.99	0.13	protonated N
6, HDPE+HCCP+HDFN	398.54	1.00	HCCP ring
	400.00	1.01	second comp. *(see text)*
	401.34	0.20	protonated N

In all cases, there is a first component that is assignable to the phosphazenic nitrogen[63] around 398.4 eV, and a second one that is about 1.4 eV higher in binding energy. This second component, already highlighted in the case of poly[bis(trifluoroethoxy)phosphazene], was attributed by Fewell to branching in the polymer during the substitution reaction.[64] Another explanation could be: (a) the presence of phosphazane segments derived from hydrolysis phenomena,[43] which may occur in spite of the care taken to keep the reaction environment anhydrous[65] or even during the final washing of the samples if the substitution reaction was not complete or (b) the engagement of phosphazene nitrogen atoms in electrostatic interactions with the polar moieties generated by plasma activation of the substrate.

Finally, a third, less important component is present around 401.5 eV that can be tentatively assigned to protonated phosphazene nitrogens. This phenomenon could arise from the interaction with hydrochloric acid molecules that are produced in step 2 of the functionalization process.

The presence of fluorine in samples 3−6 indicates that substitution of chlorine atoms with the fluorinated alcohols actually occurs. Moreover, curve-fitting studies carried out on C_{1s} spectra of these samples reveal the appearance of new components around 293.3 eV, assigned to CF_3 groups, and around 292.2 eV in samples 4 and 6, arising from CF_2 moieties.

As far as PDCP-containing samples is concerned, the measured F/P ratios are 2.59 and 26.20 for TFE and HDFN, respectively, as reported in Table 3. Stoichiometric substitution of PDCP with the same alkoxides in solution would induce a F/P ratio of 6 for TFE and 34 for HDFN. This discrepancy could be accounted for by invoking either the incomplete substitution of the P−Cl bonds in the grafted PDCP and/or the engagement of a significant portion of the phosphorus atoms in covalent bonds with the surface of the substrates.

Moreover, looking at Tables 3 and 4, it appears evident that the higher the presence of the second component in the nitrogen spectra of the phosphazene, the lower the percentage of the grafted fluorinated alcohols.

Conclusion

This paper deals with a new, innovative method to functionalize the surface of an industrially important organic polymer, i.e., high-density polyethylene, with a variety of fluorinated alcohols using cyclic $(NPCl_2)_3$ and polymeric $(NPCl_2)_n$ chlorinated phosphazene derivatives as coupling agents.

The first step of this process implies the surface functionalization of the apolar HDPE using an argon cold low-pressure plasma to introduce a variety of polar groups on the surface of this substrate, including free hydroxylic functionalities.

These functions were reacted in a second step with chlorine-containing cyclo- and polyphosphazenes to graft these derivatives onto the surface of the HDPE substrates through the formation of strong covalent bonds such as Cl−P−O−HDPE.

The residual chlorines were eventually substituted in a third step with nucleophiles, thus changing the surface properties of HDPE plates.

The functionalized samples obtained were characterized by a variety of surface techniques, e.g., water contact angle, FTIR-ATR, and XPS spectroscopy. All the results we obtained were consistent with the effectiveness of the designed synthetic strategy to achieve surface functionalization of the HDPE material.

It should be pointed out that the surface functionalization technique we presented in this paper is completely general and could be applied in principle to a variety of polar groups to modify the surface features of any polymeric material with an almost infinite number of nucleophiles, as already explored in classical phosphazene chemistry.[66]

In the next papers of this series, in fact, we will report the plasma-induced surface functionalization of polyamide-6 plates[67] following the same synthetic procedure described in this paper and the surface functionalization of polyethylene-*co*-vinylalcohol copolymer films, which already contain free hydroxylic groups in their chemical structure.[68]

CM071002M

---

(63) Dake, L. S.; Baer, D. R.; Ferris, K. F.; Friedrich, D. M. *J. Electron Spectrosc.* **1990**, *51*, 439.

(64) Fewell, L. L. *J. Appl. Polym. Sci.* **1990**, *41*, 391.

(65) Carriedo, G. A.; Fernandez-Catuxo, L.; Garcia, Alonso, F. J.; Elipe, P. G.; Gonzalez, P. A.; Sanchez, G. *J. Appl. Polym. Sci.* **1996**, *59*, 1879.

(66) Gleria, M.; De Jaeger, R. *Top. Curr. Chem.* **2005**, *250*, 165.

(67) De Jaeger, R.; Mazzah, A.; Gengembre, L.; Frere, M.; Jama, C.; Milani, R.; Bertani, R.; Gleria, M. *J. Appl. Polym. Sci.* **2007**, submitted.

(68) Milani, R.; Gleria, M.; Gross, S.; De Jaeger, R.; Mazzah, A.; Gengembre, L.; Frere, M.; Jama, C. *Surf. Coat. Technol.* **2007**, submitted.