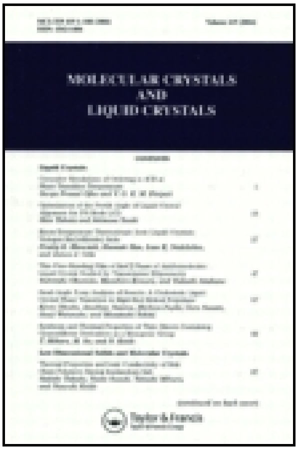

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Surface Modification of Plasma-Treated Polyamide-6 with Fluorinated Alcohols and Azobenzene Compounds using Chlorinated Phosphazenes as Coupling Agents

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Surface Modification of Plasma-Treated Polyamide-6 with Fluorinated Alcohols and Azobenzene Compounds using Chlorinated Phosphazenes as Coupling Agents

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A three-step procedure for surface functionalization of polyamide-6 plates is presented. The substrate was first treated with cold, low pressure Ar plasma to generate surface OH groups, which were successively reacted with chlorophosphazenes to ensure grafting of these molecules. Substitution of the residual chlorines of the phosphazenes with fluorinated alcohols and 4-hydroxyazobenzene yielded the final surface modification. Characterization was performed by contact angle, XPS and UV-Vis techniques.

Keywords: cold argon plasma; phosphazenes; polyamide-6; surface functionalization

INTRODUCTION

Surface functionalization allows to modify important properties of materials such as wettability, flame resistance, adhesion, biocompatibility, optical response, surface conductivity, tribology, catalytic

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activity etc, leaving bulk properties unaltered and requiring small quantities of the compounds needed for functionalization [1].

Chlorophosphazenes are compounds of formula $(NPCl_2)_n$, with n ranging from 3,4,5... units (cyclic oligomers) to over 15000 (linear polymers). As well established in literature [2], the P–Cl groups in these compounds can react with alcohols, phenols and primary or secondary amines to form covalent P–OR, P–OAr, P–NHR or $P{-}NR_2$ bonds, respectively.

In this work a three step strategy for the surface functionalization of polyamide-6 (PA6) plates is proposed, as illustrated in Figure 1.

In the first step, PA6 substrates were treated with cold, low pressure argon plasma and subsequently re-exposed to air. This process brought about several effects on the surface of the samples, including cleaning, chain scission, volatilization of small fragments and formation of radicals, that led to crosslinking and production of oxidized species at the contact with atmospheric oxygen and moisture. These oxidized species include hydroxyl, ether, carbonyl and carboxyl moieties [3].

In the second step of the procedure, plasma-treated PA6 samples were immersed in solutions of hexachlorocyclophosphazene ($N_3P_3Cl_6$, HCCP) or poly(dichlorophosphazene) ($[NPCl_2]_n$, PDCP), and the surface hydroxyls reacted with the P–Cl groups of the phosphazenes to form strong covalent P–O–C bonds.

Only a part of the reactive chlorines are utilized in this process, the remaining ones being substituted in the third step with suitable nucleophiles. This is simply performed by immersing phosphazene-grafted samples into THF solutions of alcoholates or phenates of the

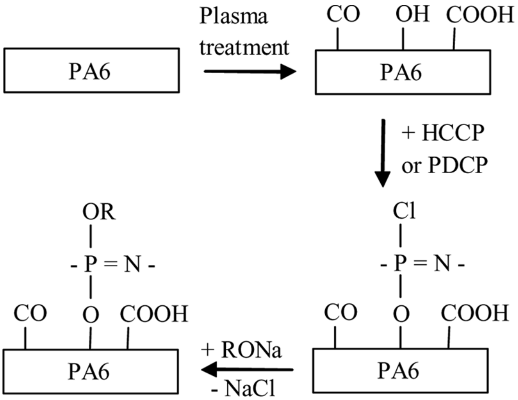

FIGURE 1 Schematic representation of the surface functionalization procedure.

selected nucleophiles, as obtained by reaction of metallic sodium with the corresponding alcohols or phenols.

In the present work, the nucleophilic substitution was performed with 2,2,2-trifluoroethanol (TFE), 1,1-*H*-heptadecafluorononanol (HDFN) and 4-hydroxyazobenzene (AzB). The fluorinated alcohols were chosen because they behave as good markers for XPS analysis, to verify the possibility of changing the hydrophilicity of the substrates, and for the known properties of poly[bis(trifluoroethoxy)] phosphazene as an antithrombogenic coating [4], while the azo compound was selected for its well-known photochromic properties [5].

Characterization of the functionalized samples was carried on by contact angle measurement, and by XPS and UV-Vis spectroscopy.

EXPERIMENTAL

Materials

Ethanol, tetrahydrofuran, chloroform, triethylamine (TEA), *n*-heptane and toluene were Aldrich products. Tetrahydrofuran, TEA and *n*-heptane were dried before use.

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. Polydichlorophosphazene, $(NPCl_2)_n$, (PDCP) was prepared as described elsewhere [6] and stored as a 37% w/w solution in 1,2,4-trichlorobenzene, with a viscosity of 44 ml/g, stabilized with 1% w/w $SOCl_2$. Before utilization, PDCP was precipitated in anhydrous *n*-heptane and redissolved in anhydrous toluene, with a concentration of 0.110 g/ml.

Metallic sodium, tetrabutylammonium bromide (TBAB), benzophenone, calcium hydride, 2,2,2-trifluoroethanol (TFE) and 1,1-*H*-heptadecafluoro-1-nonanol (HDFN) were Aldrich products used as received.

Polyamide-6 (PA6) was purchased from Goodfellow as 0.5 mm thick films, with a density of 1.13 g/cm^3. The substrate was previously cut in squares or rectangles with dimensions ranging from 10 × 10 mm to 25 × 35 mm depending on characterization needs, and cleaned by sonication in ethanol bath for 18 minutes. The samples were then dried overnight in an oven at 60°C before use.

Step 1: Plasma Treatment

Plasma treatments were performed with a Europlasma 300 PC-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-litre capacity connected to an Edwards rotative vacuum pump.

PA6 samples were put into the treatment chamber, that was evacuated to 130 m Torr pressure. Argon gas was introduced with a flux of 0.30 dm^3/min while keeping vacuum pumping going, and allowing the system two minutes to reach a steady state. The microwave generator was turned on at a power of 300 W, and the treatment was continued for three minutes. Then plasma was turned off and the chamber was brought back to atmospheric pressure by the introduction of air.

All plasma-treated samples were utilized for chlorophosphazene grafting immediately after the treatment.

Step 2: Grafting of Chlorophosphazenes

PDCP grafting. Plasma-treated PA6 plates were dipped into 20 ml of PDCP toluene solution and kept at room temperature for 7.5 h. After extraction from solution they were washed with 20 ml of anhydrous THF under stirring for 10 minutes before nucleophilic substitution in step 3.

HCCP grafting. Plasma-treated PA6 plates were dipped into a solution of 0.35 g (1.0 mmol) of HCCP and 0.9 ml (6.5 mmol) of anhydrous TEA in 10 ml of anhydrous THF, at 50°C for 24 h. After extraction from solution they were washed with 20 ml of anhydrous THF under stirring before nucleophilic substitution in step 3.

Substitution Reaction

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 added (*warning: hydrogen evolution*). At the completion of sodium consumption, a phosphazene-functionalized sample was put into the solution, which was kept stirring for 16 h at room temperature. First washing was with 10 ml of THF for PDCP-grafted samples and with 10 ml of chloroform for HCCP-grafted samples. Successive washings were the same in both cases, with 10 ml of THF, 10 ml of distilled water and again 10 ml of THF. Samples were dried in an oven at 50°C before characterization.

HDFN and AzB. 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 or 0.99 g (5.0 mmol) of AzB were added (*warning: hydrogen evolution*). The mixture was stirred for 7 h at room temperature, then residual sodium was removed, 0.02 g (0.06 mmol) of TBAB were added and a phosphazene-functionalized sample was put into the solution, which was stirred for 16 h at room temperature. First washing was with 10 ml of THF for PDCP-grafted samples and with 10 ml of chloroform for HCCP-grafted samples. Successive washings were the same in both cases, with 10 ml of THF, sonication for 30 minutes in a 15 ml THF/6 ml distilled water mixture, washing with 10 ml of distilled water and then with 10 ml of THF. Finally, HDFN-functionalized samples also underwent an 8 h soxhlet extraction with THF and were eventually dried in an oven at 50°C before characterization.

RESULTS AND DISCUSSION

Contact Angle Characterization

The results of contact angle measurements are shown in Table 1.

It appears evident that plasma treatment lowered contact angle with water and increased surface energy as an effect of the creation of new polar moieties; this was confirmed also by the marked increase of the polar component of surface energy.

Nucleophilic substitution in step 3 caused contact angle with water to grow back, especially when fluorinated alcohols were used, reaching values higher than that of virgin PA6. In the case of sample 4, where surface modification was performed with PDCP and HDFN, a contact angle with water as high as 123° was reached, with a value of surface energy as low as 7.1 mJ/m^2. These findings supported the success of the functionalization reaction.

TABLE 1 Contact Angles with Water and Values of Surface Energy, with Polar and Dispersive Components

Sample	Water contact angle (°)	Surface energy (mJ/m^2)		
		Total	Polar	Disp.
1-Virgin PA6	76.5	39.6	5.2	34.4
2-PA6 + Ar plasma	43.3	60.9	21.0	40.0
3-PA6,Ar + PDCP + TFE	103.1	15.3	3.0	12.3
4-PA6,Ar + PDCP + HDFN	123.2	7.1	1.0	6.2
5-PA6,Ar + PDCP + AzB	92.3	45.6	0.3	45.3
6-PA6,Ar + HCCP + TFE	99.0	36.4	0.2	36.2
7-PA6,Ar + HCCP + HDFN	99.7	23.8	0.8	23.0
8-PA6,Ar + HCCP + AzB	81.6	45.1	2.4	42.8

TABLE 2 Atomic Percentages as Revealed from XPS Analysis

Sample	C	O	N	P	F
1	77.1	12.4	10.4	—	—
2	70.6	16.9	11.1	—	—
3	58.6	14.6	10.3	2.2	14.3
4	49.6	8.2	6.0	1.3	34.8
5	73.7	13.3	11.7	1.3	—
6	67.5	14.0	11.1	1.5	5.8
7	59.6	14.3	8.9	2.1	15.1
8	68.4	15.8	12.2	3.3	—

XPS Characterization

The atomic percentages for the surface composition of the samples, as revealed from XPS analysis, are exposed in Table 2.

The oxidizing effect of the plasma treatment was assessed by the growth in oxygen content (O/C ratio grew from 0.16 to 0.24 as a consequence of plasma exposure) and by the appearance of two new components in the curve fitting of C_{1s} spectrum, shown in Figure 2, at 286.9 eV and at 288.6 eV, assigned to alcohol/ether [7] and carboxyl groups [8]; the other visible components of the spectrum at 285.9 eV and 287.9, already present in virgin PA6, are assigned to nitrogen-bonded and amidic carbon, respectively.

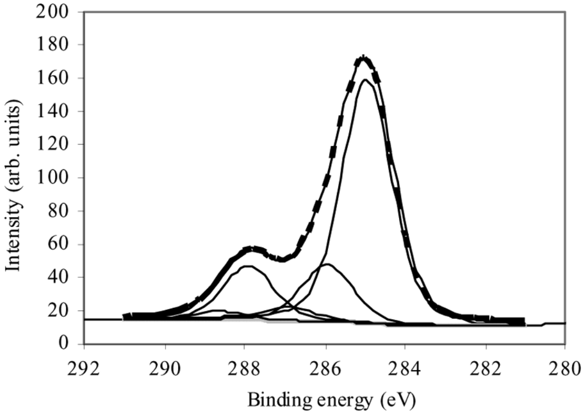

FIGURE 2 Curve fitting of C_{1s} XPS peak; the envelope is represented by the dashed curve.

The effectiveness of phosphazene grafting was indicated in samples 3 to 8 by the presence of phosphorus at 134.0 eV, and by the appearance of a new component in the curve fittings of N_{1s} spectra at 398.1 eV. Both signals are assignable to the phosphazene ring [9]. The revealed phosphorus percentages seem to indicate that an extremely thin layer was grafted, as expected. The fact that reported P percentages were quite similar when HCCP and PDCP were used might be surprising, in consideration of the different dimensions of these compounds and the higher reactivity of PDCP chlorines [10], but could be explained on the basis of the different experimental conditions employed for the grafting of these two compounds (higher temperature, longer reaction time and presence of triethylamine catalyst in the case of HCCP), of steric reasons, and possibly of the effect of an incomplete substitution of chlorine atoms in step 3 that would expose the phosphazene chain or ring to hydrolysis and degradation phenomena, towards which PDCP is more prone than HCCP [10].

Similarly, the success of the substitution of residual chlorine atoms with fluorinated alcohols in the third step of the procedure was assessed by the presence of fluorine in the XPS spectra of samples 3, 4, 6 and 7, together with the appearance in their C_{1s} curve fitting spectra of components at about 293.1 eV and 291.9 eV (samples 4 and 7 only), that were assigned to CF_3 and CF_2 carbons, respectively.

As far as azobenzene-functionalized samples (5 and 8) are concerned, their relatively higher content of carbon and nitrogen in comparison to the other functionalized samples gave an indication of the presence of this moiety on the surface of the PA6 plates; anyway, an unequivocal support to the success of the grafting of AzB came from the UV-Vis spectroscopic analysis, reported below.

UV-Vis Characterization

Samples functionalized with AzB were analyzed also by means of UV-Vis spectroscopy in reflectance conditions, to verify the photochromic properties induced by the presence of the azo compound and their reversibility. The azobenzene molecule in fact can exist in a *trans* and in a *cis* form, characterized by different absorption bands at 330 nm and 430 nm, respectively; interconversion between the two isomers can be induced photochemically from *trans* to *cis* and *vice versa*, or thermally from *cis* to *trans* [5].

Thus samples were exposed to 365 nm radiation collecting spectra at different irradiation times, and subsequently underwent a thermal relaxation treatment in an oven at 50°C.

The collected spectra for sample 5 are reported in Figure 3.

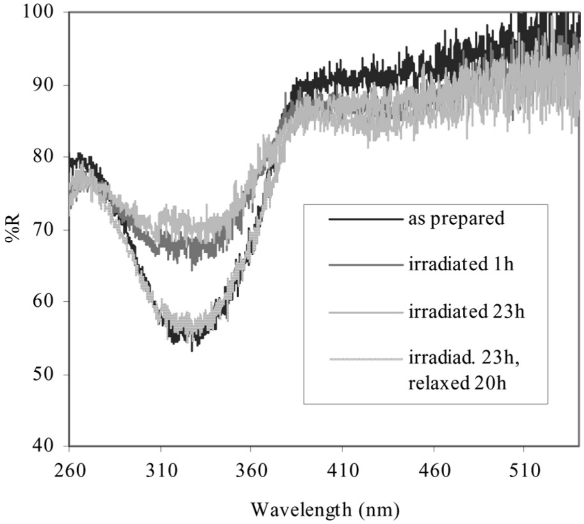

FIGURE 3 UV-Vis spectra of sample 5 in reflectance conditions, collected at different irradiation times with 365 nm light and after subsequent thermal relaxation at 50°C.

The presence of the bands associated with the two azobenzene isomers accounted for the success of the substitution reaction with AzB in step 3. As the functionalized PA6 plates were exposed to UV radiation, the absorption band associated with the *trans* isomer decreased in intensity, while the one relative to the *cis* form grew.

Moreover, as it appeared from the reported spectra, the subsequent thermal relaxation afforded an almost complete recovery of the initial status of the system, therefore demonstrating the reversibility of the photochromic transition.

CONCLUSION

Surface modification of Ar plasma-treated PA6 with 4-hydroxyazobenzene and with fluorinated alcohols of different length was obtained using cyclic and polymeric chlorophosphazenes as functionalization intermediates. Samples were characterized by contact angle measurement, XPS and UV-Vis spectroscopy, and the results supported the effectiveness of the proposed functionalization pathway.

It should be noted that the proposed procedure is of general nature, and could in principle allow the surface modification of substrates different from PA6, and the introduction on their surface of a great number of different organic compounds able to grant a range of different chemical and physical properties. This is possible thanks to the remarkable synthetic versatility of phosphazene chemistry, as widely demonstrated in literature [2].

In this regard, we have already obtained similar results for the surface functionalization of high density polyethylene, a polymer that is apolar in nature [11].

REFERENCES

[1] Allcock, H. R. (1998). *Appl. Organomet Chem.*, *12*, 659.

[2] Gleria, M. & De Jaeger, R. Eds. (2004). *Phosphazenes. A Worldwide Insight*, NOVA Science Publishers: Hauppauge, New York, USA.

[3] Guruvenket, S., Mohan Rao, G., Komath, M., & Raichur, A. M. (2004). *Appl. Surf. Sci.*, *236*, 278.

[4] Grunze, M. (2001). *PCT Int. Appl. WO*, 01 70,296 (2001). *Chem. Abstr.*, *135*, 262311, assigned to Polyzenix GmbH, Germany.

[5] Irie, M. (1990). *Pure Appl. Chem.*, *62*, 1495.

[6] Helioui, M., De Jaeger, R., Puskaric, E., & Heubel, J. (1982). *Makromol. Chem.*, *183*, 1137.

[7] Yip, J., Chan, K., Sin, K. M., & Lau, K. S. (2003). *J. Appl. Surf. Sci.*, *205*, 151.

[8] Davies, M. C., Lynn, R. A. P., Hearn, J., Paul, A. J., Vickerman, J. C., & Watts, J. F. (1996). *Langmuir*, *12*, 3866.

[9] Dake, L. S., Baer, D. R., Ferris, K. F., & Friedrich, D. M. (1990). *J. Electr. Spectr.*, *51*, 439.

[10] Allcock, H. R. (1972). *Phosphorus-Nitrogen Compounds. Cyclic, Linear, and High Polymeric Systems*, Academic Press: New York, USA.

[11] Milani, R., Gleria, M., Sassi, A., De Jaeger, R., Mazzah, A., Gengembre, L., Frere, M., Jama, C. (2007). *Chem. Mater.*, *19*, 4975.