Functionalization of Sisal Fibers and High-Density Polyethylene by Cold Plasma Treatment

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ABSTRACT: Chopped sisal fibers and finely powdered high-density polyethylene were surface functionalized using dichlorosilane (DS) under radio frequency (RF)-plasma conditions and characterized by electron spectroscopy for chemical analysis (ESCA) and fluorescence labeling techniques. A high-capacity (10 L), rotating, 13.56 MHz, electrodeless plasma installation, specially designed to allow the uniform surface modification of powdery and particulate matter of irregular shape, was used. A three-factor fractional experimental design was employed to evaluate the effect of RF-power, pressure, and reaction time on the ESCA-based relative atomic composition of plasma-treated samples. It was demonstrated that —SiH_xCl_y functionalities are present on plasma-exposed surfaces and these functionalization reactions can be controlled by selecting proper plasma parameters. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 2145–2154, 2002

Key words: cold plasma; sisal; polyethylene; dichlorosilane plasma; surface functionalization

INTRODUCTION

The cold plasma technique is a very promising approach for the surface functionalization of different types of materials. It has been demonstrated that efficient surface-modification reactions can be carried out even on inert polymer surfaces, such as Teflon and polypropylene.[1–13] Natural polymer- and thermoplastic-based composites represent a very attractive approach to create products with properties that combine the desired characteristics from each constituent component.[14,15] Characteristics like biodegradability, advanced mechanical properties, etc. can

be tailored in this way. However, generation of high-tech composites from these dissimilar materials requires surface modification of one or both constituents to achieve the necessary compatibility of surface energies.[14–16] Conventional compatibilization techniques involve wet chemical methods for the modification of lignocellulosic components and involve mainly the primary and secondary hydroxyl groups of the polysaccharide chains.[17–19] The surface functionalization of thermoplastics (polyolefins) is much more difficult because of the strong chemical inertness of these materials. Current modification methods are primarily based on aggressive surface oxidation reactions involving mineral acids (e.g., chromic acid) or the utilization of expensive copolymers.[20–22] Many of these approaches are not cost effective and are not environmentally friendly.[17]
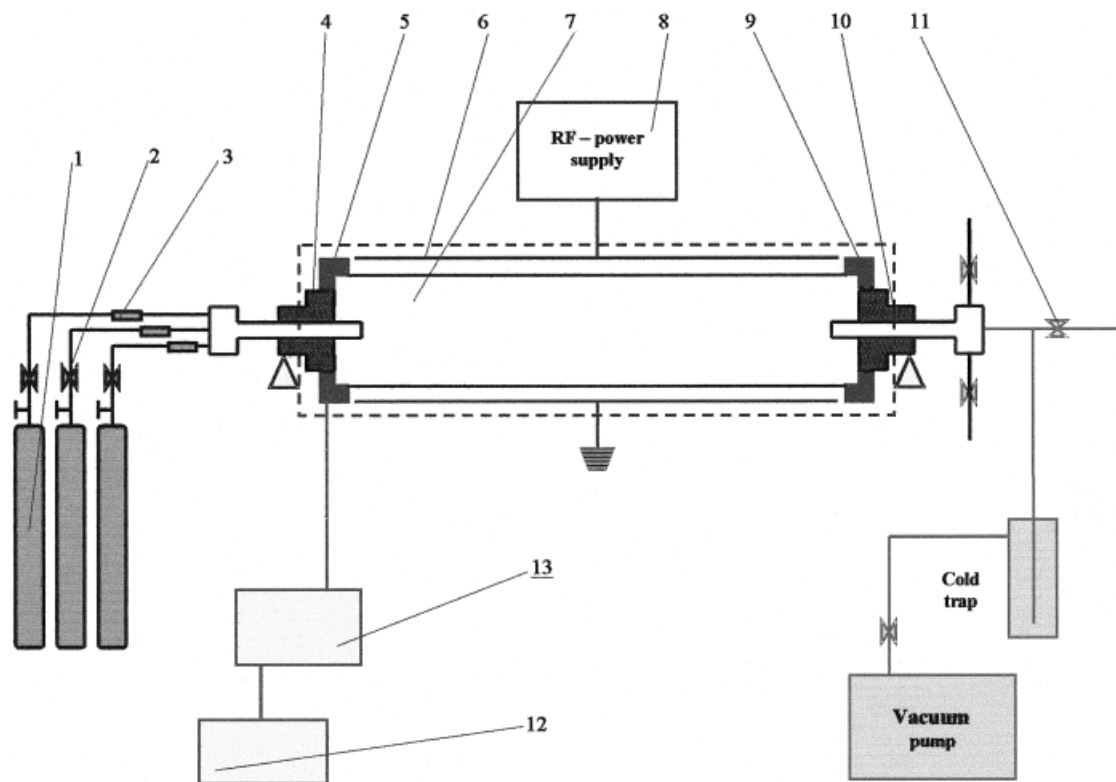
Figure 1   Scheme of originally designed rotating, 13.56 MHz-RF-plasma installation.

Cold plasma chemistry opens up a new way for the surface modification of materials for composites and other applications.[15,16] The energies of neutral and charged plasma species, including electrons, ions of either polarity, free radicals, excited species, atoms, molecules, and photons, are comparable to the bond energies involved in all organic compounds and, as a consequence, both the gas phase and surface molecular fragmentation and recombination processes can be controlled by selecting the proper plasma parameters.[17,23]

Cold plasma-enhanced functionalization reactions will only be adequate for the modification of components for melt processing compounding if the surface area of the substrate is very large relative to its volume, which is crucial for the development of interaction between the fibers and the matrix.[15,24,25] In this paper the functionalization of sisal fibers (chopped form) and high-density polyethylene (powder) with dichlorosilane on a radio frequency (RF)-plasma reactor was investigated under different conditions, and the nature of plasma-generated surface functionalities of specimens was analyzed and discussed.

MATERIALS AND METHODS

Materials

High-density polyethylene (PE) powder (type IE-59 U3), with a melt-index of 5.0 g/10 min (ASTM-1238) and density of 0.959 g/cm^3 (ASTM-D792), and sisal (S) fibers were supplied by Politeno S.A. and Incomar-Brazilian Industry Company, respectively. Dichlorosilane (DS, SiH_2Cl_2) and diamine propane vapor [PD, $NH_2(CH_2)_3NH_2$] were purchased from Gelest Company and Aldrich, respectively. Fluorescamine ($C_{17}H_{10}O_4$) was purchased from Aldrich.

DS Plasma Treatment

DS plasma treatment was used to functionalize the surfaces of PE and S samples, as described next. All plasma treatments were carried out in an originally designed, rotating, 13.56 MHz, RF-plasma installation capable of uniform surface treatment of powdery and fiber-type substrates (Figure 1). The plasma installation is composed of a Pyrex glass chamber (7) with connecting rubber and stainless steel rings[5,9] on both ends. The vacuum-tight connections of the reactor to the liquid

Table I Relative Atomic Composition of Untreated and DS Plasma-Treated and PD-Derivatized PE Samples

No.	Power (W)	Time (min)	Pressure (mTorr)	C (%)	O (%)	Si (%)	Cl (%)	N (%)
Untreated	—	—	—	98.2	1.8	—	—	—
1	200	9	150	55.2	23.1	6.0	5.0	10.6
2	200	5	150	60.3	22.2	5.5	4.2	7.8
3	200	1	150	60.9	25.7	5.7	1.8	5.8
4	270	7.8	150	50.3	27.9	9.1	3.2	9.3
5	270	2.2	150	50.4	28.5	9.6	3.0	8.5
6	130	2.2	150	64.5	18.3	5.3	2.7	8.2
7	250	5	150	69.0	13.9	4.7	3.9	8.5
8	100	5	130	66.7	22.7	5.7	4.9	2.4
9	100	5	200	51.8	29.8	8.9	3.4	6.0
10	200	5	130	65.6	21.3	5.7	2.6	4.8
11	300	5	200	67.4	18.3	3.6	2.9	7.9
12	130	7.8	170	50.8	25.3	8.7	6.0	9.2
13	130	2.2	170	61.5	22.9	5.6	2.7	7.2

and gas supply systems and to the vacuum line are assured with the aid of two ferrofluidic feedthroughs.[4,10] The hollow shaft of the stainless steel chambers is made of special magnetic material, which is a part of the ferrofluidic sealing system. The RF-power is transferred to the reactor through two semicylindrical copper electrodes[6] located outside the reactor, from a 1000 W, 13.56 MHz RF-power supply and matching network assembly.[8] A large cross-section gate valve[11] separates the reactor from the vacuum line and controls the outflow of the plasma gases. The vapor and gas flow into the reactor is controlled by individual flow controllers.[2,3] The rotation of the reactor at various angular velocities is assured by a digitally speed-controlled electric engine transmission system.[12,13]

PE and S samples were submitted, respectively, to 13 and 16 different plasma treatments (Table I and II) to investigate the influence of external plasma parameters (power, treatment time, and pressure) on the relative atomic composition of the samples.

Diamine propane (PD) Derivatization

PD derivatization of DS plasma-treated PE substrates was carried out, as described later, to investigate the formation of C—Si bonds during the DS plasma treatment of PE surfaces.

Right after the DS plasma treatment of PE in the rotating reactor, PD was allowed to react with the treated PE for 30 min vacuum conditions. Every 5 min, the reaction chamber was evacuated

to remove the byproduct of the reaction (HCl), and fresh reagent was added. The product was then collected and one portion was examined by ESCA. The other portion was subjected to a fluorescamine test to investigate the presence of primary amine groups on the plasma-treated and PD-derivatized PE, using a fluorescence labeling technique.[26] For this technique, a solution of fluorescamine (10% by weight in acetone) was sprayed three times over a control sample (pure untreated PE) and the DS plasma-treated and PD-derivatized PE samples. The fluorescence of the substrates was revealed with the aid of a Black-Ray UV lamp (model UBL 21; UVP Inc., San Gabriel, CA) and an FCR-10 photo camera (Fotodyne Inc., Hartland, WI). The derivatized sample was then rinsed with acetone (good solvent for fluorescamine), washed with water, and re-tested for fluorescence.[26]

Electron Spectroscopy for Chemical Analysis (ESCA)

Survey and high-resolution ESCA multiplex spectra were taken with a Perkin-Elmer PHI 5400 Spectrometer (Mg X-ray source; 15 kV; 300 W; 45°). ESCA survey spectra were collected in the range 0–1000 eV binding energy, with a resolution of 1.0 eV. The pass energy of the electron energy analyzer was set at 89.45 eV. The high-resolution ESCA multiplex spectra were collected for all the elements identified from the survey scan (C_{1s} and O_{1s}, for untreated samples, and Si_{2p}, Cl_{2p}, Si_{2s}, and N_{1s} for treated samples). The

Table II   Relative Atomic Composition of Untreated and DS Plasma-Treated Sisal Samples

No.	Power (W)	Time (min)	Pressure (mTorr)	C (%)	O (%)	Si (%)	Cl (%)
Untreated	—	—	—	71.7	28.3	—	—
1	200	0.5	200	51.3	38.3	9.7	0.7
2	200	4.5	200	83.7	14.7	1.6	—
3	200	2.5	100	57	37.1	4.5	1.0
4	200	2.5	300	45.7	42.6	9.9	1.8
5	100	2.5	200	33.3	52.1	13.7	0.9
6	300	2.5	200	69.3	26.6	4.1	—
7	140	1.3	140	78.7	20.3	1.0	—
8	140	3.7	140	79.0	18.0	3.0	—
9	140	1.3	260	39.6	43.3	15.6	1.5
10	140	3.7	260	50.1	41.4	6.7	1.8
11	260	1.3	140	46.0	43.1	7.4	3.4
12	260	3.7	140	59.2	30.4	9.1	1.4
13	260	1.3	250	36.1	50.2	12.8	1.0
14	260	3.7	250	48.6	39.6	11.8	—
15	200	2.5	200	76.2	20.9	2.9	0.0
16	200	2.5	200	79.9	18.8	1.3	—

energy resolution for a multiplex scan was 0.05 eV, with a pass energy of 35.75 eV. The surface atomic composition was calculated with the provided system software based on the peak intensity corrected for atomic sensitivity factors. It should be mentioned that the assignments of C_{1s} and Si_{2p} high-resolution, deconvoluted binding energy peaks resulting from virgin and plasma-treated PE and sisal substrates were made according to "The Scienta ESCA300 Database"[27] and to similar assignments used for chemical linkages identified on plasma-synthesized and plasma-treated polymeric surfaces.[28-37]

Influence of External Plasma Parameters

A three-factor fractional experimental design was used to evaluate the effect of RF power, pressure, and reaction time on the ESCA-based relative atomic composition of plasma-treated PE samples. The least squares equations that best described the silicon, chlorine, and nitrogen ESCA relative atomic concentrations in terms of power, time, and pressure for DS-RF-plasma-treated PE (second order, 3 polynomial variables) are:

$$Si = -2.604 - 2.833 \cdot 10^{-3} \cdot w - 2.378$$
$$\times t + 0.188 \cdot p + 4.279 \cdot 10^{-4} \cdot w^2 + 0.102 \cdot t^2$$
$$- 3.584 \cdot 10^{-4} \cdot p^2 - 2.948 \cdot 10^{-3}$$
$$\times w \cdot t - 9.078 \cdot 10^{-4} \cdot w \cdot p + 0.014 \cdot t \cdot p \quad (1)$$

$$Cl = -32.941 - 0.033 \cdot w + 2.873$$
$$\times t + 0.409 \cdot p + 4.93 \cdot 10^{-5} \cdot w^2$$
$$- 0.05 \cdot t^2 - 1.257 \cdot 10^{-3}$$
$$\times p^2 - 4.83 \cdot 10^{-3} \cdot w \cdot t + 1.776 \cdot 10^{-4} \cdot w$$
$$\times p - 6.792 \cdot 10^{-3} \cdot t \cdot p \quad (2)$$

$$N = -70.431 + 0.024 \cdot w - 1.243 \cdot t + 0.91$$
$$\times p - 3.023 \cdot 10^{-5} \cdot w^2$$
$$+ 0.0024 \cdot t^2 - 2.72 \cdot 10^{-3} \cdot p^2$$
$$+ 1.476 \cdot 10^{-3} \cdot w \cdot t - 4.907 \cdot 10^{-5} \cdot w$$
$$\times p + 6.893 \cdot 10^{-3} \cdot t \cdot p \quad (3)$$

where Si, Cl, and N are the theoretical relative atomic concentrations, w is the power (W), p is the pressure (mTorr), and t is the treatment time (min).

RESULTS AND DISCUSSION

ESCA Analysis of DS Plasma-Treated-PE

The external plasma parameters employed for the surface modification of PE and the relative surface atomic composition of untreated, and plasma-treated and PD-derivatized PE samples are presented in Table I. The virgin PE contains only a low percent (1.8%) of processing origin oxygen.
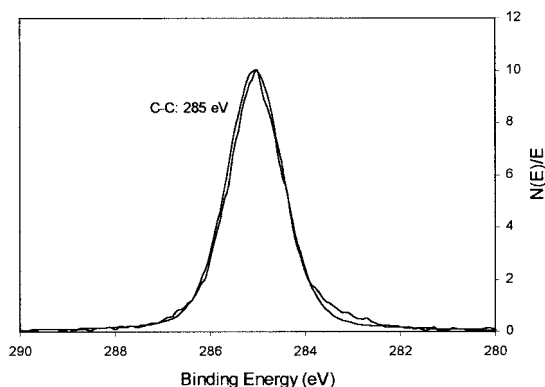
Figure 2 High-resolution ESCA diagram of Cls peak of untreated PE.

The high-resolution diagram of unmodified PE (Figure 2) shows a very symmetrical 285 eV binding energy peak, which is in good agreement with the survey ESCA results, indicating a very low level of processing origin oxidation.

Because the DS plasma-induced reactions only functionalized the PE surface, the resulting modified layers are thinner than 100 Å and the C—C (285 eV) binding energy peak will dominate all spectra. It should also be assumed that a part of the plasma-generated SiH_xCl_y species will not be directly connected to the PE surfaces through C—Sl bonds. The non-bound species are removed by vacuum during the plasma processes, and their higher molecular weight derivatives will generate SiO_2 under open laboratory conditions. In addition, the binding energy value of the C—Si bond (284.4 eV) is fairly close to that of the C—C linkage and, as a result, the identification on the PE surfaces of C—Si bonds, based on deconvoluted high-resolution ESCA data, is difficult. To solve this problem, *in situ* PD-based derivatization reactions were carried out on DS plasma-functionalized PE surfaces because the presence of nitrogen in the relative surface atomic composition is indicative of the formation of C—Si(Cl)$_y$ functionalities on the PE surfaces.

The relative surface atomic composition of DS plasma-treated and PD-derivatized PE substrates (Table I) clearly shows that fairly high Si (3.6–9.6%) and N (4.8–10.6%) concentrations can be achieved. Two typical high-resolution ESCA diagrams of DS plasma-treated, and DS plasma-treated and PD-derivatized PE are presented in Figures 3A and 3B, respectively. The C—C (285 eV) and C—O and C≡O (286.7 and 288 eV, respectively) binding energy peaks dominate the spectra and C—N (285.6 eV) and C—Si (284.4 eV) bonds are also present. The existence of C—O and C≡O functionalities on the DS plasma-treated PE substrate surfaces are probably related to the generation of free radical sites by dehydrochlori-
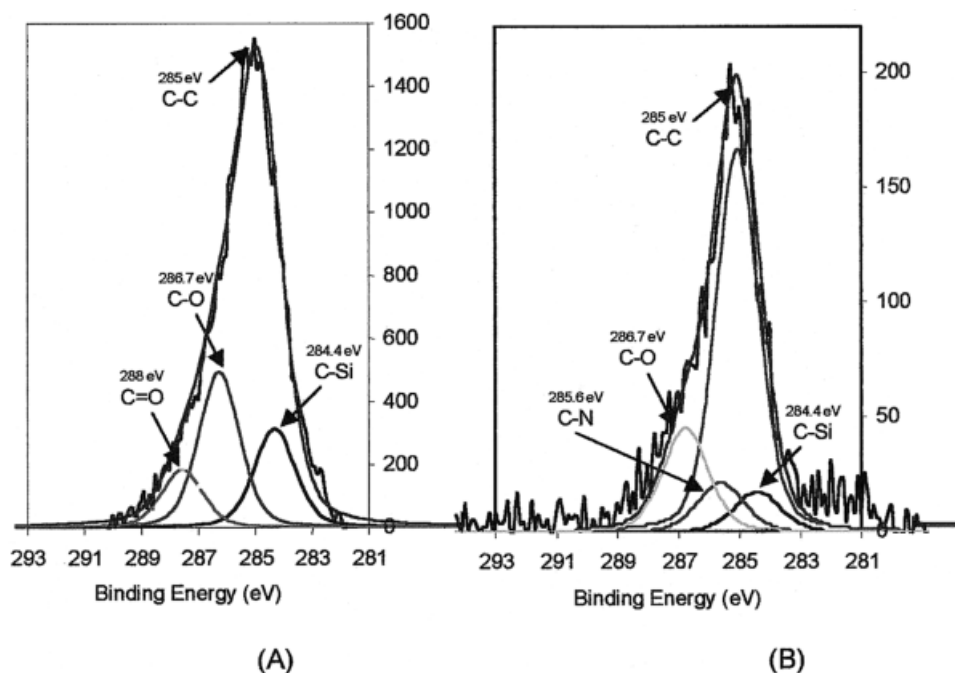

Figure 3 High-resolution ESCA diagram of Cls peak: (A) DS plasma-treated PE; (B) DS plasma-treated and PD-derivatized PE.
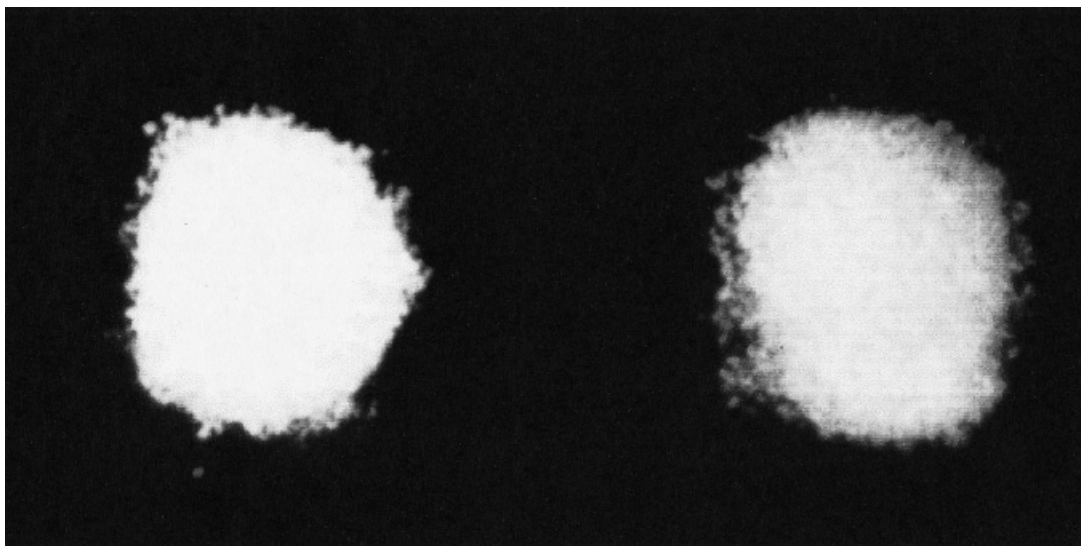
Figure 4 Fluorescence images of DS plasma-treated and PD-derivatized PE (left) and untreated PE (right).

nation mechanisms; under open laboratory conditions (OLC), these active species will certainly initiate oxidation processes. The slightly higher C—C : C—Si peak area ratio (10.71) of DS plasma-treated and PD-derivatized PE in comparison with the DS plasma-exposed PE (6.02) also is indicative of the presence of a C—C-containing deposition, as a result of the PD derivatization reaction.

Identification of the PD-Based Primary Amine Surface Functionalities

Fluorescamine-labeled virgin and DS plasma-treated and consecutively PD-derivatized PE substrates show that fluorescence is associated with both plasma-exposed and virgin PE substrates. However, it should be noted that the fluorescence of plasma-modified PE is significantly more intense in comparison with untreated PE (Figure 4) because of the presence of primary amines in the DS plasma-treated and PD-derivatized PE. The fluorescence of PE can be related to synthesis or processing origin contamination of PE (e.g., catalysts, initiators, etc.).

Influence of Plasma Parameters on the Relative Surface N, Si, and Cl Atomic Compositions of DS Plasma-Treated PE

The magnitudes of external plasma parameters (treatment time, pressure, and power) show a strong influence on the relative surface atomic composition. Surface responses under various

plasma parameter conditions (pressure, power, and treatment time) of relative Si atomic concentrations are presented in Figures 5A, 5B, and 5C; respectively. It should be noted that the Si concentration variation in each diagram is presented under two variable parameter conditions, whereas one of the parameters selected from the center of the parameter range has been maintained constant. High power and high pressure conditions generate the highest Si concentrations (Figure 5A). The influence of power, at various DS pressure values, generates Si concentration variations that are developing always through minimal values. This result suggests that at least two different Si-based deposition reaction mechanisms are present under different pressure and RF-power conditions. It can be assumed that not all of the plasma-generated SiH_xCl_y species will be covalently linked to the PE chains. Some of them can result in the formation of polysilane- and polyhalosilane-type structures, which will undergo, under OLC, hydrolyzation reaction mechanisms associated with the generation of SiO_2 or polysilicic acid-type derivatives.

The simultaneous influence of the RF-power and treatment time on the Si atomic concentrations (Figure 5B), at constant pressure environments, shows a dependence that indicates that both parameters induce Si concentration variations, which are passing through minimal values. However, the influence of pressure and treatment time (at constant RF-power) on the Si atomic concentrations is slightly different relative to the
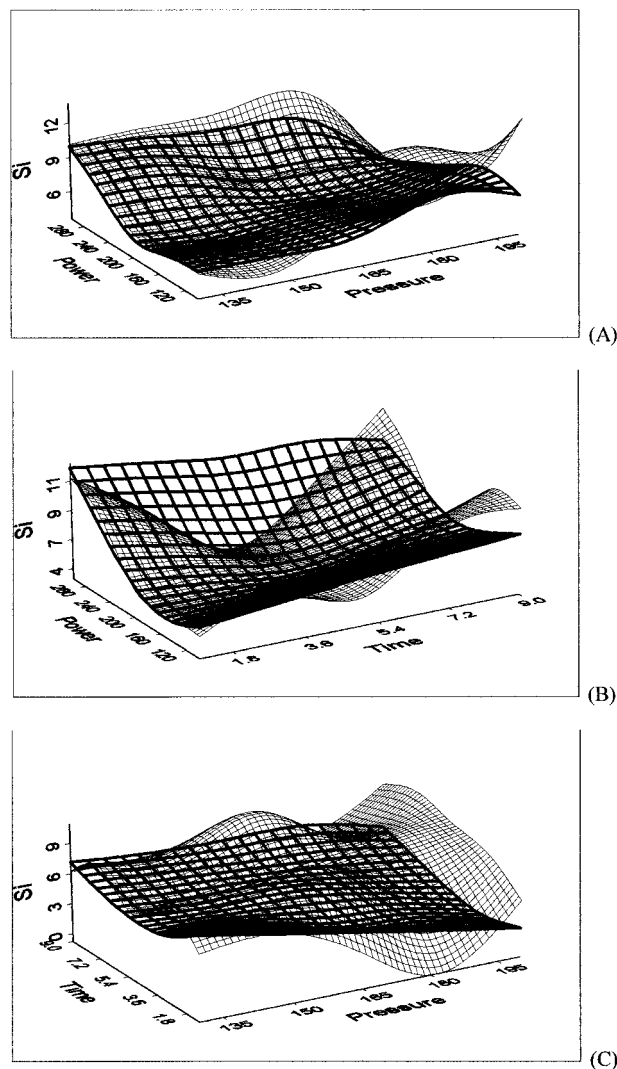
Figure 5 Experimental and theoretical (thick mesh lines) PE surface responses of relative silicon atomic concentrations generated under various plasma parameter conditions: pressure (mTorr), power (W), and treatment time (min).

other parameter pairs. High pressure and low treatment time conditions generate the lowest concentration values, whereas low pressure and low and high treatment time environments create the highest Si atomic concentrations.

Earlier it has been established, using actinometric evaluations,[38] that both the DS pressure in the reaction chamber and the RF-power dissipated to the electrodes have a significant influence on the 13.56 MHz, DS plasma-generated, relative chlorine atomic concentrations (Figure 6). It was demonstrated that at RF powers (at constant DS pressure) < 150 W, the Cl/Ar line intensity ratios indicate the presence of negligible

amounts of atomic chlorine, whereas higher powers significantly increase the chlorine atomic concentrations, followed by a Cl/Ar line intensity plateau starting around 300 W. Conversely, low DS pressure conditions (at constant RF-powers) in the vicinity of 150 mT, generate intense chlorine-splitting reactions, whereas high pressures of DS significantly diminish the chlorine concentrations.

The presence of chlorine atoms will mainly generate dehydrochlorination reactions in the presence of SiH_xCl_y (x and y < 2) species because the affinity of chlorine is higher to hydrogen than to carbon. The corresponding bond energies reflect these affinities: C—H 5.3 eV; Cl—H, 4.52 eV; and Si—H, 3.1 eV. Accordingly, the chlorine concentration of DS plasma-exposed PE substrates should be fairly low.

The relative surface chlorine concentration and the plasma-parameters-dependent chlorine concentration surface responses (Table I and Figure 7) also reflect these affinities. According to the actinometric evaluations, low pressure (130 mT) and high power (300 W) conditions generate the highest Cl atomic concentrations in the gas phase of the DS discharges. These environments will obviously lead to the development on the PE substrate surfaces of strong dehydrochlorination reactions with the generation of fairly stable and volatile HCl. These molecules will easily leave the system due to the vacuum conditions. Chlorine atoms recombined with plasma-generated free radical sites on PE surfaces can be extracted by subsequent dechlorination reactions by the omni-
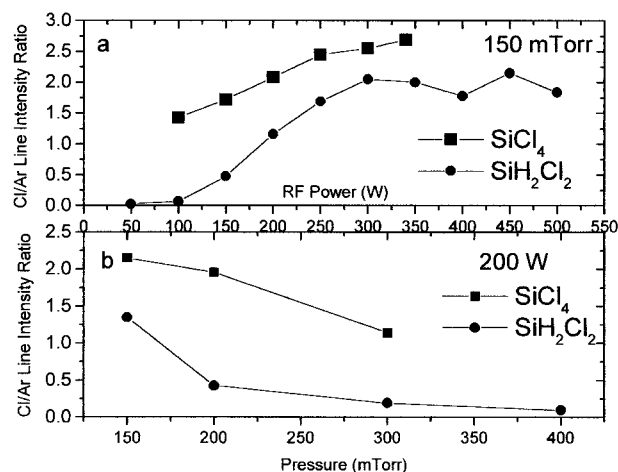

Figure 6 Chlorine-to-argon line intensity ratios in SiH_2Cl_2 and $SiCl_4$ plasmas, using an RF frequency of 13.56 MHz and rotating electrodless reactor, as a function of (A) RF power and (B) pressure.
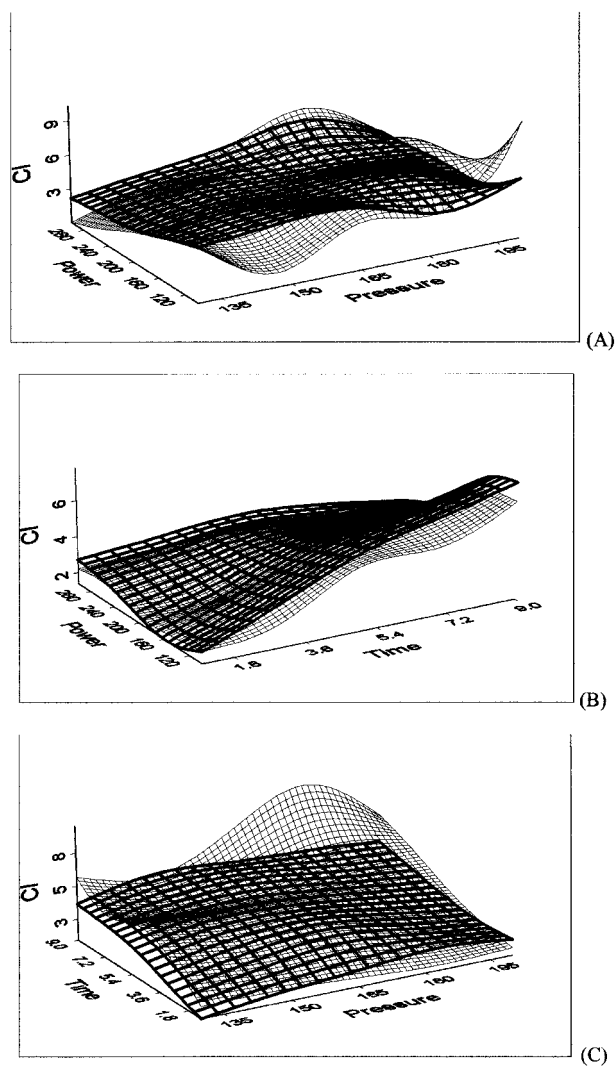
Figure 7 Experimental and theoretical (thick mesh lines) PE surface responses of relative chlorine atomic concentrations generated under various plasma parameter conditions: pressure (mTorr), power (W), and treatment time (min).

alities are indicative of the existence of C—Si bonds, and the surface responses of nitrogen atomic concentrations will actually reflect the plasma parameter-dependent concentrations of PE-Si-Cl_y functionalities (Figure 8). At constant treatment time values, the RF-power does not have a significant influence on the primary amine functionalities and the nitrogen concentrations record the highest values in the middle of the pressure range (Figure 8A). Similarly, the pressure/time dependence shows only a slight increase in the concentration of primary amine
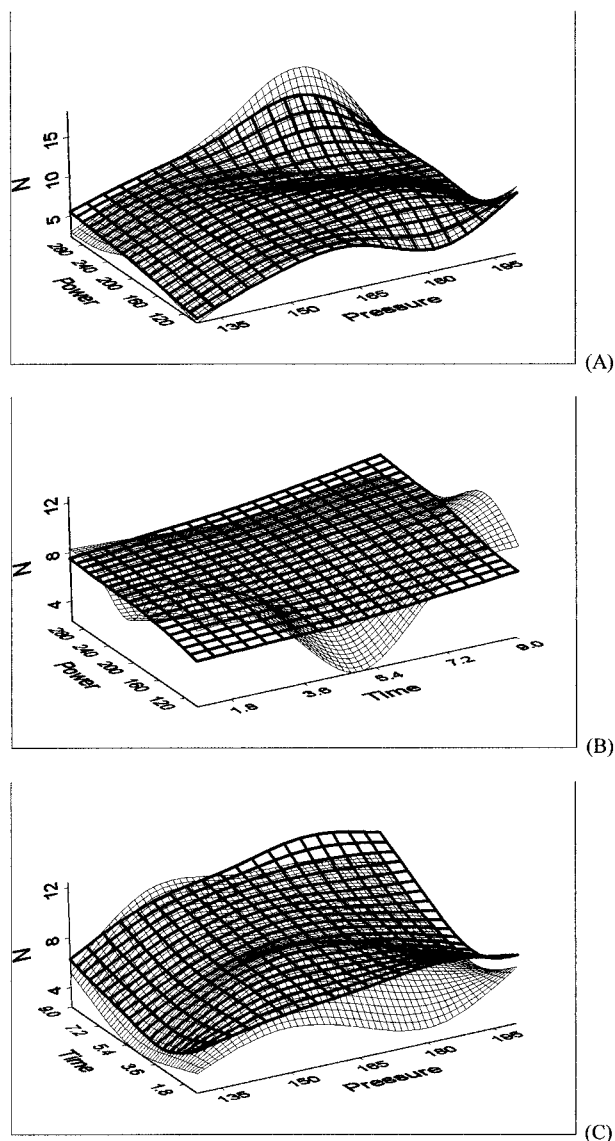

Figure 8 Experimental and theoretical (thick mesh lines) PE surface responses of relative nitrogen atomic concentrations generated under various plasma parameter conditions: pressure (mTorr), power (W), and treatment time (min).

present SiH_xCl_y species. These suggested mechanisms might also explain the presence of low chlorine concentration under high power and low pressure environments (Figure 7A).

The time/power and time/pressure dependence of chlorine atomic concentrations on PE surfaces are more complex (Figures 7B and 7C). Further actinometric evaluations would be required to understand the reaction mechanisms.

The surface responses of plasma parameter-dependent N relative atomic concentrations are most relevant for the surface functionalization of DS plasma-exposed PE. The presence of nitrogen atoms and especially the primary amine function-

functionalities, as a result of increased treatment time period, whereas the pressure generates the highest nitrogen atomic concentrations in the middle of the pressure interval, under similar conditions (Figure 8C). The time/power dependence clearly indicates the generation of the highest N concentrations at the highest power and treatment time environments (Figure 8B).

ESCA Analysis of Surface-Modified Sisal Fibers

Sisal fibers contain $\sim$ 74% cellulose, 10% lignin (locate mainly in the extra-crystalline zone), 11% hemicelluloses and pectins, 3.5% waxes, and 1.5% ash. Because of the high polysaccharide content, the surface characteristics and functionalities of these high tensile strength and modulus fibers should be comparable to those of cellulose. The presence of OH functionalities in the cellulosic and hemicellulosic macromolecular chains make these fibers functional (polar functionalities).

The experimental conditions employed during the DS plasma treatment of sisal fibers and the ESCA-based relative surface atomic compositions are shown in Table II. In general, the presence of
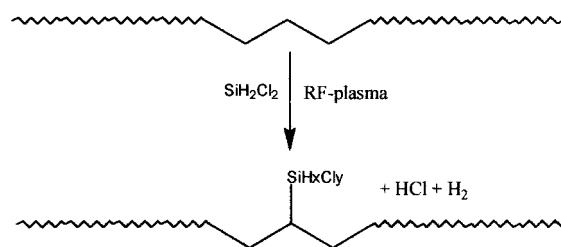
Scheme 1   Sisal fibers exposed to DS plasma result in the formation of C–O–SiH$_x$Cl$_y$ groups on the fiber surfaces.

a significantly diminished carbon and substantially increased oxygen contents can be observed as a result of the DS plasma treatment. This result might be related partly to the plasma-enhanced etching of lignin and waxy materials[39] from the fiber surfaces. In addition, significant Si and low Cl atomic concentrations can also be observed.

The high-resolution deconvoluted C1s ESCA diagram of virgin sisal (Figure 9A) reveals the main nonequivalent carbon functionalities (C—O, 286.7 eV; O—C—O, 288 eV), which usually are characteristic for polysaccharide type structures. However, two fairly intense C—C (285 eV) and O—C=O (289.3 eV) binding energy peaks are also present in the spectrum. The presence of these linkages can be related to compounds that accompany the cellulose in the structure of the sisal. The diagram of DS plasma-exposed sisal (Figure 9B) shows peaks at identical binding energy values; however, in this case, the relative peak areas are notably different. A significantly decreased C—O/O—C—O = 1.96 and C—O/O—C=O = 2.66 peak area ratios of plasma-modified sisal in comparison with the virgin substrate (C—O/O—C—O = 2.75 and C—O/O—C=O = 4.75) allow us to suggest that in addition to O—C—O and O—C=O functionalities, identical binding energy value C—O—Si and O=C—O—Si linkages are also present on the DS plasma-treated sisal surfaces. The increased C—O/C—C = 8.6 peak area ratio of modified sisal, relative to the original substrate (C—O/C—C = 7.7), also indicates that the hydrocarbon-type components have been partly removed from the sisal surface as a result of the plasma exposure.
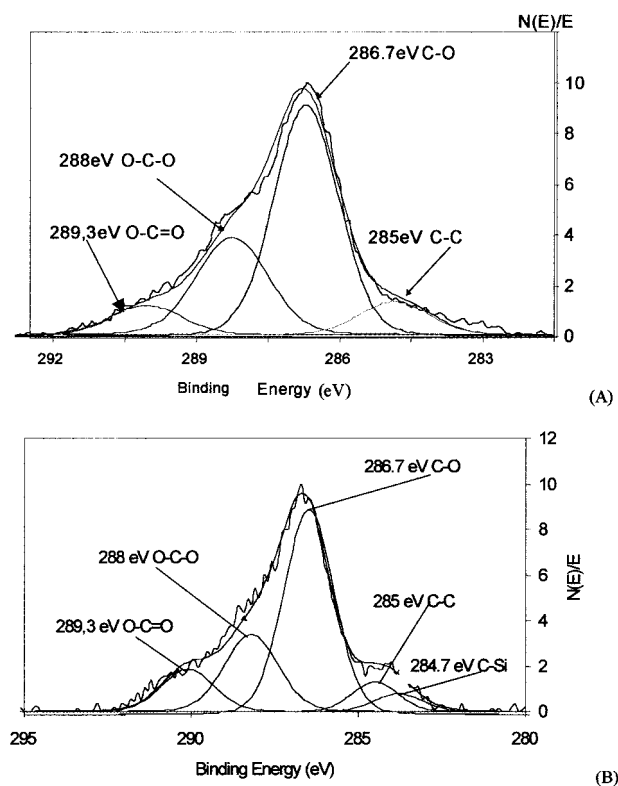
Figure 9   High-resolution deconvoluted C1s ESCA diagrams of (A) virgin sisal and (B) DS plasma-exposed sisal.

CONCLUSIONS

DS RF-plasma treatment results in the successful surface functionalization of high-density PE and

sisal substrates. It has been demonstrated that —SiH$_x$Cl$_y$ functionalities are present on plasma-exposed surfaces and the functionalization reactions can be controlled by selecting proper plasma parameters. The reaction mechanism shown in scheme 1 can be suggested for the implantation onto PE surfaces of —SiH$_x$Cl$_y$ functionalities.

REFERENCES

1. Mahlberg, R.; Niemi, H. E.-M.; Denes, F. S.; Rowell, R. M. Langmuir 1999, 15(8), 2985.
2. Denes, F.S., Hua, Z. Q.; Hop, C. E. C. A.; Young, R. J Appl Polym Sci 1996, 61, 875.
3. Lee, S. D.; Sarmadi, M.; Denes, F.; Shohet, J. L. Plasma Polym 1997, 2(3), 177.
4. Ganapathy, R.; Wang, X.; Denes, F.; Sarmadi, M. J Photopolym Sci Technol 1996, 9(2), 181.
5. Denes, F.; Young, R. A.; Sarmadi, M. J Photopolym Sci Technol 1997, 10(1), 91.
6. Hua, Z. Q.; Denes, F.; Young, R. A. J Vac Sci Technol A 1996, 14(3), May/Jun.
7. Hopkins, J.; Wheale, S. H.; Badyal, H. P. S. J Phys Chem 1996, 100, 14062.
8. Hopkins, J., Badyal, J. P. S. J Phys Chem 1995, 99(1), 4261.
9. Greenwood, O. D.; Tasker, S.; Badyal, J. P. S. J Polym Sci, Part A: Polym Chem 1994, 32, 2479.
10. Shard, A. G.; Badyal, J. P. S. Macromolecules 1992, 25 (7), 2053.
11. Shard, A. G.; Badyal, J. P. S. Polym Commun 32(7), 217 (1991)
12. Rahmati, P. M.; Arefi, F.; Amoroux, J. Surface Coating Technol 1991, 45, 369.
13. Arefi, F.; Rahmati, P. M.; Andre, V.; Amoroux, J. J Appl Polym Sci, Appl Polym Symp 1990, 46, 33.
14. Denes, F.; Nielsen, L. D.; Young, R. A. In Lignocellulosic-Plastic Composites; Eds. Leao, A. L.; Carvalho, F. X.; Frollini, E., Eds.; UNESP: São Paulo, Brazil, 1997, p. 61.
15. Rowell, J.; Manolache, S.; Mattoso, L. H. C.; Sarfaty, M.; Young, R. A.; Denes, F. S. In Anais do Second International Symposium on Natural Polymers and Composites; Mattoso, L. H. C.; Frollini, E.; Leão, A.; Eds.; UNESP: São Paulo, Brazil, 1998; p. 45.
16. Hua.; Z. Q.; Sitaru, R.; Denes, F.S.; Young, R. Plasmas Polym 1997, 2 (3), 199.
17. Denes, F.; Young, R. A. In Polysaccharides Structural Diversity and Functional Versatility; Dumi-triu S., Ed.; Marcel Dekker: New York, 1998, p. 1087.
18. Joseph, K.; Mattoso, L. H. C.; Toledo, R. D.; Thomas, S.; Carvalho, L. H. In Natural Polymers and Agrofibers Based Composites; Frollini, E.; Leão, A.; Mattoso; L. H. C., Eds.; UNESP: São Paulo, Brazil, 2000; p. 159.
19. Denes, F.; Young, R. A. In Proceedings of Wood Adhesives; Christiansen, A.W.; Conner, A.H., Eds.; Forest Products Society: Portland, OR; 1995; p. 61.
20. Rowell, R. M.; Young, R. A.; Rowell, J. K. Paper and Composites from Agro-Basead Resources; Editora Lewis Publishers: New York, 1997.
21. Kazayawoko, M.; Balatinecz, J. J.; Woodhams, R. T.; Sodhi, R. N. S. J Wood Chem Technol 1998, 18(1), 1.
22. Gauthier, R.; Gauthier, H.; Joly, C. In Proceedings of 5th International Conference on Woodfiber-Plastic Composites; Forest Products Society: Madison, WI, 1999; p. 153.
23. Denes, F. Trip, 1997, 5(1), 23.
24. Martin, A. R.; Manolache, S.; Mattoso, L. H. C.; Rowell, R. M.; Denes, F. S. In Third International Symposium on Natural Polymers and Composites (ISNAPOL) Proceedings; Brazil, 2000; p. 431.
25. Martin, A. R.; et al., submitted.
26. Underfriend, S.; Stein, S.; Bohlen, P.; Dairman, W. Science 1972, 178, 871.
27. Beamson, G.; Briggs, D. High Resolution XPS of Organic Polymers, The Scienta ESCA 300 Database. John Wiley & Sons: New York, 1992.
28. Mukherjee, S. P.; Evans, P. E. Thin Solid Films 1972, 14, 105.
29. Inagaki, N.; Kobayashi, H.; Shimohira, K. Polym Bull 1984, 11, 29.
30. Inagaki, N.; Kondo, S.; Hirata, M.; Urushibata, H. J Appl Polym Sci 1985, 30, 3385.
31. Tajima, I.; Yamamoto, M. J Polym Sci, Polym Chem Ed. 1985, 23, 615.
32. Park, S. Y.; Kim, N.; Kim, U. Y.; Hong, S. I.; Sasabe, H. Polym J 1990, 22(3), 242.
33. Wrobel, A. M. Plasma Chem Plasma Proc 1987, 7(4), 429.
34. Cai, S.; Fang, J.; Yu, X. J Appl Polym Sci 1992, 14, 135.
35. Fonseca, J. L. C.; Apperley, D. C.; Badyal, J. P. S. Chem Mater 1993, 5, 1676.
36. Vasilets, V. N.; Yuranova, T. I.; Ponomarev, A. N. J Polym Sci Technol 1994, 7(2), 309.
37. Alexander, M. R.; Short, R. D.; Jones, F. R.; Stollenwerk, M.; Zabold, J.; Michaeli, W. J Mater Sci 1996, 31, 1879.
38. Manolache, S.; Sarfaty, M.; Denes, F. Plasma Sources Sci Technol 1999, 9(1), 37.
39. Mattoso, L. H. C.; Ferreira, F. C.; Curvelo, A. A. S. In Lignocellulosic-Plastic Composites, Leao, A. L.; Carvalho, F. X.; Frollini, F.; Eds.; UNESP: São Paulo, Brazil, 1997; p. 241.