

Lignin–Polypropylene Composites. II. Plasma Modification of Kraft Lignin and Particulate Polypropylene

G. Toriz,^{1,2,3} J. Ramos,³ R. A. Young^{1,2}

¹Department of Forest Ecology and Management, University of Wisconsin–Madison, Madison, Wisconsin 53706

²Center for Plasma Aided Manufacturing, University of Wisconsin–Madison, Madison, Wisconsin 53706

³Department of Wood, Cellulose and Paper, University of Guadalajara, Guadalajara 45020, Mexico

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ABSTRACT: Indulin kraft lignin and polypropylene were subjected to plasma treatments in a rotating electrodeless plasma reactor at 13.56 MHz radio frequency, with the goal of improving the strength properties of the composites made from these materials. It was shown that efficient surface modification could be achieved by these plasma treatments, avoiding long reaction times and large volumes of reactants for modification by conventional wet chemistry. SiCl₄-plasma treatments of lignin at 100 and 200 W resulted in silicon implantation in the range of 4–10% that depended on the treatment time. However, the effect of power in the treatments was minimal, given that changes in silicon implantation were not observed for changes in this parameter. SiCl₄-plasma treatment of polypropylene at 80 W, 1 and 10 min, resulted in silicon implantation in the order of 10–15%, for the two different treatment times, showing that low

power and short treatment times were sufficient to significantly alter the polypropylene surface. However at high power (250 W), the longer treatment time of polypropylene apparently led to formation of oligohalosilanes. Other plasma treatments in the rotating reactor such as plasma-induced copolymerization of acryloyl chloride on both lignin and polypropylene, and plasma-state polymerization of acryloyl chloride on polypropylene under pulsing conditions, resulted in thin film depositions. Evaluation of composites from these treated materials is described in the next contribution (Part III) from this series. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 1920–1926, 2004

Key words: plasma; kraft lignin; polypropylene modification; functionalization of particles; graft copolymers

INTRODUCTION

Surface modification of lignin and polypropylene (PP) was carried out with the goal of developing lignin–PP composites. These modifications were achieved by use of cold plasmas. In this article the modification of the materials is presented and the performance of the composites is described in the next article of this series.¹ The previous article described the properties of composites from unmodified lignin and inorganic fillers in a polypropylene matrix.²

Plasmas can be defined as partially ionized gases that have a collective behavior. Plasma refers to a state of matter in which a significant number of atoms and/or molecules are electrically charged or ionized.³ In cold plasmas, there is no thermal equilibrium between the electrons and the remaining fragments that compose the plasma, with the temperature of the electrons greater by around two orders of magnitude to that of the gas (i.e., $T_{\text{electron}}/T_{\text{gas}} \sim 10\text{--}100$). The temperature of the electrons can reach around 1 to 10 electron volts at an electron density between 10⁹ and

10¹² electrons/cm³. Hot plasmas are almost totally ionized gases, whereas the degree of ionization in cold plasmas is between 1 and 5%.^{3,4}

The transfer of energy to the molecules leads to the formation of a variety of new species including metastables, free radicals, and ions. All these products are chemically active and therefore can serve as precursors for the formation of new stable products. Excited electrons gain enough energy and reach high temperatures generating UV radiation and photons, phenomena that are collectively known as glow discharge.⁴

To initiate a plasma it is necessary to have a certain field strength, whose magnitude depends on the pressure and the nature of the gas. The electrical field accelerates the electrons and these transfer their energy to molecules by collisions; therefore, the higher the field strength, the more energy electrons can pick up between collisions, which leads to a greater number of inelastic collisions that finally increase the number of active chemical species. An increase in pressure reduces the average mean free path of the electrons with the consequence that electrons pick up less energy between collisions.⁵ Hence, an increase in pressure reduces the rate constant for inelastic collisions. The energy of the electrons also depends on the dimensions and geometry of the reactor.

Correspondence to: R. Young (ryoung@facstaff.wisc.edu).

Plasma processing of materials offers an edge over conventional processes for surface modification because the process is dry and does not penetrate more than 10 microns of the material, leaving intact the bulk properties. Furthermore, controlled tailoring of surfaces with reactive functional groups is now possible by means of pulsed discharges. Several investigations have dealt with the use of pulsed discharges for surface modifications to control the molecular composition of the surface modifications achieved.⁶⁻¹³ For instance, deposition and polymerization of fluorocarbons as Teflon-like films have been studied by means of pulsed discharges. Savage et al.⁶ deposited perfluoropropylene oxide on silicon and KCl disks, and studied the variation on molecular composition of the surface as a function of the radio frequency (RF) duty cycles by electron spectroscopy for chemical analysis (ESCA) and FTIR spectroscopy. It was found that decreasing the RF duty resulted in progressive and substantial incorporation of fluorine as CF_2 groups, which in turn resulted in a less-branched polymeric structure. In another study on the deposition of fluorinated monomers Hynes et al.⁷ found that pulsed discharges favored the control of film deposition of perfluorocyclohexane, with regard to a higher retention of CF_2 functionality along with a decrease in crosslinking. Mackie et al.⁸ found as well that pulsed discharges allow for better control of bulk and surface film properties for $\text{C}_2\text{F}_6/\text{H}_2$ systems, where primarily CF_2 species were deposited. Wang et al.⁹ also showed that controlled plasma synthesis of perfluorocarbon films dominated by CF_3 groups could be achieved by means of pulsed discharges. Incorporation of functional groups was achieved by pulsed plasma polymerization monomers such as allyl alcohol,¹⁰ maleic anhydride,¹¹ and acryloyl chloride.¹² Nanoscale control of film chemistry in pulsed plasma polymerization of tetramethyltin has been reported as well.¹³ In general it can be said that functionality retention and better film control can be achieved with pulsed plasma discharges at low RF duty cycles.⁶⁻¹³

Plasma treatment of lignin is a method to efficiently implant reactive functional groups on the surface; although lignin has been considered as a polyol in many applications, the surface of lignin in the solid state consists mainly of ether and carbon-carbon bonds.¹⁴ The use of lignin as a cocomponent with olefins would involve mainly surface interactions and therefore it is important to incorporate reactive functional groups on the surface of the polymers. SiCl_4 -plasma modification of lignin was carried out and the effects of silicon implantation and the chemistry developed were evaluated with regard to composite performance.

Polypropylene (PP) is one of the most important olefinic polymers; features such as chemical inertness, fair thermal stability, low specific gravity (0.9-0.92), excellent mechanical properties (high tensile strength,

impact resistant), excellent dielectric properties, non-toxicity, and low cost (38-41 ct/lb.) are some of the most important characteristics of PP. The historical growth of PP has been in the order of 6% per year. The uses of PP encompass injection molding (31%); fibers and filaments (30%); distributors and compounders (23%); films and sheets (11%); blow molding (2%); and others including wires and cables (3%).¹⁵

To reduce cost and to increase certain properties, fillers are often introduced in PP matrices; glass fibers increase modulus and reduce impact resistance, and also reduce the price of the final product. However, the use of inorganic fillers in polymeric matrices causes high abrasion to the processing equipment and an increment in the weight of the product resulting from the higher specific gravity of mineral fillers. An alternative to the use of inorganic fillers is the use of lignocellulosics. Either mineral or organic fillers have to be compatibilized with the polymeric matrix; otherwise, the excellent mechanical properties exhibited by PP are diminished. The use of coupling agents and compatibilizers has been investigated thoroughly for lignocellulosic fibers/PP composites and mechanical properties are often improved when these substances are incorporated into the composites. In this study the modification of PP with different plasmas is viewed as a way to improve interactions between PP and lignin with the aim of producing superior composites with these materials.

Previous investigations explored the use of SiCl_4 , oxygen, and argon plasmas to modify PP in a parallel-plate reactor.¹⁶⁻¹⁹ Denes et al.¹⁶ modified PP fibers with SiCl_4 for incorporation of PP into cementitious matrices; it was found that treatments for 5 min at 20 W and 200 mT were sufficient to implant at the surface almost 20% of silicon, increasing the oxygen content more than 60% and dramatically reducing the carbon content to 15%. The treatment decreased the contact angle of PP fibers about 30% and resulted in improved flexural properties of the composites. In further investigations it was found that PP films plasma treated with SiCl_4 at 150 mT, 100 W for 1 min contained up to 13.5% of Si and oxygen increased to 42.7%, chlorine to 5.8%, whereas carbon decreased to 38%.^{17,18} A 5-min treatment under the same plasma conditions gave 22.4% Si content, 62.3% oxygen, and a very low carbon content (15.3%). Argon- and oxygen-plasma treatment of PP resulted in oxidation of the surface (up to 40% of oxygen incorporation).¹⁹

Plasma treatment of polypropylene flakes to improve compatibility would be advantageous compared to the use of the usual coupling agents because the resins are expensive and the effects of plasma processes are confined exclusively to the surface. In this investigation, treatments of polypropylene with silicon tetrachloride, acryloyl chloride, and helium-

activated postgrafting with acryloyl chloride were performed.

EXPERIMENTAL

Materials and methods

Indulin AT is a purified form of kraft lignin from the Westvaco Co. (Charleston, SC); it is claimed by the supplier to be completely free of all hemicellulosic materials and is ideal for use in a wide range of polymeric applications. Isotactic polypropylene flakes were kindly provided by Solvay Polymers (Houston, TX). This PP has a melt flow index of 10 g/10 min according to the ASTM standard test D1238-90b.²⁰ The onset of the melting point was at 152°C, measured with a Netsch DSC 200 apparatus (Chicago, IL). The particles had an average diameter of about 10 μm . Argon and helium were obtained from Liquid Carbonic Co. (Oak Brook, IL). Silicon tetrachloride (99% bp 57.6°C) and acryloyl chloride (96%, bp 72–76°C), were purchased from Aldrich Co. (Milwaukee, WI).

Plasma treatments

Plasma treatments were carried out in the rotating RF-plasma reactor described elsewhere.²¹ The development of the reduced pressure, rotating plasma reactor with ferro-fluidic seals in our laboratory has now made possible the modification of particulate materials such as lignin and other polymer in sufficient quantities for detailed surface analysis and preparation of composite materials. The surface modification of lignin and polypropylene was accomplished through the implantation of plasma-generated molecular fragments (e.g., Si—Cl, —C=COCl, etc.) of reactive vapors (e.g., SiCl₄, acryloyl chloride) followed by grafting reactions, where applicable. In a typical experiment one of the reactor's stainless-steel removable caps was opened and a determined quantity of lignin powder (~ 100 g) was fed, after which the reactor chamber was closed. The rotation of the reactor was then started, the particles were mixed with removable deflectors made of glass rods fixed within the reactor with ceramic rings, and the system was evacuated to base pressure level, followed by repressurizing cycles with argon and evacuating to base pressure for removing any volatile contaminants.

Five argon gas-washing cycles were used and the pressure level then reestablished. By operating the reactive-gas feeding system valves the preselected pressure and steady-state flow rate were created in the reactor. The plasma was ignited by dissipating power to the electrodes from the power supply and sustained for a predetermined period of time. At the end of the reaction the plasma source was disconnected, base pressure reestablished, and the reactor pressurized

with argon to atmospheric level. The reaction chamber was then opened and the product removed and stored under dry conditions for later analysis. The experimental parameter ranges used in this investigation were as follows:

- 13.56 RF power: 100–300 W
- Base pressure: 30–50 mT
- Pressure in the absence of plasma: 100–400 mT
- Gas flow rate: 2–7 sccm
- Treatment time: 1–10 min
- Inert gases: Argon, He
- Reactive plasma gases SiCl₄ and CH₂=CH—COCl
- Temperature: room temperature

Grafting reactions were carried out immediately after the plasma treatment (*in situ*) to avoid further reactions that might occur under open laboratory conditions and the product was stored under dry conditions for later analysis.

Electron spectroscopy for chemical analysis

Survey and high-resolution ESCA multiplex spectra were obtained with a Perkin–Elmer PHI 5400 Spectrometer (Mg X-Ray source; 15 kV and 300 W; 45°; Perkin Elmer Cetus Instruments, Norwalk, CT). ESCA survey spectra were collected in the range of 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} and Cl_{2ps} for treated samples). The 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.

RESULTS AND DISCUSSION

SiCl₄-plasma treatment of lignin

Indulin kraft lignin was first subjected to SiCl₄-plasma treatment at 100 and 200 W and treatment times in the range of 2–10 min. A longer treatment time generally resulted in higher silicon and oxygen surface atomic concentration (Table I). These results are compared to a previous treatment of lignin in a parallel-plate reactor operated at 40 kHz RF²¹ where the treatment conditions (i.e., power, pressure, and time) were the same as those for the treatments in this study (Table I). Differences arose here in reactor geometries, radio frequency, nature of the discharge (electrodeless versus electrode), and the quantity of material treated (much greater quantity of material can be treated in

TABLE I
Atomic Concentration of Lignin Determined by ESCA Analysis
of Samples After SiCl₄-Plasma Treatment

Time (min)	Reactor type						
	Rotating 13.56 MHz reactor				Parallel-plate 40 kHz ^a reactor		
	C	O	Si	Cl	C	O	Si
					Untreated lignin		
					72.8	26.6	0.1
				100 W			
0.5					52.1	37.7	6.9
2	62.8	29.8	3.7	3.7	55.9	38.4	5.7
5	55.1	33.8	4.9	6.2	42.8	43.6	8.8
10	40.3	42.7	10.6	6.5	24.5	57.3	18.0
				200 W			
0.5					48.5	44.2	9.3
2	58.1	33.0	4.0	4.9	50.9	40.8	8.2
5	61.6	30.7	4.7	3.0	41.9	44.6	10.9
10	46.0	37.6	9.0	7.5	38.0	45.6	10.2

^a From previous results²¹ and included for comparison with current data.

the rotating reactor). Essentially the trend for the modification of lignin in both reactors is similar with regard to silicon implantation in the sense that it depended on treatment time; lignin modification in the parallel reactor, however, was more intense as seen in Table I. In Table I one may also observe that similar amounts of silicon were implanted at 100 and 200 W at the different treatment times in the electrodeless rotating reactor. Therefore plasma treatments were carried out for 2 and 10 min varying the power applied to the discharge. Table II shows that at 10 min the silicon implantation on lignin ranged from 7 to 10%, whereas after the 2-min treatment, the silicon concentration on lignin ranged from 4 to 5% for all powers from 80 to 300 W. Hence, the effect of power is not apparent in the electrodeless discharge even at a long treatment

time (Table II). This can be seen more clearly in Figure 1 where, especially at a short treatment time (2 min), the surface atomic concentration for all the elements remains practically constant, although at a long treatment time (10 min), powers lower than 200 W appear

TABLE II
Surface Atomic Concentration Determined by ESCA for
SiCl₄-Plasma Treatment of Lignin Under Different
Power and Time in the Rotating Reactor

Power (W)	Element			
	C	O	Si	Cl
	10 min			
80	68.0	23.6	8.3	3.1
100	40.3	42.7	10.6	6.5
200	46.0	37.6	9.0	7.5
250	38.9	48.4	7.1	5.6
300	55.5	30.5	7.8	6.1
	2 min			
80	59.2	33.6	4.4	2.8
100	62.8	29.8	3.7	3.7
200	58.1	33.0	4.0	4.9
250	58.0	31.0	5.4	5.7
300	—	—	—	—

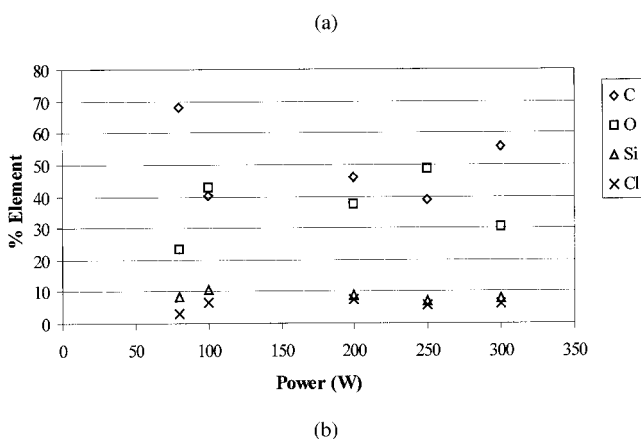
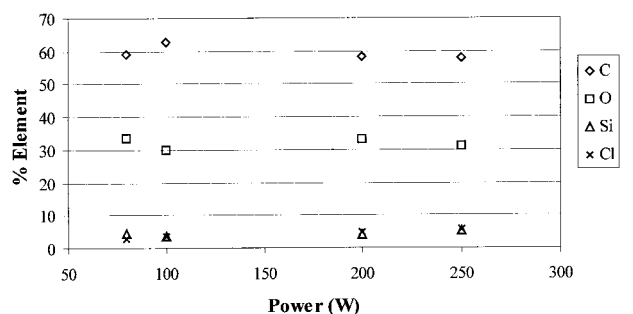


Figure 1 Effect of power on the surface atomic concentration in SiCl₄ plasma treatment of lignin at (a) 2 min and (b) 10 min.

to favor silicon implantation. These results contrast from previous results reported for polypropylene treated in a parallel-plate reactor at 40 kHz, where changes in power led to significant differences in silicon implantations.¹⁶⁻¹⁸

Manolache et al.²² investigated the effects of RF power and pressure on SiCl₄ and SiCl₂H₂ fragmentation in parallel-plate and rotating reactors. It was found that in SiCl₄ plasma discharges, the free chlorine density (FCD) determined by actinometry (a measure of species dissociation) was not affected at 40 kHz and 13.56 MHz under equivalent plasma conditions in the parallel-plate reactor. It is important to point out that experiments in the rotating reactor cannot be carried out at 40 kHz. In the rotating reactor at 13.56 MHz, power had a stronger effect on the dissociation of SiCl₄ at low pressure, whereas at a fixed power (200 W), lower pressures (150 mT) resulted in higher FCD. At 13.56 MHz the FCD was almost twice as high in the rotating reactor compared to that in the parallel reactor at 40 kHz. This means that a more intense fragmentation of the vapor occurred in the rotating reactor at 13.56 MHz compared to earlier work at 40-kHz frequency. According to Manolache et al.²² a similar FCD can be detected at 150 mT and 100 W (Cl/Ar line intensity = 1.5) and at 200 mT and 200 W (Cl/Ar line intensity = 2) at 13.56-MHz frequency in the rotating reactor. Likewise the differences for silicon implantation on lignin in the rotating reactor at different powers could not be detected.

SiCl₄-plasma treatment of polypropylene in the rotating reactor

Modification of PP flakes in the rotating reactor at 13.56 MHz RF was performed under two different powers and two different times. The surface atomic concentration recorded by ESCA measurements revealed that low power and short times are sufficient to significantly alter the surface of PP (Table III). High powers and short time resulted in a moderate implantation of Si as well as oxygen. As in the case of lignin modification, this might be attributable to high fragmentation of the vapor at higher powers, although at longer times the extent of the modification is similar to that obtained at the low power. The analysis of the nonequivalent C_{1s} surface areas (Table III) shows that similar chemistries are obtained at 80 W (both at 1 and 10 min) and at 250 W for 10 min; it is important to note that all the oxygen incorporated in the sample treated at 1 min and 250 W must be part of Si because bonded oxygen was not detected in the C_{1s} peak. Also, it is noteworthy that in one of the samples, treated at 250 W and 10 min, only 2.5% of the C_{1s} nonequivalent surface area was detected as C—Si bonds, whereas a significant amount of silicon was implanted and oxygen was incorporated in a high quantity as well. That

TABLE III
Atomic Concentration and Relative Surface Areas of Nonequivalent ESCA C_{1s} Peaks for SiCl₄ Plasma-Treated PP at 1 and 10 min and 80 and 250 W

Sample	80 W		250 W			
	1 min	10 min	1 min	10 min		
Atomic concentration (%)						
C	44.1	42.2	43.2	80.7	45.1	45.3
O	39.4	40.7	40.5	14.0	37.6	37.6
Si	9.3	14.8	13.9	2.8	13.6	13.6
Cl	7.2	2.2	2.3	2.5	3.7	3.5
Nonequivalent C _{1s} surface area (%)						
C—Si	12.6	15.5	11.6	17.0	8.6	2.5
C—C	69.5	63.7	71	83.0	69.2	83.1
C—O(C,H)	12.6	16.5	13.6		14.8	11.1
C=O	5.2	4.4	3.8		4.9	3.2
COO(C,H)					2.6	

fact suggests that formation of oligohalosilanes occurred under these treatment conditions.

Modification of PP in the rotating reactor is more moderate than that in the parallel-plate plasma reactor, and as mentioned previously, RF effects as well as the reactor geometry play an important role in the fragmentation. A power effect was not observed because of the fact that at 13.56 MHz RF the fragmentation of the gas phase is very similar at different powers when the pressure is above 150 mT.²²

Plasma-induced polymerization of acryloylchloride on polypropylene

Another approach to improve the compatibility of PP with lignin was performed by helium plasma treatment and grafting *in situ* of an acid chloride compound onto the surface of PP. The attached C(O)Cl groups are expected to react with OH groups present in lignin when compounded into composites. Helium-plasma treatment was carried out at 200 mT, 100 W, for 1 and 10 min and then the plasma was turned off. Then, acryloyl chloride vapor was introduced to the reactor for 2.5 h to allow the grafting reaction to occur. ESCA results showed incorporation of oxygen at 9 and 13% for 1- and 10-min treatment times, respectively. Figure 2 is a schematic of acryloylchloride plasma-induced polymerization both on lignin and on PP. When acryloylchloride is grafted onto lignin particles [Fig. 2(b)], abstraction of the proton in the tertiary carbon in PP would covalently link lignin and PP.

Plasma-state polymerization of acryloylchloride under pulsing conditions on polypropylene and silicon wafers

Calderon and Timmons¹² previously showed that significant C(O)Cl group retention on substrates can be

obtained under conditions of very low power input in acryloyl chloride plasmas. Continuous-wave plasmas cannot be operated at low power input because of instabilities. Therefore the natural choice was to apply pulsed discharges. It is valuable to investigate this approach as another means for derivatization and compatibilization of PP with lignin because the acid chloride on PP would be expected to condense with OH groups present in the lignin [see Fig. 2(a)].

Several experiments were carried out to select the appropriate plasma parameters and deposition of the plasma-polymer was done on both a silicon wafer and on PP. The surfaces were first cleaned with an argon plasma (5 min, 200 W, 100 μ s, 20% duty, 400 mT) and then subjected to acryloyl chloride plasma-polymerization under the following conditions: 15 min, 25 W, 500 μ s, 20% duty, and 190 mT. Under these conditions, deposition of a film was achieved, given that on the silicon wafer it was no longer possible to detect silicon at the surface.

For detection, derivatization of the acid chloride group on the surface of the Si wafer was performed with trifluoroethanol. The sample derivatized with $\text{CF}_3\text{CH}_2\text{OH}$ showed an almost 11% fluorine concentration (Table IV), which is an indication that the acid chloride group was retained at about 3% on the surface. Calderon and Timmons¹² $\text{CF}_3\text{CH}_2\text{OH}$ -derivatized the films they obtained under acryloyl chloride plasmas and concluded that complete conversion of the acid chloride was not achieved based on surface analysis. The atomic concentration at the surface of PP, after the treatment with acryloyl chloride, suggests that the reaction on PP and on the silicon wafer both proceed in the same manner; furthermore, the shapes of the C_{1s} HR spectra revealed a small peak at 288.4 in PP corresponding to the acid chloride group. The effect of the plasma surface modification on the proper-

TABLE IV
Surface Atomic Concentrations Determined by ESCA for an Acryloyl Chloride-Modified Silicon Wafer and PP^a

Sample	Atomic concentration (%)			
	C	O	Cl	F
Silicon wafer, deriv.	61.1	18.3	9.8	10.8
PP	74.6	14.4	11	—

^a Plasma conditions: 15 min, 25 W, 500 μ s, 20% duty, and 190 mT.

ties of lignin-PP composites is described in the next article of this series.

CONCLUSIONS

Modification of lignin with silicon tetrachloride plasma in a rotating electrodeless reactor at 13.56 MHz resulted in silicon implantation in the range of 4–10%, which depended on treatment time. In general, modification of lignin in this reactor was more moderate compared to previous results in a parallel-plate reactor at 40 MHz.²¹ The effect of power on the modification of lignin in the rotating reactor was not noticeable, especially at a short treatment time. Strong fragmentation of the SiCl_4 vapor in the plasmas at 13.56 MHz might be the cause of not seeing the effects of changes in power, at least for silicon implantation.

As in the case of lignin, the modification of PP flakes in the rotating reactor was moderated compared with that in the parallel-plate reactor. Treatments as short as 1 min gave 9% Si implantation on PP flakes at 80 W. At higher power (250 W) and 1-min treatment time, silicon implantation was more modest, reaching about 3%. At longer treatment time (10 min) the implantation of silicon and the chemistry appeared to be similar, even at different powers, similar to plasma treatment of lignin. However, Si—C bonds were scarce, and large amounts of silicon and oxygen were found at the surface in a treatment at 250 W and 10 min. This suggested formation of oligohalosilanes on the surface of polypropylene.

Acryloyl chloride was also grafted to PP flakes by plasma-induced polymerization and pulsed plasma-state polymerization. Changes in PP from plasma-induced polymerization of acryloyl chloride were barely noticeable because of very thin film formation; however, the properties of composites made with PP-modified flakes were improved as described in the next article in this series. Pulsed plasma-state polymerization of acryloylchloride on PP resulted in retention of the acid chloride functionality of at least 3%. Cold plasmas offer a sound and efficient approach for modification of particulate polymeric materials in a rotating reactor under a wide range of conditions.

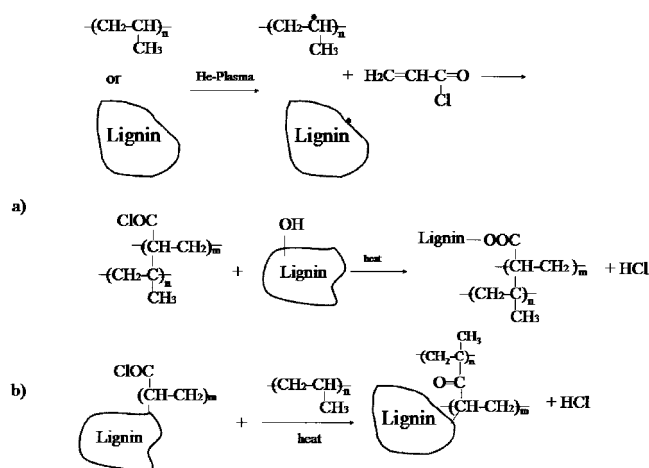


Figure 2 Plasma-induced graft copolymerization of acryloylchloride on (a) PP and (b) lignin for compatibilization of lignin and PP.

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