Hydrophilic Surface Modification of Polypropylene Films by CCl_4 Plasma

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SYNOPSIS

The CCl_4 plasma treatment of polypropylene films was investigated from the viewpoint of hydrophilic surface modification using a contact-angle meter, ATR FTIR spectroscopy, and angular XPS. Hydrophilicity and chemical composition of the CCl_4-plasma-treated polypropylene films were discussed. The CCl_4 plasma treatment was effective in hydrophilic modification. The advancing contact angle of water for polypropylene films was decreased from 99° to 81–7° by the CCl_4 plasma treatment, and the surface energy increased from 27.2 to 38.9–67.7 mJ/m^2 when the discharge current varied from 50 to 150 mA. The CCl_4 plasma initiated chlorination, oxidation, and aluminum sputtering reactions. The chlorination of polypropylene films was favorable in a mild CCl_4 plasma operated at a discharge current of 50 mA. The oxidation and aluminum sputtering reactions were predominant over the chlorination in strong CCl_4 plasmas operated at discharge currents of more than 75 mA. The chlorination initiated by the mild CCl_4 plasma was restricted near the film surface within 36 Å deep. The regions modified with the strong CCl_4 plasma reached inner layers of 36–49 Å deep. Hydrophilicity caused by the CCl_4 plasma treatment may be due not only to chlorine functionalities but also to oxygen and aluminum functionalities. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Polypropylene is a hydrophobic polymer and is difficult to paint and adhere to other materials such as polymers, metals, and ceramics using adhesives. Typical methods for hydrophilic surface modification of polypropylene are the trichloroethylene vapor, corona discharge, primer, and plasma treatments.[1–16] These surface modifications except for the trichloroethylene vapor treatment and primer treatment change the surface property of polypropylene from hydrophobic to hydrophilic.

The plasma treatment is a distinguished surface-modification process. Gas molecules such as oxygen and nitrogen in a plasma reactor are activated by plasma energy, i.e., the collision of electrons, and the activated oxygen and nitrogen atoms attack polypropylene surfaces. Oxides and nitrides are formed at the polypropylene surfaces, and then the hydrophilic surface modification is accomplished. Therefore, what gas is used for the plasma treatment is closely related to the hydrophilicity caused by the plasma treatment. From the viewpoint of high hydrophilic effects of hydroxyl, carbonyl, carboxyl, amine, and amide groups, oxygen, carbon oxide, carbon dioxide, nitrogen oxide, nitrogen dioxide, nitrogen, and ammonia are generally used as gases for the plasma treatment.[17,18]

Chlorine moieties also could be expected to have good hydrophilic functionality if the chlorination of polypropylene occurs in plasma treatment, because polyvinyl chloride is rather hydrophilic. The surface energy of polyvinyl chloride is 41.5 mJ/m^2 and that of polypropylene, 29.6 mJ/m^2.[19] The direct chlorination by elemental chlorine gas has been reported for the purpose of promoting adhesion.[20] This investigation describes the CCl_4 plasma treatment of polypropylene films to improve hydrophilicity.

EXPERIMENTAL

Materials

The polypropylene film used in this study was kindly provided from Idemitsu Petrochemical Co. and received as 215 mm wide and 25 μm thick. Carbon tetrachloride was analytical grade (Tokyo Kasei Co.) and used without further purification.

Plasma Treatment

The polypropylene film was mounted on the sample stage shown in Figure 1 and was plasma-treated using a homemade reactor that was a capacitively coupled system at a 20 kHz frequency. It consisted of a bell jar (400 mm diameter, 470 mm height) with a monomer inlet, a pair of parallel aluminum electrodes (150 × 150 mm), a substrate stage, a pressure gauge, and a vacuum system consisting of a rotary and a diffusion pump. A schema of the reaction system is shown in Figure 1.

The experimental procedures for the plasma treatment of the polypropylene films were essentially the same as reported elsewhere.[18] The reaction system was evacuated to approximately 0.13 Pa, and then the vapor of CCl_4 at a flow rate of 10 cm^3 (STP)/min adjusted by a metering valve was introduced into the reaction chamber. The plasma treatment was performed at a given discharge current of 50–150 mA at a 20 kHz frequency at a system pressure of 13.3 Pa for a given duration of 1–30 min.

Advancing Contact Angle of Water and Surface Energy

The advancing contact angles of water, glycerol, formamide, diiodomethane, and tricresyl phosphate on the plasma-treated polypropylene film surfaces were measured at 20°C using an Erma contact-angle meter with a goniometer, model G-1. The advancing contact angle of the liquids (1 μL) was determined from an average of 10 specimens. The surface energy of the plasma-treated polypropylene film was estimated from the data of the advancing contact angles of the five liquids according to Kaelble's method.[21]

Infrared and X-ray Photoelectron Spectra

The plasma-treated polypropylene film was supplied as a specimen for IR and XPS measurements. The attenuated total reflection (ATR) IR spectra for the surface of the polypropylene film were recorded on a Horiba Fourier transform spectrometer FT 300 with a MTC detector. The crystal of KRS-5 was used for ATR measurement, and the incidence angle of infrared light was 45°. The penetration depth of IR light in the ranges of 3000–400 cm^{-1} is estimated to be about 0.66–5.0 μm. The spectral resolution was 0.5 cm^{-1}, and 500 scans were recorded on each sample.

The XPS spectra of the surface of the plasma-treated polypropylene films were obtained on an Ulvac-Phi spectrometer 5400 using MgK_α photon source. The anode voltage was 15 kV; the wattage, 400 W; and the background pressure in the analytical chamber, 1 × 10^{-7} Pa. The analysis area of the film specimen was 1.1 mm diameter. The takeoff angle of the analyzer against the face of the film specimen was 20, 45, and 80°. Otherwise, the takeoff angle was 45°. The C_{1s} and Cl_{2p} spectra were decomposed by fitting Gaussian functions to the experimental curve using a nonlinear, least-squares curve-fitting program supplied by Ulvac-Phi. The decomposed Cls component appearing at the lowest
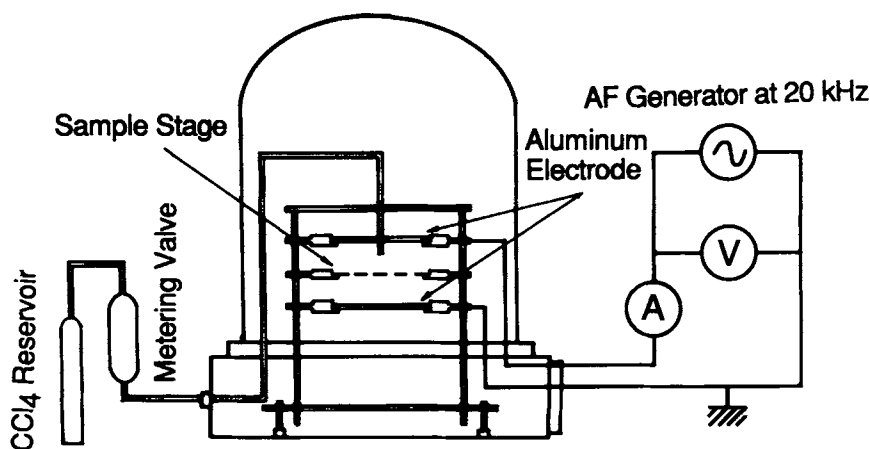

Figure 1   Schema of reaction for plasma treatment.

binding energy scale was corrected at 285.0 eV to eliminate charging effects. The sensitivity factors (S) for core levels were $S(C_{1s}) = 0.296$, $S(Cl_{2p}) = 0.891$, $S(O_{1s}) = 0.711$, and $S(Al_{2p}) = 0.234$.

RESULTS AND DISCUSSION

Water Contact Angle and Surface Energy of Plasma-treated Polypropylene Films

CCl_4 plasma exposure made the polypropylene film surface hydrophilic. Figure 2 shows an advancing contact angle of water on the CCl_4-plasma-treated polypropylene surface as a function of the CCl_4 plasma exposure time and CCl_4 plasma discharge current. The advancing contact angle, as shown in Figure 2, decreases gradually with increasing the CCl_4 plasma exposure time, and, then, the decrease in advancing contact angle levels off. The leveling-off point depends on both of the plasma exposure time and plasma discharge current. The plasma exposure time reaching the leveling-off point is 4 min at a discharge current of 50 mA and 15 min at discharge currents of 75, 100, and 150 mA. The advancing contact angle at the leveling-off point depends also on the plasma discharge current: 81° at 50 mA, 39° at 75 mA, 22° at 100 mA, and 7° at 150 mA. The dependence of the leveling-off point on the plasma exposure time and plasma discharge current suggests that the surface modification of polypropylene films by the CCl_4 plasma is not a simple reaction but a complex one of at least two reactions, one of which is initiated only by a large magnitude of the plasma discharge current, because if the surface modification proceeds through simple reaction,
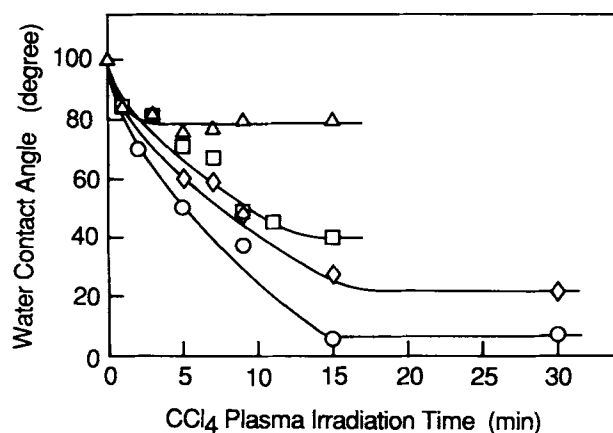

Figure 2   Advancing contact angle of water against CCl_4-plasma-treated polypropylene films; discharge current: ($\triangle$) 50 mA; ($\square$) 75 mA; ($\diamond$) 100 mA; ($\bigcirc$) 150 mA.

the degree of the surface modification occurring at the polypropylene film surface, which we evaluate as a decrease in the advancing contact angle, will be a function of the plasma exposure time and plasma discharge current. Also, the CCl_4 plasma operated at a low plasma discharge current is expected to require longer plasma exposure time to reach the leveling-off point than that at high plasma discharge current. The experimental evidence is converse to the expectation. The plasma exposure time at the leveling-off point is 4 min at a plasma discharge current of 50 mA and 15 min at 150 mA. Therefore, we speculate that the surface modification by the CCl_4 plasma involves at least two reactions, one of which becomes predominant at a high plasma discharge current. This speculation will be discussed in later sections.

Comparison with the surface modification by the oxygen, nitrogen, and argon plasmas shows that the CCl_4 plasma operated at plasma discharge currents of more than 100 mA is more effective in hydrophilic modification than are these plasmas. The advancing contact angle of water for polypropylene film surface-treated with the CCl_4 plasma, as shown in Table I, is 22–7°, and the advancing contact angles for the oxygen plasma-, nitrogen plasma-, and argon plasma-treated polypropylene films are 60°, 46°, and 50°, respectively. Independently, Marchant et al.[10] reported effects of nitrogen plasma in hydrophilic surface modification of polypropylene films, but the effectiveness was low. (The advancing contact angle of water on the nitrogen-plasma-treated polypropylene films was 34.6°.)

From the advancing contact angles of five liquids (water, glycerol, formamide, diiodomethane, and tricresyl phosphate), the surface energy of the polypropylene surfaces treated with the CCl_4 plasma was estimated according to the Kaelble's method (Table I) and was plotted with the discharge current (Fig. 3). The surface energy for the CCl_4-plasma-treated polypropylene films increases linearly from 27.2 to 67.7 mJ/m^2 with increasing the plasma discharge current to 150 mA (Fig. 3). The analysis of surface energy by Kaelble's method[21] divided the surface energy (γ_s) into a dispersive (γ_s^d) and a polar component (γ_s^p). The contribution of each of the components to the surface energy, as shown in Figure 3, is different among the CCl_4-plasma-treated polypropylene films. For the polypropylene films CCl_4-plasma-treated at a discharge current of 50 mA, the dispersive component (γ_s^d) is somewhat larger than the polar component (γ_s^p). On the other hand, for the films CCl_4-plasma-treated at discharge currents of more than 75 mA, the polar component (γ_s^p) is

Table I   Advancing Contact Angle of Water and Surface Energy of Plasma-treated Polypropylene Films

Plasmas	Plasma Treatment Conditions		Advancing Contact Angle of Water (°)	Surface Energy (mJ/m²)
Untreated	—	—	99	27.2 (25.9 + 1.3)ᵃ
CCl₄	50 mAᵇ	7 minᶜ	78	38.9 (33.8 + 5.1)
	75 mAᵇ	13 minᶜ	39	54.0 (20.5 + 33.5)
	100 mAᵇ	20 minᶜ	22	63.2 (19.4 + 43.8)
	150 mAᵇ	20 minᶜ	7	67.7 (18.8 + 48.9)
O₂	25 Wᵈ	2 minᵉ	60	
N₂	25 Wᵈ	2 minᵉ	46	
Ar	25 Wᵈ	2 minᵉ	50	
CF₃Cl	1.5 MW/molᶠ		97	52 (52 + < 1)
	2.3 MW/molᶠ		98	53 (53 + < 1)
	3.7 MW/molᶠ		99	52 (52 + < 1)
	7.5 MW/molᶠ		98	51 (51 + < 1)

ᵃ Dispersive and polar contribution.
ᵇ Discharge current at 20 kHz.
ᶜ Plasma irradiation time.
ᵈ Rf power at 13.56 MHz.
ᵉ Plasma irradiation time.
ᶠ Rf power/CF₃Cl mol.

larger than the dispersive component (γ_s^d). This analysis suggests that the CCl₄-plasma discharge current will change the course of modification reactions initiated by the CCl₄ plasma. We could speculate that the CCl₄ plasma operated at a discharge current of 50 mA forms predominantly dispersive groups such as chlorine functionalities, and the CCl₄

Figure 3   Surface energy of CCl₄-plasma-treated polypropylene films as a function of discharge current: (○) surface energy (γ_s); (□) dispersive contribution (γ_s^d); (△) polar contribution (γ_s^p).

plasma operated at discharge currents of more than 75 mA forms predominantly polar groups such as oxygen. We have already speculated a similar alteration in the surface-modification process by the CCl₄ plasma discharge current from the plasma exposure time at the leveling-off point. This speculation is supported by the elemental composition determined with XPS (Table II). We will discuss the elemental composition for the CCl₄-plasma-treated polypropylene in a latter section.

Recently, Strobel et al.[22,23] reported on the hydrophilic surface modification of polypropylene films with CF₃Cl plasma. The CF₃Cl plasma showed notable surface modification reactions. The chlorination and fluorination of polypropylene occurred in the CF₃Cl plasma. Which of the reactions occurred depended on the rf power. They characterized the rf power in the term of the rf power per mol of CF₃Cl molecules in the plasma zone. In the CF₃Cl plasma operated at low rf powers per CF₃Cl mol (1.5–3.7 MW/mol), the chlorination of polypropylene films occurred predominantly, and at high rf powers per CF₃Cl mol (more than 7.5 MW/mol), the chlorination and fluorination occurred simultaneously. They concluded that the CF₃Cl plasma operated at low powers of 1.5–3.7 MW/mol was effective in hydrophilic modification of polypropylene films. The advancing contact angle of water and surface energy for the CF₃Cl-plasma-treated polypropylene films were 97–98° and 52–53 mJ/m², respectively.

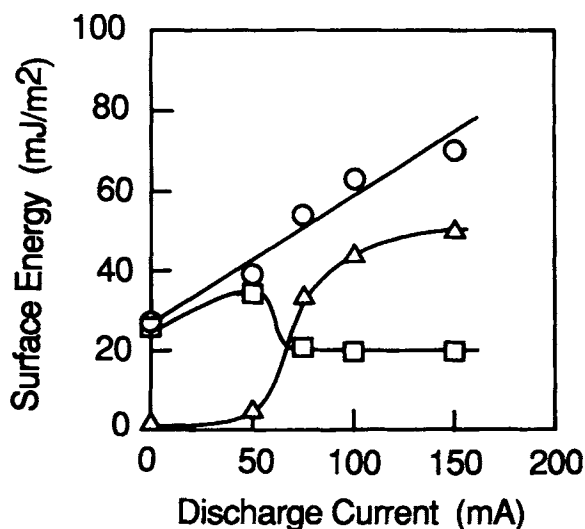**Table II Elemental Composition of Polypropylene Films Treated with CCl_4 Plasma**

Plasma Treatment Conditions			Atomic Ratios Determined by XPS		
Discharge Current (mA)	Irradiation (min)	Ar^+ Ion-etching Treatment[a]	Cl/C	O/C	Al/C
Untreated	—	No	< 0.01	0.02	< 0.01
		Yes	< 0.01	0.02	< 0.01
50	7	No	0.35	0.20	0.04
		Yes	0.02	0.07	0.03
75	13	No	0.15	0.85	—
100	20	No	0.16	0.76	—
150	20	No	0.23	0.60	0.19
		Yes	0.68	3.35	1.67

[a] A sputtered-off film is about 30 Å thick.

From comparison with our polypropylene films treated with the CCl_4 plasma and Strobel's ones treated with CF_3Cl plasma, we conclude that the CCl_4 plasma treatment, especially at high plasma discharge currents of more than 100 mA, is more effective in hydrophilic modification than is the CF_3Cl plasma treatment. The advancing contact angle is 22–7° for the CCl_4-plasma-treated polypropylene films at more than 100 mA and 97–98° for the CF_3Cl-plasma-treated ones.

Elemental Composition of CCl_4-plasma-treated Polypropylene Films

Polypropylene films treated with CCl_4 plasma at various discharge currents were analyzed with XPS, and the elemental composition of the films was determined from the signal intensities of XPS spectra (Table II). The CCl_4-plasma-treated polypropylene films, as shown in Table II, possess chlorine, oxygen, and aluminum as well as carbon. This indicates that the chlorination of polypropylene films occurred with the CCl_4 plasma. A source of oxygen incorporated into the CCl_4-plasma-treated polypropylene film surfaces may be due to two possible processes: One is postreactions of radicals generated at the polypropylene film surfaces with air, when taken out from the plasma reactor after finishing the plasma treatment, and the other is water vapor adsorbed on the wall of the reaction chamber, which will be decomposed into atomic oxygen and hydroxyl groups by plasma. At high plasma discharge current, the sputter reactions of the aluminum oxide layer of the aluminum electrodes may be a possible origin of the incorporated oxygen. Foerch et al.[24] investigated the elemental composition of the nitrogen plasma-

treated polyethylene by XPS. Prior to the plasma treatment, a plasma reaction chamber was carefully baked at 130°C for 12 h, after which base pressure of the reaction chamber was 2×10^{-8} Torr. Once the chamber reached such pressure, polyethylene films were introduced into the reaction chamber and treated with nitrogen plasma. The treated polyethylene films were inserted without air exposure directly into an analysis chamber of the XPS instrument, which was connected through a gate valve to the plasma reaction chamber. Nevertheless, the plasma-treated polyethylene films were contacted with air; the films contained some oxygen as well as nitrogen. The O/C atomic ratio was 0.09–0.12, and the N/C atomic ratio, 0.09–0.26. This emphasizes that a source of the incorporated oxygen is water vapor-adsorbed at the wall of the reaction chamber. Therefore, in the CCl_4 plasma treatment, it is reasonable that water vapor is a possible origin of the incorporated oxygen. However, the interpretation does not exclude the postreactions with air. Sputter reactions of aluminum electrodes may be an origin of aluminum incorporated into the plasma-treated polypropylene film surfaces.

The Cl/C, O/C, and Al/C atomic ratios for the CCl_4-plasma-treated polypropylene films are strongly influenced by the plasma discharge current. At a discharge current of 50 mA, the Cl/C atomic ratio is high (0.35) and the O/C and Al/C atomic ratios are low (0.2 and 0.04, respectively). On the other hand, at discharge currents of more than 75 mA, the Cl/C atomic ratio is low (0.15–0.23) and the O/C atomic ratio is high (0.60–0.85). Also, the polypropylene films plasma-treated at 150 mA possess a greater amount of aluminum (Al/C atomic ratio = 0.19). The elemental composition shown in

Table II indicates that the chlorination of polypropylene films is favorable in the CCl_4 plasma operated at a low discharge current of 50 mA. In the CCl_4 plasma operated at high discharge currents of more than 75 mA, the oxidation of polypropylene rather than the chlorination becomes predominant, and the sputtering reactions of aluminum occur.

The chemistry of the CCl_4 plasma is distinguished from the CF_3Cl plasma investigated by Strobel et al. In the CF_3Cl plasma, the chlorination of polypropylene films occurs predominantly and the oxidation scarcely occurs. The Cl/C and O/C atomic ratios for the polypropylene films treated with the CF_3Cl plasma were 0.22–0.36 and 0.01–0.06, respectively. On the other hand, in the CCl_4 plasma, the chlorination and oxidation occur consequently, although when the oxidation in the CCl_4 plasma occurs, during the plasma treatment by incorporation reactions of oxygen atoms decomposed from water vapor or after the treatment by reactions between polymer radicals and air, is not clear at the present time.

The parachor concept[25] is able to estimate the contribution of chlorine functionalities to hydrophilicity of polypropylene films. When a part of the hydrogen atoms in polypropylene is substituted with chlorine atoms, the estimation from the parachor concept shows that the surface energy is 32.0 mJ/m^2 for polypropylene (C_3H_6), 33.2–40.7 mJ/m^2 for one-chlorine-substituted polypropylene (C_3H_5Cl), and 36.7–43.5 mJ/m^2 for two-chlorine-substituted polypropylene $(C_3H_4Cl_2)$. The distribution of the surface energy for the chlorine-substituted polypropylenes indicates which of the hydrogen atoms bonded to primary, secondary, and tertiary carbon in polypropylene is substituted with the chlorine atom. A comparison in surface energy between the experimental results shown in Table I and the es-

timation from the parachor concept indicates that hydrophilicity caused by the CCl_4 plasma treatment, especially operated at high discharge currents, is not explained only by the chlorine functionalities. It is not unreasonable that hydrophilicity caused by the CCl_4 plasma treatment is related to oxygen functionalities as well as to chlorine functionalities.

The depth profile of chlorine, oxygen, and aluminum introduced into polypropylene films by the CCl_4 plasma treatment was determined by an angular XPS and an Ar^+ ion sputter etching technique (Tables II and III). The takeoff angles of electrons against the polypropylene film face were 20°, 45°, and 80°, which correspond to a sampling depth of 17, 36, and 49 Å, respectively, under the assumption that the escape depth of electrons is 50 Å. Table III shows that the chlorine profile is influenced by how much discharge current was applied for the CCl_4 plasma. In the CCl_4 plasma treatment operated at a low discharge current of 50 mA, the Cl/C atomic ratio is almost equivalent at sampling depths of 17 and 36 Å, but is lower at 49 Å. This indicates that most of the incorporated chlorines exist near the surface layer within 36 Å deep from the topmost layer of the polypropylene films. On the other hand, in the CCl_4 plasma treatment at high discharge currents of more than 75 mA, the Cl/C atomic ratio is higher at 36 Å than at 17 Å. Most of chlorines do not exist at the topmost layer but at inner layers of 36–49 Å deep. This lack of chlorine near the surface layer may be due to sputtering-off of chlorine from the surface by electrons.

The polypropylene films CCl_4-plasma-treated at discharge currents of 50 and 150 mA were sputteretched at about 30 Å deep with Ar^+ ions, and the new surfaces were analyzed with XPS (Table II). The Cl/C, O/C, and Al/C atomic ratios at the new surfaces were 0.02, 0.07, and 0.03, respectively, for

Table III Depth Profile of Chlorine and Oxygen Incorporated into Polypropylene Films by CCl_4 Plasma

Electron Takeoff Angle (°)	Untreated Polypropylene Film		Polypropylene Films CCl_4-plasma-treated at a Discharge Current of 50 mA		Polypropylene Films CCl_4-plasma-treated at a Discharge Current of 150 mA	
	Cl/C	O/C	Cl/C	O/C	Cl/C	O/C
20 (17 Å)[a]	0.02	0.38	0.31	0.29	0.14	0.47
45 (36 Å)	< 0.01	0.02	0.35	0.20	0.23	0.60
80 (49 Å)	< 0.01	0.15	0.11	0.71	0.28	0.83

[a] Sampling depth.

the polypropylene film CCl_4-plasma-treated at 50 mA, and 0.68, 3.35, and 1.67, respectively, for the polypropylene film treated at 150 mA. The Cl/C, O/C, and Al/C atomic ratios for the polypropylene film treated at 150 mA are surprisingly high. Why such high Cl, O, and Al atoms are concentrated is not known. These results support the conclusion derived from the angular XPS spectra. Chlorine and oxygen incorporated into polypropylene films by the CCl_4 plasma operated at a discharge current of 50 mA are concentrated near the surface layer within 30 Å deep from the topmost layer of the film. Most of chlorines, oxygens, and aluminums incorporated into polypropylene films by the CCl_4 plasma at a discharge current of 150 mA exist at inner layers of more than 30 Å deep.

In conclusion, the CCl_4 plasma treatment leads to chlorination and oxidation of polypropylene films and to aluminum deposition on the films by sputtering reactions. The chlorination is favorable in the CCl_4 plasma operated at a low discharge current of 50 mA, and chlorine is concentrated near the surface within 30 Å deep. In the CCl_4 plasma operated at large discharge currents of more than 75 mA, the chlorination is unfavorable, and the oxidation and aluminum sputtering reactions occur predominantly.

Figure 4 ATR IR spectra of CCl_4-plasma-treated polypropylene films: (A) untreated; (B) treated at a discharge current of 50 mA; (C) treated at 150 mA.

Chemical Composition of CCl_4-plasma-treated Polypropylene Films

Figure 4(a) and (b) compare ATR IR spectra for the CCl_4-plasma-treated polypropylene films (at discharge currents of 50 and 150 mA) with that for the untreated film. There are differences between the untreated and the plasma-treated films in the broad peaks in wavenumber ranges of 1700–1600 cm^{-1} due to C=O and C=C groups [Fig. 4(a)] and characteristic absorptions at 653 and 605 cm^{-1} due to C—Cl stretching vibration[26] [Fig. 4(b)]. The untreated film shows no absorption peak at 1700–1600 cm^{-1}, but the plasma-treated films show a strong absorption peak. The intensity is higher for the polypropylene film treated at a discharge current of 150 mA than for the film treated at 50 mA. Moreover, the absorption peaks related to C—Cl groups at 653 and 605 cm^{-1} also are observed. The intensity is stronger for the polypropylene film treated at a discharge current of 50 mA than for that at 150 mA. This indicates that the chlorine content is higher for the polypropylene film treated at a discharge current of 50 mA than for that at 150 mA, and the oxygen content is inverse. This observation corresponds to the conclusion derived from the XPS
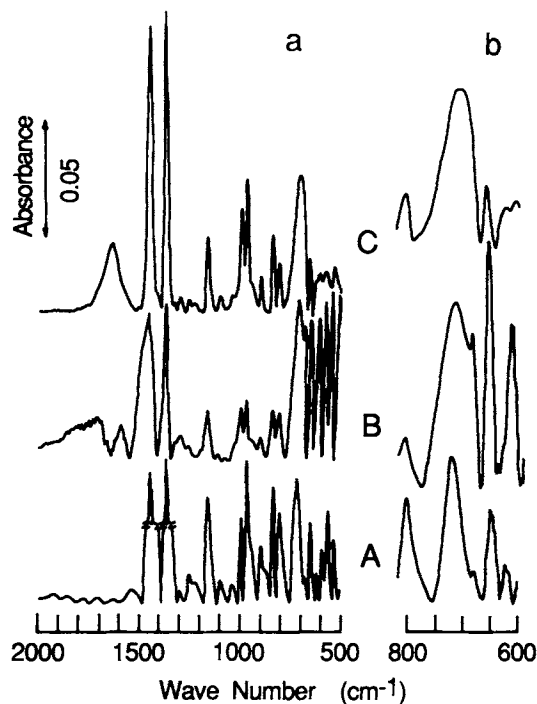
results. Other strong absorption peaks are related to polypropylene. These are characteristic absorption peaks related to CH, CH_2, and CH_3 groups at 1450 (asymmetric deformation vibration of CH_3 groups), 1369 (symmetric deformation vibration of CH_3 groups), 1300 (wagging vibration of CH_2 groups and bending vibration of CH groups), 1250 (twist vibration of CH_2 groups and bending vibration of CH groups), 1163 (stretching vibration of C—C bonds and rocking vibration of CH_3 groups), 1100 (rocking vibration of CH_3 groups and stretching vibration of C—C bonds), 1040 (stretching vibration of C—CH_3 and C—C bonds), 994 (rocking vibration of CH_3 groups, stretching vibration of C—CH_3 bonds, and twist vibration of CH_2 groups), 969 (rocking vibration of CH_3 groups, stretching vibration of C—C bonds, and stretching vibration of C—CH_3 bonds), 894 (rocking vibration of CH_3 and CH_2 groups, and bending vibration of CH groups), 800 (rocking vibration of CH_2 groups and stretching vibration of C—CH_3 and C—C bonds), and 719 cm^{-1} (deformation vibration of CH_2 zigzag chains).[27]

Furthermore, XPS analysis gave detailed information on the chemistry of chlorine and oxygen incorporated into the polypropylene films by the CCl_4
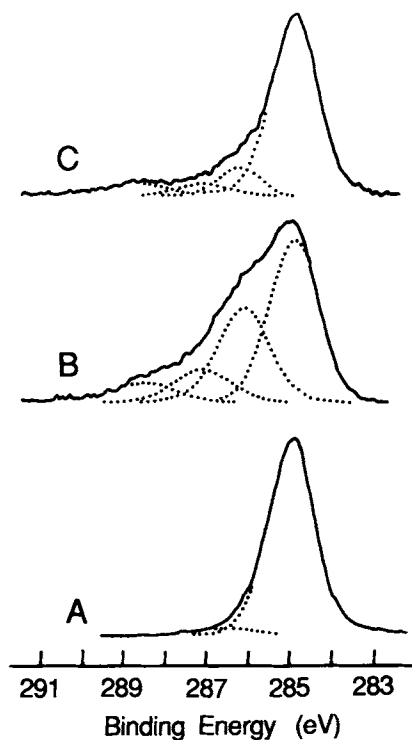
Figure 5 XPS (C_{1s}) spectra of CCl_4-plasma-treated polypropylene films: (A) untreated; (B) treated at a discharge current of 50 mA; (C) treated at 150 mA.

Figure 6 XPS (Cl_{2p}) spectra of CCl_4-plasma-treated polypropylene films: (A) treated at a discharge current of 50 mA; (B) treated at 150 mA.

plasma treatment. Figures 5 and 6 show typical C_{1s} and Cl_{2p} core level spectra for the polypropylene films CCl_4-plasma-treated at discharge currents of 50 and 150 mA. The C_{1s} spectra, as shown in Figure 5, are expanded into high binding energy regions by the CCl_4 plasma treatment. A full width at half-maximum of the C_{1s} core level spectra increases from 1.3 eV for the untreated polypropylene film to 2.6–1.5 eV for the polypropylene films CCl_4-plasma-treated at discharge current of 50 and 150 mA. The
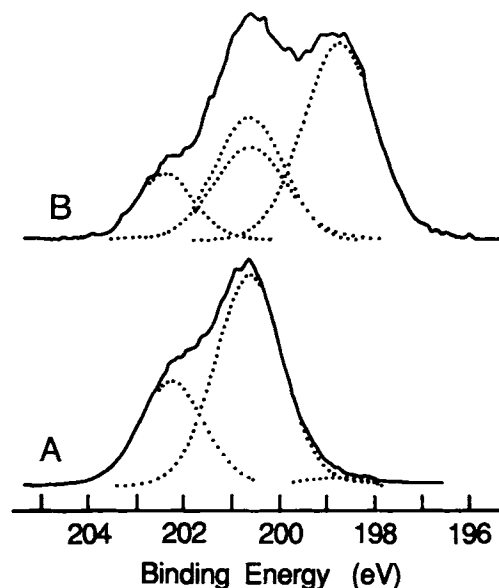
C_{1s} core level spectra are decomposed into four components, CH, C — O and C — Cl, C = O, and C(O)O groups, which appear at 285, 286.4–286.9, 287.4–287.7, and 289.1–289.6 eV.[28] A relative concentration of the four components is listed in Table IV. The polypropylene films CCl_4-plasma-treated at a discharge current of 50 mA possess a greater amount of C — O and C — Cl and C = O components compared with the other films treated with the CCl_4 plasma at a discharge current of more than 75 mA.

The Cl_{2p} core level spectra show noticeable chlorine chemistry of the CCl_4-plasma-treated polypropylene films. The Cl_{2p} core level spectra, as shown in Figure 6, distribute complicatedly and are decomposed into four components, noionic $Cl_{2p3/2}$ (at

Table IV Relative Concentration of C_{1s} and Cl_{2p} Components for CCl_4-plasma-treated Polypropylene Films

| Plasma Conditions Discharge Current (mA) | C_{1s} Components (%) | | | | Cl_{2p} Components (%) | | | |
| | | C — O | | | Nonionic Cl | | Ionic Cl | |
	CH	C — Cl	C = O	C(O)O	2p3/2	2p1/2	2p3/2	2p1/2
Untreated	96	4	< 0.1	< 0.1	—	—	—	—
50	48	32	12.0	8.0	65	32	2	1
75	76	8	4.0	12.0	13	7	53	27
100	85	5	0.0	9.0	15	7	52	26
150	77	10	6.0	7.0	21	12	43	24

200.0–200.7 eV) and $Cl_{2p1/2}$ (201.9–202.5 eV) (C—Cl) and ionic $Cl_{2p3/2}$ (198.3–198.8 eV) and $Cl_{2p1/2}$ (200.1–200.9 eV) (Cl$^-$).[29] The noionic Cl may be a product of chlorination of polypropylene with the CCl_4 plasma and the ionic Cl may be a product of sputter-etching reactions of the aluminum electrode. This assumption could be supported by the evidence that the Al_{2p} core level spectra appeared at about 74 eV, which was somewhat higher than pure aluminum (72.9 eV),[28] although the spectra are not represented here for the sake of brevity. If the assumption is true, an efficiency in the chlorination of polypropylene films with the CCl_4 plasma could be estimated from the ratio of the noionic and ionic Cl components. The effective chlorine in the 13 chlorination is 97, 20, 22, and 33% of the total chlorine incorporated into the polypropylene films by the CCl_4 plasma operated at discharge currents of 50, 75, 100, and 150 mA, respectively. This emphasizes that the chlorination is favorable under a mild CCl_4 plasma operated at a discharge current of 50 mA. In strong CCl_4 plasmas operated at discharge currents of more than 75 mA, chlorine is consumed by the aluminum sputtering reactions rather than by the chlorination.

CONCLUSION

The CCl_4 plasma treatment of polypropylene films was investigated from the viewpoint of hydrophilic surface modification. The results are summarized as follows:

1. The CCl_4 plasma treatment is effective in hydrophilic modification. Hydrophilicity caused by the CCl_4 plasma treatment strongly depends on plasma conditions, especially on the discharge current. When the discharge current varies from 50 to 150 mA, the advancing contact angle of water decreases from 81° to 7° and the surface energy increases from 38.9 to 67.7 mJ/m^2 when the discharge current varies from 50 to 150 mA.
2. The CCl_4 plasma initiates chlorination, oxidation, and aluminum sputtering reactions. The chlorination of polypropylene films is favorable in a mild CCl_4 plasma operated at a discharge current of 50 mA. The oxidation and aluminum sputtering reactions are predominant over the chlorination in strong CCl_4 plasmas operated at discharge currents of more than 75 mA.

3. The chlorination occurring in the mild CCl_4 plasma is restricted within 36 Å deep from the topmost layer of polypropylene films. The modification in the strong CCl_4 plasma occurs predominantly at inner layers of 36–49 Å deep rather than near the surface.
4. The chlorine functionalities incorporated by the CCl_4 plasma contain nonionic and ionic chlorine. The oxygen functionalities involve $C=O$ and $C(O)O$ groups. The aluminum functionalities contain aluminum chloride as well as aluminum oxides.
5. Hydrophilicity caused by the CCl_4 plasma treatment is due to not only chlorine functionalities but also to oxygen and aluminum functionalities.

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