

Glow Discharge Polymerization of Reactive Functional Silanes on Poly (methyl Methacrylate)

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Synopsis

Glow discharge polymerization among such reactive functional silanes as 3-methacryloxypropyltrimethoxysilane (MSL), 3-glycidioxypropyltrimethoxysilane (ESL), and vinyltrimethoxysilane (VSL) on poly (methyl methacrylate) was investigated by means of Fourier transform infrared spectroscopy, ESCA analysis, and contact angle measurement. Flow rate of monomer influenced both polymer deposition rate and polymer elemental composition. Infrared spectra showed differences in chemical structure among the polymers prepared from the different silanes. All of the polymers obtained contained similar chemical groups such as $-\text{CH}_3$, $-\text{CH}_2-$, $\text{Si}-\text{O}-\text{Si}$, and $\text{Si}-\text{O}-\text{C}$. Polymers deposited from MSL and ESL contained highly hydrophilic functional groups like $\text{C}-\text{OH}$, $\text{Si}-\text{OH}$, and $\text{C}=\text{O}$ on the uppermost layer while that from VSL contained highly hydrophobic functional groups like $-\text{CH}_3$ groups. Chemical analysis by ESCA and contact angle measurement gave evidence for the similarity of the polymers prepared from MSL and ESL, in contrast with the differences of the polymers prepared from VSL.

INTRODUCTION

Plasma polymerization prepared in glow discharges is a polymer-forming process substantially different from various conventional polymerizations. The chemical reactions are complex. They have been extensively studied to understand how organic molecules are excited by the discharge of electrons, ions, radicals, etc., and also how these fragmentations can rearrange simultaneously to form complex polymers. There are at least two major types of the polymerization mechanisms involved in the process. The first is conventional plasma-induced polymerization, and the second is plasma-state polymerization.^{1,2} Today, plasma polymerization is generally assumed to be a combination of the induced and state mechanisms.

Plasma processes have been used for the chemical modification of polymer surfaces (100 Å to 100 μm thick) without affecting their bulk properties.³⁻⁵ The process may be more promising than the high energy radiation grafting technique,^{6,7} where materials are affected throughout the bulk. Therefore, glow discharge polymerization processes have been applied to improve adhesion,⁸⁻¹⁰ biocompatibility,¹¹ and wettability^{12,13} in the area of polymers and coatings.

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Poly(methyl methacrylate) (PMMA) has been widely used for its bulk chemical, mechanical, and optical properties especially in the areas of implantable biomedical materials and structural materials like aircraft windows. The bulk properties of PMMA are totally acceptable and even the desired ones for certain applications. However, the surface properties may not be satisfactory. Therefore, chemical modification restricted to the surface region of PMMA could provide the desired surface properties while leaving the bulk materials unchanged. PMMA has a hydrophobic surface with the critical surface energy (γ_c) of 36 dyn/cm.¹⁴ The surface modification, by incorporating hydrophilic groups on the polymer, could place a hydrophilic layer on the hydrophobic surface. Gardella and Hercules^{15,16} found the simple process to hydrolyze methacrylate functional groups of the PMMA. But since the polymer has a low surface area, the technique was found to be ineffective. Gregonis and Andrade¹⁴ have taken the approach of making the copolymers from the monomers with different sidechain ester functional groups as a means of changing the surface properties.

From the literature survey, a number of silicon-containing plasma polymers prepared under different operational conditions have been reported. Hoffman¹⁷ and Hudis¹⁸ have discussed extensively the technique of surface modification by plasma processes. Inagaki and colleagues^{19,20} have investigated the influence of the parameter of energy input per unit mass (W/FM) on the structure and composition of films from several silicon-containing compounds. Smolinsky and Vasile^{21,22} studied vinyltrimethylsilane containing reactions in plasma system by mass spectrometry. Evans and Prohaska²³ prepared thin films of vinyltrimethylsilane and also copolymerized them with styrene in a glow discharge. Nguyen and co-workers²⁴ have applied plasma prepared organosilicon polymers to photolithography. However, no report has been found in the literature that deals with plasma polymers of silane coupling agents.

The primary objective of our investigation in the field of plasma polymerization was to investigate plasma films of silicon containing compounds deposited on the surface of a glassy amorphous polymer, like poly(methyl methacrylate), and to characterize the surfaces of the unmodified and modified polymers. The monomers used in this study were silanes with the terminal reactive functional groups such as methacrylate-terminated silane (MSL), epoxy-terminated silane (ESL), and vinyl-terminated silane (VSL). These silanes have been widely used in the area of composite materials as coupling agents for filler-resin interfaces. The deposition of the selected silane polymers on PMMA by plasma processes may offer possibilities for altering the surface properties of PMMA to be compatible with subsequent selective coatings.

EXPERIMENTAL

Materials

The silicon-containing compounds used for the plasma polymerization were 3-methacryloxypropyltrimethoxysilane (Dow-Z6030), 3-glycidoxypropyltrimethoxysilane (Dow-Z6040), and vinyltrimethoxysilane (Dow-Q9-6300), sup-

plied by Dow-Corning Corporation, Miami, FL. The chemicals were used as received. Prior to use, these compounds were subjected to multiple freeze-pump-thaw cycles after placing them in a monomer reservoir. The polymer substrates were Plexiglas (PMMA) sheets, provided by Rohm and Haas. The substrate was cut to the volume dimensions of $5 \times 25 \times 50$ mm. Prior to the experiments, the substrate samples were washed with 5% KOH in aqueous solution, rinsed with distilled water, and dried with methanol. The clean substrate samples were kept in an oven at 70°C for 2 h and then stored in a desiccator over night.

Plasma Reactor and Polymerization Procedures

An inductively-coupled glow discharge tubular reactor (75 mm inner diameter, 600 mm long) was used for the film preparation. The main reactor system is the same as that used by Kny et al.²⁵ The configuration of the process system including the rf copper coil, the monomer inlet, the pressure gauge, and the vacuum unit are schematically illustrated in Figure 1. The impedance of the glow discharge and the generator was tuned through a matching network for the inductive coupling of a 3.9 MHz radio frequency source. The reactor system was evacuated to the millitorr range by means of a rotary pump. The pressure was monitored with a capacitance manometer (Baratron type 220B, MKS Instruments). The flow rates of Ar and monomers were adjusted through suitable setting of "NUPRO" fine metering valves.

In general, the experimental procedures are as follows: Precleaned substrates were mounted by adhesive tape to the inner wall of annular glass sleeves which were placed in the tubular reactor. The system was then pumped to a pressure of about $10 \mu\text{m Hg}$. Argon gas was introduced into the reactor chamber. The substrate surfaces were exposed to argon plasma for 10 min. The system was evacuated again to about $10 \mu\text{m Hg}$ to eliminate most of the residual gases. The monomer reservoir was then opened to the plasma chamber. The flow rates of the monomer vapor were determined by measuring the pressure increase per minute when the vapors were introduced into the

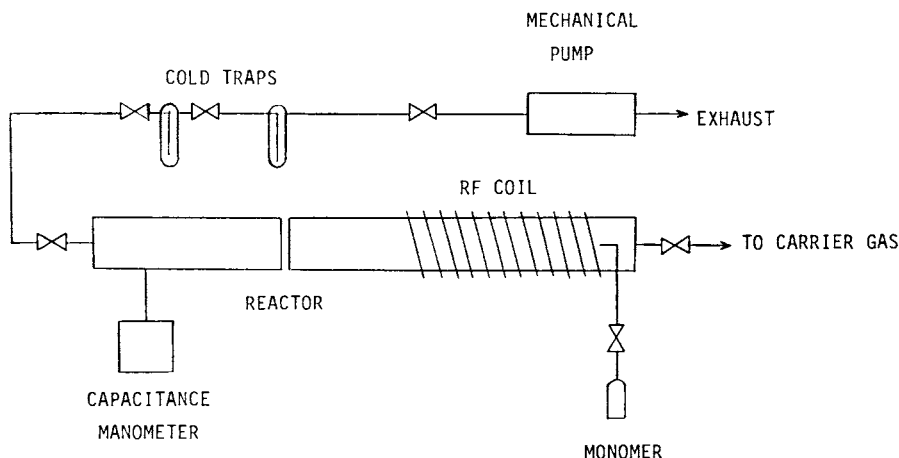


Fig. 1. Inductively-coupled glow discharge tubular reactor.

TABLE I
Operating Conditions for Glow Discharge Polymeric Film Deposition^a

Operating Condition	Batch Number		
	P-34	P-39	P-41
(I) Pressure before process I ($\mu\text{m Hg}$)	10.8	10.6	10.4
Inert gas for etching	Argon	Argon	Argon
System pressure before Rf power is applied ($\mu\text{m Hg}$)	106.4	111.7	106.2
System pressure after Rf power is applied ($\mu\text{m Hg}$)	116.3	122.1	118.7
Rf power input (Ws)	37	37	37
Duration (min)	10	10	10
(II) Pressure before process II ($\mu\text{m Hg}$)	11.1	10.6	10.5
Starting monomers	MSL	ESL	VSL
Flow rate of monomer [$\text{cm}^3(\text{STP})/\text{s}$]	1.73×10^{-3}	1.90×10^{-3}	4.33×10^{-3}
System pressure before Rf power is applied ($\mu\text{m Hg}$)	39.3	42.4	56.7
System pressure after Rf power is applied ($\mu\text{m Hg}$)	52.6	59.9	83.3
Rf power input (watt)	37	37	37
Standing wave ratio (SWR)	1	1	1
Duration (mins)	60	60	60
W/FM (MJ/kg)	1.92×10^3	1.84×10^3	1.29×10^3

^aMSL = 3-methacryloxypropyltrimethoxysilane (Dow-Z6030); ESL = 3-glycidioxypropyltrimethoxysilane (Dow-Z6040); VSL = vinyltrimethoxysilane (Dow-Q9-6300); W/FM = energy input per unit mass.

closed reactor system of known volume. After the vapor flow rates and chamber pressure stabilized, the rf power was applied and the glow discharge polymerization was initiated. The operating conditions for a typical run are shown in Table I. After the plasma was terminated and the monomer line was turned off, the system was pumped to a pressure of about 10 $\mu\text{m Hg}$ and maintained at this pressure for about 30 min. The pressure was then allowed to rise to atmospheric pressure (under air); the samples were removed and kept in a dessicator.

The plasma polymer deposition rate was calculated from the weight increase of aluminum foil sheets (10 \times 20 mm, 0.005 mm thickness), which were horizontally lined along the reactor chamber starting from the monomer inlet. The sheets were mounted with tape on a glass plate (25 \times 300 mm). An average weight gain of 13 pieces of aluminum foil placed at locations between monomer inlet to 26 cm was taken for the calculation of polymer deposition rate.

Film Characterization

Elemental Analysis

The chemical properties of polymers are often determined by the presence or absence of certain surface functional groups. Electron spectroscopy for chemical analysis (ESCA) has been used for studying polymer surfaces. For the elemental analysis of substrates and films of this study, the photoelectron spectrometer (Model 548, Physical Electronics, Eden Prairie, MN) was used with an X-ray source of $\text{MgK}\alpha$ (1253.6 eV). Typical operating conditions were as follows: X-ray gun, 10 kV, 40 mA; pass energy, 50 eV, chamber pressure,

5×10^{-9} torr; sputtering rate, 65 Å/min. Data acquisition and analysis were done by computer (IBM-PC model) linked to the spectrometer. Under the experimental conditions, the Au_{4f} core level at 83.7 eV was used for the energy scale calibration. The broad complex spectra of the C_{1s} and the Si_{2p} core levels were deconvoluted by computer (IBM-PS/2 Model 50) and using a curve fitting program developed by the Material Research Center, University of Missouri-Rolla, Rolla, MO. A Gaussian distribution was assumed, and the observed broad envelopes were resolved with several component peaks. The curve fitting was carried out by variation of three parameters: the position of the peaks, the height of the peaks, and the full width at half maximum (FWHM). It is well known that the shift in the electron binding energy can be caused by calibration errors as well as the effects of sample charging. The degree of the effect depends on the thickness of the insulated film to be analyzed. Therefore, in this study the binding energies of the component peaks were calibrated by assuming that the component peak of the C_{1s} with the highest intensity be assigned as an aliphatic carbon and C—Si centered at 284.6 eV as reported in the literature.^{26,27} The shift in binding energy of the peak was then used as a reference to correct the centers of the remaining peaks.

Infrared Spectroscopy

KBr pellets were prepared and placed in the plasma reactor. The plasma films were deposited onto the pellets as described previously. The film samples were then analyzed using a Perkin-Elmer 1750 infrared Fourier transform spectrometer which was connected to a Perkin-Elmer 7300 professional computer.

Wettability of Films

Contact angles of liquids on solid surfaces are generally used to describe how wettable the particular surface is with respect to a certain liquid. In this study, the contact angles to water on untreated and treated surfaces were measured using a sessile drop measurement in which a drop of water (0.03 cm³) was placed on the surface and its dimensions measured using a microscope fitted with a goniometer eye piece.

RESULTS AND DISCUSSION

Polymer Deposition Rate

When the reactive functional silanes, 3-methacryloxypropyltrimethoxysilane, 3-glycidoxypopyltrimethoxysilane, and vinyltrimethoxysilane, were used for the glow discharge polymerization, colorless transparent polymer films were deposited on the surfaces of the PMMA. The deposition rate of the polymers determined as a function of the distance from the monomer inlet was illustrated in Figure 2. Generally, when a tubular reactor was used for the film preparation, the polymer films were not uniformly deposited. The distribution of film thickness may arise from different concentrations of monomer vapor and that of the various species generated by the plasma at different

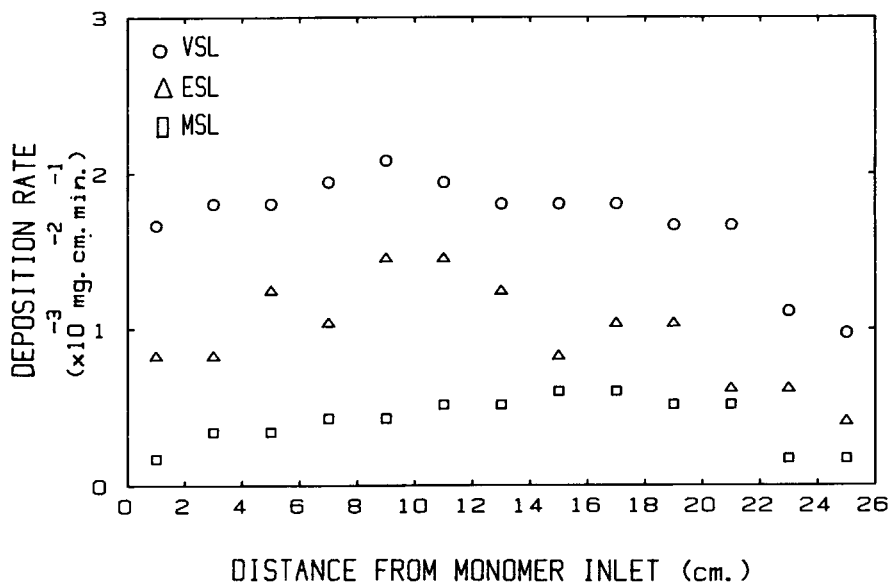


Fig. 2. Deposition rate profile observed at 37 W.

points in the reactor. In this study, the deposition rate was expressed as an average value of polymer deposited on positions between monomer inlet to 26 cm from the monomer inlet. The deposition rates of MSL, ESL, and VSL on the PMMA were 0.41, 0.98, and 1.70 $\text{mg cm}^{-2} \text{min}^{-1}$, respectively. This may be due to the different flow rate of the monomers, even though all control valve settings were the same.

Polymer Structure

After the film preparation, the structures of the plasma polymers were documented by FT-IR analysis. Figure 3 represents the IR spectra of the polymers. The IR spectral peak positions^{28,29} are tabulated in Table II. In the spectrum of the polymers prepared from VSL, strong absorptions were observed at 2950 (CH_3), 2846 (CH_2), 1460 (C-H), 1269 (Si-CH_3), 1191 (Si-OCH_3), 1100-1000 (Si-O-Si , Si-O-C), 810-800 (Si-C) cm^{-1} . The spectrum indicates that the polymers consist mainly of Si-CH_3 , Si-OCH_3 , and Si-O-Si groups. The polymers prepared from MSL and ESL show similar spectra. The strong absorptions of MSL were found at 3400-3200 (OH), 2936 (CH_3), 2872 (CH_2), 1708 (C=O), 1453 (C-H), 1375 (Si-CH_3), 1100-1000 (Si-O-Si , Si-O-C), 950-830 (Si-O), and 810-800 (Si-C) cm^{-1} , while the absorptions of ESL were found at 3400-3200 (OH), 2943 (CH_3), 2865 (CH_2), 1705 (C=O), 1453 (C-H), 1372 (Si-CH_3), 1100-1000 (Si-O-Si , Si-O-C), 950-830 (Si-O), and 810-800 (Si-C) cm^{-1} . For both polymers, the band observed within the 3400-3200 cm^{-1} range is typical of the stretching vibrations of hydroxyl groups. The marked broadening of this band indicates that it may arise from hydrogen-bonded hydroxyls from the Si-OH groups as well as the C-OH group.²⁸ The weak broad band which originates from the Si-O stretching vibration

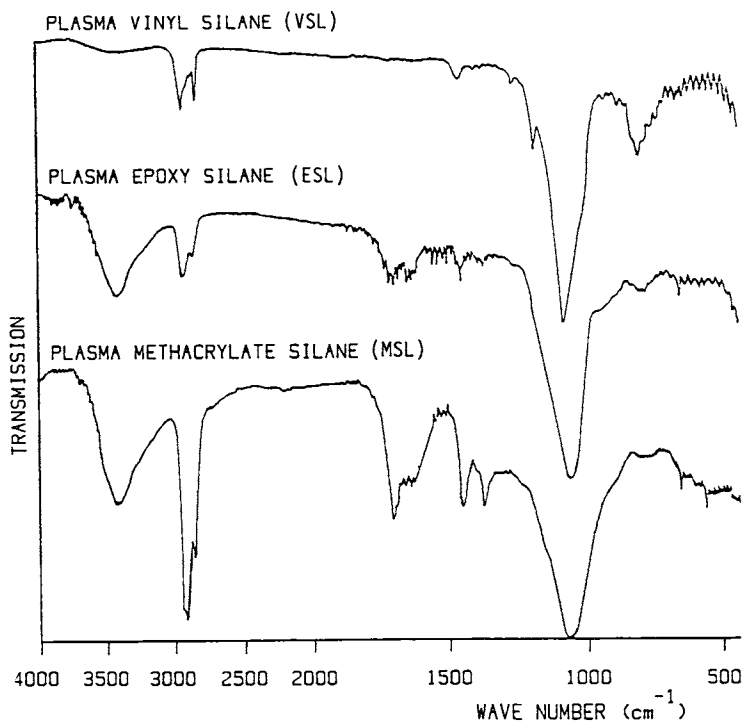


Fig. 3. IR spectra of plasma polymers from MSL, ESL, and VSL.

at the 950–830 cm^{-1} region suggests the appearance of the Si—OH functional groups of the films. The C=O stretching gives a strong absorption within the 1708–1705 cm^{-1} region. Hydrogen bonding and resonance effects are known to increase the C=O bond length and cause a reduction of the frequency of absorption. The shift of the carbonyl band from the typical 1720 cm^{-1} to a lower wavelength of 1708–1705 cm^{-1} implies the formation of carboxylate type structure of the films.²⁹ The strong absorption in the 1100–1000 cm^{-1} region arise from the asymmetric stretching of Si—O—Si and Si—O—C. This single broad band possibly originates from the short siloxane chains rather than the split band of the longer siloxane chains.²⁸ The weak absorption within the 810–800 cm^{-1} region indicates the appearance of Si—C linkages at the surface.

Chemical Analysis by ESCA

Two types of information were accessed through the ESCA studies. The elemental composition (in atomic percent) and the atomic ratio of Si/C, Si/O, and O/C of the integrated peak areas yield compositional data and list in Tables III and IV. The curve fits of the carbon 1s and silicon 2p core-level signals yield relative concentrations of functional groups as shown in Table V and Figures 4–7.

The ESCA studies of the unmodified PMMA provides a complementary information on the substrate for the plasma process. The O/C ratios and

TABLE II
IR Peak Positions of Plasma Films^a

Monomers	Wave length (cm ⁻¹)	Possible functional groups
MSL	3400–3200	OH stretching
	2936	CH ₃ stretching
	2872	CH ₂ stretching
	1708	C=O stretching
	1453	CH ₃ asym. deformation
	1375	CH ₃ sym. deformation
	1100–1000	Si—O—C, Si—O—Si stretching
	950–830	Si—O stretching
	810–800	Si—C asym. rocking
	ESL	3400–3200
2943		CH ₃ stretching
2865		CH ₂ stretching
1705		C=O stretching
1453		CH ₃ asym. deformation
1375		CH ₃ sym. deformation
1100–1000		Si—O—C, Si—O—Si stretching
950–830		Si—O stretching
VSL	810–800	Si—C asym. rocking
	2950	CH ₃ stretching
	2846	CH ₂ stretching
	1460	CH ₃ asym. deformation
	1269	Si—CH ₃ sym. deformation
	1191	CH ₃ asym rocking
	1100–1000	Si—O—C, Si—O—Si stretching
	810–800	Si—C asym. rocking

^aFrom Refs. 28 and 29.

carbon 1s core-level curve fits evaluated the surface composition of the PMMA reference sample. Prior to plasma treatment, the O/C ratio was high in the near surface region and decreased with depth. This reflects the arrangement of the oxygen-rich functionality like carbonyl group or methoxy groups on the PMMA surface. The topmost layer with high oxygen content may also involve incorporation of oxygen functionality from either moisture chemisorption or other reactions during surface cleaning process.

TABLE III
Elemental Composition of Surface Layer of Substrate and Polymers^a

Sample	W/FM (MJ/kg)	Elemental composition			
		C	O	Si (at. %)	Others
PMMA	—	74.90	24.30	0.20	0.60
MSL	1.92×10^3	66.00	24.80	9.10	0.10
ESL	1.84×10^3	61.80	28.30	9.70	0.20
VSL	1.29×10^3	54.00	28.70	16.80	0.50

^aPrepared by glow-discharge polymerization and determined by ESCA.

TABLE IV
Elemental Ratios for PMMA Surface and Polymers as Determined by ESCA

Sample	Depth (Å)	Atomic ratio by ESCA		
		Si/C	Si/O	O/C
PMMA	0	0.0027	0.0082	0.3244
	32.5	0.0021	0.0488	0.0433
	65.0	0.0021	0.0645	0.0323
	130.0	0.0021	0.0690	0.0301
	325.0	0.0021	0.0870	0.0237
MSL	0	0.1379	0.3669	0.3758
	32.5	0.2188	0.6860	0.3190
	65.0	0.2234	0.7617	0.2933
	130.0	0.2314	0.8042	0.2877
	325.0	0.2104	0.8788	0.2395
ESL	0	0.1570	0.3428	0.4579
	32.5	0.3057	0.7314	0.4180
	65.0	0.2973	0.7619	0.3902
	130.0	0.2967	0.8054	0.3683
	325.0	0.2707	0.9301	0.2911
VSL	0	0.3111	0.5854	0.5315
	32.5	0.5516	0.8227	0.6704
	65.0	0.5667	0.8916	0.6356
	130.0	0.5185	1.0161	0.5103
	325.0	0.4706	0.7860	0.5987

TABLE V
Calibrated C_{1s} and Si_{2p} Core-Level Spectra of the Surface of Polymers

Core-level spectra	Deconvoluted peak position (eV) and peak area (%)		
	Component I	Component II	Component III
PMMA C _{1s}	284.6 (71%)	286.6 (12%)	288.2 (17%)
	MSL C _{1s}	284.6 (80%)	286.4 (14%)
Si _{2p}		100.9 (14%)	102.2 (82%)
ESL C _{1s}	284.6 (73%)	286.5 (22%)	287.9 (5%)
	Si _{2p}	100.9 (13%)	102.2 (29%)
VSL C _{1s}	284.6 (85%)	286.7 (15%)	—
	Si _{2p}	100.9 (6%)	102.2 (41%)

^aCalibrated C_{1s} and Si_{2p} core-level spectra of the surface of substrate and polymers prepared from MSL, ESL, and VSL.

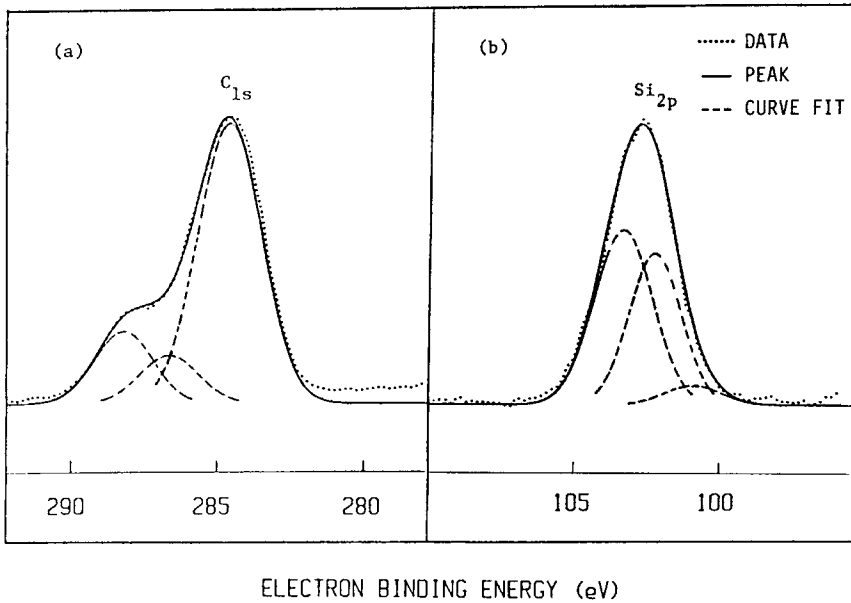


Fig. 4. Examples of typical C_{1s} and Si_{2p} ESCA spectral curve fits obtained from (a) PMMA surface and (b) VSL film deposited on PMMA surface by plasma polymerization.

The polymers prepared from the silicon-containing compounds (MSL, ESL, VSL) were examined by ESCA analysis. The elemental compositions of the polymers are tabulated in Table III. Yasuda¹ has suggested that, at high W/FM levels, the polymer deposition rate is independent of W/FM but dependent upon monomer flow rate. In this study, the W/FM levels were higher than 1000 MJ/kg. The flow rate of the monomer was found to be the main influence on the polymer deposition rate and elemental compositions of the films. Since the monomers used contain only one silicon atom in each molecule, the silicon content of the film indirectly reveal information for the polymer deposition rate. The silicon content of the polymers prepared from MSL and ESL were similar, but less than that of the polymers from VSL. At a constant rf power level of 37 W, the VSL with the highest flow rate (Table I)

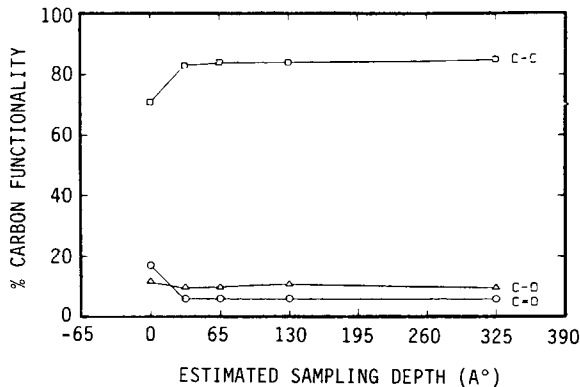


Fig. 5. Curve-fit depth profiles of C_{1s} core level spectra of PMMA.

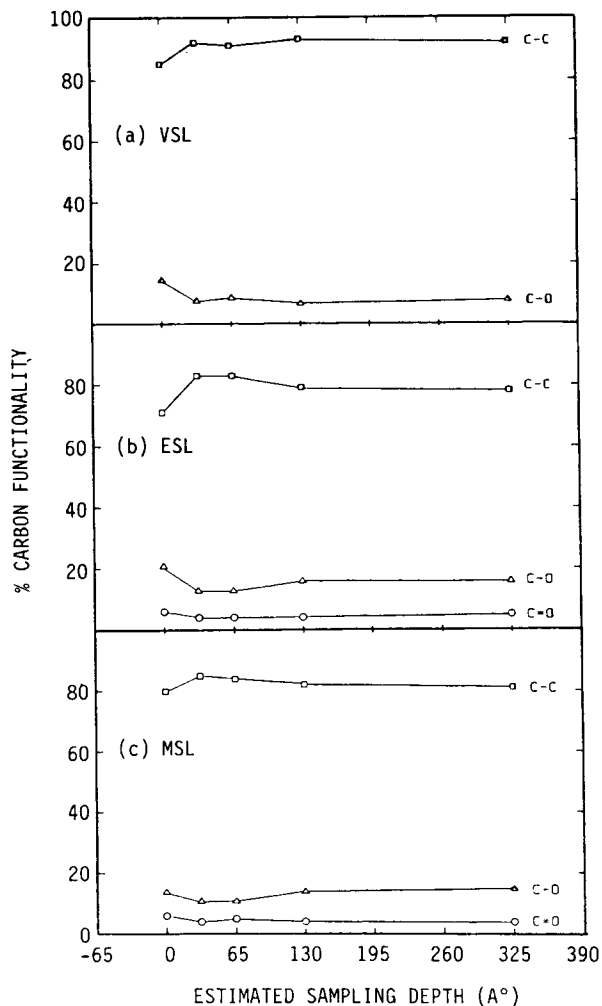


Fig. 6. Curve-fit depth profiles of C_{1s} core level spectra of (a) VSL, (b) ESL, and (c) MSL plasma films deposited on PMMA.

gave the highest deposition rate (Fig. 2) and also the highest silicon content (Table III). In all three monomer systems, the polymer deposition rates were found to increase with increasing monomer flow rate.

The elemental ratios of plasma polymer are illustrated in Table IV. For the MSL film, oxygen and carbon concentrations were highest in the uppermost layer of the film, while the silicon concentrations were highest at deeper layers. These observations imply that at the outermost layer of the film, the oxygen-rich functional groups like carbonyl, carboxyl, hydroxyl, alkoxy, and silanol groups may be formed. The same results were observed for the ESL film. For the case of VSL film, the opposite results were found. The O/C ratio which increases with depth indicates the deposition of the carbon-rich functionality like methyl or methylene groups at the outer layer. The Si/C and Si/O ratios in Table IV showed that silicon content of VSL film was about

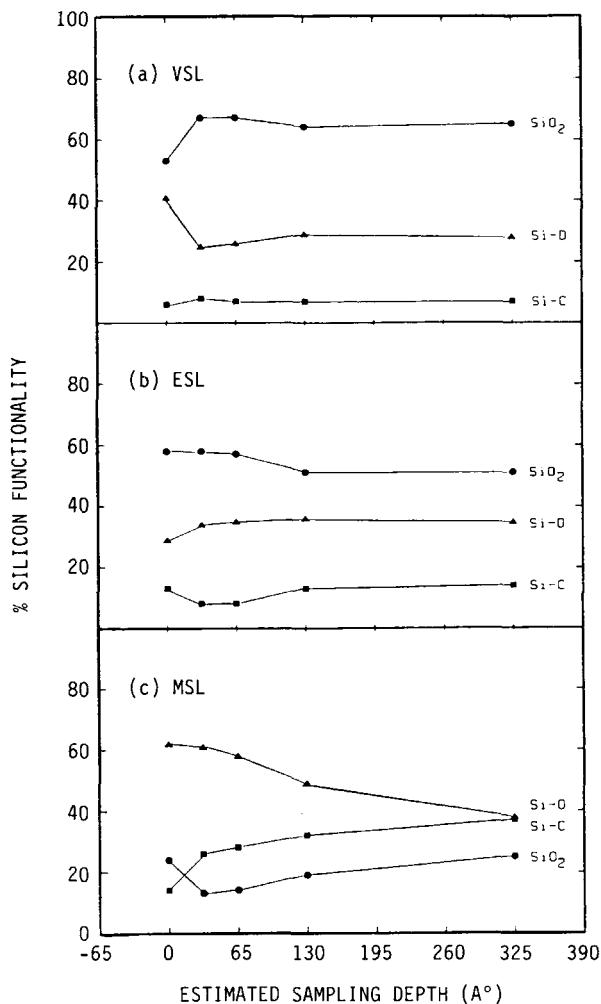


Fig. 7. Curve-fit depth profiles of Si_{2p} core level spectra of (a) VSL, (b) ESL, and (c) MSL plasma films deposited on PMMA.

half that of the carbon content and was nearly equal to the amount of oxygen. Such results may suggest the formation of alkylsiloxane chains and carbon chains of polymers.

The plasma polymers prepared from the reactive functional silanes showed ESCA features that were combinations of two or more component peaks. Assignments were made to individual components on the basis of the mathematical deconvolution by computer. Differentiating carbonyl, carboxylated, and hydroxylated oxygen was not possible from O_{1s} spectra, but the oxidized carbon functionalities were evident as a high-binding energy shoulder on the saturated C_{1s} signal. The line width of the high binding energy C_{1s} shoulder and that of the Si_{2p} spectra suggest the presence of the multiple functionalized carbon and silicon species. Such results are summarized in Figures 5-7

and Table V. In Figures 4, the dashed lines show the Gaussian component peaks; their sum (solid line) almost equals the dotted line observed experimentally. In this study, sample charging gave a shift in the binding energy value and introduced an indeterminate increase in peak widths. Thus, the identification of specific functional groups was complicated. Calibration of the peak positions was used to adjust the position of the deconvoluted component peaks of C_{1s} and Si_{2p} to correspond to the reference peaks reported in the literature.^{26,27} For the C_{1s} core-level spectra, the peaks centered at 284.6, 286.6, and 287.9 eV are assigned to aliphatic carbon as well as C—Si, C—O, and —C=O groups, while, for the Si_{2p} core-level spectra, the peaks centered at 100.9, 102.2, and 103.3 eV are assigned to Si—C, Si—O, and SiO_2 groups, respectively.

In the untreated PMMA surface analysis, C_{1s} spectra were resolved into three peaks centered at 284.6, 286.6, and 288.2 eV, which are assigned to aliphatic carbon (methyl and methylene groups), C—O (methoxy groups) and —O—C=O (ester carbonyl groups). The relative areas of the peaks for the outermost layer were 71, 12, and 17%, while those at deeper layers were 84, 10, and 6%, respectively. The data obtained confirm the homogeneity of the functional groups over the various depths near surface region sampled by ESCA analysis (see Fig. 6).

For the MSL film, the peaks of aliphatic carbon and C—Si, C—O, and —C=O groups were positioned at 284.6, 286.4, and 287.9 eV. The outermost surface layer analysis indicates a 13.3 : 2.3 : 1 (C—C : C—O : C=O = 80% : 14% : 6%) ratio of the functional groups. After the depth of 130 Å, a 20.5 : 3.5 : 1 (C—C : C—O : C=O = 82% : 14% : 4%) ratio of the functional groups was found (see Fig. 6). From the Si_{2p} core-level spectra of the MSL top layer shown in Fig. 7, the 1 : 4.4 : 1.7 (Si—C : Si—O : SiO_2 = 14% : 62% : 24%) ratio of functional groups was obtained. Si—O group content was diminishing with depth while Si—C and SiO_2 increased. Such trend suggests that the oxygen-rich functionalities like hydroxyl, silanol, and carbonyl groups are to be found in the upper layers of the films while the presence of the siloxane structure are found in the deeper layers.

The curve-fit results of C_{1s} core-level spectra of ESL film illustrated in Figure 6 were similar to that of MSL. The ratio of C—C : C—O : C=O of 14.6 : 4.4 : 1 (73% : 22% : 5%) was found at the outermost layer and the ratio of 20 : 4 : 1 (80% : 16% : 4%) was found at deep layer. But the results from Si_{2p} core-level spectra of ESL shown in Figure 7 were different from the ones found in MSL film. The content of SiO_2 groups was higher than the content of Si—O groups and Si—C groups. A 1 : 2.2 : 4.5 (Si—C : Si—O : SiO_2 = 13% : 29% : 58%) ratio of functionality was found at the top layer and a 1 : 2 : 3.9 (Si—C : Si—O : SiO_2 = 13% : 36% : 51%) ratio was found at the deep layer. The results indicate that the film consists of the combination of carbon chains, siloxane chains, and oxygen-rich functional groups which agree with the results obtained from FT-IR analysis.

The ESCA analysis of chemical groups on the surface of the polymer prepared from VSL is illustrated in Figures 6 and 7. The polymer contains about 85% of aliphatic carbon and C—Si, and about 15% of oxidized carbon at the surface layer. No carbonyl functional groups were observed. The Si_{2p}

TABLE VI
Contact Angles of Water on PMMA
and Plasma Films^a

Solid surface	Water contact angle (θ_{adv}) (deg)
Plexiglass (PMMA)	63.0
Plasma MSL film	20.0
Plasma ESL film	45.0
Plasma VSL film	69.5

^aFilms were deposited on PMMA substrates.

core-level spectra contains only 6% of Si—C groups with high amounts of Si—O (41%) and SiO₂ (53%). But for the deep layer, the polymer contains about 92% of aliphatic carbon and C—Si, 8% of oxidized carbon, 7% of Si—C groups, 29% of Si—O groups, and 64% of SiO₂ groups. It is pointed out that the film consists of the combination of carbon chains, siloxane chains, and some hydroxylated groups of carbon and silicon.

Wettability of Films

The surface properties of the smooth solid polymer are strongly dependent upon the chemical constitution of molecules in the surface layer. Therefore, the surface which has been modified can be characterized from the interfacial reactions between an aqueous solution and a polymer surface. Contact angle methods are one of the simple techniques capable of evaluating the polymer–water interface directly. The results of the “advancing” contact angles of water on the unmodified and modified PMMA are tabulated in Table VI.

The topmost layer of the polymers prepared from MSL and ESL were dominated by oxygen rich functional groups as observed from FT-IR and ESCA analyses. The results obtained from the water contact angle measurement on these solid films provide additional supporting evidence. PMMA surface structures modified by MSL and ESL plasma polymers were more wettable than the unmodified surface. For the VSL-plasma-modified surface, the arrangement of the hydrophobic functional groups, i.e., methyl groups, at the outermost layer exhibited the hydrophobic properties to the water contact. Such results suggest that MSL-plasma-modified surface with the highest hydrophilicity may be considered as the most favorable surface for the subsequent selective coatings.

CONCLUSIONS

Glow discharge polymerization of reactive functional silanes on the surface of poly(methyl methacrylate) provided an opportunity to investigate the surface alteration of the polymer. The concluding remarks of this study were

summarized as follows:

1. By plasma polymerization, the surface of PMMA was coated with silicon-containing polymers. All of the polymers consist of a combination of carbon chains and siloxane chains with varying functional groups at the surface. Therefore, glow discharge polymerization may be viewed as a surface modification technique which provides low alteration of the bulk properties of polymer substrates.
2. The polymers formed by the glow discharge are different from the corresponding conventional polymers which one would expect from the chemical characters of the starting monomers. Since there is a large extent of chemical fragmentation taking place during the glow discharge, the polymers were virtually formed and deposited on the solid surface through the recombination and/or neutralization reactions. These plasma deposited polymers may retain a certain degree of the functionality of their starting materials.
3. The surface of PMMA can be modified by the glow discharge polymerization of the reactive functional silanes. The desired surface properties of PMMA for particular applications can be achieved by the proper choice of starting monomers, and with optimization of the glow discharge operating conditions.

Finally, further study on this subject is currently being undertaken in our laboratory, so that a better understanding of these surface modification techniques might be more fully realized.

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