Glow Discharge Polymerization of Tetramethylsilane by Capacitive Coupling of 20 kHz Frequency and Surface Hardening of Polyethylene Sheet

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Synopsis

Glow discharge polymerizations of tetramethylsilane (TMS) were performed by the capacitive coupling of a 20 kHz frequency in comparison with those by the inductive coupling of a 13.56 MHz frequency. The polymers prepared by the former coupling were poorer in carbon and hydrogen, but richer in silicon than those prepared by the latter coupling. These two polymers showing similar infrared spectra contained CH_3, CH_2, CH, Si–O–C, Si–O–Si, Si–CH_3, and Si–CH_2–CH_2–Si groups. Some physical properties involving surface energy, thermal stability, and absorption spectra in the regions of the UV and visible light were determined. This coating procedure was applied for surface hardening of a polyethylene sheet. The surface hardness of the polyethylene sheet was enhanced by a coating of plasma films prepared from TMS or the TMS/O_2 mixtures. Surface hardness was determined by the pencil method and hardness was enhanced from 2B to 2H. The adhesion between these plasma films and polyethylene sheet was good even when immersed in 0.9% NaCl solution at 40°C for 10 days.

INTRODUCTION

Glow discharge polymerization is a unique polymer-forming technique whereby polymers are deposited as thin films on substrate surfaces. This process is frequently applied for surface modification including water repellancy, wettability, and surface hardening.[1-4] This polymerization has an inherent feature in that chemical structures and properties of the formed polymers are strongly influenced by the operational conditions to sustain the glow discharge. From only one monomer polymers with various properties can result by changing the operational conditions, but the properties of forming polymers are difficult to predict before the polymerization occurs. The influence of flow rate of the monomer, pressure, discharge power, discharge method, and reactor design on glow discharge polymerizations have been investigated to seek optimum conditions for preparation of desired polymers.[5-9]

Surface modification of polymeric substrates are important in making membranes for reverse osmosis and plastic lenses. Uniform plasma films are important, because film thickness directly affects efficiency.

In this study to coat uniformly polymeric substrates, a reactor in which a glow discharge is driven by the capacitive coupling of a 20-kHz frequency source is used and some physical properties of the formed polymers are compared with those of the polymers prepared by the inductive coupling of a 13.56-MHz frequency source. This coating procedure, finally, is applied for surface hardening of a polyethylene sheet.

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EXPERIMENTAL

Glow Discharge Polymerization

Two different apparatuses for the glow discharge polymerizations were used in this study: a tubular-type and a bell-jar-type reaction chamber.

The tubular reaction chamber (35 mm inner diameter, 400 mm long) was made of Pyrex glass and fitted with a monomer inlet, a pressure gauge, a vacuum system, and a matching network for the inductive coupling of a 13.56-MHz radio frequency source. A relative position of these elements are schematically illustrated in Figure 1(a). The electric power to sustain the glow discharge was supplied by the inductive coupling of a 13.56-MHz frequency using a coil (nine turns) place out of the chamber. The experimental procedures for the glow discharge polymerizations using the tubular reaction chamber are essentially the same as reported elsewhere.[10] The substrates were horizontally placed in the reaction chamber, and the system was evacuated to approximately 0.1 mtorr using a diffusion and a rotary pump. Argon gas was introduced into the reaction chamber, and, to eliminate water adsorbed on the surfaces of the substrates, the surfaces were exposed to argon plasma for 10 min. Again the system was evacuated to 0.1 mtorr, and the monomer gas, adjusted at a fixed flow rate at a pressure of 30 mtorr, was injected into the reaction chamber. The rf power was turned on, and the glow discharge polymerization was continued at a level of the rf power of 25 W for a suitable duration.

The other apparatus for the glow discharge polymerization is a bell-jar-type reaction chamber (400 mm diameter, 470 mm high). The basic polymerization system is essentially the same as reported elsewhere.[11] The reaction chamber was composed of a monomer inlet, a pressure gauge, a vacuum system and a parallel pair of aluminum electrodes separated from each other by 100 mm. A disk (aluminum or glass, 340 mm in diameter), on which the substrates to be modified by the glow discharge polymerization were mounted was positioned midway between the aluminum electrodes and was rotated around an axis placed on the top of the electrodes during the coating process. A relative position of these elements is schematically illustrated in Figure 1(b). The glow discharge was driven by the capacitive coupling of a 20-kHz audio frequency, and magnetic enhancement was employed. The experimental procedures for the glow discharge polymerization in the bell-jar-type reactor are not essentially different from those employed in the system of the tubular reaction chamber. The sub-
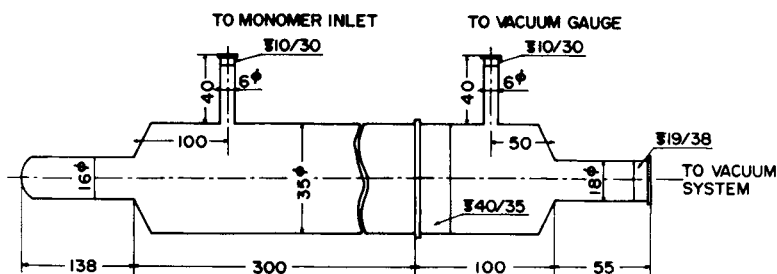

Fig. 1(a). Schematic presentation of the tubular-type reactor (mm).

strates were mounted on the aluminum disk, and the system was evacuated to approximately 10^{-2} mtorr.   To eliminate water adsorbed on the surfaces of the substrates, the surfaces were exposed to argon plasma for 20 min.   Again the system was evacuated to 10^{-2} mtorr, and the monomer gas, adjusted at a fixed flow rate at a pressure of 200 mtorr, was injected into the reaction chamber.   The af power was turned on, and the glow discharge polymerization continued at a constant current of the af power for a suitable duration.   The pressure changes in the system and the voltage level between the electrodes were continuously recorded through the polymerization with a Pirani gauge and a digital multimeter, respectively.

A chemical used for the glow discharge polymerization in this study was tetramethylsilane (TMS) (provided by the Ventron Co.).

Elemental Analysis

The polymers deposited on a glass plate were scraped with a knife, and analyzed for C, H, N, and Si.   The C, H, and N content in the polymers were determined using a CHN Recorder MT-2 (Yanagimoto Co.), and the Si content was determined by gravimetric analysis.

Infrared Spectra

The KBr ground to approximately 150 mesh was thinly sprinkled on the glass plate, and the glow discharge polymerization was performed according to the same procedure as above.   The KBr powder coated with the polymer films by the glow discharge polymerization was provided for preparation of the KBr disk. The spectrometer used was a Nihon Bunko Spectrometer A-3.
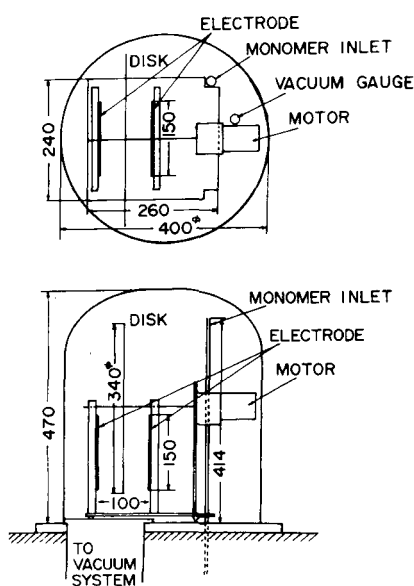

Fig. 1(b). Schematic presentation of the bell-jar-type reactor (mm).

Surface Energy

The contact angles of the polymer films deposited on a polyethylene sheet against water, glycerol, formamide, diiodomethane, and tricresyl phosphate were measured by a drop-on-plate method using a Kyowa Kagaku contact angle meter CA-1. The contact angle data were analyzed to estimate a dispersive contribution, γ_s^d, and a polar contribution, γ_s^p, according to Kaelble's method.[12]

Evaluation of Adhesion between Plasma Films and Polyethylene Substrate

To evaluate adhesion between the plasma films and polyethylene substrate lap-shear strength was measured. Special specimens were provided: with the aluminum coupon ($25 \times 100 \times 1$ mm) of which the surface was sandblasted, the polyethylene substrate was bonded using epoxide adhesive consisting of the mixture of Epicoat 828 and Tomide 235-S at a mixing ratio of 100:70 by weight. The dimension of the overlapping part was 25×12.5 mm long. The construction of the joint, therefore, was polyethylene/plasma film/epoxide adhesive/aluminum coupon. The specimens were pressed at 5 kg/cm^2 at a temperature of 80°C for 0.5 h.

The lap-shear strength of the joint was measured using an Instron universal testing instrument at a peeling speed of 5 mm/min.

RESULTS AND DISCUSSION

Comparison of Glow Discharge Polymerizations at 20 kHz and 13.56 MHz Frequency

Polymer Deposition Rate

Glow discharge polymerizations operated at a 20 kHz frequency were compared with those at a 13.56 MHz frequency. When the tubular reaction chamber was used [Fig. 1(a)] for glow discharge polymerization, a glow expanded over the whole reaction chamber, and the formed polymers were deposited on the whole wall of the chamber. Generally, the polymer disposition rate varies at a location of the reaction chamber, and the distribution in the thickness of the deposited polymers appears. Concerning the distribution of the polymer deposition rate, Yasuda and Hirotsu[13] have investigated in detail influences of type of discharge, reactor design, and operational conditions. They have concluded that this distribution arises from concerted effects of the flow of the starting monomer and activated species generated by plasma, and have proposed a basic reactor design to obtain uniform polymer-deposition rate. Based on their findings, an apparatus was designed [Fig. 1(b)]. To average the polymer deposition rate at any location of substrates placed in a glow discharge, the substrates, which were mounted on a disk positioned midway between the electrodes, were rotated at 60 rpm throughout the glow discharge polymerization. To confine the glow within the space between the parallel electrodes and to minimize the shift of the glow to the back side of the electrodes, the back sides of the electrodes were insulated with Teflon and the relatively high pressure of 0.2 torr was used in the reactor.

Figure 2 shows the distribution of the polymer deposition rate as a function of a distance from the center of the disk in the radial direction. The polymer
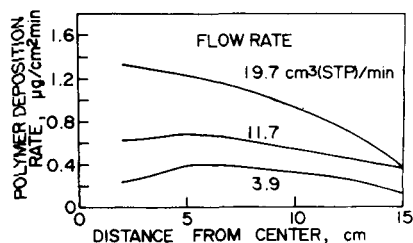
Fig. 2. Distribution of polymer deposition rate as a function of the flow rate of TMS (in the bell-jar-type reactor).

deposition rate was not completely but satisfactorily uniform when the flow rate of TMS was less than 11.7 cm³ (STP)/min. Extremely high flow rate, e.g., 19.7 cm³ (STP)/min, does not exist in uniform deposition. It is not clear why high flow rate of the monomer yielded narrow distribution of the polymer deposition.

Features of the operation in the bell-jar-type reactor are emphasized by comparison with that in the tubular reactor [Fig. 1(a)]. In the operation of the tubular reactor the fairly low pressure of 0.03 torr in the reactor was chosen to enlarge the mean free path of electrons. Figure 3 shows the distribution of the polymer deposition rate as a function of the distance from the monomer inlet. The comparison between Figures 2 and 3 shows that (1) the polymer deposition rate distributes more narrowly in the tubular reactor than in the bell-jar-type reactor and (2) the distribution is strongly sensitive to the monomer flow rate in the operation of the tubular reactor. A small drift of the monomer flow rate directly affects the polymer film thickness. Hence the bell-jar-type reactor is a suitable reactor for coating over a wide area of substrates with less drift in polymer film thickness. The mass of the deposited polymers in the operation of the bell-jar-type reactor, although the relationship between the mass of deposited polymers and polymerization times is not presented here, was linearly proportional to the duration of the polymerization. The thickness of the polymer films can be easily controlled by varying the duration of the polymerization.
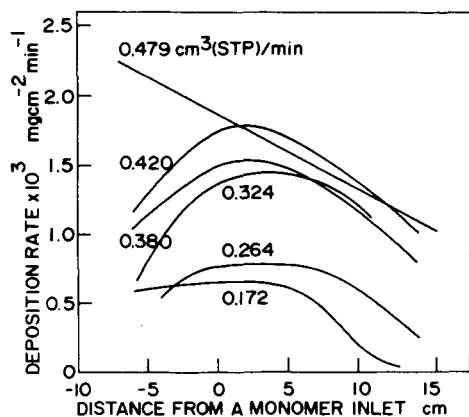

Fig. 3. Distribution of polymer deposition rate as a function of the flow rate of TMS (in the tubular-type reactor).

TABLE I
Comparison of Polymers Prepared from TMS in Capacitively Coupled Discharge (20 kHz) and Inductively Coupled Discharge (13.56 MHz)

Discharge method	Flow rate (cm^3(STP)/min)	Pressure (torr)	Current (mA)	Average deposition rate (mg/cm^2·min)	Appearance	Empirical formula of polymers
Capacitively coupled (20 kHz)	3.9	0.2	70	0.33×10^{-3}	Colorless, film	$C_{2.58}H_{4.94}N_{0.04}O_{0.76}Si$ (threshold temp 240°C residue at 500°C: 71%)
	8.0			0.66	Colorless, film	
	11.7			0.84	Colorless, film and powder	
	19.8			1.06	Colorless, film and powder	
Inductively coupled (13.56 MHz)	0.17	0.03	25[a]	0.48	Colorless, film	$C_{3.72}H_{8.23}N_{0.19}O_{1.09}Si$ (threshold temp 270°C residue at 500°C: 80%)
	0.26			0.66	Colorless, film	
	0.38			1.32	Colorless, film	
	0.43			1.52	Colorless, film	
	0.48			1.62	Colorless, film	

[a] rf power in wattage.

Chemical Composition of the Deposited Polymers

Appearance and elemental composition of the polymers prepared from TMS using the bell-jar-type and the tubular-type reactor, which were operated at a 20 kHz and a 13.56 MHz frequency, respectively, are listed in Table I. The polymers prepared from TMS in the bell-jar-type reactor were deposited as colorless films, but colorless powder was deposited when the monomer flow rate increased to more than 11.7 cm^3 (STP)/min, while the polymers prepared in the tubular reactor were always deposited as colorless films.

The elemental composition of the polymers prepared at the same deposition rate of 0.66 $\mu g/cm^2$·min in the two reactors were compared. The polymers prepared in the bell-jar-type reactor (Table I), had a lower content of carbon and hydrogen than those prepared in the tubular reactor, indicating that the polymers in the bell-jar-type reactor were highly crosslinked.

These polymers showed similar infrared spectra, but there were some differences in intensity of absorptions due to CH_3, CH_2, and CH groups (Fig. 4). On the infrared spectrum of the polymers prepared in the bell-jar-type reactor, absorptions appeared at 3400 (OH), 2950, 2880 (CH_2, CH), 2180 (Si–H), 1450, 1435, 1400, 1370 (C–H), 1255 (Si–CH_3), 1030 (Si–O–C, Si–O–Si), 838 (CH_3), and 798 cm^{-1} (Si–CH_2–CH_2–Si, Si–CH_3). These absorptions were also observed on the spectrum of the polymers prepared in the tubular reactor. The absorptions at 2950, 2880, 1450, 1400, 1370, and 1255 cm^{-1} assigned to CH_3, CH_2, and CH groups were lower in intensity for the polymers prepared in the bell-jar-type reactor than for those prepared in the tubular reactor. This indicates that TMS underwent more vigorous fragmentation in the bell-jar-type reactor than in the tubular reactor and therefore yielded crosslinked polymers.

The influence of oxygen on the glow discharge polymerization of TMS was examined in preparing siloxanelike polymers. The polymers prepared from the TMS/O_2 mixture were deposited tightly on the glass disk and were too hard to be scraped off with a knife. Without performing elemental analysis the poly-
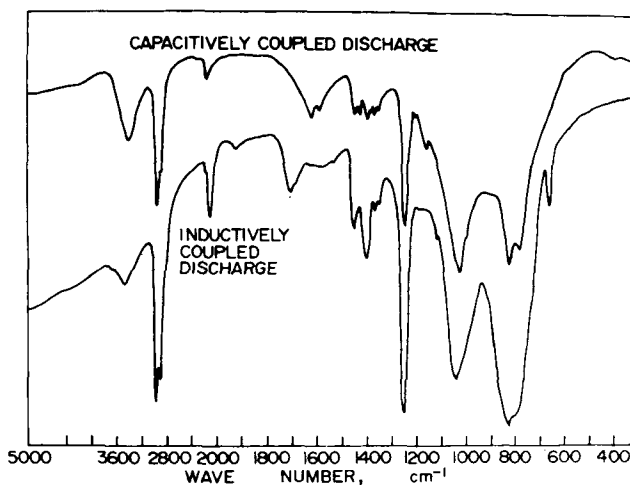

Fig. 4. Infrared spectra of polymers prepared from TMS by the capacitive coupling at 20 kHz frequency and by inductive coupling at 13.56 MHz frequency.
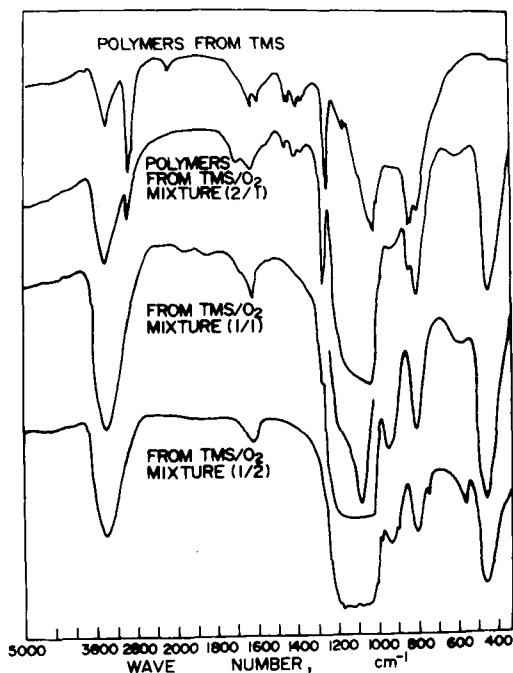
Fig. 5. Infrared spectra of polymers prepared from TMS/O$_2$ mixture as a function of the mixture composition.

merization in the TMS/O$_2$ mixture was prepared for infrared spectroscopy. Figure 5 shows infrared spectra of the polymers prepared from the TMS/O$_2$ mixture as a function of the concentration of oxygen in the mixture. With increasing oxygen concentration, the absorptions due to CH$_3$, CH$_2$, and CH groups became less intense, and the absorptions due to Si–O groups increased. New absorptions at 940 (Si–H$_2$) and 450 cm^{-1} (unknown) appeared. These changes on infrared spectra show that mixing oxygen of more than 50 mol % yielded siloxanelike polymers containing less CH$_3$, CH$_2$, and CH groups.

Physical Properties of the Polymers

The polymers prepared from TMS in the bell-jar-type reactor, (Table II) had surface energies of 26.8 dyn/cm which were lower than that of the polymers prepared in the tubular reactor ($\gamma_s = 33.7$, $\gamma_s^d = 27.9$, $\gamma_s^p = 5.7_6$ dyn/cm).[10]

Thermal stability of the two polymers prepared from TMS in the bell-jar-type and in the tubular reactor are shown in Table I. The polymers prepared in the tubular reactor were superior to those prepared in the bell-jar-type reactor in the threshold temperature for weight loss and in the residual products remaining at 500°C.

Absorption spectra of the two polymers (Fig. 6) showed that these polymers had absorption only in the UV light region. The absorption curve of the polymers prepared in the bell-jar-type reactor shifted to shorter wavelength. This indicates that the polymers may be rich in Si–O structures.

TABLE II
Surface Hardness and Surface Energy of Polymers Deposited on Polyethylene Substrate from TMS/O$_2$ Mixture

Polymers from	Current (mA)	Thickness (μm)	Hardness[a]	Steel wool scratch[b]	Surface energy (dyn/cm)		
					γ_s	γ_s^d	γ_s^p
TMS	70	3.1	2H	+	26.8	25.0	1.8
TMS/O$_2$ (2/1)[c]	70	3.6	2H	+	30.4	26.9	3.5
(1/1)	40	2.0	H	+	30.0	24.3	5.7
(1/1)	70	0.8	HB	+	29.6	22.5	7.1
(1/1)	70	1.5	F	+			
(1/1)	70	2.7	H	+			
(1/2)	70	2.2	H	+			
Uncoated			2B	−	61.4	22.4	39.0
					33.2	33.2	0

[a] Evaluated by the pencil hardness method.
[b] ++, excellent; +, good; −, poor.
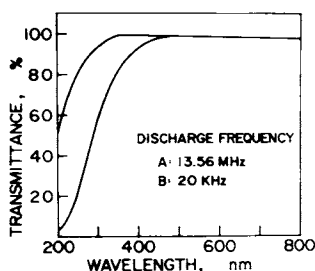[c] Mixing ratio in moles.

Fig. 6. Absorption curves of polymers prepared from TMS by the capacitive coupling at 20 kHz frequency and by inductive coupling at 13.56 MHz frequency.

Surface Hardening of Polyethylene

A preliminary investigation showed that surface properties, including hardness and surface energy of the polymers prepared by glow discharge polymerization, were strongly influenced by the nature of substrates on which plasma polymers were deposited.[14]   For example, the polymers which were deposited from the TMS/O_2 mixtures on a slide glass were as hard as glass, but the polymers deposited from the same mixture on polyethylene substrate were not as hard.   This discrepancy in hardness arises not only from rheological properties, but also from plasma susceptibility of these substrates.   Because the substrates, especially polyethylene, are subjected to degradation with evolution of small molecules by exposure to plasma during the polymerization process, changes of composition in the gas phase were followed, and these changes might directly affect the alteration of the polymers formed in a discharge state.   Therefore, either the inhibition of the degradation reactions in a discharge state or the formation of polymers being rich in siloxane structures is necessary to improve surface hardness of substrate such as polyethylene.

In processing in the bell-jar-type reactor the polymers prepared from TMS, as described in the previous section, are rich in silicon and poor in carbon and hydrogen.   This polymer-formation process in the bell-jar-type reactor was applied for the improvement of surface hardness of the polyethylene sheet. Table II shows the surface hardness of polyethylene modified by glow discharge polymerizations in the systems TMS or TMS/O_2.   The surface hardness was evaluated by the pencil hardness method (JIS K5400).   The hardness of polyethylene surfaces (Table II) was enhanced from 2B to 2H.   Such improvement was never accomplished in processing in the tubular reactor.   By increasing the oxygen concentration in the TMS/O_2 mixture, the surface energy of the polymers deposited on polyethylene, especially the polar contribution, increased.   This indicates that some oxygen mixed with TMS was incorporated into the polymers prepared from TMS by the glow discharge polymerization.   However, there was not a remarkable improvement in the surface hardness of polyethylene substrates when modified with the TMS/O_2 mixture (Table II).   The extent of the improvement by the glow discharge polymerization (Table II) is closely related to the thickness of polymer films deposited and not to *what* polymer films were deposited.   A film thickness of more than 3 μm is required to enhance surfaces to 2H hardness.

TABLE III
Adhesion between Plasma Films and Polyethylene Substrate

Polymers from	Current (mA)	Lap-shear strength (kg/cm^2)	
		Not immersed	Immersed in NaCl Solution
TMS	70	20.7	38.3[b]
TMS/O$_2$ (2/1)[a]	70	33.2	29.8
(1/1)	40	27.5	23.8
(1/1)	70	36.8[b]	37.4[b]
(1/1)	110	31.0	32.2
(1/2)	70	34.0[b]	36.5[b]
Uncoated		0	0

[a] Mixing ratio in moles.
[b] Constructive failure occurred.

Adhesion between Plasma Films and Polyethylene Substrate

The adhesion between the polymer films deposited from TMS or the TMS/O$_2$ mixture on polyethylene and the polyethylene substrate was examined in connection with durability of these modified surfaces. Polyethylene sheets (25 × 50 × 1.5 mm) modified with TMS or the TMS/O$_2$ mixture were placed in two different aging environments for 10 days: One was exposed to air at room temperature, and the other was immersed in 0.9% NaCl solution, the isotonic sodium chloride solution, at 40°C. After these exposures, the specimens were bonded with aluminum coupons using epoxide adhesive, and the lap-shear strength of these joints was determined.

A magnitude of the lap-shear strength for most of these joints (Table III) was more than 30 kg/cm^2, indicating good adhesion between the plasma films and polyethylene. For polyethylene sheets modified by the glow discharge polymerization of the TMS/O$_2$ mixtures at 1/1 and 1/2 molar ratios that were operated at 70 mA, constructive failure occurred. The polyethylene sheets modified with TMS showed the latest lap-shear strength of 20.7 kg/cm^2. The failure occurred at an interface between the plasma films and the epoxide adhesive layer, indicating poor adhesion between the plasma films and the epoxide adhesive. The adhesion strength between the plasma films and polyethylene sheets is more than 20.5 kg/cm^2.

Even when these modified polyethylene sheets were immersed in the NaCl solution, the lap-shear strength was maintained without diminishing the strength. SEM pictures of the surfaces of broken joints showed that the failure occurred at an inner layer of the plasma films or of polyethylene substrates, and never occurred at an interface between the plasma films and polyethylene layer. Consequently, it can be concluded that the adhesion between the plasma films and polyethylene sheet is tight enough for practical applications.

CONCLUSION

This study presented comparisons between the glow discharge polymerization of TMS performed by the capacitive coupling at 20 kHz frequency and the inductive coupling at 13.56 MHz frequency.

1. The polymers prepared by the capacitive coupling at 20 kHz frequency possessed lower carbon and hydrogen content than those by the inductive coupling at 13.56 MHz frequency, and were rich in silicon.

2. These two polymers consisted of similar structural groups such as CH_3, CH_2, CH, Si–O–C, Si–O–Si, Si–CH_3, and Si–CH_2–CH_2–Si groups.

3. The surface hardness of polyethylene sheets was enhanced from 2B to 2H by plasma films prepared from TMS or the TMS/O_2 mixtures using capacitive coupling at 20 kHz frequency.

4. The adhesion between the plasma films and polyethylene sheets was good even when immersed in 0.9% NaCl solution at 40°C for 10 days.

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