Silicone Polymerization by Glow Discharge Application

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Synopsis

Polymerization of hexamethyldisiloxane (HMDS) on aluminum by application of capacitively coupled plasma was carried out under different polymerization conditions. The effect of applied frequency, power, and discharge duration on polymerization rate was investigated. Film adhesion was found to be directly related to applied frequency and power. Polymer deposits were examined with SEM and ATR, and the effect of the coat on wettability was sought by measuring the contact angles. The chemical structure of the coat was affected by the energy density applied during coat preparation.

INTRODUCTION

Recently, plasma polymers prepared with glow discharge are gaining great attention. Obtaining pinhole-free and highly cross-linked films by using no ingredients besides the monomers results in very pure polymers that also have a high resistance to wear and abrasion. These films are being used in very different areas.[1-3] The starting materials do not need functional groups, and the chemical structure of these glow discharge polymers are quite different from that of the starting materials. The mechanism of the polymerization is also very different than conventional polymerization. Many parameters affect the chemical structure of the polymer deposits and also the rate of polymerization. The most important parameters are the chemical and physical structure of the substrate, the type of monomer, the monomer flow rate, and the applied frequency, power, and duration.[4-8]

EXPERIMENTAL

Polymerization experiments were carried out by using the capacitively coupled system shown in Figure 1. The reaction chamber was a cylindrical Pyrex column (50 cm in length and 5 cm in diameter) that had copper electrodes (12×2 cm^2). Electrodes were connected to a matching network, which in turn was connected with copper wires to a variable-frequency radio-frequency (RF) generator up to 200 kHz. The reaction chamber was connected to a flowmeter from one end to adjust the monomer flow rate and to a vacuum pump from the other. HMDS was kept in a container under vacuum and was degassed a few times before it was used in the polymerization experiments. Aluminum sheets (2×7 cm^2) were cleaned with alcohol, weighed, and placed on the lower electrode of the reaction chamber. After the system was evacuated, the monomer was let in at a constant flow rate (30 cm^3/min)
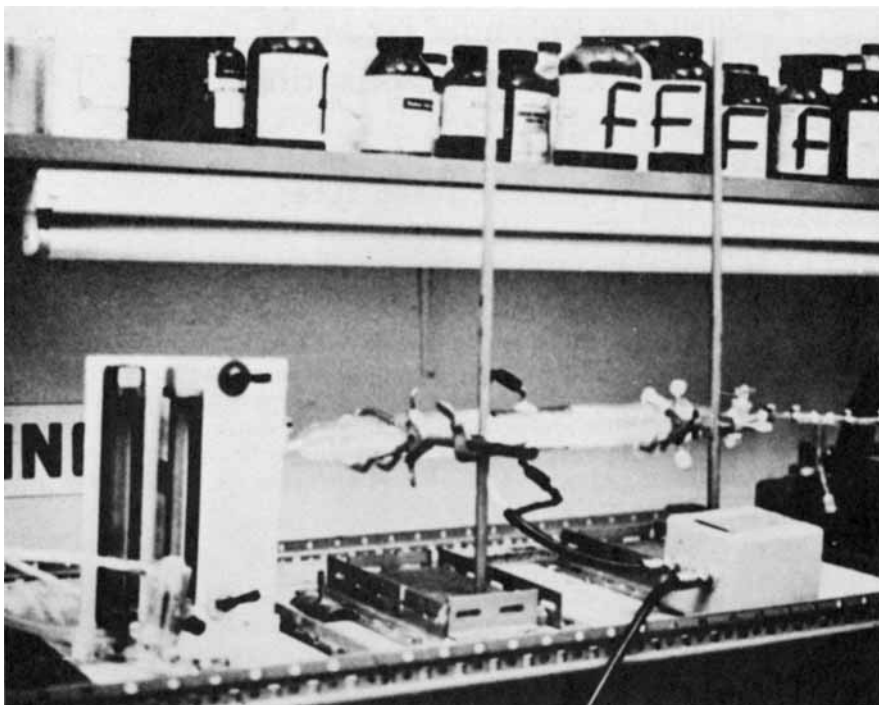
Fig. 1.   Plasma setup.

and discharge was applied. The amount of polymer deposited was determined gravimetrically.

Contact angle measurements were done by drop method. A drop of distilled water was placed on the freshly prepared samples, and the angles were measured from photographs.
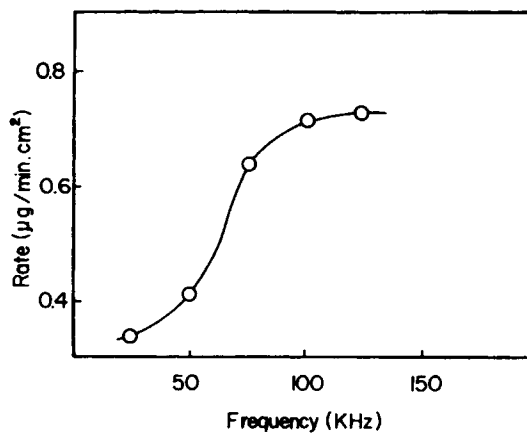

Fig. 2.   Effect of frequency on polymerization rate (power = 10 W; monomer flow rate = 30 cm^3/min; duration = 30 min).
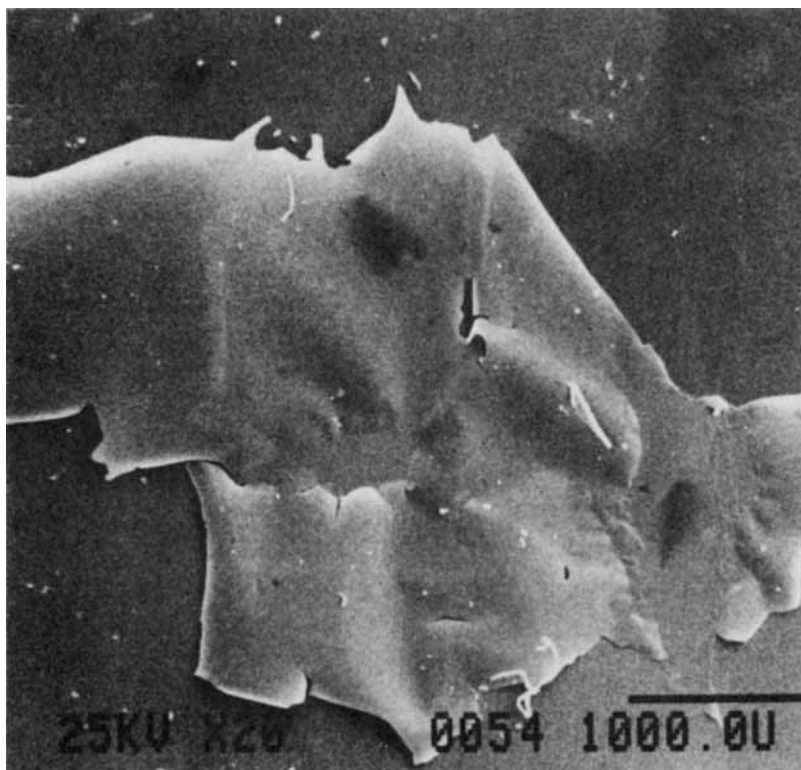
Fig. 3.   SEM of HMDS coat prepared under the following conditions: frequency = 50 kHz, power = 10 W, monomer flow rate = 30 cm³/min, duration = 30 min.

Results and Discussion

The effect of frequency on polymerization rate is given in Figure 2. It was observed that the amount of the polymer deposit increased up to 100 kHz and did not change significantly between 100 and 125 kHz under the conditions in which monomer flow rate, applied power, and discharge duration were 30 cm³/min, 10 W, and 30 min, respectively. Scanning electron microscope (SEM) results showing the physical structure of these samples are presented in Figures 3 through 5. It was observed that when the frequency was 50 kHz a definite polymer film that did not adhere to the aluminum surface was obtained. The adhesion of the film to the substrate was increased with the frequency. The polymers prepared at 100 and 125 kHz had some very smooth areas defining adhesion to the surface and some crisp and broken areas defining a weak adhesion. All the samples prepared under these conditions had a pinkish-green color the instant they were taken out of the reaction chamber. This glittering color can be explained as the diffraction of light on the ultrathin film deposit. Attenuated Total Reflectance Infrared (ATR) examinations of these samples showed the same absorption peaks at 1050 cm^{-1} for Si—O—Si stretching, at 1250 cm^{-1} for —Si(CH$_3$) bending, and at 800 cm^{-1} for —CH$_3$ wagging absorption (Fig. 6). There were slight differences
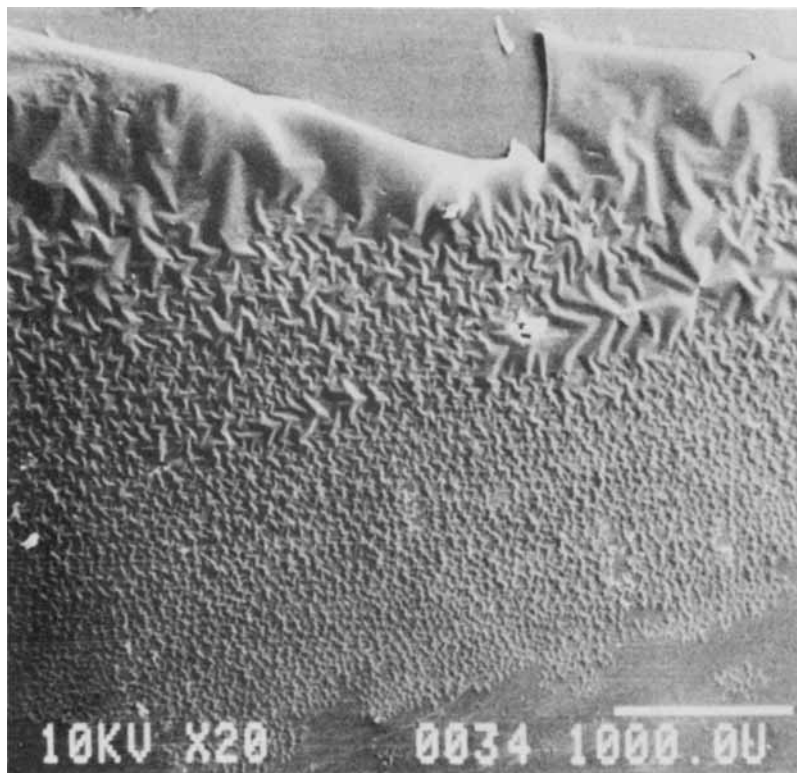
Fig. 4. SEM of HMDS coat prepared under the following conditions: frequency = 100 kHz, power = 10 W, monomer flow rate = 30 cm³/min, duration = 30 min.

in the intensities of the absorption peaks. The presence of the same type of spectra indicate that the chemical structure of the HMDS coat is the same when it is polymerized under these conditions. Since the increased frequency seems to increase adhesion to the aluminum surface and since 125 kHz was the maximum frequency at which the apparatus works, the remainder of the studies were carried out at this frequency.

The effect of discharge duration on polymerization rate is shown in Figure 7. Linear relationships were obtained with 10 W up to 30 min, with 50 W up to 10 min, and with 100 W up to 3 min. Deviations from the linearity at higher durations can be explained as the degradation of the polymer because of the heat evolving in the system. Thus, the removal rate of the degraded polymer seems to be higher than the rate of polymer deposition, leading to an overall decrease in the amount of polymer deposited.

When the power was increased to 100 W and applied for 1 min, no color was seen on these samples when they were taken from the reaction chamber and no absorption peaks were detected with ATR. SEM results were, however, interesting (Figs. 8 and 9): growing macrochains were observed instead of a continuous coat. Measurements made on the SEM indicate that every fiber has a thickness of $\simeq 450$ Å, which is roughly equal to about 50 times the thickness of an individual chain (if the theoretical thickness of an individual
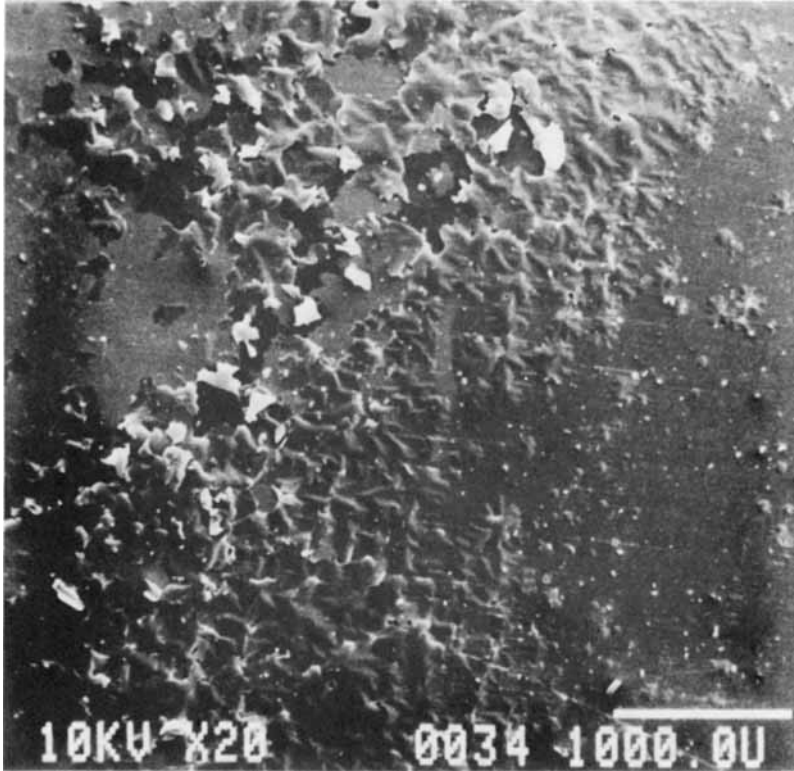
Fig. 5. SEM of HMDS coat prepared under the following conditions: frequency = 125 kHz, power = 10 W, monomer flow rate = 30 cm^3/min, duration = 30 min.
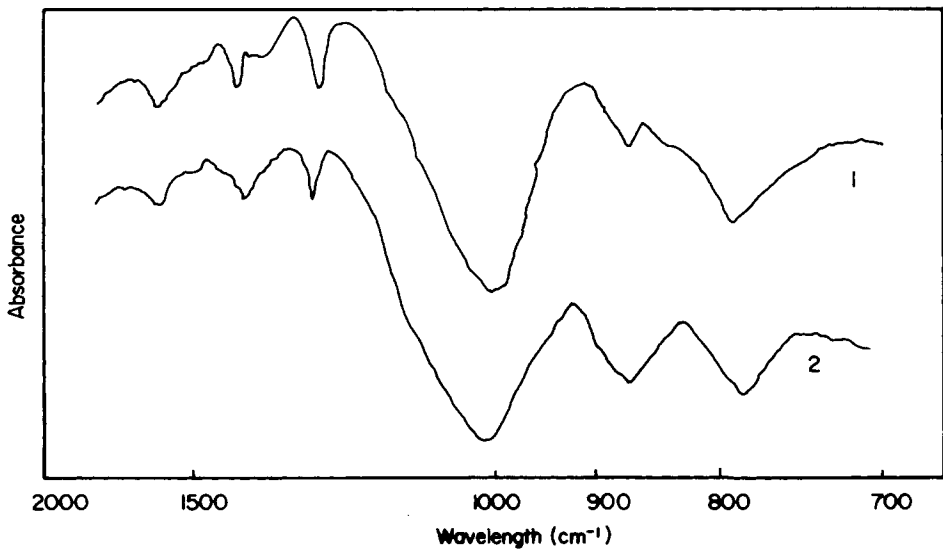

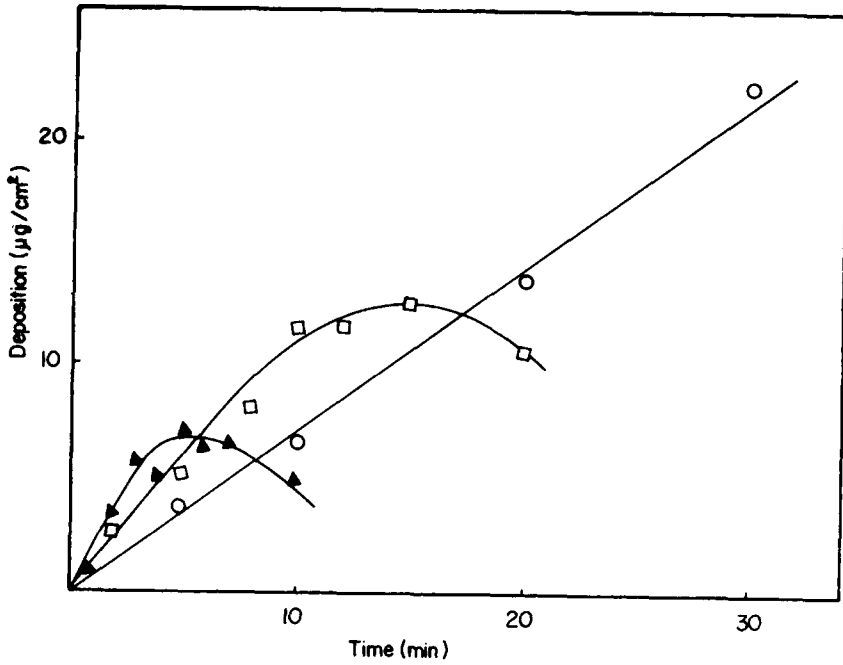Fig. 6. ATR spectra of HMDS coats prepared by application of (1) 50 kHz; (2) 125 kHz (power = 10 W).

Fig. 7. Effect of discharge duration on polymerization rate: $\bigcirc$, 10 W; $\square$, 50 W; $\blacktriangle$, 100 W (frequency = 125 kHz, monomer flow rate = 30 cm^3/min).

Fig. 8. SEM of HMDS coat prepared under the following conditions: frequency = 125 kHz, power = 100 W, monomer flow rate = 30 cm^3/min, duration = 1 min.
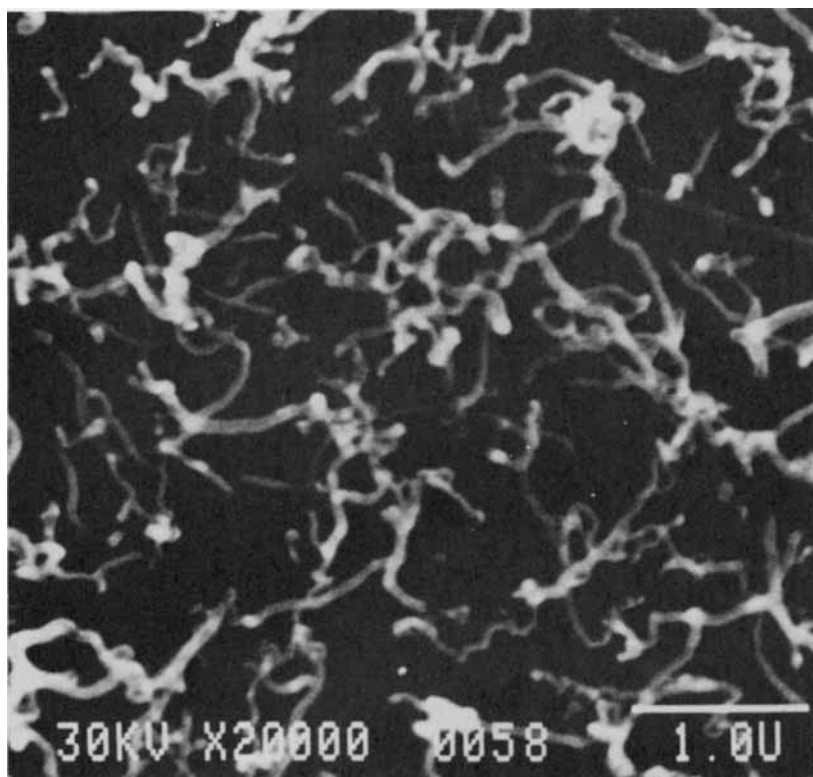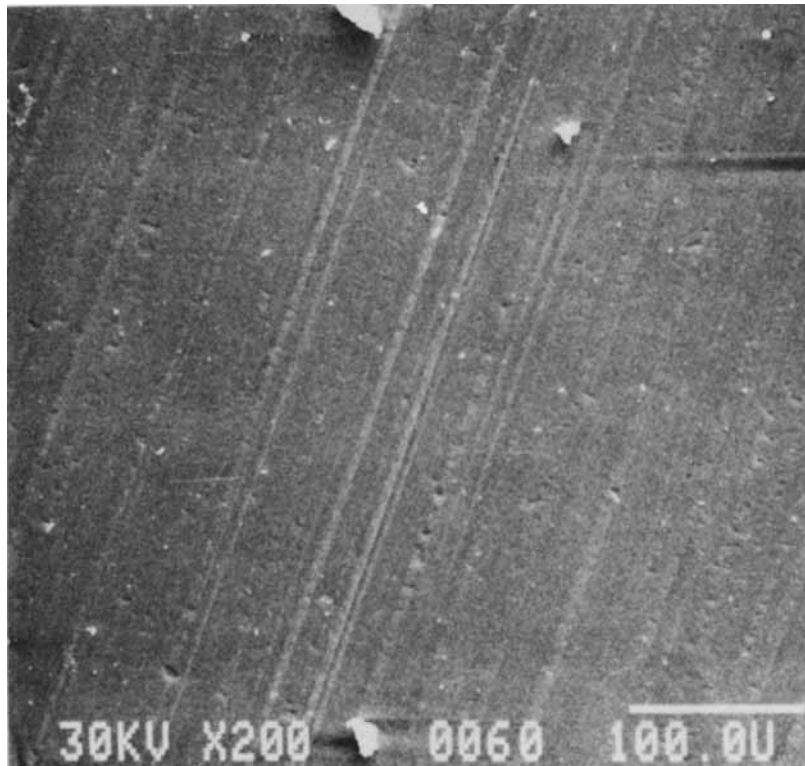
Fig. 9.   HMDS macrochains.

Fig. 10.   SEM of HMDS coat prepared under the following conditions: frequency = 125 kHz, power = 100 W, monomer flow rate = 30 cm^3/min, duration = 5 min.
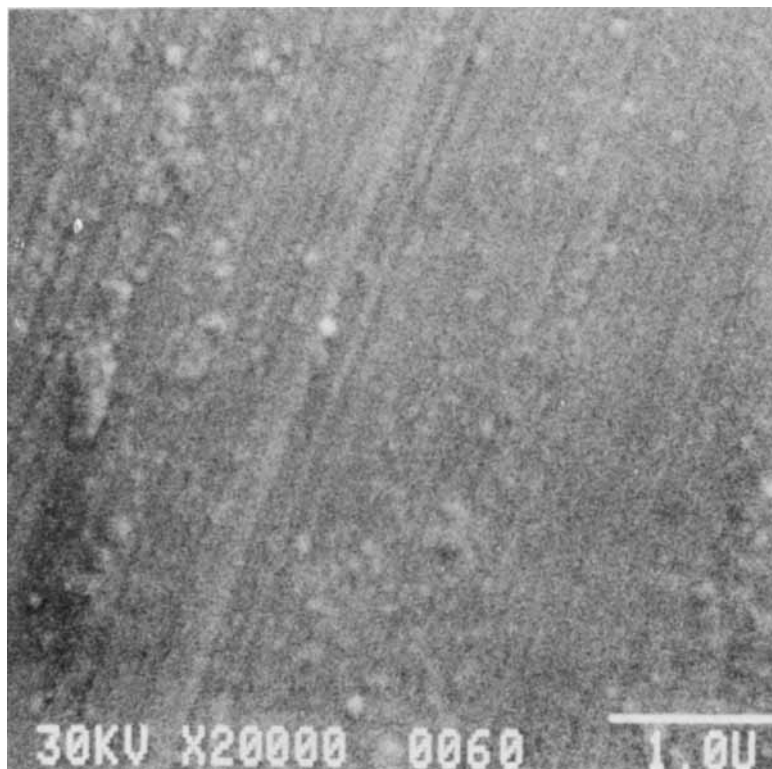
Fig. 11. SEM of HMDS coat prepared under the following conditions: frequency = 125 kHz, power = 100 W, monomer flow rate = 30 cm^3/min, duration = 5 min.

chain is $\simeq$ 9 Å, calculated from bond lengths of HMDS). We believe these are the first SEM showing the macromolecules formed under plasma. These macrochains seem to be evenly distributed over the whole surface. When the discharge duration was extended to 5 min, a continuous and strongly adhered coat was obtained (Figs. 10 and 11). The samples did not have glittering color after the coating process, and the coat was so smooth that it looked as if there was no coat even when magnified 20,000 times. ATR examination of these samples gave intense absorption peaks that are quite different from those obtained with the other polymer coats (Fig. 12). The decrease in the intensity of Si-O-Si stretching (at 1050 cm^{-1}) and the increase in the intensities of the peaks observed at 1070 cm^{-1} and at 1170 cm^{-1} (defining —CH$_2$—O—Si and C—O bonds, respectively) indicate drastic changes in the chemical structure of the monomer. Since the bond energies for C—H, C—Si, and O—Si are given as 337, 435, and 799 kJ/mol, respectively, it can be concluded that by application of higher energy it became possible to break the more energetic bonds. Thus, unlike the previous cases presented above, the polymer formed under these conditions does not seem to have a —C—Si—O—Si—C— backbone.

Contact angle results are presented in Table I. Samples 1, 2, and 3 have quite similar contact angles, emphasizing quite similar chemical structures that are different from those of samples 4, 5, and 6. The very low contact
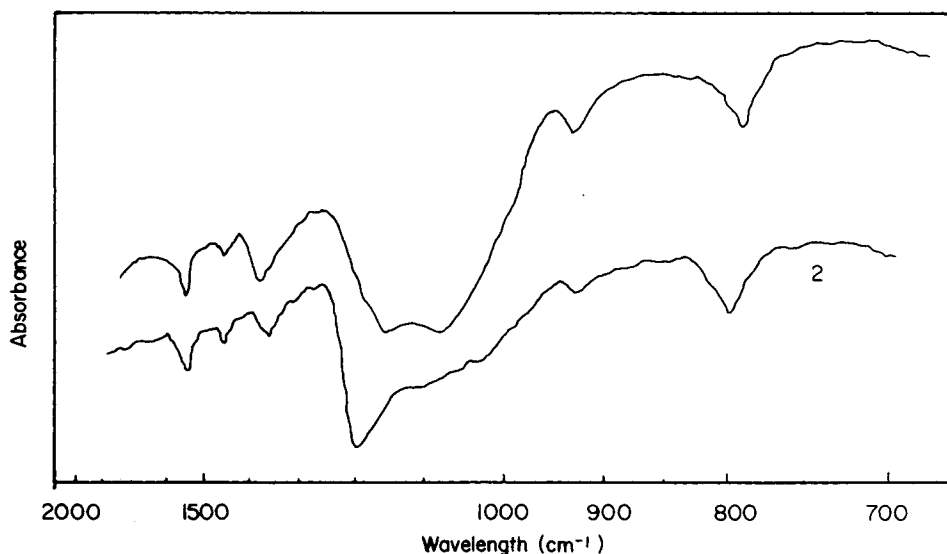
Fig. 12.   ATR spectra of HMDS coats prepared by application of (1) 125 kHz for 3 min; (2) 125 kHz for 5 min (power = 100 W).

TABLE I
Contact Angle Measurements

| | Polymer preparation conditions | | | |
Sample no.	Frequency (kHz)	Power (W)	Time (min)	Contact angles
A1	0	0	0	70.0
1	50	10	30	75.5
2	100	10	30	73.0
3	125	10	30	75.0
4	125	50	10	61.0
5	125	100	1	52.5
6	125	100	5	64.0

angle value of the fifth sample may be caused by incomplete coverage of the surface by the film, resulting in surface roughness.

It can be hypothesized from the data presented above that, when the energy density is low, polymerization takes place in the gas phase, resulting in weak adhesion between the polymer film and the surface. Upon increasing the energy density, surface activation and initiation occur with a resultant strong adherence of the film to the substrate.

CONCLUSION

Polymerization of HMDS, which has no functional groups, is possible by application of glow discharge. The rate of polymerization increases with frequency in the kilohertz region. The rate of polymerization has a linear relation, with duration up to a certain point, and then the abrasion rate

overcomes the polymerization rate. The chemical structure of the coat shows some differences when the preparation parameters are changed. A very uniform and strongly adhered coat is obtained when the frequency, power, and duration were 125 kHz, 100 W and 5 min.

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