

Fourier Transform Infrared Analysis of Plasma-Polymerized Hexamethyldisiloxane

V. KRISHNAMURTHY and IHAB L. KAMEL, *Department of Materials Engineering*, and YEN WEI, *Department of Chemistry*, Drexel University, Philadelphia, Pennsylvania 19104

Synopsis

The plasma-induced polymerization of hexamethyldisiloxane onto solid surfaces is studied by FTIR. An inductively coupled RF reactor was used to produce the thin polymer coatings. Analysis of the plasma polymer indicates a long chain polysiloxane structure resulting from the removal of some methyl groups from the monomer structure. Increasing the plasma power level from 30 to 100 W increased the chain length in the resultant polymer as indicated by the widening and splitting of the Si—O stretching absorptions. Thermal aging of the vapor phase polymer at 120°C for 1 h in vacuum and at 410°C for 30 min in a nitrogen atmosphere revealed the removal of some methyl groups from the polymer structure with temperature. TGA runs on the vapor phase polymer at 20°C/min in air showed the polymer retaining almost 65% of its weight at 1000°C. The residue remaining after the TGA run had very little organic content and may represent a glass type silicate network. Wettability values determined on coated glass slides revealed the hydrophobicity of the coatings with water contact angle values > 100°. SEM micrographs showed uniform and featureless coating on glass fibers which was etched by boiling water and was attributed to the loss of vapor phase polymer on the surface.

INTRODUCTION

In polymer matrix composites, coupling agents are molecular bridges at the interface between the inorganic surface and the polymer matrix. Tetrafunctional organometallic compounds based on titanium, silicon, and zirconium make useful coupling agents because of the metal's electron sharing ability. When the inorganic surface is glass, the extra strength of the Si—O—Si bonds is preferred to either Ti—O—Si or Zr—O—Si because of chemical compatibility. Consequently, organosilanes are the most common coupling agents used to promote adhesion between glass fibers and polymer matrices.¹⁻⁴

Silane coupling agents have the general formula R_3SiX , where X is the inorganic functionality and R the organophilic group. X is a hydrolyzable group typically alkoxy, acyloxy, amine, or halogen and following hydrolysis a reactive silanol is formed which can condense with other silanols to form siloxane linkages.¹ The choice of the organophilic group depends on the matrix of interest and the extent of coupling desired.

These organosilanes are applied from aqueous solutions and would normally result in fairly thick coatings (of the order of few microns). Thick coatings are detrimental to properties in most cases as this would result in a low strength interphase as the coupling layer cannot be expected to be a high strength layer unless it is a polymer of high molecular weight or significant degree of crosslinking. Thus, ideally only a monomolecular layer is needed for coupling

between the fibers and the matrix. Thick coatings, however, can be advantageous particularly to improve impact properties if the coating layer is tough.⁵⁻⁸ But such improvements are favored in the presence of strong bonding between the organosilane and the glass surfaces.

One of the problems associated with organosilane coupling agents is their hydrolytic instability. A possible mechanism suggested to explain the hydrolytic failure of glass fiber composites is the hydrolysis of the Si—O—Si linkages formed by the glass surface and the coupling agent⁹ as a result of a weak bond. The hydrolytic stability can be improved by a strong and crosslinked interface.

Covalent linking of glass fibers and polymer matrices is being studied by plasma polymerization of a selected monomer onto the fiber surface. The plasma grafted layer is a structurally flawless, highly crosslinked layer which has excellent adhesion to the substrate. Functional groups on the surface of this organic layer will then act as coupling agents and readily bond with their chemical complement in the organic matrix. The type and extent of the generated bonds is controlled by the choice of the monomer and the processing conditions. The strong bonding between the matrix and the fiber and the crosslinked nature of the plasma grafted film will provide for maximum strength at the interface and the necessary hydrolytic stability. This approach has been investigated to a limited extent in the graphite/epoxy system^{10,11} and in mica-filled polyethylene and polystyrene systems.¹²

This investigation centers on glass fibers and high temperature thermoplastic matrices like polyphenylene sulfide (PPS) and polyetheretherketone (PEEK). Hexamethyldisiloxane (HMDSO) was selected as the monomer because of its ease of plasma polymerization and its siloxane functionality which would be beneficial in coupling the silicate network of the glass fibers to the polymer matrices. The plasma polymerization of HMDSO has been previously studied for noncomposite applications by Gazicki et al.¹³ and Inagaki et al.¹⁴ The resulting plasma polymer has also been evaluated for its electrical¹⁵ and moisture barrier properties.¹⁶ In addition, plasma-polymerized HMDSO was evaluated as an adhesion promoter for Kevlar/epoxy system¹⁷ and another derivative, tetramethyldisiloxane, was found to improve the adhesion to glass surfaces.¹⁸ As a first step in evaluating the potential of the plasma-grafted HMDSO layer as a coupling agent for glass fibers and thermoplastic matrices, the structure of the plasma polymer and its thermal and hydrolytic stability are studied by Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM).

EXPERIMENTAL

The plasma equipment used was an inductively coupled plasma reactor (Branson/IPC 3000) operating at the RF frequency of 13.56 MHz. The plasma treatment scheme consisted of an argon plasma treatment (5–15 min) followed by the introduction of the monomer (hexamethyldisiloxane, Aldrich Chemicals). The plasma chamber was evacuated to a pressure of 0.02–0.05 torr before initiation of the discharge.

Substrates are thoroughly solution cleaned in an ultrasonic bath to remove any grease due to handling before coating. Argon plasma treatment (0.5 torr,

100 W) was then performed to activate, and clean the substrates of molecular level contaminants. Following this initial treatment in argon plasma, the substrates are coated with the plasma polymer for 10–20 min (0.5 torr, plasma power variable).

FTIR may be used directly to examine the grafted films on the above substrates using the attenuated total reflectance (ATR) technique. Another approach is to use the transmission spectra on a nonabsorbing substrate (e.g., NaCl plates) or to use the vapor-phase-polymerized residue. The last two approaches provided better results and are presented in this study. In particular, the residue provided a simple way to evaluate directly the thermal stability of the polymer without the influence of the substrate. The thermal aging was done at two temperatures: 120°C for 1 h in vacuum and 410°C for 30 min in a nitrogen atmosphere. In addition, TGA (DuPont 9900) of this polymer was performed under a rapid heating cycle (20°C/min in air). IR transmission spectra of the residue left after the TGA run was also recorded. Interpretation of all the infrared spectra were based on standard references.^{19–22}

Changes in surface energies as a result of the plasma treatment were evaluated by water droplet contact angle measurements performed on glass slides coated with the plasma polymer. The glass slides were cleaned in 5% NaOH solution and the contact angles were the average of five measurements. E-glass fibers coated with the plasma polymer of HMDSO and exposed to boiling water environment for 1 h were viewed under the SEM (JEOL JSM-35CF) to determine the hydrolytic stability of the coatings.

RESULTS AND DISCUSSION

Comparison of the infrared spectra of the monomer and the plasma polymerized film at 100 W (Figure 1) reveals the conversion of the monomer to the plasma polymer. The monomer shows CH stretching in the methyl groups (2958 and 2902 cm^{-1}) and CH bending within the methyl groups (1438 and 1412 cm^{-1}). The Si—Me stretching due to the Si—(Me)₃ end groups are present at 837 and 756 cm^{-1} , the Si—Me rocking vibration is also a strong absorption at 1254 cm^{-1} and the Si—O stretching absorption has a broad signal at 1059 cm^{-1} .

Characteristic absorption peaks for the plasma polymer show a CH stretching absorption at 2960 cm^{-1} and the Si—Me rocking vibrations at 1258 cm^{-1} . The Si—Me stretching vibrations are present at 842 and 796 cm^{-1} . The absorption at 796 cm^{-1} could be due to the Si—Me stretching vibration in either Si—(Me)₂ or Si—Me groups indicating the removal of some methyl groups from the monomer. The Si—O stretching absorption shows a doublet in the 1150–1000 cm^{-1} region (1115 and 1040 cm^{-1}), showing that the resultant polymer is a long chain polysiloxane.^{21,22} The removal of the methyl groups might be one of the possible reactions during the formation of the plasma polymer as was shown by a previous NMR study.²³ In addition, hydrogen abstraction and the formation of disilyl—methylene links [Si—(CH₂)_n—Si] may contribute to the 1150–1000 cm^{-1} absorption band.^{24–26}

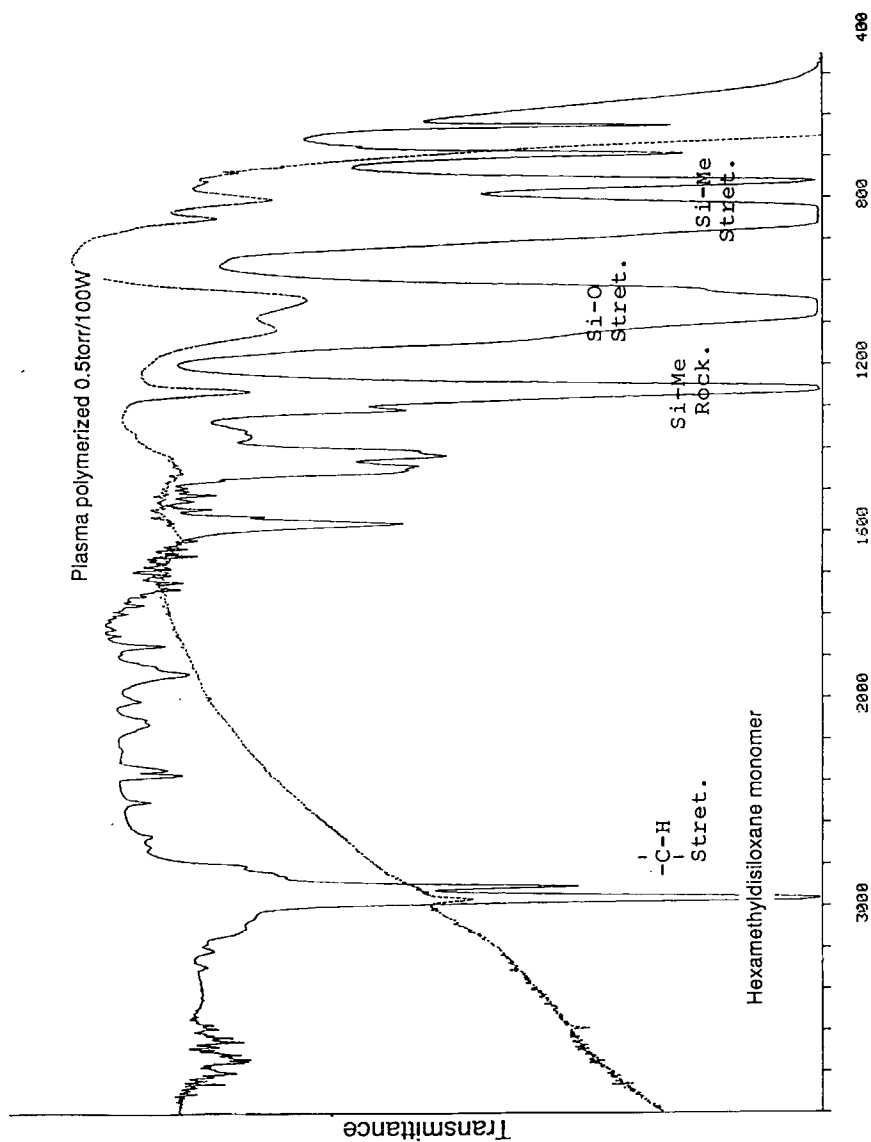
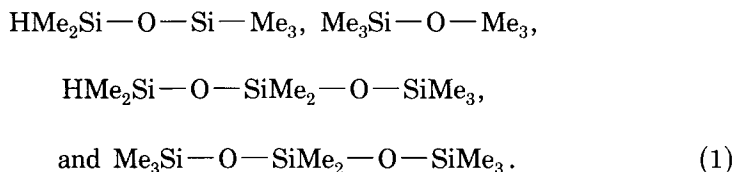
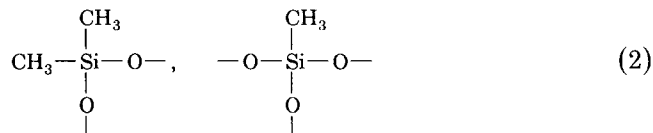


Fig. 1. FTIR spectra of hexamethyldisiloxane (—) and its plasma polymer (---).

Plasma polymerization is believed to be initiated by the collision of free radicals and other excited species in the plasma with the monomer molecules.^{27,28} Predicting the structure of plasma polymers is not an easy task because of the complexity of the process and possible structures can only be speculated upon from the changes observed in, e.g., the IR spectra. Pyrolysis coupled with chromatography has been used to study the structure of plasma polymerized organosilicones.¹³ These authors reported that low temperature pyrolysis at 300°C of plasma-polymerized HMDSO under mild conditions (monomer pressure = 0.3 torr and current density = 1 mA/cm²) yielded certain volatile oligomers such as



This also augments the proposed scheme that some methyl groups are knocked off from the monomer structure during the plasma polymerization process. Thus the plasma polymer structure can be speculated upon to be containing the following units in its backbone, consistent with earlier observations^{23,26}:



To study the effect of the plasma parameters on the polymerization behavior of the monomer, the plasma power was changed from 30 to 100 W, keeping the monomer flow rate constant. This in effect increases the energy per unit mass of the monomer²⁹ and may bring about a change in the fragmentation process of the monomer in the plasma field. Figure 2 shows the infrared spectra of the polymer film deposited on NaCl plates at different plasma power levels. The Si—O stretching absorption (and possibly —CH₂— wag in disilyl—methylene groups) show systematic changes with plasma power level. The single absorption at 1042 cm⁻¹ for the 30 W plasma polymer becomes a doublet at 1115 and 1040 cm⁻¹ when a 100 W plasma power level was used. The widening and splitting of the Si—O stretching absorption is indicative of increased siloxane chain length.^{21,22} In addition, due to the nature of the plasma polymer and its thermal stability (discussed below), a significant degree of branching/crosslinking is expected in that structure.

Increasing the plasma power also increases the relative proportion of the 796 cm⁻¹ absorption (Si—Me stretching in Si—Me₂ or Si—Me groupings) compared to the 842 cm⁻¹ absorption (Si—Me stretching in Si—Me₃ groups). Hence the removal of the methyl groups is a function of wattage with more groups being knocked off at higher power levels. There is a weak absorption at 2100 cm⁻¹ which is well resolved at low power levels and could be assigned to Si—H stretching vibrations.

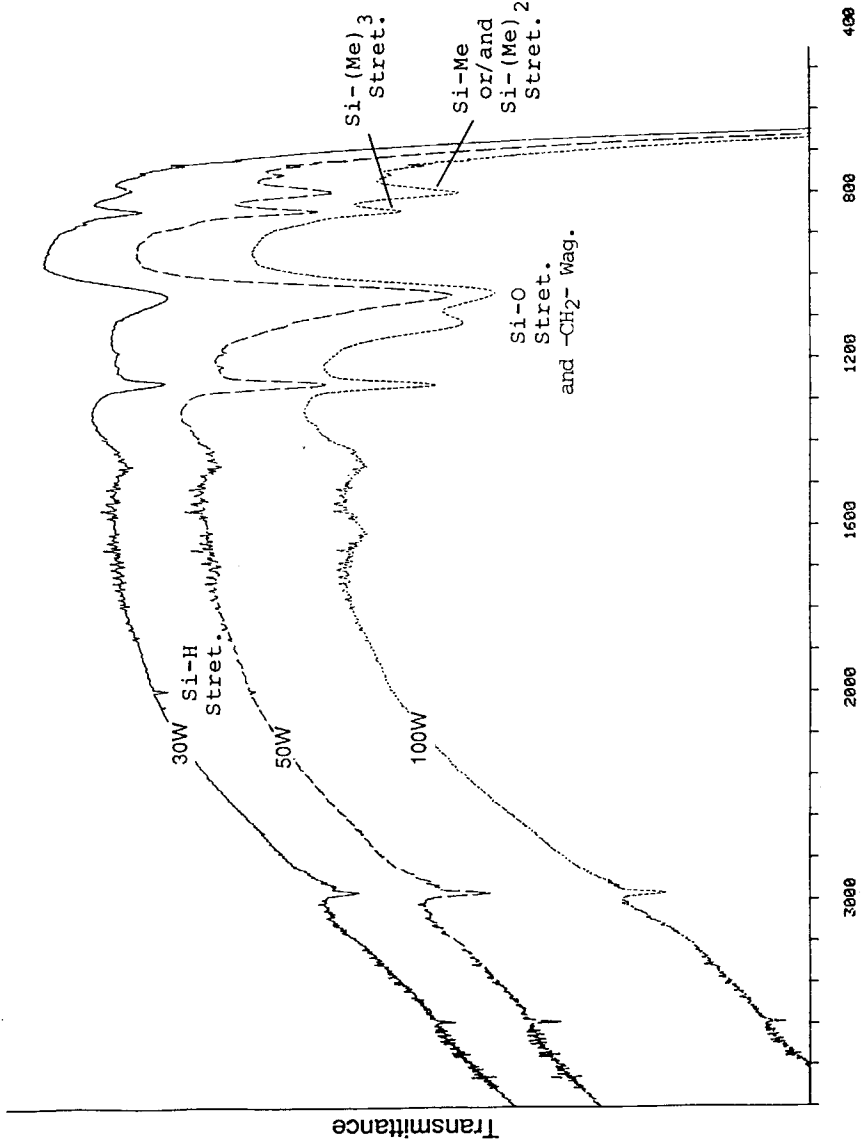


Fig. 2. FTIR spectra of plasma polymerized hexamethyl/disiloxane as a function of plasma power.

Both argon and monomer overlap for a relatively short time during the plasma treatment. The residual argon active species will bombard the substrate surfaces and also increase the monomer fragmentation in the vapor phase. Thus, simultaneously a grafted coating on the substrate and vapor phase polymer are created under the influence of plasma. The vapor phase polymerization of the monomer leads to deposition of residues on the walls of the chamber and on the substrates leading in some cases to a coarse texture for the deposited film.

In the case of HMDSO, however, significant residue deposition occurred only when both argon and the monomer were present appreciably in the discharge. During a previous study dealing with the plasma polymerization of allylamine³⁰ it was observed that the vapor phase polymerization took place very easily even when the monomer was the main specie present in the discharge. The olefinic double bond ($C=C$) present in allylamine structure is easily attacked providing for the active species necessary to initiate the vapor phase polymerization. In this investigation, the lack of a radiation sensitive bond in HMDSO produced coatings on substrates of the order of a few hundred angströms which were difficult to study. The vapor phase polymer thus collected provided an easy way to determine the thermal stability and structure of the polymer.

The plasma grafted layer has the role of a coupling agent; therefore, it should have sufficient thermal stability to withstand the molding temperatures of the resins of interest, e.g., PPS-300°C and PEEK-400°C. The infrared spectra of the vapor phase polymer of HMDSO is shown in Figure 3 and can be compared to a deposited film on NaCl plates (Fig. 1). The major differences between the two spectra lies in the Si—O stretching (and the absorptions due to the disilyl—methylene groups) and Si—Me stretching vibrations. The Si—O stretching, which appears as a doublet in the polymer film on NaCl plates, is a broad absorption in the vapor phase polymer. This may be indicative of a difference in the degree of branching and crosslinking between the two, the vapor phase polymer being less branched or crosslinked than the film. In addition, the Si—Me stretching absorptions due to the Si—(Me)₂ and Si—Me groups are stronger in the polymer film when compared to the absorptions due to the Si—(Me)₃ groups; these two are comparable in the vapor phase polymer, another indication that the vapor phase polymer is less branched/crosslinked than the polymer film.

Figure 3 also shows the IR spectra of the vapor phase polymer upon thermal aging at 120°C for 1 h in vacuum and then at 400°C for 30 min in a nitrogen atmosphere. The two temperatures were chosen to simulate a typical PEEK molding cycle:

- (i) a drying operation at 120°C for 1 h in vacuum to remove the absorbed water before molding
- (ii) molding of PEEK matrix at 400°C

It should also be noted in Figure 3 that the Si—Me stretching absorption at 798 cm^{-1} is increasing in proportion compared to the 842 cm^{-1} peak, indicating a reduction in the methyl groups. The broadening of the Si—O stretch-

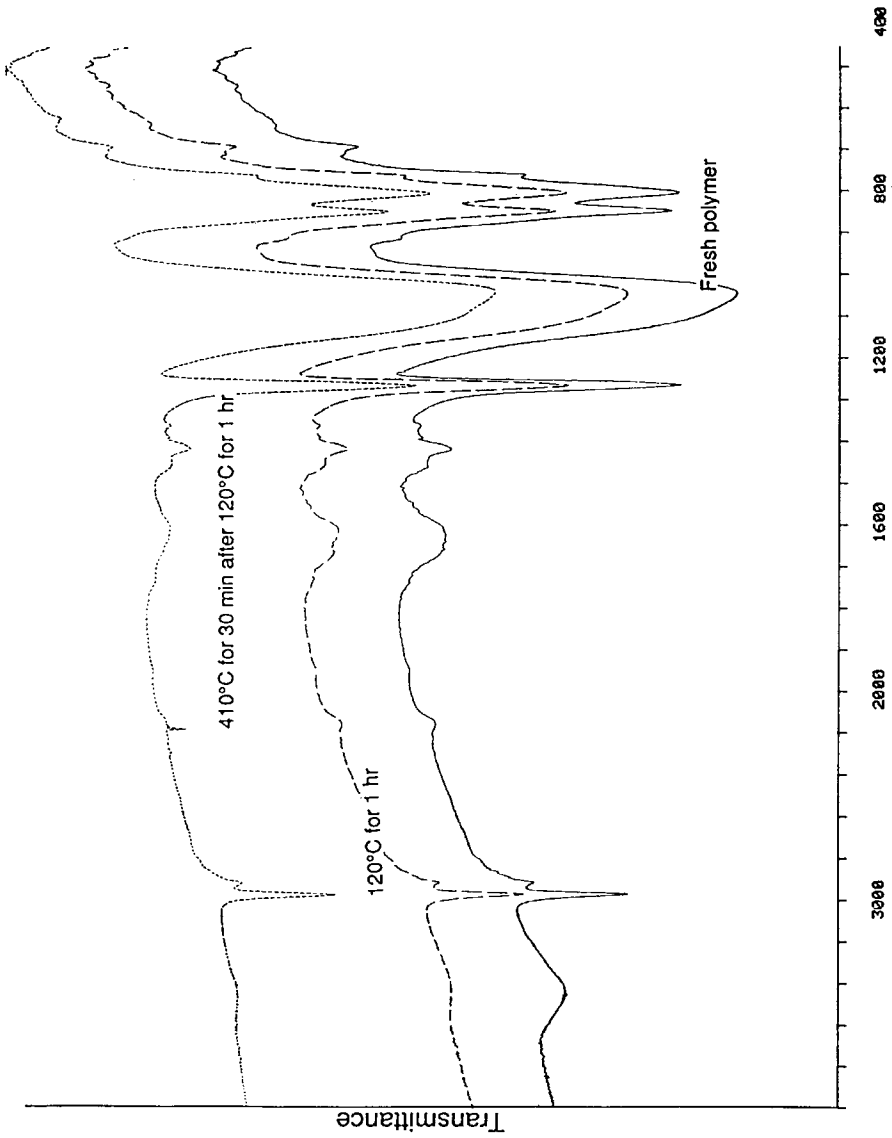


Fig. 3. Effect of thermal aging on the IR spectra of the vapor phase polymer produced at 100 W.

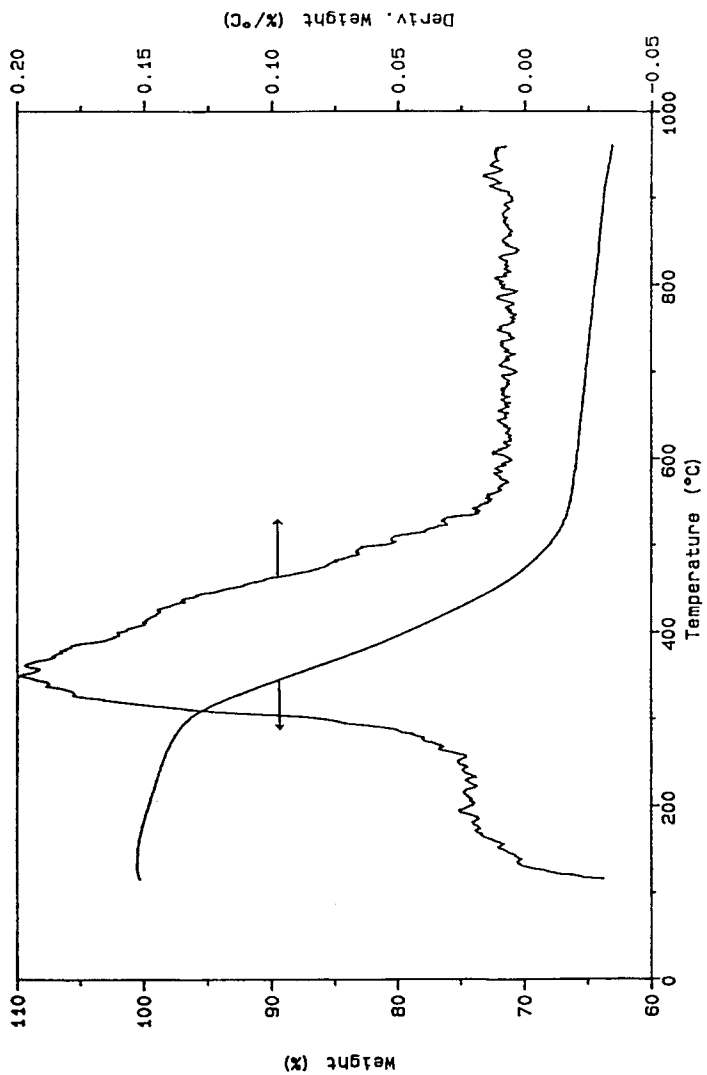


Fig. 4. TGA of the vapor phase polymer produced at 100 W at a heating rate of 20°C/min in air.

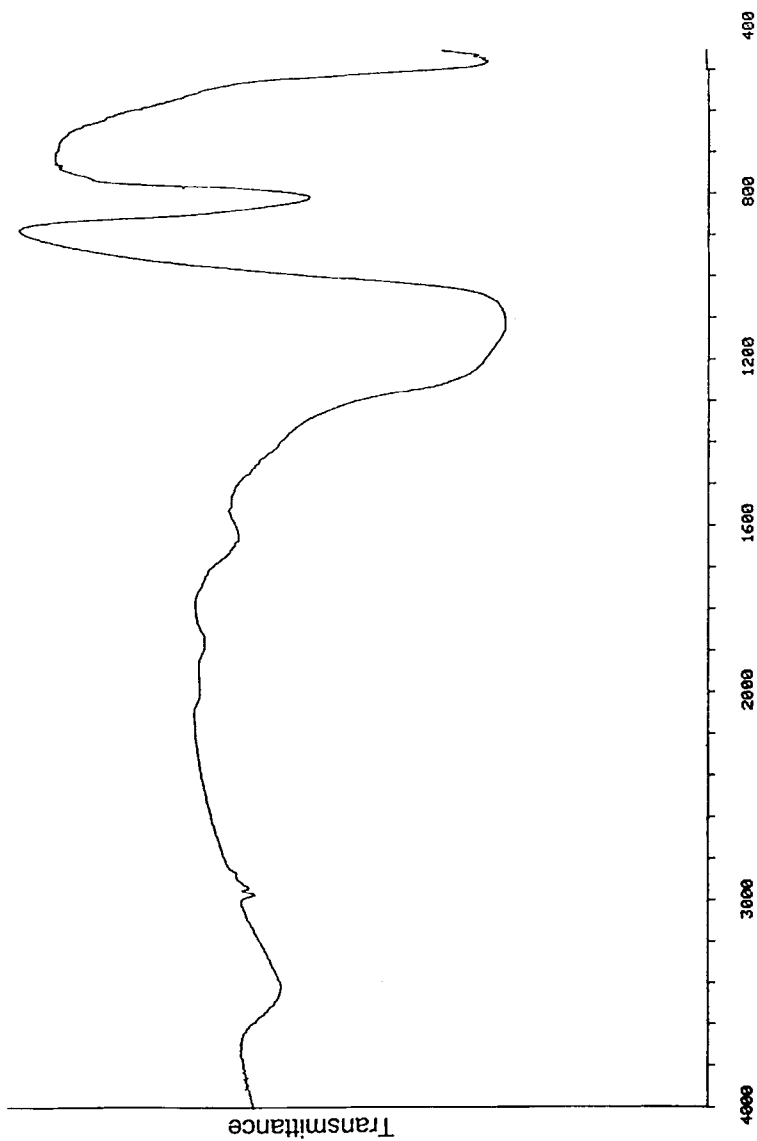


Fig. 5. FTIR spectra of the TGA residue remaining after heating up to 1000°C at 20°C/min in air.

ing absorption at 1040 cm^{-1} could be attributed to a more branched/crosslinked polymer as a result of thermal aging.²³

Figure 4 shows the result of the TGA run on the vapor phase polymer at $20^\circ\text{C}/\text{min}$ in air. The experiment was conducted in air as a severe environment rather than nitrogen in order to determine the lower limit of thermal stability. The polymer retains almost 65% of its original weight at 1000°C and this high thermal stability could be attributed to the inorganic nature of the plasma polymer. The plot also shows a reaction zone around 350°C . Usually the coupling layer is expected to be stable to beyond the molding temperature of the matrix. However, if this layer were to partially degrade at the molding temperature, covalent linking of the coated fiber to the matrix would be facilitated. In the case of the plasma polymer of HMDSO the partial degradation at around 350°C may result in a direct bonding with the matrix and provide for maximum strength at that interface.

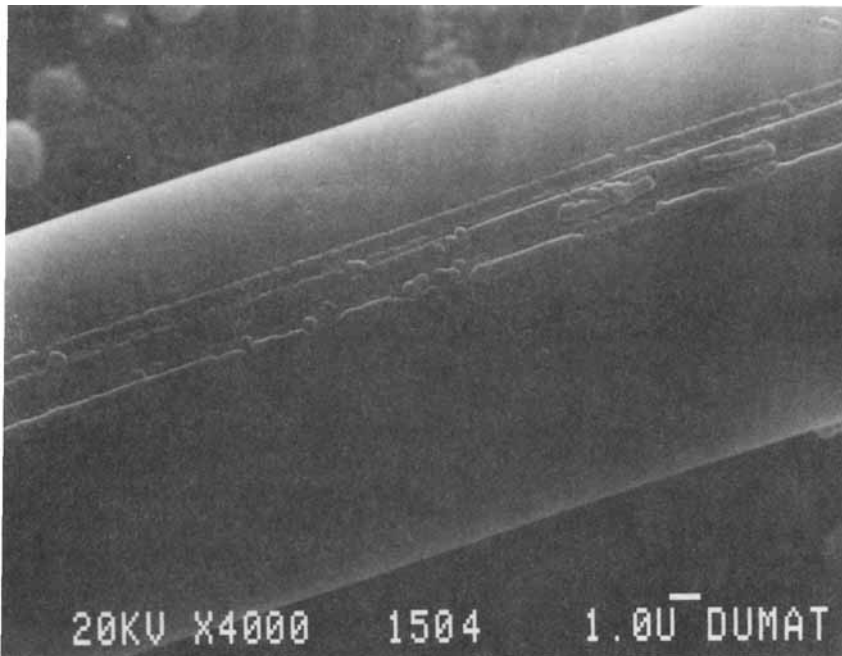
To understand the nature of the reaction taking place during the heating cycle of up to 1000°C , IR transmission spectra of the polymer residue following the TGA run was analyzed (Fig. 5). The spectra shows that the CH absorptions near 3000 cm^{-1} are considerably weaker compared to the broad absorption in the $1300\text{--}1000\text{ cm}^{-1}$ region which can be assigned to Si—O stretching. In addition, the Si—Me stretching absorption due to Si—(Me)₃ groups is completely absent, but the Si—Me stretching absorption in the Si—(Me)₂ and the Si—Me groups near 800 cm^{-1} overlap with the amorphous SiO₂ absorption expected in this region.²² Because of the temperature range and the presence of air, the Si—O mode is expected to dominate that signal. The resultant compound is very low in organic content and may essentially represent a glass type silicate network.

Wettability measurements (Table I) on glass slides coated with the plasma polymer of HMDSO revealed the hydrophobic nature of the coating. Contact angle values were 103° for samples coated at 100 W. To study the hydrolytic stability of the coatings and the influence of the vapor phase polymer that drifts to the substrates, the samples were washed in boiling water for 15 min. The water contact angle value dropped to 98° , which may be the true contact angle value of the coating as the excess vapor phase polymer (low in branching and crosslinking) is expected to wash off.

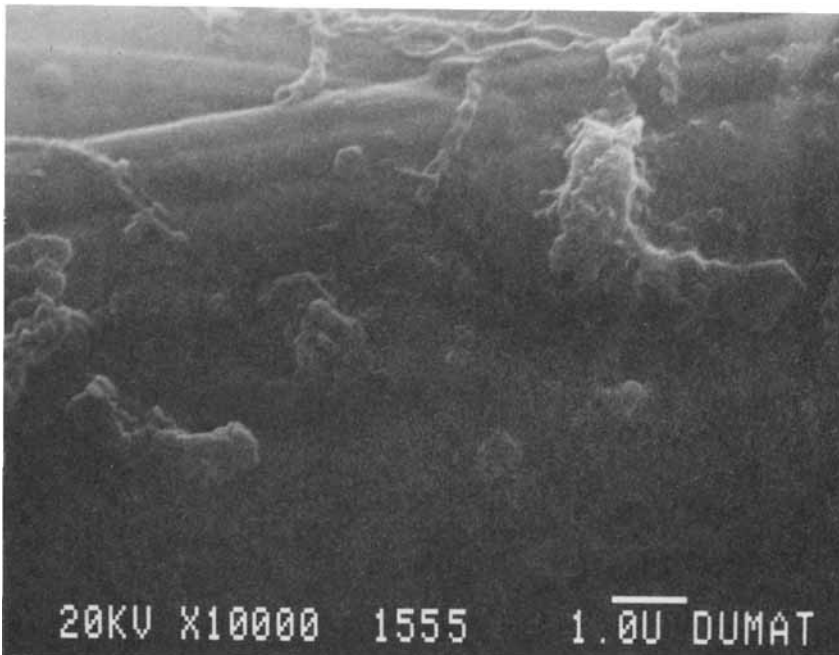
The wettability of the coating can be altered by a post-coating argon plasma treatment to further modify the surface chemistry. The contact angle

TABLE I
Wettability Values for HMDSO Coatings

Treatment	Water contact angle (deg)
Cleaned glass slides	53
Argon plasma (0.5 torr, 100 W, 10 min)	36
Coated with HMDSO (0.5 torr, 100 W, 15 min)	
As coated	103
Aged in boiling water for 15 min	98
Argon plasma etching (0.5 torr, 50 W, 3 min)	
Left in vacuum for 15 min after discharge power off	90
Air purged immediately after discharge power off	77



(a)



(b)

Fig. 6. SEM micrographs of hexamethylsiloxane coatings on glass fibers: (a) as coated; (b) aged in boiling water for 1 h.

was determined to be 90° if the chemically active sample surfaces were left in vacuum for 15 min after the plasma modification. If, however, the chamber was air purged immediately after turning the discharge power off, the contact angle value dropped to 77°, which could be attributed to the formation of some peroxides on the surface.³¹

Finally, the coatings on glass fibers before and after exposure to a boiling water environment for 1 h are shown in Figures 6(a) and (b) respectively to determine the hydrolytic stability. Figure 6(a) shows a uniform and featureless coating on the glass fiber surface. Figure 6(b) shows that the coating is etched by the boiling water. This may be due to the loss of excess polymer that drifts to the fiber surface due to polymerization in the vapor phase and which is loosely crosslinked to the grafted layer. Therefore, the hydrolytic stability can be controlled by the choice of the plasma processing conditions which favor grafting/crosslinking to the substrate over vapor phase polymerization.

CONCLUSIONS

The plasma polymer of hexamethyldisiloxane is a long chain polysiloxane, resulting from the removal of methyl groups from the monomer structure. The plasma polymerization behavior was a function of the plasma power, with higher power levels resulting in increased siloxane chain length. Thermal aging of this polymer showed it to have sufficient thermal stability to withstand the molding cycles of the resins of interest, e.g., PPS and PEEK matrices. TGA runs at 20°C/min in air showed the polymer retaining almost 65% of its weight at 1000°C with a partial degradation at around 350°C, which may prove beneficial for direct bonding with the matrix and the concomitant formation of a crosslinked interpenetrating network at the interface. The residue remaining at 1000°C was very low in organic content and represented a glass type silicate structure. Wettability measurements showed the hydrophobic nature of the coating with contact angles of around 103° which could be lowered by an argon plasma etching of the coatings. SEM micrographs showed uniform and featureless coatings on glass fiber surfaces which were etched by boiling water. This uniformity is attributed to the loss of vapor phase polymer loosely crosslinked to the grafted layer.

This study was sponsored by the Office of Naval Research under the University Research Initiative Composite Materials Program.

References

1. B. Arkles, *Chemtech*, **7**, 766 (1977).
2. H. Ishida, *Polym. Compos.*, **5**(2), 101 (1984).
3. D. F. Sounik and M. E. Kenney, *Polym. Compos.*, **6**(3), 151 (1985).
4. H. Inoue and S. Kohama, *J. Appl. Polym. Sci.*, **19**, 1939 (1975).
5. D. G. Pfeiffer and L. E. Nielson, *J. Appl. Polym. Sci.*, **23**, 2253 (1979).
6. B. Schlund and M. Lambla, *Polym. Compos.*, **6**(4), 272 (1985).
7. R. V. Subramanian and A. S. Crasto, *Polym. Compos.*, **7**(4), 201 (1986).
8. J. P. Bell, J. Chang, H. W. Rhee, and R. Joseph, *Polym. Compos.*, **8**(1), 46 (1987).
9. E. Pluedemann, *Silane Coupling Agents*, Plenum, New York, 1982, p. 120.
10. G. Dagli and N. H. Sung, *Proceedings of the ACS Division of Polymeric Materials: Science and Engineering*, Spring Meeting, Denver, Am. Chem. Soc., Washington, DC, 1987, Vol. 56, p. 410.

11. A. Benatar and T. G. Gutowski, *Polym. Compos.*, **7**(2), 84 (1986).
12. H. P. Schreiber, M. R. Wertheimer, and A. U. Sridharan, *Plasma Polymerization*, M. Shen and A. T. Bell, Eds., ACS Symp. Ser. 108, Am. Chem. Soc., Washington, DC, 1979, p. 287.
13. M. Gazicki, A. M. Wrobel, and M. Kryszewski, *J. Appl. Polym. Sci., Appl. Polym. Symp.*, **38**, 1 (1984).
14. N. Inagaki, S. Konda, M. Hirata, and H. Urushibata, *J. Appl. Polym. Sci.*, **30**, 3385 (1985).
15. J. Tyczkowski and M. Kryszewski, *J. Appl. Polym. Sci., Appl. Polym. Symp.*, **38**, 149 (1984).
16. E. Sacher, J. E. Klemberg-Sapieha, H. P. Schreiber, and M. R. Wertheimer, *J. Appl. Polym. Sci., Appl. Polym. Symp.*, **38**, 163 (1984).
17. M. R. Wertheimer and H. P. Schreiber, *J. Appl. Polym. Sci.*, **26**, 2087 (1981).
18. A. K. Sharma and H. Yasuda, *Thin Solid Films*, **110**, 171 (1983).
19. L. J. Bellamy, *Infrared Spectra of Complex Molecules*, Methuen, London, 1958.
20. R. M. Silverstein, G. C. Bassler, and T. C. Morrill, *Spectrometric Identification of Organic Compounds*, Wiley, New York, 1981.
21. A. L. Smith, *Spectrochim. Acta*, **16**, 87 (1960).
22. R. Anderson, B. Arkles, and G. L. Larson, *Silicon Compounds: Register and Review*, Petrarch Systems, Bristol, PA.
23. R. A. Assink, A. K. Hays, R. W. Bild, and B. L. Hawkins, *J. Vac. Sci. Technol.*, **A3**(6), 2629 (1985).
24. A. M. Wrobel, J. Kowalski, J. Grebowicz, and M. Kryszewski, *J. Macromol. Sci. Chem.*, **A17**(3), 433 (1982).
25. A. M. Wrobel, M. Kryszewski, and M. Gazicki, *J. Macromol. Sci. Chem.*, **A20**(5), 583 (1983).
26. I. Tajima and M. Yamamoto, *J. Polym. Sci., Polym. Chem. Ed.*, **23**, 615 (1985).
27. A. T. Bell, T. Wydeven, and C. C. Johnson, *J. Appl. Polym. Sci.*, **19**, 1911 (1975).
28. H. Yasuda, *J. Macromol. Sci. Chem.*, **A10**(3), 383 (1976).
29. H. Yasuda, *Thin Film Processes*, J. L. Vossen and W. Kern, Eds., Academic, New York, 1978, p. 361.
30. V. Krishnamurthy, I. L. Kamel, and Y. Wei, *J. Polym. Sci., Polym. Chem. Ed.*, **27**, 1211-1224 (1989).
31. R. P. Ouellette, M. M. Barbier, and Paul N. Cheremisinoff, *Electrotechnology, Vol. 5: Low Temperature Plasma Technology Applications*, Ann Arbor Science, Ann Arbor, MI, 1980, p. 41.

Received May 4, 1988

Accepted July 20, 1988