

Effect of Filament Temperature on the Chemical Vapor Deposition of Fluorocarbon–Organosilicon Copolymers

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ABSTRACT: The effect of filament temperature on the hot-filament chemical vapor deposition (HFCVD) of fluorocarbon–organosilicon copolymer thin films from 1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane (V_3D_3) and perfluorooctane sulfonyl fluoride (PFOSF) was examined. Significant changes in chemical structure occur as the filament temperature is varied, and these changes give rise to differences in thermal and mechanical properties. When the filament temperature is low, the films consist primarily of carbon-backbone polymer chains with siloxane ring pendant

groups. When higher filament temperatures are used, the film structure consists of siloxane-backbone chains with some degree of crosslinking. Films produced with low filament temperatures have a greater degree of thermal stability and flexibility than those produced with high filament temperatures. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 2176–2185, 2004

Key words: fluoropolymers; silicones; pyrolysis; thin films; structure–property relations

INTRODUCTION

Fluorocarbon and organosilicon polymers have several attributes that make them useful separately. Fluorocarbon thin films are biocompatible, hydrophobic, and have low dielectric constants.^{1,2} Organosilicon thin films produced by chemical vapor deposition (CVD) have higher dielectric constants, but they are biocompatible, have low surface roughness, and adhere well to silicon substrates.^{3–7} The synthesis of a fluorocarbon–organosilicon copolymer offers the opportunity to incorporate the useful characteristics of both fluorocarbon and organosilicon polymers into a single thin film. Fluorocarbon–organosilicon copolymers are currently under investigation as candidate materials for biopassivation coatings on neurological implants. These coatings need to be biocompatible, adherent, electrically insulating, and also thermally stable at the temperature of assembly of the implants (typically $\sim 150^\circ\text{C}$). CVD is an attractive synthetic technique for this application because it is single-step,

requires no solvent, and allows coatings to be deposited on substrates with complex topographies and small overall dimensions.

In a prior investigation,⁸ we described the synthesis of fluorocarbon–organosilicon copolymer thin films from hexamethylcyclotrisiloxane and hexafluoropropylene oxide by hot-filament chemical vapor deposition (HFCVD). The copolymer films had well-resolved bonding environments and the presence of covalent bonds between the fluorocarbon and siloxane polymeric units was confirmed by various spectroscopic techniques. The same synthetic method was used to demonstrate the use of an initiator, perfluorooctane sulfonyl fluoride (PFOSF), in the synthesis of fluorocarbon–organosilicon copolymer films.⁹ The organosilicon precursor used in this work was 1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane (V_3D_3). The presence of an initiator allowed deposition at relatively low filament temperatures (370°C), and under these conditions, chemical characterization showed that polymerization occurs across the vinyl bonds of V_3D_3 . The resulting films consisted of polymer chains with carbon backbones and siloxane rings as pendant groups.

This article examines the effect of filament temperature on the chemical and physical properties of fluorocarbon–organosilicon copolymer thin films produced from V_3D_3 and PFOSF by HFCVD. Significant changes in chemical structure are observed as the filament temperature is varied, and these changes in turn influence the mechanical and thermal properties of the copolymer films.

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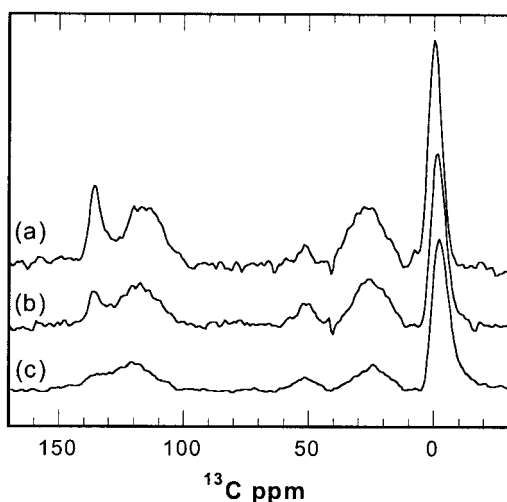


Figure 1 ^{13}C -NMR spectra of the HFCVD films deposited at filament temperatures of (a) 370°C, (b) 440°C, and (c) 540°C. Spectra were obtained by direct polarization with proton decoupling.

EXPERIMENTAL

Film depositions were carried out in a custom-built vacuum chamber described previously.⁸ Precursor breakdown was achieved by use of a resistively heated Nichrome wire (diameter 0.038 cm; 80% nickel, 20% chromium; Omega Engineering, Stamford, CT). The filament temperature was measured using a 2.2- μm infrared pyrometer with a spectral emissivity of 0.85. V_3D_3 (Gelest, Morrisville, PA) was fed to the chamber from a stainless steel vessel heated to $110 \pm 5^\circ\text{C}$ and a line maintained at $140 \pm 5^\circ\text{C}$. PFOSF (Aldrich, Milwaukee, WI) was vaporized in a glass container that was heated to $60 \pm 5^\circ\text{C}$ and fed through a line held at $90 \pm 5^\circ\text{C}$. The flow of both precursors into the chamber was regulated by needle valves. The flow rates of V_3D_3 and PFOSF were 23 and 12 sccm, respectively, and the chamber pressure was 0.5 Torr for all depositions. Substrates for the film depositions were placed on a stage within the chamber. The temperature of the stage was maintained at $25 \pm 2^\circ\text{C}$ by backside water cooling.

Films were deposited on silicon wafers using filament temperatures of 370, 440, and 540°C. For chemical characterization by solid-state NMR spectroscopy

and thermal stability studies by thermogravimetric analysis (TGA), longer-duration depositions (~ 60 min long) were carried out to prepare 14–16 mg samples for each of the three filament temperatures. NMR spectroscopy was performed using a home-built spectrometer consisting of a 6.338 T Oxford superconducting magnet and a 3.2 mm Chemagnetics magic angle spinning (MAS) probe. For NMR analysis, films were scraped off wafers and packed into zirconia rotors of 11 mm³ internal volume. Sample spinning was performed at speeds of 10 and 5 kHz for ^{13}C and ^{29}Si , respectively. ^{13}C -NMR spectra were obtained by direct polarization with proton decoupling, requiring about 17 h of signal averaging per spectrum. ^{29}Si spectra were obtained with proton cross-polarization and proton decoupling, requiring about 25 h of signal averaging per spectrum. Other experimental details for NMR analysis were described previously.⁸ Sample preparation for TGA was done by scraping films off wafers and loading into a platinum pan covered with aluminum foil. TGA was performed on a Perkin-Elmer TGA 7 analyzer (Perkin Elmer Cetus Instruments, Norwalk, CT) using nitrogen as the purge gas with a flow rate of 20 mL/min. Samples were held at 40°C for 3 min and then heated to about 450°C at a rate of 10°C/min.

Films were also deposited on platinum wires (diameter 50 μm ; A-M Systems, Everett, WA). These wires were mounted on an aluminum ring with posts, and the distance between the wires and the reactor stage was 0.5 cm. The distance between the substrate wires and the Nichrome filament was 1.8 cm. The structure of the coatings was observed using a FEI/Philips XL30 environmental scanning microscope (ESEM; Philips, The Netherlands).

RESULTS AND DISCUSSION

^{13}C -NMR spectroscopy

Figure 1 shows the ^{13}C -NMR spectra of the films produced at three different filament temperatures. Chemical shift assignments for these spectra are given in Table I. Peak areas were obtained using a nonlinear least-squares regression. Because the ^{13}C -NMR spectra

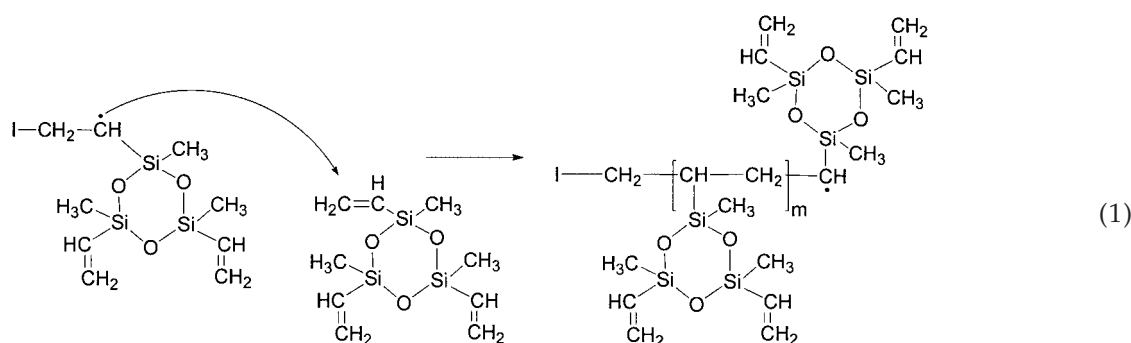
TABLE I
Chemical Shift Assignments for the ^{13}C -NMR Spectra of Figure 1

Chemical shift (ppm)	Structure	Normalized peak area (arbitrary units)			Ref.
		370°C	440°C	540°C	
-2 to 0	CH_3	1.000	1.000	1.000	23
12–41	CH_2 and $\text{CH}(\text{Si})$	0.536	0.468	0.220	24
51	$\text{CH}(\text{Si})\text{SO}_2\text{F}$	0.043	0.114	0.059	25
109	CF_2	0.435	0.354	0.178	26
117	CF_3	0.208	0.219	0.161	26
135	Vinyl group	0.314	0.142	0.117	27

were obtained by direct polarization, these areas provide a quantitative measure of the concentrations of the respective carbon moieties.

In our prior investigation of the chemical structure of films deposited from V_3D_3 and PFOSF at a filament temperature of 370°C ,⁹ the peak between 12 and 41 ppm was shown to be evidence of carbon-backbone

polymer chains with siloxane ring pendant groups. These chains are formed by chain propagation along the vinyl bonds of V_3D_3 , as shown in reaction (1). Here, "I" represents a fluorocarbon initiator fragment produced by the thermal decomposition of PFOSF.⁹ This initiator fragment is of the form $\text{CF}_3(\text{CF}_2)_n$, where n varies from 0 to 7.



The 12- to 41-ppm peak corresponds to CH_2 and $\text{CH}(\text{Si})$ groups in the carbon backbone, and decreases in intensity as the filament temperature is increased. The peak at 135 ppm, which corresponds to unreacted vinyl groups, follows the same trend. If reaction (1) were the only pathway available to the vinyl groups in V_3D_3 , the decrease in intensity of the 135 ppm peak should be accompanied by an increase in the 12- to 41-ppm peak. Because both of the peaks decrease in intensity with increasing filament temperature, the ^{13}C -NMR spectra suggest the presence of an alternative reaction pathway [in addition to reaction (1)], which becomes more dominant at higher filament temperatures. Such a pathway could be one that involves abstraction of vinyl groups from the V_3D_3 molecules. An abstraction reaction would result in a lower intensity for the 135-ppm peak, and also leave fewer vinyl groups available for polymerization according to reaction (1), thereby giving a lower intensity for the 12- to 41-ppm peak.

The 0-ppm peak in the ^{13}C -NMR spectra decreases in intensity and becomes broader as the filament temperature is increased. This trend indicates a decrease in methyl group content at higher temperatures. The extent of Si-methyl bond cleavage is, however, not as significant as that of Si-vinyl bond cleavage in the range of filament temperatures being examined. Michalczyk et al.¹⁰ examined the thermal stability of crosslinked siloxane polymers prepared from 1,3,5,7-tetravinyl-1,3,5,7-tetramethyl-cyclotrisiloxane (V_4D_4), an eight-membered ring, and its hydrogen-substituted analog, 1,3,5,7-tetramethylcyclotetrasiloxane (H_4D_4), by thermogravimetric analysis coupled with mass spectrometry. The cleavage of Si-vinyl bonds was found to occur at a lower temperature compared to

that of Si-methyl bonds, and the latter was not significant at temperatures lower than 550°C . This observation is consistent with the preferential abstraction of vinyl groups observed in the films deposited from V_3D_3 and PFOSF.

^{29}Si -NMR spectroscopy

Figure 2 shows ^{29}Si -NMR spectra of the same set of films, with peak assignments listed in Table II. Because ^{29}Si -NMR was performed using proton cross-polarization, the spectra are not quantitative and thus no peak areas are given in Table II.

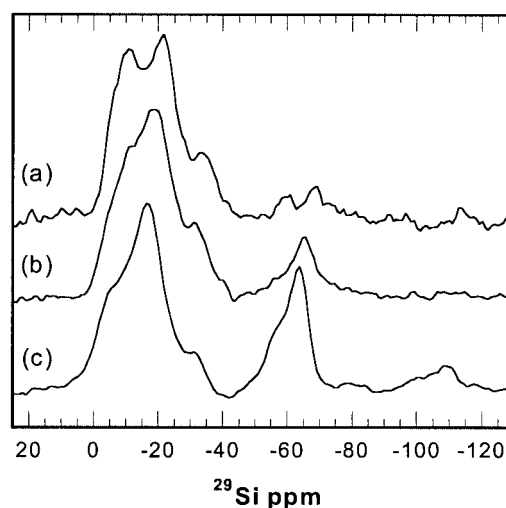


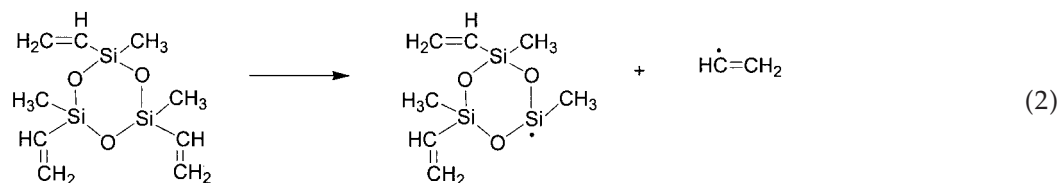
Figure 2 ^{29}Si -NMR spectra of the HFCVD films deposited at filament temperatures of (a) 370°C , (b) 440°C , and (c) 540°C . Spectra were obtained with proton cross-polarization and proton decoupling.

The ^{29}Si -NMR spectrum of the precursor V_3D_3 contains only one peak at -22 ppm. This peak appears in the spectrum of the film deposited at the lowest filament temperature [Fig. 2(a)] and is assigned to the vinylmethylsiloxane group in a ring structure of three siloxane units (peak iv in Table II). Also present in Figure 2(a) is a peak at -10.9 ppm, which is assigned to the siloxane group in a pendant ring that is directly bonded to a carbon-backbone chain [peak i in Table II; see reaction (1)]. Given that both of the carbon atoms attached to the silicon atom of interest in this moiety are sp^3 hybridized, its chemical shift is close to the -10 ppm shift reported for the dimethylsiloxane groups in hexamethylcyclotrisiloxane.⁶ As the filament temperature is increased, these two peaks are replaced by a single peak at -16.4 ppm. This peak is assigned to the linear-siloxane chain version of the $(\text{CH}_2)\text{CH-Si}(\text{O})_2(\text{CH}_3)$ group.¹⁰

The peak lying between -31.0 and -33.7 ppm (peak v in Table II) represents the vinylmethylsiloxane group in a linear chain.¹¹ This peak decreases in intensity with filament temperature, along with peak iv. Because both of these peaks correspond to siloxane

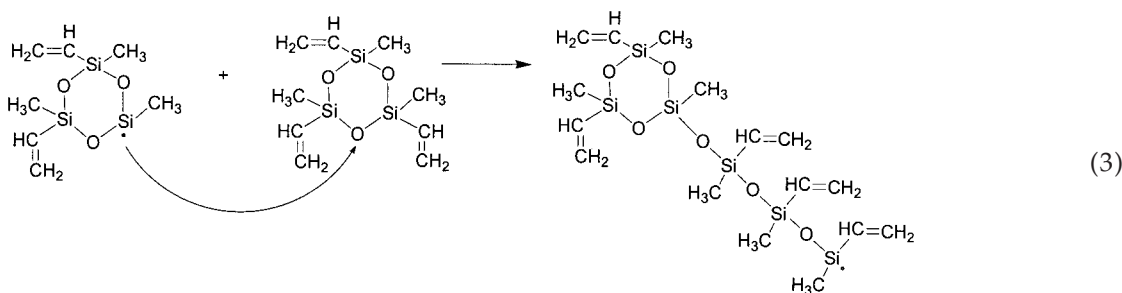
moieties with vinyl groups, their decreasing trend indicates a greater degree of vinyl group abstraction at higher filament temperatures. This trend is consistent with the decrease in vinyl group concentration with increasing filament temperature observed in the ^{13}C -NMR spectra. The decrease in methyl group content with increasing filament temperature observed in the ^{13}C -NMR spectra is reflected by the increasing intensity of peak viii, which corresponds to $\text{Si}(\text{O})_4$ (commonly known as "Q") groups.⁶

The most significant effect of increasing filament temperature, however, is the increase in intensity of the peak located between -64 and -69 ppm. This peak is assigned to the $(\text{O})_3\text{Si}(\text{CH}_3)$ (commonly known as "T") group.⁶ The formation of T-groups requires abstraction of vinyl groups from the siloxane units in V_3D_3 . The increasing intensity of the T-group peak with increasing filament temperature is therefore indicative of greater vinyl group abstraction and is consistent with the trends followed by peaks iv and v. The vinyl group abstraction reaction (2) is shown as follows:



In addition to vinyl abstraction, a second requirement for T-group formation is the creation of a third Si—O bond in the siloxane moiety produced in reaction (2). The formation of such a bond could occur by a reaction between this moiety and another V_3D_3 molecule, as shown in reaction (3). The resulting radical species is a ring structure attached to a linear vinylmethylsiloxane chain that is three monomer units in

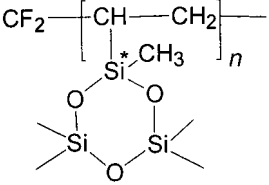
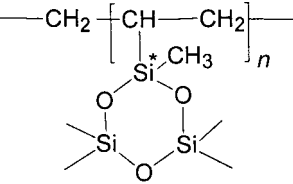
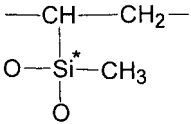
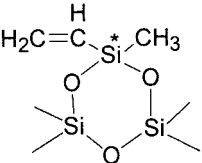
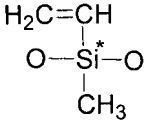
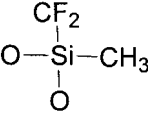
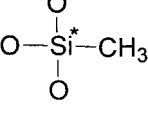
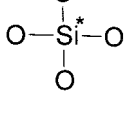
length. This moiety may react further with other V_3D_3 rings or undergo a termination reaction with a siloxane or fluorocarbon radical. Another possible reaction pathway for the formation of T-groups is the decomposition of the six-membered V_3D_3 ring into three vinylmethylsilanone molecules,¹² followed by a reaction between the silanone molecules and vinyl-abstraced siloxane groups.



The reaction pathways proposed in reactions (2) and (3) indicate that the formation of T-groups is accompanied by the conversion of some six-membered V_3D_3

rings into linear chains. The increase in T-group concentration observed at higher filament temperatures should therefore occur with a greater extent of ring opening.

TABLE II
Chemical Shift Assignments for the ^{29}Si -NMR Spectra
of Figure 2

Peak	Chemical shift (ppm)	Structure
i	-4.0 to -6.0	
ii	-10.9	
iii	-16.4	
iv	-21.9	
v	-31.0 to -33.7	
vi	-56.4 to -60.1	
vii	-63.7 to -69.2	
viii	-108.4 to -114.0	

This is indeed what is observed in the ^{29}Si -NMR spectra, in the region between -4 and -34 ppm.

FTIR spectroscopy

Figure 3 shows the FTIR spectra of films for the same series of filament temperatures. Absorption band as-

signments made from the literature are given in Table III. The asymmetric stretching mode (ASM) of the siloxane (Si—O—Si) group appears as a doublet in all of the films, indicating the presence of linear siloxane chains or ring structures.^{13,14} In their investigation of organosilicon films deposited from D_3 by HFCVD, Pryce Lewis et al.⁶ observed a larger concentration of ring structures relative to linear chains under conditions where the lower wavenumber band of the ASM was more intense than the higher wavenumber band. This trend in the ASM is observed in the spectrum of the copolymer film deposited at the lowest filament temperature [Fig. 3(a)]. As the filament temperature is increased, the relative height of the higher wavenumber band increases, indicating a transition from siloxane rings to linear siloxane chains. This is consistent with the ^{29}Si -NMR data and provides further support for the ring-opening pathway shown in reaction (3).

The FTIR data can also be quantitatively analyzed in conjunction with the ^{13}C -NMR data to examine the relationship between vinyl group abstraction and T-group formation. Figure 4 shows the region between 1240 and 1300 cm^{-1} of the FTIR spectra for the three HFCVD films. This is the region where the symmetric bending mode of CH_3 groups in Si— CH_3 appears. The position of this band depends on the oxidation state of the silicon atom. For example, the position of this band in $\text{O}_2\text{Si}(\text{CH}_3)_2$ (commonly known as "D") groups is around 1260 cm^{-1} .¹⁵ In T-groups, where the silicon atom has a higher oxidation state, it appears around 1270 cm^{-1} .¹⁵

In each spectrum, this band can be deconvoluted into two peaks that denote siloxane groups with silicon atoms having oxidation states of +2 and +3, respectively. The lower wavenumber peak (centered at 1265 cm^{-1}) thus represents all of the groups that are analogous to the D-group (groups corresponding to peaks i-v in Table II), and the higher wavenumber peak (centered at 1279 cm^{-1}) corresponds to T-groups. The area under these peaks provides a measure of the concentration of the respective moieties. These areas, expressed as percentages of the overall area of the Si— CH_3 FTIR band, are given in Table IV for each of the three filament temperatures.

The loss of vinyl groups from the V_3D_3 molecules can be quantified from the ^{13}C -NMR data. Using the normalized areas given in Table I, the lost vinyl content can be evaluated by adding the areas corresponding to the vinyl groups and the CH_2 and $\text{CH}(\text{Si})$ groups and subtracting the result from the area of the methyl groups. The last subtraction step is valid because the precursor V_3D_3 contains equal numbers of methyl and vinyl groups and the methyl groups do not undergo appreciable abstraction under the present conditions. The results of this calculation for all three filament temperatures are given in Table IV.

Comparison between the values of %T and the lost vinyl content indicate similar trends with increasing

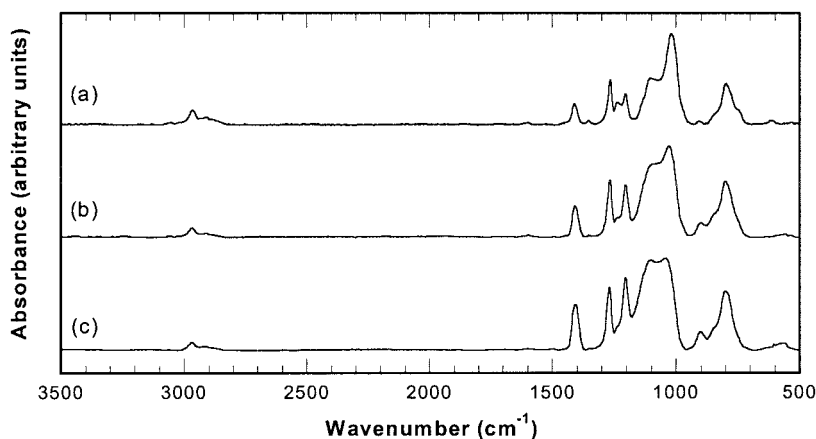


Figure 3 FTIR spectra of the films deposited at filament temperatures of (a) 370°C, (b) 440°C, and (c) 540°C.

filament temperature. For example, the percentage concentration of T-groups increases by a factor of 4 (approximately) as the filament temperature is increased from 370 to 540°C. Over this temperature range, the degree of vinyl group loss also increases by approximately the same factor. The %T-group concentration for films deposited using a filament temperature of 440°C is about 2.7 times greater than that for films deposited using a filament temperature of 370°C. Correspondingly, the lost vinyl content for the former is about 2.6 times greater than that of the latter. These calculations show the close relationship between vinyl group abstraction and T-group formation, and support the hypothesis that the former must precede the latter, as indicated by reactions (2) and (3).

Thermal analysis

Figure 5 shows the TGA results for films deposited at the three filament temperatures under consideration.

The six-membered cyclic siloxane, hexamethylcyclotrisiloxane, is known to be more thermally stable than linear poly(dimethylsiloxane) (PDMS).¹⁰ It is also known that crosslinking siloxane rings into network structures improves thermal stability.¹⁰ In this arrangement, the siloxane rings are the repeat units, and the structure takes advantage of the superior thermal stability of the siloxane rings relative to linear PDMS. The HFCVD film deposited using a filament temperature of 370°C is similar to this type of architecture, given that the structure consists primarily of carbon-backbone chains with siloxane ring pendant groups. Individual siloxane rings can be connected to more than one carbon chain because more than one vinyl group on a ring can undergo polymerization. The HFCVD film deposited at 540°C, on the other hand, is almost completely devoid of ring structures, and would therefore be expected to have lower thermal stability relative to the film deposited at 370°C.

TABLE III
Absorption Band Assignments for the FTIR Spectra of Figure 3

Assignment	HFCVD films (cm ⁻¹)	Literature (cm ⁻¹)	Ref.
SO ₂ scissoring	575	504–586	28
Si—CH=CH ₂	614	610	29
Si—C stretching, CH ₃ rocking in Si(Me)(Vi) ^a	800	805	29
Si—O—Si asymmetric stretching (doublet)	1018–1104	1020–1075	6
CF ₂ asymmetric stretching	1204	1220	30
CF ₃ —CF ₂ stretching	1239	1270–1340	31
CH ₃ symmetric bending in Si—CH ₃	1265–1279	1260–1270	28, 29
SO ₂ asymmetric stretching in CH(Si)SO ₂ F,	1409	1409	9
=CH ₂ scissoring		1400	28, 29
C=C stretching in vinyl groups	1599	1600	29
C—H symmetric stretching in sp ³ CH ₃	2912	2900	29
C—H asymmetric stretching in sp ³ CH ₃	2967	2960	29
=CH ₂ symmetric stretching in vinyl groups	3020	3020	29
=CH ₂ asymmetric stretching in vinyl groups	3060	3060	29

^a Vi denotes vinyl groups.

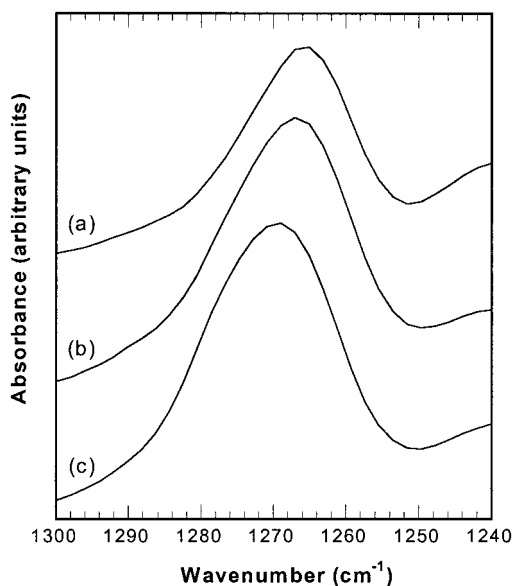


Figure 4 Expanded FTIR spectra of the films deposited at filament temperatures of (a) 370°C, (b) 440°C, and (c) 540°C showing the region of the CH₃ symmetric bending mode in Si—CH₃ groups.

As anticipated, using a filament temperature of 370°C produces a more thermally stable film than a filament temperature of 540°C film (Fig. 5). The film deposited with a filament temperature of 440°C lies in between, consistent with a mixture of rings and linear units in the film structure.

For the film deposited at a filament temperature of 370°C, 5% of the film mass is lost at 378°C. For linear PDMS polymers examined by Kendrick et al.,¹⁶ the estimated temperature for 5% weight loss ranges between 340 and 420°C, depending on the molecular weight of the polymer. For crosslinked siloxane glasses prepared from V₄D₄ and H₄D₄ by Michalczyk et al.,¹⁰ the temperature corresponding to 5% weight loss was about 575°C (these crosslinked glasses consist entirely of eight-membered siloxane rings linked together by methylene bridges). These values indicate that the HFCVD film deposited with a filament temperature of 370°C is more thermally stable than low molecular weight linear PDMS chains, but not as stable as the crosslinked glasses. The preservation of siloxane

TABLE IV
FTIR Peak Fit Areas and Vinyl Group Loss Quantification

Filament temperature (°C)	%D	%T	Lost vinyl content (arbitrary units)
370	95.98	4.02	0.15
440	89.11	10.89	0.39
540	83.24	16.76	0.66

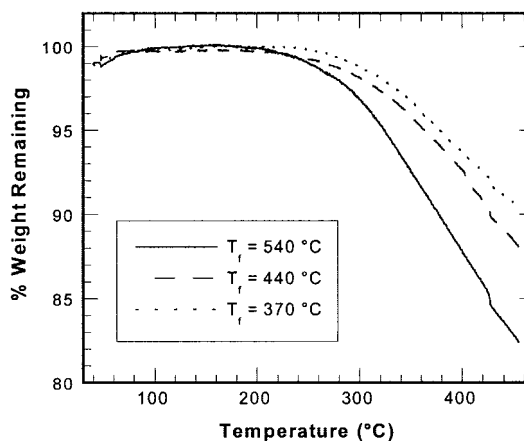


Figure 5 TGA results of the HFCVD films deposited at three different filament temperatures.

ring structures is most likely the cause of the former, whereas the latter could be a result of insufficient ring immobilization within the film structure.

For the film deposited using a filament temperature of 540°C, the temperature for 5% mass loss is 324°C. Comparison with the above-mentioned value for linear PDMS suggests that this film consists primarily of low molecular weight linear siloxane chains.

Wire coatings

Figure 6 shows ESEM images of wire coatings made from V₃D₃ and PFOSF with filament temperatures of 370, 440, and 540°C. The wires were tied into loops to examine the flexibility of the copolymer coating. The difference in chemical composition manifests itself in the form of brittleness, which increases as filament temperature is increased. The film deposited with a filament temperature of 540°C cracks extensively when the wire is bent and peels off almost completely. The 440°C coating is marginally better, and the 370°C coating shows no apparent cracking. This trend is consistent with the brittleness observed with increasing T-group concentration in organosilicon films deposited by plasma CVD by Cech et al.¹⁷ and also with the higher rigidity of ladderlike siloxane polymers (consisting almost entirely of T-groups) relative to linear polysiloxanes.¹⁸

This test demonstrates a qualitative similarity between these coatings and fluorocarbon coatings deposited from hexafluoropropylene oxide by Limb et al.¹⁹ Fluorocarbon coatings with a high degree of crosslinking were found to be more brittle than those consisting of mostly linear chains.

The increase in brittleness with filament temperature can be related to the chemical composition of the coatings using the continuous random network theory and percolation of rigidity concepts.^{19–21} In a com-

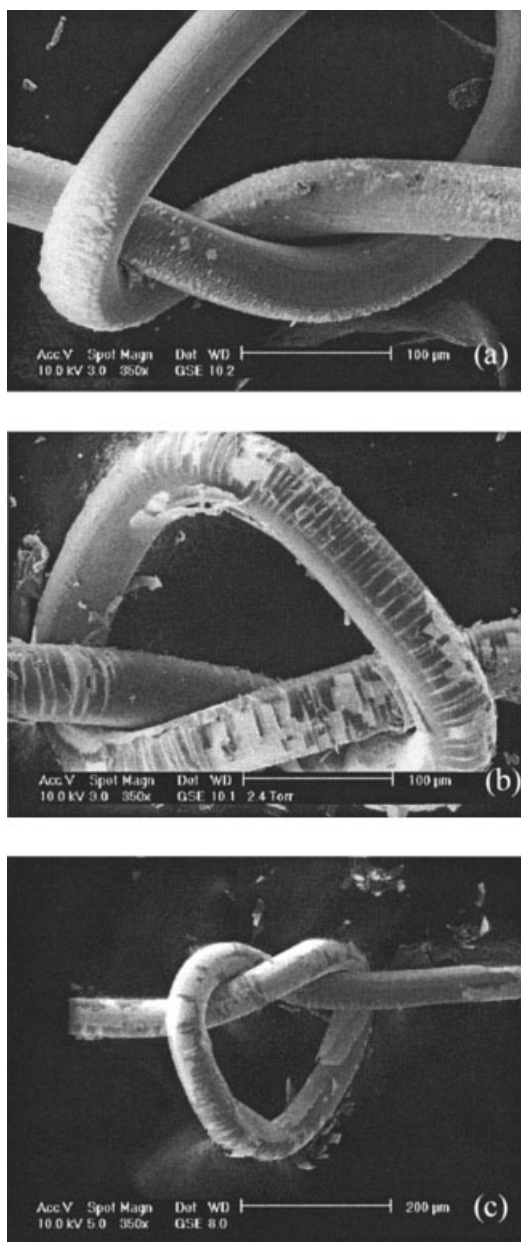


Figure 6 Environmental SEM micrographs of fluorocarbon-organosilicon copolymer wire coatings on platinum wires (diameter 50 μm) deposited using filament temperatures of (a) 370°C, (b) 440°C, and (c) 540°C.

pletely amorphous material consisting of random covalent bonds, the percolation of rigidity represents a threshold above which the network is said to be overconstrained and below which it is considered underconstrained.²⁰ This threshold is related to the average connectivity number $\langle r \rangle$ of the covalent network, which is defined as the average number of bonds per network-forming atom. Atoms that have a valence of two or higher that are bonded to other such atoms are considered to be network-forming atoms. Atoms with only one bond, such as hydrogen or fluorine, do not contribute to the network and are therefore not

counted. When a material consists entirely of atoms that are able to form two or more bonds, the percolation of rigidity occurs at an average connectivity number of 2.4.²² When the value of $\langle r \rangle$ is less than 2.4, the material is underconstrained, meaning that it has a low degree of crosslinking and is flexible. When $\langle r \rangle$ is greater than 2.4, the material is overconstrained and rigid.

Values of $\langle r \rangle$ for the present series of films can be estimated using the NMR and FTIR data. This is done by calculating $\langle r \rangle$ for each chemical moiety and using the composition data to determine $\langle r \rangle$ for the sample as a whole. The most significant contributions to the changes in $\langle r \rangle$ come from the siloxane moieties listed in Table II.

Because the ^{29}Si -NMR spectra were obtained by cross-polarization with protons, the spectra in Figure 2 are not quantitative. However, approximate compositions for each siloxane moiety can be obtained by using peak areas from the ^{29}Si -NMR spectra along with the quantitative FTIR data shown in Table IV. The first step is to assume that all of the moieties lying within the "D" region of the ^{29}Si -NMR spectra (-4 to -34 ppm) have the same cross-polarization efficiency. Next, fractional areas are calculated for each moiety by taking the peak area and dividing this by the sum of the areas of all peaks lying between -4 and -34 ppm. The fractional area can then be multiplied with the %D value in Table IV for the relevant filament temperature to obtain an estimate of the composition of each D-like moiety. A similar calculation can be done for each T-like moiety. The results of these calculations are shown in Tables V, VI, and VII for each of the three filament temperatures under consideration.

The next step is to calculate the value of $\langle r \rangle$ for each moiety. A general formula for $\langle r \rangle$ is given in eq. (4) where n_r is the number of network-forming atoms and r is the number of bonds:

$$\langle r \rangle = \frac{\sum_r r n_r}{\sum_r n_r} \quad (4)$$

For example, $\langle r \rangle = 2.57$ for the moiety corresponding to peak iii in Table II. In this moiety, the silicon atom has three network-forming bonds (the Si-CH₃ bond is non-network forming) and each oxygen atom forms two network bonds. The -(CH-CH₂)- group is considered as a single moiety capable of forming three network-forming bonds. To avoid double counting, each oxygen atom is counted as one-half an atom, and the -(CH-CH₂)- group as one-third an atom. The numerator of eq. (4) for this moiety is then $[(3 \times 1) + (2 \times \frac{1}{2}) + (2 \times \frac{1}{2}) + (3 \times \frac{1}{3})]$ and the denominator is given by the sum $(1 + \frac{1}{2} + \frac{1}{2} + \frac{1}{3})$. Division gives $\langle r \rangle = 2.57$. Values of $\langle r \rangle$ for each siloxane moiety are given in Tables V-VII.

TABLE V
Percolation of Rigidity Calculations for the HFCVD Film Deposited with a
Filament Temperature of 370°C

²⁹ Si-NMR peak position (ppm)	Area (arbitrary units)	Fractional area	Composition	< <i>r</i> >
-6	114,188	0.148	14.17	2.57
-11	166,871	0.216	20.71	2.57
-21	417,858	0.540	51.85	2.00
-34	74,574	0.096	9.25	2.00
-60	19,384	0.310	1.25	2.40
-69	43,159	0.690	2.77	2.40
Overall average connectivity number: 2.16				

Once $\langle r \rangle$ values for each moiety have been calculated, the average connectivity number for the entire sample is calculated by summing the weighted contributions from each moiety ($\langle r \rangle$ multiplied by composition value obtained from ²⁹Si-NMR and FTIR) and dividing the result by the sum of the composition values. These values are also given in Tables V–VII.

The trend in the values of the average connectivity number indicates a progression from an underconstrained and flexible network to one that is overconstrained and rigid as the filament temperature is increased from 370 to 540°C. This correlates well with the trend observed with the wire coatings in Figure 6. The coating deposited with a filament temperature of 370°C remains intact upon bending, whereas the coating deposited using a filament temperature of 540°C undergoes extensive cracking. The electron micrographs suggest that the transition point where the percolation of rigidity occurs lies between filament temperature values of 440 and 370°C. In this region, however, the values of the average connectivity number would have to lie between 2.24 and 2.16 according to the calculations. The calculated value for the transition point would then be below the threshold of 2.4 predicted by theory. This discrepancy is probably attributable to errors resulting from the assumption of equal cross-polarization efficiency of moieties within each group (D-like or T-like) in the ²⁹Si-NMR spectra. Nevertheless, the trend in the calculated values of the

average connectivity number shows the effect of increasing T-group concentration on the rigidity of the wire coatings.

CONCLUSIONS

The chemical structure of fluorocarbon–organosilicon films synthesized from V₃D₃ and PFOSF by HFCVD depends strongly on filament temperature. When the filament temperature is low, the films consist of carbon-backbone polymer chains with siloxane rings as pendant groups. Higher filament temperatures result in films that consist of linear siloxane chains crosslinked by T-groups. This difference in chemical structure gives rise to significant differences in thermal and mechanical properties. The retention of the siloxane ring structure confers greater thermal stability on the film deposited with a low filament temperature. In addition, the chemical structure of this film is of an underconstrained nature, giving it a greater degree of flexibility. In the films deposited with higher filament temperatures, the greater concentration of T-groups results in an overconstrained and brittle structure with poorer thermal stability. Using a low filament temperature thus allows more selective chemistry that results in films with better properties.

TABLE VI
Percolation of Rigidity Calculations for the HFCVD Film Deposited with a
Filament Temperature of 440°C

²⁹ Si-NMR peak position (ppm)	Area (arbitrary units)	Fractional area	Composition	< <i>r</i> >
-6	230,332	0.164	14.59	2.57
-11	301,627	0.214	19.11	2.57
-20	671,576	0.477	42.54	2.00
-32	203,268	0.144	12.88	2.00
-60	98,437	0.401	4.37	2.40
-65	146,772	0.599	6.52	2.40
Overall average connectivity number: 2.24				

TABLE VII
Percolation of Rigidity Calculations for the HFCVD Film Deposited with a
Filament Temperature of 540°C

²⁹ Si-NMR peak position (ppm)	Area (arbitrary units)	Fractional area	Composition	<r>
-6	115,203	0.296	24.61	2.57
-17	255,378	0.655	54.56	2.57
-32	19,062	0.049	4.072	2.00
-58	78,528	0.522	8.749	2.40
-64	9,109	0.478	8.011	2.40
Overall average connectivity number: 2.52				

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