# STUDY ON THERMAL DECOMPOSITION OF PLASMA-POLYMERIZED ORGANOSILICON THIN FILMS

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## ABSTRACT

Thermal decomposition of plasma-polymerized hexamethylcyclotrisilazane films was studied. Pyrolysis-gas chromatography and IR investigations showed that methylsilyl groups of monomer are highly susseptible to form disilymethylene and disilyethylene crosslinkages in the polymer. Abstraction of methyls and scission of Si-C bonds in the polymer network appeared to be dominating decomposition reactions. A significant improvement of the film adhesion to metal substrate followed by thermal treatment agreed reasonably with the increase in the surface energy of the film.

## 1. INTRODUCTION

Our recent studies (1) have shown that the chemical structure and properties of plasma-polymerized organosilicon films can be modified selectively by a controlled post-thermal treatment. Such treatment results in highly crosslinked materials with increasing, inorganic character which display a strong adhesion to the metal substrates and outstanding resistance to aggressive environments. In view of these promising results the current work has been devoted to a complex study on thermal decomposition of plasma-polymerized hexamethylcyclotrisilazane (PP-HMCTSN) films using various analytical methods such as: pyrolysis-gas chromatography (PGC) combined techniques, IR spectroscopy, thermogravimetry (TGA), transmission electron microscopy (TEM) and contact angle measurements.

## 2. EXPERIMENTAL

Plasma polymerizations were carried out in the electrode system described previously (2). Polymer films were deposited on the surface of two parallel stainless steel electrodes spaced 3 cm apart, each having a surface area of 50 $cm^2$. Glow discharge was generated at frequency f=20 kHz, current density j=0.4-2.7 $mA/cm^2$, monomer vapour pressure p=0.3 Torr and discharge duration t=30 s. Thickness of the films was found to be 1.5 µm. Polymer samples of ~0.2 mg removed from the electrodes were pyrolysed in argon at 750°C for 15 s, using a Jeol, Model PL723, pyrolyser unit.The gaseous products were fed directly to the injection part of a Jeol, Model JGC1100, gas chromatograph equipped with a flame ionization detector and a 1mx3mm stainless steel separation column filled with a 5A 60/80 mesh molecular sieve. The products were identified using the retention time coincidence with pure standard compounds. TGA measurement was performed for polymer sample of 8mg in vacuum ($10^{-5}$ Torr) at a heating rate of 2 deg/min using a Mettler "Thermoanalyzer". TEM examinations were carried out for films of 600 Å in the initial thickness, deposited on copper foil and pyrolysed in vacuum at 800° for various periods of time. Film samples separated from the substrate by dissolving copper foil in nitric acid were examined directly in a Tesla, Model BS-500, transmission electron microscope. The dispersion and polar components of the surface energy were calculated from the contact angle measurements of water and methylene iodide according to a surface energy model by Owens et al.(3).

## 3. RESULTS

PGC studies showed that the gaseous residue following thermal decomposition of PP-HMCTSN consists mostly of light hydrocarbons (Fig.1) such as methane, ethane, ethylene and some amount of acetylene and propylene. The formation of these products is associated with thermal scission of $\equiv Si-CH_3$, $\equiv Si-H$, and $\equiv Si_2N-H$ bonds in the polymer (1). The methyl and hydrogen radicals released in this way may be then converted in the gaseous phase into secondary products shown in Fig.1. PGC examination of PP-HMCTSN obtained at different discharge current densities revealed a marked change in concentration of decomposition products. PGC data were evaluated as the concentration ratios $C_2H_6/CH_4$ and $C_2H_4/CH_4$, which express the ratios of the areas under the respective gas chromatographic peaks. These ratios are presented in Fig.2 as a function of j. The plots show that the $C_2H_4/CH_4$ ratio increases with current density whereas the $C_2H_6/CH_4$ remains constant. The points at zero current density correspond to the respective ratios determined for monomer. Assuming that $CH_4$, $C_2H_6$ and $C_2H_4$ are formed as a secondary decomposition products, thus their relative content under the same pyrolysis conditions will be independent on the number of methyl groups in the polymer and should remain constant. This agrees well with a distinct plateau in the $C_2H_6/CH_4$ curve observed for whole density range under investigation. The increase of the $C_2H_4/CH_4$ ratio with current density (Fig.2) results from the increase in ethylene content and indicates clearly that ethylene is produced not only as a secondary product of thermal reactions but it can also be evolved as a primary product. The IR analysis of PP-HMCTSN provided the evidence for the presence of disilymethylene $\equiv Si-CH_2-Si\equiv$ and disilyethylene $\equiv Si-CH_2-CH_2-Si\equiv$ linkages which are identified by the appearance of the absorption bonds at 1350 and 1020 $cm^{-1}$ (Fig.3B) corresponding to $\delta_s(CH_2)$ and $\omega(CH_2)$ vibrations (4), respectively. These bands are absent in the monomer spectrum (Fig.3A). The broadening of the band at 1020 $cm^{-1}$ is due to the overlapping of $\omega(CH_2)$ absorptions from disilymethylene and disilyethylene bonds which fall in a close vicinity and proves the presence of both types of these bonds in the polymer. The rise in the intensity of the discussed bands observed in the spectrum of polymer deposited at higher current density (Fig.3C) results from the increased content of $\equiv Si-CH_2-Si\equiv$ and $\equiv Si-CH_2-CH_2-Si\equiv$ crosslinkages. Comparison of the relative bond energies for Si-C (74 kcal/mole) and C-C (83 kcal/mole) bonds indicates that the former bond will undergo thermal scission more readily than the latter. This proves that ethylene may also be produced by Si-C bonds rupture in $\equiv Si-CH_2-CH_2-Si\equiv$ crosslinkages and, hence, the rise in the $C_2H_4/CH_4$ ratio with current density (Fig.2) is caused by the increasing content of these links in the polymer as it was documented by IR spectra (Fig.3B and C). Moreover, the extrapolation of the $C_2H_4/CH_4$ curve to the ordinate axis exactly yields the value of the $C_2H_4/CH_4$ ratio found for the monomer. This value seems to represent the relative content of ethylene in the decomposition products produced via secondary thermal reactions. In general, PGC and IR data indicate that methylsilyl structural units of monomer are highly susceptible under plasma conditions towards formation of disilymethylene and disilyethylene crosslinkages in the polymer film. TGA examination showed that thermal decomposition of PP-HMCTSN takes place in three distinctly separated stages. A rapid weight loss noted in TGA curve (Fig.4) during the first stage is due to the volatilization of low molecular products whose presence in this polymer was testified by PGC and mass spectrometry studies (5). The second stage associated with the largest weight loss can be attributed to the scissions of $\equiv Si\text{-}CH_3$, $\equiv Si\text{-}(CH_2)_2\text{-}Si\equiv$ , $\equiv Si\text{-}H$ and $\equiv Si_2N\text{-}H$ bonds (1) which involve the evolution of methane, ethane and ethylene as was detected by PGC. These processes may produce in the polymer residue Si-N crosslinkages with tertiary nitrogen. A small weight loss observed during the third stage of decomposition proceedings within a high temperature range may result from dehydrogenation of $\equiv Si\text{-}CH_2\text{-}Si\equiv$ linkages, retained in the polymer residue, and their transformation into Si-C inorganic bonds. This was confirmed by the results of IR analysis of the residue after TGA measurement which showed the absence of absorption bands to be assigned to C-H bonds. A very intense and broad band appeared at 1000-800 $cm^{-1}$ was characteristic of inorganic material containing Si-C and Si-N linkages. A three-stage mechanism of thermal decomposition proves a great complexity of thermal reactions involved in this process and indicate for a very complex structure of plasma polymer. TEM examination of PP-HMCTSN films subjected to a vacuum pyrolysis at 800°C revealed a marked effect of thermal decomposition on their morphological structure. The microporosity appeared in the film after 30 s of pyrolysis was caused by a vigorous evolution of decomposition products determined by PGC. The rapid change in film microstructure was consistent with the kinetics of thermal decomposition which showed the most sharp decrease in content of organic groups in the initial stage of this process (1). With increase in pyrolysis time the microporosity appeared to decay completely and the structure of film became almost uniform. This was due to thermally-induced crosslinking reactions (1) which cause the increase of inorganic structural content in the film and its densification. The structural changes of PP-HMCTSN films involved in thermal treatment were also manifested by a significant variation in their properties. Scratch and abrasion qualitative tests showed a progressive hardening of the film and increase of its adhesion to the metal substrates with treatment time. The pyrolysed films were found to be colourless glassy materials which adhered tenaciously to a wide range of metal substrates including carbon steel, stainless steel, copper and brass. Passivation tests revealed that the metal substrates coated with the pyrolysed films displayed outstanding stability to highly corrosive environments such as: saline, acidic or sulfurrich media, over a broad range of temperature. The examination of the films surface by the contact angle measurements showed a strong effect of thermal treatment on the surface free energy. Data in Table 1 indicate that the dispersion, $\gamma_s^d$ , and polar, $\gamma_s^p$, components of the surface energy, $\gamma_s = \gamma_s^d + \gamma_s^p$, increase markedly after thermal treatment. The increase of $\gamma_s^d$ may be due to the densification of polymer film resulting from thermally-induced crosslinking. The density was found to vary from 1.2 $g/cm^3$ for untreated film to nearly 2 $g/cm^3$ for film treated at 800°C. It is evident that the distance between the elements of the polymer structure decreases with increasing density and this gives rise to the dispersion forces since they are proportional to the inverse sixth power of this distance. The increase of ${}^{p}_{s}$ is considered to be due mainly to the rise in concentration of Si-N bonds in the pyrolysed film as was proved by IR study (1). It should be noted, that the increase in the surface energy observed for thermally-treated films reasonably agrees with the improvement in their adhesion to the metal substrate.

## REFERENCES

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TABLE 1. Effect of Vacuum Thermal Treatment on Surface Energy of PP-HMCTSN Film

| Treatment conditions | | Contact angle(deg) | | Surface energy(erg/cm$^2$) | | |
|---|---|---|---|---|---|---|
| Temperature ($^o$C) | Time (hr) | $H_2O$ | $CH_2J_2$ | $\gamma_s^d$ | $\gamma_s^p$ | $\gamma_s$ |
| Untreated film | | 81 | 50 | 30.1 | 5.3 | 35.4 |
| 600 | 2.0 | 74 | 40 | 34.3 | 7.1 | 41.4 |
| 800 | 0.5 | 70 | 30 | 38.4 | 7.8 | 46.2 |

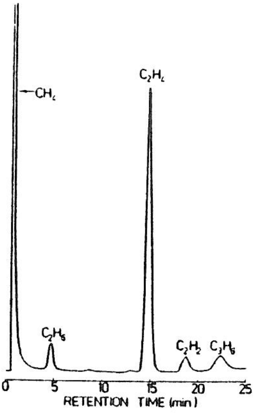

Fig.1. Gas chromatogram of thermal decomposition products of PP-HMCTSN.

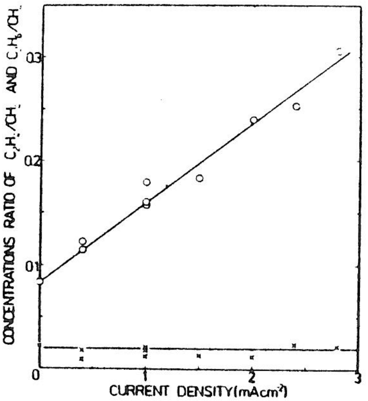

Fig.2. Concentrations ratio of $C_2H_4/CH_4$(O) and $C_2H_6/CH_4$(X) in gaseous pyrolyzate of PP-HMCTSN as a function of discharge current density.

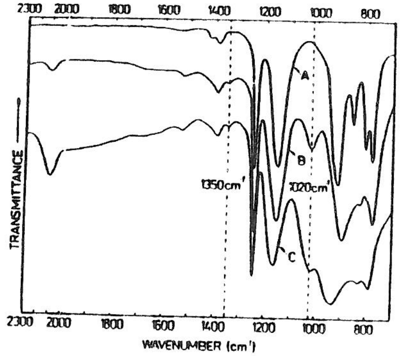

Fig.3. IR-ATR spectra of PP-HMCTSN films deposited at various discharge current densities: (A) monomer spectrum, (B) 1mA/$cm^2$, (C) 2mA/$cm^2$.

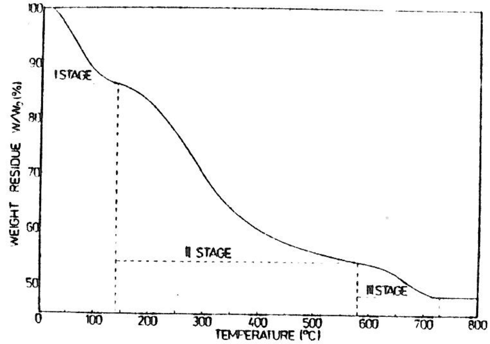

Fig.4. Thermogram of PP-HMCTSN deposited at p=0.3 Torr, j= 1mA/$cm^2$, t= 30 s.