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POLYIMIDES CONTAINING PENDENT SILOXANE GROUPS

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ABSTRACT

The incorporation of siloxane units into the backbone of aromatic polyimides has been shown to impart certain advantages over the unmodified polyimides. These include enhanced solubility, lower moisture adsorption, lower dielectric constant, improved toughness and surface modification. In addition, when exposed to an atomic oxygen environment these materials form an in-situ silicate (SiO_2) surface coating which protects the underlying material from further erosion. These unique advantages make polyimide-siloxanes useful in a variety of electronic and aerospace applications. For example, these materials find use in the microelectronic industry as interlayer dielectrics where thermal stability, low dielectric constant, low water adsorption and good adhesion to various substrates is required. Materials of this type may find use as films and coatings in a space environment where resistance to atomic oxygen erosion is needed.

As part of an effort on high performance polymeric materials for potential aerospace applications, polyimides containing pendent siloxane groups are under investigation. These materials were prepared by reacting a functionalized siloxane compound with polyimides containing benzhydrol groups. Thin films of the polymers exhibited glass transition temperatures ranging from 167 to 235°C. Tensile strengths and moduli measured at 23°C ranged from 11-14 ksi and 250-450 ksi, respectively. The dielectric constant was lowered substantially from that of the unmodified polyimide. Preliminary data after exposure to a simulated atomic oxygen environment (Asher) indicates that these materials form a silicate surface coating. The chemistry, physical and mechanical properties of these materials as well as potential applications will be discussed.

INTRODUCTION

Organic polymeric materials are currently being considered for long term use (> 10 years) in structural (adhesives and composites) and functional (films and coatings) applications on spacecraft. Polymeric materials offer attractive features such as low density, low thermal expansion over a relatively large temperature range, high strength and stiffness. In addition, they can provide unique performance in specialized applications where optical transparency, surface smoothness or adhesion is of critical importance. Although organic polymeric materials have been utilized successfully on spacecraft for short term missions, the long term durability of these materials in space is uncertain. Of particular concern is the durability of polymeric materials in low earth orbit (LEO) where atomic oxygen (AO) is prevalent.. Due to the high erosion rates of polymeric materials by atomic oxygen, they must be protected by a surface coating. Coatings that appear to eliminate or substantially reduce erosion of polymeric materials by AO include aluminum oxide[1], silicon dioxide[1], polytetrafluoroethylene[2], chromium oxide[2], copper-sapphire[2] and indium-tin oxide[3]. To be effective the coatings must be uniform, ~500-2000Å thick and pinhole and defect free.

A number of literature reports concerning polyimides containing siloxane groups in the mainchain (i. e., polymer backbone) are available. A U. S. patent describing polyimides of this type dates back to 1961[4]. The first report in the open literature appeared in 1966[5]. Since then a number of literature reports[6-11] and U. S. patents[12-17] concerning polyimides containing siloxane groups in the backbone have been disclosed. Recently, a report on polyimides containing pendent siloxane groups was published[18].

As part of a NASA effort to develop materials technology for potential space applications, a series of polyimides containing pendent siloxane groups were synthesized, characterized and evaluated under a simulated atomic oxygen environment using a radio frequency generated oxygen plasma asher. The oxygen plasma asher contains some species that are not present in LEO and therefore does not accurately or adequately represent that orbital environment. Also, other types of radiation (i. e., ultraviolet, electron and proton) and temperature cycling are present in LEO and may cause synergistic effects resulting in accelerated degradation. However, the device is useful for testing the hypothesis that the polyimides containing pendent siloxane groups will form an in-situ SiO_2 surfacing coating during exposure. Pendent siloxane groups should be advantageous as compared to backbone siloxane groups since cleavage of the organo-silicon bonds would not necessarily result in molecular weight degradation (i. e., backbone cleavage). The results of this study are presented herein.

EXPERIMENTAL

The polyimides containing pendent siloxane groups were prepared from polyimides containing benzhydrol groups. One polyimide containing benzhydrol groups used in this study is commercially available and the other was an experimental material that was synthesized in-house. A detailed representative experimental procedure is given below for the preparation of the polyimides containing pendent siloxane groups from commercial and experimental polyimides containing benzhydrol groups.

Experimental Polyimide Containing Benzhydrol Groups

Into a 100 ml three neck round bottom flask equipped with a mechanical stirrer, nitrogen gas inlet and drying tube filled with calcium carbonate was placed 3,3'-diaminobenzhydrol (3.3210g, 15.5 mmol) and DMAc (15.0 ml). The mixture was stirred at 23°C until the diamine dissolved (~15 minutes). To this solution was added 3,3',4,4'-benzophenonetetracarboxylic dianhydride (4.9944g, 15.5 mmol) and DMAc (10.0 ml) to give a final concentration of 25.0% solids. The solution was stirred at 23°C for ~16 hr under nitrogen to give a viscous poly(amide-acid) solution (inherent viscosity of a 0.5% solution in DMAc at 25°C was 0.81 dL/g). The poly(amide-acid) solution was diluted to 15% solids by the addition of DMAc (8 ml) and transferred to a pressure equalizing addition funnel which had previously been flushed with nitrogen.

Into a 250 ml three neck round bottom flask equipped with a mechanical stirrer, thermometer, nitrogen gas inlet, Dean Stark trap and reflux condenser was placed DMAc (20 ml) and xylenes (30 ml). The liquids are heated to reflux (~150°C) and maintained for ~5 hr. The poly(amide-acid) solution was subsequently added dropwise to the refluxing DMAc/xylenes mixture over ~1 hr period. Refluxing was continued for 1 hr after all of the poly(amide-acid) solution had been added. The xylenes was subsequently removed via the Dean Stark trap and the polyimide was precipitated into water in a high speed blender. The polymer was washed repeatedly in water and dried at 150°C for ~4 hr under vacuum. The polyimide had a glass transition temperature (T_g) of 267°C and an inherent viscosity of 0.43 dL/g measured on a 0.5% solution in DMAc at 25°C.

Polyimide Containing Pendent Siloxane Groups

Into a 100 ml three neck round bottom flask equipped with a mechanical stirrer, nitrogen gas inlet and pressure equalizing addition funnel was placed the previously described polyimide containing benzhydrol groups (1.56g, 3.1 mmol based on hydroxy group content, assuming a molecular weight of 20,000 g/mole) and DMAc (9 ml, 15% solids). The mixture was stirred at 23°C until the polyimide dissolved (~1 hr) and platinic acid (55 mg) was subsequently added. Into the pressure equalizing addition funnel was placed 1,1,2,2,3,3,3-heptamethyltrisiloxane (0.73g, 3.25 mmol) and toluene (5 ml). The siloxane dissolved rapidly in the toluene and the solution was subsequently added dropwise to the polymer solution over a 30 minute period. The solution was stirred at 23°C for 16 hr, filtered through 5.0 micron filter paper under ~20 psi and cast into a thin film. The film was stage-dried to 235°C and held for 1 hr at 235°C under vacuum. The translucent orange film exhibited a T_g of 235°C. Infrared spectroscopic analysis of the film indicated that the reaction had proceeded as anticipated. Tensile strength and modulus of thin film specimens at 23°C of 12.5 and 391 ksi, respectively were obtained.

Polyimide Containing Pendent Siloxane Groups From Commercial Polyimide

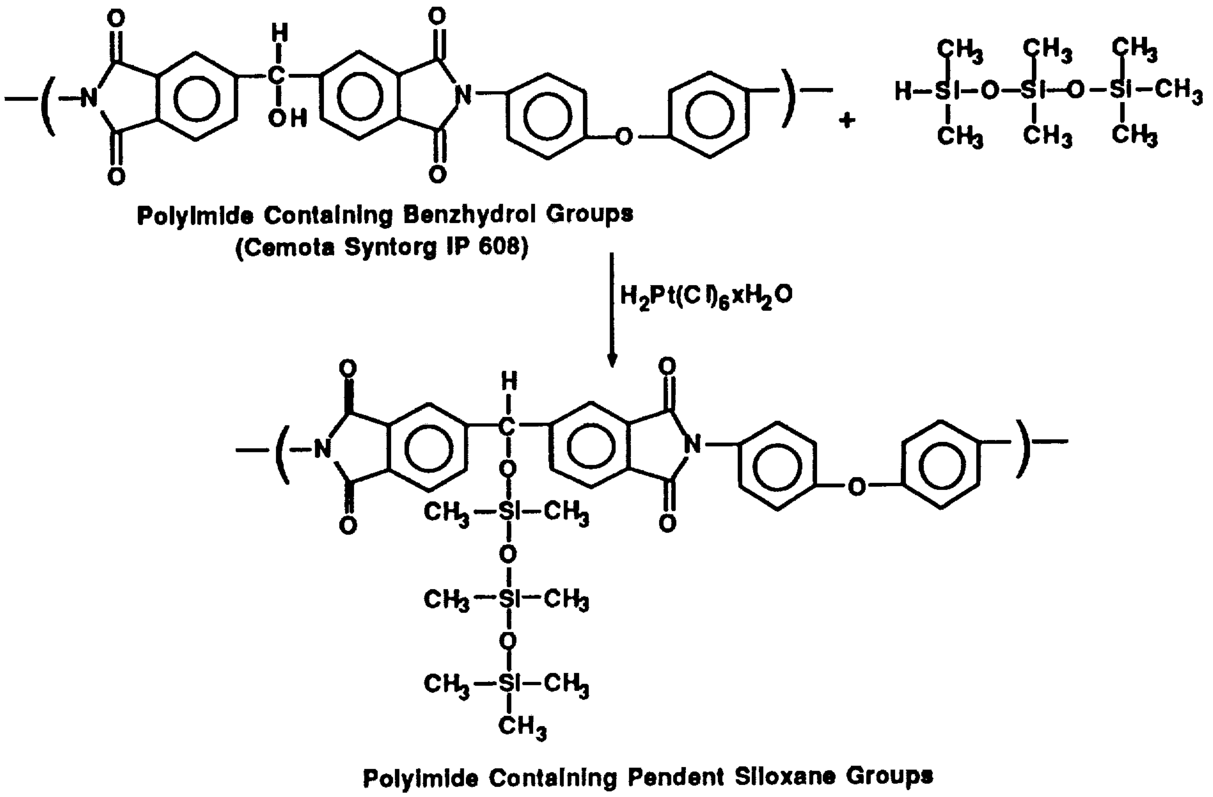
Into a 100 ml three neck round bottom flask equipped with a mechanical stirrer, nitrogen gas inlet, and pressure equalizing addition funnel was placed Cemota Syntorg IP 608 polyimide containing benzhydrol groups (10.12g, 40.2 mmol based on hydroxy group content, assuming a molecular weight of 36,000 g/mole) and N-methyl-2-pyrrolidinone (NMP) (58 ml, 15% solids). The mixture was stirred at 23°C under nitrogen until the polymer had dissolved (~1 hr) and platinic acid (105 mg) was subsequently added. Into the pressure equalizing addition funnel was placed 1,1,2,2,3,3,3-heptamethyltrisiloxane (9.86g, 44.3 mmol) and toluene (25 ml). The siloxane solution was added to the polyimide solution dropwise over a 1 hr period. The solution was stirred at 23°C under nitrogen for 16 hr and subsequently filtered through a 5.0 micron filter under pressure (~20 psi). A thin film was cast from the solution onto plate glass. The film was dried to a tack-free state in a dust-proof chamber and stage-dried to 225°C and held at 225°C for 1 hr under vacuum. The translucent yellow/green film exhibited a T_g of 167°C. Tensile strength and modulus of thin film specimens at 23°C of 11 and 250 ksi, respectively were obtained.

Asher Exposure

Simulated atomic oxygen exposures were performed on thin films (0.5 x 0.5 in., ~1-3 mils thick) of the polyimides containing pendent siloxane groups in a Tegal Plasmod Asher. The Asher was operated at 500 millitorr, 100 Watts of radio frequency, O_2 pressure of 3 psi and a flow rate of 50 standard cubic centimeters per minute. Since the Asher was not calibrated, simultaneous exposures of Kapton® and Ultem® were performed with each experimental polyimide containing pendent siloxane groups. The Kapton® and Ultem® films served as standards allowing for direct comparison with the films of the polyimides containing pendent siloxane groups. Exposures were performed for up to 8 hours and the weight loss of the films were monitored as a function of exposure time.

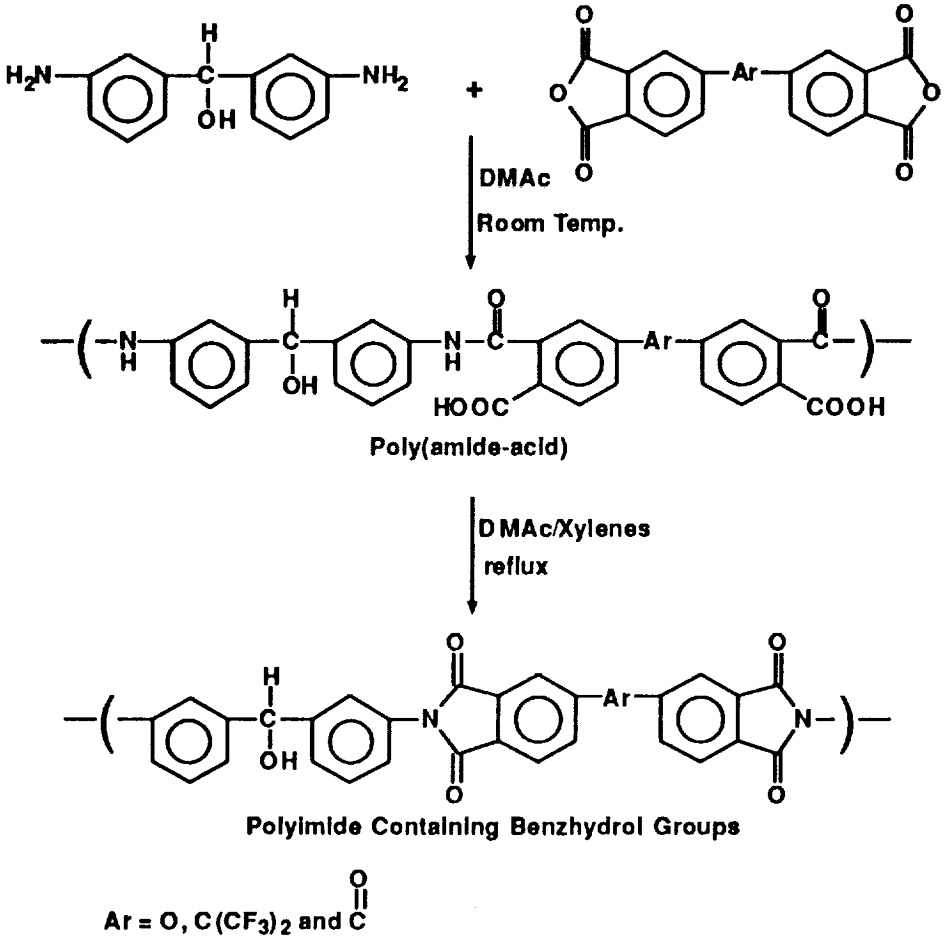
RESULTS AND DICUSSION

The polyimides containing pendent siloxane groups were prepared by reacting polyimides containing benzhydrol groups with heptamethyltrisiloxane as shown in equation 1. The reaction solution was subsequently used to cast thin films. After stage-drying the polymer films up to ~ 225-250°C to remove residual solvent the films were characterized by infrared spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and measurement of thin film tensile properties.



Equation 1. Synthesis of polyimides containing siloxane groups.

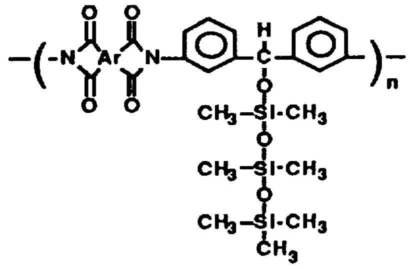
The synthesis of the experimental polyimides containing benzhydrol groups is depicted in equation 2. After isolation and characterization these polyimides were reacted with the heptamethyltrisiloxane as shown in equation 1.

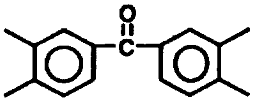
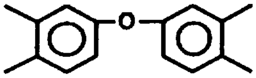
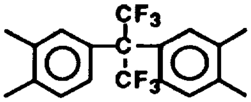


Equation 2. Synthesis of Polyimides Containing Benzhydrol Groups.

Polymer characterization is shown in Table 1 for the polyimides containing pendent siloxane groups prepared from the experimental benzhydrol containing polyimides. All of these films were translucent which is indicative of some degree of phase separation, although only one T_g was detected by DSC. As expected the T_gs of the polyimides containing siloxane groups are significantly lower than the corresponding polyimides containing benzhydrol groups. Also, the polyimides containing pendent siloxane groups exhibited a reduction in thermal stability as measured by TGA as compared to the corresponding polyimides containing benzhydrol groups. The temperature of 5% weight loss by TGA for the polyimides containing pendent siloxane groups was ~380°C in air versus 490°C for the corresponding polyimides containing benzhydrol groups. All of the films in Table 1 were fingernail creasable whereas films from the corresponding benzhydrol derivative were not creasable. Polymers that contain benzhydrol units can undergo a thermally induced crosslinking reaction which may cause embrittlement.

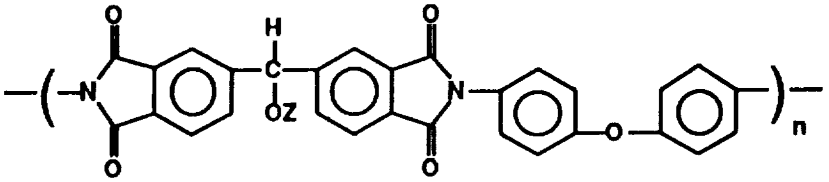
TABLE 1
POLYMER CHARACTERIZATION

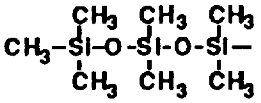


Ar	Glass Transition Temperature,°C	Film Appearance, Quality
	235	orange, translucent, tough, creasable
	219	brown, translucent, tough, creasable
	211	light tan, translucent, tough, creasable

Polymer characterization for the commercial polyimide containing benzhydrol groups and the siloxane derivative are presented in Table 2. The introduction of the pendent siloxane group in this polymer caues a similar effect, most notably the lowering of the Tg. The film of the polyimide containing pendent siloxane group was semi-translucent, but clearer than the films from the polymers in Table 1.

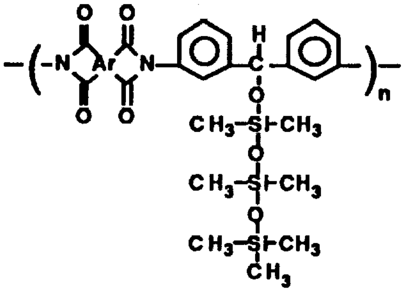
TABLE 2
POLYMER CHARACTERIZATION

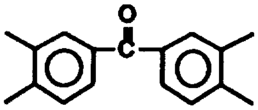
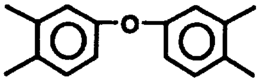
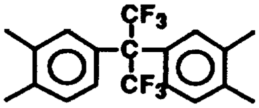


Z	Glass Transition Temperature,°C	Film Appearance, Quality
 $CH_3-Si(CH_3)_2-O-Si(CH_3)_2-O-Si(CH_3)_2-$	167	yellow/green, semi-translucent, tough,creasable
H (Cemota Syntorg IP 608 Polyimide)	250	orange,clear, tough,creasable

Thin film tensile properties of the polyimides containing pendent siloxane groups are presented in Tables 3 and 4. All of the polyimides containing pendent siloxane groups exhibited a reduction in tensile strength and tensile modulus compared to the corresponding polyimides containing benzhydrol groups. However a noticeable increase in elongation to break was observed. These property changes are expected since chain to chain interactions, hydrogen bonding and the ability to crosslink are effectively eliminated by the incorporation of the pendent siloxane groups. In addition, the polyimides containing pendent siloxane groups exhibited a significantly lower dielectric constant (Table 4).

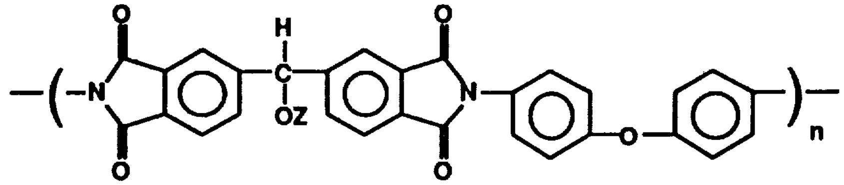
TABLE 3
THIN FILM PROPERTIES*

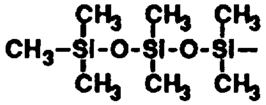


Ar	Tensile Strength,ksi	Tensile Modulus,ksi	Elong.,%
	12.5	390.6	9.4
	13.3	453.3	4.1
	8.2	360.6	12.0

* Tensile properties determined at 23°C.

TABLE 4
THIN FILM PROPERTIES*

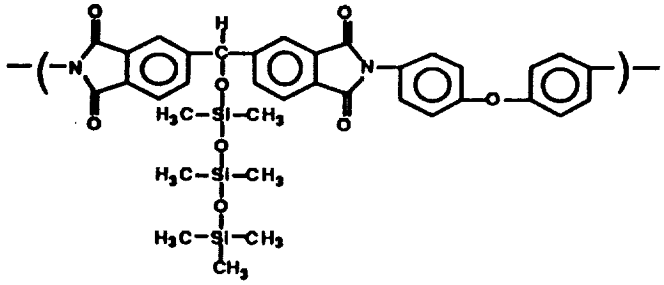


Z	Tensile Strength,ksi	Tensile Modulus,ksi	Elong.,%	Dielectric Constant
 $CH_3{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}O{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}O{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}$	10.9	250.0	34.3	2.8
H (Cemota Syntorg IP 608 Polyimide)	18.1	442.3	10.4	3.4

*Tensile properties determined at 23°C.

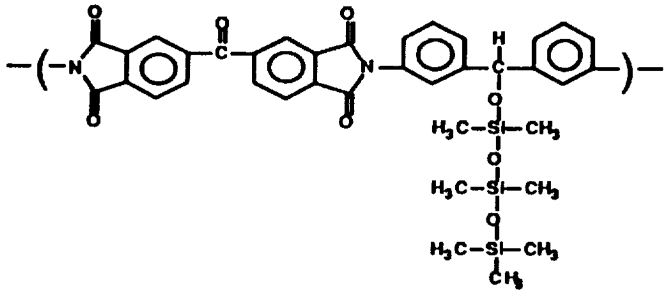
The results of the oxygen plasma exposures are given in Tables 5 and 6 for two different polyimides containing pendent siloxane groups. Each exposure was performed simultaneously with thin film samples of Kapton® and Ultem® for comparative purposes. The polyimides containing pendent siloxane groups used in this study contain ~12% silicon by weight. The polyimides containing pendent siloxane groups exhibited ~ 63-64% weight loss after 8 hours of exposure whereas Kapton® and Ultem® exhibited 100% weight loss. The weight loss data for the polyimides containing pendent siloxane groups fluctuates. For example, in Table 5 the sample after 5 hours of exposure shows a 50% weight loss and after 6 hours shows a 40% weight loss or net weight gain of ~ 10%. This weight gain is most likely due to the formation of oxides. Preliminary X-ray photoelectron spectroscopy (ESCA) results indicate the presence of silicon oxide on the film surfaces after exposure to the oxygen plasma. The polyimides containing pendent siloxane groups did not exhibit the stability (i. e., weight retention) that was anticipated. Examination of the polymer films by scanning electron microscopy (SEM) before exposure revealed the presence of pinholes. After exposure to the oxygen plasma the films were reexamined by SEM, many cracks in the films were observed all of which appeared to originate from pinholes. The pinholes act as stress concentraters and the films subsequently crack during exposure and expose fresh surface area, some of which is erroded away, resulting in additional weight loss. Pinhole-free films prepared from these polyimides containing pendent siloxane groups are expected to exhibit better resistance to the oxygen plasma.

TABLE 5
ASHER EXPOSURE DATA



	Weight Loss, %		
Exposure Time, hr	Ultem®	Kapton®	Sample
4	37.0	38.6	6.3
5	41.2	39.8	50.5
6	62.6	43.2	40.4
8	100.0	100.0	62.2

TABLE 6
ASHER EXPOSURE DATA



	Weight Loss, %		
Exposure Time, hr	Ultem®	Kapton®	Sample
4	55.5	48.0	67.5
5	45.6	52.1	59.5
6	100.0	81.3	70.6
8	-----	100.0	63.8

CONCLUSIONS

A series of polyimides containing pendent siloxane groups were prepared and characterized. The T_gs, tensile moduli, thermal stability and dielectric constant of the polyimides containing pendent siloxane groups were lower than that of the corresponding precursor polyimides containing benzhydrol groups. The polyimides containing pendent siloxane groups exhibited significantly lower weight loss than Kapton® and Ultem® when exposed to an oxygen plasma. Preliminary results indicate that the polyimides containing pendent siloxane groups formed a protective silicate-type surface layer during oxygen plasma exposure.

ACKNOWLEDGMENT

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