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Effect of oxygen plasma asher on poly(methylphenylsiloxane)-polyimide blends

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Variable concentrations of low molecular weight poly(methylphenylsiloxane) were added to polyimide at its precursor poly(amic acid) stage to produce blends of different compositions. Ultimately cured poly(methylphenylsiloxane)/polyimide blends (PMSI) were exposed to radio frequency oxygen plasma. The stability of the blends to the oxygen plasma was assessed by monitoring the weight loss of the films as a function of exposure time. After 24 h exposure blends exhibited weight losses that were much lower than neat polyimide. The effect of oxygen plasma on polyimide and its blends has been analyzed by scanning electron microscopy and changes in surface chemistry of the exposed films were subsequently examined using X-ray photoelectron spectroscopy. The mechanical properties of oxygen plasma exposed and unexposed neat polyimide and its blends have been evaluated. © *2004 Kluwer Academic Publishers*

1. Introduction

Design of any system demands consideration of the environment in which it is to operate, to ensure proper system function, reliability and lifetime, and space systems are no exception to this rule. The extent of degradation of polymeric materials due to atomic oxygen (AO) attack clearly indicates that none of the materials are acceptable for long duration use in low earth orbit (LEO) spacecraft applications. Mitigation techniques would ideally avoid the use of AO sensitive materials and/or orient the critical spacecraft surface to avoid the direct impingement of the AO environment. Unfortunately, these solutions may not always be possible and it is therefore necessary to apply a protective mechanism, which can reduce the amount of damage or replace with AO—resistant materials. The selection of a protective mechanism candidate is primarily based on the following requirements [1]

(a) It should be resistant to AO attack
(b) It should be thin, light weight and adhere strongly to the base material
(c) It should be free from defects, pores and scratches
(d) It should be non contaminating
(e) It should not alter the basic properties of the base material.
(f) It should have good physical integrity with the base material to withstand ground handling and manufacturing.
(g) It should be stable in the LEO environment synergism, which includes particulate radiation, ultraviolet (UV) radiation, micrometeroids, and orbital debris impact, plasma charging and thermo vacuum cycling.
(h) The application process should not damage the base material
(i) It should be cost effective and easily scalable to large components

The application of a thin protective coating to base material is one of the most commonly used methods of preventing AO degradation. The purpose of coating is to provide a barrier between the base material and the AO environment or, in some cases, to alter AO reactions to inhibit AO diffusion. The effectiveness of a coating depends on its continuity, porosity, degree of adhesion and durability in the environment. In addition to the technicalities of forming an effective barrier, such factors as cost, convenience of application and ease of repairs are some of the important considerations in the selection of a coating for a particular application [2]. The role of polyimide as a protective blanket for polymeric base components is well known [3, 4], but unfortunately polyimide itself undergoes degradation on long time exposure and needs a protective coating on the surface. Experimental data obtained after LEO exposures [5], indicate that silicone coatings provides good protection to the Kapton® polyimide substrate from AO attack. Hence a modified polyimide matrix with siloxane appears to be resistant to AO attack and precludes the degradation of polymer-derived components in the LEO environment [6–9]. In this communication an effort has been made to study the effect of reactive oxygen on recently synthesized novel blends.

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2. Experimental

2.1. Materials

Analytical grade benzene-1,2,4,5-tetracarboxylic-1,2,4,5-dianhydride and 4,4′-diaminodiphenyl ether were supplied by Merck chemical company, Germany and were used as received. Analytical grade tetrahydrofuran and N,N′-dimethylacetamide were supplied by Aldrich chemical company, USA and were purified by distillation under reduced pressure and dried over calcium hydride for 24 h. Analytical grade dimethyldichlorosilane was supplied by Across chemical Ltd. and was 99.7% pure hence was used as such. Water used in this study was double distilled.

2.2. Synthesis of polyamic acid (PAA)

Into a 500 ml three-necked round bottom flask fitted with mechanical stirrer, nitrogen inlet and drying tube of $CaCl_2$, was taken 0.05 mol of 4, 4′-diaminodiphenyl ether (ODA) in 188 g of dry dimethylacetamide. 0.05 mol of benzene-1,2,4,5-tetracarboxylic-1,2,4,5-dianhydride (PMDA) was added slowly to the above solution with vigorous mixing. After complete addition reaction mixture was stirred for additional 2 h in nitrogen atmosphere. The concentration of solution was 10% having inherent viscosity of 0.157 m^3/kg at 26°C when stored at −10°C temperature [10].

2.3. Synthesis of poly(methylphenylsiloxane) (PMPS)

Polymethylphenylsiloxane was synthesized by the hydrolysis of 25×10^{-6} m^3 dichlorophenylmethylsilane (DCPMS) with icy cold water in a three necked round bottom flask equipped with nitrogen inlet, water condenser and magnetic stirrer [11]. The resultant viscous oily layer was extracted with diethylether and washed several times with water and finally with very dilute solution of Na_2CO_3 to remove last traces of acid. The polymer obtained was a transparent low viscous having intrinsic viscosity of 1.31 m^3/kg and density 970 kg/m^3.

2.4. Preparation of PAA/PMPS blends

PMPS in various concentrations (i.e., 4.76, 9.09, 13.04, 16.67, and 20.0% w/w) were taken in a known volume of tetrahydrofuron (THF) and added to the fixed quantity of polyamic acid (PAA) to result into the blends of required concentrations and were designated as PMSI-5, 10, 15, 20 and 25 respectively. THF was chosen as solvent on the basis of its miscibility with dimethylacetamide (DMAC) and its use as a solvent for the preparation of polyamic acid. Additionally, it was also necessary to ensure that two solvents should not interact each other. Various compositions comprising two polymers were prepared by mixing them for 2 h with the help of magnetic stirrer operating at 200 rpm in flowing nitrogen atmosphere. The resultant blends were kept under nitrogen atmosphere at −10°C for 72 h. These blends were used for casting and curing process.

2.5. Casting and curing

Blends of different compositions were spread over clean dry glass plates in a dust free chamber by means of a doctor blade to ensure uniform ultimate thickness of 25 ± 2 microns. The films on glass plates were kept overnight at ∼50°C followed by soft backing (slow increase in temperature at the rate of 1°C/min) up to 100°C and thereafter retained for one hour at this temperature. The films were then heated in steps i.e., at 160°C for two hours (to ensure slow removal of DMAC), 200°C for one hour (to ensure cyclization or imidization), and ultimately at 350°C for two hours (to ensure the maximum possible ordering and crystal growth). Films were cooled to room temperature and removed from the glass plates.

2.6. Oxygen plasma asher conditions

Oxygen plasma exposures were performed on thin films (100 mm × 200 mm, ∼25 micron thick). Treatment was carried out in a plasma CVD 301 unit from Anelva Corporation Japan, operating at a radio frequency 13.56 MHz, and 200 V. The oxygen flux rate was 50 Sccm (approx. 3.0×10^{23} atoms/m^2/h) and inter electrode distance was 30 mm.

2.7. FTIR microscopy and spectroscopy

FTIR images and corresponding spectra of thin films were taken on a Perkin-Elmer instrument having autoimage microscope and SPECTRUM One software.

2.8. Microscopic analysis

The oxygen plasma exposed surfaces of the blend samples were coated with gold and studied by Jeol JSM-35CF scanning electron microscope (SEM).

2.9. Thermogravimetric analysis

Dynamic thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA-7 instrument using Pyris software. The heating rate was 10°C/min in air and nitrogen atmosphere. All analysis was conducted on samples in the form of fully cured films.

2.10. X-ray photoelectron studies

XPS was performed on thin films using Perkin-Elmer 5400 instrument with a hemispherical analyzer and an MgK-alpha source (1253.7 ev), with X-ray voltage of 10 kV and X-ray current of 20 mA. The scan area was 5×5 mm and depth profiling was achieved by Ar etching for different time interval at 4 kV electron beam. The data was smoothed, incident beam linewidth was removed and data were fitted using the operating instrument software.

2.11. Mechanical analysis of blends

Mechanical properties of the blends were evaluated before and after the oxygen plasma exposure as per ASTM

D882 on a universal testing machine from R & D Equipment India, at ambient temperature (i.e., 27°C). Thin film samples were cut into rectangular shape and were conditioned at 50°C for 24 h, before testing. The width and thickness of the samples were measured with a suitable micrometer to the nearest 0.03 mm at several points.

3. Results and discussion

Most of the physicochemical and mechanical properties of the blends seem to pivot around the molecular packing arrangement and also the introduction of free volume in the resultant polymeric system due to incorporation of foreign flexible molecules. Our previous studies [12] have shown that the major force contributing towards the stability of the components in the blend is probably due to the formation of charge transfer complexation between the moieties. In synthesized polysiloxane, the presence of telechelic PMPS containing hydroxyl functionality can be recognized from FTIR spectra shown in Fig. 1, as appearance of Si—OH stretching at 3130 cm^{-1} and hydrogen bonded hydroxyl stretching at 3445 and 3620 cm^{-1} is seen. Si-ph stretching is found at 1429 cm^{-1} while $Si—CH_3$ stretching at 1263 cm^{-1} and Si—O—Si stretching at 1050 cm^{-1}. Since the product obtained after the hydrolysis of dichlorosilane compounds consists of linear hydroxyl terminated polysiloxane in predominance along with the cyclic fractions (Fig. 1), any possibility for the reaction of amic acid and silanol functionality needs to be explored. Fig. 2 shows a FTIR microscopic image and corresponding spectra of blends having 20 wt% of polysiloxane. The presence of phase separated domains of poly(methylphenylsiloxane) in polyimide appears clearly in the FTIR microscopic image. It has been documented previously [13] that none of the phases present in a blend composition are pure phase as each phase is a mixture of a minor component in the major one. Corresponding spectra for the region where polyimide dominates shows a sharp band at 1774 cm^{-1} indicating that an essentially imidized structure is obtained even after the incorporation of high concentration (20 wt%) of polysiloxane, while spectra for the region where polysiloxane dominates as blend component shows distinct methyl group at 2900 cm^{-1} and phenyl group at 1500 cm^{-1} (from PMPS) along with the imide peak at 1774 cm^{-1}. The above premise suggests that PMPS retains its identity even after the complete curing cycle of the blends to 350°C. Incorporation of a high concentration of PMPS leads to the loss in degree of imidization and may result in the overall drop in macroscopic properties. The degree of imidization

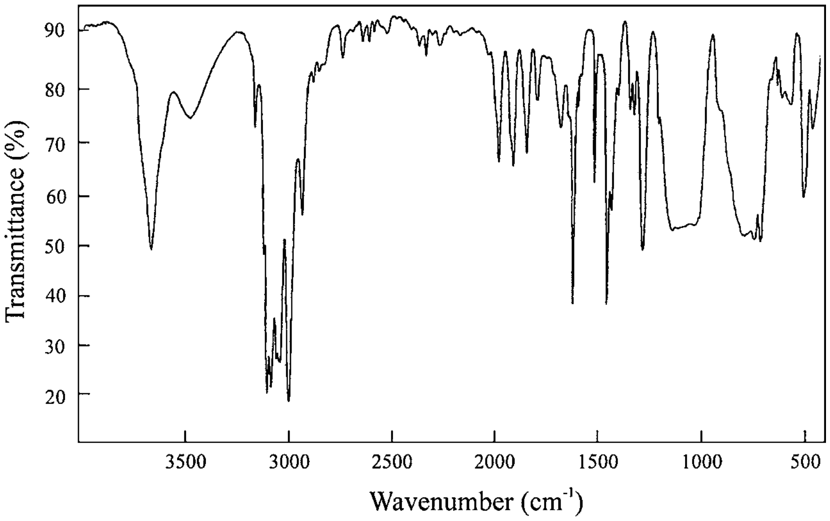

Figure 1 FTIR spectra of poly(methylphenylsiloxane).

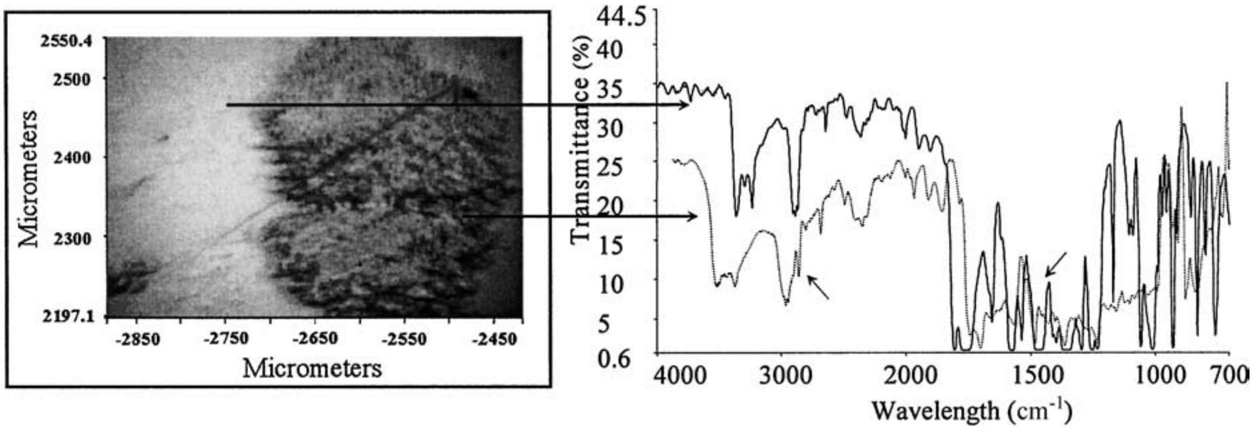

Figure 2 FTIR microscopic image and corresponding spectra of PMSI-20 blend film.

TABLE I Calculated parameters of oxygen plasma exposed and unexposed polyimide and blends

					Weight loss rate	
Polymers	PMPS content (%)	Degree of imidization (%)	$D_{0.1}$ (°C)	Calculated OI	0–7 h (mgh^{-1})	7–24 h (mgh^{-1})
PI-0	0.0	100	600	0.387 ± 0.01	0.73	0.60
PMSI-5	4.76	88	664	0.405 ± 0.01	0.61	0.33
PMSI-10	9.09	79	668	0.406 ± 0.01	0.54	0.20
PMSI-15	13.04	71	679	0.411 ± 0.01	0.41	0.05
PMSI-20	16.66	64	661	0.415 ± 0.01	0.28	0.01

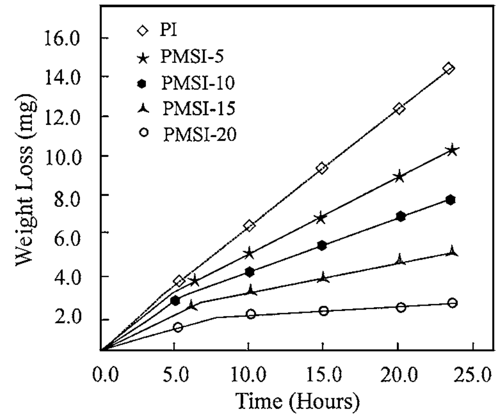

Figure 3 Weight loss versus exposure time in the oxygen plasma asher for polyimide and PMSI blends.

of 350°C cured blends were compared with the neat polyimide cured to the same temperature. The degree of imidization (%) is commonly determined from the height of the 1360 cm^{-1} band (C—N stretch) normalized to the height of the 1500 cm^{-1} as internal [14, 15]. This ratio is then referenced to the ratio obtained on a fully cured film. Although the bands at 1776 and 1730 cm^{-1} have also been used to study the degree of imidization in polyimide [16, 17], work by Pryde has shown that the 1774–1776 and 1730 cm^{-1} bands overlap anhydride absorption bands. In addition, these bands can be influenced by the degree of molecular orientation in the film, while the band at 1360 cm^{-1} is relatively unaffected by dichroic effects. Despite all these suggestions regarding the use of absorption bands for determining the degree of imidization by above methods, the technique suggested by Ginsburg and Susbu [14] has been adopted wherein the area of symmetrical carbonyl stretch at 1776 cm^{-1} was ratioed with the area of reference aromatic vibration [18] at 1012 cm^{-1} and the results for different blend compositions are summarized in Table I. A regular drop in the degree of imidization can be seen with the increase in PMPS concentration. This drop may be due to either the reaction of carboxyl group of poly(amic acid) with silanol functionality of PMPS or due to the shielding effect caused by flexible polysiloxane chains by the entanglement of poly(amic acid) chain.

3.1. Calculated limiting oxygen index

The limiting oxygen index was determined by using an equation reported elsewhere [19].

$$\mathrm{LOI} = [17.5 + 0.4\,(\mathrm{CR})]/100$$

where CR is the char residue obtained after the complete decomposition of the polymer determined by TGA at 900°C under the nitrogen atmosphere. The thermal stability of neat polyimide and blends in terms of temperature for 10% decomposition is given along with the calculated limiting oxygen index in Table I.

3.2. Oxygen plasma asher exposure

Thin films of various blend compositions were exposed to oxygen plasma under high vacuum. Since the asher instrument was not calibrated hence a simultaneous exposure was conducted on neat polyimide film for the relative comparison with the experimental polymers. Exposures were performed continuously on each sample for 24 h, with the samples being periodically removed from the asher, placed immediately in a desiccator having silica gel to avoid exposure to open atmosphere, and weighed. The weight losses in the films were monitored as a function of exposure time and represented graphically in Fig. 3. All the blend compositions exhibited lower rate of weight losses as compared to neat polyimide. Typically these blends have shown higher initial weight loss up to 7 h of exposure. In general, it could be pointed out that polymeric blends have exhibited two distinct regions of differing weight loss rate as visualized from the change of slope of the weight loss versus exposure time curves. The first region of weight loss seems to occur within the first 7 h of exposure to the oxygen plasma asher and with a subsequent decrease in weight loss rate thereafter. On the other hand neat polyimide film has shown nearly constant and linear weight loss rate (~0.59 mgh^{-1}) throughout the exposure time period. The higher rate of weight loss in blends, observed in the first 7 h of exposure is probably due to the conversion of polysiloxane to silica. The second region of weight loss in the blends occurs in the range 7 to 24 h of exposure. The overall rate of weight loss with respect to exposure time appears to drop with the increase of polysiloxane content in the polyimide blends. The polyimide blend containing 20-wt% of PMPS exhibited relatively lower weight loss rate over 7 to 24 h of exposure (Table I). This material exhibited an overall weight loss rate of 0.10 mgh^{-1}, much lower than neat polyimide for the same time of exposure. Nearly a constant or linear weight loss observed in the case of neat polyimide may possibly be due to the degradation of polyimide via oxidation reaction involving the breaking of bonds within the backbone of the macromolecule.

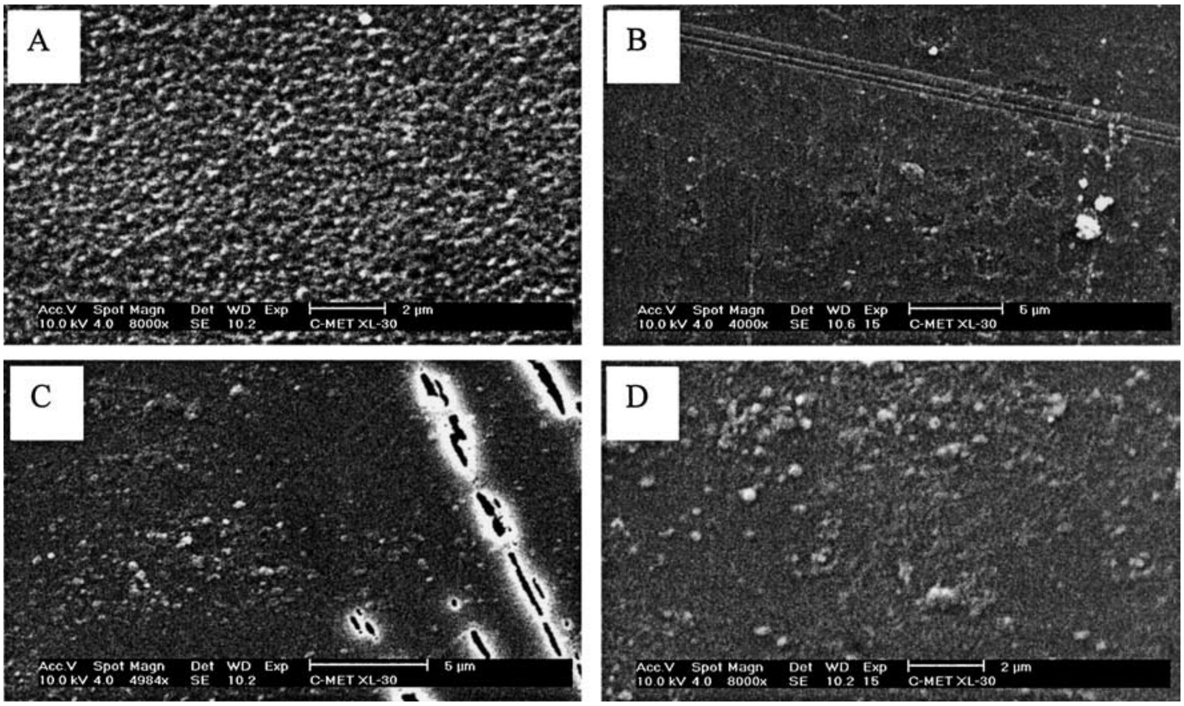

Figure 4 SEM of oxygen plasma exposed neat polyimide (A), PMSI-5 showing surface erosion (B), PMSI-10 showing oxidized silica particles and cavitation on surface (C), PMSI-20 showing dispersed silica particles and unaffected surface (D).

The change in weight loss rate observed in blends after the 7 h of oxygen plasma exposure is due to formation of a higher oxidized silicate type of surface layer having superior resistance to oxygen plasma. Formation of the silicate layer acts as a protective barrier for the incoming atomic oxygen to penetrate the surface molecules and the presence of flexible polysiloxane in continuous polyimide matrix enables the blends to sustain against lengthy plasma exposures [20]. Fig. 4 shows scanning electron microscopic image of surface morphology resulted from the oxygen plasma exposure of neat polyimide and blends. Surface corrosion of neat polyimide due to oxygen plasma bombardment can be clearly seen from SEM. Silica particles generated as a result of oxidation of PMPS seems to have particle diameter in the range of 58 to 450 nm with the average particle radii of about 60 nm. The distribution of silica particles appears clearly in blends having high a concentration of PMPS. At low concentration of PMPS, patches are observed resulting from the surface degradation of the blends due to atomic oxygen attack.

3.3. X-ray photoelectron spectroscopic analysis

In order to determine the changes in oxidation state of the surface atoms, thin films of blends were subjected to XPS before and after the exposure to oxygen plasma. All photo peaks were referenced to that of carbon having a maximum at 285.0 eV. Unexposed PMSI-5, PMSI-10, PMSI-15 and PMSI-20 have shown silicon content ranging from 2.99 to 13.62% (±0.1% in all the cases) respectively while, after the exposure, these values were very high as shown in Table II. Ion milling was done with the help of argon to determine the percentage of various atoms in different layers of blends. It was found that the percentage of silicon remains practically constant in different layers of unexposed blends, while in the case of exposed blends the percentage of silicon was found to decrease with depth. This anomalous behavior could not be understood so far, and further research is still under progress and will be communicated very soon. Experiments done so far indicate that, due to the low surface energy of polysiloxanes they tend to migrate towards the surface of the film to provide a measure of healing to the degraded film surface. The behavior is still under investigation and the mechanism appears to be similar to that reported for the self-healing of polymeric composites [21]. Blends have shown a change in binding energy of oxygen and silicon atoms on the surface with the increase in relative concentration of the species. Neat polyimide exhibits an oxygen peak at 532.1 eV due to carbonyl oxygen whereas the peak at 533 eV is from oxygen singly bonded to carbon [22]. In the case of unexposed blends, the carbonyl oxygen peak was relatively the same but oxygen bonded to carbon has shown a shift in binding energy (534 eV) due to its interaction with the silicon atom of polysiloxane. After the exposure to oxygen plasma, binding energies increased to 532.7 eV for carbonyl oxygen and 533.2 eV for oxygen bonded to carbon and silicon atoms. The binding energy peak for the silicon atom Si(2p) in unexposed blends was found at 102.5 eV corresponding to $Si{-}CH_3$ bonding while that at 101.5 eV corresponds to Si—O linkage. The positions of these photo peaks indicate the presence of silicone in the form of polysiloxane. After exposing the blends, the intensity of the peak at 102.5 ($Si{-}CH_3$) was found to be very low, while the intensity of the peak at 103.1 eV was increased, indicating that the conversion of polysiloxane to silica has taken place on exposure to the oxygen plasma [23] and the same appears from the SEM analysis (Fig. 4).

TABLE II Position of photo peaks and atomic concentration in oxygen plasma exposed and unexposed polyimide and blends

		Binding energy (eV)		Atomic concentration (%)		
Polymers	Photopeaks	Before	After	Before	After	Theoretical
PI-0	C 1s	285.0	284.6	75.68	71.97	69.11
	O 1s	532.1	532.8	19.82	22.36	20.94
	N 1s	400.3	398.7	4.50	5.67	7.33
PMSI-5	C 1s	285.0	285.0	72.84	56.74	68.41
	O 1s	532.1	533.0	22.40	33.98	20.93
	N 1s	401.9	399.1	1.77	2.88	6.98
	Si 2p	102.5	103.1	2.99	9.39	0.86
PMSI-10	C 1s	285.0	285.0	71.22	48.82	67.79
	O 1s	532.1	533.0	18.79	35.80	20.92
	N 1s	401.9	399.1	1.74	2.60	6.66
	Si 2p	102.5	103.1	8.25	12.78	1.65
PMSI-15	C 1s	285.0	285.0	68.95	41.48	67.21
	O 1s	532.1	532.8	16.77	38.56	20.92
	N 1s	401.9	399.1	1.62	1.35	6.37
	Si 2p	102.5	103.1	12.66	18.61	2.37
PMSI-20	C 1s	285.0	285.0	66.34	44.87	66.67
	O 1s	532.1	532.9	18.63	32.54	20.91
	N 1s	401.9	399.3	1.41	0.07	6.11
	Si 2p	102.5	103.1	13.62	22.52	3.14

3.4. Mechanical properties of blends

The mechanical properties of a glassy polymeric system depend on the crystallanity introduced into the chains, orientation of the macromolecular segments, and the amount of crosslinking between the macromolecular units. When stress is applied to such materials, the weakest link, i.e., the nonbonded interchain interaction, deforms much easier than the strong covalent bonds along the individual chains. Thus the network of nonbonded interchain interactions plays a crucial role in determining the magnitude of the strength in that particular polymer. The presence of the crystalline region can lead the polymer to behave like a rigid rod while the amorphous region will compel the polymeric chain to act as an elastomer. The increase in the crystalline region can act as a stress raiser and thereby weakens the polymer network to cause premature failure [24, 25]. The addition of silicone polymer with a bulky phenyl group may contribute towards the overall increase in free volume and thereby an additional free space for the folded chains of macromolecules to uncoil, capable of reversible deformation. The mechanical properties of blend films were analyzed before and after the oxygen plasma exposure and the results are shown in Table III. It can be inferred from the table that the tensile strengths (TS) of unexposed blends are vastly improved inspite of the increase in polysiloxane concentration. Nearly 25% enhancement was observed in TS for PMSI-20 while its elongation was increased by 47% as compared to the neat polyimide. After 24 h oxygen plasma exposures, various blend films were analyzed for the change in their mechanical properties. Nearly 25% drop was observed in TS and elongation for exposed neat polyimide as compared to unexposed polyimide, while TS for various compositions of exposed blends have shown only a slight drop in TS (~8.0%) for unexposed PMSI-20 sample. The TS observed in case of exposed PMSI-20 blends was nearly 75% higher as compared to exposed neat polyimide. It should also be noted that the elongation shown by these blends increases with increases in polysiloxane concentration and the maximum value (72% higher as compared to unexposed neat polyimide) was found for PMSI-20. On the other hand the tensile modulus decreases regularly in both the cases with the increase in concentration of polysiloxane in blends. The above results give an idea about the probable mechanism involved during the mechanical cleavage of backbone bonds in the blends. A remarkable drop in TS was found in the case of exposed neat polyimide as compared to unexposed film, while TS was not severely affected in the case of blends. It appears that the film surface degraded as a result of atomic oxygen bombardment, but was healed up by the polysiloxane present in the succeeding layers. The above argument can be strengthened by the close observation of elongation at break as exposed neat polyimide film has shown nearly

TABLE III Mechanical properties of oxygen plasma exposed and unexposed polyimide and blends

	Before the exposure			After the exposure		
Polymers	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation (%)	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation (%)
PI-0	88	2988	17	73	2761	13
PMSI-5	92	3321	19	91	3318	18
PMSI-10	98	3575	21	93	3495	19
PMSI-15	102	3926	23	99	3856	21
PMSI-20	110	4280	26	100	4126	23

25% less elongation as compared to unexposed polyimide while only 7.0% drop was observed in exposed PMSI-20 blend film (as compared to unexposed PMSI-20) which still retained higher elongation then the neat polyimide. This suggests that neat polyimide is much more adversely affected by the attack of oxygen plasma as compared to blends.

4. Conclusions

At this point it can be postulated that thin films of the blends exhibited better resistance to oxygen plasma bombardment as compared to neat polyimide films. Blends have shown better retention of weight after the exposure and exhibited non-linear weight loss due to the formation of inorganic silica (SiO_2) layer acting as a barrier for the incoming oxygen plasma. Blends are thermally stable and mechanical properties of the exposed blends were found far better than similarly exposed neat polyimide. A self-healing mechanism seems to operate in these blends but needs to be explored in detail.

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