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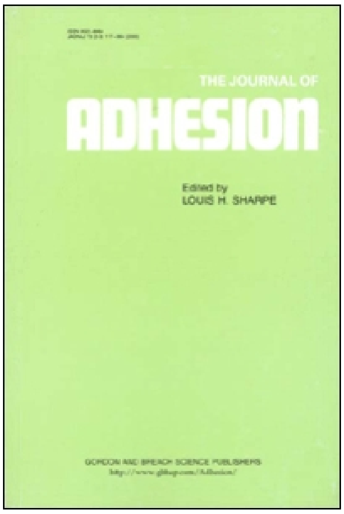

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Synthesis and Characteristics of Novel Poly(Imide Siloxane) Segmented Copolymers†

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New poly(imide siloxane) copolymers for possible use as tough environmentally stable structural matrix resins and structure adhesives have been prepared. Thus, 3,3′-4,4′-benzophenone tertracarboxylic dianhydride was reacted with various $\bar{M}n$ aminopropyl-terminated polydimethylsiloxane oligomers and a meta-substituted diamine "chain-extender" such as 3,3′-diaminodiphenyl sulfone or 3,3′-diaminobenzophenone to produce the siloxane-modified poly(amic acid). Thin films were cast from the reaction mixtures and subsequent thermal dehydration produced the poly(imide siloxane) block or segmented copolymers. Upper "cure" temperatures of 300°C were used to insure complete imidization. By varying the amount and molecular weight of the siloxane oligomer, a variety of novel copolymers of controlled composition have been synthesized. Tough, transparent, flexible soluble films were produced by this method. The thermal and bulk properties of films having low to moderate siloxane content closely resemble those of the unmodified polyimide controls. However, toughness and surface behavior can be enhanced.

KEY WORDS Segmented Copolymers; Poly(imide siloxanes); Moisture Durability; Atomic Oxygen Resistance; Surface Segregation; Synthesis.

INTRODUCTION

Polyimides synthesized from aromatic monomers are of great interest for high performance applications due to their excellent

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thermal and mechanical properties. However, these polymers are often insoluble in their fully imidized form unless carefully designed. Many approaches to enhancing the solubility and processability of polyimide systems have been investigated which also attempt to maintain their high performance properties. Successful attempts to accomplish this goal have involved the incorporation of flexible bridging units into either the diamine or dianhydride monomers, which imparts mobility to the otherwise rigid polyimide backbone.[1-3] Incorporation of bulky side groups[4] and utilization of diamines containing meta linkages[5,6] also enhance processability.

Incorporation of flexible siloxane segments into the polyimide backbone can yield soluble, processable copolyimides while still maintaining fairly good thermal-mechanical properties.[7] In addition to enhanced solubility, incorporation of polysiloxane blocks imparts a number of other desirable characteristics, such as improved weatherability to aggressive environments, improved impact resistance, decreased sensitivity to water absorption and surface modification.[7,8]

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This improved processability and environmental resistance to moisture and atomic oxygen suggests these materials as candidates for specialized adhesive applications. Although the low surface energy of poly(dimethyl siloxane) suggests that it should behave as a release agent, preliminary results in our laboratories suggest that the decrease in bond strength due to incorporation of low levels of siloxane (<20% w/w) is small. Thus, these materials may find utility in applications where environmental resistance is paramount. It is also expected that the hydrophobic nature of the polysiloxane segments should add an improved degree of resistance to moisture over the unmodified polyimides. This paper will describe the synthesis, characterization and initial adhesive properties of several novel poly(imide-siloxane) copolymers having the representative structure shown in Figure 1.

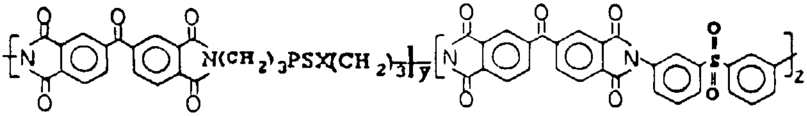

FIGURE 1 Representative structure for poly(imide siloxane) segmented copolymers.

EXPERIMENTAL

Synthesis of Poly(imide-siloxane) Copolymers of Controlled Composition

The 3,3′-4,4′-benzophenone tetracarboxylic dianhydride (BTDA) was obtained in high purity from the Chriskev Company and subjected to a thermal treatment prior to use. 3,3′-diaminodiphenylsulfone (DDS) was obtained from FIC Corporation and recrystallized from a deoxygenated methanol/water solution (90% yield, m.p. 172–173°C). The α, ω-aminopropyl polydimethylsiloxane oligomers were synthesized by methods previously disclosed[9] and their corresponding molecular weights were determined by potentiometric titration of the amine end groups. N-methylpyrrolidinone (NMP, Fisher), tetrahydrofuran (THF, Fisher), and N-cyclohexylpyrrolidinone (CHP, GAF) were distilled from calcium hydride under reduced pressure and stored in round bottom flasks sealed with rubber septa.

Synthesis of the poly(amic acid siloxane) intermediates was conducted in a 3-neck, 250 mL round bottom flask fitted with a mechanical stirrer, nitrogen inlet, drying tube, and addition funnel. The actual cosolvent ratio used to synthesize the amic acids varied with the amount of siloxane oligomer to be incorporated. A representative synthetic procedure will be outlined to synthesize a copolymer containing 10 weight percent of a siloxane oligomer whose molecular weight is 950 g/m.

The entire apparatus was assembled and flamed to remove residual moisture from the system. BTDA (11·3546 g, 0.0352 moles) was added to the flask and rinsed in with 40 mL of NMP and 30 mL of THF. Next, 2.0000 g of the siloxane oligomer (0.0009 moles) and 20 mL of THF were placed in the addition funnel and added dropwise to the stirring dianhydride solution. After stirring for an additional 15 min, 6.7016 g (0.0334 moles) of 3,3′-DDS was added as a chain extender along with 20 mL of NMP and 10 mL of THF. The reaction was allowed to proceed for 8 hours. The resulting clear viscous solution was stored at ~10°C until needed.

"Curing" of the poly(amic acid siloxane) intermediate to the imide form was accomplished by casting the amid acid solution onto glass plates at thicknesses ranging from 5 to 50 mils. The plates were

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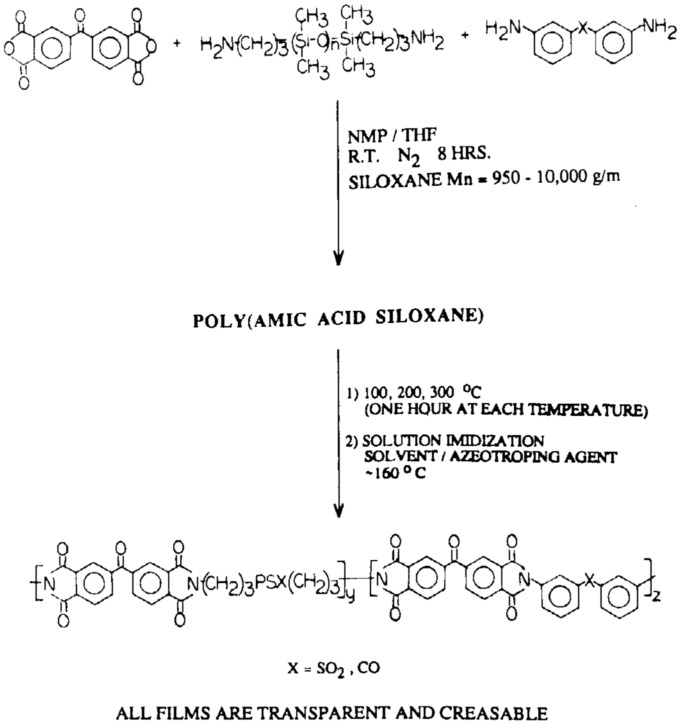

FIGURE 2 Synthetic scheme for poly(imide siloxane) segmented copolymers.

then placed in a vacuum oven to remove the reaction solvents. After this treatment, the films on the plates were imidized in a forced air convection oven at temperatures of 100°C, 200°C and 300°C, each for one hour. The synthetic scheme is summarized in Figure 2.

Characterization of poly(imide-siloxane) copolymers

Viscosity measurements Intrinsic viscosity measurements yielded relative molecular weights and were performed in NMP at 25°C using a Cannon–Ubbelohde viscometer.

Thermal analysis Differential scanning calorimetry (DSC) was used to determine the glass transition temperatures (Tg) of the

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copolymers with a Perkin–Elmer Model DSC-4. Scans were run at 10°C/min with a sensitivity of 10 mcal/sec in a nitrogen atmosphere. Reported values were obtained from a second scan after heating and rapid cooling. Some copolymer transitions were obtained by dynamic mechanical thermal analysis (DMTA) at a frequency of 1 Hz using a Polymer Laboratories instrument.

Thermal gravimetric analysis and thermal mechanical analysis TGA was performed on a Perkin–Elmer TGS-2 instrument on samples in film form. Scans were run at 10°C/min in an air atmosphere. TMA was performed on a Perkin–Elmer TMS-2 with a 10°C per minute heating rate with a 50 gram quartz penetration probe.

Stress strain analysis An Instron Model 1122 was used to determine the mechanical behavior of dogbone-shaped specimens of the copolymers. Specimen gauge lengths were 10 mm. Specimen widths were 2.76 mm. The extension rate was 5 mm per minute.

Contact angle measurements Water contact angles were measured on samples prepared by spin-coating the amic acid intermediate in its reaction solution onto a ferrotype plate and then imidizing by thermal treatment. In some cases, recast fully imidized films were also examined.

X-ray photoelectron spectroscopy Samples for XPS were prepared by spin-coating the amic acid intermediate in its reaction solution onto ferrotype plates which had been washed in hexane three times prior to coating. The samples were covered with a watchglass to prevent contamination during thermal imidization by the standard method in a forced air convection oven. After imidization, the samples were thrice washed in hexane and placed in clean glass containers with lids. Analysis was performed on a Kratos instrument at exit angles of 15° and 90°.

Oxygen plasma stability Samples of the siloxane-polyimide copolymers were analyzed in an oxygen plasma environment to determine qualitative physical degradation and weight loss. A Plasmod unit from the Tegal Corporation of Richmond, CA, was used. Film samples were maintained in an oxygen-charged environment for

45 minutes, under a vacuum of 1.5 torr. The applied radio frequency was 50 KHz. Oxygen flow rate to the analysis chamber was approximately 30 cc per minute.

Initial adhesion results Single lap shear specimens were prepared by sandwiching a scrim cloth (112 E glass) coated with the poly(imide siloxane) resin between two primed titanium adherends. The poly(amic acid siloxane) solution in NMP/THF, which was molecular weight controlled by the addition of phthalic anhydride, was coated onto the scrim cloth and cured in a forced air convection oven using the following schedule:

60° – $\frac{1}{2}$ hr
100° – $\frac{1}{2}$ hr
160° – $\frac{1}{2}$ hr
160 in vac – $\frac{1}{2}$ hr.

This procedure was repeated until an overall thickness for the cloth and resin of 9–13 mils was achieved.

The titanium adherends were sandblasted, treated with Pasa Jell 107, ultrasonically cleaned, and immediately primed with a coating of amic acid solution to preserve the surface treatment. This primer coat was imidized using the same thermal schedule as the scrim cloth.

Single lap shear specimens ($\frac{1}{2}$-inch overlap) were prepared by pressing the coated scrim cloth between two primed adherends using the following bonding cycle:

R.T. to 325°C, apply 200 PSI at 280°C
Hold for 15–60 min, @ 325°C
Cool under pressure.

RESULTS AND DISCUSSION

Thermal analysis and thermal stability

Values of the upper glass transition temperatures of the siloxane modified polyimides were found to be a function of both the level of incorporated siloxane as well as the siloxane molecular weight (Table I). Generally, the upper transition temperature will increase

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TABLE I
Upper glass transition temperatures of poly(imide siloxane) copolymers

PSX wt%	PSX Mn	DSC	Tg(°C) DMTA
Control	—	272	—
10	950	256	260
10	2100	267	267
10	5000	264	—
10	10,000	264	266
20	950	246	248
20	2100	259	—
20	5000	262	—
40	950	†	225

† No transition detected in DSC scan.

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with greater siloxane oligomer molecular weight and with decreasing siloxane incorporation. In many cases, the copolymers' upper transition temperature is depressed only slightly relative to that of the control, indirectly indicating that good microphase separation was achieved. The lower temperature siloxane transition is difficult to detect by DSC for low levels of siloxane incorporation, <20 weight percent. At greater levels of incorporation, however, the transition is detected by both DSC and DMTA within the range −117 to −123°C, representing 20 to 50 weight percent siloxane, respectively.

Copolymer thermal stability also varied with both siloxane oligomer molecular weight (Figure 3) and level of siloxane incorporation (Figure 4), increasing with the former variable and decreasing with the latter. From this observation, one may conclude that thermal degradation begins at the aliphatic *n*-propyl segments linking the siloxane oligomers to the polyimide matrix. As the siloxane oligomer molecular weight is increased, the concentration of *n*-propyl linkages in the copolymer backbone decreases, thus increasing the overall thermal stability. Copolymers containing higher amounts of siloxane show decreased resistance to probe penetration by TMA (Figure 5). The TGA traces indicate, however, that the copolymers possess fairly high stability values at elevated temperatures. Even at high siloxane levels of 60 weight

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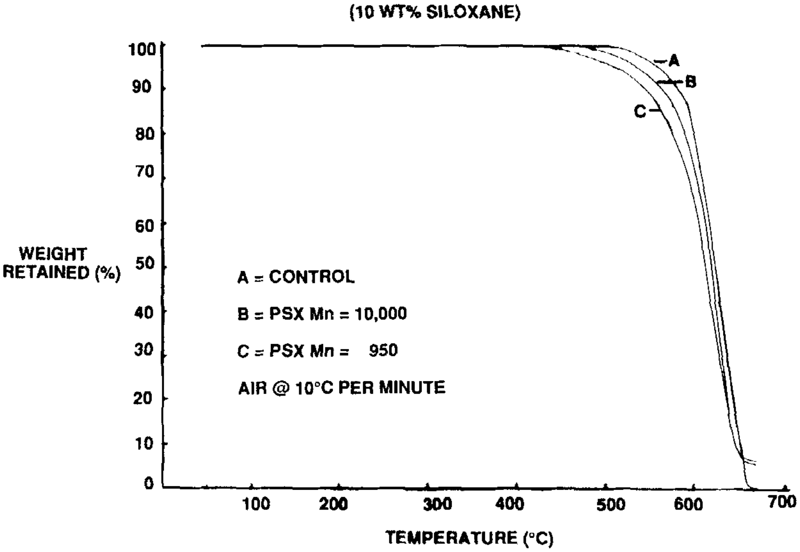

FIGURE 3 Thermogravimetric analysis of poly(imide siloxane) copolymers (10 weight % siloxane).

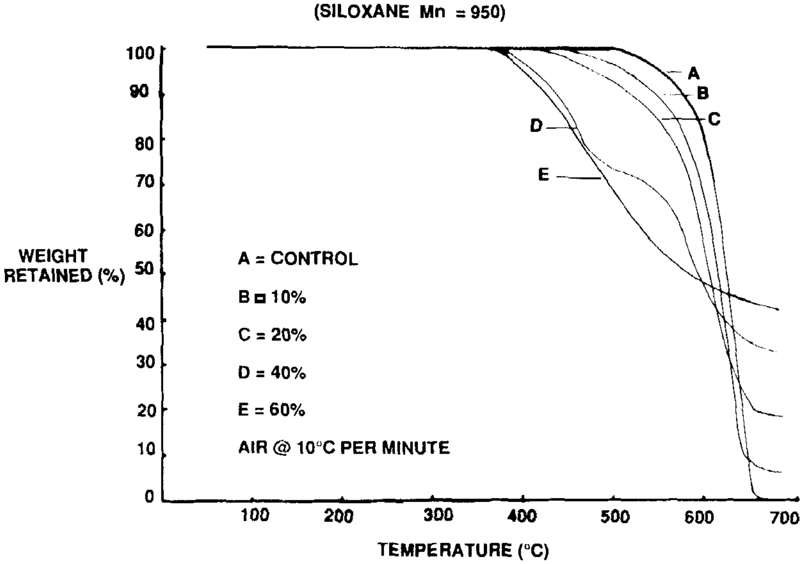

FIGURE 4 Thermogravimetric analysis poly(imide siloxane) copolymers (siloxane Mn = 950).

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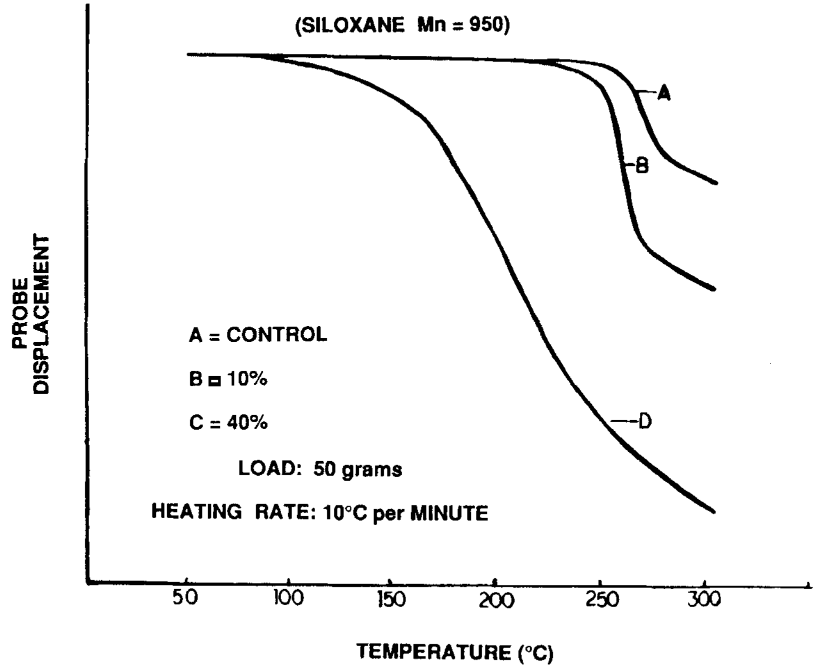

FIGURE 5 TMA penetration curves for poly(imide siloxane) copolymers.

percent, the copolymers maintained good thermal stability, although as the siloxane content is increased, degradation occurs at lower temperatures. The char yield at high temperatures, proportional to the siloxane content, suggests that a silicate-type structure is the principal degradation product in an air atmosphere.

Mechanical property analysis

An initial investigation of the mechanical behavior of these copolymers indicated that this property is highly dependent upon the level of siloxane incorporation (Figure 6). While copolymers containing low to moderate amounts of siloxane maintained good rigidity and ductile mechanical properties, a significant decrease in modulus and an increase in elongation occurred for high amounts of siloxane, no doubt due to inversion of the imide matrix to a continuous siloxane phase in the latter case.

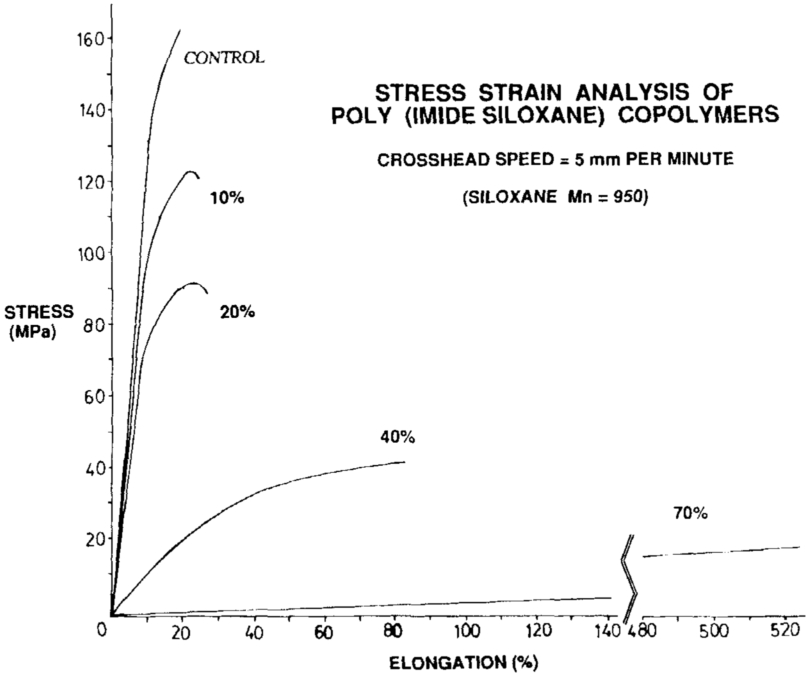

FIGURE 6 Stress strain analysis of poly(imide siloxane) copolymers.

Surface properties

Since the surface composition of these macromolecular materials is directly related to such properties as coefficient of friction and atomic oxygen stability, X-ray photoelectron spectroscopy (XPS or ESCA) was employed in order to characterize the surface composition of the siloxane-modified polyimide copolymers. By varying the angle of the sample relative to the analyzer, different depths of the polymer were sampled, such that a 15° grazing take-off angle characterizes molecules from the uppermost surface (~10 to 20 Å) more so than molecules from the bulk. The 90° take-off angle, on the other hand, yields compositional information more characteristic of the subsurface regions (~50 to 70 Å).

The results of the XPS experiments are listed in Table II. The results conclusively demonstrate that the siloxane component dominates the surface of the copolymer. Furthermore, the extent of

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TABLE II
XPS analysis of poly(imide siloxane) copolymers

PSX wt%	PSX Mn	Take-off angle	wt% PSX at surface
5	950	15°	85
5	950	90°	34
10	950	15°	77
10	950	90°	35
10	10,000	15°	87
10	10,000	90°	39
20	950	15°	87
20	950	90°	53
40	950	15°	86
40	950	90°	63

Grazing angles (15°) sample depths of ~10–20 Å; normal angles sample depths of ~50–70 Å.

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TABLE III
Water contact angle measurements of poly(imide siloxane) copolymers

PSX wt%	PSX Mn	Water contact Angle (degrees)
Control	----	68
5	950	92
10	950	98
10	2100	100
10	5000	98
10	10,000	100
20	950	101
20	2100	102
20	5000	102
40	950	106
40 (recast)	950	105
60	2100	106

domination is independent of the weight percent of the siloxane incorporated into the copolymer. Thus, one is able to achieve a surface characteristic of the siloxane component while tailoring the physical properties which are characteristic of the bulk.

These results are supported by the data obtained by contact angle measurements. Unlike XPS, however, contact angle measurements provide no direct quantitative information.

Water contact angle measurements are listed in Table III. A significant increase in contact angle is observed between the unmodified control and copolymer samples containing only 5 to 10 weight percent siloxane. In fact, the copolymer contact angles approach those of pure polydimethylsiloxane. The water absorption is also significantly reduced upon siloxane incorporation. Both of these properties are attributed to the hydrophobicity of siloxanes.

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Oxygen plasma stability

The copolymers examined were based upon BTDA-PSX-DDS as well as their oxydianiline (ODA) analogue, and had siloxane

TABLE IV
Oxygen plasma stability of poly(imide siloxane) copolymers (PSX Mn of 1000; based upon either 3,3'-DDS or 3,3' ODA; averages of multiple runs)

Sample	Weight loss (Mg per cm^2)
Kapton	0.86
DDS-Control	0.86
DDS-10% PSX	0.75
DDS-20% PSX	0.67
DDS-30% PSX	0.24
DDS-50% PSX	0
ODA-Control	1.13
ODA-30% PSX	0.30
ODA-50% PSX	0.14
DDS-30% PSX on kapton†	0.35
DDS-50% PSX on kapton†	0.10

† Spray-coating of poly(imide siloxane) copolymer ~0.03 mm thickness on kapton.

contents of 30 and 50 weight percent and siloxane segment molecular weights of 1000. Results obtained thus far are listed in Table IV. In every run, the DDS-based 50 weight percent siloxane samples lost no weight after exposure to the oxygen environment and their ODA analogues performed similarly well. Interestingly, the ODA-based systems seemed to perform somewhat less successfully than the DDS-based copolymers. Additionally, the 30 weight percent siloxane copolymers lost more weight during exposure than the 50 weight percent siloxane analogues, in both the DDS and ODA systems. Consistently, Kapton® lost more weight than either the DDS- or ODA-based siloxane-modified polyimides, and coating Kapton with the DDS-based copolymers enhanced the stability of the Kapton film under the aggressive environment for both the 30 and 50 weight percent siloxane levels. Under these latter conditions, the performance of the Kapton-coated film resembled the performance of the siloxane-modified polyimides which constituted the coated layer.

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Initial adhesion results

Preliminary adhesive data on controlled molecular weight copolymers are shown as lap shear strengths in Table V. The incorporation of low to moderate amounts of siloxane ($M_n = 950$ g/m) does not significantly alter the adhesive characteristics of these materials. Only at high levels of siloxane do the lap shear strengths fall below 2000 psi, indicating the potential utility of these materials as atomic oxygen resistant structural adhesives.

The data presented in this table represent tests on a comparable series of polymers synthesized using the same techniques and

TABLE V
Compositions, molecular weight considerations and preliminary adhesive results

PSX wt%	PSX Mn	[n] 25°C, NMP	Lap shear strength (psi)
Control	—	—	2500
5	950	—	2400
10	950	0.40	2300
20	950	0.36	2100
40	950	0.34	1800

bonded using the same cure schedules. This is significant since these materials are only produced in 1–10 gram quantities at present, and there has been continuing improvement in both synthesis and bonding techniques. The goal of this adhesion research is to evaluate the potential utility of this class of new materials for specialized applications without becoming overwhelmed with optimization of processing variables. The cure and bonding cycles chosen have been used in similar systems and were therefore thought to be appropriate for this initial evaluation.[6] The failures of these bonds were cohesive in the polymer/scrim cloth layer.

More recently, attention has been focused on the measurement and comparison of bond durability in a hot/wet environment for these poly(imide-siloxane) copolymers. This testing involves the use of lap shear specimens which are placed under load (some percentage of the ultimate strength measured at R.T.) then placed into an 80°C, 100% R.H. environment. The time to failure is then measured. Initial results in this area have been promising although only a limited number of samples have been tested to date. In this study a comparison was made between the polyimide sulfone control and a poly(imide-siloxane) containing 10% by weight of a ~900 (g/m) poly(dimethyl siloxane) segment. The control polymer (no siloxane) had a room temperature lap shear strength of 2500 psi, and the polymer containing 10% siloxane was approximately equal at 2560 psi. This difference does not appear significant in light of the data scatter evident in this test. However, in terms of durability a significant difference is apparent. When these specimens were tested in a hot/wet environment, the control polymer was loaded to 1100 psi for a 0.5 in.^{2} overlap sample corresponding to ~40% of the ultimate load at room temperature. The 10% siloxane containing sample was loaded to 1700 psi or 66.7% of the ultimate R.T. strength. Interestingly, both samples failed after the same amount of time in the 80°C/100% R.H. environment: 60 hrs. This result, although not conclusive due to the limited number of samples tested, does suggest an enhancement of durability with respect to moisture in the case of the siloxane containing material. Also of interest is that again in this durability test, both samples failed cohesively so that material rather than interfacial properties appears to control the ultimate bond strength. Currently, new synthetic methods which involve the imidization of the copolymer

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prior to bonding are being explored in order to evaluate the role of the amic acid in bonding as well as the effect of volatiles. In the present cases, thermogravimetric analysis suggests that up to 5% (w/w) volatiles due to water of imidization and residual solvent may be lost during the bonding cycle. This relatively high percent volatiles is expected to be reduced significantly due to prior imidization of the copolymer and solubility in more volatile solvents which could be more thoroughly removed prior to bonding. More extensive durability testing on a series of siloxane containing copolymers is also underway.

CONCLUSIONS

High molecular weight, randomly coupled, segmented siloxane modified polyimides were synthesized. These materials show good mechanical and thermal properties. Preliminary adhesive results suggest that incorporation of low levels of siloxane does not detract significantly from the room temperature lap shear strength compared to the unmodified controls. Also, preliminary durability studies at 80°C in a 100% relative humidity environment suggest that the incorporation of hydrophobic siloxane segments may significantly enhance the durability of those materials under these conditions.

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