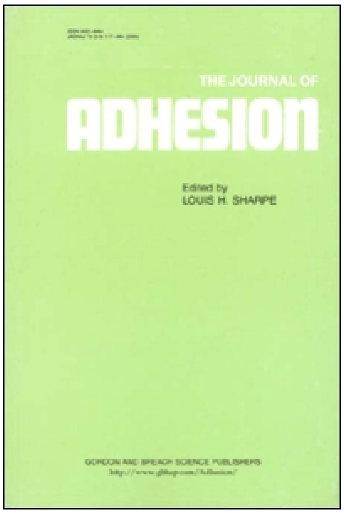

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Investigation of Polyimidesiloxanes for Use as Adhesives by Electron Spectroscopy for Chemical Analysis*

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Angle-dependent electron spectroscopy for chemical analysis (ESCA) was used to examine the air facing surface (20–100 Å thick) composition of polyimidesiloxanes with different processing variations, and of varying polydimethylsiloxane (PDMS) content and block length (number of PDMS repeat unit varies from 1 to 9). Polyimide was clearly detected (due to the nitrogen content) in the 20–100 Å surface regions. This shows that a small amount of PDMS and short PDMS segment lengths in polyimidesiloxanes give a surface region with both PDMS and polyimide present. The surface composition, particularly that in the *ca.* 100 Å region, was correlated to the peel strength of polyimidesiloxane melt pressed to a metal substrate. Our results suggest that both PDMS and polyimide are essential components to rendering a needed peel strength. PDMS, having a good diffusive ability, readily reaches the substrate upon being pressed, achieving intimate contact, while imide groups interact with the substrate, presumably through chemical bonding; these two factors act synergistically to result in a high peel strength. In addition, the interaction mechanism and the failure mechanism involved in bonding polyimidesiloxane and metal substrate were also elucidated based on the ESCA results.

Keywords: Angle-dependent ESCA; polyimidesiloxane; adhesion; relationship between peel strength and surface composition

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*One of a collection of papers honoring Robert J. Good, the recipient in February 1996 of *The Adhesion Society Award for Excellence in Adhesion Science, sponsored by 3M.*

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INTRODUCTION

Due to the attractive properties of polyimides, such as high glass transition temperatures, good thermal and mechanical properties, and low dielectric constants, their surface chemistry has been intensively investigated. Targeted as an adhesive material, the adhesion behavior of polyimides seems to be fairly well established. A sizable body of literature has appeared addressing the nature of interactions between polyimides and various metal substrates both experimentally [1] and theoretically [2], and the effects of structure and molecular weight of polyimides on the adhesion strength have been determined [3, 4]. Nonetheless, conventional polyimides can not meet the increasingly demanding requirements of structural adhesives. Surface modification of polyimides has been tried by some researchers [5–8] to enhance the adhesive strength, but only with limited success. It was for this reason and the concern about the poor processability of conventional polyimides that prompted researchers to seek alternative approaches. Among others, siloxane incorporation into polyimides [9–15], which results in polyimidesiloxanes, has proven to be an effective scheme to improve the adhesive characteristic and processibility.

There is only a limited amount of published literature on the understanding of the surface characteristics of diverse polyimidesiloxanes, and of the nature of interactions between polyimidesiloxanes and adherends (in most cases metal substrates). Dwight *et al.* [16] have measured the surface composition of various siloxane-containing copolymers including polyimidesiloxanes by electron spectroscopy for chemical analysis (ESCA). The polyimidesiloxanes they used are copolymers of dimethylsiloxane, 3,3′, 4, 4′-benzophenonetetracarboxylic dianhydride (BTDA) and 4,4′-oxydianiline (ODA). They observed segregation of the lower surface energy siloxane block at the surface of formulations containing 1–10% siloxane in the bulk. They found many similarities in the various classes of siloxane-copolymer systems investigated. In the bulk, microphase domains range from 100 to 400 Å depending on block size, siloxane chemistry and preparation. The gradient of siloxane overlayer thickness depends upon siloxane block length and its content; and a siloxane molecular weight between 6800–12800 is required to form a complete siloxane monolayer, according to their work.

William *et al.* [17, 18] have studied the microstructural characteristics of polyimidesiloxanes using transmission electron microscopy (TEM) and energy-dispersive X-ray analysis (EDX). They found that heating to 100°C resulted in the appearance of discrete siloxane domains measuring 20 to 160 Å in diameter. The spherical domains increased significantly in number upon further annealing to 212°C. The samples were commercially available solutions in *N*-methylpyrrolidone (NMP) obtained from M&T Chemicals (grade 3510) and General Electric (10–15 $-Si(R)_2-O-$ units), and details of the structure were not divulged.

McGrath *et al.* [14] have investigated the effect of test temperature, molecular weight and siloxane amount on the adhesive strength of polyimidesiloxanes deriving from BTDA and 3,3′-diaminodiphenyl sulfone (DDS). They found that bond strengths measured by lap-shear tests do not significantly depend on overall molecular weight (20–50,000 g/mol) at a bonding temperature of 200°C. At this temperature, they also measured a drop in adhesion in a 20% siloxane blend compared with the 10% siloxane copolymer, and a dramatic drop in adhesion for the pure polyimide.

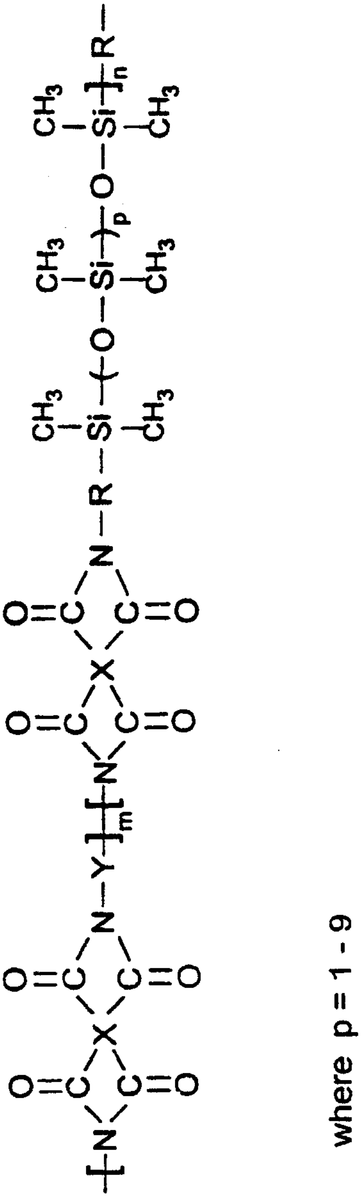
Another research group [19] has examined the factors governing adhesion between pyromellitic dianhydride-4,4′-oxydianiline (PMDA-ODA) polyimidesiloxane and glass. The adhesion energy increases with increasing content of polydimethylsiloxane (PDMS). The adhesion energy was also found to be a function of PDMS molecular weight at a constant 2% (wt.) of diamine. The adhesion energy is around 600 J/m^2 in the case of 248.5 g/mol but it decreases abruptly to around 10 J/m^2 in the cases of 900 and 1680 g/mol, respectively. The adhesion energy for high molecular weight PDMS incorporation is even less than the initial adhesion energy of polyimide. The abrupt decreases of adhesion energy with increasing molecular weight of PDMS were attributed to the different degree of microphase separation with PDMS molecular weight and the nature of interphase between the polyimidesiloxane and glass. The degree of microphase separation increases with increasing molecular weight of PDMS. Above 900 g/mol, a new phase, the composition of which is similar to pure PDMS, is formed and separated from bulk polyimide.

In recent years, the Occidental Chemical Corporation developed and commercialized a series of adhesives for microelectronics packaging, based on polyimidesiloxanes. In the present study, two types of these polyimidesiloxanes, designated as type I and type II, were studied with angle-dependent ESCA. The surface composition of polyimidesiloxane type I produced from various treatments and preparations, and that of polyimidesiloxane type II with varying compositions and PDMS block lengths were evaluated. The measured surface composition, particularly that in the *ca.* 100 Å region, was correlated to the peel strength between the polyimidesiloxane and the metal substrate. An *a priori* knowledge was garnered regarding the significance of various factors influencing the surface composition and subsequently the peel strength of polyimidesiloxanes.

EXPERIMENTAL

The two types of polyimidesiloxanes used were produced by the Occidental Chemical Corporation, with a trade name of SumiOxy®. Their general chemical structure is shown in Scheme 1. The specific chemical structure of the polymer backbone is proprietary, and thus is not divulged. Due to the nature of the application of the polyimidesiloxanes as adhesives, high purity is required, *i.e.*, no other ingredient is present in the adhesive except polyimidesiloxanes. The solutions used to cast films contained 22% (wt.) preimidized polymer in *N*-methylpyrrolidone (NMP). Silicone-treated poly(ethylene terephthalate) (PET) sheet was used as casting substrate. The thickness of PET is 100 or 150 μm, and its surface has been chemically modified. In silicone-treated PET-1, the surface modification was performed by Douglas Hanson's electron beam treatment, while for PET-2 a wet surface treatment was applied. The temperature for casting was ramped from room temperature at 5°C/min. to 220°C and held at 220°C for 30 min., unless otherwise noted. Film thicknesses typically measured 3 mils (75 μm). Residual NMP was typically ~2400 ppm. The air sides of such films were analyzed using ESCA, and their hot melt adhesive strengths were tested. Each reported peel strength is the average of 5 specimens.

The ESCA experiments were performed on a Perkin Elmer PHI 5100 ESCA instrument. Angle-dependent mode was used; take-off angles of 10°, 15°, 45°, and 90° were set and employed, which lead to sampling depths of *ca.* 20Å, 30Å, 70Å, and 100Å, respectively. A survey spectrum



SCHEME 1 General structure of polyimidesiloxanes.

of each sample was first acquired to detect all elements present ($\geqslant 0.1$ mole %) except hydrogen. Then high resolution spectra of each element in a sample were collected with an energy window of 20.eV and sufficient scans to achieve an acceptable signal-to-noise ratio. For the purpose of gaining maximum signal within a given data acquisition time duration, limited by the possible sample degradation, pass energies of 178.95 eV and 71.55 eV were chosen for survey and high resolution spectrum acquisition, respectively. No detectable sample degradation was observed during twice the regular data acquisition time. The data in high resolution mode were normalized based on all the elements detected with peak area integration scheme taking into account of appropriate atomic sensitivity factors [20]. The instrumental precision for these samples was found to be 1–3% at all take-off angles for all the elements, with the exception of signals near the detection limit ($\leqslant 1.0$ mole %) which yielded $<25\%$ relative standard deviations.

The specimens for the peel strength testing consisted of 1/4″ × 1″ (6.3 mm × 25 mm) strips of polymer which were laminated onto alloy 42 substrates using a laboratory press at 300°C, with 500 psi (3.45 MPa) pressure applied for 1 minute. Alloy 42 was cleaned with methylene dichloride three times before use. The composition of alloy 42 is 42% Ni and 58% Fe by weight. The surface composition of alloy 42 was not investigated. The authors believe that the surface consists of an oxide layer of unknown thickness. The peel tests were performed on a Diventro Peel Tester adapted with a 5 kg Omega Digital Force Gauge connected to a strip chart recorder. The test was done in a 90 degree geometry, with the alloy substrate clamped horizontally and the tip of the polymer film clamped and pulled in an upward direction. The peel rate was 2 cm/min.

RESULTS AND DISCUSSION

ESCA survey spectra of polyimidesiloxanes indicate the presence of both polyimide and polydimethylsiloxane. For instance, Figure 1, an ESCA survey spectrum of sample 44A (See Tab. I for sample ID), shows a peak at a binding energy of ~400 eV due to the presence of nitrogen (indicative of polyimide), and a peak at a binding energy of

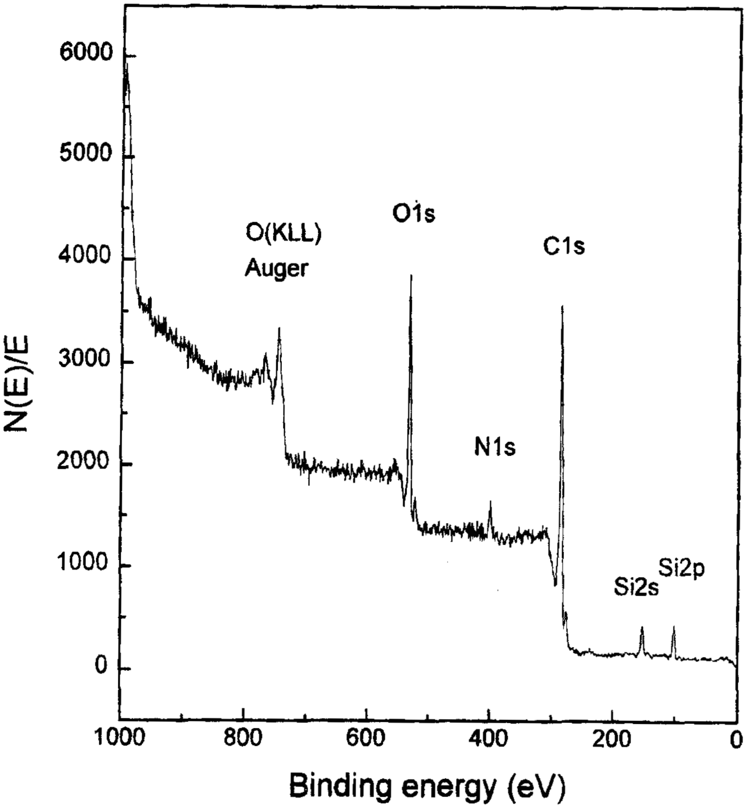


FIGURE 1 ESCA survey spectrum of sample 44A taken at a take-off angle of 45°.

~101 eV due to the presence of silicon (indicative of polydimethylsiloxane). This is further evidenced by high resolution carbon 1s (C1s) spectra, as exemplified by the C1s spectrum of sample 44A (Fig. 2). Figures 2a, 2b, 2c and 2d are C1s spectra of sample 44A taken at take-off angles of 10°, 15°, 45°, and 90°, respectively. The large peak at 285.0 eV of each of the four traces is attributed to carbon singly bonded, and the small but noticeable peak at around 288.5 eV is due to —C (=O)—N— characteristic of polyimide. The intensity of the peak at ~285.5 eV in Figure 2 increases progressively with increasing sampling depth (see Figs. 2a, 2b, 2c to 2d). This trend suggests that the concentration of polyimide is lower at the topmost surface than in the near surface region, while the concentration of PDMS exhibits the

TABLE I Various preparations or treatments of the type I polyimidesiloxane

Polymer	*Substrate*	*Sample ID*	*Description*	*Peel Strength (kg/cm, ±10%*)*
Oxy-1-9	Silicone-treated PET-1	41B	Dried 1 hr. @ 220°C	1.4
Oxy-1-9	Silicone-treated PET-2	41A	Dried 1hr. @ 200°C	1.0
Oxy-1-9	Silicon-treated PET-1	43C	Dried 1 hr. @ 240°C	1.8
Oxy-1-9	Silicone-treated PET-2	43A	Dried 1 hr. @ 240°C	1.5
Oxy-1-9	Silicone-treated PET-2	43B	1 hr 160°C, peel, 1 hr-220°C	1.6
Oxy-1-1	Silicone-treated PET-1	44B	Dried 1 hr. @ 240°C	1.4
Oxy-1-1	Silicone-treated PET-2	44A	Dried 1 hr. @ 240°C	1.4

Note: Oxy-1-9: the number of PDMS repeat units in the polyimidesiloxane is 1 (minor content), and 9 (major content).
Oxy-1-1: the number of PDMS repeat units in the polyimidesiloxane is 1.
*: relative standard deviation.
The peel strength of pure polyimide comprising the type I polyimidesiloxane is 0.2 kg/cm.

opposite trend. The actual composition of polyimidesiloxanes within different surface regions ranging from ~20 Å to ~100 Å was obtained by integrating the high resolution peaks of N1s, O1s, C1s and Si2p, and then normalizing them to yield their atomic percentages [20]. The atomic ratio of nirogen to silicon is used to represent the surface composition throughout this work.

The peel strength of the type I polyimidesiloxane prepared at different conditions, including varying casting temperature and substrate (see Tab. I for detailed information), was plotted against the nitrogen (N) to silicon (Si) atomic ratio determined by ESCA over the 100 Å region, as shown in Figure 3. The justification for using the composition over the 100 Å region instead of that of the topmost surface region lies in the fact that lamination of the polyimidesiloxane film for subsequent peel strength measurement was done by hot melting at ~500 psi, which means a thick surface layer is likely involved in interactions with the metal surface. Figure 3 shows that the peel strengths, ranging from 1.0–1.8 kg/cm, of all the polyimidesiloxane samples are much

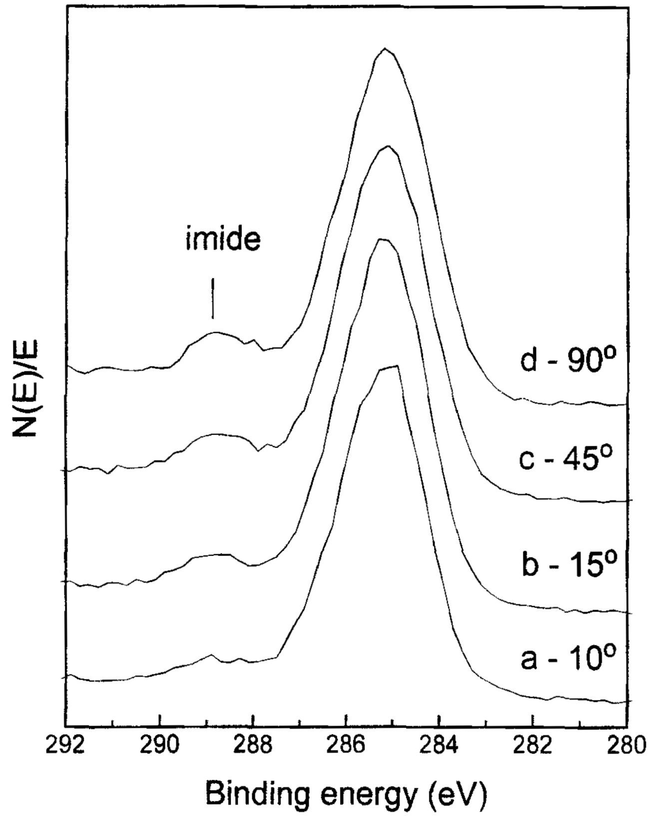


FIGURE 2 ESCA C1s spectra of sample 44A taken at take-off angles of (a) 10°, (b) 15°, (c) 45°, and (d) 90°.

greater than that of non-silicone polyimide (0.2 kg/cm) from which the type I polyimidesiloxane was synthesized.

This is direct experimental evidence of the significance of incorporating PDMS into polyimides in terms of the hot-melt adhesive strength. In fact, in order to achieve satisfactory adhesion between an adhesive and an adherend, there must not only be a component (polyimide in the current case) contained in the adhesive which presumably assumes the role of interacting with the adherend *via* chemical bonding, electrostatic attraction, or other strong interactions [21], but it is also equally important that the adhesive must have a sufficient diffusive ability or ductility to reach the adherend, achieving intimate

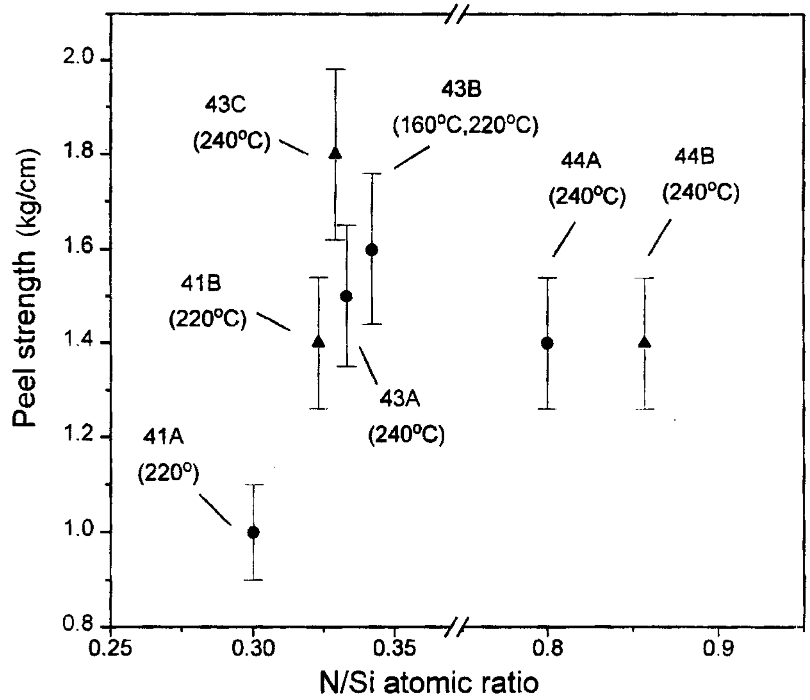


FIGURE 3 Correlation between the N/Si atomic ratio and the peel strength of the type I polyimidesiloxane cast on silicone-treated PET-2 (●) and on silicone-treated PET-1 (▲) at different temperatures. In contrast, the peel strength of pure polyimide from which the type I polyimidesiloxane was synthesized was measured to be 0.2 kg/cm.

contact, and facilitating the interaction of the imide groups with the adherend [21]. Polydimethylsiolxane is physically flexible at room temperature, rendering the polyimidesiloxanes the required ductility and needed processability lacked by pure polyimides.

The bulk morphology of Oxy-1–9 revealed by a small-angle X-ray scattering measurement [22] indicates a microphase separated morphology consisting of siloxane-rich domains on the order of 90 Å in diameter, dispersed in a polyimide-rich continuous phase.

Film preparation plays a significant role in influencing the surface composition, hence the variation in the peel strengths of the air sides of polyimidesiloxanes. The peel strength (1.0 kg/cm) of sample 41A prepared on silicone-treated poly(ethylene terephthalate) (PET)-2 is remarkably lower than that (1.4 kg/cm) of sample 41B prepared on silicone-treated PET-1, implying that selection of substrates for film formation is important. Note that both sample 41A and 41B were dried for 1 hr. at 220°C. Alternatively, if a sample is prepared by being dried for 1 hr. at 240°C, as were samples 43A and 43C, the peel strength increases: from 1.0 kg/cm for 41 A to 1.4 kg/cm for 41B, and from 1.5 kg/cm for 43A to 1.8 kg/cm for 43C. Sample 43B was dried for 1 hr. at 160°C, then peeled and dried for 1 more hr. at 220°C; the peel strength of this sample was 1.6 kg/cm, still greater than that of sample 43A.

The structure of polyimidesiloxane is another variable that can be tailored to achieve a better peel strength. For instance, both sample 43C and 44B were cast on silicone-treated PET-1, dried for 1 hr. at 240°C; the only difference is that the PDMS block length in sample 44B is 1 PDMS repeat unit, whereas in sample 43C the PDMS block is primarily comprised of PDMS blocks of 9 PDMS repeat units with minor amount of PDMS blocks of 1 PDMS repeat unit; however, they exhibit significantly different peel strength, with sample 43C of 1.8 kg/cm and sample 44B of 1.4 kg/cm (see also Fig. 3). A similar disparity is observed between sample 43A and 44A, but to a much less extent.

In order to examine systematically such a structural effect, type II polyimidesiloxanes with the number of PDMS repeat unit(s) being 1, 2, 3, 4, 5, and 9 were designed and synthesized. The corresponding bulk compositions are listed in Table II. They were cast from their NMP solutions on silicone-treated PET at 220°C for 1 hr. Figure 4 shows the correlation between the peel strength and the N/Si atomic ratio over the 100 Å surface region of the type II polyimidesiloxanes. At the lower N/Si range end, corresponding to a higher PDMS content

TABLE II Bulk compositions and peel strengths of the type II polyimidesiloxanes

Sample ID	*Gp* $p=$	*% PDMS (wt.)*	*Peel Strength (kg/cm, ±10%*)*
7415-137	9	7.01	1.3
7415-138	5	4.58	1.5
7415-139	4	3.96	1.4
7415-140	3	3.38	1.6
7415-141	2	2.78	1.7
7415-142	1	2.08	1.9

Note*: relative standard deviation.

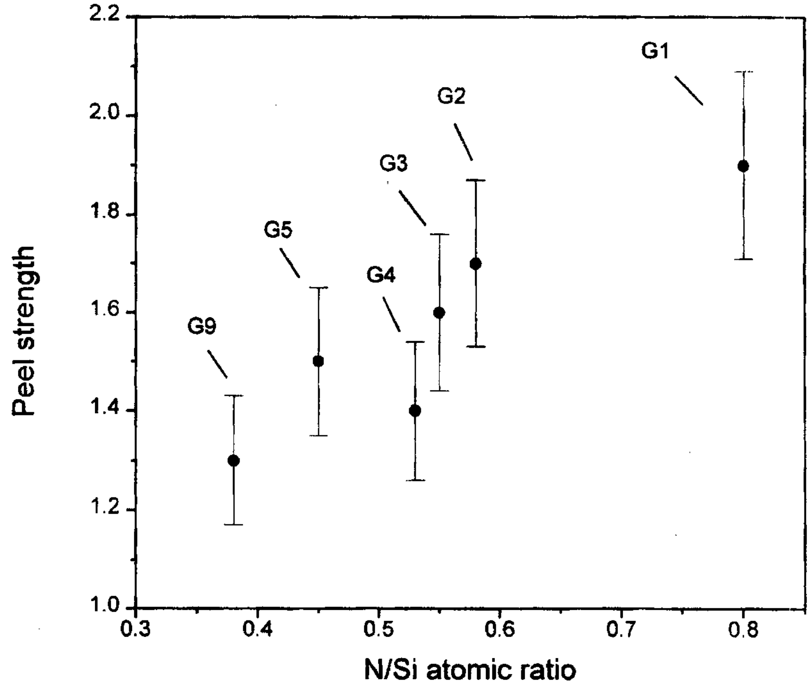


FIGURE 4 Correlation between the N/Si atomic ratio and the peel strength of the type II polyimidesiloxane.

and longer PDMS block length, the peel strength is low; it then increases with decreasing amount of PDMS at the surface of the polyimidesiloxane, corresponding to lower PDMS contents and shorter PDMS block lengths. As for the case of the type I polyimidesiloxanes, the values of the peel strength of the type II polyimidesiloxanes are all much higher than that of the pure polyimide. This observation, on the one hand, demonstrates again the effectiveness of incorporating PDMS into polyimides to enhance the peel strength of the resultant copolymers; on the other hand, too much long-block PDMS in the copolymers, resulting in a high surface concentration of PDMS, could hinder the efficacy of this scheme, as for the cases at the lower end of the N/Si range.

We performed a simple experiment to determine the interaction mechanism and the failure mechanism involved in bonding the polyimidesiloxane to Fe/Ni alloy 42 (a metal substrate). The film was laminated onto the metal substrate. The peel strength of the subsequent film measured 1.2 kg/cm, representing good adhesion. A strip of film bonded to the alloy was peeled off, and the polymer side in contact with the metal and the metal side in contact with the polymer were immediately analyzed. The measured composition is given in Table III. Compared with the surface composition of the film prior to bonding, the nitrogen content in the top 20 Å of the film after bonding has risen ~4 fold and the silicon content dropped by ~4 fold. In the meantime, a significant amount of polyimidesiloxane is observed on alloy 42 after peeling. This indicates that a cohesive failure is involved and that metal-imide interactions may be involved in the adhesive bond. During the lamination procedure (300°C for 1 min. at 500 psi (3.45 MPa) the polar imide moieties are drawn to the Fe/Ni metal centers, inducing counter migration of siloxane toward the bulk. These findings are supported by a published ESCA study of various

TABLE III Surface composition (atomic percentages) of sample Oxy-1-9, before and after bonding to Fe/Ni alloy 42, and that of polymer-contacting side of alloy 42 after peeling

Take-off angle Sampling depth	10° ~20 Å	15° ~30 Å	45° ~70 Å	90° ~100 Å
Air-facing surface of polymer, before bonding				
N	0.8	0.9	2.5	2.9
Si	18.3	17.6	11.2	8.7
O	24.1	24.2	21.8	20.3
C	56.8	57.3	64.5	68.1
Alloy 42-contacting side of peeled polymer				
N	3.6	3.5	3.9	3.8
Si	4.1	4.0	3.6	3.8
O	16.2	16.4	16.2	16.2
C	76.2	76.1	76.4	76.3
Polymer-contacting side of alloy 42 after peeling				
N	0.8	1.0	0.8	0.8
Si	4.1	4.6	4.5	4.1
O	19.3	20.0	23.4	24.3
C	75.8	74.4	71.0	69.8
Fe	0.0	0.0	0.2	0.6
Ni	0.0	0.0	0.1	0.4

metals deposited by sputtering on the surface of a PMDA-ODA polyimide [23]. Effects for Al, Cu and Au metals were all similar; initial reaction occurs preferentially at the PMDA carbonyl oxygen. Subsequent reactions at other sites such as PMDA and ODA aromatic rings were not observed, and no metal-carbon bond formation was found. It is, thus, likely that the carbonyl oxygen of the imide groups are responsible for adhesion to metals like Fe/Ni alloy 42. Of course, the effect of deformation caused by the peeling process on the surface composition of the polyimidesiloxane might also contribute to the decrease of silicon content and the increase of nitrogen content. The effect of deformation on the surface composition of multicomponent polymers has been investigated by Gorelova *et al.* [24]. Nevertheless, it is worth further study to evaluate the extent of change in the surface composition caused by the peeling process.

CONCLUSIONS

ESCA enables us to determine the surface composition of polyimidesiloxanes of different compositions, prepared as films under various conditions. Bulk compositions and PDMS block lengths were varied as well as casting substrates and temperature profiles. Polyimide was clearly detected (due to the nitrogen content) along with siloxane in the 20–100 Å regions of the polyimidesiloxane. From the ESCA results we conclude:

(1) A small amount of PDMS and short segment length PDMS in the polyimidesiloxane give a surface region with both siloxane and imide present.

(2) The peel strength of the polyimidesiloxane is related to the surface concentrations of both imide and siloxane; the surface composition, hence the peel strength, of the polyimidesiloxane is heavily determined by the polyimidesiloxane structure and bulk composition as well as by film preparation conditions.

(3) For the type II polyimidesiloxanes, shorter PDMS block lengths and lower PDMS content in the bulk give rise to higher peel strengths; too much long-block PDMS in the copolymers, resulting in a high surface concentration of PDMS, could hinder the efficacy of peel strength enhancement by incorporating PDMS into polyimides.

(4) During the lamination procedure, the polar imide moieties are drawn to the Fe/Ni metal centers of Fe/Ni alloy 42, including counter migration of siloxane toward the bulk. It is likely that the —C(=O)—N— groups of the polyimidesiloxane are responsible for adhesion to metals. Upon peeling the polymer from its metal substrate, a cohesive failure mechanism is observed.

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