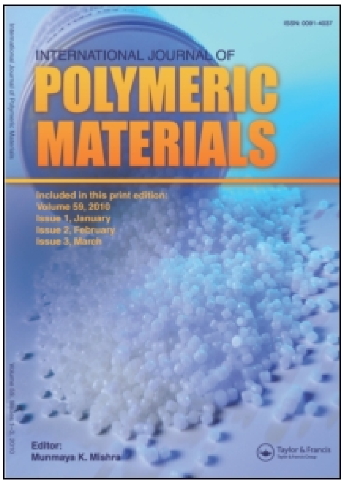

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Preparation and Properties of Silane End-capped Polyimide Adhesives: Structure–Property Relationship

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High temperature resistant adhesives consisting of silane end-capped polyimides were prepared by reacting anhydride terminated poly(amic-acid), obtained from pyromellitic dianhydride and a diamine (diaminodiphenyl methane, diaminodiphenyl ether, p-phenylenediamine, or benzidine), with an aminosilane in dimethylformamide. The polymers were precipitated in toluene and thermally cyclized to the corresponding polyimides. Polymers were characterized by viscosity, infrared, X-ray diffraction patterns and thermogravimetric analysis. The presence of silane was confirmed by silicon estimation and IR. The polymers were isothermally aged at various temperatures and the extent of degradation was established by IR. The poly(amic-acid) solutions were brushed onto the surface of chemically oxidized or anodized aluminium panels. Curing was done at 150 psi for varying periods of time and at different temperatures. Lap shear strengths of adhesives were determined. Effects of curing time, temperature, silane incorporation and nature of diamine were evaluated. Panels were aged for prolonged periods of time at high temperatures to analyse the effect of structure on lap shear strength.

INTRODUCTION

The unique applicability of polyimides at high temperatures in the form of fibres, films, plastics, varnishes and adhesives have made them the object of interest for many research workers.[1] The application of polymides in the form

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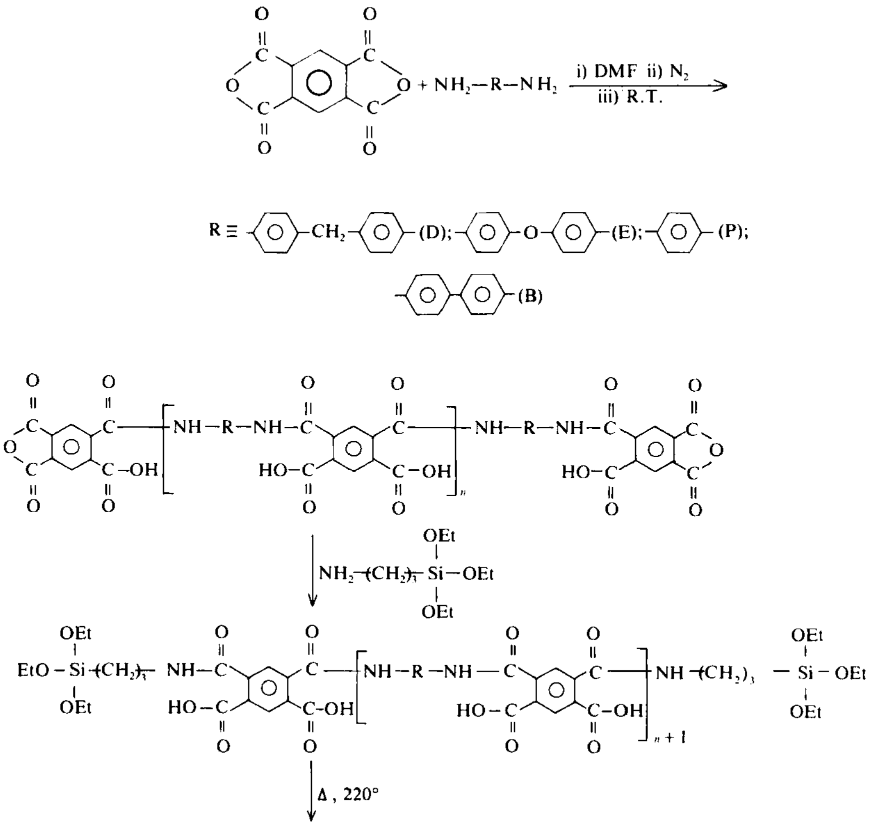
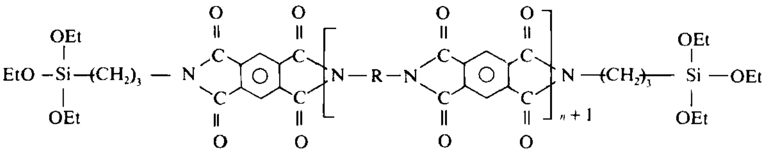
of adhesives was first investigated by DuPont in 1960–62. Since then, a number of recipes involving polyimides have been reported.[2–5] The present work deals with the structure–property correlation of silane end-capped polyimide adhesives.

EXPERIMENTAL

Materials All materials used were either obtained in sufficiently pure grade or were purified by conventional techniques before use.

Polymer synthesis Anhydride terminated prepolymer was prepared as described earlier.[6–7] The prepolymer was further reacted with aminopropyltriethoxysilane to complete the stoichiometry. The reaction scheme is as follows:





Homopolymers were prepared by conventional procedures.

Characterization Silicon percentage was determined gravimetrically.

Intrinsic viscosity measurements were made in DMF at 30°C using Ubbelohde suspended level viscometer.

IR spectra were run in nujol mull using a Perkin–Elmer spectrophotometer.

X-ray diffraction patterns were obtained using Phillip's X-ray unit PW 1140/90 with Ni-filtered CuK_α radiation at 40 KV.

Thermal analysis of the polymers was carried out in static air using a Stanton–Redcroft STA-780 thermal analyser. Samples (5 mg) were heated at a rate of 10°C/min from ambient temperatures to 900°C.

Preparation of adherends Aluminium panels measuring 3.8 cm (1.5 in) by 15 cm (6 in) were degreased by treatment with 5% NaOH solution for 10 minutes followed by sandblasting the surfaces. The aluminium surfaces were then oxidized by standard procedure.[8] A solution of 17 g of potassium dichromate in 170 ml distilled water and 50 ml concentrated sulphuric acid (98%) was prepared. The panels were then immersed in the solution maintained at 70°C for 10 minutes after which they were washed thoroughly with deionized water and dried under vacuum at 80°C. The surfaces were primed with polymer solution within 30 minutes.

Specimens were anodized potentiostatically in 0.1 M H_2SO_4 at different voltages (1, 1.5, 2 volts) for constant time (1 minute) to give a linearly increasing thickness of oxide film. The panels were washed thoroughly with distilled water and dried under vacuum as described earlier. The thickness of the oxide layer is given by the formula

$$\text{Thickness} = 12.45\ V + t_i$$

where V is voltage; t_i is initial thickness of oxide layer and has an approximate value of 30 Å.[9]

Bonding process The aluminium panels treated as described above were brush coated with poly(amic-acid) solutions in DMF. The panels were heated at 140°C for 5 minutes until the solvent evaporated. Panels were overlapped an area 2.5 cm (1 in) × 3.8 cm (1.5 in) and bonding was effected by placing samples in a hand press under a pressure of 150 psi at a temperature, 160–260°C ± 5° for 0.5 to 3 hours.

Isothermal ageing The bond aluminium specimens were aged isothermally in an air oven at 350° ± 5°. Sets of 5 specimens were removed for testing after 0, 24, 50, 100, 150 and 200 hours.

Testing Lap shear tests of adhesively bonded aluminium strips were performed on an Instron Universal Testing Instrument Model 1195 according to ASTM designation D882-61T. Specimens were tested at a cross head speed of 5 mm/min using a gauge length of 7.6 cm (3 in).

Resin properties Adhesive flash was subjected to IR studies to confirm complete conversion to polyimide. Thermal characteristic of the flash was studied by subjecting to TGA.

RESULTS AND DISCUSSION

The results of polymer syntheses are summarized in Table I.

Viscosity studies On the basis of viscosity studies, the order of reactivity of diamines is

$$D < E < P < B$$

This may be due to the rigid, rod-like structure of *B* and, to a lesser degree, of *P*, which results in high viscosity polymers.

Introduction of silane monomer does not result in significant change in viscosity as the increase in molecular weight of the prepolymer corresponds to the addition of two γ-aminopropyltriethoxysilane units at both ends (i.e. the increase in molecular weight of the propolymer is by 600).

Infrared studies Figures 1a and b give the infrared spectra of *P*, *P*(Si) poly(amic-acids) and their cyclodehydration products. Figure 1c gives the infrared spectrum of adhesive *P*(Si) flash and the polymer when heated to 350°C for 200 hours.

The poly(amic-acid) peak at 1650 cm^{-1} is replaced by polyimide peaks at 1780, 1080 and 800 cm^{-1} indicating complete cyclization (Figures 1a and b). In

TABLE I

Preparation of adhesive poly(amic-acids)

S. No.	Polymer code	PMDA : R[a] (mole ratio)	weight (gs) in prepolymer of		Intrinsic[b] [η] viscosity (dl/g)	weight of amino silane (g)
			PMDA	D		
1.	D	1 : 1	2.620	2.380	0.56	—
2.	*D*(Si)	3 : 2	2.572	1.557	0.39	0.869
3.	*E*	1 : 1	2.607	2.392	0.86	—
4.	*E*(Si)	3 : 2	2.564	1.568	0.43	0.866
5.	*P*	1 : 1	3.344	1.657	1.63	—
6.	*P*(Si)	3 : 2	2.998	0.990	0.62	1.013
7.	*B*	1 : 1	2.712	2.289	2.16	—
8.	*B*(Si)	3 : 2	2.632	1.481	1.31	0.893

[a] R ≡ diamine.

[b] Intrinsic viscosity determined in DMF at 30°C.

case of P(Si), the broad band due to ν as (Si—O—C) in the region 1050–1130 cm^{-1} conforms the presence of silane in polyimide.

IR of the flash is identical to that of the silane treated polyimides showing completion of imidization (Figure 1c). Further, IR of the polymer aged at 350°C for 200 hours shows the structure to be unchanged indicating the high temperature stability of the polyimide at service temperatures.

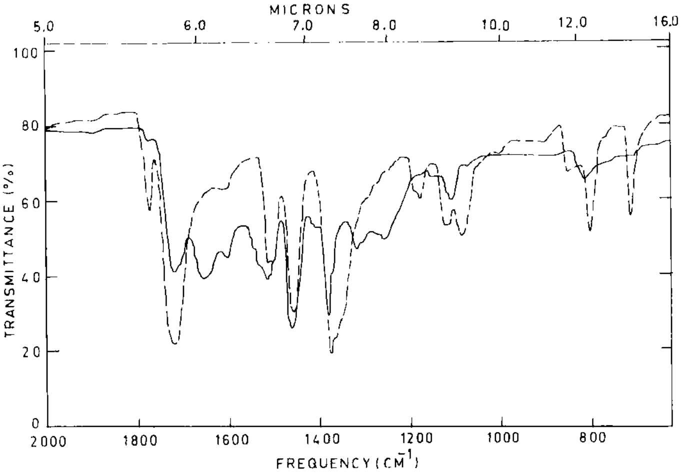


FIGURE 1a Infrared spectra of P(——) and its cyclodehydration product (------).

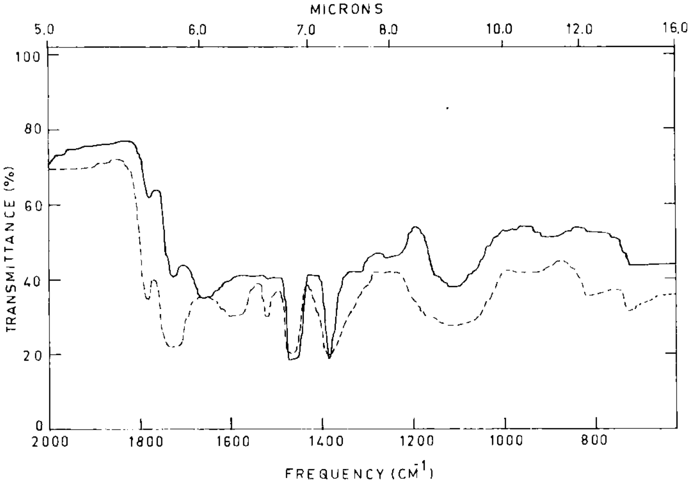


FIGURE 1b Infrared spectra of P(Si) (——) and its cyclodehydration product (------).

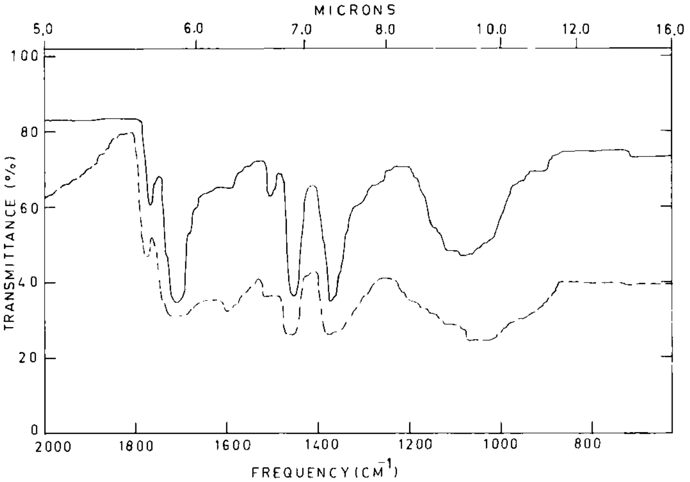


FIGURE 1c Infrared spectra of *P*(Si) adhesive flash (——) and *P*(Si) polymer aged at 350°C for 200 hours (- - - - - - -).

Solubility The polymers were found to be largely insoluble in a range of organic solvents such as DMF, DMAc, DMSO, NMP, HMPA indicating the existence of strong intermolecular interactions between the polymer chains.

X-ray diffraction studies X-ray diffraction patterns of poly(amic-acids) and polyimides of various diamine composition and the corresponding silane treated poly(amic-acids) and polyimides are shown in Figures 2a, b and c. All three polymers showed a peak at $2\theta = 19$–$22°$, while the silane end-capped polymers showed an additional peak at $2\theta = 9.4$–9.8 which is due to the silyl moiety. Although the introduction of silane monomer reduces the crystallinity as reflected in the lowering of crystalline peak height and resolution, the Bragg's spacing remains unchanged in the case of *B* and *B*(Si). This implies that the silyl monomeric units do not affect the highly rigid crystal structure of *B* (Figure 2a).

On the other hand, incorporation of silyl units in less crystalline polymers such as *P* and *D*, not only changes the crystal structure but also reduces crystallinity (Figures 2b and c). The peak maxima in *P* and *D* observed respectively at $2\theta = 19.4$ and $2\theta = 24.6$ shifted to $2\theta = 22.0$ and $2\theta = 22.1$ upon incorporation of silyl unit. A similar phenomenon is indicated for the polyimides of silane end-capped polyimides.

Polyimides are found to have much higher crystallinity than the corresponding poly(amic-acids). The imidization process leads to a lowering of molar volume and hence the observed increase in crystallinity.

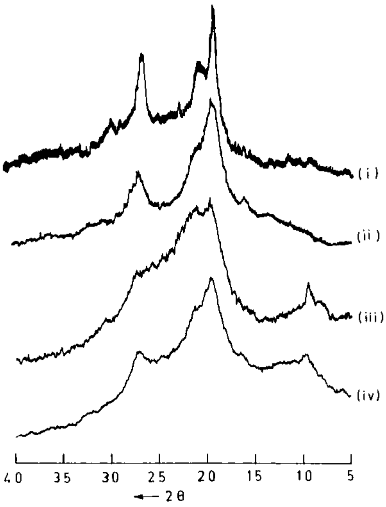


FIGURE 2a X-ray diffraction patterns of i) *B* poly(amic-acid), ii) *B* polyimide, iii) *B*(Si) poly(amic-acid), iv) *B*(Si) polyimide.

FIGURE 2b X-ray diffraction patterns of i) *P* poly(amic-acid), ii) *P* polyimide, iii) *P*(Si) poly(amic-acid), iv) *P*(Si) polyimide.

FIGURE 2c X-ray diffraction patterns of i) *D* poly(amic-acid), ii) *D* polyimide, iii) *D*(Si) poly(amic-acid), iv) *D*(Si) polyimide.

The figures show the order of crystallinity for different diamines to be: $D < E < P < B$. This observation reflects the higher rigidity of the *B* and, to a lesser extent, *P* structures in comparison to *E* and *D*.

Thermal Studies Figure 3a gives the primary thermograms of the polyimides *B*, *P* and *D* and the corresponding silane treated polyimides *B*(Si), *P*(Si), and *D*(Si). The silane treated polymers are found to be substantially less thermally stable. Results also show the order of stability to be:

$$D < E < P < B$$

for both silane treated and non-silane treated series. These results reflect the crystallinity data. A polymer having high crystallinity could be expected to possess higher stability since thermal decomposition is initiated in amorphous regions. The source of degradation of the polymer may also be derived from the methylene groups attached to silyl units.

P(Si) polymers were subjected to isothermal ageing at 250, 300 and 350°C for periods up to 200 hours. Results are shown in Figure 3b. As seen from the plots there is virtually no degradation at 250°C whereas at 350°C the polymer loses 6% weight. This may be attributed to loss of absorbed moisture and volatilization of low molecular weight products.

Samples aged at 250, 300 and 350°C for 200 hours were subjected to thermogravimetric analysis (Figure 3c) and their thermal stabilities were compared with the unaged *P*(Si) and the adhesive flash. The aged samples are significantly more stable than unaged samples indicating the formation of

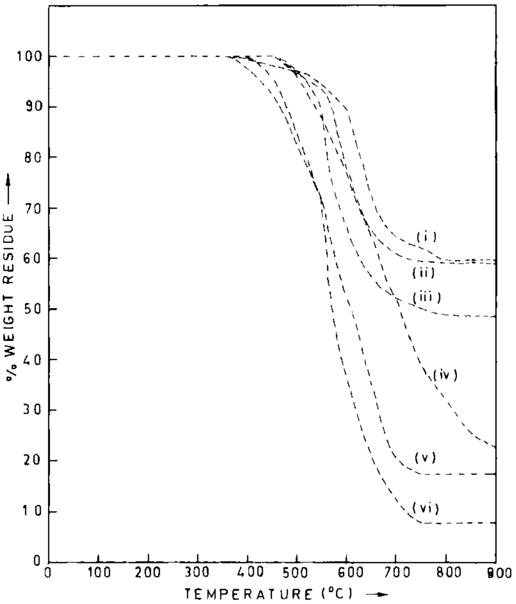


FIGURE 3a Primary thermograms of polyimides: i) *B*, ii) *P*, iii) *D*, iv) *B*(Si), v) *P*(Si), vi) *D*(Si).

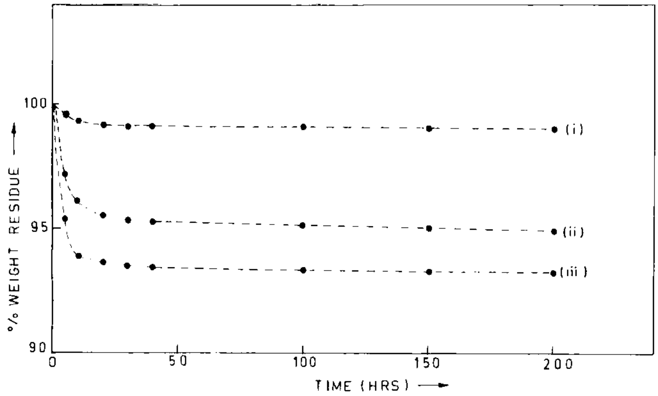


FIGURE 3b Isothermal ageing of polyimide *P*(Si) at i) 250°, ii) 300°, iii) 350°C.

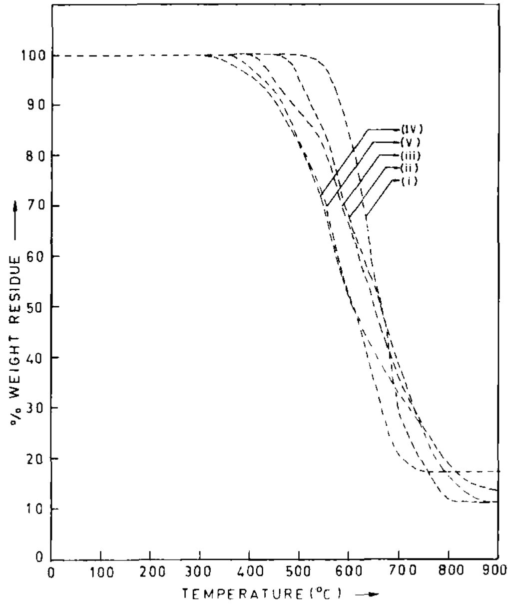


FIGURE 3c Primary thermograms of polyimide *P*(Si): i) aged at 250°C for 200 hours, ii) aged at 300°C for 200 hours, iii) aged at 350°C for 200 hours, iv) adhesive flash, v) unaged sample.

cross linking at high temperature which results in a more thermally stable polymer.

Adhesive characteristics In order to find the optimum bonding conditions, *P*(Si) bonded aluminium specimens were subjected to various curing temperature (160°, 210°, 260°C) and for varying lengths of time (0.5, 1, 1.5, 2 and 3 hours). Results are presented in Figures 4a and b. For relative comparison specimens were cured at 210°C for 1 hour.

Figures show lap shear strength for *P* and *P*(Si). The marked increase in strength of the bond as a result of silane incorporation is due to the lowering of crystallinity of the polymer as compared to the homopolymer and also due to the affinity of silyl units towards the oxide surface.

Room temperature lap shear strengths of the bondlines obtained after 0, 24, 50, 100, 150 and 200 hours of ageing are shown in Figure 4c. After ageing for 200 hours the bondlines darkened. Room temp. strengths of all the adhesives showed a peak in the region 25–75 hours (except for *D*(Si) sample where the peak occurs after 100 hours) indicating post curing effects. The order of lap shear strengths of the various silane treated polymers is found to be

$$D(\mathrm{Si}) > E(\mathrm{Si}) > P(\mathrm{Si}) > B(\mathrm{Si})$$

The poor lap shear strength of *B*(Si) and *P*(Si) is due to their higher crystallinity which results in poor wetting of the oxide layer.

Since the adhesive bonding depends on the oxide layer on the aluminium samples, it was considered of interest to study the effect of anodizing the aluminium panels. The resulting oxide surface was expected to be of far higher uniformity than that from chemical oxidation. Table II shows the result of the anodizing experiment.

The higher lap shear strength in samples 2, 3 and 4 as compared to samples 1 and 5 may be due to the porous structure of the oxide layer which allows the polymer molecules to diffuse into its interstices. On the other hand, the relatively lower lap shear strength in sample 5 is ascribed partly to the nonporous nature of the chemically formed oxide film and also to the weak adhesion between oxide layer and the aluminium surface.

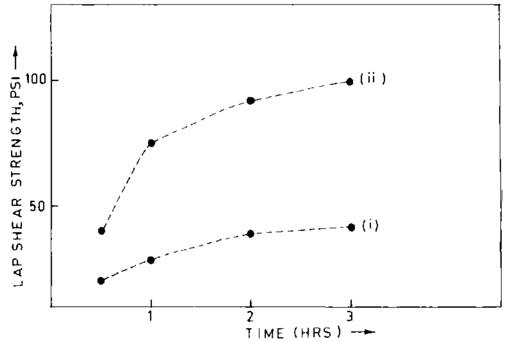


FIGURE 4a Plot of lap shear strength *vs.* bonding time at 210°C: i) *P*, ii) *P*(Si).

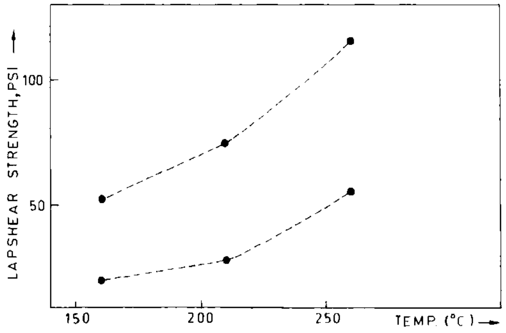


FIGURE 4b Plot of lap shear strength *vs.* bonding temperature for 1 hour: i) *P*, ii) *P*(Si).

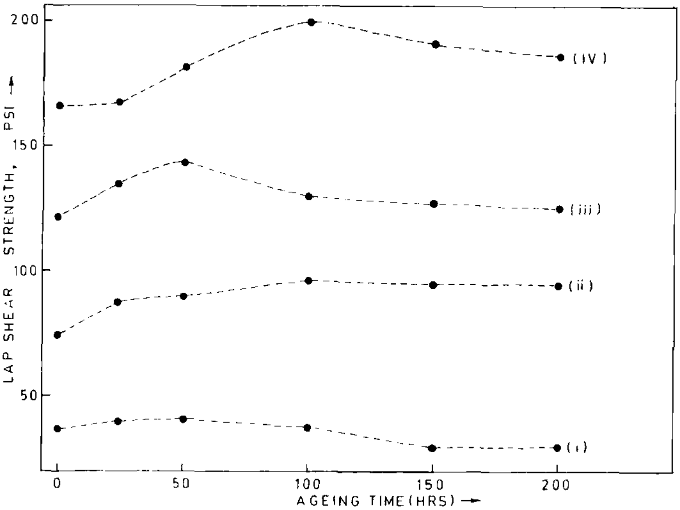


FIGURE 4c Plot of lap shear strength *vs.* ageing time at 300°C: i) *B*(Si), ii) *P*(Si), iii) *E*(Si), iv) *D*(Si).

CONCLUSIONS

Silane treatment of all polymer adhesives gave rise to improved lap shear strength of the resultant bond. The use of a more flexible dianhydride such as benzophenonetetracarboxylic dianhydride may lead to enhanced lap shear strengths. Investigations in this direction are in progress.

TABLE II

Lap shear strengths of *D*(Si) bonded anodized aluminium specimens

Sr. No.	Treatment applied	Thickness of oxide layer (A°)	Lap shear[a] strength (psi)	Mode of failure[b]
1.	no oxidation	30	117	A
2.	anodized (1.0 volt)	42.5	410	C
3.	anodized (1.5 volt)	48.7	302	C
4.	anodized (2.0 volts)	54.9	288	C
5.	chemical oxidation	>100	166	A

[a] Each result is average of 5 sample points.
[b] A = Adhesive, C = Cohesive.

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