

# Influence of adsorption behaviour of a silane coupling agent on interlaminar fracture in glass fibre fabric-reinforced unsaturated polyester laminates

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The relationship between the interphase consisting of physisorbed and chemisorbed silane on glass fibres and the resultant composite Mode I delamination fracture toughness in glass fibre fabric laminate, was studied. The Mode I interlaminar fracture toughness of the laminate specimen was obtained by using a double cantilever beam (DCB) specimen. The delamination resistance of the laminate specimen finished with two silane concentrations and washed in methanol solvent, is discussed on the basis of the interlaminar fracture toughness. In order to determine the amount of physisorbed and chemisorbed silane on the glass fibre, the amount of total carbon was determined using an analysis instrument. The physisorbed silane migrated into the resin matrix and influenced the mechanical properties and interlaminar fracture of the laminate specimen. The amount of unsaturated polyester resin blended with a silane coupling agent was measured using dynamic mechanical spectroscopy, and a DCB specimen for mechanical properties and fracture toughness.

## 1. Introduction

Glass fibre fabrics have been used as materials of reinforcement and electrical insulation for printed circuit boards. An increase in the density of patterns for printed circuit boards has been required in the electronics industry, and important properties, such as heat resistance, dimensional stability and resin impregnation, have increasingly been improved. The heat resistance is the most important property which is currently a limiting factor in many design applications. Silane coupling agents are widely used as finishing agents for glass fibre fabrics of glass fibre/matrix laminates in order to obtain the good heat resistance required of printed circuit boards. A silane coupling agent is an adhesive material which is like a bridge between glass fibre and matrix and the heat resistance of the laminate is greatly influenced by them [1].

It is well known that the mechanical properties of composites are influenced by the adhesive property of the glass fibre/matrix interface. The contribution of the silane coupling agents on the glass fibre/matrix

interface is based on the chemical bonding of the silane to both the resin and the glass surface [2, 3]. The chemical bonding theory has been modified to accommodate some mechanical properties of glass fibre reinforced plastic, such as stress relaxation and water susceptibility. The modified theories are as follows: deformable layer theory, surface wettability theory, restrained layer theory, reversible hydrolytic bond mechanism, interdiffusion and interpenetrating network model [3-7]. These theories have been proposed on the basis of the molecular structure of silane coupling agents and the mechanical properties of composites. Ishida and co-workers [8, 9] proposed that silane coupling agents on a glass fibre form multilayers with a structural gradient as an "interphase", i.e. the region surrounding a glass fibre where the properties of the interphase differ from those of the bulk matrix. The multilayer with a structural gradient is considered to consist of physisorbed and chemisorbed silane.

We have attempted to evaluate the interfacial strength obtained from a single-filament coupon test.

This test is a useful technique to evaluate the interfacial strength between a glass fibre and the matrix resin. We proposed a parameter, the “interfacial transmissibility”, to estimate the interfacial strength using the single-filament coupon test and attempted to investigate the correlation between the interfacial transmissibility and the amount of silane coupling agent in the interphase, with or without physical adsorption [10].

The mechanical properties and the heat resistance of glass fibre fabric laminates (GFFL) are influenced by the adhesive property of the glass fibre/matrix interphase. Crick *et al.* suggested that the interlaminar fracture morphology of carbon fibre/PEEK interphase can be examined using the Mode I interlaminar fracture toughness test [11]. Because the crack propagation behaviour of the double cantilever beam (DCB) test is similar to the growth of the delamination of GFFLs in industrial tests, fracture toughness values can be used as a simulation for the delamination. The observation of crack propagation during DCB tests is also important to evaluate the delamination resistance.

The relationship between the adhesive properties of the interphase of glass fibre/resin and the resultant composite Mode I interlaminar fracture toughness in GFFLs was studied. The Mode I interlaminar fracture toughness of GFFL was obtained using a DCB specimen. There was an optimum amount of silane on the glass fibre to accomplish maximum fracture toughness from DCB test results [12]. The reduction of fracture toughness of GFFL was caused by an excessive amount of silane.

Nishiyama *et al.* [13] proposed that changes in mechanical properties were correlated with changes in the silane adsorption behaviour of a silica-filled methacrylate composite, using dynamic mechanical spectroscopy (DMS). The dramatic differences in  $\tan \delta$  accompanied by an increase in modulus were assigned to a reinforcement mechanism, which only occurred after the appearance of the physisorbed silane.

The goal of this research was to understand the effect of the physisorbed and chemisorbed layers on the dynamic mechanical properties and the resultant Mode I interlaminar fracture. The unsaturated polyester resin blended with a silane coupling agent was measured using DMS and a DCB specimen for its mechanical properties and fracture toughness. Mode I interlaminar fracture toughness of GFFLs which were finished with a silane coupling agent and washed in methanol solvent, was measured.

## 2. Experimental procedure

### 2.1. Silane treatment

Plain E-glass fibre fabric, WE 18W 44 (warp) × 34 (weft) strand count/ inch was supplied by Nitto Boseki Company. The fibre strand from the E-glass fibre fabric consisted of 400 glass fibre filaments (9 μm diameter) and the calculated surface area was 0.175 m<sup>2</sup> g<sup>-1</sup>. γ-methacryloxypropyltrimethoxysilane: A-174 (methacryl silane) purchased from Nippon Unicar Company were used as silane coupling agents. The

methacryl silane has an organic function which can react with the double bond of vinyl ester resin as a matrix and a good adhesive agent at the glass fibre/resin interface [12]. The aqueous solutions of silane coupling agents were acidified with acetic acid at pH = 4.0. Glass fibre fabrics were dipped into the silane aqueous solutions of 0.4 and 1.0 wt % methacryl silane. They were squeezed between squeeze rollers and dried at 110 °C for 10 min.

The 0.4 and 1.0 wt % methacryl silane-finished glass fibre fabric was sufficiently washed with methanol solvent to remove the physisorbed silane from the surface of the glass fibre. After washing the glass fibre fabric with methanol, it was dried at 110 °C for 10 min.

### 2.2. Preparation of vinyl ester resin blended with methacryl silane for fracture toughness test and dynamic mechanical measurement

Vinyl ester resin (Ripoxy R-806B), an unsaturated polyester resin which was used as matrix, was polymerized with 0.7 wt % methyl-ethyl-ketone-peroxide and was purchased from Showa High Polymer Company. Hydrolysed and oligomeric methacryl silane was blended with the vinyl ester resin in order to simulate the interphase of glass fibre/resin. The oligomeric methacryl silane was prepared as follows [14]: the 20 wt % methacryl silane was hydrolysed in pH 3.5 distilled water. The hydrolysed silane separated from the aqueous solution after several days. This viscous siloxane oil was dried in a vacuum oven at 80 °C for 3 h. Then the resin blended with the oligomeric silane was cured with the peroxide for 48 h at room temperature.

### 2.3. Preparation of DCB and dynamic mechanical torsion laminate specimens

Fig. 1 shows a schematic diagram of GFFL for DCB specimens. Four surface finishes, unwashed and methanol-washed 0.4 wt %, unwashed and methanol-washed 1.0 wt % methacryl silane finished glass fibre fabrics, were provided for the reinforcement of GFFL. Twenty-ply glass fibre fabrics for DCB testing and eight-ply glass fibre fabrics for DMS testing were fabricated by the hand lay-up technique. The volume

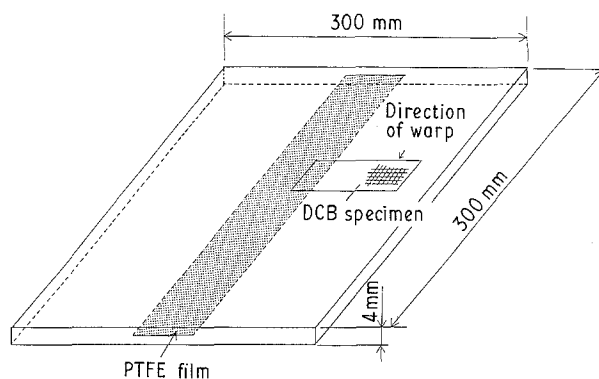


Figure 1 Schematic diagram of the glass fibre fabric laminate for the DCB specimen.

fraction of each laminate material was about 44%. PTFE 40  $\mu\text{m}$  thick film was inserted on the midplane as a starter slit during fabrication, shown in Fig. 1. The DCB and DMS fabricated materials were cured for 48 h at room temperature. The laminate materials were cut into pieces approximately 100 mm long, 25 mm wide and 4 mm thick for the DCB specimens. The dynamic mechanical torsion specimens were 55 mm long, 10 mm wide and 1.5 mm thick. The longitudinal direction of the DCB specimen was parallel to the weft glass fibre strand shown in Fig. 1.

#### 2.4. Quantitative analysis of silane coupling agent

In order to determine the amount of the silane coupling agent on the glass fibre, the total amount of carbon in the silane was determined using an analysis instrument: N. C.-Analyser Sumigraph Model NC-80, Sumitomo Chemistry Company. The measurements were made on the following basis. The total carbon content of the silane adsorbed on the glass fibre was perfectly oxidized by an electric hearth at 830  $^{\circ}\text{C}$ . The oxidized carbon was measured using a TCD detector of a gas chromatograph. The total amount of carbon was calculated in comparison with acetanilide as a reference material.

#### 2.5. Fracture toughness of vinylester resin blended with methacryl silane and the laminate specimen

The fracture toughness of the vinylester resin blended with the oligomeric methacryl silane was measured using a three-point bend specimen in accordance with ASTM E 399-83. The fracture toughness specimens were 50 mm long, 5 mm wide and 10 mm thick. The specimens were loaded at a crosshead rate of 1.0  $\text{mm min}^{-1}$ .

The interlaminar fracture toughness,  $G_{\text{IC}}$ , of the laminate specimen was measured by the technique described previously [12].

#### 2.6. Dynamic mechanical measurements

The dynamic mechanical measurements were carried out as a function of temperature from 50–200  $^{\circ}\text{C}$  under a torsion mode using a Rheometrics Dynamic Analyser model 700. The measurements were done at 1 Hz, 0.1% strain for the laminate specimens and 1% strain for the cured vinylester resin. The specimen sizes of the silane-blended resin and laminate were 55 mm long, 10 mm wide and 1.5 mm thick.

### 3. Results

#### 3.1. Quantitative analysis

Fig. 2 shows the total carbon content of the silane adsorbed on the unwashed and methanol-washed glass fibre fabrics as a function of the concentration of the silane in the treatment solution. The total amount of carbon in the silane on the unwashed glass was proportional to the concentration of the silane in the

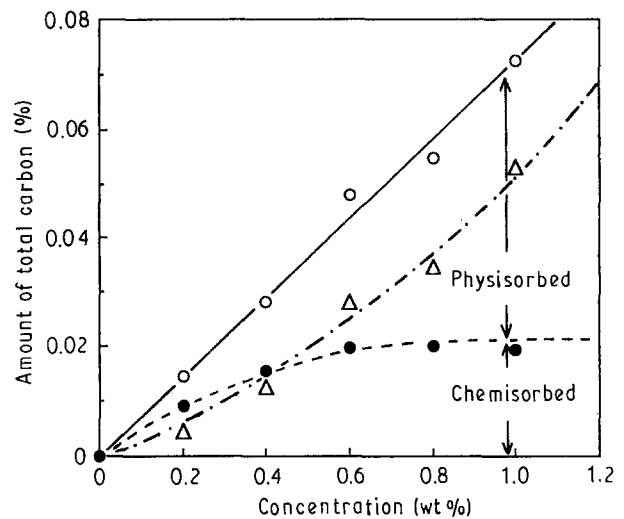


Figure 2 Amount of methacryl silane adsorbed on the glass fibre fabric as a function of concentration in the treatment solution. (○) Unwashed specimen, (△) methanol-washed specimen, (●) the difference between unwashed and methanol-washed specimen (chemisorbed silane).

treatment solution. However, the total amount of carbon in the silane on the methanol-washed glass fibre fabrics approximately indicates a constant value above 0.6 wt % silane concentration, and is considered to be the quantity of chemisorbed silane. The difference between the total amount of carbon in the unwashed and methanol-washed glass fibre fabrics increases with increasing concentration of silane, and is equal to the amount of the physisorbed silane [10, 13, 15]. The greatest amount of silane adsorbed on the unwashed 1.0 wt % silane glass fibre fabric is the physisorbed silane from the results in Fig. 2.

#### 3.2. Fracture toughness measurements of vinylester resin blended and cured with methacryl silane

Fig. 3 shows the relation between the fracture toughness,  $K_{\text{IC}}$ , and the amount of the methacryl silane blended with the vinylester resin. The value of  $K_{\text{IC}}$  decreases in proportion to the increase in methacryl silane in the vinylester resin.

#### 3.3. Dynamic mechanical measurements

Fig. 4 shows the effect of the addition of the methacryl silane on the visco-elastic properties of the vinylester resin. There is a dramatic change in  $\tan \delta$  as a function of the amount of silane blended with the resin. Three peaks, at 134.1, 144.0 and 148.3  $^{\circ}\text{C}$ , correspond to second-order transition. These temperatures are known as glass transition temperatures,  $T_g$ . The value of the resin glass transition temperature increased with increasing additional silane content and cross-link density.

Fig. 5 shows the dynamic modulus,  $G'$ , and  $\tan \delta$  data in the unwashed and methanol-washed 1.0 wt % silane laminate specimens. The  $G'$  values of the unwashed specimen are higher than those of the methanol-washed specimen between 50 and 150  $^{\circ}\text{C}$ .

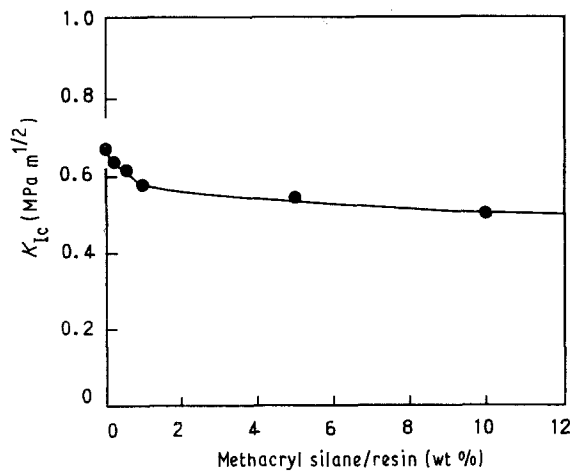


Figure 3  $K_{IC}$  of the vinyl ester resin mixed with three concentrations of methacryl silane as a function of silane content.

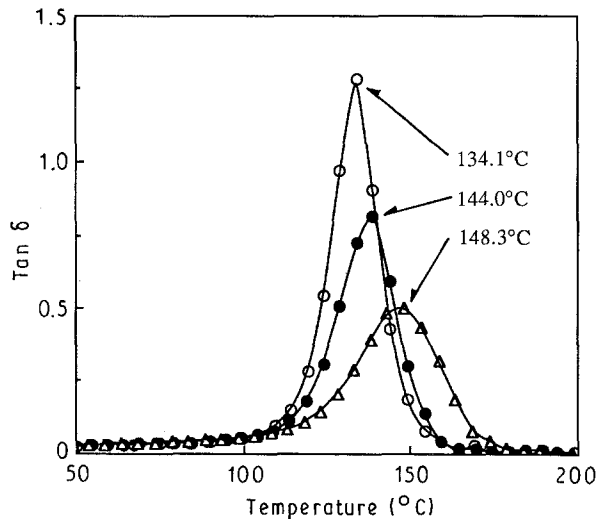


Figure 4  $\tan \delta$  for the vinyl ester resin mixed with three different amounts of silane as a function of temperature. (○) 100:0, (●) 95:5, (△) 90:10.

The  $G'$  values of the unwashed and methanol-washed specimen over  $150^\circ\text{C}$  show nearly the same constant value. The  $\tan \delta$  peaks at  $138.0$  and  $140.2^\circ\text{C}$  correspond to glass transition temperatures. The  $T_g$  point of the unwashed specimen is higher than that of the methanol-washed specimen. These  $T_g$  results in Figs 4 and 5 are in agreement.

### 3.4. Mode I fracture toughness test

Fig. 6a–d show the representative load–displacement curves for four silane–finished specimens. These load–displacement curves can be divided into two patterns in terms of crack propagation behaviour: one is a stable crack propagating growth pattern, the other is an unstable crack propagating growth pattern [11, 12]. The value of load dropped drastically (unstable fracture behaviour) and decreased slowly (stable fracture behaviour) in the load–displacement curve in Fig. 6a. On the other hand, only the unstable fracture behaviour was seen in the methanol-washed 0.4 wt % silane concentration of Fig. 6b. The unstable fracture behaviour was only observed in the unwashed

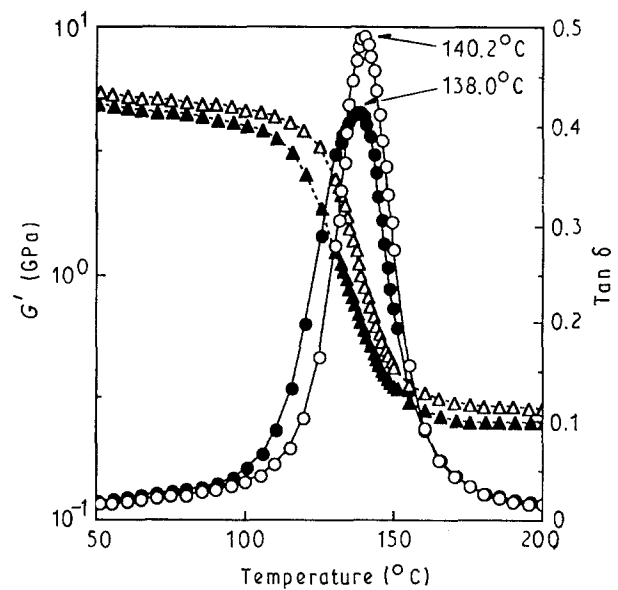


Figure 5 Dynamic modulus and  $\tan \delta$  for (○, △) unwashed and (●, ▲) methanol-washed 1.0 wt % methacryl silane laminate specimen as a function of temperature.

1.0 wt % and methanol-washed 1.0 wt % silane concentration specimens.

### 3.5. Macroscopic and microscopic observation of fracture surfaces

Fig. 7a–e show the macroscopic photographs of the fracture surfaces of five specimens. The light region on the fracture surface corresponds to the stable crack propagation and the dark region corresponds to the unstable crack propagation in each specimen. Fig. 7a shows a photograph of the stable fracture surfaces of the unwashed 0.4 wt % silane finished specimen. The upper picture of Fig. 7a illustrates the fracture surface covered with vinyl ester resin, whereas the lower picture reveals the glass fibre fabric. The only unstable fracture behaviour in terms of the load–displacement curve was observed in the methanol-washed 0.4 wt % silane, unwashed and methanol-washed 1.0 wt % silane-finished specimens. The large stable and small unstable crack propagation from the macroscopic photographs of the fracture surface are seen in the same specimens in Fig. 7b–e, respectively.

Fig. 8a and b show scanning electron micrographs of fracture surfaces for representative DCB specimens. Fig. 8a shows the stable crack growth and the exposed glass fibre strands without resin; Fig. 8b shows the unstable crack growth. The unstable fracture surface is mainly covered with resin and no glass fibre strand is seen on the fracture surface. It can be concluded that the stable crack propagates along the glass fibre/resin interface and the unstable crack propagates through the resin between the glass fibre fabric.

### 3.6. Relation between fracture toughness and crack length

Fig. 9a–d illustrates the relation between the fracture toughness,  $G_{IC}$ , and the normalized crack length,  $a/H$ , for four specimens. Fig. 9a and b correspond to the

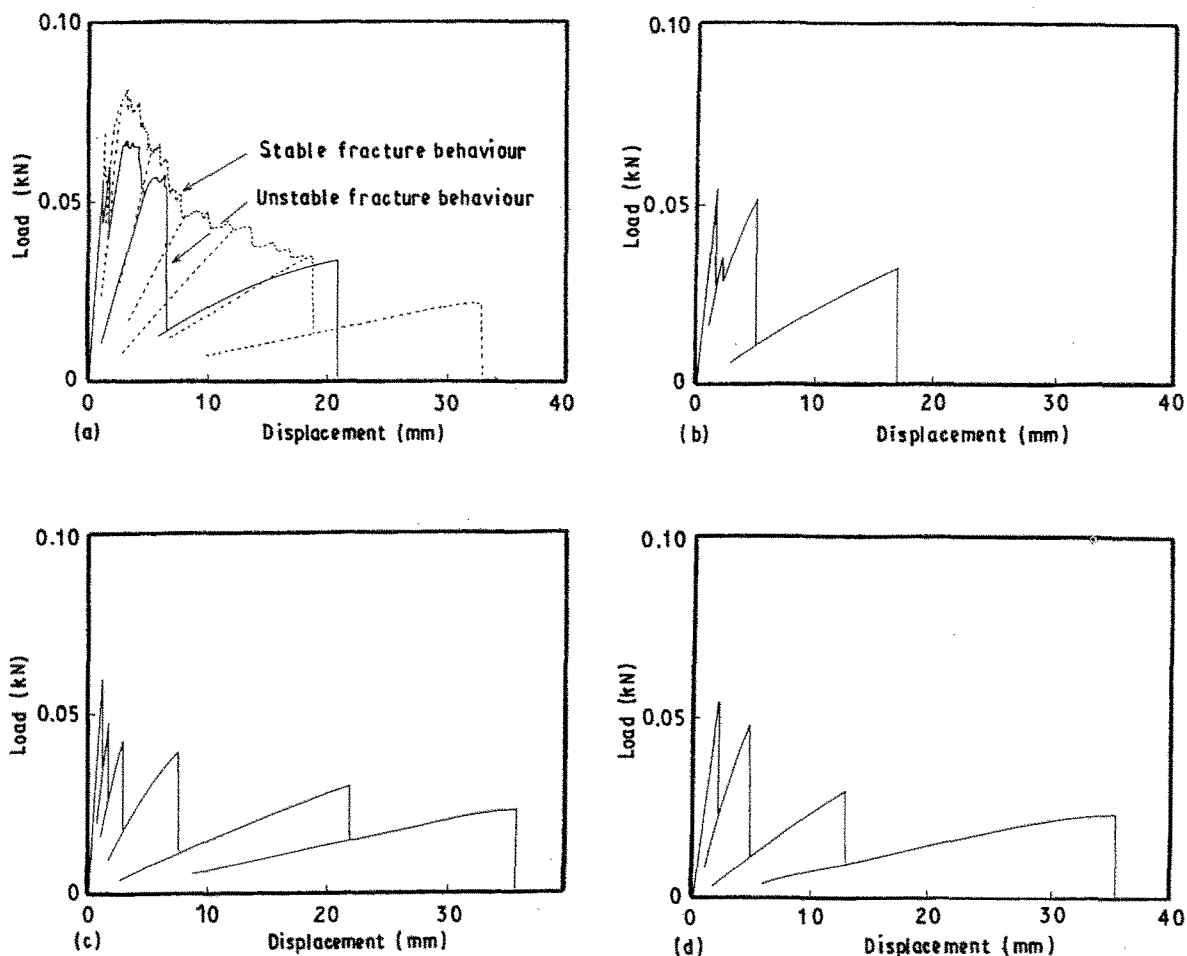


Figure 6 Load–displacement curves for (a) unwashed 0.4 wt % methacryl silane, (b) methanol-washed 0.4 wt % methacryl silane, (c) unwashed 1.0 wt % methacryl silane, and (d) methanol-washed 1.0 wt % methacryl silane laminates.

load–displacement curves in Fig. 6a–d. Fig. 9b–d indicate that fracture toughness values increase in proportion to the increase in the normalized crack length. The fracture toughness at the initiation of crack propagation is almost equal to that of neat cured vinylester resin. The fracture toughness values at  $a/H = 10$ – $20$  in Fig. 9a are much higher than those in Fig. 9b–d.

## 4. Discussion

### 4.1. Physisorbed and chemisorbed silane adsorption on the glass fibre fabric

Graf *et al.* [14] suggested that the physisorbed layers of methacryl silane could be dissolved by organic solvent, and that the chemisorbed layers were insoluble. The physisorbed layers of methacryl silane reduced the flexural strength of the polyester laminate. This strength reduction was caused by migration of the physisorbed layers into the resin, forming a blend of methacryl silane and polyester near the fibre surface. However, they did not investigate the amount of physisorbed and chemisorbed silane on the glass fibre fabric which affected the mechanical properties of the polyester composites.

Miller and Ishida [8] calculated that the hydrolysed methacryl silane molecule occupied an area parallel and perpendicular in relation to the glass fibre surface.

If the methacryl silane is perpendicular to the glass fibre surface, it occupies  $0.24 \text{ nm}^2/\text{molecule}$ . The monolayer equivalent as a function of total carbon content shown in Fig. 2 can be obtained from as follows: the number of monolayer equivalents,  $L$ , can be calculated by

$$L = T/84 \times 6.02 \times 10^{23} \times 0.24/0.175 \quad (1)$$

where  $T$  is the total carbon content (%), and 84 is the molecular weight of the organic function of methacryl silane.

The physisorbed silane layer is 1.2 monolayer equivalents and the chemisorbed layer 1.6 monolayer equivalents for the 0.4 wt % silane-finished specimen. For the 1.0 wt % silane-finished specimen, the physisorbed and chemisorbed silane layers are 5.1, 2.2 monolayer equivalents, respectively. The calculation proved that there were the physisorbed silane layers on the glass fibre that can affect the properties of the interphase. The high-concentration silane specimens have, therefore, many physisorbed silane layers that can affect the properties of the interphase. The physisorbed silane layers can influence the properties of the interphase and the mechanical properties of the laminate are dependent on the interphase. Methanol washing removed the physisorbed layers on the glass fibre and can affect the mechanical properties.

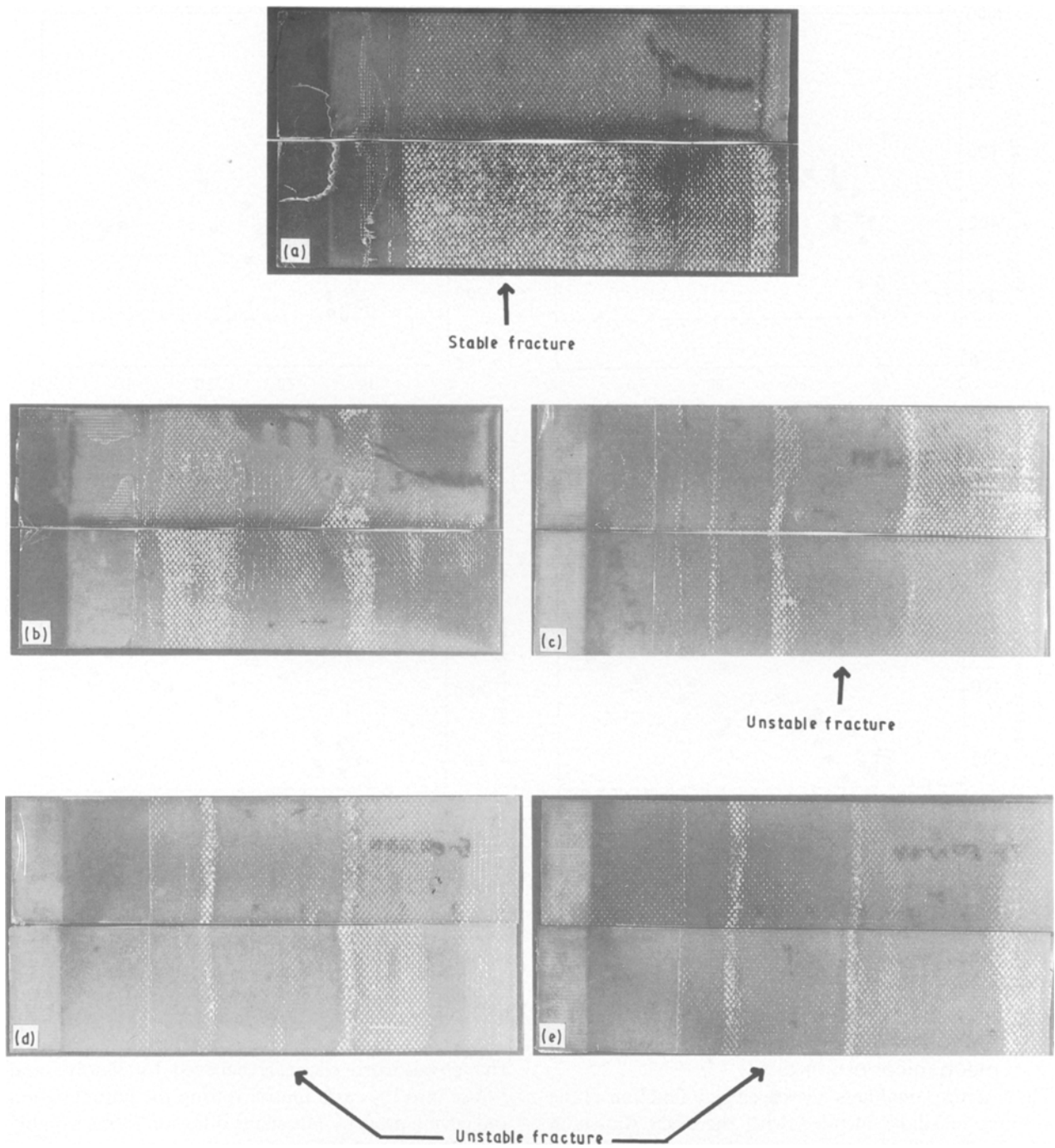


Figure 7 Macroscopic observation of the DCB specimen fracture surfaces for (a, b) 1, 2 unwashed 0.4 wt % methacryl silane, (c) methanol-washed 0.4 wt % methacryl silane, (d) unwashed 1.0 wt % methacryl silane, and (e) methanol-washed 1.0 wt % methacryl silane laminates.

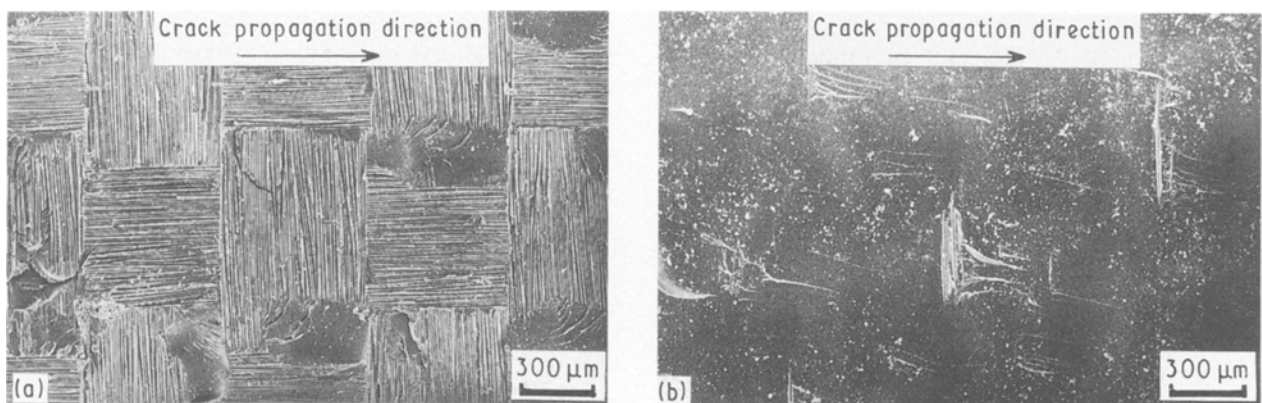


Figure 8 Scanning electron micrographs of the DCB specimen fracture surfaces: (a) stable crack growth and (b) unstable crack growth of unwashed 0.4 wt % methacryl silane specimen.

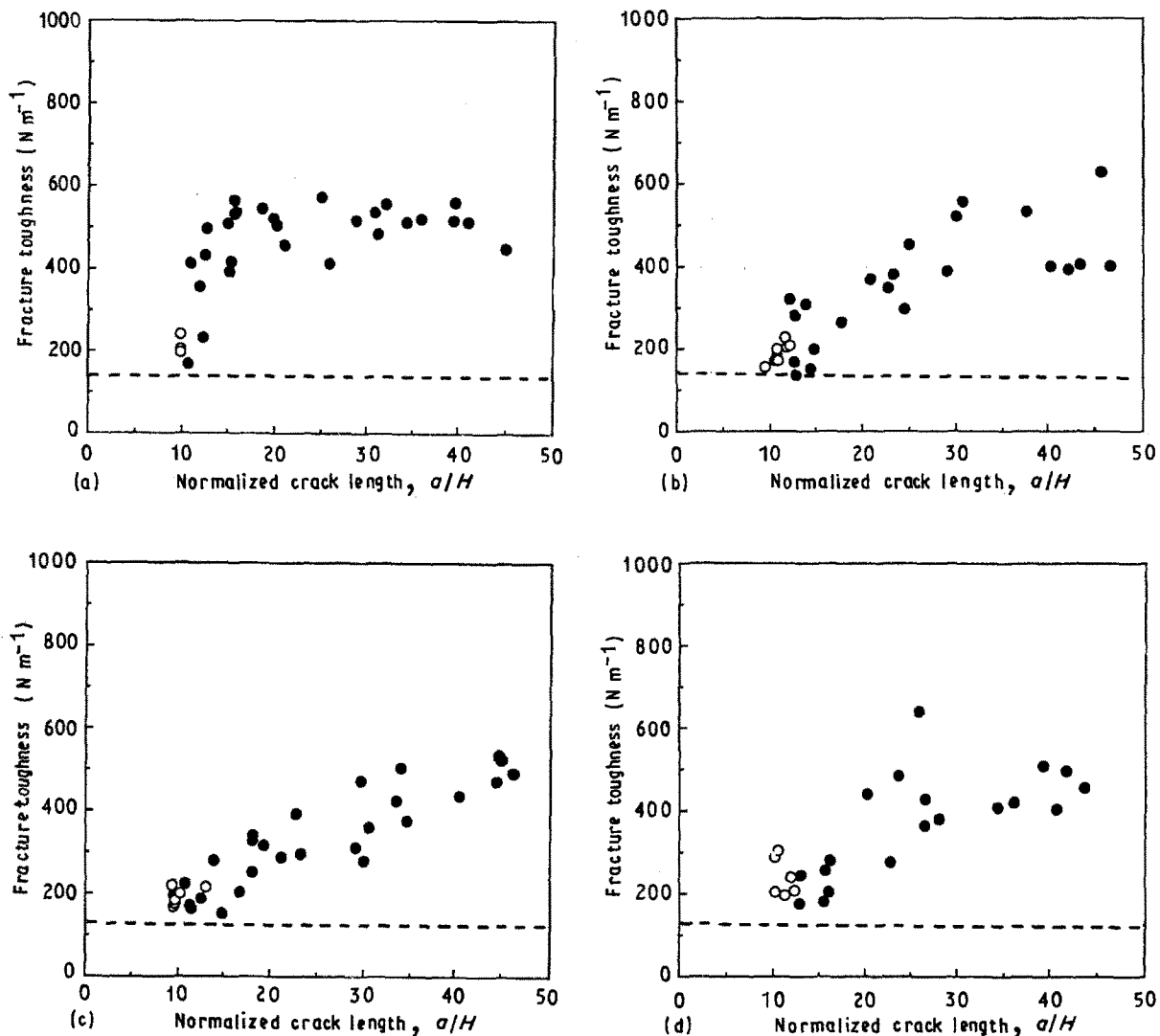


Figure 9 Relation between fracture toughness,  $G_{IC}$ , and crack propagating length for (a) unwashed 0.4 wt % methacryl silane, (b) methanol-washed 0.4 wt % methacryl silane, (c) unwashed 1.0 wt % methacryl silane, and (d) methanol-washed 1.0 wt % methacryl silane laminates. (○) Initiation, (●) propagation, (---) resin.

#### 4.2. Influence of physisorbed silane on fracture toughness and dynamic mechanical properties.

The fracture toughness decreased as a function of the amount of silane blended with the resin shown in Fig. 3. The fracture toughness of the silane-blended and cured resin was measured in order to study a simulated interphase of glass fibre/resin. The low fracture toughness of the silane-blended and cured resin indicates that the blended resin becomes a brittle material.

The value of  $T_g$  increases in proportion to the amount of silane cured with vinylester resin, as shown in Fig. 4. The value of  $T_g$  for the silane-blended and cured resin is connected with the cross-link density of the resin. The methacryl silane, which has a double bond chemical function, is an agent which can react with the double bond of the vinylester resin. From the results of  $T_g$  measurements, the silane-blended resin is seen to become a brittle material.

There is a difference in  $\tan \delta$  and dynamic modulus,  $G'$ , between the unwashed and methanol-washed methacryl silane 1.0 wt % specimen shown in Fig. 5. The  $T_g$  value at 140.2 °C for the unwashed specimen is higher than that at 138.0 °C for the methanol-washed

one. The unwashed specimen has much more physisorbed silane than the methanol-washed specimen. The physisorbed silane is believed to dissolve and diffuse into the resin matrix during the impregnation and curing process. The silane diffusion forms a highly cross-linked and brittle blend in the interphase; we presumed that in the unwashed 1.0 wt % silane specimen this was more cross-linked than that in the methanol-washed specimen. The  $G'$  value of unwashed specimen is higher than that of methanol-washed specimen over the temperature range 50–150 °C due to the cross-link density difference. The  $G'$  values over 150 °C in Fig. 7 had almost the same values because the laminate specimens were ductile above  $T_g$ . These results indicate that physisorbed silane affected not only properties of the interphase but also mechanical properties of the laminate.

#### 4.3. Influence of physisorbed silane and methanol-washed surface treatment on interlaminar fracture

Stable and unstable fracture were observed in the unwashed 0.4 wt % silane specimen. The stable fracture surface in Fig. 7a corresponds to the stable

fracture behaviour in Fig. 6a. However, after the 0.4 wt % silane specimen was washed by methanol solvent, the stable fracture behaviour disappeared in Fig. 6b. Fig. 8a and b demonstrate that the stable crack propagates along the glass fibre/resin interface and the unstable crack propagates through the resin between glass fibre fabrics. If the interfacial strength of the glass fibre/resin is excellent, the crack must propagate into the matrix resin. On the other hand, if the interfacial strength is poor, the crack must propagate along the interface. The interlaminar fracture pattern can be dependent on the adhesive strength of the interphase. For the unwashed 0.4 wt % silane specimen, the small amount of physisorbed silane on the glass fibre migrated into the resin and reduced the interfacial strength because the physisorbed silane could not bond with the glass fibre. The crack propagated along the interface and the stable fracture was observed in the unwashed 0.4 wt % silane specimen. However, when the amount of physisorbed silane for the unwashed 1.0 wt % silane specimen is sufficient, large amounts of physisorbed silane diffused into the resin and increased the cross-link density of the resin. The fracture toughness of the resin with the large amount of physisorbed silane became low, and then unstable fracture was observed. On the other hand, because the physisorbed silane for the methanol-washed 0.4 wt % and 1.0 wt % silane specimens was removed and the interfacial strength was improved, the crack propagated through the resin between glass fibre fabrics, and unstable fracture was produced.

The interlaminar fractures of each specimen shown in Fig. 7c–e illustrate almost the same fracture surface pattern. The large unstable fracture regions and small stable fracture regions shown in Fig. 7c–e are located in the same place in each specimen. In addition to the results in Fig. 7c–e, Fig. 9b–d indicates that the  $G_{IC}$  values increase with the increment of normalized crack length,  $a/H$ . The  $G_{IC}$  values of each specimen are therefore dependent on the normalized crack length. The fracture toughness,  $G_{IC}$ , at three normalized crack

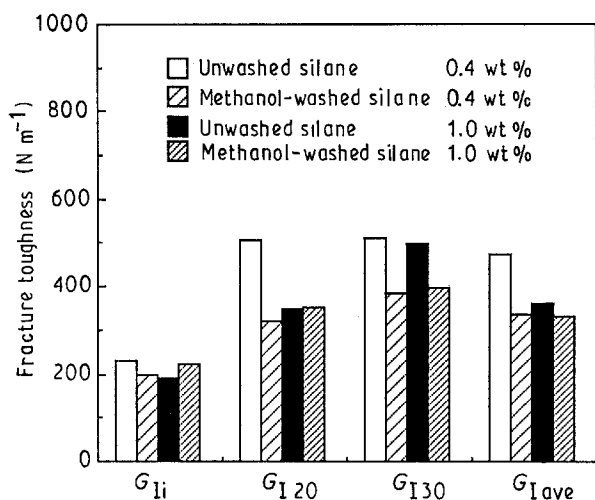


Figure 10 Relation between fracture toughness,  $G_{IC}$ , and crack propagating position for (a) unwashed 0.4 wt % methacryl silane, (b) methanol-washed 0.4 wt % methacryl silane, (c) unwashed 1.0 wt % methacryl silane, and (d) methanol-washed 1.0 wt % methacryl silane laminates.

lengths may be summarized as follows, avoiding the influence of the crack propagating position for fracture toughness: (i) the mean fracture toughness at initiation,  $G_{II}$ ; (ii) the mean fracture toughness at  $a/H = 20, 30$  ( $G_{I20}, G_{I30}$  respectively); (iii) the mean fracture toughness without  $G_{II}$  ( $G_{Iave}$ ). Fig. 10 shows  $G_{II}$ ,  $G_{I20}$ ,  $G_{I30}$  and  $G_{Iave}$  values for the laminate specimens. The  $G_{II}$  value of each specimen is close to that of the neat polymerized vinyl ester resin because cracking began from the space between the PTFE film/resin and propagated into the resin-rich region between the glass fibre fabrics. For the methanol-washed 0.4 wt % and 1.0 wt % silane specimens,  $G_{IC}$  values (except  $G_{II}$ ) are lower than those of unwashed specimens because the interfacial strength was improved and the crack propagated through the resin between glass fibre fabrics.

## 5. Conclusions

We conclude that the reduction of the fracture toughness of a laminate specimen was caused by an excessive amount of methacryl silane which made the vinyl ester resin brittle [12]. In addition, four conclusions were also drawn.

1. The physisorbed and chemisorbed silane layers adsorbed on glass fibre fabrics utilized for the printed circuit board industry were characterized. The amount of chemisorbed silane did not increase above a certain amount; on the other hand, the amount of physisorbed silane increased with increasing concentration of the silane solution. Methanol washing is possibly one way in which we can modify the interphase state and mechanical properties.

2. The value of fracture toughness,  $K_{IC}$ , in the silane-blended resin decreased and the cross-link density increased in proportion to the increase in the amount of the silane blended with the resin.

3. The cross-link density difference in the interphase between the unwashed and methanol-washed laminate specimen was observed in the DMS measurements. The physisorbed silane on the glass fibre fabric in the laminate specimen reacted with and hardened the vinyl ester resin.

4. The unstable fracture behaviour was caused by two factors. First, the large amount of physisorbed silane produced the unstable fracture because it increased the cross-link density of the resin and made it brittle. The crack propagated quickly through the physisorbed silane-blended resin. Second, because the physisorbed silane was removed by methanol washing, the chemisorbed silane directly bonded with the resin and the interfacial strength of the glass/resin was improved. The crack therefore propagated through the resin between the glass fibre fabrics. On the other hand, stable fracture behaviour was caused by poor interfacial strength. The small amount of physisorbed silane migrated into the resin and decreased the interfacial strength.

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