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Silane Coupling in Carbon Fibre-Reinforced Polyester Resin

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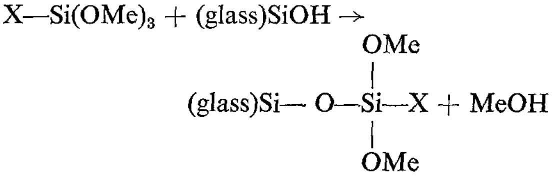
Previous work has suggested that organosilanes applied to carbon fibres do not improve the interlaminar shear properties of reinforced plastics containing these fibres. However, by first oxidising the fibres in an aqueous environment, hydroxyl groups can be put onto the surface and the silanes are then able to form silanol bonds to the fibre surface as they do in glass fibre-reinforced plastics.

This has been shown to occur in polyester resins containing carbon fibres that were first boiled in 70% nitric acid and then coated with two epoxysilanes. Tensile and interlaminar shear properties of these composites are presented, together with Stereoscan studies of the fracture surfaces.

1. Introduction

Considerable attention has been given to the problems of fully utilising the available strength of a reinforcing fibre and of reducing the propensity towards interlaminar shear in filament-reinforced plastics both by workers in the glass fibre field and, more recently, by those investigating carbon fibre-reinforced plastics. In the manufacture of glass-reinforced plastics (GRP) it is usual to coat the glass fibres with a bifunctional coupling agent – one of the organosilanes for example – prior to their incorporation in a resin. The coupling agent is supposedly capable of reacting with and forming covalent bonds with both polymer and glass, giving good adhesion and resistance of the interfacial bond to degradation by moisture absorption. Initially the glass fibre has a high surface energy, being covered with silanol (–SiOH) groups. Silane coupling agents react with these surface silanols through hydrolysable groups bonded to the silicon atom of the silane molecule. This may occur either directly or through silanol condensation with other silane molecules that have been prehydrolysed to silanols. The treatment lowers the surface energy of the glass and facilitates wetting by the low-polarity liquid resin. Many of the organofunctional groups available in silanes make them highly reactive with the majority of common thermosetting resins, but unlike the hydrolysable groups employed in the glass/silane bond, these groups must be bonded to the silicon in a hydrolytically and thermally stable manner. In simple terms, the bridging reaction might be represented, for the system glass/vinyltrialkoxysilane/polyester for example, as given by Schwaber and Rodriguez [1]:



$$\text{X—Si(OMe)}_3 + \text{(glass)SiOH} \rightarrow \text{(glass)Si— O—}\overset{\displaystyle \text{OMe}}{\underset{\displaystyle \text{OMe}}{\text{Si}}}\text{—X} + \text{MeOH}$$

The vinyl group, X, is able to co-polymerise with the styrene in the polyester by a free radical mechanism during cure.

This simple picture invites criticism, for it is difficult to show directly that covalent bonds occur. The evidence for the mechanism is largely circumstantial, although in a recent paper Johannson *et al* [2] conclude from tracer and electron microscopy studies that, contrary to previous experience, continuous silane films are formed which are covalently bonded to the glass. A discussion of some of the arguments for and against the covalent bridge is given by Sterman and Marsden [3] and we shall not enlarge upon them. But of relevance to carbon fibre work are some experiments of Schwaber and Rodriguez [1] which suggest that a direct silanol bond between resin and filler is not a *sine qua non* for improved properties of an ethylene/propylene terpolymer in which precipitated silica or calcined clay (aluminium silicate) were used as fillers. They found that considerable reinforcement occurred in both systems when silane coupling agents were used. While it may be acceptable to use the concept of the silane bridge between SiO_2 and the resin, it would be questionable to talk of covalent bonding in the case of the clay which has virtually no reactive –OH groups on its surface. They suggest that even in the absence of surface functionality there may be enough moisture present to enable hydrolysis of the silane to occur and a condensation between two or more silanols in the coupling agent could lead to the formation of a strong membrane of di- or polysiloxane around the filler particles. The membrane could then react with the resin and form a combined mechanical/chemical bridge between particle and resin.

Attempts have already been made to modify the surface of carbon fibres in order to improve the interfacial bond. The simplest methods used have been oxidation treatments of various kinds – boiling the fibre in concentrated nitric acid, for example. An early report by Herrick *et al* [4] describes the results of many surface treatment experiments. They show that the shear strength of CFRP is increased by 50% or more after boiling the fibres in concentrated HNO_3, although composite tensile strength is reduced. Oxidation in air and simple vacuum desorption at elevated temperatures also improve the shear strength somewhat. However, they report that the application of silane finishes not only did not raise the shear strength of their CFRP but in some cases brought about a deterioration in properties.

Prosen *et al* [5] also tried silane treatments, anticipating that the high adsorbed moisture content on the carbon would serve the same purpose as the silanols in glass. They used both a chlorisilane (NOL24) and an alkoxysilane (A186), applied either from solution or by the integral blend method in filament-wound composites. They found, for example, that the NOL24 finish applied to roving containing about 10 wt % of water gave higher shear strengths than when the finish was applied to pre-dried roving. However, neither result was as good as the properties of composites in which no finish was used. In view of the considerable amelioration of the properties of polymers reinforced with silane-coated clay particles cited earlier, these conclusions are unexpected, and the experiments now to be described were initiated in an attempt to improve upon these early results.To increase the chance of success it was decided to try to make the system as closely analogous to the glass/silane/resin system as possible. Therefore, instead of applying the silane to the carbon fibres as they were received from the manufacturer, the fibres were first oxidised by boiling in HNO_3.

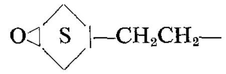
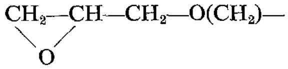
Hennig has discussed the graphitic oxide formed when graphite is treated with aqueous oxidising mixtures such as concentrated HNO_3/H_2SO_4 [6]. He suggests that such oxides always contain some hydroxyl and carboxyl groups, and although the concentration of —OH never approaches the total concentration of oxygen in the compound, there is nevertheless a large amount of residual hydrogen. There are various models for the structure of the oxide. Hennig proposes that most of the oxygen in graphitic oxide is bonded by meta-ether links to two separate carbon atoms, and that some of these ether groups may be hydrolysed to form hydroxyls. Ruess [7] had suggested earlier that the —OH groups were more probably a result of disorder among the meta-ether groups which results occasionally in available bonds occurring in the para- position. The oxygen in such a position would presumably not form an ether bridge but rather an —OH. Hennig also discusses a model due to Hofmann *et al*, who proposed that the —OH groups are vicinal to carbon double bonds: their model predicts an "ideal" composition of $C_8O_2(OH)_2$ for graphitic oxide. But, whatever the model, it appears that graphite oxidised under aqueous conditions could contain a large enough concentration of —OH groups to allow the carbon/silane/resin system to be treated as analogous to the glass/silane/resin system, provided the chosen silane and resin be compatible.

2. Experimental Work

The carbon fibre used in this work was Morganite fibre, described as RAE type I (high modulus), for which the following properties were supplied, with the fibre, by Mr L. N. Phillips at RAE: tensile strength mean value, 159 kg/mm^2 (standard deviation 27.9 %); elastic modulus 36.7 × 10^3 kg/mm^2 (s.d. 8.6 %); fibre diameter 7.93 μm (s.d. 7.67 %). The resin system was the Bakelite polyester SR 17449, using MEK peroxide catalyst and cobalt naphthanate accelerator, the constituents being compounded in the ratio 100 : 2 : 2, by weight. The fibres were given various treatments prior to fabrication into composites by the "leaky mould" technique.

Fibres were boiled in 70 % HNO_3 for 2 h and allowed to cool in the acid to room temperature, after which they were washed and dried. No weight change occurred during this treatment. The silanes listed in table I were then applied to samples of the boiled fibre from 30 vol % solutions in MEK. They were immersed in these solutions for 1 h and then removed and dried at room temperature. The silane coating increased the weight of the fibres by ~ 15 % which corresponds to a uniform coating thickness of approximately 0.5 μm. It is not likely, however, that coatings applied in this manner were uniform.

TABLE I Trialkoxysilanes, X—Si (—OR)$_3$

Organofunctional group X	Manufacturer's reference number*
1. β-(3,4-epoxycyclohexyl-) ethyl 	A186
2. γ-glycidoxypropyl  $CH_2—CH—CH_2—O(CH_2)—$	A187
3. mercaptopropyl $HS—CH_2CH_2CH_2—$	A189

*Union Carbide Corporation.
R is everywhere a methyl group.

The silane-coated fibres were combed out and 12 g samples of each were made up into composite bars measuring 300 mm × 24 mm × 2 mm which then contained a standard volume fraction of fibre of 0.40. Samples of untreated fibre, and others boiled in HNO_3 were also used to prepare control material. For comparison, a few specimens were prepared which contained fibre that had been oxidised by heating in air at 550°C for 5 h and 16 h. The properties of these were so poor compared with other materials that no attempt was made to put silanes onto fibres oxidised in this way.

In general the handling properties of treated fibres were similar to those of untreated ones. However, the mercapto-silane shortened the gel time of the polyester by about half, with the result that perfect penetration of the fibres by the resin was difficult to obtain with the leaky mould technique. There was a great deal of porosity and the distribution of fibres in the resin was non-uniform. As the table of results will show, all the mechanical properties of this material were poor. Nevertheless, in view of the results of Schwaber and Rodriguez with this silane, a second batch of specimens was prepared in an attempt to improve the quality of the composite.

The bars were sliced with a water-cooled diamond cutting wheel to give pieces 12 mm wide and of various lengths for tensile, flexure and interlaminar shear (short-beam flexure) testing. Waisted samples for tensile tests were made by grinding a continuous radius into each edge, the minimum width at the centre being about 1.5 mm. This was sufficient to give tensile failures at the minimum section rather than shear in the shoulders. For interlaminar shear strength determinations the short-beam flexure method was used, with a span/thickness ratio of about 5 (i.e. with a 1 cm span). All the specimens tested in this way, with the special exception of those made from air-oxidised fibre discussed later, failed by shear at the neutral plane. For long-beam flexure tests a span/thickness ratio greater than 12 was used. At least three and frequently up to six specimens of each material were tested by each method, the quoted results being mean values. The results of all mechanical tests are summarised in table II. Fracture surfaces of selected samples were examined in the scanning electron microscope for the effects of the treatments on the fibre surface and fibre/resin bonding.

3. Discussion of Results

3.1. Mechanical Properties

For a composite containing 40 vol % of high modulus fibre, the upper bound value of tensile strength should be roughly 63.5 kg/mm^2; and values of this order are given by Phillips [8] and others working with similar fibre. The composites containing untreated fibre used in this work therefore apparently develop only 83 % of the available fibre strength. The interlaminar shear strength is identical with that reported by Prosen

TABLE II Summary of mechanical test results

Fibre treatment ($V_f = 0.40$)	Tensile failure strength kg/mm^2	Flexural strength kg/mm^2	Interlaminar shear strength kg/mm^2	Ratio shear strength to tensile strength
As-received	52.8	38.4	2.06	0.039
Boiled 2 h in conc. HNO_3	56.6	47.5	2.52	0.045
Boiled in HNO_3 + A186	63.7	53.0	2.77	0.044
Boiled in HNO_3 + A187	62.0	56.8	2.66	0.043
Boiled in HNO_3 + A189 (1)	39.5	24.8	1.82	0.046
Boiled in HNO_3 + A189 (2)*	23.5	18.3	2.58	0.11
Heated in air at 550° C for 5 h	26.6	49.5	Tensile failure at 28.8	—
Heated in air at 550° C for 16 h	20.7	39.0	Tensile failure at 26.1	—

*In this repeat sample the resin cured so prematurely that specimens were nearly twice as thick as the standard and $V_f \sim 0.25$.

and Simon [9], but is somewhat lower than Phillips' own value of 2.37 kg/mm^2. After oxidising in HNO_3, the tensile strength is improved by some 7% and the shear strength is 23% higher. (For comparison, Herrick *et al* [4] improved the shear strength of epoxy-carbon composites by up to 40% by boiling for 24 h in 70% HNO_3.) Subsequent treatment with the epoxysilane, A186, was successful in increasing the tensile strength by a further 12% and the shear strength by 10% over those of the control (HNO_3 boil) samples. Thus, a total improvement of 35% in the shear strength has been obtained, and this is close to that obtained by Herrick *et al* [4] after a much longer treatment in HNO_3 alone. In view of the relatively crude method of applying the silane used in these experiments, it is expected that even better coupling could be obtained with a controlled process of application.

The A187 silane was only slightly less effective than A186, but at the first attempt the mercaptosilane (A189) appeared to reduce both the tensile and shear strengths by significant amounts. Because of the poor quality of the material a second batch of specimens was produced with the same fibre surface treatment. In this material the shear strength was found to be just a little higher than that of the control, but the tensile strength was again very low. In this instance the premature curing of the polymer caused the finished thickness of the composite bar to be too great and the volume fraction of fibre was only 0.25. The tensile strengths of both sets of mercaptosilane treated samples are therefore roughly the same on a strength/volume fraction basis. Only about 62% of the available fibre strength is being developed, perhaps because the excessively rapid curing rates of resins containing this silane resulted in high void contents. The ratio shear strength/tensile strength increases from 0.039 for the untreated fibre, to about 0.044 for all treated fibres (excluding the final mercaptosilane samples).

The properties of the composites containing fibres oxidised in air are so poor as to be of no direct value. The low tensile properties imply that the strength of the fibre is greatly reduced by the treatment, and, as will be seen later, the fibre surface is so badly pitted that this is not surprising. As might be expected, however, the interlaminar shear strengths are higher and in this case it appears that the improved bond arises simply from mechanical locking. In short-beam tests with a span/thickness ratio of 5 no shear failure could be induced in these samples.

Since the ratio "tensile stress at outer surface/shear stress at neutral plane" is given by $\sigma/\tau = 2l/d$, failure in tension at about 27 kg/mm^2 implies that the interlaminar shear strength may be at least as high as 2.7 kg/mm^2. However there is no practical gain if the tensile strength of the composite is so poor.

The apparent improvement in tensile properties shown by the results ought not, strictly, to have occurred. We conclude that the mode of gripping used, which was the conventional ceramic testing method of gripping dog-bone specimens without positive lateral pressure on the specimen faces, allowed some early shear failure in poorly-bonded materials even when the final failure appeared to be purely tensile. The improvement in tensile properties therefore merely reflects the real result, which is an improved interfacial bond. The true tensile strength would appear from the results to be about 63 kg/mm^2, which was the expected value for these composites, Similarly, the ratio of 12 used for long-beam flexure tests would, for the poorly-bonded specimens, have been sufficiently short to cause some shear as well as tensile failure and the improvement in flexure properties again only reflects the improved shear strength.

3.2. Structural Features

Fracture surfaces of composites containing untreated fibres showed the usual features that are characteristic of this kind of material. Fig. 1 shows that the surfaces of the pulled-out fibres are perfectly clean and smooth, and that the release of matrix contraction stresses has resulted in the complete separation of fibre and resin in the vicinity of the fracture surface.

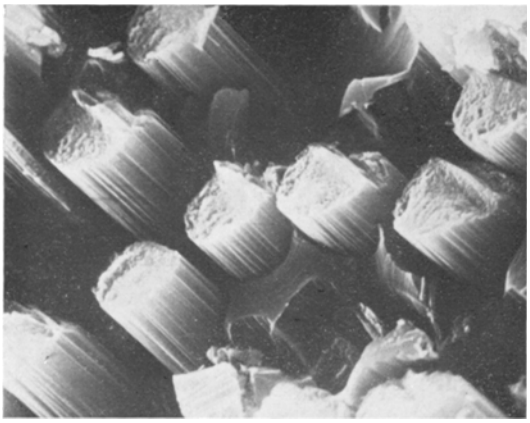


Figure 1 Fracture surface of polyester resin containing untreated carbon fibres (× 1540).

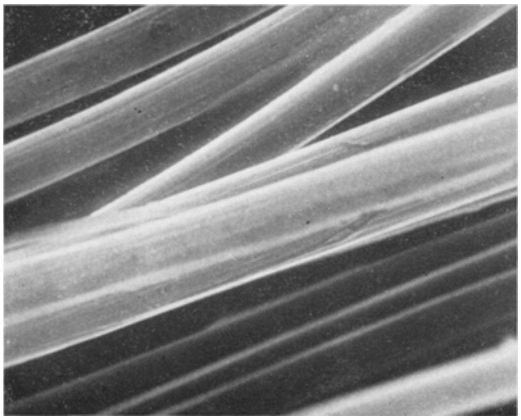


Figure 2 Surfaces of fibres boiled in 70% HNO_3 after fracture in shear of the composite containing them (× 1040).

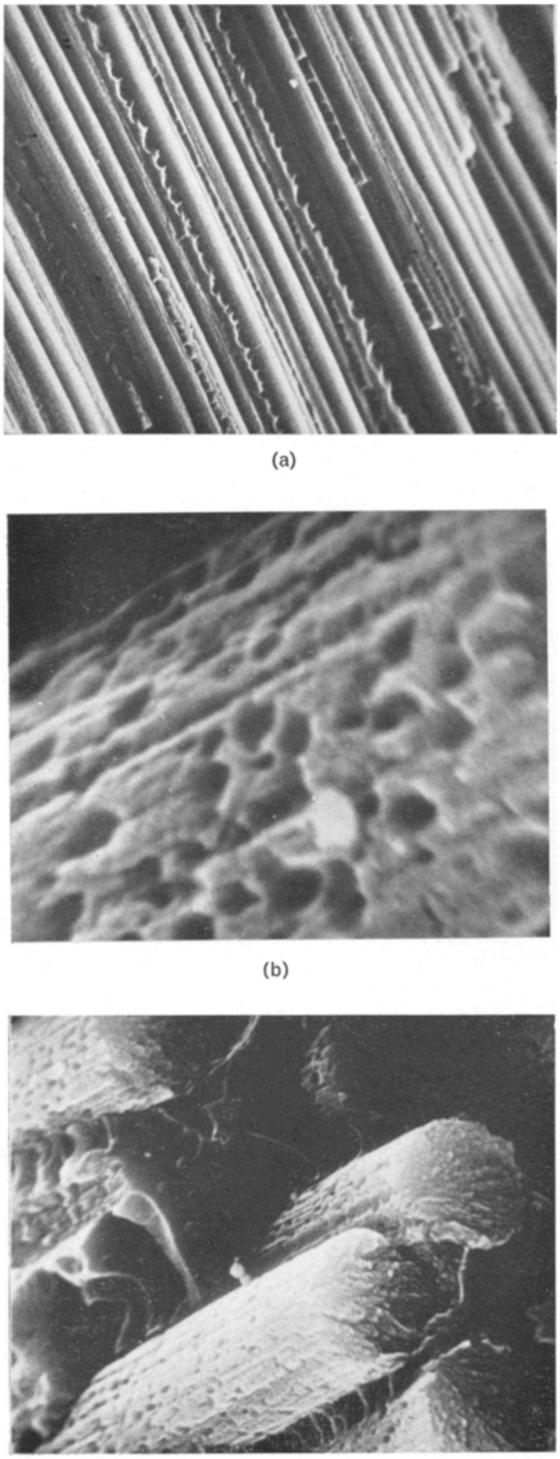
After boiling in HNO_3 the surface of the fibre apparently remains unchanged. The suggestion has been made that slight pitting occurs and thereby increases mechanical keying at the interface, but this is not visible at a magnification of 1040 × (fig. 2). Despite the improved shear strength of the composite, there is little difference in the overall appearance of the fracture.

Oxidation in air causes marked pitting of the fibre surface. Fig. 3 shows that the resin surface, where it has broken away from the fibre, is very ragged and quite unlike the usual clean, almost replica-like surfaces which can be seen when the fibre has not been treated. This is seen again in fig. 3b where the surface pitting of the fibre is more clearly shown. It can also be seen that the character of the fracture surface of the fibres is quite different, which suggests that the oxidation damage is not restricted to the fibre surface. There is also good residual adhesion between fibre and resin after fracture. The surface pits are shown at high magnification in fig. 3c. Fracture surfaces in this material usually show very short broken fibres rather than long pulled-out lengths.

Fig. 4 shows the fracture of a silane-treated specimen, in which it can be seen that there are both long pulled-out fibres and also short stubby ones. There remains tight adhesion at the interface after failure, which always appears to be associated with an improved shear strength. The surfaces of pulled-out fibres (fig. 5) show no traces of residual silane such as are normally observed by electron microscopy on treated glass fibre. The appearance is no different from that of the untreated fibre, but this may be because the silane/resin bond is stronger than the silane/ carbon bond.

4. Conclusion

In view of the work of Herrick *et al* [4] and Prosen *et al* [5] the results of our experiments strongly suggest that silanes can act as true coupling agents between the carbon surface and the polyester resin provided that the carbon is first treated to produce surface —OH groups. Both the epoxy- and the glycidoxysilanes are used commercially for coupling between glass fibre and polyester resin [3], the organofunctional groups both being able to co-polymerise with the styrene monomer contained in the resin. However, these silanes do not contain double bonds and could well react with the polyester by a chain transfer mechanism rather than by a free



(a)

(b)

(c)

Figure 3 Fracture of composite containing fibres oxidised in air: (a) fibres heated for 5 h at 550° C (× 410); (b) fibres heated for 16 h at 550° C (× 2190); (c) as 3b (× 10880).

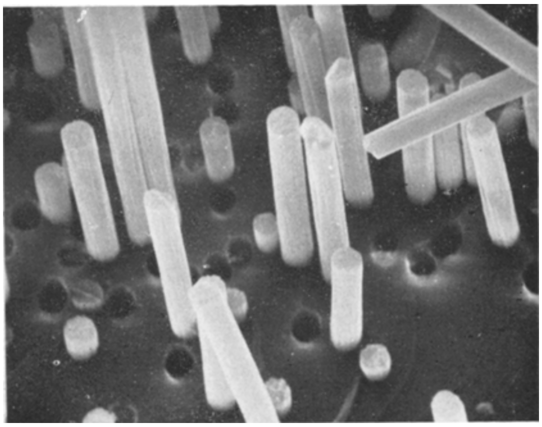


Figure 4 Fracture of composite containing silane-treated fibre (× 460).

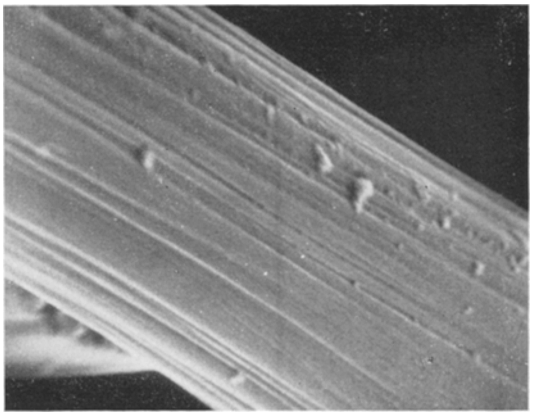


Figure 5 Higher magnification photograph of silane-treated fibre (× 5410).

radical mechanism. They are known to be only moderately effective in glass/polyester systems, compared with the highly reactive methacryloxypropylsilane, for example, whose structural similarity with the resin considerably enhances the compatibility of the two [10]. Treatment of the oxidised carbon fibre surface with this silane should therefore produce even greater improvements in dry strength. Both epoxysilanes should work successfully in a carbon fibre/epoxy resin system.

The reaction between the silane and the hydroxyl groups on the fibre is clearly more efficient for stress transfer than the formation of a mechanically tough membrane by polymerisation of the silane in the presence of adsorbed moisture which is the mechanism discussed by Schwaber and Rodriguez [1] and which has presumably occurred in the experiments of Herrick *et al* [4].

The properties of the mercaptosilane-treated composites are disappointing; there is some evidence of improved shear properties, but this improvement is masked by the poor structural quality of the composite resulting from the accelerating effect of the mercaptan group on the resin cure.

Schwaber and Rodriguez [1] carried out hysteresis loss measurements on their materials. They expected that if a covalent bridge was formed between filler particles and polymer then the damping of the material would be significantly reduced. They found that the samples with the mercaptosilane treatment, which showed greatest reinforcement, also had the highest hysteresis loss. On this evidence, principally, they concluded that there was not a full covalent bridge between filler and matrix. It is proposed to carry out stress/relaxation and damping experiments on the carbon fibre/polyester composites in order to confirm our suggestion that we have in this case obtained a covalent bond.

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References

1. D. M. SCHWABER and F. RODRIGUEZ, *Rubber & Plastics Age* **48** (1967) 1081.
2. O. K. JOHANNSON, F. O. STARK, G. E. VOGEL, and R. M. FLEISCHMANN, *J. Composite Materials* **1** (1967) 278.
3. S. STERMAN and J. G. MARSDEN, in "Fundamental Aspects of Fibre-Reinforced Plastic Composites", edited by R. T. Schwartz and H. S. Schwartz (Interscience, New York, 1968) ch. 7.
4. J. W. HERRICK, P. E. GRUBER, and F. T. MANSUR, (AVCO Corporation, Lowell, Mass.) Technical Report AFML-TR-66-178, part 1 (July 1966).
5. S. P. PROSEN, J. V. DUFFY, P. W. ERICKSON, and M. A. KINNA, Proc. 21st SPI Annual Technical Conference (1966) section 8-D.
6. G. R. HENNIG, "Progress in Inorganic Chemistry", Vol. 1, edited by F.A. Cotton (Interscience, New York, 1959) p. 125.
7. G. RUESS, *Monatsh. Chem.* **76** (1947) 381
8. L. N. PHILLIPS, RAE, Farnborough, Technical Report 67088 (1967).
9. S. P. PROSEN and R. A. SIMON, *Plastics and Polymers* (June 1968) p. 241.
10. K. H. GRUNDY, "Chemical Finishes for Glass Fibres", paper presented at the British High Polymer Research Group Meeting at Moretonhampstead, April 1967.