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STUDY OF BONDING BETWEEN GLASS AND PLASTIC
IN GLASS-REINFORCED PLASTICS--EXTENDED WORK

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INTRODUCTION

The general objective of this research program is to evaluate the effect of deliberate and known chemical bonding between the glass reinforcement and the plastic matrix of a glass-reinforced plastic composite material.

Previous reports¹⁻³ described studies of the methods by which siliceous surfaces can be modified with organic groups that are bonded to surface-based silicon atoms by silicon-carbon bonds. These surface-modifying organic groups can be chosen for specific interaction with the resin matrix of the composite material. Surface modification was accomplished in two steps:

- (1) Reactive-intermediate groups such as chlorine atoms, fluorine atoms, or alkoxyl groups were bonded to surface-based silicon atoms.
- (2) Reactive-intermediate groups were converted to surface-modifying organic groups by reaction with an organometallic compound.

The objectives of the present phase of this project are (1) to evaluate the effects of surface modification upon a realistic composite material (such as a filament-wound NOL ring or a woven glass cloth laminate), (2) to study optimum characteristics for surface-modifying groups and improved methods for obtaining them, and (3) to study methods for application of surface modification to reinforcement materials other than glass and silica.

This is the fourth quarterly report for this phase of the project. Work during this quarter was directed primarily toward the preparation of experimental laminates for evaluation.

SUMMARY

Procedures for the fluorination and alkylation of glass fabric for subsequent use in the production of laminates have been established.

Several test specimens were made from untreated glass fabric in order to perfect a technique for the production of laminates. The lay-up procedure for the specimens to be used in the evaluation studies has been chosen.

A detailed study of the effect of surface modification upon the position of the Si-O fundamental stretching frequency was made. The study required attenuated total reflection (ATR) spectral techniques for the attainment of highly resolved spectra.

DISCUSSION AND EXPERIMENTAL

Fluorination of Glass Fabric

Fluorination of a glass fabric serves a twofold purpose. First, residual carbon remaining after the manufacturing procedure is burned off with fluorine gas leaving a clean surface. Second, reactive-intermediate groups ($-\overset{|}{\text{Si}}-\text{F}$) formed on the surface can be converted to a desired surface modifying group ($-\overset{|}{\text{Si}}-\text{R}$).

Table I shows the results of carbon analyses before and after fluorination of the "E"-glass fabrics which will be used for laminate production. The small variation in carbon content after fluorination of the three samples indicates that this is not surface contamination but carbon which is trapped in the matrix of the "E"-glass fiber. Therefore, the first purpose of fluorination is met--the removal of surface contamination.

Table I

CARBON ANALYSIS OF GLASS FABRICS
BEFORE AND AFTER FLUORINATION

Glass Fabric ^a	Carbon Analysis before Fluorination (ppm carbon)	Carbon Analysis after Fluorination (ppm carbon)	Remarks
2P181 ^b	215	89	Samples were degassed at 5×10^6 mm Hg and 100°C for 24 hours before carbon analysis.
1P81 ^c	238	88	
1P81	247	91	

^a2P181 and 1P81 "E"-glass fabric supplied by Coast Manufacturing and Supply Co., Livermore, Calif.

^b2P181 supplied with starch oil sizing.

^c1P81 heat cleaned and washed to neutral pH by manufacturer.

Fluoride analysis for 1P81 glass fabric and Cab-O-Sil after fluorination and high vacuum degassing indicated surface population of 5.6 and 5.3 fluorine atoms per 100 Å, respectively. The presence of polyvalent cations should result in ionic fluorides and a somewhat higher fluoride population. Since the 1P81 glass fabric was water washed to neutral pH, its surface should contain few, if any, cations such as Ca⁺⁺, and therefore approximate the surface of silica. This appears to be the case since the fluorine atom population for both Cab-O-Sil and 1P81 glass fabric are very nearly the same.

Alkylation Reactions

A series of fluorinated glass fabric samples was alkylated with selected organometallics to gain information about the generation of organic surface groups with terminal substituents that may undergo reaction with the resin phase. The data on these samples are summarized in Table II.

Table II

ALKYLATION REACTIONS OF FLUORINATED GLASS FABRICS

Glass Fabric	Reagent	Solvent	Product (-Si = Silicon Atom in Glass Surface)	Carbon Analysis Groups per 100 Å
1. 2P181	Allyl-magnesium bromide	Tetrahydrofuran	$-\text{Si}-\text{CH}_2-\overset{\text{H}}{\underset{ }{\text{C}}}-\overset{\text{H}}{\underset{ }{\text{CH}}}$	5.52
2. 1P81	Allyl-magnesium bromide	Diethyl ether	$-\text{Si}-\text{CH}_2-\overset{\text{H}}{\underset{ }{\text{C}}}-\overset{\text{H}}{\underset{ }{\text{CH}}}$	18.1
3. 1P81	Pentane-1,5-di-magnesium bromide followed by oxidation of the terminal -CH ₂ -MgBr group	Diethyl ether	$-\text{Si}-(\text{CH}_2)_5-\text{OH}$	12.1

The terminal hydroxyl group on a five-carbon chain (No. 3, Table II) and 1P81 glass fabric will be used for the preparation of epoxy laminates in the present work.

Since diethyl ether is a poor solvent for alkoxides and polymers of acetone, the high surface population of groups (Nos. 2 and 3, Table II) can be reasonably attributed to organic residues which were not removed by this solvent. Polymers of acetone can possibly be formed by aldol condensation catalyzed by basic magnesium alkoxides formed in the Grignard reaction. In future, tetrahydrofuran will replace diethyl ether in the pentane-1,5-dimagnesium bromide system and acetone will be omitted from the fabric washing procedure.

Laminate Preparation

To investigate various lay-up techniques, several 4 in. x 4 in. test specimens were made using untreated 2Pl81 glass fabric. The results obtained from four 8-ply laminates and one 14-ply laminate, using differing lay-up techniques, were very satisfactory. The calculated void contents of the 8-ply specimens ranged from 0.1 to 1% by volume. The calculated value for the 14-ply specimen was 10%.

The resin formulation used for the test laminates is as follows: 100 parts Epon 825, 91 parts Nadic Methyl Anhydride, and 0.3% by weight (based on total charge) N-benzyl dimethylamine initiator.

The 6 in. x 6 in. x 0.125 in. 12-ply laminates which will be used for the evaluation studies will be prepared from the above resin formulation, using the following lay-up procedure suggested by Eakin.⁴ The resin is divided into five equal portions, the first of which is placed on a sheet of cellophane. Three 6 in. x 6 in. squares of glass fabric are placed on the resin, and the squares are covered with another portion of the epoxy formulation. This procedure is repeated in 3-ply increments until the lay-up contains 12 plies. The cellophane is folded over the laminate and sealed on three sides. The fourth side is folded loosely to allow venting of gases. The lay-up is then carefully and gently rolled to work the resin into the fabric and to displace trapped air. The lay-up is placed in a cold laminating press and the platens closed very slowly against 0.125 in. gauge blocks. The pressure is increased to 125 psig, and this pressure is maintained throughout the curing cycle at 240° F.

Infrared Studies of Surface Modified Silica

In the course of other work in this laboratory, an infrared spectral technique was developed⁵ which allows semi-quantitative investigation of broad, intense absorption regions such as the Si-O stretching frequency of silica. Spectral data are obtained for inorganic solids by applying a thin film of dry, finely divided solid, e.g., Cab-O-Sil, to the face of a single reflection KRS-5 ATR prism.* The spectrum is run at high sensitivity and 5X scale expansion. The high degree of resolution obtained allows assignment of spectral band positions reproducibly within $\pm 2 \text{ cm}^{-1}$.

From the infrared spectra of a series of surface modified silicas it appears that the frequency at which lattice Si-O bonds of Cab-O-Sil absorb is related to the surface environment. Using untreated Cab-O-Sil (175-180 m^2/g specific surface), containing surface silanol groups, as a reference silica, it was shown that surface modification results in a shift (Δ value) in the position of the absorption band due to asymmetric Si-O stretching. The direction of the shift (positive or negative Δ value) is related to the tendency of the surface modifying groups to withdraw or donate electrons. Positive shifts (to lower frequencies) resulted from electron donating groups such as methoxy, and negative shifts (to higher frequencies) resulted from electron withdrawing groups such as halogen. No shift in the Si-O position was observed with methyl or phenyl as surface-modifying groups.

A study of these effects should contribute to a better understanding of the chemistry of surface modification, and of the role that surface modified inorganic fibers may play in the production of improved reinforced materials. A detailed study of this nature must be reserved for a future effort.

Hydrogen bonding of polar adsorbates to the surface Si-OH groups has the overall effect of withdrawing electrons from the surface. The effect is observed as a shift in the lattice Si-O absorption band. Table III

* Connecticut Instrument Corporation single ATR assembly.

summarizes the effect of adsorbed phenol (500 mole % on SiO₂) on the position of the Si-O stretching frequency of Cab-O-Sil M₇.

Table III

EFFECT OF ADSORBED PHENOL ON THE
INFRARED SPECTRUM OF CAB-O-SIL

Sample	Untreated	A	B	C	Control
SiO ₂ lattice frequency (cm ⁻¹)	1080	$\frac{\Delta}{1085 - 5}$	$\frac{\Delta}{1083 - 3}$	$\frac{\Delta}{1078 + 2}$	$\frac{\Delta}{1079 + 1}$

Samples A-C illustrate the effect of adsorbed phenol and the step-wise attempts to remove the adsorbate.

Sample A represents the material after absorption of phenol and vacuum degassing at 1 mm Hg at room temperature for 1/2 hour. Sample B is an aliquot of A after it was rigorously degassed at 1 mm Hg at 70° C for 66 hours. Sample C is an aliquot of A which was thoroughly washed with benzene and vacuum dried. The control sample represents Cab-O-Sil after washing with benzene and vacuum drying.

Replacement of the surface hydroxyl group with the more electro-negative chlorine atom has the overall effect of shifting the Si-O absorption to higher frequencies (1091 cm⁻¹, $\Delta = -11$). This effect, as reported earlier,⁶ is presently attributed to the electron withdrawing tendency of the halogen. Hydrolysis of the surface Si-Cl groups to Si-OH groups restores the lattice Si-O band to its original position, as can be seen in Table IV.

It has been observed that replacement of surface hydroxyl groups with less polar methyl, phenyl, or β -hydroxyldodecyl groups does not alter the position of the lattice Si-O band within the limits of sensitivity of the method.

Methoxylation of the surface causes a large shift in the positive direction. This is understandable on the basis that the highly polarizing -OCH₃ group may serve as an electron donor to the silica surface. The

resultant increase in electron density between surface Si and O lattice atoms should be reflected in a shift of the Si-O stretching frequency at 1080 cm^{-1} to longer wavelengths. Table IV illustrates the magnitude of the effects of alkylation and alkoxylation on the position of the lattice Si-O stretching frequency in the high-surface Cab-O-Sil.

Table IV

EFFECT OF SURFACE MODIFICATION ON LATTICE Si-O FREQUENCY

Surface Species	Si-O (cm^{-1})	Δ (cm^{-1})	C-H Stretching Position ^a (cm^{-1})
-CH ₃	1081	-1	2979, 2959, 2856
control	1081	-1	
-C ₆ H ₅	1079	+1	3082, 3062
control	1078	+2	
$\begin{array}{c} \text{OH} \\ \\ -\text{OCH}_2\text{CC}_{10}\text{H}_{21} \end{array}$	1078	+2	2964, 2932, 2860
control	1081	-1	
hydrolyzed	1082	-2	
-OCH ₃	1073	+7	2993, 2961, 2859
control	1081	-1	-- 2965, 2862
hydrolyzed ^b	1075	+5	2994, 2960, 2858
hydrolyzed ^c	1079	+1	-- -- 2859

^aValues obtained from transmission spectra of thin powder samples between NaCl discs on a linear wave number Perkin Elmer 221 spectrophotometer.

^bSample boiled in H₂O for 20 min and dried.

^cSample boiled in dilute NaOH, rinsed with dilute HCl, then rinsed with H₂O, and dried.

Alkylated surfaces were prepared through the reaction of the appropriate metal alkyl with halogenated Cab-O-Sil. The control samples received the identical treatment except for the halogenation step.

β -hydroxydodecoylated silica was prepared from the BF_3 -etherate catalyzed reaction of dodecene oxide with the silanol surface of Cab-O-Sil. The control was a similar reaction uncatalyzed.

Methoxylation of the Cab-O-Sil surface was carried out in a stainless steel high pressure bomb reactor at 200°C for 21 hours. The control was obtained by boiling Cab-O-Sil in CH_3OH for five minutes. The appearance of weak C-H bonds in the control indicates a small degree of hydroxyl replacement resulting from this mild treatment. The presence of C-H bonds in the transmission spectrum was a positive indication of the surface environment. The intensity of these bonds in relation to the lattice Si-O intensity was used as a qualitative measure of the extent of surface coverage and the degree of hydrolysis. No attempt has been made to account for the small differences in the C-H frequencies that appear in these samples.

Analytical Studies

Fluoride analyses were carried out using an Orion fluoride-ion electrode and a Corning Model 12 expanded scale pH meter. The glass sample was hydrolyzed in 2N NaOH . An equal volume of $2\text{N H}_2\text{SO}_4$ was added, and the electrode response to the solution is read in millivolts. The corresponding F^- concentration is determined from a standard curve for fluoride ion in $1\text{N Na}_2\text{SO}_4$ solution.

FUTURE WORK

The preparation and evaluation of experimental laminates will receive all effort expended in the remaining work period.

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