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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 reports[1,2] 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 (Cl), fluorine atoms (F), or alkoxyl groups (OR) 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: first, 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); second, to study optimum characteristics for surface modifying groups, and improved methods for obtaining them; and last, to study methods for application of surface modification to reinforcement materials other than glass and silica.

This is the second quarterly report for the current phase of work.

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[1] D. L. Chamberlain, Jr., Summary Technical Report No. 1, "A Study of Bonding Between Glass and Plastic in Glass-Reinforced Plastics, Phase I," Contract NASr-49(14), July 31, 1964.

[2] D. L. Chamberlain, Jr., Summary Technical Report No. 2, "A Study of Bonding Between Glass and Plastic in Glass-Reinforced Plastics, Phase II," Contract NASr-49(14), November 15, 1965.

DISCUSSION

Rate-of-Chlorination Studies

The rate of formation of surface-based Si-Cl groups must be known to carry out a continuous treatment process such as in the preparation of NOL ring test specimens.

Rate-of-chlorination studies were carried out on low-iron silica, using phosgene ($COCl_2$) at 500°C. Samples were degassed for 16 hours at 125 to 160°C, and at a pressure of less than 10^{-5} torr. The data in Table I represent only one determination at each temperature and indicate that the rate is not rapid enough to be useful in a continuous process at 500°C.

Table I

RATE OF CHLORINATION OF LOW-IRON SILICA WITH PHOSGENE AT 500°C

Time (minutes)	Chlorine Content (micrograms per gram)
0.75	0.7
18	19
60	32
120	62
180	35

Another method for following the rate of chlorination or fluorination of a siliceous surface is infrared spectrophotometry. Attempts to use this optical tool early in this study were not very fruitful because of the lack of resolution of the broad intense Si-O absorption band that occupies the region between 1000 and 1300 cm^{-1} in the usual transmission spectrum of finely divided silica. The Si-Cl, Si-F, and Si-C stretching frequencies also found in this region are either completely or partially

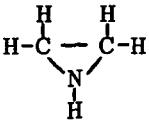
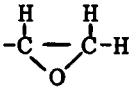
obscured by the Si-O band. Other work in this laboratory has resulted in the development of infrared spectral techniques that permit much better resolution in regions of intense absorption. (Details of this technique will be described in a later report.) With this technique one may observe the Si-O stretching absorption as a sharp well-defined peak. This absorption peak is due to the lattice Si-O bonds in the bulk of the material, and we have found that the position of this sharp peak is determined by the environment of the surface Si-O bonds. In this particular case, the replacement of surface OH groups with chlorine atoms results in a shift in the position of lattice Si-O absorption. This point is illustrated in Table II by the data on the chlorination of silica (Cab-O-Sil) with phosgene at 500°C. The Si-O lattice absorption appeared at 1080 cm^{-1} in the original silica. After a reaction time of 105 minutes, the position of this peak shifted 11 cm^{-1} to a higher frequency of 1091 cm^{-1}. The hydrolysis of this sample of chlorinated silica resulted in the return of the lattice absorption to 1081 cm^{-1}. Further, the OH absorption at 3757 disappeared upon chlorination for 105 minutes, and reappeared at 3750, instead of 3757, when the Si-OH group was regenerated by hydrolysis. We have no explanation for this discrepancy at present, but it would seem to be related to a rearrangement of the surface as the OH groups are either displaced or regenerated.

Table II

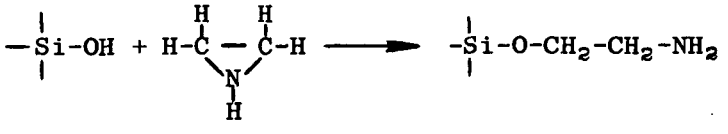
EFFECT OF CHLORINATION UPON THE SPECTRUM OF FINELY DIVIDED SILICA

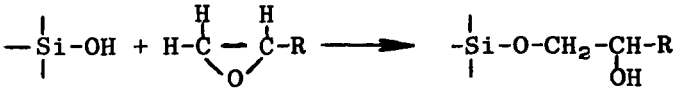
Reagent	Reaction Time (min)	Halogen Concentration (ppm)	Infrared Absorption Bands (CM^{-1}) OH	Si-O	Comments
Phosgene ($COCl_2$)	0	0	3757	1080	The OH band (Si-OH) gradually disappeared.
	10	--	3757	1080	
	15	--	3757	1081	
	60	1,634	3757	1087	Chloride analyses were run after 4 months storage in a dissicator.
	105	23,160	absent	1091	
	105 after hydrolysis		3750	1081	The OH band returned after hydrolysis of the Si-Cl.

Reactive Intermediate Studies

Surface modification of high-surface silica was studied with two reagents that may be useful in the diagnostic study of bonding mechanisms: ethylenimine,  , and dodecene oxide,  .

The imine and the epoxide rings should both open, with proper catalysis, by reaction with surface silanol groups:





The 2-aminoethyl and 2-hydroxyethyl side chains provide functional groups for reaction with an epoxy resin. The Si-O-C linkage between the substrate and the organic group should provide sensitivity to water and other reactive agents.

The reaction of low-iron silica with ethylenimine catalyzed by boron trifluoride gave a product which, after thorough solvent extraction and thorough desorption, contained 210 ppm of carbon. This corresponds to 25 ethylenimine groups per 100 Å^2, from which, assuming complete coverage of available Si atoms with polymeric chains, one may calculate an average of 3.4 ethylenimine units per chain. The degree to which this homopolymer is chemically bonded is not known, but it was not removed by exhaustive extraction with ethanol, in which the low molecular weight polymer is soluble. However, any conclusions based upon this one experiment must be verified.

A similar experiment was carried out with 1,2-epoxydodecane (dodecene oxide) on high-surface silica of 196 meter^2/gram specific surface. After thorough washing and desorption, the carbon analysis was 18,800 ppm. This value corresponds to 4.8 carbon atoms/100 Å^2 or 0.4 dodecyl groups per 100 Å^2 (5% coverage).

Alkylation Studies

Chlorinated low-iron silica, of 0.21 meter^2/gram specific surface, was treated with the appropriate organometallic reagent to produce surface-modified silica with functional modifying groups that would permit chemical interaction with a resin matrix. In the equations to illustrate this (below), $-\overset{|}{\underset{|}{Si}}-Cl$ represents a silicon atom, in a silica surface, bonded to the reactive intermediate chlorine atom.

10-Carboxydecyl groups were produced by using the bifunctional Grignard reagent from 1,10-dibromodecane:

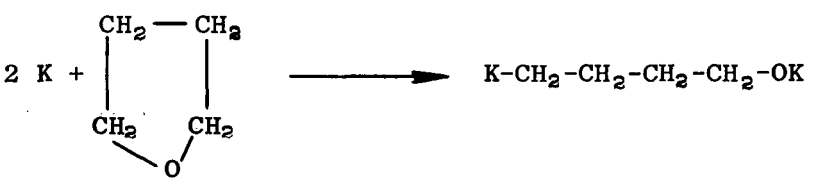
$$-\overset{|}{\underset{|}{Si}}-Cl + BrMg(CH_2)_{10}MgBr \longrightarrow -\overset{|}{\underset{|}{Si}}-(CH_2)_{10}MgBr$$

$$-\overset{|}{\underset{|}{Si}}-(CH_2)_{10}MgBr + CO_2 \xrightarrow{\text{(hydrolysis)}} -\overset{|}{\underset{|}{Si}}-(CH_2)_{10}\overset{O}{\overset{\|}{C}}-OH$$

The final product (after thorough cleaning) had a carbon content of 24.7 ppm, which corresponds to about 7% replacement of the available surface hydroxyl groups with $-(CH_2)_{10}-C\overset{O}{\underset{OH}{}}$ groups.

Allyl groups were produced on silica surfaces by using the Grignard reagent. The allyl group, useful in its own right, offers potential routes for the synthesis of terminal acid and glycol functions. A carbon content of 38.7 ppm was achieved for allyl groups on low-iron silica. This corresponds to 3.2 allyl groups per 100 $Å^2$, or a conversion of 43% of the theoretical surface sites.

4-Hydroxybutyl modified silica should be readily prepared from the organometallic reagent derived from the cleavage of tetrahydrofuran with potassium. Certain ethers are readily cleaved by alkali metals.[3] Recent difficulties with the use of tetrahydrofuran in this laboratory indicated that ring cleavage had occurred, and an attempt was made to capitalize on this otherwise undesirable reaction. The reaction of potassium with tetrahydrofuran,



was attempted several times. In no attempt was it possible to isolate an identifiable product.

Analytical Studies

The capability to quantitatively analyze siliceous material for surface-bonded organic species is a must for this work. To facilitate this capability a Leco Analyzer (Model 516-000) was made available by the Institute for use on this project. This apparatus is currently being completely renovated to obtain maximum accuracy and reproducibility. This renovation will be done at no expense to the project and should be completed during the next quarter.

[3] R. G. Jones and H. Gilman, Chem. Rev. 54, No. 5, 839-40 (1954).

Dilatometer Studies

Previous dilatometer studies[2] were carried out with polyurethane rubbers. To accurately evaluate the effect of autohesion as a bonding mechanism, it was necessary to use a castable rubber that was compatible with hydrocarbon surface-modifying groups. The PBAN polymer, used for castable rubber propellants, appeared to be the best choice for our purpose. This polymer was formulated with 14.28% DOA (dioctyl adipate), 17.41% DER-332 (diglycidyl ether of Bis Phenol-A), 3.50% NMA (Nadic Methyl Anhydride), and 64.81% polybutadiene-acrylonitrile copolymer. Dilatometer strips were prepared with 55% low-iron silica.

The PBAN polymer proved to be useless for dilatometer experiments because of a very low cohesive strength. As a result, the samples ruptured at a very low extension, and no useful information was obtained.

Filament Reinforcement Studies

The major objective of this phase of the work is to evaluate the effect of surface modification upon the physical properties of a glass-filament reinforced plastic.

Two systems will be evaluated more or less concurrently: NOL rings by the interlaminar shear test and fabric laminates (hand lay-up) by the ASTM D790-63 flexural test. All equipment for this test is available except the ringwinder. This apparatus will be supplied as capital equipment by the Institute.

The details for this work are being formulated.

FUTURE WORK

Future work will be concerned primarily with evaluation studies. Surface modification studies will be pursued where necessary to support the evaluation program.