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A STUDY OF BONDING BETWEEN GLASS AND PLASTIC IN GLASS-REINFORCED PLASTICS: PHASE II

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I INTRODUCTION AND SUMMARY

This report covers work done during the third quarter of Phase II of this study of direct bond formation between glass and plastic in glass-reinforced plastic materials. Phase II is concerned with alkylation of surface-based silicon atoms (to produce Si-R groups) from reactive intermediate surface groups. Phase I was a study of the preparation of reactive intermediate surface groups (e.g. Si-Cl groups) from the available surface-based silanol (SiOH) groups.

Peel tests were run on glass and silica rings that had been treated to produce n-butyl groups on the surface.

Contact angle measurements were made for a series of organic liquids in cleaned and on surface-treated glass microscope slides.

Dilatometric measurements were made on six specimens of glass-filled GE RTV-615 Silicone elastomer. This polymer is not satisfactory for dilatometric evaluation of adhesion, because of its low cohesive strength. Polyurethane rubber appears to be a satisfactory replacement for the silicone rubbers.

Direct measurement of organic groups on glass or silica of low specific surface continues to be a challenge. The procedure for determination of carbon in steel was adapted to analysis for carbon compounds on glass surfaces. The method is basically satisfactory. Further work is necessary to permit differentiation between carbon <u>on</u> the glass and carbon <u>in</u> the glass.

II DISCUSSION

Peel Tests

Peel tests were performed on glass cylinders, by the method described earlier,[1] for the purpose of evaluating the effect of surface modification on glass and silica materials. In Table I are summarized the data on preparation and testing of the samples. In Figure 1 are shown the recorder traces obtained during these peel tests. Because of the wide fluctuations in the average peel force, the precise value of the average was not calculated. The erratic nature of the traces is readily explained as due to small, but frequent, areas of the tape that did not adhere to the substrate. These areas are readily visible on these transparent tapes before the tape is unrolled for application. The extent of occurrence of these areas of poor bonding vary from roll to roll. They are, apparently, related to aging of the tape in the roll.

Specimens 1 and 2 (Figs. 1a and 1b) were untreated Pyrex glass. Specimens 3,4, and 5 (Figs. 1c, 1d, and 1e) were fluorinated with fluorine gas and then hydrolyzed with water. This treatment was used to maximize the concentration of surface-based hydroxyl groups, which should result in a maximum value for the critical surface energy, and therefore maximum adhesion. Specimens 6, 7, and 8 (Figs. 1f, 1g, and 1h) were fluorinated and alkylated with n-butyl lithium. The reaction

$$\geq Si - Cl + n - C_4H_9Li \rightarrow$$

$$\geq Si - n\ C_4H_9 + LiCl$$

should result in a surface in which $\geq SiOH$ groups, originally present, are replaced with $\geq$ Si-butyl groups. Among the many factors which

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[1] Report No. 6, Quarterly Report No. V, Contract NAsr-49(14), May 26, 1965.

Table I

PEEL TEST DATA ON 2 INCH-o.d. PYREX RINGS

Sample No.	Surface Treatment Prior to Tape Application	Tape Width and Type	Conditioning	
			Before Wrapping	After Wrapping
1	No treatment.	3/4 in. - Scotch glass filament	5 days	24 hours
2	No treatment.	3/4 in. - Scotch glass filament	5 days	24 hours
3	Fluorination with F_2 at 180°C in 1 hour Hydrolyzed with distilled water	1 in. - Scotch Core No. 0300	16 hours	22 hours
4	Fluorination with F_2 at 180°C in 1 hour Hydrolyzed with distilled water	3/4 in. - Scotch glass filament	5 days	24 hours
5	Fluorination with F_2 at 180°C in 1 hour Hydrolyzed with distilled water	3/4 in. - Scotch glass filament	5 days	24 hours
6	Fluorination with F_2 at 180°C in 1 hour Alkylated with a 15% n-butyl lithium sol.	1 in. - Scotch Core No. 0300	16 hours	22 hours
7	Fluorination with F_2 at 180°C in 1 hour Alkylated with a 15% n-butyl lithium sol.	3/4 in. - Scotch glass filament	5 days	24 hours
8	Fluorination with F_2 at 180°C in 1 hour Alkylated with a 15% n-butyl lithium sol.	3/4 in. - Scotch glass filament	5 days	24 hours

NOTES:

1. Full-scale deflection on chart = 4 lb
2. [illegible] peel rate, 2 in./min.
3. All trichloroethylene degreased before tape application
4. Conditioning done at 58% relative humidity at 76°F.

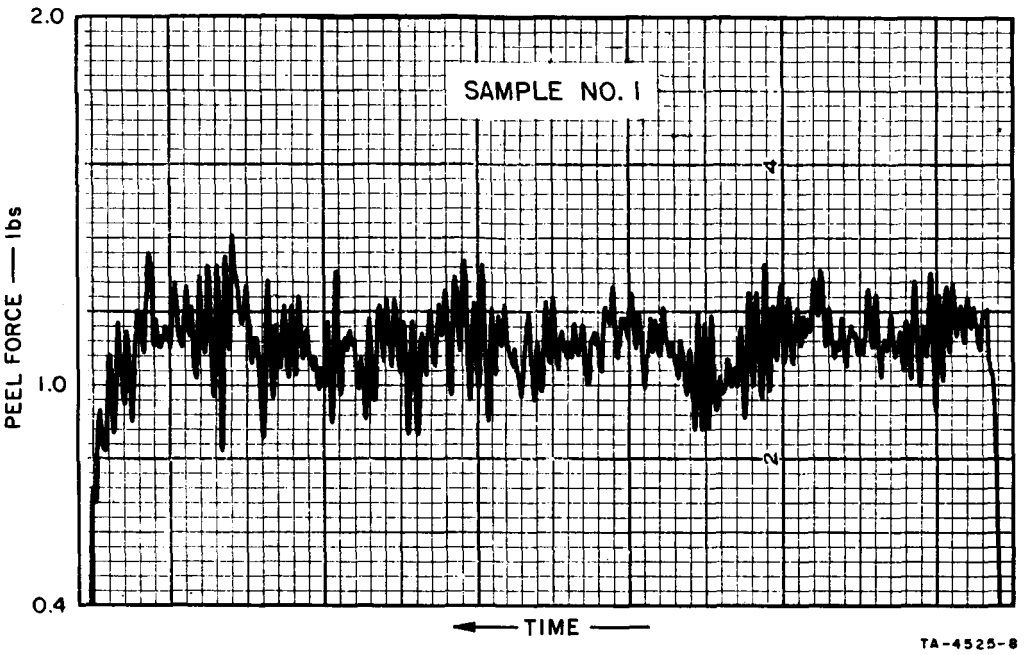

FIG. 1a PEEL TEST DATA FOR CLEAN GLASS

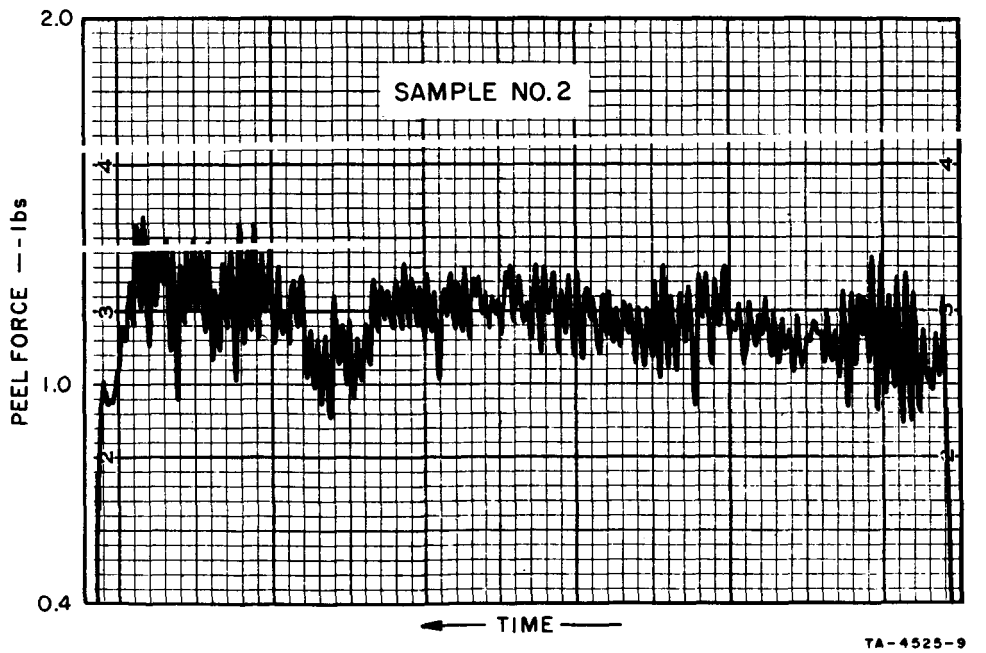

FIG. 1b PEEL TEST DATA FOR CLEAN GLASS

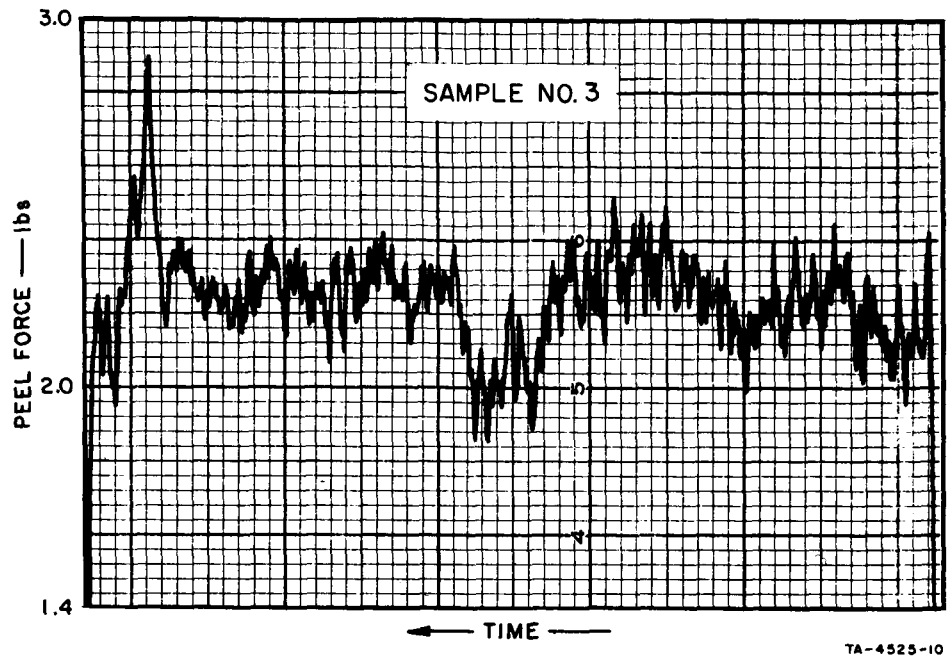

FIG. 1c PEEL TEST DATA FOR FLUORINATED-HYDROLYZED GLASS

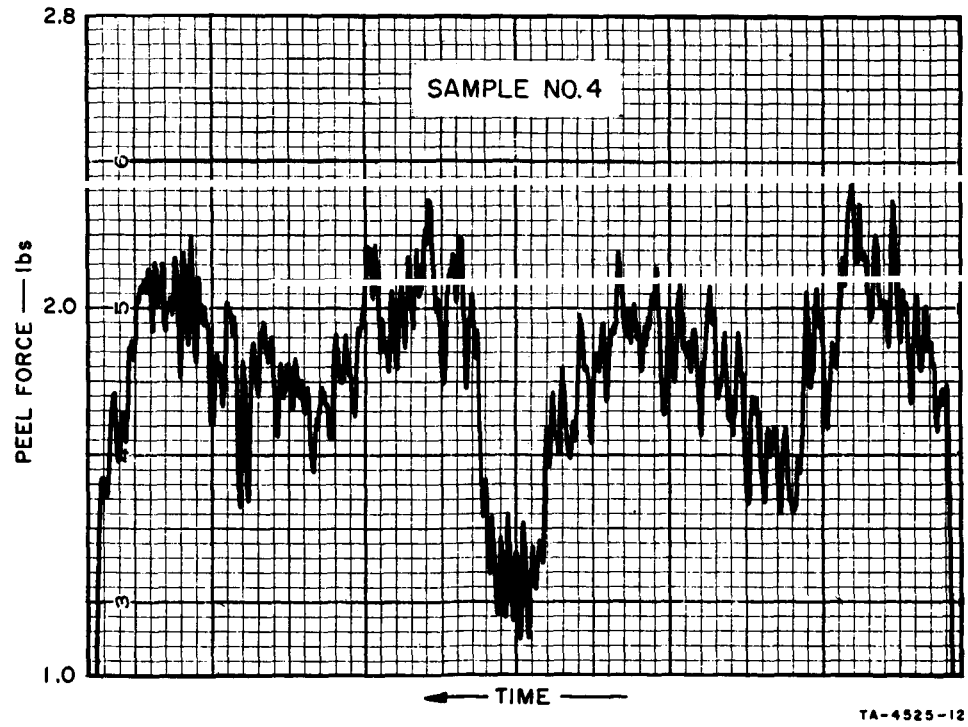

FIG. 1d PEEL TEST DATA FOR FLUORINATED-HYDROLYZED GLASS

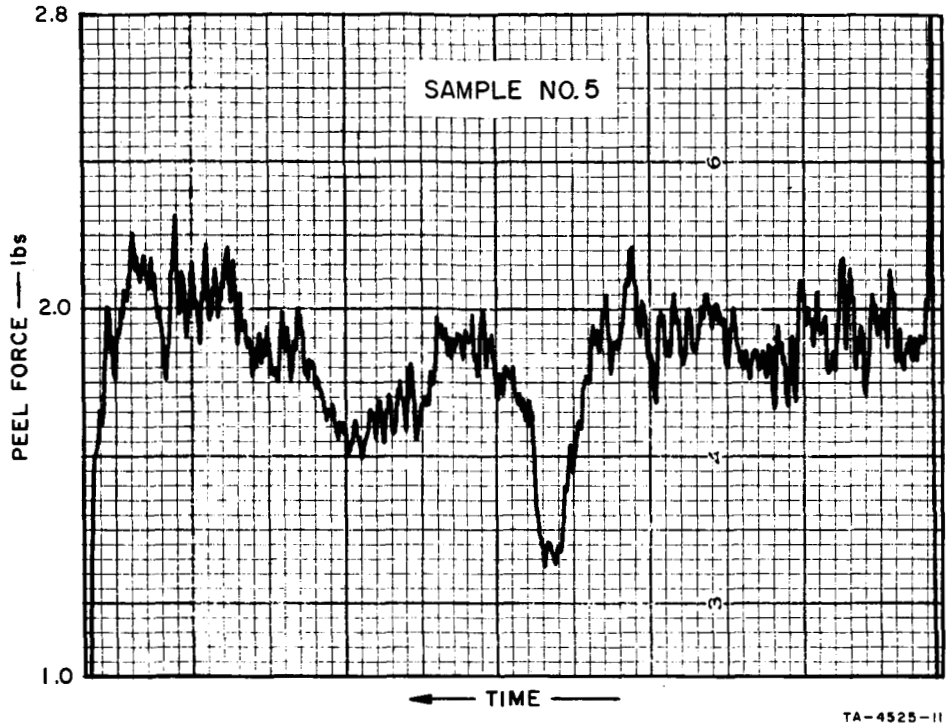

FIG. 1e PEEL TEST DATA FOR FLUORINATED-HYDROLYZED GLASS

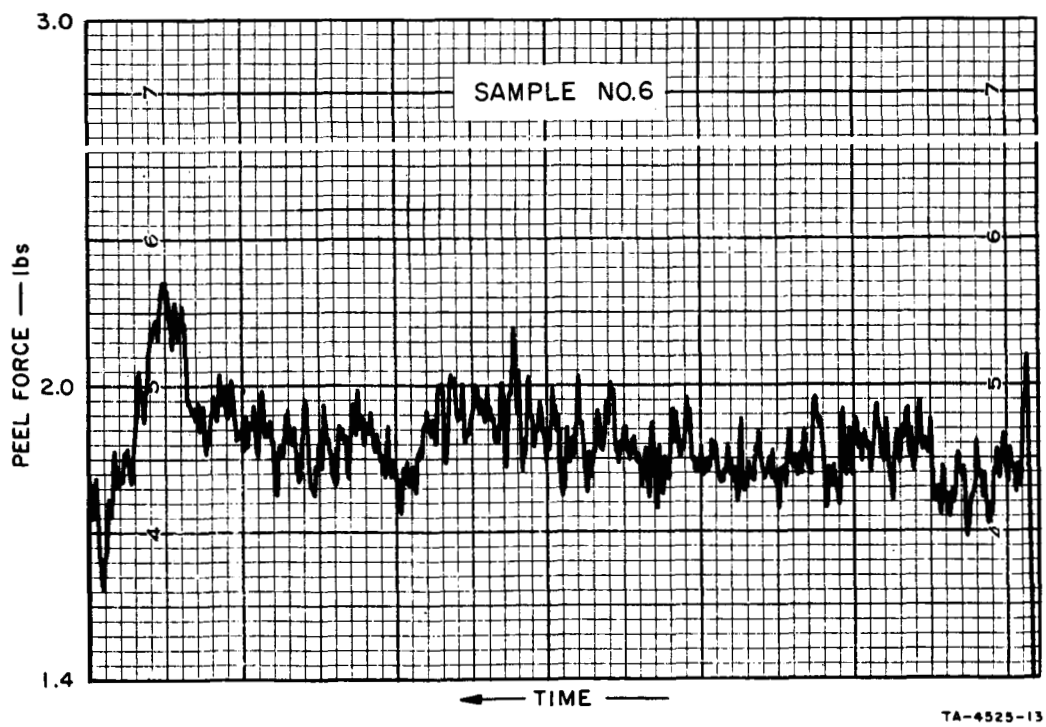

FIG. 1f PEEL TEST DATA FOR FLUORINATED-BUTYLATED GLASS

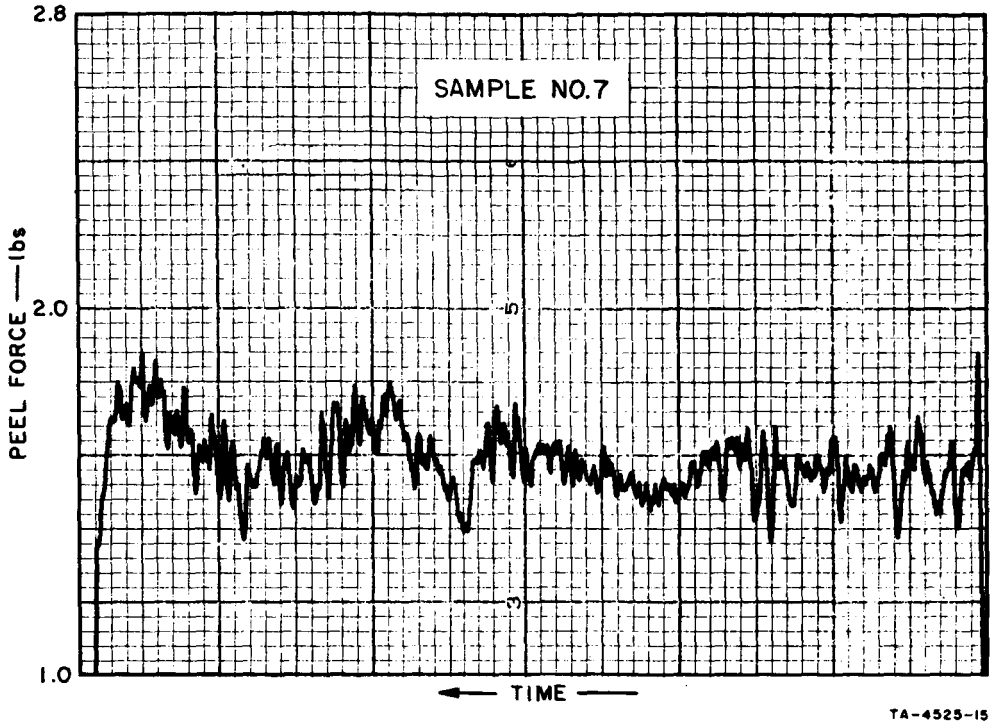

FIG. 1g PEEL TEST DATA FOR FLUORINATED-BUTYLATED GLASS

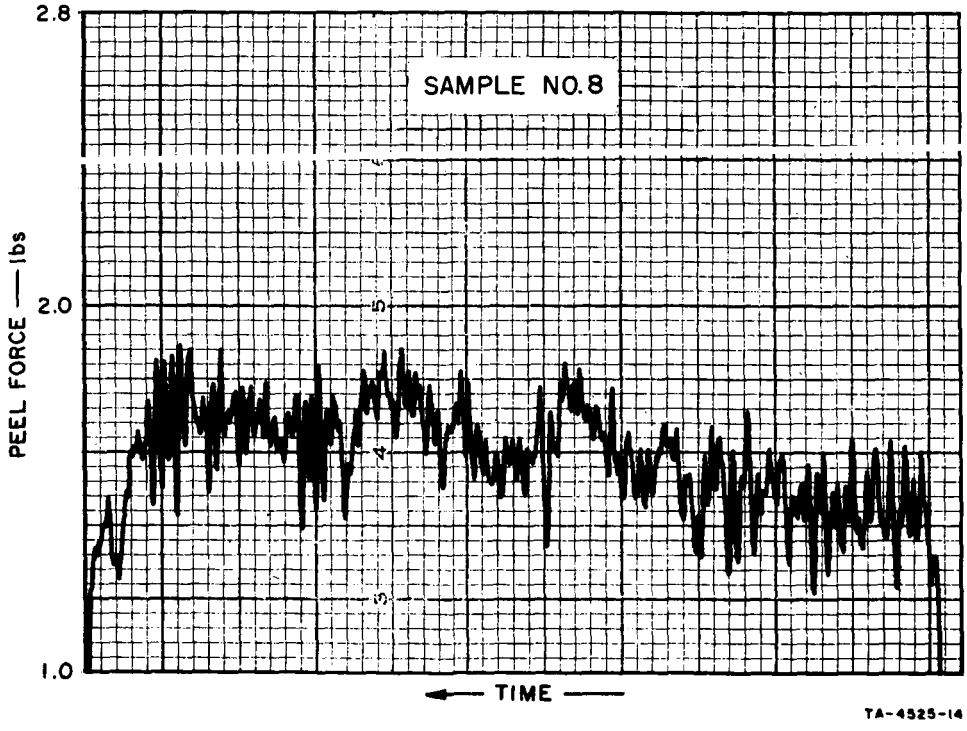

FIG. 1h PEEL TEST DATA FOR FLUORINATED-BUTYLATED GLASS

may contribute to adhesion to this surface, two should be considered here: the extent of butylation (i.e., the population of butyl groups on the surface), and the extent of autohesion obtainable from the 4-carbon butyl group. Under the conditions of this experiment it is probable that the over-all conversion of Si-OH groups to $Si-C_4H_9$ groups is not more than 50% of the theoretical maximum of 7.5 - 7.8 groups per 100 square Å.

The anticipated effect of such a surface layer of organic groups on glass would be to reduce the surface free energy of the glass. Two consequences should arise from this effect: the contact angles between polar liquids and the surface should be greater than for unmodified glass (i.e., the modified surface is more difficultly wet by liquids); and the work of adhesion of an organic adhesive bonded to the modified glass surface should be less than for a clean glass surface.

The effect of autohesion, in this case the intertwining or enmeshment of the straight-chain butyl groups with the polymer chains in the adhesive, may serve to increase the work of adhesion. However, this effect may be small for the short, 4-carbon, butyl group.

In summary, one may predict that two opposing effects may be at work, one to lower the work of adhesion, and one to raise the work of adhesion. Further, the wettability of the surface should be lowered.

The peel test data show that adhesion of commercial pressure-sensitive tapes to a freshly generated, hydroxyl-rich glass surface (Figs. 1c, 1d, and 1e) is about twice that for ordinary glass surfaces (Figs. 1a, 1b). Comparing Figs. 1c, 1d, and 1e sample No. 3 for a 1.0-in.-wide tape required approximately 20% higher peel force than samples 4 and 5 (Figs. d and e), which were for 0.75-in.-wide tape.

The same difference is found between sample 6 and samples 7 and 8 (Figs. 1f, 1g, and 1h), where sample 6 was 1.0 in. wide and 7 and 8 were 0.75 in. wide.

It will be noted that duplicate pairs of samples showed almost identical average peel strengths, in spite of the point-by-point scatter

in the pen traces. (Compare sample 1 with 2, sample 4 with 5, and sample 7 with 8.) These results, though limited, show that the method gives reproducible results, and that it is sensitive to changes in the substrate surface.

Finally, a comparison of sample No. 6 (Fig. 1f) for 1.0 in. tape on a butylated surface with sample No. 3 (Fig. 1c) for a 1.0 in. tape on a hydroxylated surface shows that butylation lowered the work of adhesion to that surface. Similar results are found with samples 7 and 8 (0.75-in. tape on butylated surfaces) compared with samples 5 and 6 (0.75-in. tape on hydroxylated surfaces. However, it is found that adhesion to a butylated glass surface is greater than to an ordinary glass surface (samples 1 and 2). With the data at hand one cannot assess the contribution, if any, of autohesion to these results.

Contact Angle Measurements

For a clean, glass surface, the contact angle for water and organic liquids should be zero (i.e., the glass should be completely wetted.) The predicted effect of butylation of a glass surface upon the contact angle between that surface and polar liquids was discussed in the preceding section on peel tests. By lowering the surface free energy of the glass, butylation should result in an increase in the contact angle for water and other polar liquids. This prediction is verified by the data in Table II and Figs. 2a, 2b, 2c, and 2d. Contact angles between a series of liquids of decreasing polarity (or surface tension) and glass were measured for a series of surface-modified glass microscope slides. For all liquids, the contact angles with clean glass slides (for reference) were zero (complete wetting). For a control series, in which clean glass surfaces received the same treatment (with n-butyl lithium, etc.) as the halogenated surfaces, contact angles were zero for all liquids except water. The 32^{o} angle for water is probably due to surface contamination, or possibly to a slight reaction between n-butyl lithium and surface Si-O-Li groups to produce butoxy groups.

Table II

CONTACT ANGLES IN DEGREES FOR LIQUIDS ON SURFACE-MODIFIED GLASS

Notebook No. and Page	Type of Surface Modification	Liquids (γ_{LV}, dynes/cm @ 20°C)*				
		Water (γ_{LV} = 72.8)*	Benzyl Alcohol (γ_{LV} = 39.0)	M-Cresol (γ_{LV} = 38.4)	Hexachloro-butadiene (γ_{LV} = 36.3)	Toluene (γ_{LV} = 28.4)
7494; pp. 3-11	Blank: Cleaned in acid-dichromate solution	0°	0°	0°	0°	0°
	Control: Cleaned and treated with n-butyl lithium	32°	0	0	0	0
	Propoxylated	53, 61	33,18	25,15	18,18	0
	Propoxylated and alkylated with n-butyle lithium	40,46, 50	4,19,10	4,22,22	14,14	0
	Fluorinated and alkylated with n-butyl lithium	67,60, 49	36,32	23,27,35	22,24,26	0

*Figures in parentheses are surface tension in dynes/cm for liquids in contact with saturated vapor at 20°.

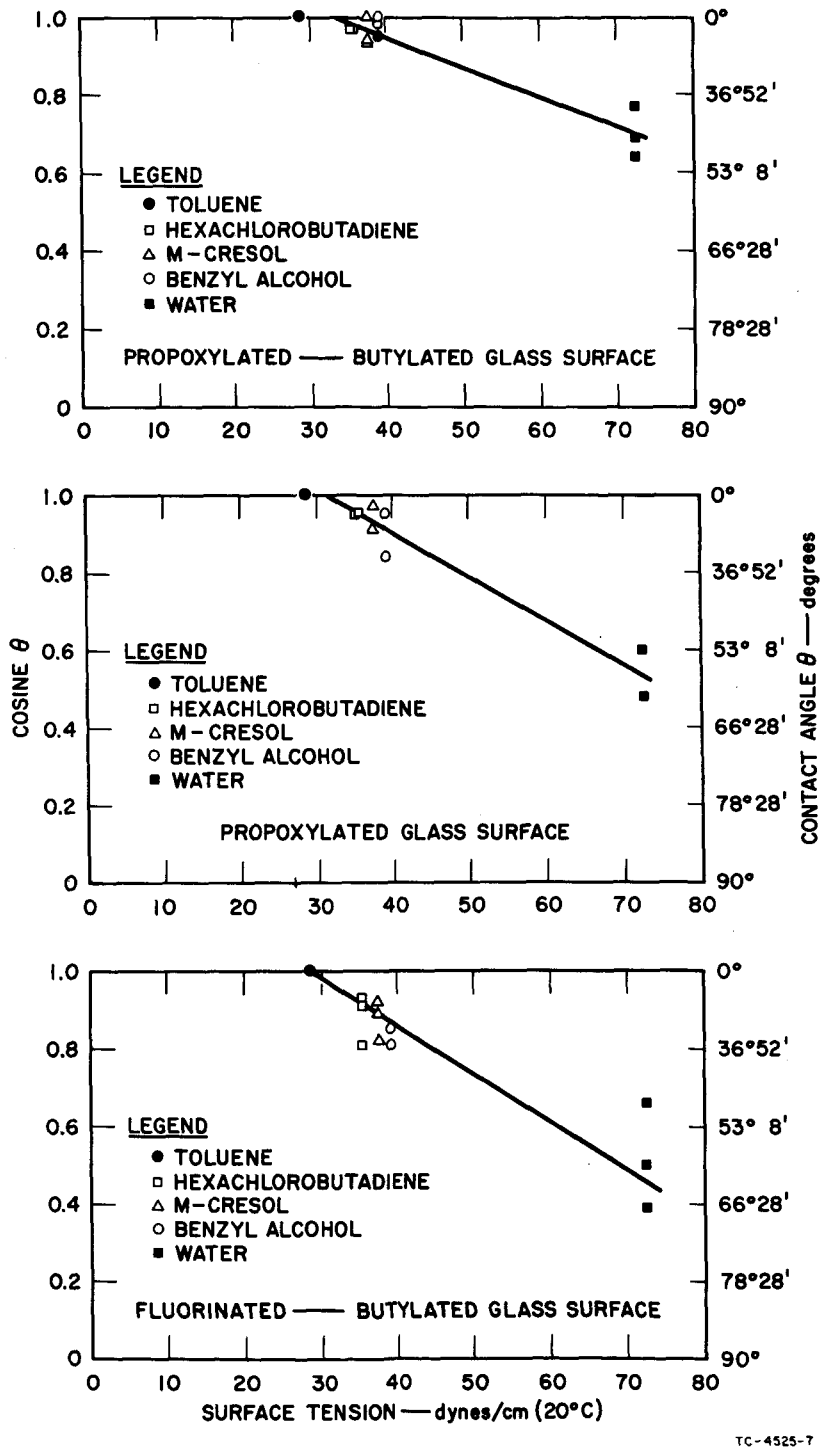

FIG. 2a,b,c CONTACT ANGLES OF LIQUIDS ON GLASS SURFACES

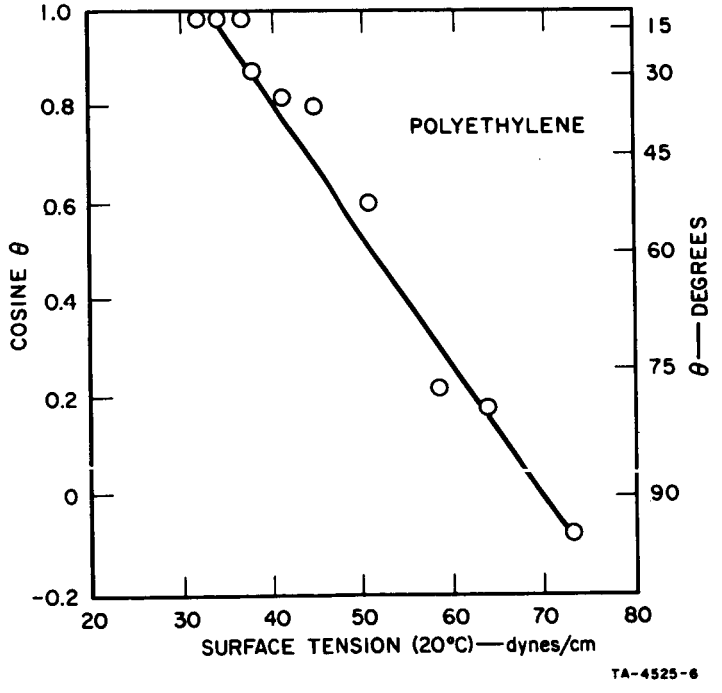

FIG. 2d CONTACT ANGLES OF LIQUIDS ON POLYETHYLENE[3]

$$\text{Si-OH} + \text{n-C}_4\text{H}_9\text{Li} \longrightarrow \text{Si-OLi} + \text{n-C}_4\text{H}_{10}$$

$$\text{Si-OLi} + \text{n-C}_4\text{H}_9\text{Li} \longrightarrow \text{Si-O-C}_4\text{H}_9 + \text{Li-O-Li}$$

Three methods of surface modification were evaluated: a surface modified by n-propoxy groups was prepared by esterification of hydroxyl groups with n-propyl alcohol; a surface modified with n-butyl groups was prepared by reaction of a propoxylated surface with n-butyl lithium; and a surface modified by n-butyl groups was prepared by reaction of a fluorinated surface with n-butyl lithium. The contact angles of the five liquids with each of the three surfaces were comparable. Theoretically, one would expect the n-butyl-modified surface to exhibit a higher contact angle than a propoxylated surface, and this was found for the fluorinated-butylated samples. The slightly lower values for the propoxylated-butylated samples, compared with the propoxylated-only sample, may be ascribed to the incomplete conversion of propoxy groups ($\geqslant$ Si-O-C_3H_7) to butyl groups ($\geqslant$ Si-n-C_4H_9). Groups that escaped alkylation were ultimately hydrolyzed to $\geqslant$ Si-OH groups, resulting in a surface of higher free energy and therefore lower contact angles.

Figures 2a, b, and c show the plot of the data in Table II. The abscissa, $\cos\theta$, is the cosine of the measured contact angle, and the ordinate, γ_{LV}, is the surface tension of the liquid, at 20°C, in contact with its saturated vapor. The plot of such data usually gives a straight line.[2] The surface tension corresponding to the point on the curve at $\cos\theta = 1.0$ is the critical surface tension for that solid surface. Figure 2d shows a similar plot, from Fox and Zisman,[3] of contact angles of a series of liquids with a polyethylene surface. The data for the surface-modified glass are parallel to those for polyethylene.

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[2]W. A. Zisman, "Relation of the Equilibrium Contact Angle to Liquid and Solid Constitution," p. 13, Chapter 1 in Contact Angle, Wettability and Adhesion, Advances In Chemistry Series No. 43, American Chemical Society, Washington, D. C., 1964.

[3]H. W. Fox and W. A. Zisman, J. Colloid Sci., I. 428 (1952).

Dilatometry

The dilatometric method for evalution of adhesion between a polymer and a solid was described earlier.[1] It is based upon a constant volume system in which the change in pressure in the sample cell is compared with the pressure in a reference cell. The sample consists of a rectangular prism of an elastic polymer which is reinforced with the solid in particulate form. As the sample is stretched, interfacial shear forces cause debonding and void formation. The volume increase of the sample, due to these voids, causes an increase in pressure in the sample cell.

The method requires an elastic polymer with sufficient cohesive strength to undergo an elongation of 50% or more. Initial experiments were carried out with the G. E. RTV-615, room-temperature-vulcanizing silicone rubber. The cohesive strength of this rubber proved insufficient for our purpose.

Future work will make use of polyurethane elastomers which have much better physical properties than the RTV-615 rubbers.

Analysis

Analysis of surface-modified glass (or silica) for the amount of bound carbon and/or hydrogen has presented a major difficulty. Until this problem is solved, an exact measure of the extent of surface modification cannot be made.

A few experiments have been performed for analysis of particulate glass by the method used for determination of carbon in steel. This method, using the Leco Combustion Apparatus, involves fusion of the sample in an oxygen environment. Successful use of this method for glass requires that residual carbon be known or eliminated. Preliminary work shows that this requirement can probably be met, and that carbon may be measured to as low as about 10 parts per million with reasonable accuracy.

III EXPERIMENTAL

Peel Tests

Peel tests were performed, using the method and apparatus previously described.[1] The effect of surface treatment of glass and silica cylinders upon the peel strength of various commerical pressure-sensitive tapes is shown in Table I and in Figures 1a-1h. The surface treatment for glass and silica rings was by fluorination followed by alkylation with n-butyl lithium. The type of surface (cleaned, butylated, etc.) is designated in each figure. The figures show the actual recording of the force-time relationships during the peeling of the tape from the glass cylinder.

Contact Angle Measurements

Contact angle measurement was used to evaluate the effect of surface treatment of glass. Standard glass microscope slides were used for this work. Five sets, of three slides each, were prepared: blank samples of glass plates were cleaned with dichromate cleaning solution; control samples of glass plates were cleaned with dichromate cleaning solution, washed, dried, and treated with butyl lithium; test samples of glass plates were cleaned as above, and alkoxylated by treatment at 180°C, for two hours, with a large excess of purified n-propyl alcohol. (The anticipated reaction was $\gtrless Si\text{-}OH + n\text{-}C_3H_7OH \rightarrow H_2O + \gtrless Si\text{-}O\text{-}C_3H_7$.) This was done in a high-pressure autoclave. After cooling, the slides were removed, air-dried, and then desorbed under vacuum); another set of test samples was alkoxylated as above, followed by alkylation with n-butyl lithium; and a final set of test samples was prepared by fluorination with gaseous fluorine, followed by alkylation with n-butyl lithium.

Contact angles were measured by photographing the drop of liquid on the plate through a microscope. Tangents were drawn on the enlarged images, and angles were measured with a protractor.

The data are shown in Table II. Data for the three treated slides are plotted in Figures 1b, 2b, and 3b. In Figure 2d is shown, for comparison, the results of Fox and Zisman regarding the contact angles of a series of liquids on a polyethylene surface.

Dilatometry

The dilatometric method for evaluation of adhesion between a filled elastomer and particulate material used as a filler is based upon the increase in total volume of a sample as voids are formed, due to adhesive failure, at polymer-particle interfaces.

The instrument used for this work was constructed at the Institute under Contract AF 33(600)-40560, and is the property of the U.S. Air Force. Permission to use this instrument on a noninterference basis was granted by the owner.

Samples for dilatometric measurement were cast from a 1:1 mixture of glass powder (200 mesh) and GE RTV-615 Silicone elastomer, in the shape of rectangular prisms 0.5 x 0.5 x 3.0 in. Aluminum end tabs were placed in the mold prior to casting. The finished samples were cured as per the recommendations of the resin manufacturer.

The samples were mounted in the dilatometer by means of the aluminum end tabs. After mounting the samples were elongated at a preset rate, and measurements were made of the force required, the elongation, and the change in pressure of the sample cell compared with a reference cell.

All samples of this class of silicone elastomer failed in cohesion at an elongation too low to be of value for adhesive studies. Therefore, the use of these elastomers was discontinued.

Materials and equipment are now being procured for preparation of polyurethane elastomer samples. This formulation of polyurethane has

proved satisfactory for dilatometric studies of solid propellant formulations.[4]

Analysis

Determination of the extent of alkylation of glass surfaces has presented a problem because of the low concentration of alkyl groups on a weight basis. The Seco Combustion Apparatus for determination of carbon in steel is under evaluation for determination of carbon on and/or in glass. Preliminary results indicate that the method may prove to be satisfactory. The method is based upon the fusion of a weighed sample of glass in a stream of purified oxygen. Carbon dioxide is removed from the combustion products by absorption in a conductivity cell. The carbon content of the sample is calculated from conductivity measurements. The data collected to date for carbon on glass are preliminary, and therefore are not presented.

IV FUTURE WORK

Work for the fourth quarter will be concentrated on analytical problems, i.e., measurement of the amount of carbon on a modified glass surface, and dilatometry as a tool for measuring changes in adhesion to glass surfaces.

ACKNOWLEDGMENTS

Mrs. Fern Jantzef and Mr. Michael Bertolucci carried out the major part of this experimental work. Dilatometric measurements were performed by Mr. James Rinde. Dr. Gunther Steinberg contributed very helpful discussions on the subject of surface chemistry.

[4]N. Fishman, and co-workers, Technical Reports on Contract AF33(600)-40560, Stanford Research Institute.