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EFFECT OF INTERFACIAL CHEMICAL BONDING ON THE
STRENGTH OF ADHESION OF GLASS-POLYBUTADIENE JOINTS

by

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20. elastomer in the former case and not in the latter. Swelling stresses were found to discriminate between relatively strongly-bonded systems of the former type, causing earlier bond failure for less firmly bonded elastomer layers.

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Effect of Interfacial Chemical Bonding on the Strength of Adhesion of Glass-Polybutadiene Joints

Summary

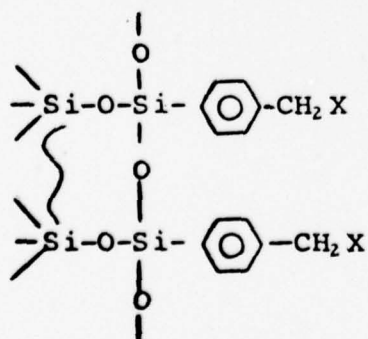
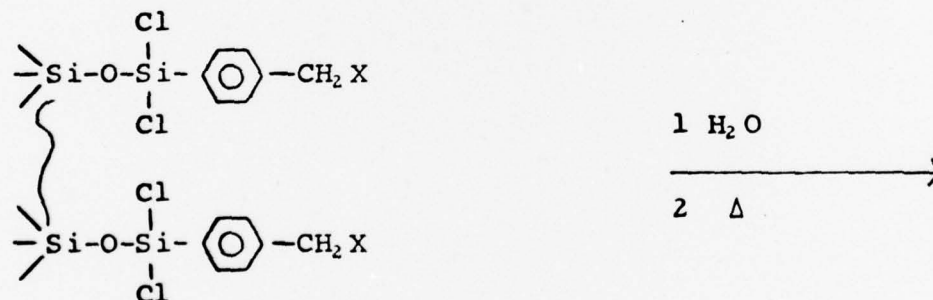
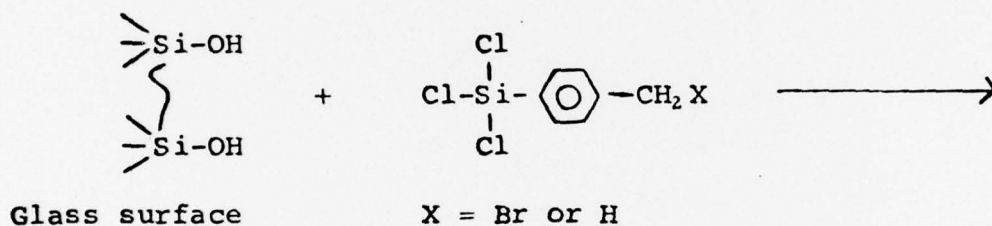
A new example of a positive effect of interfacial chemical bonding on the strength of adhesive bonds is reported. The chemical bond was formed between a p-bromomethylphenylpoly-siloxane coated glass slide and a liquid dicarboxyterminated polybutadiene which was subsequently bonded to an elastomeric polybutadiene by crosslinking with dicumylperoxide. Peel tests at 180° led to cohesive failure in the elastomer layer for two different proportions of p-bromomethylphenyl groups on the glass slides, whereas uncoated slides and slides coated with an inert polysiloxane layer, p-tolylpolysiloxane, showed interfacial failure. Further confirmation of interfacial bonding was obtained from SEM studies. When peel tests resulted in cohesive failure it was found possible to distinguish between different degrees of interfacial bonding by the different times required for failure at the interface on swelling the elastomer layer with pentane.

Introduction

The importance of interfacial bonding on the strength of an adhesive joint is still a subject of controversy (1-3). Some investigators believe that covalent bonding at an interface is not necessary to form a strong joint. Others argue that adhesion is improved by forming chemical bonds between adherends. Ahagon and Gent (4) have shown that when the presence of chemical bonds at an interface can be inferred from the method of preparation of the joint, then a corresponding increase in the work of adhesion is observed. In their work bonding to the substrate, a glass surface treated with varying amounts of vinyltriethoxysilane, and crosslinking of the adhesive, polybutadiene, were carried out simultaneously during a peroxide cure of the adhesive. It was assumed that the bonding to vinyl groups on the substrate was quantitative or at least proportional to the number of groups present. No attempt to measure the number of vinyl groups was made, although earlier work by Hsu and Gent had shown that the proposed reactions should occur (5).

We have now developed a second system that shows a significant effect of interfacial chemical bonding on adhesive strength and that also allows us to vary the number of interfacial chemical bonds and the degree of crosslinking of the

elastomer in separate steps. In designing this system we have used well-established chemistry developed for use in solid phase peptide syntheses with glass beads as the stationary phase (6,7). The following sequence of reactions is first carried out on a clean glass slide:



Thus a hard film consisting of a three dimensional functionalized polysiloxane network is formed on the surface of the glass slides. This system is particularly attractive because it has been shown that the linkage between the glass slide and the bonded organic layer is hydrolytically stable (6,7). These prepared slides with varying amounts of $-\text{CH}_3$ and $-\text{CH}_2\text{Br}$ groups are then treated with a liquid polybutadiene terminated at both ends with carboxylic acid groups and finally the liquid polybutadiene is bonded to an elastomeric polybutadiene overlayer during a curing reaction. The strengths of adhesion of these model joints were measured in 180° peel tests and correlated with debonding times in pentane and micrographs taken with a scanning electron microscope.

Experimental

Materials. p-Tolyltrichlorosilane ($\text{CH}_3-\text{C}_6\text{H}_4-\text{SiCl}_3$) was prepared according to the method of Chvalovsky and Bazant (8).

p-Bromomethylphenyltrichlorosilane ($\text{BrCH}_2-\text{C}_6\text{H}_4-\text{SiCl}_3$) was made by Grohmann's procedure (6). The liquid dicarboxyterminated polybutadiene was B. F. Goodrich's Hycar CTB (2000X156), $\bar{M}_n$ 4130, functionality 1.9, cis/trans/vinyl (%): 20.5/54.9/24.6. The

elastomeric polybutadiene was Firestone's Diene 35, an anionic polybutadiene of $\bar{M}_n \sim 150,000$ and cis/trans/vinyl (%): 36/54/10. Dicumyl peroxide (recrystallized, Hercules, Inc.) was used as a curing agent. Reagent grade benzene (Mallinckrodt Chemical Works) was dried over lithium aluminum hydride and distilled. Other solvents were reagent grade and were used as received. The glass slides were cleaned by standing in freshly prepared chromic acid solution for several days and then rinsing several times with distilled water followed by drying in a vacuum oven at 120°C for six days.

Polysiloxane Coating of Glass Slides. The glass slides were treated for 4 days at room temperature with one of three different silane solutions in dry benzene: A, 10g of p-bromomethylphenyltrichlorosilane in 250ml of dry benzene; B, 10g of p-tolyltrichlorosilane in 250ml of dry benzene; or C, 5g of p-bromomethylphenyltrichlorosilane and 5g of p-tolyltrichlorosilane in 250ml of dry benzene. They were removed and placed in Soxhlet extractors and washed with refluxing dry benzene for 24 hours in order to remove any of the silane compounds not chemically bonded to the slides. The glass slides were then

placed in a solution of benzene, ethanol and water (50/45/5 by volume) for four hours to hydrolyze the remaining Si-Cl bonds and then heated in a vacuum oven at 115°C for 24 hours to polymerize the silane compounds on the surface of the glass.

Reaction With Liquid Polybutadiene. Three clean glass slides which had not been treated with any of the silane solutions, three slides treated with A, three slides treated with B, and three slides treated with C were suspended in a reaction kettle. In accord with the usual procedure for coupling amino acids to chloromethylated supports a solution of 30g of di-carboxyterminated liquid polybutadiene in 750ml of ethyl acetate and 5ml triethylamine were added (9). The kettle was heated to 60-70°C. After four days, the solution was removed and the glass slides were washed twice with ethyl acetate and once with methylene chloride in order to remove all of the liquid rubber which was not chemically bonded to the glass slides. The coated glass slides were then air dried. Two of each type of slide were used for adhesion testing and the third was examined by scanning electron microscopy.

Application of Elastomer Layer. Dicumyl peroxide (0.1%) was mixed with the elastomeric polybutadiene on an open mill. Before bonding the elastomer was pressed into a thin layer on a sheet of finely-woven cotton cloth. The cloth-backed

layer was then pressed against the prepared glass slide for 2.5 hrs. at 150°C in a press to cure the elastomer and bond the two polybutadienes. The thickness of the elastomer interlayer in the resulting cloth-elastomer-glass sandwich was ~ 0.7mm. Peeling experiments were carried out on strips of cloth-backed elastomer layer after trimming them to a uniform width on the glass of 2 cm.

Measurement of Work of Adhesion, W . The cloth-backed elastomer layer was peeled off a short distance, bent back through 180°, and then stripped off at constant rate. Work of adhesion W per unit area of interface was calculated from the time-average of the peel force P per unit width of the detaching layer (4):

$$W = 2P$$

Scanning Electron Microscopy. Slides were gold coated and examined with a JSM-V3 Scanning Electron Microscope.

Results and Discussion

The results of the 180° peel tests of the bonds prepared as described above are given in Table I. As would be expected if chemical bonding plays a role in improving the strength of adhesion the p-tolylpolysiloxane coated slides and the clean glass slides led to low work of adhesion W since chemical

bonding with the dicarboxyterminated polybutadiene is not expected in either case. The slides with the p-tolylpolysiloxane coating gave a lower W than the uncoated slides. This is consistent with the known release agent characteristics of silane compounds and indicates that there is some intrinsic attraction between clean glass surfaces and polybutadiene that is reduced by the siloxane coating. Similar results were obtained by Ahagon and Gent (4); higher values of W for clean glass compared to methyltriethoxysilane treated glass were found and can be accounted for in the same way. Wong has also noted a strong attraction between polybutadiene and clean glass (10).

The existence of strong attraction between the dicarboxyterminated polybutadiene and clean glass was confirmed by the scanning electron microscope study. (See Figure 1.). Uncoated glass slides were covered by a significantly larger amount of debris, presumably rubber, after treatment with the dicarboxyterminated polybutadiene than were slides coated with p-tolylpolysiloxane. This attraction could be of the same nature as that noted by Ahagon and Wong but covalent bonding might also have occurred under the reaction conditions used.

In contrast, when some degree of interfacial chemical bonding was expected, as with the 50/50 p-bromomethylphenylpolysiloxane/p-tolylpolysiloxane coated slides and with p-bromomethylphenylpolysiloxane coated slides, a much larger value of W that resulted in cohesive failure in the polybutadiene layer was observed. As shown in Figure 2 the scanning electronmicrographs of the siloxane coated slides before and after treatment with the dicarboxyterminated rubber also revealed a definite coating on the glass. Micrographs of the rubber treated slides showed evidence of rubber particles in addition.

A further difference between the slides where chemical bonding is expected and those where it is not was found in the time required for failure of the adhesive bond by swelling in pentane of the polybutadiene layer (See Table I). When chemical bonding could not occur the bond failed in a few minutes. When chemical bonding was possible much longer times were required. The rubber-glass bond on the slide coated with the 50/50 p-bromomethylphenylpolysiloxane/p-tolylpolysiloxane failed after several hours in pentane. The corresponding bond on the glass slide coated with p-bromomethylphenylsiloxane did not fail even after being submerged

in pentane for three days. This indicates, as would be expected, that there is a higher density of bonds in the case of the glass slides coated with the p-bromomethylphenylpolysiloxane than in the case of those coated with the 50/50 p-bromomethylphenylpolysiloxane/p-tolylpolysiloxane. Time to debond the elastomer from the substrate by swelling in pentane seems to be a very sensitive criterion for determining the existence and relative density of chemical bonds.

Conclusion

A new example of a positive effect of interfacial chemical bonding on the strength of adhesive bonds is reported. The chemical bond was formed between a p-bromomethylphenylpolysiloxane coated glass slide and a liquid dicarboxyterminated polybutadiene which was subsequently bonded to an elastomeric polybutadiene by crosslinking with dicumyl peroxide. Peel tests at 180° led to cohesive failure in the elastomer layer for two different contents of p-bromomethylphenyl groups. The two levels of functionalization could be distinguished by the time necessary for failure of the adhesive bond by swelling in pentane. Peel tests of similarly treated uncoated slides

and p-tolylpolysiloxane coated slides led to interfacial failure. Further confirmation of the existence of the coatings was obtained from scanning electronmicroscope studies.

Acknowledgement

This work forms part of a program of research on the adhesion of elastomers supported by a research grant from the Office of Naval Research. We are indebted to A. N. Gent for helpful comments and suggestions throughout this work. We also thank K. Riew of the B. F. Goodrich Co. for supplying the sample of CTB and the Firestone Tire and Rubber Co. for samples of Diene 35 NFA.

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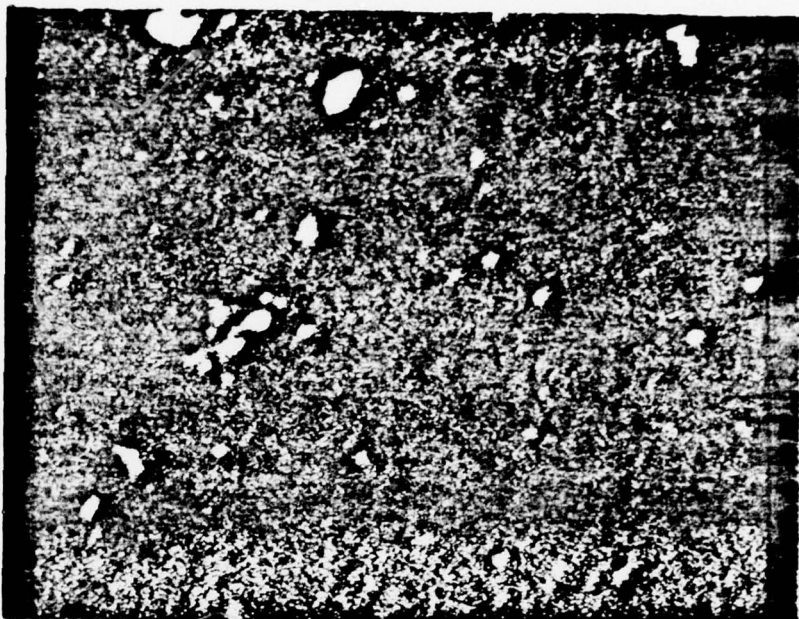
Table I

Effect of p-Bromomethylphenylpolysiloxane and p-Tolylpolysiloxane Coatings on Work of Adhesion Between Dicarboxyterminated Polybutadiene and Glass and on Time for Bond Failure in Pentane

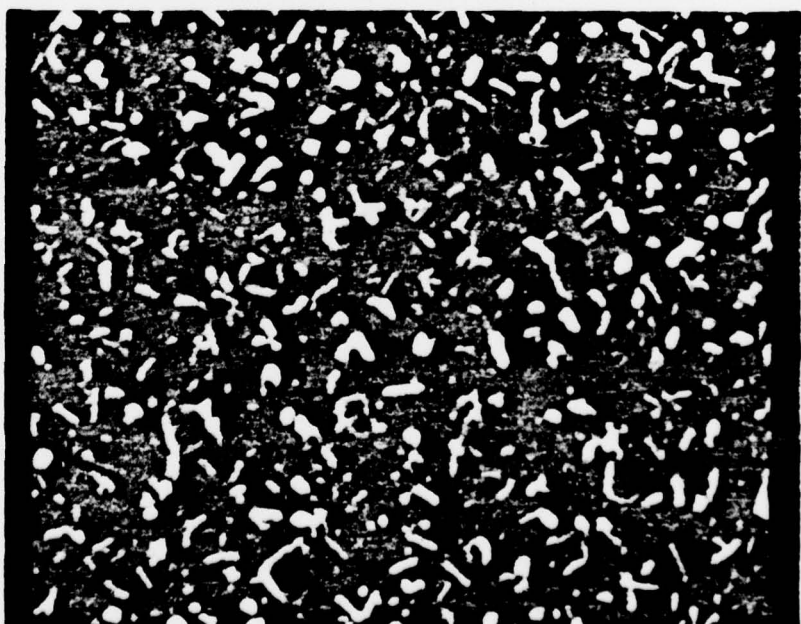
% of silane in Coating Solution

<u>-Si--CH₃</u>	<u>-Si--CH₂ Br</u>	<u>W(J/m²)^a</u>	<u>Time for Bond Failure in Pentane(hrs)</u>
0	0	34(I)	~0.08
100	0	20(I)	~0.08
50	50	450(C)	~3
0	100	470(C)	> 72

^aDetermined in a 180° peel test with 0.5 cm per min crosshead speed and 0.1% dicumyl peroxide cure of the polybutadiene. I = interfacial failure. C = cohesive failure of the elastomer.

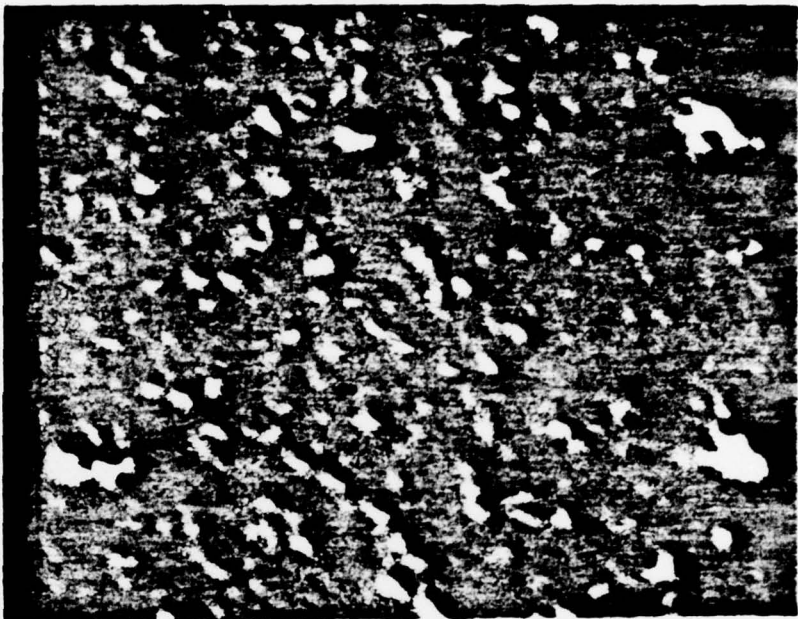


COATED

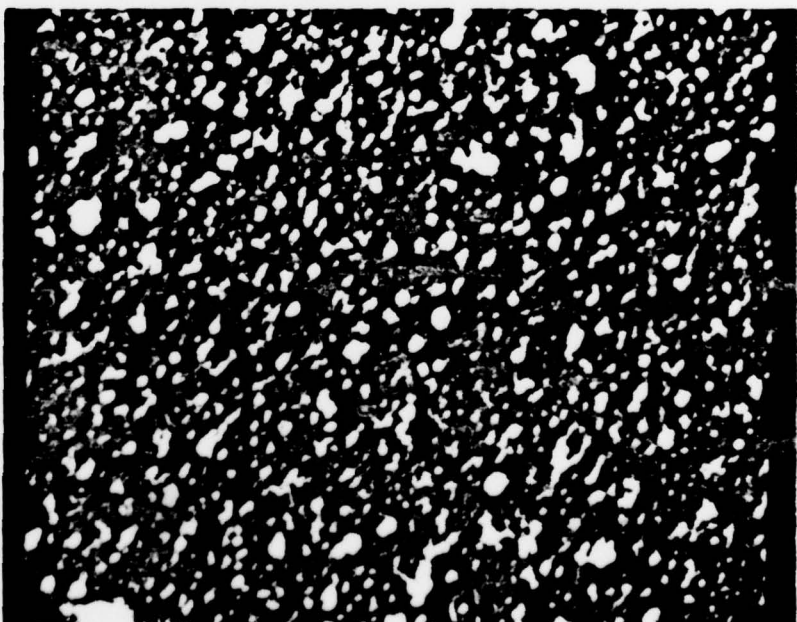


UNCOATED

Figure 1: Comparison of scanning electronmicrographs of uncoated glass slide and p-tolylpolysiloxane coated glass slide after treatment of each with dicarboxy-terminated polybutadiene. ~ x 10,000.



BEFORE



AFTER

Figure 2: Comparison of scanning electromicrographs of 50/50 p-bromomethylphenylpolysiloxane/p-tolylpolysiloxane coated slides before and after treatment with di-carboxyterminated polybutadiene. ~ x 10,000.

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