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OFFICE OF NAVAL RESEARCH
Contract N00014-76-C-0408
Project NR 092-555

Technical Report No. 6

EFFECT OF NUMBER OF CHEMICAL BONDS ON THE STRENGTH OF ADHESION BETWEEN GLASS AND POLYBUTADIENE

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December 1979

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report 6	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Effect of Number of Chemical Bonds on the Strength of Adhesion Between Glass and Polybutadiene		5. TYPE OF REPORT & PERIOD COVERED Technical Report 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) P. Dreyfuss, Y. Eckstein and Q. S. Lien and H. H. Dollwet		8. CONTRACT OR GRANT NUMBER(s) N00014-76-C-0408
9. PERFORMING ORGANIZATION NAME AND ADDRESS		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 092-555
11. CONTROLLING OFFICE NAME AND ADDRESS		12. REPORT DATE December 14, 1979 13. NUMBER OF PAGES
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

DISTRIBUTION STATEMENT A
Approved for public release;
Distribution Unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

Submitted for publication in Adv. in Chem.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

^{14}C labelled interfacial bonds, adhesion, polybutadiene, glass substrate, silane coupling agents, locus of failure

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Studies of the effect of chemical bonding on the joint strength of bonds formed between polybutadiene and glass were carried out. The number of chemical bonds was determined using ^{14}C labelled interfacial bonds and measuring the resulting radioactivity. The strength of the joint was found to increase as the number of chemical bonds increases. The presence of

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essentially all the radioactivity on the glass surface after peeling at 180° indicated that fracture occurred without breaking the interfacial bonds.

Effect of Number of Chemical Bonds on the Strength of Adhesion Between Glass and Polybutadiene

Summary

Studies of the effect of chemical bonding on the joint strength of bonds formed between polybutadiene and glass were carried out. The number of chemical bonds was determined using ^{14}C labelled interfacial bonds and measuring the resulting radioactivity. The strength of the joint was found to increase as the number of chemical bonds increases. The presence of essentially all the radioactivity on the glass surface after peeling at 180^0 indicated that fracture occurred without breaking the interfacial bonds.

Introduction

There are conflicting reports in the literature about the importance of interfacial covalent bonds on the strength of an adhesive joint (1-2). Recent studies from our laboratories have led to the conclusion that covalent bonds between an adhesive and an adherend improve their adhesion (3-5). Furthermore, the accumulated evidence indicates that joint strength increases with the inferred number of bonds at the interface. A major objective of the present study was to establish a quantitative relationship between the measured number of interfacial chemical bonds and the resulting joint strength. Demonstration of such a relationship would be definitive evidence that chemical bonding plays a positive role in adhesion.

This paper shows that the required relationship does exist. The interfacial bonds were labelled with ^{14}C and their number was determined by counting the resulting β-emissions. The work of adhesion was obtained from peel tests at 180^0.

Experimental

Materials

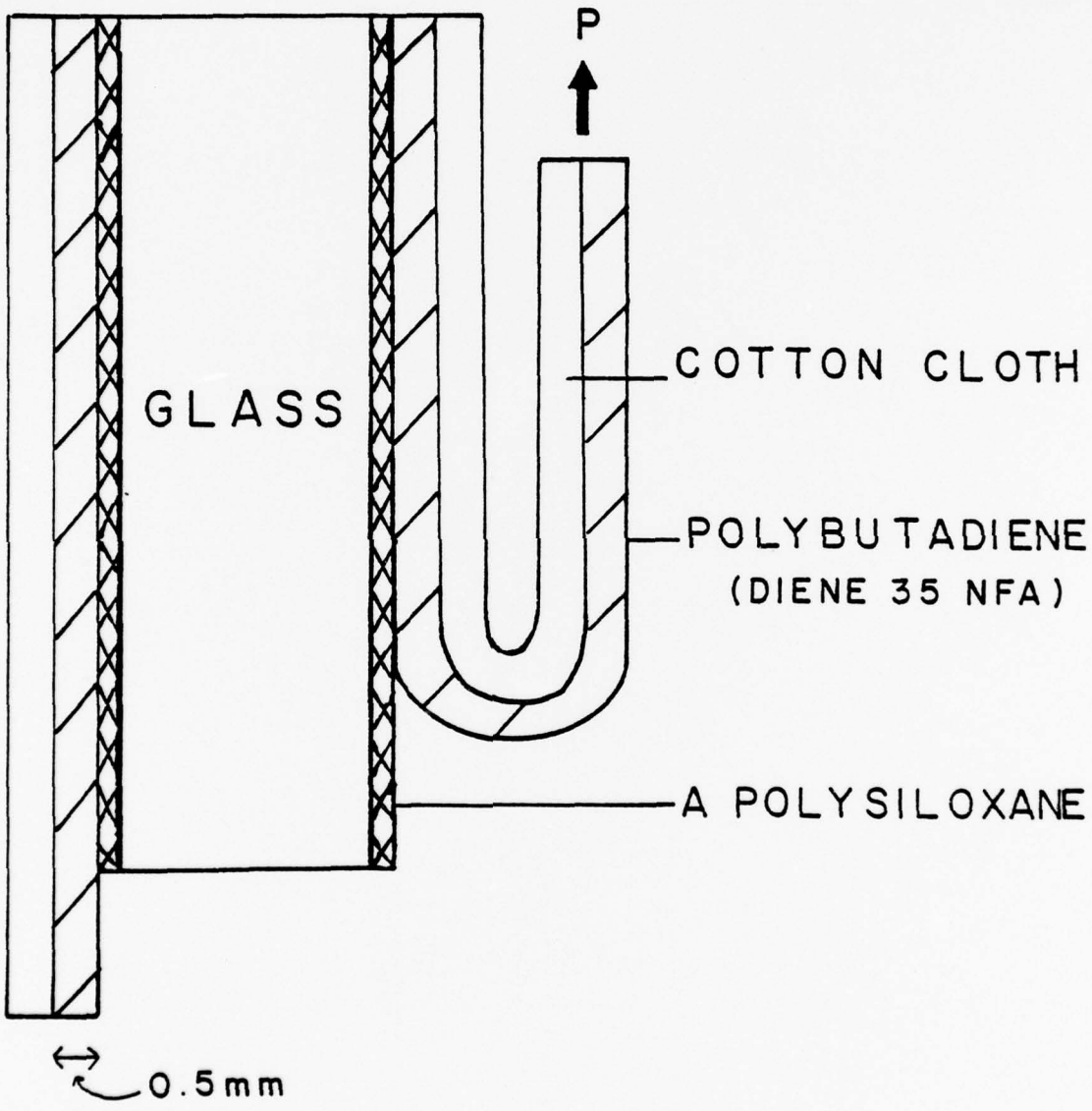
β-Phenethyltrichlorosilane and 1-trichlorosilyl-2-(p,m-chloromethylphenyl)ethane were synthesized from trichlorosilane

and styrene or vinylbenzyl chloride, respectively, according to the methods of Chuang (6). Glycine (U-^{14}C) from ICN Pharmaceuticals, Inc. had a specific activity of 140 mCi/mmole. The liquid dicarboxy-terminated polybutadiene was BFGoodrich's Hycar CTB (2000 x 156) with $\overline{M}_n$ = 4130, functionality of 1.9, cis:trans:vinyl (%) = 20.5:54.9:24.6, and was converted to the di-p-nitrophenyl ester by coupling with p-nitrophenol using N,N'-dicyclohexylcarbodiimide according to standard procedures (7). Dicumyl peroxide (Dicup-R, recrystallized) was a gift of Hercules, Inc. The elastomeric polybutadiene used as adhesive was Firestone's Diene 35 NFA, an anionic polybutadiene of $\overline{M}_n \simeq 150{,}000$ and cis:trans:vinyl (%) = 36:54:10. Slides made from sheet glass were obtained from Sargent-Welch.

Typical Test Specimen

A modified 180^0 peel test specimen with the configuration shown in Figure 1 was prepared from carefully cleaned glass slides. The specimen differs from those used in earlier work (3-5) in that the adhesive was applied to both sides of the slide instead of to one only in order to make more efficient use of the ^{14}C labelling, which was distributed over the entire surface of the slide. Previous work has shown that each layer of the specimen is required before the effect of chemical bonding of polybutadiene to glass on the strength of their adhesion can be demonstrated (8).

Figure 1. Diagram of Peel Test Specimen

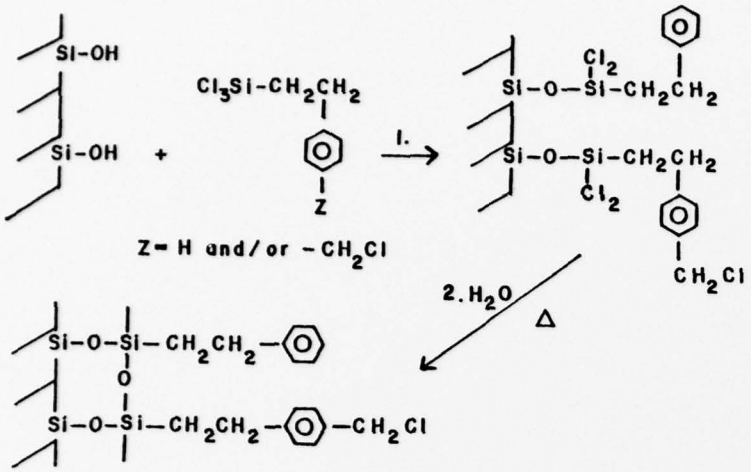


The preparation was similar to the one described by Runge and Dreyfuss (5) except that additional steps were required to insert the radiotracer in the form of uniformly labelled glycine. The preparation is shown schematically in Figure 2. Details will be published elsewhere and are only summarized here.

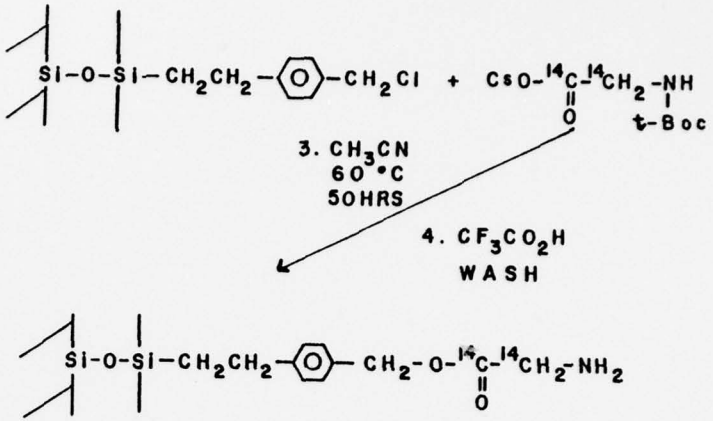
In step 1 the glass surface was treated with 5% benzene solutions containing varying proportions of 1-trichlorosilyl-2-(p,m-chloromethylphenyl)ethane and β-phenethyltrichlorosilane, Z = CH_2Cl and H, respectively. (The relative rates of reaction of the two trichlorosilanes were assumed to be about the same and so the number of $-CH_2Cl$ groups attached to the surface should be proportional to the concentration of the 1-trichlorosilyl-2-(p,m-chloromethylphenyl)ethane). In step 2 the remaining chlorines attached to the silicon were hydrolyzed and the glass slides were heated at 110°C in vacuum to form the polysiloxane layer. Through step 2 the groups with Z = CH_2Cl and Z = H will behave the same. From step 3 onward, only the groups with Z= CH_2Cl will react and only those are used to illustrate the rest of the scheme. The number of $-CH_2Cl$ groups thus determines the maximum number of chemical bonds that form. In step 3 partially protected glycine (t-Bu-O-C(=O)-O-NH-$^{14}CH_2$-^{14}COOH) was bonded to the polysiloxane coating by reaction of the

Figure 2. Schematic Representation of the Preparation of the Peel Test Specimen Shown in Figure 1

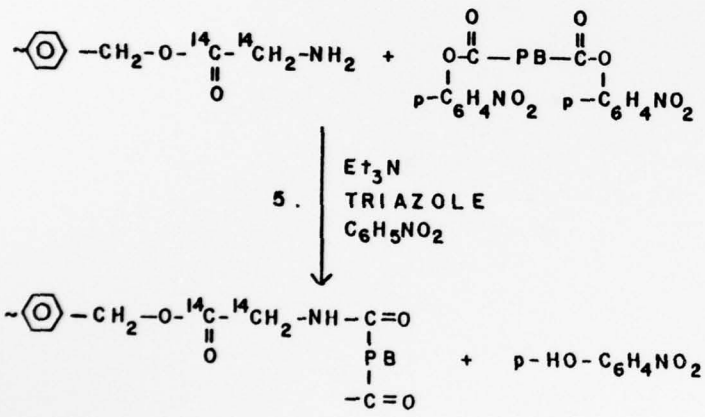
ADDING THE POLYSILOXANE



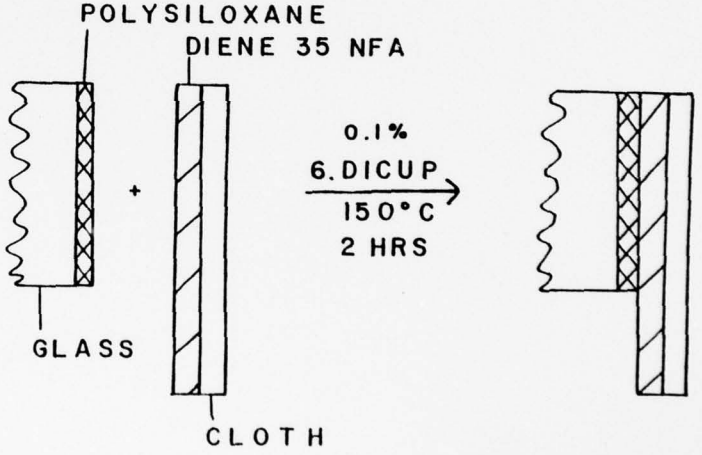
ADDING RADIOACTIVE GLYCINE



ADDING POLYBUTADIENE (CTB)



ADDING THE ADHESIVE



cesium (9) salt of the partially protected glycine with the chloromethyl group of the polysiloxane to form an ester linkage. In step 4 the t-Boc group was removed with trifluoroacetic acid (CF_3COOH) and in step 5 the free amine was coupled to the dicarboxy-terminated liquid polybutadiene via its p-nitrophenylester forming an amide bond (10). Finally, in step 6 the polybutadiene overlayer containing dicumyl peroxide was pressed against the treated slides and cured at 150°C to complete formation of covalent bonds from the glass surface to the polybutadiene adhesive.

Measurement of Radioactivity

β-Emission from the glycine molecules was measured after step 5 and again after the peeling test using a Picker Compact Scalar Model 644010. A modified gas flow-through system with Q-gas (1.3% Butane in Helium) as the counting gas was used. Background count was about 40 counts per minute (CPM) and observed counts due to glycine ranged from about 200 to 5000 CPM. A Glycine Standard was provided by ICN.

Measurement of Work of Adhesion, W

Measurements of the peel force were carried out sequentially on the two sides of the slides using the same procedure previously

described by Runge and Dreyfuss (5). Work of adhesion, W, per unit area of interface was calculated from the time average peel force, P, per unit width, w, of the detaching layer: W = 2P. All tests were carried out at 0.5 cm/min crosshead speed.

Results

The Observed Work of Adhesion

The results of our study are plotted in Figure 3 where the observed work of adhesion is plotted against both β-emission and the number of glycine molecules per 100 $\mathring{A}^2$. The number of glycines is equal to the number of interfacial bonds. The data are based on what appears to the eye to be interfacial failure at the glass-rubber interface. Several conclusions can be drawn from the results shown in the Figure:

1. As the number of glycine/100 $\mathring{A}^2$ increases, the work of adhesion increases.
2. There are relatively few instances in which the number of glycine/100 $\mathring{A}^2$ is greater than 4. By far the largest number of points lie between two and four glycine/100 $\mathring{A}^2$, although the mole fraction of 1-trichlorosilyl-2-(p.m-chloromethylphenyl)-ethane in the treating solution was varied from 0 to 1. This measured number of chemical

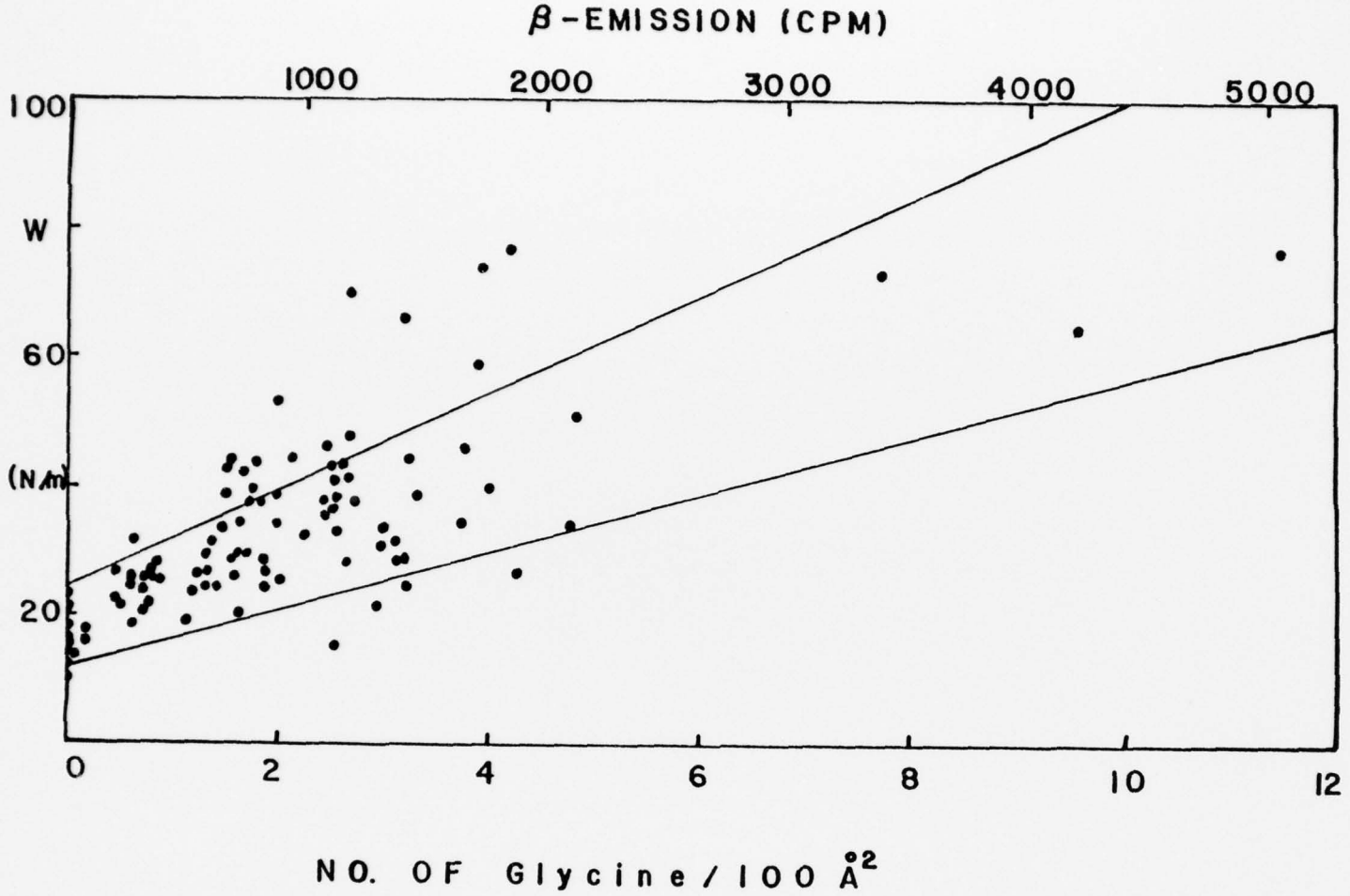


Figure 3. Effect of Number of Chemical Bonds on the Observed Work of Adhesion between Silanated Glass Surfaces and a Polybutadiene Adhesive

bonds is of about the same order of magnitude as the number of OH groups/100 $\mathring{A}^2$ usually quoted for glass dried under our conditions (11-13). This suggests a near 1:1 correlation between the number of interfacial bonds and indicates that the polysiloxane layer is probably no more than 1-2 layers thick.

3. As the number of glycine/100 $\mathring{A}^2$ increases, the scatter in the data also increases. We believe the scatter is real and results from an increasing amount of tearing through the polybutadiene toward the cloth. At higher peel forces patches of rubber on the glass were always visible to the eye. Therefore, instead of making a statistical analysis which would give one line and a coefficient of correlation, we have elected to draw two lines that encompass most of the data and give slightly greater weight to the lower values.
4. The slope of the lines is a measure of the increase in the work per interfacial chemical bond. This slope lies between 5 and 8 x 10^{-18} J/bond and is of the same order of magnitude as C-N, C-C, and C=C bond strengths found in the literature (14). Table 1 shows

Table I

Comparison of Typical Bond Strengths With Observed Increase in Work of Adhesion per Chemical Bond

Bond	E: J/Bond[a]	Slope/E[b]
C-N	0.5×10^{-18}	9-15
C-C	0.6×10^{-18}	8-13
C=C	1.2×10^{-18}	4-6

[a] Values in reference 14 are at 298^{0}K.

[b] The experimental slope is $(4.8\text{-}7.7) \times 10^{-18}$ J/glycine

the numerical comparisons. The experimental value is only one order magnitude higher than the bond strengths. The comparison would be even better if dispersion and van der Waals forces are considered (3). Furthermore, experimentally at any given time it is not possible to stress only one bond of a crosslinked network. Some work must be expended stretching several bonds simultaneously and this would lead to observed forces being higher than theoretical forces. Thus we feel that there is reasonable agreement between the slope and bond strengths.

The Locus of Failure

Bonds between silicon and oxygen or between silicon and carbon were not included in Table 1 because after peeling, essentially all the radioactivity remained on the glass surface. Considering that the interface has the structure shown in Figure 4, this indicates that fracture must have occurred within the polybutadiene or at one of the C-N bonds.

Conclusion

A quantitative relationship exists between the number of interfacial bonds of the model adhesive system described in this paper and the strength of the resulting joint. We conclude that chemical bonds at the interface improve adhesion.

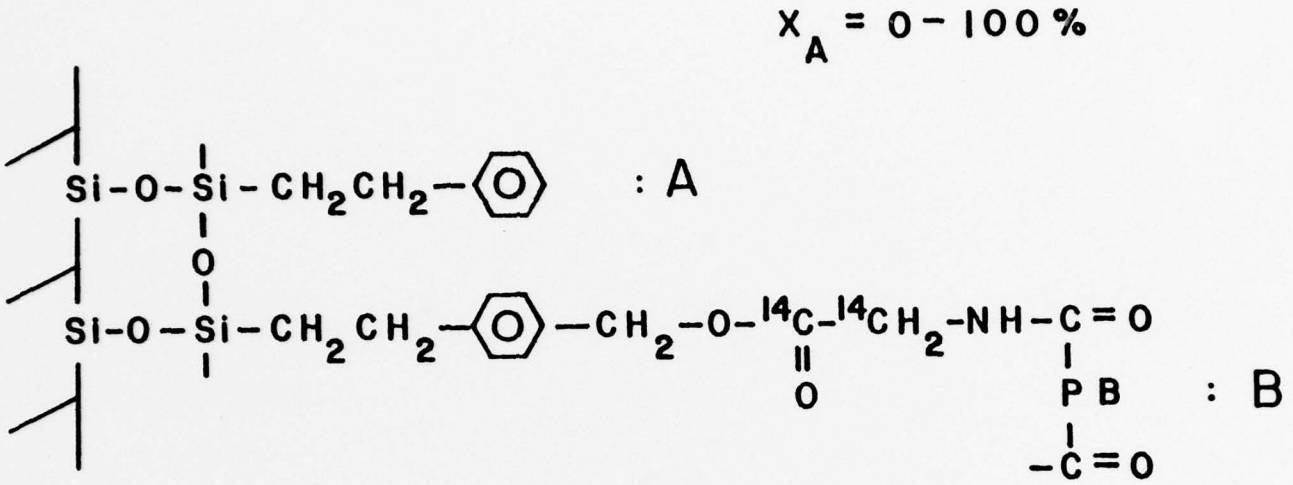


Figure 4. Structure of the Interface to which Polybutadiene Adhesive is Bonded

Acknowledgement

This work forms part of a program of research on the role of chemical bonding in adhesion supported by a research grant from the Office of Naval Research. The authors thank K. Riew of the BFGoodrich Co. for supplying the sample of CTB, Hercules, Inc. for the Dicup-R, and the Firestone Tire and Rubber Co. for samples of Diene 35 NFA. We are indebted to A. N. Gent for helpful comments and suggestions throughout the work.

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