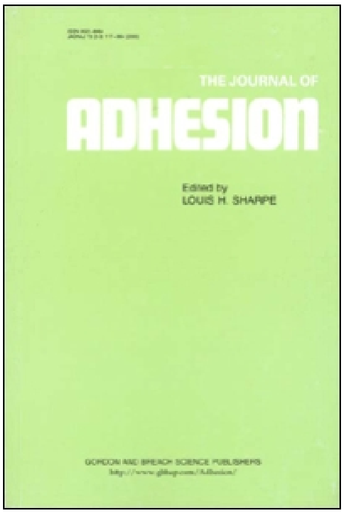

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Role of Amines in Adhesion of Polybutadiene to Glass Substrates. III. Effect of Amines on the Reaction of Peroxide with Olefinic Groups

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To cite this Article Eckstein, Y. and Dreyfuss, P.(1983) 'Role of Amines in Adhesion of Polybutadiene to Glass Substrates. III. Effect of Amines on the Reaction of Peroxide with Olefinic Groups', The Journal of Adhesion, 15: 2, 179 — 191
To link to this Article: DOI: 10.1080/00218468308073225
URL: http://dx.doi.org/10.1080/00218468308073225

J. Adhesion, 1983, Vol. 15, pp. 179–192
0021–8464/83/1502–0179 $18.50/0

Role of Amines in Adhesion of Polybutadiene to Glass Substrates.

III. Effect of Amines on the Reaction of Peroxide with Olefinic Groups

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(*Received June 7, 1982; in final form October 20, 1982*)

An attempt to elucidate the role of amines in general, and of 3-aminopropyltriethoxysilane in particular, has been made through a study of the title subject by several different approaches. This paper describes a near infrared study of the influence of amines on the reactions of model olefins with dicumyl peroxide. The model olefins were chosen to be representative of typical internal and external double bonds found in polybutadiene. The study has shown that in addition to serving as radical traps the amines participate in other ways. Exactly what occurs depends on the structure of the amine.

INTRODUCTION

The initial paper in this series showed that, contrary to expectations, amines do participate in free radical reactions leading to crosslinking of polybutadiene (PB).[1] Previous studies have indicated that the function of amines is to serve as radical traps (antioxidants), which either decrease[2] or have no effect[3] on the efficiency of crosslinking of unsaturated polyolefins. The reason that the earlier studies failed to detect the participation of amines in crosslinking reactions is that these studies were carried out either at high concentration of amine or at a high ratio of amine to peroxide.[2,3] Our study showed clearly that the effect of an amine on crosslink density is greatest when

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Presented at the Annual Meeting of The Adhesion Society, Savannah, GA, U.S.A., February 22–25, 1981.

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the concentration of the amino group approaches that of the peroxide. Such low concentrations are comparable to those that would be found in glass beads treated with 3-aminopropyltriethoxysilane. Trapping of free radicals takes place only at high excess of the amine. This phase of our study was undertaken to obtain a better understanding of the chemistry of the reactions that lead to crosslinking. Instead of polybutadiene itself, model compounds have been used as the source of the double bonds. In particular, 1-decene (D) and 2-hexene (H) were used as models for the internal and external double bonds of PB, respectively. Figure 1, which presents the near infrared spectra of PB, D and H, shows that the choice of these compounds as models for the PB is fully justified. The spectrum of the elastomer is almost reproduced by superposition of the spectra of the model compounds. As before, triethylsilanol (S) has been used as a model for the glass surface.

The study was made in the near infrared region because this region provides more specific information, both qualitative and quantitative, about hydrogen atoms in unique environments than is available from the remainder of the infrared region. Some additional information was obtained from gas liquid chromatography (GLC).

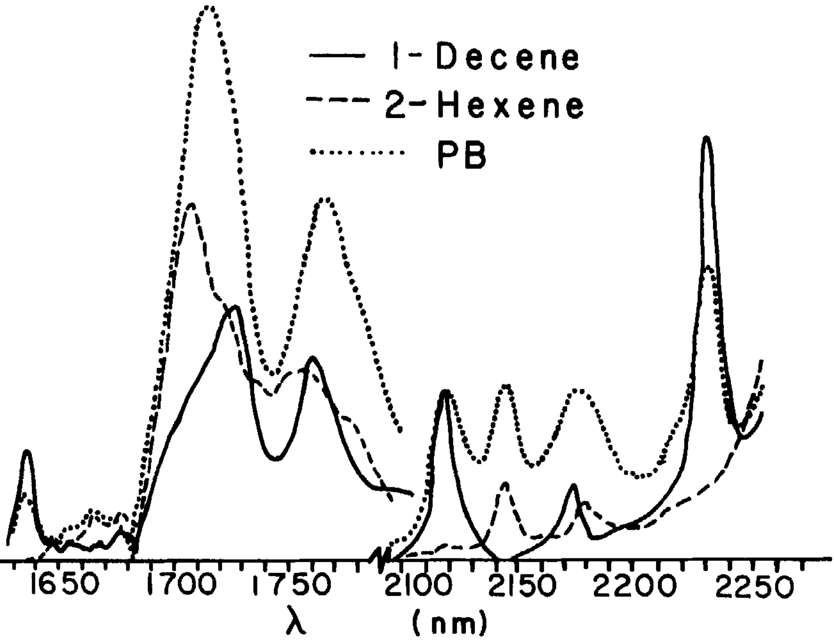


FIGURE 1 Comparison of near infrared spectra of ——— 1-decene, — — — 2-hexene, and ········· polybutadiene (Diene 35NFA).

EXPERIMENTAL

Materials

The reagents used consisted of *m*-phenylenediamine, "Aldrich"; 3-aminopropyltriethoxysilane and triethylsilanol, "Petrarch Systems Inc."; chloroform and carbon tetrachloride, spectranalyzed "Fisher Scientific Company"; dicumyl peroxide, dry "Hercules" DiCup®, 2-hexene 99+% (mixture of cis and trans, "Aldrich"), and 1-decene 99%, "Chem Samp Co".

Reactions

The reactants were mixed in a round bottom flask equipped with a condenser and heated at a constant temperature of 148°C for 17 hr, using a silicone oil bath. This temperature was used because it is above the decomposition temperature of dicumyl peroxide and near 150°C, the usual curing temperature for polybutadiene containing DiCup. In Table I are listed the quantities of each of the reactants in various reaction mixtures. In the last column of the table, a description of the reaction products is given. When two immiscible phases were formed, only the phase soluble in CCl_4 was analyzed.

Spectra

Known amounts (200–500 μl) of the reaction mixture were diluted with CCl_4 in a 10 ml volumetric flask. The near infrared spectrum of this mixture was recorded using a Cary 17 spectrophotometer. When three or more reagents were used in a given reaction, additional spectra were recorded for each of the reagents above and for pairs of reagents in different combinations. Spectra of known compounds suspected to be products were also recorded and used to confirm the identity of the proposed products. The assignments were consistent with those reported in the literature.[4]

Gas liquid chromatography

As a check on the credibility of our interpretation of the near infrared spectra, the reaction product mixtures were also examined by gas liquid chromatography using a Hewlett Packard 5710A Chromatograph equipped with an SE 30 column and a flame ionization detector. The retention time of pure known compounds was used to verify the identity of the products. Data were taken in real time by a computer and subsequently analyzed by computer.

TABLE I

Reaction mixtures

Mixture of reactants[a]	Concentration in mole/l						Remarks
	D	H	PO	AS	S	DA	
PO in 5 ml CCl_4	—	—	0.5	—	—	—	yellow oily solution
AS+PO	—	—	1.5	1.5	—	—	dark brown oily solution
D+AS	2.64	—	—	0.5	—	—	colorless solution + white fine precipitate
D+PO+AS	2.64	—	0.5	0.5	—	—	brown oily solution + white fine precipitate
D+PO+AS+S	2.64	—	0.5	0.5	0.6	—	brown oily solution + traces of white precipitate
D+2PO+AS+S	2.64	—	1.0	0.5	0.6	—	same as above
S+PO	—	—	1.5	—	1.5	—	brown oily solution
D+PO	2.64	—	0.5	—	—	—	yellow oily solution
D+PO+DA	2.64	—	0.5	—	—	0.5	very dark brown solution + tarry dark precipitate not soluble in CCl_4
D+2PO+DA+S	2.64	—	1.0	—	0.6	0.35	same as above
H+PO	—	8.06	1.0	—	—	—	yellow oily solution
H+PO+DA	—	4.03	0.5	—	—	0.5	yellow oily solution + heavier blue-green oily solution soluble in acetic acid

[a] PO = dicumyl peroxide.
D = 1-decene.
H = 2-hexene.
AS = 3-aminopropyltriethoxysilane.
S = triethylsilanol.
PDA = *m*-phenylenediamine.

RESULTS

Characteristics of the near infrared spectra of products from different reaction mixtures are summarized in Table II. The table includes assignment of the spectral bands to vibrational modes, position of the bands and comparison of their intensities. The intensities given in the table were calculated by dividing the measured absorbance by the concentration (mole/l) of the substance which is believed to be responsible for a given absorption band. For example, the intensities of vinyl group peaks at 2.23 μm and 1.633 μm were calculated from the initial concentration of 1-decene, while those of the primary amino group at 2.0 μm and 1.5 μm were calculated from the initial concentrations of the amines. The intensities of —OH bands due to the presence of cumyl alcohol, at 2.03 μm and 1.418 μm, were calculated from the initial concentration of dicumyl peroxide, since it was assumed that the alcohol resulted from hydrogen abstraction by an alkoxy radical. The intensities of peaks at 1.38 μm due to presence of the silanol group, at 1.408 μm due to ethanol (formed during reaction of triethylsilanol with 3-aminopropyl-triethoxysilane) and at 1.87 μm due to the presence of H_2O were calculated from the initial concentrations of triethylsilanol.

I. Control reactions

a) Decomposition of dicumyl peroxide (PO)

The near infrared spectra of the peroxide before and after decomposition are similar in appearance and in intensity. This is attributed to the mechanism of decomposition of the peroxide, in which the total concentration of the aromatic component remains unchanged throughout the decomposition:[5]

$$\phi C(CH_3)_2OO(CH_3)_2C\phi \rightarrow 2\phi C(CH_3)_2O^{\cdot} \quad (RO^{\cdot}) \tag{1}$$

$$\phi C(CH_3)_2O^{\cdot} \rightarrow \phi C(CH_3) = O + CH_3^{\cdot} \tag{2}$$

$$CH_3^{\cdot} + CH_3^{\cdot} \rightarrow C_2H_6 \tag{3}$$

The cumyloxy radicals formed in the reaction shown in Eq. (1) are not stable. They may decompose according to Eq. (2) to form acetophenone or they may abstract a hydrogen from other reagents, if present, and form cumyl alcohol. Since the solvent used throughout the study was CCl_4, no cumyl alcohol was formed when dicumyl peroxide was decomposed alone. The concentration of cumyl alcohol formed in other reaction mixtures provided a measure of the reactivity of the free radicals toward abstraction of hydrogen from the other reagents. Acetophenone is not visible in the near infrared region investigated but was found among the reaction products observed by gas liquid chromatography.

TABLE II

Intensities of absorption bands from near infrared spectra of reaction products[a,b]

	Double bond bands (μm)			Amine bands (μm)				—OH bands (μm)			
	Vinyl[c]		Aromatic or internal	Aliphatic[d]				Cumyl alcohol[e]		Ethanol[f]	S[a,f]
Reaction mixtures[a]	2.23	1.63	2.14	2.02	1.995	1.525	1.490	2.03	1.418	1.408	1.384
D	0.83	0.325									
H			0.13								
PO			1.28					0.24	0.22		
S											0.475
Ethanol										0.41	
D+PO	(−)	(−)	overlap					0.65	1.25		
H+PO		(+)						(+)	(+)		
S+PO	tail		1.4					0.48	0.88		0.26
AS				0.58	0.51	0.72	0.07				
AS+D	0.78	0.29	overlap	0.32	0.33	0.49	overlap				
AS+PO			0.08	(−)	(−)	(−)		1.76	2.24	(+)	
AS+D+PO	0.15	0.07	overlap	(−)	(−)	(−)		0.91	1.55		
AS+D+S+PO	0.64	0.18	overlap	(−)	(−)	(−)		1.3	2.2	1.43	0.49
AS+D+S+2PO	0.11	0.05	overlap	(−)	(−)	(−)		0.85	1.65	1.37	0.45
				Aromatic[g]							
				1.965	1.93	1.49	1.45				
PDA				1.52	0.37	1.27	0.45				
PDA+D+PO	0.48	0.18	overlap	1.02	0.26	0.88	0.16	3.92	3.85		0.32[e](H_2O?)
PDA+D+S+2PO	0.47	0.17	overlap	0.30	v.w.[h]	0.17	v.w.[h]	0.96	1.95		0.90[f] (H_2O?)
PDA+H+PO			(+)	(−)	(−)	(−)	(−)	(−)	(−)		

[a] The symbols have the same meaning as in Table I.

[b] (+) indicates the presence of the compound but its concentration was too low to be measured; (−) indicates total disappearance of the bands from the spectrum.

[c] Intensities were calculated from concentrations of D.

[d] Intensities were calculated from concentrations of AS.

[e] Intensities were calculated from concentrations of PO.

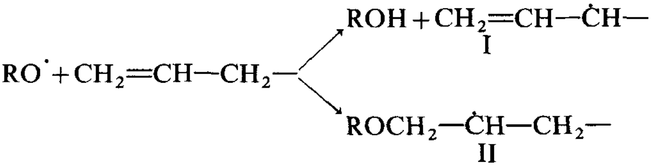
[f] Intensities were calculated from concentrations of S.

[g] Intensities were calculated from concentrations of PDA.

[h] v.w. = very weak.

b) Reaction of 1*-decene with peroxide* $(D+PO)$

When peroxide was added to 1-decene and allowed to react for 17 hr at 148°C, the vinyl peaks at 2.23 and 1.63 μm, characteristic of 1-decene, disappeared completely, and cumyl alcohol, absorbing at 1.418 μm, formed. The reactions which took place in the system are well known and can be represented by the scheme:



$$RO^{\cdot}+CH_2{=}CH{-}CH_2{-}\begin{array}{l} \nearrow ROH+\underset{\text{I}}{CH_2{=}CH{-}\dot{C}H{-}} \\ \\ \searrow \underset{\text{II}}{ROCH_2{-}\dot{C}H{-}CH_2{-}} \end{array} \qquad (4)$$

where ROH stands for cumyl alcohol ($\phi C(CH_3)_2OH$). The radical I formed in reaction 4 is reactive and may, therefore, add to a nearby double bond, initiating a sequence of further additions. Formation of radical II has not been shown directly, but if it forms, it would be expected to be very reactive and add readily to other double bonds.[6]

c) Reaction of triethylsilanol with dicumyl peroxide $(S+PO)$

This reaction mixture turned brown. The products of the reaction were cumyl alcohol and a thick oil. Since the decomposition of PO alone gives acetophenone and ethane, the presence of cumyl alcohol among the products implies the participation of S in a free radical reaction. This is not surprising. It is known that polyorganosilanes containing methyl and ethyl groups can be converted to elastomers by curing with small amounts of peroxide.[7,8] The alkoxy radical formed by decomposition of the peroxide presumably abstracts a hydrogen from one of the alkyl groups and cumyl alcohol forms. The resulting alkyl radicals condense to give a rubbery or oily product of unknown structure. The dark color suggests that oxidized and/or unsaturated condensed products form simultaneously.

d) Reaction of 3*-aminopropyltriethoxysilane with dicumyl peroxide* $(AS+PO)$

This reaction mixture also turned dark brown. As shown in Table II, the $-NH_2$ bands of the AS disappeared completely and a large quantity of cumyl alcohol formed. The disappearance of the amino group can be ascribed to the known ability of primary and secondary amines to induce decomposition of peroxides in a chain reaction.

$$R_2CHNH_2+RO^{\cdot}\rightarrow R_2\dot{C}NH_2+ROH \qquad (5)$$

$$R_2\dot{C}NH_2+ROOR\rightarrow \underset{\text{III}}{R_2C{=}NH}+ROH+RO^{\cdot} \qquad (6)$$

Here ROOR denotes a molecule of peroxide. In the case of primary amines product III may undergo a condensation reaction with unreacted amine[9] resulting in formation of $R_2C{=}N{-}CH_2R$ (IV). Oxidation of amine or of compound IV could give a dark color to the reaction mixture. However it should be noted here that formation of compound IV may not be solely responsible for the dark color of the reaction mixture. A similar color was obtained in the S + PO system in the absence of the amino group. There it was deduced that the ethyl groups participated in the free radical reaction. Ethoxy groups should be even more reactive toward alkoxy radicals than ethyl groups. It seems therefore that both the amino and ethoxy groups of the AS participated in the reaction. This explains the relatively large quantities of cumyl alcohol formed by interaction of AS and PO.

e) Reaction of 1-decene with 3-aminopropyltriethoxysilane (D + AS)

This reaction gave a mixture of soluble products plus a fine precipitate. The near infrared analysis of the soluble products from this reaction indicated that, compared to the starting materials, the concentration of both the AS and D were reduced. This conclusion is based on the reduced intensity of the $-NH_2$ group peaks at 2.0 and 1.526 μm, and of the vinyl group peaks at 2.23 and 1.65 μm. (See Table II.) The precipitate was insoluble in conventional solvents and left no residue on burning. It was probably a gel of unknown structure formed by interaction of AS and D.

II. Model reactions for the polybutadiene phase

a) Reaction of 1-decene and 3-aminopropyltriethoxysilane in the presence of dicumyl peroxide (D + AS + PO)

As described above, when peroxide was added to 1-decene alone, the vinyl peaks at 2.23 and 1.63 μm disappeared completely. In the presence of AS, about 20% of the vinyl groups remained. The bands at 2.0 and 1.525 μm, characteristic of the primary amino group of AS, disappeared totally from the spectra. GLC confirmed these observations and in addition a new product was observed at very long retention time.

In view of the reactions described above in the control reactions with D + PO, AS + PO and D + AS, these results imply higher or at least similar reactivity of the alkoxy radicals toward AS molecules than toward D molecules. Disappearance of the NH_2 group of AS and the product at long retention time in the GLC suggest polycondensation of the AS. Simultaneous reaction of AS with D by a free radical mechanism cannot be excluded.

b) Reaction of 1-decene with m-phenylenediamine in the presence of peroxide (D + PDA + PO)

On addition of PDA to the reaction mixture consisting of D + PO, about only 50% of the total concentrations of vinyl and amino groups reacted with the alkoxy radicals, yet the concentration of the cumyl alcohol formed was higher by a factor of about 4–6 than in the reaction of D + PO and by factor of ~2.0 than in AS + PO.

Nozaki and Bartlett[10] concluded that, in general, more stable free radicals show a greater tendency to react with other radicals instead of with other molecules. Therefore in the case of PDA, the radicals (V) formed by action of the alkoxy radicals in reaction 7,

$$NH_2\phi NH_2 \xrightarrow{RO^{\cdot}} \underset{V}{NH_2\phi\dot{N}H} + ROH \tag{7}$$

which are stabilized by resonance with the aromatic ring, will react with other radicals rather than induce further decomposition of the peroxide or polymerization of D. This accounts for the high concentration, about 50%, of the unreacted vinyl compound in the reaction products from the D + PDA + PO mixture. Alternatively, the high concentration of unreacted vinyl compound may result from greater reactivity of the PDA compared to D toward alkoxy radicals.

The reason for the formation of the high concentration of cumyl alcohol is obvious, if it is recalled that one mole of PDA has four abstractable hydrogens on the nitrogen atoms and thus can give rise to four moles of cumyl alcohol by reaction with alkoxy radicals. This result lends support to our conclusion in Part I of this series that all four hydrogens on PDA are available to participate in crosslinking reactions.[1]

This product mixture was dark colored probably as a result of oxidation of the aromatic amine groups and condensation of radicals of PDA.[11] These condensation products precipitated from CCl_4 in time and could be redissolved in acetic acid but not in CCl_4.

c) *Reaction of 2-hexene with m-phenylenediamine in the presence of peroxide (H + PDA + PO)*

1-Decene was used as a model for the vinyl group present in polybutadiene. 2-Hexene and its reactions were used to study the reactivity of the internal double bonds in the same elastomer. Qualitatively, the reaction products of 2-hexene with PDA in the presence of peroxide were similar to those described above for D + PDA + PO. The reaction products consisted of two phases; namely, a liquid soluble in CCl_4 and rich in cumyl alcohol and a solid phase, which was soluble in acetic acid but not in CCl_4. Because of the high volatility of H at the reaction temperature of 148°C from the simple apparatus used, quantitative analysis was not possible (2-hexene boils at 67–69°C).

III. Model reactions for the polybutadiene-glass interphase

a) Reaction of 1-decene with dicumyl peroxide in the presence of 3-aminopropyltriethoxysilane and triethylsilanol (D + AS + PO + S)

A comparison of the near infrared spectra of D + AS + PO + S, D + AS + PO and D + PO is given in Figure 2. In the presence of the silanol, a strong peak of ethanol at 1.408 μm in the near infrared spectrum was observed; but the silanol concentration did not change. The ethanol peak was absent from the spectrum of D + AS and appeared only as a shoulder in the spectrum of D + PO + AS. Moreover, in the presence of silanol, as shown in Table I, more than 75% of the vinyl groups of 1-decene did not react. When the concentration of peroxide was doubled, 20% of the vinyl groups still did not react, and the final concentrations of ethanol and silanol were the same as before. Also, in contrast to the system of D + AS or D + AS + PO, only traces of precipitate were found here. All these facts point to a different reaction mechanism in the presence of silanol when compared to the system D + AS + PO.

The fact that the concentration of silanol groups remained unchanged throughout the experiment suggests the absence of a condensation reaction of

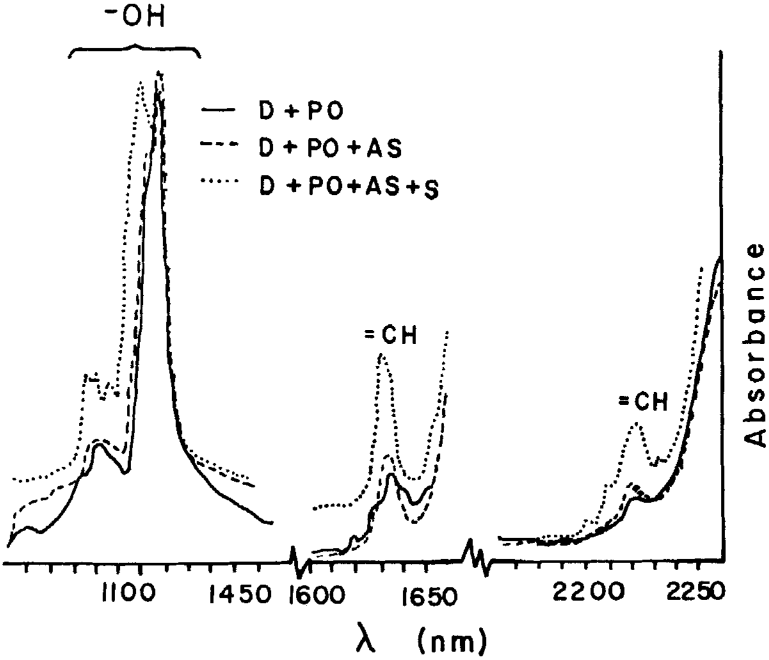


FIGURE 2 Near infrared spectra of reaction products: ——— D + PO, — — — D + PO + AS, ········· D + PO + AS + S.

the type:

$$(EtO)_3Si{-}R' + HOSiEt_3 \rightleftharpoons EtOH + Et_3Si{-}O\overset{|}{\underset{|}{Si}}{-}R' \tag{8}$$

The ethanol found in the products (Table II) must have been formed, therefore, at a later stage by interchange between the cumyl alcohol and the AS:

$$(EtO)_3Si{-}R' + ROH \rightleftharpoons EtOH + RO{-}\overset{|}{\underset{|}{Si}}{-}R' \tag{9}$$

Such reactions are normally slow in the absence of catalysts, but equilibrium is rapidly established in the presence of acid or bases.[12] Here the silanol acts as an acid. Broadening of near infrared spectral bands, dependence of the 20 μm spectral characteristics on concentration and the shift of the 1.525 μm band to lower energies indicates that at the earliest stage of the reaction the S forms a complex with the amino group of the AS:

$$(EtO)_3Si{-}(CH_2)_3NH_2 + HO{-}SiEt_3 \rightarrow [(EtO)_3Si(CH_2)_3NH_3]^+[OSiEt_3]^- \tag{10}$$

The details of these studies were described in Part II of this series of papers.[13] Later, because of the high temperature and the presence of peroxide, oxidation might take place resulting in formation of covalently bonded nitrogen groups or irreversible absorption of amino groups as opposed to the reversible reaction with single silanol groups shown in Eq. (8). Some possible amine oxidation products have been described above in section I—d and in Ref. 9. In the presence of S, the bonding would occur as a result of free radical reactions between the amine of the AS and the ethyl groups of the S. With glass, coordinate bonds are still possible through the amine group. Others have previously shown that coordinate bonds form between some surface species in glass and ammonia.[14–16] The possibility of such coordinate bonds suggests that in the presence of peroxide, bonding of a compound like AS to a glass surface can take place through the amino group and not exclusively through a siloxane group as is usually proposed.

Amine groups, which do not participate either in the reaction shown in Eq. (10) or in reactions like those described in the previous paragraph, would be consumed in reactions described by Eqs. (5) and (6).

b) Reaction of 1-*decene with m-phenylenediamine in the presence of triethylsilanol and dicumyl peroxide* ($D+PDA+S+PO$)

As can be seen from Table II, on inclusion of silanol in the reaction mixture of D + PDA + PO, the concentration of the unreacted vinyl groups remained unchanged, even when the concentration of the peroxide was doubled. At the same time, the concentration of the —NH_2 groups decreased dramatically. The decrease in amino group concentration must have resulted from an interaction of the amine with the silanol at a very early stage, due to formation of an acid-base compound similar to the one shown in Eq. (10) for AS. Subsequently, this complex may disintegrate to form a variety of products.[3] The sharp decrease in the concentration of cumyl alcohol in the system containing silanol is in agreement with this mechanism. Since the concentration of the cumyl alcohol was reduced by a factor of two, only one amine group seems to be involved in formation of the salt, $[NH_2\phi NH_3]^+[OSiEt_3]^-$, while the second amine group reacts with free radicals to form products of the type given by Eq. (7).

CONCLUSIONS

The reactions with model compounds provided insight into the effect of amines on the reactions occurring during peroxide curing of polybutadiene in contact with glass. The studies with model compounds indicate that aminosilanes and aromatic amines participate in the free radical crosslinking of polybutadiene to form Si—O—C, C—N—C, ϕ—N—C in addition to C—C and Si—O—Si links. 3-Aminopropyltriethoxysilane may bond to the polybutadiene network through the ethoxy groups as well as through the amino group, while the aromatic amines bond to polybutadiene through the amino group. Reactions with triethysilanol as a model for the glass surface showed that the mechanisms of interaction of 3-aminopropyltriethoxysilane and of aromatic amines are different. With the primary aliphatic amine carbamates form readily[13] and an acid-base ionic complex of the type $[RNH_3]^+[OSiEt_3{}^-$ forms at an early stage. In the presence of peroxide and heat covalent bonds may form between the silanol and the amine. Bonding to the rubber phase can occur through the ethoxy groups. With aromatic diamines the results indicate that one amino group reacts with the silanol to form the same initial ionic complex given above while the other reacts later with the polybutadiene matrix.

Acknowledgement

This work forms part of a program of research on the adhesion of elastomers sponsored by a research grant from the Office of Naval Research. The authors thank Hercules, Inc. for a sample of dry dicumyl peroxide, DiCup®.

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