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An attempt to elucidate the role of amines in general, and of 3-amino-propyltriethoxysilane in particular, has been made through a study of the title subject by several different approaches. This paper describes the interactions of amines during curing of the rubber phase. When aromatic or cyclic amines were added, maximum stress at break and minimum swelling ratios were observed when the number of alkoxide radicals generated was equal to the number of hydrogen atoms on the nitrogen of the amines. The order of			

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reactivity was thus no amine < aniline < piperazine < m-phenylenediamine. The greatest effect of aliphatic amines also occurred when the concentration of primary amino groups was equal to the concentration of peroxide; but the behavior was complex and dependent on the backing against which samples were molded. The higher rigidity and reinforcement of the polybutadiene in the presence of low concentrations of amines was attributed to formation of chemical bonds between the amines and the polybutadiene. ↗

OFFICE OF NAVAL RESEARCH
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Technical Report No. 22

ROLE OF AMINES IN ADHESION OF POLYBUTADIENE TO GLASS SUBSTRATES
I. REACTIONS OF AMINES DURING PEROXIDE CURING OF POLYBUTADIENE

BY

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October, 1982

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- (1) the effect of amine structure and amine/peroxide concentration on the mechanism of interaction with a polybutadiene backbone
- (2) the effect of amine on the reaction of peroxide with internal and external olefinic groups in model compounds
- (3) the effect of amine structure on the mechanism of interaction with inorganic surfaces such as glass
- (4) the effect of amine structure and concentration on the strength of adhesion of peroxide cured polybutadiene to a glass surface.

The first study consisted of an examination of the effects of the presence of amines on the mechanical properties of peroxide cured polybutadiene and is the subject of this paper. The results of the other three studies will be reported separately.

EXPERIMENTAL

Materials

1,4-Diaminobutane (99%), anhydrous piperazine (99%), and *m*-phenylenediamine (99+%) from Aldrich Chemical Company, Inc., aniline ("Baker Analyzed" Reagent) from J. T. Baker Chemical Co., 3-aminopropyltriethoxysilane and triethylsilanol from Petrarch Systems, Inc. and dry dicumyl peroxide (Di-Cup^R R) from Hercules, Inc. were used as received. The structures and properties of these materials are given in Table I. Two criteria were used in the selection of amines for this study. First, a variety of

structures was desired, so selected compounds include primary and secondary amines as well as aliphatic, aromatic, linear and cyclic amines. Second, since curing of the elastomer was carried out at 150°C, compounds with boiling points close to or above 150°C were chosen. The polybutadiene (PB) was Firestone's Diene 35, an anionic polybutadiene of $\bar{M}_n = \sim 150,000$ and cis:trans:vinyl (%) = 36:54:10. Chloroform (Spectroanalyzed) from Fisher Scientific Co. was used as received.

Mixing of Amines with Polybutadiene

The solid amines were ground in a mortar and incorporated into PB during mill mixing of the rubber with peroxide on an unheated mill. The liquid amines were first diluted with chloroform and then appropriate quantities of the solution (50-800 μ l) were added to the rubber with the aid of a syringe by filling with the solution voids adventitiously and randomly present in the rubber as received. Usually the PB-amine mixture, covered with aluminum foil, was allowed to sit on the bench overnight. Only after the chloroform had evaporated or dissolved in the rubber, was the rubber mill-mixed with peroxide. Any chloroform still present should have evaporated during milling.

Curing

Each of the mixtures, containing a constant level of peroxide, 0.05 phr (or 1.85×10^{-5} mole/100 gr PB), was premolded for 3 mins. at 65°C and finally molded usually between Mylar 300A sheets for 2 hrs at 149°C at a pressure >30000 psi/5" ram on a PHI press. The molded and cured sheets had a thickness of 1.5 mm. Mylar 300D, cellophane, and Teflon coated aluminum sheets were sometimes used for molding samples containing diaminobutane or 3-propylaminotriethoxysilane.

Tensile tests. The tests were carried out at room temperature using dumbbell shaped specimens (11.5 cm long, 0.65 cm wide at the narrow central part) cut from the molded sheet with a sharp die. The breaking stress was determined from the breaking force by dividing by the cross-sectional area of the narrow central part of the specimen. All the measurements were carried out at a cross-head speed of 50 cm/min. (0.83 cm/sec). The deviation in measured tensile strength was $\pm 3-4\%$.

Linear swelling ratio measurements.

Samples were cut in the same direction from all molded sheets. The same sample of polybutadiene was used for all comparisons. For each compound measurements on two separate strips were carried out. The lengths of strips of rubber of about 1 cm wide and about 8 cm long were measured before, L_0 , and after, L_f , immersion in n-heptane solvent at room temperature for 40-70 hrs. The swelling ratio, q , was calculated from the ratio L_f/L_0 . If there is an orientation effect, it should have been the same for all specimens and would not have been observed by this procedure.

RESULTS

The mechanical properties studied were tensile strength and swelling ratio. Any effect caused by the presence of amine, resulting in reduced or increased crosslinking density, should be easily identified by measuring these properties.

Aromatic and Cyclic Amines

PB compounds containing these amines handled normally after being molded between Mylar 300A sheets. The effects of amine concentration on mechanical properties, at constant level of peroxide

(0.05 phr or 1.85×10^{-1} moles/100 gr PB) are given for aromatic and cyclic amines in Figure 1. The figure shows that in the presence of these amines the degree of change in the mechanical properties of PB depends on both the amine structure and its concentration. The greatest changes are observed in the presence of m-phenylenediamine (PDA); aniline (A) has only a small effect. As the amine concentration increases, the swelling ratio first decreases gradually, while the tensile strength increases. The two properties reach a limiting value at the same concentration, specific for a given amine, and then return gradually to near their values in the absence of amine.

Diaminobutane (AB) and 3-Aminopropyltriethoxysilane (AS)

PB compounds containing these amines adhered tenaciously to the backing after being molded between Mylar 300A sheets. This type of Mylar is known to have a silicone lubricant on its surface. Zeller (14) has shown by ESCA analysis that the Mylar surface contains 0.5% Si even after molding against PB. We presumed that the amines being considered in this section are able to react with this lubricant and thereby form strong bonds to the Mylar. Therefore, experiments using other backings during curing were carried out. The results are summarized in Table II. The assumption that the amines of this section can react with the lubricant seems justified, since molded specimens could readily be separated from the backing in the absence of the lubricant but adhered tenaciously whenever it was present.

Plots of swelling ratio and tensile strength versus amine concentration presented in Figure 2, show that in the case of the PB and AB compound molded between Mylar sheets, the swelling ratio increases in value with an increase of the amine concentration, while the tensile strength decreases. Similar behavior, but less pronounced, was observed in the case of PB + AS compounds. This is in contrast to the observation made in the case of aromatic and cyclic amines, presented in Figure 1, which showed an opposite effect. When PB + AS compounds were molded between Teflon sheets, the swelling ratio decreased, and was accompanied, surprisingly, by a simultaneous decrease in tensile strength. The mechanical properties observed after molding between cellophane were different again.

The effect of the amine concentration on mechanical properties seems to be inconsistent and depends strongly on molding conditions and especially on the backing used during molding. However, the plots have one thing in common; namely, the greatest changes in mechanical properties always take place when the molar ratios of amine to peroxide is about 1. This fact implies that the aliphatic amines or 3-aminopropyltriethoxysilane do participate in the radical crosslinking of PB, even though the specific results depend strongly on the surfaces against which the PB is molded.

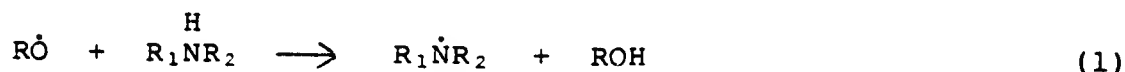
DISCUSSION

A comparison of Figure 1 with Figure 2 suggests that the interactions of aromatic and cyclic amines with PB and peroxide during curing are different from those of aliphatic amines and

3-aminopropyltriethoxysilane. However, regardless of the nature of the interactions, at concentrations near those of the peroxide each of the amines does participate in the free radical cross-linking reactions of PB. This conclusion is totally unexpected, since amines are known to act as radical traps. Data in the literature indicate that addition of amine antioxidants decreases (15) or has no effect (16) on the efficiency of crosslinking of unsaturated polyolefins. But these studies were carried out either at high concentration of the additive or at high ratio of the additive to peroxide (15,16). Our study shows clearly that the effect of an amine on crosslinking density is greatest when the concentration of the amino groups approaches that of the peroxide; trapping of free radicals takes place only at high excess of the amine.

Aromatic and Cyclic Amines

Figure 1 shows that the magnitude of enhancement of tensile strength and crosslink density (inversely related to swelling ratio) increases in the order: aniline < piperazine < m-phenylenediamine. The maxima in the plots given in Figure 1 occur at molar ratios of amine to peroxide of 0.5 for m-phenylenediamine and 1 for aniline or piperazine. These numbers suggest that a relationship exists between the mechanical properties, and the relative concentrations of the amine and the peroxide. Such a relationship can be explained by assuming that the reaction proceeds via abstraction of the labile hydrogens on the amino groups, according to the scheme:



where $\text{R}\dot{\text{O}}$ represents alkoxy radicals.

This mechanism conforms with the conclusions of Bartlett and Nozaki (17). These authors state that when a peroxide decomposes in the presence of an amine, it appears that, if a nitrogen-hydrogen (N-H) bond is present, the N-H bond is attacked before all others. They ascribed this course of reaction to greater accessibility of the N-H bond to attack and resonance stabilization of the amine radical formed.

Calculation of the ratios of molar concentration of labile hydrogens of the amine group at the point of maximal changes in mechanical properties, to the molar concentration of peroxy radicals present in the curing system, reveals that in each case the ratio equals 1 (Table III). These results imply that the aromatic and the cyclic amines do indeed participate in reactions with free radicals, as described by eq. (1).

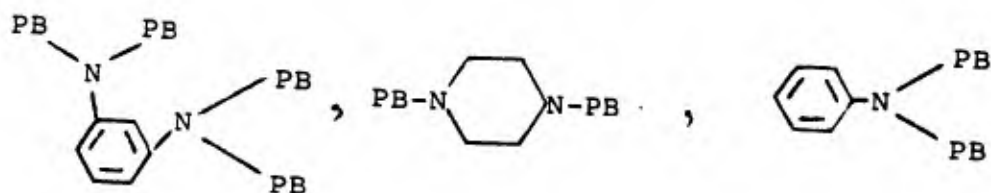
In order to determine whether crosslink density is the only factor in our systems that influences the stress at break and swelling ratio of the PB, compounds with different concentrations of peroxide were prepared and their properties were examined. Both stress at break and swelling ratio varied linearly with peroxide concentration. These data were used to predict the maximum percent increase in tensile strength at break attributable to an increase in crosslink density alone. It was assumed that compounds with the same swelling ratio have the same crosslink density and that the small amount of amine present in some compounds did not influence

their swelling behavior. The percent increase was calculated relative to the tensile strength of PB cured by peroxide alone at the same peroxide concentration used when amines were present. The results are compared in Table IV with the percent increases actually observed in the presence of amine. Good agreement between predicted and observed percent increases was obtained only for aniline. Much larger increases than predicted were observed in the presence of PDA and P. We conclude that part of the observed enhancement of tensile strength must have resulted from factors other than crosslink density.

Loan (18), studying the effect of adding sulfur to ethylene-propylene rubber before curing with peroxide, made an observation similar to the above. He suggested that the sulfur was incorporated into the crosslinks and changed the network structure. By analogy to Loan's hypothesis, the possibility of incorporation of the amines into the crosslinks of PB rubber needs to be examined as the factor that might be responsible for the measured enhancement of tensile strength.

As indicated in eq. (1), abstraction of hydrogen from an amino group by an alkoxy radical results in formation of an amine radical. This radical may later react with a polymeric chain, most likely by combination with a radical on the rubber. (Addition of the free radicals formed from an amine to a double bond in the rubber to form an active free radical on the chain is not expected (17). Bartlett and Kozaki observed very little polymerization when benzoyl

peroxide was decomposed by triethylamine in the presence of vinyl acetate, a monomer capable of undergoing free radical polymerization (17).) Since each molecule of PDA contains four labile hydrogens on the nitrogen, one molecule of PDA should be able to react with four polymeric chains. In contrast, aniline or piperazine, each having only two labile hydrogens, should be able to react with only two polymeric chains. Such reactions would result in formation of crosslinks of the following form:



In the case of PDA, the polymeric chains would be linked together through the aromatic ring; in the case of piperazine also through the cyclic structure, but in the case of aniline only through the nitrogen atom. Since aromatic or cyclic structures are more rigid and less flexible than the aliphatic chain, the enhancement of tensile strength observed in the case of PDA and P can be attributed to incorporation of these rigid units into the crosslinked network of PB. In the case of A the aromatic ring is left out of the main polymeric chain, and has no effect on tensile strength.

Diaminobutane(AB) and 3-Aminopropyltriethoxysilane(AS)

As mentioned already, the consideration of the results shown in Figure 2 leads to the conclusion that aliphatic amines and

aminosilane participate in the free radical crosslinking of PB. This conclusion is in agreement with the observation made by Ranney et al. (2) and Plueddemann (3). They concluded that aminosilane influences the vulcanization process and provides a higher state of cure in the base rubber blend.

The mechanism by which aminosilane interacts with the polymeric network is unclear. The decreases in tensile strength and in elongation at break of PB compounds containing AS, molded between Mylar or teflon sheets, as the concentration of the amine increased, suggest incorporation of siloxane units into the crosslinks. This hypothesis is supported by Noll's observation (19) that the presence of ethoxy groups has an effect on crosslink density similar to that of vinyl groups. It is also supported by the evidence gained from studies of reactions of model compounds (20) and described in Part II of this series.

CONCLUSIONS

1. At concentrations of amines comparable to those of the peroxide used to cure PB, amines participate in rather than inhibit the free radical crosslinking of PB.
2. Interactions of aromatic and cyclic amines with PB and peroxides during curing are different from those of aliphatic amines.
3. The effect of aromatic and cyclic amines on the mechanical properties of PB increases in the order: aniline < piperazine < m-phenylenediamine. It is postulated that incorporation of the amines into the network of crosslinked PB is responsible

for increased stiffness and enhanced tensile strength at break of peroxide cured polybutadiene if amines are added before curing.

4. Properties of PB cured in the presence of diaminobutane or 3-propylaminotriethoxysilane are strongly influenced by the surfaces against which the PB is molded.

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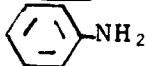
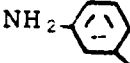
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TABLE I

List of Compounds Incorporated into Polybutadiene

<u>Compound</u>	<u>Structure</u>	<u>b.p. (°C)</u>	<u>m.p. (°C)</u>	<u>Symbol</u>
1,4-diaminobutane	$\text{NH}_2(\text{CH}_2)_4\text{NH}_2$	159	27	AB
piperazine		145	109	P
aniline		184	-6.3	A
<i>m</i> -phenylene diamine		283	65	PDA
3-aminopropyl-triethoxysilane	$\text{NH}_2(\text{CH}_2)_3\text{Si}(\text{OEt})_3$	122/30mm	AS
triethylsilanol	Et_3SiOH	75/24mm	
dicumyl peroxide	$\text{C}(\text{CH}_3)_2\text{OO}(\text{CH}_3)_2\text{C}$	~ 150 (decomp)		

16
TABLE II

Backings Used for PB Compounds Containing AB and AS

<u>Backing</u>	<u>Ease of Removal of Backing</u>	
	<u>from AB</u>	<u>from AS</u>
Mylar 300A ^a	Adhered tenaciously; could be separated by soaking in water for 36 hrs.	Adhered tenaciously could not be sepa- rated even after soaking in water for one month
Cellophane	— — — — —	Easy to separate
Cellophane with Mylar 300A backing	— — — — —	Could not be sep- arated
Mylar 300D ^b	— — — — —	Easy to separate
Teflon clad aluminum	— — — — —	Easy to separate

^aSurface is covered with an unknown lubricant used in processing.

^bSurface is untreated.

TABLE III

Ratios of Molar Concentrations of Amine to Peroxide at the Point
of Maximal Changes in Mechanical Properties of the Cured PB

<u>abbreviation</u>	<u>amine</u>	<u>[amine]/[ROOR]^a</u>	<u>[amino group]/[ROOR]</u>	<u>H/RO[·]^b</u>
PDA	NH ₂ ∅NH ₂	0.5	2	1
A	∅NH ₂	1	1	1
P	HN∅NH	1	2	1

a) ROOR denotes dicumyl peroxide

b) RO[·] denotes alkoxy radicals

TABLE IV

Comparison Between Tensile Strength of Peroxide Cured Polybutadiene
in the Presence and in the Absence of Amines^a

<u>Amine</u> ^c	<u>Predicted Increase (%)</u> ^b	<u>Observed Increase (%)</u>
PDA	7	31
P	3.5	12
A	2	2

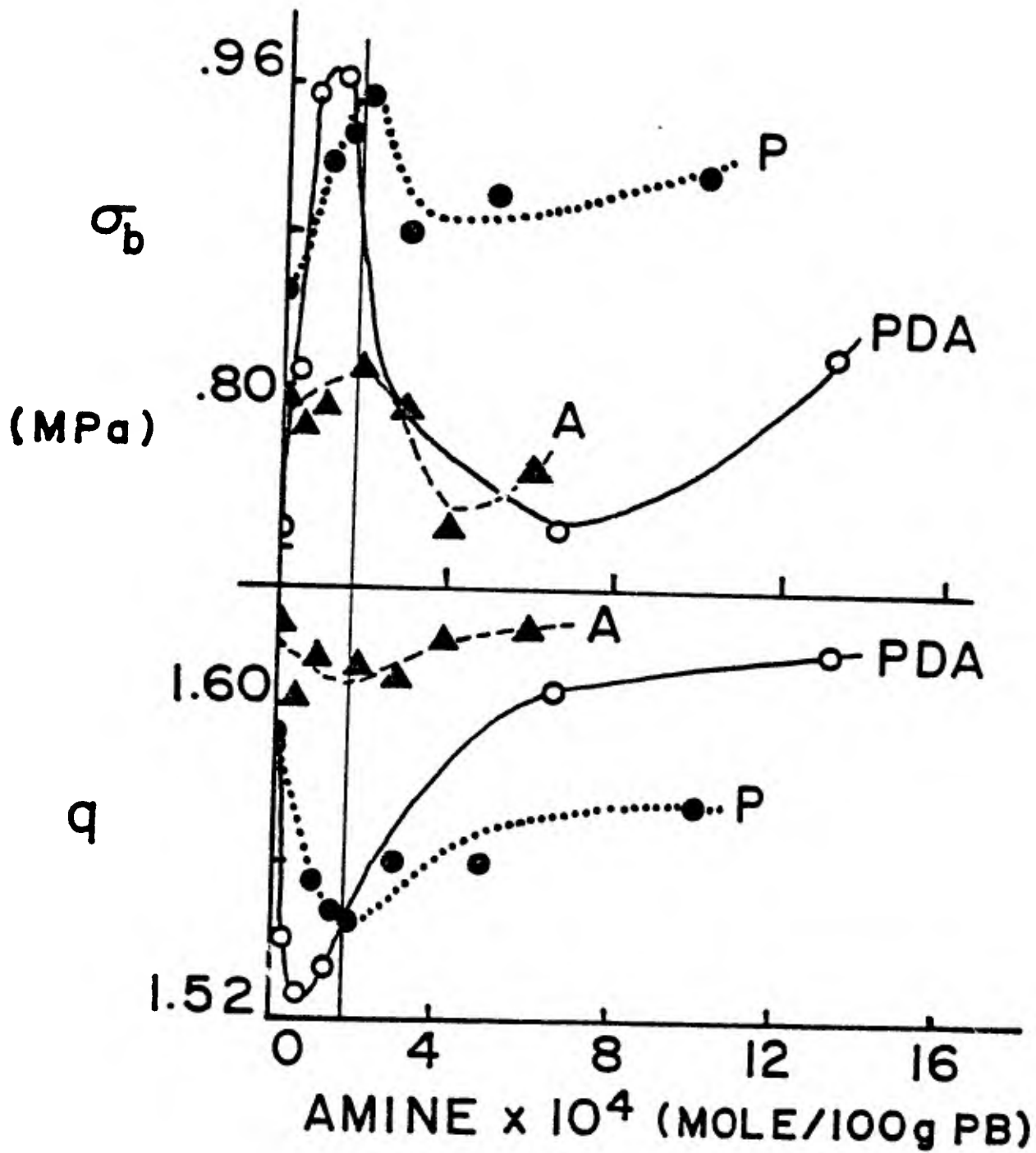
^aThe same peroxide concentration, 0.05%, was used in all samples.

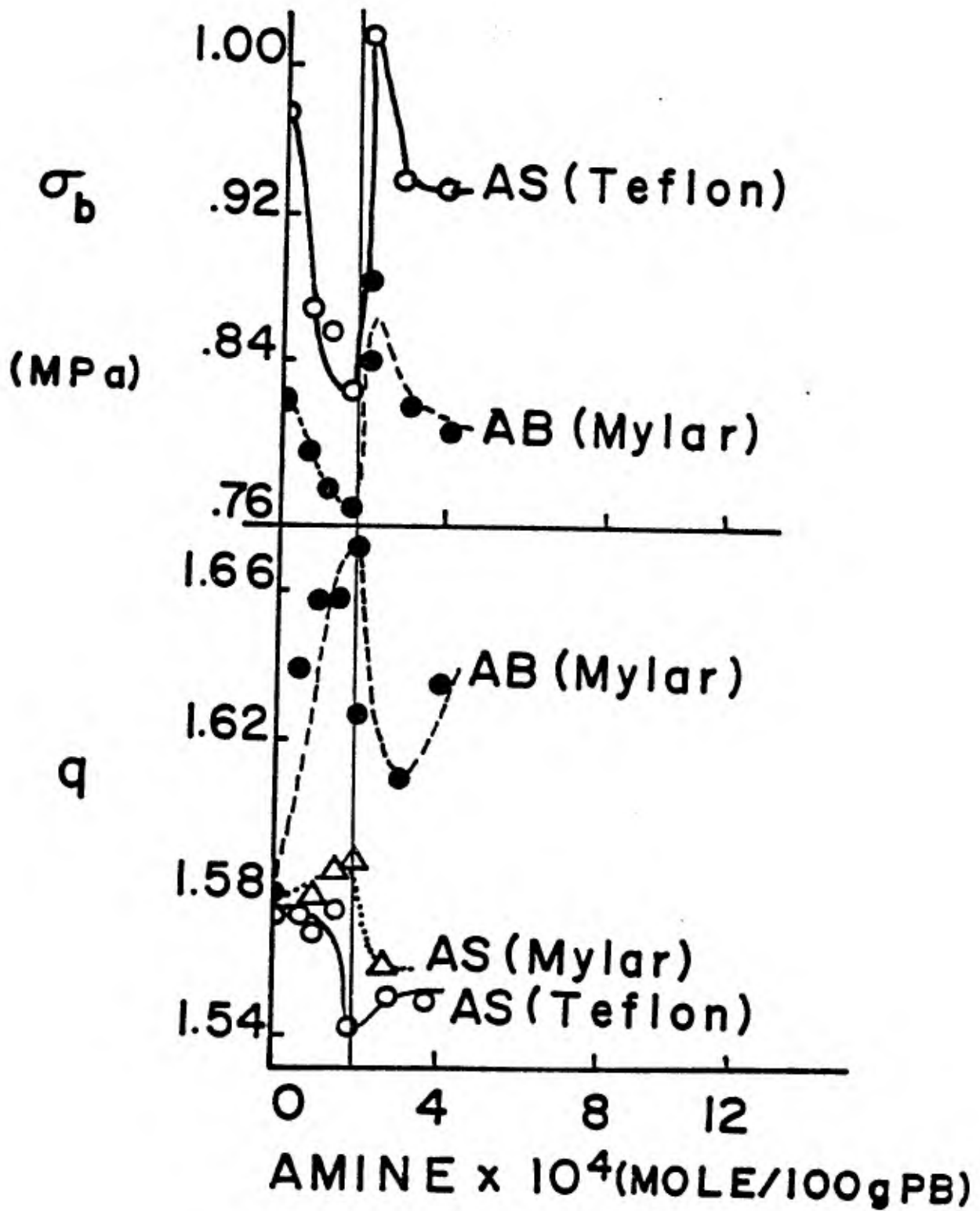
^bBased on values observed for peroxide cured samples having the same swelling ratio

^cPDA, P, A = m-phenylenediamine, piperazine, and aniline, respectively.

Figure Legends

- Figure 1. Effect of Concentration of Aromatic and Cyclic Amines on Breaking Stress and Swelling Ratio of Peroxide Cured Polybutadiene. The vertical line is drawn at 1.85×10^{-4} moles/100g PB, the concentration of peroxide in the PB. (This concentration is equivalent to 0.05 phr peroxide.) A, P, and PDA correspond to aniline, piperazine and m-phenylenediamine, respectively.
- Figure 2. Effect of Concentration of Diaminobutane (AB) and 3-Aminopropyltriethoxysilane (AS) on the Breaking Stress and Swelling Ratio of Peroxide Cured PB. The vertical line is drawn at the same concentration as in Figure 1.





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