

Estimation of Butadiene in Vulcanized BR and SBR by Thermographic Analysis

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Synopsis

A method for the determination of butadiene in vulcanized polybutadiene (BR) and styrene-butadiene rubber (SBR) has been proposed. The method is based on determining the area under the exothermic peak (around 380°C) of the differential scanning calorimetry thermograph in nitrogen. The exotherm area was found to be linearly related to the butadiene content of the polymers and was unaffected by vulcanization or by loading with carbon black. This approach supplements and extends the existing methods of BR determination, which depend upon the estimation of styrene content. The existing evidence indicates that the exothermic reaction is due to cyclization of BR. The energy of activation calculated from the Arrhenius plot is 32-35 kcal/mole; it does not change with vulcanization, loading, or nature of the polymer.

INTRODUCTION

In a previous investigation,¹ an exotherm having a peak temperature of around 380°C was seen in the differential scanning calorimetry thermographs of SBR copolymers heated in nitrogen to 500°C. It was shown that the exotherm area was linearly related to the butadiene content for SBR copolymers containing up to 50% BR. The present work is an extension of the above investigation and shows that the method can also be used to estimate the butadiene content of vulcanized BR and SBR compounds.

EXPERIMENTAL

A du Pont Model 900 thermal analyzer fitted with a DSC module was used to obtain the thermographs. The experimental procedure was the same as that employed in the previous study, except that larger samples (5-15 mg) were used for the vulcanized elastomers. The nitrogen flow was 0.2 l./min and the heating rate was 10°C/min. Areas were determined with a planimeter and divided by the sample weight in milligrams. The per cent composition of BR in the vulcanized stocks was obtained from the following formula:

$$\% \text{ BR} = \frac{\text{area (in.}^2\text{)/sample weight (mg)}}{\text{area of 1 mg raw polymer (in.}^2\text{/mg)}}$$

Average area/mg values were computed from the results of five individual test results. Based on 20 actual tests with Ameripol CB-220, it was seen that the standard deviation at the 95% confidence level was $\pm 4.9\%$, using this procedure. When individual test results were used to estimate BR contents, the standard deviation at the 95% confidence level was $\pm 11\%$. The areas can be converted to calories/mg by using the equation²

$$\Delta H = E \frac{A \Delta T_s T_x}{M a}$$

where E = calibration coefficient, mcal/°C-min; A = peak area, sq. in.; ΔT_s = Y -axis sensitivity setting; T_x = X -axis sensitivity setting; M = sample mass, mg; and a = heating rate, °C/min. The calibration coefficient E was determined experimentally from the thermograph areas of the melting transition of pure metals and their known heats of fusion. The value of E for peak temperature of 380°C is 218 mcal/°C-min. The calculated value of ΔH for Ameripol CB-220 is 226 mcal/mg or 12 kcal/mole of butadiene. The TGA apparatus used was a Cahn balance with a programmed heating arrangement which was assembled in this laboratory. The recipe of the stocks used is given in the Appendix. Elastomers investigated were of technical grade and were used without further purification. Per cent cis contents of commercial BR as cited in the literature were used.

RESULTS AND DISCUSSION

Thermographs of raw BR, BR gum, and black-loaded BR vulcanizates are shown in Figure 1. It is evident from this graph that the shape of the BR exotherm is unaffected by vulcanization or by the addition of compounding ingredients. In further confirmation of this, thermographs were obtained for all the compounding ingredients employed in this study. No transitions were observed for zinc oxide or carbon black in the temperature range studied; and with the exception of Circosol 4240 (a naphthenic oil), the transitions of the other materials occurred below 250°C. Also, the concentration of these materials in the recipe is too small to distort the baseline.

Figure 2 depicts the relationship between exotherm area and sample weight for BR and SBR vulcanizates. In each case the relationship is linear, indicating that this approach can be used to estimate the BR content of these vulcanizates.

Table I shows a comparison of BR contents calculated from the exotherm areas for various BR's, OE-BR's, SBR's and SBR/BR blends to the values calculated from the stated compositions of these materials. The experimental agreement between the two sets of values is very good. Additional tests revealed that there is a slight difference in exotherm area per mg of BR, depending upon the cis content of the BR, the exotherm area decreasing linearly with the percent cis content (Fig. 3). Since this could introduce an error of approximately 10% in the BR estimate, it is sug-

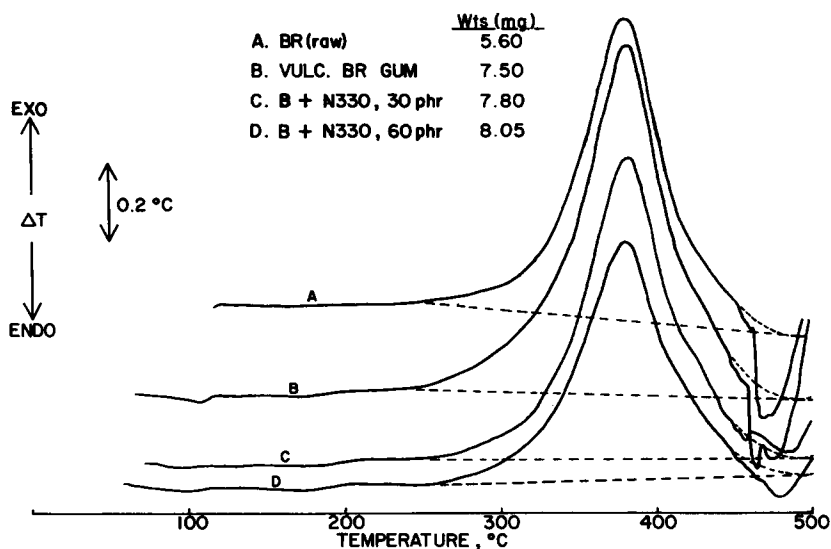


Fig. 1. Thermographs of vulcanized BR with increasing carbon black loading.

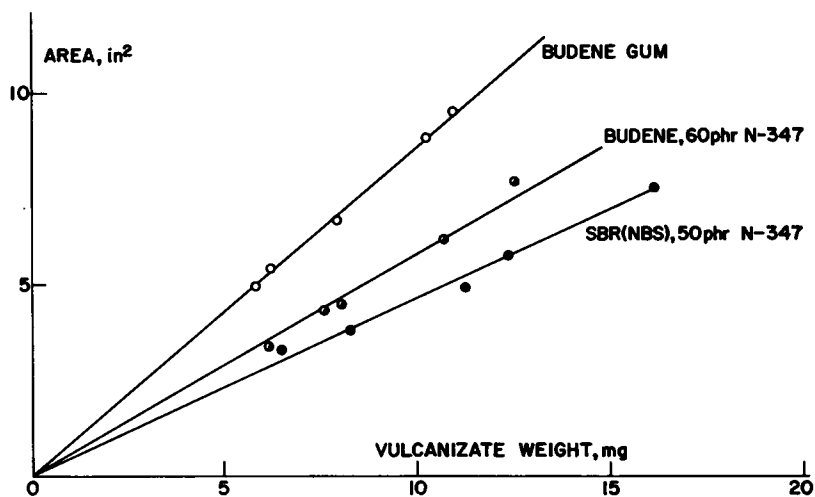


Fig. 2. Exotherm area vs. weight of SBR and BR vulcanizates.

gested that this approach be limited to vulcanizates whose polymer type is known. If this latter condition is fulfilled, it is also possible to estimate blend compositions from the exotherm areas. For example, an area of $0.695 \text{ in.}^2/\text{mg}$ for an Ameripol CB-441/SBR-1712 blend (sample 18) suggests that the polymers are present in the ratio of 50.5:49.5, respectively, which is very close to the actual 50:50 ratio. However, as the percentage of BR in the blend decreases below 30%, the area/mg of the blend approaches that of pure SBR and it becomes progressively more difficult to determine the polymer composition of the vulcanizate.

TABLE I
Determination of BR in BR and SBR Vulcanizate

Sample no.	Description	Area, in. ² /mg	BR present, %	BR found, %	Difference, %
1	Budene 501	1.038	100	100	—
2	Budene gum compd.	0.869	85.1	84.1	-1.0
3	Sample 2 + N-330, 30 phr	0.709	67.8	68.3	+0.5
4	Sample 2 + N-330, 60 phr	0.577	56.3	55.6	-0.7
5	Ameripol CB-441, OEER	1.137, ^a 0.827	100	100	—
6	Ameripol CB-441, gum compd.	0.755	64.4	66.4	+2.0
7	Sample 6 + N-347, 60 phr	0.514	46.5	45.2	-1.3
8	Sample 6 + N-347, 75 phr	0.481	43.4	42.3	-1.1
9	Sample 6 + N-347, 100 phr	0.406	39.2	35.7	-3.5
10	SBR-1500 NBS	0.778	72.0	71.6	-0.4
11	SBR-1500, N-330, 10 phr	0.581	59.2	59.4	+0.2
12	SBR-1500, N-330, 30 phr	0.527	51.1	53.8	+2.7
13	SBR-1500, N-330, 50 phr	0.468	45.0	47.9	+2.9
14	SBR-1712	0.560	54.5	49.2	-5.3
15	SBR-1712, N-347, 50 phr	0.312	36.5	32.0	-4.5
16	SBR-1712, N-347, 60 phr	0.332	34.8	34.0	-0.8
17	SBR-1712, N-347, 75 phr	0.306	31.7	31.3	-0.4
18	Ameripol CB-441/SBR-1712, 50:50	0.695	63.6	61.1	-2.5
19	Sample 18 + N-347, 50 phr in vulc. compd.	0.394	42.6	37.6	-5.0
20	Sample 18 + N-347, 75 phr in vulc. compd.	0.356	33.7	38.0	+4.3
21	Ameripol CB-441/SBR-1712, 75:25	0.762	68.2	68.2	—
22	Sample 21 + N-347, 75 phr in vulc. compd.	0.417	40.7	37.3	-3.4
23	Ameripol CB-441/SBR-1712, 25:75	0.592	59.1	58.7	-0.4
24	Sample 23 + N-347, 75 phr in vulc. compd.	0.338	35.3	33.1	-2.2
25	Ameripol CB-441, N-347, 75 phr in vulc. compd., cure 15 min	0.481	43.4	42.3	-1.1
26	Sample 25, cure 30 min	0.460	43.4	40.5	-2.9
27	Sample 25, cure 60 min	0.460	43.4	40.5	-2.9
28	Sample 25, cure 100 min	0.496	43.4	43.6	+0.2

^a Converted to 100% polymer.

The presence of carbon black does not interfere with the estimation of BR content, though it does make it very difficult to determine the composition of BR-SBR blends unless the black loading is known. An approximate idea of the black loading may be obtained by weighing the sample pan after the DSC experiment. The weight remaining corresponds to the percentage of carbon black, zinc oxide, and polymer ash, to within 1%. This was also confirmed by TGA in nitrogen and oxygen atmospheres and agrees with the observation of Jasper.³

The state of cure of the elastomers does not have a significant effect on the BR determination. This is shown for compounds 25-28, which were

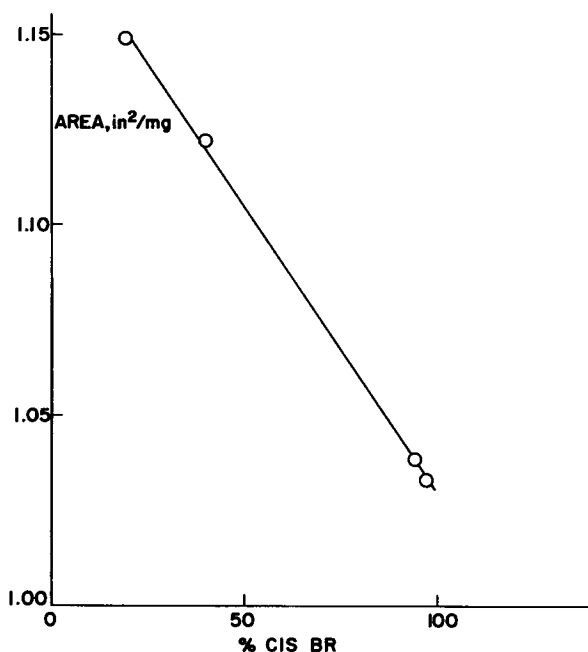


Fig. 3. Relationship between exotherm area in N_2 vs. per cent cis content.

cured at 15, 30, 60, and 100 min, the optimum cure being around 60 min. Also, a sample aged for four days at 100°C in a Geer oven did not show any change in per cent BR found, although physical properties showed a drastic deterioration.

Nature of the Reaction

The mechanism of thermal degradation of organic polymers is presumably very complex.⁴ An exothermic reaction in an inert atmosphere precludes oxidation and indicates crosslinking and/or cyclization reactions. Also, the differential thermogravimetric curve (Fig. 4) for BR and SBR shows that the highest rate of weight loss occurs at the end of the reaction zone ($450\text{--}500^\circ\text{C}$). This indicates that the reaction under study precedes significant decomposition of the vulcanizate by pyrolysis. A similar exotherm in the case of Neoprene W was explained by Schwenker et al.⁵ as due to crosslinking following the elimination of HCl . Coffman⁶ studied the effects of heating vulcanized polybutadiene at 250°C for several days. Because an impermeable crust formed rapidly, the subsequent reaction was anaerobic and was therefore very similar to the reaction being studied here. From the combined evidence of the change of such physical properties as hardness, density, flexural modulus and swelling as well as the second-order transition (which rose to approximately 150°C after five days), he concluded that both crosslinking and cyclization took place.

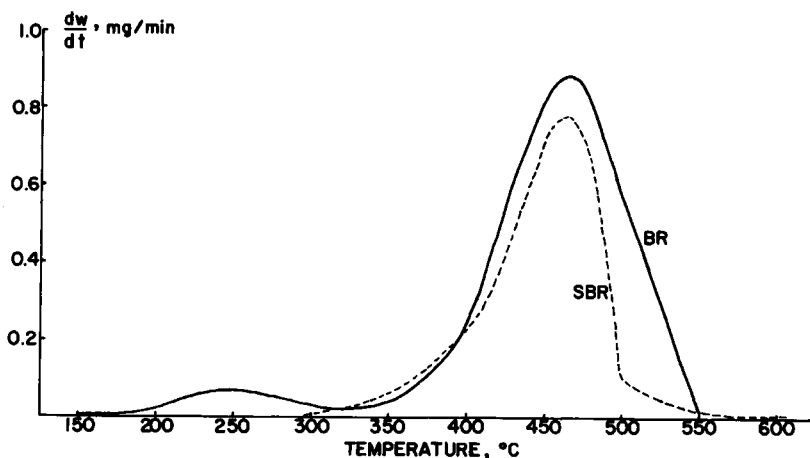
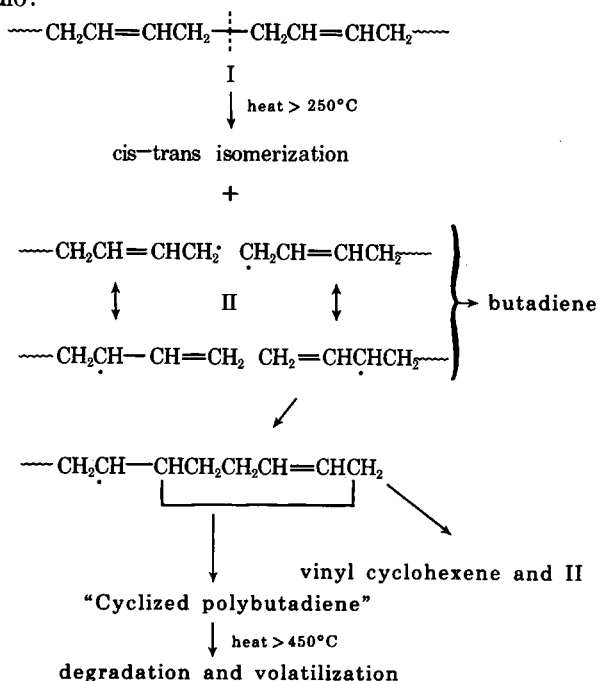


Fig. 4. Differential thermogravimetric curves for BR and SBR.

A recent IR and NMR study by Golub and Gargiulo⁷ provides convincing evidence that the reaction is indeed a saturation-cyclization process, probably accompanied by a cis-trans isomerization. The latter would explain the slightly lower heat of reaction values observed in this study as the cis content of the polymer increases, since isomerization is presumably an endothermic process. A scheme for the cyclization and depolymerization of polybutadiene may be enunciated along the same lines as that of Golub and Gargiulo:



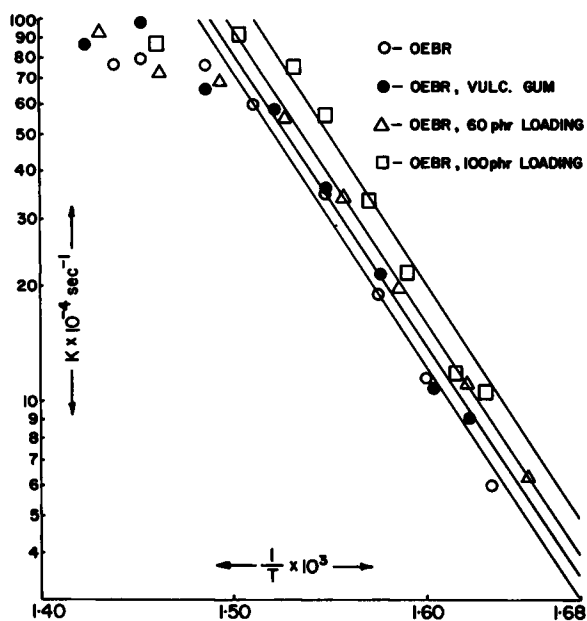


Fig. 5. Arrhenius plot for OE-BR.

First-order rate constants were calculated from the formula⁸

$$k = \frac{[\text{height (in.)}][\text{heating rate (}^\circ\text{C/sec)}]}{[A - a \text{ (in.}^2\text{)}][\text{temp. sensitivity (}^\circ\text{C/in.)}]}$$

where A = total area under the peak, and a = peak area up to time t

Figures 5 and 6 show the Arrhenius plot for the first-order rate constants. The activation energy calculated from the slope of these straight lines is 32–35 kcal/mole. This value is somewhat lower than the strength of a carbon-carbon bond activated by two double bonds (43 kcal/mole, as calculated by Ballard and Orr⁹ in the temperature range 220–270°C) and is closer to 38 kcal/mole calculated by Coffman. Figures 5 and 6 show that the activation energy is the same for BR and SBR and remains unaffected by vulcanization and loading of carbon black as well as by blending of SBR and BR. In fact, the points for SBR and a blend of 50:50 SBR:BR fall on the same line (Fig. 6). This demonstrates that the fundamental reaction being studied is the same in all cases. The slight curvature at the high-temperature end of the Arrhenius plot is due to depolymerization and volatilization reactions being superimposed on the cyclization reaction.

Advantages and Limitations

The advantages of the present method are that no sample preparation or pretreatment is needed; and unlike the chemical method by ASTM,¹⁰ no operator attention is necessary once the experiment is started. The unique

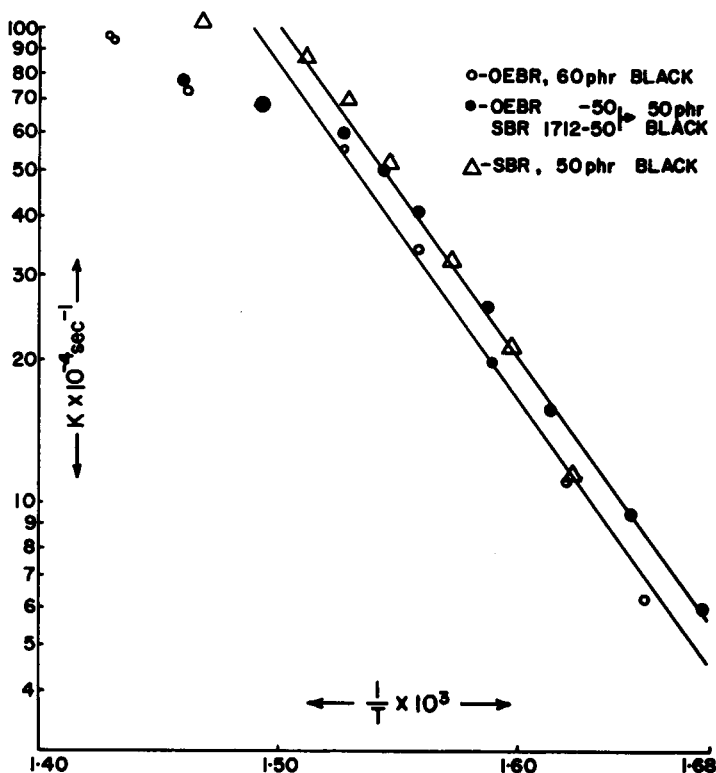


Fig. 6. Arrhenius plot for OE-BR, SBR, and blend.

advantage of the present method is that it is based on the determination of butadiene, whereas most of the other methods,¹¹⁻¹⁸ including the chemical method,¹⁰ are based on styrene, butadiene being determined by difference. The method may therefore be used as an excellent check on other methods. Moreover, with the exception of the nitration procedure described by Hilton et al.⁹ and by ASTM,¹⁰ the existing methods are limited to SBR's that are free from fillers, antioxidants, soaps, fatty acids, and gels.

Exotherm areas/mg for various butadiene elastomers decrease slightly with per cent cis content (increase with per cent 1:2 structure) of the polymer. Also, a slight difference exists in the exotherm area/mg (based on known BR content) between oil-extended (Ameripol CB-441) and non-extended BR (Ameripol CB-221) of the same microstructure. The latter can be remedied by acetone extraction of the oil-extended rubber which then gives the same value as the unextended counterpart, within the accuracy of the method.

The above factors will contribute to a slightly higher margin of error if the type of elastomer is not known. However, once the type is established by auxiliary methods, an estimation of the butadiene component may easily be obtained from the thermograph area.

Appendix

Recipe

Polymer ^a	100
Black	variable
Zinc oxide	5.0
Stearic acid	1.5
Naphthenic oil ^b	7.5
Santocure ^c	1.0
Sulfur	1.8
PBNA ^d	1.0

^a For BR compounds, Budene 501, Ameripol CB-220, or Ameripol CB-441 (137.5 for 100 rubber); for SBR compounds, SBR-1500 or 1712 (137.5 for 100 rubber).

^b Circosol 4240, Sun Oil Company.

^c N-Cyclohexyl-2-benzothiazole sulfenamide.

^d Phenyl- β -naphthylamine.

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