

Brominated Phenolic Resin Based Vulcanization of Butyl Rubber

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Summary: Brominated phenol formaldehyde resin was utilised to vulcanize butyl rubber in the presence of carbon black as well as in the absence of carbon black. Unfilled vulcanizates were found to conform to the Mooney-Rivlin equation in their stress elongation behaviour. Cross-linking efficiency of the resin was deduced and the gel point was found in the vicinity of the concentration 0.5 PHR of resin.

Introduction

The first recorded phenolic resin based vulcanization of butyl rubber was carried out in 1956 by a French chemist Bitterich.¹ At that time sulphur was a common vulcanizing agent for rubbers. The comparative studies² of sulphur based vulcanization and phenolic resin based vulcanization of butyl rubber were carried out to evaluate the effect of vulcanizing agent on vulcanizate. It was reported that when a sulphur based butyl rubber vulcanizate softens during exposure to high temperature, the disulphide link between polymer chains breaks down to thiol group, while such a phenomenon was not observed in phenolic resin based vulcanizates. Later on substituted^{3,4} phenolic resins were tried for butyl rubber vulcanization. Halogenated phenolic resins were reported to be better vulcanizing agents. In 1954⁵ and 1956⁶ phenolic resins were used commercially and patents were filed. According to the patent reports, butyl rubber can also be vulcanized with phenol formaldehyde resin to give vulcanizates which are extremely stable.

After this brominated phenolic resin was used for further investigations. It was observed that the vulcanization^{7,8,9,10,11} temperature of butyl rubber decreased with increase in the bromine content in the brominated phenolic resin. It^{12,13} has also been reported in the literature that the brominated phenolic resin gave the best vulcanizate with a higher modulus (20%) and short (40 vs 80 min) vulcanization time. In this paper the aspects of stress elongation behaviour, cross-linking efficiency and gel points were evaluated using

brominated phenolic resin vulcanizate of butyl rubber.

Material and Methods

Butyl rubber: (BK 1675 T/USSR, mole percent unsaturation 1.4 - 1.6 antioxidant of amine type. Density 0.9g/cm^3 , was used for investigation.

Poly-isobutylene: Oppanol B 150/Base, Ger/density 0.92g/cm^3 , was used for experimentation.

Chloroprene rubber: Bayprem 230/Bayer, Ger/density 1.25g/cm^3 , was used for research.

Brominated methylol phenolic resin: Schenectady¹⁰⁵⁵/Schenectady Chemicals USA/brominated 3.5-3.5-4%, density 1.1g/cm^3 , was used for vulcanization without further purification.

Methylol phenolic resin: Super bekacite 1001/Reichhold Chemie, Ger, density $1.02 - 1.04\text{g/cm}^3$, was used without further purification.

Zinc oxide: Density 5.5g/cm^3 , was used in vulcanization reaction without further purification.

Carbon black: HAF density 1.8g/cm^3 , was used for investigation without further treatment.

Acetone: Analar Grade was used without further purification.

Benzene: Analar Grade was used without further purification.

Cyclohexane: Analytical Grade was used without further purification.

Equipment

Banbury mixture: Laboratory type 40 cm³/PAPRA, U.K., was used for the mixing purposes.

Two-roll mill: Laboratory type 250x400 mm, was utilised for milling.

Curing press: 200x200 mm, electrically heated, was used for pressing.

Cathetometer: Uican was used for measurement.

Equilibrium Swelling Measurements

Acetone soluble fractions ASF containing non-rubber constituents, unbounded resin and anti-oxidants were determined by extraction of weighed samples of rubber vulcanizates measuring 35 x 15 x 0.6 mm, taken in capped bottle with three separate portions of acetone which were changed every twenty four hours for four days at room temperature (20°C). The extracted samples were first dried at room temperature under the stream of air for twenty four hours and then in an oven at 70°C for another twenty four hours. All weighing were carried out on an analytical balance.

Solution fractions were determined by extraction of the dried acetone extracted samples with cyclohexane.

The equilibrium swelling volumes V_r were determined by weighing the swollen samples, calculating the amount of cyclohexane and the volume of the net polymer.

The P₁B-Cr vulcanizates were first extracted with cyclohexane to remove poly-iso-styrene, the unbounded resin and other non-rubber constituents. Then the sam-

ple was extracted with benzene to remove the soluble portion of cycloprene. The weight of the gel swollen in benzene was recorded for further calculation. Only traces of the unreacted vulcanizing agent were detected. Quantitative analysis of these traces were not possible.

Compounding and Vulcanization

Six gum compounds were prepared using brominated methylol phenolic resin by the following compositions.

| | |
|---------------------|---------------------|
| Methyl-iso-butylene | 100 parts by weight |
| Chloroprene rubber | 5 |
| Zinc oxide | 4 |
| Methylol resin | 10 |

The mixing of the compound was performed in a Banury mixer for 20 minutes, followed by milling for 10 minutes at room temperature (20°C).

The other six compounds were prepared by adding 55 PHR of HAF black as a reinforcing filler.

Results and Discussion

Effects of the Absence of Carbon Black on Vulcanization

The vulcanization experiments based on brominated phenolic resins in the absence of carbon black were carried out. It was observed that the density of the vulcanizate slightly increased with the increase of resin. See Fig. 1, Table 1).

TABLE 1

| Composition: II R, ZnO 80%, stearic acid 1% | | | | |
|---|-----------------|------------------|--------------|--|
| No | Code | Brominated resin | Carbon black | Density of vulcanizate g/cm ³ |
| 1 | CV ₁ | 0.5 | — | 0.936 |
| 2 | CV ₂ | 1.0 | — | 0.938 |
| 3 | CV ₃ | 2.0 | — | 0.940 |
| 4 | CV ₄ | 4.0 | — | 0.942 |
| 5 | CV ₅ | 8.0 | — | 0.947 |
| 6 | CV ₆ | 16.0 | — | 0.956 |

TABLE 2

| Composition: II R 100 ZnO 8, stearic acid 1 (by weight) | | | | |
|---|------------------|-------------------------------------|---------------------|---------------------------|
| No | Code | Conc. of brominated resin by weight | HAF parts by weight | Density g/cm ³ |
| 1 | BCV ₁ | 0.5 | 55 | 1.138 |
| 2 | BCV ₂ | 1.0 | " | 1.138 |
| 3 | BCV ₃ | 2.0 | " | 1.137 |
| 4 | BCV ₄ | 4.0 | " | 1.137 |
| 5 | BCV ₅ | 8.0 | " | 1.136 |
| 6 | BCV ₆ | 16.0 | " | 1.136 |

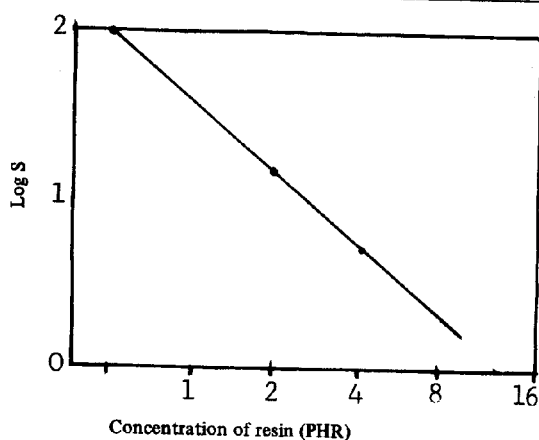


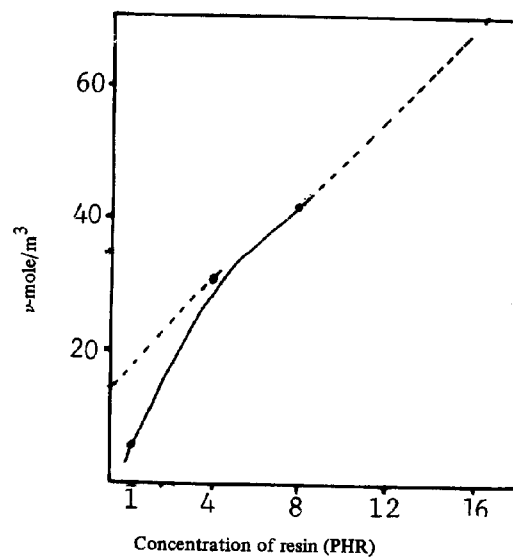
Fig. 1. The dependence of sol on the concentration of resin.

Effect of Carbon Black on Brominated Phenolic Resin Based Vulcanization

The vulcanization reaction in the presence of fixed concentration of carbon black and variable concentration of brominated phenolic resin was carried out. Almost negligible effect was observed on the density of vulcanizate as shown in Fig. 2, Table 2.

Solubility and Equilibrium Swelling Measurements

The results of the solubility and equilibrium of unfilled vulcanizate have been summarized in Table 3, and similar results of the reinforced composition have been collected in Table 4. The mutual relationship between V_0 and V_r was calculated by applying the Flory and

Fig. 2. The dependence of network density $= 2C_1/V_0RT$ on resin concentration.

Rehner equation in reinforced and unfilled compositions. These results have been summarized in Table 4.

Calculation of the Mooney Rivlin Constant and Interaction Parameters

In Table 5, Mooney Rivlin Constant and interaction parameters have been summarized. Polymer solvent parameters increased with the increase of resin. The parameters were calculated by using Flory Equation and Flory Rehner Equation.

Table 3. Measurement in Unfilled Compositions Solubility and Equilibrium Swelling.

| Code | Resin/DHR | SSF % | S x 100% | V _o | V _r ⁻ |
|-----------------|-----------|-------|----------|----------------|-----------------------------|
| CV ₁ | 0.5 | 100 | | | |
| CV ₂ | 1.0 | 0.09 | 16.27 | 0.836 | 0.023 |
| CV ₃ | 2.0 | 0.3 | 14.3 | 0.854 | 0.050 |
| CV ₄ | 4.0 | 0.12 | 4.68 | 0.951 | 0.100 |
| CV ₅ | 8.0 | 0.23 | 3.53 | 0.962 | 0.142 |
| CV ₆ | 16.0 | 0.57 | 3.53 | 0.959 | 0.168 |

Table 4. Solubility and Equilibrium Swelling Measurement in Reinforced Composition.

| Code | Resin/PHR | ASF% | S x 100% | V _o | V _r |
|------------------|-----------|------|----------|----------------|----------------|
| BCV ₁ | 0.5 | 0.19 | 47.39 | 0.524 | 0.041 |
| BCV ₂ | 1.0 | 0.16 | 38.52 | 0.613 | 0.058 |
| BCV ₃ | 2.0 | 0.11 | 19.52 | 0.802 | 0.078 |
| BCV ₄ | 3.0 | 0.27 | 2.05 | 0.977 | 0.165 |
| BCV ₅ | 4.0 | 0.43 | 0.01 | 0.995 | 0.206 |
| BCV ₆ | 5.0 | 0.50 | 0.18 | 0.993 | 0.218 |

Discussion

It is a well known fact that the incorporation of halogens in the polymer chain greatly effects the characteristics of the polymer¹⁴. Such results have also been noticed in the case of polyethylene-polyvinyl chloride-polyvinylidene chloride system. Similar types of results have also been observed by the incorporation of bromine in the butyl rubber chain before vulcanizing or using brominated vulcanizing agents. The presence of halogens usually increases melting point, glass transition temperature, tensile strength and modulus of the polymer³. Butyl rubber can also be vulcanised with halogen-free resins but their characteristics are far inferior to those vulcanized with halogenated resin. Bromine especially plays a significant role in butyl rubber vulcanization. A certain amount of bromine in the elastomer good workable polymer.¹⁵

Tables 1 and 2, clearly indicate the importance of carbon black in the vulcanizate. According to the

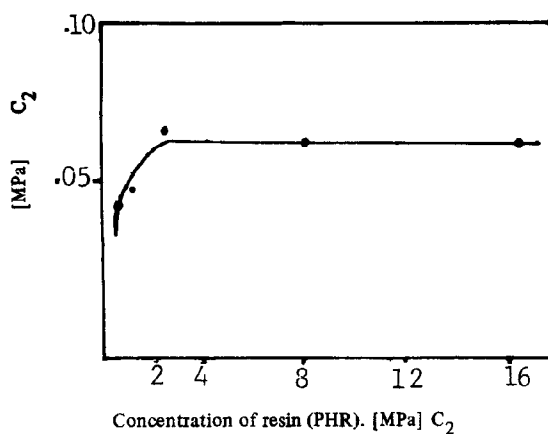
authors' point of view, the action of carbon black is purely physical and dependent on its particle size and surface energy.

Tables 2 and 3 indicate that a very slight change in density was noticed on increasing the amount of resin above 0.5 PHR.

Table 2 clearly shows that PHR 0.5 of bromine resin is the amount required for vulcanization. But on the other hand the amount of vulcanized rubber in the vulcanizate has minimum value with 8 part of resin per HPR. This phenomenon was observed in both filled and unfilled vulcanizate (see Tables 3 and 4). Fig. 2 clearly shows that dependence may be taken as a rough measure of cross linking efficiency of the brominated resin. It also shows the increase in network density for 10 PHR of resin which is equal to 35 mole/m², which corresponds roughly to 1.75 mole/m³ of chemical link per 1 HPR of resin. This value is lower as compared with other systems¹⁶, like natural rubber/dicumyl peroxide system. According to the another's view this difference

Table 5. Mooney Rivlin Constant and Interaction Parameters.

| Code | Resin PHR | G MP _a | C ₁ MP _a | C ₂ MP _a | C ₁ V ₀ RT Mole/m ³ | X Flory Eq. | X ₁ Flory Rehner Eq. |
|-----------------|--------------|----------------------|-----------------------------------|-----------------------------------|--|-------------------|---------------------------------------|
| CV ₁ | 0.5 | 0.081 | 0.0020 | 0.0385 | | | |
| CV ₂ | 1.0 | 0.104 | 0.0065 | 0.0455 | 6.38 | 0.179 | 0.160 |
| CV ₃ | 2.0 | 0.157 | 0.0100 | 0.0685 | 9.61 | 0.384 | 0.373 |
| CV ₄ | 4.0 | 0.178 | 0.0325 | 0.0565 | 28.06 | 0.410 | 0.394 |
| CV ₅ | 8.0 | 0.227 | 0.0490 | 0.0645 | 41.82 | 0.450 | 0.434 |
| CV ₆ | 16.0 | 0.264 | 0.0680 | 0.0640 | 85.21 | 0.459 | 0.439 |

Fig. 3. The dependence of C₂-constant on resin concentration.

is due to the higher molecular weight of the resin and the lower cross-linking efficiency.

Fig. 3 the dependence of C₂ (the deviation from the kinetic theory of rubber elasticity) is seen to increase at first with resin concentration but to assume a constant value in the region of higher crosslinking degree. Such a behaviour has been observed in other rubber systems³.

Table 5 shows that chloroprene rubber which is being used as an activator in the resin vulcanization of II R becomes effective by cross-linked to an appreciable degree comparable to that of II R and this contributes to the modulus. This property can be noticed in butyl rubber resin cured articles, e.g. cured bladder. Practically the whole amount of the curing agent was used up in polymer chain during vulcanization process.

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