

## Characterization of Sulfur-Cured Styrene-Butadiene Copolymer Rubbers and Their Polybutadiene Blends

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### Synopsis

Dissolution of sulfur-cured, carbon black-loaded copolymers and their blends with *cis*-1,4-polybutadiene (PBD) are brought about by boiling with *o*-dichlorobenzene which contains a small amount of 2,2'-dibenzamidodiphenyl disulfide. The resulting slurries are subjected to a sequence of separations which include high-speed centrifugation to remove solids, and solvent precipitation followed by filtration to isolate the precipitates. The precipitates are washed with solvent to remove soluble organic materials followed by carbon disulfide washing to dissolve the polymers. Cast films of the polymers are obtained by evaporating the carbon disulfide washings onto sodium chloride discs. The infrared spectra of the cast films of these preparations are very similar to those of their respective polymers prior to loading and curing. Calculations for relative concentrations of bound styrene and PBD microstructures permit nominal identification of the kinds of styrene-butadiene rubber and the amounts of *cis*-1,4-PBD used in a cured rubber formulation. Absorption bands used are near 3.35  $\mu$  for *cis*-1,4-PBD, 6.65  $\mu$  for bound styrene, 10.35  $\mu$  for *trans*-1,4-PBD; and 11.0  $\mu$  for vinyl-1,2-PBD. Efforts are being made to improve the data by using a grating infrared instrument and also to extend the calibrations to include other rubber blends.

### INTRODUCTION

Techniques are needed to identify the microstructures of cured, carbon black-loaded styrene-butadiene copolymers and also of their blends with other rubbers. MacKillop<sup>1</sup> characterized pyrolyzates by infrared spectroscopy and Phillips<sup>2</sup> made use of pyrolysis in conjunction with mass spectrometry. Corish<sup>3</sup> microtomed the cured rubbers to prepare samples for infrared spectroscopy while Dinsmore and Smith<sup>4</sup> used boiling *o*-dichlorobenzene to bring about dissolution of the cured rubbers as a method of sample preparation for spectroscopic examination. Pyrolysis appears to yield products which are correlatable with total styrene, butadiene, and natural rubber contents; but it is hazardous to extrapolate data, even on low temperature pyrolyzates, back to the microstructures of the original rubbers. It is often difficult or impossible to bring about dissolution of cured rubber with boiling *o*-dichlorobenzene while the preparation of samples for infrared examination by microtoming requires considerable time and skill.

The procedure used in this work has brought about the devulcanization of sulfur-cured, carbon black-loaded styrene-butadiene copolymers and of blends with high *cis*-1,4-polybutadiene to provide pentane-insoluble fractions which have infrared spectra similar to those of the rubbers before curing. Appropriate spectral measurements permit identification of the styrene-butadiene copolymer composition and also a good estimate of the amount of any *cis*-1,4-polybutadiene used in a blend. The technique is applicable to polyisoprene but a modification will be needed to allow estimates of polyisoprene content in mixed rubber formulations. Hereafter, styrene-butadiene copolymers will be referred to as SBR and polybutadiene as PBD.

## EXPERIMENTAL

### Loaded and Cured Rubbers

Three SBR rubbers with dissimilar concentrations of bound styrene and three blends of an SBR with varying amounts of *cis*-1,4-PBD served as experimental samples (see Tables I and II). A portion of each sample was loaded as follows: 100 parts rubber, 50 parts carbon black, 3 parts zinc oxide, 5 parts naphthenic oil, 2 parts sulfur, and 2 parts of mixed organic accelerators. These loaded rubbers were pressed in a mold at 10,000 psig for 30 min at 290°F to produce cured sheets of 4 in. × 6 in. × 0.07 in.

### Devulcanization and Purification

The following steps were used to prepare pentane-insoluble but carbon disulfide-soluble fractions of rubber from the loaded, cured samples:

(a) Two-gram portions of each sample were shredded by passing them through a tightly adjusted laboratory roll mill. The shredded samples, along with 0.08 g Pepton 22 (American Cyanamide Co. trade name for 2,2'-dibenzamidodiphenyl disulfide) and 50 ml orthodichlorobenzene, were placed into a 125-ml pyrex, flat-bottomed boiling flasks with  $\nabla$  24/40 necks. The flasks were fitted with water-cooled Liebig condensers and refluxed for 7 hr on a hot plate.

(b) After cooling overnight, 10-ml volumes of the partially devulcanized slurries were added with stirring to 40-ml portions of cyclohexane. Fifteen-milliliter volumes of each of the cyclohexane mixtures were centrifuged for 3 hr in a Custom Scientific Instrument, Model CS-26, high-speed angle centrifuge. The instrument rheostat was operated at a setting of 85.

(c) The clear, brownish liquids were withdrawn from the centrifuge tubes with a long-needle Luer syringe. This provided about 12 ml of each sample solution which was precipitated by slow addition with stirring to 200 ml pentane in a 400-ml beaker.

(d) Pyrex fritted, D porosity, 100-mm × 20-mm Büchner filter funnels were packed with consecutive layers of 1/2 in. sea sand, then 2 in. of Johns Manville Supercel-Hyflo filter aid, and another 1/2 in. of sea sand. These

TABLE I  
 Normalization of Bound Styrene and *trans*-1,4-PBD and Vinyl-1,2-PBD to 100 Parts by Weight. *cis*-1,4-PBD Excluded in the Normalization

Sample <sup>a</sup>	Infrared film analysis		
	Bound styrene, parts	<i>Trans</i> -1,4-PBD, parts	Vinyl-1,2-PBD, parts
A: <i>Cis</i> -1,4-PBD	(refer to Table II)		
B: SBR (23% Styrene)	(refer to Table II)		
No load, no cure, no devulcanization	28.1	59.9	12.0
Loaded, cured, devulcanized	30.5	58.2	11.3
	29.1	59.1	11.8
C: 10 parts A plus 90 parts B	(refer to Table II)		
No load, no cure, no devulcanization	27.8	59.6	12.6
Loaded, cured, devulcanized	26.6	61.5	11.9
	29.0	58.2	12.8
D: 20 parts A plus 80 parts B	(refer to Table II)		
No load, no cure, no devulcanization	27.3	59.1	13.6
Loaded, cured, devulcanized	26.2	61.8	12.0
	25.2	62.7	12.6
E: 40 parts A plus 60 parts B	(refer to Table II)		
No load, no cure, no devulcanization	24.4	60.8	14.8
Loaded, cured, devulcanized	23.6	64.2	12.2
	22.5	65.7	11.7
F: SBR (40% Styrene)	(refer to Table II)		
No load, no cure, no devulcanization	47.6	42.3	10.1
Loaded, cured, devulcanized	49.9	42.0	8.1
	47.0	45.2	7.6
G: SBR (10% Styrene)	(refer to Table II)		
No load, no cure, no devulcanization	11.0	73.0	16.0
Loaded, cured, devulcanized	13.0	72.6	14.4
	13.2	70.5	16.4

<sup>a</sup> Loaded, cured, devulcanized samples were analyzed in duplicate.

filter funnels were attached to 250-ml vacuum flasks through perforated rubber stoppers, and the flasks were attached by rubber vacuum tube to a water tap aspirator. The pentane-precipitate mixtures were added slowly to the filter funnels under vacuum suction and washed through with additional 50 ml pentane. The pentane filtrates were discarded.

(e) Each column was washed through with 50 ml carbon disulfide, and these carbon disulfide washings contained the desired rubber fractions. The carbon disulfide washings were evaporated down in a vacuum oven, without heat, to about 1-3 ml. These concentrated solutions were used to cast films for infrared spectra.

TABLE II  
Normalization of Bound Styrene and PBD Microstructures to 100 Parts by Weight

Sample <sup>a</sup>	Infrared film analysis <sup>b</sup>			
	Bound styrene, parts	<i>cis</i> -1,4-PBD, parts	<i>trans</i> -1,4-PBD, parts	Vinyl-1,2-PBD, parts
A: Polybutadiene				
No load, no cure, no devulcanization	—	89.6	5.9	4.5
B: SBR (23% Styrene)				
No load, no cure, no devulcanization	23.8 <sup>c</sup>	15.4 <sup>c</sup>	50.7 <sup>c</sup>	10.1 <sup>c</sup>
Loaded, cured, devulcanized	23.3	17.1	49.6	10.0
	25.0	18.1	47.7	9.2
	24.0	17.0	49.1	9.9
C: 10 parts A plus 90 parts B				
No load, no cure, no devulcanization	23.9 <sup>c</sup>	26.0 <sup>c</sup>	42.0 <sup>c</sup>	8.1 <sup>c</sup>
	21.0 <sup>d</sup>	24.4 <sup>d</sup>	45.0 <sup>d</sup>	9.5 <sup>d</sup>
	20.3	26.7	43.8	9.2
Loaded, cured, devulcanized	20.1	31.0	40.2	8.7
	18.7	29.6	43.3	8.4
D: 20 parts A plus 80 parts B				
No load, no cure, no devulcanization	21.4 <sup>c</sup>	35.0 <sup>c</sup>	36.4 <sup>c</sup>	7.2 <sup>c</sup>
	18.6 <sup>d</sup>	31.6 <sup>d</sup>	40.9 <sup>d</sup>	8.9 <sup>d</sup>
	18.3	32.2	40.3	9.2
Loaded, cured, devulcanized	17.4	33.3	41.3	8.0
	17.1	32.0	42.5	8.4
E: 40 parts A plus 60 parts B				
No load, no cure, no devulcanization	16.4 <sup>c</sup>	49.0 <sup>c</sup>	29.4 <sup>c</sup>	5.2 <sup>c</sup>
	14.0 <sup>d</sup>	46.1 <sup>d</sup>	32.2 <sup>d</sup>	7.7 <sup>d</sup>
	13.0	46.4	32.6	7.9
Loaded, cured, devulcanized	13.9	41.4	37.5	7.2
	12.3	45.7	35.6	6.4
F: SBR (40% Styrene)				
No load, no cure, no devulcanization	40.0 <sup>c</sup>	14.8 <sup>c</sup>	37.3 <sup>c</sup>	7.9 <sup>c</sup>
	38.8	18.6	34.4	8.2
Loaded, cured, devulcanized	41.3	17.4	34.6	6.9
	40.0	15.0	38.5	6.5
G: SBR (10% Styrene)				
No load, no cure, no devulcanization	11.9 <sup>c</sup>	21.8 <sup>c</sup>	55.5 <sup>c</sup>	10.8 <sup>c</sup>
	8.8	21.4	57.4	12.4
Loaded, cured, devulcanized	12.6	16.7	57.6	13.1
	10.5	20.5	56.8	12.2

<sup>a</sup> The loaded, cured, devulcanized samples were analyzed in duplicate.

<sup>b</sup> Except where stated otherwise.

<sup>c</sup> Near-infrared solution analysis.

<sup>d</sup> Blend values.

### Nonloaded and Noncured Rubbers

Portions of the three SBR rubbers and the three SBR-PBD blends were made up into 20 g/l. solutions in carbon disulfide. These solutions were

used to provide cast films for the infrared spectra of the rubbers prior to loading and curing.

### Calibration Samples

Six polymer blends of polystyrene and *cis*-1,4-PBD, *trans*-1,4-PBD, and vinyl-1,2-PBD made up to 20 g/l. in carbon disulfide solutions served as calibrating standards. These blends simulated rubbers containing 21%–31% bound styrene, 10%–36% *cis*-1,4-PBD, 30%–46% *trans*-1,4-PBD, and 7%–16% vinyl-1,2-PBD. These mixtures cover a common range of microstructures found in SBR and SBR-PBD rubber blends, but other compositions could be equally valid.

### Infrared Spectra

A Perkin-Elmer 21 prism instrument was used with a slit program of 984, a response setting of 1.0, a gain of 4.8, a scanning speed of 2 min/ $\mu$ , a suppression of zero, a pen speed of 1100, and a Nernst glower current of 0.3 amperes to produce spectral scans over the range of 2–15  $\mu$ .

Cast films made by evaporating the carbon disulfide solutions, for 1 hr at ambient temperature on sodium chloride discs of 25-mm diameter and 5-mm thickness, provided the samples for spectral scanning. Appropriate film thicknesses gave absorption maxima between 20%–40% transmission for the most intense band among the peaks at 3.35  $\mu$ , 6.65  $\mu$ , 10.35  $\mu$ , and 11.0  $\mu$  (Fig. 1). Measurements made from lines drawn tangent to the bases of the bands yielded the absorbance data.

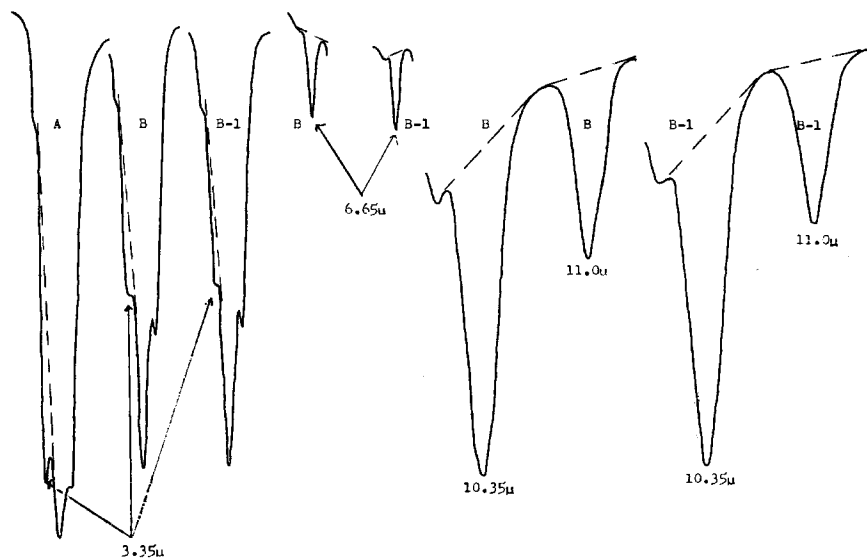


Fig. 1. Infrared absorption spectra of cast films: (A) *cis*-1,4-PBD; (B) SBR (23% bound styrene); (B-1) B after cure and devulcanization.

### Absorptivities

Spectra of the six calibration mixtures provided pseudoabsorptivities. The absorbances were divided by the known molar concentrations of the mixtures and these results were normalized to a *trans*-1,4-PBD absorptivity of unity. Following is an example of the calculations where  $a$  represents the absorptivities;  $A$ , the absorbances, and the last column results from the normalization step, in this case division of all the results by 0.766:

$$a_{6.65\mu} \text{ for bound styrene} = \frac{A_{6.65\mu}}{\text{mol conc styrene}} = 0.425 - 0.555$$

$$a_{3.35\mu} \text{ for } cis\text{-1,4-PBD} = \frac{A_{3.35\mu}}{\text{mol conc } cis\text{-1,4-PBD}} = 0.147 - 0.192$$

$$a_{10.35\mu} \text{ for } trans\text{-1,4-PBD} = \frac{A_{10.35\mu}}{\text{mol conc } trans\text{-1,4-PBD}} = 0.766 - 1.00$$

$$a_{11.0\mu} \text{ for vinyl 1,2-PBD} = \frac{A_{11.0\mu}}{\text{mol conc vinyl-1,2-PBD}} = 1.35 - 1.75$$

### Calculations on Unknowns

Following is an example of the calculations for an unknown where the absorptivities are averages of the values determined for the six calibrating blends:

$$\text{bound styrene} = \frac{A_{6.65\mu} \times \text{mol wt styrene}}{a_{6.65\mu}} = \frac{0.0529 \times 104}{0.551} = 10.0 \text{ parts}$$

$$cis\text{-1,4-PBD} = \frac{A_{3.35\mu} \times \text{mol wt butadiene}}{a_{3.35\mu}} = \frac{0.0576 \times 54}{0.177} = 17.6 \text{ parts}$$

$$trans\text{-1,4-PBD} = \frac{A_{10.35\mu} \times \text{mol wt butadiene}}{a_{10.35\mu}} = \frac{0.432 \times 54}{1.00} = 23.3 \text{ parts}$$

$$\text{vinyl-1,2-PBD} = \frac{A_{11.0\mu} \times \text{mol wt butadiene}}{a_{11.0\mu}} = \frac{0.084 \times 54}{1.60} = 4.6 \text{ parts}$$

The terminology "parts" is used because a sample weight term cannot be included in the calculation.

### Characterization of Unknowns

Considerable flexibility may be used in applying the data to characterize the unknown rubbers. Some examples are included in this work:

(a) Advantage may be taken of the observations that there is relatively small variation in the microstructure of SBR rubbers for any particular level of bound styrene and that the addition of *cis*-1,4-PBD or natural rubber in blends would not change the relative ratios of the bound styrene, *trans*-1,4-PBD, and vinyl-1,2-PBD concentrations. Table I shows that

an SBR of nominal 23% bound styrene would be recognized readily in spite of blending and that SBR rubbers of nominal bound styrene levels of 10% and 40% also have very different and distinctive relative concentrations of microstructure.

(b) After ascertaining the class of SBR used, it is essential to know if any other polymers have been included as blends, and this requires a careful examination of the entire infrared spectrum. If only SBR and PBD are observed in a spectrum, the relative concentrations of bound styrene, *cis*-1,4-PBD, *trans*-1,4-PBD, and vinyl-1,2-PBD may be all normalized to 100 parts (Table II). The bound styrene concentrations show that the 23% bound styrene SBR has been diluted to about 80%–90%, 70%–80%, and 50%–60% of its original concentration, which is well within  $\pm 10\%$  of the actual dilutions. The increasing *cis*-1,4 concentrations resulting from blending is apparent but it is a tedious measurement at  $3.35 \mu$  which could be improved with grating instrument resolution.

(c) Natural rubber may be detected by a band at  $12.0 \mu$  but in some cases it may be removed with the pentane washing and a procedure has not been evolved for making concentration estimates.

(d) Polybutadiene alone may be simply identified by its spectrum.

(e) A library of data derived from a variety of SBR rubbers and SBR blends may be compiled to permit immediate comparisons with unknowns.

**Reagents.** Reagent grade chemicals were used but it is likely that technical grade materials would suffice.

## DISCUSSION

Attempts to devulcanize the cured samples with boiling *o*-dichlorobenzene alone did not result in any visual evidence of rubber dispersion over a period of 7 hr. The use of Pepton 22 along with *o*-dichlorobenzene produced black dispersions within 30 min of the initial boiling. After 7 hr of boiling, the slurries were gritty and they did not appear to have any elastomeric nature. In addition to the analysis, attempts were also made

TABLE III  
Pentane-Insoluble Polymer Recovered from Devulcanization of  
Loaded and Cured Samples

Sample <sup>a</sup>	Nominal weight of bound styrene, %	Pentane-insolubles recovered in weight, % <sup>b</sup>
F	40	49
B	23	33
G	10	16
A	0	8
C	21	45
D	19	44
E	14	36

<sup>a</sup> See Table I for compositions.

<sup>b</sup> Based upon weight of rubber used in formulations.

to recover, weigh, and estimate the amounts of rubber recovered as pentane-insoluble fractions. Table III illustrates that the pentane-insoluble fractions increase with higher bound styrene contents and it is relatively low for polybutadiene alone. Since the data in Tables I and II show excellent microstructure correspondence before and after devulcanization, the distribution of rubber fractions after devulcanization was not studied in detail. The amounts of devulcanized blends recovered were even slightly higher than that of their nonblended SBR polymer, so there may be other factors affecting the amounts of the devulcanized fractions recovered.

The 11.0- $\mu$  and 10.35- $\mu$  bands are the well-known carbon-hydrogen bending mode absorptions which are associated with vinyl and *trans*-vinylene structures, respectively. The 6.65- $\mu$  band is an aromatic carbon-carbon stretching mode band. These bands are well isolated from other absorptions, so they are easily baselined and provide absorption references for strong structure correlations. The data in Table I show that the relative concentrations of these three structures form a good basis of correlation for identifying the origin of an SBR rubber even though it may be blended with another rubber such as *cis*-1,4-PBD. This is because the SBR rubbers tend to be in fairly constant microstructure ratios for any particular level of bound styrene. In any case, any anomalous departures from these ratios could be easily recognized and probably interpreted.

The 3.35- $\mu$  band used to measure *cis*-1,4 content originates from a carbon-hydrogen stretching mode absorption. Below the 25% *cis*-1,4 concentration level, the 3.35- $\mu$  peak is only a shoulder and the baseline drawings and absorbance measurements are best accomplished with the aid of a magnifying glass. The correct peak position is located by measuring from the strong 3.45- $\mu$  band which is to be found in all SBR spectra. It is surprising that these determinations for low *cis*-1,4 concentrations reproduce as well as the data shown in Table II. At higher concentrations of *cis*-1,4-PBD structure, the 3.35- $\mu$  band is easily located, baselined, and measured, and this is really where the measurement becomes most meaningful. Nonetheless, the problem of measuring the 3.35- $\mu$  band should justify the use of a grating instrument for better resolution because more accurate evaluations of *cis*-1,4-PBD blending along with the accompanying dilutions of the other microstructures would result.

The SBR rubbers and the SBR-PBD rubber blends were analyzed, prior to loading and curing, as carbon disulfide solutions, in the near infrared region. An analytical matrix was employed with a 2.10- $\mu$  band for the vinyl-1,2-PBD element, a 1.75- $\mu$  band for the *trans*-1,4-PBD element, a 1.69- $\mu$  band for the *cis*-1,4-PBD element, and a 1.66- $\mu$  band for the bound styrene element. This procedure is not part of the analytical method and it was carried out only to provide an independent check on the results from the infrared film analyses. Table II shows that the near-infrared analyses provide good support and justification for the infrared film data. The devulcanized samples are not suitable for near-infrared analysis because of the small sample sizes and the color.



Work is in progress to include SBR-natural rubber in a characterization scheme. Natural rubber appears to be more soluble than SBR in pentane, so it may be desirable to substitute methanol in place of pentane for the precipitation and washing steps.

While it was postulated that the 2,2'-dibenzamidodiphenyl disulfide would devulcanize the cured rubbers by virtue of replacing some of the polymeric sulfide linkages, an exact knowledge of the mechanism is not essential for the analytical application. It has been observed that the devulcanized polymer spectra exhibit small extraneous absorption bands, of materials which do not seem to be separable, in the 5.75- to 6.75- $\mu$  region. These bands are thought to originate from Pepton attached to the polymeric material. Small quantities of Pepton 22 are used to minimize the possibility of interferences with spectral characterizations. Also, very little absorption evidence for oxidation is to be found in the spectra of the devulcanized rubbers.

Inorganic materials are removed in the centrifuging and the filtration steps. Excess oils and possibly other organics such as accelerators and excess Pepton 22 are removed in the precipitation and filtration steps.

While the analysis of any unknown may extend over a two-day period, it is *estimated* that one analysis would require about 3 man-hours of work.

## CONCLUSIONS

Sulfur-cured, loaded SBR and SBR-*cis*-1,4-PBD blends may be devulcanized to produce pentane-insoluble fractions which have infrared spectra that are very similar to those of the rubber or blends prior to loading and curing. This permits identification of the SBR and also estimates of the amount of *cis*-1,4-PBD used in blends. Best results would probably be obtained from a grating infrared spectrophotometer.

PBD alone can be identified by simple qualitative examination of the spectrum. Natural rubber can be recognized in the spectra of blends but it would be desirable to substitute methanol in lieu of pentane. A procedure has not been developed for estimating natural rubber contents.

## References

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