

Flammability and Degradation Characteristics of Styrene-Butadiene Rubbers

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Synopsis

Uncured styrene-butadiene gum, a known cured composition, and four SBR beltings used in underground coal mining were subjected to thermal oxidative degradation in static and dynamic systems. The room temperature volatiles produced under the static conditions at 370°C were identified and quantitated. Monomers and their interaction products were liberated by the raw gum; the cured composition formed together with the above products materials traceable to the curing ingredients. The four beltings gave a large spectrum of products; an attempt was made to correlate these with possible components used in belts manufacture. In the dynamic system, the occurrence of glow, the rate of smoke generation, and char yields were determined at 400° and 500°C. None of the materials glowed at 400°C. At 500°C, the raw gum volatilized completely, and the cured rubber and two beltings glowed. One of the beltings, which failed to glow, liberated the smallest quantity of toxic products.

INTRODUCTION

Styrene-butadiene rubbers constitute one of the major elastomers employed in the manufacture of conveyor beltings used in underground coal mining. The flammability characteristics of these materials, as well as the potential for smoke and toxic product formation, are thus of utmost importance if the hazards created by the utilization of these materials underground are to be assessed. To provide valid comparison data, the current study included SBR raw gum, a known cured composition, and four different beltings composed of SBR and the carcass. These materials were investigated under static and dynamic degradation environments.

EXPERIMENTAL

The samples tested are listed in Table I. The composition of the cured styrene-butadiene rubber following a standard vulcanizing recipe is given in Table II.

The experimental details of the quiescent degradation apparatus have been discussed previously.^{1,2,3} The stagnation burner arrangement employed in the dynamic tests was described elsewhere,⁴ with the exception that provisions were also made to determine smoke density changes during the entire decomposition

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TABLE I
List of Materials Studied

Uncured styrene-butadiene gum
Cured styrene-butadiene rubber
Belting E3, SBR, FR
Belting E5, SBR, FR
Belting F9, SBR/nylon, FR
Belting E4, SBR, non-FR

period. The light emission and detection system was constructed and installed using the specifications of ASTM method D 2843-70⁵ as a guideline. The optical path length of this arrangement was 390 mm. The volume of the burner system is ~1.5 liters; the volume of the ASTM smoke test chamber is ~71 liters.

Product analyses were performed using 8 ft × 1/8 in. stainless steel Porapak Q and 10 ft × 1/8 in. Apiezon L on Chromosorb G columns programmed for 50–220°C, utilizing flame ionization and thermal conductivity detectors as well as a du Pont Model 491B mass spectrometer equipped with a data acquisition and processing system.

RESULTS AND DISCUSSION

The experimental data for the thermal oxidative degradations are presented in Table III, while the volatile products compilation is given in Table IV. The extent of decomposition, as determined by weight loss, was relatively minor, particularly so in the case of the uncured gum and the known cured composition. With the exception of material E3, the TGA data are in very good agreement with the sealed system findings, especially if one considers that in programmed thermogravimetric analysis the residence time at temperature is significantly lower than the 30 min used here. On the other hand, it should be noted that in all the instances, the 370°C region was laying on the flat portion of the TGA curves. The appearances of TGA curves were found to be fairly specific for a material's composition in the case of chlorinated polymers.¹ This is also true to a degree here. Thus, the TGA curves of the known cured SBR and composition E4 bear close resemblance which is reflected in their parallel thermal oxidative behavior (see Tables IV and V).

TABLE II
Composition of Cured Styrene-Butadiene Rubber

Ingredient	Ingredient description	%
SBR-1502	styrene-butadiene raw gum	60.50
ISAF	oil furnace black filler	30.26
Zinc oxide	—	3.03
Circolite	processing oil	2.42
Stearic acid	—	0.61
MBT	2-mercaptobenzothiazole	0.61
TMMS	tetramethylthiuram monosulfide	0.30
Sulfur	—	1.06
Antioxidant 22446	2,2-methylenebis(4-methyl-6- <i>tert</i> -butyl phenol)	1.21

TABLE III
Experimental Data for Thermal Oxidative Degradations of
Styrene-Butadiene Rubbers at 370°C

Sample ^a	Initial <i>P</i> , mm	Final <i>P</i> , mm	Sample wt, mg	Resi- due, ^b (TGA),		Oxygen consumed		Total volatile products	
				% ^c	%	mg	% ^d	mg	% ^e
SBR Gum	479	493	5174	93	94	17.9	1.8	349.1	98.9
SBR Cured	513	495	5232	91	91	19.8	1.9	328.9	68.0
E3	507	519	1918	73	85	27.5	2.8	250.0	46.2
E5	502	522	5897	80	80	15.2	1.6	533.7	44.6
F9	499	537	5044	82	80	35.3	3.7	656.4	68.4
E4	505	552	5971	83	85	31.1	3.2	719.5	69.6

^a For material identification, see Table I; the sample was exposed to 370°C for 30 min.

^b This is only the solid removable portion of the residue and does not include any tars and oils deposited on the sides of the tube.

^c Percent of the weight of the starting material.

^d Percent of oxygen available.

^e Percent of total products based on sample weight loss.

The extent of oxidation as shown by the relative concentration of oxygenated compounds (CO₂ and oxygenated hydrocarbons) and the amount of oxygen consumed (see Table III) were relatively minor for all the compositions tested. Thus, it can be deduced that at 370°C, pyrolytic conditions prevailed. However, the amount of weight loss transformed into room-temperature volatiles was significantly lower in materials E3 and E5 (ca. 45%) than in the known cured composition and materials F9 and E4 (ca. 70%). Almost all the weight loss of the uncured gum resulted in volatiles production, the latter being derived from depolymerization processes.

The volatiles produced are given in Table IV in the form of milligram of product per gram of sample subjected to degradation. All definitely identified compounds are entered in the table separately. The relative toxicity of these specific species may be obtained by inspection of, for example, the threshold limit values adopted by the American Conference of Governmental Industrial Hygienists.⁶ Other products, for which the structures were not absolutely identified, are listed in Table IV as groups of species.

Examining Table IV, it is apparent that the three major products derived from the raw gum are the monomers 1,3-butadiene and styrene and 4-vinyl-1-cyclohexene (8.98 mg/g) formed by dimerization of 1,3-butadiene. This dimerization was also observed by Madorsky⁷ in his studies of polybutadiene. The other compounds identified and quantitated were various aromatics and materials derived from these primary products.

The cured composition afforded a somewhat different product mix than the raw gum. The monomer concentration was significantly decreased. The volatiles accounted for 68% of the weight loss; the remainder constituted room temperature-involatile oils and tars. The main toxic species formed were carbon disulfide, phenol, and cresols. If one considers phenol and cresols to be derived exclusively from the 2,2-methylenebis(4-methyl-6-*tert*-butylphenol) antioxidant, the quantity of phenol and cresol combined accounts for 18% of this constituent (see Table II). On the other hand, only four sulfur-containing compounds were

TABLE IV
Volatile Products Obtained on Thermal Oxidative Degradation of Styrene-Butadiene Rubber Compositions^{a,b}

Product	Uncured, mg/g	Cured, mg/g	E3, mg/g	E5, mg/g	F9, mg/g	E4, mg/g
CO	n.d. ^c	n.d.	12.0	3.67	?	2.53
CH ₄	0.67	0.89	0.27	0.21	0.39	1.23
H ₂ O	6.63	18.8	71.4	33.9	20.2	42.8
HCl	—	—	2.8	14.1	39.4	15.9
CO ₂	0.95	4.69	18.7	12.5	10.8	25.5
SO ₂	?	?	0.17	0.09	—	T
COS	0.13	0.14	0.56	1.34	0.36	0.45
CS ₂	0.29	0.68	0.03	0.33	1.72	—
H ₂ S	T ^d	T	0.02	0.74	7.63	0.25
HCN	—	—	—	0.50	T	—
C ₂ Species	0.99	0.53	0.58	0.60	3.34	5.25
C ₃ Species	1.19	0.51	0.26	0.48	2.69	0.76
C ₄ Species	0.22	3.47	0.55	0.51	2.91	0.66
1,3-Butadiene	11.2	3.80	0.01	0.11	—	0.29
C ₅ Species	3.27	2.21	0.23	0.60	5.32	0.88
C ₆ Species	3.09	2.11	1.06	1.59	2.81	0.71
C ₇ Species	1.19	1.05	0.34	0.12	0.99	0.56
C ₈ Species	0.64	1.05	6.87	0.90	2.49	0.05
4-Vinyl-1-cyclohexene	8.98	1.73	—	—	—	—
C ₉ Species	—	—	—	—	0.03	—
1-Methyl-4-isopropenyl- 1-cyclohexene	—	—	—	—	—	8.21
C ₁₁ Species	—	—	—	—	0.01	—
C ₁₂ Species	—	—	—	—	0.07	—
C ₁₃ Species	—	—	—	—	0.02	—
Benzene	0.95	0.58	0.50	0.32	1.98	0.35
Toluene	3.40	2.25	1.03	0.17	0.16	0.79
C ₂ Benzenes	2.11	4.15	0.61	1.10	0.34	1.79
C ₃ Benzenes	0.34	1.04	0.27	0.03	0.15	0.05
C ₄ Benzenes	0.11	0.14	0.02	0.02	0.04	0.05
C ₅ Benzenes	0.01	0.11	—	—	0.02	—
C ₆ Benzenes	0.38	0.07	—	—	—	—
Styrene	13.8	2.79	0.95	0.27	0.56	1.12
Methylstyrene	0.46	0.66	0.08	0.03	0.12	0.11
C ₂ Styrenes	—	—	0.06	0.02 ^e	0.21	T
Methylnaphthalenes	—	—	0.01 ^e	0.03 ^e	T	?
Tetrahydronaphthalenes	—	0.08	0.01 ^e	0.02 ^e	0.02	0.02 ^e
Methyltetrahydro- naphthalenes	0.14	0.08	0.01 ^e	0.02 ^e	0.01 ^e	0.01 ^e
Dimethyltetrahydro- naphthalenes	0.01	—	—	—	—	—
Indene	0.01	0.02	0.02 ^e	0.02 ^e	0.10 ^e	0.06 ^e
Dimethylindenenes	0.09	—	—	—	—	—
C ₃ Indenes	0.02	—	—	—	—	—
Indan	0.05	0.37	0.02 ^e	0.03 ^e	0.10	0.06 ^e
Methylindans	0.03	0.10	0.01 ^e	0.02 ^e	0.01	0.01 ^e
Dimethylindans	—	0.03	T	0.03 ^e	0.01	0.01 ^e
Santene	—	0.05	—	—	—	—
Azulene	—	0.02	?	?	0.10	?
Methyl chloride	—	—	T	0.39	10.39	0.01
Vinyl chloride	—	—	—	—	0.34	T
Ethyl chloride	0.05	—	—	0.12	2.77	0.13

continued

Table IV Contd

Product	Uncured, mg/g	Cured, mg/g	E3, mg/g	E5, mg/g	F9, mg/g	E4, mg/g
2-Chloropropene	—	—	—	—	0.26	—
Chloroprene	—	—	—	—	0.27	—
2-Chloro-2-butene	—	—	—	—	0.63	—
3-Chloro-2-methyl- propane	—	—	—	—	0.06	—
Chlorobenzene	—	—	0.01	0.01	0.09	T
Chlorotoluenes	—	—	0.02	?	0.12	—
Chloro-C ₂ -benzenes	—	—	—	—	0.01	—
Dichlorobenzenes	—	—	—	0.01	0.03	—
Methanol	0.01	0.03	0.23	T	2.74	0.04
Ethanol	0.02	0.01	0.04	T	T	0.11
Allyl alcohol	—	—	—	—	—	0.02
C ₃ Alcohols	T	T	—	—	—	T
C ₄ Alcohols	T	—	0.08	0.05	0.01	T
C ₅ Alcohols	—	—	—	—	T	—
Phenol	—	0.04	0.02	0.67	0.03	0.06
Cresols	—	0.59	?	?	1.77	?
4-Methyl-2-ethyl- phenol	—	—	—	—	0.02	—
Methylbenzyl alcohols	0.02	0.28	—	—	—	—
2-Chloroethanol	—	—	0.01	T	0.03	0.04
Acetaldehyde	0.01	0.02	—	—	0.46	0.71
Butyraldehyde	T	—	—	—	—	—
Acetone	0.04	0.07	0.02	0.09	0.06	0.21
Methyl ethyl ketone	—	0.04	0.03	0.02	0.06	0.10
Methyl <i>n</i> -propyl ketone	—	—	—	—	T	—
Methyl isopropenyl ketone	—	—	—	—	—	0.07
4-Methyl-2-pentanone	—	—	—	—	—	0.07
Methyl furyl ketone (4'-Methyl-2-furyl)-2- cyclopentane-2-one	0.11	—	—	—	—	—
Cyclopentanone	—	—	2.46	1.78	0.02	0.02
Methylcyclopentanone	—	—	—	—	0.06	—
Cyclohexanone	—	—	—	0.10	0.02	0.02
Dimethylindanones	—	—	?	?	0.01	?
Trimethylindanones	—	—	?	?	0.03	?
2-Ethyldimedone	—	T	—	—	—	—
<i>p</i> -Dioxane	—	—	—	0.04	0.01	—
Formic acid	—	—	—	—	2.91	—
Acetic acid	0.06	T	T	0.14	0.71	0.23
Methoxyacetic acid	—	—	—	1.73	—	—
Propionic acid	0.02	—	—	—	—	—
Methyl formate	T	—	—	—	—	—
Ethyl formate	—	—	0.01	—	T	—
Methyl acetate	T	—	0.12	—	0.02	T
Ethyl acetate	—	—	0.08	—	—	?
Vinyl acetate	—	—	—	—	—	0.07
2-Methylfuran	—	—	—	0.01	—	0.28
Dimethylfuran	—	—	—	0.12	—	?
Ethylmethylfurans	—	—	—	—	0.02	—
Methyl mercaptan	—	—	?	?	0.01	?
Dimethyl sulfide	—	—	T	T	0.02	?
Dimethyl disulfide	—	—	?	?	0.21	?

continued

Table IV Contd

Product	Uncured, mg/g	Cured, mg/g	E3, mg/g	E5, mg/g	F9, mg/g	E4, mg/g
Methylthiophenes	—	—	?	?	0.08	?
2-Acetylthiophene	—	T	—	—	—	—
Thiacyclopentane	—	—	?	?	0.01	?
Acetonitrile	—	—	—	0.22	—	—
5-Cyano-hexene	—	—	—	—	0.25	—

^a Material identification is given in Table I. All values are given in mg of product formed per gram of test sample.

^b For the curing recipe, see Table II.

^c n.d. = not determined.

^d $T = < 0.005$ mg/g.

^e Tentatively identified.

identified, namely, hydrogen sulfide, carbon disulfide, carbonyl sulfide, and 2-acetylthiophene. All these added up to ca. 0.64 mg/g sulfur, whereas the total sulfur present in the actual rubber amounted to at least 14.3 mg/g. Thus, it is apparent that under the degradation conditions employed, the bulk of sulfur remained in the residue or tars. This is not surprising, since less than 10% of material was actually decomposed; however, only about 4% of the sulfur present was liberated.

For none of the four beltings was the carcass identified by the supplier, nor was the weight percent of carcass given. The fibers most commonly employed in carcasses are nylon 66, dacron polyester, and, to a lesser degree, viscose rayon.

TABLE V
Summary of Stagnation Burner Studies Performed on Styrene-Butadiene Rubbers

Sample ^a	Temp., °C ^b	Resi- due, %	Residue (TGA), %	Glow, min	Smoke ^c		Total duration, min
					Maximum intensity %	Duration, min	
SBR Gum	404	59	94	—	95	4.2-4.6	4.0-7.0
	505	0.5	10	—	100	1.3-2.8	1.0-5.0
SBR Cured ^d	399	84	91	—	10	4.0-4.5	3.7-5.5
	500	14	40	8-15	100	1.2-1.9	1.0-4.0
E3	402	84	84	—	60	3.2-4.6	2.0-7.0
	507	37	53	—	85	4.7-5.3	1.0-11.0
E5	399	69	80	—	50	5.0-7.0	1.5-6.0
	499	35	45	—	80	3.2-6.0	1.0-9.0
F9	399	64	78	—	89	4.0-6.0	1.5-8.0
	499	29	52	5-15	90	1.8-5.2	0.5-8.0
E4	401	70	78	—	50	6.8-7.7	3.0-9.0
	507	15	40	9-15	80	3.3-4.0	1.0-12.0

^a For sample identification, see Table I.

^b This is the average temperature of heating block and air in the stagnation burner; the difference between the two temperatures was always less than 5°C; a given sample was exposed to stagnation burner environment for a total of 15 min.

^c Smoke was measured in conformance with ASTM method D 2843-70.

^d For the curing recipe, see Table II.

All the beltings with the exception of E4 were fire resistant. Poly(vinyl chloride) and other chlorinated materials are commonly used to impart fire resistance; thus, it is not surprising that each of the belting compositions liberated hydrogen chloride. However, the chlorinated moieties would not be expected to be present in the nonfire-resistant composition E4, wherein the quantity of liberated hydrogen chloride (see Table IV) was larger than in the case of fire-resistant sample E3. Regarding material E5, ammonium chloride and amine hydrochlorides were found in the involatile deposits; accordingly, the reported value for HCl of 14.1 mg/g must be increased if one would consider the total hydrogen chloride liberated.

Comparing the types and relative proportions of products formed by these belts, it is obvious that F9 produced the largest variety and quantity of toxic species as represented by hydrogen chloride, sulfur dioxide, carbon disulfide, hydrogen sulfide, cresols, vinyl chloride, formic acid, acetic acid, methyl mercaptan, and other sulfur-containing compounds (dimethyl sulfide, dimethyl disulfide, methylthiophenes, and thiacyclopentane). The presence of sulfur-containing moieties in all of these styrene-butadiene formulations is to be expected since sulfur is one of the constituents of rubber curing recipes (see Table II). However, it is the relative proportion of the toxic species formed which is of importance. The *m*-cresol (1.77 mg/g) found in the volatiles of material F9 is probably derived from a cresyl phosphate additive. The origin of acetonitrile and, most likely associated with it, hydrogen cyanide in the products of E5 is unknown. This belting did afford caprolactam, ammonium chloride, and amine hydrochlorides in the involatile deposits, pointing clearly to the presence of nylon 6 in the carcass.

Based on literature data,⁸⁻¹⁰ polyamides do not produce hydrogen cyanide below 400°C. This conclusion is also supported by our studies.¹¹ On the other hand, it is plausible that the other ingredients present in the actual belting can alter the decomposition mechanism of a polyamide and thus the products formed. It should be stressed that the value given for hydrogen cyanide is most likely too low since it is based only on the hydrogen cyanide present as gas in the -196°C fraction and does not include the HCN dissolved in the aqueous portions of the -23°C, -78°C, and room-temperature fractions. The same applies to hydrogen sulfide. The total quantity of sulfur-containing species formed was relatively high here, 2.41 mg/g. Of particular significance is the relatively large amount (1.34 mg/g) of COS found, which would indicate that the reactive and therefore difficult-to-determine sulfur-containing compounds were produced in larger quantities than reported. Phenol is another toxic compound found in the volatiles of material E5.

It is of interest that 1-methyl-4-isopropenyl-1-cyclohexene (8.21 mg/g) was the main organic compound found in the volatiles produced by sample E4; that sample also produced terephthalic acid found in the involatile residue. One is thus tempted to speculate that 1-methyl-4-isopropenyl-1-cyclohexene is derived from the alcohol portion of a terephthalate ester plasticizer employed in this formulation.

To obtain data on the degree of decomposition in dynamic environment and to evaluate glow and smoke formation characteristics of the styrene-butadiene rubbers, the stagnation burner tests were performed and are summarized in Table V. None of the compositions produced high char yields at 500°C. Virtually

no residue remained in the case of polystyrene–butadiene raw gum at the higher temperature, showing that under these conditions the material completely volatilized. This fact explains the absence of glow. Materials F9 and E4 and the cured SBR compositions glowed at 500°C; no glow and relatively less smoke production and shorter time periods of high smoke intensity were observed for materials E3 and E5. Of the two beltings, E3 afforded lower quantities of toxic products. It thus may be concluded that increased “flame resistance” (as evidenced by the absence of glow at 500°C) must not be associated with high smoke and increased toxic product formation, even in conventional compositions as represented by styrene–butadiene rubbers.

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