High Temperature Tensile Properties of Elastomers Containing Carboxyl Groups

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The development of elastomers which are serviceable at elevated temperatures has been emphasized in the past few years. Most of this work has been directed toward the preparation of thermally stable elastomers without regard to the actual physical properties of the elastomer at these elevated temperatures. Smith (*9*, *10*) recently pointed out that the tensile strength of all of the commercially available elastomers is very low at 400° F.

This article describes the vulcanization of butadiene elastomers containing carboxyl groups with epoxy resins and metal oxides and shows the exceptionally good tensile properties of these vulcanizates at elevated temperatures.

EXPERIMENTAL

Polymers. The 85–15 butadiene–methacrylic acid polymer (prepared in an acid emulsion system by the incremental addition of the methacrylic acid, and known to contain 0.17 equivalent of carboxyl groups per 100 grams of polymer), and the 70–30 butadiene–methyl methacrylate copolymer (prepared in emulsion at 50° C.) were available in experimental quantities at the Firestone Chemical and Physical Research Laboratories.

The 75–15–10, 75–19–6, and 75–22–3 butadiene–methyl methacrylate–methacrylic acid terpolymers were prepared in 28-ounce beverage bottles according to the following recipes.

	No. 1	No. 2	No. 3
Butadiene (BD)	75	75	75
Methyl methacrylate (MMA)	15	19	22
Methacrylic acid (MAA)	10	6	3
Aquarex G	3	3	3
$K_2S_2O_8$	0.4	0.4	0.4
Sulfole B8	0.3	0.3	0.3
Sequestrene AA	0.05	0.05	0.05
Distilled water	180	180	180

The polymerizations were run at 50° C. to a conversion of 65%, which required 6 to 8 hours. They were shortstopped at the desired conversion, and antioxidant was added prior to coagulation with 10% aqueous calcium chloride solution. The polymers were washed on a wash mill and dried in an oven at 70° C. Although no analytical data were obtained on these polymers, it is known that methacrylic acid enters the copolymer more rapidly than butadiene (*2*). This fact plus the conversion of 65% ensures that the methacrylic acid content in the rubber lies between 3 and 4.5%, 6 and 9%, and 10 and 15%, respectively. Furthermore, the presence of a third monomer such as methyl methacrylate which alternates with the butadiene effectively reduces the rate at which the methacrylic acid enters the polymer (*4*). Thus, the resulting polymers contain approximately 3, 6, and 10% methacrylic acid.

Mixing. In general, the polymer, carbon black, stearic acid, antioxidant, and softener were mixed in a laboratory Banbury at 300° F. The remaining ingredients were added on a mill. For the carboxyl polymers, batch size was limited to 50 to 400 grams, and the metal oxide and epoxy resin were added to the stock with the mill rolls as cold as possible. Using larger batches and subsequent higher mixing temperatures nearly always resulted in setting up the batch on the mill. The barium hydroxide octahydrate was added to the butadiene–methyl methacrylate masterbatch at temperatures of 160° to 200° F. This pigment does not disperse completely until it melts at about 160° F.

Curing and Testing. The stocks were cured as 6 × 6 × 0.070 inch slabs and cut into dumbbell strips for testing. The tensile strengths and elongation were measured on a modified Scott tester enclosed in an oven held at the desired temperature (*6*, *9*). A 6-minute preheat period was used to allow the strips to reach the desired temperature. The carboxy stocks must be vulcanized within 24 hours after they are mixed in order to prevent precure.

DISCUSSION

The vulcanization of carboxylic elastomers and their resulting physical properties have been adequately reviewed by Brown (*1*). Included in this review and in an article by Lufter and Duke (*7*) are data indicating that an improvement in stress-strain properties up to 250° F. can be obtained from a carboxylic elastomer when cured with a combination of sulfur and zinc oxide. Werner (*11*) and Mika (*8*) showed that epoxy resins may be used to vulcanize elastomers containing carboxy groups. Satisfactory cures can be obtained with a variety of epoxy compounds (Table I). The differences in the results are not particularly significant because establishing optimum loadings or curing conditions was not attempted with any of the epoxides except Epon 828. Epon 828 was selected for the rest of the study because of its availability and relatively high epoxy content.

The effect of the amount of zinc and cadmium oxides on the tensile properties of the epoxy cured 85–15 butadiene–methacrylic acid copolymer is shown in Table II. The tensile strength and elongation are greatly improved as the amount of metal oxide is increased to an equivalent of the carboxyl groups present. The relatively constant elongation over the 73° to 400° F. range is of particular interest.

Table III shows that many other metal oxides and hydroxides give improved tensile properties at temperatures up to 500° F. The stock containing magnesium oxide holds its properties somewhat better than the others at 500° F. All have very high modulus and relatively low elongations at 73° F.

To lower the modulus and increase the elongation of the epoxy–metal oxide vulcanizates, polymers containing approximately 3, 6, and 10% methacrylic acid were examined (Table IV). The magnesium oxide vulcanizates of the polymer with 3% methacrylic acid and the cadmium oxide vulcanizates of the polymer containing 6% methacrylic acid have as good high

Table I. Effect of Epoxides on Vulcanization of 85–15 Butadiene–Methacrylic Acid Copolymer

Basic recipe. Polymer, 100 parts; HAF black, 40; stearic acid, 2; N-phenyl-2-naphthylamine, 2.

Cure. 60 minutes at 300° F.

Epoxy Compound	Parts/100 of polymer	200% Modulus, P.S.I.	Tensile, P.S.I.	Elongation, %
Epon 828 [a]	4	700	3150	400
EP-201 [b]	3	650	3250	520
Vinyl cyclohexene dioxide	1.5	325	2075	620
Paraplex G62 [c]	8	550	2875	500
Emery 3051R [d]	9	225	2250	660

[a] Shell Chemical Co., reaction product of bisphenol A and epichlorohydrin.

[b] Union Carbide Chemicals Co., 3,4-epoxy-6-methylcyclo-hexylmethyl-3,4-epoxy-6-methylcyclohexane carboxylate.

[c] Rohm & Haas Co., epoxy plasticizer.

[d] Emery Industries, Inc., epoxy plasticizer.

Table II. Effect of Zinc and Cadmium Oxides in Epoxy Vulcanization of 85–15 Butadiene–Methacrylic Acid Copolymer

Basic recipe. Polymer, 100 parts; HAF black, 40; Epon 828, 4; stearic acid, 2; *N*-phenyl-2-naphthylamine, 2; variable metal oxide
Cure, 60 minutes at 300° F.

Test Temp., °F.		Parts of Metal Oxide/100 of Polymer						
		0	2 ZnO	5 ZnO	8 ZnO	6 CdO	8 CdO	11 CdO
73	200% modulus, p.s.i.	700	875	2225	2800	2750	3575	3375
	Tensile, p.s.i.	3150	3300	4975	4750	4275	4275	4400
	Elongation, %	500	520	340	280	280	250	260
300	200% modulus, p.s.i.	710	260	310	460	600	750	840
	Tensile, p.s.i.	710	710	900	1210	1340	1290	1760
	Elongation, %	200	390	430	400	320	280	320
400	200% modulus, p.s.i.	...	...	340	390	...	...	770
	Tensile, p.s.i.	190	300	800	930	420	700	1090
	Elongation, %	80	180	380	380	130	190	260

Table III. Effect of Oxides and Hydroxides in the Epoxy Vulcanization of 85–15 Butadiene–Methacrylic Acid Copolymer

Basic recipe. Polymer, 100 parts; HAF black, 40; Epon 828, 4; stearic acid 2; *N*-phenyl-2-naphthylamine, 2; variable metal oxide
Cure, 60 minutes at 300° F.

Test Temp., °F.		Parts of Metal Oxide/100 of Polymer					
		0	7 ZnO	11 CdO	13.4 BaO	4 MgO	6.6 $Ca(OH)_2$
73	200% modulus, p.s.i.	700	2800	3375	...	...	...
	Tensile, p.s.i.	3150	3900	4400	4025	4850	3650
	Elongation, %	500	250	260	150	170	160
300	200% modulus, p.s.i.	710	500	840	...	...	...
	Tensile, p.s.i.	710	940	1760	1430	1400	1000
	Elongation, %	200	310	320	170	200	120
400	200% modulus, p.s.i.	...	520	770	...	900	...
	Tensile, p.s.i.	190	870	1090	1500	1300	900
	Elongation, %	80	300	260	170	260	110
500	200% modulus, p.s.i.	...	...	...	...	420	...
	Tensile, p.s.i.	...	380	300	500	570	400
	Elongation, %	...	110	80	70	280	70

temperature tensile strength and elongation as those containing more carboxyl groups, and they have a lower modulus and higher elongation at room temperature.

In spite of their exceptionally good high temperature properties, carboxy polymers containing relatively large amounts of metal oxides are considered to be impractical for tire stocks because of extreme processing difficulties. The stocks must be mixed in small batches on a very cold mill to avoid scorching; still, an occasional batch is lost. Alleviating this problem by using salts containing the desired metal or metal oxide has been attempted. In general, when salts of carboxylic acids are used, the vulcanizate fails to show the outstanding high temperature properties. Thus far, no material gives satisfactory properties and permits conventional mixing techniques with the carboxy rubbers.

However, the good high temperature properties can be obtained by the hydrolysis of a butadiene–methyl methacrylate copolymer with barium hydroxide octahydrate during the vulcanization step. These stocks can be mixed either in a Banbury or on a warm mill. The results of two different formulations for the vulcanization are shown in Table V. Cooper and Bird (*3*) reported a similar "in situ" hydrolysis of butadiene-acrylate copolymers with calcium hydroxide, barium hydroxide, and similar reagents using a polyhydric alcohol as a catalyst for the system. This system fails in the case of the butadiene–methyl methacrylate copolymer. In fact, the hydrated barium hydroxide appears to be the only reagent which operates satisfactorily for the methacrylate copolymer.

In all of these vulcanization systems, both an ionic cross-linking agent and a covalent cross-linking agent are necessary. If the epoxide or dicumyl peroxide is removed, the stock is thermoplastic. If the ionic cure is omitted, the good high temperature properties are lost.

All of the high temperature test results reported were made on stocks quickly brought to temperature and tested without any further aging. Table VI shows the results of aging these carboxy polymers compared with some commercial elastomers. Apparently, none of the vulcanizates are adequate after 8 hours' aging at 400° F. and testing at 400° F.

The data do show that the butadiene–methyl methacrylate copolymer vulcanized with barium hydroxide octahydrate and dicumyl peroxide gives a vulcanizate which is better both for aging and for high temperature properties than other diene polymers. Unaged, it is better than either silicone or Viton A at temperatures up to 500° F.

Probably, introducing ionic cross links into the polyacrylates, Viton A, and the silicones will result in vulcanizates which will retain their properties both before and after aging at tempera-

Table IV. Epoxy–Metal Oxide Vulcanizates of Butadiene–Methyl Methacrylate–Methacrylic Acid Terpolymers

Terpolymers used	BD-MMA-MAA
1	75-15-10
2	75-19-6
3	75-22-3

Basic formula. Polymer, 100 parts; HAF black, 40; *N*-phenyl-2-naphthylamine, 2; stearic acid, 2; Epon 828, 4; variable metal oxide
Cure, 60 minutes at 300° F.

		A	B	C	D	E
		Terpolymer				
		1	1	2	3	3
Test Temp., °F.		Metal Oxide, Parts/100 of Polymer				
		11 CdO	4 MgO	11 CdO	11 CdO	4 MgO
73	200% Modulus, p.s.i.	3625	...	1875	625	1650
	Tensile, p.s.i.	4300	4225	4225	2475	3300
	Elongation, %	250	180	370	540	420
200	200% Modulus, p.s.i.	950	...	590	280	1000
	Tensile, p.s.i.	1550	1900	1600	900	1780
	Elongation, %	280	190	380	550	340
300	200% Modulus, p.s.i.	640	...	450	220	720
	Tensile, p.s.i.	1200	1300	1300	650	1330
	Elongation, %	300	190	420	460	330
400	200% Modulus, p.s.i.	440	...	450	260	670
	Tensile, p.s.i.	800	840	910	550	870
	Elongation, %	300	190	330	350	260

Table V. Vulcanization of 70–30 Butadiene–Methyl Methacrylate Copolymer with $Ba(OH)_2 \cdot 8H_2O$

		A	B
Recipe			
Polymer		100	100
HAF black		40	40
Stearic acid		2	2
N-Phenyl-2-naphthylamine		2	2
Pine tar		5	5
$Ba(OH)_2 \cdot 8H_2O$		15	20
Di Cup 40 C[a]		2	...
Epon 828		...	5
Barium oxide		...	10
Cure, 60 min. at 320° F.			
Test Temp., °F.		A	B
73	Tensile, p.s.i.	4025	3425
	Elongation, %	450	230
300	Tensile, p.s.i.	1490	...
	Elongation, %	470	...
400	Tensile, p.s.i.	960	1760
	Elongation, %	500	370
500	Tensile, p.s.i.	300	...
	Elongation, %	190	...

[a] Hercules Powder Co., 40% dicumyl peroxide on calcium carbonate.

tures from 400° to 550° F. Studies on some of these modifications and further compounding of the butadiene-methyl methacrylate copolymer are in progress.

Table VI. Aged High Temperature Properties of Carboxy Rubbers and Some Commercial Elastomers

	Aged 8 Hours °F.			
	. . .	300	. . .	400
	Test Temperature, °F.			
Polymer	300	300	400	400
BD-MMA-MAA, 3% MAA (Table IV, E)				
Tensile, p.s.i.	1330	590	870	190
Elongation, %	300	100	260	10
BD-MMA-MAA, % MAA (Table IV, C)				
Tensile, p.s.i.	1300	1050	910	280
Elongation, %	420	230	330	50
BD-MMA (Table V, A)				
Tensile, p.s.i.	1490	950	960	380
Elongation, %	470	360	500	70
SBR [a]				
Tensile, p.s.i.	890	270	260	170
Elongation, %	180	30	100	60
Hevea [b]				
Tensile, p.s.i.	1530	690	500	125
Elongation, %	400	440	500	80
Cohrlastic HT655 [c]				
Tensile, p.s.i.	560	510	360	330
Elongation, %	500	490	340	240
Viton A [d]				
Tensile, p.s.i.	. . .	. . .	220	210
Elongation, %	. . .	. . .	60	70
Butyl [e]				
Tensile, p.s.i.	1140	850	790	360
Elongation, %	260	180	150	90

[a] Stock 2405 (*9*). [b] Stock 2404 (*9*). [c] Stock 5065 (*9*). [d] Stock 104A-410 (*5*). [e] Stock 8787 (*9*).

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Component Analysis of Naphtha Fractions of Three Venezuelan Crudes

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Quality and quantity data on petroleum fractions boiling up to 210° F. were needed in isolating high yields of high octane number isopentane, isohexanes, and isoheptanes in virgin naphthas for inclusion in aviation gasoline. As part of the over-all program, a complete analysis was made of the naphthas from three Venezuelan crudes boiling up to 210° F.

The project consisted of fractionating each 310° F. final boiling point naphtha into the C_5, C_6, C_7, and C_8 fractions. The C_6 and C_7 fractions were refractionated into 2% cuts, and infrared and ultraviolet techniques applied to determine their compositions. Low temperature distillation methods were used to determine those compounds boiling below normal pentane.

To adhere as closely as possible to plant operations, no treatment affecting the composition of the sample was made prior to distillation or to the small cuts prior to analysis. Distillations were carried out under conditions designed to simulate those in the units and no attempt was made to isolate pure compounds.

Refractive index and specific gravity measurements were made on each cut as aids in the analyses. At the time the work was done gas chromatography was not available at these laboratories. Since then, several units have been acquired, and future analyses will utilize this technique. The work was repeated on a less extensive scale using gas chromatography; the results were essentially the same. One interesting development, however, was the identification of hydrocarbons not suspected.

MATERIALS AND EQUIPMENT

Distillation. Three distillation units were used in this work. Podbielniak Hyd Robot low temperature fractional distillation units were used to analyze the naphthas for those compounds boiling below normal pentane. This equipment is conventional, commercially available, and adequately covered in the literature (*10-14*).

The initial separations of the samples into broad isomer cuts were made in a Fenske-type distillation column (*5*), of a semi-automatic nature having a nominal capacity of 1 to 5 liters. The apparatus consists of a still pot, packed column, still head, receiver, and temperature measuring devices. The column is a vacuum-jacketed glass tube with an inside diameter of 25 mm. and with a packed section 1.5 meters long. The packing is 3/32-inch stainless steel Fenske-type helices supported by a 12-mesh stainless steel conical screen 80 mm. from the bottom of the column. The still head is of the total reflux-intermittent take-off-liquid dividing type. It consists of a reflux chamber, condenser, and product cooler. A solenoid-actuated plunger controlled by a Flexopulse timer of variable setting is used to control liquid product removal and thus control reflux ratio (*1,6*). Copper-constantan thermocouples and an L&N manually operated portable potentiometer are used to measure overhead vapor temperatures. The still pot is heated by a Variac-