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Boron-Filled Elastomers (SANL 252-056)

Robert E. Schneider and Lawrence W. Hartzel

April 20, 1976

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Abstract

A series of boron filled vinyl copolymer elastomer (VCE) and Viton A fluoroelastomer formulations was prepared and the physical characteristics of the cured formulations determined. Their weight loss on heating to 300°C, as determined by two different analytical methods, did not agree.

Values for the percent weight loss at 300°C differed depending on the analytical method used. The presence of up to 0.23% boric acid in the boron powders used to fill a standard boron filled VCE elastomer did not appear to affect the physical characteristics of the cured formulation. This work was done at the request of Lawrence Livermore Laboratory.

Introduction

Studies to determine the ability of two elastomers to accept high loadings of crystalline boron powder were carried out at the request of Lawrence Livermore Laboratory. Authorization for this work was by SANL 252-056 dated April 1974. This report describes the preparation of various formulations and their evaluation.

Accomplishments

Boron powder containing 0.23% boric acid was washed with methanol to remove boric acid. The boron contained 0.015% boric acid after washing.

Densities of various boron powders and their particle size distribution by Andreason pipette were determined (Table 1).

The density, swell ratio, percent weight loss at 300°C, percent solvent extractables, Shore D hardness and tensile strength were determined on samples of ten formulations of 60 volume % washed boron loaded Viton A fluoroelastomer. These data are listed in Tables 2 and 3. The effect of the order of ingredient addition during mixing on the physical characteristics of one cured formulation was also determined (Table 7).

The density, swell ratio, percent weight loss at 300°C, percent solvent extractables, Shore D hardness and tensile strength were determined on four samples of 60 volume % boron filled standard vinyl copolymer elastomer (VCE MI-24) cured with tolylene-diisocyanate dimer (TDID). The four samples were: unwashed boron loaded press cured (1); press and post cured (2); washed boron loaded press cured (3); and press and post cured (4). Table 5 lists the physical properties of the four samples.

Four nonstandard VCE formulations filled with 60 weight percent of washed boron powder were prepared and their density, swell ratio, percent weight loss at 300°C, hardness, tensile strength and elongation characteristics were determined. This data is shown in Table 6 together with similar data obtained from the standard VCE-TDID formulation.

Experimental

Boron Purification

Two liters of anhydrous methanol were stirred in a one-gallon polyethylene container while 1500 g of unwashed boron, supplied by LLL, was added slowly. After all the powder was added, the slurried mixture was transferred to a stainless steel drying tray. A small amount of methanol was used to transfer traces of boron from the container. The supernatant methanol was decanted from the mixture after standing overnight. The tray was covered with porous paper and dried under vacuum at 200°C for four hours. Upon completion of drying, the boron cake was broken up and the powder transferred to a polyethylene bag which was then sealed. The unwashed boron powder contained 0.23% boric acid; the washed boron contained 0.015% boric acid.

Elastomer Formulation and Curing

Sixty volume % loaded VCE MI-24 was milled on a cold mill. The boron powder was added slowly until it was dispersed in the polymer. After the boron was fully dispersed in the elastomer, the curing agent was added and milled to a homogeneous mixture. It was removed from the mill at a thickness of approximately 110 mils. A 2½ x 5 in. slab was stamped out with a die cutter. A Teflon film was placed on either side of the slab and the laminate placed in a hot 2½ x 5 in. compression mold. The VCE was pressed at 10,000 psi (69 megapascals) at 130°C for 1 hour. The slabs were cut in half and one piece of each slab was post cured in an oven under no load for 24 hours at 130°C.

The Viton A elastomer formulations (60 volume % loaded) were also milled on a cold mill in the same manner as the VCE elastomer. Filled material formulations were press cured at 10,000 psi pressure (69 megapascals) and 177°C for 30 minutes. Half of each 2½ x 5 in. slab was post cured in an oven under no load 30 minutes at 177°C, 2 hours at 191°C, and 24 hours at 204°C.

Unfilled formulations of both polymers were cured at the same temperatures as filled formulations but at a reduced pressure (about 900 psi, 6.2 megapascals) to prevent extrusion of the polymer from the mold.

Testing

Density

Densities of the cured samples were determined by the liquid displacement method using cyclohexane (d - 0.772 g/ml). Only weighings taken immediately upon immersion (before absorption of the suspending medium) were used in the calculations. The sample densities, in grams per milliliter, were determined by the relation

$$\text{Sample Density} = \frac{0.772 \times \text{wt sample in air}}{\text{wt sample in air} - \text{wt sample in medium}}$$

Swell Ratio

One-half inch diameter disks were die cut from milled and cured slabs and swelled in a solvent for 24 hours at 23°C. Toluene was the solvent used for VCE and methyl ethyl ketone for Viton A. Weights were taken before and after swelling. Calculations were made based on the polymer matrix only. (Reference letter, J. Stuart, LLL to L. Hartzel, MRC, dated 7/12/74).

$$\frac{\frac{(W_1)(X)}{P_1} + \frac{W_2 - W_1}{P_2}}{\frac{(W_1)(X)}{P_1}} = \text{Swell Ratio}$$

W_1 = initial weight of sample
W_2 = swollen weight of sample
P_1 = density of the polymer matrix
P_2 = density of solvent used
X = weight % of the polymer in the sample

Weight Loss at 300°C

A. A 1.0 g sample was placed in an Aminco TGA apparatus and heated at the rate of 10°C/min. The weight loss from room temperature up to and beyond 300°C was automatically recorded. The actual weight loss at 300°C was used to calculate the weight loss of the matrix at that temperature:

$$\text{Weight loss at 300°C} = \frac{W_1}{W_S \times X}$$

where W_1 = weight loss at 300°C
W_S = weight sample
X = % polymer matrix in sample

B. A 10 mg sample was placed in a DuPont TGA apparatus and heated at the rate of 10°C/min. The weight loss was automatically recorded and the weight loss at 300°C determined using the same formula as in A.

% Solubles

The filled cured material was ground in a Wiley Mill and the portion passing through a 20 mesh screen used for the weight loss and extractables measurements. The sample was weighed into a coarse fritted glass extraction thimble and extracted with 100 ml of solvent for 20 hours in a Soxhlet extraction apparatus. A 5 g sample was used for VCE formulations with toluene as the solvent while a 2 g sample of the Viton A formulation was used with methyl ethyl ketone as the solvent. After refluxing the material for 20 hours the solvent was removed from the warmed flask under vacuum by means of a Rinco Rotary evaporator. Both the sample in the thimble and the flask were vacuum dried for 4 hours at 60°C then cooled. The percent weight loss, based on polymer matrix in the sample, was calculated as follows:

$$\%\ \text{wt. loss} = \frac{W_1 - W_2 \times 100}{W_S\ X}$$

where: W_1 = initial weight of thimble and sample
W_2 = final weight of thimble and sample
W_S = original weight of sample
X = weight % polymer matrix in sample

$$\%\ \text{extractables} = \frac{W_3 - W_4 \times 100}{W_S\ X}$$

where: W_3 = final weight of flask and extractable
W_4 = initial weight of flask
W_S = weight of sample
X = % polymer matrix in sample

Tensile and Elongation

An Instron floor model tensile tester was used with ASTM tensile test specimens to obtain tensile and elongation data. A "D" cell was used with 2 inch per minute crosshead speed. Specimens were cut from sample slabs with an LLL furnished die cutter measuring ⅛ x ½ inch in the stretch area of the specimen.

Results and Conclusions

- There appeared to be no significant difference in physical characteristics between the unwashed boron powder filled and the washed boron powder filled VCE formulations.
- Of the ten boron powder filled Viton A formulations prepared and evaluated in this study (Tables 2 and 3) cured Formula No. 3 containing 2.5 parts magnesium oxide and 1.5 parts of Diak No. 1 per 100 parts of Viton A had the best physical characteristics.
- The scorching of one Viton A formulation (60 parts boron powder 10 parts magnesium oxide and 2 parts Diak No. 3 per 100 parts of Viton A) appeared to depend on the order of addition of the boron powder and the magnesium oxide. Addition of the boron before the magnesium oxide appeared to be preferable. Results are given in Table 7.
- The values obtained for the weight loss of VCE elastomer formulations at 300°C were found to depend on whether the Aminco or DuPont TGA apparatus was used. The DuPont instrument using a 10 mg sample gave much higher values than did the Aminco instrument using a 1 gm sample (Table 4).

Table 1

AVERAGE PARTICLE SIZE AND DENSITY OF VARIOUS BORON POWDERS[a]

	Average Particle Size (μ)	Density (g/ml)
washed, unclassified	28	2.42
coarse	35	2.38
medium	22	2.44
fine	12	2.40

[a] - By Andreason pipette

Table 2

PHYSICAL CHARACTERISTICS OF BORON[a] FILLED VITON A ELASTOMERS

Formulation No.*	No. 1		No. 2		No. 3		No. 4		No. 5	
Cure	Press	Post	Press	Post	Press	Post	Press	Post	Press	Post
Density - Filled	2.037	2.029	2.023	2.004	2.137	2.148	2.167	2.166	2.13	2.188
(g/ml) - Unfilled	1.782	1.781	1.775	1.778	1.809	1.816	1.822	1.833	1.856	1.860
Swell Ratio	2.50	2.46	2.00	2.53	3.66	3.15	3.59	3.47	3.14	2.94
Wt. Loss at 300°C (Aminco) (%)	2.40	1.20	2.70	1.20	0	0	0.30	0	0	0
Hardness										
Shore D - Filled	51	52	41	47	53	63	51	58	49	58
- Unfilled	17	21	13	20	13	16	16	17	16	18
Tensile p.s.i.	*b*	*b*	*b*	*b*	740[c]	1110[c]	959	943	523[c]	557[c]
Max. Elongation (%)										
Max. Elongation (in.)	*b*	*b*	*b*	*b*	0.44	0.76	0.88	0.75	0.38	0.33
Solubles:										
(A) Wt. Loss %	31.34	26.97	34.34	28.29	12.96	14.40	21.22	19.37	23.16	20.62
(B) Extractables % Based on matrix only	33.89	28.48	35.10	28.95	14.10	15.12	23.25	22.17	23.87	20.85
Wt. % Matrix (includes additives)	32.93	32.93	32.84	32.84	33.26	33.26	33.41	33.41	33.85	33.85

*Formulations:

No. 1 = Li_2O @ 10 phr plus Diak No. 1 @ 1.5 phr
No. 2 = Li_2O @ 10 phr plus Diak No. 3 @ 2.0 phr
No. 3 = MgO @ 2.5 phr plus Diak No. 1 @ 1.5 phr
No. 4 = MgO @ 5.0 phr plus Diak No. 1 @ 1.5 phr
No. 5 = MgO @ 10.0 phr plus Diak No. 1 @ 1.5 phr

[a] = Boron was nonfractionated and was washed in methanol.

[b] = Suitable tensile specimens could not be cut from this sheet material.

[c] = Breaks were laminar in character.

Table 3

PHYSICAL CHARACTERISTICS OF BORON[a] FILLED VITON A ELASTOMERS

Formulation No.*	No. 6		No. 7		No. 8		No. 9		No. 10	
Cure	Press	Post	Press	Post	Press	Post	Press	Post	Press	Post
Density - Filled	2.141	2.141	2.131	2.167	2.166	2.176	2.068	2.071	2.052	2.141
(g/ml) - Unfilled	1.796	1.815	1.817	1.835	1.840	1.859	1.783	1.785	1.778	1.783
Swell Ratio	6.77	6.98	4.19	4.25	3.61	3.35	4.09	3.74	3.29	3.60
Wt. Loss at 300°C (Aminco) (%)	1.80	1.50	0.50	0.50	0.50	0.30	0.90	1.80	0.90	0.90
Hardness										
Shore D - Filled	44	51	52	57	40	59	47	54	50	58
- Unfilled	8	13	12	13	13	15	16	18	13	16
Tensile p.s.i.	404	524	507	867	479[c]	691[c]	[b]	[b]	424	631
Max. Elongation (%)									15	15
Max. Elongation (in.)	2.24	2.61	1.08	1.03	0.79	0.80	[b]	[b]		
Solubles:										
(A) Wt. Loss %	49.30	42.54	36.75	25.51	35.90	26.67	16.12	15.76	26.09	25.33
(B) Extractables %	45.04	2.56	25.63	25.62	41.09	29.45	19.85	15.94	26.30	25.81
Wt. % Matrix (includes additives)	33.24	33.24	33.52	33.52	33.69	33.69	32.94	32.94	32.89	32.89

*Formulations:

No. 6 = MgO @ 2.5 phr plus Diak No. 3 @ 2 phr
No. 7 = MgO @ 5.0 phr plus Diak No. 3 @ 2 phr
No. 8 = MgO @ 10.0 phr plus Diak No. 3 @ 2 phr
No. 9 = Li_2O @ 5.0 phr plus Diak No. 1 @ 1.5 phr
No.10 = Li_2O @ 5.0 phr plus Diak No. 3 @ 2.0 phr

[a] = Boron was nonfractionated and was washed in methanol.

[b] = Suitable tensile specimens could not be cut from this sheet material.

[c] = Breaks were laminar in character.

Table 4

WEIGHT LOSS IN PERCENT[a] OF VARIOUS FORMULATIONS AT 300°C AS DETERMINED ON THE AMINCO (1 g sample) AND DuPONT (10 mg sample) INSTRUMENTS

	Aminco	DuPont
VCE-TDID Unfilled p + p	1.3	35.3
VCE-TDID Unwashed B	1.0	31.3
VCE-TDID Washed	1.4	32.5
LLL 9-3A 70% B	5.3	72.6
LLL 9-3B 70% B	3.3	62.4
VCE-MDI 8.6 phr	0.5	5.4
Viton A B + MgO + Diak No. 3	0	0

[a]For elastomers after removal of boron powder contribution.

Table 5

PHYSICAL CHARACTERISTICS OF CURED 60 VOLUME % BORON POWDER FILLED VINYL COPOLYMER ELASTOMER (VCE MI-24) FORMULATIONS UNWASHED vs WASHED BORON FILLER

Powder	Unwashed		Washed	
Cure	Press	Post	Press	Post
Density, g/ml	1.840	1.853	1.844	1.856
Swell Ratio (Toluene)	2.34	2.32	2.28	2.24
Wt. Loss at[a] 300°C	2.2	0.9	2.2	1.4
Solubles, %				
Wt. Loss	16.28	10.67	11.45	9.11
Extractables	16.91	6.12	10.63	7.91

[a]Wt. loss at 300°C of VCE MI-24 only 1.3%.

Table 6

PHYSICAL CHARACTERISTICS OF 60 VOLUME PERCENT BORON FILLED VCE ELASTOMER FORMULATIONS

Formulation No.[a]	No. 1		No. 2		No. 3		No. 4		Standard	
Cure	Press	Post	Press	Post	Press	Post	Press	Post	Press	Post
Density - Filled	1.840	1.845	1.840	1.850	1.834	1.838	1.804	1.818	1.844	1.856
(g/ml) - Unfilled	0.990	0.993	0.988	0.992	0.990	0.991	0.966	0.969	1.005	1.004
Swell Ratio	2.17	2.25	2.14	2.13	2.29	2.29	2.85	2.77	2.24	2.21
[b]Weight Loss at 300°C (%)	0.90	0.90	1.40	0.90	1.40	0.50	2.70	2.70	2.10	1.40
Hardness										
Shore D - Filled	65	70	69	72	69	71	61	68	64	74
- Unfilled	17	20	20	18	20	22	14	15		
Tensile p.s.i.	2102	1987	1906	1917	1956	1984				
Max. Elongation (%)	15	20	20	20	30	33				
Solubles:										
(A) Wt. Loss %	11.62	10.60	12.54	10.48	10.87	9.11	15.59	14.44	11.45	9.11
(B) Extractables %	10.73	9.52	9.21	9.36	9.71	8.47	13.10	12.78	10.63	7.91
Weight % Matrix (nonboron fraction)	21.42	21.42	21.38	21.38	21.72	21.72	21.59	21.59	21.74	21.74

[a]Formulations per 100 parts of VCE MI (24)

No. 1 = Isonate 143 L 10 parts
No. 2 = PAPI 901 9.2 parts
No. 3 = MDI 8.6 parts
No. 4 = DDI 21.2 parts
Standard TDID 12 parts

[b]Weight loss at 300°C of unfilled VCE MI (24) is 1.3%.

Table 7

EFFECT OF ORDER OF MAGNESIA ADDITION ON THE PHYSICAL CHARACTERISTIC OF A 60 VOLUME PERCENT BORON FILLED VITON A-MgO-DIAK No. 3 ELASTOMER FORMULATION (10 phr MgO+2 phr DIAK No. 3)

Order of Addition	MgO-B		B-MgO	
Cure	Press	Post	Press	Post
Density, g/ml	2.166	2.177	2.160	2.181
Swell Ratio (MEK)	3.61	3.35	4.09	3.27
Wt. Loss at 300°C, %	0.5	0.3	0	0
Hardness Shore D	40	59	50	63
Tensile Strength, psi	480	690	690	1200
Max. Elongation (%)	53	53	70	55
Solubles %				
Wt. Loss	35.9	26.7	35.4	20.6
Extractables	41.1	29.5	56.4	20.5

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