

**Use of Polybutadiene Coagents
in Peroxide Cured Elastomers
for Wire and Cable Compounds**

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ABSTRACT

This paper is a continuation of work done to enhance properties and processes for peroxide cured elastomers. The present work demonstrates how polybutadiene resins can be used to enhance properties. The paper also compares these coagents with others currently available in the marketplace. For example, some coagents work well with certain peroxides and give poor results with other peroxides. Other coagents are useful at low levels but are not compatible at high concentrations. Polybutadiene resins are compatible over a much higher concentration range and can provide special benefits at these higher concentration levels.

Work is directed primarily to wire and cable elastomers and explores variation in properties with coagent type. Also discussed is the relationship of properties such as compression set, moduli and heat and fluid resistance with the structure of the elastomer and the coagents affect on these relationships.

INTRODUCTION

During the peroxide vulcanization of rubber, peroxides decompose to produce highly reactive free radicals which in turn react with rubber molecules to produce crosslinks. One of the strongest interchain bonds in a rubber matrix is formed by peroxide vulcanization. Its C-C bonds are stronger than sulfur cured C-S-C bonds and much stronger than C-SX-C bonds. Peroxide vulcanization also allows rubber to be used in harsh environments; peroxide cured rubber articles have superior heat and set resistance compared to rubber articles manufactured via other cure systems. Peroxide vulcanization not only produces stronger, better-aging rubber, but also gives the compounder a wide variety of elastomers with which to work. Saturated elastomers, like EPM, cannot be vulcanized by sulfur, due to a lack of double bonds. Use of these saturated elastomers requires the compounder to use peroxide cure agents. One of the drawbacks to peroxide vulcanization is that the same free radicals which produce crosslinks can also cause beta scission. Also, in some elastomers peroxide vulcanization is not highly efficient, so a preponderance of peroxide is required to obtain acceptable properties. Both of these difficulties may be alleviated by addition of coagents to the peroxide cure package.¹

Coagents are polyfunctional, multi-unsaturated organic compounds which readily form free radicals when exposed to the products of heat or light induced peroxide decomposition. These free radicals are more stable than those resulting from the decomposition of peroxide alone, thus when coagents are added to peroxide cured elastomer compounds, they often improve the efficiency of crosslink formation during vulcanization. Coagents have been categorized into two groups: Type I and Type II. During vulcanization, Type I coagents undergo hydrogen abstraction, producing radicals which lead to chain crosslinking. They also experience free-radical addition, resulting in homopolymerization. These two functions give higher cure states and faster cure rates than does peroxide vulcanization without coagents. Type I coagents include acrylates, methacrylates, bismaleimides, and vinyl esters. Type II coagents include allylic compounds and low molecular weight high vinyl polymers, both of which typically increase cure state without increasing cure rate. When undergoing hydrogen abstraction, Type II coagents tend to produce more stable radicals than the small, polar radicals produced by Type I coagents. So Type I coagents tend to be more reactive than Type II coagents, but they are also more prone to beta scission and radical coupling reactions.³

Research has proven that coagents are very effective in generic EPDM and EPM rubber formulations. They are widely used in the automotive industry in NBR, HNBR, EPDM, and EPM under-the-hood applications. Coagents have also found a niche in the dynamic downhole applications of the mining and petroleum exploration industries. This paper, however, focuses on the use of coagents in wire and cable (w/c) applications. It is a summary of test results obtained from EP elastomers (EPM and EPDM), EVA, EVM, and CPE.

The first elastomers discussed in this study are the EP copolymers and terpolymers. They are extensively used in the w/c industry due to their excellent moisture and weather resistance, combined with very good electrical properties. EPM is a copolymer of ethylene and propylene which, due to its lack of unsaturation in the backbone, can only be peroxide cured. Incorporation of a diene (such as ethylidene norbornene

or hexadiene) pendant to the backbone of EPM produces EPDM. Both of these elastomers are used in power transmission cables, portable power cables, control cables, and mining cables. They are also used in many flexible cord, automotive ignition wire, and appliance wire formulations, as well as in jacketing compounds. Uncured EPM is also used as an electrical insulating material in many high voltage power cables.

The second elastomer discussed in this paper is ethylene vinyl acetate, a saturated copolymer of ethylene and vinyl acetate (VA). The saturation of this copolymer provides outstanding ozone, weather, and temperature resistance. Varying the VA content of these materials changes both nomenclature and compound properties. Ethylene vinyl acetate copolymers with VA contents less than 40% or greater than 80% are thermoplastics and in this paper will be called EVAs. Those with VA contents between 40% and 80% are elastomers and will be denoted as EVMs. The higher the VA content of one of these copolymers, the more resistance they have to heat, oil, and solvents. Though this material has exceptional age properties, the polarity of the VA harms its electrical properties, hence it is not as widely used for insulation by the w/c industry as are the EP elastomers.

CPE is the final elastomer discussed in this investigation. It is produced by random chlorination of an aqueous solution of high density polyethylene. This chlorination produces a highly saturated polymer with many useful qualities such as excellent ozone, weather, and heat resistance, which are desirable to the w/c industry. CPEs are used in power transmission cables, portable power and control cables, and mining cables.

Coagents from both the Type I and Type II categories were milled into these elastomers. The Type I coagents chosen for study were trimethylolpropane trimethacrylate (TMPTMA) and a scorch retarded trimethylolpropane trimethacrylate (SRTMPTMA). The Type II coagents were represented by triallyl cyanurate (TAC), triallyl isocyanurate (TAIC), high 1,2-vinyl polybutadiene resin (PBD), PBD adducted with maleic anhydride functionality (PBD/MA), and solid PBD/MA. TMPTMA, TAC, and PBD were studied in the EP elastomers, while TAC, PBD, and SRTMPTMA were tested in EVM. SRTMPTMA, TAIC, and PBD/MA were studied in CPE. All of the coagents tested were shown to be useful compounding tools, but there are definite toxicity, performance, and cost advantages obtained by the use of PBD based coagents (Table 1).

Table 1
Volatility Properties of Coagents

Comparison of Molecular Weight and Boiling Points of Coagents				
Coagent	Type	Molecular Wt.	Boiling Point	Volatility
TMPTMA	I	338.4	>200°C/1mm	Moderate
EGDMA	I	198.2	83°C/1mm	High
HVA-2	I	268.3	195°C mp	Moderate
ZDA	I	235.4	>250°C mp	Low
70% 1,2 PBD/S	II	2400	>300°C/1mm	Low
70% 1,2 PBD	II	2400	>300°C/1mm	Low
90% 1,2 PBD	II	3200	>300°C/1mm	Low
TAC	II	249.3	110°C mp	Moderate
TAIC	II	249.3	149°C/4 mm	Moderate
TATM	II	330.3	175°C/0.1mm	Moderate

EXPERIMENTAL

Chemicals

All ingredients used in this study are commercially available compounds and are listed in Appendix I. Three common wire and cable elastomers were studied in this investigation: chlorinate polyethylene, ethylene propylene rubber, and ethylene vinylacetate (Table 2). Five coagents commonly utilized in both the rubber

and plastics industries were evaluated. Type I coagents compounded in the test formulations were trimethylolpropane trimethacrylate (TMPTMA) and a scorch retarded trimethylolpropane trimethacrylate (SRTMPTMA). Type II coagents selected were liquid high 1,2-vinyl polybutadiene (PBD), liquid and solid maleinized high 1,2-vinyl polybutadiene (PBD/MA), triallyl cyanurate (TAC) and triallyl isocyanurate (TAIC).

Table 2
Polymers Studied

Compound	Diene* (%)	Ethylene (%)	Vinyl Acetate (%)	Chlorine (%)
EPDM A	7.9	52	--	--
EPDM B	2.6	52	--	--
EPM A	0.0	68	--	--
WCEPDM	6.0	72	--	--
WCEPM	0.0	65	--	--
EVA	---	---	18	--
EVM	---	---	50	--
CPE	---	--	--	36

* All diene types are ethylidene norbornene, except WCEPDM which contains hexadiene

Procedure

Lab size masterbatches were prepared off-site to provide consistent formulations for use in this study (Table 3). The peroxide and coagents were mixed

into these masterbatches on a two roll lab mill at a temperature of 125 °F (52 °C), except for the EVA compounds which were milled at 212 °F (100 °C). Formulations were sheeted and allowed to rest 24 hours then sampled for testing.

Table 3
Test Formulations

Compound	EPDM A	EPDM B	EPM A	WCEPDM	WCEPM	EVA	EVM	CPE
EPDM	100.0	100.0	--	100.0	--	--	--	--
EPM	--	--	100.0	--	100.0	--	--	--
EVA	--	--	--	--	--	100.0	--	--
EVM	--	--	--	--	--	--	100.0	--
CPE	--	--	--	--	--	--	--	100.0
N550 carbon black	50.0	50.0	50.0	35.0	35.0	2.0	45.0	35.0
calcium carbonate	--	--	--	105.0	105.0	--	--	150.0
hydrated alumina	--	--	--	--	--	75.0	--	--
red lead (90%)	--	--	--	5.6	5.6	--	--	--
antioxidant	0.5	0.5	0.5	2.0	2.0	3.0	2.0	--
zinc oxide	5.0	5.0	5.0	5.0	5.0	--	--	--
paraffinic oil	--	--	--	25.0	25.0	--	--	--
stearic acid	--	--	--	--	--	1.0	1.0	--
silane	--	--	--	--	--	1.0	--	--
magnesium oxide	--	--	--	--	--	--	2.0	5.0
PE wax	--	--	--	--	--	--	2.0	--
paraffinic wax	--	--	--	--	--	--	--	2.0
plasticizer	--	--	--	--	--	--	--	38.0
dicumyl peroxide (40% dispersion)	8.0	8.0	8.0	7.0	7.0	--	--	7.0
Butylperoxy-di-isopropyl benzene (40% dispersion)	--	--	--	--	--	6.0	6.0	--

Appendix II lists the appropriate ASTM methods and test equipment used for this study. Test plaques were cured at various temperatures with two familiar peroxides: 40% active di-cumyl peroxide dispersion and 40% active t-butylperoxy-diisopropyl benzene dispersion. Electrical testing was performed by independent laboratories.

A careful log of mill time, temperatures, and observations was kept on the compounding work. This allowed for consistent and reliable data to be generated. The material balances were determined for all compounds and found to be satisfactory (>99.5%).

DISCUSSION AND RESULTS

EP Elastomers

The first investigations of EP elastomers were performed on the EPDM A, EPDM B, and EPM A formulations shown in Table 3. The three elastomers chosen varied in diene content and ethylene to propylene ratio. These compounds were cured at 160°C with 8.00 parts per hundred (phr) of 40%

active dicumyl peroxide dispersion (DCP) with equivalent phr of Type I coagent trimethylolpropane trimethacrylate (TMPTMA) and of the Type II coagents high 1,2-vinyl polybutadiene (PBD) and triallyl cyanurate (TAC).

The study proceeded by formulation of model wire and cable (w/c) compounds varying only in base elastomer and coagent. The base elastomers compounded were EPDM and EPM; these model w/c formulations were denoted as WCEPDM and WCEPM, respectively. The coagents utilized in these two formulations were TMPTMA and PBD. The following results reveal clear advantages with the use of the nontoxic PBD coagents.

Rheometry

Rheometric data for the non-w/c formulations are presented in Table 4. The most noticeable difference between the coagents in these compounds was their scorch times. The scorch times of the TMPTMA formulations were 14-25% lower than those of the three controls.

Table 4
Properties of EP Elastomers

Elastomer: (no coagent)	EPDM A control				EPDM B control				EPM A control			
PBD	.	3			.	3			.	3		
TAC	.	.	3		.	.	3		.	.	3	
TMPTMA	.	.	.	3	.	.	.	3	.	.	.	3
Rheometric Data: ODR 1°arc, 160°C												
Min. torque (dNm)	13.3	12.9	13.9	13.2	12.9	11.4	11.3	12.5	8.3	7.8	7.0	7.3
Max torque (dNm)	74.1	75.8	77.3	77.5	62.8	68.0	68.1	64.0	62.1	66.4	70.0	65.4
Ts ₁ (min)	1.3	1.3	1.3	1.1	1.6	1.4	1.5	1.2	1.4	1.4	1.4	1.2
T ₉₀ (min)	23.6	24.7	20.8	23.4	24.5	25.2	21.8	23.8	21.4	20.4	19.4	19.4
Physical Properties:												
Press cure T90 at 160°C												
Tensile Strength (Mpa)	12.0	15.1	12.7	17.2	14.5	14.3	11.6	13.9	14.6	12.5	10.9	11.0
50% modulus (Mpa)	2.3	2.8	2.9	2.9	1.6	2.1	2.2	2.0	1.9	2.0	2.0	2.0
100% modulus (Mpa)	8.2	9.4	11.9	8.7	3.2	4.9	5.4	4.0	4.0	4.8	5.2	4.4
Ultimate elongation (%)	150	130	105	140	230	165	145	205	205	150	135	160
Hardness (shore A)	76	78	80	79	73	76	76	75	76	78	78	77
Aged Physical Properties: Air, 166 hours at 150°C (percent/pts. Change)												
Tensile Strength	+ 5.8	- 3.8	-28.0	-13.3	- 4.8	-17.5	-44.0	-34.2	- 5.5	-47.2	-75.2	-48.2
50% modulus	+21.7	+ 1.7	+38.6	+11.2	+25.0	+ 8.7	+ 4.5	+15.8	+35.0	+25.0	+35.0
100% modulus	+ 3.7	- 2.8	+22.7	+18.8	+ 9.3	+ 9.3	+12.5	+17.5	+43.8	+13.6
Ultimate elongation	-20.0	- 9.2	-21.0	- 9.3	- 8.7	- 9.1	- 9.3	-31.7	- 4.0	-33.3	-63.0	-28.1
Hardness (shore A)	- 2	+ 4	+ 2	+ 2	+ 3	+ 3	0	- 2	0	0	- 1	0
Compression Set: 166 hrs. at 150°C (%)												
	25.6	18.7	19.5	18.4	32.2	22.8	23.7	26.5	29.8	23.2	25.0	25.9
Fluid Resistance: Toluene, 22 hrs. at 25°C												
% volume change	115.7	103.4	103.1	109.6	138.5	120.2	120.2	128.1	138.6	127.6	128.3	130.4

Differences in scorch safety were more apparent in the w/c formulations (Table 5). For example, both

control formulations' scorch times were reduced more than 40% when compounded with TMPTMA.

Table 5
Properties of W/C EP Elastomers

Elastomer: (no coagent)	WCEPDM Control			WCEPM Control		
	PBD (phr)	TMA (phr)				
	3	2		2	2	
Rheometric data: ODR 1°arc, 160°C						
Min. torque (dNm)	7.0	6.1	6.5	6.3	6.6	6.5
Max torque (dNm)	27.3	32.0	30.3	17.4	25.0	22.3
T _{s1} (min)	2.8	2.5	1.6	2.9	2.3	1.6
T ₉₀ (min)	28.7	28.2	28.0	28.1	27.1	24.6
Physical Properties:						
Press cure T90 at 160°C						
Tensile strength (Mpa)	10.7	11.5	11.1	6.5	7.4	6.8
50% modulus (Mpa)	3.9	4.1	4.1	2.3	2.8	2.4
100% modulus (Mpa)	6.5	6.9	7.4	3.5	4.0	3.5
Ultimate elongation (%)	235	195	205	425	390	395
Hardness (shore A, pts.)	86	87	86	79	82	81
Aged Physical Properties: Air, 166 hours at 150°C (percent/pts. Change)						
Tensile strength	+1.9	-6.1	0.0	-16.9	-2.7	-10.3
50% modulus	+15.4	+7.3	+14.6	+26.1	+25.0	+33.3
100% modulus	+7.7	+7.2	+2.7	+17.1	+17.5	+17.1
Ultimate elongation	-14.9	-17.9	-12.2	-23.5	-29.5	-18.7
Hardness (shore A)	+1	+1	+2	+3	+1	+2
Compression Set: 166 hrs. at 150°C (%)						
	70.3	50.7	55.9	92.3	56.9	78.9
Fluid Resistance: Water, 25°C						
% volume change, 70 hrs.	0.14	0.08	0.12	0.27	0.02	0.00
% volume change, 168 hrs.	0.23	0.18	0.14	0.30	0.14	0.18
Electrical data:						
vol. resistivity at 25°C (E+13 ohm-cm)	4.8	6.7	6.5	4.6	4.5	4.4
dielectric strength (volts/mil)	275	296	380	299	342	334

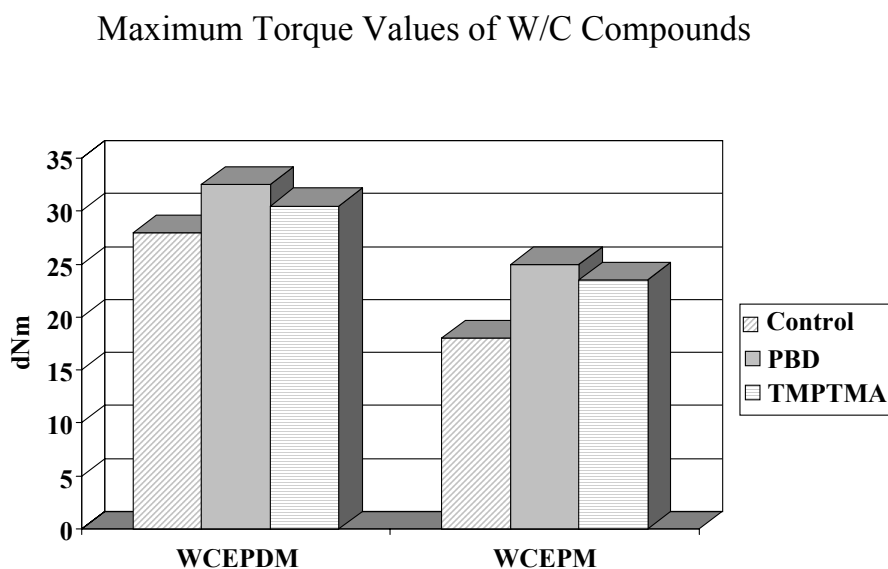
The most effective indicator of increased crosslink density among rheometric properties is maximum torque. The base elastomer had the largest effect on the maximum torque of these compounds. The maximum torque values for the non-w/c compound's controls (no coagent) were 74.1, 62.8, and 62.1 dNm for EPDM A, EPDM B, and EPM A, respectively. EPDM A contains the highest ethylidene norbornene

(ENB) content, causing the highest maximum torque value. EPDM B and EPMA both contain low amounts of ENB, 2.9% and 0.0% respectively, and their control compounds' maximum torques were approximately equivalent. Although EPM does not contain any diene in its backbone, the high ethylene content of this elastomer helped its maximum torque value to be comparable to the maximum torque value of EPDM B.

The only other factor affecting this property was the selection of coagent. All the coagents increased the maximum torque value of the control compounds, indicating an increase in crosslink density. The largest changes in maximum torque values included an 8.3% increase in EPDM B with the addition of the PBD and TAC coagents and a 12.7% increase in EPM A compounded with the TAC. The compounds modified with the PBD coagent recorded the largest increases

in maximum torque figures in both w/c formulations. A dramatic 48% increase in maximum torque occurred in WCEPM due to the addition of PBD (Figure 1). Higher maximum torque values were also reported in the WCEPDM formulations – 17% for the PBD formulation and 10% with the TMPTMA addition. All rheometric data indicated that increased scorch safety and crosslink density were obtained with the utilization of the Type II coagents.

Figure 1



UNAGED AND AGED PHYSICAL PROPERTIES

The physical properties indicate that all the coagents increased crosslink density since they increased tensile moduli and hardness while decreasing ultimate elongations (Eb) and tear strength. In the WCEPM formulation, PBD produced slightly lower Eb and higher moduli values than the TMA coagent modified formulation. This is a clear indication that the PBD increased peroxide efficiency in comparison to the TMPTMA.

As the demand for higher temperature performance of elastomers increases, so does the importance of accelerated age testing. Table 4 displays the heat aged results of all the EP elastomers. Most of the EP formulations aged very well, which was not surprising because heat aging is one property where EP elastomers excel.

Comparatively, the non-w/c TAC formulations did not age as well as the other coagent modified compounds. For instance in the EPM A compound, the TAC formulation posted changes of -75.2% and -63.0% for tensile strength and Eb, respectively. Similar results occurred with these two properties in EPDM A and B, with the exception of the Eb in EPDM B, which only changed -9.3%. All the other coagent altered compounds had changes less than 50% in both tensile strength and Eb. Also, all the percent changes for Eb were negative, and positive for the moduli, indicating additional crosslinking. Curing the test samples beyond their T_{90} s and/or a post cure of these parts would probably increase the heat aged performance of these compounds.

ELECTRICALS

Electrical properties are obviously very important to w/c compounds. Volume resistivities and dielectric strengths of the w/c formulations were tested by an independent laboratory (Table 5). The results suggest that volume resistivity and dielectric strength were inconsistent with respect to each other. For example, in the WCEPDM compounds the PBD formulation posted a higher volume resistivity than did the TMPTMA compound. In contrast, the PBD reported lower dielectric strength than did the TMPTMA material. Therefore, it was difficult to draw a concise conclusion; however, both coagents did improve the electrical performance compared to the control formulation. In the WCEPM compound, the PBD compound reported higher values than did the TMA compound, for both electrical properties tested.

FLUID RESISTANCE

Because water resistance is very important to electrical properties, testing of the w/c compounds were preceded by measurements of water resistance. Test samples were immersed in water at 82 °C for 70 and 166 hours. The data showed that both coagent modified w/c masterbatches resisted water penetration more than did the formulations without coagents (Table 5). In WCEPDM, the 70 hour results indicate that the PBD modified elastomers had higher resistance to water molecules compared to the resistance of the control. However, after 166 hours, the TMPTMA compound reported the highest resistance to water at elevated temperatures. In the WCEPM formulation the opposite trend was noticed. The TMPTMA samples posted a 0.0% mass change after a 70 hour

test period compared to a 0.02% mass change for the PBD compound. After 166 hours, the PBD and TMPTMA samples averaged 0.14% and 0.18% mass change, respectively. It is very interesting to note that the lowest reported mass percent changes for the 70 and 166 hour testing were those of the compounds based on the ethylene propylene copolymer (EPM) and not the ethylene propylene terpolymer (EPDM). PBD modified EPDMs have been reported by Drake et. al. to perform as well as or in many cases better than EPDMs formulated with or without coagents.²

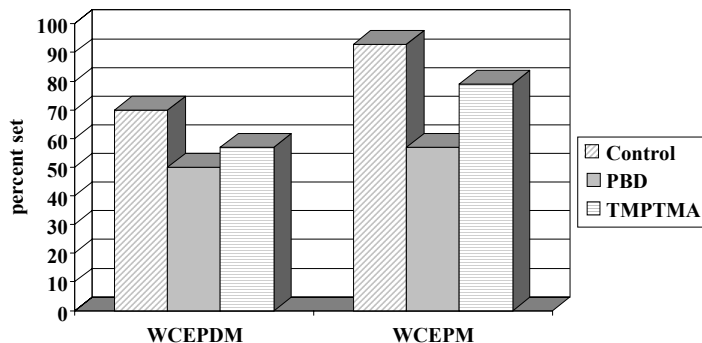
COMPRESSION SET

Although compression set testing is not as important for many w/c compounds as it is for hose or bridge bearing compounds, there are w/c applications where compression set properties are important. In addition to being directly related to crosslink density, compression set testing at elevated temperatures helps predict heat aged characteristics of the material.

The results in Table 4 indicate that in all the EP formulations, the PBD coagent produced lower compression set figures, with the exception of EPDM A. In the w/c formulations the PBD coagent outperformed the TMPTMA coagent during compression set testing (Figure 2). For example, in the PBD WCEPDM compound the compression set was 50.7% compared to 55.9% for the TMPTMA compound. Also in the WCEPM tested samples, the PBD and TMPTMA compression set values were 56.9% and 78.9%, respectively. This indicates that the PBD coagent increased the crosslink density of these systems.

Figure 2

Compression Set of W/C Compounds
166 hrs @ 150C



EVA AND EVM ELASTOMERS

The test formulations compounded were based on an EVA elastomer containing 18% vinyl acetate (VA) and an EVM compound with 50% VA content (Table 3). The coagents employed were a scorch retardant version of TMPTMA (SRTMPTMA), TAC, and PBD. These compounds were cured at 180 °C for two additional minutes beyond their 90% cure times (T_{90}).

RHEOMETRY

Rheometric data shows considerable changes in the maximum torque values with utilization of these different coagents (Table 6). For the coagent modified EVAs and EVMs, the ascending order of maximum torque values were TAC, PBD, then SRTMPTMA.

The cure times revealed that the TAC material was the fastest compound to reach its T_{90} in both the EVA and EVM compounds. The PBD and SRTMPTMA reached their T_{90} s at approximately the same time. These faster cure times demonstrated by the compound formulated with the TAC contradicted the traditional classification of Type I and Type II coagents. By definition, Type I coagents cure faster and scorchier than Type II coagents. The Type II coagent, TAC, cured faster than the Type I coagent SRTMPTMA. Also in the EVM formulation, the TAC and PBD modified compounds had lower scorch times than those of the control compounds, while the Type I coagent, SRTMPTMA, had an increased scorch time compared to the scorch time of the control compound.

Table 6
Rheometric Properties of EVA and EVM Compounds

Rheometer Data, ASTM D-2084

Model: TechPro Range: 100 Clock: 24min.
Die: Micro Arc: 1° Temperature: 180 °C

Compound	phr	min. torque dNm	max. torque dNm	scorch time min.	cure time min.
EVA Control	-	3.9	38.9	1.3	7.3
PBD	2	6.1	51.4	1.2	6.9
TAC	2	4.1	56.1	1.2	5.8
SRTMPTMA	2	4.3	42.8	1.1	7.1
EVM Control	-	4.6	25.2	1.7	9.6
PBD	2	5.4	36.6	1.4	8.3
TAC	2	5.1	46.2	1.4	6.1
SRTMPTMA	2	4.9	34.3	1.8	8.1

UNAGED PHYSICAL PROPERTIES

The unaged physical property data are shown in Table 7. In the EVA formulations, the addition of TAC increased peroxide efficiency more than the other coagents increased it. For example, the EVA

formulation compounded with the TAC produced the largest decreases in tear strength and Eb compared to the control. The PBD coagents clearly outperformed the SRTMPTMA, for the same reasons stated above. The order of performance was not as clear for the EVM compounds (Figure 3).

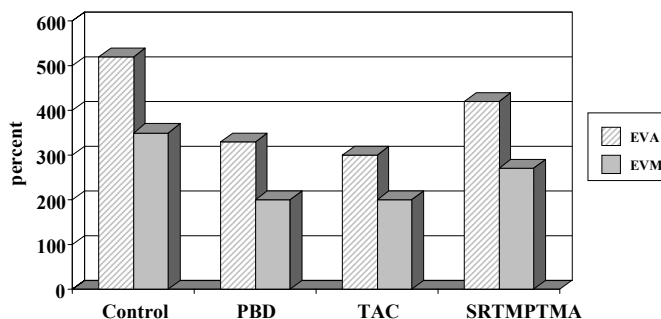
Table 7
Unaged Physical Properties of EVA and EVM Compounds

**Unaged Physical Properties, ASTM D-412
Press Cure @180°C, T90 + 2 mins.**

Compound	phr	tensile Mpa	tear KN/m	50% mod. Mpa	100% mod. Mpa	elong. %	hrd. A pts.	hrd. D pts.
EVA Control	-	15.1	63.4	7.0	7.7	525	92	44
PBD	2	12.8	55.7	7.3	7.5	325	93	46
TAC	2	11.3	50.6	7.2	7.8	300	93	45
SRTMPTMA	2	11.3	56.6	7.1	7.4	410	93	46
EVM Control	-	15.2	44.1	2.2	3.5	350	68	—
PBD	2	15.1	34.1	2.2	5.4	205	72	—
TAC	2	17.6	34.0	2.3	5.8	200	73	—
SRTMPTMA	2	16.9	45.3	2.3	4.8	255	69	—

Figure 3

Ultimate Elongation of EVA/EVM Compounds



In the EVM compounds, data indicated that the SRTMPTMA did not increase the crosslink density to the same extent as did the PBD and TAC coagents. In addition, the data suggested that the TAC and PBD compounds reached approximately equivalent cure states.

All the physical properties of these two compounds were equivalent; the largest difference was in the 100% modulus. The TAC formulation produced a 100% modulus of 5.8 MPa, compared to a 5.4 MPa 100% modulus for the PBD compound. Since tensile strength has a “bell-shaped” relationship with crosslink density, this property is not considered to be an accurate measure of crosslink density.

It was noticed that the PBD coagent performed more efficiently in the EVM formulation than in the EVA

compound. A possible theory for this phenomenon pertains to the polarities of the EVM and PBD. As the VA content increases, so does the compatibility of the PBD with the EVM, due to the inherent polarity contained in the unsaturation of the PBD. With increased compatibility between PBD and EVM, the high 1,2-vinyl polybutadiene became more efficient in increasing crosslink density by suppressing unwanted chain terminating reactions such as beta scission and disproportionation.

FLUID RESISTANCE

The EVA and EVM compounds were tested for water resistance by immersing all compounds in distilled water for 166 hours at 82 °C (Table 8). The most distinguishable differences were the small percent changes produced by the lower VA materials (EVAS) relative to the higher VA materials (EVMs). For

example, the EVA control compound reported a 0.64% volume change compared to the EVM control compound's 7.21% volume change. Although these base elastomers' formulations varied in additives, VA and carbon black content were believed to have the greatest influences on water absorption.

In the EVA materials, all coagents tested relatively equivalent by decreasing water absorption

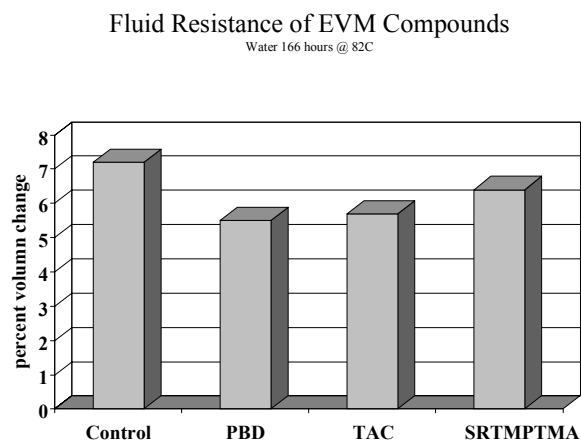
approximately 50 percent from the control's values. In the EVM compounds, Type II coagent modified formulations (PBD and TAC) outperformed the SRTMA altered formulation (Figure 4). For instance, Type II coagent systems decreased water absorption 23 percent compared to a 10 percent decrease produced by the SRTMPTMA additive from the control's absorption.

Table 8
Aged Physical Properties of EVA and EVM Compounds

Fluid Resistance: Water 166 hrs. @82°C

Compound	phr	% Vol. Chg	% Mass chg
EVA Control	—	0.64	0.65
PBD	2.0	0.28	0.54
TAC	2.0	0.25	0.67
SRTMPTMA	2.0	0.31	0.69
EVM Control	—	7.21	6.87
PBD	2.0	5.50	5.50
TAC	2.0	5.62	5.44
SRTMPTMA	2.0	6.48	6.30

Figure 4



CPE

The primary motivations for the use of coagents in CPE are to improve physical and aged properties. They improve physical properties through increased crosslink density caused by increased peroxide efficiency⁴. Coagents improve aged properties by redirecting harmful radicals produced by ozone attack, into cross-linking reactions rather than backbone unsaturation reactions or by side chain radical scavenging. The physical properties which are

influenced by coagents and discussed in this paper are: ultimate elongation (Eb), tensile strength, tensile modulus, maximum torque, and fluid swell properties. The coagents examined in this study were: triallyl isocyanurate (TAIC), scorch retarded trimethylolpropane trimethacrylate (SRTMPTMA), liquid high 1, 2-vinyl polybutadiene resin adducted with maleic anhydride functionality (PBD/MA), and solid PBD/MA. TAIC was tested at 1 phr, 2 phr, and 3 phr. SRTMPTMA was tested at 3 phr and 5 phr. BD/MA

was tested at 2.5 phr and 3 phr. These levels reflect both the usage ranges found in industry and the product manufacturers' recommended levels. The coagents were milled into a toll manufactured masterbatch.

RHEOMETRY

Cure schedules must be considered along with physical properties when compounding with coagents. A quick glance at the rheometer data for these compounds indicates that all of the tested coagents decreased both

scorch and cure times from the times of the control (Table 9). The SRTMPTMA formulations were much scorchier than the other two coagent formulations. The rheometer data also shows the maximum torque values of the TAIC and SRTMPTMA formulations to be higher than the PBD/MA formulations' torque values. Maximum torque values are usually good indicators of coagency, but as other properties will demonstrate, they are deceptive indicators of coagency in this instance.

Table 9
Rheometric Properties of CPE Compounds

Rheometer Data, ASTM D-2084

Model: MP10		Range: 100		Clock: 60 min.	
Die: Micro		Arc: 1°		Temperature: 160°C	
Compound	phr	min. torque dNm	max. torque dNm	scorch time min.	cure time min.
Control	—	7.1	19.3	4.1	23.2
TAIC	1.0	7.1	27.8	2.3	19.3
SRTMPTMA	3.0	7.4	25.6	0.7	13.6
	5.0	6.5	27.0	1.8	19.3
PBD/MA solid	2.5	6.5	20.3	2.8	19.3

UNAGED PHYSICAL PROPERTIES

The effects of these coagents on CPE's physical properties are best compared by the properties of Eb, modulus, and fluid swell resistance. The better a coagent performs, the more it will decrease Eb, increase modulus, and improve fluid resistance. Tensile strength is also affected by coagents, but due to its "bell-shaped" curve in relation to crosslink density it is not the best indicator of coagency. However, it is still important for a compounder to know what influence an additive will have on tensile strength.

All three of the tested materials increased tensile strength (Table 10). There was a clear trend for these formulations--the higher the coagent level, the more the formulation's tensile strength was increased over the control's. TAIC had the biggest impact on tensile strength. At 2 phr, it gave a larger increase over the control's tensile strength than did any of the other tested coagents. Even at 1 phr it had more influence on tensile strength than did SRTMPTMA at both 3 phr and 5 phr. The PBD/MA coagent formulations at 2.5 phr and 3 phr also had a greater influence on tensile strength than did both of the SRTMPTMA formulations. So TAIC had more influence on tensile strength than did PBD/MA which was followed by SRTMPTMA.

Table 10
Unaged Physical Properties of CPE Compounds

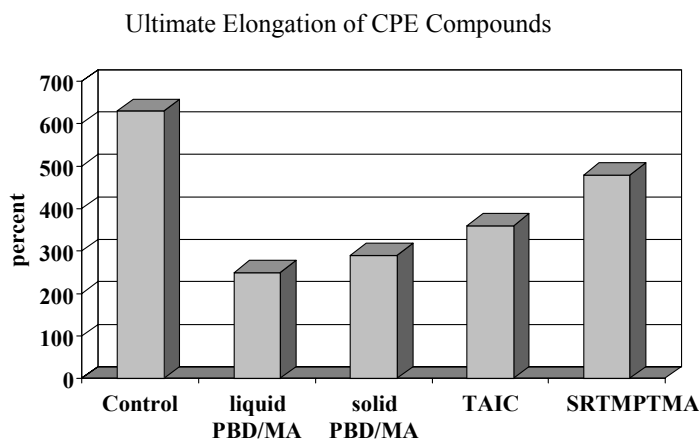
Unaged Physicals ASTM D-412, Press Cure @160°C, T90

Compound	phr	tensile Mpa	tear KN/m	100% mod. Mpa	200% mod. Mpa	elong. %	hrd. pts
Control	–	5.1	30.7	2.1	2.7	640	75
TAIC	1.0	7.5	33.5	2.7	3.6	510	76
	2.0	8.5	33.1	3.1	4.3	450	77
	3.0	8.7	3–5	3.6	5.1	360	79
SRTMPTMA	3.0	7.3	34.7	3.1	4.1	470	78
	5.0	7.0	38.0	3.8	4.5	470	82
PBD/MA liquid	2.5	7.5	28.0	4.5	7.1	250	79
	3.0	7.9	34.9	4.4	7.1	325	83
PBD/MA solid	2.5	7.8	33.5	4.9	7.5	280	80

An increase in crosslink density usually results in a decrease in Eb. This physical property is one of the primary indicators of how much a coagent has increased peroxide efficiency⁶. The PBD/MA coagent at 2.5 phr decreased the Eb from that of the control more than the other tested coagents decreased Eb. It reduced Eb to 250% from the control's 640%. Solid

PBD/MA was also very active in lowering Eb. Both SRTMPTMA formulations gave Ebs of 470%. TAIC at 2 phr resulted in lower Eb than both of the SRTMPTMA formulations, but at 1 phr it was outperformed by the SRTMPTMA formulations. The PBD/MA materials clearly had the greatest effect on Eb, followed by TAIC, then SRTMPTMA (Figure 5).

Figure 5.



A decrease in Eb, especially when accompanied by an increase in tensile strength, will be evidenced by increased modulus strength. Therefore, the coagents which decreased elongation the most also gave the most increase in modulus. The PBD/MA formulations had the highest 100% and 200% moduli. The solid PBD/MA formulation broke at 280% elongation, and the liquid PBD/MA modified compound at 2.5 phr broke at 250% elongation, so they had no 300% modulus, but the 300% modulus of the liquid PBD/

MA formulation at 3 phr was the highest obtained by the tested coagents. TAIC gave the next highest moduli and, following the elongation trend, SRTMPTMA had the lowest moduli.

It was observed that the stress-strain profiles of the PBD/MA formulations were very different in shape from the curves of the other formulations. The control, SRTMPTMA, and TAIC samples had stress-strain curves which were steep for the first 100% elongation

(slope about 2), but tapered off to more gentle slopes after reaching 100% elongation (slopes from 3/5 to 1). The PBD/MA compound's stress-strain profiles did not taper off until the materials reached 200% elongation. They maintained slopes of about 5 up to this point and then tapered to slopes of about 2. This indicates that PBD/MA modification of CPE formulations results in mechanical properties which are not obtained by other coagent modified CPE compounds.

AGED PHYSICAL PROPERTIES

All of the physical properties were measured after aging the test parts in air at 121 °C for 70 hours (Table

11 and Table 12). Two of the most common indicators of age resistance used in industry are retention of tensile strength and retention of elongation. The TAIC formulations had the smallest magnitude changes in both properties, with changes in tensile strength under 6% and changes in Eb under 15%. PBD/MA and SRTMPTMA had comparable aging properties. The formulations containing SRTMPTMA had tensile strengths that were 4%-5% higher after aging than they were prior to aging. The tensile strengths of the PBD/MA formulations were 6%-14% higher after aging. Both the PBD/MA and SRTMPTMA formulations had Eb changes in the 14%-20% range.

Table 11
Aged Physical Properties of CPE Compounds

Heat Aged Physicals ASTM D-412 166 hrs. @150°C

Compound	phr	tensile Mpa	tear KN/m	100% mod. Mpa	200% mod. Mpa	elong. %	hrd. pts.
Control	—	5.7	37.5	3.6	4.0	530	83
TAIC	1.0	7.7	35.2	3.5	4.9	450	82
	2.0	8.0	35.2	3.8	4.7	385	81
	3.0	8.5	33.3	4.3	5.8	325	83
SRTMPTMA	3.0	7.7	40.6	5.1	6.0	380	82
	5.0	6.7	36.1	4.6	5.2	375	86
PBD/MA liquid	2.5	8.6	25.7	5.8	8.5	215	85
	3.0	7.4	33.5	5.2	7.3	265	85
PBD/MA Solid	2.5	8.7	32.2	6.5	8.6	220	86

Table 12
Aged Percent Change of CPE Compounds

Heat Aged Physicals ASTM D-412 percent change							
Compound	phr	tensile %	tear %	100% mod. %	200% mod. %	elong. %	hrd. pts.
Control	---	+ 10.8	+ 22.3	+ 74.3	+ 48.5	- 17.2	+ 8
TAIC	1.0	+ 2.3	+ 5.2	+ 30.5	+ 35.3	- 11.8	+ 6
	2.0	- 5.9	+ 6.4	+ 21.0	+ 11.3	- 14.4	+ 4
	3.0	- 1.9	+ 9.2	+ 18.5	+ 12.5	- 9.7	+ 4
SRTMPTMA	3.0	+ 5.4	+ 17.2	+ 65.5	+ 45.1	- 19.2	+ 4
	5.0	- 4.1	- 5.1	+ 22.0	+ 16.0	- 20.2	+ 4
PBD/MA liquid	2.5	+ 14.0	- 8.1	+ 29.2	+ 20.2	- 14.0	+ 6
	3.0	- 6.0	- 4.0	+ 17.8	+ 2.5	- 18.5	+ 2
PBD/MA Solid	2.5	+ 10.8	- 3.7	+ 32.3	+ 15.2	- 21.4	+ 6

ELECTRICAL PROPERTIES

If a coagent enhances a compound's physical properties but destroys its electrical properties, it should not be used in the w/c industry. The volume resistivities (VR) and dielectric strengths (DS) of the control compound and the three modified compounds which contained 3 phr of coagent were determined. Only one of the coagent modified formulations,

TAIC'S, had a VR lower than that of the control. Both of the other tested coagents produced compounds with VRs greater than the control's. 3 phr of PBD/MA yielded the most resistive compound. Its VR was $9.4 \times 10^{12} \text{ } \Omega \text{ cm}$, more than triple the control's $3.1 \times 10^{12} \text{ } \Omega \text{ cm}$. The SRTMPTMA formulation's VR ($4.7 \times 10^{12} \text{ } \Omega \text{ cm}$) was also higher than that of the control. TAIC at 3 phr had the lowest VR of the group, $2.3 \times 10^{12} \text{ } \Omega \text{ cm}$.

Table 13
Electrical Properties of CPE Compounds

Compound	Phr	Vol. Resistivity ASTM D-257 (ohm-cm) (E+12)	Dielectric Strength ASTM D-149 (volts/mil)
Control	–	3.1	170
PBD/MA	3.0	9.4	270
TAIC	3.0	2.3	240
SRTMPTMA	3.0	4.7	250

All three of the coagent modified materials increased DS from the control. The highest DS value belonged to the PBD/MA modified vulcanizate. It was 270 V/mil, 100 V/mil higher than the 170 V/mil DS of the control. The SRTMPTMA and TAIC compounds tested at 250 V/mil and 240 V/mil respectively for DS. This information shows PBD/MA to be the best coagent for use in compounds which must have good electrical insulation properties (Figure 7).

FLUID RESISTANCE

Perhaps the best indicator of how well a coagent performs is its affect on fluid resistance. As crosslink

density increases, the rubber matrix becomes more tightly knit, promoting greater fluid resistance. Since an increase in peroxide efficiency yields a greater crosslink density, and since coagents added to peroxide cure packages increase peroxide efficiency, low fluid swell values are evidence of effective coagency⁶. CPE is used in many w/c applications, so it is vital that compound ingredients decrease water swell to ensure maintenance of electrical properties. At 70 hours in 82 °C water, the PBD/MA coagents reduced mass swell from 23.4% for the control to 6.5%-7.0% for the PBD/MA formulations (Table 14).

Figure 7

Electrical Properties of CPE Compounds

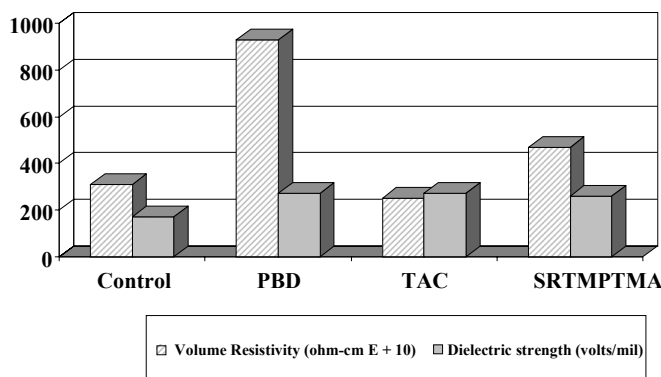


Table 14
Fluid Resistance of CPE Compounds

Fluid Resistance: Water @82°C

Compound	phr	70 hours		166 hours	
		% Volume	% Mass	% Volume	% Mass
Control	—	28.7	23.4	48.7	35.4
TAIC	1.0	36.3	23.5	54.3	34.6
	2.0	31.0	19.9	47.6	30.4
	3.0	26.4	17.4	41.3	26.6
SRTMPTMA	3.0	17.8	10.1	24.4	15.2
	5.0	17.5	11.5	30.1	19.2
PBD/MA liquid	2.5	9.8	6.5	16.9	11.0
	3.0	10.2	6.5	18.2	11.9
PBD/MA Solid	2.5	10.2	7.0	12.5	12.5

At 166 hours, PBD/MA reduced mass swell from 35.4% for the control to 11.0%-12.5% for the PBD/MA formulations. The SRTMPTMA coagents were the next best protection against water, reducing the 70 hour mass swell to 10.9% at the 3 phr level, and 11.5% at the 5 phr level. At 168 hours, the SRTMPTMA modified compounds gave mass swells of 15.2% and 19.2% (3 phr and 5 phr, respectively). TAIC formulations were the least water resistant of the coagent formulations. At the 70 hour milestone, 1 phr TAIC actually increased mass swell to 23.5% while at 2 phr and 3 phr it reduced mass swell to only 19.9% and 17.4%, respectively. All of these numbers either nearly tripled, or more than tripled, the PBD/MA swell numbers. The TAIC mass swells at 166 hours ranged

from 26.6% to 34.6%, again roughly tripling the PBD/MA swell values (Figure 6). The volume swell, as expected, followed the same trend as the mass swell. Since the study's experimental CPE formulation was not compounded for a specific industrial application, the water swell numbers are higher than expected for industrial use. However, this is not a poor reflection on the use of coagents in CPE. Because the coagents decreased the swell from that observed in the control, it can be deduced that they will have a similar impact in formulations compounded for swell reduction. The PBD/MA materials can be expected to decrease swell more than either SRTMAPTM or TAIC will, and SRTMPTMA can be expected to give more improvement than will TAIC.

CONCLUSION

Properties of EP elastomers, EVAS, EVMS, and CPEs are greatly improved with the addition of coagents in peroxide cured compounds. The reason for this improvement is that more C-C bonds are formed during peroxide vulcanization when coagents are added than when they are absent. The peroxide cured compounds with coagents are superior to sulfur cured compounds in many room temperature and heat aged physical properties, fluid resistance, and electrical properties.

This research compared commonly utilized coagents primarily in wire and cable formulations. In the EP,

EVA and EVM elastomers, liquid high 1,2-vinyl polybutadiene (PBD) coagents outperformed and often exceeded the performance of the Type I coagents, trimethylolpropane trimethacrylates, and the Type II coagent, triallyl cyanurate. The PBD modified compounds particularly excelled in heat aged, water resistance, and electrical properties. The reason to use any coagent in a peroxide cured formulation is to increase peroxide efficiency hence increasing crosslink density. The main advantage of the polymeric PBD systems is the stability of the PBD radical (Table 15). With increased radical stability, PBD coagents give better properties due to the suppression of competing reactions like beta scission, disproportionation, and homopolymerization^{2,3,4,7}.

Table 15
Bond Dissociation Energies of Free Radicals

Free Radical	Symbol	Dissociation Energy Kcal/Mole at 0°K
Methyl	CH ₃ *	102
Primary	RCH ₂ *	101
Secondary	R ₂ CH*	96
Tertiary	R ₃ C*	89
Vinyl stabilized	CH ₂ =CH-CH ₂ *	77
Benzyl stabilized	C ₆ H ₅ -CH ₂ *	78

Solid and liquid maleinized PBD (PBD/MA) were developed as coagents for CPE elastomers during the course of this study. PBD/MA resins have an effect on the vulcanization of chloroprene rubber. This is believed to be due to the chlorine on the rubber backbone interacting with the MA sites on the PBD/MA chain⁸. There is also an increased amount of conjugation on the PBD chain, due to maleinization, which can increase peroxide efficiency. These chemistries are most likely responsible for the outstanding coagent properties obtained from PBD/MA materials in CPE. The stress-strain profiles for the PBD/MA formulations were completely different in shape from the curves for the control, TAIC, and SRTMPTMA formulations, indicating that unique mechanical properties are imparted to CPE by PBD/MA. Further study is underway to determine the mechanisms for this phenomenon which is clearly a benefit to the CPE compounder.

Liquid PBD resins are currently used in geothermal and oil well cable compounds because they are among the few coagents which can adequately perform in these harsh environments. With the utilization of non-toxic PBD coagents, compounders will be able to produce improved wire and cable jackets, insulators, and connectors by improving cost effectiveness and physical and electrical properties of peroxide cured formulations.

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REFERENCES

1. Michael Fath, "Vulcanization of Elastomers," Course Notes of Compounding, Processing and Testing of Elastomers, American Chemical Society, 1994
2. R.E. Drake, J.M. Labriola and J.J. Holliday, "Improving Properties of EPM and EPDM with Coagents," American Chemical Society, Chicago, IL, April 19-22, 1994
3. R.E. Drake, Coagent Bulletin: Introduction, April 27, 1992. Ricon Resins, Inc., Grand Junction, Colorado
4. R.E. Drake, J.M. Labriola and J.J. Holliday, "1,2 Polybutadiene Coagents for Improved Elastomeric Properties," American Chemical Society, Nashville, TN, November 3-6, 1992
5. William H. Davis Jr., Raymond L. Laukso Jr., Loyd B. Hutchinson and Sandra L. Watson, "Peroxide-Cured Chlorinated Polyethylene Compounds Having Enhanced Resistance to Ozone-Induced Creaking," American Chemical Society, May 29-June 1, 1990
6. J.W. Martin, "1,2-Polybutadiene Resin Coagents for peroxide Cure of Rubber Compounds," Rubber Chemistry and Technology, Vol. 47, No. 1, American Chemical Society, October 3-6, 1972
7. Robert C. Keller, "Peroxide Curing of Ethylene-Propylene Elastomers," American Chemical Society, October 6-9, 1987
8. R.E. Drake and J.M. Labriola, "New Polymeric Curative for Polychloroprene," American Chemical Society, Atlanta, GA, October 7-10, 1986

Appendix 1

Chemical Name and Suppliers of the Ingredients

Supplier	Compound	Grade
Akzo Chemicals	Dicumyl Peroxide	Perkadox BC 40KPD
Akrochem	Stearic Acid	Stearic Acid (RG)
	Magnesium Oxide	Akro-Mag
	Bis tert-butylperoxy	
	Diisopropylbenzene	Retilox F 40KE
	Zinc Oxide	Zinco Oxide
Alcoa	Hydrated alumina	Hydral 710
Argus	Dilauryl thiodipropionate	DLTDP
Ashland Chemical	Trioctyl Trimellitate	Irganox 1010
Ciba-Geigy	Antioxidant	Cylink TAC Monomer
Cyanamid	Triallyl Cyanurate	Tyrin 0136
Dow Chemical	Chlorinated Polyethylene	Epsyn 55
DSM/Copolymer	EPDM	Elvax 460
Dupont	Chlorinated Polyethylene EPDM	Nodel 2722
E.C.C. America	Calcium Carbonate	Atomite
Eagle Picher	Red Lead	EP202
Engelhard	Calc./surface mod. Kaolin	Engelhard
Huber	Carbon Black	N550
Miles/Polysar	EPM	Polysar 306
	Ethylene Vinylacetate	Levapren 500 HV
	Styrenated Diphenyl amine	Vulkanox DDA
Nippon Kasei Chem.	Triallyl Iso cyanurate	TAIC
R.T. Vanderbilt	Polymerized trimethyl di-hydroquinoline	AgeRite Resin D
RiconResins, Inc.	1,2 Polybutadiene	Ricon 154
	1,2 Polybutadiene adducted w/maleic anhydride	
Cray Valley	Trimethylolpropane Tri-methacrylate	SR-350
	Scorch retarded Trimethylolpropane Trimethacrylate	Saret 517
Sun Oil Co.	Paraffinic oil	Sunpar 2280
Union Carbide	Silane	Silane A-172
Uniroyal	EPDM	Royalene 580HT
Special thanks to Colonial Rubber for supplying the masterbatch formulations used in this study		

Appendix II

Test Methods and Equipment

Vulcanization Using Oscillating Disk Cure Meter	2084	TechPron Oscillating Disk Rheometer
Measurement of Rubber Properties in Tension	412	GCA/Precision CRE 500 Universal Tester
Tear Resistance (Die C)	624	GCA/Precision CRE 500 Universal Tester
Compression Set Method B	395	Ames 202 Thickness Gauge
Determination of swell in Liquids	471	Ames 202 Thickness Gauge
The Impact Resilience of Rubber by Vertical Rebound	2632	Shore Resiliometer
Deterioration in an Air Oven	573	GCA/Precision CRE 500 Universal Tester
Durometer Hardness	2240	Rex Durometer model 1600
Standard Temperatures and Atmospheres for Conditioning and Testing	1349	

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