

Polybutadiene and Functionally Adducted Polybutadiene Additives for Enhancing Wire and Cable Compounds

Abstract

Polybutadiene resins and functionally adducted polybutadiene resins have been shown to be effective in the improvement of wire and cable compounds. High 1,2-vinyl polybutadiene coagents produce physical and electrical properties in EP elastomers and EVA/EVM elastomers which are as good as or better than those obtained from other coagents which are commonly used by the wire and cable industry today. Also, functionally adducted polybutadiene resins are shown to improve the physical, electrical, and fluid-swell properties of CPE and CSM elastomers. In peroxide-cured CPE and CSM formulations, maleinized polybutadiene forms an ionomeric network via maleic anhydride. During the vulcanization step, this ionomeric network is bound to the elastomeric network through the polybutadiene chain, enhancing physical and electrical properties as well as improving fluid-swell properties. When used in sulfur-cured CSM formulations, the maleinized resins allow for the maintenance of physical properties with increased filler levels. In peroxide-cured CSM formulations, functionalized polybutadiene resins show promise for partially or completely replacing lead compounds as scavengers and stabilizers.

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. These crosslinks allow rubber to be used in harsh environments; peroxide-cured rubber articles are among the most weatherable, heat-resistant, and set-resistant elastomeric materials available. Peroxide

vulcanization also gives the compounder a wide variety of elastomers with which to work. Due to a lack of double bonds, saturated elastomers like EPM cannot be vulcanized by sulfur. Use of these saturated elastomers requires the compounder to utilize 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 (not very many crosslinks are formed per peroxide radical formed), 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.² 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 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 coagents give higher cure states and faster cure rates than does peroxide vulcanization without coagents. Type I coagents include acrylates, methacrylates, bis-maleimides, 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 radicals which are more stable 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.⁴ 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, CPE, and CSM.

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 very good electrical properties combined with excellent moisture and weather resistance. 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 which may be sulfur cured. 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 results in 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 these copolymers, the more resistance it has to heat,

oil, and solvents. Though this material has exceptional age properties, the polarity of the VA increases its conductivity, nevertheless it has found its niche as a semi-conductive insulator in the w/c industry.

CPE is the third 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 in the w/c industry. CPEs are used in power transmission cables, portable power and control cables, and mining cables.

CSM, or chlorosulfonated polyethylene, is the final elastomer studied herein. It is widely used as a sheathing material for cable due to its insulating properties. It is also selected for w/c applications due to its heat resistance, good water resistance, and superior weatherability. Unfortunately, many CSM compounds require the addition of lead as a stabilizer, HCL scavenger, and moisture-resistance promoter.

Experimental

Chemicals

All ingredients used in this study are commercially available compounds and are listed in Appendix I. Four common wire and cable elastomers were studied: chlorinated polyethylene (CPE), chlorosulfonated polyethylene (CSM), ethylene propylene rubber (EPM and EPDM), and ethylene vinylacetate (EV and EVM) (Table 1). 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), a scorch-retarded trimethylolpropane trimethacrylate (TMPTMA) and metallic diacrylate (ZDA). 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). A potential lead replacement, epoxidized 1,4-polybutadiene (PBD/EP), was also examined. TMPTMA, TAC, and PBD were studied in the EP elastomers, while TAC, PBD, and TMPTMA were tested in EVM. TMPTMA, TAIC, and PBD/MA were studied in CPE

and CSM; PBD/EP was also examined in CSM. All of the coagents tested (Table 2) 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

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

Table 2

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/4mm	MODERATE
TATM	II	330.3	175°C/0.1mm	MODERATE

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, allowed to rest 24 hours, and then sampled for testing.

Appendix II lists the ASTM methods and test equipment used for this study. Test plaques were cured at various temperatures and prepared for testing. 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%).

Results and Discussion

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 phr of 40% active dicumyl peroxide dispersion (DCP) with varying phr of the 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 which differed 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 to the use of the PBD coagents.

Table 3

Test Formulations							
Compound	EPDM A	EPDM B	EPM A	WCEPDM	WCEPM	EVA	EVM
EPDM	100.0	100.0	--	100.0	--	--	--
EPM	--	--	100.0	--	100.0	--	--
EVA	--	--	--	--	--	100.0	--
EVM	--	--	--	--	--	--	100.0
N550 CARBON	50.0	50.0	50.0	35.0	35.0	2.0	45.0
CaCO ₃	--	--	--	105.0	105.0	--	--
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
ZnO	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	--
MgO	--	--	--	--	--	--	2.0
Polyethylene Wax	--	--	--	--	--	--	2.0
Paraffinic Wax	--	--	--	--	--	--	--
Plasticizer	--	--	--	--	--	--	--
Dicumyl Peroxide (40% dispersion)	8.0	8.0	8.0	7.0	7.0	--	--
Butylperoxy-Di-Isopropyl Benzene (40% dispersion)	--	--	--	--	--	6.0	6.0

Rheometry

Rheometric data for the non-w/c formulations are presented in Table 4. The vulcanization property which was most useful for comparison of the different coagents was scorch time. The scorch times of the

TMPTMA formulations were 14-25% lower than those of the three controls. Differences in scorch safety were more apparent in the w/c formulations (Table 5); both control formulations' scorch times were reduced more than 40% when compounded with non-scorch retarded TMPTMA.

Table 4

Properties of EP Elastomers												
Elastomer:	EPDM A				EPDM B				EPM A			
(no coagent)	cnt'l				cnt'l				cnt'l			
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	66.4	70.0	65.4
T _{s1} (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	20.4	19	19.4
Physical Properties: Press Cure to T ₉₀ @ 160°C												
Tensile Str. (MPa)	12.0	15.1	12.7	17.2	14.5	14.3	11.6	13.9	15	12.5	11	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
Elongation %	150	130	105	140	230	165	145	205	205	150	135	160
Shore A Hardness	76	78	80	79	73	76	76	75	76	78	78	77
Aged Physical Properties: Air, 166 hrs. @ 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
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
Shore A Hardness	-2	+4	+2	+2	+3	+3	0	-2	0	0	-1	0
Compression Set: 166 hrs. @ 150°C (%)												
	25.6	18.7	19.5	18.4	32.2	22.8	23.7	26.5	30	23.2	25.0	25.9
Fluid Resistance: Toluene, 22 hrs. @ 25°C												
% Volume Change	115.7	103.4	103.1	109.6	138.5	120	120	128	139	128	128	130.4

Table 5

Properties of W/C EP Elastomers						
Elastomer:	WCEPDM			WCEPM		
No Coagent	Control			Control		
PBD (phr)		2			2	
TMPTMA (phr)			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 to 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
Shore A Hardness (pts.)	86	87	86	79	82	81
Aged Physical Properties: Air, 166 hrs. 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 Elongatin	-14.9	-17.9	-12.2	-23.5	-29.5	-18.7
Shore A Hardness	+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: Volume 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. Selection of base elastomer had the largest effect on the maximum torque of these compounds. The maximum torque values for the non-w/c compounds' controls (which utilized no coagent) were 74.1, 62.8, and 62.1 dNm for EPDM A, EPDM B, and EPMA, respectively. EPDMA contains the highest

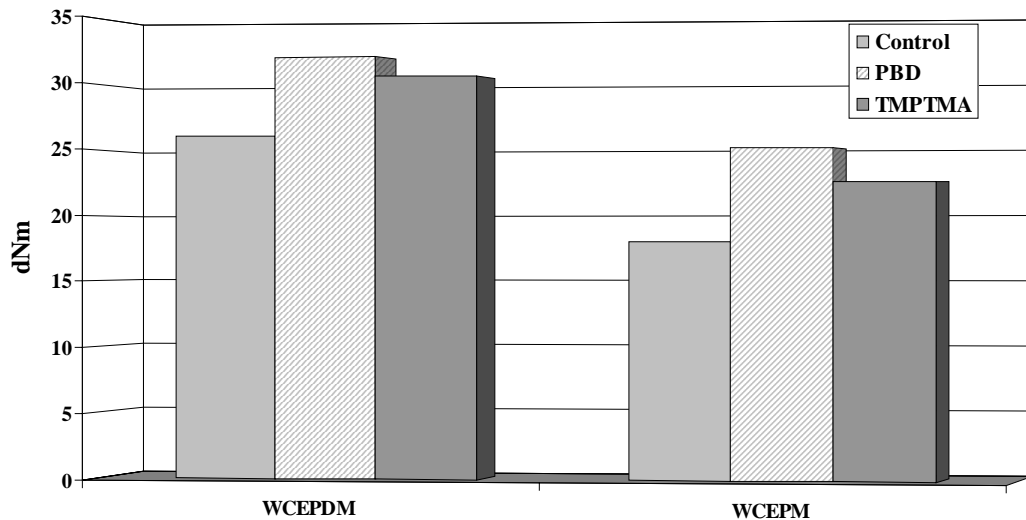
ethylidene norbornene (ENB) content, causing the highest maximum torque value. EPDM B and EPMA both contain low amounts of ENB — 2.9% and 0.0%, respectively — and their control compounds' maximum torques were approximately the same. Although EPM does not contain any diene in its backbone, the high ethylene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

The 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

Maximum Torque Values of W/C Compounds



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 (E_b) and tear strength. In the WCEPM formulation, PBD produced lower E_b and higher moduli values than the TMPTMA coagent modified formulation. This is a clear indication that the PBD increased peroxide efficiency more than did the TMPTMA.

Table 4 displays the heat-aged results of all the EP elastomers. Most of the EP formulations aged very well; this was not surprising because heat aging is one

property in which EP elastomers excel. 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 E_b , respectively. Similar results occurred with these two properties in EPDM A and B, with the exception of the E_b in EPDM B, which only changed -9.3%. All the other coagent-altered compounds had changes less than 50% in both tensile strength and E_b . Also, all the percent changes for E_b were negative, and for the tensile moduli the changes were positive, indicating that crosslinking continued during the aging process.

Curing the test samples beyond their T_{90s} and/or a post cure of these parts would undoubtedly minimize the heat-age-induced changes in 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. The results are displayed in Table 5. The changes caused by coagents in the volume resistivity and dielectric strength were inconsistent. For example, in the WCEPDM compounds the PBD formulation had a higher volume resistivity than did the TMPTMA compound. In contrast, the PBD compound reported lower dielectric strength than did the TMPTMA material. Although no particular trend was clear for the relationship between particular coagents and electrical properties, it was obvious that both coagents did improve the electrical performance relative to the control formulation. In the WCEPM compound, the PBD compound had higher values for both electrical properties tested than did the TMPTMA compound (Table 5).

Fluid Resistance

Because water resistance is very important for maintenance of electrical properties, testing of the w/c compounds proceeded 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 indicated that the PBD modified elastomers had the best water resistance of the materials tested. However, after 166 hours at elevated temperatures, the TMPTMA compound showed the highest

resistance to water. In the WCEPM formulation, the opposite trend was noticed. The TMPTMA coagent 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 changes, 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

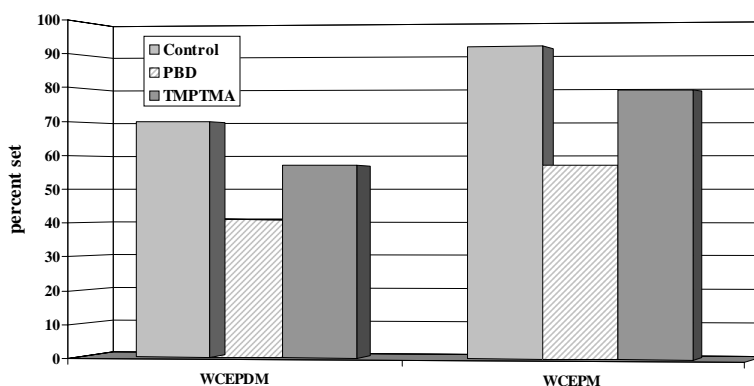
Compression Set

Although compression set testing is not as important for many w/c compounds as it is for other 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 high-temperature characteristics of the material.

The results in Table 4 indicate that in all the EP formulations except EPDM A, the PBD coagent produced lower compression set figures. 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, the PBD and TMPTMA compression set values were 56.9% and 78.9% respectively. This indicates that the PBD coagent gave the highest crosslink density of these two coagents.

Figure 2

Compression Set of W/C Compounds



EVA and EVM

The test formulations compounded were based on an EVA elastomer containing 18% VA and an EVM compound with 50% VA content (Table 3). The coagents employed were a scorch-retarded version of TMPTMA, TAC, and PBD. These compounds were cured at 180°C for two 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 was TMPTMA, PBD, then TAC. The cure times

revealed that the TAC formulations were the fastest-curing formulations among both the EVA and EVM compounds. The PBD and TMPTMA reached their T_{90} s at approximately the same time. The faster cure times demonstrated by the compound formulated with the TAC contradicted the traditional classification of Type I and Type II coagents; type I coagents typically cure faster and are scorchier than Type II coagents. The Type II coagent TAC, however, cured faster than the Type I coagent TMPTMA. 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, TMPTMA had an increased scorch time relative 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: 24 min.					
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
TMPTMA	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
TMPTMA	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. For example, the EVA formulation

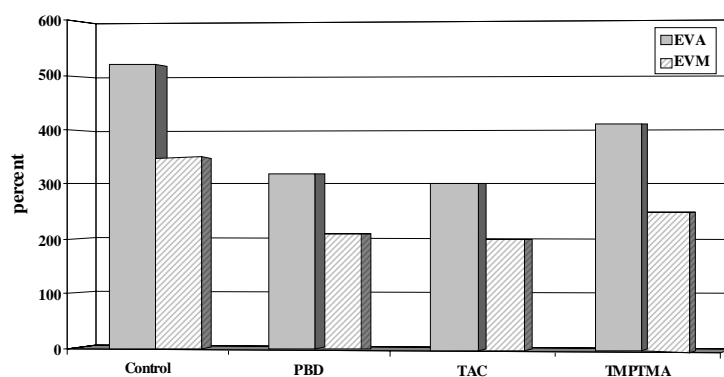
compounded with TAC produced the largest decreases in tear strength and E_b compared to the control. The PBD coagents clearly outperformed the TMPTMA as evidenced by E_b (Figure 3). The order of performance was not as clear for the EVM compounds.

Table 7

Unaged Physical Properties of EVA and EVM Compounds								
Unaged Physical Properties, ASTM D-412								
Press Cure @ 180°C, $T_{90} + 2$ 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
TMPTMA	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	--
TMPTMA	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 TMPTMA 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 had approximately equivalent crosslink densities. All the physical properties of these two compounds were essentially equivalent; the largest

difference was in the 100% modulus. The TAC formulation produced a 100% modulus of 5.8 MPa, compared to 5.4 MPa for the PBD compound. It was noticed that the PBD coagent performed more efficiently in the EVM formulation than in the EVA compound.

Heat-Aged Physical Properties

The heat-age data for the EVA compounds (Tables 8 & 9) indicate that the PBD and TAC coagents both out perform the control in the area of tensile-strength retention, while the TMPTMA performs very poorly in this area. In the retention of E_b, PBD showed the greatest change, and that was only +9.2%. Considering all of the physical properties, it is clear that the TAC and PBD coagents give the best aging properties.

In the EVM formulations, TAC had the best age properties, and the PBD and TMPTMA compounds both gave sporadic enough results to make a vis a vis comparison difficult. They gave similar changes in tensile strength, but the TMPTMA gave a smaller change in E_b than did the PBD — +13.7% vs. +25.0%. The PBD generally posted smaller changes for the properties of tear strength, modulus strength, and hardness (Tables 8 & 9).

Table 8

Aged Physical Properties of EVA and EVM Compounds								
Aged Physical Properties, ASTM D-412, 166 hrs. @ 150°C								
Compound	phr	Tensile MPa	Tear KN/m	50% Mod. Mpa	100% Mod. MPa	Elong. %	Hrd. A pts.	Hrd. D pts.
EVM Control	-	13.1	70.7	7.4	8.8	520	93	46
PBD	2	12.6	61.5	7.9	8.6	355	93	47
TAC	2	12.3	51.1	7.7	8.5	300	93	47
TMPTMA	2	13.3	64.4	7.7	8.6	420	93	47
EVA Control	-	13.0	48.3	1.5	3.5	360	74	--
PBD	2	16.0	37.8	2.1	4.9	255	75	--
TAC	2	16.9	29.6	2.3	7.1	200	76	--
TMPTMA	2	16.2	41.0	1.7	4.4	290	73	--

Table 9

Aged Percent Change of EVA and EVM Compounds								
Aged Physical Properties, ASTM D-412, percent change								
Compound	phr	Tensile %	Tear %	50% Mod. %	100% Mod. %	Elong. %	Hrd. A chg	Hrd. D chg
EVA Control	-	-13.2	+11.5	+5.7	+14.3	-1.0	+1	+2
PBD	2	-1.6	+10.4	+8.2	+14.6	+9.2	0	+1
TAC	2	-8.8	+1.0	-6.9	+9.0	0.0	0	+2
TMPTMA	2	-17.7	+13.8	-8.5	+16.2	+2.4	0	+1
EVM Control	-	-14.5	+9.5	-31.8	0.0	+2.9	+6	--
PBD	2	+6.0	+10.9	-4.8	-9.3	+25.0	+3	--
TAC	2	-4.0	-12.9	0.0	+22.4	0.0	+3	--
TMPTMA	2	-4.1	-11.7	-26.1	-8.3	+13.7	+4	--

Water Swells

The EVA and EVM compounds were tested for water resistance by immersing all compounds in distilled water for 166 hours at 82°C (Figures 4 & 5). The most notable 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 0.72% 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.

Figure 4

Fluid Resistance of EVA Compounds

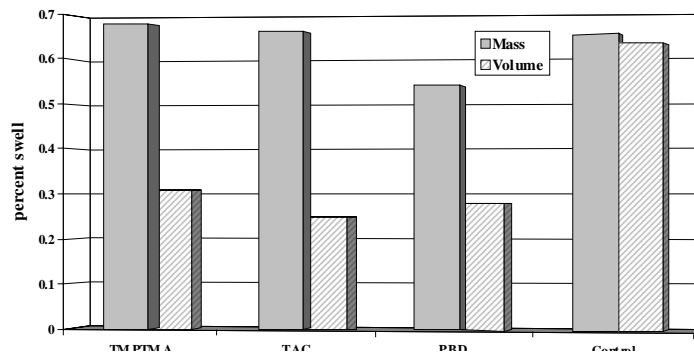
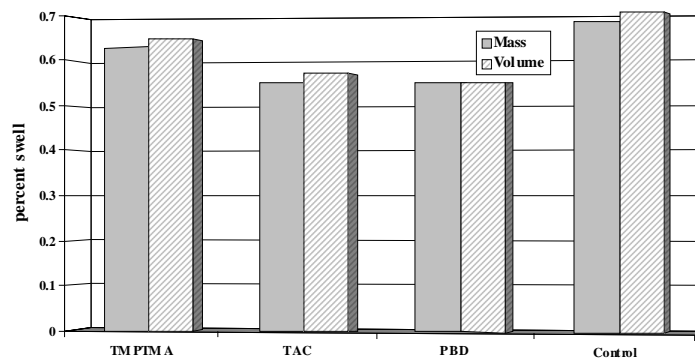


Figure 5

Fluid Resistance of EVM Compounds



In the EVA materials, all coagents performed comparably by decreasing water absorption approximately 50% from the control's values. In the EVM compounds, Type II coagent modified formulations (PBD and TAC) outperformed the TMPTMA-altered formulation (Figure 4). For instance, Type II coagent systems decreased water absorption 23% compared to a 10% decrease from

the control's absorption produced by the TMPTMA additive.

CPE Elastomer

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

efficiency.⁵ 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.⁶ The physical properties which are influenced by coagents and discussed in this section are: ultimate elongation (E_b), tensile strength, tensile modulus, maximum torque, and fluid swell properties. The coagents examined in CPE were: triallyl isocyanurate (TAIC), scorch-retarded trimethylolpropane trimethacrylate (TMPTMA), high 1,2-vinyl polybutadiene liquid resin adducted with maleic anhydride functionality (PBD/MA), and solid PBD/MA. TAIC was tested at 1 phr, 2 phr, and 3 phr. TMPTMA was tested at 3 phr and 5 phr. PBD/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 (Table 10).

The PBD/MA coagent takes a novel approach to coagency in CPE. As previously mentioned, coagents traditionally increase crosslink density by increasing peroxide efficiency. The PBD/MA coagent not only increases peroxide efficiency through its PBD backbone, but also forms an ionomeric network in the CPE through the MA sites adducted to its PBD chain. During CPE vulcanization, HCl is liberated only to be scavenged by MgO (or a similar additive to the CPE formulation), forming $MgCl_2$ and H_2O . The H_2O formed during this reaction catalyzes ring opening of the MA which reacts with MgO to form a magnesium salt of the MA. These salts form an ionomeric network in the CPE which is bound to the rubber chains via peroxide crosslinking between the PBD and CPE. This dual network yields increased strengths in physical properties as well as improved fluid resistance and electrical properties.

Table 10

CPE Formulations	
Ingredient	phr
CPE	100.0
CaCO ₃	150.0
N550 Carbon Black	35.0
Plasticizer	38.0
Paraffin Wax	2.0
MgO	5.0
Dicumyl Peroxide (40%)	7.0
Coagent	*
* See Following Tables	

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 11). The TMPTMA formulations were much scorchier than the other two coagent formulations. The rheometer data also shows the

maximum torque values of the TAIC and TMPTMA 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, possibly because the ionomeric network formed by PBD/MA is past its softening point at the vulcanization temperature.

Table 11

Rheometric Properties of CPE Compounds					
Rheometer Data, ASTM D-2084					
Model: MP10 Range: 100 Clock: 60 min.					
Die: Micro Arc: 1° Temperature: 160°C					
Comp'd	phr	Min. Torque dNm	Max. Torque dNm	Scorch Time min.	Cure Time min.
Cnt'l	---	7.1	19.3	3.1	23.2
TAIC	1.0	7.1	27.8	2.3	19.3
	2.0	7.0	31.8	2.1	17.4
	3.0	6.9	35.2	2.2	17.2
TMPTMA	3.0	7.4	25.6	0.7	13.6
	5.0	6.5	27.0	1.8	19.3
PBD/MA liquid	2.5	7.4	20.7	2.2	15.7
	3.0	7.5	20.7	2.2	17.8
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 E_b , modulus, and fluid-swell resistance. The better a coagent performs, the more it will decrease E_b , 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 12). 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 TMPTMA 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 TMPTMA both at 3 phr and 5 phr.

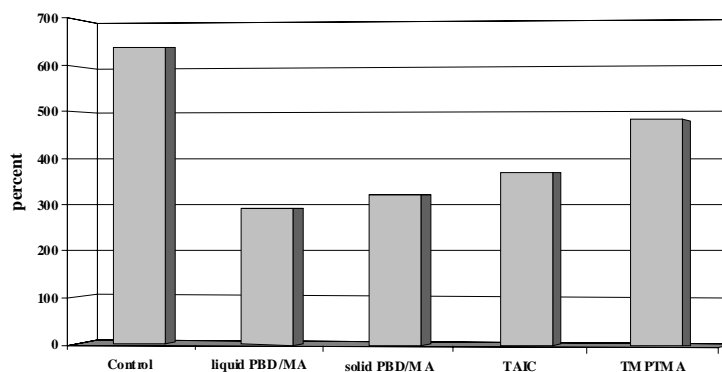
An increase in crosslink density usually results in a decrease in E_b . This physical property is one of the primary indicators of how much a coagent has increased peroxide efficiency.⁴ The PBD/MA coagent at 2.5 phr decreased the E_b from that of the control more than did the other tested coagents. It reduced E_b to 250% from the control's 640%. Solid PBD/MA was also very active in lowering E_b . Both TMPTMA formulations gave E_b s of 470%. TAIC at 2 phr resulted in lower E_b than both of the TMPTMA formulations, but at 1 phr it was outperformed by the TMPTMA formulations. The PBD/MA materials clearly had the greatest effect on E_b , followed by TAIC, then TMPTMA (Figure 6).

Table 12

Unaged Physical Properties of CPE Compounds							
Unaged Physicals ASTM D-412, Press Cure @ 160°C, T90							
Comp'd	phr	Tensile Mpa	Tear KN/m	100% Mod. Mpa	200% Mod. Mpa	Elong. %	Hrd. Pts.
Cnt'l	---	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	30.5	3.6	5.1	360	79
TMPTMA	3.0	7.3	34.7	3.1 3.8	4.1	470	78
	5.0	7.0	38.0		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

Figure 6

Ultimate Elongation of CPE Compounds



A decrease in E_b , especially when accompanied by an increase in tensile strength, will be evidenced by increased modulus. Therefore, the coagents which decreased elongation the most also gave the most increase in modulus strength. 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 neither had a 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 modulus and, following the elongation trend, TMPTMA had the lowest modulus (Table 12).

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, TMPTMA, 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 0.6 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 improved mechanical properties 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 13 and Table 14). 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 E_b under 15%. PBD/MA and TMPTMA had comparable aging properties. The formulations containing TMPTMA 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 TMPTMA formulations had E_b changes in the 14%-20% range.

Table 13

Aged Physical Properties of CPE Compounds							
Heat Aged Physicals ASTM D-412 70 hrs. @ 121°C							
Comp'd	phr	Tensile MPa	Tear KN/m	100% Mod. MPa	200% Mod. MPa	Elong. %	Hrd. Pts.
Cnt'l	---	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
TMPTMA	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 14

Aged Percent Change of CPE Compounds							
Heat Aged Physicals, ASTM D-412, percent change							
Comp'd	phr	Tensile %	Tear %	100% Mod. %	200% Mod. %	Elong. %	Hrd. pts.
Cnt'l	---	+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
TMPTMA	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

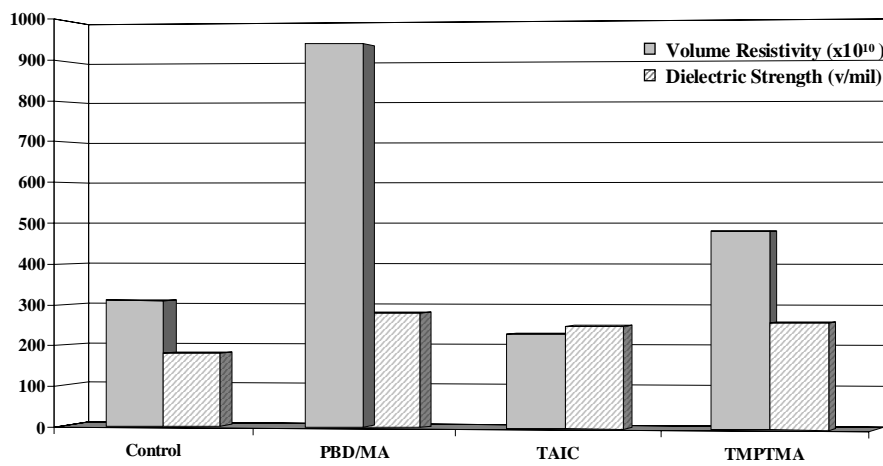
Electrical Properties

If a coagent enhances a compound's physical properties but destroys its electrical properties, it should not be used in the wire and cable 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 $9.4 \times 10^{12} \text{ } \Omega \cdot \text{cm}$ — more than triple the control's $3.1 \times 10^{12} \text{ } \Omega \cdot \text{cm}$. The TMPTMA formulation's VR ($4.7 \times 10^{12} \text{ } \Omega \cdot \text{cm}$) was also higher than that of the control. TAIC at 3 phr had the lowest VR of the group, $2.3 \times 10^{12} \text{ } \Omega \cdot \text{cm}$ (Figure 7).

Figure 7

Electrical Properties of CPE Compounds



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 TMPTMA 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).

Water Swell Properties

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 coagency.⁴ 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 15). 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 TMPTMA coagents were the next best protection against water, reducing the 70 hour mass swell to 10.1% at the 3 phr level, and 11.5% at the 5 phr level. At 166 hours, the TMPTMA 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.

Figure 8

Fluid Resistance of CPE Compounds

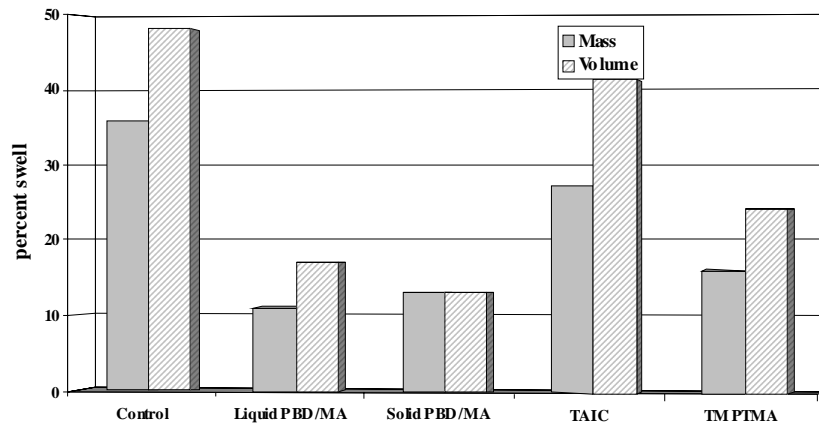


Table 15

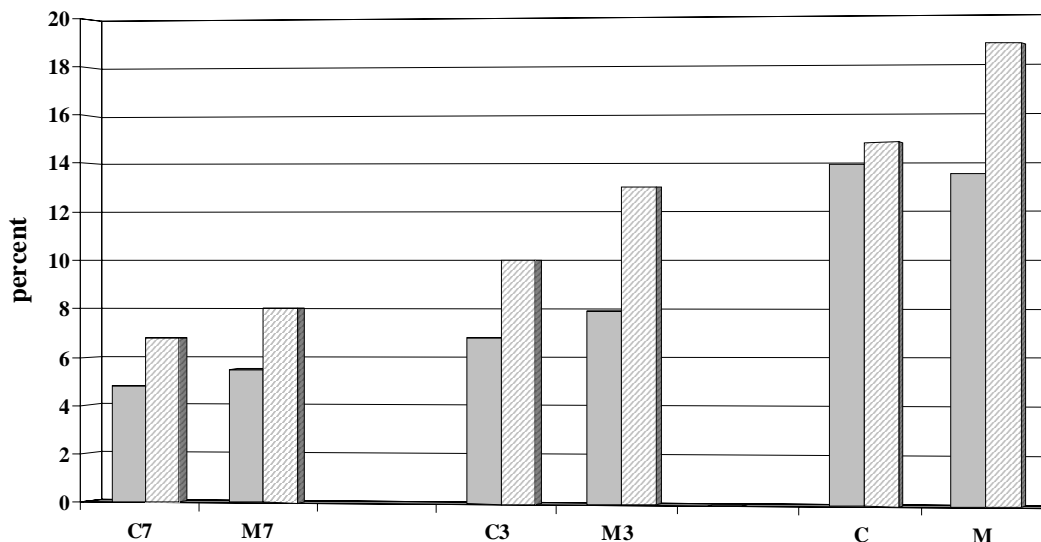
Fluid Resistance of CPE Compounds					
Fluid Resistnace: Water @ 82°C					
		70 Hours		166 Hours	
Comp'd	phr	% Volume	% Mass	% Volume	% Mass
Cnt'l	---	28.7	23.4	48.7	35.4
TAIC	1.0	36.3	23.5	54.3	34.6
	2.0	31.0	19.9	47.6	30.4
	3.0	26.4	17.4	41.3	26.6
TMPTMA	3.0	17.8	10.1	24.4	15.2
	5.0	17.5	11.5	30.1	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

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 9). The volume swell, as expected, followed the same trend as the mass swell.

Figure 9

70 Hour Water Swells, MgO vs. CaO in CPE



MgO vs. CaO in PBD/MA Modified CPE

A similar ionomeric network to that formed with MgO and PBD/MA can also be created using CaO. It was hypothesized that the CaO network would be stronger than the MgO network since the presence of the larger Ca atom in the salt would produce a more polar moiety, yielding stronger ionic interactions. This hypothesis was tested along with the effects of higher PBD/MA

loadings. The formulations in Table 16 were mixed on a two roll mill and tested for rheometric, physical, and fluid swell properties. The “M” compounds contain 5 phr MgO, and the “C” compounds contain 5 phr CaO. The number after the letter indicates the phr of PBD/MA in the formulation (ex. M3 contains MgO with 3 phr of PBD/MA). The control compounds, M and C, contain no PBD/MA.

Table 16

Formulations Comparing MgO to CaO in CPE						
Compound	M	M3	M7	C	C3	C7
CPE	100.0	100.0	100.0	100.0	100.0	100.0
CaCO3	150.0	150.0	150.0	150.0	150.0	150.0
N550 Carbon Black	35.0	35.0	35.0	35.0	35.0	35.0
Plasticizer	38.0	38.0	38.0	38.0	38.0	38.0
Paraffin Wax	2.0	2.0	2.0	2.0	2.0	2.0
MgO	5.0	5.0	5.0	---	---	--
CaO	---	---	--	5.0	5.0	5.0
PBD/MA	---	3.0	7.0	---	3.0	7.0
Dicumyl Peroxide (40% dispersion)	7.0	7.0	7.0	7.0	7.0	7.0

Rheometry

The addition of PBD/MA to the rubber increased the maximum torque over the control's no matter which metal oxide was used (Table 17). However, in the C compounds, the effects of the PBD/MA were greater than they were in the M compounds. The scorch time of the resin-modified materials was lower than the control's in both the CaO and MgO formulations. In the C compounds, increasing the resin level slowed the cure time.

Physicals

In both metal oxide formulations, the addition of the resin increased the tensile strength while decreasing

elongation (Table 18), but again the effects of the PBD/MA were larger in the C compounds. The one hundred percent and two hundred percent modulus strengths increased as the PBD/MA level increased. The metal oxides with PBD/MA also had higher hardness than the control.

In both rheometric and physical properties, the C compound performed more poorly than the M compound, but the C3 and C7 compounds had superior properties to those of the M3 and M7 formulations. This observation supports the hypothesis that the CaO-network is stronger than the MgO-based network.

Table 17

Rheometry Data for MgO vs. CaO Study in CPE				
Comp'd	Min. Torque	Max. Torque	Scorch Time	Cure Time
M	7.08	15.76	3.08	17.25
M3	6.02	17.08	2.58	14.75
M7	5.37	22.91	2.50	17.17
C	8.21	14.96	3.42	15.67
C3	5.95	20.26	2.50	19.33
C7	5.37	26.88	2.25	21.75

Table 18

Physical Data For MgO vs. CaO in CPE						
Compound	Tensile MPa	Elong. %	100% Mod. MPa	200% Mod. Mpa	Tear KN/m	Hrd. A pts.
M	3.7	550	2.6	3.0	31.5	66
M3	7.0	280	4.7	6.8	36.2	73
M7	8.3	230	5.7	8.1	33.4	80
C	3.2	510	2.2	2.5	26.3	67
C3	7.8	260	5.1	7.6	35.5	76
C7	8.7	230	5.8	8.5	33.4	83

Fluid Swells

The water-swell tests show that there is no difference between the metal oxides when it comes to crosslink density. The CaO formulations absorbed less water than did the MgO formulations after 70 hours (Figure 10), but after 166 hours of immersion, the differences between the PBD/MA-modified M and C compounds were small (Figure 11). For elastomeric networks, water swell is directly related to crosslink density. Assuming this to be true for ionomeric networks as

well, we conclude that the crosslink densities for MgO and CaO networks are the same.

The ionomeric network formed by PBD/MA reacting with CaO is stronger than the one formed by PBD/MA reacting with MgO. The CaO-containing formulation consequently has stronger physical properties than the MgO containing formulation. The single drawback to using CaO rather than MgO is slower cure time.

Figure 10

166 Hour Water Swells, MgO vs. CaO in CPE

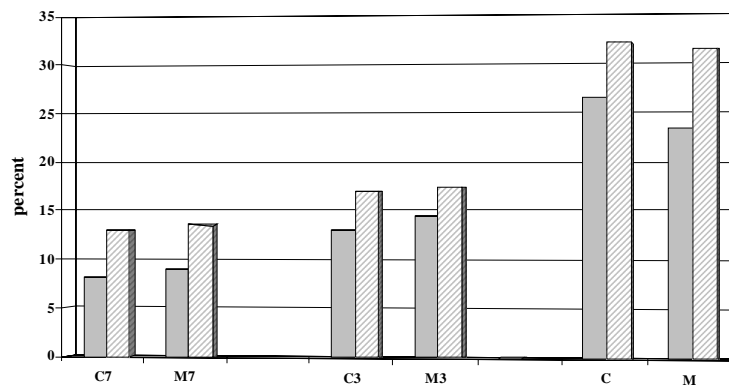
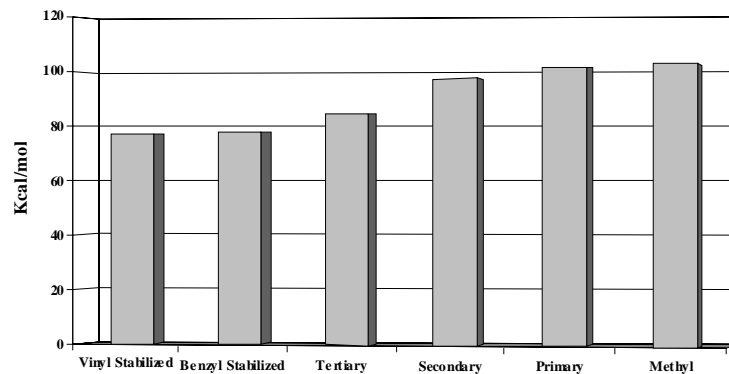


Figure 11

Bond Dissociation Energies of Free Radicals



CSM Elastomer

It is desirable to find a non-hazardous material which can replace lead in CSM compounds. Lead acts as an HCl scavenger, stabilizer, and additive for moisture resistance in CSM. Two functionally adducted PBD materials were tested as possible replacements for lead, an epoxidized PBD (PBD/EP) and the same PBD/MA coagent tested in CPE. Both PBD/EP and PBD/MA were tested in peroxide-cured CSM. PBD/MA was also tested as a coagent in sulfur-cured CSM.

Peroxide-Cured CSM, Rheometer Properties

The control formulation contained 40 phr dibasic lead phthalate and was compared to formulations containing 20 phr dibasic lead phthalate with 20 phr PBD/EP half replacement, 40 phr PBD/EP full replacement, and 5 phr PBD/MA with 20 phr MgO (Table 19).

Table 19

Rheometer and Physical Properties of Lead-Substitute Compounds				
Compounds	Lead	PBD/EP 1/2	PBD/EP full	PBD/MA w/ MgO
Rheometer Data, ASTM D-2084				
Model: Tech Pro	Range: 100		Clock: 60 min.	
Die: Micro	Arc: 1°		Temperature: 177°C	
Min. Torque dNm	4.70	2.92	2.59	3.84
Max. Torque dNm	30.65	35.88	22.64	23.31
Scorch Time min.	2.50	1.83	2.25	1.67
Cure Time min.	16.17	14.83	25.42	30.83
Physical Properties, ASTM D-412				
Press Cure @ 177°C to T ₉₀				
Tensile MPa	8.7	12.1	9.1	7.9
Elongation %	475	280	275	470
100% Modulus MPa	3.5	5.1	4.3	3.7
200% Modulus MPa	6.1	10.4	8.0	6.4
Shore A Hardness pts.	76	76	77	83
Die C Tear KN/m	44.3	42.7	32.0	50.1

All of the formulations had comparable scorch times (Table 20). The PBD-modified formulations had lower maximum torque values than the control with the exception of the PBD/EP half-replacement formulation.

The PBD modified formulations also had longer cure times than the control except for the half-replacement formulation.

Table 20

Formulations Testing Possible Lead Replacements in CSM				
Compounds	Lead	PBD/EP 1/2	PBD/EP full	PBD/MA w/MgO
CSM	90.0	90.0	90.0	90.0
EPDM	10.0	10.0	10.0	10.0
EVA Resin	20.0	20.0	20.0	20.0
Dibasic Lead Phthalate	40.0	20.0	---	---
Calcined Clay	60.0	60.0	60.0	60.0
TiO ₂	5.0	5.0	5.0	5.0
Vinylsilane	1.0	1.0	1.0	1.0
Paraffin Wax	5.0	5.0	5.0	5.0
Antioxidant	1.0	1.0	1.0	1.0
Antiozonant	2.0	2.0	2.0	2.0
t-butylperoxy-diiso-propyl benzene, 40%	8.0	8.0	8.0	8.0
PBD/EP	---	20.0	40.0	---
MgO	---	---	---	20.0
PBD/MA	---	---	---	5.0

Peroxide-Cured CSM, Physical Properties

The PBD/MA formulation's physical properties were the most similar to the control's (Table 20). Its elongation and modulus strengths were very similar to the control's while its tear strength was higher, and its tensile strength was slightly lower. The most significant difference between the PBD/MA and control formulation is that the PBD/MA vulcanizate was 7 points harder (Shore A scale) than the control vulcanizate. The PBD/EP half-replacement formulation's physicals exhibited higher tensile, lower elongation, and subsequently higher modulus strengths than did the control. The PBD/FP full-replacement formulation also had lower elongation as well as higher modulus strength than the control's along with lower tear strength.

Peroxide-Cured CSM, Water-Swell Properties

The PBD/EP improved water-swell properties while the PBD/MA hurt the water-swell properties in comparison to the control's (Table 20). The PBD/EP half-replacement formulation had the lowest water-swell properties with a mass swell of only 1.01%. The PBD/EP full-replacement formulation followed with a mass swell of 1.36%, and the next lowest swell was obtained by the control with a mass swell of 1.76%. The water swells of the PBD/MA formulation were not in the neighborhood of these other formulations; its mass swell was 11.9%.

Sulfur-Cured CSM, Physical Properties

Further study explored the effect's of forming the PBD/MA-based ionomeric network in a sulfur-cured CSM,

since much of the CSM utilized in the w/c industry is sulfur-cured. The initial physical properties showed the potential to extend PBD/MA modified CSM formulations with additional fillers while maintaining physical properties. Extended formulations were milled and tested for physical properties. Table 21 shows all of the sulfur-cured CSM formulations.

The initial physical properties which prompted us to mill the extended formulations showed that PBD/MA in sulfur-cured CSM gave comparable physical properties to the control formulation's except that it gave higher elongation (665% vs. 605%) and higher tear strength (50.1 kN/m vs. 37.4 kN/m) (Table 22). This combination of properties often permits the addition of affordable fillers to reduce the cost of a formulation while obtaining the desired physical properties.

The two fillers whose levels were increased were CaCO₃ and hydrated alumina. In one formulation they were increased by 25%, and in a second they were increased by 50%. Increasing the filler levels caused a decrease in elongation and tensile strength, while increasing modulus strength and hardness (Table 22). While the tensile strength of the extended formulations was considerably lower than the control, the modulus strengths and tear strengths were superior to the control. So unless the formulation were to be used to the point of failure, the extended formulations could be used to replace the control.

Table 21

Sulfur-Cured CSM Compounds				
Compound	Control	PBD/MA	PBD/MA +25% flrs	PBD/MA +50% flrs
CSM	100.0	100.0	100.0	100.0
MgO	4.0	4.0	4.0	4.0
CaCO ₃	30.0	30.0	37.5	45.0
Hydrated Alumina	60.0	60.0	75.0	90.0
Plasticizer	20.0	20.0	20.0	20.0
TiO ₂	5.0	5.0	5.0	5.0
Paraffin Wax	5.0	5.0	5.0	5.0
LMWPE	3.0	3.0	3.0	3.0
Stearic Acid	2.0	2.0	2.0	2.0
Pentaerythritol	3.0	3.0	3.0	3.0
Ni Dibutylthiocarbamate	3.0	3.0	3.0	3.0
Dipentamethylene Thiuram	0.5	0.5	0.5	0.5
Hexasulfide				
m-Phenyl Dimaleimide	1.0	---	---	---
PBD/MA	---	3.0	3.0	3.0

Table 22

Rheometer and Physical Properties of Sulfur-Cured CSM Compounds				
Compound	Control	PBD/MA	PBD/MA +25% fillers	PBD/MA +50% fillers
Rheometer Data, ASTM D-2084				
Model: TechPro Range: 100 Clock: 60 min				
Die: Micro Arc: 1° Temperature: 177°C				
Min. Torque dNm	4.97	5.03	6.62	6.95
Max. Torque dNm	25.23	23.07	25.95	27.61
Scorch Time min.	1.33	1.42	1.42	1.33
Cure Time min.	22.50	23.08	24.67	23.75
Physical Properties, ASTM D-412				
Press Cure @ 177°C to T ₉₀				
Tensile MPa	11.5	10.0	8.7	8.1
Elongation %	605	665	630	575
100% Modulus MPa	1.9	2.3	2.8	2.9
200% Modulus MPa	2.9	4.0	4.7	4.9
Shore A Hardness pts	68	70	74	76
Die C Tear KN/m	37.4	50.1	49.9	49.4
Water Swell, Mass %	1.81	1.01	0.93	11.9
Water Swell, Vol. %	1.72	0.75	0.50	16.0

Conclusion

This research compared commonly utilized coagents primarily in w/c 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 coagent, trimethylolpropane trimethacrylate, and the Type II coagent, triallyl cyanurate. The PBD-modified compounds particularly excelled in heat-age, 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. PBD coagents do this via a highly stable radical. With increased radical stability, PBD coagents give better properties to those obtained with other coagents due to the superior suppression of competing reactions like beta scission and disproportionation. PBD is also less prone to homopolymerization than are the less stable Type I coagents and low molecular weight Type II-coagents.^{2,3,5,7}

Solid and liquid maleinized PBD (PBD/MA) were developed as coagents for halogenated elastomers during the course of this study. The PBD/MA coagent utilizes a dual approach to coagency. During

maleinization, portions of the PBD backbone become conjugated, increasing its already good propensity to act as a coagent. Also, during the vulcanization of chlorinated materials, the reaction of MA with metal oxides is catalyzed by the products of HCl scavenging. This reaction forms an ionic network which enhances the physical and electrical properties of a compound. These chemistries are responsible for the out-standing coagent properties obtained from PBD/MA materials in CPE. The stress-strain profiles of the PBD/MA formulations were completely different in shape from the curves of the control, TAIC, and TMPTMA formulations, indicating that unique mechanical properties are imparted to CPE by PBD/MA. This phenomenon is clearly a benefit to the CPE compounder.

In CSM, this same ionic network can be used to replace lead in peroxide-cured formulations. If it is used as such, water-swell properties are harmed, but ecological difficulties are alleviated. The PBD/MA can also be used to increase the level of fillers in sulfur-cured CSM, thus reducing the cost of a compound. PBD/EP also has the potential to serve as a lead replacement in CSM. If it is used as such, the authors

recommend that it be used in conjunction with a metal oxide when heat stability is an issue.

The competitive pricing of PBD coagents and the levels at which they must be used in order to obtain desired properties give them an economic advantage to go along with their performance.

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, physical properties, and electrical properties of their formulations.

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Appendix I		
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	A kro-Mag
	Bis (t-Butylperoxy) Diisopropylbenzene	Retilox F 40KE
	Zinc Oxide	Zinc Oxide
Alcoa	Hydrated Alumina	Hydral 710
Argus	Dilauryl Thiodipropionate	DLTDP
Honeywell Corporation	Low Molecular Weight Polyethylene	Polyethylene 1702
BASF	Antioxidants/Antiozonants	Irganox 1010
		Irganox 1024
C.P. Hall	Polyester Adipate	Paraplex G-50
	Diisononyl Phthlate	Plasthall DINP
	Calcium Oxide	Calcium Oxide HP
	Paraffin Wax	Paraffin Wax
Cytec	Triallyl Cyanurate	Cylink TAC Monomer
Evonik	Titanium Dioxide	Titandioxide P25
Dow Chemical	Chlorinated Polyethylene	Tyrin 0136
DSM/Copolymer	EPDM	Epsyn 55
Dupont	Chlorosulfynated Polyethylene	Hypalon 4085
	EPDM	Nordel 2722 & 2522
	m-Phenyl Dimaleimide	HVA-2
	Dipentamethylene Tiuram Hexasulfide	TETTRONE-A
	Ethylene Vinylacetate Resin	Elvax 40
E.C.C. America	Calcium Carbonate	Atomite
Eagle Picher	Red Lead	EP202
Engelhard - BASF	Calcined/Surface Modified Kaolin Clay	Engelhard
Hercules	Pentaerythritol	PE-200
Huber	Carbon Black	N550
Miles/Polysar	EPM	Polysar 306
	Ethylene Vinylacetate	Levapren 500 HV
	Styrenated Diphenylamine	Vulkanox DDA
Nippon Kasei Chem.	Triallyl Isocyanurate	TAIC
R.T. Vanderbilt	Polymerized Trimethyl Dihydroquinoline	AgeRite Resin D
	Nickle Dibutyldithiocarbamate	Vanox NBC
Cray Valley	1,2 Polybutadiene	Ricon [®] 154
	Maleinized 1,2 Polybutadiene	Ricon [®] 156MA17
	Epoxidized 1,4 Polybutadiene	Ricopoxy 30
	Metallic diacrylate	SR-633
Sun Oil Co.	Paraffinic Oil	Sunpar 2280
SynPro Ware	Dibasic Lead Phthalate	Dythal
Momentive	Vinylsilane	A-172
Uniroyal	EPDM	Royalene 580HT
Colonial Rubber milled the masterbatch formulations used in this study.		

Appendix II		
Test Methods and Equipment		
Test	ASTM D#	Equipment
Vulcanization Using Oscillating Disk Cure meter	2084	TechPro 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 Guage
Determination of swell in Liquids	471	Ames 202 Thickness Guage Sartorius Analytical Balance
The Impact Resilience of Rubber by Vertical Rebound	2632	Shore Resiliometer
Deterioration in an Air Oven	573	GCA/Precision CRE 500 Universal Tester Hotpack Digimatic Oven Model 213024
Durometer Hardnes	2240	Rex Durometer Model 1600
Standard Temperatures and Atmospheres for Conditioning and Testing	1349	

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