

Metallic Coagents for Rubber-To-Metal Adhesion

By Richard Costin* and Walter Nagel

Cray Valley USA, LLC
Exton, Pennsylvania
USA

INTRODUCTION

We have previously reported on the use of metallic coagents as crosslinkers for peroxide cured elastomers⁽¹⁾. The metallic coagents are effective crosslinkers for both saturated and unsaturated elastomers and can be used over a wide concentration range to tailor mechanical properties for a variety of applications. We have now found that, in addition to improving mechanical properties, they also significantly increase adhesion of the vulcanized rubber-to-metal substrates.

Conventional metal reinforced rubber products require both an adhesive to bond the metal to the rubber and a separate curing system to increase the mechanical properties of the rubber. This entails an intensive, time-consuming series of procedures: first the metal surface has to be prepared, then the adhesive has to be applied and dried; next the elastomer compound has to be prepared. The product is then molded and cured, and finally, post-cure treated.

In contrast, the metallic coagents yield stronger rubber-to-metal bonds without the use of external adhesives or a separate curing step. Instead, the rubber compound is simply prepared with the coagents and cured against the metal surface. During curing, metallic coagents develop adhesive bonds at the metal-rubber interface, while simultaneously producing crosslinks in the rubber.

The metallic coagents discussed in this paper are zinc diacrylate and zinc dimethacrylate, which are commercially available under the trade names of SR633 and SR634, respectively.

EXPERIMENTAL

Materials

A masterbatch containing 100 phr Hycar 1042, 65 phr N365 carbon black, 15 phr dioctyl phthalate, 5 phr zinc oxide and 1 phr stearic acid was used in all experiments pertaining to nitrile rubbers. Hycar 1042 was supplied by Zeon Chemicals and is a general purpose nitrile rubber with good processing characteristics and high physical properties.

A masterbatch containing 100 phr Nordel 1040, 100 phr N762 carbon black, 50 phr Sunpar 2280, 5 phr zinc oxide and 1 phr stearic acid was used in all experiments related to EPDM rubbers. Nordel 1040 was obtained from the DuPont Company.

Hypalon and ethylene vinyl acetate copolymer were obtained from the DuPont Company; silicone rubber was obtained from General Electric; and natural rubber was obtained from the Malaysian Rubber Bureau.

The zinc salts of acrylic acid and methacrylic acid were supplied by the Cray Valley Company. The scorch retarded versions of zinc diacrylate and zinc dimethacrylate are marketed by the Cray Valley Company under the tradenames of SR633 and SR634, respectively.

Formulations

The rubbers were compounded according to the formulations given in Tables 1-8 using a laboratory six-inch two roll mill. The masterbatches described above were masticated on a two roll mill until a flux was created at the nip of the rollers. At this point, the Agerite Resin D, dicumyl peroxide and coagent were slowly added to the flux roll. The band was then sheeted and folded and then rebanded for mixing. This process was repeated many times to ensure thorough mixing. The coagent concentration was varied as noted. The compounded rubbers were then cured in a chelsea mold for twenty minutes at 160°C-166°C.

Table 1

Aged Lap Shear Adhesion, Mpa
EPDM To Cold Rolled Steel
10 phr SR633

Unaged Control	8.0
Heat Age 300°F	
96HR	8.3
165HR	8.5
Water Submersion, 70°F	
66HR	8.6
165HR	7.9

Table 2

Physical Property Comparison in EPDM

Nordel 1040 (1)	100	100	100
N762 Black	100	100	100
Sunpar 2280 (3)	50	50	50
Zinc Oxide	5	5	5
Stearic Acid	1	1	1
Agerite Resin (4)	1	1	1
DiCup 40 KE (5)	7.5	7.5	7.5
TMPTA SR-351	10	—	—
SR633	—	10	—
SR644	—	—	10
Scorch TS, min.	1.4	1.7	3.2
TC (90) min.	6.4	6.8	11.1
Tensile, PSI	1000	1240	1190
Elongation, %	680	710	820
Modulus ₁₀₀ PSI	140	180	150
Shore A Hardness	56	57	56

(1) DuPont EPDM

(2) SRF Furnace Black

(3) Sun Oil Company Plasticizer

(4) Monsanto Company, Antioxidant

(5) Hercules, Inc., Dicumyl Peroxide

Table 3Formulation for
Ethylene Vinyl Acetate Copolymer

<u>MATERIAL</u>	<u>PARTS</u>
Elvax 240	100
HI SIL 230	25
Zinc Oxide	3
Stearic Acid	3
Tris (2-Ethylhexyl)	
Tri Mellitate (TOTM)	3
Perkadox 1440	2
SR633	3

Table 4

Formulation for Sulfur-Cured EPDM Rubber

<u>MATERIAL</u>	<u>PARTS</u>
Nordel 1040	100
N762 Black	100
Sunpar 2280	50
Zinc Oxide	5
Stearic Acid	1
Agerite Resin D	1
Sulfur	1.5
TMTM	1.5
MBT	0.5

Table 5

Formulation for Silicone Rubbers

<u>MATERIAL</u>	<u>PARTS</u>
GE 6140	100
GE 6916 HA Stabilizer	1
Triganox 101-45	2
SR633	10
Cure, 166°C, 20 minutes	

Table 6

Formulation for Natural Rubber

<u>MATERIAL</u>	<u>PARTS</u>
SMR5CF60 NR	100
Sunthene 4240	3
Zinc Oxide	4
HI SIL 233	5
N660 Black	20
Trimethyldihydroquinoline	2
Stearic Acid	1
Dicumyl Peroxide 40 KE	5
SR633	10
Cure, 160°C, 20 minutes	

Table 7

Formulation for Hypalon

<u>MATERIAL</u>	<u>PARTS</u>
Hypalon 40	100
T (HRL) D-90 (Polydispersion)	44
N990 Black	22
N550 Black	5
Whitetex Clay	40
Kenflex A	20
Sundex 790	15
Paraffin Wax	6
Dicumyl Peroxide 40 KE	5
SR633	5

Table 8

Formulation for EPDM Rubbers

<u>MATERIAL</u>	<u>PARTS</u>
Nordel 1040	100
N 762 Black	100
Sunpar 2280	50
Zinc Oxide	5
Stearic Acid	1
Agerite Resin D.	1
DiCup 40 KE	5
Coagent	0-20

The remaining formulations were compounded in a similar manner to the masterbatches with the dicumyl peroxide being added last.

Measurement

Physical tests were conducted for all molded compounds after molding and again after heat aging at 100°C for 70 hours. Tensile strength, modulus and elongation were determined according to ASTM method D-412 using a Thwing Albert model 1451-42 tensile tester at a crosshead speed of 20 in/min.

Shore A hardness tests were determined for samples after molding using a hand-held Shore A durometer.

Cure characteristics which include scorch time, cure rate and torque values were measured over a twenty minutes period at 160°C using a Monsanto oscillating-disk rheometer according to ASTM method D-1084.

Compression set was determined by compressing a one inch diameter specimen built up with four plies to 50% original thickness for 22 hours at 100°C. The specimen was then removed and the permanent set measured as a percentage of original thickness (ASTM D395).

Rubber-to-metal adhesion was determined by tensile testing a rubber specimen cured between two metal coupons. The tensile test was run at 1.0 IPM cross-head speed and the force in pounds to break the lap joint in shear was measured. The rubber specimen,

approximately 0.030 inch in thickness, was cured at 160°C-166°C for 30 minutes between two 1x3x.030 inch metal coupons overlapped 1.0 inch in a plaque mold under 30,000 PSI pressure. The metal coupons were methanol washed and dried before curing.

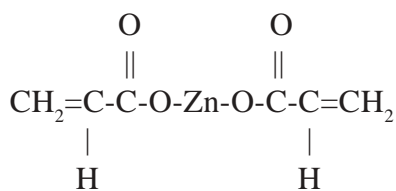
Adhesion peel tests were run by curing a 1/4 inch thick rubber specimen against a metal coupon and then tensile testing at 180°C with 1.0 IPM crosshead speed. The rubber specimen was hand-pressed against the metal coupon.

RESULTS AND DISCUSSION

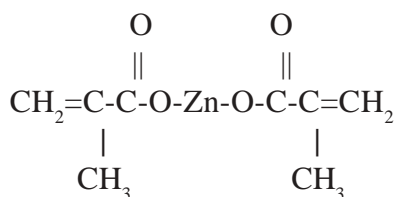
Physical Properties

SR633 and SR634 are the difunctional zinc salts of acrylic acid and methacrylic acid as shown in Figure 1.

Figure 1
Metallic Coagents*



[Zinc Diacrylate]



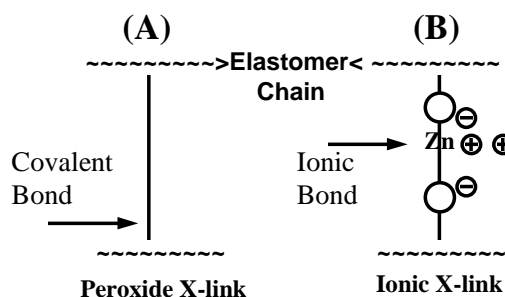
[Zinc Dimethacrylate]

*Coagents contain non-nitroso scorch retarder.

They are free-flowing, 100% reactive solids that can be readily compounded with a variety of elastomers. They exhibit excellent high temperature stability as well as outstanding fluid-resistance. They derive many of their unique physical and mechanical properties from the ionic bonds that are formed between the zinc cations and the carboxylate anions.

Metal cations, particularly zinc, are known to increase the mechanical properties of metal-neutralized ionomers by forming ionic crosslinks⁽²⁾. The same ionic crosslink mechanism is believed to occur with elastomers that are cured with SR633 and SR634, and is illustrated in Figure 2.

Metallic Coagent Cure



Crosslinking with peroxide results in the formation of a covalent bond as shown in (A) of Figure 2. This carbon-carbon bond is quite rigid and stable, and accounts for the lower tensile and tear strength of peroxide-cured stocks compared with sulfur vulcanates. The good heat stability of this covalent bond also explains the superior heat-aged characteristics of peroxide-cured systems.

In contrast, polysulfide crosslinks formed in sulfur cure are thermally weak but are mobile under stress and can slip along the hydrocarbon chain. This mobility has been used to explain the superior tensile and tear strength in sulfur-cured stocks.

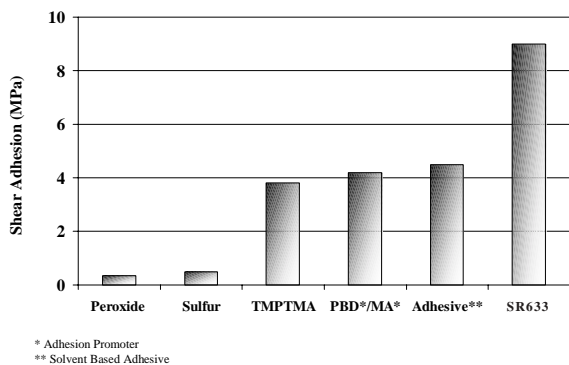
The metallic coagent-peroxide crosslink bond is “ionic” as shown in (B) of Figure 2. This ionic bond exhibits both good heat-aged stability and the ability to slip along the hydrocarbon chain and reform. Thus, this unique system embodies the best characteristics of both the peroxide and sulfur crosslink systems, giving high tensile and tear strength and excellent heat-aged properties.

Adhesion

The data in Figure 3 shows the lap shear adhesion of SR633 versus solvent-based adhesives, commercial adhesion promoters and conventional sulfur and peroxide cure systems for bonding EPDM to steel. In

an effort to compare each adhesive system on an equal basis, the EPDM in each case was formulated and cured to a 56 Shore A hardness. It is normally very difficult to bond EPDM to most metals without extensive metal cleaning and the use of solvent-based adhesives. This is illustrated in Figure 3 with low adhesion for the samples cured with either sulfur or peroxide alone. As expected, an improvement in adhesion was obtained when either a polar coagent, a commercial adhesion promoter or a solvent-based adhesive was used with the peroxide cure formulation. SR633, without any special metal treatment, is clearly superior to all other materials tested.

Figure 3
EPDM Adhesion to Steel 56 Shore A Hardness



The SR633 cure system also promotes good adhesion to other untreated metals including aluminum, zinc and stainless steel (Figure 4). The effect of SR633 concentration on EPDM to these metals is shown in Figure 5. Adhesion increased rapidly as the SR633 concentration was increased from 0 to 20 phr. This means that strong adhesive bonds can be created economically at low coagent levels.

Figure 4
EPDM Adhesion

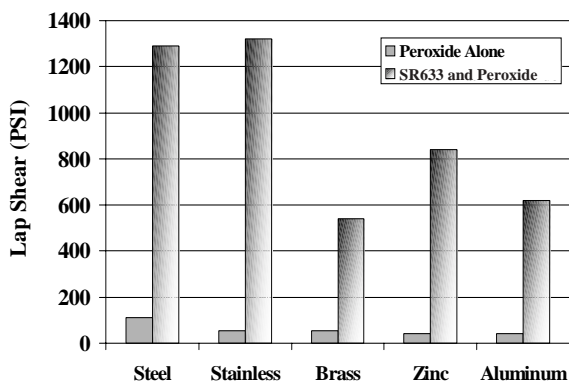
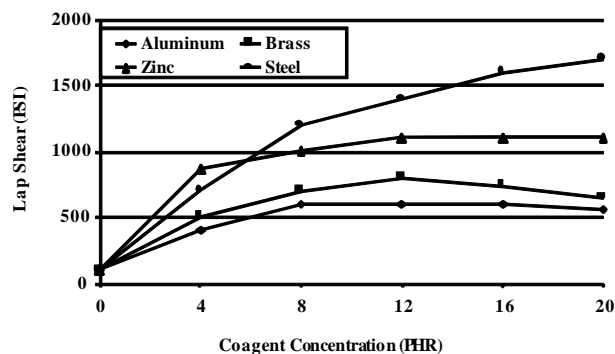
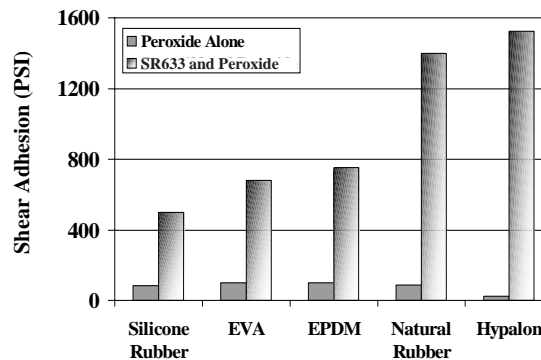


Figure 5
EPDM Adhesion
Effect of SR633 Coagent Concentration



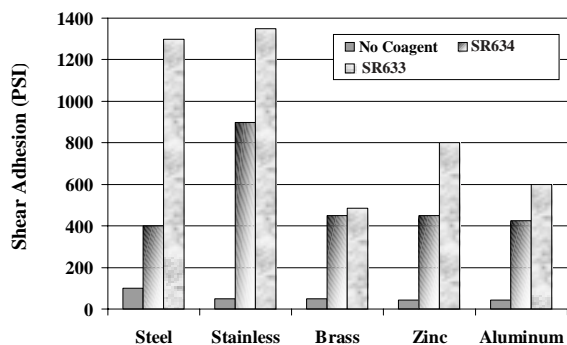
Strong rubber-to-metal bonding can be obtained with SR633 for a variety of rubbers as shown in Figure 6 for silicone rubber, EVA, EPDM, natural rubber and Hypalon. In each case, shear adhesion is significantly increased with the SR633 cure system over the peroxide control. Cohesive failure is the predominant mode of failure in each rubber compound.

Figure 6
Rubber-To-Steel Adhesion



SR634, while not as effective as SR633, also increases rubber-to-metal adhesion in peroxide-cured elastomers as illustrated in Figure 7. In applications where high tear strength, abrasion resistance, exceptional scorch safety and slow cure are needed, SR634 can be used. Metallic monomers based on other metal salts, such as calcium and magnesium, also increase rubber-to-metal adhesion, but not to the extent that SR633 and SR634 do.

Figure 7
EPDM Adhesion to Metals



Aged Adhesion

The SR633 rubber-to-metal adhesive bond remains strong even when exposed to heat and moisture. Table 1 shows no deterioration in lap shear strength under heat aging at 300°F and submersion under water at room temperature for 165 hours.

Mechanical Properties

The mechanical properties of rubber cured with SR633 and SR634 are superior to those obtained with conventional coagent systems. The SR634 is noted for its elongation and tear strength, while SR633 gives excellent tensile strength and modulus as shown in Table 2.

Compounding and Curing

The SR633 and SR634 coagents can be mixed with most rubbers using a two roll mill or a Banbury internal mixer. Curing the resulting rubber compound against the metal substrate creates the adhesive bond as well as the mechanical properties of the rubber. For example, the EPDM formulations described in Table 2 were mixed on a two roll mill and sheeted out to a thickness of 0.03 inches. Strips of the rubber sheeting

were then placed between the appropriate metal panels and cured in a compression mold for 20 minutes at 330°F. The shear adhesion values and the mechanical properties reported in this bulletin were determined according to ASTM test methods D816-55 and D412-80, respectively.

CONCLUSIONS

Based on the data reported in this paper, it is evident that SR633 and SR634 can be used to create extremely strong adhesive bonds between a variety of rubbers and untreated metal substrates. The metallic coagents are readily compounded into the rubber stock where they crosslink into the rubber when cured with peroxides. Thus, they function as adhesion promoters as well as crosslinkers to enhance both the adhesive and mechanical properties of the cured rubber. SR633 is the best coagent for adhesion, but SR634 is good alternative when abrasion resistance and tear strength is needed in addition to adhesion

ACKNOWLEDGMENT

The authors, Richard Costin and Walt Nagel, would like to acknowledge the many contributions of Gary Ceska and Al Tuccio in developing this technology. This paper was presented at the Rubber Division, American Chemical Society in Pittsburgh, PA., October, 1994.

REFERENCES

1. Richard Costin, Walter Nagel and Raymond Eckwall, Rubber Division Meeting, American Chemical Society, Washington, DC., October 9-12, 1990
2. H. Xie and Y. Feng, *Polymer*, 29, 1216, July (1988).