CRAY VALLEY
A BRAND OF TOTAL

Blending Specialty Coagents for Improved Rubber Compound Performance

Benefits

- Increased crosslink density
- Rubber adhesion while optimizing compression set
- Improved tear properties at high modulus
- Improved flexural fatigue properties
- Ultra-high hardness while minimizing migration/blooming of coagent
- Moderate scorch safety while maintaining modulus and compression set

Suggested Applications

- Cured-in-place adhesion to metal or reinforcing textiles (e.g., belts and hoses)
- High-hardness compounds (e.g., rubber rollers, engineered products)
- Peroxide-cured compounds demanding high tear or flexural fatigue (e.g., vibration mounts, belts, tires)

Additional Information

SDS: Dymalink® 633, Dymalink® 634, Ricon® 154

Description

Multifunctional coagents are used to modify the cure kinetics and ultimate physical properties of elastomers cured with organic peroxides. Total Cray Valley offers several high-quality coagents, each having unique structure-property relationships. Among these are Dymalink® series metallic coagents and Ricon® 154 polymeric coagent (Table I).

Table I: Coagent types evaluated in this update.

Type	Total Cray Valley Coagents	
I	Dymalink 633	Zinc diacrylate (solid)
I	Dymalink 634	Zinc dimethacrylate (solid)
II	Ricon 154	High vinyl polybutadiene (liquid)
	Controls	
I	TMPTA	Trimethylolpropane triacrylate (liquid)
II	TAIC	Triallyl isocyanurate (liquid)

CRAY VALLEY
A BRAND OF TOTAL

It is possible to achieve significant enhancement in elastomer performance by carefully selecting an appropriate coagent. However, improvements in certain physical properties may come at the expense of others. For example, it is not uncommon for physical property specifications to be gained at a loss of processing characteristics.

By blending certain classes of coagents, it may be possible to optimize physical properties that might otherwise be mutually exclusive if only working with a single coagent. In addition, coagent blends may allow for both physical property and processing improvements. Examples provided below will demonstrate how metallic and liquid (meth)acrylate esters can be blended to optimize a variety of physical properties.

Total Cray Valley's metallic monomer coagents Dymalink 633 (DL633) and Dymalink 634 (DL634) are often selected to promote adhesion of rubber to polar substrates (metal, textiles) or to improve the tear and dynamic properties of the compound. However, the unique structure and cure mechanism of these coagents can negatively impact compression set. Replacing part of the coagents loading with a liquid monomer (TMPTA, TAIC, HVA-2) will retain adhesion or dynamic properties at an acceptable level while improving compression set.

TMPTA/Dymalink 634

A model EPDM formulation cured with coagents and peroxide (Table II, Appendix) was used to demonstrate trends in physical properties across the spectrum of TMPTA/DL634 blend ratios. Total coagent loading was held constant at 10 phr, which resulted in a 100% modulus of nearly constant value (2.60 +/- 0.7 MPa, Figure 1). Results are shown below as a function of percent DL634 in the coagent blend.

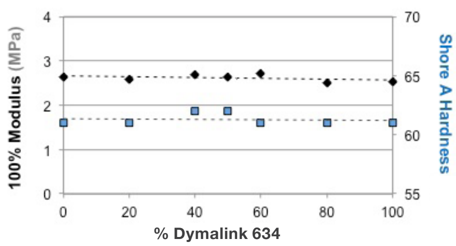

Figure 1: 100% modulus and hardness can be maintained regardless of Dymalink 634 concentration in the coagent blend.

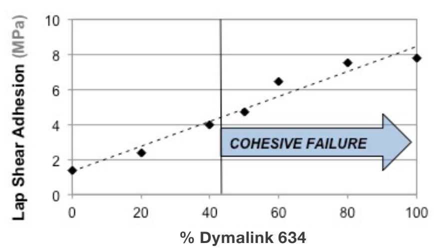

Figure 2: Lap shear adhesion can be dramatically improved with only 40% of Dymalink 634 in blend with TMPTA in peroxide-cured EPDM.

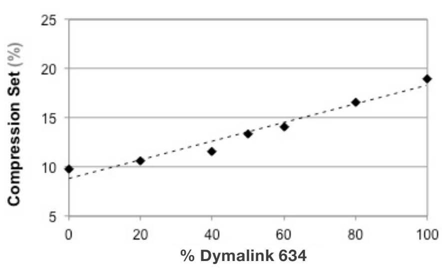

Figure 3: Effect of increasing Dymalink 634 loading in the coagent blend on compression set in peroxide-cured EPDM.

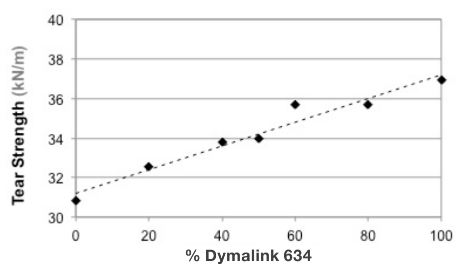

Figure 4: Effect of increasing Dymalink 634 loading in the coagent blend on tear strength in peroxide-cured EPDM.

Adhesion (Figure 2) was maintained even with reduced levels of liquid monomer (~60% TMPTA), which provide improved compression set (Figure 3). Tear strength (Figure 4) was also improved with DL634 loading while maintaining modulus and hardness (Figure 1). The results show a predictable relationship between coagent blend ratio and physical properties. Through judicious selection of blend components and ratio, the specified physical properties of the compound may be optimized.

TMPTA/Ricon 154

Most acrylate and (meth)acrylate ester liquid coagents have very limited solubility in hydrocarbon rubber and can migrate to the surface – a phenomenon also known as "blooming." Blooming is especially common when a compound contains elevated levels of polar coagent. Substituting part of the coagent loading with a polymeric Type II coagent (Ricon 154) may help alleviate blooming effects while maintaining hardness and other physical properties, and extending scorch safety, as the diene-based polymeric coagent is much more soluble in the rubber compound than the liquid coagent. As a result of improved compatibility with hydrocarbon rubber, excellent surface characteristics can also be observed when using Ricon 154 in the blend.

The same model EPDM formulation was used to evaluate TMPTA/Ricon 154 blend at 10 phr total coagent loading. Again, modulus was constant (2.83 +/- 0.2 MPa) as TMPTA was replaced with Ricon 154. As the percentage of Ricon 154 was increased in the blend, uncured shear modulus (Figure 5) is maintained (processing) and aged surface characteristics are improved. Scorch time (Figure 6) was greatly increased with increasing Ricon 154 content, while tensile and compression properties (Figure 7) were largely maintained. Results are shown below as a function of percent Ricon 154 in the coagent blend.

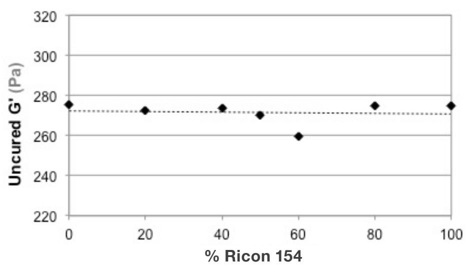

Figure 5: Effect of increasing Ricon 154 loading in the coagent blend on processing characteristics (uncured G' modulus) in peroxide-cured EPDM.

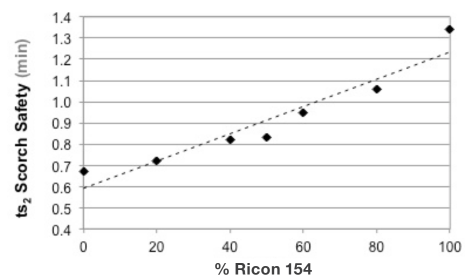

Figure 6: Effect of increasing Ricon 154 loading in the coagent blend on scorch safety in peroxide-cured EPDM.

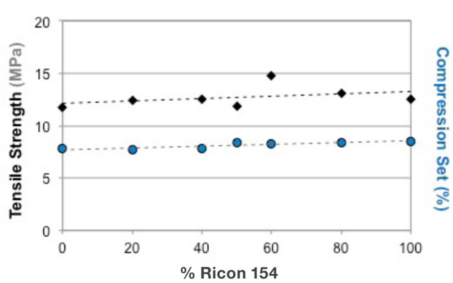

Figure 7: Effect of increasing Ricon 154 loading in the coagent blend on tensile strength and compression set in peroxide-cured EPDM.

TAIC/Dymalink 633

Curing FKM-type elastomers can pose a challenge due a limited number of allylic hydrogen atoms available for abstraction during peroxide vulcanization. TAIC is commonly used in FKM peroxide cure to obtain low compression set values and build modulus. However, it is hard to achieve adequate adhesion when using TAIC alone, especially with FKM rubber. In this example, a model FKM compound (Table III, Appendix) (HFP-VF-TFE terpolymer) was used to demonstrate how adhesion to metal (Figure 8) can be considerably improved with Dymalink 633 metallic coagent comprising only 25% of the coagent blend (5 phr total coagent loading) without having any significant impact on 100% modulus (Figure 9). Low compression set and delta torque (Figure 10) were also unaffected at up to 25% of DL633 in the blend.

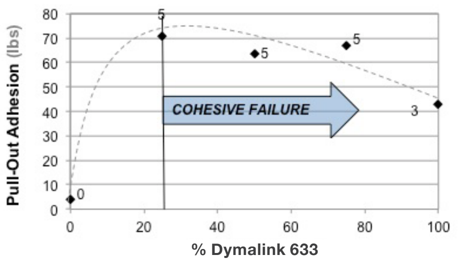

Figure 8: Pull-out adhesion force of a model FKM compound cured with Dymalink 633/TAIC coagent blend and dicumyl peroxide. Numbers above data points indicate rubber coverage after pull-out: 0 – no rubber coverage, 5 – complete rubber coverage.

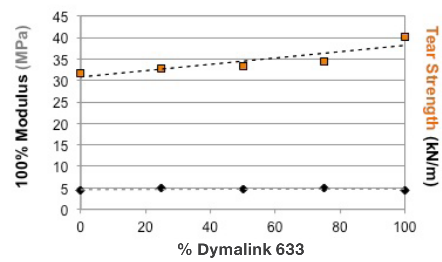

Figure 9: 100% modulus and tear strength of a model FKM compound cured with Dymalink 633/ TAIC coagent blend and dicumyl peroxide.

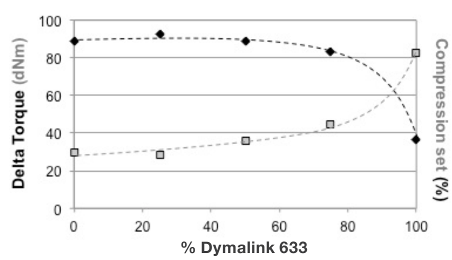

Figure 10: Delta torque and compression set properties of model FKM compound cured with Dymalink 633/TAIC coagent blend and dicumyl peroxide.

Summary

Coagents play an important role when it comes to attaining better physical properties in peroxide-cured elastomers. However, improving one property of an elastomeric compound without sacrificing others can be difficult, which is why a careful selection of coagent is critical to optimizing compound properties. By blending certain classes of coagents, a compounder can achieve a better balance of physical properties or improve upon cured properties without sacrificing cure or processing characteristics. Total Cray Valley provides a high-quality portfolio of Type I (Dymalink) and Type II (Ricon) coagents with a number of different high-performance products available for a variety of demanding applications where physical property optimization can be difficult.

Appendix

Table II: Model EPDM Formulation

Ingredient	phr
EPDM (Nordel™ IP 4640)[1]	100.0
Carbon black (N 660)	100.0
Oil (Sunpar® 2280)[2]	50.0
Stearic acid	1.0
TMQ (Naugard® Q)[3]	1.0
Coagent Blends	10.0
Dicumyl Peroxide (Di-Cup® 40KE)[4]	7.5

Table III: Model FKM Formulation

Ingredient	phr
FKM (Viton® GF-600S)[5]	100.0
Carbon black (MT 990)	30.0
VPA#2 (Processing aid)	1.0
Coagent Blends	5.0
Zinc Oxide	3.0
Varox® DBPH50[6] (45% actives)	3.0

[1]Nordel is a trademark of The Dow Chemical Company
[2]Sunpar is a trademark of Holly Frontier Corporation
[3]Naugard is a trademark of Addivant
[4]Di-Cup is a trademark of Arkema, Inc.
[5]Viton is trademark of DuPont™
[6]Varox is a trademark of Vanderbilt Chemicals, LLC

Table IV: Test Methods

Test	ASTM	Comments
Scorch Safety	D5289	ts_2
Tensile Modulus	D412	Die C
Tear Strength	D624	Die C
Compression Set	D395	100 °C, 22 hrs.
Hardness	D2240	Shore A
Processability	D6204	G' (8.33 Hz, 15%)
Lap Shear Adhesion	D816	Method B
Pull-Out Force	D2229	Brass/Steel

CRAY VALLEY
A BRAND OF TOTAL

About Total Cray Valley

Total Cray Valley is the premier global supplier of specialty chemical additives, hydrocarbon specialty chemicals, and liquid and powder tackifying resins used as ingredients in adhesives, rubbers, polymers, coatings and other materials. Total Cray Valley has pioneered the development of these advanced technologies, introducing hundreds of products that enhance the performance of products in energy, printing, packaging, construction, tire manufacture, electronics and other demanding applications.