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Reduced Zinc Loading:
Using Zinc Monomethacrylate to Activate
Accelerated Sulfur Vulcanization

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INTRODUCTION

Zinc is a ubiquitous component of rubber compounds cured by accelerated sulfur vulcanization. Early in the history of curing unsaturated rubber it was discovered that metal oxides can greatly improve the efficiency of sulfur-based cure systems, and the most useful metal oxide applied in the "activating" role is zinc oxide (ZnO). The role of zinc salts in accelerated vulcanization is thoroughly reviewed in a recent article.[1] Today, activators for sulfur cure are typically zinc salts of fatty acid carboxylates. Zinc stearate is the most popular activator used today, necessarily formed *in-situ* for optimum effect. Zinc species have been implicated in a number of intermediate reactions in the proposed mechanism of accelerated sulfur vulcanization, and are thought to influence scorch safety and the quantity and quality of the crosslinks formed. By influencing the structure of the cured network, zinc species can change physical properties such as hysteresis, abrasion resistance, and dynamic properties. Zinc salts of fatty acids are also used to improve the uncured processing characteristics of rubber compounds. The presence of zinc oxide is claimed to benefit aged properties in certain formulations by acting as an acid scavenger. Zinc may also play a key role in post-cure maturation of the sulfur network through initiation of desulfuration reactions.

Despite the beneficial role of zinc in the chemistry of sulfur vulcanization, there are questions regarding the impact of heavy metals on human health and ecological systems when they are released into the environment.[2] These environmental concerns have lead to discussion regarding potential governmental regulation of heavy metal compounds in rubber articles, and prompted many manufacturers to proactively evaluate strategies to reduce the amount of zinc in formulations. Technologies considered for reducing zinc levels include zinc oxide loading rationalization, the use of alternative zinc carboxylates,[3,4] activators based on other metal centers,[5,6,7] or new activators which either do not include heavy metals or use them sparingly.[8,9] In general, these strategies have at best shown no clear advantage over conventional zinc activation, or compromised the process safety or desirable physical properties inherent to zinc stearate activated cure systems.

Recently, zinc salts of methacrylic acid have been demonstrated to be a viable alternative to conventional zinc activators. Previous work has shown the monobasic adjuvant, zinc monomethacrylate (ZMMA, Resin Solutions Dymalink® 709), can improve upon the activating efficiency of *in-situ* derived zinc stearate.[10] In studies where Dymalink® 709 fully replaced ZnO as the activating species at molar equivalent loadings, crosslink density was increased resulting in higher tensile strength and modulus. Reversion resistance was also improved. The findings were consistent with results in earlier work which also incorporated zinc salts of methacrylic acid into sulfur-cured formulations and noted improvements in physical properties.[11,12,13,14,15] The data suggested that Dymalink® 709 activation results in more crosslinks of lower sulfur rank.

The present study expands upon earlier work through a more complete analysis of how sulfur crosslink formation is influenced by the presence of Dymalink® 709. Swelling experiments and chemical probe desulfuration studies confirm previous theories regarding the changes in the distribution of crosslinks in Dymalink® 709 versus ZnO activated cure. Dymalink® 709 is also compared to several other zinc salts of carboxylic acids in an attempt to determine structure-property relationships governing activation. The performance of Dymalink® 709 as an activating species is also studied as a function of the loading and relative ratio of sulfur and accelerator. Finally, the increased efficiency of activation is applied to various model formulations in order to demonstrate the potential for reductions in zinc content in a variety of applications.

EXPERIMENTAL

Materials

Synthetic poly(isoprene) (*cis*-PI, Natsyn 2205) was supplied by The Goodyear Tire and Rubber Company and natural rubber (NR, SMR CV 60) was supplied by Akrochem Corporation. Poly(butadiene) (*cis*-BR, Buna BR23) and solution poly(styrene-co-butadiene) (SSBR, VSL 5025-0 HM) were produced by Lanxess Corporation. Poly(acrylonitrile-co-butadiene) (NBR, Nipol 1052) was supplied by Zeon Chemicals. An N330-grade carbon black (Vulcan 3) was supplied

by Cabot, and precipitated silica (ZS 1165MP) was acquired from Rhodia. The silane coupling agent used, Z-6945 (50% active on carbon black) was supplied by Dow Corning. Aromatic oil (Sundex 790TN) was produced by Sunoco Inc. Polymerized 2,2,4-trimethyl-1,2-dihydroquinoline (Flexol TMQ) and N-isopropyl-N'-phenyl-p-phenylenediamine (Santoflex IPPD) antioxidants and the accelerators N-cyclohexylbenzothiazole-2-sulfenamide (Santocure CBS), N-t-butylbenzothiazole-2-sulfenamide (Santocure TBBS), diphenylguanidine (Perkacit DPG), and tetramethylthiuram disulfide (Perkacit TMTD) are commercial products of Flexsys America L.P. Rubbermaker's sulfur was provided by International Sulphur Inc.

The zinc oxide and stearic acid used in the study were supplied by Sigma-Aldrich Company. The ZnO grade was reported to have a surface area of 9 m2/g. Zinc acetylacetonate (Zn(AcAc)2) was provided by Sachem Europe B.V. and zinc 2-ethylhexanoate (ZEH) was supplied by Gelest Inc. Activator 73 (aryl zinc soap) is a product of Struktol Company of America. Zinc monomethacrylate (ZMMA, Dymalink® 709) and zinc diacrylate (ZDA, Dymalink® 705), are products of Resin Solutons Calcium dimethacrylate (CDMA), and magnesium dimethacrylate (MDMA) are experimental samples prepared by Cray Valley Company, Inc. All materials were used as supplied.

Rubber Compounding

Each compounded stock was mixed in a 350cc internal mixer with cam blades (Brabender Prep Mixer). Two-stage mixing was used for each compound. Non-productive stage initial conditions were 100ºC heating and 100 rpm mixing for 3 minutes after the ingredients were added. The productive stage used initial conditions of 60ºC and 60 rpm and mixing for 2 minutes. Compounded stock was passed on a two roll mill between stages and prior to testing.

Physical Testing

Cure kinetics and tensile properties. An oscillating die rheometer (ODR, TechPro rheoTech) was used to determine extent of cure and cure kinetics according to ASTM D 2084. The cure temperature used was 160ºC, using an arc deflection of 3º. Physical testing

was performed on samples cured in a press to t_{90} times (time to 90% of maximum torque, optimal cure) at the same temperature. Tensile, elongation and tear data was acquired on a tensile machine (Thwing-Albert Materials Tester) following ASTM D 412 and D 624.

Dynamic testing

A Dynamic Mechanical Analyzer (DMA 2980, TA Instruments) was operated in tension to obtain temperature sweeps of the cured vulcanizates from -100ºC to 100ºC at 11 Hz and 0.1% strain amplitude.

Crosslink density and sulfur rank distribution

Sulfur rank distributions were measured based on a published method using thiol cleavage agents.[16] Chemical probe reactions were conducted in the swelled state using toluene as the swelling agent. The crosslink density was calculated using Flory-Rehner methodology.[17] Filler loading was corrected by volume. The volume fraction of rubber in the swollen gel, V_r, is calculated by Equation 1. The effective number of chains in a real network per unit volume, n_e, is subsequently calculated according to Equation 2.

$$V_r = [m_0\phi(1 - \alpha)/\rho_r]/[\ m_0\phi(1 - \alpha)/\rho_r + (m_1 - m_2)/\rho_r] \qquad (1)$$

$$\nu_e = - [\ln(1-V_r) + V_r + \chi V_r^2]/[V_s(V_r^{1/3} - V_r/2)] \qquad (2)$$

Here m_0 is the sample mass prior to swelling, and m_1 and m_2 are the masses before and after drying of the swelled sample, α is mass loss during swelling, ϕ is the mass fraction of rubber in the sample, and ρ_r and ρ_s are the densities of the elastomer and solvent, χ is the polymer solvent interaction parameter and V_s the molar volume of solvent.

RESULTS AND DISCUSSION

Relative Activity of Zinc Monomethacrylate

Zinc salts have been recognized as activators of sulfur vulcanization since the early 1920s, when they were found to further improve the cure rate in combination with organic accelerators. In-situ formed complexes of zinc stearate from zinc oxide and stearic acid can improve the kinetics of unaccelerated sulfur vulcanization,[18] but are particularly effective when used with thiazole accelerators. It is believed that soluble

zinc can form complexes with accelerator fragments that, when reacted with sulfur, may form the active sulfurating agents. Figure 1 shows the commonly proposed structure of the active polysulfide complex.[19,20] The role of this structure as a crucial intermediate in forming sulfur crosslinks is supported by extraction studies[21] and NMR/HPLC analysis.[22]

Structure-property relationships of activator species

Previous work has demonstrated that the zinc salts of methacrylic acid can be used as activators. Cure analysis and the resulting physical properties of vulcanizates cured using Dymalink® 709 in place of ZnO demonstrate that the monomethacrylate salt is a much more efficient activator which produces a higher crosslink density. Figure 2 summarizes the results of replacing zinc oxide with Dymalink® 709 and Dymalink® 705 (ZDA) at molar equivalent loadings in a model *cis*-PI formulation. ZDA provided no apparent activation strength, as the cure kinetics are similar to the compound containing no zinc source. However, the zinc carboxylates based on methacrylic acid increased the apparent crosslink density of the compound significantly. Rheometer delta torque was nearly doubled when Dymalink® 709 was employed. As reported earlier, Dymalink® 709 also provided a considerable increase in scorch safety. The increase in scorch time may be related to differences between Dymalink® 709 and the other zinc salts in the intermediate reactions with the accelerator (TBBS) which lead to zinc-accelerator intermediates.[19,23]

Figure 3 provides a direct comparison of Dymalink® 709 with other available zinc salts. In a formulation based on NR, Dymalink® 709 was compared with $Zn(AcAc)_2$, ZEH, and commercially available aryl zinc soap. The zinc salts were all compared at 5 phr. It can be seen that the alternative zinc salts did not activate cure as efficiently when compared to Dymalink® 709 or ZnO. Again, Dymalink® 709 provided a measure

of scorch safety while increasing the overall crosslink density. The aryl Zn soap produced the least scorch resistance. The organic groups found on $Zn(AcAc)_2$ are structurally similar to Dymalink® 709, but $Zn(AcAc)_2$ was not an efficient activator of sulfur cure. $Zn(AcAc)_2$ has a significantly different chelate structure, based on b-ketone enolate ions. These results indicate that the steric size and binding strength of the methacrylic acid moiety to the metal center are likely the critical parameters in the efficiency of activation. The nature of the ligand in the resulting active sulfurating species is thought to strongly influence both the kinetics of crosslink formation and the final network structure. While Dymalink® 709 does have terminal unsaturation, additional crosslinks attributed to radical reactions involving the monofunctional monomer have not been detected.[10]

Other metal oxides and their fatty acid salts have also been considered as alternative activating systems. Calcium and magnesium oxide are two examples that have been evaluated previously. In the present study, samples of CDMA and MDMA were produced and compared to Dymalink® 709 and ZnO in a model *cis*-PI formulation. All metal salts were compared at 5 phr. The results are provided in Figure 4. Neither CDMA nor MDMA demonstrated measurable levels of activation. Consistent with other work comparing organic salts of various metal centers, zinc derivatives are the most effective activators.

Investigation of the network structure

The results of previous studies demonstrate that physical properties related to the number of the crosslinks formed and the sulfur rank distribution of the network were influenced by the application of Dymalink® 709 as the activator. Reversion and compression set were reduced compared to ZnO when measured at molar equivalent loading. The physical testing results provided circumstantial evidence that the sulfur rank distribution was altered.
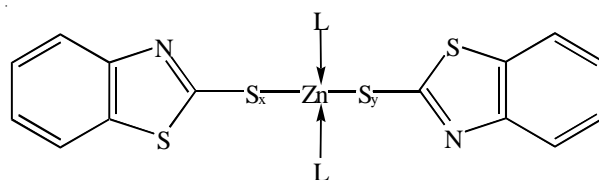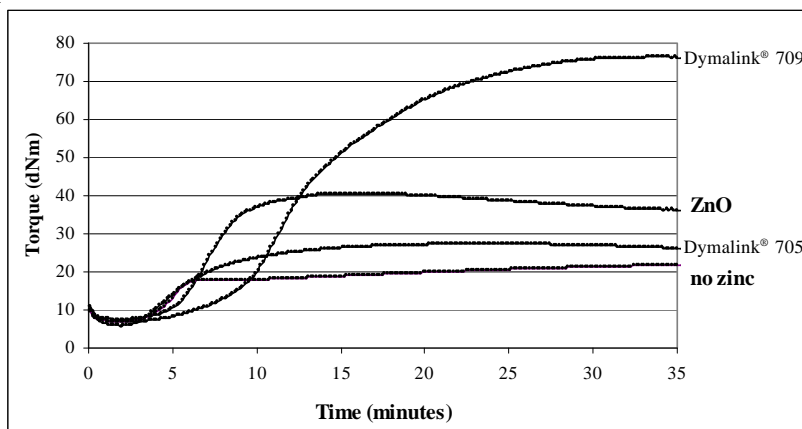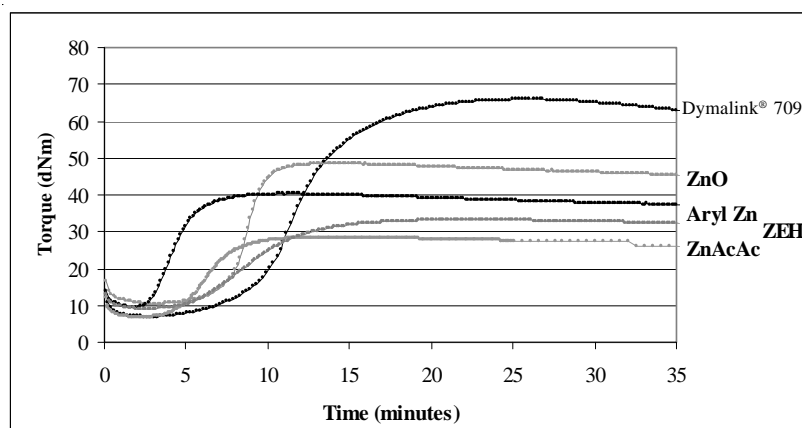

**Figure 1. MBT accelerator-zinc polysulfide complex; L represents a ligand.**

Figure 2. ODR results for various zinc species used as activators in a model *cis*-PI formulation. Molar equivalent loading of zinc equal to 0.063 moles/ phr (ZnO at 5.0 phr, Dymalink® 709 at 10.4 phr, and Dymalink® 705 at 12.8 phr).

Figure 3. ODR results for various zinc species used as activators in a model NR/*cis*-BR formulation. Activating species were present at 5 phr.
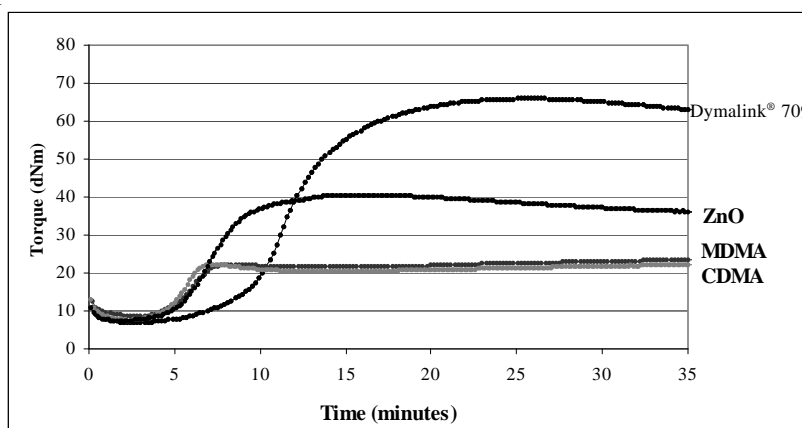
Figure 4. ODR results for CDMA and MDMA compared to Dymalink® 709 and ZnO as activators in a model *cis*-PI formulation. Activating species were present at 5 phr.

The current work compared Dymalink® 709 and ZnO in a model NR/*cis*-BR formulation and quantifies the influence of the activating species on crosslink density and structure. A model sidewall formulation was used to determine the actual crosslink density from swelling experiments and further determine the sulfur rank distribution through chemical probe desulfuration. Figure 5 summarizes the ODR data comparing Dymalink® 709 and ZnO as a function of loading. As demonstrated in other formulations, Dymalink® 709 provided increased apparent crosslink density. Hardness, tensile strength and modulus were predictably increased for the Dymalink® 709 containing vulcanizates.

The vulcanizates prepared above (NR/*cis*-BR formulation) were subjected to swelling experiments. Figure 6 contains the comparative results of total crosslink density for Dymalink® 709 and ZnO prepared networks. The results are consistent with ODR data. At a given activator loading, Dymalink® 709 provided significantly higher crosslink density. The density of the Dymalink® 709 activated compounds increased with loading, and was consistently higher than ZnO at a given loading.

The compounds investigated were formulated with identical loadings of sulfur and accelerator, such that only the activating species could effect changes in crosslink formation. For a given amount of sulfur loading, a higher crosslink density necessitates changes in the sulfur rank distribution. Figure 7 quantifies the relative changes in the sulfur rank distribution as a function of activator species and loading of the compounds by using chemical probe techniques. The expectation for ZnO activated compounds in a conventional vulcanization system (high sulfur to accelerator ratio) is for a majority of polysulfidic crosslinks to be formed.[24] In the current analysis, ZnO activation resulted in a network containing approximately 60% polysulfidic crosslinks, and the distribution of sulfur ranking did not significantly change with ZnO loading. In comparison, the application of Dymalink® 709 as an activating species produced significantly different distributions. In accordance with the increased crosslink density from Dymalink® 709 activation, the sulfur rank distribution shifted to a higher percentage of shorter crosslinks (mono- and disulfidic) as Dymalink® 709 loading was increased. At 2 phr Dymalink® 709, the distribution was similar to ZnO at 5 phr with a majority of polysulfidic linkages. However, as Dymalink® 709 loading increased, the population of monosulfidic linkages increased at the expense of polysulfidic such that at 10 phr Dymalink® 709 (the molar zinc equivalent of 5 phr ZnO) the distribution resembled what would be expected for an efficient cure system. Monosulfidic crosslinks comprised the majority, with disulfidic also representing a major population. It should also be noted that the disulfidic population was elevated in all the compounds using Dymalink®709, and was relatively constant with loading.

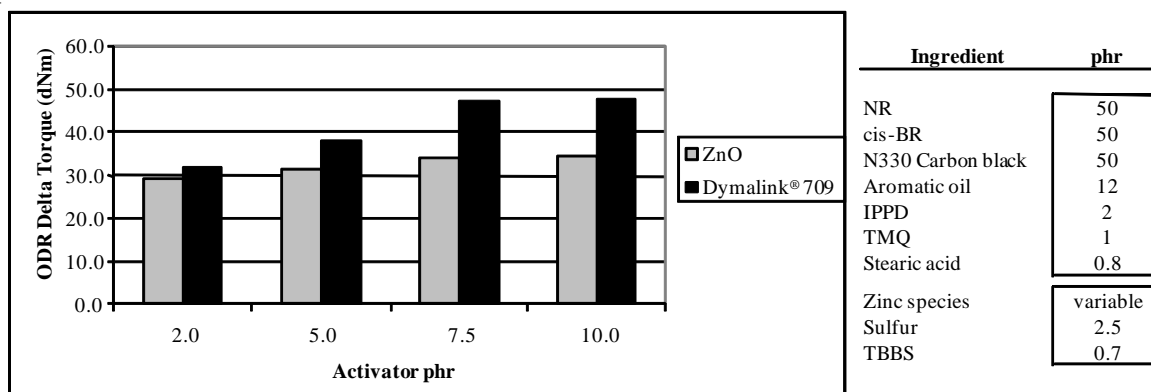| Ingredient	phr
NR	50
cis-BR	50
N330 Carbon black	50
Aromatic oil	12
IPPD	2
TMQ	1
Stearic acid	0.8
Zinc species	variable
Sulfur	2.5
TBBS	0.7

Figure 5. ODR results for Dymalink® 709 and ZnO at increasing loading in a model NR/*cis*-BR formulation.
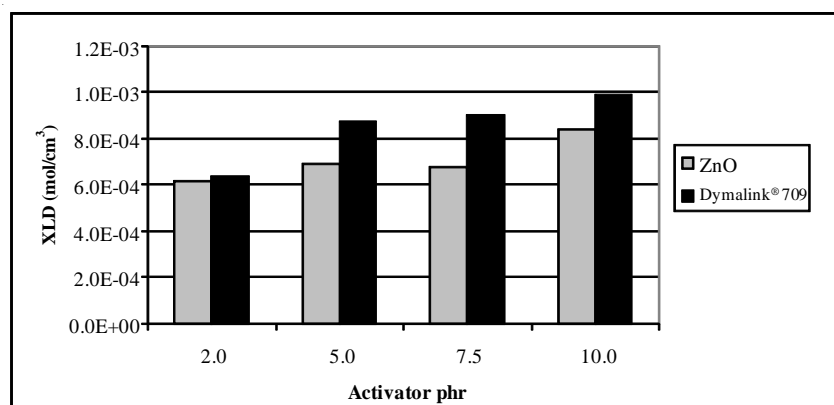
Figure 6. Crosslink density (XLD) as a function of loading for vulcanizates containing ZnO and Dymalink® 709 as activating species in a model NR/*cis*-BR formulation.
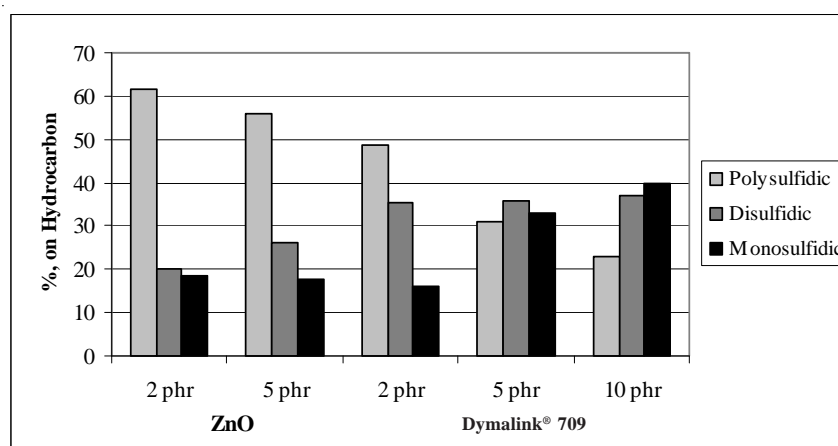

Figure 7. Sulfur rank distribution for vulcanizates containing ZnO and Dymalink® 709 as activating species in a model NR/*cis*-BR formulation. Data reported as a percentage on hydrocarbon content of compound.

ZINC REDUCTION POTENTIAL

As the efficiency of the activating species increases, there is potential to maintain the crosslink density in the vulcanizate at a lower concentration of zinc. The results suggest that there is an opportunity to reduce the amount of zinc in certain rubber formulations by taking advantage of both the increased activity and higher molecular weight of Dymalink® 709. Based on relative activation efficiency, there are opportunities to maintain physical properties of ZnO-activated vulcanizates at reduced levels of Dymalink® 709. In addition, the higher molecular weight of Dymalink® 709 results in a reduction of zinc level even at equivalent phr loadings of ZnO.

In the model formulations investigated above, it was demonstrated that at molar equivalent loadings

Dymalink® 709 increases the crosslink density when compared to ZnO. At a constant sulfur level in the cure package, the result is a shift in the sulfur rank distribution to mono- and disulfidic linkages. In contrast, a net reduction in zinc loading should be possible if the objective is to maintain a given crosslink density. Figure 8 compares the rheometer profiles for Dymalink® 709 as a function of increased loading in a model *cis*-PI formulation. A control compound using 5 phr ZnO is also included. Using the same model formulation, it was shown previously that addition of zinc oxide increased the rate and state of cure but only to a limiting value. In the given formulation, no additional benefit was seen by increasing the ZnO loading (with appropriate increase in stearic acid) from 5 to 10 phr.[10] There is prior evidence available supporting the finding

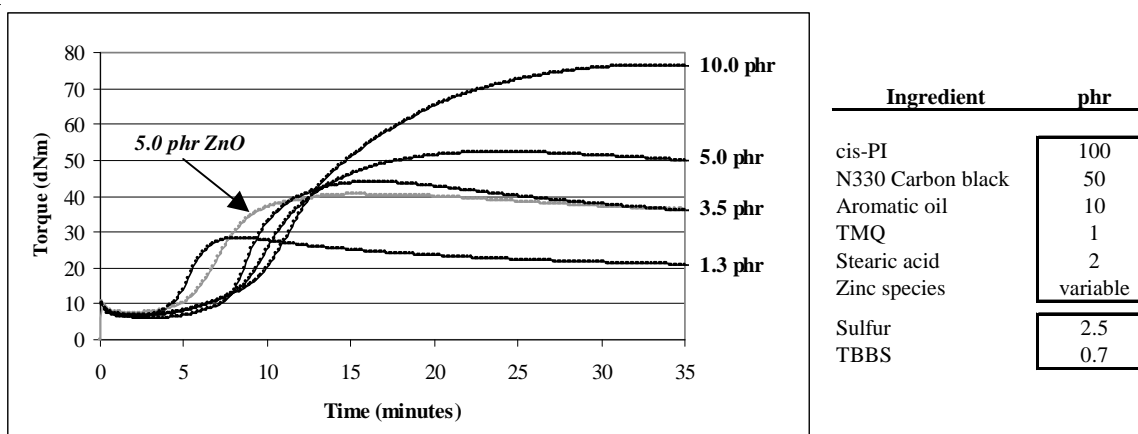| Ingredient	phr
cis-PI	100
N330 Carbon black	50
Aromatic oil	10
TMQ	1
Stearic acid	2
Zinc species	variable
Sulfur	2.5
TBBS	0.7

Figure 8. ODR results for Dymalink® 709 at increasing loading in a model *cis*-PI formulation. ZnO at 5 phr is provided as a control.

Formulation	Sulfur	TBBS	TMTD	Type
A	6.0	1.2		Conventional
B	3.5	0.7		Conventional
C	2.5	0.7		Conventional
D	1.2	1.6		Semi-Efficient
E	0.2	2.0	2.0	Efficient
F			5.0	Sulfur Donor

Table I. Characterization of the vulcanization systems investigated.

of a limiting concentration of zinc oxide beyond which cure state is no longer affected.[25] In the current study, delta torque increases consistently with Dymalink® 709 loading. Also, the cure profile generated using 3.5 phr Dymalink® 709 was similar to that of ZnO at 5 phr. The data suggests that a reduction in the phr loading of activator required to maintain cure state is possible. In addition, the loading reduction represents a significant molar reduction of zinc in the compound when the formula weights of ZnO (81 g/mol) and Dymalink® 709 (167 g/mol) are considered.

To adequately explore the potential for zinc reduction using Dymalink® 709 in place of ZnO, both activators were compared as a function of cure type at both equal phr loading (5 phr) and molar equivalent loadings (5 phr ZnO, 10 phr Dymalink® 709). A model formulation based on NR was utilized, and Table I outlines the vulcanization systems implemented in the study. Sulfur loading decreases through the series of cure systems (6.0 phr to 0 phr). The sulfur to accelerator ratio is also varied, such that conventional (CV), semi-efficient (S-EV), efficient (EV), and sulfur donor (SDV)

vulcanizations are represented.[26] Previous studies have explored the effect of sulfur to TBBS ratio on the resulting network structure at a constant ZnO (5 phr) activator level, and demonstrated the shift in crosslink structure at various sulfur to accelerator ratios.[27]

Figure 9 provides the delta torque (ODR) data from the formulations using molar equivalent loadings of activators in a model NR formulation. First, it is seen that overall apparent crosslink density decreased with decreasing sulfur loading. However, for the formulations incorporating ZnO, the crosslink density decreased quickly to a plateau. Comparative analysis of these trends indicates that Dymalink® 709 activation is most effective for CV and S-EV formulations which represent most standard rubber cure packages.

Figure 10 summarizes the data by comparing the difference in delta torque between Dymalink® 709 and ZnO in these formulations. The differentiation between the activators is maximized in CV and S-EV formulations with typical sulfur loadings (1-3 phr). In the formulation with elevated sulfur level, there was no

comparative difference. In low sulfur (EV) formulations, or those with no free sulfur (SDV), the benefit in crosslink density from a more efficient activator was also not realized. The mechanism for accelerated sulfur vulcanization predicts the zinc-accelerator intermediate, when reacted with free sulfur, forms the active sulfurating species. The stoichiometry of the three components (activator, accelerator, and sulfur) has been demonstrated to be a parameter which influences the kinetics of cure and the final network structure. It is proposed that at high sulfur loading, any contribution to vulcanization efficiency attributed to the activator is minimized by the excess of available sulfur in the system. Conversely, when there is little or no free sulfur to utilize, the differences due to the activator species are again negligible.

The potential to reduce the concentration of zinc in several model tire and engineered rubber product formulations will be demonstrated below. A typical activator loading of 5 phr ZnO was chosen for the control compounds in each case. Optimization of cured properties by altering the ZnO loading of the control was not in the scope of the present study. For each compound, Dymalink® 709 loading was varied in the same formulation to best match cured kinetics and ultimate physical properties of the given ZnO activated control.

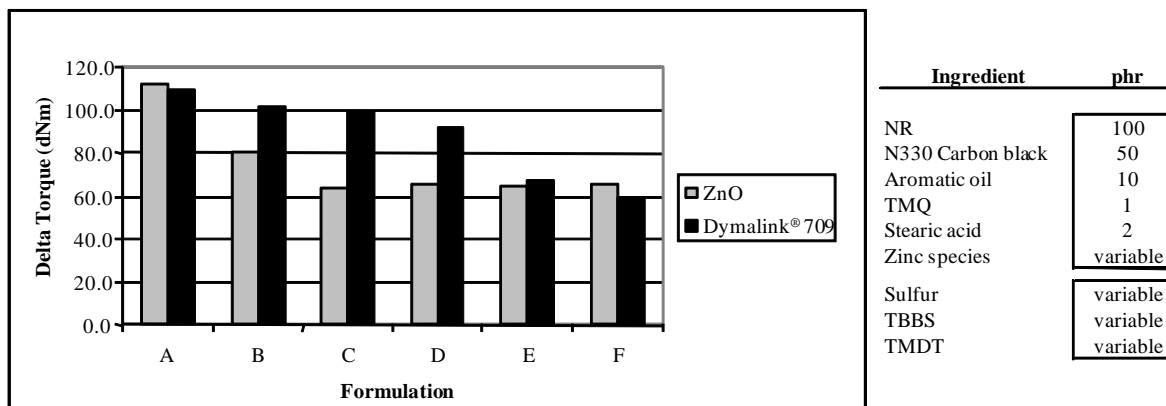| Ingredient	phr
NR	100
N330 Carbon black	50
Aromatic oil	10
TMQ	1
Stearic acid	2
Zinc species	variable
Sulfur	variable
TBBS	variable
TMDT	variable

Figure 9. ODR delta torque results for Dymalink® 709 and ZnO at molar equivalent loading as a function of vulcanization system in a model NR formulation.
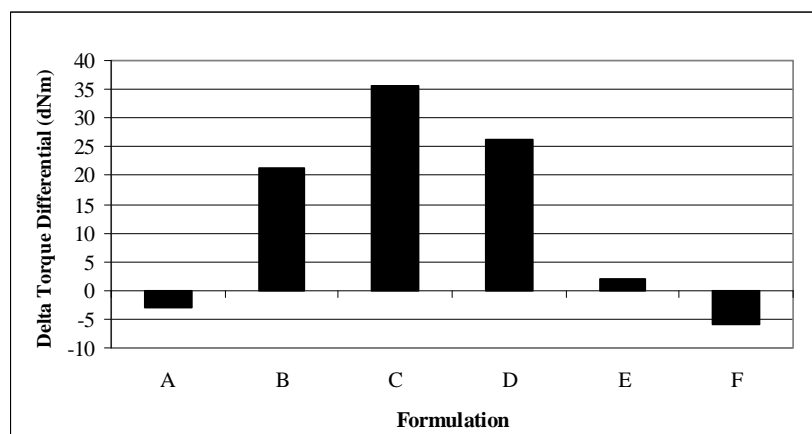

Figure 10. Differentiation in ODR delta torque results for Dymalink® 709 and ZnO at molar equivalent loading as a function of vulcanization system in a model NR formulation.

Model silica tire tread formulation

A model silica tread formulation containing both high vinyl SSBR and cis-BR was evaluated. The compound contains silane coupling agent and was mixed using conventional heat treatment techniques to promote hydrolysis of the silane and reaction with the silica filler surface. Table II contains the model tread formulation and the comparative results. Approximately 2.5 phr Dymalink® 709 was required to produce similar physical properties as 5.0 phr ZnO in the S-EV cure system. Apparent crosslink density (ODR delta torque), hardness, and modulus were similar. The Dymalink® 709 loading represents a 50% reduction in zinc on a phr basis, and a 75% reduction of zinc on a molar basis.

Dynamic properties of the compounds were also investigated. Figure 11 compares the tangent delta values of the ZnO and Dymalink® 709 activated compounds as a function of temperature under tensile strain (DMA). The results indicate that there appears to be a slight positive shift in peak tangent delta temperature when Dymalink® 709 is employed. Comparison of 0ºC tangent delta would suggest that Dymalink® 709 may produce improved wet traction properties. High temperature tangent delta behavior (60ºC) is similar for the two compounds studied.

Table II. Zinc reduction in a model silica tire tread formulation.

| Ingredient	phr		Properties	ZnO	Dymalink® 709
cis-BR	25.0	25.0	t_2 (minutes)	2.1	2.8
SSBR	75.0	75.0	t_{90} (minutes)	10.4	6.6
Silica	65.0	65.0	ML (dNm)	5.6	5.8
Silane (50%)	10.4	10.4	MH (dNm)	32.9	33.8
Aromatic oil	25.0	25.0	MH-ML (dNm)	27.4	28.1
IPPD	2.0	2.0			
Stearic acid	1.0	1.0	Shore A	53	52
ZnO	**5.0**		Tensile Strength (MPa)	18.2	17.5
Dymalink® 709		**2.5**	Elongation, Break (%)	450	385
Sulfur	1.4	1.4	Modulus, 100% (MPa)	2.1	2.6
CBS	1.7	1.7	Modulus, 300% (MPa)	10.1	12.4
DPG	2.0	2.0			
			Die C Tear (kN/m)	43.9	38.0
moles Zn/ 100g polymer	**0.063**	**0.015**			
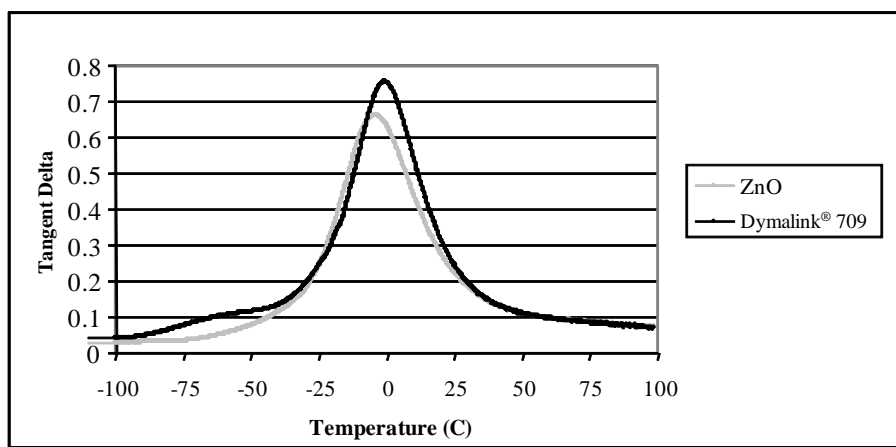
Figure 11. Tangent delta as a function of temperature measured in tension (DMA) in a model silica tread formulation. ZnO at 5 phr and Dymalink® 709 at 2.5 phr loading.

Model tire sidewall formulation

In a formulation using a carbon black filled NR/cis-BR blend, physical properties were again approximated by a net reduction of zinc when Dymalink® 709 was applied as the activating species in a CV cure system. Table III provides the formulation used and the physical property results. Apparent crosslink density, tensile modulus and tear were matched. The reduced Dymalink® 709 loading represents an 80% reduction in molar zinc for this compound compared to ZnO.

Dynamic properties were also compared for these compounds using DMA. Figure 12 shows that the profiles for both vulcanizates were identical. Peak tangent delta temperatures and values at 0ºC and 60ºC also appeared to be similar.

Model wirecoat formulation

A model wirecoat formulation based on NR and an elevated sulfur loading was evaluated. The formulation and results of physical testing are provided in Table IV. With 3.5 phr sulfur, the same loading (5 phr) of activator was required to match cured physical properties, so no net phr reduction was achieved. However, when considering the molecular weight of the activators, approximately 50% less zinc was incorporated into the compound on a molar basis using Dymalink® 709.

Table III. Zinc reduction in a model tire sidewall formulation.

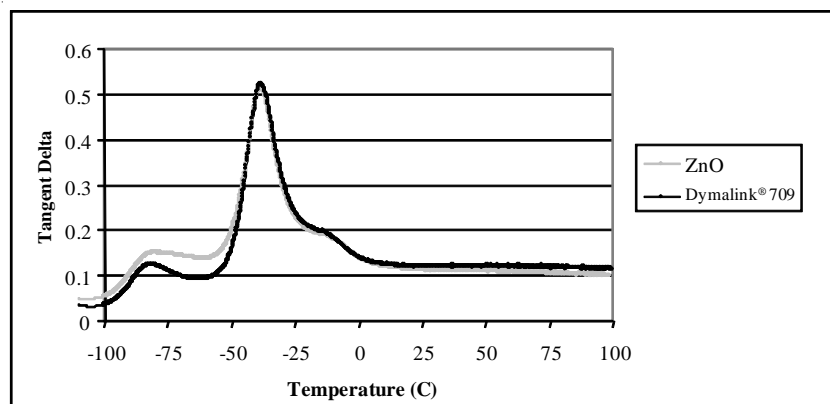| Ingredient	phr		Properties	ZnO	Dymalink® 709
cis-BR	50.0	50.0	t_2 (minutes)	3.6	3.2
NR	50.0	50.0	t_{90} (minutes)	6.3	5.9
Carbon Black	50.0	50.0	ML (dNm)	4.1	3.4
Aromatic oil	12.0	12.0	MH (dNm)	30.9	30.3
IPPD	2.0	2.0	MH-ML (dNm)	26.9	26.8
TMQ	1.0	1.0			
Stearic acid	0.8	0.8	Shore A	51	56
ZnO	**5.0**		Tensile Strength (MPa)	22.8	23.2
Dymalink® 709		**2.0**	Elongation, Break (%)	738	758
Sulfur	2.5	2.5	Modulus, 100% (MPa)	1.7	1.7
TBBS	0.7	0.7	Modulus, 300% (MPa)	6.5	6.5
moles Zn/ 100g polymer	**0.063**	**0.012**	Die C Tear (kN/m)	86.1	84.6

Figure 12. Tangent delta as a function of temperature measured in tension (DMA) in a model sidewall formulation. ZnO at 5 phr and Dymalink® 709 at 2.0 phr loading.

Table IV. Zinc reduction in a model wirecoat formulation.

Ingredient	phr		Properties	ZnO	Dymalink® 709
NR	100.0	100.0	t_2 (minutes)	0.9	1.1
Carbon black	65.0	65.0	t_{90} (minutes)	3.1	5.4
Aromatic oil	3.0	3.0	ML (dNm)	6.3	4.9
TMQ	1.0	1.0	MH (dNm)	50.7	56.4
Stearic acid	2.0	2.0	MH-ML (dNm)	44.5	51.5
ZnO	**5.0**				
Dymalink® 709		5.0	Shore A	66	69
Sulfur	3.5	3.5	Tensile Strength (MPa)	26.4	25.1
CBS	0.8	0.8	Elongation, Break (%)	518	481
IPPD	1.0	1.0	Modulus, 100% (MPa)	4.4	4.6
			Modulus, 300% (MPa)	16.0	16.5
moles Zn/ 100g polymer	**0.063**	**0.030**	Die C Tear (kN/m)	133.0	157.0

Table V. Zinc reduction in a model rubber roll formulation.

Ingredient	phr		Properties	ZnO	Dymalink® 709
NBR	100.0	100.0	t_2 (minutes)	2.8	3.7
Carbon black	50.0	50.0	t_{90} (minutes)	4.9	6.5
Aromatic oil	10.0	10.0	ML (dNm)	3.5	3.3
IPPD	2.0	2.0	MH (dNm)	22.5	21.3
Stearic acid	0.8	0.8	MH-ML (dNm)	19.0	18.0
ZnO	**5.0**				
Dymalink® 709		**2.0**	Shore A	62	64
Sulfur	1.0	1.0	Tensile Strength (MPa)	19.7	18.8
CBS	1.2	1.2	Elongation, Break (%)	957	1005
			Modulus, 100% (MPa)	1.6	1.6
moles Zn/ 100g polymer	**0.063**	**0.012**	Modulus, 300% (MPa)	5.1	4.6
			Die C Tear (kN/m)	64.1	62.8

Model rubber roll formulation

In a final example, a model sulfur-cured rubber roll formulation based on NBR was considered. Table V contains the formulation and testing results. Again, key physical properties were maintained, such as modulus, tensile strength and tear while a significant reduction in activator loading was realized when 2.0 phr Dymalink® 709 was used in place of 5.0 phr ZnO. The lower loading corresponds to an 80% reduction in zinc content for the model compound.

The results from comparing ZnO and Dymalink® 709 activation in model formulations suggest that reductions in molar zinc concentration of 50-80% may be achieved in sulfur cured rubber compounds.

SUMMARY AND CONCLUSIONS

Zinc monomethacrylate can be formulated into accelerated sulfur vulcanization systems as an activating species. Comparison with other zinc-based organic acid salts indicated that Dymalink® 709 was a more efficient activator, and suggested through structure-property relationships that the steric size of the methacrylate group and the binding energy of the zinc-acid pair may contribute to increased activity. Methacrylic acid salts of other metal centers did not produce significant activation, consistent with previous work investigating alternative metal oxide/stearic acid complexes.

When compared to ZnO at molar equivalent loadings, Dymalink® 709 produced increased crosslink density. In addition, it was shown that the sulfur rank distribution was altered significantly using Dymalink® 709 as the activating species. Despite application of a conventional vulcanization system (high sulfur to accelerator ratio), the crosslink distribution was shifted to a higher population of mono- and disulfidic linkages with increased Dymalink® 709 loading. The same trend was not seen using ZnO. At a given molar equivalent loading, more crosslinks of lower sulfur rank were produced using Dymalink® 709 compared to other zinc species

The increased efficiency of Dymalink® 709 was employed in a number of model formulations to demonstrate the ability to reduce both the loading and molar concentration of zinc in the compound by replacing ZnO with Dymalink® 709 as the activating species. Compounds were subsequently formulated to equivalent physical properties. The largest reductions in comparative activator loading were demonstrated for conventional and semi-efficient vulcanization systems. In practical formulations, from 50% to 80% of the molar zinc concentration was eliminated from the compound.

The results of the reported evaluations suggest that for most tire and engineered rubber product formulations, Dymalink® 709 should be considered as a candidate in a zinc rationalization program.

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