

**“Fundamentals of Curing Elastomers with
Peroxides and Coagents II:
Understanding the Relationship
Between Coagent and Elastomer”**

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ABSTRACT

Previously, the structure-property relationships of multifunctional monomeric and polymeric coagents were explored using a compound based on a standard peroxide-curable elastomer, EPDM. While the system represented a good model to compare the relative activity of coagent structures, it did not address the more complex relationships between coagent and elastomer.

A larger study has been recently completed in which a select group of representative coagents were evaluated in a series of model formulations based on commercially significant elastomers that can be cured with organic peroxides (NR, NBR, HNBR, EPDM, EVA, CM, CSM, FEPM, FKM). Cure kinetics and cured physical property data are summarized. The results are interpreted by considering the relative reactivity of different polymers towards hydrogen abstraction and other radical reactions, and the proposed chemistry of coagent vulcanization. The results provide a better understanding of coagent selection based not only on coagent structure but also on the composition and microstructure of the elastomer being cured. The investigation furthers the understanding of coagent activity by exploring coagent and elastomer structure-property co-relationships.

INTRODUCTION

By crosslinking elastomeric polymers, useful compositions can be formed that exhibit physical properties such as high tensile strengths, low compression set, recoverable elongations, high tear energies, and improved dynamic performance. The quantity and quality of the linkages formed by the crosslinking reactions determine the properties of the resulting network. Networks formed from radical-based vulcanization typically possess good heat-ageing stability and low compression set. These qualities are a direct manifestation of the chemical composition of the crosslinks that are formed. Synergistic use of multifunctional coagents can improve upon these properties by increasing the crosslink density of the network and by altering the crosslink composition.

The use of organic peroxides in the radical vulcanization of elastomers is well established. Through model reactions and analysis of *in-situ* derived networks, previous work has established the fundamental chemistry and mechanism of radical cure for the basic allyl ester, allylic, and (meth)acrylate ester functional coagents monomers.¹ Other work has further determined the structure-property relationships of a wide group of coagents through empirical studies.^{2,3} Most studies made available in the literature which highlight coagents utilize ethylene-propylene or ethylene-propylene-diene rubber as the model elastomer vulcanized by peroxide-coagent systems.^{4,5,6} Where the use of coagents has been expanded into other elastomer grades, the focus is primarily on the elastomer and a small selection of coagents are utilized to enhance specific physical properties.^{7,8,9} An expanded survey of several coagent types across a wide variety of commercially significant elastomers has not been available.

A design study evaluating a select group of coagents of very different structure and activity in a series of model formulations based on the most commercially significant elastomers cured with organic peroxides was recently completed. Comparisons between coagents in a given elastomer and the relative activity of specific coagents across a spectrum of elastomers are presented. The relative activity of coagents was found to be highly dependent on the elastomer in which it is being reacted, as cure kinetics and cured physical property data demonstrate. The results provide a better understanding of coagent selection based not only on coagent structure but also the context of the elastomeric matrix being cured.

EXPERIMENTAL

Materials

Table I outlines the commercially available coagent grades used in the study. They are available from Cray Valley Company, Inc. Table II provides a summary of the elastomer grades and manufacturers used in the model compound formulations evaluated. Both dicumyl peroxide (Di-Cup[®] 40KE, Geo Specialty Chemicals) and 2,5-dimethyl-2,5-di-*t*-butylperoxyhexane (Varox[®] DBPH 50, R.T. Vanderbilt Company, Inc.) were used as curing agents at 3 phr active peroxide. A listing of model formulations is provided in the Appendix.

Table I. Coagent identification and commercial products.

COAGENT DESCRIPTION	CODE	TYPE	COMMERCIAL PRODUCT
trifunctional (meth)acrylate ester	TMA	I	
N,N'-m-phenylene dimaleimide	PDM	I	
poly(butadiene) diacrylate	PBDDA	hybrid	
triallyl cyanurate	TAC	II	
triallyl isocyanurate	TAIC	II	
high vinyl poly(butadiene)	HVPBD	II	Ricon [®] 154

Table II. ASTM designations for common elastomer grades.

ELASTOMER TYPE	ASTM DESIGNATION	COMMERCIAL GRADE
natural rubber	NR	SMR CV-60
nitrile rubber	NBR	Nipol [®] DN 3335, Zeon Chemicals
hydrogenated nitrile rubber	HNBR	Zetpol [®] 2010L, Zeon Chemicals
ethylene propylene diene rubber	EPDM	Nordel [™] IP4640, Dow Chemical
ethylene-vinyl acetate copolymer	EVM	Levapren [®] 600HV, Lanxess
chlorosulfonated poly(ethylene)	CSM	Hypalon [®] 40, DuPont Elastomers
chlorinated poly(ethylene)	CM	Tyryn [™] 0136, Dow Chemical
fluorocarbon rubber	FKM	Viton [®] GF-S, DuPont Elastomers
fluorocarbon rubber	FEPM	Aflas [®] 150P, AGC Americas

Rubber Compounding

A set of compound evaluations was conducted using six different coagents in model formulations based on nine different elastomers. To limit systematic error derived from the mixing step, masterbatches containing all ingredients except the coagent and peroxide were prepared in an internal mixer to which the curatives were later added on a two-roll mill. Curative incorporation time was approximately 7 minutes at an average mixing temperature of 85°C. In each formulation, the selected coagents were evaluated at loading levels of 1, 5, and 10 phr; 7.5 phr peroxide (3.0 phr actives) was also added to the compound. A control compound for each formulation using no coagent (peroxide only) was included for comparison.

Physical Testing

Cure kinetics. A moving die rheometer (MDR, TechPro MDPT) was used to determine the extent of cure and cure kinetics according to ASTM D 5289. The cure temperature used was dependent upon the peroxide (160°C for dicumyl peroxide, 180°C for 2,5-dimethyl-2,5-di-*t*-butylperoxyhexane). Cure rheometry was conducted using an arc deflection of 3°. Cure times were sufficiently long to ensure near complete decomposition of the peroxide (35 minutes for dicumyl peroxide, 15 minutes for 2,5-dimethyl-2,5-di-*t*-butylperoxyhexane).

Tensile and compression properties. Physical testing was performed on samples cured in a press under the same temperature and time conditions outlined above. Tensile, elongation and tear data was acquired on a tensile machine (Thwing-Albert Materials Tester) following ASTM D 412 and D 624. Compression set was evaluated after heating at 100°C (200°C for FKM, FEPM model formulations) for 22 hours following ASTM D 395.

RESULTS AND DISCUSSION

An important factor that determines the final architecture of the vulcanized network is the relative reactivity between coagent and the polymer chain towards radicals. Polymer radicals can be formed when a radical species abstracts hydrogen from the polymer chain. The ease of abstraction is dependent on the structure of the polymer. A list quantifying the relative difficulty of hydrogen abstraction from various chemical groups is available.⁵ For most commercially relevant polymers cured by peroxides, the following list is sufficient to describe the ease that polymer radicals can form through hydrogen abstraction based on the microstructural elements of the polymer:

benzylic = allylic > tertiary carbon > secondary carbon > primary carbon > vinyl >> phenyl

By default, the above list can also be used to determine the relative reactivity of polymers to peroxide cure assuming attack by an alkoxy radical. For poly(dienes), other factors are also of importance in comparing the relative reactivity to hydrogen abstraction, including steric hindrance and the effects of microstructure.

Radical addition across C=C unsaturation is the other mechanism by which polymer radicals can form. Terminal, or pendant double bonds (vinyl) have low steric hindrance and are more likely to participate in addition reaction than internal double bonds (cis/trans). Radical addition reactions compete with allylic abstraction to form polymer radical species. Crosslinks can be subsequently formed through polymer radical coupling reactions.

Peroxide Cure of Elastomers

In order to provide a baseline of polymer reactivity, an equivalent amount of peroxide was added to the elastomers in our evaluation group, and the delta torque ($M_H - M_L$) was determined by rheometry. The results are provided in Figure 1. Delta torque has been shown to correlate to crosslink density in peroxide cured systems, and in the present example serves to measure only the increase in torque due to vulcanization which provides normalized data enabling meaningful comparisons across the disparate model formulations used in the study.

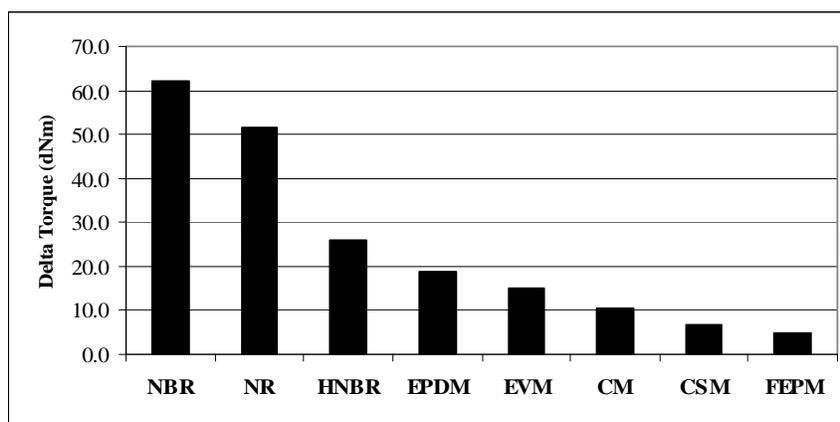


Figure 1. Delta torque values as a function of elastomer for model formulations cured with 3 phr peroxide.

The polymer order in Figure 1 follows the percent unsaturation in the diene-based elastomer materials (NR, NBR > HNBR » EPDM). The fully saturated materials (EVM, CM, CSM, FEPM) are listed last. The unsaturated materials as a group generated the highest delta torque with the actual value roughly correlating to percent unsaturation. However, details regarding the actual polymer structure can better explain the trends observed in the data.

NR contains more unsaturation than the NBR copolymer, but NBR typically builds higher crosslink density than NR in radical systems. Both are diene-based polymers, but an addition reaction would be favored at the less sterically hindered butadiene (vs. isoprene) monomer cure site.¹⁰ Also, in poly(isoprene) the result of addition would be a tertiary radical, which is subsequently less reactive to coupling reactions. As abstraction may be the dominant mechanism, there is a higher allylic hydrogen concentration in isoprene (7 vs. 4 for butadiene). Again, steric hindrance may limit the accessibility of the allylic sites on poly(isoprene) to other macroradicals. HNBR and EPDM contain low amounts of unsaturation (4-5%) resulting from partial hydrogenation and the incorporation of cure site monomer, respectively. Residual butadiene will be more reactive to radical attack than the ethylidene norbornene monomer, with reasoning parallel to the butadiene/isoprene comparison.

The fully saturated elastomers are also peroxide-curable, relying exclusively on hydrogen abstraction as the mechanism for polymer radical formation. For EVM, the methyl hydrogen is the most likely site for abstraction.¹¹ Abstraction on CM and CSM polymers occurs at the carbon adjacent to the halogenated site. Crosslinking efficiency of polymer radicals in halogenated elastomers is typically reduced through dehydrohalogenation reactions. Fluorocarbon rubbers can be peroxide cured, but fluorine is much more difficult to abstract than hydrogen, resulting in reduced crosslinking efficiency. Certain grades of fluoroelastomers may utilize cure site monomers or have reactive groups added to the polymer structure to promote crosslinking with peroxides (FEPM).^{12,13} The FKM grade produced negligible delta torque when peroxide was used without co-curatives.

Crosslink formation is the desired reaction pathway for a radical species, but competitive reactions can limit the efficiency of radical cure.⁵ Unfortunately, many of the destructive reactions are kinetically and thermodynamically favored, and typically only a very high concentration of reactive sites on the polymer backbone allows for effective crosslink formation to occur at all. However, productive crosslink formation can be favored through the use of very reactive, multifunctional coagent products. Coagents favor network formation by increasing the local concentration of highly reactive groups. The incorporation of coagents into the network can also favorably impact the physical properties of the vulcanizate.

Comparing Coagent Activity as a Function of Elastomer

Coagent classification. Coagents are classified based on their contributions to cure and divided into two basic classes (Type I and Type II). Type I coagents increase both the rate and state of cure. Type I coagents are typically polar, low molecular weight multifunctional compounds which propagate very reactive radicals primarily through addition reactions. These “monomers” can be homopolymerized or grafted to polymer chains. Type II coagents form less reactive radicals and contribute only to the state of cure. Type II coagents can include allyl-containing cyanurates, isocyanurates and phthalates, and high vinyl poly(butadiene) resins. Those Type II coagents that contain extractable allylic hydrogen have been shown to participate in intramolecular cyclization reactions as well as intermolecular propagation reactions.¹ High vinyl poly(butadienes) simply increase the concentration of reactive pendant unsaturation, further promoting crosslinking predominantly via addition reactions through the pendant vinyl group. Examples representing the structural diversity of coagents are provided in Figure 2.

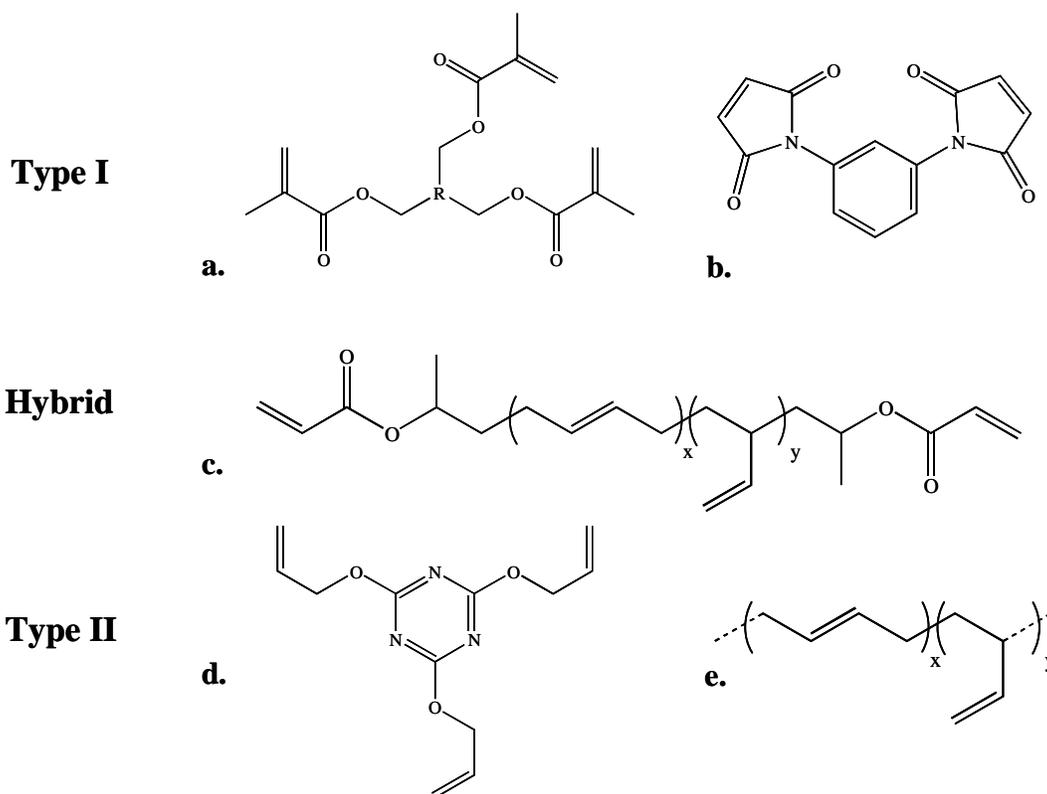


Figure 2. Examples demonstrate the structural diversity of Type I and Type II coagents. Type I (a. tri(meth)acrylate ester, b. N, N'-m-phenylene dimaleimide), hybrid (c. poly(butadiene) diacrylate resin), and Type II (d. triallyl cyanurate, e. high vinyl poly(butadiene) resin) coagents are represented.

Coagent reactivity. Because of their reactivity, coagents generally make more efficient use of the radicals derived from peroxides, whether acting to suppress non-network forming side reactions during cure^{14,15} or to generate additional crosslinks.¹⁶ The mechanism of crosslink formation using coagents appears to be at least partially dependent on their class. Figure 3 demonstrates the change in crosslink density (as measured by MDR delta torque) when either a Type I coagent (tri(meth)acrylate, TMA) or Type II coagent (high vinyl poly(butadiene) resin, HVPBD) was added to the peroxide cure system at 5 phr. Addition of Type I coagent increased the delta torque for each compound. The Type I coagent is a very reactive monomer, favoring addition reactions leading to homopolymerization and subsequent grafting to polymer chains, through either direct addition reactions (unsaturated polymers) or through abstraction/coupling reactions with saturated or unsaturated polymer chains. Regardless of mechanism, the Type I coagent increased crosslink density in each compound.

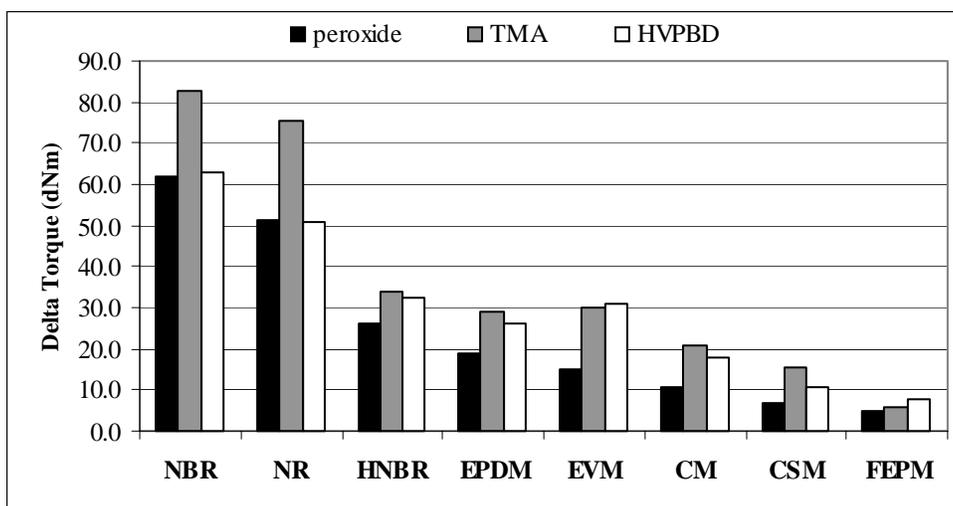


Figure 3. Delta torque values as a function of elastomer for model formulations cured with 3 phr peroxide and 5 phr coagent.

In general, the addition of a Type II coagent had less of an impact on crosslink density. Vinyl (1,2) microstructure dominates the poly(butadiene) resin (90% of monomer units), and addition reactions may dominate the cure mechanism. Homopolymerization may proceed, but at a slower rate than monomeric coagents due to group reactivity and steric hindrance associated with the polymeric form. These factors may lead to a decrease in the overall state of cure when the poly(butadiene) resin is used. The Type II coagent provided no increase in delta torque for highly unsaturated polymers, perhaps due to the relative ease of allylic hydrogen abstraction from the polymer backbone compared to the vinylic group of the coagent. The relative concentration of vinylic groups on the coagent compared to unsaturation on the polymer may also contribute to the negligible impact on crosslink density by the coagent in the NR and NBR compounds. However, the Type II coagent appeared to become more effective as unsaturation decreased. In EVM and FEPM the Type II coagent produced higher delta torque than the Type I coagents.

Figure 4 summarizes the percent increase in delta torque data (over peroxide alone) as a function of elastomer when applying the Type I and Type II coagents. The Type I coagent increased delta torque for every formulation, with the greatest improvements seen in saturated EVA, CM and CSM systems. The more reactive coagents may limit the amount of dehydrohalogenation occurring in these compounds, providing the most positive effect in cure state. Type II coagents, most notably allylic-containing monomers, increase the cured physical properties of fluorocarbon rubber.⁸ (Meth)acrylate esters have not been shown to be as effective in FEPM grades.

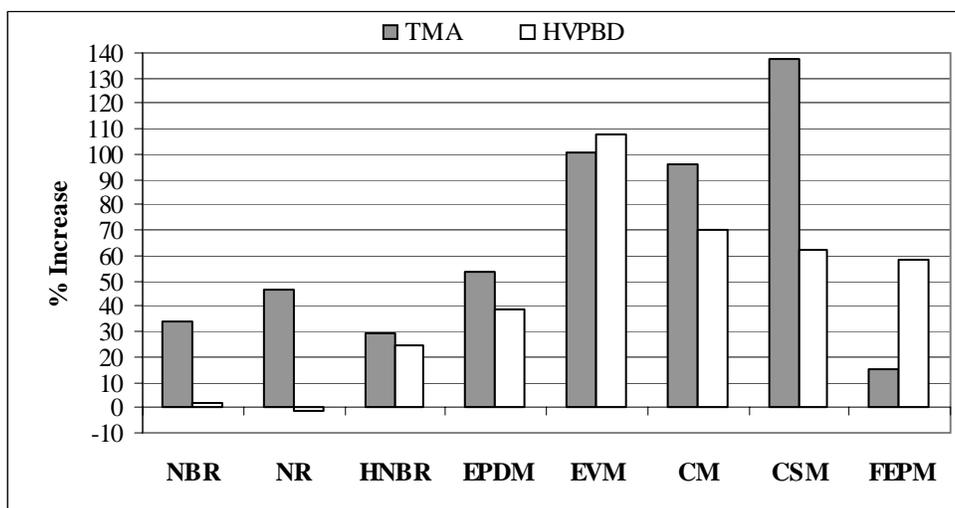
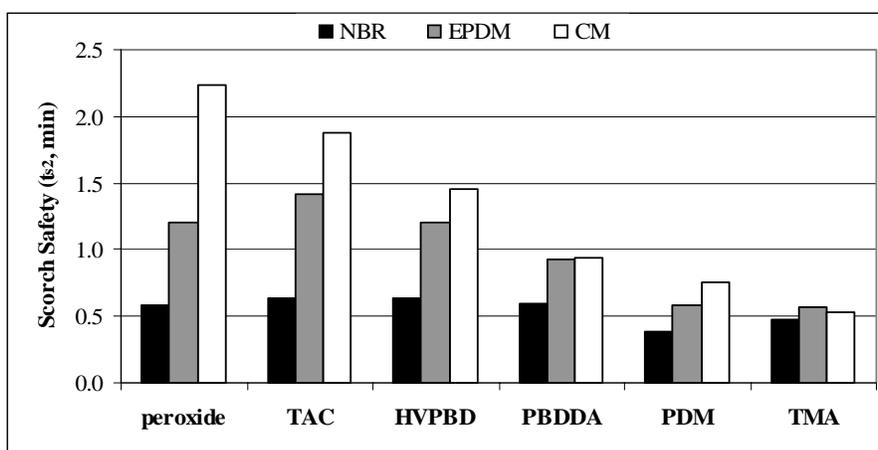


Figure 4. Percent increase in delta torque over that for peroxide alone due to the addition of 5 phr coagent as a function of elastomer.

What is clear is that many kinetic and mechanistic factors must be considered when explaining the complex behavior observed. A direct manifestation of the competition for peroxy radicals and other macroradicals by coagent and elastomer is seen in the final cured physical properties of the compounds. However, the competition must be considered within the context of all the possible competitive reactions. The fact that many elastomers are cured to form useful commercial products attests to the domination of crosslink-forming reaction in these systems.

Cure kinetics. The reactivity of coagents can have negative effects on process safety, typically manifested by a decrease in scorch time. The addition of highly reactive monomers and resins to compounds can result in a fast onset of cure once the peroxide begins to decompose. The few initial peroxy radicals react with coagents and will propagate quickly. The relative decrease in process safety is typically measured by the time to a two-point increase in rheometer torque (t_{s2}). Figure 5 compares scorch times for model NBR, EPDM, and CM compounds as a function of coagent (TAC, HVPBD, PBDDA, PDM, TMA). Again the control (peroxide only) provides a baseline reference for the inherent reactivity of the elastomer itself to peroxide cure. Scorch time increases as unsaturation decreases (NBR < EPDM < CM), perhaps due to the relative efficiency of addition reactions generating crosslink density compared to abstraction, as the polymer plays less of a role in the cure mechanism with increased saturation.



5. Scorch safety as measured by t_{s2} times for NBR, EPDM, and CM model formulations as a function of coagent (5 phr loading).

Adding coagent (5 phr) negatively affected scorch safety. Structure-property relationships can predict the direction and degree of the change. In general, the Type II coagents (TAC, HVPBD) provided the most scorch safety. In the NBR compound, the addition of these coagents maintained scorch times; in EPDM, the scorch times were increased. In each formulation, the Type I monomers (PDM, TMA) provided the least scorch safety. The hybrid coagent PBDDA contains structural elements of both Type I and Type II coagents; the scorch safety provided was also characteristically intermediate of the two classes. As CM contains no unsaturation, the addition of any reactive component to the formulation decreased scorch time. Reviewing the scorch times for the CM compound provides a good illustration of the gradual increase in reactivity of the selected coagents.

Figures 6, 7 and 8 provide more insight as to the effect of coagent addition on the cure kinetics and state of cure for the same three compounds (NBR, EPDM, CM, respectively). A coagent loading ladder (1, 5, and 10 phr each coagent) was used to generate the data. Looking at the change in scorch time as a function of delta torque provides a relative comparison of the crosslink density/scorch safety trade-off often associated with each coagent. The data indicate that for most coagent-elastomer systems a negative slope was obtained; scorch safety decreases with an increase in delta torque. The few exceptions typically involve a Type II coagent and a saturated elastomer (HVPBD, NBR). In general, the Type I monomers possess a much more negative slope than Type II coagents. It is also instructive to consider the y axis range of each figure: the relative magnitude of scorch safety again aligns with elastomer reactivity towards radical species (NBR < EPDM < CM).

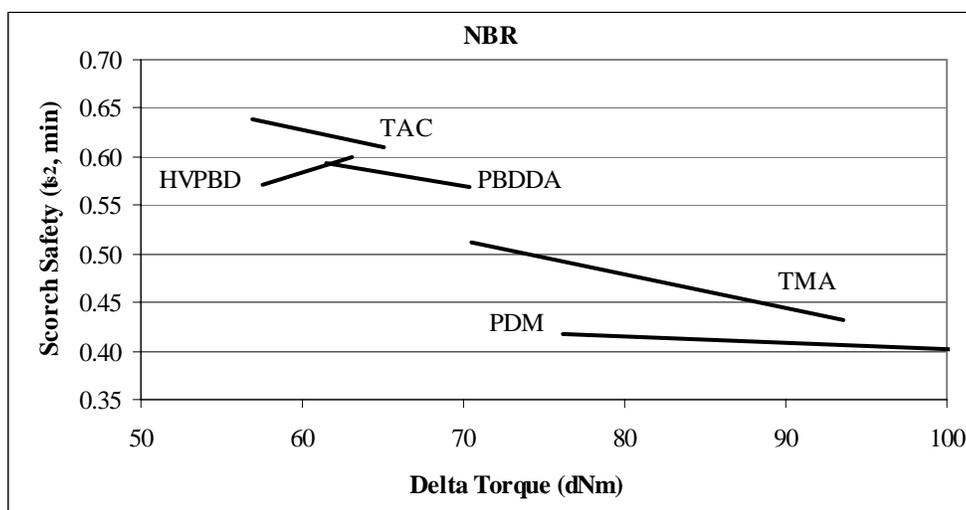


Figure 6. Scorch safety as a function of delta torque for selected coagents in the NBR model formulation.

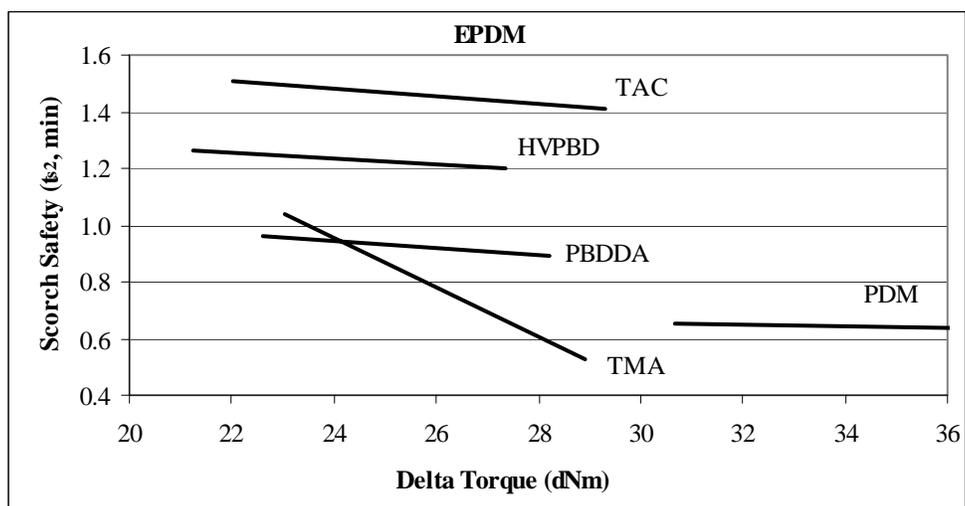


Figure 7. Scorch safety as a function of delta torque for selected coagents in the EPDM model formulation.

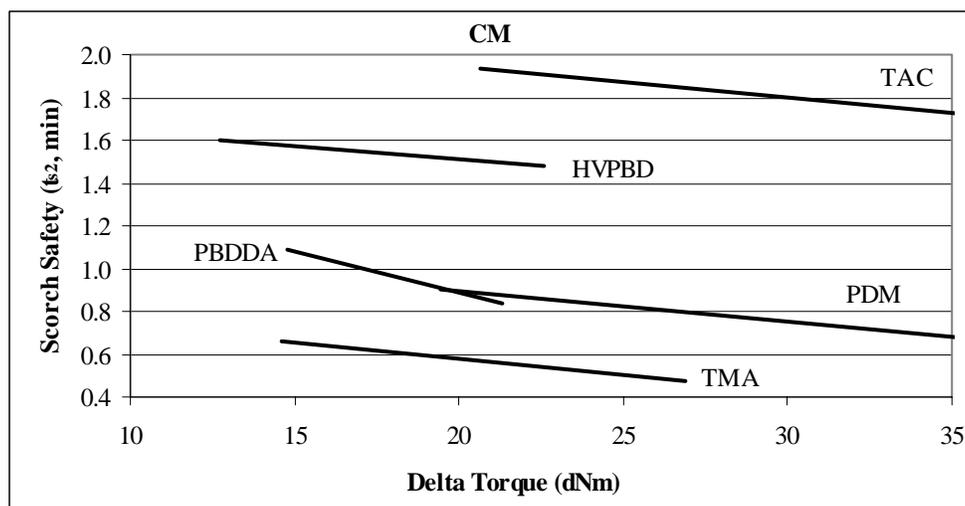


Figure 8. Scorch safety as a function of delta torque for selected coagents in the CM model formulation.

Physical Properties. The cured physical properties exhibited by the model compounds are determined by the crosslinked network and the composition of the formulation. To normalize the effect of the formulation composition, the relative improvement in tensile and compression properties as a function of coagent in the NBR, EPDM, and CM model formulations is compared. In Figure 9 the increase in 50% modulus is compared in these compounds with the addition of 5 phr coagent (based on the peroxide-only control). The Type I coagent monomers (TMA, PDM) provided the greatest increases in modulus. As seen earlier, the coagent effect on cure typically increases as polymer unsaturation decreases. The trend was evident for the TAC, HVPBD, and PBDDA coagents. However, for the compounds formulated with PDM the modulus-building effect followed the opposite trend, with the relative increase in modulus becoming larger with higher levels of polymer unsaturation.

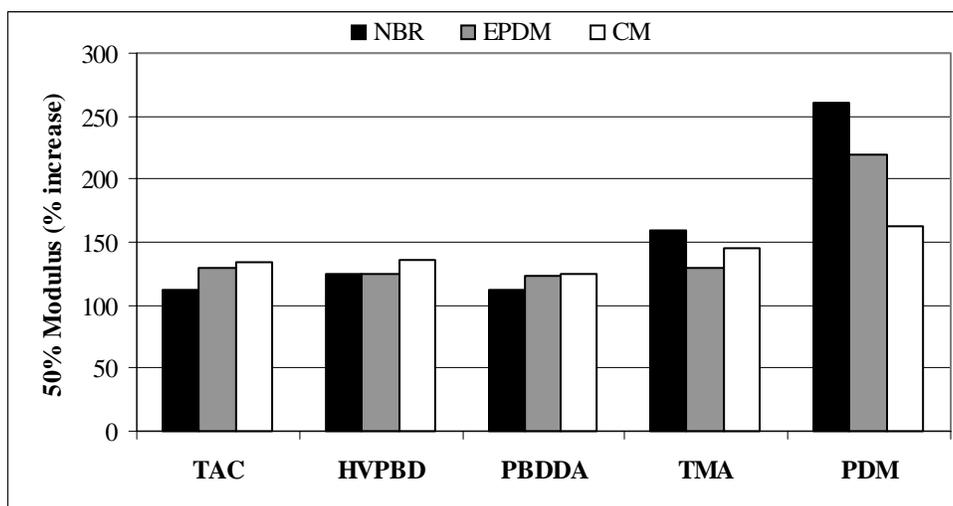


Figure 9. Percent increase in tensile modulus value by the addition of 5 phr coagent to the BNR, EPDM, and CM model formulations (based on peroxide-only cure).

Figure 10 compares compression set data of the same compounds. Again, the effects of coagent addition generally increased as a function of polymer saturation. However, no clear trends can be seen as a function of coagent type. The results suggest that in compression testing the effect of the coagent is highly dependent on the elastomer being crosslinked and the property more sensitive to other factors.

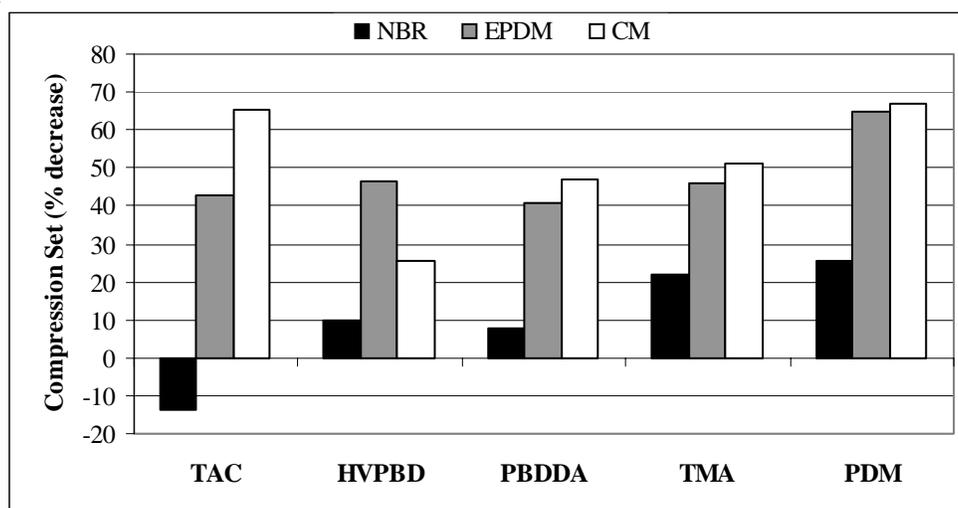


Figure 10. Percent decrease in compression set value by the addition of 5 phr coagent to the NBR, EPDM, and CM model formulations (based on peroxide-only cure).

Compression set is particularly sensitive to the homogeneity of crosslink density. The relative amount of permanent set can therefore be a diagnostic tool for the final structure of the network based on the relative solubility of the coagent in the elastomer matrix and the mechanism for which crosslinks are formed. Several models have been put forth to describe the architecture of the network formed when coagents are employed in the radical cure of elastomers. Network enhancement through the grafting of coagents between polymer chains,^{16,17} the formation of an interpenetrating network of homopolymerized coagents,¹⁸ and the formation of higher modulus filler-like domains of thermoset coagent¹⁹ has been suggested. Rather than the above cases being distinct or mutually exclusive outcomes of vulcanization, the resulting network is likely defined by a distribution of the above crosslink structures. The actual population of the distribution is determined by a host a factors including coagent loading, solubility of the

coagent in the elastomer, and the relative reactivity of the coagent compared to the elastomer. In most cases where monomeric Type I and Type II coagents are employed, a limited solubility in the elastomer phase and the ability to homopolymerize leads to the formation of domains of thermoset coagent. This has been demonstrated for allylic²⁰ and (meth)acrylate-based monomeric coagents.²¹ However, high vinyl poly(butadiene) resins possess solubility parameters much closer to common elastomers, and have been shown to greatly improve physical properties at coagent loadings above the solubility limit of monomeric forms.²²

By measuring compression set as a function of modulus for select coagents, a more informative comparison can be made across elastomer model formulations. Figures 11 through 13 provide the compression set / modulus analysis for the NBR, EPDM, and CM model formulations, respectively. The results were again generated through a coagent loading ladder (1, 5, and 10 phr) in each formulation. In Figure 11 (NBR) increased loading of the Type II coagents (TAC, HVPBD) resulted in compression set improvement over a relatively narrow modulus range. PBDDA, the hybrid diene-acrylate resin, provided an incremental improvement in compression at equal modulus versus the HVPBD resin. The Type I monomers PDM and TMA produced consistently low compression set values over a much higher modulus range. It is possible that the reactivity of the highly unsaturated NBR polymer chain may compete favorably with radical addition reactions of these monomers, the effect being a higher percentage of well distributed crosslinks.

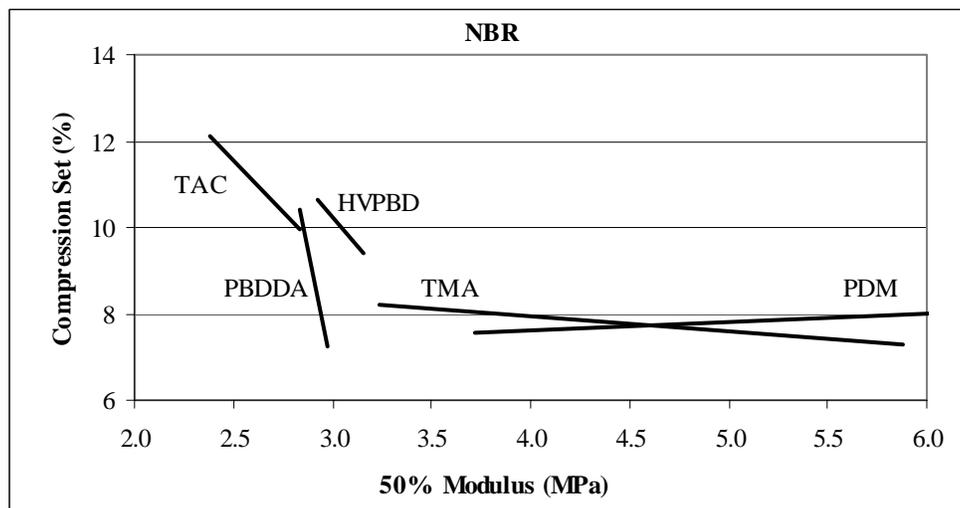


Figure 11. Compression set as a function of modulus for selected coagents in the NBR model formulation.

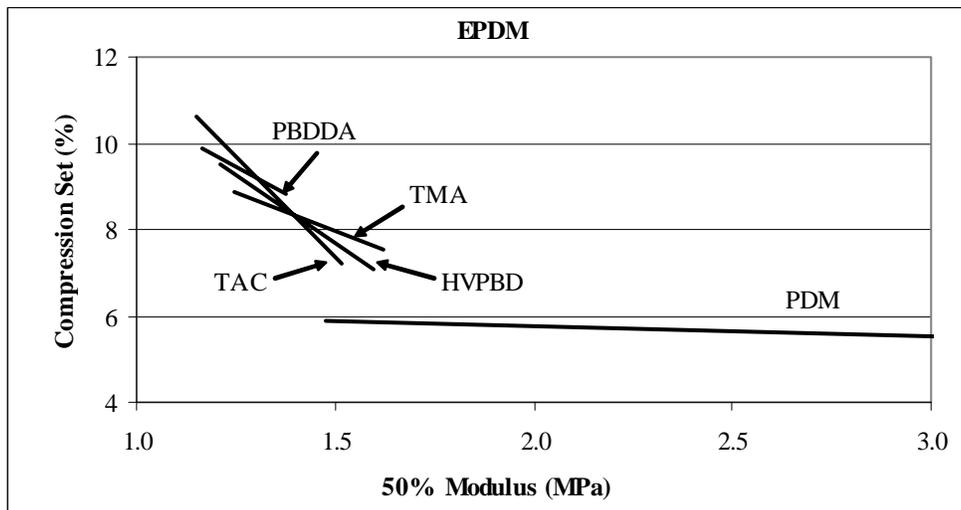


Figure 12. Compression set as a function of modulus for selected coagents in the EPDM model formulation.

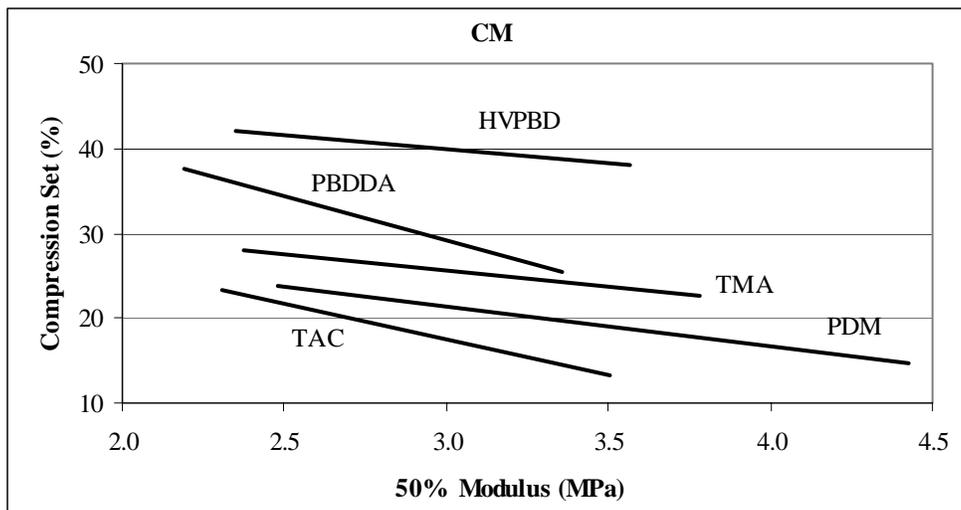


Figure 13. Compression set as a function of modulus for selected coagents in the CM model formulation.

Figure 12 provides the data for the EPDM formulation. Trends are similar to the NBR data set, with the exception of the TMA monomer which groups with the Type II coagents in this formulation. The PDM monomer again provides a very low compression set across an extended modulus range. It is possible that addition reactions between PDM monomers are not favored, limiting the monomers ability to homopolymerize. Alternatively, the PDM coagent can also react with in-chain unsaturation through ionic mechanisms in the absence of radicals.²³ The efficiency that the addition of PDM increases crosslink density and minimizes compression set suggests that a majority of the crosslinks formed consist of well distributed linkages grafted between polymer chains.

Figure 13 summarizes the experiment utilizing the CM model formulation. Coagent loading produced a more uniform range of moduli, and more equally distributed differentiation by coagent structure. With the exception of TAC, the coagent efficacy follows a trend based on reactive structures and Type (HVPBD < PBDDA < TMA < PDM). For CM elastomers, TAC provided optimal tensile-compression properties.

Additional Comparisons of Elastomers

The results summarized above offer some insight as to mechanism of peroxide/coagent cure within the context of the relative degree of diene unsaturation of the host elastomer. However, many polymers utilize cure site monomers to either increase the inherent cure reactivity or enable alternative cure chemistries. The most notable commercial examples include EPDM (diene monomer) and butyl rubber (isoprene monomer). Many other elastomer grades utilize different comonomers to increase the reactivity to peroxide cure, or in other cases utilize post-polymerization derivatization to add reactive groups. The presence of these reactive groups can alter the activity of peroxide/coagent cure systems. In many cases the reactive group can be more selective to specific coagents, or as outlined earlier may increase the participation of the polymer chain in curing reactions and favorably alter the cure mechanism.

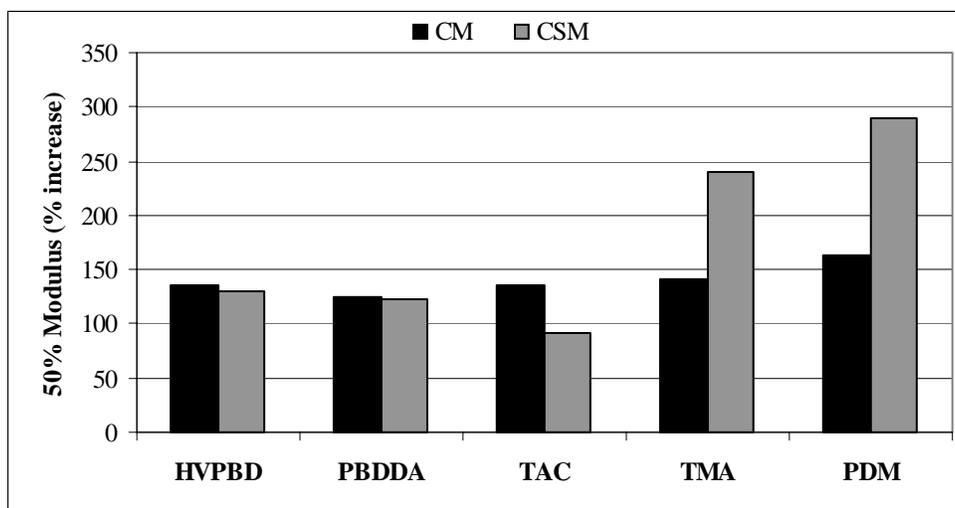


Figure 14. Percent increase in tensile modulus value by the addition of 5 phr coagent to the CM and CSM model formulations.

CM / CSM elastomers. CM and CSM elastomer grades contain cure sites that increase the reactivity of the polymer to standard cure systems. The chlorination process decreases crystallinity and also adds a reactive site. Coagents are often used in the peroxide cure of these grades as they can promote crosslinking reactions and limit dehydrohalogenation reactions. The CM and CSM grades evaluated in the present study have the same chlorine content (~35%), with the CSM grade also having 1% chlorosulfonyl groups added. Model formulations containing these grades were cured using 5 phr of various coagents. The relative increase in 50% modulus (calculated as a percent increase over the modulus value for the addition of peroxide without a coagent) for the two compounds are provided in Figure 14. In general, the addition of coagent increases the modulus value by at least 100%. For the CM masterbatch, the increase in modulus is fairly constant, regardless of coagent Type or chemistry. The Type I monomers TMA and PDM do provide a marginal increase in physical properties when compared directly to the Type II grades. In contrast to the CM case, the Type I coagents increased the modulus values more significantly than the Type II coagents when applied to the CSM formulation. While there are minor formulation differences between the model compounds, the manner with which the Type I monomers improved the crosslink density and cured physical properties in the CSM compounds relative to the CM grade suggests that the chlorosulphonyl groups may contribute preferentially in the radical cure when Type I monomers are added.

HNBR / NBR elastomers. The residual diene monomer in HNBR can be considered a cure site monomer, the result of removing unsaturation through hydrogenation. The HNBR grade used contains 4% residual unsaturation, compared to the 67% butadiene content NBR. Figure 15 summarizes the increase in modulus provided by 5 phr coagent as a function of elastomer. Similar to the CM/CSM comparison, the relative effect of coagent addition is

greater for the Type I monomers in both base elastomers. For each coagent surveyed, the impact on physical properties, including modulus, was greatest in the highly unsaturated elastomer.

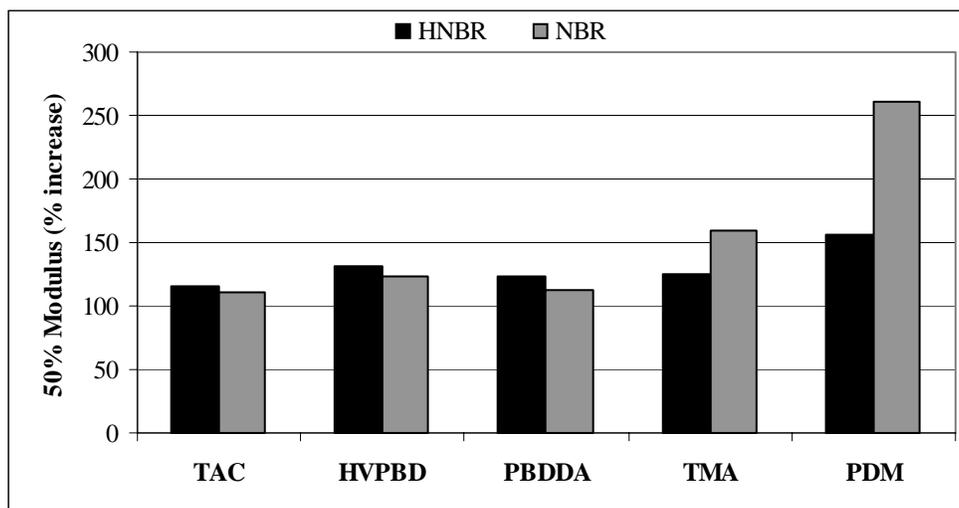


Figure 15. Percent increase in tensile modulus value by the addition of 5 phr coagent to the HNBR and NBR model formulation.

FKM/FEPM elastomers. A final comparison of commercial polymer grades focuses on fluoroelastomers. The FKM grade is a copolymer of hexafluoropropylene, vinylidene fluoride, and tetrafluoroethylene with a cure site monomer. In many cases, the cure site is a bromine-substituted fluorinated monomer.⁸ In contrast, the FEPM grade is an alternating copolymer of tetrafluoroethylene and propylene with a cure site added to the polymer. Figures 16 and 17 summarize the relative effect of coagent on the two fluoroelastomer model formulations for the FKM and FEPM compounds, respectively. The coagents were added at 2 phr; a post cure step (200°C, 4 hrs) was included prior to physical testing. In both systems, the allylic monomers produced a significantly higher relative increases in modulus compared to other Type II coagents. The Type I coagent was least effective. It must be noted that the relative increase in modulus is an order of magnitude greater for FKM than FEPM. Again, the results are shown as a percent increase in property based on the peroxide-only compound, a useful way to remove formulation differences and focus on coagent-elastomer structure effects. In the FKM compound, straight peroxide cure produced a very low state of cure. In contrast, the FEPM compound was adequately cured by peroxide alone. The cure site incorporated into the FEPM grade appears to be more effective at participating in the cure mechanism, with all Type II coagents providing measurable increases in cured modulus.

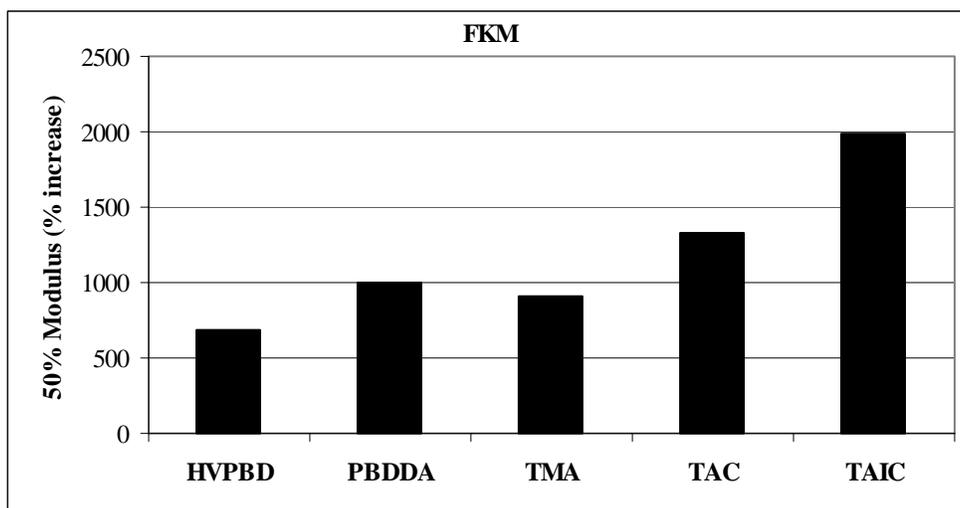


Figure 16. Percent increase in tensile modulus value by the addition of 5 phr coagent to the FKM model formulation.

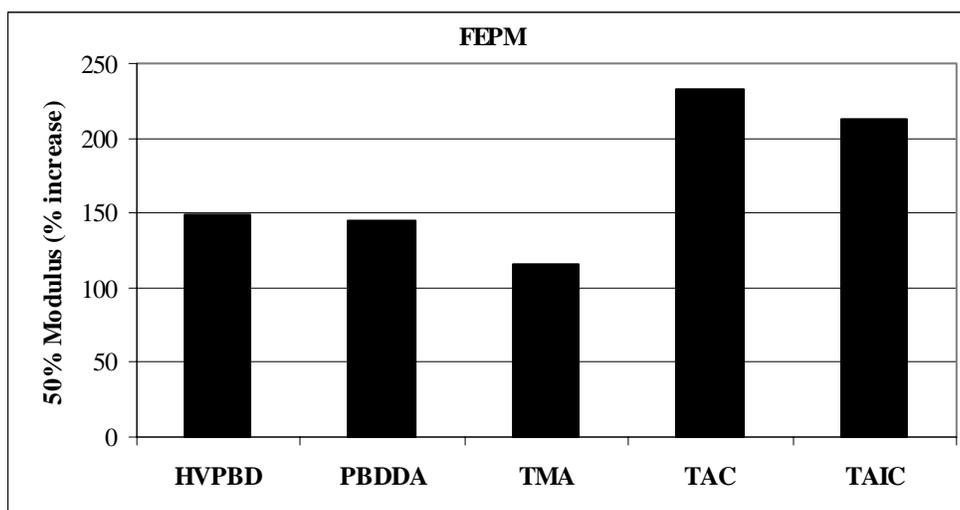


Figure 17. Percent increase in tensile modulus value by the addition of 5 phr coagent to the FEPM model formulation.

SUMMARY AND CONCLUSIONS

Generalizations regarding the absolute ranking of coagent performance must be reconsidered to take into account the context of the elastomer being cured. As previous work has concentrated on particular aspects regarding the mechanism of peroxide vulcanization, coagent chemistry, or specific improvements imparted to an elastomer grade through coagent selection, little focus was given to understanding coagent/elastomer structure-property co-relationships. By considering the favored reactions of a particular coagent within the context of a selected elastomer, it is more likely to be able to understand and predict the cure kinetics and physical properties of the one chosen system relative to another.

The tendency towards addition reactions of monomeric Type I coagents can, in general, result in compounds with very good tensile and compression properties, albeit at the expense of process safety. While the difference between solubility parameters of monomeric coagents and elastomers results in the likely formation of highly crosslinked domains and a heterogeneous crosslink density, more reactive host polymers may help balance the tendency

towards coagent homopolymerization by actively participating in cure reactions through easily abstractable hydrogen or even addition reactions. Type II coagents react more slowly, either due to the tendency towards intramolecular cyclization reactions (monomeric forms) or steric/structural effects (polymeric resins) and thus may exhibit a more balanced reactivity when used in the radical cure of saturated elastomers.

The results of the current study were culled from a database of information documenting the relative activity of a wide spectrum of coagents in an equally broad selection of elastomers grades. Careful analysis of the data has provided a better understanding of coagent selection based not only on coagent structure but also on the composition and microstructure of the elastomer being cured.

Appendix. Model formulations.

NR Masterbatch	
Ingredient	phr
NR CV-60	100
N330 Carbon Black	50
total	150

NBR Masterbatch	
Ingredient	phr
Nipol® DN 3335	100
N550 Carbon Black	50
PlastHall® 7050	5
Stearic Acid	1
Agerite® Resin D	1
total	157

HNBR Masterbatch	
Ingredient	phr
Zetpol® 2010L	100
N550 Carbon Black	50
TOTM	5
total	155

EPDM Masterbatch	
Ingredient	phr
Nordel™ IP4640 EPDM	100
N660 Carbon Black	100
Sunpar® 2280	50
Stearic Acid	1
total	251

EVM Masterbatch	
Ingredient	phr
Levaprene® 600HV	100
MT 990 Carbon Black	50
Rhenogran® PCD 50	3
Naugard® Q	2
Maglite® D	2
Stearic Acid	1.5
total	158.5

CM Masterbatch	
Ingredient	phr
Tyrin™ 0136	100
N550 Carbon Black	60
CaCO ₃	40
DIDP	30
Maglite® D	5
Agerite® Resin D	1
total	236

CSM Masterbatch	
Ingredient	phr
Hypalon® 40	100
N330 Carbon Black	60
Sunpar® 2280	10
PE Wax	2
Agerite® Resin D	1
total	173

FKM Masterbatch	
Ingredient	phr
Viton® GF-600S	100
MT 990 Carbon Black	30
VPA #2	1
total	131

FEPM Masterbatch	
Ingredient	phr
Aflas® 150P	100
MT 990 Carbon black	25
Sodium Stearate	1
total	126

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