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"Fundamentals of Curing Elastomers with Peroxides and Coagents I: Coagent Structure - Property Relationships"

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INTRODUCTION

By crosslinking elastomeric polymers, useful materials can be formed which possess 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.

There are many types of vulcanization systems. Deciding which system is optimal for a given application depends on the required curing conditions, the elastomer or elastomer blend employed, and the desired physical properties of the final vulcanizate. Peroxides are capable of vulcanizing most polymer types, including standard unsaturated and saturated elastomer grades, fluoroelastomers, and silicones. The use of coagents synergistically with peroxides helps expand the utility of this vulcanization process.

Networks formed from peroxide vulcanization typically possess good heat-ageing stability and low compression set. These qualities are a direct manifestation of the chemical composition of the covalent crosslinks 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. Greater adhesion to polar substrates and a better balance of heat-aged and dynamic properties result from a judicious choice of coagent. There are many functional compounds that have been used as coagents for peroxide cure. The final properties of the formed network will depend on the reactivity and structure of the coagent. Understanding these structure-property relationships will allow for more informed coagent selection.

The present article will review the use of peroxides to cure elastomer systems, and introduce the concept of improving vulcanizate performance by proper coagent selection through an understanding of structure-property relationships. Many commercially available coagent types will be discussed, along with relevant application data supporting their use.

PEROXIDE VULCANIZATION

Unlike the reaction mechanism of accelerated sulfur vulcanization, the basic chemistry of peroxide decomposition and subsequent crosslink-forming reactions is well established for the various unsaturated and saturated elastomer systems.[1,2,3,4] An excellent review article outlines the scope of peroxide cure and discusses the complexity of reaction pathways in terms of competing reactions, only some of which result in effective crosslink formation.[5]
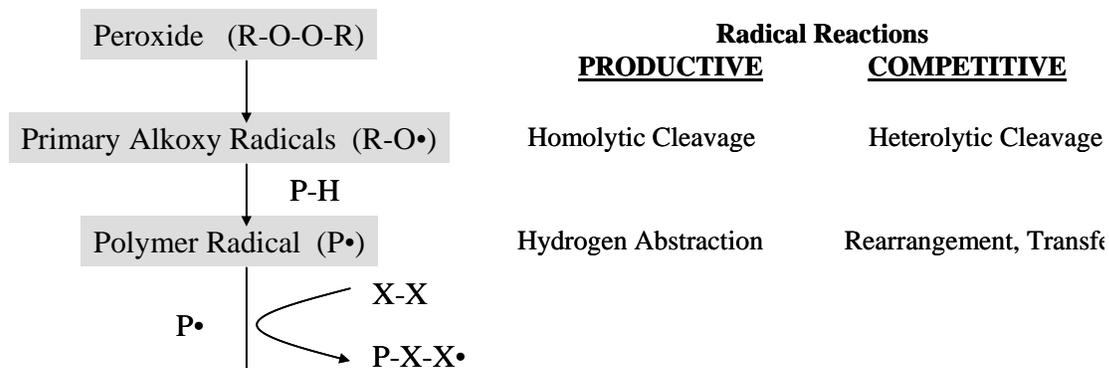
Peroxide   (R-O-O-R)

Primary Alkoxy Radicals (R-O•)

P-H

Polymer Radical (P•)

P•   X-X

P-X-X•

Radical Reactions

PRODUCTIVE	COMPETITIVE
Homolytic Cleavage	Heterolytic Cleavage
Hydrogen Abstraction	Rearrangement, Transfe

Figure 1. Scheme for peroxide vulcanization.

Figure 1 provides a mechanistic scheme for peroxide vulcanization, describing both the desirable reactions which lead to effective crosslink formation and those competing reactions which detract from productive use of radicals. Of course the desired reaction pathways for a polymer radical (P•) is crosslink formation either through coupling with another polymer radical or addition reactions through in-chain or pendant double bonds (unsaturated elastomers). The competitive reactions include polymer scission or other degradation reactions. The balance between productive and non-productive competing reactions depends on many factors, including the elastomer microstructure, the presence of hydrogen donors in the formulation (fatty acids, oils, anti-oxidants, etc.) and the ubiquitous presence of dissolved oxygen. Unfortunately, many of the destructive reactions are kinetically favored, and typically only the very high concentration of reactive sites on the polymer backbone allows for effective crosslink formation to occur at all.

However, the balance can be further tipped toward productive crosslink formation through the use of very reactive, multifunctional coagent compounds. Represented in Figure 1 as difunctional (X-X), these compounds favor network formation through increased local concentrations of easily-abstractable allylic hydrogens or other very reactive sites of unsaturation. So in borrowing the theme of competing reactions, the utility of coagents is derived from promoting more efficient crosslink formation by establishing a higher concentration of reactive sites and reducing the chance of deleterious radical side reactions.

COAGENT REACTIONS
Coagents are classified based on their contributions to cure. Type I coagents increase both the rate and state of cure. Type I coagents are typically polar, multifunctional low molecular weight compounds which form very reactive radicals 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. They form radicals primarily through hydrogen abstraction. Type I coagents include multifunctional acrylate and methacrylate esters and dimaleimides. The zinc salts of acrylic and methacrylic acid also belong to this class. Type II coagents can include allyl-containing cyanurates, isocyanurates and phthalates, homopolymers of dienes, and co-polymers of dienes and

vinyl aromatics. Table I identifies commonly used coagent types by common name, abbreviation, and commercially available products.

I.   Commonly used Type I and Type II coagents.

COAGENT DESCRIPTION	CODE	TYPE	COMMERCIAL PRODUCT
trifunctional (meth)acrylate ester	**TMA**	I	
N,N'-m-phenylene dimaleimide	**PDM**	I	
zinc diacrylate, scorch retarded	**ZDA**	I	SR633
zinc dimethacrylate, scorch retarded	**ZDMA**	I	SR634
poly(butadiene) diacrylate	**PBDDA**	hybrid	
triallyl cyanurate	**TAC**	II	
triallyl isocyanurate	**TAIC**	II	
high vinyl poly(butadiene)	**HVPBD**	II	Ricon® 154

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[6,7] or to generate additional crosslinks.[8] The mechanism of crosslink formation using coagents appears to be at least partially dependent on their class. Most Type I coagents exclusively homopolymerize and form viable crosslinks through radical addition reactions. The dimaleimide coagent (PDM) can also react with in-chain unsaturation through an "ene" reaction mechanism.[9] Certain Type II coagents, containing extractable allylic hydrogens, have been shown to participate in intramolecular cyclization reactions as well as intermolecular propagation reactions.[10] Trifunctional coagents (TAC and TAIC) may form crosslinks through the cyclopolymerization products as well as grafting through pendant allyl groups. The polymeric coagents, typically of high vinyl microstructure, simply increase the concentration of reactive pendant unsaturation, further promoting crosslinking reactions.

Network enhancement through the grafting of coagents between polymer chains,[8,11] the formation of an interpenetrating network of homopolymerized coagents,[12] and the formation of higher modulu filler-like domains of thermoset coagent[10,13] has been suggested. The resulting measurable outcome is higher crosslink density. Many of the final physical properties of vulcanizates are dependent to a large extent on the number of effective crosslinks. Increasing the crosslink density increases compound modulus and hardness, while decreasing elongation and permanent set. Properties associated with bond rupture energies are dependent on both the number of crosslinks and the hysteresis of the network. As hysteresis generally decreases with an increase in crosslink density, properties such as tear strength and fatigue to failure often display local maxima, typically at different crosslink densities.

Proper selection of coagent type can also influence the cured properties through mechanisms other than simply increasing crosslink density. The quality of crosslink can be changed as well as the quantity. It will be shown that while the peroxide provides radicals capable of crosslink formation, the coagent, through varied reactivities and crosslink structures, affords differentiation in the physical properties of the vulcanizate. The structure-property relationships of coagents will be discussed in the next section.

STRUCTURE-PROPERTY RELATIONSHIPS

For the purpose of this article it will be advantageous to create an ideal representation of a multifunctional coagent, as in Figure 2. Several structural components are represented. The groups through which reaction occurs are shown, and the number of these groups, or functionality, can vary. Also represented is the structural member bridging the reactive groups. This model best represents a Type I coagent, but is also applicable to most Type II products (non-polymeric).
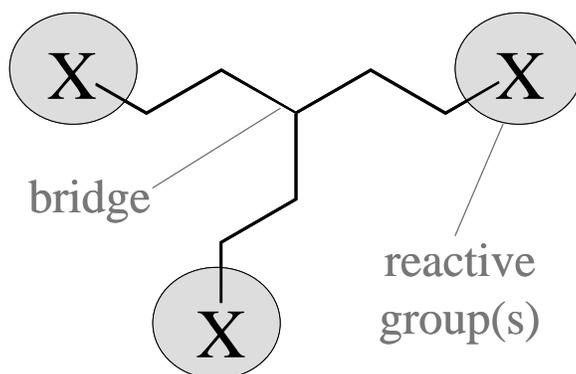

Figure 2. Idealized representation of a multifunctional coagent.

The utility of coagents is derived from the combinations of different structural components commercially available. For example, the reactive groups can vary in form from simple allylic and pendant vinyl moieties, to maleimides, acrylates and methacrylates. The functionality can range from one (monofunctional) to five (pentafunctional) or greater. Many of the more subtle vulcanizate property changes can be realized by altering the structure of the bridging group. This group can take the form of a straight chain (difunctional) or branch structure (multifunctional) or consist of a cyclic alkyl or aromatic ring. Linear structures can be either nonpolar (alkyl) or polar (polyether) and of varying length, providing proximal or widely separated reactive groups. The bridge may also include highly ionic bonds (metal salts) or other bonds with weaker dissociation energies.

The balance of this article will summarize in detail the effects of changing the structural elements on final vulcanizate properties in model peroxide-cured formulations.

REACTIVE GROUPS

Effect on Cure Profile. The chemical nature of the reactive groups dominates the mechanism of coagent reactivity. The influence of structure on reactivity is manifested in the kinetics of cure. In general, less stable radicals formed from more reactive functional groups will increase the rate of cure, effectively decreasing the scorch times (t_2) and time to optimal cure (t_{90}). The extent of cure is determined by the final torque value (S). Figure 3 depicts the departure from a standard peroxide cure rheometer profile when coagents are used. Compared to a standard peroxide-only cure, the very reactive Type I coagents decrease scorch times (t_2*) but improve cure rates (t_{90}*). Type II coagents do not affect cure rate or scorch safety. Typically the extent of cure (S*) is increased for both Type I and II coagents, as more effective crosslinks have been formed.[10]
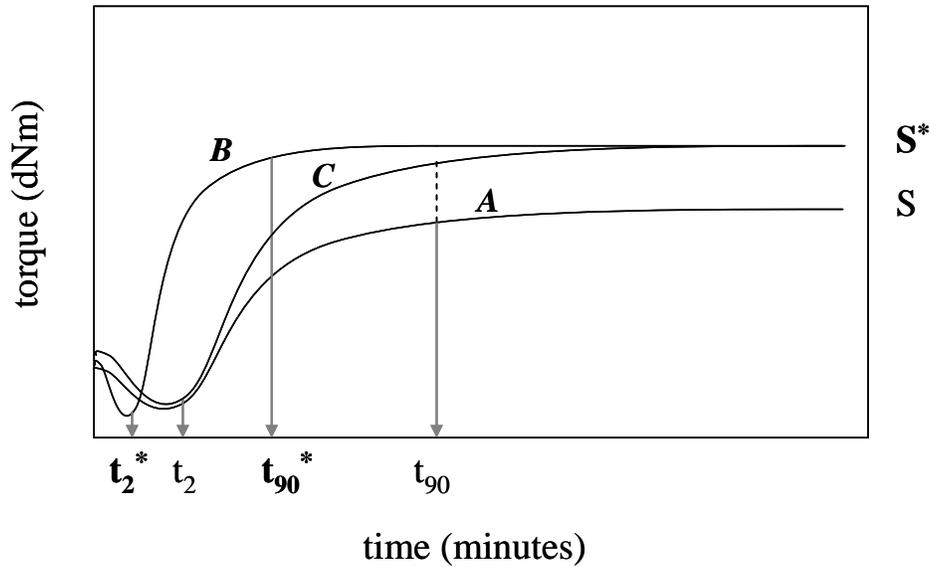
Figure 3. Difference in cure profiles between standard peroxide cure (A), that using Type I coagents (B), or Type II coagents (C).

Cure Kinetics. To better clarify the influence of coagent structure on vulcanization kinetics, various Type I and II coagents were compared (ASTM D 2084).[5] A model EPDM formulation was used with 5 phr coagent and 2.56 phr active dicumyl peroxide. Figures 4 and 5 summarize the changes in cure rate and state, respectively, as normalized plots (control = 100). Type I coagents detract from scorch safety, but also provide faster cure rates, while the Type II coagents exhibit equivalent scorch safety, but longer t_{90} times. The most reactive coagents are those with acrylate or maleimide groups. All coagents provide higher states of cure.
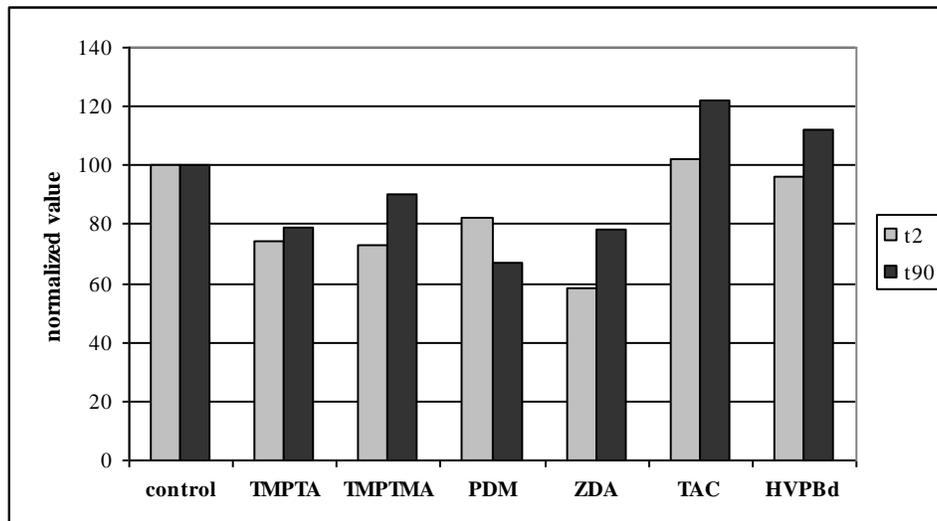
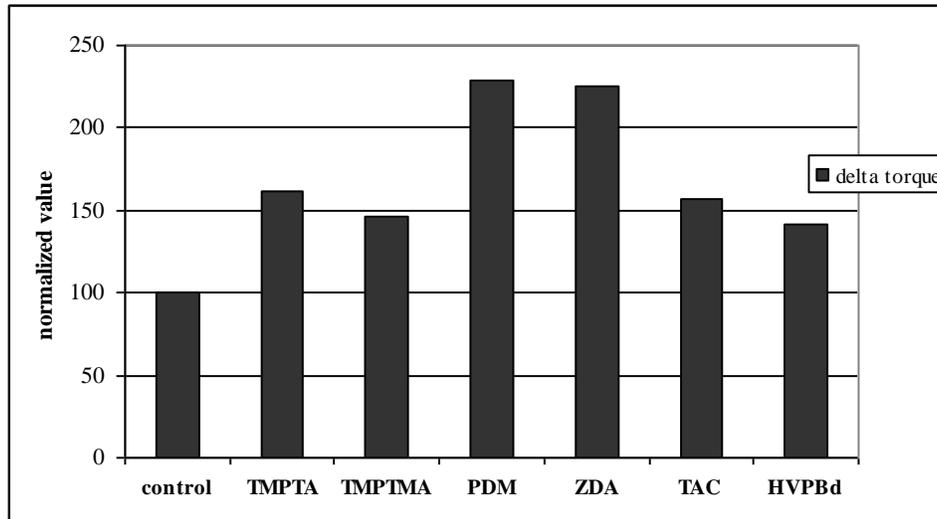**Figure 4. Normalized cure kinetics data.**

Figure 5. Normalized cure state data.

It has been suggested that the loss in scorch safety is primarily attributed to the elimination of degradative chain transfer reactions as the groups of Type I coagents quickly react with the alkoxy radical and do not possess an allylic hydrogen. Type II coagents, however, can still delay the onset of effective crosslink formation by participating in competing, non-productive reactions.[10]

Structural features are primarily responsible for the differences in cure behavior. Type II coagents produce allylic radicals that are stabilized through resonance structures and are less reactive. Acrylate and methacrylate radicals are not stabilized as well and are more reactive. However, methacrylates do form radicals that are tertiary and therefore more stable than the secondary radicals of the acrylate group. In addition, the methyl group of the methacrylate structure may provide a degree of steric hindrance to reactivity.

A good measure of the efficiency with which coagents of varying structure promote crosslink formation is the reduction in compression set of the vulcanizate. Figure 6 provides a comparison between both Type I and Type II coagents in a model EPDM/carbon black formulation with a coagent loading of 5 phr and 3 phr active dicumyl peroxide. Test conditions were 24 hours at 150°C (ASTM D 395). Improvements in set follow the order acrylates > methacrylates > HVPBd > HVSBR. These improvements parallel the reactivity of each coagent and can be attributed to the effect of structural characteristics on activity.
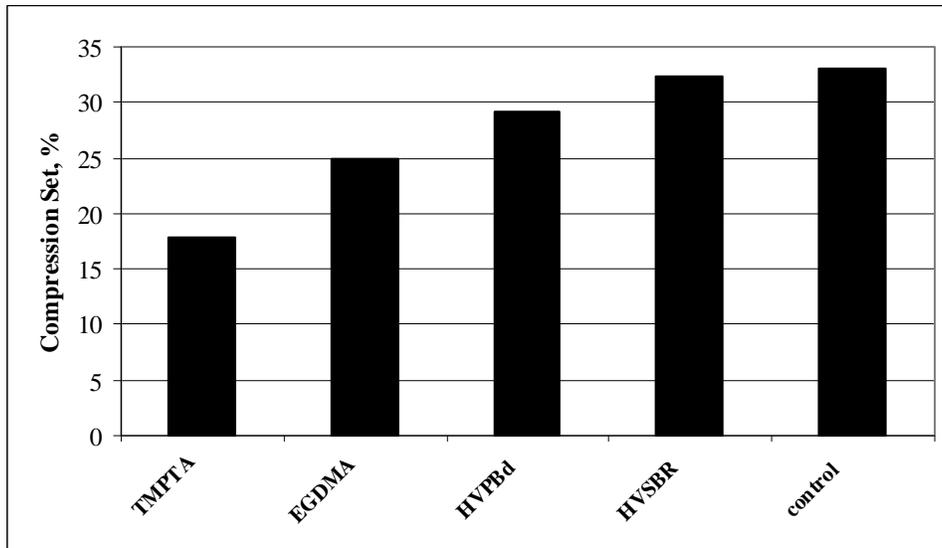
Figure 6. Comparing compression set results for various coagents.

Scorch Safety and Retarders. It should also be noted that the loss in scorch safety exhibited by the Type I coagents can be mediated by the use of cure retarders. The mechanism of retardation and the effect on vulcanization profiles has been published for weakly acidic, hydrogen-donating species.[1,10] Type I coagents are often available as proprietary mixtures including radical-scavenging retarders, providing prolonged scorch safety while maintaining cure rate and greater crosslink density.[14] Figure 7 provides information detailing the utility of a scorch-retarded coagent system (Cray Valley product line). The addition of a scorch retarder to the coagent produces equal to better scorch safety versus the control. With a slight increase in peroxide level, total crosslink density and final vulcanizate properties can be maintained.
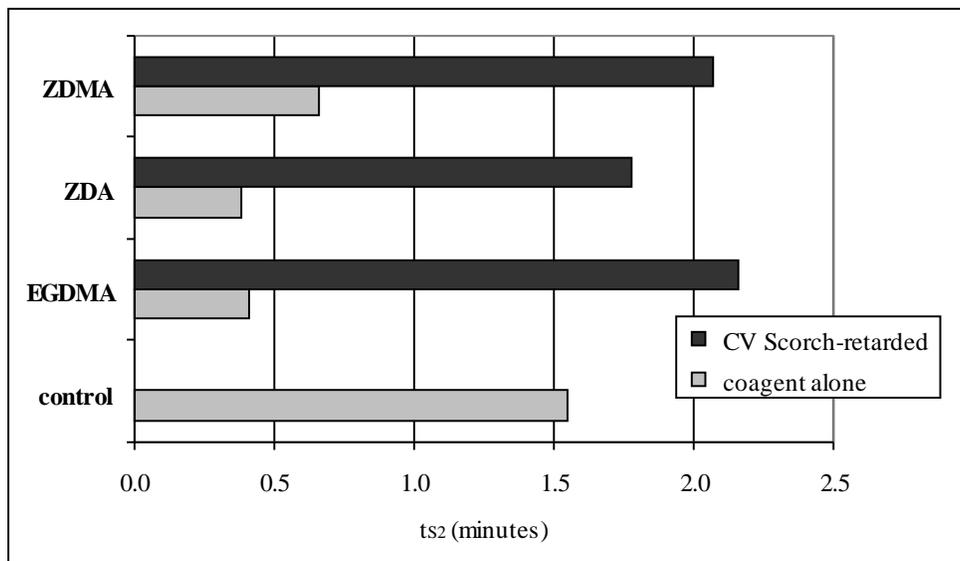

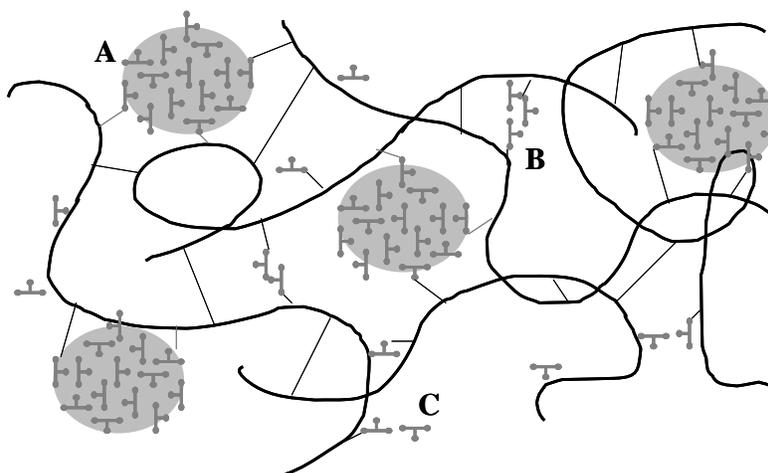**Figure 7. The utility of a scorch-retarded coagent system.**

Figure 8. Idealized network derived from a poorly soluble coagent. (A) coagent domains grafted to network, (B) coagent forming effective crosslink, (C) pendant coagent graft forming no effective crosslink.

BRIDGING STRUCTURES

Effect on Coagent Solubility. The second crucial structural parameter that must be considered when selecting a coagent is the nature of the bridging group. While not directly contributing to the reactivity of the coagent, apparent reaction rates may be affected by the influence of bridging group polarity on the solubility and local concentration of the actual reaction centers.

Most Type I coagents show poor solubility in hydrocarbon-based elastomers (dienes, EPM, EPDM) as they are quite polar.[15,16,17] The largest impact on cure kinetics and vulcanizate properties are often derived from structures having the least solubility—multifunctional acrylates or maleimides with a high reactive group density—translating to a high molar concentration of reactivity per phr of coagent. The addition of hydrocarbon character to improve solubility—longer alkyl bridging groups, pendant methyl to tertiary butyl structures, etc.—may also decrease the apparent reactivity by either steric hindrance or molar dilution effects.

Most Type I coagents produce phase-separated domains of high local concentration. As the peroxides used are also polar in nature, it is likely that a disproportionate amount of the radicals formed are partitioned in the coagent domains as well, promoting thermoset filler-like particles produced from radical addition reactions.[10] If grafted to the polymer chains, the effect can be similar to the addition of a reinforcing filler of high modulus. Figure 8 provides an idealized schematic of a crosslinked elastomer network derived from a coagent of poor solubility.

The polymeric Type II coagents tend not to increase modulus upon curing to the extent of the Type I diene-based coagents. These materials are typically much more soluble in the elastomeric matrix, as the difference in solubility parameters is much less pronounced. Domain formation is typically not exhibited. They can provide improvements in compression set and other tensile properties while not adversely effecting elongation or tear strength.

Effect of Crosslink Strength. The quality of crosslink formed when coagents are employed can exhibit great influence on the dynamic and fatigue properties of the composite. The bridging structure

of the coagent is often the member which will carry the load under network deformation. Covalent carbon-carbon double bonds have high dissociation energies and produce vulcanizates of high strength and heat-aging resistance but poor flex fatigue and tear strength. The latter properties rely on internal energy dissipation mechanisms to reduce stresses and delay rupture. Crosslinks that rupture and reform can dissipate energy and reduce local stresses to provide improved properties.

It has recently been discovered that certain peroxide coagents based on zinc salts of acrylic and methacrylic acid provide improvements in applications where heat resistance is required under dynamic strains.[18,19] The dissociation energy of the $C-O-Zn^{2+}-O-C$ (293 kJ/mol) ionic bond is intermediate to that of C-C (335 kJ/mol) and $C-S_x-C$ (147 kJ/mol) covalent crosslinks.[4] The ability of the ionic bond to break and reform under strain to alleviate stresses has been suggested. This mechanism should be similar in principle to that proposed for networks of polysulfidic linkages.[20,21] It has been shown that the zinc-based coagents do improve the dynamic flex properties of peroxide-cured compounds, while maintaining resistance to heat ageing and compression set.[4,22]

Figure 9 shows the influence of the ionic crosslink character on DeMattia flex fatigue properties (ASTM D 813). A model EPDM formulation was used with 5 phr coagent and 1.4 phr active dicumyl peroxide compared to an efficient sulfur system.[4] At similar modulus, the peroxide/ZDMA system provides superior flex fatigue resistance versus a network derived from sulfidic linkages.

Figure 10 demonstrates the improvement in aged tear strength (ASTM D 624) when ionic crosslinks are formed using zinc salts (ZDA and ZDMA) compared to a traditional triacrylate coagent (TMPTA).[23] Again, a model EPDM formulation was employed with varied coagent phr and 2 phr active dicumyl peroxide. Samples were aged for 70 hrs at 100°C.
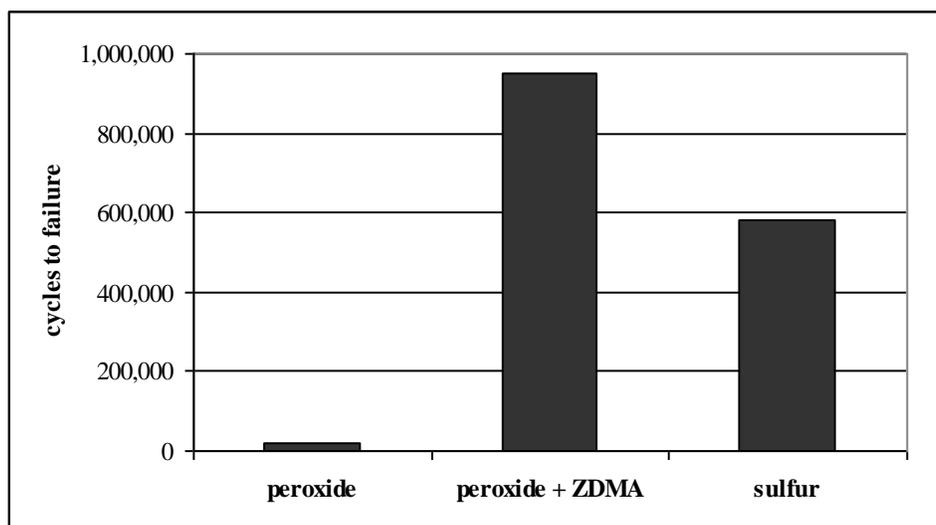

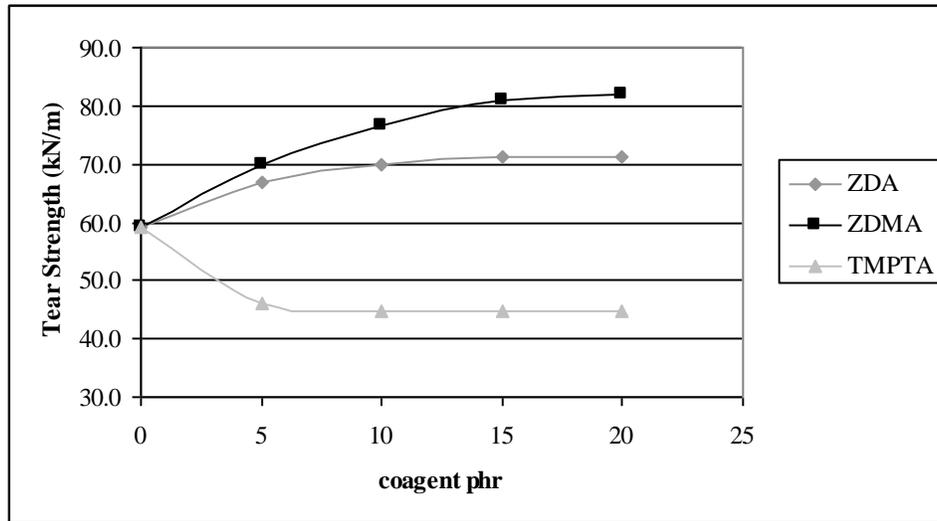**Figure 9. Flex fatigue as a function of crosslink type.[4]**

Figure 10. Tear strength as a function of crosslink type.[23]

Adhesion Promotion. The zinc salts of acrylic and methacrylic acids also increase the adhesion strength of composites containing these coagents to more polar substrates. By increasing the polarity of the rubber network, adhesion of various hydrocarbon elastomers to both metal and fabric surfaces can be greatly improved. Several authors have suggested that the utility of the zinc cation lies in its ability to expand valence in certain complexes.[24,25,26] Regardless of the mechanism, the ionic nature of the crosslink bridge contributes to cured adhesion. It is important, however, that the ionic coagent is an integral part of the cured network to provide maximum benefit.

Figure 11 demonstrates the advantage of using 5 phr ZDA as a coagent for increasing the adhesion to steel in various elastomer systems (ASTM D 816). Figure 12 provides evidence of increased adhesion of an EPDM formulation using 5 phr of ZDA to aramid fabric both with and without resorcinol-formaldehyde-latex (RFL) treatment (ASTM D 413). The disadvantage of coagents which provide exceptional adhesion to metal is that mold fouling is often an issue. However, the proper use of release agents or the use of coagent blends containing an effective anti-fouling component such as adventitious zinc stearate can mediate this problem.[27]
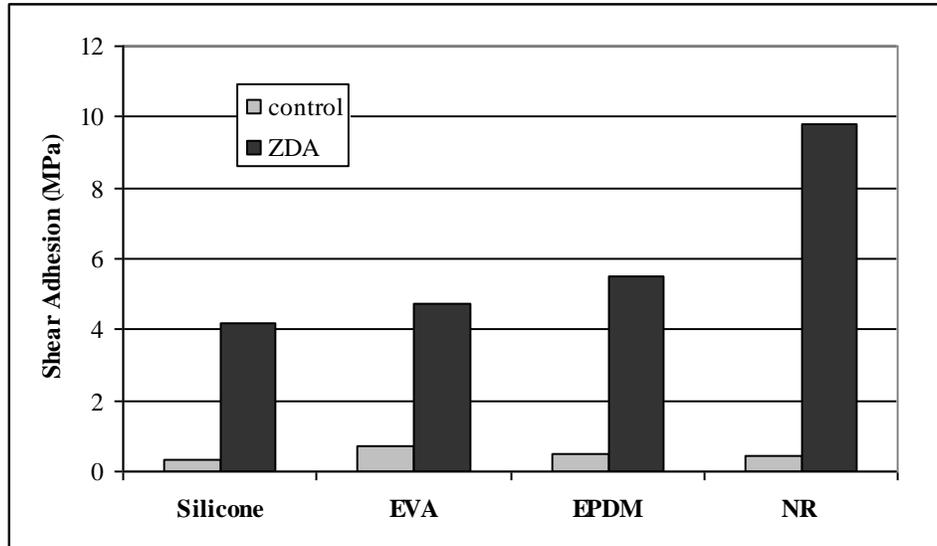
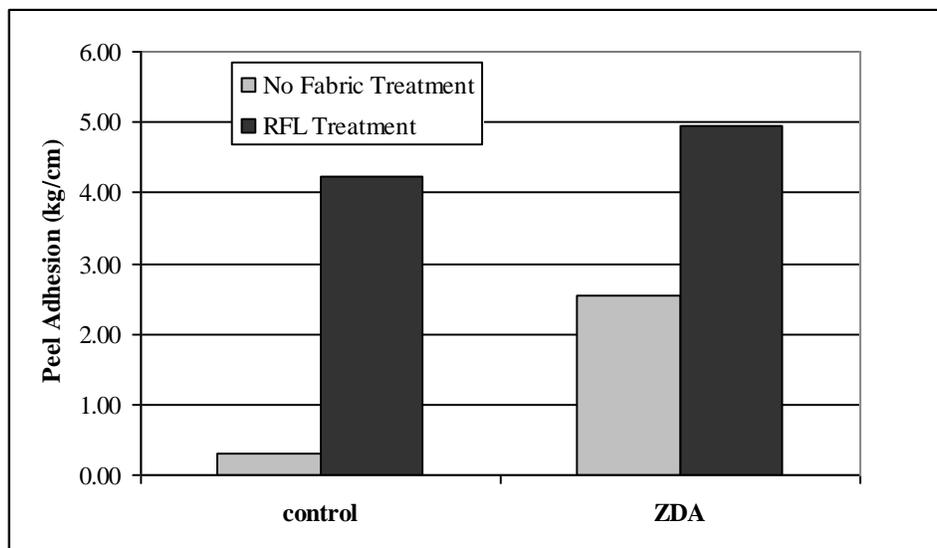**Figure 11. Shear adhesion to steel using zinc diacrylate as a coagent in various elastomer systems.**

Figure 12. Peel adhesion of EPDM compound to aramid fabric with and without treatment using zinc diacrylate as a coagent.

Coagent Functionality

In order to explore the impact of varying the number of reactive groups per coagent molecule on cure kinetics and physical properties, a series of acrylate esters having mono- through penta-functionality were evaluated. Table II lists the coagent products by number of reactive groups per molecule.

Table II. Multifunctional acrylate coagents.

Common Name	Functionality
octyl/decyl acrylate	mono
1,6-hexanediol diacrylate	di
trimethylolpropane triacrylate	tri
pentaerythritol tetraacrylate	tetra
dipentaerythritol pentaacrylate	penta

These products were compounded in an EPDM/carbon black formulation with 5 phr active dicumyl peroxide. Two loading strategies were utilized: 1) each coagent was compared at 10 phr loading and 2) the mono-, tri-, and penta-functional coagents were loaded to a molar equivalency of acrylate groups. In the latter strategy, the phr of the mono- and penta-functional products were matched to provide the same concentration of acrylate in the compound based on 10 phr of the tri-functional product (43.70 phr and 3.38 phr, respectively). The control (no functionality) represents the same formulation without coagent. Physical testing was carried out on samples cured for 20 minutes.

Figures 13 and 14 provide the t_2 and t_{90} times, respectively, as a function of the acrylate number for each coagent at equivalent loading (10 phr) and at equivalent molar concentration. Complex behavior is evident, as the scorch times appear to decrease with increasing functionality, but the time to optimal cure follows the opposite trend. Calculating the actual acrylate molar concentration helps explain the scorch time data. At a constant loading of 10 phr, the molar concentration of acrylate increases to a limiting value that is nearly equivalent for the tri-, tetra-, and penta-functional products. A higher concentration of reactive group will increase the initial cure rate and lower scorch safety. However, this argument does not hold for the time to optimal cure (t_{90}). Here, the higher concentrations of acrylate also require longer cure cycles. Some of the structure-property relationships outlined earlier may help explain this phenomenon. As the acrylate group concentration per molecule increases, it is possible that both the solubility of the coagent decreases and that steric hindrance increases. The net result could be to make a percentage of the acrylate groups unavailable for reaction, effectively lowering their apparent local concentrations and reactivity in the compound. This theory is supported by the data from the series compounded to molar equivalency of reactive groups, as similar trends are seen regardless of an attempt to normalize acrylate concentrations.
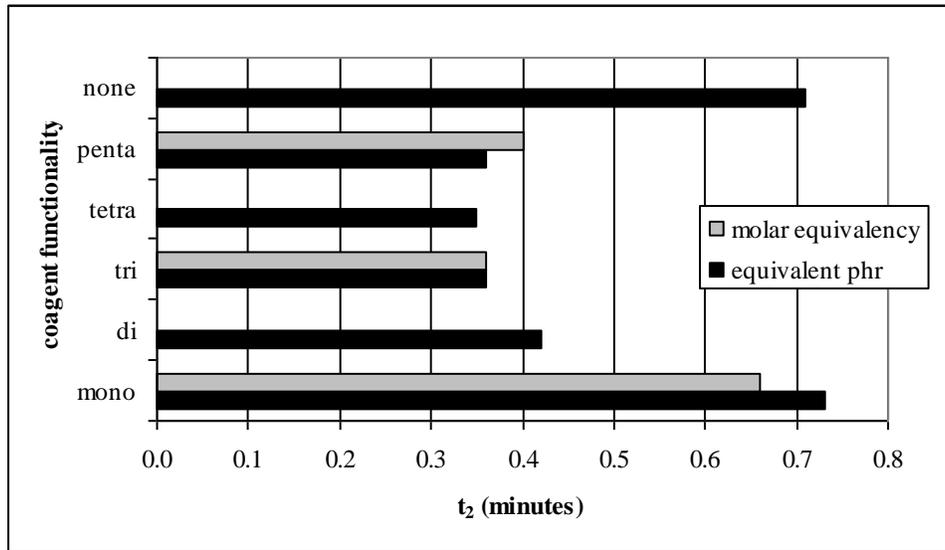
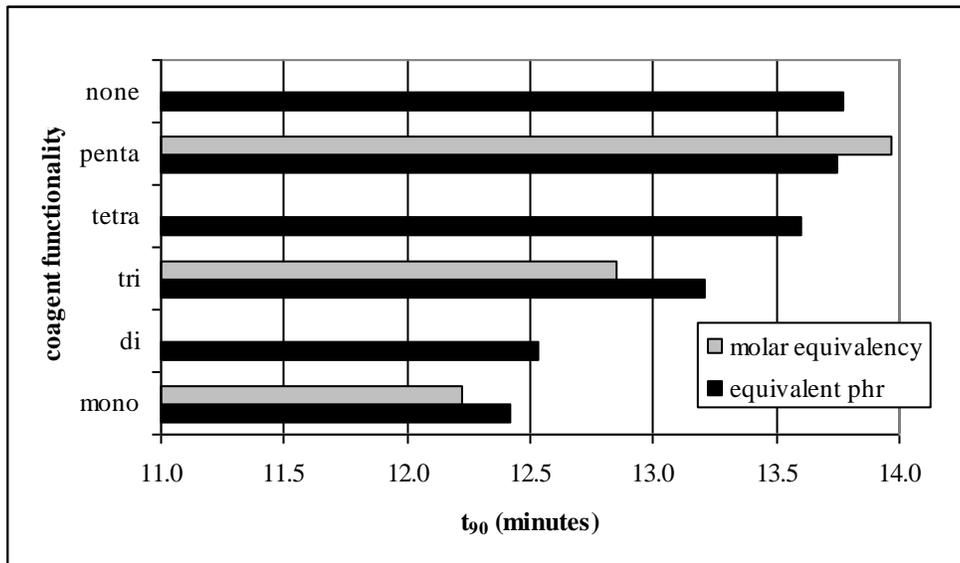**Figure 13. Scorch safety as a function of the number of reactive groups per coagent molecule.**

Figure 14. Cure time as a function of the number of reactive groups per coagent molecule.
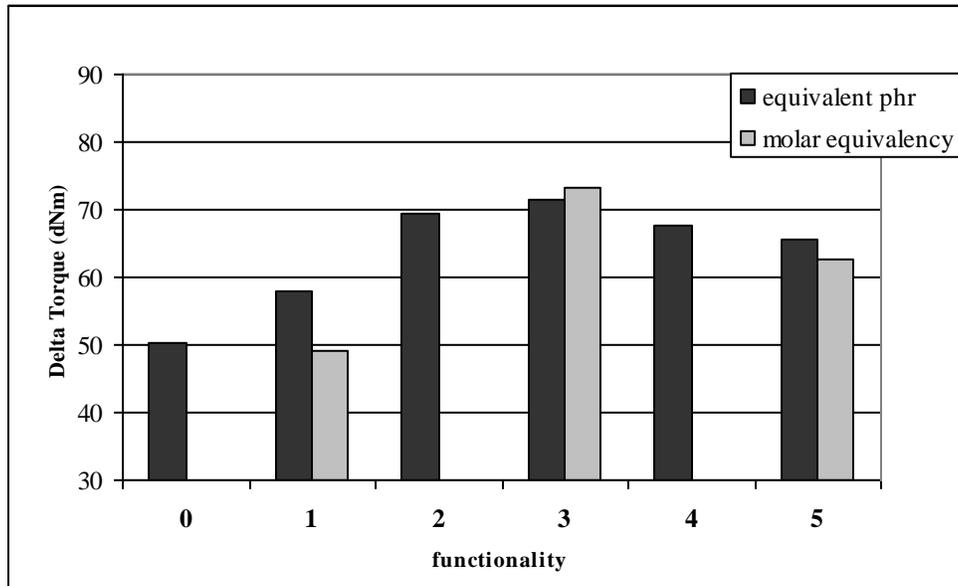
Figure 15. Delta torque as a function of the number of reactive groups per coagent molecule.
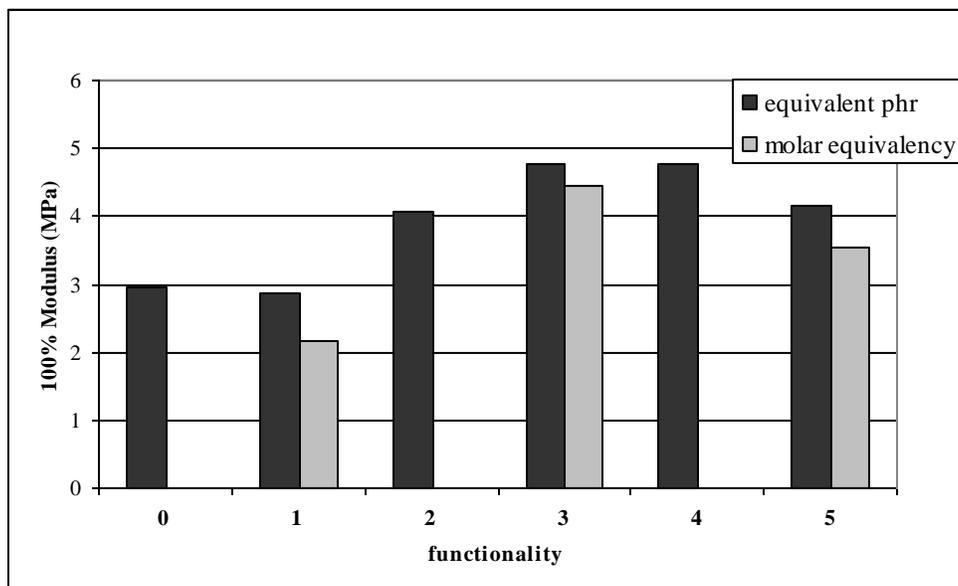

Figure 16. 100% modulus as a function of the number of reactive groups per coagent molecule.
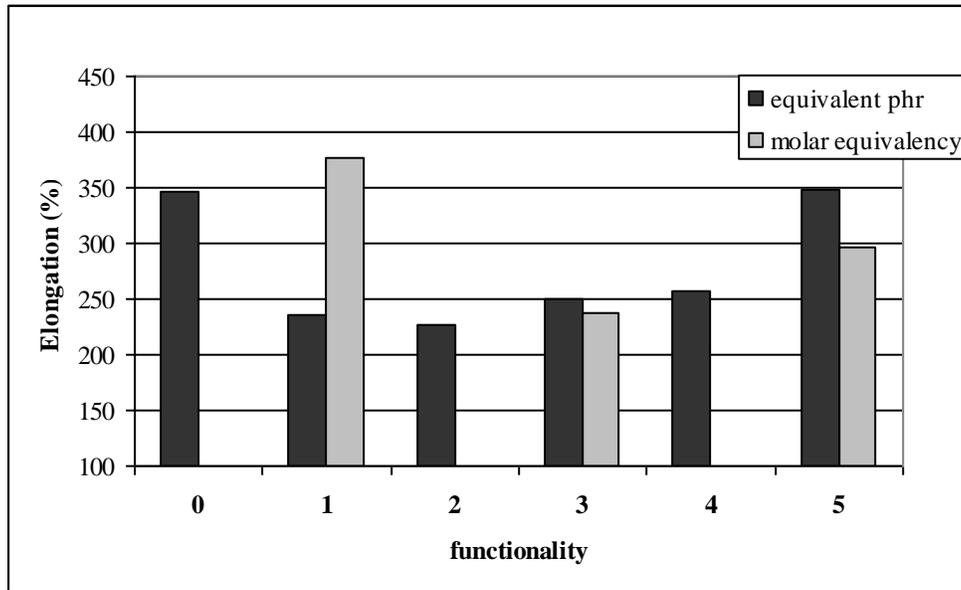
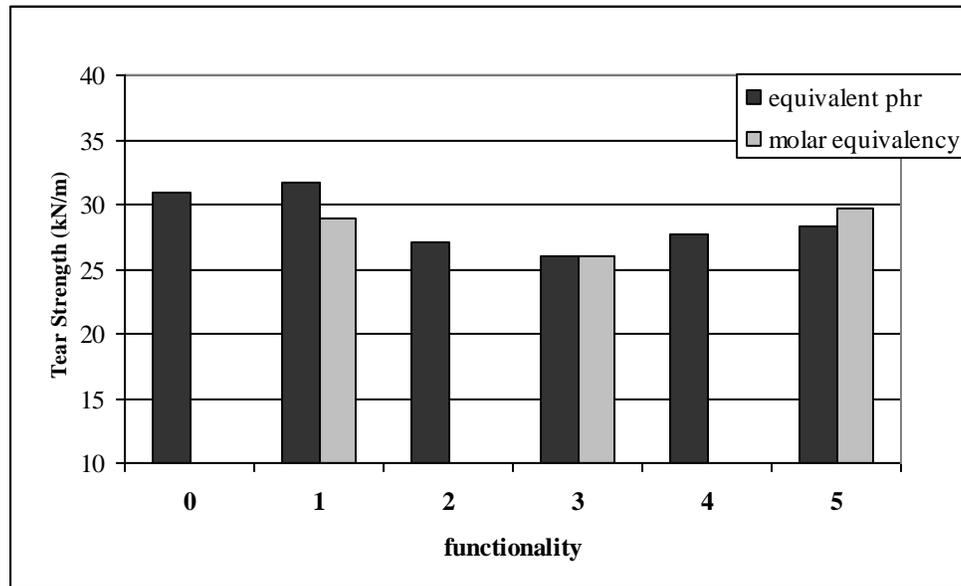**Figure 17. Ultimate elongation as a function of the number of reactive groups per coagent molecule.**

Figure 18. Tear strength as a function of the number of reactive groups per coagent molecule.

The efficiency with which the different coagent structures produce effective crosslinks was also investigated using the same formulation. Delta torque data is provided in Figure 15. It is shown that the trifunctional coagent (TMPTA) is the most effective network building species. Again, the structure of this coagent may provide the best balance of reactivity and solubility in the given compound. The physical properties measured correlate to the crosslink density, with modulus having a maxima and elongation and tear showing minima values at the functionality with the highest delta torque (trifunctional). Tensile strength was largely maintained across the series. Figures 16-18 provide physical property data as a function of acrylate density per molecule (ASTM D 412).

Maximizing effective crosslink formation relies on an understanding of both the reactivity of a given coagent, and its solubility in the compound. It appears that there are structural factors that may limit the benefits delivered by the coagent. Optimized performance of the vulcanizate can be realized if both reactivity and solubility are controlled in the specific application.

CONCLUSIONS

Coagents were originally used to increase the crosslink density of peroxide-cured systems by increasing the efficiency of productive radical reactions. The technology has progressed forward such that today the improvements in crosslinking are generally taken for granted, and coagent selection is now driven by the desire to improve more than just the modulus or tensile strength of the compound. Coagents can impart physical properties such as greater tear strength, improved adhesion to polar substrates, and dynamic fatigue properties rivaling networks derived from sulfur linkages—all while maintaining heat aged properties and lower compression set.

It is now clear that many of the beneficial properties associated with coagent use are directly related to the chemical structure of the products. Reactivity and cure kinetics, the inherent strength and flexibility of the formed network, and the affinity of the resulting compound for polar substrates can in large part be accounted for by an inventory of the structural components of the coagent molecule. To realize the greatest improvements in a given application, it is crucial to understand the structure-property relationships directing coagent performance.

ACKNOWLEDGEMENTS

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