The Chemical Reactions of Network Structures in Elastomers

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Introduction

Elastomers are one of the most widely used industrial polymers. Historically, vulcanized natural rubbers have been used since their discovery in the 19th century. The elastic property of natural rubber, i.e., elongation up to several hundred percent with recovery of its initial state upon removal of the external stress, is the characteristic property of this class of polymers. Rubbers are the only materials capable of reversible extension to strains of 6−700%. No other materials exhibit an increase in modulus with increase in temperature.

A rubber is generally defined as a material which can be stretched to at least twice its original length and which will retract rapidly and forcibly to substantially its original dimensions on release of the force. An elastomer is a rubber-like material from the standpoint of modulus but has limited extensibility and incomplete retraction.

The resistance to deformation in conventional elastomers is largely entropic. The number of conformations accessible to a chain diminishes when its end points are separated. When entropy drops, the free energy rises and an external applied stress is required to impose such a deformation.

Vulcanization

Useful rubber articles are made by vulcanization. Unvulcanized rubbers are generally not very strong, do not maintain their shape after a large deformation, and can be very sticky (about the same consistency as chewing gum). To produce a rubber having the proper elastomeric physical properties, the polymer chains must be very flexible and chemically cross-linked. Vulcanization can be defined as a chemical cross-linking process that generates a rubber material with useful properties. The ultimate goal of understanding vulcanization chemistry is to be able to tailor formulations to produce desired mechanical and chemical properties. If we can develop a full understanding of the relationship between vulcanization chemistry and the resulting network, then this goal can be obtained.

In the rubber industry a sulfur-based cross-linking system is generally used. Since the vulcanization rate with sulfur alone is slow, chemical accelerators and activators are necessary, so there are two general categories of sulfur vulcanization—unaccelerated and accelerated. Unaccelerated sulfur formulations consist of rubber and sulfur, while accelerator systems contain rubber, accelerator, and sulfur. In addition, zinc oxide and stearic acid are often included in both types of systems. The vulcanization process may occur via different reaction mechanisms, depending on the chemicals/fillers used. There are also accelerator systems in which elemental sulfur is not present; instead, the accelerator provides the sulfur for

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vulcanization. These sulfurless systems are generally referred to as sulfur donor formulations.

Vulcanization Mechanism

The exact mechanism under which accelerated sulfur vulcanization occurs is a function of the class of accelerators/activators. Typically benzothiazole or sulfenamide accelerators are used. Zinc oxide is the activator, and a fatty acid such as stearic acid is the coactivator. A generally accepted sequence of reactions is as follows.[1,2]

(1) An interaction of the curatives occurs to form the active sulfurating agent, $Ac-S_x-Ac$ by a reaction of accelerator (Ac) and activator with sulfur:

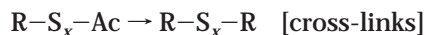$$Ac + S_8 \rightarrow Ac-S_x-Ac \quad [\text{active sulfurating agent}]$$
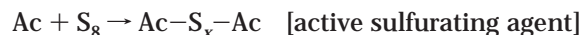
(2) The polymer chains interact with the sulfurating agent to form polysulfidic pendant groups terminated by accelerator groups:
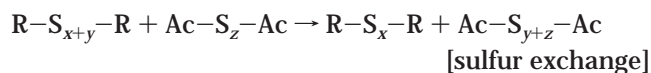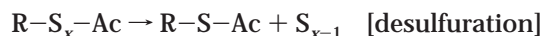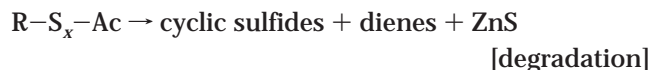
$$Ac-S_x-Ac + RH \rightarrow R-S_x-Ac$$
$$[\text{pendant sulfurating agent}]$$
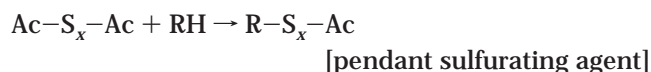
RH is the rubber chain.

(3) Polysulfidic cross-links are formed:

$$R-S_x-Ac \rightarrow R-S_x-R \quad [\text{cross-links}]$$

(4) Network maturing and competing side reactions also occur which do not lead to effective cross-links. Thermal decomposition leads to the following reactions:

$$R-S_x-Ac \rightarrow \text{cyclic sulfides} + \text{dienes} + ZnS$$
$$[\text{degradation}]$$

$$R-S_x-Ac \rightarrow R-S-Ac + S_{x-1} \quad [\text{desulfuration}]$$

$$R-S_y-R \rightarrow R-S-R + S_{y-1} \quad [\text{monosulfidic cross-links}]$$

$$R-S_{x+y}-R + Ac-S_z-Ac \rightarrow R-S_x-R + Ac-S_{y+z}-Ac$$
$$[\text{sulfur exchange}]$$

During the curing and network maturing periods, there are at least three competing reactions: cross-linking, desulfuration, and degradation reactions. The network structures formed depend on not only temperature but also accelerator types and concentration. The ratio of poly-, di-, and monsulfidic cross-links strongly depends on the ratio of sulfur to accelerator in the formulation.

Role of Carbon Black

Carbon black is a universal reinforcing filler and light stabilizer used in rubber compounds.[3] Carbon black imparts strength and toughness to a tire and also improves the rubber's resistance to tearing, abrasion, and flex fatigue and also increases traction and durability. A tire would last less than 5000 miles without the addition of carbon black.

Carbon black, produced largely from oil, consists of irregular, branched aggregates of firmly fused nodular subunits. The dispersed carbon black agglomerates form a network themselves in the polymeric media.[4] With increasing filler content, the network chains become shorter and the number of entanglements between two cross-links decreases.[5] Single molecules are likely to adsorb on several carbon black surface sites, so the bound rubber is essentially immobile. Reactive groups including acid groups, phenolic groups, quinonic groups, and lactone groups have all been identified on the carbon black surface and influence adsorption.

Carbon black not only improves the "strength" of the rubber but also influences the curing characteristics. Carbon black decreases the vulcanization induction time and decreases the cure rate as the amount of surface acid groups on the carbon black increases. The mechanism appears to be one of a competitive reaction between the rubber and the filler for the zinc oxide activator. Channel carbon blacks exhibit high amounts of surface groups (due to about 3.5% oxygen content) as opposed to furnace carbon blacks which have a very small amount of these surface groups. Carbon black (regardless of the type) acts as a catalyst for the initiation of vulcanization. The initiating effect of carbon black increases with loading.

Recently, there has been a trend to replace carbon black with silica to improve tire rolling resistance and tire mileage rating and to decrease auto fuel consumption.[6]

Characterization of Network Structures of Elastomers

A variety of techniques have been used to study rubber vulcanization. One of the most effective, in terms of the determination of specific molecular structures, is high-resolution solid-state nuclear magnetic resonance (NMR).[7]

Advances in instrumentation and experimental techniques, such as dipolar decoupling, magic-angle spinning, and cross-polarization, have made it possible to routinely acquire high-resolution ^{13}C NMR spectra of solid polymers.[8] Information about structure and dynamics previously buried in broad featureless solid-state spectra is now available.[9] One can take advantage of the large chemical shift dispersion of ^{13}C to resolve nuclei in different chemical environments. Measurements of the relaxation rates at each resolvable carbon are also possible because the low abundance of ^{13}C precludes averaging of relaxation rates by spin diffusion. In this manner, structural information can be obtained and the CP/MAS spectra give quantitative indications of the type and amount of the chemical cross-linked structures. It has been possible to relate the reinforcement mechanism of carbon black to the relative amount of chemical versus physical cross-links (entanglements) using NMR and equilibrium swelling measurements.

Identification of Chemical Structures Developed in the Vulcanization of Rubbers Using High-Resolution Solid-State NMR

The chemical structural information obtainable from high-resolution NMR spectroscopy includes main chain microstructures, comonomer composition and sequence, terminal structures, branching, abnormal structures (cyclic
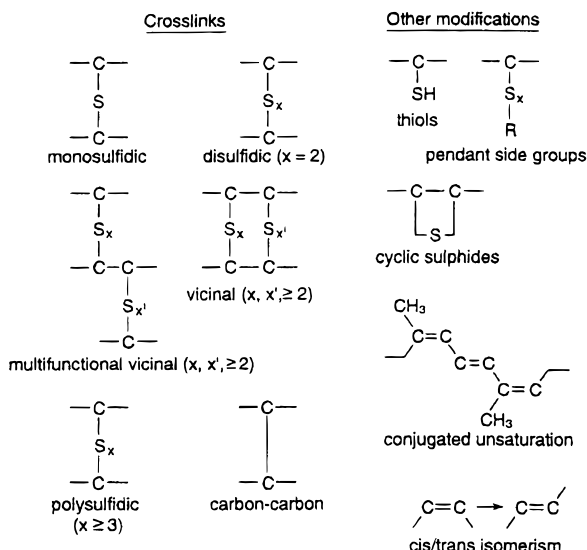
Crosslinks

monosulfidic disulfidic (x = 2)

vicinal (x, x',≥2)

multifunctional vicinal (x, x',≥2)

polysulfidic (x ≥ 3) carbon-carbon

Other modifications

SH thiols S_x R

pendant side groups

cyclic sulphides

conjugated unsaturation

cis/trans isomerism

FIGURE 1. Schematic representation of different types of sulfur cross-links.

A1c
30 ppm A1cpβ
40 ppm A1cmβ
45 ppm A1cmα
51 ppm A1cpα

A1t
45 ppm A1tm
51 ppm A1tp

Saturated A2
51 ppm

Unsaturated A2
45 ppm
51 ppm A2cpα

B1c
12 ppm B1cpβ
17 ppm B1cpβ
57 ppm B1cmα

B1t
14 ppm B1tpβ
58 ppm B1tmα
64 ppm B1tpα

C1c
45 ppm C1cpα

FIGURE 2. Specific network structure with calculated NMR resonances for chemically distinguishable carbons.

and isomerized structures), bonding direction, and the cross-link structure in the sample. In modern solid-state NMR spectroscopy, high-resolution spectra with sharp resonance lines are obtainable with solid bulk samples by applying specific line-narrowing techniques. Under magic-angle spinning (MAS) conditions, high-quality spectra can be recorded for the lightly cross-linked elastomers above the glass transition temperature. Recently, solid-state ^{13}C NMR has been widely applied for the characterization of vulcanized rubber systems.[10] The chemistry of sulfur vulcanization of natural rubber was studied by using standard ^{13}C FT-NMR with magic-angle spinning (MAS).[11] Prior to the actual NMR observation of the natural rubber vulcanizates, model compounds were examined to determine where the chemical shifts of the cross-link sites occur, and how different cross-link structures may be resolved. On the basis of the chemical shifts of the model compounds having different levels of sulfurization, it is found that the chemical shift of the α-carbon in a disulfide is about 7 ppm downfield compared to that in the corresponding monosulfide. Hence, one could expect to resolve monosulfidic and disulfidic cross-links attached to the polymer chain. On the other hand, there is usually little difference between the α-carbon chemical shift in a trisulfide and that in the corresponding disulfide.

The reaction of diene rubber produces a variety of sulfurized and other structures. A schematic representation of the different types of sulfurized structures is shown in Figure 1. The structures include monosulfide, polysulfide, and multifunctional vicinal cross-links produced by the sulfurization reactions. Non-cross-linked structures such as thiols and pendant side groups and cyclic sulfides are byproducts of the reaction. In addition, the temperature of the cure also generates some cis isomerism and introduces conjugated unsaturation. The type of sulfur attachment resulting from attack at the different available proton sites occurring in natural rubber is designated A1, A2, B1, and C1 as seen in Figure 2.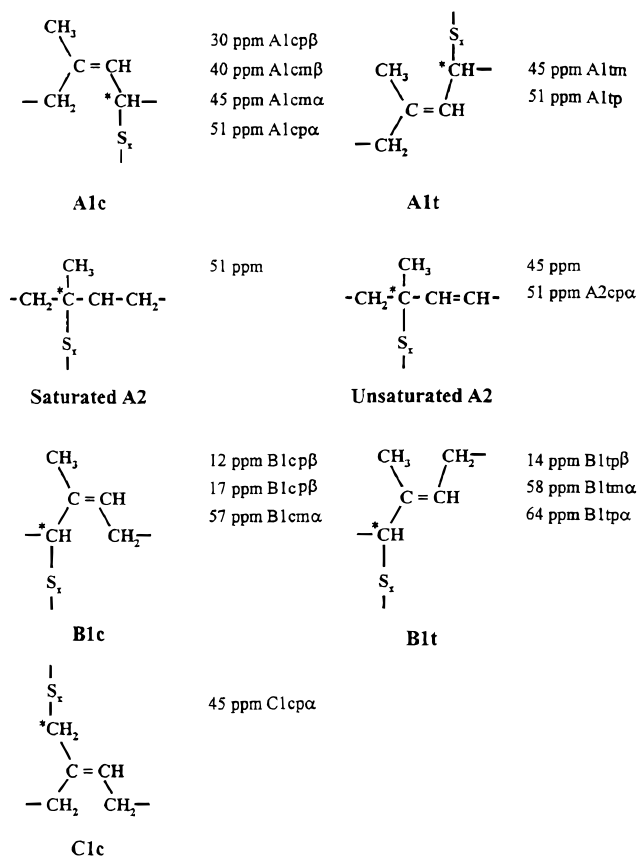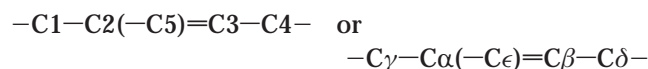 From the perspective of the NMR measurements the carbon numbers in 1,4-isoprene units in natural rubber are designated as follows:

$$-C1-C2(-C5)=C3-C4- \quad \text{or}$$
$$-C\gamma-C\alpha(-C\epsilon)=C\beta-C\delta-$$

From the NMR perspective, these structures can be identified on the basis of the chemical shifts of the chemically distinguishable carbons in each structure. The approximate chemical shifts for carbons in these structures have been calculated by using ^{13}C chemical shift substituent effects. The initial substituent-effect values used are taken from Wehrli and Wirthlin[12] but were slightly modified on the basis of model compound studies.[13] The values are, for monosulfidic, α = +18 ppm, β = +6 ppm, and γ = −4 ppm, and, for di- and polysulfide, α = +25 ppm, β = +6 ppm, and γ = −4 ppm. Thus, the chemical shift at 30 ppm corresponds to the resonance of the β-carbon of the A1 unit with the attachment of a polysulfide (p) cross-link for the cis (c) isomer. The structure corresponding to this 30 ppm resonance is symbolized by the combination of these four different contributions as A1cpβ. The calculations of chemical shift suggest that the cis and trans isomers can be resolved from each other. The resonances of the monosulfide and di- and polysulfide structures can be differentiated by their NMR resonances, but the di- and polysulfide structures are not distinguishable from each other. The theoretical predictions are confirmed by measurements on model compounds. Finally, it should be noted that the sulfur

cross-link structures and the sulfur accelerator fragments have the same resonances.

Unaccelerated Sulfur Vulcanization

Unaccelerated sulfur vulcanization (sulfur-only) is the oldest form of vulcanization practiced and as such has been widely studied. One would expect that the sulfur-only vulcanization would lead to simple chemistry and network structures. However, the opposite is true. The sulfur-only vulcanization chemistry involves many reactions such as double bond migration, chain isomerization, and saturation as well as chain cleavage, cyclization, and formation of vicinal cross-links. The first use of high-resolution solid-state ^{13}C NMR to study sulfur-only cross-linked carbon structure was by Zaper and Koenig.[14] An increase in line widths and a decrease in the resolution are observed with an increase in cure time. A dominant new resonance is observed at 58 ppm which is assigned to the polysulfide or vicinal cross-links. Other new resonances appear at 47 and 129 ppm which are assigned to monosulfide and *trans*-NR species, respectively. Broad resonances are observed in the 18−21 and 30−33 ppm regions which are attributed to the products of chain scission and cyclic structures, respectively.

Samples containing zinc oxide, stearic acid, natural rubber, and sulfur were vulcanized at 140−150 °C, varying the percent sulfur at 10, 20, and 30 wt %. In ^{13}C NMR spectra with increasing cure time at each sulfur concentration, new peaks began to appear as a result of the sulfurization of the chains. After 10 min of cure, peaks at 57.5, 50.2, 44.6, 40.1, 30.0, 18.0, 16.1, and 14.0 ppm were observed. At longer cure states peaks at 58, 64, 73, and 81 ppm were found which are probably the result of oxidation. The peaks at 16.1 and 14.0 ppm are possibly due to the chain end methyl groups occurring by chain scission.

In a further study,[15] inversion recovery spin-relaxation time measurements and computer fitting of overlapping spectra regions were used to identify additional peaks in vulcanized natural rubber cured with 1, 3, and 5% sulfur for different time intervals. Those overlapping cross-linked carbons with different T_1 times showed different peak intensities which could be determined by computer fitting of the peaks. Two new peaks at 37.8 ppm and 25.5 were identified.

Initial studies were made on sulfur vulcanization of *cis*-polybutadiene.[16] The NMR of the vulcanized rubber showed peaks representing cross-linked structures. With increasing cure at 10% sulfur, new peaks at 50, 38, and 33 ppm emerged, with an additional peak at 29 ppm appearing in the 20% sulfur vulcanization.

Clough and Koenig also examined sulfur-vulcanized polybutadiene using a higher field NMR at 75.5 MHz.[17] As shown in Figure 3, after 30 min of cure, a total of 25 new peaks emerged in addition to the normal 1,2- and 1,4-cis and trans isomers present in uncured polybutadiene in a range of 51−25 ppm. A DEPT (distortionless enhancement by polarization transfer) experiment showed
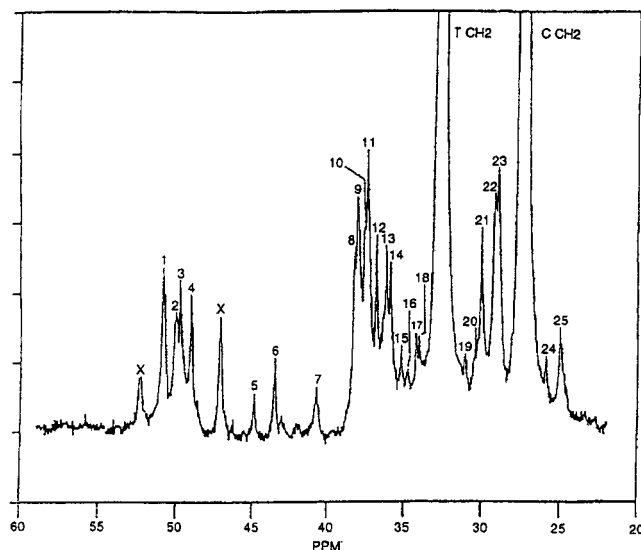

FIGURE 3. Aliphatic region of the ^{13}C GHPD-MAS spectrum of *cis*-polybutadiene cured with 10 phr sulfur at 150 °C for 30 min. The numbers refer to assignments for NMR resonances (see assigned reference).

that the peaks in the range from 40 to 52 ppm were methine carbons while at the lower range below 40 ppm the peaks represented methylene carbons. The different resonances correspond to isomeric forms of cross-linked and cyclic butadiene structures.

A major focus of the unaccelerated sulfur vulcanization has been on the nature of the reaction mechanism. At issue is the question of whether the mechanism is polar (ionic), radical, or mixed. The basis of the argument is the potential of the S_8 ring to undergo homolytic (radical) and heterolytic (polar/ionic) ring-opening reactions. The general conclusion to date is that unaccelerated sulfur vulcanization occurs via a polar reaction mechanism. A free radical mechanism would result in a quaternary radical in isoprene-based elastomers, and the stability of this radical would favor double bond migration which is not observed except at low levels (possibly induced by chain scission).

Accelerated Sulfur Vulcanization

Accelerated sulfur formations are the most common vulcanization systems used in commercial and industrial applications. Although there is a large amount of research on binary accelerator systems, the majority of the research concentrates on single accelerator systems. In our laboratory, we have concentrated our efforts on accelerated sulfur vulcanization of *cis*-polyisoprene and natural rubber.[18] Three different single accelerator systems were studied: tetramethylthiuram disulfide (TMTD), *N*-oxydiethylene-2-benzothiazole sulfenamide (MOR), and *N*-cyclohexylbenzothiazole-2-sulfenamide (CBS). The NMR spectra of vulcanizates of these three different accelerators were found to give similar peaks as in unaccelerated sulfur-cured samples. The differences in network structure were reflected in differences in the relative peak intensities between the sulfur and accelerated sulfur cures

as well as differences between the three accelerator-cured samples. Varying the accelerator/sulfur ratio also produced changes in peak intensities. Sulfurization of NR resulted in cis–trans isomerization and polysulfidic sulfurization of the types A1 and C1. There was not evidence for double bond migration or saturation of the double bond which had been observed in unaccelerated systems. Examination of vulcanizations with and without the activator, ZnO, yielded spectra where the peaks at 57 and 44 representing monosulfide linkages were absent.

Krejsa and Koenig studied the behavior of the sulfur-cross-linked carbons using *N-tert*-butyl-2-benzothiazole (TBBS) with conventional, semiefficient, and efficient formulations.[19] ^{13}C NMR was used to follow the nature of the cross-linked carbon structures with increasing cure time. At low cure states, polysulfide-cross-linked peaks at 38 and 51 ppm appeared. As these resonances decreased in intensity, new resonances appeared at 44, 57, 64, 17, 14, and 12 ppm. The majority of the later peaks are monosulfide cross-links while the 64 peak is a trans poly-linkage. Similar behavior was shown among the three formulations. Gronski and co-workers found evidence of several monosulfidic structures of the A, B, and C types.[20]

The induction period early in the vulcanization is when the majority of the accelerator chemistry occurs. The length of the induction period (termed scorch delay in terms of the rubber technologist) varies widely between accelerators. There is little, if any, induction time when using the thiuram accelerator systems. Mercaptobenzothiazole also has a short induction time, while the amine condensation products of MBT, the sulfenamides and sulfenimides, are used because of the long induction times. Studies have shown that specific complexes are formed as activated intermediates which may or may not be the actual sulfurating agent.

Effect of Carbon Black Filler on Vulcanization Chemistry

More recently, the TBBS accelerator was used in a system containing natural rubber and HAF-HS grade carbon black (N347)[21] and compared with synthetic polyisoprene.

As the carbon black content increases, the NMR resonance lines become broader due to molecular immobilization of the rubber chains by the carbon black. In addition there is a decrease of the signal-to-noise (S/N) ratio of the spectra due to the decrease in the amount of rubber displaced by the carbon black. Line broadening also occurred with an increase in cure time as a result of the decrease in molecular mobility due to cross-linking, but this line broadening was less significant than the broadening due to the presence of the carbon black.

The new resonances which appeared with vulcanization were qualitatively the same as observed for the unfilled formulation systems; i.e., new resonances at 50.7, 50.2, and 37 ppm were detected at lower cure times. At longer cure times these three resonances disappeared and new resonances were detected at 58, 64, and 45 ppm along
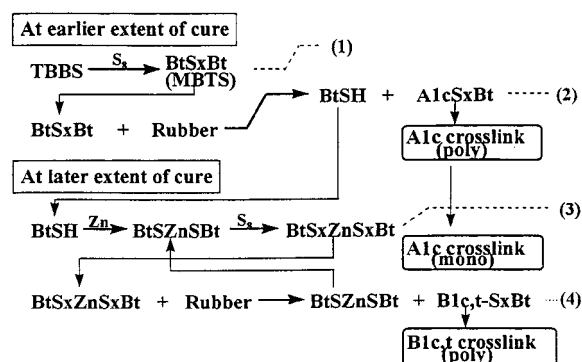

FIGURE 4. Scheme of A1 and B1 type sulfide formation upon vulcanization of natural rubber.

with new peaks at 17 and 12 ppm and the growing of the intensity of the peak at 14 ppm. As the amount of carbon black content increased, the latter features were observed at an earlier stage of cure.

At low cure times, doublet peaks at 50.7 and 50.2 ppm were detected along with the peak at 37 ppm, and these peaks disappeared at longer cure times. The intensities of these two peaks were comparable for every detected pair. In the previous studies, the peaks at 50.7, 50.2, and 37 ppm were assigned to a quaternary carbon of A1c polysulfide, a methine carbon of A1c polysulfide, and a β methylene carbon of A1c polysulfide, respectively.

At longer cure times, resonances at 58, 64, 45, 17, and 12 ppm were detected along with increasing intensity of the 14 ppm peak. The peaks at 58, 64, 17 and 12, and 14 ppm are assigned to B1t monsulfide (α methine), B1t polysulfide (α methine), B1c polysulfide (β methylene), and B1t polysulfide (β methylene), respectively.[10]

Accordingly, there are observed two phenomena involving the effect of carbon black. One is the reduction in sulfur rank for the A1c sulfide structure, and the other is the formation of the A1 type product at an earlier cure stage and an increase in the B1 products at a later stage.

The first effect was interpreted to be due to an entropy change. The disulfide cross-links have less mobility than the monosulfide cross-links due to the rigid nature of the –S–S– linkage. Similarly, the mobilities of the polysulfidic cross-links are probably lower than those of the monosulfidic cross-links. Therefore, the polysulfidic cross-link would occupy more space in the network structure than the monosulfidic cross-link. Considering this fact, the change in sulfur rank from polysulfide to monosulfide would occur along with the increase in entropy when the curing process is extended. Since the system becomes more rigid by the incorporation of the carbon black, the reduction in sulfur rank to monosulfide would eventually be accelerated.

The second phenomenon due to carbon black on a proposed scheme based on the vulcanization process is shown in Figure 4. During the vulcanization process, the reactions 1 and 2, and 3 and 4 form polysulfidic A1c and B1t, respectively. Considering the fact that A1c polysulfide reduces its sulfur rank to monosulfide and reactions 3 and 4 are the predominant process in the later stage of cure,

the system may favor reactions 3 and 4 rather than 1 and 2 in the whole reaction scheme. BtSH is formed from the reaction producing polysulfidic A1c at the earlier stage of cure, which is the reactant for reaction 4 producing the B1 structure. As previously mentioned, the sulfur and accelerator-to-rubber ratio may be higher for the system with high carbon black content. As a result, reactions 1 and 2 would occur more rapidly and, consequently, produce enough BtSH for the initiation of reactions 3 and 4, which means that the B1t polysulfides initiate at the earlier stage of cure for the sample with higher filler content. Since reactions 3 and 4 would occur until the elemental sulfur is consumed, the total amount of B1 structure would be larger for the sample with higher carbon black content.

The network chain density measured by equilibrium swelling includes both the chemical and physical cross-links while the ^{13}C NMR measurements determine only the chemical cross-links. The observed differences in network chain density between the results of the two measurements ($n_{SWELL} - n_{NMR}$) reflect differences in the physical cross-links induced by entanglements involving polymer–polymer interactions and polymer–carbon black interactions. The magnitude of the differences between the two methods of measuring the network chain density increases with the volume fraction of the carbon black for the same stage of cure. The differences in network density values reach a maximum at around the 90% cure stage for the filled formulations. These results coincide with a similar observation from tensile tests where the maximum filler reinforcement effect occurs at an optimum (90%) stage of cure. Consequently, the comparisons of the network densities determined by the swelling and ^{13}C NMR measurements give a measure of the effectiveness of the filler reinforcement at the molecular level.

Effect of Silica Filler on Vulcanization Chemistry

Solid-state ^{13}C NMR spectroscopy was used to identify and characterize the effects that silica has on the network structures that form during the vulcanization of zinc-activated, sulfur-cured *cis*-1,4 polyisoprene.[22] It was determined that the cis–trans isomerism and chain scission were enhanced when silica was added as a filler. The monosulfidic linkages, especially the A1cis and the B1trans type monosulfide linkages, had an increased concentration in the silica-filled systems. Also, the polysulfidic linkages, namely, the A1cis and B1trans type linkages, decreased in concentration. Finally, it was also determined that the intermolecular cross-links decreased in the presence of silica, while the intramolecular structures, including pendant side groups and cyclic sulfides, increased in the presence of silica, resulting in a lower overall cross-link density when silica is used as a filler.

When silica is used as a filler, the cure ingredients are adsorbed, causing the initial overall lower cure rate mentioned above. Several ways exist to counteract this effect by inhibiting the silica absorption by adding a silane

coupling agent or poly(ethylene glycol). Both additives have been shown in the literature to improve the vulcanizate properties. Therefore, solid-state ^{13}C NMR spectroscopy was used to identify and characterize the effects on the network formation when additives, such as a coupling agent and poly(ethylene glycol), were added along with silica filler. It was determined that cis–trans isomerization was inhibited by the inclusion of both the coupling agent and the poly(ethylene glycol). However, there was only a slight influence on the chain scission of the main chain carbons. The presence of coupling agent or polyethylene caused an increase in the concentration of the polysulfidic structures, especially the A1cis and B1trans type linkages, as well as a decrease in the monosulfidic structures, namely, the A1cis and B1trans type structures. Therefore, the intermolecular cross-links, mainly the polysulfidic structures, increased with the use of the additives, while the intramolecular structures, which are mainly monosulfidic in nature, decreased. Therefore, the network chain density of the silica-filled rubber system increased when additives were included in the formulation.

Thermal Oxidation of Network Structures

Elastomeric materials undergo both thermal and oxidation degradation over time. Main chain scission and loss of sulfur cross-links can occur with either factor or by both factors by a thermooxidative mechanism. The chemical changes that occur in thermal and oxidative degradation of sulfur-cured natural rubber were investigated using ^{13}C NMR analysis.[23] The cross-linked carbons formed during TBBS-accelerated vulcanization appear in the NMR spectra as peaks representing the various structures formed. Samples of vulcanized rubber were heated at 100 and 150 °C under both air (oxidative) and nitrogen (inert) environments to assess both temperature and oxidative effects. Changes were observed by measuring peak areas under the cross-linked carbon resonance peaks. A and B type monosulfide linkages were found to decompose much faster by oxidative factors at both 100 and 150 °C than under nitrogen at either temperature. The polysulfide linkages, however, showed the opposite result of thermal degradation predominating over oxidative factors. Cis–trans isomerization of the main chain carbons was observed at the higher temperature while absent at 100 °C.

Future Developments

Liquid Crystalline Elastomers. Nematic elastomeric networks exhibit a number of distinctive features such as anisotropic mechanical properties, a mechanical critical point, and a history-dependent phase diagram. These features result from the coupling between the elasticity of the networks and the nematic order. In liquid crystalline elastomers, applying a directional mechanical field orients the director in the nematic phase and the nematic polydomain structure is transformed into an anisotropic monodomain texture. Removing the mechanical field

reverses the process. So the nematic elastomer exhibits anisotropic mechanical response and recovery compared to the isotropic response of normal elastomers. Additionally, the liquid crystalline response of the mesogen to magnetic and electromagnetic fields is observed in nematic networks.

With liquid crystalline elastomers, one can couple the elastomeric network to externally applied static mechanical stresses to generate much larger effects. For example, the transition temperature can only be increased by external electric or magnetic fields by 10^{-3} K whereas in liquid crystalline elastomers it can be increased by as much as ~ 10 K.[24]

Perhaps the most surprising effect is that the optical properties of liquid crystalline elastomers change as a result of the application of a mechanical field. A turbid polydomain sample can be converted to an optically transparent monodomain sample by an applied mechanical stress.

LC elastomers are shape-memory polymers since they can relax to their undeformed shape when heated above their glass transitions. LC elastomers can be easily deformed into specific shapes and undergo unique phase transitions when they are anisotropically deformed. Elasticity and the capacity to store dispersed molecules make LC elastomers unique materials with high potential to be designed as smart materials.

Nematic monodomain elastomers have been prepared. Chains are first cross-linked in the isotropic swollen state. They are then stretched, and the solvent is removed while a second-stage cross-linking using rigid rod cross-links proceeds in an aligned, nematic state. After this slower reaction is complete, the stress is removed and the system is a clear monodomain. The system is being cross-linked in the same nematic state that deformations are being carried out. This monodomain structure is stable even after being held at elevated temperatures where it is isotropic and then cooled back down to the nematic state.[25] Cooling results in a nematic state that sees spontaneous distortions of both the elastomer and nematic networks.

Electric fields generally have no effect on the mechanical properties of conventional elastomers. In the liquid crystalline elastomers, electric and magnetic fields have been used to advantage for alignment and orientation.[26]

The elastic and electrical properties of LC elastomers in the isotropic and nematic states differ significantly.[27] The isotropic elasticity of a single chain is much stiffer than that of a nematic chain. One effect of this is an exponential temperature dependence of the elastic modulus, E, and its associated force law. In marked distinction, networks of flexible, nonliquid crystalline polymers exhibit a linear T dependence as is found in most materials. Dielectric studies reveal information on molecular dynamics; as an example, the glass transition[28] can be correlated with the degree to which local structure engenders steric constraints on the relaxation from neighboring unbonded segments and thus serves as a useful design tool.

More recently there has been a report of mechanically induced second-order harmonic optical generation (SHG) in LC elastomers.[29] A chiral smectic C phase (S_C*) liquid crystalline elastomer was prepared which could be macroscopically oriented by mechanical deformation. After the deformation, cross-linking was performed which locked in the mechanically induced anisotropy network structure and the subsequent uniform director orientation was chemically locked in. However, because of the conic layer structure, the elastomer did not exhibit macroscopic C_2 symmetry, and no SHG was observed. To obtain a uniform layer orientation, a second uniaxial stress was applied at an angle of 90° to the director, and SHG was observed. The observed nonlinear susceptibilities are on the same order as those for similar chromophores in low molecular weight systems.

Soon we will be able to utilize these unique physical, optical, and mechanical properties of LC elastomers as well as the chemical and optical properties of nematic networks to develop "smart elastomers". These LC elastomers can be made to be responsive and adaptive in a predetermined manner as required by the end-use engineering application.

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