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Solid state carbon-13 NMR studies of silica-filled, TBBS-accelerated, sulfur vulcanized, *cis*-1,4 polyisoprene

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Summary

The network formation of silica-filled, TBBS accelerated sulfur vulcanization of cis-1,4 polyisoprene (Natsyn 2200) was studied by solid state ^{13}C NMR spectroscopy, and equilibrium swelling measurements. Samples with varying silica levels at different stages of cure were analyzed. It was observed that silica retards the cure reaction, and results in an overall lower cure state. Silica also has an influence on the vulcanization chemistry causing an enhancement of the cis-trans isomerization, chain scission, and the formation of monosulfidic linkages. It was also determined that the polysulfidic linkages decreased as silica level was increased. Intermolecular crosslinks decreased, while intramolecular structures (including pendant side groups and cyclic sulfur structures) increased. Cross link density, as determined by swelling measurements, decreased as the silica level was increased.

Introduction

Nuclear magnetic resonance spectroscopy has been useful in studying the formation of network structures during vulcanization in both unfilled and filled rubber systems.[1-7] Usually an elastomer that is above the glass transition temperature (Tg) has high frequency molecular motions in the chains that average the dipolar interactions in the sample, thereby causing the NMR line widths in the spectrum to be narrow. As a result, high resolution NMR spectra can be obtained for the rubber in the solid state by applying a single pulse method with high power proton decoupling and magic angle spinning.[1] The NMR technique is sensitive to the very small modifications of the rubber molecules occurring as a result of vulcanization. Therefore, the different sulfide structures whether monosulfidic, or polysulfidic, and main chain modification like cis-trans isomerization can be detected. Also, the samples can be analyzed in the solid state, so very little sample preparation is needed.

Recently, ^{13}C NMR spectroscopy was used to characterize the influence of carbon black on the vulcanization chemistry and network formation.[8-10] It was determined that reversion reactions, such as cis-trans isomerization, were enhanced by the incorporation of carbon black. Also, carbon black caused an increase in the formation of the B1-type sulfurization structures. Similar studies have not been performed when silica is used as the filler.

Therefore, the focus of this study was to identify and characterize the effects that silica may have on the network formation during vulcanization of zinc activated, sulfur cured cis-1,4 polyisoprene. Compounds with various levels of silica filler, but constant curatives, at different stages of cure were examined.

Experimental

The rubber used in this study is Natsyn 2200, a synthetic high-cis-1,4-polyisoprene. Five samples were prepared following a standard wire coat formulation with various amounts of silica and fixed contents of rubber, cure agents, and accelerators. Table 1 shows the sample designations, formulations, and processing conditions for all the samples used in this study.

The batches were vulcanized in a Monsanto ODR-100 oscillating disk rheometer at 320°F, using a special die that produced button like samples, to obtain the characteristic rheometer curve. Times to 25%, 50%, 75%, and 90% cure were calculated, and samples were then cured to the different cure states. After the allotted time, the samples were removed from the ODR-100, and placed immediately into a cold water bath to quench the cure reaction.

NMR experiments were performed on a Bruker MSL 300 NMR spectrometer at a ^{13}C frequency of 75.47 MHz. All experiments were performed at room temperature on a cross polarization / magic angle spinning (CP/MAS) probe. Magic angle spinning was used under gated high power decoupling (GHPD) conditions. The sample-spinning rate was approximately 3.5 kHz. The signals from about 12000 - 15000 were accumulated with a recycle delay of six seconds for quantitative measurements.

Between five and six of the small sample discs of the diameter of the NMR tube were placed into the NMR sample tube for analysis.

Quantitative measurements in ^{13}C NMR require a recycle delay that is longer than five times the longest spin-lattice (T_1) relaxation time.[11] These times were determined in a previous study for both cis-polyisoprene and trans-polyisoprene.[12] The T_1 relaxation time of the backbone carbon was only slightly increased by the addition of carbon black.[8] It was assumed that the same applies for the addition of silica. Therefore, a recycle delay time of six seconds was decided to be sufficient for the spins of the cis carbons to recover, and may result in a loss of signal of less than 1% for the C-2 and C-5 trans carbons in the filled systems.

The spectra were transferred from the MSL 300 to a SGI/UNIX workstation using Ethernet, where the data was analyzed by IMAGE software. Assignment of the NMR peaks was performed using previously published work, as well as a current study.[8-10, 12-13] The concentrations of the different sulfurization structures were evaluated by using relative intensities, which were calculated by dividing the area of the peak due to a particular sulfurization structure by the average area of the main chain aliphatic carbons located at 32.5 ppm, 26.7 ppm, and 23.7 ppm. The peak area was calculated by in house software using peak integration and curve fitting routines, and the average value was used for the experimental data.

Table 1: Formulations and Processing Conditions (all in units of parts per hundred (phr) rubber).*

Min.	Banbury 1	AK 1	AK 2	AK 3	AK 4	AK 5
0’	Natsyn 2200	100	100	100	100	100
0.5’	Wingstay	1.00	1.00	1.00	1.00	1.00
0.5’	HiSil 255G	--	15	15	30	25
1.5’	HiSil 255G	--	--	15	30	20
3.0’	Stearic Acid	2.00	2.00	2.00	2.00	2.00
Dump after 4’ at 145-150 °C						
	Mill:					
0’	Sundex	3.00	3.00	3.00	3.00	3.00
0’	Zinc Oxide	8.00	8.00	8.00	8.00	8.00
0’	Sulfur	4.50	4.50	4.50	4.50	4.50
0’	Santocure NS	0.80	0.80	0.80	0.80	0.80
*Mix thoroughly. The batches were put back into the Banbury for 2 additional minutes after mixing on the mill.						

Results

The rheometer traces obtained from the Monsanto ODR-100 showed that the overall torque, as determined by subtracting the maximum and the minimum torque, was found to decrease as the level of silica increased.

All samples showed similar high resolution NMR spectra under gated high power decoupling, magic angle spinning conditions. Spectral differences were observed when the aliphatic region of the spectrum is enlarged, and the small resonances due to the sulfur crosslinks are compared.

At low stages of cure, the NMR spectra are dominated by peaks at 16 ppm, 40 ppm, 18 ppm, and 51 ppm. At longer cure times, new peaks at 64 ppm, 58 ppm, and 45 ppm are seen in addition to those previously mentioned. Figure 1 shows a typical ^{13}C NMR spectrum for high (90%) stages of cure, with peaks identified as to sulfurization structure.

The resonances of the trans isomer and the fatty acid in the rubber were observed at 40 ppm, for the trans C-1 methylene carbon, and at 16 ppm, due to the trans C-5 methyl carbon. Cis-trans isomerization in the rubber compound was quantified using only the 16 ppm peak because the peak at 40 ppm is overlapped by another resonance at a later cure state. There is an overall increase in the transformation of this structure as the cure reaction proceeds. Silica does not seem to greatly affect the formation of this structure.

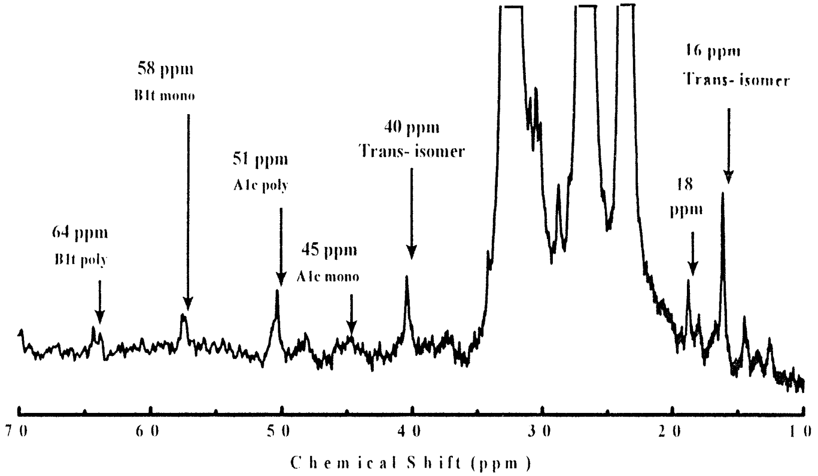

Figure 1. - High resolution ^{13}C NMR spectrum for high state of cure (90%) for silica-filled cis-114 polyisoprene. Main sulfur structures are at 64 ppm, 58 ppm, 45 ppm, and 51 ppm. Other features are at 40 ppm and 16 ppm (trans isomer), and 18 ppm (3,4-isoprene unit).

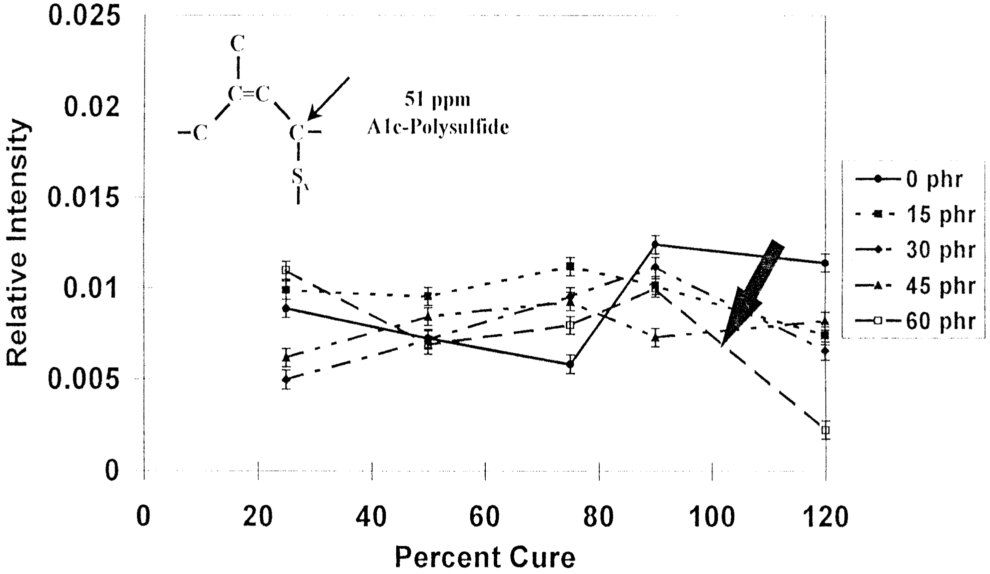

Figure 2. - 51 ppm NMR peak trends for varying silica levels. The structure is the A1c-Polysulfide, as shown. At the later cure states, there is a decrease in the formation of this structure as silica is added.

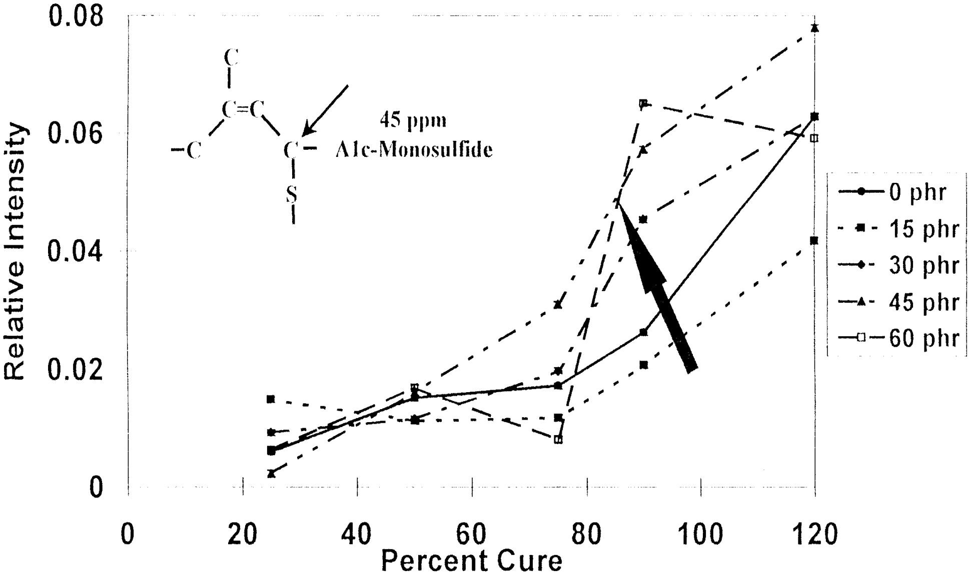

Figure 3. - 45 ppm NMR peak trends for varying silica levels. The structure is the A1c-Monosulfide, as shown. There is an increase in the formation of this structure as amount of silica is increased.

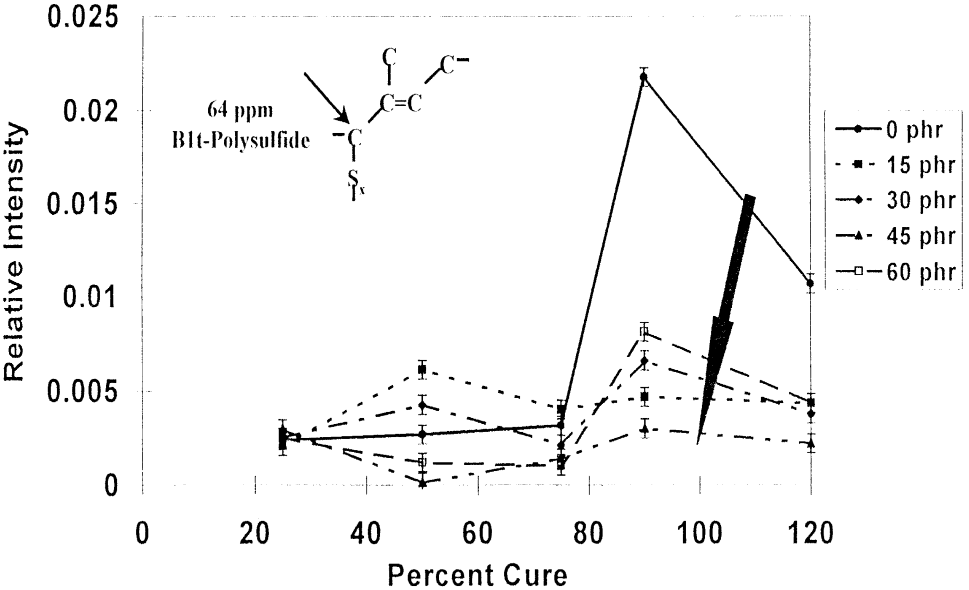

Figure 4. - 64 ppm NMR peak trends for varying silica levels. The structure is the B1t-Polysulfide, as shown. At the later cure states, there is a decrease in the formation of this structure when silica is added.

The 51 ppm peak was observed as a doublet, occurring at 50.7 ppm and 50.3 ppm. These peaks were assigned mainly to the A1-cis type polysulfide along with a small contribution of the A2-cis monosulfide. At later extents of cure, it was determined that the formation of this structure decreased as silica was added, as can be seen in Figure 2.

The peak at 45 ppm was mainly assigned to the A1-cis type monosulfide with a possible contribution of C1-cis polysulfide. Figure 3 shows the relative concentration of this structure as a function of percent cure. As the cure reaction proceeds, there was an overall increase in the formation of this structure, and with an increased production as the amount of silica was increased.

The 64 ppm peak was also observed as a doublet at 64.3 ppm and 63.6 ppm. These were assigned to the B1-trans type polysulfide structure, and were observed only at later extents of cure. Figure 4 shows the plot of the relative intensity of this peak as the cure reaction proceeds. It was observed that when silica was added as a filler, there was a decrease in the formation of this structure.

Discussion

Solid - State ^{13}C NMR Studies

Reversion Reactions. -

1. Cis-Trans Isomerization. In the rubber compound, cis-trans isomerization was evaluated by monitoring the changes in peak intensity of the 16 ppm peak, which is due to the C-5 methyl carbon, because the 40 ppm peak, due to the C-1 methylene carbon, is overlapped by another resonance at the later extent of cure. By observing any changes in this peak at the various stages of vulcanization, cis-trans isomerization occurring in the isoprene rubber backbone can be characterized.

2. Chain Scission. The change in content of the 3,4-isoprene isomer was characterized by examining the change in intensity of the 18 ppm peak, which has been assigned to the C-5 methyl carbon in the 3,4-isoprene unit. A decrease in this particular structure would indicate chain scission in the 3,4-isoprene unit during the vulcanization since 3,4-to-cis to 3,4-to-trans isomerization is rare.

In summary, it is apparent that the reversion reactions - cis-trans isomerization and chain scission - are enhanced by the incorporation of the silica, especially at the later cure times. This is similar to what was found when carbon black is used as a filler.[8-10] One possible explanation of the increased reversion reactions is that the polymer with the higher filler content experiences a longer effective cure history during the fixed states of cure. Silica retards the cure reaction, and therefore, the samples with the higher filler level are exposed to elevated temperatures for longer periods of time, as seen in Table 2.

Network Structure Formation. - The new resonances appearing upon vulcanization are the same as those observed for unfilled systems[12] as well as for systems with carbon black as a filler.[8-10] At shorter cure times, the dominant sulfurization structures are the A1c-polysulfides, with possible contributions from the saturated or unsaturated A2c structures, all characterized by the peaks at 50.7 and 50.2 ppm, combined under the 51 ppm peak. Figure 2 shows a plot of the relative concentration of the A1c polysulfidic crosslinks as a function of percent cure for all five formulations. At lower cure times, there is only a slight difference in the amount of this structure as silica level is increased. However, at the longer cure times, there is a decrease in the concentration of this structure as silica is added, as shown in Figure 2. Therefore, silica causes a decrease in the formation of this type of crosslink at longer cure times.

As the vulcanization reaction proceeds, there is a reduction in rank from polysulfide crosslinks to monosulfide crosslinks with time.[11] The peak at 45 ppm was assigned to the A1c type monosulfide structure, shown in Figure 3. It also shows a plot of the relative concentration as a function of percent cure for all five formulations examined in this study. As the cure proceeds, the graph traces show a positive slope, indicating that there is an increase in the formation of this structure with time. Figure 3 also shows that as the silica level is increased, the formation of this structure is enhanced.

Also at longer cure times, the formation of the B1-type sulfide structures begin to form,[11] and are characterized by the peaks at 64 ppm and 58 ppm. In this study, the change in the relative peak intensity at 64 ppm, assigned to the B1-trans type polysulfide structure, is shown in Figure 6 for all samples. When silica was added, there was a decrease in the formation of this structure.

Total Sulfurization. - The total sulfurization increases as percent cure increases. This appears to be inconsistent with the fact that silica adsorbs the curatives, and therefore, results in a lower overall cure state, which was indicated by the rheometer traces. However, when the total sulfurization is broken down into the components due to the polysulfide structures and the monosulfide structures, a large difference is observed. The monosulfidic structures greatly increased as the silica is added, while the polysulfidic structures remained about the same or decreased as silica was added. As was mentioned earlier, it was recently found in another study[9] that most of the monosulfidic structures existed as inefficient structures, such as pendant side groups or intramolecular structures, while the polysulfidic structures existed as intermolecular crosslinks. The results of the current NMR study indicate that the presence of silica appears to enhances the formation of inefficient structures, such as cyclic sulfur structures (intramolecular crosslinks) and pendant side groups, and decrease the formation of efficient crosslinks, thus causing a lower overall cure state.

Conclusions

Nuclear magnetic resonance (NMR) spectroscopy was used to examine and characterize changes in the sulfurization structures that form during the vulcanization of zinc activated, sulfur cured cis-1,4 polyisoprene. The rheometer studies indicate that the silica retards the cure and results in a lower overall cure state. A similar vulcanization chemistry as in the carbon black system was observed, in which a change in sulfur rank from polysulfide to monosulfide and the formation of B1-type linkages were accelerated by the incorporation of silica. Equilibrium swelling studies also indicated a lower overall network chain density when silica is added as filler.

It was also found that silica enhances the reversion reactions, including cis-trans isomerization, and chain scission. The formation of monosulfide structures, mainly of the A1cis-type and B1-trans type, increased as silica level increased, while the formation of polysulfide structures, namely the A1-cis type and B1-trans type, decreased as silica loading increased. It was determined that the monosulfidic structures may exist mainly as inefficient groups, including pendant side groups, and intramolecular crosslinks, while the polysulfidic structures exist as intermolecular crosslinks. Therefore, while the total sulfurization increased as silica level increased, the intermolecular crosslinking, involved in the overall cure state, decreased.

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