

Solid-State ^{13}C -NMR Studies of Changes in Crosslinked Carbon Structure of Natural Rubber during Heating under Air and Nitrogen Environments

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ABSTRACT: The chemical changes that occur in thermal degradation of sulfur-cured natural rubber were investigated using ^{13}C -NMR analysis. The crosslinked carbons formed during the vulcanization process appear in the NMR spectra as peaks representing the various structures formed. Samples of vulcanized rubber were heat-aged 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 crosslinked carbon peaks. A- and B-type *cis* monolinkages were found to decompose much faster by oxidative factors at both 100 and 150°C than under nitrogen at either temperature. The polylinkages, 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. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 1371–1383, 1998

Key words: natural rubber; NMR; oxidation; degradation; thermal

INTRODUCTION

The literature contains a vast amount of information on the study of the degradation of rubber by different factors such as oxidation, ozonolysis, UV irradiation, and heat.¹ The degradation factors can also affect each other in different ways: For example, it is known that oxidative degradation occurs at a higher rate with increased temperature especially on the outer surfaces of exposed rubber.² Most methods of analyzing changes are by physical methods or chemical means of measuring by-products given off during the degradation process. Study of the degradation process on a molecular level has been restricted for the most part to model compounds.

Our research group has employed several spectroscopic methods such as infrared,^{3–5} Raman,^{6,7}

and ^{13}C -NMR^{8–19} to examine rubber networks on the molecular level. Most of the past ^{13}C -NMR studies have centered on changes in the crosslinked carbons distribution during the vulcanization process. The concentration of the different crosslinked structures, $^{13}\text{C}-\text{S}_x-^{13}\text{C}$, can be observed in an NMR spectrum in the range of 10–70 ppm.

In this article, the changes in the concentration of different $\text{C}-\text{S}_x-\text{C}$ crosslink structures under thermal-oxidative conditions were examined. Samples were heat-aged at different temperatures under both air (oxygen) and nitrogen environments to observe differences in crosslink structure due to temperature and thermal-oxidative degradation.

EXPERIMENTAL

Materials

All rubber samples used in the experiment were supplied by Dr. Gary Hamed of the University of

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Table I Formulation of TBBS-vulcanized Natural Rubber

Materials	Formulation (phr)
Natural rubber	100
Zinc oxide (activator)	5.0
Stearic acid	1.0
Agerite stalite S (antidegradant)	1.0
Sulfur	2.6
TBBS (accelerator)	1.4

Akron. The samples were natural rubber samples that were sulfur-vulcanized to 100% cure using *t*-butylbenzothiazole sulfenamide (TBBS) as an accelerator. All samples were press-cured at 150°C with a curing time of 25 min. The samples were supplied as 10 × 10-cm sheets approximately 2 mm thick. The formulation is given in Table I. The cure time at 150°C was 25 min. The samples were used for thermal analysis within a time frame of 1–3 months after preparation.

Methods

A representative portion of the natural rubber sheet was taken and the surface abraded to remove surface oxidation products and contaminants. The samples were then swollen in chloroform for several days and dried under a vacuum to remove residual vulcanization compounds. The samples were heated for different time periods at

100 and 150°C in both air and nitrogen environments. Samples were removed at different time intervals and bore samples removed for ¹³C-NMR analysis. The samples were heated using a standard heating oven which varied in temperature not more than ±2%.

The bore samples used for ¹³C-NMR analysis were approximately 5 mm in diameter, which fit the NMR sample tube. All NMR measurements were performed on a Bruker MSL 300 at a ¹³C frequency of 75.47 MHz. Measurements were performed at room temperature on a CP/MAS probe using magic angle spinning at 3500 kHz under gated high-power decoupling conditions. Scans around 15,000 were obtained with a recycle delay of 5 s.

The data from NMR measurements were transferred to an SGI work station where an ASCII file of the data was obtained. After processing to remove the imaginary points, the files were imported into a Win-IR software program (Biorad Win-IR tm Version 2.04 B) where quantitative analysis of the crosslinked carbons was performed.

In the Win-IR program, the ¹³C spectra were first smoothed using a Savitsky–Golay smoothing function which fits the data to a selected polynomial. In the program, parameters of five smoothing points with a degree of polynomial of 2 were selected and employed over the entire spectral region. After smoothing, a multiple-point baseline correction was applied. The peaks were then analyzed by the curve-fitting routine which deter-

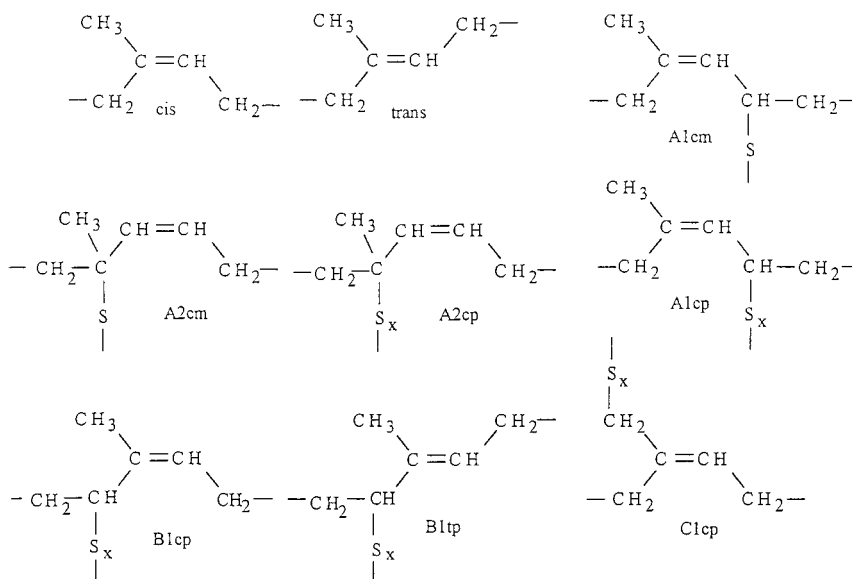


Figure 1 List of possible structures occurring during vulcanization of natural rubber.

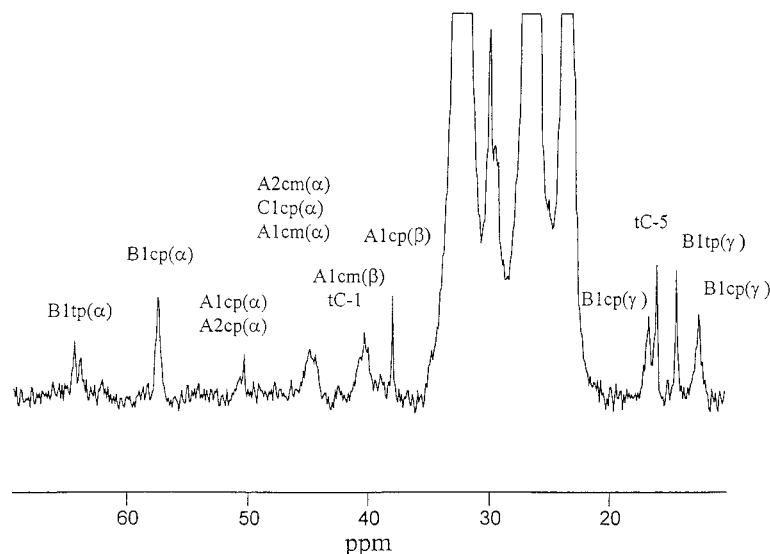


Figure 2 ^{13}C -NMR spectrum of sulfur-vulcanized natural rubber cured with TBBS accelerator.

mined the area under the peaks. In the curve-fitting program, the peaks were fit to Lorentzian line shapes with a linear baseline. In the larger peaks, the curve-fitting area value and an area value determined by a trapezoidal integration function were found to give the same values. For smaller peaks, the curve-fitting routine seems to break down, giving a calculated peak shape spread broadly over the baseline. Therefore, for the smaller peaks, the integration routine was used. When the peak to be examined was so small that the peak could not be distinguished from the baseline, the area was recorded as zero although a residual amount was present. The area found under the carbon crosslinked peaks were recorded as a percentage of the *cis* main chain carbon peaks, which effectively became our internal standard. The recorded percent was then normalized to the peak percentage at zero time for each of the crosslinked carbon peaks. To make this comparison, however, it must be assumed that the NMR intensity of the main-chain carbon peaks is constant throughout the experiment. To test this hypothesis, the NMR samples were run with a known amount of polybutadiene as a standard. It was found in the oxygen-exposed samples that some differences in intensity were observed and, hence, the main-chain carbon area was multiplied by a compensating factor.

RESULTS

During TBBS sulfur vulcanization of natural rubber, several different crosslinked structures are

formed as shown in Figure 1. The rate of formation of the different crosslinked carbon peaks have been previously studied.¹⁵ At low cure times, the only new resonance peak is a doublet in the region of 51 and 38 corresponding to A-type polysulfide linkages. These peaks reach a maximum and then gradually decrease as they are converted to monosulfide linkages assigned to the peaks around 44, which increase during vulcanization in proportion to the decrease in the poly peaks. Later in the vulcanization, the appearance of B-type peaks at 58, 63, and 64 coincide with the peaks formed at 17, 14, and 12. The appearance of the B-type peaks late in the vulcanization process is postulated due to the zinc salts of BtSH becoming the active accelerator, forming primarily a B1

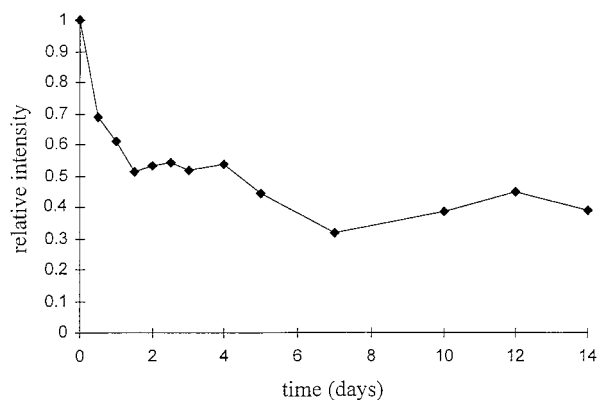


Figure 3 Graph of the decrease in intensity of the ^{13}C -NMR signal of the main-chain carbons exposed to oxygen over time at 150°C.

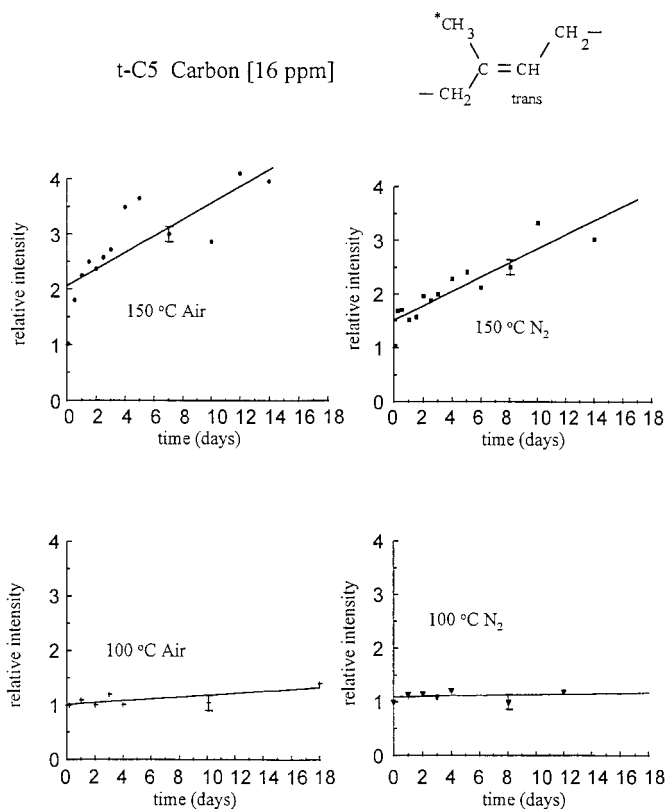


Figure 4 Relative intensity versus time graph of the C-5 *trans* carbon peak located at 16 ppm on the ^{13}C -NMR spectrum: (●) 150°C in air; (■) 150°C in nitrogen; (+) 100°C in air; (▼) 100°C in nitrogen.

structure which can undergo *cis-trans* isomerization during formation.^{18,20}

These different structures can be observed in ^{13}C -NMR spectra as small peaks in the range of 10–70 ppm as shown in Figure 2. The assignments were previously determined^{8,10,15,16,18} using calculated chemical shifts, the rate of crosslinked carbon peak formation as vulcanization proceeds, and NMR techniques such as DEPT. However, the peaks at 12, 17, and 57 ppm which were previously reported as polylinkages have been reassigned as monolinkages. This is based on two different factors: Polysulfide linkages are reduced by LiAlH_4 while monosulfides are relatively stable. On treatment of the crosslinked rubber with LiAlH_4 , the peaks at 38, 51, 63, and 64 decreased in intensity while the peaks at 12, 17, 40, 44, and 57 retained their original intensity.²¹ Second, the results of this study also support this reassignment.

In the NMR spectrum, the di- and polysulfidic linkages cannot be differentiated but monosulfide crosslinks appear at different parts per millions. In

the labeling of the peaks, the first letter and number represent the structure; the *c* or *t*, for the *cis* or *trans* isomer; and the *p* or *m*, for poly or mono linkage, and the Greek letter is the proximity of the carbon to the crosslinked carbon. For example, the methyl carbon would be γ to the crosslinked carbon in a B1 structure. Also shown in Figure 2 is the methylene and methyl carbon of the *trans* isomer present in small amounts in natural rubber. Unfortunately, not all structural peaks can be resolved into individual peaks and overlap in the spectra. Attempts at using curve-fitting routines to separate the areas gave ambiguous results. Therefore, these peaks were integrated as a single peak.

As stated earlier, the crosslinked carbon peaks are reported as a percentage of the main carbon peaks. This assumes that the main-chain carbon peaks are constant in the NMR signal intensity over time. Using a constant amount of polybutadiene as a standard, the intensity of the NMR signal of the main-chain carbons exposed to oxygen decreases with time at 100 and 150°C. Multiplying by a compensating factor, the main-chain

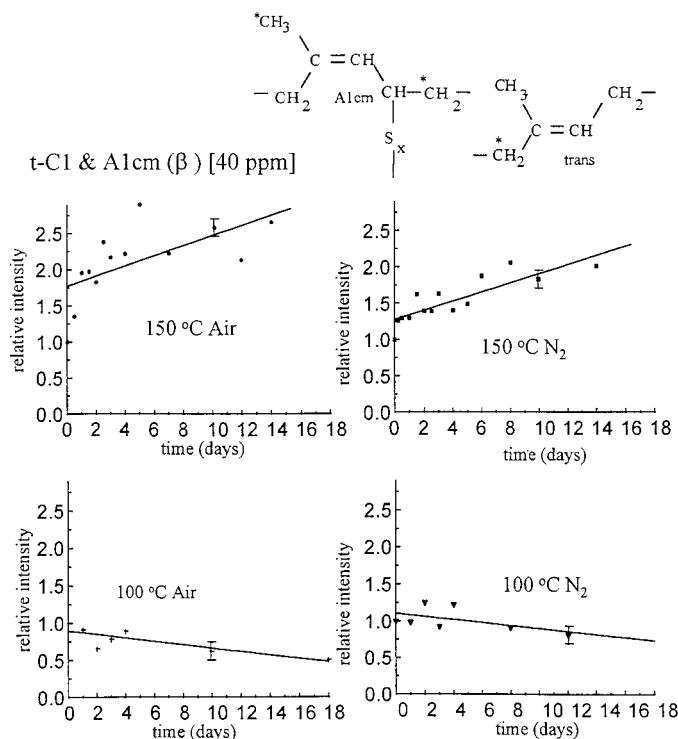


Figure 5 Relative intensity versus time graph of the C-1 *trans* and A1cm (β) carbon peaks located at 40 ppm on the ^{13}C -NMR spectrum: (●) 150°C in air; (■) 150°C in nitrogen; (+) 100°C in air; (▼) 100°C in nitrogen.

peak became standardized. The decrease is caused by increased crosslinking due to oxidation in the samples. No significant decrease in the NMR signal intensity in the nitrogen-exposed carbons was found at either 100 or 150°C as shown in Figure 3. Swelling measurements on the samples gave the same results as did the NMR measurements, showing a decrease in swelling with time in the oxygen-aged samples, while almost no effect was seen with those in the nitrogen environment.

An assumption was made that oxidative crosslinking would affect only the main-chain peak intensity and not the intensity of the crosslinked carbons. This assumption seems plausible due to the fact that the crosslinked carbons have restricted motions already due to attachment of the crosslinked sulfur chain. Therefore, no correction would be needed for the presence of the small crosslinked carbon peaks. However, the oxidative factors which reduce the intensity in the main chain should also affect the small *trans* peaks which occur at 16 and 40 ppm. The peaks were therefore reported as a percentage of the uncorrected main-chain peak area. Because the peak at 40 ppm also contains an unresolvable

A1cm (β) peak, a small error will be introduced into the percent reported.

One change in the distribution of the smaller peaks is *cis-trans* isomerization. As shown in Figures 4 and 5, the amount of *cis-to-trans* isomer-

Table II. Calculated Averages, Standard Deviations, and Percent Error on the Unheated Natural Rubber Using the NMR Peak Areas under Each Peak at Zero Heating Time for Each of the Four Conditions in the Experiment

NMR Peak (ppm)	Average	Std Dev	% Std Dev
12	.829	.078	9.40
14	.787	.09	11.4
16	.601	.085	14.1
17	.325	.036	11.1
38	.246	.037	15.0
40	.989	.121	12.2
44	2.54	.286	11.3
51	.465	.034	7.31
57	1.3	.201	15.5
63	.397	.035	8.82
64	.293	.058	19.8

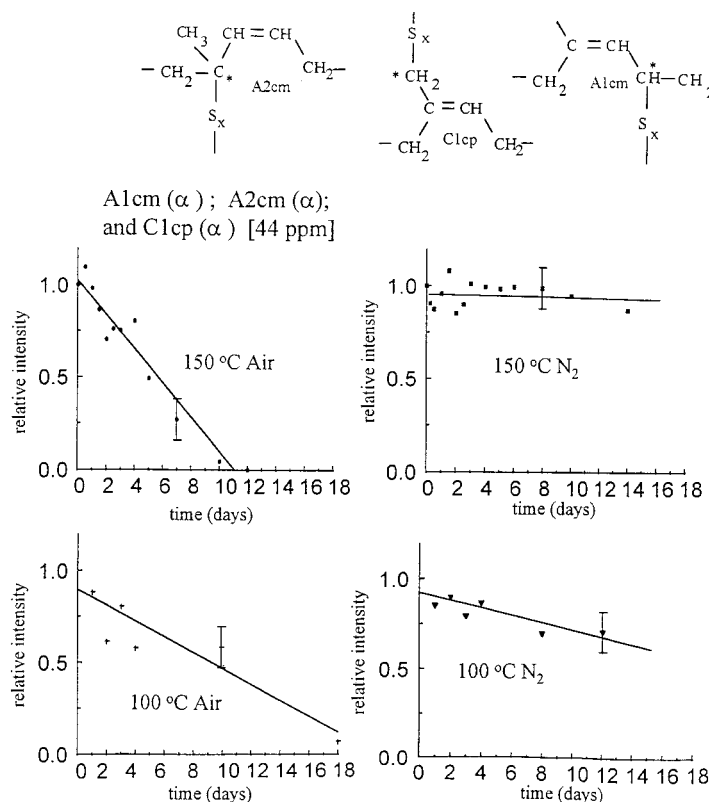


Figure 6 Relative intensity versus time graph of the A1cm (α), A2cm (α), and C1cp (α) carbon peaks located at 44 ppm on the ¹³C-NMR spectrum: (●) 150°C in air; (■) 150°C in nitrogen; (+) 100°C in air; (▼) 100°C in nitrogen.

ization is higher at elevated temperatures as would be expected.

Graphs of the relative intensities versus heating time for the major crosslinked carbon peaks are shown in Figures 6–14. The data points of all the graphs were fitted to a linear regression line. Although the majority of the data gave the best fit as a linear plot, some of the data gave a best fit as a log plot. In all the crosslinked carbon peaks analyzed, the samples exposed to oxygen at 150°C showed the largest decrease in concentration over time and those in nitrogen at 100°C showed the least change. The pattern of the samples exposed at 150°C in nitrogen and 100°C in oxygen varied from peak to peak depending on the crosslinked structure. Averages, standard deviations, and percent standard deviations were calculated on unheated rubber from the four different NMR experiments and are shown in Table II.

On heat aging in oxygen at 150°C, the sample turned a light brown after 24 h, which darkened as heating progressed. The outer surface was very

brittle, although below the surface some elasticity of the sample was still noted even after several days. The sample at 100°C in oxygen turned light brown after several days, darkening slightly as time progressed, while the samples exposed to nitrogen remained the original color.

An attempt was made to abrade off the outer layer of the 150°C oxygen-exposed sample to obtain a ¹³C-NMR spectrum to examine the *trans* and crosslinked carbon peaks. However, on abrasion, both the outer dark brown layer and the more elastic middle came off together and could not be easily separated. To simulate the outer layer's oxidation structure, a piece of the original rubber was abraded and divided into two portions. Both portions were aged at 150°C for 5 days, one under air and the other under nitrogen. A ¹³C-NMR spectrum of the nitrogen-exposed sample showed little difference from the corresponding intact sample. The abraded material under oxygen conditions became very brittle and gave a very low S/N ratio, making NMR analysis impossible.

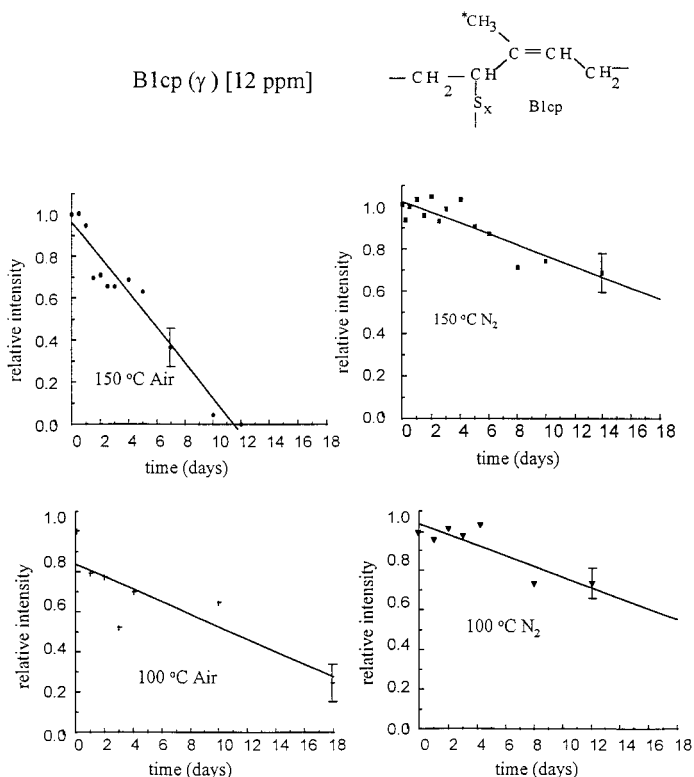
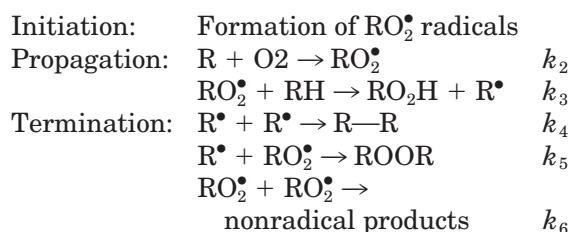


Figure 7 Relative intensity versus time graph of the B1cp (γ) carbon peak located at 12 ppm on the ^{13}C -NMR spectrum: (●) 150°C in air; (■) 150°C in nitrogen; (+) 100°C in air; (▼) 100°C in nitrogen.

DISCUSSION

Oxidation of Main Chain and Outer Surface

The autooxidation of natural rubber proceeds by the following mechanism²²:



Under conditions of high oxygen, the rate (r), $r = r_i^{1/2} k_3 k_6^{-1} [\text{RH}]$, whereas under low oxygen conditions, $r = r_i^{1/2} k_2 k_4^{-1/2} [\text{O}_2]$. The rate of initiation is given by $r_i = k_i [\text{ROOH}]^2$. As oxidation increases, competitive reactions of oxidative crosslinking such as k_4 and k_5 and chain scission from formation of RO_2^\bullet radicals in k_2 exist. At high temperatures, an inelastic highly crosslinked coating is formed. The coating is

known to decrease the diffusion of oxygen into the interior of the sample because of the high crosslink density due to oxidative crosslinking.²³ This coating is also known to protect the mechanical properties in thick-walled samples.²⁴ The outer coating is also much thinner when formed at higher temperatures, which would indicate that oxygen diffusion is severely retarded from the surface to the interior of the sample.²⁵ The effect of the decreased oxygen diffusion of the outer coating on the results in this study is hard to assess. Because our samples are relatively thin, the effect would be minimized compared to thicker samples. However, the crosslink density of the outer coating is known to increase with heat aging²⁵ which would further diminish available oxygen to the interior of the sample with increasing heating time.

Sulfide Crosslink Degradation by Oxidative and Thermal Factors

Sulfide crosslinkages are also known to undergo oxidation by reactions with the peroxide [RO_2H]

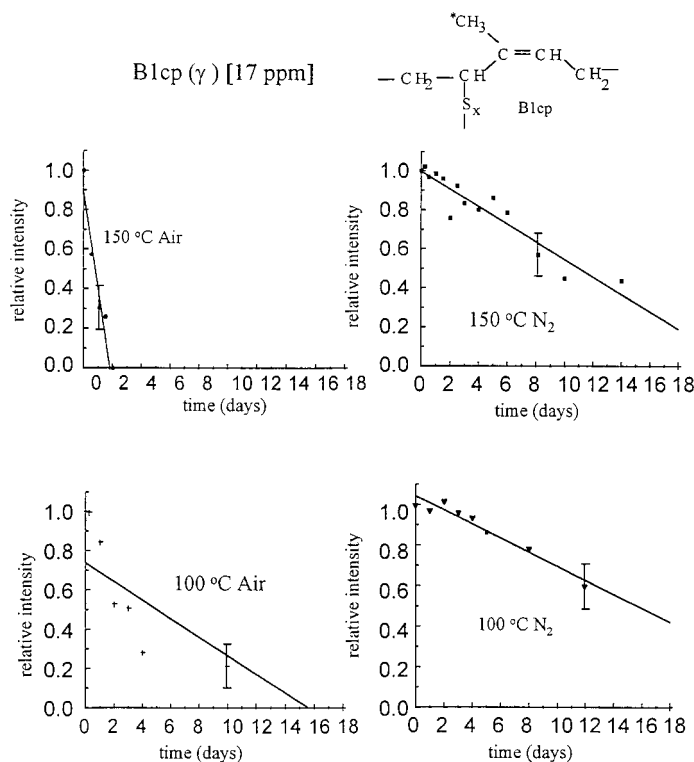


Figure 8 Relative intensity versus time graph of the B1cp (γ) carbon peak located at 17 ppm on the ^{13}C -NMR spectrum: (●) 150°C in air; (■) 150°C in nitrogen; (+) 100°C in air; (▼) 100°C in nitrogen.

formed during main-chain oxidation. Monosulfides are first oxidized to the sulfoxide. Decomposition of the sulfoxide results in chain scission with the formation of sulfenic acids: $[\text{R}-\text{S}-\text{R} + \text{RO}_2\text{H} \rightarrow \text{R}-\text{S}(=\text{O})-\text{R} \rightarrow \text{R}-\text{SOH} + \text{conjugated olefin}]$. Di- and polysulfides react with RO_2H to form thiolsulfonates which can further decompose into sulfinyl and sulfonyl radicals: $[\text{R}-\text{S}-\text{S}-\text{R} + \text{RO}_2\text{H} \rightarrow \text{RS}(=\text{O})\text{SR} \rightarrow \text{RSO}^\bullet + \text{RS}^\bullet]$.¹ Thus, mono- and disulfides at first show a marked increase in oxygen uptake but quickly are inhibitory in due to the sulfoxides and sulfonates formed.²⁵ Polysulfides are also inhibitory to oxygen uptake,²⁶ probably due to the formation of thiolsulfonates. Reactions of mono- and disulfides would show a difference in the NMR spectrum while those with polysulfide may or may not. However, it is known that under thermal conditions polysulfide linkages reduce in rank to di- and monosulfides.

From studies of natural rubber vulcanizates and model studies, A-type monosulfide linkages are very thermally stable with minimal decomposition even at 140°C.¹ Polysulfides are known to reduce in rank to form shorter polysulfide chains. In addition, in model studies, di- and trisulfide

linkages between methylpentenyl sulfides are known to give mono- and diene decomposition products plus the formation of thiol compounds.¹

Analysis of the Results

cis-trans Isomerization

The results show increased *cis-trans* isomerization at the higher temperature of 150°C under both nitrogen and oxygen with no appreciable increase at 100°C in either environment (Figs. 4 and 5). The increase in temperature shows a slight increase in the presence of oxygen over the inert nitrogen at 150°C as shown in peaks 16 and 40, probably due to addition of the double bond by radical oxidation products. However, *cis* to *trans* is mostly a thermal process. The increased temperature must provide enough activation energy to cause rotation about the double bond.

Decomposition of Monosulfidic Linkages

The peaks at 12, 17, 44, and 58 ppm (Figs. 6–9) indicate the concentration of A- and B-type monosulfide carbon crosslinks. The thermal stabil-

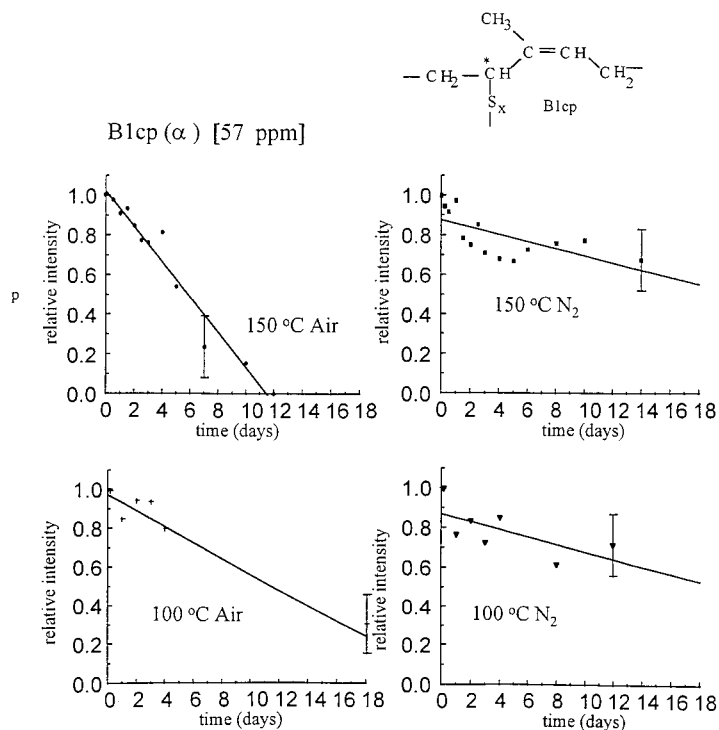


Figure 9 Relative intensity versus time graph of the B1cp (α) carbon peak located at 57 ppm on the ^{13}C -NMR spectrum: (●) 150°C in air; (■) 150°C in nitrogen; (+) 100°C in air; (▼) 100°C in nitrogen.

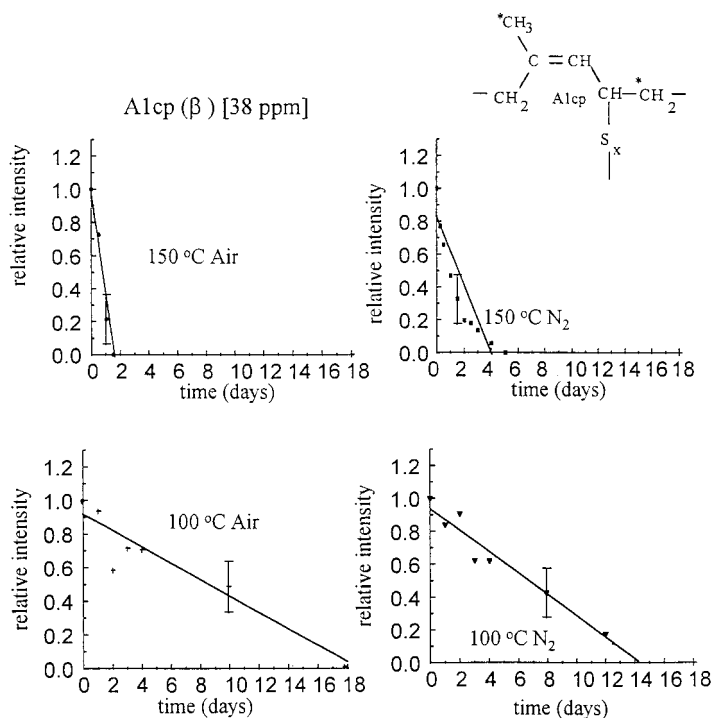


Figure 10 Relative intensity versus time graph of the A1cp (β) carbon peak located at 38 ppm on the ^{13}C -NMR spectrum: (●) 150°C in air; (■) 150°C in nitrogen; (+) 100°C in air; (▼) 100°C in nitrogen.

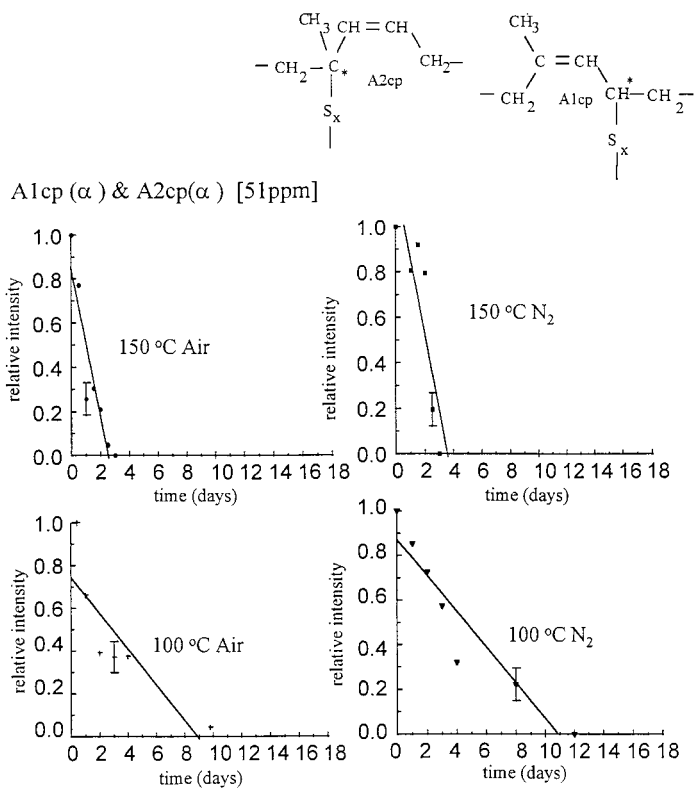


Figure 11 Relative intensity versus time graph of the A1cp (α) and A2cp (α) carbon peaks located at 51 ppm on the ^{13}C -NMR spectrum: (●) 150°C in air; (■) 150°C in nitrogen; (+) 100°C in air; (▼) 100°C in nitrogen.

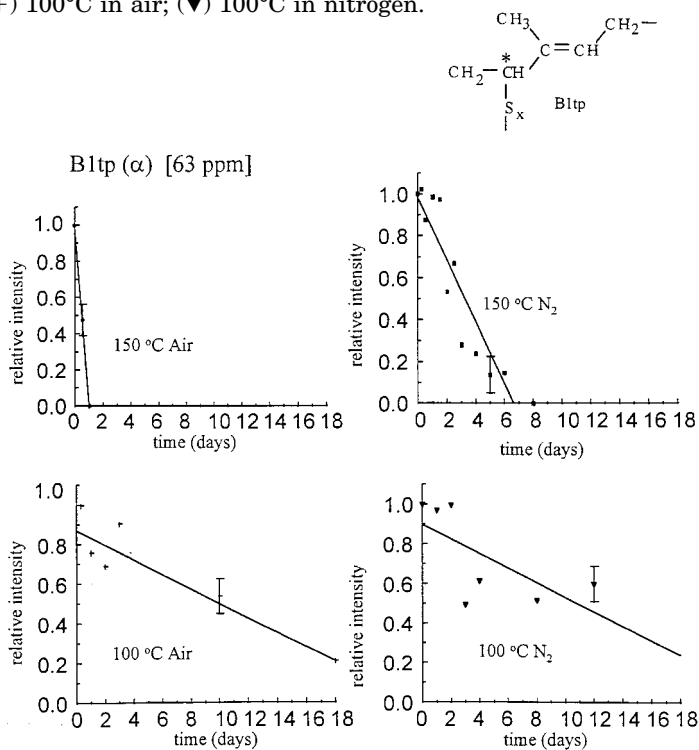


Figure 12 Relative intensity versus time graph of the B1tp (α) carbon peak located at 63 ppm on the ^{13}C -NMR spectrum: (●) 150°C in air; (■) 150°C in nitrogen; (+) 100°C in air; (▼) 100°C in nitrogen.

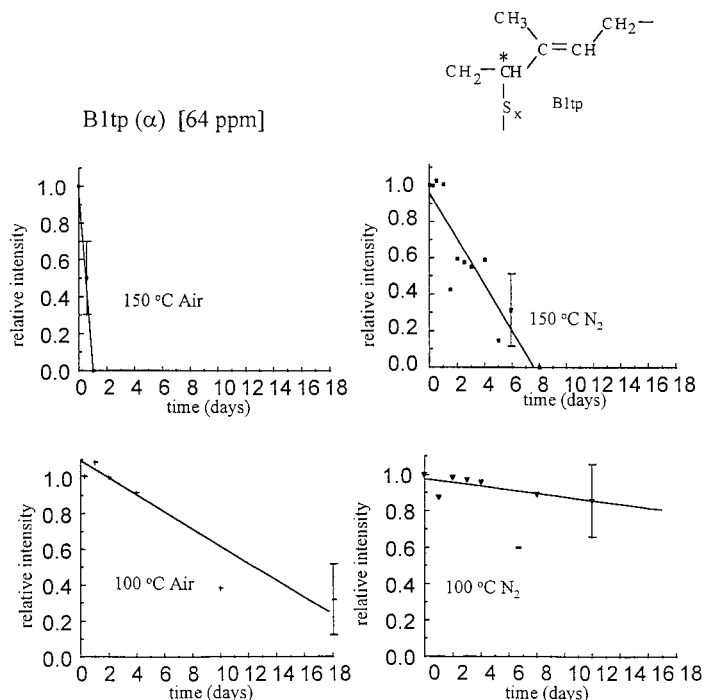


Figure 13 Relative intensity versus time graph of the B1tp (α) carbon peak located at 64 ppm on the ^{13}C -NMR spectrum: (●) 150°C in air; (■) 150°C in nitrogen; (+) 100°C in air; (▼) 100°C in nitrogen.

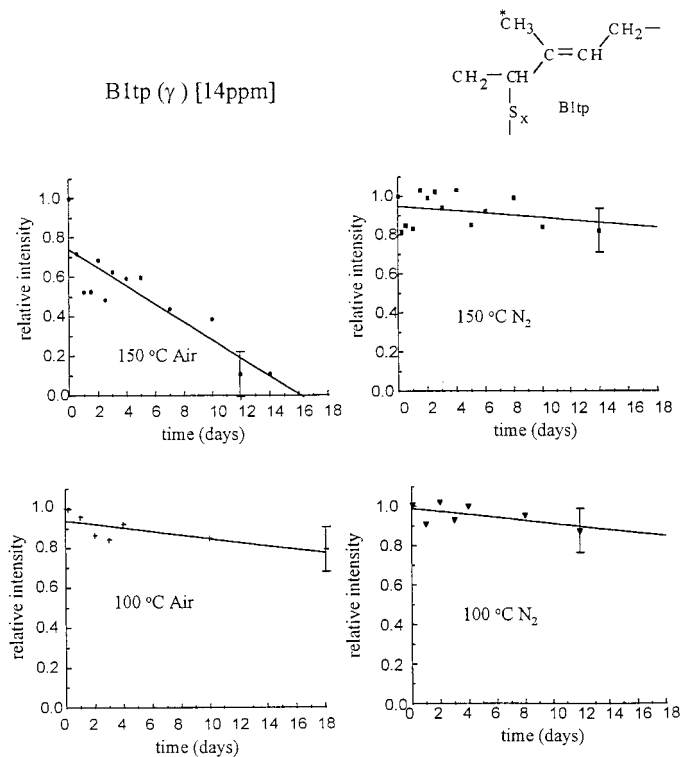


Figure 14 Relative intensity versus time graph of the B1tp (γ) carbon peak located at 14 ppm on the ^{13}C -NMR spectrum: (●) 150°C in air; (■) 150°C in nitrogen; (+) 100°C in air; (▼) 100°C in nitrogen.

ity of monosulfide crosslinks would explain the lower degree of degradation under nitrogen conditions at both 100 and 150°C. In an oxygen environment, the peroxides formed react with the monosulfide linkages, forming sulfoxides, which would account for the larger decomposition in air at both temperatures.¹ Two different peaks are shown for the B1cm (γ) structure. The two structures have been previously postulated to be due to two different conformations of the same structure.¹⁵ The degradation graphs seem to confirm all the peaks as B1 structures due to similar rates of decomposition. The notable exception is the 17-ppm graph at 150°C under oxidative conditions. Perhaps that particular structure reacts faster with oxygen due to its conformation or possibly the peak assignment could be in question. This phenomenon will require further investigation. The C1cp (α) structure is formed in only small concentrations by reversion during vulcanization and will offer little effect on the total area of the 44-ppm peak.

Decomposition of A-type Polylinkages

The NMR peaks at 38 and 51 ppm for the A1cp and A2cp carbons show the result of a much faster degradation rate of the polylinkages (Figs. 10 and 11). In addition, oxidative factors seem almost negligible compared to thermal factors as the rates of degradation between the air and nitrogen environments are almost identical. This is surprising in that one would postulate that both thermal and oxidative factors would play a role in degradation. It is apparent that such thermal degradation reactions such as desulfurization, formation of cyclic compounds, and conjugated di- and triene formation occur at a much faster rate than does oxidation. Because polylinkages can be reduced to monolinkages, an increase in A-type monolinkages should occur. This is not seen in our data probably due to side reactions as well as the small amount of the polysulfides as compared to monosulfides after vulcanization.

The B1tp

The peaks at 14, 63, and 64 ppm are assigned to B1tp structures. The two α carbons at 63 and 64 (Figs. 12 and 13) which are postulated to represent two different conformational isomers of B1tp (ref. 15) decrease at the same rate under all conditions. As with the A-type polylinkages, thermal

factors take precedence over oxidative factors. However, the rate of degradation of the 63 and 64 ppm does not coincide with the decrease of the γ carbon at 14 ppm (Fig. 14). This result would raise the question of peak assignments for the 14-ppm structure. These discrepancies will require further investigation.

CONCLUSIONS

The experimental results show that all monosulfide crosslinked structures decompose mainly by oxidative factors as is expected due to their thermal stability. The polysulfide crosslinkages were found to decompose faster by thermal factors over oxidative factors. *cis-trans* isomerization was found to increase at 150°C while minimal change was observed at the lower temperature. NMR analysis of the dark brown outer surface at 150°C proved to be impossible due to its highly crosslinked nature.

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