Network Structure and Reaction Mechanisms in High Pressure and Peroxide Vulcanization of Polybutadiene: Microstructural Changes Studied by ^{13}C Solid-State NMR

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ABSTRACT: This article is concerned with the microstructural changes during peroxide and high pressure vulcanization of polybutadiene that is unfilled and filled with carbon black. The main tool is ^{13}C solid-state NMR; it shows that vinyl unsaturations are consumed in both filled and unfilled samples under peroxide and high pressure vulcanization. Chemical shift calculations of unvulcanized polybutadiene show good agreement with the observed peaks. Calculations of proposed structures, based on a possible reaction mechanism, suggest that a large number of peaks will appear, each at very low intensity. Nevertheless, some changes can be seen as a result of the crosslinking reaction, and the results provide support for the suggested reaction mechanism. Thus, the proposed addition crosslinking mechanism over vinyl unsaturations seems to be a reasonable explanation of the crosslink formation in high pressure vulcanization. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2799–2806, 1999

Key words: crosslinking; high pressure; peroxide; polybutadiene; solid-state NMR

INTRODUCTION

High pressure vulcanization (HPV) refers to crosslinking of rubber materials at high temperature and elevated pressure, which are typically 240–260°C and up to 300 MPa for a polybutadiene rubber without any crosslinking agents present. However, the reactions leading to crosslinks in HPV of unsaturated elastomers, such as polybutadiene, have not been studied in detail. The resulting molecular structure in particular has not been revealed up to date. On the other hand, peroxide vulcanization of polydienes, which is believed to be very similar to HPV, has

been the focus of numerous studies; today there is an accumulated knowledge about the reaction mechanisms and the formed structures.[1,2]

It has long been known that unsaturated rubbers, such as polybutadiene and styrene–butadiene rubbers, are crosslinked to a high degree without vulcanization agents by mere thermal treatment at elevated pressure. In 1960 Okhrimenko[3] observed that polybutadiene could be crosslinked in this way, and IR spectroscopy studies revealed that the 1,2-vinyl units in the polymer chain were consumed as the degree of crosslinking increased. Frenkin et al.[4] investigated a number of different rubber types and their ability to crosslink by HPV. They concluded that the presence of unsaturations in the polymer chain was a prerequisite for success, but they presented no possible mechanisms for the crosslinking reaction. Lavebratt et al.[5] investi-

Table I   Composition and Treatment of Samples Investigated by NMR

Ingredients	Control	HPV	Peroxide	Control$_{black}$	HPV$_{black}$	Peroxide$_{black}$
Buna CB55	100	100	100	100	100	100
DiCup 40	—	—	3	—	—	3
N220	—	—	—	45	45	45
Treatment	1. 250°C, 6 min	1. 250°C, 6 min 2. 250°C at 293 MPa for 20 min	1. 170°C, 12 min	1. 250°C, 6 min	1. 250°C, 6 min 2. 250°C at 293 MPa for 20 min	1. 170°C for 12 min

Amounts are given in parts per hundred rubber (phr).

gated the dynamic compression stress relaxation properties of carbon black filled polybutadienes crosslinked by HPV and suggested some kind of radical mechanism, which may be expected due to the rather high temperatures of up to 250°C. Recent studies on the HPV process have focused on the time, temperature, and pressure dependence on the reaction, as well as the effect of carbon black on the network formation.[6,7]

The thermal degradation of polydienes at high temperature, at atmospheric pressure, or in a vacuum has been studied in detail by many authors. Golub[8] shed light on the reactions taking place in polybutadienes with different microstructures: polybutadiene with 10% 1,2-vinyl units treated up to 250°C showed loss of 1,2 unsaturations but almost no consumption in 1,4-cis and trans unsaturations.[9] Crosslinking was mentioned as one route of reaction together with intramolecular cyclization reactions. More recently, Doskocilova et al.[10] performed FTIR and solid-state NMR studies on polybutadiene heated in an inert atmosphere at 200 and 250°C, respectively. They found that crosslinking was one main reaction and that the reaction was of a nonradical nature.

In this study the focus was on microstructural changes in polybutadiene (11% vinyl) crosslinked by HPV (250°C and 293 Mpa), as well as by dicumyl peroxide, the latter acting as a model system for valuable comparisons. The main task was to suggest a reasonable reaction mechanism and to establish the resulting network structure on a molecular scale. The main tools were ^{13}C-NMR and estimation of the degree of crosslinking by swelling measurements. A related article on the effect of the pressure on the molecular mobility and the resulting changes in the network structure of HPV will be published soon.[11]

EXPERIMENTAL

Materials

Polybutadiene (Buna CB55; microstructure of 51% trans, 38% cis, and 11% vinyl) was used as supplied without further purification. The peroxide was DiCup40, which is dicumyl peroxide on a silica carrier of 40% active peroxide. The hindered phenol used was Irganox 1098, which is N,N'-hexamethylene bis(3, 5-di-tert-butyl-4-hyroxy-hydrocinnamamide). Table I gives the composition of the compounds used for the NMR measurements and the specifications of the crosslinking treatments used. All samples were treated in a plunger type mold designed for high pressure treatments (up to 400 MPa) at temperatures up to 300°C, which is described in more detail elsewhere.[6] It is worth commenting that the control samples were inserted in the hot mold for 6 min, which was the calculated time for the unfilled sample to reach thermal equilibrium at 250°C. In this way we were able to observe the changes occurring only during the crosslinking phase (i.e., when the pressure was applied).

NMR Measurements

The ^{13}C-NMR spectra were recorded on a 400-MHz Chemagnetics at ambient temperature during proton decoupling. Magic angle spinning (MAS) at 12 kHz was applied on the 4-mm ZrO rotor containing the sample. Comparisons of spectra using cross polarization (CP) showed no differences, and therefore 90° single pulse experiments were used (a more skillful adjustment of the the parameters of the CP experiment may have yielded different results). The pulse repetition time was 9 s, and 128 free induction decays

were accumulated before processing the spectra into the shift domain.

Crosslink Density

The rubber samples were swollen in *n*-heptane for 24 h at ambient temperature. Crosslink densities were calculated using the Flory–Rehner equation[12]:

$$\nu_{\text{phys}} = \frac{1}{2 \cdot V_S} \cdot \frac{\ln(1 - \nu_r) + \nu_r + \chi \cdot \nu_r^2}{\nu_r^{1/3}} \quad (1)$$

where ν_{phys} is the number of crosslink points per unit volume (including chemical and physical interactions), V_S is the molar volume of the solvent, ν_r is the volume fraction of rubber in the swollen gel, and *c* is the interaction parameter. The value used for *c* was $0.7 + 0.52 \nu_r$ in accordance with Kraus.[13] The ν_r values were calculated using the weights of the samples in the swollen state and after drying to constant weight. In the carbon black filled samples, the filler volume was excluded but compensation was not made for rubber–filler interactions.

RESULTS AND DISCUSSION

Control Samples

Figure 1 shows an NMR spectrum of the control sample, which is polybutadiene (unfilled) treated at 250°C for 6 min without any pressure. The aliphatic and olefinic parts are magnified to clearly show the designations of the peaks. The numbering emanates from the study of Clague et al.,[14] who performed solution NMR on polybutadienes with different vinyl content. As can be seen, around 17 peaks can be separated due to the different sequences of cis, trans, and vinyl units; the corresponding carbons in the polymer chains are given in Figure 2. However, some carbons could not be separated: no 11, 14, and 19 (overlap with 1), and no 18 (overlap with 3).

The observed aliphatic shifts are given in Table II along with those observed by Clague et al.[14] and calculated shifts using the method and parameters suggested by Lindeman and Adams.[15] For unsaturations in the α position to the observed carbon, compensations were made by the parameters given by Clague et al.[14] The prediction of the shifts is indeed very good, even for the carbons in the vicinity of branched structures (vi-

Figure 1   ^{13}C solid-state NMR spectra of the control sample of unfilled polybutadiene treated at 250°C for 6 min without any pressure. The numbering is from the study of Clague et al.[14]

nyl groups). This congruence is important to bear in mind in the prediction of unknown structures resulting from the crosslinking processes. Buna CB55, which is a lithium catalyzed polybutadiene, has a random incorporation of the cis, trans, and vinyl units.[14] With this knowledge as a basis, the powerful ^{13}C-NMR technique as a tool, and the peroxide system as a model, speculations about possible reactions mechanisms for the HPV crosslinking can be useful.

Peroxide Vulcanization

Peroxide vulcanization of diene rubbers has been well investigated and it is established that the crosslinking is achieved by either of two mechanisms[15] (see Fig. 3): hydrogen abstraction followed by combination of polymer radicals or the addition of a peroxide radical to a double bond followed by further addition of the polymer radical formed to a double bond in a nearby chain. The relative importance of the two mechanisms is dependent on the peroxide concentration and the vulcanization temperature as shown by Gonzalez et al.[16] They also demonstrated that the addition mechanism leads to a heterogeneous network.

HPV

No concrete evidence for a special type of reaction mechanism has been published so far for HPV.

Figure 2 Microstructure of polybutadiene and different sequences. The numbering is from the study of Clague et al.[14]

Table II   Calculated and Observed Shift in Control Sample

Carbon	Calcd Shift (ppm)	Observed (ppm)	Observed[a] (ppm)
2	32.9	33.2	32.3
4	27.4	28.0	27.7
7	37.1	38.8	38.3
8	43.0	44.1	43.6
13	31.6	31.1	30.6
16	30.4	30.8	30.3
17	34.2	34.7	34.4
20	24.9	25.5	25.1

[a] Values reported by Clague et al.[14]

or by addition. The latter has the ability to involve more than two chains, thus resulting in many crosslinks per initiated radical concurrently with a loss of unsaturations.

Figure 4 shows some possible structures that may be formed in HPV if addition is the main route. For reasons of convenience, the radical is shown only on the reactant side. The abstraction–combination mechanism is also possible and will result in structure (A) or (B) modified with an additional unsaturation in the lower chain in the picture, because no unsaturations are consumed

Table III shows the effect of a radical scavenger (hindered phenol) on the resulting degree of crosslinking. At both short (5 min) and long (30 min) vulcanization times the crosslink density was drastically reduced by the addition of the hindered phenol, making it clear that a radical reaction was involved in the crosslink formation. This is in accordance with earlier reports by Okhrimenko.[3] Due to the high thermal energy of the system it is reasonable to expect some cleavage of C—H bonds, preferably allylic hydrogens, which are the weakest bonds. The radical formed in this way is identical to the polymer radical formed in reaction (1) in peroxide vulcanization (see Fig. 3). After the initiation step, the crosslinking may proceed either by combination

Figure 3 Reaction mechanisms in peroxide vulcanization of diene rubber: (A) abstraction–combination mechanism and (B) addition mechanism.

Table III   Effect of 2 phr Radical Scavenger (Hindered Phenol) on Degree of Crosslinking in HPV

Vulcanization Time (min)	Crosslink Density $\times 10^4$ (mol/mL)	
	Polybutadiene	Polybutadiene + 2 phr Radical Scavenger
5	1.60	1.21
30	2.92	2.27

The crosslinking pressure was 293 MPa, and the temperature was 250°C.

in that case. Structures (C) and (D) result from one single addition over a vinyl group. Structure (E) is the result of intramolecular cyclization and (F) is one possible result if the addition takes place in many steps over vinyl groups (here four steps) like a polymerization reaction. All carbons in these structures will give rise to many different peaks in a ^{13}C-NMR spectra, but due to the low concentration of crosslinks in a rubber material they will be difficult to detect. Nevertheless, it is of interest to try to predict the values of the chemical shifts of these structures. Table IV is a list of calculated shifts of the aliphatic carbons nonadjacent to unsaturations, as the shift is affected by adjacent functional groups. The values were calculated by the method and parameters outlined by Lindeman and Adams.[15] Bearing Table II in mind, it is obvious that most of the proposed peaks may overlap with the original peaks. They will also be distributed over a wide range of shifts, thus making the intensity of each signal very weak.

Figure 5 shows the spectra from the control, HPV, and peroxide samples. Just as expected, no new isolated strong peaks can be detected in either HPV or peroxide. However, there are some small differences observed, which are indicated by arrows in Figure 5. Small increases can be seen in the HPV and peroxide at 29.5, 36, 46.5, and 48 ppm. The two former may be associated with some of the proposed structures: D1 (29.6 ppm); F5 (30.1 ppm); C3 (36.7 ppm); F4 (35.4 ppm); F6 (36.8 ppm); and F7, F8, and F14 (35.0 ppm). Further, in HPV slight increases can be observed at around 31, 37.5, and 41 ppm, which may be explained by carbon F13 (31.4 ppm), D3 (37.0 ppm), F1 and F2 (37.9 ppm), and F10 (37.1 ppm). The common feature of all these carbons is that they are associated with branched struc-

tures, which is also the result of crosslinking. Finally, the 39.5- and 42.5-ppm peaks are observed only in the peroxide spectrum. These two peaks cannot be explained by any of the proposed structures. If cyclization reactions take place,

Figure 4   Possible structures formed in HPV of polybutadiene. The abbreviations and the calculated chemical shifts are found in Table IV.

Table IV   Calculated Chemical Shift for Proposed Structures

Carbon	Calcd Shift (ppm)
A1	44.1
B1	37.5
C1	32.0
C2	32.0
C3	36.7
D1	29.6
D2	32.3
D3	37.0
E1 = E2	32.0
F1	37.9
F2	37.9
F3	34.3
F4	35.4
F5	30.1
F6	36.8
F7	35.0
F8	35.0
F9	34.5
F10	37.1
F11	32.3
F12	34.4
F13	31.4
F14	35.0
G1	34.5
G2	27.8
G3	27.8[a]
H1	27.8
H2	28.4
H4	20.6[a]

[a] Corrections for unsaturation in the α position were not made.

they will result in structures such as E1 and E2, which would appear at around 32 ppm. Unfortunately, they cannot be separated due to their closeness to the large peak at 33 ppm. Therefore,

Figure 5 ^{13}C solid-state NMR spectra of control, HPV, and peroxide samples of unfilled polybutadiene.

Table V   Quantitative Analysis of NMR Spectra from Unfilled Samples and Crosslink Density for Samples as Measured by Swelling

	Percentage Peak Area		
	Control	HPV	Peroxide
Carbon no.			
1 + 1a	23.9	24.2	23.3
2	21.8	23.5	22.8
3 + 3a	16.5	17.7	17.7
4	16.3	17.3	17.7
5	2.1	1.3	1.3
6 + 6a	3.4	3.0	3.4
7	1.4	1.7	1.3
8	2.3	2.1	2.0
9	3.4	2.2	2.2
10	4.7	2.5	2.7
16	1.5	1.9	1.9
17	1.8	1.7	2.3
20	0.8	1.1	1.3
Crosslink density $\times 10^4$ (mol/mL)	0.0825[a]	1.28	1.93

[a] Highly swollen, almost solvable gel.

it cannot be excluded that cyclization reactions take place to some extent. It is interesting to relate the chemical shift of the indicated changes in Figure 5 with the work of O'Donnell and Whittaker. They crosslinked polybutadienes of different microstructure by γ radiation. Except for cis–trans isomerizations, they also revealed new peaks at 30.5 and 45.8 ppm, which were ascribed to methylene carbons adjacent to crosslinks and methine carbons in crosslinked structures, respectively. O'Donnell and Whittaker utilized CP in their experiments, which is known to be sensitive to more rigid structures. In the present work, only single pulse experiments were used. Nevertheless, the spectra obtained revealed some new resonances that are in accordance with those resulting from crosslinking by γ radiation.

More information of interest is obtained by quantitative analysis of the NMR spectra. In Table V the percentage area and its change after vulcanization are given for each carbon with an isolated peak, together with the crosslink density as measured by swelling. The carbons belonging to cis and trans structures in 1,4 sequences (carbons 1–4 in Fig. 1) seem to be almost unaffected by the crosslinking process. The cis/trans ratio is not changed, indicating an absence of cis to trans isomerizations. At the crosslinking conditions (250°C for HPV), isomerizations are expected to

Figure 6 ^{13}C solid-state NMR spectra of HPV (unfilled polybutadiene) and HPV$_{black}$ (carbon black filled polybutadiene). Both samples are crosslinked.

take place,[8] but the fact that this does not happen may be explained by the cis/trans ratio already being close to its equilibrium value. Further analysis of Table V shows that the signal from carbons 9 and 10, the olefinic carbons in vinyl groups, decreases readily during the vulcanization. Carbon 8 is not reduced to the same extent as expected, but that may be explained by the overlap of formed structures. In summary, there is no doubt that the vinyl groups are consumed to a large extent.

Another interesting observation in Table V is the increase of carbon 20, contrary to what Doskocilova et al.[10] found. They suggested that the observed crosslinking takes place between a vinyl unit and carbon 20, because the intensity of this peak decreased during the heat treatment. The increase of carbon 20, as well as carbon 16, may be the result of new structures appearing in this region as proposed in Table IV. Furthermore, carbon 5 decreases while its original neighbors 6 and 7 behave somewhat ambivalently, depending on the crosslinking process.

Carbon Black Filled Samples

Figure 6 shows spectra from samples of HPV and polybutadiene filled with 45 phr N220 carbon black (HPV$_{black}$). The peaks, especially the two largest, are broadened in the filled samples. This is probably due to the reduced mobility of the polymer chains closest to the filler particles. Table VI gives the percentage area for some of the carbon atoms in the carbon black filled samples and the crosslink density as measured by swelling. From the intensities of carbons 1–4 it can be seen that the cis/trans ratio seems to be unaffected by the crosslinking reactions, just as for the unfilled samples. Furthermore, the decrease in vinyl content that could be observed in the unfilled samples is not so clearly seen in the filled samples. Only carbon 9 shows a significant decrease in both HPV and peroxide vulcanization. Whether this is an indication of an alteration in the reaction mechanism in the carbon black filled samples is difficult to conclude from these measurements.

CONCLUSIONS

The microstructural changes in polybutadiene crosslinked by HPV and peroxide vulcanization were investigated by ^{13}C solid-state NMR. As

Table VI   Quantitative Analysis of NMR Spectra from Filled Samples and Crosslink Density for Samples as Measured by Swelling

	Percentage Peak Area		
	Control$_{black}$	HPV$_{black}$	Peroxide$_{black}$
Carbon no.			
1 + 1a	18.7	19.2	18.3
2	21.9	21.9	21.6
3 + 3a	22.2	21.7	22.7
4	16.6	16.8	16.7
7	0.6	0.8	0.4
8	1.2	1.2	1.0
9	2.2	1.8	1.6
10	3.7	4.0	3.6
Crosslink density $\times 10^4$ (mol/mL)	0.192[a]	1.93	1.29

[a] Highly swollen, almost solvable gel.

shown earlier by FTIR studies, the vinyl unsaturations are consumed during crosslinking of unfilled samples. However, in this study it was shown to be valid even for carbon black filled samples. Furthermore, we showed that the cis/trans ratio was unaffected during the crosslinking in both the unfilled and the carbon black filled samples, probably because of an original cis/trans ratio close to the equilibrium value. A radical reaction mechanism was proposed for the HPV of polybutadiene, based on the observed affect of a radical scavenger on the resulting crosslink density. The crosslinking reactions yielded many different structures, each of which were expected to be difficult to detect. However, changes that supported the suggested reaction mechanism were observed in the NMR spectra.

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