

Influence of 1,2-polybutadiene on properties of dicumyl peroxide cured brominated butyl rubber

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ABSTRACT: Peroxide curing of brominated butyl rubber (BIIR) is an attractive topic, but the degradation of BIIR during the curing is a drawback needed to be overcome. Coagent assisted peroxide curing system is an attractive and effective choice in order to increase the crosslink density of rubbers. 1,2-polybutadiene (1,2-PB) is used as a crosslinking coagent for the curing of BIIR by dicumyl peroxide (DCP), and the effect of 1,2-PB on the curing characteristics, crosslink density, and mechanical properties is investigated. The addition of 1,2-PB affects the curing characteristics of BIIR compound and significantly increases the crosslink density of BIIR vulcanizates. With increasing 1,2-PB content, the tensile strength and stresses at a given extension of BIIR vulcanizates increase, but the elongation at break decreases. A stress-softening effect of the carbon black filled BIIR vulcanizates is observed and becomes more pronounced with increasing 1,2-PB content. The addition of 1,2-PB increases the stress relaxation index of BIIR. GPC and ¹³C-NMR results indicate 1,2-PB participates in the crosslinking reaction, and the existence of 1,2-PB component in the insoluble fraction of BIIR/1,2-PB vulcanizates is confirmed by solid-state ¹³C-NMR. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43280.

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INTRODUCTION

Isobutylene isoprene rubber (IIR) is a random copolymer prepared by cationic polymerization of isobutylene and 0.5–3.3 mol % isoprene.¹ It owes superior oxidative stability and low gas permeability to its isobutylene-rich polymer backbone.² Brominated butyl rubber (BIIR) has not only air impermeability but also the cure activity. It is generally believed that the increscent reactivity of the allylic bromide functionality derived from bromination of IIR gives rise to the improved vulcanization rates.³ Other types of cure chemistry also become available through bromination of IIR, including peroxide cures.⁴

Peroxide-initiated cure chemistry is used to produce crosslinked rubber articles whose carbon-carbon crosslinks provide good thermal stability and compression set resistance.⁵ However, polyisobutylene and isobutylene-rich copolymers incur radical degradation when activated by organic peroxides.^{6–8} The crosslink density of dicumyl peroxide (DCP) cured BIIR vulcanizates is low and the vulcanization reversion exists.⁹

Coagents are basically multifunctional organic compounds which are highly reactive towards free radicals. They are mainly used to boost the efficiency of peroxides and improve the

mechanical properties in peroxide cured elastomers.¹⁰ Since 1,2-polybutadiene (1,2-PB) was synthesized in 1955, considerable concern has been aroused in both industry and academia, and most researches were focused on the properties of 1,2-PB/polypropylene (PP) blends. The structure and properties of PP/1,2-PB blends were investigated.^{11–14} 1,2-PB can also be used as a coagent to peroxide cured PP and ethylene-octene copolymer thermoplastic vulcanizates (TPVs) to avoid the β -chain scission in PP, increase the crosslink density in ethylene-octene copolymer phase and induce the interfacial reactions.¹⁵ However, the effect of 1,2-PB on the properties of peroxide cured BIIR has not been reported. Because of the exceptional impermeability, oxidative resistance, and excellent electrical insulation of BIIR, this study will be helpful for manufacturing peroxide-curable BIIR products, with great potentials in special electrical wires and cables.

In this work, 1,2-PB was added into BIIR as a crosslinking coagent for DCP. The effect of 1,2-PB on the curing characteristics, crosslink density, mechanical properties, stress softening and stress relaxation behavior of BIIR was studied in details. The insoluble and soluble fractions of BIIR/1,2-PB vulcanizate were characterized.

Table I. Formulation of BIIR Compounds in phr (Parts by Weight per Hundred Parts of Rubber by Weight)

Component/designation	1	2	3
BIIR	100	90	80
DCP	2	2	2
1,2-PB	0	10	20
Microcrystalline wax	2	2	2

For the sample used for stress softening and stress relaxation behavior test, 40 phr carbon black N330 was added.

EXPERIMENTAL

Materials

BIIR (Bromobutyl 2030, M_n is ca. 2.7×10^5) with 1.8 wt % halogen content and Mooney viscosity [ML(1 + 8)] of 125°C of 32 and 1,2-PB (Ricon[®] 153, M_n is ca. 7.0×10^3) with 85 mol % 1,2-vinyl content and specific gravity of 0.89 g/cm³, Brookfield viscosity of 6.0×10^4 cps at 45°C, were kindly provided by Lanxess, Germany. DCP was purchased from Sino-pharm Chemical Reagent, China. Carbon black (N330) was made by Cabot Co. Microcrystalline wax (654) was made by Rhein Chemie.

Sample Preparation

BIIR compounds were prepared by melt mixing at 30°C with a rotor speed of 60 rpm in the mixing chamber of a Haake rheometer. First, BIIR was mixed with microcrystalline wax for 2 min, following by separately adding 1,2-PB and 2 phr DCP and mixing for 7 and 3 min, respectively. The compositions of BIIR compounds are shown in Table I. The resulting compounds were mixed on a two roll mill at room temperature, and cured at 160°C under a pressure of 10 MPa, at the curing time of t_{90} .

BIIR/1,2-PB (80/20) vulcanizates with curing time of 1, 1.8, 3, 4.5, 7, 13 min, respectively, were extracted by a Soxhlet extractor for 60 h at 85°C using hexane as a solvent to remove small molecules, uncrosslinked macromolecules and degradation products. The insoluble fraction was dried for 72 h at 50°C in vacuum and the soluble fraction was got by rotary evaporation and vacuum drying at 50°C for 72 h. Finally, the soluble fraction was characterized by gel permeation chromatography (GPC) and ¹³C-NMR spectroscopy, and the insoluble fraction was characterized by solid ¹³C-NMR spectroscopy.

Characterization

Curing curves were recorded using a Rubber Processing Analyzer (RPA 2000, Alpha Technologies Co. USA). A sample was directly loaded between the dies maintained at 160°C with the frequency of 1.7 Hz and the strain of 7%.

The crosslink density of BIIR was determined by swelling ratio and the Flory-Rehner equation using equilibrium swelling method.^{16,17} The crosslinked BIIR sample was cut into the dimensions of $1 \times 2 \times 0.1$ cm³, and swollen in hexane. A sample was weighed (W_1), and then swollen to equilibrium for 6 days at room temperature. Excess surface liquid was removed from the swollen sample, and the sample was immediately

weighed (W_2), and dried in an oven to remove all the solvent and reweighed (W_3).

The swelling ratio was calculated using eq. (1),

$$\Delta m(\%) = \frac{W_2 - W_1}{W_1} \times 100 \quad (1)$$

The crosslink density is defined as the number of elastically active network chains totally included in a perfect network per unit volume and evaluated according to the following Flory-Rehner eq. (2),¹⁸

$$n = \frac{-[\ln(1 - V_r) + V_r + \chi V_r^2]}{V_s \times (V_r^{1/3} - \frac{V_r}{2})} \quad (2)$$

where V_r is the volume fraction of the rubber in the swollen sample, χ the solvent-rubber interaction [given by eq. (3)], V_s the molar volume of the solvent (124.54 cm³/mol), n the crosslink concentration (mol/cm³).

$$\chi = \frac{V_s}{RT} (\delta_1 - \delta_2)^2 \quad (3)$$

where δ_1 and δ_2 are the solubility parameters of the solvent and polymer, respectively, $\delta_1 = 14.9$ MPa^{1/2} and $\delta_2 = 17.45$ MPa^{1/2},^{19,20} R , the gas constant; and T , the absolute temperature. χ of BIIR and hexane was calculated to be 0.33.

To solve eq. (2),²¹ the rubber volume fraction in the swollen sample, V_r is calculated by the following eq. (4),

$$V_r = \frac{\left(\frac{X_r}{\rho_r}\right)}{\left(\frac{X_r}{\rho_r}\right) + \left(\frac{X_s}{\rho_s}\right)} \quad (4)$$

where X_r is the mass fraction of rubber, ρ_r the density of rubber (BIIR, $\rho_r = 0.93$ g/cm³), X_s the mass fraction of hexane and ρ_s the density of the solvent (hexane, $\rho_s = 0.69$ g/cm³).

X_r and X_s can be obtained using eqs. (5) and (6),

$$X_s = \frac{W_2 - W_1}{W_2} \quad (5)$$

$$X_r = 1 - X_s \quad (6)$$

Tensile properties were measured with dumbbell specimens ($75 \times 4 \times 1$ mm³) according to ASTM D412-97, using a universal test machine (Instron 4465, USA) at a crosshead speed of 500 mm/min. Shore A hardness was measured according to ASTM D2240.

Stress softening behavior was tested in strain sweep mode with a Rubber Processing Analyzer (RPA 2000). After curing at 160°C for 15 min, three consecutive scans were carried for the vulcanizates at 60°C with the strain of 1.4 – 140% at 1 Hz, and then heated to 100°C and kept for 30 min, keeping the chamber closed. The temperature was again reduced to 60°C subsequently to conduct the fourth scan with the strain of 1.4 – 140% at 1 Hz. The whole procedure was done as a measurement to study the stress-softening behavior. Among these, the fourth scan for the vulcanizate was defined as a recovery sweep.

Stress relaxation behavior was tested with a universal test machine (Instron 4465, USA). The sample was stretched at the speed of 1000 mm/min until the strain reached 150%, then its

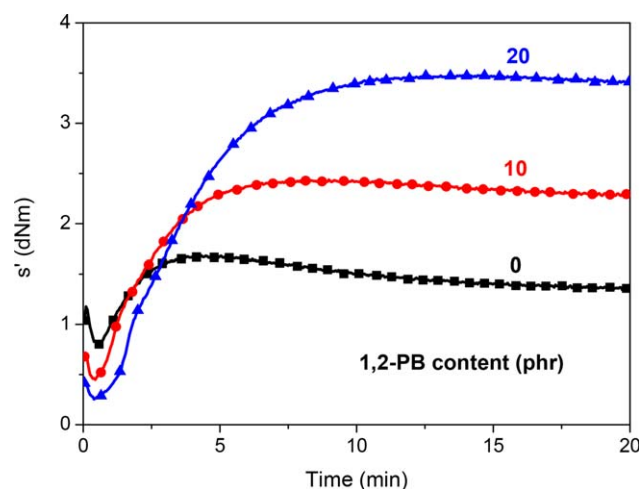


Figure 1. Curing curves of BIIR/1,2-PB vulcanizates at 160°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

stress relaxation behavior was recorded. The stress relaxation index σ_R was calculated by eq. (7),

$$\sigma_R(\%) = (\sigma_t / \sigma_0) \times 100 \quad (7)$$

where σ_t is the stress of the sample at time t , and σ_0 the initial stress of the sample.

GPC was performed in THF using a Perkin Elmer Series 200 equipped with polystyrene standards (PSS, Mainz) columns (5 μm PSS SDV gel, 102, 103, 104, 105 \AA , 30 cm each) calibrated with narrow PSS and detected by Waters 410 differential refractometer and Waters photodiode array detector operated at 254 nm.

^{13}C -NMR and solid-state CP/MAS ^{13}C -NMR spectra were recorded at a frequency of 100.6 MHz by a Bruker AVANCEIII 400 spectrometer. 1024 scans for a sample were collected. Solid-state CP/MAS ^{13}C -NMR was measured with a spinning rate of 5 KHz. The contact time was 1.5 ms and the relaxation delay was 4 s. A sample for ^{13}C -NMR was dissolved in CDCl_3 and purified by a solution-precipitation process before testing, in order to remove stabilizers (epoxidized soybean oil) and antioxidants in the rubber with hexane as solvent and acetone as precipitant, and dried in a vacuum oven at 60°C for 24 h.

RESULTS AND DISCUSSION

Curing Characteristics

The effect of 1,2-PB content on the curing characteristics of BIIR compounds is shown in Figure 1. With increasing 1,2-PB content, the maximum torque (M_H) increases significantly. With increasing 1,2-PB content from 0 to 10 phr, M_H increases by 45%. M_H of BIIR/1,2-PB (80/20) vulcanizate reaches 3.48 dNm, increasing by 107% in comparison with that of BIIR vulcanizate. M_H of BIIR compound reaches its maximum value at 4 min, and then decreases with time. This change that appears after the early crosslinking of BIIR macromolecules with 4 min at 160°C reflects the degradation of BIIR network is more obvious than crosslinking with increasing time at elevated temperature. It looks like the vulcanization reversion that appears

in sulfur crosslinked natural rubber. After the addition of 20 phr 1,2-PB, M_H of BIIR/1,2-PB (80/20) reaches its maximum value at 13 min and keeps nearly unchanged with time. It can be concluded that the addition 1,2-PB favors to the crosslinking of BIIR.

As shown in Figure 1, the minimum torque (M_L) decreases apparently with increasing 1,2-PB content. It indicates the addition of 1,2-PB can improve the processing capacity of BIIR compound to some extent.

Crosslink Density

To obtain crosslink density by a swelling test is a commonly used method to characterize the crosslinking structure of a rubber vulcanizate. Figure 2 presents the dependence of the swelling ratio and crosslink density of BIIR vulcanizates on the 1,2-PB content, and their values were calculated by using the Flory-Rehner equation.

With increasing 1,2-PB content, the swelling ratio of BIIR vulcanizates decreases while the crosslink density significantly increases as shown in Figure 2, which is in accordance with the rule of curing characteristics. The crosslink density of BIIR/1,2-PB (80/20) vulcanizate is $3.1 \times 10^{-4} \text{ mol/cm}^3$, which is much higher than the reported value of $2.6 \times 10^{-4} \text{ mol/cm}^3$ in the DCP curing system of BIIR, even the sulfur and ZnO curing systems.²⁰ Considering the low toxicity, low odor, and olefin nature of 1,2-PB, it can be concluded that 1,2-PB is an excellent coagent in enhancing the crosslink density.

The mechanism by which coagent augments crosslinking is the combination of, (a) network enhancement through the grafting of coagent between polymer chains (b) formation of an interpenetrating network of homopolymerized coagent and (c) formation of hard coagent domains (filler-like particles) grafted in the polymer chains.¹⁵ The mechanism by which 1,2-PB augments crosslinking is more likely to be the first case, as 1,2-PB is a macromolecular coagent with M_n of ca. 7.0×10^3 that is more likely to enhance the crosslinking network through the crosslink of 1,2-PB and BIIR.

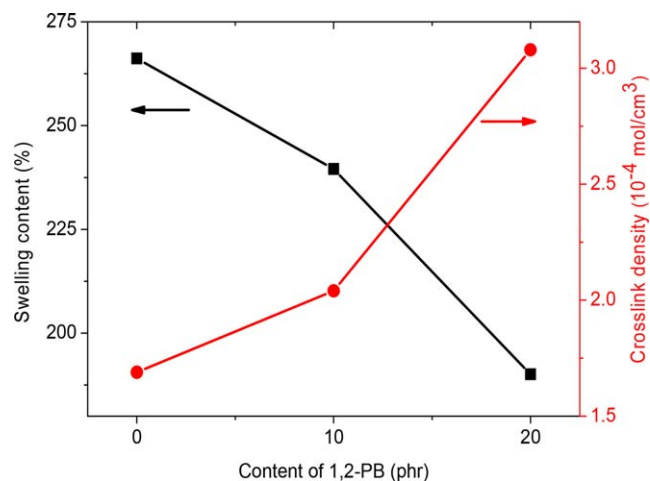


Figure 2. Swelling content and crosslink density of BIIR/1,2-PB vulcanizates. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Mechanical Properties of BIIR/1,2-PB Vulcanizates

BIIR/1,2-PB ratio	Tensile strength (MPa)	Elongation at break (%)	Stress at 100% extension (MPa)	Stress at 300% extension (MPa)	Set at break (%)	Shore A hardness
100/0	2.0 ± 0.2	679 ± 17	0.3 ± 0.0	0.5 ± 0.0	5.0	12
90/10	3.4 ± 0.1	406 ± 16	0.4 ± 0.0	1.4 ± 0.2	2.5	12
80/20	4.2 ± 0.1	307 ± 12	0.9 ± 0.1	4.1 ± 0.1	5.0	12

Mechanical Properties

The addition of 1,2-PB has a significant effect on the mechanical properties of BIIR vulcanizates as shown in Table II. With increasing 1,2-PB content, the tensile strength and stress at 100% extension of BIIR vulcanizates increase, while the elongation at break decreases. Compared with BIIR vulcanizate, BIIR/1,2-PB (90/10) has a 70% increase in tensile strength. When the 1,2-PB content is 20 phr, the tensile strength of BIIR vulcanizate increases from 2.0 MPa to 4.2 MPa, increases as much as 110%, and the stress at 100% extension increases from 0.3 to 0.9 MPa.

This trend suggests the enhanced crosslinking capacity of DCP cured BIIR by adding 1,2-PB as a crosslinking coagent. All the vulcanizates have reasonable low set at break, much lower than 10%. It can be concluded that the addition of 1,2-PB will increase the tensile strength and stresses at given extension, decrease the elongation at break, and have slight effect on the hardness and set at break.

Stress Softening Behavior

Stress softening effect is also called as “Mullins effect,” which could be observed a pronounced decrease in the stress when the

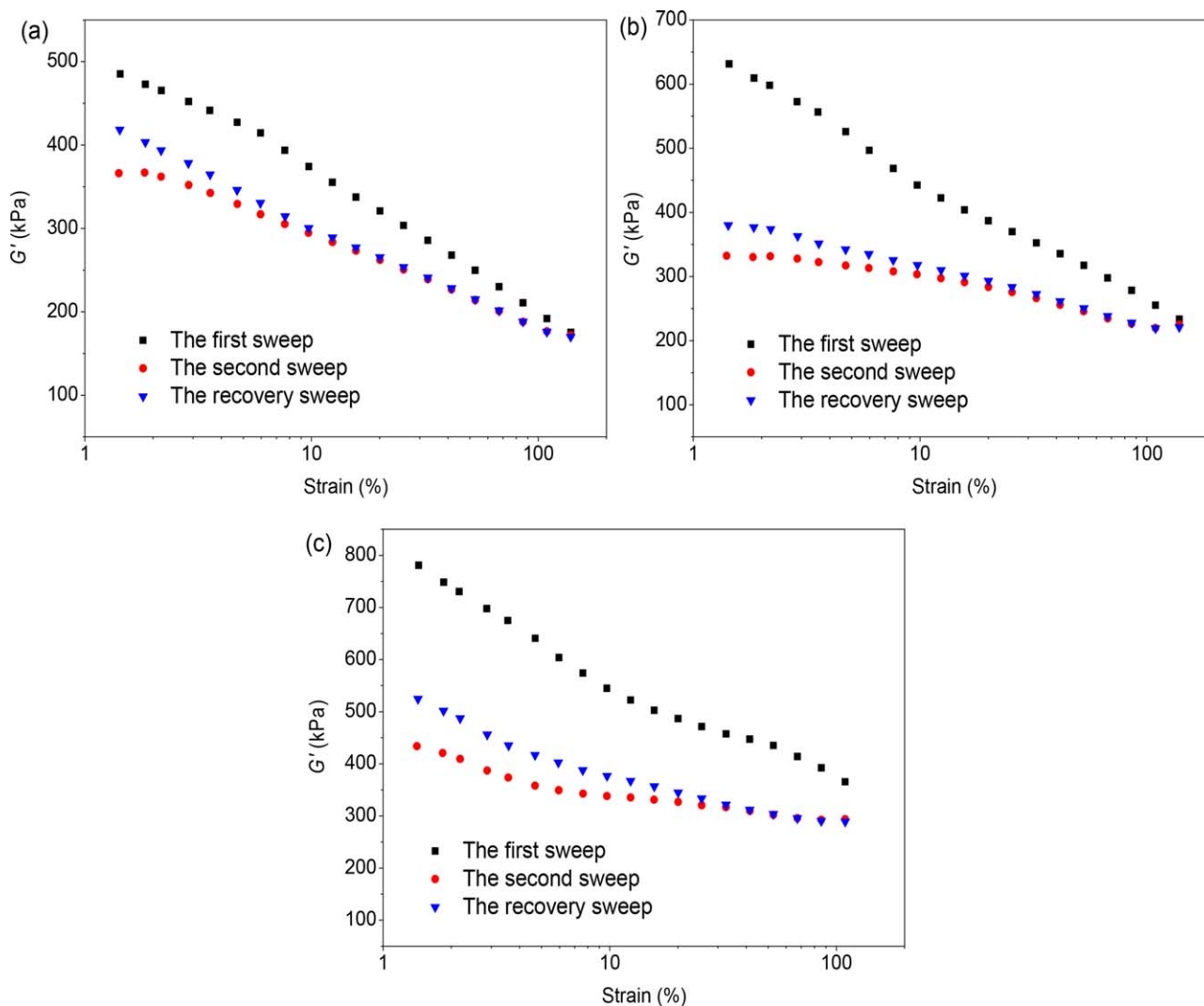


Figure 3. Stress Softening of BIIR/1,2-PB vulcanizates filled with N330 at 60°C, 1 Hz. BIIR/1,2-PB (a) 100/0. (b) 90/10. (c) 80/20. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

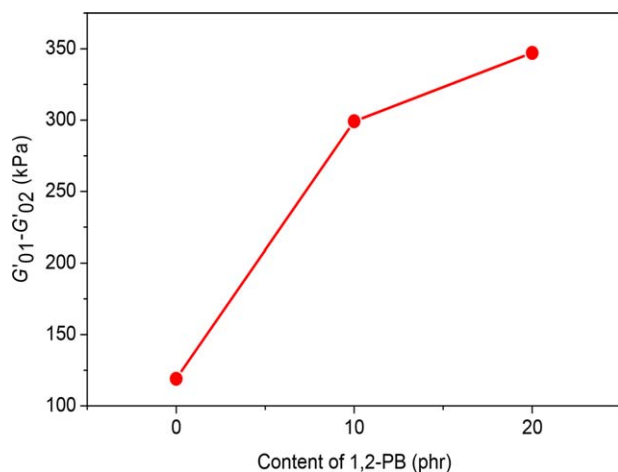


Figure 4. The influence of 1,2-PB content on the $G'_{01} - G'_{02}$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

filled vulcanizate is stretched for a second time.²² To understand the stress softening resulting from the Mullins effect, several physical interpretations were proposed, from chain breakage at the interface between the rubber and the fillers, slipping of molecules, rupture of the clusters of fillers, chain disentanglements, to more complex composite structure formation.²³ In our study the chain breakage at the interface between BIIR/1,2-PB and carbon black is the main factor leading to the stress softening effect.

Carbon black-filled BIIR vulcanizates were tested in strain sweep mode with a Rubber Processing Analyzer to check the effect of 1,2-PB content on the stress softening behavior. The stress softening of vulcanizates is shown in Figure 3. First, three consecutive scans were conducted at 60°C. To accelerate the recovery of stress softening, the temperature was raised to 100°C and kept at this temperature for 30 min. After that the temperature was reduced to 60°C to perform the fourth scan. All the carbon black filled BIIR vulcanizates show a remarkable stress-softening behavior, and higher 1,2-PB content leads to more pronounced softening behavior.

The initial G' values of the second sweep are lower than those of the first sweep, indicating an obvious stress softening effect existed in all the carbon black filled BIIR vulcanizates. Stress-softening behavior can be attributed to the weakening of filler-filler and filler-rubber interactions for filled rubber vulcanizates. For the carbon black-filled BIIR vulcanizates in the first sweep, when the strain amplitude increases to a certain extent, the filler-filler networks will break down, which results in the decrease of the initial G' of the second sweep.

After kept at 100°C for 30 min, all the vulcanizates show a recovery of G' . When heating up, the filler will gather again thus the filler-filler structure will reconstruct. It can be speculated that irreversibly broken happened leading to the incomplete recovery.

G'_{01} and G'_{02} are defined as the G' values of the first and second strain sweeps at 1.4% strain amplitude.²⁴ $G'_{01} - G'_{02}$ is

used to characterize the extent of stress softening behavior quantitatively. The influence of 1,2-PB content on the $G'_{01} - G'_{02}$ is displayed in Figure 4. $G'_{01} - G'_{02}$ increases gradually with increasing 1,2-PB content, which means that the higher the 1,2-PB content, the more pronounced the stress softening effect. Because BIIR/1,2-PB vulcanizate has higher crosslink density than BIIR vulcanizate, the pronounced stress softening effect of carbon black-filled BIIR/1,2-PB vulcanizate should be attributed to the chain breakage at the interface between BIIR/1,2-PB and carbon black.

Stress relaxation of a polymer is actually a process in which polymer segments move along the direction of an external force in order to reduce or eliminate internal stress, and the movement speed directly influences the stress relaxation rate. Jiang *et al.*²⁵ researched on the stress relaxation of EPDM/PP TPVs and found the stress relaxation index of EPDM/PP with more crosslinking agent was higher.

Carbon black-filled BIIR vulcanizates were tested with Instron 4465 to check the effect of 1,2-PB content on the stress relaxation behavior. The stress relaxation of vulcanizates is shown in Figure 5. The stress relaxation behavior of BIIR without 1,2-PB is 43.5%. With increasing 1,2-PB content to 10 and 20 phr, the stress relaxation index of BIIR increases to 47.2% and 47.7%, respectively. This change should be attributed to the increased crosslink density of BIIR by addition of 1,2-PB. As a result, the movement speed of polymer segments becomes slower.

Characterization of Insoluble and Soluble Fractions of BIIR/1,2-PB Vulcanizate

A BIIR vulcanizate was extracted at 85°C for 60 h, to obtain soluble and insoluble fractions. In Figure 6, the proportion of insoluble fraction (gel content) of BIIR/1,2-PB (80/20) vulcanizate increases with curing time at 160°C. The gel content of BIIR/1,2-PB (80/20) vulcanizate reaches 87% at 3 min, and reaches the maximum value of 90% in 7 min. It indicates the effective crosslinking of BIIR/1,2-PB compound at elevated temperature.

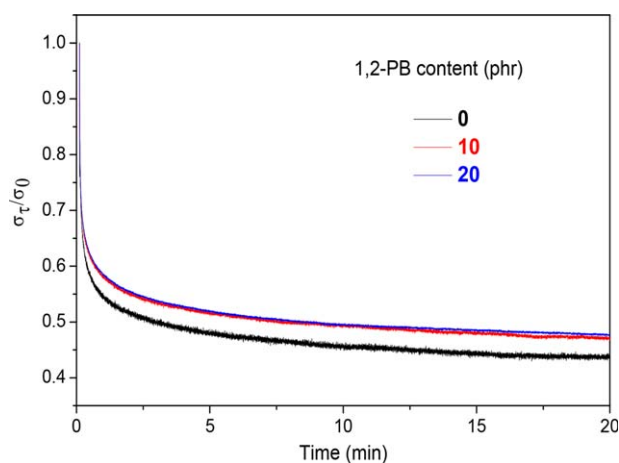


Figure 5. Stress relaxation behavior of BIIR/1,2-PB vulcanizates filled with N330. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

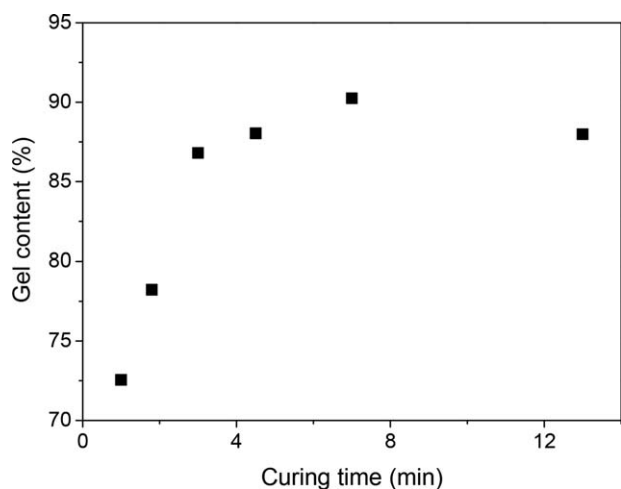


Figure 6. Dependence of gel content of BIIR/1,2-PB(80/20) vulcanizates on curing time.

The soluble fraction of BIIR/1,2-PB (80/20) vulcanizate should consist of small molecules, uncrosslinked macromolecules, and degradation products. GPC traces of BIIR and the soluble fraction of the vulcanizate at different curing time are shown in Figure 7. It is observed that, as the curing time increases, the peak of BIIR (M_n is ca. 2.7×10^5) cannot be seen in the GPC traces of the soluble fraction of the BIIR/1,2-PB vulcanizates, indicating that BIIR molecules have taken part in reactions, either crosslinking or degradation after vulcanization initiated by free radicals decomposed from DCP. On the contrast, the peak of 1,2-PB (M_n is ca. 7.0×10^3) gradually becomes weaker. Meanwhile, a new signal (M_n is ca. 1.5×10^4) generates at the shorter elution time than 1,2-PB along with the vulcanization. The results are likely ascribed to the crosslinking reaction of 1,2-PB and the degradation of BIIR. Compared the signal of neat 1,2-PB we can find the amount of 1,2-PB decreases with

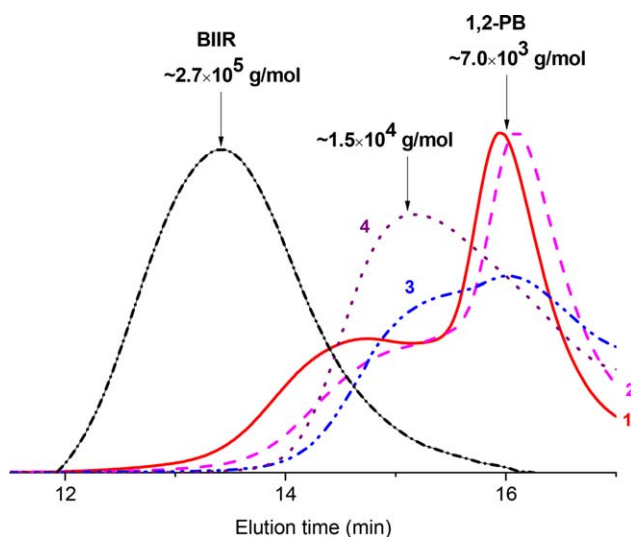


Figure 7. GPC traces of BIIR and the soluble fraction of BIIR/1,2-PB (80/20) vulcanizate at different curing time. (1—1, 2—1.8, 3—7, 4—13 min). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

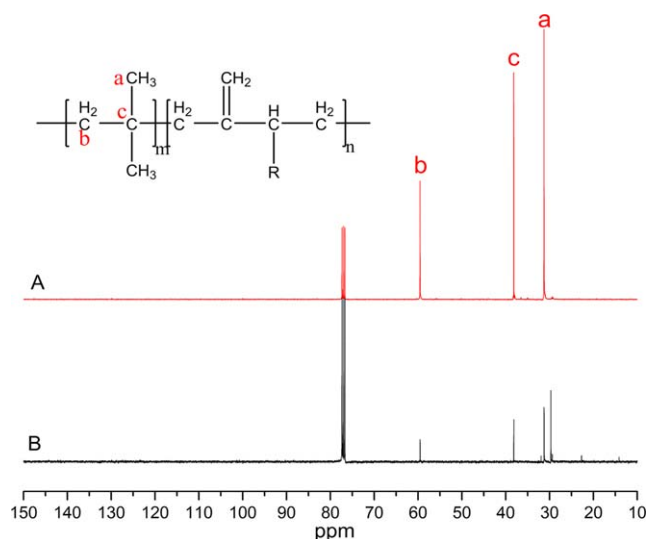


Figure 8. ^{13}C -NMR spectra of BIIR (A) and soluble fraction of BIIR/1,2-PB (80/20) vulcanizate (B). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the curing time, which indicates that 1,2-PB participates in the crosslinking reaction.

^{13}C -NMR spectroscopic measurements of the soluble fraction was also used to get an insight into the chemical nature of the degradation products. The chemical shift peaks of neat BIIR and soluble fraction of BIIR/1,2-PB (80/20) vulcanizate are shown in Figure 8. The assignment of BIIR's carbon is according to Chia Yeh Chu's work.^{26,27} In Figure 8(B), there are no resonances at 114 and 144 ppm that are corresponded to the secondary carbon and tertiary carbon of $-\text{C}=\text{CH}_2$ in 1,2-PB, which demonstrates that all 1,2-PB have taken part in the crosslinking reaction. This results are in good agreement with GPC results that the peak of 1,2-PB (M_n is ca. 7×10^3) cannot be seen in the GPC traces of the soluble fraction of the BIIR/1,2-PB vulcanizates after 13 min vulcanization. Compared Figure 8(A) with (B), it can be seen that there are new peaks occurred

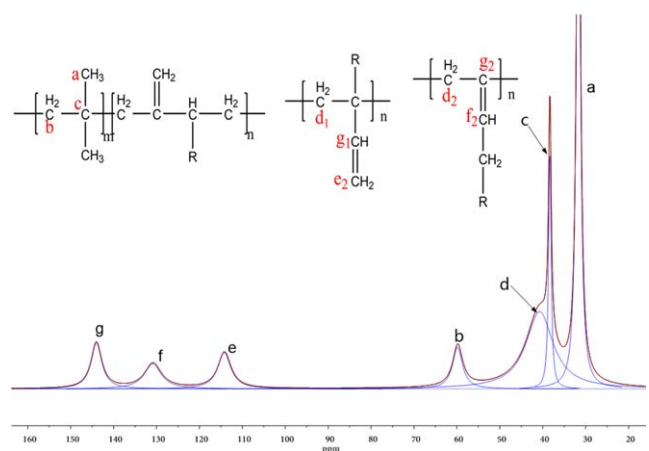


Figure 9. Solid-state ^{13}C CP/MAS spectrum of in soluble fraction of BIIR/1,2-PB (80/20) vulcanizate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

at 14.2, 29.7, and 31.9 ppm, which should be corresponded to the carbon of degradation products.

The structure of the insoluble fraction of BIIR/1,2-PB (80/20) vulcanizate was investigated by solid-state ^{13}C -NMR spectroscopy using CP/MAS method, and their chemical shift peaks and assignment are shown in Figure 9. The lower trace shows the spectrum after GSD (Global Spectral Deconvolution) peak analysis and the GSD peaks are colored blue. In the ^{13}C CP/MAS NMR spectra, signals overlap in downfield, so the GSD method was used for peak picking,²⁷ and followed by peak classification. Compared with the ^{13}C spectrum of BIIR in Figure 8(A), the new resonances occurred at 41, 114, and 144 ppm are corresponded to the secondary carbon of $-\text{CH}_2-$ in the main chain of 1,2-PB, secondary carbon and tertiary carbon of $-\text{C}=\text{CH}_2$ in 1,2-PB, respectively, indicating the existence of 1,2-PB component in the insoluble fraction of the vulcanizate. It also indicates 1,2-PB have taken part in the crosslinking reaction of BIIR.

CONCLUSIONS

1,2-PB can significantly affect the crosslinking characteristics and mechanical properties of DCP cured BIIR. The crosslink density of BIIR increases with the addition of 1,2-PB and prolonging curing time. With addition of 20 phr 1,2-PB, the maximum crosslinking torque of BIIR compound and the tensile strength of BIIR vulcanizate increase by 107% and 110%, respectively. 1,2-PB with low toxicity, low odor, and olefin nature structure is a good coagent for the peroxide curing of BIIR. With increasing 1,2-PB content, the stress softening behavior of carbon black-filled BIIR/1,2-PB vulcanizates becomes more obvious. BIIR/1,2-PB vulcanizates have higher stress relaxation index than BIIR vulcanizate. GPC and ^{13}C -NMR results indicate 1,2-PB participates in the crosslinking reaction, and the existence of 1,2-PB component in resulting BIIR/1,2-PB vulcanizates is confirmed by solid-state ^{13}C -NMR.

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