Formation of Multiple Networks in Cis-1, 4-Polybutadiene: Dynamical Viscoelasticity, Gel Content and Cross-Link Density

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Abstract. The formation of multiple networks of cis-1, 4-polybutadiene rubber (BR) with sulfur and carbon black (CB) were discussed by analysing the curing curve, gel content, cross-linking density (XLD) and dynamic viscoelasticity. XLD and gel test show the network from chains entanglement and sulfur cross-link existing in unfilled BR, in addition there is another network from CB in filled BR. Networks from sulfur and CB cross-links has two different peaks of loss modulus ($G''$) and loss tangent at different dynamic strain. Furthermore, the average bonding number of each chain to form the network is calculated from the sulfur cross-link density. There is two percolation of $G'_{0.01Hz}$ or gel content as the average bonding number increased in curing.

1. Introduction
The cross-linking of rubber is the reaction from linear macromolecule to three-dimensional networks. Previous researches on cross-linking or curing of rubber covered reaction mechanism, effect of chemical structure on property and so on [1-5]. However, the condensation of chains or fillers in curing has not been paid enough attention, which is crucial to the mechanical properties of vulcanizate. In preceding report [6], the gel content, NMR XLD and the curing curve are used to study the network structure of vulcanizate. In this report, the shearing oscillation is used to characterize the mechanical response of the condensation structure of network, which has been used to study the branching chains, phase structure and interaction of polymer/fillers [7-10]. Further, the percolation of bonding number of chains in the formation of networks is discussed.

2. Experimental Section

2.1. Raw Materials
Cis-1, 4-polybutadiene (BR), Sinopec Qilu Company; carbon black (N330), Degussa Qingdao Company. Formulation (phr) is: BR 100, ZnO 5, SA 2, TBBS 1, RD 2, sulfur 2; N330 0, 30 and 60.

2.2. Sample Preparation
BR and N330 are mixed in two-roll opening mixer (SK-168, Shanghai Rubber Machinery Plant). Vulcanizates are obtained at the Rubber Process Analyzer (RPA2000, Alpha Technologies) and immediately put into ice water to stop the curing reaction.
2.3. Measurement
Curing curves are tested in RPA2000 at temperature 150 ℃, frequency 1.67 Hz and strain 7%. XLD is tested at 60 ℃ by Nuclear Magnetic Cross-link Density Tester (MR-CDS 3500, Germany); the magnetic field intensity B_0 is 15 MHz. The dynamic viscoelasticity is tested by RPA2000 in which strain sweep is from 0.28% to 280% at 60 ℃ and 0.1 Hz, and frequency sweep is from 0.01 Hz to 20 Hz at strain of 7% and 60 ℃. The specimen is cut and weighed as M_1, then it is placed in a nickel cage and dipped into toluene for 72 hours. The toluene is washed off by dipping into acetone and dried to unchanged mass (M_2) in vacuum at 60 ℃. Gel content is calculated as \((M_1 - M_2)/M_1\)*100%.

3. Results and Discussion

3.1. Multiple Networks of Cis-1, 4-Polybutadiene Rubber
As well known, in induction period of rubber curing the macromolecular radicals or ions is formed by reaction of chains and sulfur radicals. Further, the cross-linking bond is formed by coupling of two macromolecular radicals to increase cure torque inclines first slowly and then abruptly. In the post-cure period, cross-linking reaction is to be completed, and then the cross-linking bond may be modified and finally stabilized. Besides, as for the carbon black (CB) filled vulcanizate, there are more complex networks involving the dynamic transient network of free chains, CB-bound rubber-CB network [11-16] and chemical network from cross-linking agent. Those three networks affect each other and determine cooperatively the final mechanical properties.

In figure 1, the torque, gel content and XLD increase slightly in the induction period \((t < 28\text{min})\), which means primary cross-links formed by several chains [6]. Then the sudden increases of XLD and gel content, as well as the big gel that cannot be dissolved, are thought as the percolation, i.e., the occurrence of primary network.

![Figure 1. Crosslink-density, gel content and curing curves of BR.](image)

Moreover, the uncured BR has a cross-link density as high as \(5\times10^5\ \text{mol/cm}^3\); the filled BR has a higher value and certainly the cured BR has the highest cross-link density. This means three kinds of cross-links in the filled BR vulcanizate: chain entanglement, carbon black particles with the bound rubber and the sulfur. The gel test and the curing curve also prove this view.

In figure 2, the unfilled BR shows linear viscoelasticity at small strain (<14%), i.e., the storage modulus \(G'\), loss modulus \(G''\) and loss tangent \(\tan\delta\) do not change when strain increases. The \(G'\) plateau of uncured BR without CB is related to the dynamic transient entanglement network. However, in the same strain region, the viscoelasticity of uncured filled BR decreases nonlinearly as unstable CB network. The increasing \(G'\) as curing time rise represents the effect of sulfur cross-linking network.

\(G'\) in high strain can be related to stable structures including chemical network and hydrodynamic interaction (figure 3). Apparently, the entanglement network and CB network are strengthened by the sulfur cross-linking, and the chemical network is strengthened by CB. Besides, the decreased hydrodynamic interaction in the induction period is related to the branching chains. Decline of modulus at high strain as cure time went is due to the slippage at the boundary of rubber/die.
Figure 2. Strain dependency of storage modulus $G'$ for BR/CB during curing.

Figure 3. Network strength during cross-linking of BR with different mass fraction of carbon black. $N_T$: total network, $H$: hydrodynamic interaction, $N_C$: chemical network mainly of sulfur cross-links, $N_E$: entanglement network, $N_{CB}$: CB-bound-CB network. $G'$ for $N_T$ is in strain 0.28%. Others are in high strain, which is 280% for zero and 30 phr CB filled BR and 140% for 60 phr CB filled BR.

The $G''$ curve can interpret more clearly the interaction of different networks. $G''$ in low strain (<14%) declined especially in the induction period, inferred the rheological behavior of branching macromolecules. Increase of $G''$ after 14% strain in cross-linking period is thought to be due to that the chains broken the restriction of sulfur network. Subsequently, the strain 14% is the beginning deformation of sulfur network, and the entanglement network 0.28% or much less strain beyond the experiment. Furthermore, in $G''$ vs. strain curves for filled BR, the first peak at low strain (0-7%) is thought to be from breakage/reconstruction of CB network [13-15]. The second one in high strain (28-
56%) is related to the sulfur networks.

3.2. Percolation of Bonding Number in the Formation of BR Networks

In the induction period \( (t < t_{10}, 28 \text{ min}) \) the slightly increasing properties are from primary cross-links by minority chains [6]. Then the sudden increases are thought as the occurrence of primary network.

Cross-linking is also found by dynamic viscoelasticity vs. frequency curves (figure 4). Slow increase of \( G' \) in induction and raise of \( G' \) plateau in cross-linking period \( (t > 28.5 \text{ min}) \) suggest separately the formation of branch and cross-links. Stable \( G' \) in low frequency is due to the chains with long relaxation time [17-21]. \( G' \) in low frequency \( (0.01 \text{Hz}) \) is taken as the mechanical response of network, while gel content represents its size and XLD difference between cured and uncured rubbers is thought to be the sulfur cross-link density \( (\text{XLD}_S) \). Subsequently, the percolation theory is applied by \( G'_{0.01 \text{Hz}} \) vs. \( \text{XLD}_S \) and gel content vs. \( \text{XLD}_S \) (figure 5). The percolation equation is taken as \( P \propto (p - p_c)\beta \), in which \( P \) is gel content or \( G'_{0.01 \text{Hz}} \), \( p \) is the bonding number of each chain while \( p_c \) is the threshold value, and \( \beta \) is the critical index. In the two percolations, the first threshold values for \( G'_{0.01 \text{Hz}} \) and gel content are 0.60 and 0.66 × 10^{-5} \text{mol/cm}^3, the second are 2.33 and 3.83 × 10^{-5} \text{mol/cm}^3.

![Figure 4](image-url)  
**Figure 4.** Frequency dependency of \( G' \) for unfilled BR.

![Figure 5](image-url)  
**Figure 5.** Effect of XLD on \( G'_{0.01 \text{Hz}} \), gel content of unfilled BR \( (\text{XLD}_S = \text{XLD}_t - \text{XLD}_{t=0}) \).

According to the Flory-Stockmayer theory [22-25], the critical bonding number of each chain in the formation of 3D network is \( p_c = 1/ (z-1) = 1/N \) (\( z \) is the coordination number and \( N \) is polymerization degree of each chain). It means that one cross-linking bond per chain would link together to form a giant 3D macromolecule. \( \text{XLD}_S \) is regarded as the molar concentration of bonding number. The mass concentration of pure rubber in vulcanize \( C \). Thus the chain number is \( C \times \rho / M \) (\( \rho \) is the mass density and \( M \) is the relative molecular weight of BR), and the average bonding number of each chain is \( \text{XLD}_S/(\rho / M)/C \). In table 1, the average bonding number is 2-3. Slight increase of bonding number in the early induction prove branching of chains. Its increase at the end of induction and the early cross-linking period inferred that bigger gel and sudden increase of \( G' \). As for the second percolation, the average bonding number is about 10, which is related to the formation of the perfect network.

Critical indexes of the power law equation for modulus vs. XLD and gel content vs. XLD are also calculated and shown in table 1. In Ref. [26] the indexes of elastic shear modulus and gel content for 3D network are 1.65 and 0.40. In table 1, the first percolation is from similar micro-gel to have close index (0.53) to the theoretical number (0.40). The cross-linking reaction happen in 2-dimensional space which resulted in the difference of index (0.44) for modulus from the theoretical one (1.65). As for the second percolation, perfect network has close index (1.32) to the theoretical value (1.65).

The percolation of bonding number in CB filled BR is also studied by the analysis of \( G'_{0.01 \text{Hz}} \) vs. frequency curve (figure 6). Bound rubber has existed in uncured BR to show XLD and gel content before curing (figure 6). The increases of XLD and gel content in the induction period also mean the forming of branching chains, and the abrupt increases are due to gigantic gel network. \( G' \) vs. frequency curves in induction period with BR/CB (30 phr) is similar to unfilled BR, while the highly filled BR...
(60 phr CB) is obviously different because of CB network [10]. Lower dependency of $G'$ in low frequency also show the formation of multiple networks as the appearance of the plateaus.

**Table 1.** Percolation analysis of sudden changes for gel content and $G'_{0.01Hz}$ of unfilled BR.

| Network property   | Gel_I | Gel_II | $G'_I$ | $G'_II$ |
|--------------------|-------|--------|--------|--------|
| Cure time (min) ($t_{10} = 28$ min, $t_{90} = 45$ min) | 20    | 31     | 26     | 33     |
| Critical XLD <sub>S</sub> ($\times 10^{-5}$mol/cm$^3$) | 0.60  | 2.33   | 0.66   | 3.83   |
| Fitted critical parameter | Critical bonding number<sup>a</sup> | 2.70  | 10.48  | 2.95   | 17.23  |
|                      | Critical index<sup>b</sup> | 0.53  | 1.08   | 0.44   | 1.32   |
|                      | 3D-network theriotical critical index [26] | 0.40  | 1.65   |        |        |

Note: <sup>a</sup> Bonding number = XLD/(ρ/M)/C, $M = 384805$ Kg/mol, $C = 0.901$ (g rubber)/(g compound), $ρ = 0.95$ g/cm$^3$. XLD is the sulfur cross-link density. <sup>b</sup> The index is obtained by analysis according to percolation theory.

**Figure 6.** Frequency dependency of $G'$ for BR filled with 30 and 60 phr CB.

In comparison to the unfilled BR with two or three abrupt increases for $G'_{0.01Hz}$ and gel content, BR with 30 phr CB (figure 7) might finish the first percolation from bound rubber to CB network at the beginning of curing. Moreover, the second percolation appears at higher cross-link density than unfilled BR (tables 1 and 2). Then the third one is in correspondence to the second abrupt increase of unfilled BR, i.e., the appearance of perfect sulfur network. Rapid increases of $G'_{0.01Hz}$ and gel content mean that CB accelerates the sulfur curing, which is different from the higher cross-link density for formation of network in filled BR.

**Figure 7.** Effect of XLD on $G'_{0.01Hz}$ gel content ($XLD_S = XLD_t - XLD_{t=0}$).
1. The response of dynamic viscoelasticity vs. strain curves for BR is very sensitive to different networks. Accordingly, it is concluded that there are three kinds of networks that enhanced each other: network of entangled chains, network of sulfur cross-links and network of CB. The sulfur cross-linking assists the CB aggregates and bound rubber to form network, and strengthen the entanglement network. Three networks have different deformation strain.

2. The cross-linking of BR is also proved by dynamic viscoelasticity vs. frequency curves. The dependency curves of gel content and low-strain $G'$ on the sulfur cross-link density show that there are two percolations of bonding number for chains in curing. The appearance of primary network is at the bonding number of 2-3 and the formation of perfect network at the bonding number of 10-20.

3. Acknowledgement

This paper was supported by National Natural Science Foundation of China (50873049).

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**Table 2. Percolation analysis of gel content and $G'_{0.01Hz}$ of BR/CB.**

| Parameter                  | 30 phr $^a$ | 60 phr $^b$ |
|----------------------------|-------------|-------------|
| Cure time (min) ($t_{10}=6$ min, $t_{10}=13$ min) | 0 | 4 | 4 |
| Critical XLD$_S$ ($\times 10^{-5}$ mol/cm$^3$) | 0 | 0.38 | 0.72 |
| Critical bonding number | 0 | 1.96 | 3.72 |
| Critical index | - | 1.56 | - |

Note: $^a$ Bonding number = XLD$_S$/($\rho$/M)/C, $M$ = 384805 Kg/mol, $C$ = 0.709 (g rubber)/(g compound), $\rho$=1.05 g/cm$^3$. $^b$ Bonding number = XLD$_S$/($\rho$/M)/C, $M$ = 384805 Kg/mol, $C$=0.585 (g rubber)/(g compound), $\rho$=1.16 g/cm$^3$. 

4. Conclusions
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