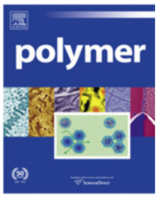
Polymer 51 (2010) 257–263

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer



Network evolution based on general-purpose diene rubbers/sulfur/TBBS system during vulcanization (I)

Ping Zhang, Fei Zhao, Yuan Yuan, Xinyan Shi, Shugao Zhao*

Key Laboratory of Rubber-Plastics, Ministry of Education, Qingdao University of Science and Technology, Qingdao 266042, China

ARTICLE INFO

Article history:
Received 16 March 2009
Received in revised form
17 July 2009
Accepted 24 October 2009
Available online 10 November 2009

Keywords:
Diene rubber
Vulcanization
Network evolution

ABSTRACT

In order to investigate the rule of network evolvement during vulcanization of diene rubber, generally used diene rubbers, including natural rubber (NR), polybutadiene rubber (BR), and styrene butadiene rubber (SBR), were cured with the same curing agents but at different time. The cured rubbers were then analyzed with Rubber Process Analyzer (RPA2000), dissolution/swell, and Magnetic Resonance Crosslink Density Spectrometer (MR-CDS 3500). Through data analysis on torques obtained from RPA2000, gel contents from dissolution/swell experiment and crosslink densities obtained from MR-CDS 3500, a new concept about the formation of rubber network during induction period of vulcanization was proposed. The experiments showed that even in scorch delay period, crosslink density, gel content and torque of the three rubbers increased as curing time went. The increase of these parameters indicated the formation of primary crosslink among several macromolecules which could be called local primary network-the first stage of network development. After this stage, both crosslink density and gel content of these three rubbers increased abruptly. The change percent of torque, crosslink density and gel content increased from 5% to 15%, 13%–33% and 2.5%–20% respectively which meant that almost one third of the vulcanization had been carried out during this period. Corresponding photographs of dissolution/swell experiments showed that whole gels which only swell but didn't solve in their solvents were formed. So the mutation point can be taken as the second stage of network development – a fundamental network had been formed. For NR, BR and SBR, the critical average change percent for crosslink density, gel content and torque were 33%, 20% and 15% respectively. BR, NR and SBR formed local primary network during induction period and a continuous fundamental network at the beginning of crosslinking period. This is different from traditional vulcanization theory.

1. Introduction

It's well known that raw rubber is a kind of linear polymer with poor mechanical properties, hence hardly of any practical value. Vulcanization causes profound changes at the molecular level. After vulcanization, the linear molecules are crosslinked and a network is formed. This imparts many important properties to it. Rubber is transformed from soft, weak material into a strong high elastic product, losing its tackiness and becoming insoluble in any solvent and is more resistant to deterioration caused by heat, light and aging process.

Since the discovery of vulcanization in 1839, researchers have devoted much effort to rubber vulcanization/crosslinking. Most of the work was focused on the study of vulcanization mechanism, vulcanization kinetics and structure and property of vulcanizates [1–8] and this contributes a lot to the theoretical investigation and engineering application of vulcanization/crosslinking.

It can be seen from research history of rubber vulcanization, related to property of vulcanizates and vulcanizing technology, most of the work about the formation of network is indirectly described by the development of apparent mechanical property. However, the description cannot discover the essence of rubber network formation systematically, and this limits the further research on rubber vulcanization process, relation between structure and property of vulcanizates, and vulcanizing technology to some degree. It's necessary to study the network evolution of rubber during vulcanization on microstructure level. Rubber process analyzer (RPA2000) and Magnetic resonance crosslink density Spectrometer (MR-CDS 3500) are applied in this work. A series of structural parameters during vulcanization of natural rubber (NR), butadiene rubber (BR), and styrene butadiene rubber (SBR) cured with sulfonamide accelerated sulfur (in order to eliminate influence of other ingredients on network, fillers are not introduced) are measured and the evolution of

---

* Corresponding author. Tel.: +86 532 84022731.
E-mail address: lindashi88@hotmail.com (S. Zhao).

0032-3861/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2009.10.057

network is analyzed. This paper deals only with the evolution of network during induction period of traditional cure curves. The evolution of network during crosslinking period will be discussed in paper II.

2. Experiment

2.1. Raw materials

Butadiene rubber (BR9000) and styrene butadiene rubber (SBR1502) are supplied by Qilu petro. Corp. of China Petro. NR (RSS1) is from Malaysia.

2.2. Sample preparation

2.2.1. Recipes

The compound formulations with different rubbers are shown in Table 1. The content of all compounded ingredients are given as usual, based on a total of 100 parts of rubber by weight.

2.2.2. Samples preparation

The raw rubber was masticated first on a two-roll mill by passing it through the rolls. After that, ZnO, stearic acid, aging resister and accelerator were added and mixed for 3 min with a rolling bank and 5 cuts on each side. Then sulfur was added and mixed for 2 min and finally 5 additional passes.

The compound was stored at room temperature for at least 8 h.

Isothermal vulcanization was performed using a rubber processing analyzer (RPA2000 from Alpha Co.). The samples underwent dynamic oscillation at 7% strain amplitude at a frequency of 1.67 Hz and temperatures of 150 °C for BR and SBR, 145 °C for NR respectively. Samples cured at different set time were taken out and cooled in pieces of ice to terminate the cure reaction, then dried and the measurements are carried out as soon as possible.

2.3. Measurement and data analysis

2.3.1. Gel content measurement

About 50 mg rubber cured at different time was put into a 200-mesh nickel sieve with constant weight and then immersed in toluene. Shook the solution periodically. Took them out of toluene after 48 h and dried them till their weight kept constant. Then weighted them and calculated the gel content.

2.3.2. Crosslink density measurement

The crosslink density (XLD) measurements were done using an IIC XLDS-3500 Magnetism Resonance crosslink density spectrometer. The measurement temperature for NR and BR samples was 60 ± 0.1 °C and for SBR was 90 °C. Data analysis was performed with the IIC Analysis Software package, using a non-linear Marquardt–Levenberg algorithm.

Table 1
Compound formulation of different rubber.

Ingredient	NR	BR	SBR
Rubber	100	100	100
Zinc Oxide	5	5	5
Stearic Acid	2	2	2
Accelerator TBBS[a]	1	1	1
Aging resister RD[b]	1	1	1
Sulfur	2	2	2

[a] TBBS: N-t-butylbenzothiazole-2-sulfenamide.
[b] RD: polymerized 1,2-dihydro-2,2,4-trimethyl-quinoline.

Table 2
Solubility parameters (SP) of rubbers and solvents.

Rubber	SP($cal^{0.5}/cm^{1.5}$)	Solvent	SP($cal^{0.5}/cm^{1.5}$)
Polyisoprene (NR)	7.9 ~ 8.3	Heptane	7.45
Polybutadiene (BR)	8.1 ~ 8.6	Tetrahydrofuran	9.9
Polystyrene-butadiene(75/25 ~ 72/28)[a]	8.1 ~ 8.6	Toluene	8.9

[a] the ratio is the weight ratio of butadiene to styrene in SBR. The ratio for SBR here is 76.5/23.5.

2.3.3. Dissolution/swell experiment

About 50 mg of rubber cured at different time were put into 15 ml toluene. Their dissolution or swell situation was observed after 48 h. According to the solubility parameters of both rubbers and solvents, toluene was chosen out of three different solvents as the best one. The solubility parameters of rubbers and solvents are shown in Table 2.

3. Result and discussion

3.1. Analysis for vulcanization process according to cure-curves

The simplest and oldest experiment to characterize vulcanization process is called the cure-curve, and can be measured using a moving-die rheometer. The rheometer measures the torque, or equivalently the shear modulus, as a function of curing time when the rubber cures, with an assumption that the modulus is proportional to the concentration of crosslinks. A typical schematic of cure-curve obtained from rheometer is shown in Fig. 1.

There are three main regions in the cure-curve: the first region is the scorch delay or the induction region. After the compound is put into the cavity of the rheometer, there is a drop of shear modulus because the softening of compound. Because the torque keeps a low plateau, it is usually thought there is no crosslink formed during this period. The second region is associated with the cure reaction, where crosslinking takes place and the crosslinked network forms. There is an abrupt increase of torque at the beginning of this period and keep going-up linearly, so do the elasticity and tensile strength of rubber. The third and final region of cure-curve is the postcure region where the modulus can increase (more crosslink is formed), decrease

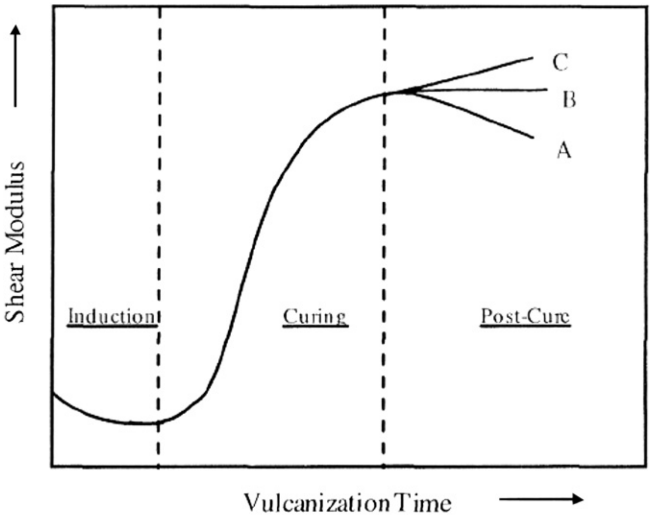


Fig. 1. A typical schematic of cure-curve obtained from rheometer.

(thermal degrading) or remain constant [10] depending on the specific cure system. In a word, the cure-curve explains the development of rubber network according to the development of mechanical property.

Cure-curve of NR, BR, SBR obtained from RPA2000 is shown in Fig. 2.

It can be seen that the shape of cure-curve is similar to traditional cure-curve. But the induction time is different due to their different chemical structure and non-rubber constituent, NR had the longest induction time, BR had the shortest, SBR fell between NR and BR [10]. If analyze the development of network in Fig. 2 according to traditional vulcanizing mechanism, the induction time of NR, BR and SBR was 4 min, 25 min and 16 min respectively. The complete network was formed at 13 min, 45 min and 30 min respectively.

3.2. The network evolution during early vulcanization process

Repeated experiments on measurement of crosslink density, gel content and dissolution/swell of rubber cured different time (that means rubber with different cure extent) were carried out to investigate the actual evolution of network during vulcanization. The results were compared with that obtained from traditional cure-curve.

Fig. 3 showed the evolution of crosslink density and gel content of NR, BR and SBR with different cure extent. For convenient observation of network evolution, the cure temperature for NR is reduced to 145 °C due to its fast cure rate. The crosslink density of rubber was measured with magnetism resonance crosslink density spectrometer. The network structure characterization of vulcanizate with solid NMR relaxation technique is described in full detail in the references [11–13]. ^{1}H NMR relaxation is caused by inter- and intramolecular diplomar magnetic interaction of protons and contains related information about mobility between nuclei of hydrogen atoms. In rubber networks at temperatures far above T_g, this interaction is averaged by the thermal molecular motion of the hydrogen atoms within the hydrocarbon backbone of the network. The extent of the motional averaging depends on the local dynamics and on the constraints of the hydrocarbon chains imposed by the network junctions. So, the mobility of chain can reflect the structure of network.

The crosslink density in Fig. 3 is total crosslink density, including physical crosslink of the uncured compound which can be understood as the entanglements of the long hydrocarbon chains, and chemical crosslink formed by chemical crosslink reaction. The evolution trend of crosslink density of NR, BR and SBR is similar to the shape of cure-curves, i.e. the evolution of crosslink density can also be divided into three regions with different slopes. But if the data is analyzed further and compared with the results of gel content, intrinsic difference can be found. The evolution of network structure will be discussed as follows.

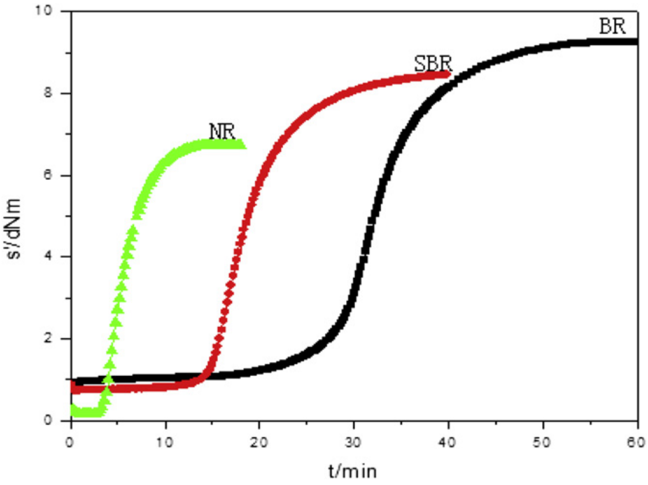


Fig. 2. Cure-curve of NR, BR and SBR NR (cured at 145 °C), BR and SBR(cured at 150 °C).

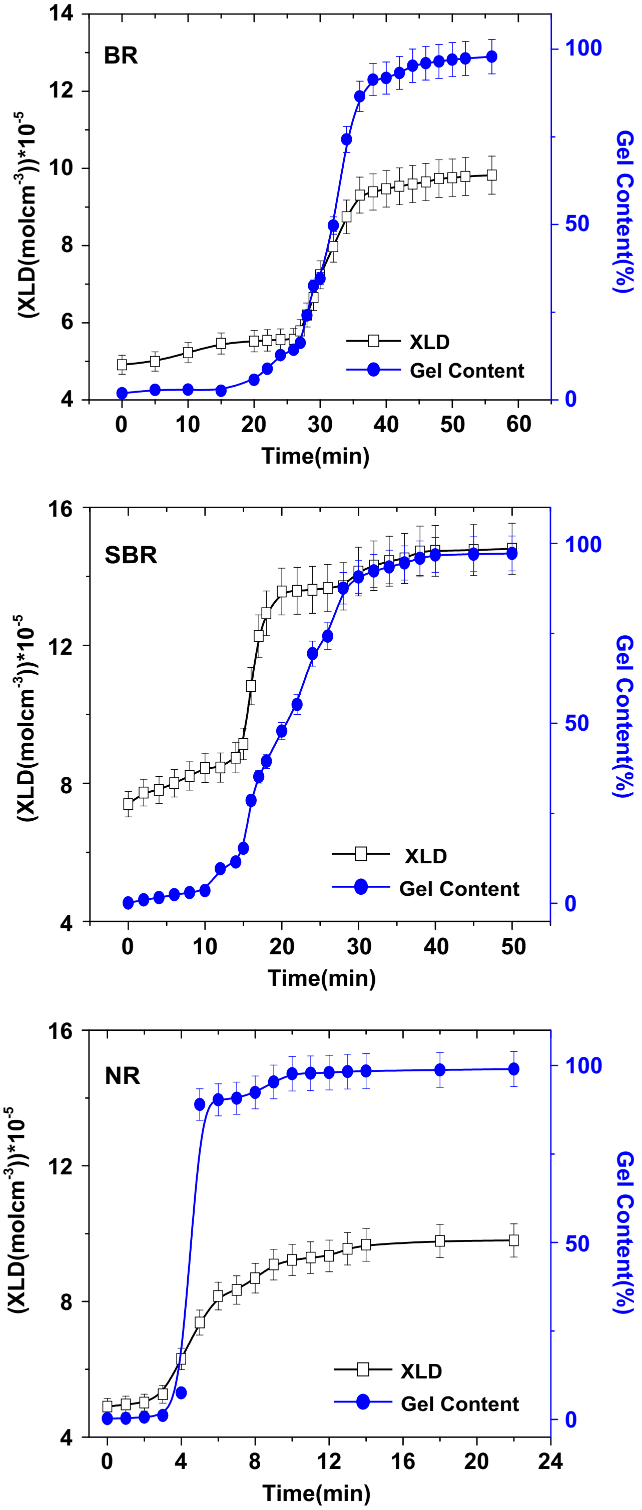


Fig. 3. Evolution of crosslink density and gel content with cure time.

3.2.1. *Local primary network forming period*

In traditional view, only reactions between activators, accelerators and sulfur take place during induction period, leading to the formation of rubber molecules with accelerator terminated pendant polysulfidic groups which is called crosslink precursors [9,10], while crosslink reactions between rubber molecules don't take place, so the torque of cure-curve during this period almost keeps constant. But if compare the first period of Fig. 3 with the first period of cure-curve (induction period), we can find that there is an apparent increase of both crosslink density and gel content of the three kinds rubber. The data of cure-curve torque listed in Tables 3–5 shows the same trend. This cannot be explained by the formation of rubber molecules with accelerator terminated pendant polysulfidic groups, the only reason is the formation of crosslink between rubber molecules.

Theoretically, only one crosslink between each rubber molecule is enough to form an insoluble gel. So, the result showed that not only reactions to form the rubber molecules with pendant polysulfidic groups took place during induction period, but also the crosslink reactions between several rubber molecules which led to the formation of local primary network by one or more crosslinks. This kind of crosslink was similar to rubber molecules with long branches. The crosslink reaction took place only in a small scale. The formed network is not strong enough to bear the force exerted by the moving die and there was relative slide between rubber molecules under force and the network contributed little to the macroscopical mechanical properties. This can be explained by Fig. 4.

Table 3
Percent change of network structure parameters during local primary network formation period.

Cure time, min	ΔSt/ΔS, %	ΔXLDt/ΔXLD, %	Gel Content, %
BR			
0	0	0	1.92
5	0.82	1.70	2.88
10	1.33	6.39	2.95
15	1.68	11.23	2.63
20	3.45	12.44	5.74
26	9.86	13.40	14.32
27	12.04	17.88	16.27
28	14.86	26.26	24.10
29	19.22	57.45	32.56
30	26.04	67.26	34.58
31	36.14	88.04	36.39
34	64.58	89.53	
SBR			
0	0	0	0.10
2	0.52	4.53	0.97
4	0.58	5.60	1.58
6	0.77	8.23	2.39
8	0.94	11.06	2.98
10	1.21	14.25	3.54
12	1.96	14.36	9.61
14	4.12	18.18	11.49
15	8.43	23.62	15.29
16	19.47	46.33	28.58
17	33.62	65.95	35.19
18	46.46	74.77	
NR			
0	0	0	0.24
1	0.30	1.30	0.32
2	0.52	2.42	0.64
3	0.79	7.49	1.12
4	12.95	28.75	7.51
5	38.70	50.65	88.99
6	58.97	66.59	
9	89.63	85.53	
12	98.22	90.71	
14	100	100	

Note: ΔSt is torque change at cure time t ($S_t - S_{min}$); ΔS is total torque ($S_{max} - S_{min}$); ΔXLDt is crosslink density change at cure time t ($XLD_t - XLD_{min}$), ΔXLD is total crosslink density change ($XLD_{max} - XLD_{min}$).

Table 4
Percent change of network structure parameters during the first part of network maturation period.

Cure Time, min	ΔSt/ΔS, %	ΔXLDt/ΔXLD, %	Gel Content, %
BR			
30	26.04	47.45	34.58
32	53.46	62.26	49.72
34	69.44	78.04	74.28
36	79.19	89.53	86.52
38	85.64	91.18	91.29
SBR			
17	33.62	65.95	35.19
18	46.46	74.77	39.44
20	65.37	83.35	47.86
22	77.00	83.58	55.23
24	84.19	84.04	69.37
26	88.99	84.74	74.22
28	92.38	85.43	87.54
30	94.76	91.21	90.67
NR			
4	12.95	28.75	7.51
5	38.70	50.65	88.99
6	58.97	66.59	90.32
7	73.38	70.22	90.77
8	83.30	77.32	92.41
9	89.63	85.53	95.38
10	93.76	88.31	97.69

Note: ΔSt is torque change at cure time t ($S_t - S_{min}$); ΔS is total torque change ($S_{max} - S_{min}$); ΔXLDt is crosslink density change at cure time t ($XLD_t - XLD_{min}$), ΔXLD is total crosslink density change ($XLD_{max} - XLD_{min}$).

It can be deduced from the above results that the first stage for network evolution is the formation of local primary network as shown in stage (1) of Fig. 6 which is corresponding to the induction period of cure-curve obtained from moving die rheometer. The size of this local primary network will be further measured and analyzed.

3.2.2. *Fundamental network forming period*

With the going of vulcanization, there is an apparent increase in torque of cure-curve which means the start of crosslink reaction in traditional view, corresponding to the reaction between crosslink

Table 5
Percent change of parameters related to network structure during the second part of network maturation period.

Cure Time, min	ΔSt/ΔS, %	ΔXLDt/ΔXLD, %	Swell Ratio, %
BR			
46	97.34	96.41	4.80
48	98.48	98.21	4.78
50	99.31	98.65	4.76
52	99.74	99.33	4.71
SBR			
38	99.50	98.98	4.95
40	99.71	99.3	4.93
NR			
10	93.76	88.31	6.39
11	96.54	89.7	5.86
12	98.22	90.71	5.55
13	99.26	95	5.10
14	99.55	97.44	5.02

Note: ΔSt is torque change at cure time t ($S_t - S_{min}$); ΔS is total torque change ($S_{max} - S_{min}$); ΔXLDt is crosslink density change at cure time t ($XLD_t - XLD_{min}$), ΔXLD is total crosslink density change ($XLD_{max} - XLD_{min}$). SR is swell ratio, SR = volume after swell/volume before swell.

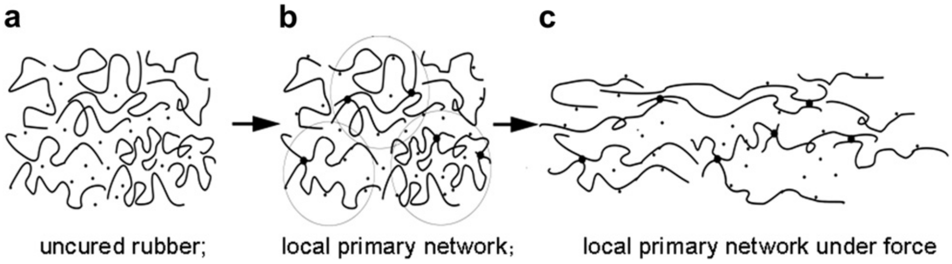


Fig. 4. Sketch for formation of local primary network with · represents polysulfidic groups and ● for crosslinks.

precursors and rubber molecules. The network becomes larger and larger which increases the modulus of the cured rubber, and so does the torque of cure-curve.

It can be seen from the fore semi-part of the second period of Fig. 3, i.e. the end of local primary network forming period that both the crosslink density and gel content increased fast and there was an inflexion in the curves. This can also be reflected from the parameters related to network structure shown in Table 3. The crosslink density, gel content and torque increased abruptly when BR, SBR and NR cured for 27–28 min, 15–16 min and 4 min respectively. At

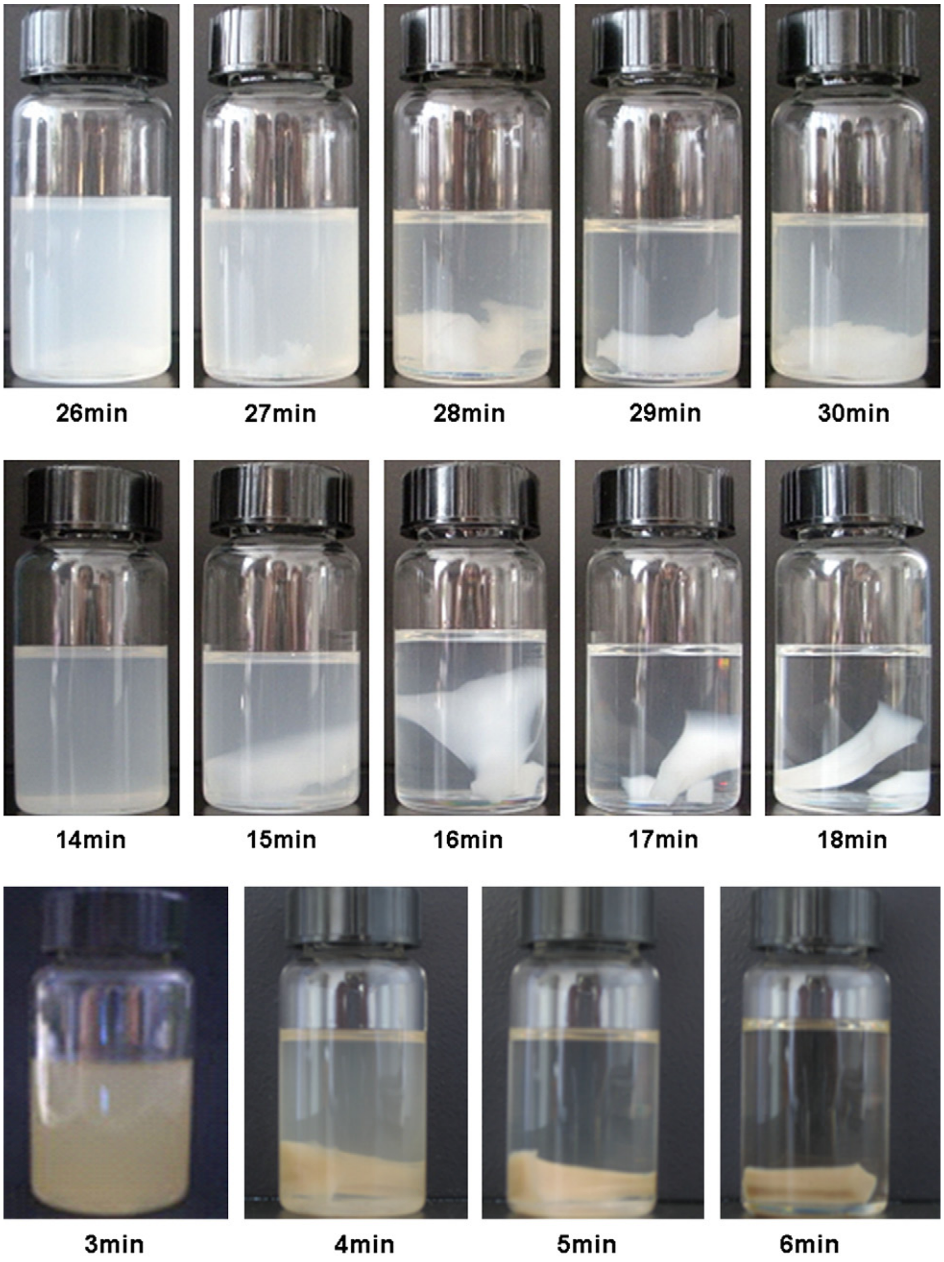


Fig. 5. Photographs of dissolution/swell experiment. (1) Photographs of dissolution/swell experiment for BR with different cure time, (2) Photographs of dissolution/swell experiment for SBR with different cure time, (3) Photographs of dissolution/swell experiment for NR with different cure time.

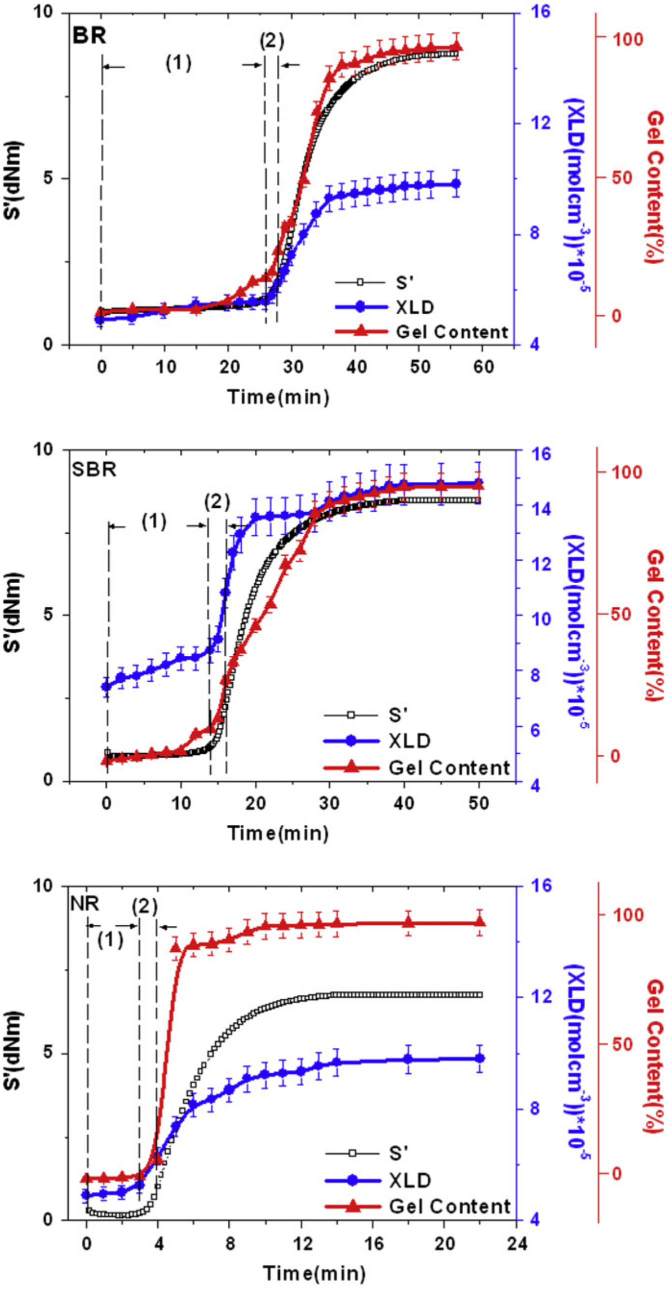


Fig. 6. Comparison of crosslink density, gel content and torque of BR, SBR and NR.

the abruptly change points, the change percent of torque, crosslink density and gel content increased from 5% to 15%, 13%–33% and 2.5%–20% respectively. It can be seen from the change of crosslink density that the crosslink reaction has completed about 1/3 during

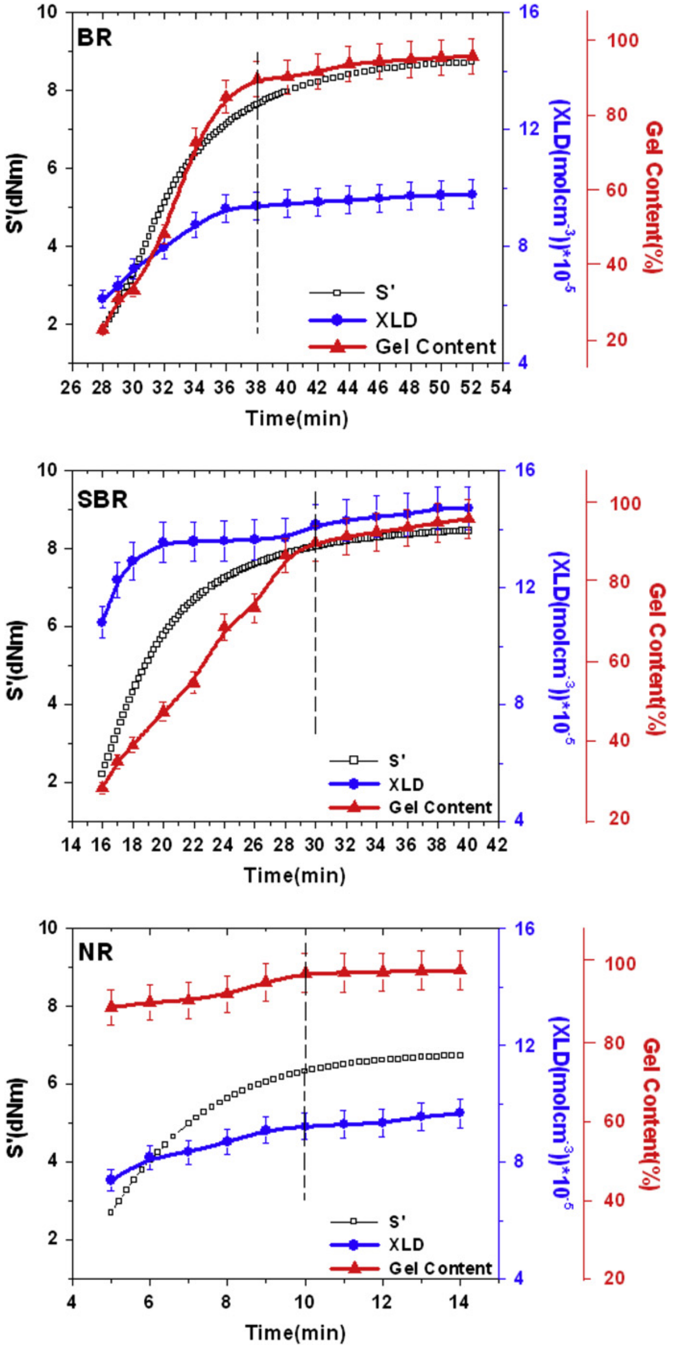


Fig. 8. Evolution of crosslink density, gel content and torque of BR, SBR and NR during the first part of network maturation period.

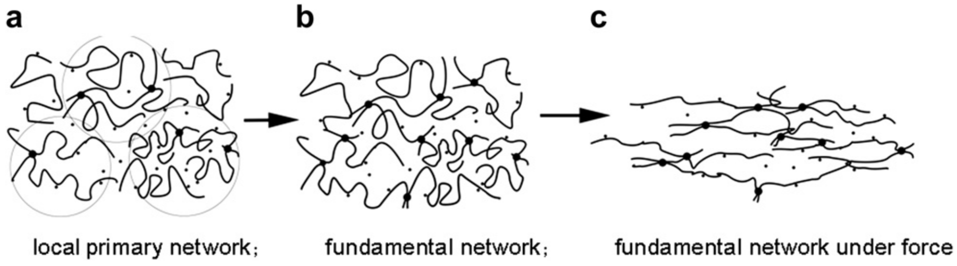


Fig. 7. Sketch for formation of fundamental network with · represents polysulfidic groups and ● for crosslinks.

this period. The low value of gel content for the three rubbers is due to the mesh size of 200-mesh sieve is invalid for filtering micro-gel, which means that the micro-gel with small size is not included in measured gel content.

To observe what has happened at the abrupt-changing points, about 50 mg rubbers cured for different time were immersed in 15 ml toluene after being taken out of the die cavity, fast cooled and dried. The photographs of dissolution/swell experiment are shown in Fig. 5.

It can be seen from Fig. 5: after having been cured for about 26 min for BR, BR dissolved in toluene or dispersed in toluene in the form of micro-gel, the whole solution was in a muddle. After having been cured for 27 min, BR had conversed into a whole swollen flocculation; for 28 min, BR had become an integral gel and the solution was transparent since then which indicated the formation of network only swell but not dissolve in toluene. The network of SBR and NR underwent the similar development. It can be seen from the experiment that the time for formation of complete network for SBR and NR is 15–16 min and 4–5 min respectively. The values tallied well with the crosslink density and gel content list in Table 3. All these experiments indicated a continuous fundamental network had been formed during this period.

What should be noted is that, if compare the crosslink density and gel content with torque in cure-curve (as shown in Fig. 6 and Table 3), it can be seen that the cure time for abrupt change of crosslink density and gel content was around the start of torque going-up point, i.e., the fundamental network had already been formed at this point. But the fundamental network was so sparse that the modulus (equivalently torque) of the rubber was still low.

So, the second stage for network evolution is the formation of fundamental network as shown in period 2 of Fig. 6. It takes only about 1–3 min to form the fundamental network from the local primary networks, the length of this period depends on the type of rubber, cure system and cure condition. The formed network is not a perfect one, but a basically infinite integrity. The formation of this kind of network can be shown in Fig. 7.

4. Conclusions

1. The experiments showed that when NR, SBR or BR cured with sulfur/TBBS at 145–150 °C, the increase of crosslink density and gel content with cure time during induction time indicated the formation of local primary network which meant that the crosslinking reaction had already taken place-the crosslink between several rubber molecules.
2. With the curing time going, the crosslink density and gel content of BR, SBR and NR increased abruptly. The dissolution/swell experiment showed the formation of continuous, integral gel which was insoluble in toluene. This can be taken as the second stage for network evolution – the formation of fundamental network.
3. In contrast with traditional vulcanizing theory, the experiments showed that BR, NR and SBR formed local al (segment) network during induction time of cure-curve and the fundamental network was formed at the beginning of hot cure.
4. The critical change of crosslink density, gel content and torque for BR, SBR and NR to form fundamental network structure is 33%, 20% and 15% respectively as shown in Fig. 8.

References

[1] Morrison NJ, Porter M. Rubber Chemistry and Technology 1984;57:63.
[2] Marzocca AJ, Goyanes S. Journal of Applied Polymer Science 2004;91:4110–1.
[3] Marzocca AJ, Mansilla MA. Journal of Applied Polymer Science 2006;101:35–41.
[4] Ding R, Leonov AI. Journal of Applied Polymer Science 1996;61:455–63.
[5] Chough Sung-Hyo, Chang Dong-Ho. Journal of Applied Polymer Science 1996;61:449–54.
[6] Marzocca AJ, Mansilla MA. Journal of Applied Polymer Science 2007;103:1105–12.
[7] Bhowmick Anil K, De Sadhan K. Journal of Applied Polymer Science 1981; 26:529–41.
[8] Mori Makio, Koenig Jack L. Journal of Applied Polymer Science 1998;70:1391–9.
[9] Yang Qifa. Chinese Synthetic Rubber Industry 1993;16(5):283–8.
[10] Yang Qingzhi. Modern rubber technology. Beijing: China Petrol Press; 1997.
[11] Kuhn W, Kelbch S. International rubber Conference Helsinki; 2000.
[12] Fratricova M, Schwarzer P, Kuhn W. Kautschuk Gummi Kunststoffe 2006;5: 229–35.
[13] Grinberg Farida, Garbaczyk Maciej, Kuhn Winfreid. Journal of Chemical Physics 1999;111:11222.