

# The Effect of Curing Parameters on the Mechanical Properties of Styrene-NR Elastomers Containing Natural Rubber-Graft-Polystyrene

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## ABSTRACT

The copolymerization of styrene on natural rubber latex was prepared by an emulsion polymerization using potassium persulfate and sodium laurylsulfate as an initiator and emulsifier, respectively. The vulcanization characteristics of styrene-NR elastomers were studied using moving die rheometer. The effect of vulcanization on styrene-NR elastomer containing natural rubber-graft-polystyrene was investigated in accelerated-sulphur curing system containing 2.0, 2.5, 3.0, 3.5 phr of sulphur with various temperatures ranging from 130 °C to 160 °C. Increase of tensile strength resulted from an increase of the crosslink density of vulcanization when compared to uncured sample. Furthermore, the accelerating action of temperature in curing system could be confirmed by increase of curing rate index and rate constant. The value of activation energy of the cure reaction could be calculated as 72.278 kJ/mol.

**Key words:** natural rubber; curing parameters; vulcanization; graft copolymerization; synthesis

## INTRODUCTION

From preliminary survey of natural rubber showed that in 2005, around 3 million tons of natural rubber (NR) can be produced in Thailand (IRG Rubber Industry, 2006). This makes Thailand the world's biggest producer and exporter of natural rubber. Therefore, more variety of products derived from or containing natural rubber should be investigated to increase its value. In addition, there is an increased consciousness about environmental preservation and an increased emphasis on the use of renewable resources, many

research works have been involved in improving the properties of natural rubber, thus enabling it to compete with synthetic rubbers. Furthermore, the improved products from natural rubber have potentially wide application as a result of physical or chemical modification. Modification of natural rubber has been performed in many different ways since 1801 (George and Swift, 1955). Further study to obtain new materials with chemical modification of natural rubber by copolymerization with vinyl monomers using various initiator systems has gained considerable important in modifying the properties of natural

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rubber (Cameron and Qureshi, 1980; Lenka *et al.* (1986) Prasassarakich *et al.*, 2001; Arayapranee *et al.*, 2002; Nampitch and Vattanatham, 2004 and 2005). The preferred processes used latex emulsion technique to obtain the particle size of smaller than 0.6 micron with effective heat removing (Rodriquez, 1970). In this polymerization, product contains grafted polystyrene rubber and compatibilizer that can lead to improve the compatibility of NR and PS in the synthesis. Similar results were also obtained by Fayt *et al.* (1981), Baetzold *et al.* (1994), Chattopadhyay and Sivaram (2001), and Arayapranee *et al.* (2002). This is because a mutual incompatibility leads to decreasing mechanical performance.

It has been a long-term practice of the rubber technologist to determine polymer compounds of desired processing and vulcanization properties (Varughese *et al.*, 1990; Asaletha *et al.*, 1999; Hanafi *et al.*, 2000, 2001). In this experiment, the curing system can be consumed by the vulcanization of the NR phase, which is more rapidly vulcanizable because of higher unsaturation level.

The objective of the present work is to study the curing parameters on mechanical properties of styrene-NR elastomers containing natural rubber-grafted polystyrene. The vulcanization characteristics of styrene-NR elastomers were studied using moving die rheometer. The effect of vulcanization on tensile strength of styrene-NR elastomers containing natural rubber-grafted polystyrene was investigated in accelerated-sulphur curing system with a various temperatures. The apparent activation energy and curing rate index for vulcanization of styrene-NR elastomers containing natural rubber-grafted polystyrene was calculated from experiments. A NR/styrene weight ratio corresponding to 60:40 has been chosen because at this composition, it is possible to maintain good mechanical properties of natural rubber while improving tensile strength of rubber material.

## MATERIALS AND METHOD

### 1. Materials

The used natural rubber latex was commercial natural rubber latex preserved with ammonia and consisted of 60% dry rubber content (DRC). Reagent-grade styrene monomer (purity  $\Delta$ 99%; Fluka) was purified by washing with 15% sodium hydroxide solution, to remove inhibitor, and followed by distilled water. The sodium dodecyl sulphate (SDS, purity  $\Delta$ 99.8%; APS Ajax Finechem) and potassium persulfate (purity  $\Delta$ 97%; Asia Pacific Specialty Chemicals Limited) were used as emulsifier and initiator in polymerization, respectively. Distilled water was used throughout the work. Other ingredients such as sulphur, zinc oxide, stearic acid, N-cyclohexyl-1-benzothiazyl sulfonamide (CBS) were obtained from Siam Metee, Univenture Co. Ltd. Cisadaneray Chemical (Indonesia) and Compton Uniroyal Chemical (China), respectively.

### 2. Preparation of styrene-NR emulsion copolymerization

The grafted polymerization was conducted in a 4-necked round bottom reactor of 1000 cm<sup>3</sup>, equipped with a two-blade impeller, condenser, and thermometer. Natural rubber latex, an aqueous solution of emulsifier and initiator were introduced to the reactor and the dissolved oxygen in the ingredients was removed by nitrogen purging for at least 30 min. The polymerization temperature was maintained constantly at 60°C using a controlled- temperature water bath. Reaction time was recorded using a stop watch. The gross polymer product was recovered and dried to constant weight in a vacuum oven. The recipe is shown in Table 1.

### 3. Structure determination of the copolymer of styrene and natural rubber

Final polymerization product was dried in vacuum oven to remove water and styrene

**Table 1** Emulsion polymerization recipe<sup>a</sup>

Ingredient	Weight (g)
Organic compound	
- Styrene	40 parts
- Natural rubber (DRC equivalent)	60 parts
Water	200 parts
Emulsifier	5 parts
Initiator	1 part

<sup>a</sup> In parts by weight.

monomer. Ungraft polystyrene and natural rubber were extracted out from product system using ethyl methyl ketone and petroleum ether respectively. Then the unextracted substance was identified by FTIR and NMR spectroscopy at 75 MHz. The C-H aromatic ring and C-H natural rubber stretching of polystyrene and natural rubber were identified. Also chemical shifts for natural rubber and polystyrene in NMR spectrum were observed.

#### 4. Morphology study

Sample of product latex was stained by potassium phosphotungstate (2% in water) and deposited on 300 mesh grid for investigation under JEM-1220 transmission electron microscope (TEM). Morphology and particle size were obtained from the pictures.

#### 5. Mixing procedure

Mixing was prepared in a two-roll mill operating at 300°C and 20 rpm. Styrene-NR elastomers was masticated for 3 minutes and other ingredients were added in the following order: zinc oxide (5 phr), stearic acid (2 phr), CBS (1.5 phr) and sulphur (variable; 2.0, 2.5, 3.0, 3.5 phr). The processing time after each component addition was about 2 minutes.

#### 6. Rheometric measurement and testing

The vulcanization parameters of the mixtures were measured using moving die rheometer (MDR 2000) at 0.5 arc degree, according to ISO 3417 method. The kinetic

parameters of the vulcanization, such as rate constant ( $k$ ) and apparent activation energy ( $E_a$ ) were calculated from the torque-time curves taken from experiments performed at 130, 140, 150 and 160 °C.

For tensile testing, the styrene-NR elastomers were vulcanized up to the optimum cure time, in the hydraulic press at 45 tonne. The optimum cure time ( $t_{90}$ ) was established as the necessary time to reach 90% of the maximum torque. Then, samples for mechanical testing were punched from the sheet according to ASTM D-412-Die C. Tensile testing was carried out using Instron (Model 1011) according to ASTM D-412-Die C. The reading were taken from an average of best three measurements.

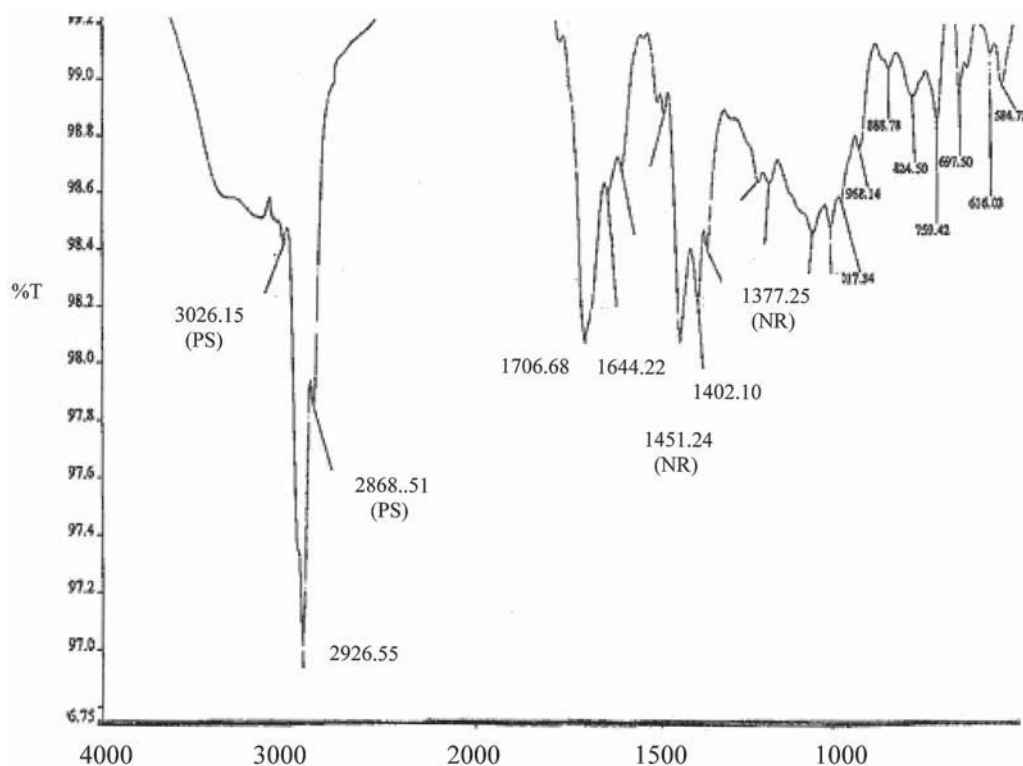
## RESULTS AND DISCUSSION

### 1. Occurrence of graft natural rubber (NR-g-PS)

To determine the presence of graft copolymer in product latex. the final polymerization product was dried in vacuum oven to remove water and styrene monomer. After treating with solvents, ungraft polystyrene and natural rubber were extracted out from product system by ethyl methyl ketone and petroleum ether respectively. The left over specimen was the reaction product which was not dissolved in petroleum ether and methyl ethyl ketone. Therefore, practically no free polystyrene and natural rubber were present. The left over product was identified by FTIR and <sup>13</sup>C NMR

spectroscopy to confirm the occurrence of styrene-graft natural rubber. Figure 1 illustrates the FTIR spectrum of the polymers. Even though the free polystyrene and natural rubber were not present, the FTIR spectrum showed polystyrene and natural rubber component in specimen. The peak at 3026.15 and 2868.51  $\text{cm}^{-1}$  were assigned to the aromatic C-H stretching ring of polystyrene. The signals at 1377.25 and 1451.24  $\text{cm}^{-1}$  were attributed to the aliphatic C-H stretching in natural rubber. The  $^{13}\text{C}$  NMR spectrum, Figure 2 exhibits the peak at 146.399, 130.067, 40.407 for polystyrene and 135.215, 128.504, 23.959, 32.881, 27.091 for natural rubber. This confirms the occurrence of grafting of styrene onto natural rubber back-bone. (Nampitch and Vattanatham, 2004)

## 2. Particle morphology



**Figure 1** FTIR spectrum of grafted natural rubber at emulsifier 4.5 parts, initiator 0.8 parts, styrene to rubber ratio; 1:1 and 60  $\text{^\circ}\text{C}$ . (Nampitch and Vattanatham, 2004)

Morphology and particle sizes were obtained from the Figure 3. From Figure 3, the grafted natural rubber particles consisting of a polyisoprene or natural rubber core and styrene shell were obtained by emulsion polymerization. The key process lies in the grafting of a significant portion of growing styrene onto the double bonds of the existing elastic compounds. Graft copolymerization with 4.5 parts by weight of emulsifier, 1 part by weight of initiator, and 50 parts by weight of monomers per 50 parts of natural rubber was performed at 60  $\text{^\circ}\text{C}$  for 4 hours. The morphology of the core-shell formation of grafted natural rubber latex is shown in Figure 3, which indicates the complete closed shell.

## 3. Vulcanization characteristics

The vulcanization characteristics of styrene-NR elastomers, cured with different amounts of

sulphur and temperature are listed in Table 2 and 3, respectively. The effect of sulphur on the rheograph profiles of styrene-NR elastomers, cured at 140°C are illustrated in Figures 4.

In all cases, the torque increased with increase of time and finally it remained constant. A NR/styrene ratio corresponding to 60:40 has been chosen because at this composition, it is possible to maintain good mechanical properties.

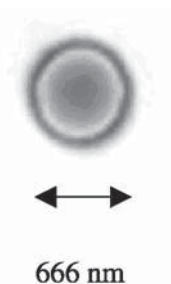
In the increase of sulphur content, the maximum torque is higher, indicating a strong influence of sulphur on the crosslink density.

Figure 5 shows the effect of the sulphur amount on tensile strength of styrene-NR elastomers. The value of tensile strength did not change significantly with the increase of sulphur because vulcanization reaction occur mainly at 2 phr of sulphur.

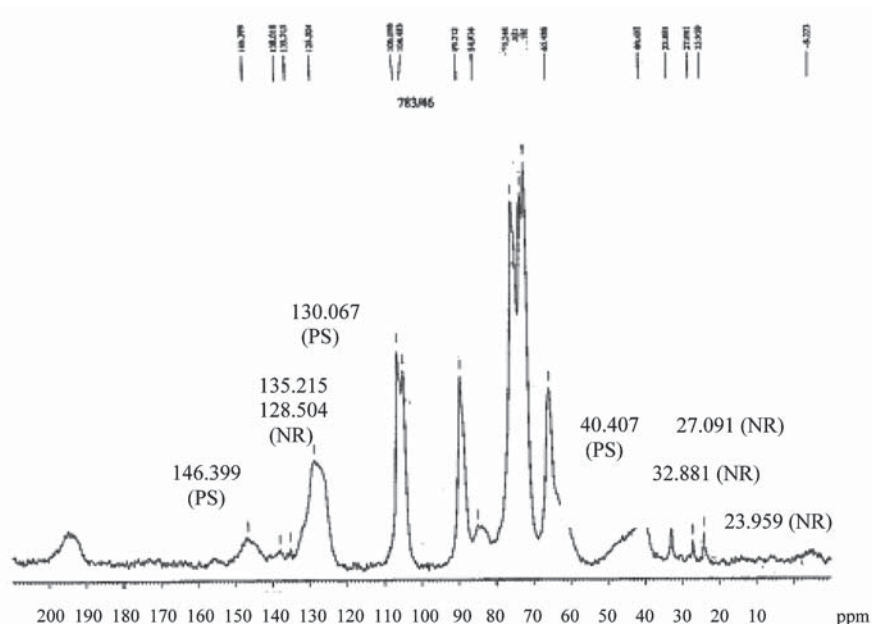
Since the product obtained in this polymerization having three components, NR, PS, NR-g-PS; the NR-g-PS is the compatibilizer of NR and PS. The addition of sulphur would help increase adhesion between the phase of NR and

PS besides NR-g-PS due to the presence of crosslinking of sulphur between phase. Then the cured samples showed a higher tensile strength compared to uncured sample. The results of the experiment are shown in Table 2.

The effect of temperature on the rheograph profiles of styrene-NR elastomers is illustrated in Figures 6. Figures 6 (a) and 6 (b)



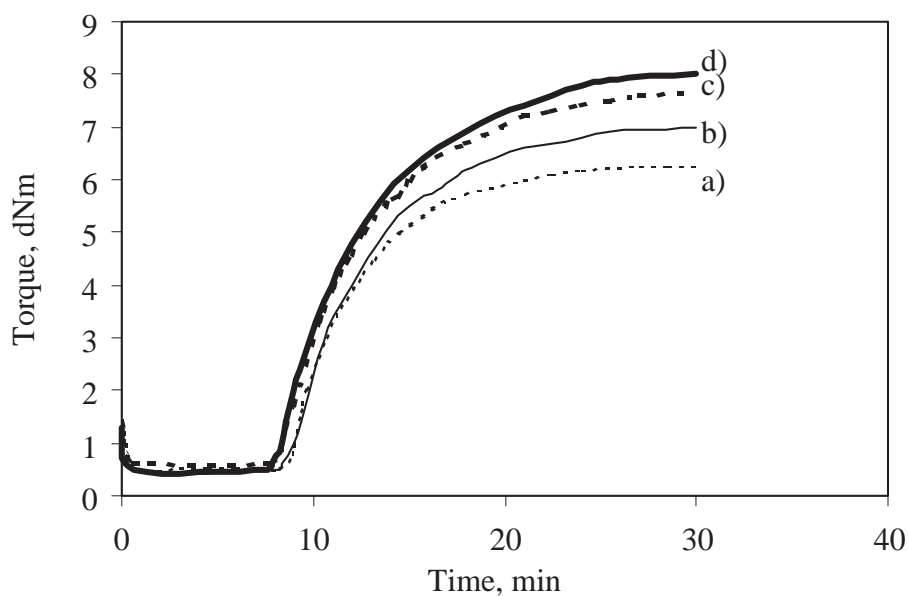
**Figure 3** Transmission electron micrograph of complete closed shell of grafted natural rubber latex (x15,000). Pictures are taken from TEM (JEM-1220) with potassium phosphotungstate. (Nampitch and Vattanatham, 2004)



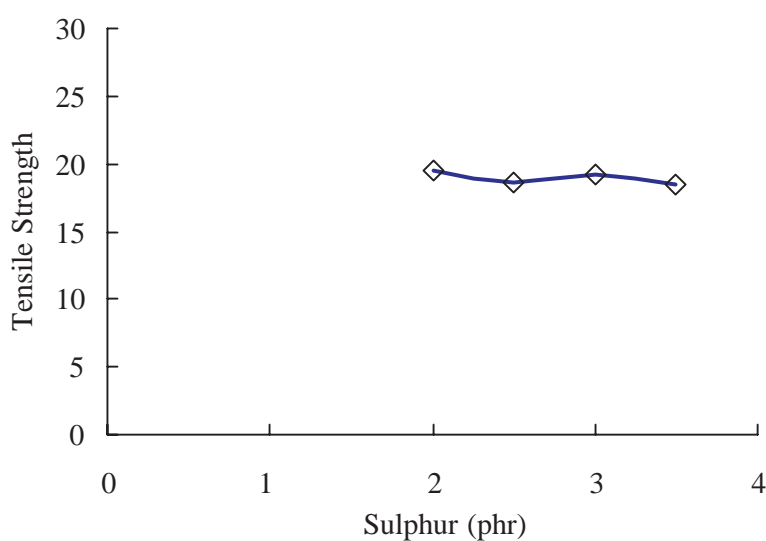
**Figure 2**  $^{13}\text{C}$  NMR spectrum of grafted natural rubber at emulsifier 6.5 parts, initiator 1 part, styrene to rubber ratio; 1:1 and 60 °C. (Nampitch and Vattanatham, 2004)

presents flat cure or plateau cure in experiment performed at 130 and 140°C which is the torque increase with increase of time and finally it remained constant when reaction was completed. After this time, the properties of cured samples did not change with time. Whereas the effect of

the temperature on the reversion phenomenon, which occur at the end of the curing process in the rheometer, are shown in Figures 6 (c) and 6 (d). The reversion tendency was only observed at higher temperature (150 and 160°C). The decrease of temperature resulted in decrease of reversion



**Figure 4** Effect of sulphur amount on the rheograph profile of styrene-NR elastomers, obtained at various sulphur content: (a) 2 phr, (b) 2.5 phr, (c) 3 phr, (d) 3.5 phr.



**Figure 5** Effect of sulphur amount on the tensile strength of styrene-NR elastomers, obtained at 140°C.

tax, indicates an improvement of thermal stability and a lower dissociation of sulphur crosslink. Normally, natural rubber shows rapid curing and high reversion effect because of its high content of allylic hydrogen. Because all allylic hydrogen are not used for crosslinking, the remaining allyl may provide site to be radicals, causing the dissociation of sulphur crosslinks. Moreover, the increase of temperature in vulcanization system leads to accelerate action because the decrease of scorch time and optimum cure time. The results of the experiment are shown in Table 3.

#### 4. Kinetic parameters of vulcanization

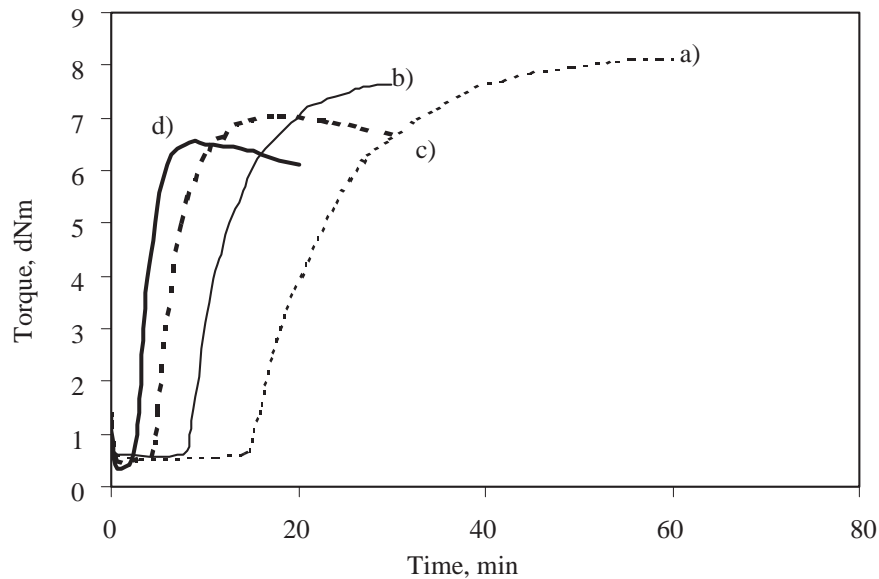
The kinetic equation describing the vulcanization process can be obtained from the torque-time values of the rheographs (Alex and Soares, 2003). If the process is considered as a first-order reaction, can be expressed by Eq. (1), as follow:

$$\ln \left( \frac{M_H - M_L}{M_H - M_t} \right) = kt \quad (1)$$

where  $M_H$ ,  $M_L$  and  $M_t$  are the maximum torque,

**Table 2** Vulcanization parameters and tensile strength of styrene-NR elastomers containing natural rubber-graft-polystyrene, obtained at 140°C.

	Uncured sample	Cured samples			
		Amount of sulphur (phr)			
		2.0	2.5	3.0	3.5
Torque max ( $M_H$ ), dNm		6.27	6.99	7.63	8.01
Torque min ( $M_L$ ), dNm		0.52	0.48	0.61	0.49
Scorch Time ( $t_{S1}$ ), minutes		9.35	9.43	8.93	8.66
Optimum cure time ( $t_{90}$ ), minutes		17.77	18.91	19.28	19.90
Tensile Strength (MPa)	0.896	19.48	18.56	19.16	18.47



**Figure 6** Effect of temperature on the curing parameters of styrene-NR elastomers at sulphur content of 3 phr, obtained at various temperatures: (a) 130 °C, (b) 140 °C, (c) 150 °C, and (d) 160 °C.

the minimum torque and the torque at a cure time  $t$ , respectively.  $k$  is the vulcanization kinetic constant.

Because the rate of the first stage, associated to the rate of conversion of the cure complex, reflects the characteristics of the main forward reaction kinetic,  $M$  values between 25 and 45% of torque change were chosen to estimate the rate constants in this work (Chough and Chang, 1996). By plotting  $\ln(M_H - M_L / M_H - M_i)$  against  $t$ , a straight line graph is obtained, indicating that the cure reaction follows first-order kinetic.

Theory and practice shows that the vulcanization rate depends on the reciprocal temperature. Therefore, it is possible to use the Arrhenius equation to express this dependence, according to Eq. (2):

$$k = A \times \exp\left(\frac{-E_a}{RT}\right) \quad (2)$$

or

$$\ln k = \ln A - \frac{E_a}{R} \times \frac{1}{T} \quad (3)$$

where  $A$  is the pre-exponential factor,  $R$  is the gas constant,  $T$  is the absolute temperature and  $E_a$  is

the apparent activation energy for the curing process. The values of the rate constants and activation energy of the cure reaction of all formulations are given in Table 4. The typical Arrhenius plot are shown in Figure 7 to estimate the activation energy. The values of the rate constants increased with the increase of temperature.

Also the cure rate index (CRI) and rate constant, obtained from Eq. (4) and Eq. (2) respectively, increased considerably with the increase of temperature in curing systems. All these results confirmed the accelerating action of temperature.

$$CRI = \frac{100}{t_{90} - t_{s1}} \quad (4)$$

where  $t_{90}$  was the optimum cure time and  $t_{s1}$  was the scorch time.

## CONCLUSIONS

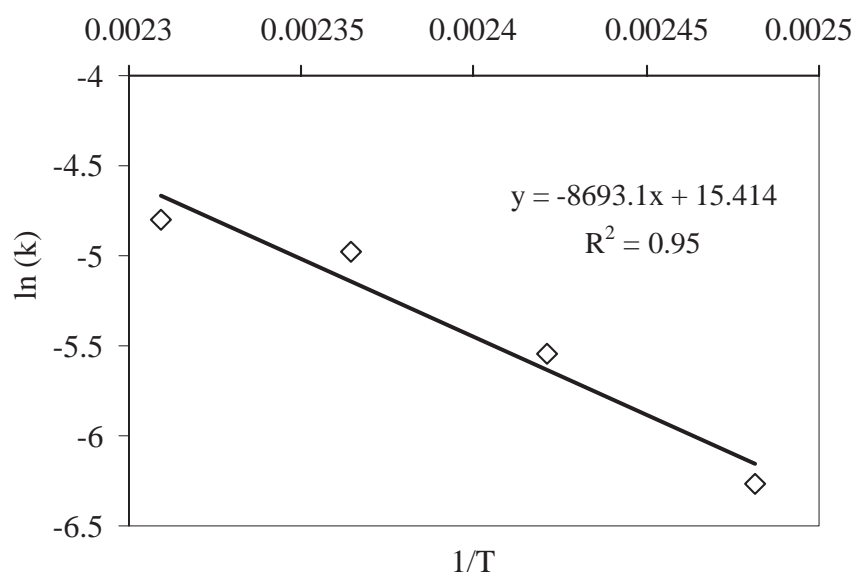
The styrene-NR elastomers containing natural rubber-graft-polystyrene was prepared by emulsion polymerization of NR and styrene using potassium persulfate and sodium laurylsulfate as an initiator and emulsifier, respectively. The

**Table 3** Vulcanization parameters of styrene-NR elastomers containing natural rubber-graft-polystyrene, obtained at sulphur content of 3 phr.

	Temperature ( $\partial C$ )			
	130	140	150	160
Torque max ( $M_H$ ), dNm	8.13	7.63	7.01	6.56
Torque min ( $M_L$ ), dNm	0.63	0.61	0.49	0.41
Scorch Time ( $t_{s1}$ ), minutes	16.25	8.93	5.19	3.01
Optimum cure time ( $t_{90}$ ), minutes	37.14	19.28	10.46	5.73

**Table 4** Kinetic parameters of vulcanization of styrene-NR elastomers containing natural rubber-graft-polystyrene, obtained at sulphur content of 3 phr.

CRI ( $\text{min}^{-1}$ )				Rate constant, $k$ ( $\text{min}^{-1}$ )				Ea (kJ/mol)
130 $\partial C$	140 $\partial C$	150 $\partial C$	160 $\partial C$	130 $\partial C$	140 $\partial C$	150 $\partial C$	160 $\partial C$	
4.79	9.66	18.98	36.76	0.0019	0.0039	0.0069	0.0082	72.278



**Figure 7** Arrhenius plot for styrene-NR elastomers obtained from the rheographs.

rheometric graphs could be carried out by moving die rheometer. The effect of vulcanization on styrene-NR elastomers containing natural rubber-graft-polystyrene was investigated in accelerated-sulfur curing system. The tensile strength did not change significantly with the increase of sulphur because vulcanization reaction occur mainly at 2 phr of sulphur and the tensile strength of cured samples increase substantially when compared to uncured sample due to increase of crosslink density. Furthermore, the increase of calculated cure rate index and rate constant could confirm the accelerating action of temperature.

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