

# Resin-Vulcanized NBR: Suitability of Rheometric Parameters for the Calculation of Cure Kinetic Constants

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**ABSTRACT:** Several mechanisms can be used to describe the vulcanization process, and study of the reactions that actually take place can be done through different techniques. In this work, two methods that used rheometric parameters to calculate the kinetic constant were compared for the cure of nitrile rubber with a system of phenolic resin, polychloroprene, and zinc oxide. The formulations and data analysis were based on a complete factorial experiment design. The results enabled the identification of the influence of each parameter involved in the vulcanization process and the suitability of the two methods used. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 505–513, 2002; DOI 10.1002/app.2354

**Key words:** nitrile rubber; phenolic resin; rheometric parameters; vulcanization kinetics

## INTRODUCTION

The reactions involved in the vulcanization process can be of the addition, substitution, or elimination types or even a combination of these reactions. In the study of the mechanism and structure of vulcanized rubber, several techniques have been developed, including chemical analysis, solid-state <sup>13</sup>C-NMR, kinetic constant determination, equilibrium swelling, differential scanning calorimetry, and so on.<sup>1</sup>

In addition to the vulcanizing agents, which effectively participate in the three-dimensional network, a number of other additives can also

take part in a typical rubber formulation. Among them, accelerators reduce the vulcanization time by increasing the rate between the vulcanizing agents and the rubber;<sup>2</sup> activators, mostly metallic oxides and fatty acids, improve vulcanization efficiency by allowing, for a given amount of vulcanizing agent, more crosslinks to be formed.<sup>3</sup>

The choice of the vulcanization system for a particular rubber depends on the set of properties required in the final product. Nitrile rubber is readily vulcanized by conventional sulfur–accelerator systems, but a phenolic resin vulcanization is used instead whenever vulcanizates with excellent heat resistance, low compression set, and good dynamic properties are desired.<sup>4</sup> In the phenolic vulcanization, the rate can be increased with halogen-containing activators such as metal halides, polychloroprene, chlorosulphonated polyethylene, and so on,<sup>4,5</sup> and several methods have been proposed for following the vulcanization kinetics.<sup>5–8</sup>

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**Table I Complete Factorial Experiment Design**

	Variable Level		
	-1	0 (Replicate Three Times)	1
Phenolic resin SP1045	7	9	11
Polychloroprene W	5	10	15
Zinc oxide	3	5	7

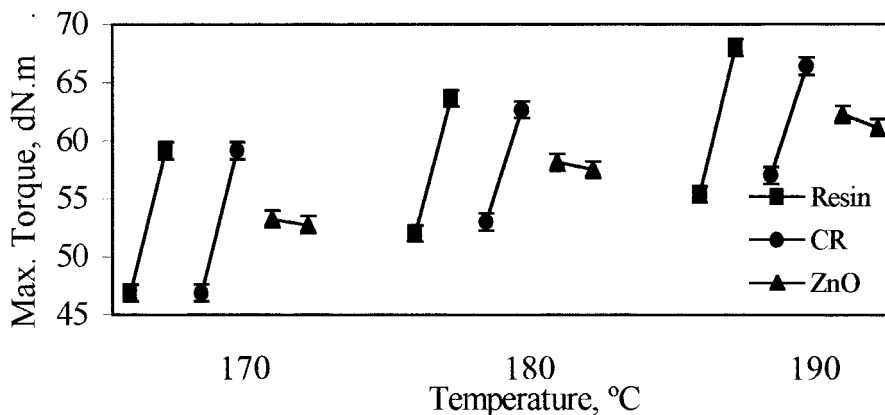
Design of Experiments	Mix Designation								
	F1	F2	F3	F4	F5	F6	F7	F8	F9
Phenolic resin SP1045	1	-1	-1	0	1	1	-1	1	-1
Polychloroprene W	-1	-1	1	0	1	-1	-1	1	1
Zinc oxide	-1	-1	1	0	-1	1	1	1	-1

NBR NP2021	phr								
	100	100	100	100	100	100	100	100	100
Phenolic resin SP1045	11	7	7	9	11	11	7	11	7
Polychloroprene W	5	5	15	10	15	5	5	15	15
Zinc oxide	3	3	7	5	3	7	7	7	3

The method based on rheometric parameters considers that the torque evolution can be directly related to the formation of crosslinks. First-order kinetics are assumed, and one then derives a mathematical expression by taking torque values at the early stages of the vulcanization reaction, considering that at these lower conversions, the rate reflects the predominant reaction toward crosslink formation.<sup>6</sup>

However, the maximum cure rate was found to be more sensitive to small variations in the amounts of the formulation ingredients than to the traditional curometer parameters,<sup>7</sup> and the knowledge of the time at which this maximum occurs allows for an improved determination of the cure kinetic constant ( $k$ ). Unlike the argument stated in the previous paragraph, this new model is based on decreasing reaction rate, and



**Figure 1** Effects of resin, polychloroprene, and zinc oxide amounts on maximum torque at different temperatures.

**Table II Influence of Polychloroprene Amount (phr)**

	Mix Designation		
	F6	F8	F8 (Resin + Zinc Oxide)
NBR NP2021	100	100	100
Phenolic resin SP1045	11	11	11
Polychloroprene W	5	15	0
Zinc oxide	5	7	0

thus, only data taken after the occurrence of the maximum cure rate are considered. Although first-order kinetics are predominantly found for most rubber compounds, this method allows for an accurate determination of the reaction order ( $n$ ) when it is different from unity.

The great interest arising from these discussions directed the objective of this work toward the investigation of the vulcanization kinetics of nitrile rubber in the presence of the phenolic resin SP-1045, polychloroprene, and zinc oxide. The effect of the amount of each of these ingredients on the reaction rate was also investigated. Thus, we elaborated a complete factorial experiment design, taking into account these three variables. Rheometric data were manipulated according to the two methods presented, and the results were compared.

## EXPERIMENTAL

The influence of the ingredients of the vulcanization system and their amounts was investigated

**Table III Influence of Zinc Oxide Amount (phr)**

	Mix Designation	
	F (resin 11 phr)	F8 (Resin + Zinc Oxide)
NBR NP2021	100	100
Phenolic resin SP1045	11	11
Zinc oxide	0	7

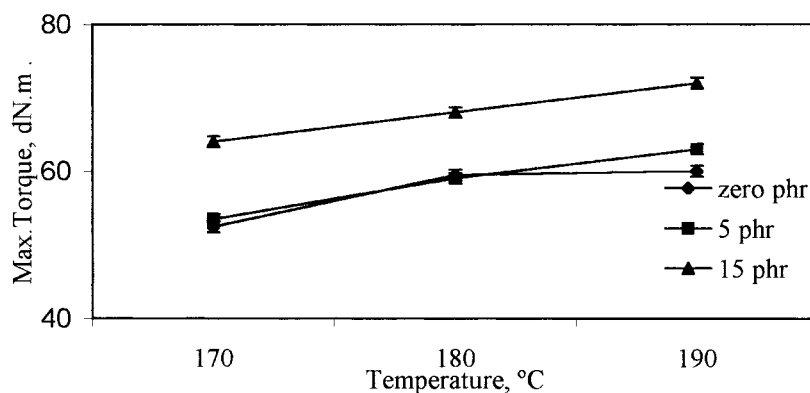
with the complete factorial experiment design shown in Table I.

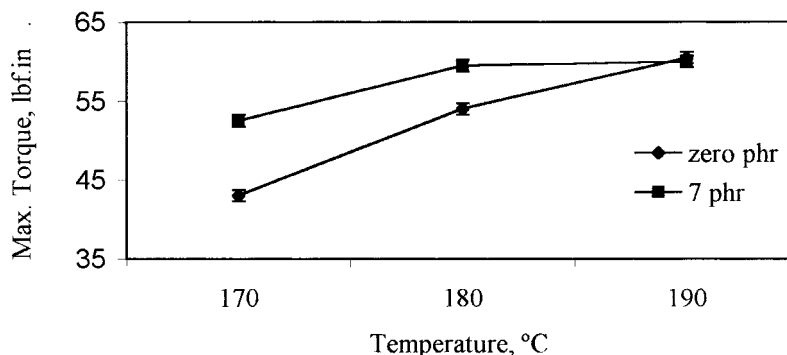
The mixes were prepared at 50°C in a Haake torque rheometer (model Rheocord RD 9000, Karlsruhe, Germany), coupled to a mixing Rheomix 600 camera and cam rotors. The rotor speed was set at 20 rpm, and the total mixture time was 10 min. Rheometric data were obtained from a Monsanto oscillatory disk rheometer (model 100S, Akron, OH), which operated with a 3° arc and at temperatures of 170, 180, and 190°C.

## RESULTS AND DISCUSSION

Figure 1 shows that the maximum torque increased as resin and polychloroprene also increased for any of the three vulcanization temperatures used.

The increase in the maximum torque as a function of the increase in the resin amount was expected because this compound acts as a reticulation agent. The polychloroprene, the activator,<sup>8</sup> also improved the vulcanization efficiency and, thus, contributed to the torque.<sup>8</sup> To confirm this fact, we prepared three additional mixtures following the formulation of Table II, in which only

**Figure 2** Influence of polychloroprene amount on maximum torque.



**Figure 3** Influence of zinc oxide amount on maximum torque.

the quantity of polychloroprene was varied and the other ingredients were kept constant.

The maximum torque data obtained for these formulations is shown in Figure 2. Figure 2 shows that increasing quantities of polychloroprene do influenced the maximum torque.

Unlike polychloroprene, zinc oxide, according to Figure 1, had no effect on maximum torque, although it was a vulcanization activator as well. For a better understanding of this behavior, the formulations of Table III were prepared, and the results obtained are presented in Figure 3. Higher values of maximum torque were reached when zinc oxide was present, but this effect was more evident at lower temperatures. Probably at 190°C, the thermal energy was sufficiently high to promote the formation of the resin degradation products necessary for vulcanization,<sup>4</sup> and thus, the presence of the oxide was not noticed. Again, as shown in Figure 1, the increase in the amount of zinc oxide did not affect the maximum torque. However, Figure 3 shows that its presence increased the torque values. From these two observations, it could be deduced that the amounts of zinc oxide employed were in excess.

For the calculation of the rate constants ( $k$ s) of the vulcanization reaction, two methods were used.

Method A considers that the torque values from the oscillatory disk rheometer obtained during vulcanization are directly related to the density of formed crosslinks and that the reaction follows elementary first-order kinetics.<sup>6</sup> Thus,  $k$  can be calculated with eq. (1) for torque values at 25 and 45% vulcanization:

$$\ln \left[ \frac{\text{Maximum Torque} - \text{Minimum Torque}}{\text{Maximum Torque} - \text{Torque}(t)} \right] = kt \quad (1)$$

where Torque ( $t$ ) is the value of torque at 25 and 45% vulcanization.

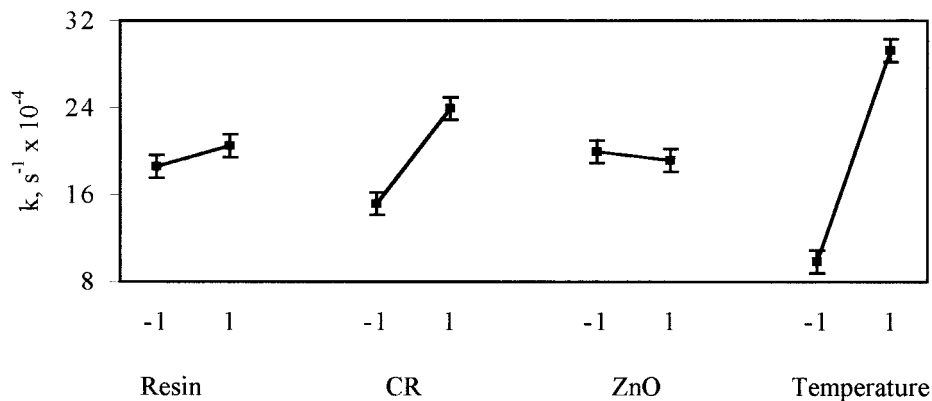
The  $k$  values calculated according to eq. (1) are presented in Table IV. These data were analyzed by analyses of variance, and information on the effect of each of the system variables and their interactions were obtained. These are shown in Figure 4(a,b). According to Figure 4, the variables influencing  $k$  were the temperature, polychloroprene, and the interaction between them.

As the vulcanization was carried out at 170, 180, and 190°C, the effect of the variables on  $k$  was investigated at isothermal conditions. The results are shown in Figure 5, which shows that polychloroprene was actually the most important variable and that only at 190°C was there any influence of the resin.

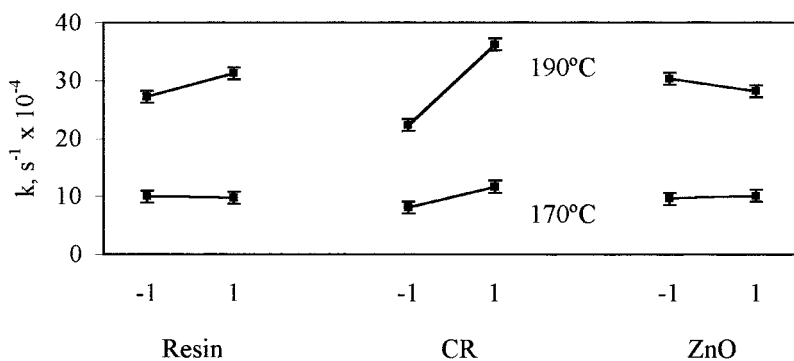
In Method B,  $n$  is determined from the conversion-versus-time curve for time values at or superior to that for which the cure rate is maximum.<sup>7</sup> The kinetic equation is given by

**Table IV** Method A:  $k$  Determination

Mix Designation	$k$ ( $s^{-1} \times 10^{-4}$ )		
	170°C	180°C	190°C
1	7.55	13.78	24.04
2	7.95	12.16	22.97
3	12.16	22.97	32.31
4-1r	8.99	16.32	28.72
4-2r	9.40	17.72	31.33
4-3r	9.40	18.14	31.33
5	11.28	20.68	39.76
6	8.74	14.77	22.97
7	8.06	13.37	19.15
8	11.49	21.39	38.29
9	11.70	20.40	34.46



(a)



(b)

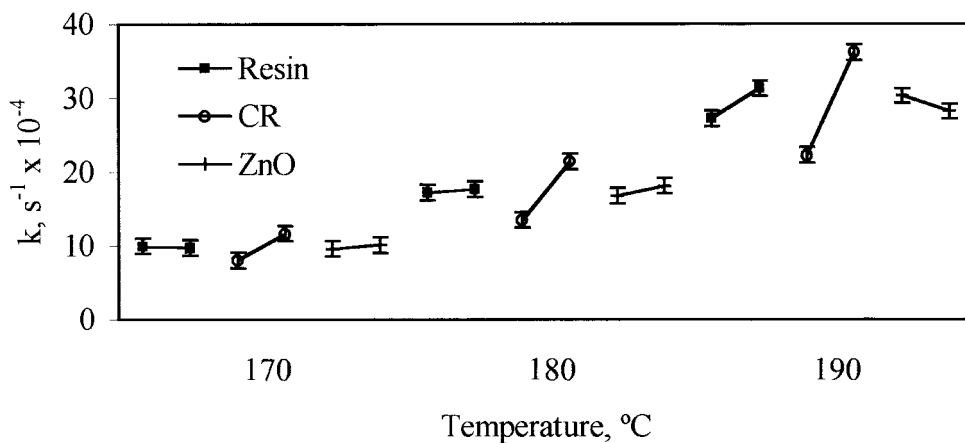
**Figure 4** Effects of resin, polychloroprene, and zinc oxide amounts and temperature (a) and interactions among them (b) on  $k$  as calculated by Method A.

$$\frac{dx}{dt} = k^n(1 - x)^n \quad (2)$$

If the reaction follows first-order kinetics,  $n = 1$  and the integrated form of the resulting equation is

where  $dx/dt$  is the conversion ratio,  $n$  is the reaction order, and  $t$  is the time.

$$\ln(1 - x) = -k(t - t_i) \quad (3)$$



**Figure 5** Effects of resin, polychloroprene, and zinc oxide amounts on  $k$  as calculated by Method A at different temperatures.

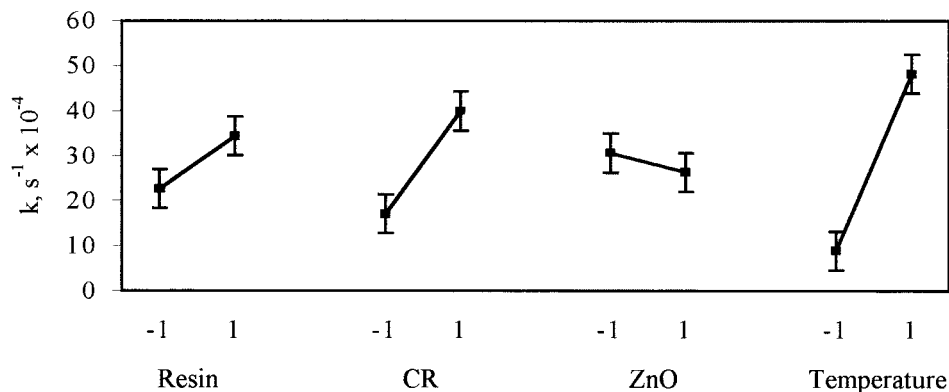
**Table V Method B:  $k$  Determination**

Mix Designation	170°C			180°C			190°C		
	$k$ ( $s^{-1} \times 10^{-4}$ )	$n$	Correction	$k$ ( $s^{-1} \times 10^{-4}$ )	$n$	Correction	$k$ ( $s^{-1} \times 10^{-4}$ )	$n$	Correction
1	6.16	0.60	0.9996	11.87	0.85	0.9998	31.99	1.35	0.9999
2	6.29	0.60	0.9993	11.10	1.00	0.9998	24.55	1.25	0.9999
3	10.68	0.85	0.9998	27.91	1.30	0.9998	42.54	1.55	0.9956
4-1r	7.51	0.70	0.9997	14.82	0.85	0.9999	56.65	1.60	0.9997
4-2r	8.50	0.75	0.9999	18.19	1.15	0.9995	59.84	1.75	0.9985
4-3r	9.13	0.80	0.9993	23.37	1.25	0.9998	51.44	1.50	0.9995
5	12.09	0.95	0.9999	26.19	1.25	0.9993	92.87	1.75	0.9996
6	7.09	0.70	0.9998	20.11	1.20	0.9959	34.47	1.45	0.9995
7	6.28	0.65	0.9996	11.64	0.95	0.9997	20.07	1.20	0.9975
8	10.66	0.85	0.9998	24.74	1.15	0.9999	79.42	1.75	0.9987
9	12.13	0.90	0.9997	28.79	1.35	0.9999	58.98	1.70	0.9988

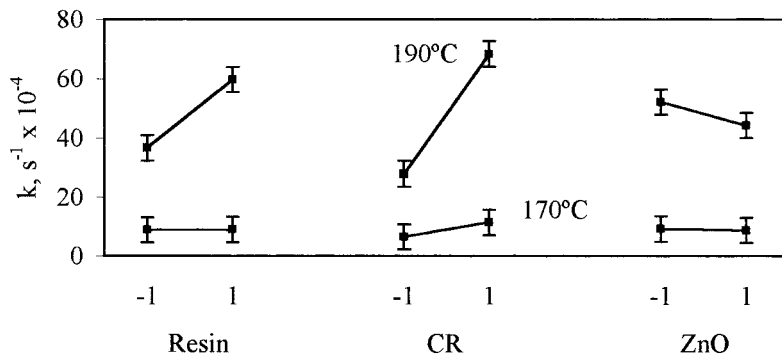
where  $t_i$  is the induction time.

Then, by the plot of  $\ln(1-x)$  versus  $t - t_i$ , a straight line of slope  $-k$  is obtained.

For  $n \neq 1$ , the reaction follows the order  $n > 1$  if the concavity of the curve  $1-x$  versus time is upward and  $n < 1$  if the concavity is downward.<sup>4</sup>

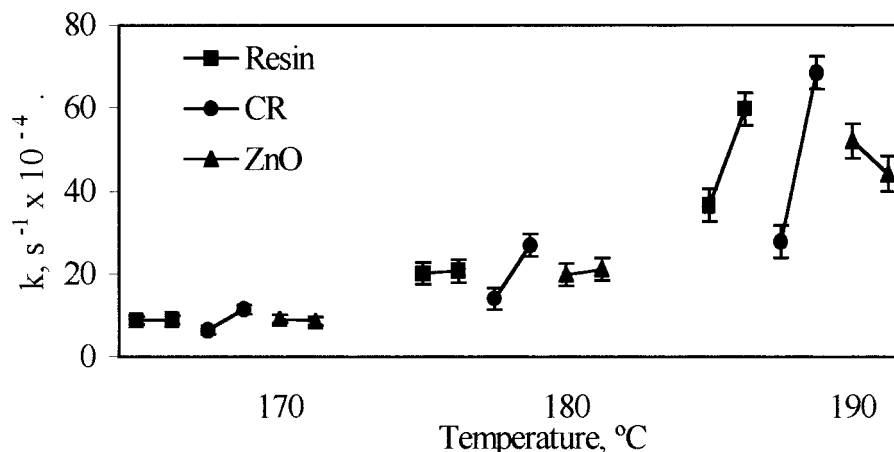


(a)



(b)

**Figure 6** Effects of resin, polychloroprene, and zinc oxide amounts and temperature (a) and interactions among them (b) on  $k$  as calculated by Method B.



**Figure 7** Effects of resin, polychloroprene, and zinc oxide amounts on  $k$  as calculated by Method B at different temperatures.

In these cases, integration of eq. (2) leads to eq. (4):

$$\frac{(1-x)^{(1-n)}}{(1-n)} = k^n(t-t_i) \quad (4)$$

The reaction order is obtained by attribution of values to  $n$  in eq. (4) until the data can be fitted into a straight line with a correlation factor higher than a preset value. In this work, a correlation factor greater than 0.999 was applied. The values of  $k$  and  $n$  calculated with eq. (4) are shown in Table V.

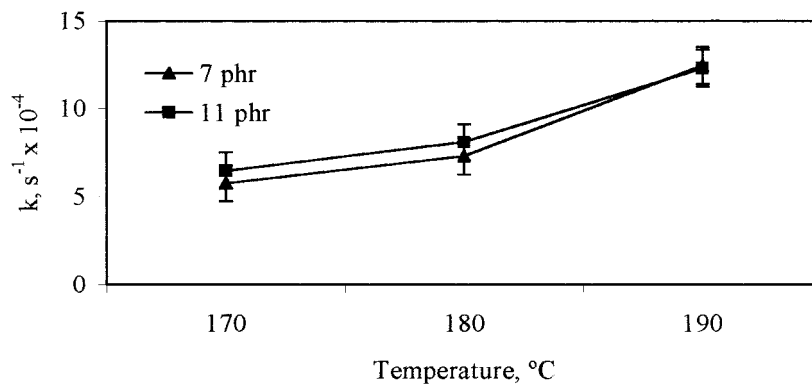
Again, analysis of variance was used in the analysis of these data, and a few conclusions were drawn. The parameters that significantly influenced  $k$  were temperature, polychloroprene, and the temperature–polychloroprene and temperature–resin interactions, as shown in Figure 6(a,b).

When each of the vulcanization temperatures is considered, it can be observed in Figure 7 that at 170 and 180°C, only polychloroprene influenced  $k$ . At 190°C, there were influences of polychloroprene and resin.

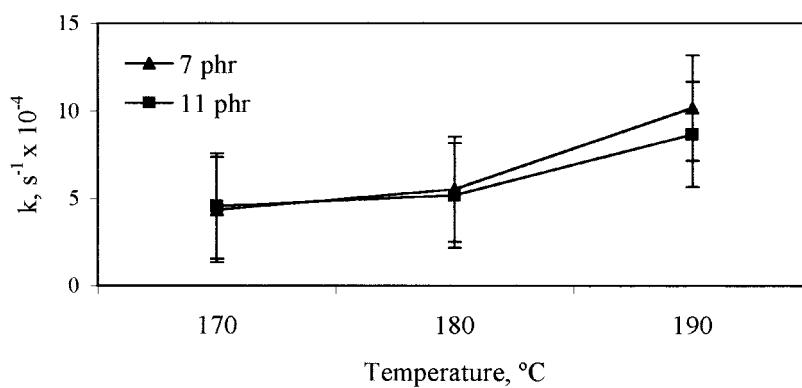
Comparison of the results obtained with the application of Methods A and B are summarized in Table VI. From the general analysis, a temperature–resin interaction was detected only with Method B. For this reason, additional experiments were carried out to verify the results of Table VI. Thus, two extra formulations were prepared with NBR and resin in the amounts of 7 and 11 phr, respectively, which were vulcanized at 170, 180, and 190°C. Figures 8 and 9 show that in the considered temperature range, no temperature–resin interaction could be detected because the two curves were practically superposed. These results suggest that Method A, in comparison to Method B, was more adequate to describe

**Table VI** Summarized Results Obtained from Methods A and B

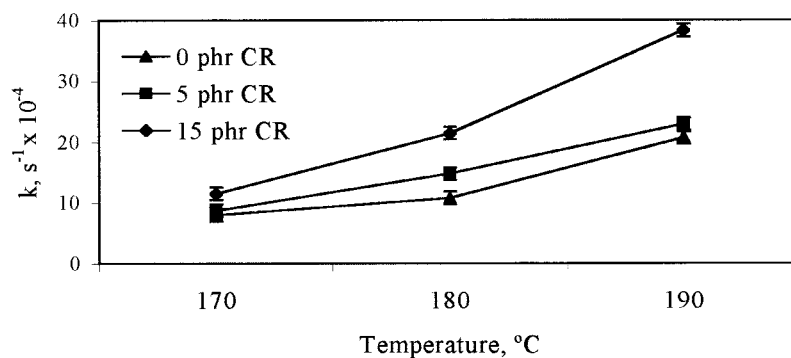
Analysis	Method	
	A	B
General	Temperature Polychloroprene Interaction: temperature and polychloroprene	Temperature Polychloroprene Interaction: temperature and polychloroprene Interaction: Temperature and resin
170°C	Polychloroprene	Polychloroprene
180°C	Polychloroprene	Polychloroprene
190°C	Polychloroprene and resin	Polychloroprene and resin



**Figure 8** Influence of resin amount on  $k$  as calculated by Method A at different temperatures.

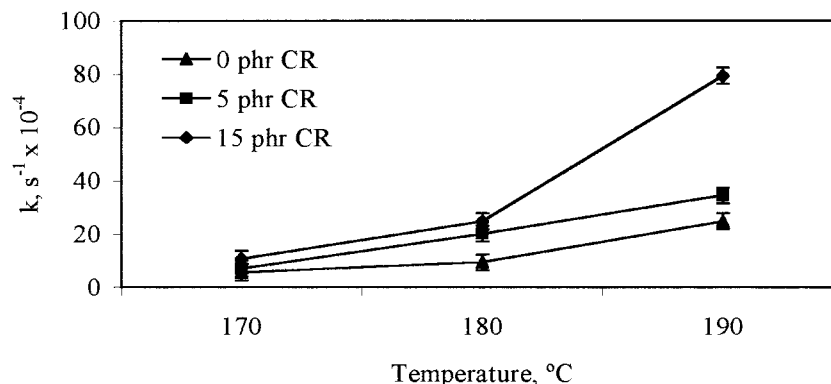


**Figure 9** Influence of resin amount on  $k$  as calculated by Method B at different temperatures.



**Figure 10** Influence of polychloroprene amount on  $k$  as calculated by Method A at different temperatures (11 phr of resin and 7 phr of ZnO).





**Figure 11** Influence of polychloroprene amount on  $k$  as calculated by Method B at different temperatures (11 phr of resin and 7 phr of ZnO).

the kinetic behavior of this system. However, from this analysis, it can also be observed that at 190°C, the increase in the amount of resin did not affect  $k$ , which contests the results previously obtained and presented in Table VI. Because of this, the influence of the other variables, namely, polychloroprene and the temperature–polychloroprene interaction, was investigated in more detail. Figures 10 and 11 show that the increase in temperature and polychloroprene led to an increase in  $k$ , and from the divergent profile of the curves, it could be said that a temperature–polychloroprene interaction did exist.

## CONCLUSIONS

For the vulcanization of NBR with system containing phenolic resin, zinc oxide, and polychloroprene at 170, 180, and 190°C, the methods used to describe the vulcanization kinetics were not found to be very accurate when the influence of the variables and their interactions on  $k$  were not very significant.

When Methods A and B were compared, Method A proved apparently more adequate because Method B showed the existence of a temperature–resin interaction that was not experimentally observed.

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