

Resin-Vulcanized NBR: Suitability of Rheometric Parameters for the Calculation of Cure Kinetic Constants—Part II

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ABSTRACT: In a previous work, two methods using rheometric parameters to calculate the kinetic constant were compared, and the results showed that the higher significant variables could be accurately determined in opposition to the lower significant ones. Thus, a modification is suggested in this article, by limiting the conversion of the cure reaction to 80% to minimize the effects due to the

deceleration curing. This allowed a precise determination of which variables have an effective influence on the cure kinetic constant. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 506–509, 2004

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INTRODUCTION

Diene rubbers can be crosslinked in the presence of certain vulcanizing agents to create a network composed of links of different natures and densities. Some examples of curing systems are: sulfur, sulfur donors, accelerated sulfur, peroxides, metal oxides, phenolic curatives, benzoquinone derivatives, and bismaleimides. The role of these crosslinks is to permit the material to stand stress and return to its original shape since such crosslinks are not permanently ruptured or rearranged.^{1,2}

Additionally, physical properties and stability upon aging of rubber materials are also affected by both the type and degree of crosslinks, which are related to the cure system and process conditions. As cure rate is closely related to manufacturing productivity, it is desirable to set up optimum conditions of cure as a compromise between cost and quality.^{2,3}

In the investigation on the mechanism and structure of the cured rubber, several techniques have been developed that include chemical analysis, solid-state

¹³C NMR, equilibrium swelling, kinetic constants determination, etc.⁴

In a previous article, an investigation on the cure kinetics of nitrile rubber in the presence of the phenolic resin SP-1045, polychloroprene, and zinc oxide was carried out using two different methods to determine the cure kinetic constant (k). To understand the curing process and establish the influence of each mixture component has on the cure kinetic constant, a Complete Three-Factor Factorial Design was used to establish the mixes composition.⁵ This technique allowed to detect those components that have greater influence on the properties and whether there is interaction between them.⁶

Regarding our previous investigation on kinetic parameters, the first method used to calculate the cure kinetic constant assumes a first-order kinetics, is based on rheometric parameters and considers that the torque evolution can be directly related to the formation of crosslinks.^{3,5} The second method allows an accurate determination of the reaction order (n), and considers that the reaction cure kinetics model is based on the decreasing rate of reaction. By using the second method, an improved determination of the cure kinetic constant was possible because reaction times, either at or after the occurrence of the maximum cure rate (Cr_{max}), were used.^{5,7} This earlier investigation allowed the fol-

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TABLE I
Three-Factor Factorial Design (phr)

Mixture designation	F1	F2	F3	F4	F5	F6	F7	F8	F9
NBR NP2021	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

Central point: F4 was replicated three times to determine experimental errors.

lowing observation: the cure kinetic constant resulted by both methods, when used in complete factorial design analysis, produced an accurate determination of higher significant variables but failed in the determination of lower significant variables.⁵

Thus, the objective of the present article is to suggest a modification in the second method (designated as method B) by inserting a maximum limit of conversion at 80%. This procedure to calculate k and n can then minimize the effect due to the deceleration curing. This modified method will be designated here as method C.

EXPERIMENTAL

The influence of the amount of the variables—resin, polychloroprene W, and zinc oxide—on the cure ki-

TABLE II
Formulation for Additional Mixtures (phr)

Mix designation	F10	F11
NBR NP2021	100	100
Phenolic resin SP1045	7	11
Polychloroprene W	0	0
Zinc oxide	0	0

netic constant was investigated using Three-Factor Factorial Design as shown in Table I.

To confirm the results of Three-Factor Factorial Design analysis, additional mixtures were prepared, following the formulation of Table II.

The mixtures were prepared at 50°C in a Haake Torque Rheometer, Rheocord RD 9000, coupled to a mixing Rheomix 600 chamber 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, 100S model, operating with a 3° arc, at temperatures of 170, 180, and 190°C.

RESULTS AND DISCUSSION

Table III shows k values from Methods B and C. Figure 1 shows a comparison between both methods for obtaining k for the F4 mixture. This analysis was done for the central point (F4) because it measures the experimental error. From Figure 1, both methods B and C produce the same average k at 170 and 180°C. However, different values of k are obtained at 190°C. Regarding variability of k , it was found that Method B produces larger variation than Method C.

Figures 2–4 show the Three-Factor Factorial Design analysis. They indicate which variables and which interactions have influence on k . The results are:

TABLE III
Cure Kinetic Constants (k , s⁻¹ 10⁻⁴), as Determined by Methods B and C

Mixture designation	Temperature (°C)					
	170		180		190	
	Method B	Method C	Method B	Method C	Method B	Method C
F1	6.2	6.9	11.9	14.0	32.0	26.7
F2	6.3	8.0	11.1	13.7	24.6	30.8
F3	10.7	10.9	27.9	22.9	42.5	44.6
F4 (1st)	7.5	8.6	19.8	18.0	56.7	38.0
F4 (2nd)	8.5	8.1	18.2	18.5	59.8	34.7
F4 (3th)	9.1	8.9	23.4	18.4	51.4	33.1
F5	12.1	11.6	26.2	28.9	92.9	51.3
F6	7.1	8.1	20.1	16.0	34.5	33.0
F7	6.3	7.0	11.6	10.9	20.1	30.1
F8	10.7	11.4	24.7	26.6	79.4	54.4
F9	12.1	11.9	28.8	29.9	59.0	46.1

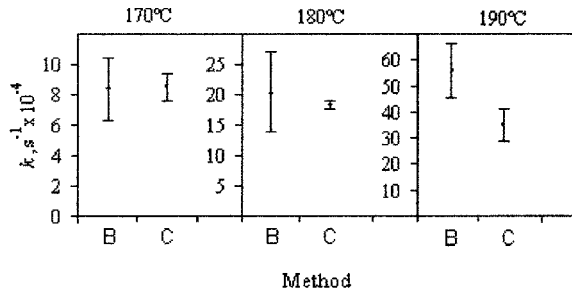


Figure 1 Cure kinetic constants (k) at F4 mixture at 170, 180, and 190°C as determined by Methods B and C.

1. Temperature: the higher the temperature, the higher k . This result was found to be true by using either Method B or Method C, and depends on the parameter being investigated, as seen in Figures 2–4;

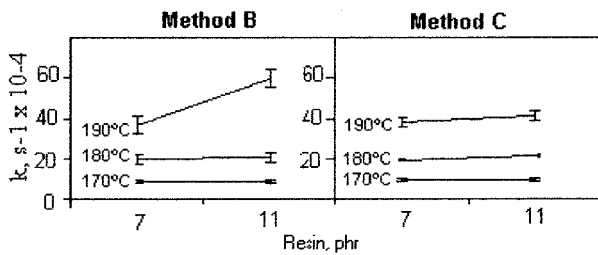


Figure 2 Influence of the amount of resin on the cure kinetic constant, at different temperatures.

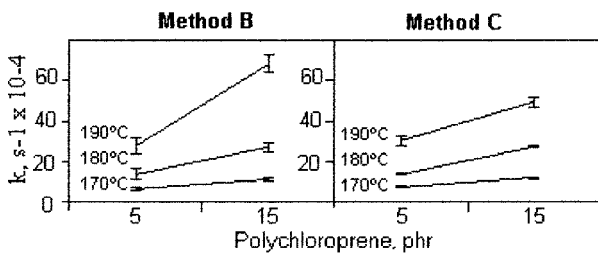


Figure 3 Influence of the amount of polychloroprene on the cure kinetic constant, at different temperatures.

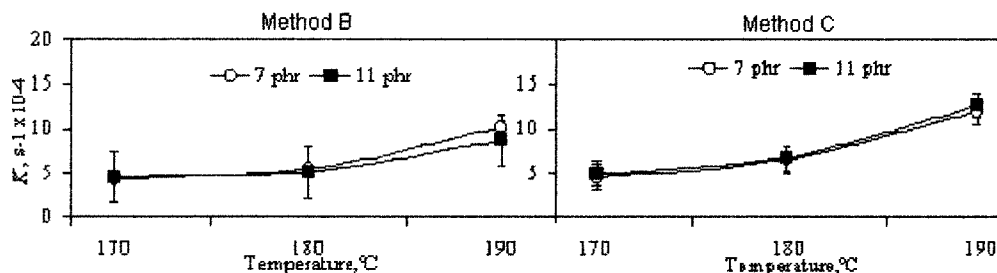


Figure 5 Application of Methods B and C in the determination of cure kinetic constant in the additional experiments.

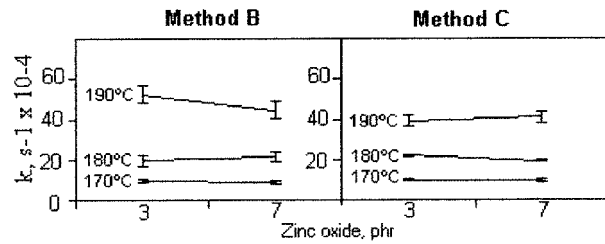


Figure 4 Influence of the amount of zinc oxide on cure kinetic constant, at different temperatures.

2. Resin: considering Method B, the resin variable affects k at 190°C. Because this effect is found only at a specific temperature, 190°C, this may be regarded as a strong indication that an interaction between temperature and resin is taking place. As for Method C, the resin does not have any influence on k , at any temperature (Fig. 2);
3. Polychloroprene W: as the amount of Polychloroprene W is increased, k also increases. From Figure 3, it can be observed that the lines are not parallel, therefore indicating the existence of an interaction temperature vs Polychloroprene W. Similar results were found either through Method B or Method C;
4. Zinc oxide: as seen in Figure 4, zinc oxide does not have any influence on k .

The results above show that the methodologies used for k determination produced different conclusions. On account of the fact that additional experiments were carried out to verify the existence of resin influence and resin vs temperature interaction. From these experiments it was possible to identify which method produces the most accurate results from the Three-Factor Factorial Design analysis. Figure 5 shows the results of the additional experiments using Method B and Method C. It was observed that the curves were exactly the same. This result proved the absence of resin influence and of temper-

ature *versus* resin interaction. Thus, Method C can be considered to produce more accurate k than Method B.

CONCLUSION

Rheometric parameters can be used to accurately calculate the cure kinetic constant in NBR/phenolic resin systems as well as the variables having effective influence on the cure process. However, care should be taken as to dismiss the stages where the deceleration process predominates, which in the present case occurs around 80% conversion.

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