

Phenomenological effect of temperature on the order n of the reaction of the curing kinetics in an EPDM polymer

Efecto fenomenológico de la temperatura en el orden n de reacción de la cinética de curado en un polímero EPDM

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Abstract

The precise control of curing reaction parameters allows a better crosslinking polymer. Modeling and optimization of this process require a correct kinetic of curing model. The kinetics of the crosslinking reaction is studied for the ethylene propylene diene monomer (EPDM) synthetic elastomer by mobile die rheometer (MDR). The kinetic parameters of reaction were calculated from Kamal-Ryan, Sestak-Berggren, and the Isayev-Deng methods at different temperatures. An Arrhenius-type function for the order of reaction n is introduced to improve the adjusting. A comparative study of Sestak-Berggren and Isayev-Deng models was made to validate and determine which model best describes the behavior of vulcanization. The best approximation was obtained with the model Isayev-Deng. Finally, taking the model with the best fit, a graphical and analytical description of the cure kinetics was developed. The order of reaction is predicted to better establishment of processing time. It was noted that for EPDM at higher temperatures, the increase of the rate of reaction occurs in short period of time, which could cause premature curing if the supply system is inadequate.

Resumen

El control preciso de los parámetros de reacción de curado permite un mejor reticulado del polímero. El modelado y la optimización de este proceso requiere una adecuada descripción de la cinética de curado. En el presente trabajo se estudia la cinética de la reacción de curado para el elastomero sintético monómero propileno-dieno (EPDM) por medio de un reómetro de cámara móvil (MDR). Los parámetros cinéticos de la reacción se calcularon a partir de los métodos de Kamal-Ryan, Sestak-Berggren e Isayev-Deng a diferentes temperaturas. Para mejorar el ajuste se introdujo una función tipo Arrhenius para el orden de reacción n . Se hizo un estudio comparativo entre los modelos de Sestak-Berggren e Isayev-Deng para validar y determinar cuál modelo describe mejor el comportamiento de vulcanizado del polímero ensayado. Se predice el orden de reacción para una mejor descripción del tiempo de procesamiento. Se observó que, para el EPDM a las temperaturas más altas ensayadas, el incremento de la fracción de curado ocurre en periodos de tiempo cortos, lo que podría ocasionar curado prematuro si el sistema de inyección es inadecuado.

Keywords:

Curing Kinetics, Polymer Rheology, Kinetic Parameters, Phenomenological Models

Introduction

Vulcanization is one of the essential processes in the rubber industry, involves an enormous amount of energy to convert a material without form into an elastic finished product [1]. Elastomers consist of independent high molecular weight molecules when they are in the monomer or non-vulcanized states. The cross-links between these molecules show nonlinear viscoelastic behavior allowing the flow and processing by injection. During the injection, a chemical reaction of vulcanization (or curing) takes place. The vulcanizing process presents three stages: induction, curing, and post-curing. In the induction stage, reactions of the accelerators take place, but crosslinks do not occur in the polymer matrix. It has great practical importance since it determines the time when the vulcanization should start and then avoid

Palabras clave:

Cinética de curado, Reología de polímeros, Parámetros cinéticos, Modelos fenomenológicos

premature vulcanization. The curing stage begins with the formation of crosslinks at a curing rate that depends on the temperature and the composition of the rubber. Up to approximately 90% of vulcanization take place, and it is measured with the proportional increase in elasticity. If curing is continued post-curing occurs (final stage); this can cause a hardening or soften of the product which are usually undesirable effects [2].

The curing rate increases with temperature and therefore a finite time for filling the mold is needed [3, 4]. The final properties of the formed polymer depend largely on reactions that occur during vulcanization, so it is necessary to study the curing kinetics of the compound to determine the time and degree of curing [5, 6].

The rubber curing is an exothermic process of high complexity in which several reactions coincide [7, 8]. The vulcanization mechanism and the rate of reaction depend on the structure of the rubber, the concentration of activators and accelerators as well as the diffusivity, and thermodynamics of each reaction [9].

The reaction rate means how quickly the concentration of a reactant or a product changes over time. Several mathematical models used to describe the semi-solid chemical kinetics present inconsistencies among them [10]. This may be due to the difficulty in distinguishing between a reaction regimen controlled by the mass, that is thermo-mechanical, or a reaction regimen controlled by diffusion [11].

On the other hand, the kinetics associated with a chemical process is not correctly characterized by the so-called kinetic triplet. That is activation energy, pre-exponential factor and kinetic model which are represented either by a differential function $f(\alpha)$ or by an integral function $g(\alpha)$. Where α is the cure rate. Knowing the $f(\alpha)$ or $g(\alpha)$ functions, the characterization of the chemical process could be solved. In the majority of cases, these functions are unknown or are too complicated. In order to have a better description of the process a simplify models are necessary to describe the system behavior approximately. Such phenomenological or empirical models tend to ignore de chemical details of the system [11].

It is common to rename the molar concentration of chemical reactions for the so-called degree of cure, conversion or cure rate α , which is normalized by any other physical time-dependent property that represents the system. In this paper, the viscosity of Mooney (rheometer torque) was used since it can be normalized as the rate of conversion α [12].

Due to the complexity of the cure kinetics, models of order n are used to describe the reaction paths since they are sequential and parallel. These models allow a better approximation to describe the behavior of the vulcanization rate in terms of an autocatalytic reaction. The most widespread and best fit include Kamal-Ryan, Sestak-Berggren, and Isayev-Deng models, from which the curing rate can be modeled by determining the kinetic parameters involved such as the order of reaction and the rate constants. Most of authors considered the order of reaction as the average of the values obtained at different temperatures [13, 14]. Recent publications present variety of polynomial models to describe order of reaction as a temperature variation dependent [15, 16].

This research consisted in adjusting the parameters of the Kamal-Ryan expression in the curing kinetics of the EPDM rubber by proposing an Arrhenius-type function for the order of reaction n (temperature variation dependent). Then a comparative study of the models of Sestak-Berggren and Isayev-Deng, for describing the cure kinetics using the proposed expression, was carried out in order to ascer-

tain which of these models better describes the behavior of EPDM polymer. By taking the model with the best fit, a graphical and analytical description of cure kinetics was developed in a three-dimensional field $\alpha(T, t)$.

Materials and Methods

Materials

Synthetic elastomer EPDM (ethylene propylene diene monomer M-class) was used, according to the standard ASTM D1418 – 17. Standard Practice for Rubber and Rubber Lattices-Nomenclature) with Sulphur as a vulcanizing agent and integrated lubricant (black carbon). Tested under standards GMW 14744 type B with reference to standards SAE J200, ASTM D2000, GMW 3232 compatible with standard FM-VSS302, GMW 3059 for substances restricted and reportable. ISO 48 (55 +/- 5) hardness IRHD, resistance to temperature 24 h (90 +/-3) °C with no changes in function and appearance. The test specimen was prepared at 20°C temperature with 5 cm³ (25 mm × 25 mm × 8 mm) sample volume.

Method

Trials were conducted in an Alpha Technologies Moving Die Rheometer (MDR 2000), property of Elastomer Solutions México S. de R. L. de C. V, according to the standard ASTM D2084 – 01. This type of cure meter measures the torque produced by an angular strain of constant amplitude in a cavity that is completely closed and sealed (see Figure 1a). The die cavity is formed by two dies (Figure 1b). In the measuring position, the two dies are fixed a specified distance apart so that the cavity is closed and sealed. A pneumatic cylinder closes the dies and holds them closed during the test with a force of not less than 8.0 kN (1820 lbf).

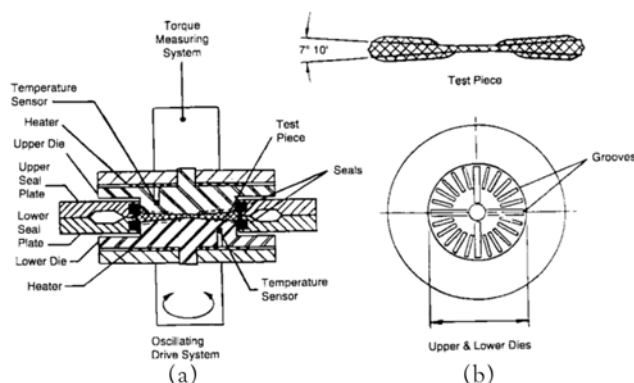


Figure 1. Sealer torsion shear rotorless curemeter, ASTM D 5289 – 12: (a) Measuring principle, (b) Reaction dies.

The die oscillating system consists of a rigid eccentric drive, which imparts a torsional oscillating movement to one of the dies, in the plane of the cavity. This action produces a sinusoidal alternating torsional strain in the test piece and a sinusoidal shear force or torque, which depends on the stiffness (shear modulus) of the rubber compound. The ampli-

tude of the oscillating torque is continuously recorded as a function of time and torque against time graphs are obtained (Figure 2).

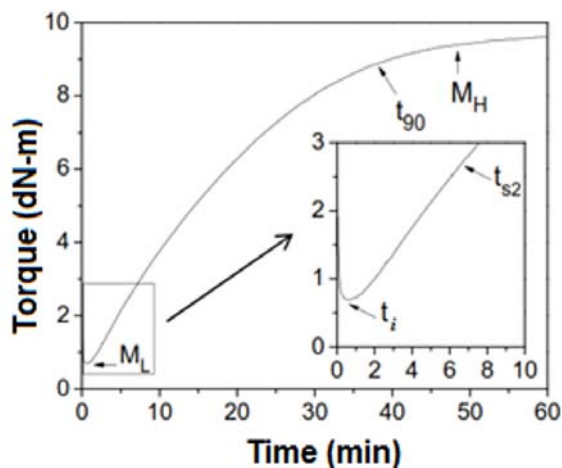


Figure 2. Standard graph time vs. torque, where M_L and M_H , represent the minimum and maximum torques; t_i is the induction time, t_{s2} is the time to incipient cure (scorch time), and t_{90} is the time to reach 90% of final crosslinking.

The trial was conducted with amplitude of oscillation from 0 to 5 degrees and a frequency of 1.66 Hz, according to the standard ISO 6502-1999 and ASTM D5289 - 12(Standard Test Method for rubber property-vulcanization using oscillating disk cure meter) with isothermal permanence of samples at different temperatures ranges, 155 to 205°C with increments of 10°C each.

In order to convert the rheometry test results into time variations of the state of cure, the following Equation was used.

$$\alpha = \frac{(M_t - M_L)}{(M_H - M_L)} \tag{1}$$

where α is the cure rate, M_t , M_L , and M_H is the instant, minimum and maximum torques, during the reaction respectively.

Models for describing the cure kinetics

Generally, the cure kinetics is expressed with the following differential equation

$$\frac{d\alpha}{dt_r} = [K(T)]f(\alpha) \tag{2}$$

Where $K(T)$ is the kinetic constant and $f(\alpha)$ is a function of the cure degree; t_r is the reaction time, that corresponds to the total process time t minus induction time t_i .

$$t_r = t - t_i \tag{3}$$

Claxton-Liska isothermal model defines the induction time t_i with an Arrhenius-type temperature dependence equation [17, 18]:

$$t_i = t_0 e^{T_0/T} \tag{4}$$

Kamal-Ryan model [19] was initially developed to describe the gradual reaction mechanism in rubber materials using two parameters for the order of reaction (m , p) and two rate constants (k_1 , k_2) as shown in equation (5). In this model, the total order of reaction n is considered as $(m+p)$.

$$\frac{d\alpha}{dt_r} = (k_1 + k_2 \alpha^m)(1 - \alpha)^p \tag{5}$$

with $(0 \leq m \leq 1, p \geq 1)$ [2], while Sestak-Berggren model presents just one kinetic constant

$$[K(T)] = k(T) \tag{6}$$

and the degree of curing function as the following expression

$$f(\alpha) = \alpha^m (1 - \alpha)^p \tag{7}$$

the reaction rate can be written as

$$\frac{d\alpha}{dt_r} = k(T) \alpha^m (1 - \alpha)^p \tag{8}$$

k is the temperature-dependent rate constant, α is experimentally calculated using equation 1, k follows the Arrhenius law:

$$k(T) = k_0 e^{\left(\frac{-E}{RT}\right)} \tag{9}$$

where k_0 is the pre-exponential factor (temperature independent), E is the activation energy, R is the universal gas constant and T is the temperature.

From equation (2) and (6), time curing is expressed as a function of α as:

$$\int_0^{t_r} k(T) dt = \int_0^\alpha \frac{1}{\alpha^m (1 - \alpha)^p} d\alpha \tag{10}$$

Solving the last equation results in

$$t_r = \frac{\alpha^{1-m}}{k(T)(1-m)} F(1-m, p; 2-m; \alpha) \tag{11}$$

where F is a hypergeometric function which can be defined as follows:

$$F(1-m, p; 2-m; \alpha) = 1 + \frac{(1-m)p}{1!(2-m)}\alpha + \frac{(1-m)(2-m)p(p+1)}{2!(2-m)(3-m)}\alpha^2 + \frac{(1-m)(2-m)(3-m)p(p+1)(p+2)}{3!(2-m)(3-m)(4-m)}\alpha^3 + \dots \quad (12)$$

Alternatively, equation (10) can be expanded using Taylor series before being integrated to obtain the same result.

On the other hand, the empirical model proposed by Isayev - Deng to determine the parameters of the cure kinetics [7, 20-22] is expressed by the following equations:

$$K(T) = k(T)^{\frac{1}{n}} \quad (13)$$

$$f(\alpha) = n\alpha^{n-1/n}(1-\alpha)^{n+1/n} \quad (14)$$

Substituting equations (13) and equation (14) in equation (2), we can obtain the following expression

$$\frac{d\alpha}{dt_r} = nk^{1/n}\alpha^{(n-1)/n}(1-\alpha)^{(n+1)/n} \quad (15)$$

Considering the empirical model proposed by Kamal-Sourour [23]:

$$\alpha = \frac{kt_r^n}{1+kt_r^n} \quad (16)$$

and substituting equations (16) in equation (15), the reduced model is obtained

$$\frac{d\alpha}{dt_r} = \frac{nk t_r^{n-1}}{(1+kt_r^n)^2} \quad (17)$$

where $n \geq 1$.

Equation (16) describes a reaction that slows down quickly as conversion progresses, such that $\lim_{(t \rightarrow \infty)} \alpha = 1$ due to the depletion of reagents so $0 < \alpha < 1$.

Expressing the curing time as a function of α , from equation (16) results:

$$t_r = \left[\frac{\alpha}{k(1-\alpha)} \right]^{\frac{1}{n}} \quad (18)$$

Using logarithms we obtain:

$$\ln(t_r) = \frac{1}{n} \text{Ln} \left[\frac{\alpha}{1-\alpha} \right] + \frac{1}{n} \ln \left[\frac{1}{k} \right] \quad (19)$$

From expression (19), plotting $\ln(t_r)$ vs $\ln[\alpha/(1-\alpha)]$, for any given test temperature, results in parallel lines with slope $1/n$ [22].

On the other hand, to obtain the reaction rate using the results obtained with the equation (1), the method of finite differences is applied as shown in equation (20):

$$\frac{d\alpha}{dt_r} = \frac{\alpha_j - \alpha_{j-1}}{\Delta t_r} \quad (20)$$

The literature cites a variety of differential models to describe the curing kinetics through a phenomenological approach.

In this work, the rheometric characterization of EPDM polymer is experimentally obtained, whereas the curing rate adjustment is made using the empirical models of Sestake-Berggen (with parameters $[k, m, p]$) and Isayev-Deng (with parameters $[k, n]$) in order to ascertain which model best describes the behavior of the polymer.

Results and Discussion

The curing kinetics of EPDM polymer obtained by non-linear adjustments from six different isothermal tests carried out in the MDR 2000 appliance. Kinetic parameters from non-linear fits are tested with the Kamal-Sourour adjustment. The analysis of variation of each parameter as a function of temperature was developed. Kinetic models of Sestake-Berggen (k, m, p) and Isayev-Deng (k, n) is used to obtain the adjusted-parameters set from each model.

Rheological tests

Figure 3 shows the graphs obtained from tests carried out at various temperatures in the MDR 2000 instrument. This shows a non-reversible behavior because the torque remains constant after reaching the maximum value. Results also shown that induction times became shorter as the test temperature was increased since it is a characteristic behavior in the vulcanization of sulfur-containing polymers [24].

Table 1 shows results obtained from a test carried out in the Alpha Technologies MDR 2000 (Moving Die Rheometer) for each of the parameters. Also, induction time (when minimum torque occurs) is included.

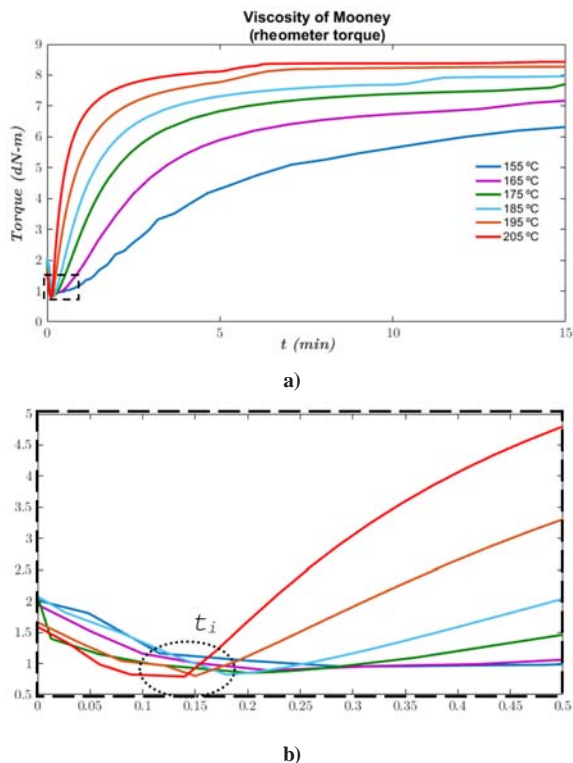


Figure 3. (a) Isothermal rheometry tests; (b) Induction times

Table 1, EPDM cure-characteristics obtained at different temperatures

T (°C)	ML dN-m	MH dN-m	t_i min	ts_2 min	t_{90} min
155	1.00	6.38	0.29	1.94	12.10
165	0.95	6.52	0.22	1.21	10.98
175	0.94	7.58	0.20	0.90	7.68
185	0.93	7.61	0.18	0.56	4.83
195	0.89	7.82	0.15	0.42	2.90
205	0.87	8.20	0.13	0.34	1.52

Figure 4 represents the degree of curing variation depending on reaction time, α is obtained from rheometric tests using equation (1). This graph shows the non-linear dependence of the degree of curing related to time and temperature. Allows us to obtain kinetic parameters from non-linear fits for each temperature being tested. Also, it was observed that during the first four minutes the polymer reaches approximately 60 to 90 percent of curing.

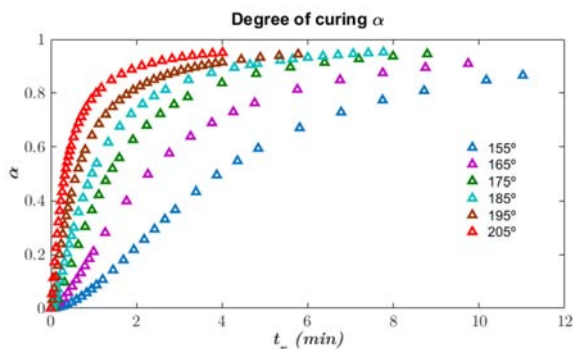


Figure 4, Standardized curing-degree graphics using equation (1)

The adjustment of these results with Kamal-Sourer expression (equation (16)) is represented in Figure 5.

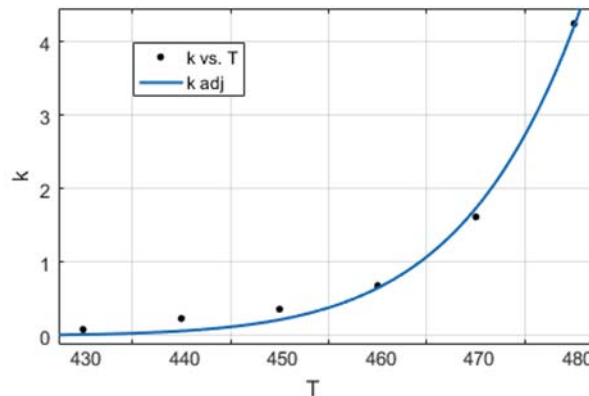


Figure 5, Curves adjustment using equation (16), based on the MDR tests

The appropriate fitting data results in a correlation R^2 of 0.99 and higher for all cases, see Table 2. The corresponding curing-kinetic parameters k , n and t_i are also reported in this table.

Table 2, Adjusted values of k , n and t_i at different temperatures using the expression (15)

T (°C)	k	n	t_i min	R^2
155	0.08	1.81	0.29	0.9992
165	0.27	1.59	0.22	0.9997
175	0.62	1.53	0.2	0.9993
185	1.05	1.43	0.18	0.9991
195	1.89	1.25	0.15	0.9995
205	3.71	1.19	0.14	0.9991

Variation of curing parameters with temperature

Once determined the isothermal behavior of the curing-degree with each tested temperatures, the analysis of variation of each parameter as a function of temperature was developed.

In Figure 6, it is observed that the constant of reaction-rate k increases rapidly as the temperature of the test increases. This behavior agrees with the Arrhenius model (equation (9)). In this case, the adjustment of $k(T)$ using Arrhenius correlates with $R^2 = 0.9951$.

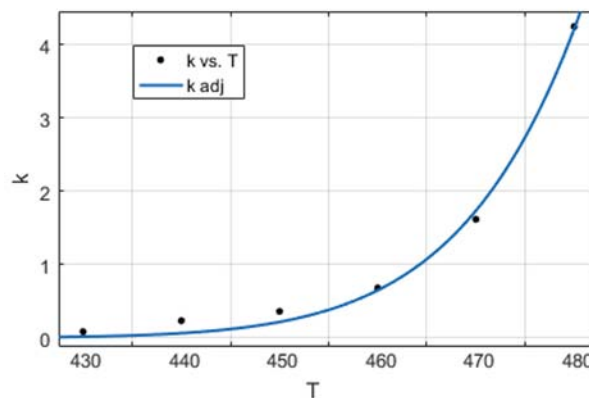


Figure 6, Adjustment of k using equation (9)

For induction-time $t_i(T)$, the adjustment was carried out with the Claxton-Liska model equation (4) obtaining $R^2 = 0.9864$. Figure 7 shows the corresponding graph.

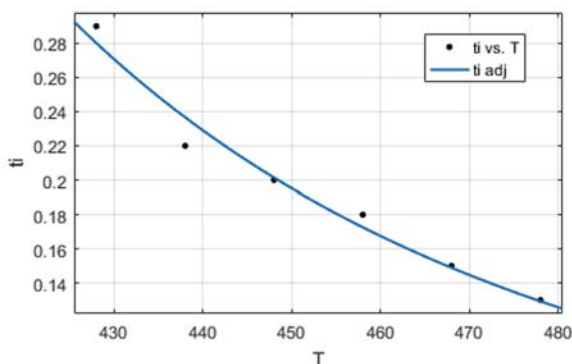


Figure 7, Fitting of t_i using Table 2 data and equation (4)

When experimental data using equation (19) it is expected to get straight parallel lines with the $1/n$ slope. However, it was found that the slopes are different for each temperature which suggests that, for the tested material, the order of reaction n also depends on temperature. Figure 8 also shows that the order of reaction n varies non-linearly as increases sampling isothermal-temperature.

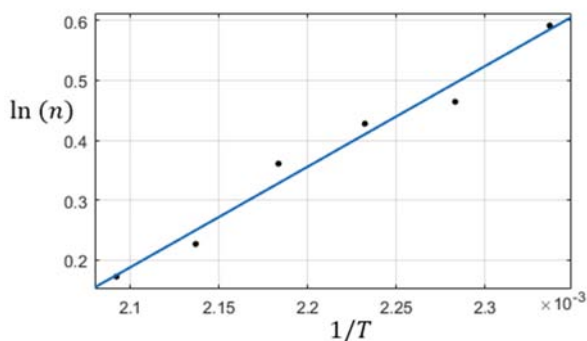


Figure 8, Behavior of $\ln(n)$ vs $1/T$

So, to describe how the order of reaction n varies, an Arrhenius-type expression was proposed based on the trend shown in Table 2 and Figure 8. The expression is indicated by equation (21).

$$n = n_0 e^{\left(\frac{T_0}{aT}\right)} \quad (21)$$

where a is the material's constant obtained by non-linear regression of experimental results, see Table 3. It can be inferred, from the curve shape of Figure 9, that $a > 1$.

In Figure 9, the fitted experimental results using the proposed expression are plotted. The reliability factor is high enough $R^2 = 0.9896$, that is an error of just 1.04%.

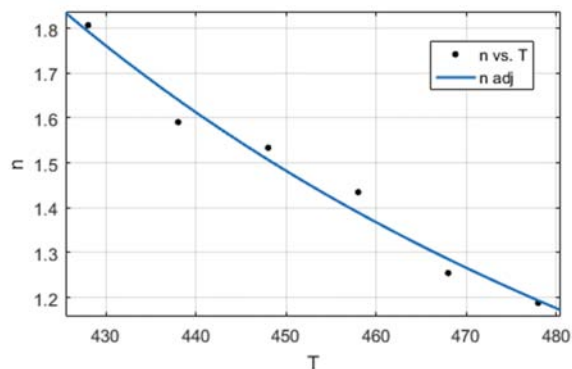


Figure 9, Adjustment of n based on the Table 2 data and equation (21)

Table 3 lists the values of the constants used in the calculation of the parameters $k(T)$, $t_i(T)$ and $n(T)$ for the Kamal-Sourour model.

Table 3, Constants for calculation of Kamal-Sourour model

T_0 (K)	k_0 (min^{-1})	n_0	a	t_0 (min)	$\frac{E}{R}$ ($\frac{\text{mol}\cdot\text{K}}{\text{Kg}}$)
3,165	3.99e+08	3.6499e-2	2.16	1.43e-4	8,822

Comparison between Isayev-Deng and Sesták-Bergger models for the curing rate

In order to validate the proposed expression for the reaction order, first the variations of the parameters $k(T)$, $t_i(T)$ y $n(T)$ were substituted in the kinetic models of Sesták-Berggen (k , m , p), equation (8), and Isayev-Deng (k , n), equation (17). Table 4 shows the adjusted-parameters set from each model.

Table 4, Parameters obtained using non-linear adjustments of kinetic models

T ($^{\circ}\text{C}$)	Isayev-Deng		Sesták-Berggen			
	$k(T)$	$n(T)$	$k(T)$	m	p	n
155	0.0856	1.805	0.4771	0.4669	1.5747	2.04
165	0.2444	1.622	0.7454	0.4081	1.6676	2.07
175	0.5589	1.504	1.2463	0.4074	1.7111	2.11
185	1.0506	1.324	1.7394	0.3866	1.7831	2.16
195	1.9547	1.278	2.9667	0.4440	1.7974	2.24
205	3.6677	1.202	4.8921	0.3073	2.0055	2.31

Subsequently, the curing rate was calculated from the experimental results using the equation (20) to make the adjustment with each of the above models. This also allowed knowing which of two models best describes the curing kinetics of EPDM polymer.

The solution obtained with equation (17) and equation (8) against the equation (20) at all considered operating temperatures, are contrasted in Figure 10. Corresponding reliability factors are shown in Table 5.

In both cases, the reliability factor R^2 is high enough to consider that the expression proposed for the temperature-dependent order of reaction is entirely accurate for the tested material. On the other hand, although both models adequately describe the phenomenon, the best fit is obtained with the Isayev-Deng model.

Table 5. Correlation coefficients between equation (20) and equations (17) and (8)

$T(^{\circ}\text{C})$	Isayev-Deng R^2	Sesták-Berggen R^2
155	0.9998	0.9981
165	0.9998	0.9982
175	0.9998	0.9986
185	0.9998	0.9888
195	0.9998	0.9879
205	0.9998	0.9874

In the case of Sestake model, after the curing rate reaches its maximum and begins to decline, the gap between experimental results and this model increases slightly. This separation respect to the Isayev model is minimal (see graphs of Figure 10). Another notable advantage of Isayev-Deng kinetic model is that it uses only two parameters (k,n), as the Sesták-Berggen model requires three (k,m,p); this advantage could make more accessible programming the rate of curing.

In Figures 11 and 12 the curing-kinetics behavior as temperature increases is described using the expression with the best fit and fewer parameters. Note that, as temperature takes higher values, the maximum reaction rate takes place in less time and becomes higher (Figure 11); this occurs in the range of curing fraction α less than 0.25 (Figure 12).

The resulting values for the maximum curing rate obtained from the Isayev-Deng model are shown in Table 6. It is also shown the drastic reduction of α at peak curing rate. These results indicate that the vulcanized can be defective if the variables of time and temperature are not adequately controlled.

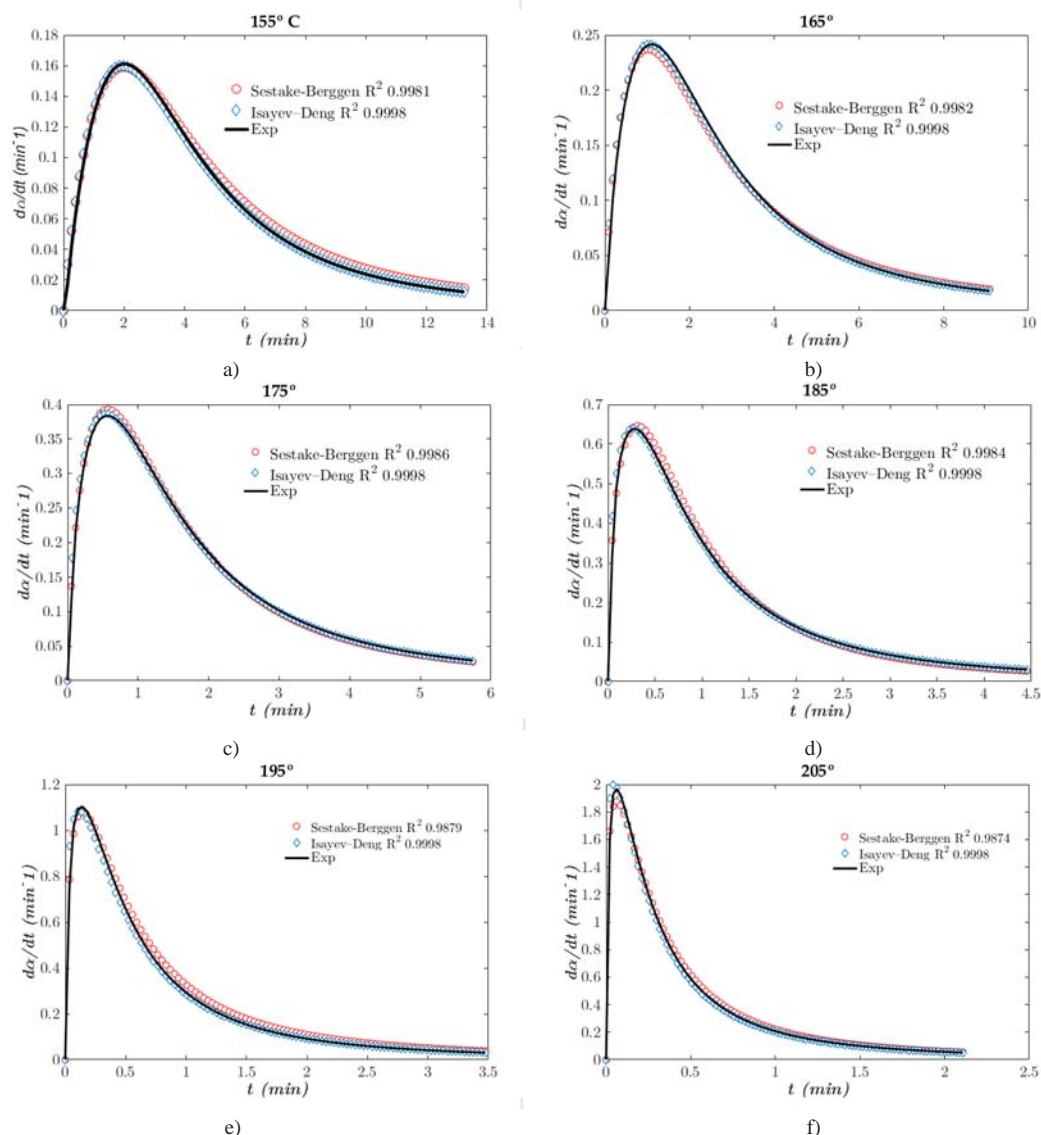


Figure 10. Plots of cure kinetics at different temperatures from standardized experimental data and the adjusted models of Sesták – Berggen and Isayev - Deng: a) EPDM to 155°, b) EPDM to 165°, c) EPDM to 175°, d) EPDM to 185°, e) EPDM to 195° and f) EPDM to 205°

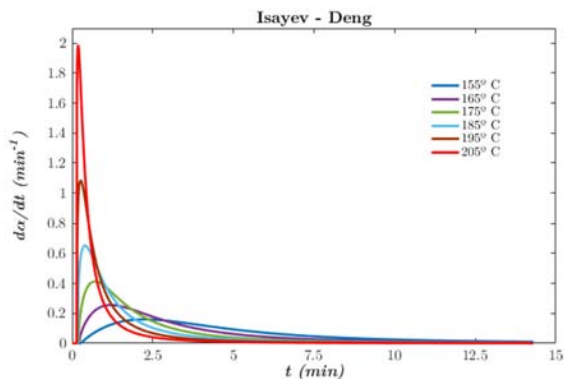


Figure 11. Reaction rate vs time

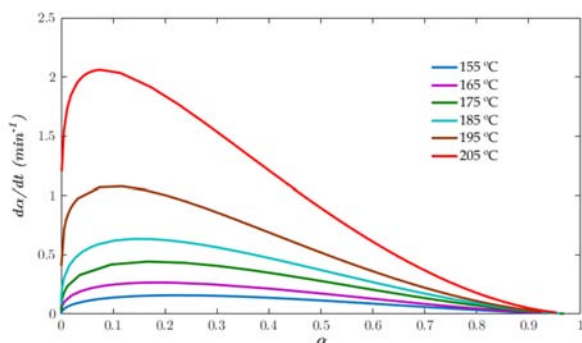


Figure 12, curing rate against the degree of curing

Table 6, Maximum curing rate $\frac{d\alpha}{dt}$ vs t and α to different temperatures

T (°C)	t_r (min)	α	$\frac{d\alpha}{dt}$ (min ⁻¹)
155	1.9696	0.2233	0.1591
165	0.9017	0.1857	0.2628
175	0.4967	0.1740	0.4438
185	0.2899	0.1515	0.6362
195	0.1061	0.1016	1.0792
205	0.0412	0.0791	2.0609

Figure 13 illustrates the three-dimensional behavior of the transformation ratio as a function of time and the reaction temperature $\alpha(T, t_r)$. This graph provides the theoretical set of values that describe in a wide range the fraction of curing for the EPDM material tested.

For future, the kinetic model could be used in the simulation of the EPDM injection process since the reaction rate is intimately related to the heat generation [25], see equation (22).

$$\dot{Q} = Q_x \frac{d\alpha}{dt} \tag{22}$$

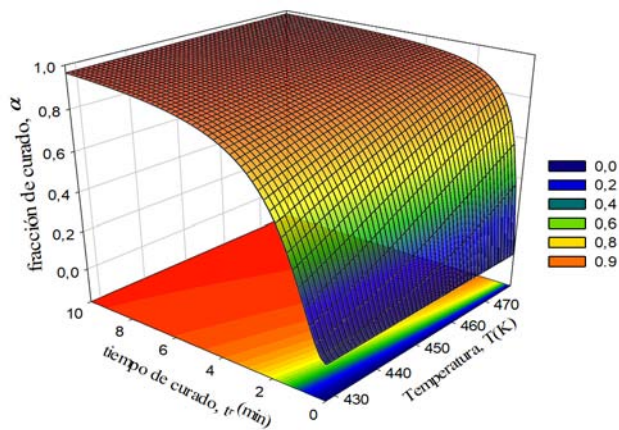


Figure 13, Surface graphics $\alpha(T, t_r)$

Conclusions

It was possible to obtain, through adjustments of nonlinear regression, the kinetic parameters of kamal-Sourour expression for the EPDM material.

From the experimental results, it was found that the order of reaction is a temperature dependent parameter and it obeys to an Arrhenius-type exponential function. The fitted experimental results using the proposed expression determine a reliability factor good enough, $R^2 = 0.9896$. That corresponds to a relative error of just 1.04%.

Each of the parameters involved in Kamal-Sourour model for the degree of curing could be expressed in function of the temperature, allowing to extend the behavior to a three-dimensional model $\alpha(T, t)$.

The adjusted model of Isayev–Deng was contrasted with the one of Sesták – Berggen. It was found that Isayev-Deng model best describes the kinetics of reaction in the tested isothermal temperature range.

As temperatures increase, the maximum reaction rate takes place in less time than the normal and rises high values for the curing processes. This could cause premature curing if the design of the rubber feeding system is not adequate.

Finally we can conclude that since Deng-Isayev model uses the minimum of parameters to describe the kinetics of curing, it can be used more efficiently to EPDM polymer injection-process simulation.

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