

Cure Kinetics of a Polymer-Based Composite Friction Material

Akbar Shojaei,¹ Farhang Abbasi²

¹Department of Chemical & Petroleum Engineering, Sharif University of Technology, Tehran 11365-9465, Iran

²Research Center for Polymeric Materials, Sahand University of Technology, P.O. Box 51335-1996, Tabriz, Iran

Received 7 April 2005; accepted 20 June 2005

DOI 10.1002/app.22465

Published online 21 December 2005 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: In the present article, cure kinetics of a commercially available composite friction material used in railroad vehicles is investigated using the rheometer measurements. Effect of ingredients of friction material compound, including rubber matrix, phenolic resin, and fillers, on overall cure kinetics of friction compound is also investigated by comparing the cure kinetics of friction material and rubber matrix compound. A phenomenological model and an Arrhenius-type equation is developed for cure kinetics and induction time of both friction material and rubber matrix. The parameters of the models are extracted from experimental data, using the rheometer at different temperatures and utilizing appropriate optimization method. The good agree-

ment between experimental measurement and models prediction indicates the good performance of the models developed in this study. The results demonstrate that phenolic resin and fillers have dominant effects on the overall cure behavior of the friction material compound. A comparison between the present results and other published data based on the differential scanning calorimetry (DSC) shows a reasonable agreement as well. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 9–17, 2006

Key words: kinetics; composites; curing of polymers; thermosets; friction materials

INTRODUCTION

Friction materials are basic elements of frictional braking systems of various vehicles, ranging from small brakes on a bicycle to large brakes for Jumbo aircraft. Depending on the end use, various types of friction materials have been developed to work in different braking conditions. Generally speaking, friction materials can be categorized into three different classes, including polymer-based composites, carbon-carbon composites, and metallic materials.¹

Polymer-based composites are the most common type of friction materials used in braking system of normal and heavy vehicles such as automotive, truck, and trains. In railroad industry, particular attention has been recently paid to use the polymer-based composite brake blocks in place of conventional cast iron ones.^{2,3}

A typical composite friction material is composed of many ingredients, which can be generally categorized into four different classes, including polymer matrix, fillers, friction modifiers, and reinforcements.^{1,4} Designing of friction material formulation, i.e., selection of a set of raw materials to meet a specific performance, and appropriate manufacturing conditions are

major concerns for composite friction material manufacturers. In producing a composite friction material, cure process or crosslinking reaction has a dominant effect on the production rate and part quality.⁵ Prediction of cure process inside the mold enables one to obtain proper processing conditions. Accurate cure kinetics data is necessary to predict the progress of cure process adequately during the cure cycle.

From cure kinetics viewpoint, above-mentioned ingredients involved in a friction material compound may be divided into two major groups⁶: (1) reactive components or thermoset polymer matrix containing curing agents, which directly take part in creating the three-dimensional crosslinked structure, and (2) nonreactive components, including different additives. An important polymer matrix that is particularly used in railroad brake block is rubber material. These materials may be natural rubber or synthetic, which is vulcanized to form a final product in which the other components are distributed uniformly. Styrene butadiene rubber (SBR) is the common type of rubber material used in the railroad friction element.^{7,8} The use of rubber material is pivotal to obtain a conformable brake block, which is an important characteristic to achieve a good braking performance.³ In addition to rubber, phenolic resin along with curing agent such as hexamethylenetetramine is also added to strengthen and stiffen the rubber matrix.^{7,8} Owing to reactive na-

Correspondence to: A. Shojaei (akbar.shojaei@sharif.edu).

ture of the resin, it can contribute in the final cure kinetics of the friction material compound.

Two important features in curing process of the friction materials are firstly the presence of phenolic resin in rubber matrix and secondly high content of additives or nonreactive components, typically between 70 and 85 wt %.^{7,8} Cure kinetics of rubber compound have been the subject of several research works, but to our knowledge, the same efforts for composite friction material with above-mentioned features have not been reported in the literature. A description of vulcanization kinetics of conventional rubber compounds has been given in the literature.⁹⁻¹¹ Jeong et al.¹² proposed a kinetics model for a highly silica and silane-modified silica-filled SBR, but the maximum amount of silica included in the compound was less than 40 wt %, which is lower than the one in friction material compound. Effect of nonreactive components on cure kinetics has been also addressed in the literature, in particular, for thermoset resins.^{13,14}

Generally, two different approaches have been used to model the cure kinetics of thermosetting polymers^{15,16}: phenomenological or empirical models and mechanistic models. Although mechanistic models can reveal the effect of chemical species taking part in the compound on the overall cure process, it is not easy to derive a mechanistic model in many cases because of complicated nature of the crosslinking reaction.¹⁷ On the other hand, phenomenological models have been successfully used to predict the cure kinetics of many rubber compounds and thermosetting resins.^{9-11,18-20}

The present article is an attempt to investigate the cure kinetics of a composite friction material used in braking system of railroad vehicle.^{21,22} A kinetic model is proposed based on the phenomenological approach and the model parameters are extracted from the cure curve obtained by rheometer. This model can easily be used in the analysis of cure process of the composite friction material during the manufacturing process.

THEORY

Cure kinetics model

A phenomenological model is a simple rate equation representing the main features of the reaction kinetics without taking into account the role of individual species separately. A variety of phenomenological models are available, which can be generally expressed as²³

$$\frac{d\alpha}{dt} = K(T)f(\alpha) \quad (1)$$

where α denotes the overall state or degree of cure, t is the time, K represents the temperature-dependent reaction rate constant, and $f(\alpha)$ is a known function of α . A simple model is n th-order rate equation, which can be expressed as

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

in which k is a rate constant obeying an Arrhenius temperature dependence as

$$k = A \exp\left(-\frac{E}{RT}\right) \quad (3)$$

where A is the pre-exponential factor, E is the activation energy, and R is the universal gas constant ($R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$).

In many cases, owing to the autocatalytic nature of the cure process, n th-order kinetic model cannot predict the progress of the entire cure process adequately. For instance, eq. (2) predicts the maximum of reaction rate at time $t = 0$, which is not correct for an autocatalytic reaction. Other models have been proposed to estimate the cure kinetics accurately, which normally are more complicated functions of conversion and temperature. An appropriate kinetic model that has been proposed by Piloyan et al.²⁴ is expressed as

$$\frac{d\alpha}{dt} = k\alpha^m(1 - \alpha)^n \quad (4)$$

where m and n are model constants. A generalized expression, which has been adequately used to predict the cure process of thermosetting polymers, is given by Kamal and Sourour¹⁹:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1 - \alpha)^n \quad (5)$$

where k_1 and k_2 are temperature-dependent reaction rate constants having Arrhenius temperature dependence.

For rubber compounds, it has been observed that there is a period in the vulcanization process during which chemical reaction does not take place and the reaction rate is zero. This period, which is called induction time, occurs at the start of vulcanization. Induction time for a given rubber compound depends on temperature, according to Arrhenius-type temperature relation:¹¹

$$t_i = a \exp\left(\frac{b}{T}\right) \quad (6)$$

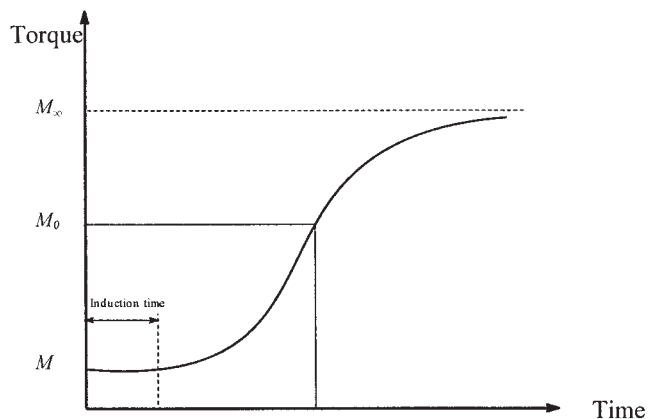


Figure 1 Typical cure curve of rheometer.

where t_i is the isothermal induction time and a and b are model constants, which are obtained based on kinetic study under isothermal conditions.

Degree of cure characterization

During the curing process, chemical structure of the polymer as well as the physical and mechanical properties of the compound changes as a result of crosslinking reaction. Cure kinetics of the thermosetting polymers can be estimated by tracing a property of the polymer that alters during the curing process. Therefore, various methods such as mechanical, spectroscopic, and thermal analyses can be used to study the cure kinetics. Differential scanning calorimetry (DSC), in both isothermal and dynamic or nonisothermal modes, is a proper method, which can be used to characterize the cure kinetics and extract the model parameters.^{11,14,19} It is based on the heat of reaction released during the crosslinking reaction. It has been pointed out that the parameters of kinetic model from isothermal and dynamic modes may be different due to the fact that the degree of conversion is a function of the curing time and temperature.¹⁵ Normally, DSC in isothermal mode is preferred to determine the kinetic parameters. However, for fast reacting thermoset or for experiments at high temperature, isothermal mode cannot be reliable, because the cure reaction takes place significantly before the DSC stabilizes at the desired temperature. In such cases, DSC experiments at dynamic mode are desirable, but the extraction of model parameters from the experimental data in this mode needs special considerations.

Another method to analyze the cure kinetics of thermosetting polymers, in particular for the rubber compounds, is to track the change of mechanical properties of the compound, during the curing process.²⁵ Various instruments such as Monsanto rheometer have been developed to do this. Figure 1 shows a

typical cure curve obtained by rheometer representing the progress of cure reaction.

In comparison with DSC, in the rheometer, one can use larger samples in the range of grams, providing better chance to get a uniform sample with predetermined composition, according to compound formulation. Consequently, the rheometer is regarded as a large specimen instrument and as a result it may suffer from thermal lag. In the present study, cure kinetics of the friction material compound is analyzed based on the cure curve obtained by Monsanto rheometer. Application of this method to characterize the curing of rubber compounds has been reported and recommended in the literature.^{11,25} More recently, Jeong et al.¹² used the cure curve obtained by rheometer to study the cure kinetics and extract the kinetic parameters for a rubber compound, and a good agreement was found between model prediction and experiments.

According to notations presented in Figure 1, the overall degree of cure or the overall state of cure, α , and the overall rate of reaction, $d\alpha/dt$, can be calculated as

$$\alpha(t) = \frac{M(t) - M_0}{M_\infty - M_0} \quad (7)$$

$$\frac{d\alpha(t)}{dt} = \frac{1}{M_\infty - M_0} \frac{dM(t)}{dt} \quad (8)$$

where M_0 , $M(t)$, and M_∞ are the modulus of the sample at the beginning, at the time t , and at the final state of cure, respectively, which are directly obtained from the curve drawn by the instrument.

EXPERIMENTAL PROCEDURE AND ANALYSIS

Materials and compound preparation

A composite friction material whose performance in the braking system of railroad vehicles has been evaluated in our previous work^{21,22} is used in this study. The recipe of this friction material, which is here indicated by **FM-100**, is presented in Table I. As illus-

TABLE I
Compound Recipes (PHR*)

Compound	R	FM-100
SBR-1502	100	100
Sulfur	7.5	7.5
Zinc oxide	5	5
Stearic acid	1.8	1.8
MBTS	1.8	1.8
Phenolic resin	—	20
Nonreactive components	—	290

*Part per hundreds of rubber by weight.

trated in the table, the compound **FM-100** contains SBR and its curing agents as main matrix, phenolic resin, and highly loaded nonreactive additives. Moreover, the cure kinetics of rubber matrix of the friction material is also investigated independently in the present work. The recipe of this compound is given in Table I, under the name of **R**.

Styrene butadiene rubber (SBR-1502) supplied by BIPC (Banadr Imam Petrochemical Company, Iran) is used in this study. Novolac phenolic resin IP502 from RC (Resitan Company, Iran) is used in the compound **FM-100**. Nonreactive components of friction material **FM-100** are mixture of different materials such as calcium carbonate, barite, iron oxide and steel wool, graphite, and so on. All of the additives are industrial grades and are provided by local companies.

The rubber and nonreactive components are mixed using a banbury mixer, and then the sulfur and resin are added in the next stage using a two-roll mill. The temperature of the two-roll mill is maintained at 50°C during the mixing process, and the mixing is completed within 20 min.

Rheometry

The Monsanto R-100 rheometer is used as a cure meter, under isothermal conditions over the test period. The isothermal experiments for both compounds are performed at three different temperatures ranging from 140 to 170°C, and each experiment is conducted at least twice to ensure the repeatability of the results. The test temperatures used are 140, 155, and 170°C, and sample sizes employed in the rheometer are in the range of 10 g.

The change of torque of the compounds is recorded as a function of time, which can be a measure of curing reaction rate. The reaction is considered complete when the cure curve levels off. The cure curves obtained from the rheometer for both compounds are illustrated in Figure 2. As expected, owing to presence of high content of additives and reactive resin, both torque and cure rate have increased in friction compound **FM-100** in comparison with compound **R**. The initial decrease in the curve shown in Figure 2 is due to nonsteady thermal effect caused by heating the samples. This zone of the cure curve is neglected in the analysis of the cure kinetics, and start of minimum point on the curve is considered as the onset of the cure process.

Data analysis

In the cure curve obtained for each compound and at each temperature, the induction time is considered as a time during which a 2 units increase in the rheometer curve is observed.²⁵ At a given time after the induction period, value of torque is extracted from the

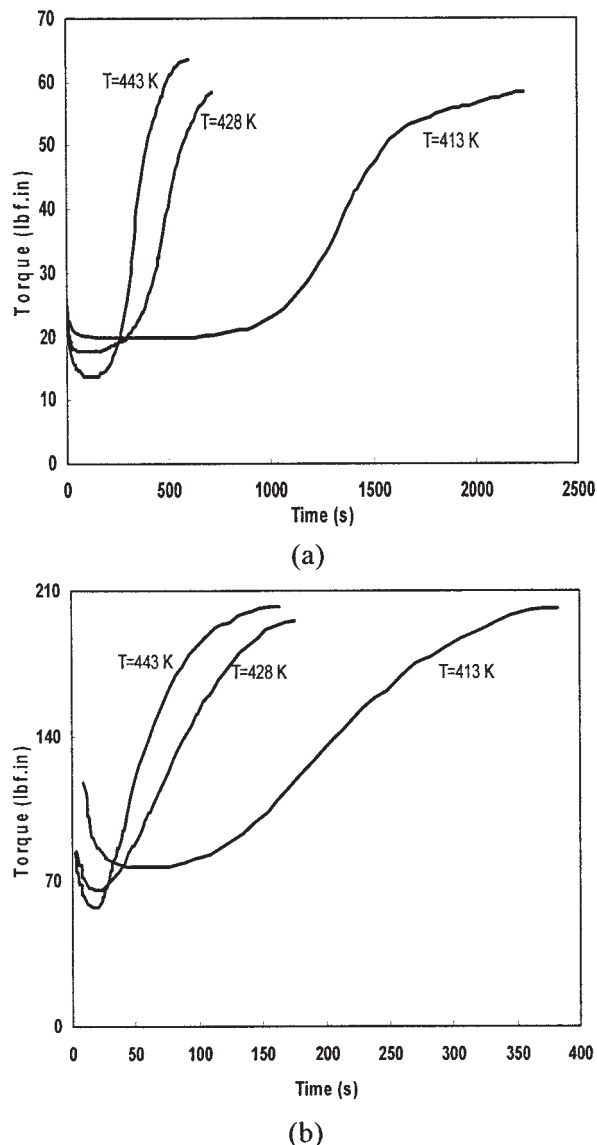


Figure 2 Isothermal cure curves obtained by rheometer for (a) rubber compound **R** and (b) friction material **FM-100**.

cure curve and then the corresponding overall conversion is directly calculated using eq. (7). The overall curing rate ($d\alpha/dt$) at each time can also be determined by the use of eq. (8); however, this needs further mathematical treatments. The slope of the curve at time t , i.e., $(dM/dt)^n$, is approximated as follows:

$$\left(\frac{dM}{dt}\right)^n \approx \frac{M^{n+1} - M^{n-1}}{\Delta t} \quad (9)$$

in which M^{n+1} and M^{n-1} are the values of M at times t_{n+1} and t_{n-1} , respectively, and Δt represents the time interval, $\Delta t = t_{n+1} - t_{n-1}$. Once the term dM/dt is determined, the overall curing rate can be obtained at any time from eq. (8).

TABLE II
Parameters of Induction Time Model, Eq. (6)

Compound	a (s)	b (K)
R	5.1×10^{-8}	9.56×10^3
FM-100	1.03×10^{-8}	9.11×10^3

The kinetic data obtained on the basis of the above-mentioned procedure can be used to calculate the parameters of induction time and curing rate models by the use of an appropriate regression method. Plotting the logarithm of the induction time, t_i , at each temperature, versus $1/T$ results satisfactorily in a straight line, whose slope and y -intercept are used to calculate the parameters a and b in eq. (6).

The values of kinetic parameters are also obtained at each isothermal temperatures by fitting the kinetics model to the measured values of $d\alpha/dt$ versus conversion. Since the kinetic model is a nonlinear equation, an appropriate optimization method is needed to extract the parameters. In this article, an optimization software called Table Curve²⁶ is used to estimate the best value of the model parameters. Curve fitting leads to a set of model parameters at different temperatures from which temperature dependence of each parameter can be evaluated. Normally, rate constants, k 's, show strong dependence on temperature, and this dependency is usually expressed by Arrhenius-type relation, i.e., eq. (3). Therefore, pre-exponential factor A and activation energy E in eq. (3) are determined by the same procedure mentioned for obtaining the constants of induction time model.

RESULTS AND DISCUSSION

The major objective of this work is to derive information on cure behavior and cure kinetics of a composite friction material, which is mainly composed of many reactive and nonreactive components. Such information would be essential for process development as well as part quality. Here, kinetic analysis of friction material is performed using the semiempirical kinetic model, without the consideration of cure reaction mechanism. Because, the exact mechanism is obscure for this complex thermosetting system containing many reactive and nonreactive components.

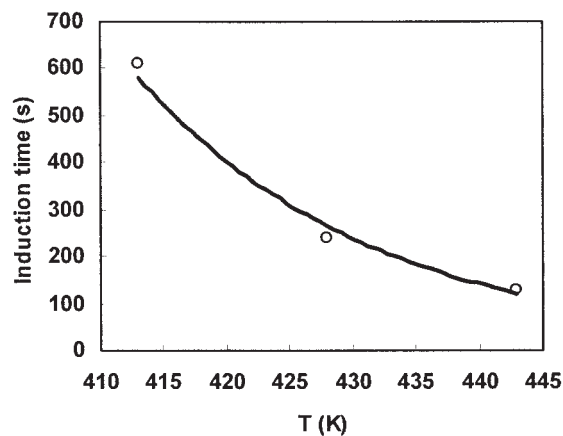
The friction material **FM-100** studied in this investigation contains two reactive components, including SBR matrix and phenolic resin added to the matrix, and many nonreactive fillers. Chemical structures and curing reactions of both reactive components are different, and therefore, these two components have different curing behaviors.²⁷⁻²⁹ SBR is a sulfur curing component, while curing of phenolic resin is activated by hexamethylenetetramine. Although the main purpose of this investigation is to characterize the cure

kinetics of friction material **FM-100**, it would be instructive to study the cure kinetics of compound **R**, namely SBR component, independently. This can help one to reveal the overall contribution of rubber component, phenolic resin, and fillers on the cure rate of the final friction compound.

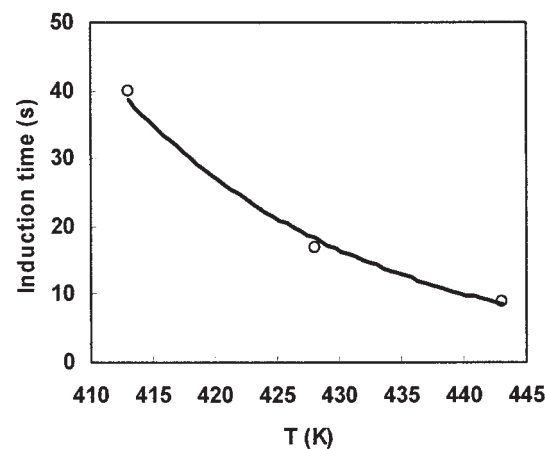
Induction time of the friction material

The parametric values of induction time model, i.e., eq. (6), for both compounds obtained using regression analysis are listed in Table II.

The comparison between the model prediction and experimental data is also illustrated in Figure 3. As seen in the figure, agreement between the calculated values and the experimental results is good, showing the good performance of the model for predicting the induction time of both compounds. The results also show that the induction time of friction material is



(a)



(b)

Figure 3 Induction time vs. temperature for (a) rubber compound **R** and (b) friction material **FM-100**.

significantly small in comparison with the induction time of compound **R**. This means that inclusion of both phenolic resin and fillers in the compound decreases significantly the induction time of the friction material. Of course, our previous results have shown that adding the fillers in the rubber matrix without phenolic resin decreases the induction time as well³⁰; however, the present results indicate the presence of both fillers and phenolic resin in the compound results in a much more reduction in induction time. As a result, it can be concluded that both fillers and phenolic resin are main cause of small induction time of the friction material compound. Fillers used in the friction material are composed mainly of different organic and inorganic materials and are actually nonreactive. Consequently, they affect the cure kinetics and induction time in a complicated manner from the viewpoint of reaction chemistry. However, different curing nature of phenolic resin with respect to rubber compound can be an interpretation for its effect on induction time as well as cure kinetics. The phenolic resin is a highly reactive component and its cure rate is high at the temperature range suitable for vulcanization of SBR, i.e. 140–170°C.^{28,29} Therefore, as the phenolic resin takes part in the chemical structure of the matrix, overall induction time of the friction compound decreases.

Cure kinetics of the friction material

The regression analysis was carried out based on two kinetic models, i.e. eqs. (4) and (5); however, eq. (5) fits well the experimental data. Therefore, only parameters of eq. (5) are reported here for both compounds. Figure 4 illustrates the values of m and n for compounds **FM-100** and **R** at different temperatures.

As can be seen in the figure, the m and n values for compound **R**; and m for compound **FM-100** remain relatively constant over the temperature range studied here. Therefore, mean values of these parameters can be used in the kinetic model. This condition is not true for the n value of compound **FM-100** and as is seen in Figure 4, it is a temperature-dependent parameter. As shown in Figure 4, n increases considerably by increasing temperature, and a temperature dependence of this parameter can be illustrated fairly well by a straight line, which can be expressed as

$$n(T) = 0.006T - 1.66 \quad (10)$$

where T is in Kelvin. The dependence of kinetic model exponents to temperature may be related to the chemistry of curing reaction of the compound, and such an observation has been reported in the literature for reactive systems such as epoxy resin.³¹ The kinetic model exponents are constant for compound **R** which is only a rubber along with its curing system; how-

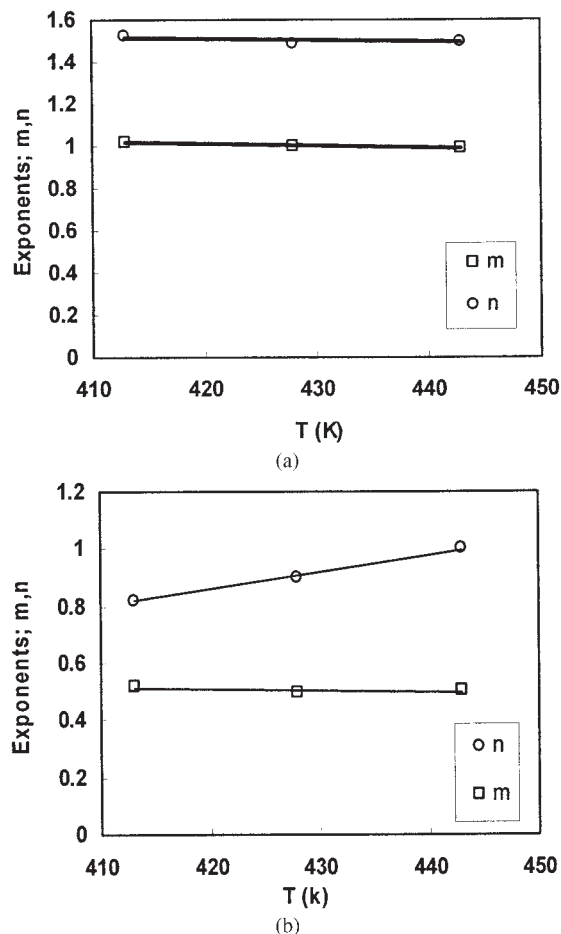


Figure 4 Model exponents m and n for (a) rubber compound **R** and (b) friction material **FM-100**.

ever, adding the resin significantly changes the cure kinetics behavior. This behavior of the friction material may be explained by different cure chemistry of rubber and phenolic resin. Owing to this matter, reaction rate for the two reactive components, i.e., rubber and resin, are different at a given temperature,^{27–29} and consequently this leads to temperature dependence of model exponents for the friction compound. Figure 5 shows the results of the regression analysis of rate constants, k 's, based on Arrhenius relationship. It is obvious that rate constants follow eq. (3) very well. Table III summarizes the parametric values of the model determined by the curve fitting for both compounds.

Figure 6 illustrates the comparison of conversion-time curves between model prediction and experimental data for both compounds at different temperatures. As can be seen, agreement between the calculated and experimental results is good, indicating the applicability of the kinetics model in predicting the cure process. It is also seen that the cure rate of the friction material has increased with respect to rubber gum (compound **R**). This conclusion is consistent with

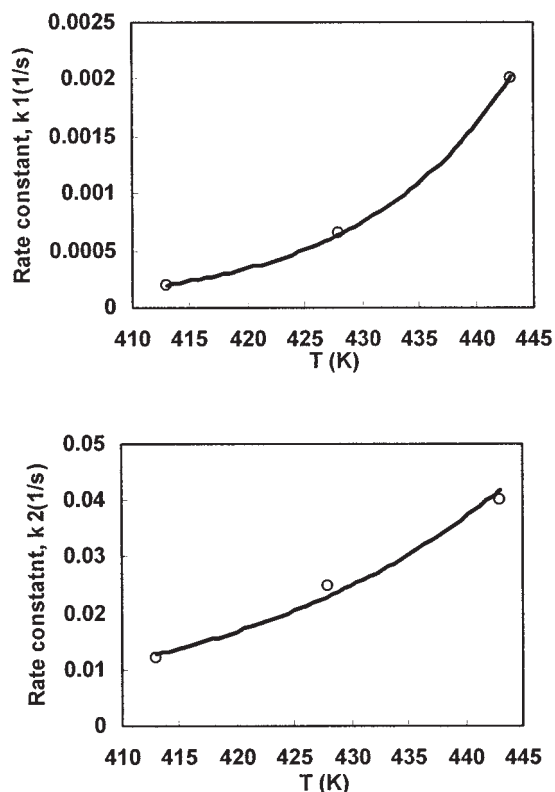


Figure 5 Comparison of model prediction and experimental values of rate constants for friction material FM-100.

the results of induction time of both compounds. Although a little effect of fillers on increasing the cure rate has been observed by rheometer measurements,³⁰ the presence of the resin can be interpreted as a major source of significant increase in overall cure rate. Because the cure rate of phenolic resin at temperature suitable to normal vulcanization of SBR is very high.

Comparison of kinetic data with published results

To the best of our knowledge, there is no report on cure kinetics of friction material compounds containing different reactive components. However, cure kinetics of SBR compound has been well documented. Figure 7 shows the cure rate versus time and induction time versus temperature for a SBR gum (named 19F), investigated by Isayev and Deng.¹¹ These curves are recalculated here using explicit finite difference method,³² based on the parameters reported by

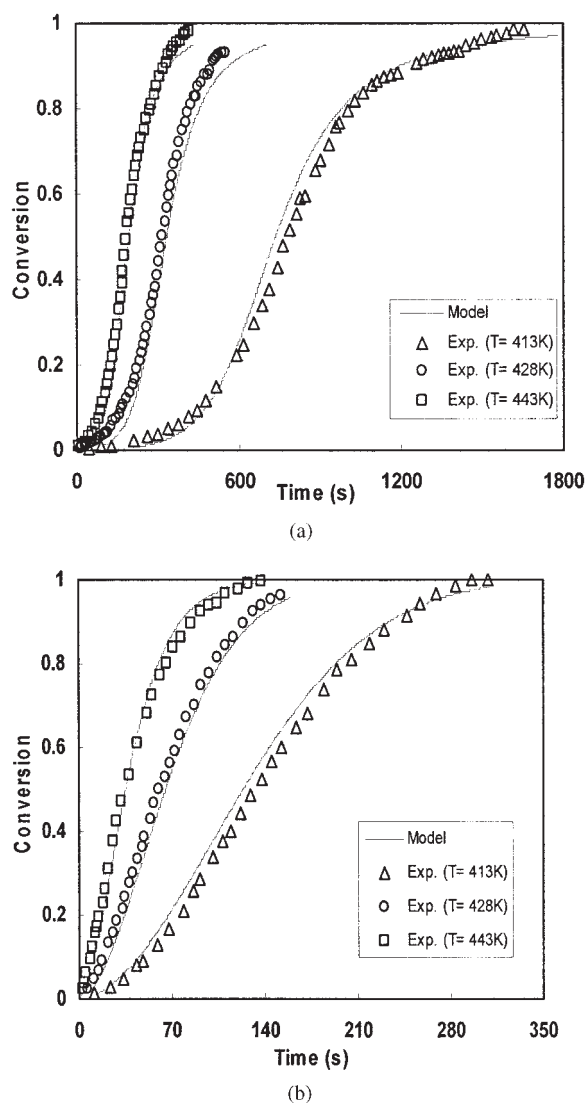


Figure 6 Comparison of model prediction and experimental data of conversion vs. time for (a) rubber compound R and (b) friction material FM-100.

them.¹¹ The parametric values of kinetic and induction time models which were obtained using DSC, are presented in the caption of Figure 7. The recipe of compound 19F is so identical to compound R except the curing system.¹¹ In both rubber compounds, i.e., 19F and R, sulfur is used as crosslinking agent in the curing system, but the other curing agents such as accelerator and its contents are different.

Cure rate–time curves are also illustrated in Figure 8 for compounds R and FM-100, based on the para-

TABLE III
Parameters of the Kinetic Model, Eq. (5)

Compound	$A_{1,0}$ (s^{-1})	$A_{2,0}$ (s^{-1})	E_1 (J/g mol)	E_2 (J/g mol)	m	n
R	9.26×10^{10}	4.78×10^5	1.26×10^5	6.07×10^4	1	1.5
FM-100	1.16×10^{11}	5.67×10^5	1.167×10^5	6.04×10^4	0.51	$0.006T-1.66$

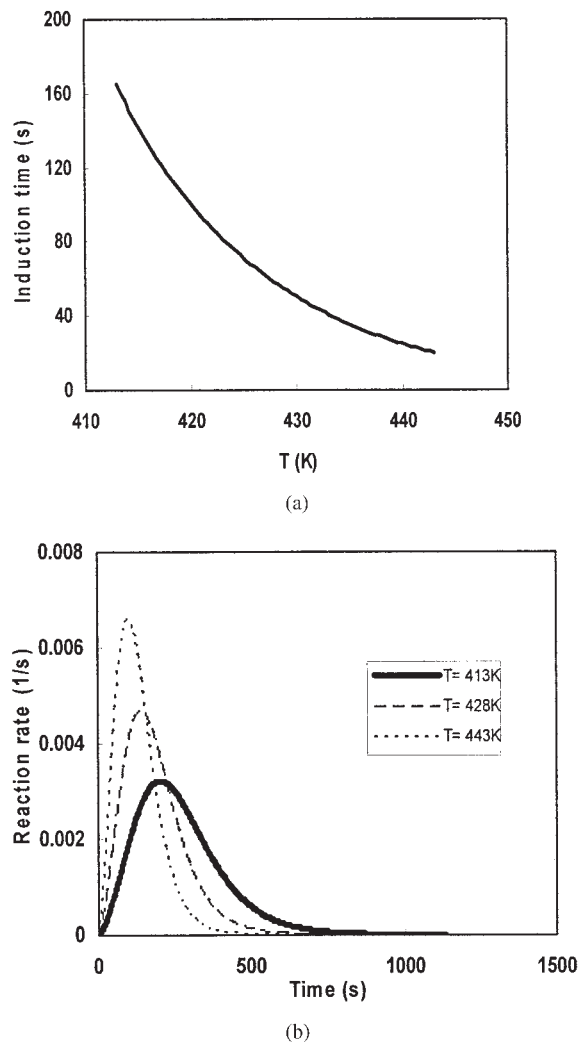


Figure 7 Calculated cure kinetics of compound **19F** with material constants reported by Isayev and Deng¹¹: (a) Induction time vs. temperature with model constants $a = 5.786 \times 10^{-12}$ s and $b = 1.28 \times 10^4$ K at (b) cure rate vs. time with model constants $A_1 = 0$, $A_2 = 352$ (s^{-1}), $E_1 = 0$, $E_2 = 3.62 \times 10^4$ (J/g mol), $m = 0.6$, $n = 1$.

metric values presented in Table III. Comparing cure rate curve for compounds **R** and **19F** shows that the cure rate for compound **R** is relatively lower than the compound **19F**, and consequently, the cure time becomes longer. The same trend can be observed for induction times of both compounds. This difference can be normal, because the curing systems of both compounds are different. A review on chemistry of vulcanization of rubbers presented by Coran¹⁷ shows the significant effect of curing agents such as accelerators on both induction time and cure rate of a rubber compound regardless of the rubber type. On the other hand, the difference for the two rubber compounds is reasonable and comparable. For example, maximum cure rate for compound **R** at 155°C is $3.55 \times 10^{-3} s^{-1}$, while for compound **19F** is $4.66 \times 10^{-3} s^{-1}$. Also the

duration of cure for compounds **R** and **19F** at the same temperature are around 17 and 10.5 min, respectively, which show comparable results.

CONCLUSIONS

Cure kinetics of a composite friction material, which is used in braking system of railroad vehicles, has been studied, and a phenomenological cure kinetics model has been developed to predict the cure process. The model is based on the rheometer measurements and its parameters are derived by the use of an appropriate optimization method. Induction time is also measured by the rheometer and a previously known Arrhenius-type equation is used to develop an expression for induction time. Good agreement is found between models predictions and experimental measurements, showing good performance of the models in predict-

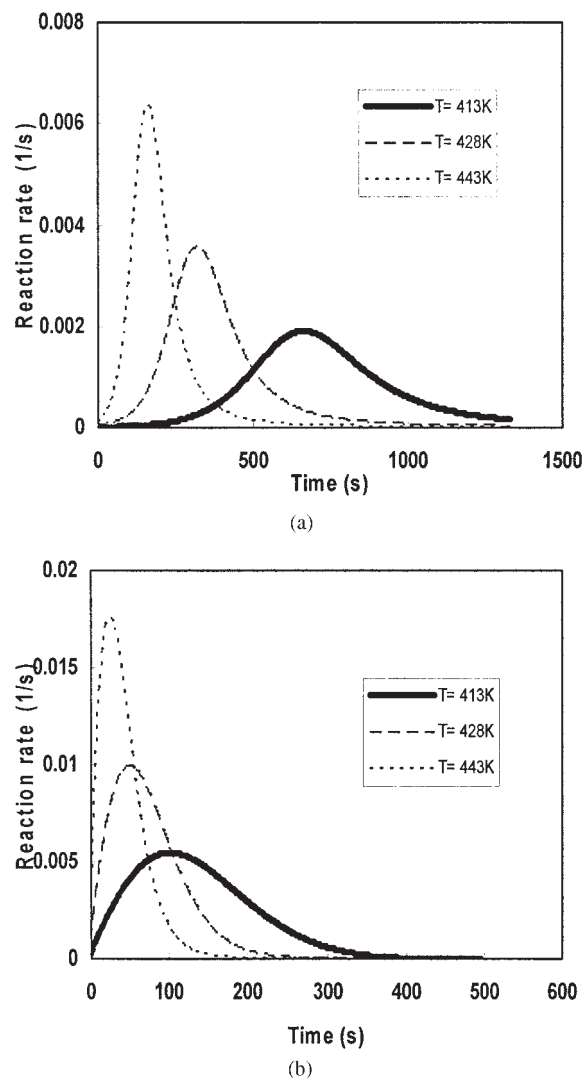


Figure 8 Calculated cure rate vs. time based on the model parameters listed in Table III: (a) rubber compound **R** and (b) friction material **FM-100**.

ing the curing process of the friction compound. The results reveal that phenolic resin and fillers significantly affect the curing behavior of the friction material compound. Predicted results from the models developed based on the rheometric measurements has been compared with the available data in the literature, which has been developed based on DSC measurements. The comparison shows reasonable agreement between two results. The models developed in this study can conveniently be employed to predict the cure cycle of a commercial friction material during the manufacturing process.

The authors thank Mr. Alaei, general director of Mashin Lent Tehran Company (Iran), for providing materials and compounding machines used in this work. The rheometer measurements were performed in Parmida Company (Iran). Their support is greatly appreciated. The authors are also grateful to the Research Center of Iran Railway for providing helpful documents required in this work.

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