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Determination of mechanical properties of silica compounds using a curing kinetic model

D. Nichetti *

CHIORINO LAB, Via S. Agata 9, 13900 Biella, Italy

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Abstract

Curing is the final step in rubber goods production and the mechanical properties of the vulcanized items, strongly depend on the processing conditions. The objective of this research is to predict the mechanical properties of SBR silica compound using kinetic data obtained from curemeter measurements. The model proposed is based on two curing parameters and on mechanical properties measured in the cured and uncured state. Results showed that the model is able to accurately predict the mechanical properties of the isothermal cured compound and therefore has potential application in the non-isothermal curing cycle optimization.

Keywords: Curing kinetic; Rubber silica compound; Mechanical properties; Isothermal curing model

1. Introduction

The rubber industry began when Goodyear [1,2], developed the first useful rubber compound: natural rubber plus sulfur. The concept of mixing materials into rubber to improve performance is still of primary importance today [3,4]. Without compounding, few rubber goods would be of any commercial value.

The curing process is the final step in tire manufacturing whereby a green rubber goods is formed to the desired shape in a press. In curing press, heat is transferred to the tire from the surfaces, which are maintained at high temperatures, inducing the curing reaction of the rubber compounds, thereby converting them to a strong elastic material. The vulcanization process is optimized to achieve an optimal curing state for the rubber goods, which ensure the mechanical properties required of each component.

The prediction of the curing state is usually determined by employing a rheometer, in which the kinetics is described by the torque variation during curing [5,6]. This approach, however, cannot give any explicit dependence of compound properties, such as dynamic modules, tensile strength hysteresis and abrasion, on the curing cycle. The purpose of this work is to develop a simple constitutive model able to predict the mechanical properties of rubber compounds during a non-isothermal curing cycle.

2. Experimental

2.1. Sample preparation

The rubber compound used is typical 100% silica formulated. The polymer used was solution-polymerized SBR oil extended. The selected silica is a granulated and high surface area type. Table 1 shows the rubber compound formulation used in this study.

A 1.5 l intermeshing internal mixer with variable rotor speed and ram pressure capability was used to mix

* Tel.: +39-15-8489345; fax: +39-15-8489320.
E-mail address: nichetti@chiorino.com (D. Nichetti).

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Table 1
Recipe of silica rubber compound

Chemicals	S-SBR	BR	Silica	Silane	Plasticizer	Antioxidant	Sulfur	Curatives
%	40.6	13.5	34.1	5.4	2.7	1.3	0.8	1.6

S-SBR Buna 5025 HM Bayer: styrene–butadiene rubber solution polymerized.
BR: polybutadiene Enichem High *cis*-type.
Silane: bis(triethoxysilylpropyl)tetrasulfide.

Table 2
Mixing sequence

Phase	Polymers + silica + silane	Addition of antiox. + sulfur	Oil injection	Cleaning	Discharge
Time (s)	0	145	185	270	360

our compounds. The mixing sequence and the working conditions were designed in order to reach a given temperature in a defined time.

The compound was discharged at 140 °C, to prevent any undesired scorch phenomenon, and the complete mixing sequence is given in Table 2. After mixing, the compound was completed, adding curatives, on an open mill keeping the rubber temperature below 110 °C.

2.2. Curing kinetics

A major focus on rubber compounds, since sulfur vulcanization was studied has been to characterize the reaction scheme during the curing process and, on this subject, a review was published by Koenig and co-workers [7]. Vulcanization is a cross-linking process that prevents permanent deformation under load and ensures elastic recovery on removal of the load. Many approaches including physical tests and chemical analysis have been attempted to relate the chemical microstructure to the physical properties of both raw and cured compounds. The curing conversion denotes the extent of the reaction and is determined by measuring the rubber properties during the cross-links formation. The most popular and practical method to measure the curing conversion is based on mechanical dynamical measurement of the isothermal torque vs. time at a given strain using a die rheometer. A first approach proposed by Kamal and Sourous [8] was to fit the curing using *n*th order kinetic model. Other authors proposed plausible kinetic reaction mechanisms of the vulcanization process to reproduce the torque curve [9,10]. Quirk and co-workers [11] modeled the cure reaction mechanism to establish the kinetic model able to predict the curemeter data.

These approaches imply that any material property can be scaled by the curing conversion curve. These models, however, do not give any explicit dependency of material parameters on curing conversion.

2.3. Test conditions

The cure kinetic was measured using Monsanto Moving Die Rheometer MDR, at four temperatures (140, 150, 160 and 170 °C) in constant test conditions (1.667 Hz, ±0.5 deg arc strain amplitude). The samples for mechanical tests were prepared by compression molding in thin layer sheet (2 mm thickness). A water ice bath was used to rapidly cool the sample to room temperature after curing. Viscoelastic behavior of each sample was measured in terms of static and dynamic properties.

The dynamic modulus E^* was measured using the servo hydraulic Instron at a frequency of 100 Hz and 3.5% of strain. A tensile strength test was carried out on a dumbbell test sample (2 mm thick) using Zwick dynamometer at 500 mm/min and 23 °C and employing a contact extensometer to collect deformation data. Abrasion and hardness were also measured following the ASTM methods respectively the rotary drum abrader (D5963) and the international rubber hardness (D1415).

3. Results and discussion

3.1. Model development

The torque profile $S'(t)$ was used to define the curing conversion $\chi(t)$ as follows:

$$\chi(t) = \frac{S'(t) - \mathrm{ML}}{\mathrm{MH} - \mathrm{ML}} \tag{1}$$

where ML, MH are the minimum and the maximum torque values and t is the curing time at a given temperature.

It is interesting to note that for this silica compound formulation, a non-reverting curing behavior has been observed. The superposition principle has been used to

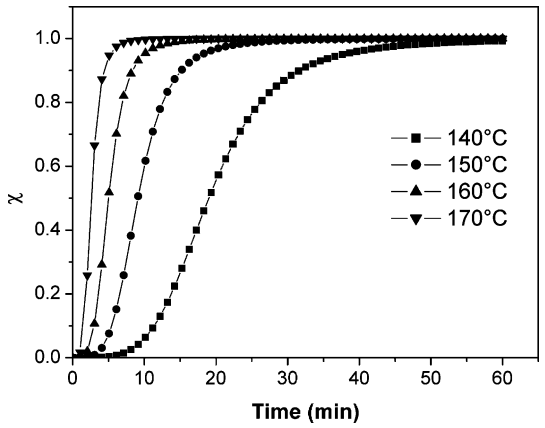

Fig. 1. Degree of curing as a function of curing time at four temperatures.

evaluate the curing kinetic at any temperature. This is accomplished by collecting data at different temperature and shifting it to one reference curing conversion curve, usually also known as degree of conversion $\chi(t)$ as shown in Fig. 1. This S shape behavior, suggests that the reaction mechanism of vulcanization could be described by simple kinetic models. The data was fitted with the induction model proposed by Isayev and Deng [12]

$$\chi(t) = \frac{t^n}{k_T^n + t^n} \tag{2}$$

where k_T is a kinetic time at a given temperature and n is the exponential rate coefficient. In Fig. 1 you can see the experimental data (dots) and the fitting curves (line) calculated using $n = 4.3$ in Eq. (2) and the kinetic times at each temperature as given in Table 3.

In order to develop a model for material properties of curing systems, it is useful to underline that the experimental method used to evaluate the degree of the curing conversion is based on torque, $S'(t)$, measurement. Therefore, it is not surprising that $\chi(t)$ cannot be explicitly used to predict the effect of curing on material viscoelastic properties.

Table 3
Kinetic time data (min) at given temperatures

Temp	140 °C	150 °C	160 °C	170 °C
K_T	18.6	9.1	5.1	3.1

Our approach to characterize the curing behavior of silica compounds was to describe the viscoelastic properties evolution, such as tensile strength, dynamical mechanical modules hardness and abrasion, by a power law model and use the kinetic time to take into account the effect of the vulcanization temperature. The equation describing the material property dependence on time and temperature, is of the form:

$$P(t) = \frac{1}{k_T^n + t^n} \cdot (P_C \cdot t^n + P_U \cdot k_T^n) \tag{3}$$

where k is a kinetic time at a given temperature and n is the exponential rate coefficient. The parameters P_U and P_C are, respectively, the material property in uncured and cured states (plateau region). We assumed that the kinetic time and the exponential rate coefficient depend only on the curative system used in the compound formulation. The values of k and n, obtained by fitting the curemeter data employing Eq. (2), were used in the material model, Eq. (3), to fit the experimental data of the mechanical properties. The cured parameter P_C, was obtained measuring the material properties of the compound vulcanized at 150 °C for 1 h. The mechanical properties of uncured materials cannot always be measured mainly because of some experimental difficulties in sample preparation. Therefore, the uncured parameter was extrapolated following Eq. (4), by measuring the mechanical properties of a partially cured (7.5 min at 150 °C). As shown in Fig. 1 such a vulcanization condition corresponds to 20% of curing degree and its curing time is usually named as t_{20}

$$P_U = P_{20} \cdot \left[1 + \left(\frac{t_{20}}{k_{150}}\right)^n\right] - P_C \cdot \left(\frac{t_{20}}{k_{150}}\right)^n \tag{4}$$

where P_{20} is the mechanical property measured for a sample cured at 150 °C and a time equal to t_{20} and k_{150} is the kinetic time at 150 °C. Model parameters are shown in Table 4. The model was used to predict the mechanical properties of samples cured at a wide range of temperature and time. The isothermal curing conditions are given in Table 5.

3.2. Mechanical properties

Modulus at 300% elongation, measured at 23 °C, versus curing time is plotted in Fig. 2. First, we should note that a model curves (line) was obtained employing the parameters k_T and n calculated by rheometric curves

Table 4
Model parameters obtained from isothermal experiments

$k = 9.1$ $n = 4.3$	M_{300} (MPa)	E' (MPa)	E'' (MPa)	IRHD	Abrasion (mg)
P_C	12.8	5.9	8.9	63	87
P_U	2.5	2.4	5.1	9.9	147

Table 5
Experimental isothermal curing conditions

Temperature			
140 °C	150 °C	160 °C	170 °C
Curing time (min)			
19	9	5	3
24	11	7	4
29	15	8	5
40	30	13	8
50	35	15	12
60	40	20	18

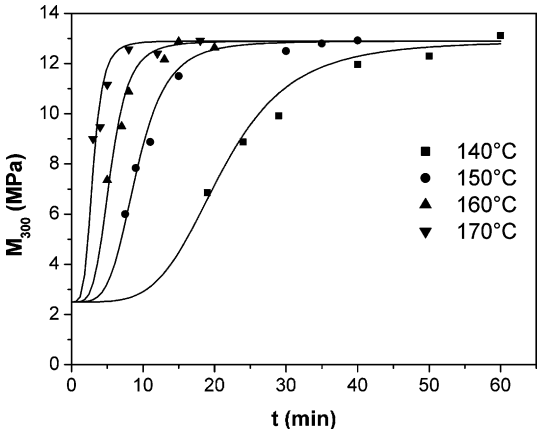

Fig. 2. Master curve of tensile stress at 300% of elongation vs. curing time. Solid lines: approximation of experimental data by Eq. (3).

and the P_U and P_C extrapolated and measured for sample cured at 150 °C. It is also interesting to point out that the model fits well the experimental data for all curing conditions. The same approach was also used to predict the behavior of the storage modulus at 70 °C as shown in Fig. 3. It should be noted that both properties monotonically increase with curing time to a plateau value.

Futamura [13] suggested, in order to predict the tread tire performance in terms of wet grip, to use the loss modulus, E'', measured at 0 °C. Experimental data of E'' at 0 °C are shown in Fig. 4. The correlation between wet friction coefficient and loss modulus at 0 °C was investigated in terms of silanization degree and mixing conditions by Nichetti and co-workers [14].

The hardness is a technological parameters used to classify rubber compounds and the comparison between data and model prediction are shown in Fig. 5. Some light on the life time of any rubber goods working by friction contact can be also given using an abrasion test. Therefore it can be expected that the lower is the abrasion the longer is the rubber life. The comparison between data and model prediction is shown in Fig. 6.

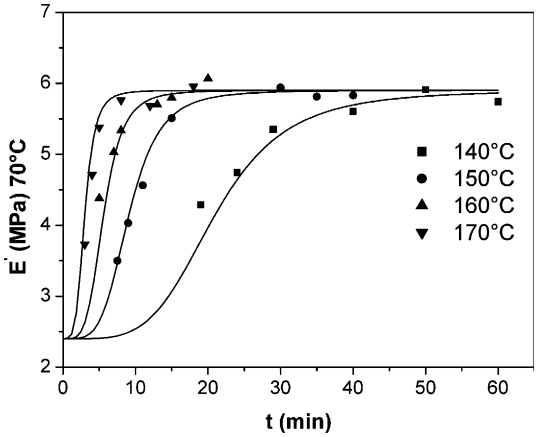

Fig. 3. Storage modulus vs. curing time. Solid lines: approximation of experimental data by Eq. (3).

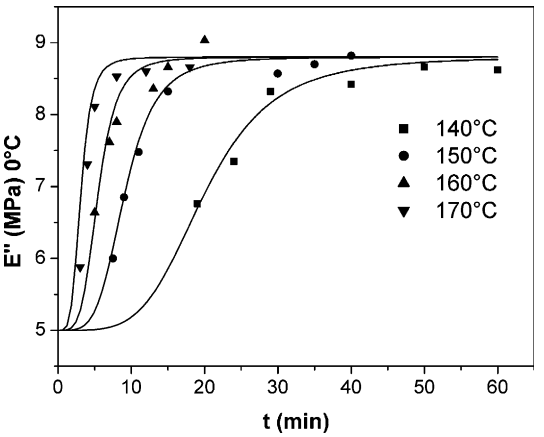

Fig. 4. Loss modulus vs. curing time. Solid lines: approximation of experimental data by Eq. (3).

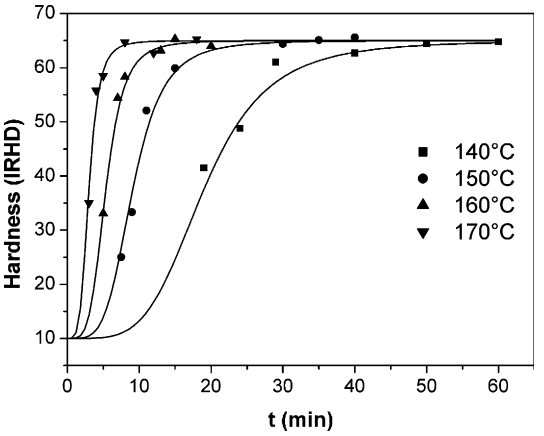

Fig. 5. Hardness (IRHD) data and model prediction (solid line), at various curing temperature.

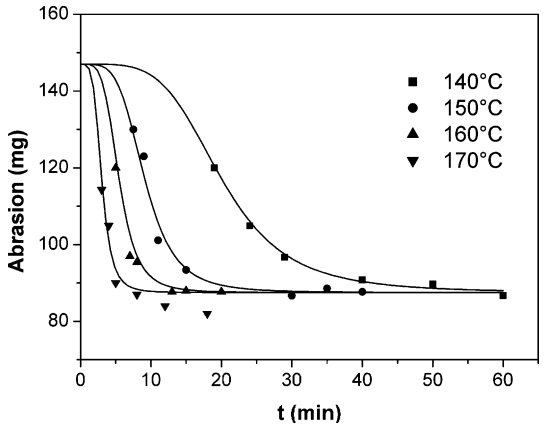

Fig. 6. Abrasion data and model prediction (solid line), at various curing temperature.

Clearly, the small discrepancy in the model prediction can be originated from intrinsic experimental errors. Moreover, this methodology requires the input of uncured data, obtained by extrapolating data in the early stage of curing, and therefore limits the accuracy of our investigation in the first vulcanization stage. On the other hand this methodology, essentially based on measuring mechanical properties of two samples vulcanized at a given reference temperature and two curing time, can be used to predict the experimental data at any isothermal curing condition.

4. Conclusions

The purpose of this work is to develop a relatively simple constitutive model able to predict the mechanical properties of silica compound cured in isothermal conditions. The model proposed, based on a very simple constitutive equation, is obtained combining rheometrical data and two mechanical properties measured at a given temperature. In this way we are able to predict the real physical properties of a sample vulcanized in isothermal conditions. One of the principle attractive features of this empirical approach is that such model can to be used in numerical simulation to predict mechanical properties evolution in non-isothermal curing process.

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