

Vulcanization kinetics study of natural rubber compounds having different formulation variables

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Abstract Vulcanization kinetics of natural rubber (NR) compounds with efficient vulcanization system was studied through phenomenological approach using the experimentally cure data obtained from a moving die rheometer. The cure kinetic parameters were defined using the proposed models by Claxton–Liska and Deng–Isayev with the support of curve fitting software. The effects of the amount of accelerators, sulfur and silica in the formulations on the cure characteristics and cure kinetic parameters at high cure temperatures were investigated. Kinetic data results showed that the above two models were able to describe the curing behaviour of the studied compounds satisfactorily. It showed that the fitting of the experimental data with Claxton–Liska and Deng–Isayev could provide a good platform to investigate the cure kinetics of the prepared NR compounds.

Keywords Rubber · Vulcanization kinetics · Fitting · Vulcanization system

Introduction

Rubber compounds are usually crosslinked by sulfur vulcanization and peroxide curing. The sulfur vulcanization is the most popular method [1, 2]. It is known that the mechanical properties of the vulcanized rubber articles are

strongly affected by the cure system and processing conditions. Efficient vulcanization (EV) system is the most suitable vulcanization system for injection moulding procedure because it provides excellent ageing resistance accompanied by appropriate scorch time and cure rate of the rubber composition in the mould cavity at high temperatures [3].

Rubber injection moulding is ideal for producing small and/or complicated parts that require precision and high productivity, or stock-fitting parts that fit inside other components [4, 5]. Compared to compression moulding technique, injection moulding can improve the uniformity of the products and permit more versatility of shape and also reduce materials cost [1, 6].

Despite the basic similarities between thermoplastics and rubber injection moulding technologies, the complication of rubber rheology, kinetic and thermal characteristics makes rubber injection moulding much more difficult to study. Therefore, the rubber injection moulding process has been somewhat neglected and the production relied mostly upon experience [2, 7, 8]. Although, natural rubber (NR) is one of the most widely used rubbers to produce diversified injection-moulded rubber products, the complicated characteristics of this kind of rubber due to their natural origin has made them difficult to study compared to other types of rubber and similar models proposed by other researches on SBR compounds could not be transferred directly to NR compounds when studying injection moulding simulation [9].

The rapid development of the computer science technologies, especially full 3D simulation software package which employs a mesh of volumetric elements as the basis for its calculations has provided a reasonable and promising solution for moulding thick, solid and complicated parts. Several injection moulding simulation studies have showed the potential of this development [8–17].

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However, the complicated material characteristics include rheological behaviour, cure kinetics and thermal behaviour of rubber compounds must be taken into account when using these softwares to simulate a reactive processing operation. Besides the primary roles of vulcanization kinetic study which are to impart the uniform cures in rubber profiles, attaining equivalent cures and achieving adequate cures in thick rubber sections are also very important to be explored to have successful simulation. Vulcanization kinetics studies provide the kinetic coefficients that are required as input for mathematical models to predict responses of rubber compound towards any type of deformation found during processing [18]. In addition, there are now increasing demands in the field of industrial process simulation, such as modelling cure behaviour of rubbers injection moulding at high temperatures.

Many mathematical models have been developed to describe vulcanization behaviour. Generally, these models could be divided into two categories, namely mechanistic kinetic approach and phenomenological or empirical approach. The mechanistic approach attempts to model and describes chemical reactions that occur during the curing process, that is, it quantifies the balance of chemical species involved in the reactions to form the mathematical relationships connecting the reaction rate path to cure time and temperature. A typical study that used this approach was the research of Ding and Leonov [19]. These authors proposed a kinetic model, which could fit well the isothermal rheometer data of NBR and NR compounds, based on the realistic model reaction scheme. As to the phenomenological or empirical approach, its basis originates from the fact that there are regression models which can fit a set of experimental data assuming a particular functional form, where the parameters are estimated from the experimental data using non-linear procedures to obtain essential parameters. In other words, the phenomenological approach is based on the experimental observations [20–22].

There are quite a number of different models to describe the cure kinetic parameters, and the main techniques used to study these parameters in previous studies involved differential scanning calorimetry (DSC), oscillating disc rheometer (ODR) and moving die rheometer (MDR). In this study, MDR technique was utilized to obtain the experimental data for the cure kinetic analysis based on Claxton–Liska and Deng–Isayev models.

Experimental

Materials

NR (SMR 20) was purchased from Kumpulan Guthrie Sdn. Bhd., Seremban, Malaysia. The grade of stearic acid used

in this study was Palmac 1500 from Acidchem International Sdn. Bhd. All other chemicals were obtained from Bayer Ltd.

Sample preparation

EV system was chosen for this study because it is considered to be suitable for injection moulding process [3]. The vulcanization characteristics and cure kinetics were investigated by varying the loading of TMTD, sulfur and silica in the compositions. The content of TMTD incorporated to the rubber compounds varied from 1.5 to 2.5 phr with the increment of 0.5 phr, the sulfur concentration was changed from 0.25 to 0.5 phr, and the silica loadings of 0, 20 and 40 phr were utilized. The combination of accelerators in which the content of CBS was maintained at 1.5 phr for all prepared compounds with the purpose to obtain sufficient induction time and desired cure rate [2, 3]. The recipes are tabulated in Table 1. The nomination is based on the ingredients content's change in the compounds, and was expressed as S_{x-y-z} , where the subscripts x is the silica loading, y is the TMTD content and z is the sulfur concentration.

The rubber was compounded at room temperature using a laboratory 2-roll mill in the size of 160 × 320 mm (model XK 160) in accordance to ASTM D 3184-80. The average time for one mixing cycle was around 25 min. The sequence of addition of compounding ingredients and the detailed time of mixing cycle are given in Table 2.

Rheometer test

The samples were characterized for their cure characteristics by means of torque curves using Monsanto MDR2000 rheometer at three different testing temperatures 160, 170 and 180 °C (433, 443 and 453 K) according to ASTM 2084-95. From the rheometer curves, scorch time (t_s), optimum curing time (t_{90}), maximum torque (M_H) and minimum torque (M_L) were obtained. These data were used to calculate the cure kinetic parameters.

Evaluation of ageing resistance of rubber compounds

To evaluate the ageing resistance of the rubber compounds at high curing temperatures, a defined parameter R_{300} was developed. R_{300} is the percentage of reversion of the rubber compound after 300 s from the time at M_H and was calculated using the following equation:

$$R_{300}(\%) = \frac{M_H - M_{300s}}{M_H} 100\% \quad (1)$$

where M_H is the maximum torque, M_{300s} is the torque after 300 s from the maximum torque.

Table 1 Compound recipes in part per hundred of rubber/phr

Sample no.	Nomination	Ingredients							
		SMR20	Zinc oxide	Stearic acid	TMQ ^a	Silica S	CBS ^b	TMTD ^c	Sulfur
1	S _{0-1.5-0.25}	100	4	2	2	–	1.5	1.5	0.25
2	S _{0-2.0-0.25}	100	4	2	2	–	1.5	2.0	0.25
3	S _{0-2.5-0.25}	100	4	2	2	–	1.5	2.5	0.25
4	S _{0-1.5-0.50}	100	4	2	2	–	1.5	1.5	0.50
5	S _{0-2.0-0.50}	100	4	2	2	–	1.5	2.0	0.50
6	S _{0-2.5-0.50}	100	4	2	2	–	1.5	2.5	0.50
7	S _{20-1.5-0.25}	100	4	2	2	20	1.5	1.5	0.25
8	S _{20-2.0-0.25}	100	4	2	2	20	1.5	2.0	0.25
9	S _{20-2.5-0.25}	100	4	2	2	20	1.5	2.5	0.25
10	S _{20-1.5-0.50}	100	4	2	2	20	1.5	1.5	0.50
11	S _{20-2.0-0.50}	100	4	2	2	20	1.5	2.0	0.50
12	S _{20-2.5-0.50}	100	4	2	2	20	1.5	2.5	0.50
13	S _{40-1.5-0.25}	100	4	2	2	40	1.5	1.5	0.25
14	S _{40-1.5-0.50}	100	4	2	2	40	1.5	1.5	0.50

^a Polymerized 2,2,4-trimethyl-1,2-dihydroquinoline

^b *N*-cyclohexyl-2benzothiazole-sulfenamide

^c Tetramethyl thiuram disulfide

Table 2 The mixing procedure and mixing time of rubber compounds

Order	Action	Time/min (based on 40 phr silica-filled NR compound)
1	Add NR (mastication)	5
2	Add ZnO and stearic acid	3
3	Add anti-oxidant	2
4	Add half silica	4
5	Add the remaining silica	4
6	Add CBS and TMTD	3
7	Add sulfur	4
Total		25

Models for characterizing the induction period

There are different definitions of induction period or scorch time for rubber compounds during injection moulding process [3, 20, 21]. In this study, scorch time was defined as the time when the test began until the time when the torque started to rise from the minimum point (M_L) due to cross-linking [20], as shown in Fig. 1. Then, the Arrhenius relationship (Eq. 2) proposed by Claxton–Liska [23] was used to fit the scorch time at three different cure temperatures of all prepared rubber compounds:

$$t_s = t_0 \exp\left(\frac{T_0}{T}\right) \tag{2}$$

where t_s is the scorch time, t_0 and T_0 are the material constants and T is the absolute temperature.

Model for describing the cure kinetic

From the cure data obtained from the rheometer curve, the state of cure (α) can be calculated using the following equation [20, 21]:

$$\alpha = \frac{M_t - M_L}{M_H - M_L} \tag{3}$$

where M_L , M_t and M_H are the minimum torque, the torque at the time t and the maximum torque, respectively.

For the purpose of injection moulding simulation, the cure kinetic parameters were determined based on the model proposed by Deng–Isayev [24]:

$$\alpha = \frac{k(t - t_s)^n}{1 + k(t - t_s)^n} \tag{4}$$

in which the rate constant k is normally expressed by an Arrhenius-type temperature dependence

$$k = k_0 \exp\left(\frac{-E_0}{RT}\right) \tag{5}$$

where t , n , k_0 , E_0 and R are time of reaction, the order of reaction, the pre-exponential factor of reaction velocity, the activation energy and the universal gas constant, respectively.

Fitting procedure

From the rheometer curve, the stages of cure of rubber compounds were obtained using Eq. 3. Then, these curves were fitted using Eq. 4 for each test temperature. For this

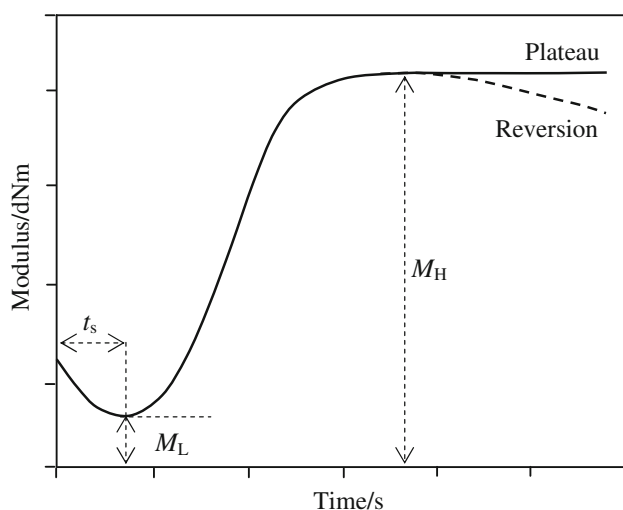


Fig. 1 Determination of induction time on MDR cure curve

fitting, it is assumed that the reaction order (n) does not vary with temperature but changes with the recipes [20, 21]. Using the Microcal Origin 7.5 software, the constants of Deng–Isayev model were determined.

Results and discussion

Vulcanization characteristics

The vulcanization characteristics of NR compounds are summarized and tabulated in Table 3.

Scorch time (t_s)

As shown in Table 3, there was a decreasing trend of scorch time when the TMTD content was increased in the recipes. However, an opposite tendency is observed when higher sulfur was introduced to rubber compounds. The incorporation of silica content led to a considerable reduction of scorch time of rubber compounds, especially with those employed 40 phr silica loading. Beyond this, it is clearly observed that the scorch time of the rubber compounds was strongly depended on the test temperature and this value decrease sharply when the test temperature was increased. The constants of Claxton–Liska model (t_0 and T_0) that used to express the scorch time of rubber compounds were calculated and represented in Table 5.

Optimum curing time (t_{90})

It can also be seen in Table 3 that the raise of accelerator and sulfur content led to the decrease of optimum cure time, however, the effect of sulfur is more visible than that of TMTD at the same test temperature. The effect of silica on

curing time is quite complex. It is found to increase at 20 phr of silica loading but significantly decrease at 40 phr. This phenomenon is in agreement of the other studies which reported the slight decrease in curing time after 30 phr silica-filled NR without using silane coupling agent [25–27]. The first reason for this may be attributed to the greater thermal history during mixing as a result of their higher compound viscosities. It is a fact that the shear heating during mixing goes up with increasing the silica loading due to the elevation of compound viscosity. The clear evidence for this explanation was given by the value of minimum torque determined from rheometer cure curves. It is obvious that compounds having higher silica content presented higher minimum torques, indicating higher viscosities compared to others. The second reason may come from the adsorption of activators and accelerators by silanol groups on the silica surface. Finally, the decrease could be originated from the silica conductivity and over loading, which cause a faster heat generation in compound and hence faster curing.

Similar to scorch time, the effect of test temperature on the cure time is remarkable. This value at 160 °C could be shortened significantly and remained two-third (2/3) at 170 °C and one-third (1/3) at 180 °C.

Maximum modulus (M_H)

As observed in Table 3, M_H increases with higher dosage of TMTD, higher amount of sulfur and higher silica loading. These effects show similar trend for the three testing temperatures. TMTD, besides the function of accelerator, can work as sulfur donor during vulcanization resulting in higher crosslink density and higher M_H . This also causes approximate M_H values between $S_{0-2.5-0.25}$ and $S_{0-1.5-0.50}$, $S_{20-2.5-0.25}$ and $S_{20-1.5-0.50}$ despite the difference in sulfur loading. The higher amount of sulfur provides more crosslink in the rubber and higher M_H . The increase of M_H with silica loading is expected, and it is projected to be due to the reinforcing role of silica in rubber compounds [27].

Reversion resistance (R_{300})

The reversion of the rubber compounds increased when higher test temperatures were applied, noticeably a considerable reversion degree was revealed in some compounds at 180 °C (refer to Table 3; Fig. 2). The same behaviour can also be found with increasing silica content in the compositions. The effect of silica became significant for those compounds with low contents of TMTD, which caused remarkable change in R_{300} values obtained from $S_{20-1.5-0.25}$, $S_{20-1.5-0.50}$, $S_{40-1.5-0.25}$ and $S_{40-1.5-0.50}$ as shown in Fig. 3. The reason for this phenomenon is that compounds with low content of TMTD have low crosslink densities. Therefore,

Table 3 The cure characteristics of compositions

Sample	T/K	M_L /dNm	M_H /dNm	t_c /s	t_{90} /s	$R_{300}/\%$
S _{0-1.5-0.25}	433	0.02	4.31	63.7	185.7	0.00
	443	0.03	4.17	43.2	118.6	0.00
	453	0.01	3.68	34.3	78.5	2.17
S _{0-2.0-0.25}	433	0.04	4.82	50.5	186.4	0.00
	443	0.03	4.67	34.1	118.6	0.00
	453	0.08	4.38	28.3	71.1	2.05
S _{0-2.5-0.25}	433	0.04	5.53	47.6	177.8	0.00
	443	0.04	5.31	29.7	118.6	0.00
	453	0.04	4.99	21.7	72.5	1.00
S _{0-1.5-0.50}	433	0.02	5.27	65.4	173.6	0.00
	443	0.01	5.24	42.8	110.1	0.00
	453	0.03	4.99	30.8	67.7	3.61
S _{0-2.0-0.50}	433	0.04	5.68	60.1	168.8	0.00
	443	0.03	5.62	39.5	101.6	0.00
	453	0.04	4.92	29.9	67.9	2.44
S _{0-2.5-0.50}	433	0.02	6.19	48.2	161.2	0.00
	443	0.02	6.01	35.2	100.5	0.00
	453	0.01	5.97	22.9	65.3	2.51
S _{20-1.5-0.25}	433	0.04	5.33	63.7	199.8	0.00
	443	0.11	4.93	42.5	117.3	2.84
	453	0.09	4.67	32.1	71.5	7.92
S _{20-2.0-0.25}	433	0.04	6.30	48.2	201.1	0.00
	443	0.08	6.22	32.5	117.4	1.29
	453	0.02	5.09	27.7	70.6	5.30
S _{20-2.5-0.25}	433	0.09	7.01	42.8	201.1	0.00
	443	0.04	6.33	27.1	121.7	0.95
	453	0.07	6.03	21.8	76.3	3.98
S _{20-1.5-0.50}	433	0.04	6.82	63.9	182.5	1.03
	443	0.04	6.28	42.7	101.5	3.03
	453	0.09	5.79	31.9	61.6	9.33
S _{20-2.0-0.50}	433	0.06	7.50	58.7	163.5	0.00
	443	0.07	7.03	37.1	102	2.85
	453	0.07	6.40	27.3	64.2	4.69
S _{20-2.5-0.50}	433	0.03	8.02	44.6	169.4	0.00
	443	0.04	7.47	24.1	116.1	1.87
	453	0.12	7.36	22.3	66.8	2.45
S _{40-1.5-0.25}	433	3.12	11.96	42.5	118.9	0.00
	443	2.10	9.90	29.7	72.3	3.03
	453	2.00	8.76	21.2	51.1	8.90
S _{40-1.5-0.50}	433	2.59	14.25	42.6	107.4	0.00
	443	2.41	12.91	34.1	65.8	2.87
	453	2.44	12.43	21.5	44.5	8.37

the rubber chains could reduce the filler holding capacity under the dynamic movement of rheometer rotor leading to lower M_{300s} to be retained and higher R_{300} . The reversion study showed that the use of EV system and TMTD accelerator had positive effect on improving the reversion resistance of NR compounds at high-temperature processing.

Fitting parameters

The fitting parameters of all compounds using Deng–Isayev model are shown in Table 4. Experimental data with their respectively fitting curves at three testing temperature of compounds S_{0-1.5-0.05} and S_{20-1.5-0.25} are shown in

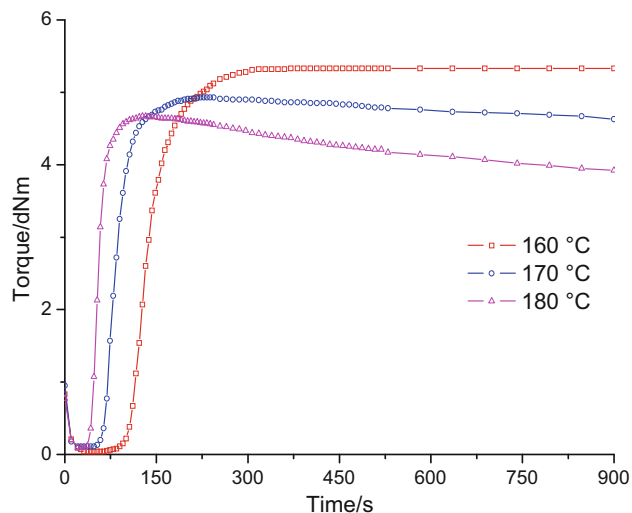


Fig. 2 Crosslinking conversion and reversion by time of sample $S_{20-1.5-0.25}$ at different curing temperatures

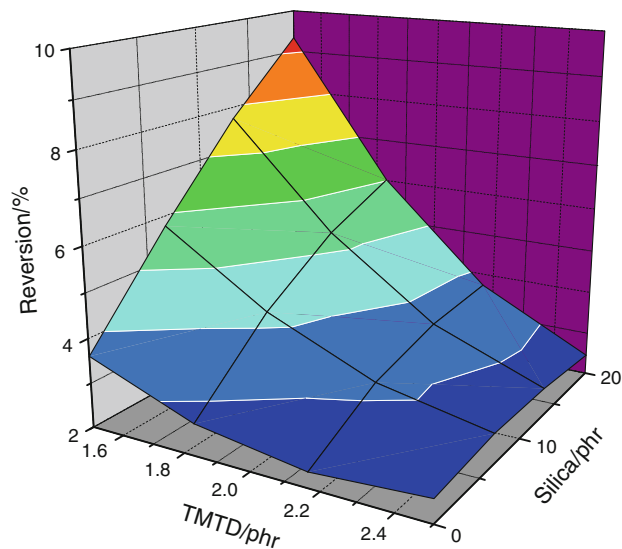


Fig. 3 The effect of TMTD and silica content on R_{300} of compounds at 0.5 phr S and test temperature 180 °C

Fig. 4a, b. It can be observed that the fitting curves at high testing temperature (453 K) show better agreement with experimental data compared to that at lower testing temperature (433 K). At high curing temperature, the curing time is faster resulting less number of practical points can be obtained, which are also almost in-line with each other and therefore makes the fitting to be more accurate. The degree of fit for the fitting procedure is verified based on the coefficient of determination, R^2 . As observed in Table 4, all the R^2 are very close to unity, therefore, it could be said that the Deng–Isayev model is able to describe very well the experimental vulcanization characteristics data of all studied compounds during the fitting process.

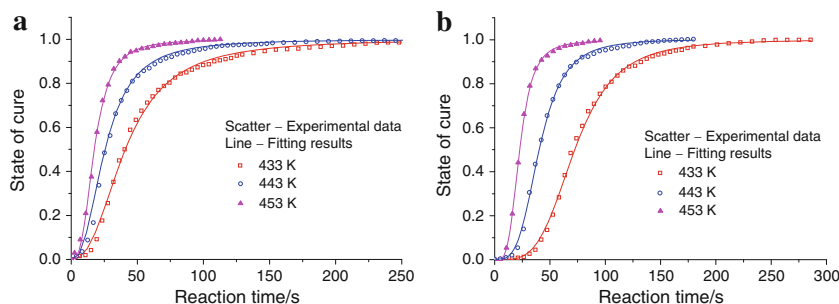
Table 4 Deng–Isayev model's fitting coefficients n , k

Sample	T/K	n	$k \times 10^{-6}/s^{-1}$	R^2
$S_{0-1.5-0.25}$	433	3.194	2.43	0.997
	443		9.64	0.996
	453		50.00	0.999
$S_{0-2.0-0.25}$	433	3.570	0.28	0.997
	443		1.70	0.996
	453		10.00	0.999
$S_{0-2.5-0.25}$	433	3.759	0.15	0.997
	443		0.61	0.996
	453		3.74	1.000
$S_{0-1.5-0.50}$	433	2.453	110.00	0.998
	443		360.00	0.996
	453		990.00	0.996
$S_{0-2.0-0.50}$	433	3.129	6.38	0.996
	443		20.00	0.996
	453		100.00	0.999
$S_{0-2.5-0.50}$	433	3.488	0.90	0.995
	443		5.29	0.997
	453		20.00	0.999
$S_{20-1.5-0.25}$	433	3.699	0.13	0.997
	443		1.13	0.999
	453		10.00	0.999
$S_{20-2.0-0.25}$	433	4.013	0.02	0.997
	443		0.21	0.998
	453		1.97	1.000
$S_{20-2.5-0.25}$	433	4.141	0.01	0.997
	443		0.08	0.998
	453		0.63	0.999
$S_{20-1.5-0.50}$	433	3.381	1.22	0.996
	443		10.00	0.999
	453		70.00	0.996
$S_{20-2.0-0.50}$	433	3.821	0.28	0.999
	443		1.65	0.998
	453		10.00	1.000
$S_{20-2.5-0.50}$	433	4.056	0.04	0.997
	443		0.16	0.999
	453		3.04	1.000
$S_{40-1.5-0.25}$	433	4.493	0.03	0.999
	443		0.41	0.999
	453		2.30	0.999
$S_{40-1.5-0.50}$	433	4.302	0.15	0.997
	443		3.51	0.999
	453		8.07	0.999

Order of reaction (n)

When analyzing the variation of n , as shown in Table 4, with the changes of accelerator and sulfur content, there were two different behaviours. If the amount of sulfur is fixed in the recipes, n increases as the accelerator amount

Fig. 4 Cure kinetic fitting curves of sample $S_{0-1.5-0.50}$ (a) and sample $S_{20-1.5-0.25}$ (b) using Microcal Origin software



increases. On the other hand, if the amount of accelerator is the same and the content of sulfur increases, the value of n decreases (Fig. 5).

The effect of silica content obviously affected the reaction order (Fig. 6). The n value increased considerably when the silica content was increased from 0 to 20 phr and continuously rising sharply at 40 phr despite of the high sulfur concentration. This result was in agreement with the curing time, which showed very short t_{90} were obtained from $S_{40-1.5-0.25}$ and $S_{40-1.5-0.50}$. This also explains the steepest slope of $S_{40-1.5-0.50}$ cure kinetics curve as compares to those of $S_{0-1.5-0.50}$ and $S_{20-1.5-0.50}$ (Fig. 7).

Reaction rate constant (k) and activation energy (E_0)

As expected, based on Eq. 5, the reaction rate constant, k , is directly proportional to temperature, hence, three values of k for each testing temperature are reported (Table 4). However, this value went down with increasing the accelerator and silica content. In contrast, k increased significantly with sulfur content. The latter behaviour reflects well the vulcanization process in which the higher amount of sulfur is used, the higher crosslink reactions can occur.

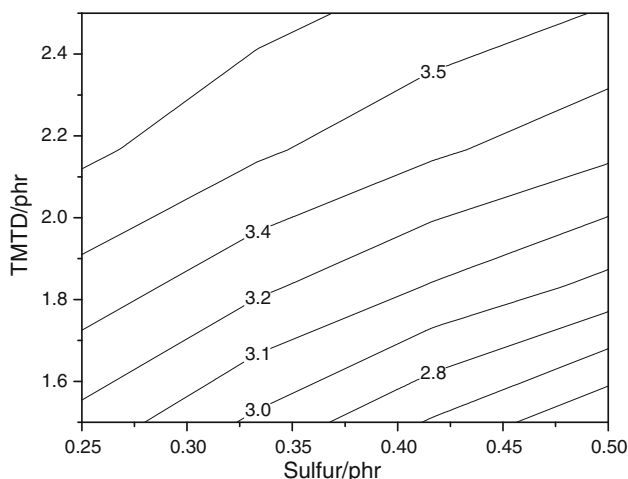


Fig. 5 Variation of n value of non-silica-filled compounds

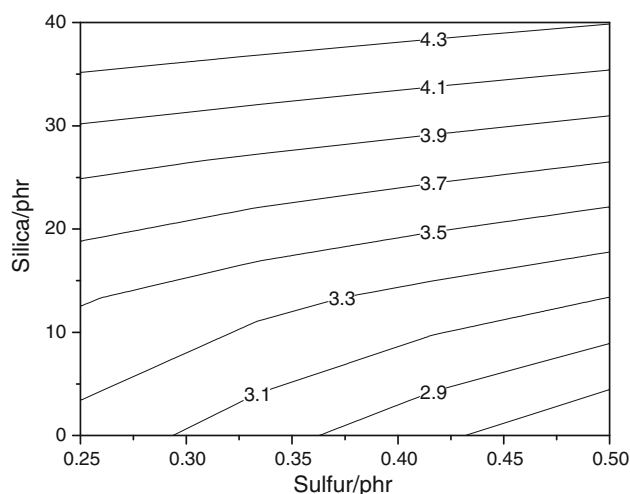


Fig. 6 Variation of n value of compounds employed 1.5 phr TMTD

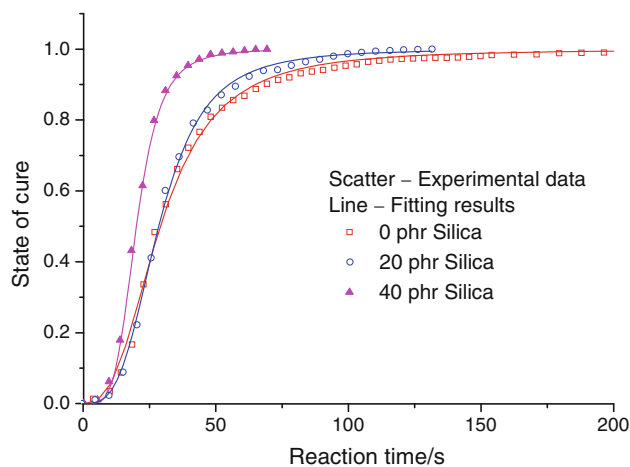


Fig. 7 Dependence of cure kinetics fitting curves on silica of rubber compound employed the same cure system (CBS:TMTD:S = 1.5:1.5:0.5) at cure testing 443 K

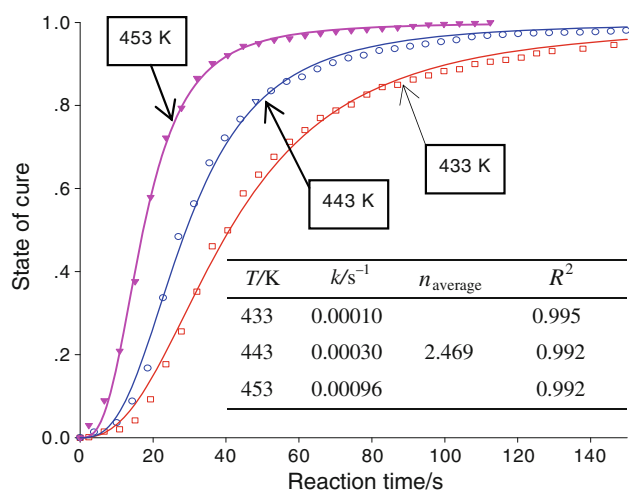
The dependence of the activation energy, E_0 , on the curing system, i.e., the amount of accelerator and sulfur were inconsistent. However, the effect of silica filler on the activation energy of the compounds is more visible (Table 5). The higher the content of silica employed, the higher the E_0 value for the compositions. It could be attributed to the silica

Table 5 The coefficients of Claxton–Liska model t_0 , T_0 and Deng–Isayev models k_0 , E_0

Sample	$t_0 \times 10^{-6}/s$	$T_0 \times 10^3/K$	k_0/s^{-n}	$E_0 \times 10^5/J \text{ mol}^{-1}$
S _{0-1.5-0.25}	49.40	6.08	1.17E + 24	2.46
S _{0-2.0-0.25}	95.20	5.69	2.71E + 28	2.90
S _{0-2.5-0.25}	0.85	7.71	6.76E + 24	2.63
S _{0-1.5-0.50}	2.49	7.39	4.71E + 17	1.79
S _{0-2.0-0.50}	7.82	6.86	6.30E + 21	2.24
S _{0-2.5-0.50}	2.05	7.29	3.40E + 24	2.53
S _{20-1.5-0.25}	11.10	6.73	3.35E + 35	3.52
S _{20-2.0-0.25}	159.00	5.45	1.46E + 37	3.72
S _{20-2.5-0.25}	9.19	6.63	2.22E + 32	3.34
S _{20-1.5-0.50}	9.08	6.82	8.28E + 38	3.20
S _{20-2.0-0.50}	1.66	7.52	2.54E + 28	2.89
S _{20-2.5-0.50}	5.71	6.84	1.19E + 35	3.53
S _{40-1.5-0.25}	6.11	6.82	5.01E + 34	3.50
S _{40-1.5-0.50}	8.69	6.69	4.62E + 32	3.26

thermal conductivity which projected that heat would go to silica first and latter to NR. Consequently, higher activation energy was required to get the sufficient curing level. Moreover, the increase of compound's stiffness could lead to the elevation of activation energy which seems to be a reasonable explanation. In addition, the activation energy has close relationship with the network structure formed during vulcanization process [21]. The slight variation of activation energy values indicated the possibility that the network structures, in which monosulfidic crosslinks took superior in quantity, where no remarkable difference was detected between the compositions.

Finally, Sigmaplot 11.0 software was employed for verification purpose. Figure 8 presents the result of Deng–Isayev model fitting (solid line) with the experimental data (dot) of sample S_{0-1.5-0.5} achieved with Sigmaplot 11.0 software. The fitting results obtained with this software

**Fig. 8** Cure kinetics fitting curves of sample S_{0-1.5-0.50} using Sigmaplot 11.0

were generally in good agreement with the parameters determined with Microcal Origin software as explained in the experimental section and all the vulcanization kinetic parameters were comparable with those of rubber compounds available in several commercial flow simulation material databases for elastomers.

Conclusions

The data obtained from MDR measurements can be used to investigate the cure kinetics of NR compounds having different formulation compositions that can be further used for injection moulding simulation purpose. It was discovered that the order of reaction, n , increased with the amount of accelerators and the loading of silica and decreased with the sulfur level. The rate constant, k , was adversely affected by these factors. The activation energy values seem to be independent of the cure systems employed, but these values had correlations to the silica contents used. In the range of cure systems used in this study, the network structures were estimated to be not much different between different compounds. Finally, the Claxton–Liska model and Deng–Isayev model, respectively, were able to describe very well the induction period and the curing process of NR compounds under specific conditions that are applied during injection moulding process.

References

1. Mark JE, Erman B, Eirich FR. The Science of rubber compounding in the science and technology of rubber, 3rd ed. Amsterdam: Elsevier; 2005. p. 401–54.

2. Gent AN. *Materials and compounds in engineering with rubber: how to design rubber components*. Munich: Hanser Verlag; 2001. p. 19–21.
3. Lindsay JA. *Rubber injection moulding: a practical guide, vol. 1. Rapra review report*; 1999.
4. Osswald TA, Turng L-S, Gramann PJ. *Injection molding materials in injection molding handbook, 2nd ed.* Munich: Hanser Verlag; 2008. p. 51–2.
5. Isayev AI. *Injection and compression moulding fundamentals*. New York: Marcel Dekker; 1987. p. 436.
6. Top 50 Innovations 1955–2005. *Injection moulding simulation*. *Plastics technology Gardner publications*; 2005.
7. Śliwa A, Matula M, Dobrzański LA. Finite element method application for determining feedstock distribution during powder injection moulding. *J Achiev Mater Manuf Eng*. 2009;37:584–91.
8. Kennedy PK. *Practical and scientific aspects of injection moulding simulation*. Technische Universiteit Eindhoven; 2008.
9. Isayev AI, Wan M. Injection moulding of a natural rubber compound: simulation and experimental studies. *Rubber Chem Technol*. 1998;71:1059–72.
10. Rafei M, Ghoreishy MHR, Naderi G. Development of an advanced computer simulation technique for the modeling of rubber curing process. *Comput Mater Sci*. 2009;47(2):539–47.
11. Cardozo D. A brief history of the filling simulation of injection moulding. *Mech Eng Sci*. 2009;223:711–21.
12. Kvas K, Staněk M, Mañas M, Mañas D, Křůmal M, Holík Z. Simulation of rubber injection molding process. *PMA 2011 & RubberCon 2011*. Bratislava, Slovakia, Chem Listy. 2011;105:354–56.
13. Cardozo D. Three models of the 3D filling simulation for injection moulding: a brief review. *J Reinf Plast Compos*. 2008;27:1963–74.
14. Ramorino G. *Injection moulding simulation of engineering rubber components. Modelling of Elastomeric Materials and Products Conference*, London; 2010.
15. Haberstroh E, Michaeli W, Henze E. Simulation of the filling and curing phase in injection moulding of liquid silicone rubber (LSR). *J Reinf Plast Compos*. 2002;21:461–71.
16. Sykutera D, Bielinski M. The use of injection moulding process simulation software Cadmould for injection mould designing. *J Pol CIMAC*. 2010;5:207–13.
17. Atre SV, Park SJ, Zauner R, German M. Process simulation of powder injection moulding: identification of significant parameters during mould filling phase. *Powder Metall*. 2007;50:76–85.
18. Nichetti D. Determination of mechanical properties of silica compounds using a curing kinetic model. *Eur Polym J*. 2004;40:2401–5.
19. Ding R, Leonov AI. A kinetic model for sulfur accelerated vulcanization of natural rubber compound. *J Appl Polym Sci*. 1996;61:455–63.
20. Arrillaga A, Zaldua AM, Atxurra RM, Farid AS. Techniques used for determining cure kinetics of rubber compound. *Eur Polym J*. 2007;43:4783–99.
21. Marzocca AJ, Mansilla MA. Vulcanization kinetic of styrene–butadiene rubber by sulfur/TBBS. *J Appl Polym Sci*. 2006;101:35–41.
22. Shojaei A, Abbasi F. Cure kinetics of a polymer-based composite friction material. *J Appl Polym Sci*. 2006;100:9–17.
23. Claxton WE, Liska JW. Calculation of state of cure in rubber under variable time–temperature conditions. *Rubber Age*. 1964;95(2):237.
24. Isayev AI, Deng JS. Non isothermal vulcanisation of rubber compounds. *Rubber Chem Technol*. 1988;61(2):340.
25. Choi S-S, Nah C, Jo B-W. Properties of natural rubber composites reinforced with silica or carbon black: influence of cure accelerator content and filler dispersion. *Polym Int*. 2003;52:1382–9.
26. Choi S-S. Influence of the silica content on rheological behavior and cure characteristics of silica-filled styrene–butadiene rubber compound. *Polym Int*. 2001;50:524–30.
27. Rattanasom N, Saowapark T, Deeprasertkul C. Reinforcement of natural rubber with silica/carbon black hybrid filler. *Polym Test*. 2007;26:369–77.