



Effect of Paraffinic Oil Plasticizer Addition on Kinetics of Rubber Vulcanization Based on Kamal-Sorour and Deng-Isayev Models

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Abstract

Plasticizer is an essential component in rubber compounding, characterized by the ability to reduce compound viscosity, improve the dispersion of additives, and significantly affect processing efficiency and vulcanization kinetics. Therefore, this study aimed to investigate the vulcanization kinetics of styrene butadiene rubber (SBR) with varying amounts of paraffinic oil plasticizer. The experimental procedures included mixing rubber and additives, followed by compound testing using a rheometer. The kinetic parameters of the Deng-Isayev and Kamal-Sorour models were determined using the sum of squared error (SSE) optimization of the rheological data. The results showed that increasing the vulcanization temperature and reducing plasticizer content caused a decrease in induction time (t_{s2}) and optimum vulcanization time (t_{c90}). Furthermore, the experimental data were accurately modeled using the Kamal-Sorour model. The vulcanization reaction occurred concurrently with the predominance of the autocatalysis mechanism ($k_2 > k_1$), while the values of m and n were inversely proportional to the amount of plasticizer. The vulcanization reaction was primarily influenced by the initial reactant compound rather than the catalytic effect on the product reaction ($n > m$), showing that high plasticizer content increased energy requirement ($E_2 > E_1$) for autocatalytic reactions.

Keywords: Paraffinic oil, Rubber, Vulcanization kinetics, Deng-Isayev, Kamal-Sorour.

1. Introduction

Rubber vulcanization is a complex multistage reaction between rubber and various additives, causing changes in physical and mechanical properties. This process requires heat input to convert an unformed elastomeric compound into an elastic material, thereby the cost of the final product is closely related to the energy consumption during vulcanization. Excessively rapid vulcanization increases compound viscosity and restricts flow, potentially causing defects such as scorch, while overly slow process reduces production efficiency [1].

Previous studies on vulcanization kinetics provide essential information for controlling and optimizing curing cycles to achieve uniform curing in rubber products [2–4]. Specifically, kinetic modeling enables detailed characterization of curing behavior [3] and prediction of optimal curing time [5,6]. Vulcanization reactivity has also been evaluated using various methods, including mechanical testing, swelling analysis, calorimetry, stress relaxation, rheological measurements, and chemical analysis [7–9]. Among these methods, rheological torque-time curves are most widely applied due to practicality and ability to describe stiffness evolution during isothermal curing, which is directly related to vulcanization conversion (α) [10].

Vulcanization kinetics have been investigated for various systems, including different rubber types and mixtures [11], systems [12], fillers [13,14], and plasticizer [15–17]. Compared to others, plasticizer is incorporated

into rubber compounds to reduce viscosity, impart softness, and provide a lubrication effect, thereby facilitating processing and improving the dispersion of other additives [18]. Previous studies have shown that plasticizer with specific oxirane values can influence vulcanization behavior [17], with the optimum torque being inversely proportional to the amount of modified soybean oil plasticizer [16]. However, systematic information regarding the effect of plasticizer amount on vulcanization kinetic parameters remains limited, particularly in terms of reaction rate constants and reaction orders.

To address the limitation, the curing behavior of thermoset polymers has been effectively analyzed using the Kamal-Sorour and Deng–Isayev kinetic models. Specifically, the Kamal-Sorour model describes curing as a complex process comprising simultaneous reactions, where the reaction product can autocatalyze other reactions [19,20]. In comparison, the Deng-Isayev model assumes that the reaction rate is proportional to the concentrations of both unreacted and reacted species [21]. Building on the theoretical framework, this study offers new kinetic insights into rubber vulcanization by systematically correlating plasticizer amount with key kinetic parameters through two widely accepted kinetic models, providing a quantitative basis for optimizing curing conditions. The kinetic models are used to systematically evaluate the effect of plasticizer amount on vulcanization kinetic parameters, including reaction rate constants, reaction orders, and activation energies, based on rheological data.

2. Materials and methods

2.1 Materials preparation

Table 1 shows the rubber compound formula used in this study, with the quantity of each component denoted in per hundred rubber (phr). For the experiment, ingredients used were weighed based on the compound formulation. SBR was initially masticated using a two-roll mill machine (Y315H-6 LEADGO), followed by the addition of carbon black and paraffinic oil. Stearic acid and zinc oxide were mixed with the compound, which was added with TMTD and DPG, as well as sulfur, in the final mixing sequence.

Table 1 Rubber compound formula.

Materials	Amount (phr)			
	Compound A	Compound B	Compound C	Compound D
Styrene butadiene rubber (SBR) Indopol	100	100	100	100
Carbon black N330 Dimacolor group	30	30	30	30
Zinc oxide C041605 HM Chemical Technology Co., Ltd	5	5	5	5
Stearic Acid DK-1838 Henan Yeedok Industry Co., Ltd.	1	1	1	1
1,3-diphenylguanidine (DPG)	2.5	2.5	2.5	2.5
Tetramethylthiuram disulfide (TMTD) S2431 Selleckchem	1	1	1	1
Sulfur CAS No. 1326-66-7 OEM	1.5	1.5	1.5	1.5
Paraffinic oil	0	3	5	7

2.2 Rheology test

Rubber compound was analyzed using a moving die rheometer under isothermal conditions. Rheology tests (Gotech GT-M2000-AN moving die rheometer) were performed at 150°C, 160°C, and 170°C to monitor the curing reaction over time at a constant temperature, with the mechanical characteristics showing crosslinking during the process. The rheology testing procedure followed ASTM D5289 and the International Standard ISO 6502. Subsequently, a moving die rheometer was used to measure a material's torsional response during the vulcanization process, which produced an autographic response separating the elastic and viscous torsional readings. The vulcanization curve refers to the elastic response obtained. Both the rubber compounding process and the rheological tests were conducted in triplicate to ensure data reliability, and the rheological data were analyzed using a one-way ANOVA method.

2.3 Kinetic study

The Kamal-Sorour is an empirical model of the curing reaction rate as expressed in Equation 1, which combines autocatalysis and n^{th} -order models [19,20]. The degree of curing or conversion (α) in the Kamal-Sorour model is calculated using Equation 2 [19].

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

$$\alpha = \frac{M_t - M_L}{M_H - M_L} \quad (2)$$

m and n are the reaction orders, k_1 and k_2 are the rate constants of the n th-order reaction and autocatalysis, respectively, and t is the reaction time. M_L , M_t , and M_H are the minimum torque, torque at time t , and maximum torque, respectively.

The degree of curing in the Deng-Isayev model of isothermal curing calculated using Equation 3. The reaction rate of vulcanization in the Deng-Isayev model is expressed using Equation 4 [21].

$$\alpha = \frac{k(t - t_{s2})^n}{1 + k(t - t_{s2})^n} \quad (3)$$

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

n , t , t_{s2} , and k respectively the reaction order, reaction time, scorch time, and curing reaction rate constants, respectively.

Output data obtained from measurements using a moving die rheometer at each temperature included minimum torque (M_L), torque at time t (M_t), maximum torque (M_H), scorch time (t_{s2}), and optimum vulcanization time (t_{c90}). To obtain the degree of curing or conversion of experimental data (α_e), the output data were processed using Equations 2 and 3. Meanwhile, Equations 1 and 4 were used to determine the kinetic parameters of the Deng-Isayev model (k and n) and the Kamal-Sorour model (k_1 , k_2 , m , dan n), respectively. Equation 1 and Equation 4 were differentiated using the *ode45* tool and optimized with multivariate sum of squared error (SSE) through the *fminsearch* tool in the open-source software (online MATLAB). Figure 1 shows the computational algorithms of the Kamal-Sorour and Deng-Isayev models.

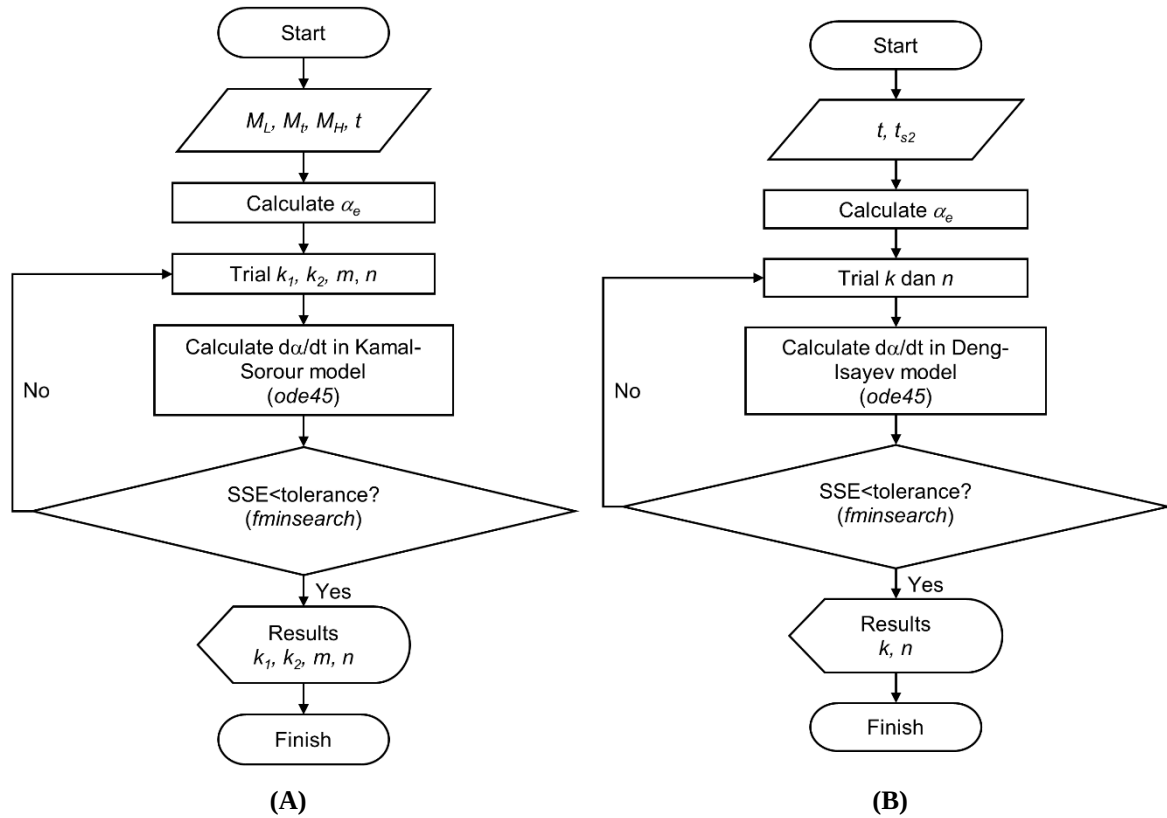


Figure 1 Model optimization computation algorithm (A) Kamal-Sorour (B) Deng-Isayev

The computation algorithms for the Kamal-Sorour and Deng-Isayev models are shown in Figure 1. Despite showing proficiency in examining the vulcanization process during the curing period, these models are not ideal for analyzing the induction period or pre-scorch time (t_{s2}) [11]. The limitation occurs because both models are constructed without considering the inversion phenomenon [1,22]. Therefore, data from the time of induction and reversion are not used in the calculations.

The activation energy (E) and curing reaction rate factor (A) were determined using the Arrhenius Equation (Equation 5), which calculated the curing reaction rate constant (k) at different temperatures. The gas constant (R) is 8.31 J/mol.K.

$$k = Ae^{-\frac{E}{RT}} \quad (5)$$

3. Results and Discussion

3.1 Vulcanization characteristics

Compound tests using a rheometer produced data in the form of rheology curves, which described the relationship between torque and time ($M=f(t)$). Figure 2 shows the rheology curve of various types of compounds at 150°C. Furthermore, the rheology test provided data on vulcanization characteristics, including minimum torque (M_L), maximum torque (M_H), induction time (t_{s2}), optimum vulcanization time (t_{c90}), and maximum vulcanization time ($t_{@MH}$), as presented in Table 2. The rheology curve showed a series of stages for each type of compound at various test temperatures. Based on observation, the torque initially decreased to its minimum point, followed by an increase over time, and gradually reduced after reaching the maximum point. This fluctuation was classified into four distinct stages, namely softening, induction, curing, and reversion. The softening stage is the initial phase during which the compound starts absorbing heat from the rheometer die and becomes soft. This is shown by a decreasing viscosity value, which leads to the rheometer die section measuring a decrease in torque value, from the initial torque (M_0) at the initial time (t_0) to the minimum torque (M_L) at the lowest time (t_L).

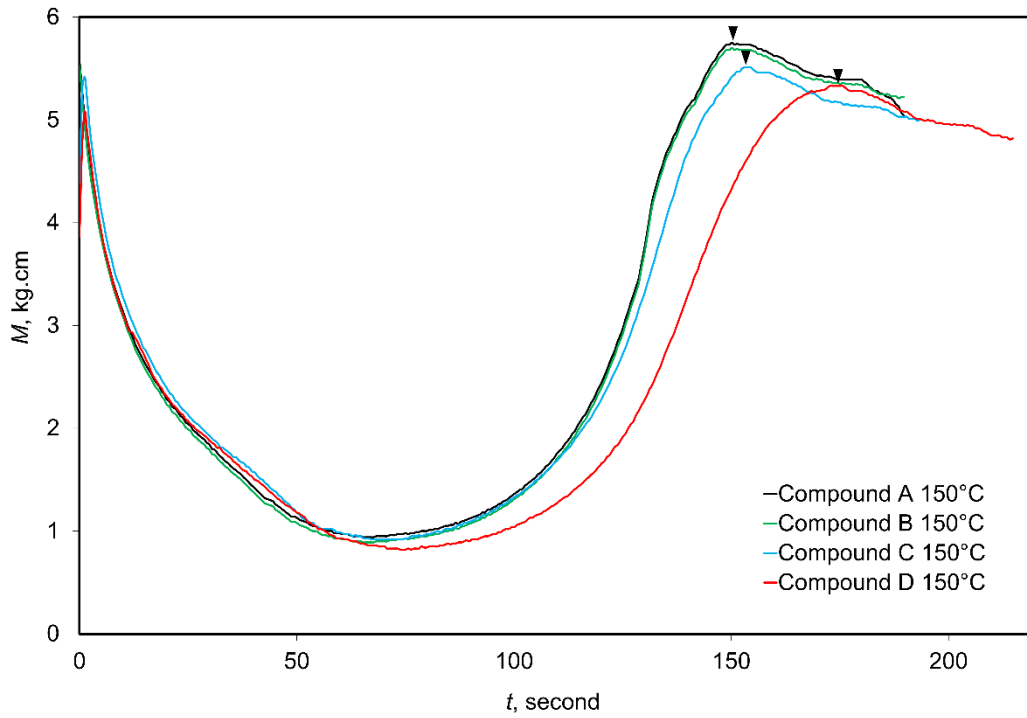


Figure 2 Rheological curve of compounds at 150°C

The vulcanization process started with an induction stage, characterized by the minimum torque (M_L) and the induction time (t_{s2}), as shown in Table 2. During this stage, chemical reactions proceed slowly, and crosslink formation has not become dominant. Furthermore, increasing the vulcanization temperature from 150°C to 170°C consistently reduced t_{s2} for all compounds, confirming that higher temperatures accelerated the onset of vulcanization. This behavior showed the temperature-dependent kinetics of sulfur vulcanization, where increased thermal energy enhanced molecular mobility and reaction rate constants, in line with previous studies [17]. As stated in the literature, the duration of induction is directly proportional to the quantity of Tudalen 65, an aromatic oil plasticizer [23]. This faster vulcanization is attributed to the increasing value of the reaction constant with the rise in vulcanization temperature [24]. At higher temperatures, the rate of molecular movement accelerates, leading to faster cross-link formation reactions [25].

Table 2 Rheological test results.

Vulcanization Characteristic	Compound A	Compound B	Compound C	Compound D
Paraffinic oil	0 phr	3 phr	5 phr	7 phr
Vulcanization temperature, 150°C				
M_L , kg.cm	0.99±0.01 ^a	0.98±0.01 ^a	0.92±0.01 ^b	0.82±0.00 ^c
M_H , kg.cm	5.76±0.01 ^a	5.75±0.01 ^a	5.51±0.01 ^b	5.33±0.00 ^c
t_{s2} , second	127±0.00 ^a	127±0.58 ^a	129±0.00 ^b	138±0.58 ^c
t_{c90} , second	140±0.58 ^a	141±0.58 ^a	144±0.58 ^b	157±1.00 ^c
$t_{@MH}$, second	152±0.58 ^a	153±0.58 ^a	165±1.00 ^b	174±1.53 ^c
Vulcanization temperature, 160°C				
M_L , kg.cm	0.96±0.58 ^a	0.95±0.00 ^a	0.91±0.01 ^b	0.77±0.02 ^c
M_H , kg.cm	5.69±0.01 ^a	5.68±0.01 ^a	5.49±0.01 ^b	4.74±0.02 ^c
t_{s2} , second	96±0.00 ^a	96±0.58 ^a	97±0.58 ^b	103±1.00 ^c
t_{c90} , second	102±0.58 ^a	103±0.00 ^a	109±1.53 ^b	114±1.00 ^c
$t_{@MH}$, second	111±0.58 ^a	112±0.58 ^a	118±1.00 ^b	133±2.00 ^c
Vulcanization temperature, 170°C				
M_L , kg.cm	1.12±0.01 ^a	1.12±0.01 ^a	0.97±0.00 ^b	0.83±0.02 ^c
M_H , kg.cm	6.39±0.01 ^a	6.38±0.01 ^a	6.25±0.01 ^b	5.18±0.00 ^c
t_{s2} , second	77±0.00 ^a	77±0.00 ^a	79±0.00 ^b	82±0.58 ^c
t_{c90} , second	87±0.58 ^a	88±0.00 ^a	90±0.58 ^b	93±0.58 ^c
$t_{@MH}$, second	94±1.00 ^a	95±1.53 ^a	111±0.58 ^b	129±1.53 ^c

Note: Different superscript letters show statistically significant differences

The inclusion of Compound A (0 phr paraffinic oil) provides a clear baseline for evaluating the plasticization effect. At all vulcanization temperatures, Compounds A and B (3 phr) showed statistically similar t_{s2} , t_{c90} , M_L , and M_H values. This result showed that the addition of paraffinic oil at 3 phr did not significantly alter the vulcanization kinetics or torque characteristics compared to the unplasticized compound. The rheological similarity between Compounds A and B is also evident in the torque-time curves in Figure 2.

In comparison, an additional increase in the paraffinic oil content to 5 phr and 7 phr (Compounds C and D) caused a statistically significant change in both torque and curing time. As the plasticizer content increased beyond 3 phr, M_L and M_H decreased significantly, showing reduced compound viscosity and lower effective crosslink density. This reduction in torque showed the plasticization effect of paraffinic oil, which enhanced chain mobility and softened the vulcanized rubber matrix [16].

The curing characteristics were similarly affected, as showed by the results. Compounds C and D showed longer t_{s2} and t_{c90} values compared to Compounds A and B at all temperatures, suggesting a retardation of the vulcanization reaction. This behavior can be attributed to the partial absorption of accelerators (DPG and TMTD) into the oil phase at higher plasticizer loadings, reducing availability in the rubber matrix and consequently slowing crosslink formation [26,27]. The results show the presence of a critical plasticizer threshold, above which the vulcanization kinetics are significantly altered.

After reaching the maximum torque (M_H), a decline in torque was observed in all compounds (Figure 2 and Table 2). The decline served as the beginning of reversion, which became more pronounced at higher temperatures, as shown by decreasing maximum time ($t_{@MH}$) values with increasing vulcanization temperature. This phenomenon is associated with the thermal breakdown of polysulfide crosslinks into shorter and more stable mono- and disulfide bonds [17]. However, compounds containing higher amounts of paraffinic oil (C and D) showed longer $t_{@MH}$ values than Compound A, suggesting that plasticization delayed the reversion process by maintaining greater chain flexibility. At higher temperatures, the effect of temperature remained dominant over formulation differences.

3.2 Vulcanization kinetics model

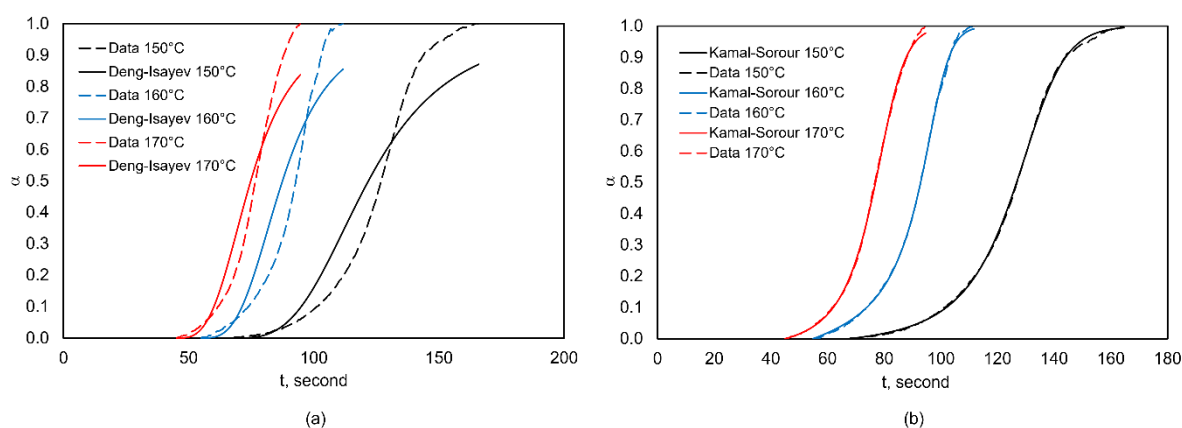
The relationship between the degree of curing or conversion (α) and time (t) at vulcanization temperatures of 150, 160, and 170°C is presented in Figure 3. The conversion (α) represents the extent of crosslink formation during vulcanization. Based on observation, higher vulcanization temperatures led to faster conversion rates, as shown by steeper α - t curves and shorter times to reach complete curing ($\alpha = 1$). At lower temperatures, the limited mobility of reactive species and rubber molecular chains led to slower conversion kinetics. Increasing the temperature enhanced molecular mobility and diffusion of the vulcanizing system, thereby accelerating crosslink network formation. However, at higher temperatures, chain scission and reversion phenomena occurred, which were shown by the torque inversion and viscosity reduction observed in Figure 2.

Figure 3 compares the experimental conversion data with the results obtained from the Deng–Isayev and Kamal–Sorour kinetic models using multivariable SSE optimization implemented through the *fminsearch* function in Octave-7.1.0. The Deng–Isayev model shows significant deviation from the experimental data, particularly in the acceleration and post-induction regions, as presented by the higher SSE values listed in Table 3. This difference suggests that the Deng–Isayev model is less capable of capturing the complex curing behavior

of sulfur-vulcanized SBR systems, where multiple reaction stages and evolving reaction mechanisms occur simultaneously.

In comparison, the Kamal-Sorour model provides a close relationship with the experimental conversion data for all compound formulations, as shown by the overlapping model and experimental curves in Figure 3 and the low SSE values reported in Table 4. This improved relationship can be attributed to the ability of the Kamal-Sorour model to account for autocatalytic effects during vulcanization. Sulfur vulcanization of SBR includes accelerator-mediated reactions, where intermediate reaction products promote other crosslinking reactions, leading to the characteristic sigmoidal conversion behavior observed experimentally. The presence of plasticizer is expected to enhance molecular mobility and diffusion, thereby facilitating the autocatalytic reactions and supporting the suitability of the Kamal-Sorour model to describe the curing kinetics of the studied systems. These results show that the vulcanization process of the investigated compounds cannot be adequately represented by a simple kinetic model, but rather requires a method that captures the multistage and autocatalytic nature of the reaction, as stated by previous studies [19,20].

(A)



(B)

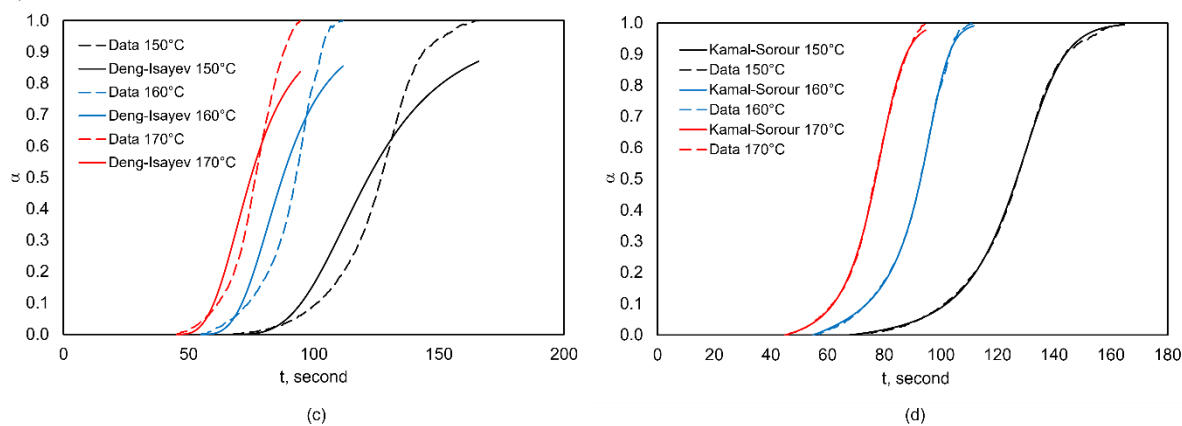


Figure 3 The degree of curing or conversion (α) at each time (t) for compound A (a-b), compound B (c-d), compound C (e-f), and compound D (g-h)

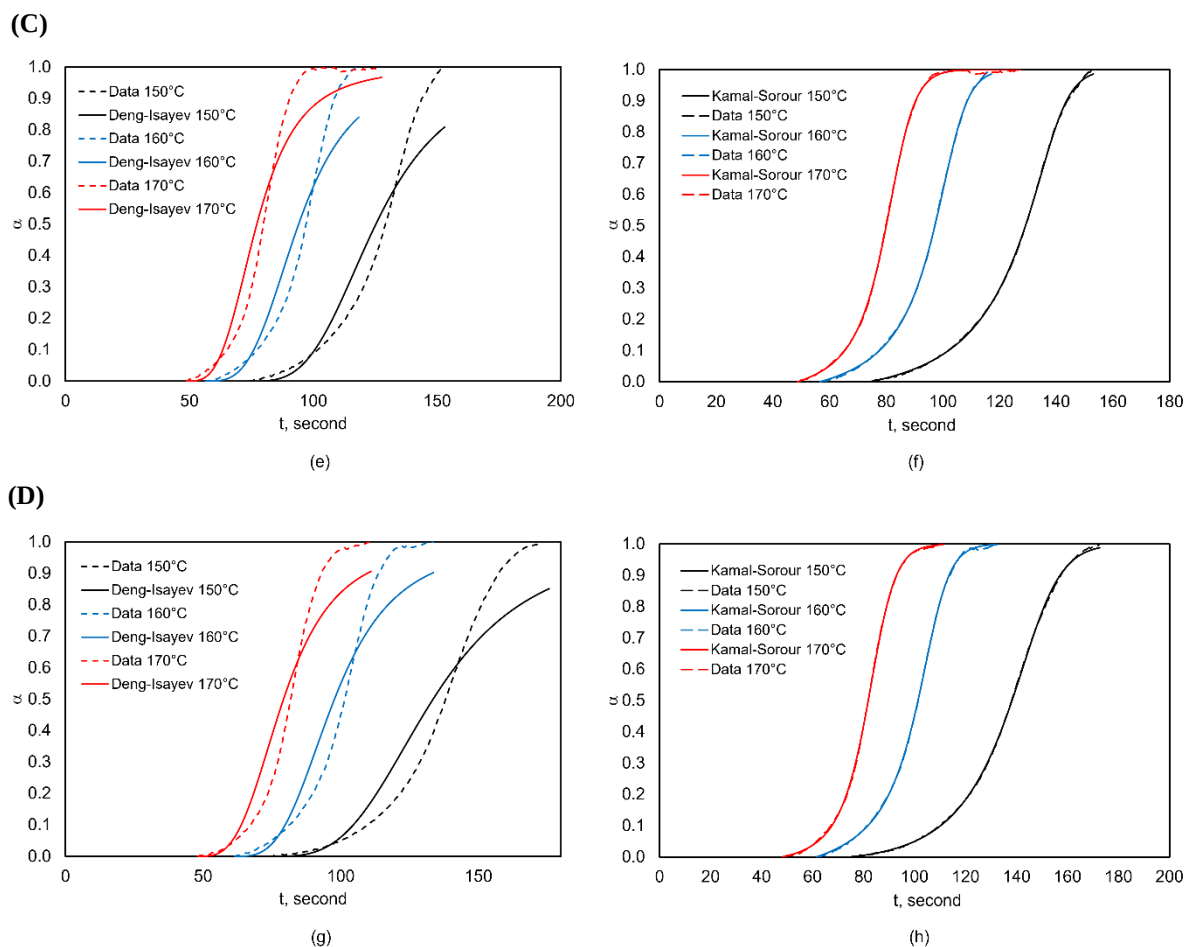


Figure 3 The degree of curing or conversion (α) at each time (t) for compound A (a-b), compound B (c-d), compound C (e-f), and compound D (g-h) (Cont.)

Table 3 Kinetic parameters of the Deng-Isayev model.

Compound	Vulcanization temperature ($^{\circ}\text{C}$)	$k \times 10^{-6} (\text{det}^{-1})$	n	SSE	E (kJ/mol)
A (0 phr)	150	2.81	3.2036	3.4104	150.2949
	160	0.14		1.0870	
	170	0.19		0.0598	
B (3 phr)	150	2.80	3.2034	3.4097	150.2947
	160	0.14		1.0865	
	170	0.19		0.5999	
C (5 phr)	150	2.18	3.3170	2.7672	150.6104
	160	6.04		0.8880	
	170	0.15		0.8259	
D (7 phr)	150	2.11	3.2111	3.6305	159.4690
	160	9.95		1.0623	
	170	0.16		0.9527	

Table 4 Kinetic parameters of the Kamal-Sorour model.

Compound	Vulcanization temperature ($^{\circ}\text{C}$)	$k_1 \times 10^{-2} (\text{det}^{-1})$	$k_2 \times 10^{-2} (\text{det}^{-1})$	m	n	SSE	E_1 (kJ/mol)	E_2 (kJ/mol)
A (0 phr)	150	0.13	8.34	1.1474	1.7561	0.0060	67.8348	34.1455
	160	0.36	12.81	1.3928	2.2486	0.0036		
	170	0.26	12.89	1.1249	1.7905	0.0043		
B (3 phr)	150	0.11	8.34	1.1473	1.7561	0.0058	67.8345	34.1458
	160	0.35	12.81	1.3927	2.2486	0.0036		
	170	0.26	12.89	1.1249	1.7905	0.0043		
C (5 phr)	150	0.19	6.09	1.1260	3.5853	0.0021	40.7331	87.6539
	160	0.28	10.96	1.2663	2.2015	0.0017		
	170	0.32	18.77	1.3110	1.2709	0.0039		
D (7 phr)	150	0.09	5.59	1.0061	2.5669	0.0024	59.1631	90.6122
	160	0.30	11.66	1.2991	1.8697	0.0019		
	170	0.19	17.86	1.2045	1.2029	0.0017		

3.3 Vulcanization kinetics parameters

The Kamal-Sorour model in Table 4 shows that the vulcanization reaction rate constant (k) is relatively directly proportional to the vulcanization temperature, both k_1 and k_2 . The result is in line with previous studies, where k is directly proportional to the vulcanization temperature [17,28]. The observation shows that higher vulcanization temperature corresponds to greater k_1 and k_2 for each type of compound. This leads to shorter (faster) vulcanization times at high temperatures, as shown in the induction time (t_{s2}) and optimum vulcanization time (t_{c90}) data in Table 2. The effect of the amount of plasticizer on the k value does not show a certain pattern based on the data in Table 4 because the k_1 and k_2 at various temperatures have different trends. At a vulcanization temperature of 150°C, the highest k_1 is in compound C, and k_2 is in compound B. At 160°C, the highest k_1 and k_2 are in compound B, while the largest is in compound C for 170°C. However, Table 4 states that the k_2 is greater than k_1 in each type of compound, showing the dominance of the autocatalysis mechanism during vulcanization [29]. At the end of the initial non-catalytic reaction stage, the viscosity of the reaction mixture becomes significantly high. Therefore, the mobility of the reactant molecules is restricted, effectively isolating and creating conditions that favor the subsequent autocatalytic reaction [30]. The data in Table 4 show that the contribution of the autocatalysis reaction (k_2) decreases as the amount of plasticizer in the compound increases at 150°C, and 160°C, while at 170°C, the contribution of the autocatalysis reaction (k_2) tends to increase as the amount of plasticizer in the compound increases.

The vulcanization reaction in the Kamal-Sorour Model follows the assumption that several reactions in vulcanization run simultaneously, and the product can catalyze the next reaction. Therefore, there is a variation in the reaction order (m and n) at different vulcanization temperatures. Table 4 shows that higher vulcanization temperature correlates with greater relative values of m and n for each type of compound. The values of m and n do not show a certain pattern in the amount of plasticizer, but have different trends at the same temperature. However, the less the amount of plasticizer used in the compound, caused an increase in m and n . At 150°C and 160°C, compounds A and B showed a higher m value than the other compounds. In line with the analysis at 160°C and 170°C, compounds A and B also showed a higher n value. Compared to m , the higher n value shows that the vulcanization reaction depends on the initial reactants of the compound rather than the effect of catalysis on the product reaction [31].

Generally, chemical reactions can be endothermic or exothermic, depending on energy absorption. Endothermic reactions occur when energy is absorbed from the environment. In the vulcanization reaction, the formation of crosslinks between rubber and vulcanizing agent (sulfur) requires heat treatment (endothermic reaction). Consistent with this behavior, t_{c90} value becomes shorter as the vulcanization temperature increases (Table 2), showing that higher temperatures accelerate the curing process [24]. However, the occurrence of the vulcanization reaction is insufficient to absorb energy from the environment, showing the need for activation energy in the form of heat. Activation energy shows the ease of the cross-link formation process. In this study, the activation energy of each compound and vulcanization temperature was calculated using Equation 5. Furthermore, the equation was linearized to establish a relationship between the reaction rate constant ($\ln k$) and the vulcanization temperature ($1/T$). The activation energy value was calculated from the slope of the curve, with results (E_1 and E_2) shown in Table 4 for each compound type.

Table 4 shows that the amount of plasticizer affects the activation energy values (E_1 and E_2). The value of E_1 is greater than E_2 in compounds A and B, showing that the autocatalysis reaction requires less energy. In comparison, E_2 is greater than E_1 in compound C and compound D, showing that the autocatalysis reaction requires more energy. Increasing the amount of plasticizer causes E_1 to decrease and E_2 to increase. A higher amount of plasticizer causes the autocatalysis reaction to require more energy. This occurs because paraffinic oil has low compatibility with SBR rubber, thereby reducing the degree of crosslinking and prolonging the vulcanization time [26]. The longer vulcanization time shows that the autocatalysis reaction requires more energy during vulcanization. The higher amount of paraffinic oil in the compound causes some of the accelerators (DPG and TMTD) to be adsorbed in the paraffinic oil. Therefore, some accelerators cannot accelerate vulcanization, suggesting the need for more energy for the autocatalysis reaction and longer vulcanization time [27]. This trend is further supported by the increase in t_{c90} values with increasing plasticizer content, as shown in Table 2.

4. Conclusion

In conclusion, increasing the vulcanization temperature and decreasing the plasticizer content reduces the induction time (t_{s2}) and optimum vulcanization time (t_{c90}). The vulcanization kinetics of the studied compounds are properly described by the Kamal-Sorour model. Although the plasticizer amount does not show a clear trend in the rate constants k_1 and k_2 , the vulcanization process is predominantly governed by an autocatalytic mechanism. The reaction order parameters (m and n) decrease with increasing plasticizer content, showing that the vulcanization reaction is more influenced by the initial reactant compound than by the catalytic effect of the reaction products. Moreover, higher plasticizer content increases the energy required for the autocatalytic reaction.

5. Author Contributions

Andri Saputra: Conceptualization, Methodology, Investigation, Writing - original draft, Project administration, Supervision, Resources. Mertza Fitra Agustian: Investigation, Data Curation. Syaifa Eza Satria: Investigation, Data Curation. Danuraja Ilmannafia: Investigation, Data Curation. Hersandy Dayu Kusuma: Visualization, Validation, Writing - Review & editing.

6. Conflicts of interest

The authors declare that there are no competing financial interests or personal relationships in this study.

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