The Effect of Ingredients Mixing Sequence in Rubber Compounding upon Vulcanization Kinetics of Natural Rubber: An Autocatalytic Model Study

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ABSTRACT

This study examined the effect of ingredients mixing sequence to the vulcanization kinetics of natural rubber. The effects of mixing temperature, vulcanization temperature, and the carbon black type upon the kinetics were also studied by using rheography and an autocatalysis reaction model approach. The results showed that this model is good in providing information on vulcanization reaction kinetics of natural rubber. High vulcanization temperature resulted in high reaction rate constant. The more black carbon mixed at the beginning of the rubber mixing process, the higher reaction rate constant would be. The mixing of carbon black and rubber chemicals mixed into the rubber subsequently resulted in the higher reaction rate constant compared with that of simultaneously.

Keywords: *autocatalysis; kinetics; mixing sequence; natural rubber*

ABSTRAK

Tujuan penelitian ini adalah untuk mempelajari pengaruh urutan pencampuran bahan kimia karet dan bahan pengisi ke dalam karet terhadap kinetika reaksi vulkanisasi karet alam. Pengaruh suhu pencampuran, suhu vulkanisasi, dan pengaruh tipe carbon black juga dipelajari dengan menggunakan rheograph dan suatu pendekatan model reaksi autokatalisis. Hasilnya menunjukkan bahwa model reaksi autokatalisis memberikan hasil yang cukup baik untuk menjelaskan kinetika reaksi vulkanisasi karet alam. Suhu vulkanisasi tinggi menghasilkan konstanta laju reaksi vulkanisasi yang tinggi. Semakin banyak carbon black dicampur di awal proses penggilingan karet, semakin tinggi konstanta laju reaksi vulkanisasi. Pencampuran carbon black dan bahan kimia karet ke dalam karet secara bergiliran menghasilkan konstanta laju reaksi vulkanisasi yang lebih besar dibandingkan dengan yang dilakukan secara simultan.

Kata Kunci: *autokatalisis; kinetika; urutan pencampuran; karet alam*

INTRODUCTION

Due to the sulfur vulcanization invented by Charles Goodyear (1839), natural rubber was used widely as it has better both physical and chemical properties, such as oxidation resistance and the change from thermoplastic to a thermoset. These properties changes cause the change of rubber characteristic from soft plastic to hard elastic [1] and were influenced by the vulcanization reaction of sulfur and rubber backbone [2-3]. This reaction initially, accelerator and activator formed active accelerator complex. The one and rubber backbones reacted to form active sulfurating agent and rubber bound intermediate, then followed by network formation with initial polysulfide crosslinks. Subsequently, network maturation process could be found. In the last stage, crosslink shortening with additional crosslink, crosslink destruction with main chain modification (cyclic sulfide) and s-s bond interchange (pendent sulfidic group) are included [4]. The rheometer is one of the equipment to observe this reaction. The rheometer principle is based on the assumption that all reactions occur during vulcanization proportional to the rubber stiffness change.

Most of researcher study the vulcanization using rheometer [5], various tools used by researchers to observe vulcanization reaction kinetics [6], utilized short wave of infrared radiation [7], monitored vulcanization reaction with online ultrasonic [8], used SANS [9], and used NMR [10] as well as used WAXD [11]. Some other researchers used DCS to observe vulcanization [12-16]. Kinetic model using rheograph has been widely

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implemented [17-21] but the autocatalytic model using rheometer to observe curing region was first done [13] and [22-23]. Another models and reaction mechanism using rheometer are reported [24-28] as well as [29-30] studied vulcanization and devulcanization kinetics models. Vulcanization kinetics is also studied by the researches using natural rubber and synthetic rubbers like that are illustrated in literature as shown in the literature [31-41]. The physical properties of rubber vulcanizates, such as abrasion resistance, not only influenced by vulcanization reaction but also influenced by the mixing process. Wang in his study, first, oil was added after the carbon black has been incorporated into the rubber, and second, oil was added into the rubber together with the carbon black. The first provided a higher abrasion resistance compared with the second one [42].

From the point of view, in this research, the autocatalytic model reported by Manchado et al. [13] was used to study the influence of the mixing sequence of rubber chemicals and filler into the rubber upon the kinetics.

EXPERIMENTAL SECTION

Materials

The ribbed smoked sheet-1 (RSS-1) produced in Indonesia and carbon black filler N 330 and N 660 type from Cobot Indonesia were raw materials employed in this research. The rubber chemicals comprised of sulfur, tertbutyl benzothiazole sulfenamide (TBBS), tetramethyl quinone (TMQ), zinc oxide (ZnO), stearic acid, and processing oil. All materials and chemicals were the commercial grades without any treatment.

Instrumentation

The equipment used in this research were open two-roll mill and rheometer. Rheograph was used to study the kinetics of vulcanization reaction.

Procedure

Sample A

Table 1 illustrates the natural rubber formula. The first sequence illustrates the mastication and milling of rubber, rubber chemicals, and filler at a mixing temperature of 60 °C and the mixing sequence, respectively. These rubber samples were called A. Meanwhile, the additional sequence of carbon black followed the sequence in Table 2 is coded as 1. Thus, this sample is then called A1. Rubber initially was masticated within 5 min, followed by additional ZnO and stearic acid that were milled within 2 min. TMQ was subsequently added into the mix and milled for 1 min. Carbon black at the amount of 10 phr was added into the mix (CB_1) and then milled for 2 min. The remains of carbon black about 40 phr were added into the mix together with oil (CB_2+oil) and then milled for 4 min. The addition of TBBS and sulfur took 1 min for milling time on each. Using the same procedure of A1, the A2, A3, and A3 could be found in the following of code 2, 3 and 4 in Table 2.

Table 1. Natural rubber formula

No	Materials	phr
1	RSS-1	100
2	ZnO	5
3	Stearic acid	2
4	Carbon Black N 330 and 660	50
5	Paraffinic oil	5
6	TMQ	2
7	TBBS	0.5
8	Sulfur	2.5

Table 2. The addition method of carbon black into natural rubber under the rubber mixing process

Code	CB_1	CB_2+oil
1	10 phr	40 phr+oil
2	20 phr	30 phr+oil
3	30 phr	20 phr+oil
4	40 phr	10 phr+oil

Sample B

The second mixing process using the formula in Table 1, was conducted in accordance with the sequence and the time each sequence needed and mixed at a mixing temperature of 60 °C. The sample in this process was then called B in which rubber was masticated for 1 min then followed by the addition of stearic acid and milled for 1 min. As subsequence of this process, sulfur and ZnO were added into the mix and milled for 2 min as well as carbon black at the amount of 10 phr that was added into the mix (CB_1) and milled for 3 min. The remains of carbon black about 40 phr were added into the mix along with oil (CB_2+oil) and milled for 7 min. Following this process, TBBS was added into the mix was milled for 6 min and TMQ needed 1 min for milling time. The addition process of carbon black into the rubber was performed using a method applied to the sequence as shown in Table 2. The samples were, at last, designated as B1, B2, B3, and B4.

Sample C

By using a procedure equal to that of in B and using the sequential addition of carbon black into rubber as listed in Table 2 code 1, sample C1, which, in this case, used carbon black type N 660 as the filler, was able to be found. The sample of C was, at last, called as C1, C2, C3, and C4.

Both samples of B1 and C1were on only milled and mixed at a mixing temperature of 60 °C, but also held at 55, 65, and 70 °C.

Sample D

The third mixing process, the formula in Table 1 was applied too for the process of mixing process as well - following the sequence and time allocated for each mixing and mixed at a mixing temperature of 60 °C. Rubber in this process was masticated for 3 min. Subsequently, of the total amount of 10 phr of the total amount of 50 phr, was added and milled for 2 min at the beginning of the mixing (CB_1). The remains of 40 phr together with oil, in turn, was added into the rubber (CB_2 + oil) and required 5 min for milling. ZnO and stearic acid were then added and milled for 2 min, followed by addition of TMQ, sulfur, and TBBS milled for 1 min on each. This process resulted in a sample of D1. The sample of D comprised also of D1, D2, D3, and D4.

All rubber compounds A, B, C, and D after the milling process were vulcanized on the temperature of 150 °C, except on the samples A1 and D1. This vulcanization were carried out at the temperature of 140, 150, 160, and 170 °C.

Study of vulcanization kinetics model

The change of rubber stiffness caused by vulcanization reaction produces torsion evaluated by rheometer and as a time function. The degree of curing (α) can be conducted using equation 1 as follows:

$$\alpha = \frac{(\text{tortion at}_t - \text{lower tortion})}{(\text{higher tortion} - \text{lower tortion})} \quad (1)$$

After that, the relationship between α and t is allocated. The slope of curve is called as dα/dt and obtained by the following equation:

$$\frac{d\alpha}{dt} = \frac{(\alpha_{after} - \alpha_{before})}{(t_{after} - t_{before})} \quad (2)$$

To get the value of m and n which is the order of the reaction then made the relationship between dα/dt and α as follows:

$$\frac{d\alpha}{dt} = k\,\alpha^m (1-\alpha)^n \quad (3)$$

$$k = k_0 \exp\left(\frac{-E}{RT}\right) \quad (4)$$

where m and n were the order of reaction, k reaction rate constant, k_0 pre-exponential, E activation energy and T absolute temperature.

Equation 3 is a representation of the chemical reaction kinetics equation introduced by Manchado et al. [13]. He observed S shape on curing region using autocatalytic model approach.

Using SSE method, the difference between the experimental data and interpolation of dα/dt, at the SSE minimum, the values of k, m and n could be determined.

RESULT AND DISCUSSION

Sample A

Rheograph on curing region in a sample of A illustrates in Fig. 1. It describes the relation between torque and vulcanization time on different rubber mixing process (RMP). It explains that the sample of A2 has the highest torque followed by A1, A3, and A4 respectively. This illustration describes RMP influences torque in a sample of A generally. A large amount of carbon black added at the beginning of RMP causes the increase of torque.

Sample A1. Fig. 2 shows that vulcanization temperature influences torque on curing region in a sample of A1. It

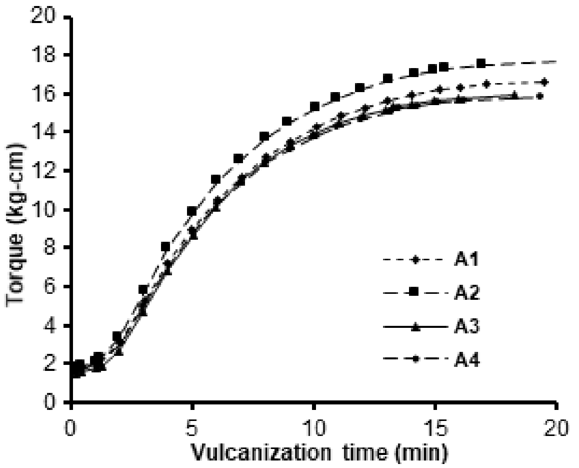

Fig 1. Relation between torque with vulcanization time in sample of A

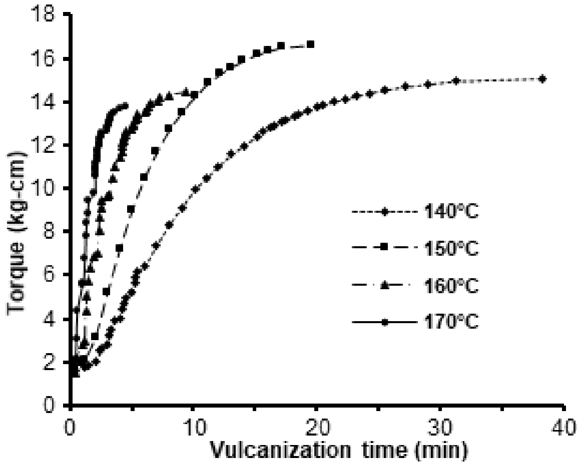

Fig 2. Relation between torque and vulcanization in sample of A1 at various vulcanization temperature

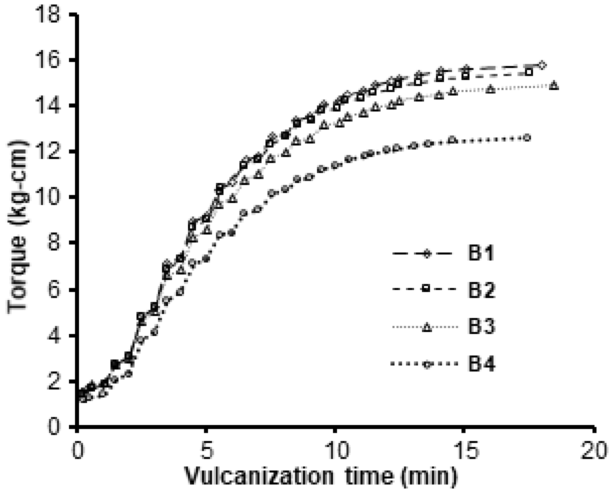

Fig 3. Relation between torque and vulcanization time in sample of B

describes the relation between torque and vulcanization time on the difference of vulcanization temperature. The highest maximum torque is on vulcanization temperature of 150 °C followed by a temperature of 140, 160, and 170 °C. The increase of vulcanization temperature causes the increase of vulcanization reaction rate to reach the optimum torque. Fig. 2 also informs that high temperature not always affects on torque or reaction rate of vulcanization, as the influence of vulcanization temperature toward torque depends on the nature of natural rubber. From this figure, high vulcanization temperature results in high reaction rate but optimum torque becomes low.

Sample B

Fig. 3 informs the influence of RMP toward torque on curing region sample of B. It describes the relation between torque and vulcanization time on different RMP. The highest torque was in a sample of B1 followed by a sample of B2, B3, and B4 respectively. A large amount of carbon black added at the beginning of the RMP of B causes the low torque.

Sample B1. Fig. 4 shows that the influence of RMP temperature in a sample of B1 on curing region toward torque. This figure describes the relation between torque and vulcanization time on different mixing temperature. In that illustration, it is clearly seen that high RMP temperature results in low torque. The highest torque is in RMP temperature of 55 °C followed by 60, 65, and 70 °C respectively. The same occurrence in a sample of B1 also happened in a sample of C1.

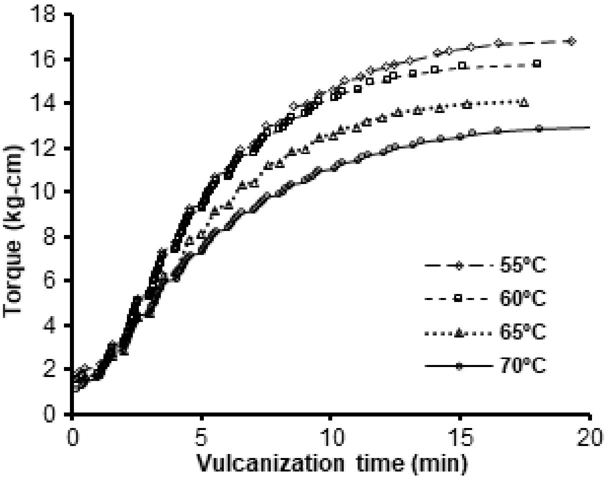

Fig 4. Relation between torque and vulcanization time in sample of B1 in various temperatures of milling process

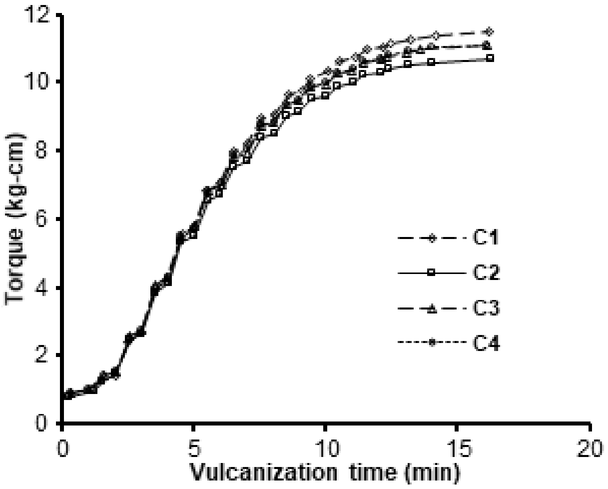

Fig 5. Relation between torque and vulcanization time in sample of C

Sample C

Fig. 5 shows that the influence of RMP on a sample of C on curing region to torque. This figure describes the relation between torque and vulcanization time on different RMP. Based on that illustration, it is clearly seen that the more carbon black added at the beginning of RMP sample of C, the torque is relatively stable. This fact shows that the large particle size of carbon black type N 660 has little influence to torque on a variety of RMP sample of C.

Sample C1. Fig. 6 explains the influence of mixing temperature in a sample of C1 toward torque too. This

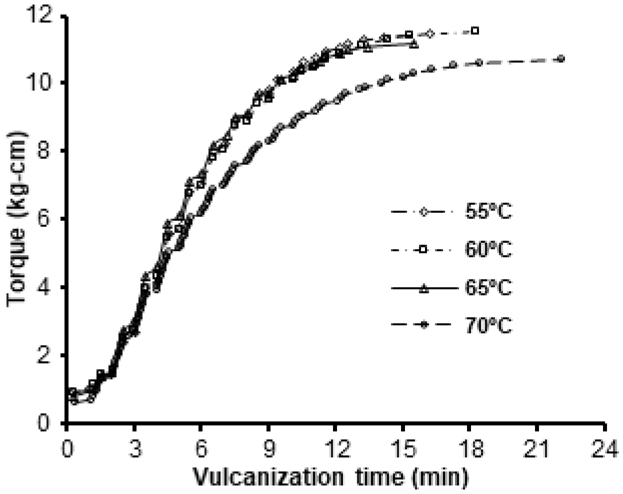

Fig 6. Relation between torque and vulcanization time in sample C1 at variety of milling temperature

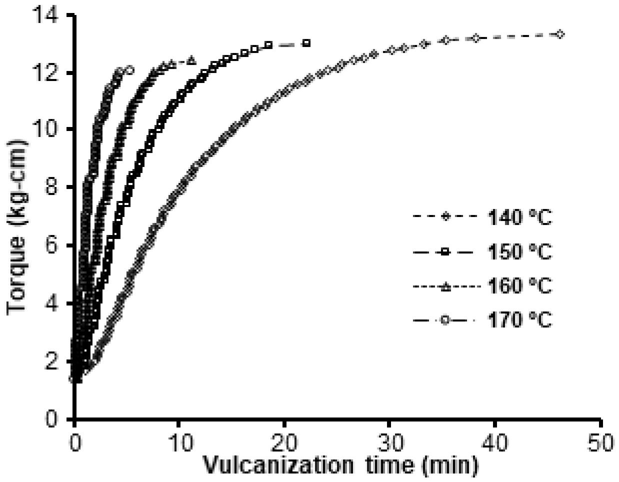

Fig 8. Relation between vulcanization time in sample of D1 at various vulcanization temperature

figure shows that the increase in mixing temperature causes the decrease of torque. High mixing temperature causes the low viscosity of rubber. In this fact, carbon black and rubber chemicals are easy to disperse into the rubber, but low rubber viscosity is unable to disperse them into smaller particles. Low rubber viscosity is proportional to the low shearing force of rubber in time of RMP and causes low breaking carbon black and rubber chemicals into small particles. Therefore, high rubber viscosity causes low torque.

Sample D

Fig. 7 shows the influence of RMP to torque on curing region sample of D. It describes the relation between torque and vulcanization time on different RMP. The highest torque in a sample of D3, followed by sample D4, D2, and D1 respectively. In general, the higher torque is caused by the more carbon black added to sample of D at the beginning of RMP. The torque increase of D1 to D4 were caused by the mixture of more carbon black at the beginning of RMP. This was the contradictive effect on samples of A, B and C. Mixing process of carbon black into the rubber of sample D is the same as the other three samples which are A, B, and C, but different in the order of mixing black carbon and rubber chemical into rubber.

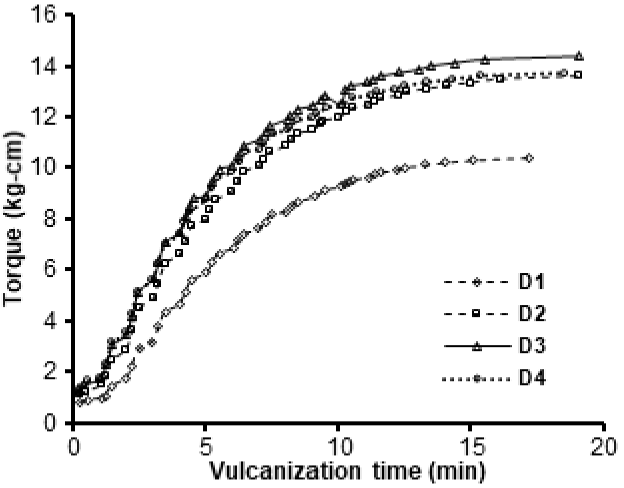

Fig 7. Relation between torque and vulcanization time in sample of D

Sample D1. Fig. 8 shows that vulcanization temperature affects on torque on curing region of sample D1. It describes the relation between torque and vulcanization time on different vulcanization temperature. The highest maximum torque is on vulcanization temperature of 140 °C followed by 150, 160, and 170 °C respectively. The higher vulcanization temperature, the lower vulcanization time to get maximum torque, therefore it concludes that vulcanization reaction is faster in line with the increase of vulcanization temperature. Fig. 8 informs us that the influence of vulcanization temperature is the same as the fact found in Fig. 2 in sample A1.

The Kinetics Model of Vulcanization Reaction Based on Rheograph

The calculation based on an autocatalysis model for vulcanization kinetics reported by Manchado et al. [13] was listed in Table A in the appendix. Calculation of the reaction rate constant k and the order reactions m and n is based on equations 1, 2, 3, and 4. The degree of curing (α) is generated rheography and calculated on the basis of equation 1 as stated in Table A column 3. Then the relationship between α and vulcanization time t is conducted. The slope of this curve is dα/dt. The relationships between dα/dt and α produce k, m, and n as

Table 3. Reaction rate constant and reaction order sample of A, A1, B, B1, C, C1, D and D1

Samples	Fitting	Kinetics variable			Vulcanization temperature (°C)
	SSE	k	m	n	
A11	0.0017	0.2199	0.4282	1.2647	140
A12	0.0017	0.3547	0.4864	1.1690	150
A13	0.1033	0.8957	0.4849	1.2556	160
A14	0.3268	0.7993	0.4845	0.6590	170
A2	0.0022	0.3826	0.4968	1.2194	150
A3	0.0016	0.3983	0.5343	1.1502	150
A4	0.0022	0.3752	0.4914	1.1577	150
B11	0.0030	0.3489	0.4330	1.1563	150
B12	0.0309	0.6936	0.5045	1.4198	150
B13	0.0030	0.3633	0.4549	1.0875	150
B14	0.0229	0.5667	0.4496	1.5096	150
B2	0.0303	0.7030	0.5315	1.3945	150
B3	0.0291	0.6988	0.5319	1.4481	150
B4	0.0316	0.6935	0.5106	1.3746	150
C11	0.0230	0.6724	0.5618	1.2310	150
C12	0.0278	0.7088	0.5929	1.3802	150
C13	0.0363	0.7827	0.5875	1.3488	150
C14	0.0216	0.4768	0.4159	1.3307	150
C2	0.0301	0.6609	0.5594	1.2255	150
C3	0.0301	0.6609	0.5594	1.2255	150
C4	0.0301	0.6789	0.5671	1.2244	150
D11	0.0062	0.2897	0.4513	1.7457	140
D12	0.0237	0.5589	0.4057	1.5607	150
D13	0.0717	0.8457	0.2933	1.2463	160
D14	2.5390	1.6975	0.2728	1.2181	170
D2	0.0262	0.5523	0.4038	1.4324	150
D3	0.0218	0.4694	0.3927	1.3658	150
D4	0.0316	0.6935	0.5106	1.3746	150

Remark: C11 and B11 were milled at temperature of 55 °C, C12 60 °C, C13 65 °C, and C14 70°C; A11 and D11 were vulcanized at temperature of 140 °C; A12 and D12 150 °C; A13 and D13 160 °C; and A14 and D14 170 °C

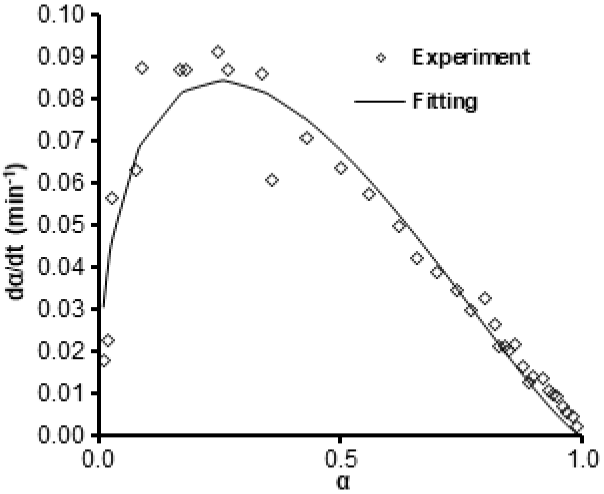

Fig 9. Relation between dα/dt and α in sample of A11 at vulcanization temperature of 140 °C

Table 4. Reaction rate constant as a function of vulcanization temperature in sample A1 and D1

Samples	ln k, min^{-1}
A1	19.913 exp (-8825.3/T)
D1	24.081 exp (-10456/T)

shown in Fig. 9 and are given in Table A in 5, 6, and 7 columns. The values of k, m, and n for samples of A, A1, B, B1, C, C1, D, and D1 were listed in Table 3. This table informs reaction rate of vulcanization based on k that it is the same information of reaction rate illustrated on Fig. 1 to 8. k in sample of A1 and D1 was listed in Table 3 then conducted the relation between k and temperature T. Fig. 10 informs the Arrhenius relation between k and T in sample of A1 and D1. The k as a function of T in a sample of A1 and D1 was listed in Table 4. This information has the same one illustrated in Fig. 2 and 8.

Samples of A12, A2, A3, and A4 had the same reaction rate as the reaction rate described in Fig. 1. From Fig. 1 and Table 3, the higher the k is, the higher the torque will be. The same k information of A12, A2, A3, and A4 were stated by a sample of D12, D2, D3 and D4 on Table 3 and Fig. 7.

Samples of B12, B2, B3, and B4 had the same information of reaction rate as samples of C12, C2, C3, and C4. The more carbon black added at the beginning of RMP was, the lower the reaction rate constant would be. It determines that carbon black cannot function as a catalyst and its surface has been tainted by rubber chemicals.

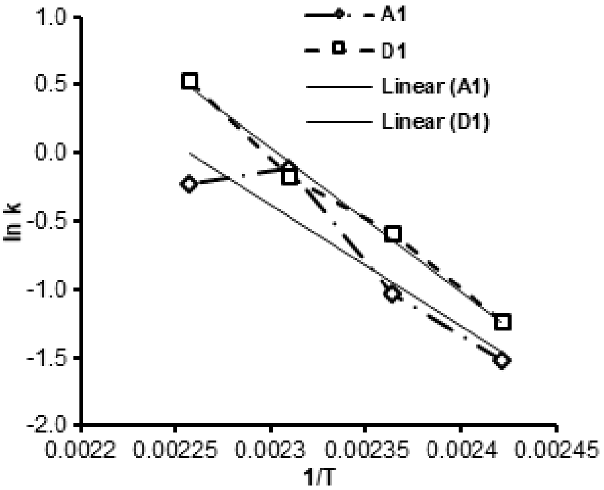

Fig 10. Arrhenius relation of A1 and D1

Mixing temperature influenced the reaction rate of vulcanization. Samples of B11, B12, B13, and B14 had the same tendency of reaction rate samples of C11, C12, B13 and C14 as described in Table 3 and Fig. 4 and 6. From these Table and Figures, high mixing temperature resulted in a low reaction rate of vulcanization. High mixing temperature causes the low shearing force of rubber. It makes a large particle of carbon black and rubber chemicals easy to disperse into the rubber. On the other hand, low mixing temperature results in a high shearing force of rubber and make carbon black and rubber chemicals dispersed into the rubber in the relatively small particle. From the explanation, reaction rate based on high shearing force is better than that of a low one.

CONCLUSION

RMP influenced the values of torque. The value of torque increased with the increase of the carbon black mixed at the beginning of RMP. The mixing sequence of rubber chemicals and carbon black into the rubber, mixing temperature and vulcanization temperature affected the values of torque too. The increase of mixing temperature caused the decrease of torque. High vulcanization temperature resulted in low torque and depended on the nature of natural rubber. Type carbon black also influenced torque, the difference of type one caused the difference of particle size. The small particle size of carbon black resulted in high torque. Reaction rate constants of natural rubber vulcanization based on autocatalysis model were rather significant to explain the vulcanization rate of natural rubber vulcanization.

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