

EFFECT OF CURING SYSTEMS ON MECHANICAL PROPERTIES AND N-PENTANE RESISTANCE OF CARBON BLACK FILLED NATURAL RUBBER VULCANIZATES

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Abstract: The mechanical properties and n-pentane resistant of carbon black filled natural rubber (NR) vulcanizate with semi efficient (SEV), efficient (EV) and the donor sulfur curing system was studied through experimental approach. Previous work about swelling behavior of NR in n-pentane has minimum information. The investigation about the swelling of NR in n-pentane is very important to inform the possibility utilization of NR in LPG rubber seal. Vulcanization kinetics of NR vulcanizates were defined using autocatalytic model, whereas the experimental cure data obtained from a moving die rheometer. The NR with SEV curing system shown the highest activation energy. In addition, NR with SEV curing system shown the highest crosslink density, which dominated with di- and polysulfidic crosslink, affect the mechanical properties and n-pentane resistance. The higher crosslink density will increase hardness and tensile strength, decrease slightly of elongation at break and compression set, and increase the n-pentane resistance.

Key words: *natural rubber, curing system, mechanical properties, n-pentane resistance*

INTRODUCTION

Natural rubber (NR) contains high molecular weight, which is based on cis-1,4-polyisoprene. It has excellent mechanical and physical properties such as; tensile strength, tensile modulus, tear strength and hardness [1-2]. However, NR has poor chemical resistance and processing ability. Degradation of natural rubber can be caused by a variety of environmental factors, such as elevated temperature, humidity, impurities, mechanical load, irradiation and chemicals. Natural rubber properties are depending on compounding ingredients, especially vulcanization system [3-4], which is determine the type of crosslink networks and crosslink density. Rubber compounds are usually crosslinked by sulfur vulcanization, peroxide and sulfur donor curing.

The sulfur vulcanization distinguished by the sulfur/accelerator ratio, which are conventional (CV), efficient (EV) and semi-efficient (SEV) [5]. The conventional system has a high sulfur ratio than accelerator, contains mostly polysulfidic crosslink. Conversely, efficient system has a high accelerator ratio than sulfur will give mainly monosulfidic crosslink. Intermediate levels of sulfur and accelerator are called semi-efficient, will produce rubber vulcanizates with higher crosslink type of di- and polysulfidic than monosulfidic. In addition,

peroxide curing has been used organic peroxide agent, while sulfur donor has been used DTDM(*dithiomorpholine*), CLD (*caprolactamdisulfide*), sulfenamide, tiazol and thiuram accelerator to replace sulfur as vulcanization agent.

Crosslinking system selection is especially important, because it significantly affects both processing and product properties. The important parameter in each rubber product was unique. The important mechanical properties of rubber seal in liquid petroleum gas (LPG) valve are compression set, tensile properties and hardness. The high compression set, tensile properties and hardness has been produced by CV, SEV and EV crosslink system consecutively [6-7]. In addition, rubber seal in LPG valve may contact with LPG that it will swell and cause deterioration of its properties. Therefore, the investigation of LPG resistance in rubber should be held. The swelling testing of rubber seal in LPG is difficult to be applied in the laboratory. According to the requirements in SNI 7655:2010, LPG can be replaced by n-pentane. Swelling test was held by immersion rubber in oil or solvent until it reaches the concentration of the liquids is uniform and equilibrium.

The swelling index percentages were related to the crosslink density of the elastomers [4], which depend on vulcanization system. Many researchers have extensively studied about the effect of the

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vulcanization system on the swelling behavior of NR in different solvent or oil. Klattanavith N [8] investigated the swelling behavior of NR with the peroxide vulcanization system in isooctane, toluene, engine oil, gear oil and brake fluid. Yahya et al. [4] studied the effect of curing systems (CV, EV and Dicumyl Peroxide) of NR on toluene swelling behaviors. Phanny et al. [9] reported the different origins of natural rubber with conventional (CV) and efficient (EV) cure systems were tested swelling properties in toluene. However, there is very little information about the effect of curing system of NR to swelling behavior in n-pentane. The investigation about the swelling of NR in n-pentane is very important to inform the possibility utilization of NR in LPG rubber seal.

The present work was undertaken to explore the effect of curing systems on mechanical properties and n-pentane resistance of carbon black filled natural rubber vulcanizate. EV, Semi-EV and sulfur donor type of vulcanization system were used to investigate this phenomena. The curing characteristics and crosslink density were also measured to accomplish this investigation.

1. Methodology

Materials

Natural rubber was used in crepe type, which is made from latex (*Hevea brasiliensis*). Fast Extrusion Furnance (FEF) carbon black was produced from Cabot Cans Sdn. Bhd. Sulfur, 4,4'-Dithiodimorpholine (DTDM), Zinc Oxide, stearic acid, N-Cyclohexyl-2-Bezothiazolesulfenaide (CBS), Dioctyl Phatalate (DOP), N-Tert-Butyl-2 Benzothiazolesulfenamamide (TBBS), and 2,2-Dibenzothiazyl Disulfide (MBTS) were supplied from local suppliers. 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ) was supplied from Kemai. Antilux as anti-ozonant was obtained from Rhein Chemie.

Compounding and curing characteristic

The NR compound was vulcanized in semi-EV, EV, and sulfur donor vulcanization system, which was code as NRSEV, NREV and NR donor respectively. The formulation of NR compounds are given in Table 1. The NR compounds were mixed using a two-roll mill with low roll speed (24 rpm) and friction ratio (1:1.4), which was maintained at $65 \pm 5^\circ\text{C}$. The NR compounds were compression molded at 150°C under a pressure approximately 100 kg/cm^2 with a cure time of t_{90} obtained from an oscillating disc rheometer (MDR 2000). The NR vulcanizate was mold as square (15x15 cm) with 2 mm thickness.

Table 1. NR compound formulation

Materials	Amount of material in each compounds (phr*)		
	NRSEV	NREV	NRDonor
NR	100	100	100
Sulfur	1.3	0.5	
DTDM			1.5
N550	50	50	50
Antilux	2	2	2
TMQ	1	1	1
DOP	5	5	5
ZnO	5	5	5
Stearic acid	2	2	2
CBS			1.5
TMTD			0.5
TBBS	1.2	2.5	2.5
MBTS	0.3	0.5	0.5

* part hundred rubber

Hardness, tensile, elongation at break and compression set properties

Hardness was determined using durometer type A according to ISO 7619-1. The test specimens with 6 mm thick were made up of three layers of rubber from the compression-molded sheets. Tensile strength and elongation at break test was held at room temperature on Lyoid Tensometer, with crosshead rate 500 mm/min. The test samples were cut from compression-mold sheets using dumbbell shaped type 2 according to ISO 37. Compression set testing was conducted at room temperature. That test was determined according to ISO 815 using the standard test specimen of cylindrical shape of 12 mm in diameter and 6.3 mm thick by compression method.

Determination of crosslink density

The crosslink density of NR vulcanizate was calculated by the Mooney-Rivlin equation based on their stress-strain behavior. The equation based on the theory of rubber elasticity which can be described as follows [10].

$$F = 2 A_0 (\lambda - \lambda^{-2}) (C_1 + C_2 \lambda^{-1}) \quad (1)$$

$$\frac{\sigma}{(\lambda - \lambda^{-2})} = 2C_1 + \frac{2C_2}{\lambda} \quad (2)$$

where F is the force required to stretch the rubber vulcanized, A_0 is the cross-sectional area of the unstretched rubber vulcanized, σ is identifiable with F/A_0 , λ is the extension ratio (which is $1 + \epsilon$), ϵ is strain, and C_1 and C_2 constans are characterizing the vulcanized. The constants C_1 and C_2 can be determined by the plot of $\sigma/(\lambda - \lambda^{-2})$ against $1/\lambda$, the intercept of the curve on the $\sigma/(\lambda - \lambda^{-2})$ axis corresponds to the value of C_1 and its slope

corresponds to the value of C_2 . The value of C_1 can be used to assess the physical crosslink density (η_{phys}) by using equation 3 as follows [10].

$$n_{phys} = \frac{C_1}{RT}$$

Where R is the gas constant ($8.314 \text{ mol}^{-1} \cdot \text{K}^{-1}$) and T is the absolute temperature.

The test was conducted at 27°C using Zwick tensometer with a crosshead speed 50 mm/min .

N-pentane resistance measurement

N-pentane resistance was obtained by swelling test of NR vulcanizate in n-pentane, conducted at room temperature. The measurement according to the immersion – weight gain method. The NR vulcanizates were cut in uniform size, then were weighed on an electronic balance with an accuracy of 0.001 g . The cut samples immersed in n-pentane. The samples were removed from the solvent at the specified time, quickly blotted with a filter paper and weighed using electronic balance. The immersing and weighing was continued till equilibrium swelling was attained. The molar percentage uptake (Q_t) of n-pentane per gram of NR vulcanized was determined using equation 4 [11].

$$Q_t = \frac{(M_t - M_0)}{\text{Molecular weight of n-pentane} / M_0} \times 100$$

where M_t is mass uptake at time t and M_0 is the initial mass of NR vulcanized. The swelling phenomenon occurs when the solvent adsorbs rapidly to rubber surface, followed by diffusion of the solvent into the rubber. The diffusion coefficient of a solvent can be obtained using Fickian's second law of diffusion [11].

$$D = \pi \left(\frac{h\theta}{4Q_\infty} \right)^2$$

Where h is the NR vulcanized thickness, θ is the slope of the initial linear portion of the plot of Q_t against $t^{1/2}$, and Q_∞ is the equilibrium absorption. The sorption coefficient (S) was calculated using equation below [11].

$$S = \frac{M_\infty}{M_0}$$

where M_∞ is mass of n-pentane absorbed at equilibrium and M_0 is the initial mass of NR vulcanized.

2. Results

Cure characteristics and kinetic study

Table 2 showed the curing characteristic of NR compound with different curing system, cured at 150°C alisted as maximum torque (S'_{max}), minimum torque (S'_{min}), delta torque ($\Delta S' = S'_{max} - S'_{min}$) and optimum cure time (t_{90}).

The vulcanization kinetic parameters were obtained according to vulcanizing curves from moving die rheometer (MDR 2000) under isothermal condition at $150, 160, 170, 180^\circ\text{C}$. The degree of conversion (α) in curing reaction is based on the crosslinking density that is proportional to the stiffness of the rubber, is defined as follows: [12-13].

$$\lambda = \frac{S'_t - S'_{min}}{S'_{max} - S'_{min}}$$

Where, S'_{min} , S'_t , and S'_{max} are the minimum torque value, the torque value at given time of curing and the maximum torque value, respectively.

Table 2. Cure characteristics of NR compounds

Sampels	S'_{max} (kg-cm)	S'_{min} (kg-cm)	$\Delta S'$ (kg-cm)	t_{90} (min)
NRSEV	2.22	0.24	1.98	7.15
NREV	1.44	0.15	1.29	11.5
NR Donor	1.16	0.18	0.98	20.16

Figure 1 shows the plot of $d\alpha/dt$ versus time for NR compounds with different curing system at different temperatures. The maximum of $d\alpha/dt$ of all NR compounds is reached at time $t > 0$, it indicates that the curing reaction of NR vulcanizate exhibited autocatalytic characteristics as given below [14].

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

Where $k(T)$ is the rate constant, m is the reaction order of autocatalytic reaction and n is the reaction order of non-autocatalytic reaction. The rate constant, k , m and n are dependent on temperature.

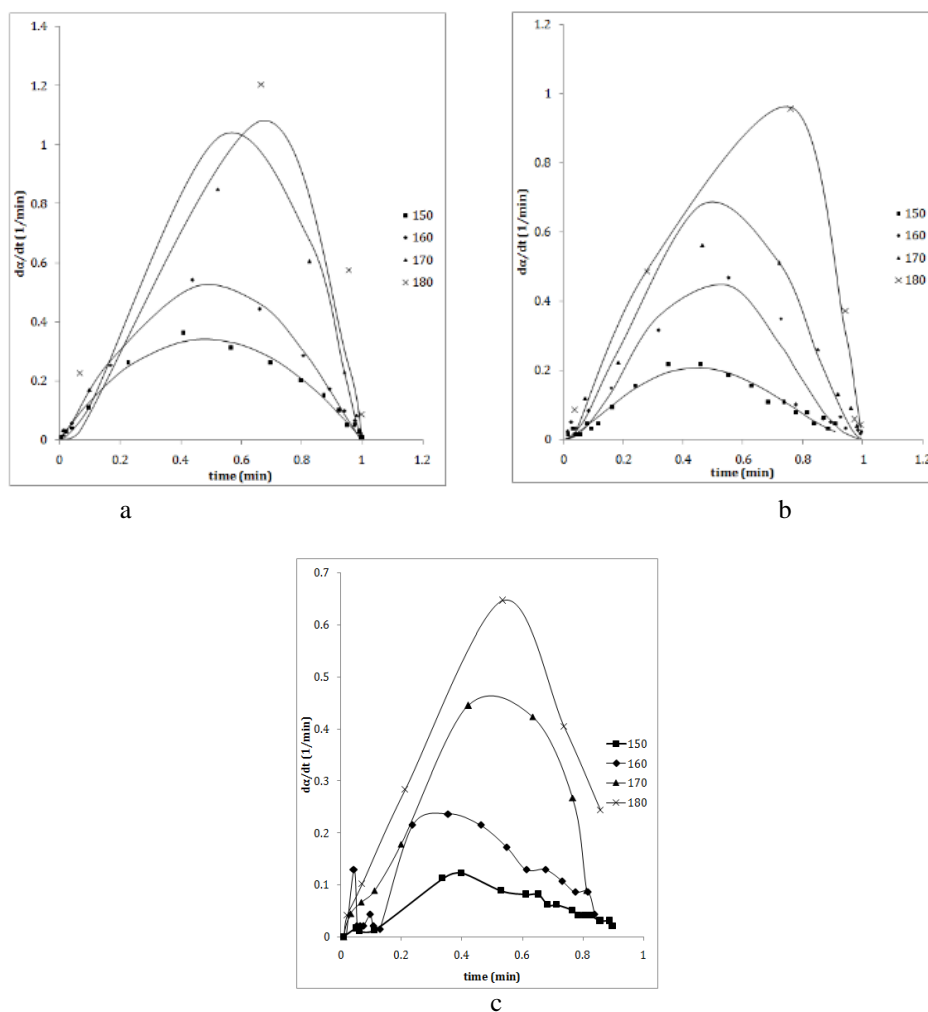


Figure 1. Vulcanizing rate versus time curves of NR vulcanizates with different curing system: (a) SEV; (b) EV; (c) Donor Sulphur.

The activation energy of NR samples can be determined using the Arrhenius equation as follows:

Table 3. Vulcanization kinetic parameters of NR samples

Samples	Vulcanization temperature (°C)	Rate constant (min ⁻¹)	Reaction order		Activation energy (kJ/mol)
			m	n	
NRSEV	150	1.38	0.97	1.04	102.38
	160	2.66	1.17	1.17	
	170	7.99	1.78	1.22	
	180	8.05	2.03	1.08	
NREV	150	2.09	1.49	1.87	59.46
	160	8.29	2.02	2.05	
	170	7.57	1.79	1.66	
	180	7.34	1.84	1.08	
NR Donor	150	1.06	1.49	1.84	79.58
	160	3.16	1.66	2.25	
	170	8.29	2.03	2.09	
	180	3.96	1.43	1.29	

(9)

$$\ln k(T) = \ln A - \frac{E}{RT}$$

Where A is the pre-exponential or frequency factor, E is the activation energy, R is the gas constant and T is the absolute temperature. The activation energy (Ea) of NR samples was determined from the slope of the plot of ln k versus 1/T and expressed in Figure 2. In addition, the vulcanization kinetic parameters are reported in Table 3.

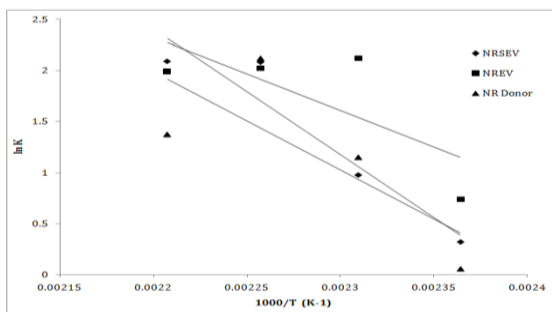


Figure 2. ln k vs. 1/T of NR vulcanizates with different curing system

Crosslink density and mechanical properties

Figure 3 shown the plot data- Mooney-Rivlin equation on NR vulcanizates with different curing system. The constants C₁ and C₂ can be determined by the plot $\sigma/(\lambda - \lambda^{-2})$ as a function of $1/\lambda$. The type and amount of crosslink density effected the mechanical properties of the rubber [4,6,15]. The effect of crosslink density affect to mechanical properties of NR vulcanized depending on the curing system of NR listed in Table 4.

N-pentane resistance measurement

The NR resistance of n-pentane was investigated by swelling test, immerse NR with different curing

system in n-pentane. The swelling behavior of the NR vulcanizate was shown in Figure 4 and Table 5.

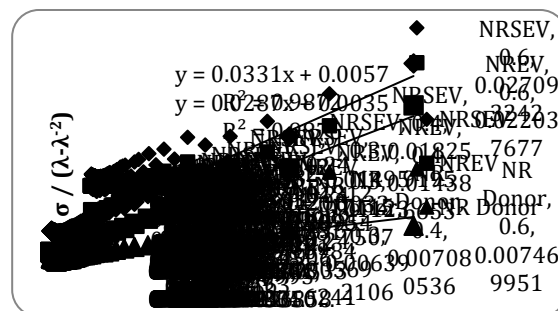


Figure 3. $1/\lambda$ vs. $\sigma/(\lambda - \lambda^{-2})$ of NR vulcanized with different curing system.

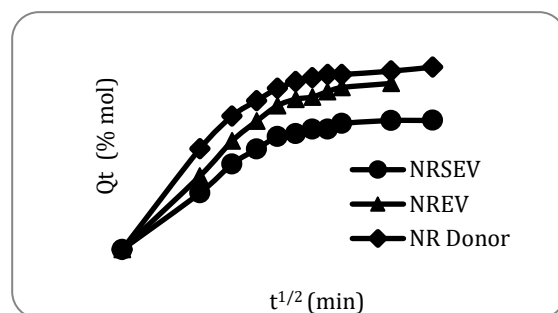


Figure 4. Molar percentage uptake (Q_t) of NR with different curing system.

3. Discussion

Cure characteristics and kinetic study

The semi efficient system showed the higher maximum, minimum and delta torque than other vulcanization system. Delta torque is related to crosslink density and stiffness of the rubber vulcanized [15,16]. Delta torque in NR donor sulfur system showed the lowest value.

Table 4. Crosslink density and mechanical properties of NR vulcanized with different acrylonitrile content

Samples	Crosslink density (mol/cm ³)	Hardness (Shore A)	Tensile strength (MPa)	Elongation at Break (MPa)	Compression set (%)
NRSEV	2.30 x 10 ⁻⁶	60	32.9	530	7.92
NREV	1.453 x 10 ⁻⁶	52	30	420	5.66
NR Donor	1.29 x 10 ⁻⁶	48	21.5	570	8.89

Table 5. Equilibrium mol uptake, diffusion coefficient and sorption of NR vulcanized with different curing system

Samples	Equilibrium mol uptake (Q _∞) (%)	Diffusion coefficient (D) (cm ² /min)	Sorption (S) (%)
NRSEV	0.9078	4.19 x 10 ⁻⁵	0.5728
NREV	1.1683	4.61 x 10 ⁻⁵	0.8423
NR Donor	1.1810	4.79 x 10 ⁻⁵	0.9228

The replacement of sulfur as vulcanization agent showed un-actively, due to the lowest crosslink formed in the donor sulfur curing system, which is dominated with mono- sulfidic crosslink. In addition, SEV curing system exhibited shorter t_{90} values than other curing systems due to crosslinks formation [17]. The low value of optimum cure time is beneficial in increasing the production rate. Increased vulcanization rates accordingly lead to increase productivity, decrease energy requirements in curing operations and increase cost savings in the curing of rubber articles.

The establishment of an optimal curing process of rubber vulcanizates depends on the understanding of the curing kinetics and curing mechanism. The isothermal vulcanization kinetics of the rubber compounds are usually characterized by two general model equations namely, n th-order and autocatalytic model equations. The n th-order kinetic equation predicts that the maximum reaction rate occurs at the very beginning of the reaction, whereas the autocatalytic equation demonstrates that the maximum reaction rate will be at any point of time other than time $t=0$ (reference). According to Figure 1, the reaction rate is observed to increase initially with conversion and passes through a maximum and then gradually slows down, finally tending to zero. Moreover, this shows that the reaction rate of the system reaches a maximum at time $t > 0$, which is autocatalytic model is more appropriate to describe the cure behavior of the system.

The activation energies for three curing systems obtained from the slope of the straight line is given in Table 3. It is seen from the Arrhenius plot that the slope of NRSEV and NR donor showed a similar trend, whereas NREV showed a moderate slope, having crossover points with the NR donor at lower temperature. This indicates that NR compound with the EV curing system need a lower amount of energy for vulcanization, as conceived in the calculation of activation energy. The rate constant (k) of each curing system shown different trend. The rate constant of NR vulcanizate with the SEV curing system was increase slightly with increase of curing temperature. In other hand, NR vulcanizate with EV and the donor sulfur curing system shown in consistency trend of rate constant to curing temperature. An increase in temperature does not change the rate constant considerably, indicating that vulcanization NR with EV and donor sulfur curing system can be done at a relatively lower temperature compared to SEV curing system. The reaction order shown same trend as the rate constant in each curing system. According to Table 3 it can be observed that SEV curing system has lower reaction order, while the donor sulfur system has higher reaction order. The higher accelerator loading in donor sulfur than others due to increase reaction order. In other hand, the higher sulfur loading in SEV curing system

than others due to decrease of reaction order. The same trend has been reported in Khang and Ariff [18].

Crosslink density and mechanical properties

The crosslink densities of NR with different curing system were given in Table 4. The crosslink density of NRSEV was the highest, correspond to NR cure characteristic (Table 2). This phenomena due to the highest sulfur loading in this curing system than others. The highest amount of sulfur provides more crosslink in the rubber [18]. Moreover, the NR donor has the lowest crosslink density. The donor sulfur curing system has only produce mono sulfidic crosslink, whereas SEV curing system produce polysulfidic, di-sulfidic and mono-sulfidic crosslink [19], so there is a little amount of crosslink in donor sulphur curing system.

Based on Table 3, it can be observed that the higher crosslink density will increase the hardness and tensile strength. While the elongation at breaking point decreased, but to a relatively small degree. In addition, the EV curing system expressed the lowest compression set. The lower loading of sulfur provides mono-sulfidic crosslink, which is express lower compression set [16,19]. The lower compression set, the better material used for rubber seal. It indicate that the EV curing system will produce better NR mechanical properties for rubber seal than other curing system.

N-pentane resistance measurement

Figure 4 shown that NR with different curing system has alike curves. The molar percentage uptake increases initially and pass through a maximum and then stable. This trend means that a number of n-pentane diffuse into rubber vulcanizates and the distance between the rubber molecules reach equilibrium. The SEV curing system shown the lowest diffusion coefficient and sorption, due to the highest crosslink density than other curing system. Crosslink restricted the expansion of rubber compounds which made it difficult for solvent to diffuse into the gap between molecules, hence decreased the swelling ratio [9]. In addition, Klattanavith [8] reported that crosslink type in NR was also influenced the swelling behavior of NR in toluene. This present work expressed that SEV curing system, predominantly di- and poly-sulfidic, showed better swelling behavior in n-pentane than mono-sulfidic crosslink.

4. Conclusion

The curing characteristic of NR vulcanizates shown that the SEV curing system was produced higher crosslink density and fastest optimum cure time. The kinetic study of vulcanizing rate determined using autocatalytic model. The activation energy of EV curing system was lower than others. The highest crosslink density was obtained from SEV, fit with the result of curing characteristic study. The crosslink density was impressed on mechanical properties and swelling

behavior. The higher crosslink density will increase hardness and tensile strength decrease slightly on elongation at breaking and compression set. In addition, the higher crosslink density will reduce the equilibrium mol uptake (Q_{∞}) and escalate diffusion (D) and sorption (S) coefficient. The lower sulfur loading in curing system was impacted on amount and type of crosslink, which is restricted the diffusion of solvent (n-pentane) to rubber. NR with SEV curing system provide the highest crosslink density, which dominated with di- and polysulfidic crosslink, give highest activation energy and lowest escalate diffusion and sorption coefficient.

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