

Effect of the Temperature on the Kinetic of Natural Rubber Vulcanization with the Sulfur Donor Agent Dipentamethylene Thiuram Tetrasulphide

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ABSTRACT: The effect of the temperature on the kinetics of vulcanization of natural rubber with the sulfur donor agent dipentamethylene thiuram tetrasulphide (DPTT) was investigated. The oscillatory disk rheometer and differential scanning calorimetry under dynamic and isothermal conditions were used. The Coran's model was applied to set the kinetic constants within each distinct step of the vulcanization process using the obtained values of the rheometer curves. During the curing period it was observed that there were two stages. Either the torque increment (ΔS) or the

crosslink density arise a maximum value at 130°C. The dynamic and isothermal thermograms showed two overlapped peaks during the curing reaction. These results were in concordance with those obtained by curemeter testing. In addition, the activation energy of the vulcanization process was also calculated by means of both techniques. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 692–701, 2010

Key words: kinetic; torque rheometer; differential scanning calorimetry; sulfur free vulcanization; elastomers

INTRODUCTION

Much empirical information on the nature of sulfur vulcanization has been accumulated since the discovery by Goodyear and Hancock of the vulcanization process in the early years of the 19th century. However, today the nature of the vulcanization process is not completely understood.¹

Analytical techniques such as nuclear magnetic resonance (NMR),^{2,3} mass spectrometry (MS),⁴ infrared (IR),⁵ and Raman spectroscopy,^{6–8} can be applied, but always with difficulties, and this cannot discriminate between different reactions that take place at the same time.⁹

Popular techniques used to study the kinetics of rubber vulcanization include differential scanning calorimetry (DSC) and oscillating disk rheometers (ODR).^{10–12} The last one is based on the fact that crosslink density is proportional to the stiffness of the rubber. A typical accelerated sulfur vulcanization curve of natural rubber is shown in Figure 1. The curve illustrates three periods of vulcanization process: scorch or induction period, curing period and over cure period. During the past years, by investigating the kinetics of rubber vulcanization, some mathematical equations have been deduced to

express the vulcanization curve. Coran¹³ deduced a famous scorch model well describing the induction period and treated¹⁴ the curing period with one first-order kinetics equation. Pal et al.^{15,16} proposed that the curing period could be treated as two stages expressed in two first-order kinetics equations with different rate constants. Furukawa et al.¹⁷ through analyzing the curve with the theory of molecular rheology suggested that curing period could be expressed in two different equations separately.

According to Coran's model, the period that corresponds to the curing process can be described by a general equation, which relates the degree of crosslink, α , with the time. For isothermal systems, this equation may be written as follows¹⁸:

$$\left(\frac{\partial\alpha}{\partial t}\right)_T = k(T)f(\alpha) \quad (1)$$

The function $k(T)$ can be expressed as an Arrhenius type relation:

$$k(T) = k_0 e^{-(E/RT)} \quad (2)$$

where k_0 is the preexponential factor, E is the activation energy, R is gas constant and T is the temperature in Kelvin degrees.

The second term of eq. (1) is a mathematical expression for the kinetic model as a function of the conversion degree as:

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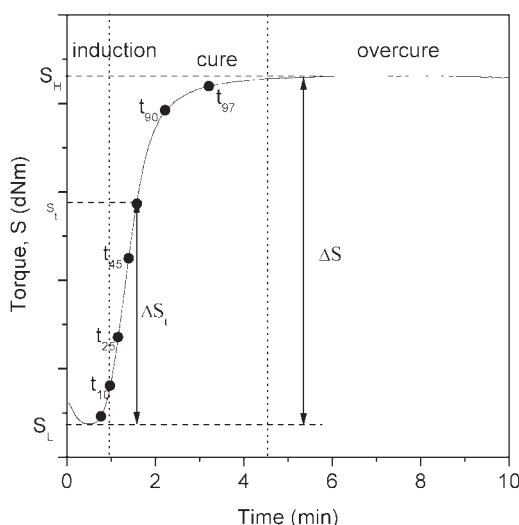


Figure 1 Typical curve of torque versus time obtained by oscillatory disk rheometry.

$$f(\alpha) = (1 - \alpha)^n \quad (3)$$

where n is the order of the vulcanization reaction.

The DSC technique is based on the assumption that the heat of reaction is that the chemical reaction rate at any given moment is directly proportional to the rate of heat release, because of many competitive reactions are occurred during the vulcanization process is very difficult to measure the enthalpy for a specific reaction.^{12,19}

The degree of conversion at the moment t is determined as a ratio between the heat released at this moment and the total heat of the reaction.²⁰

$$\alpha = \frac{\Delta H_t}{\Delta H_0} \quad (4)$$

Numerous research workers, including Wang et al.¹⁰ and Sirqueira et al.,¹¹ studied the kinetics of rubber vulcanization only used ODR; Ding and Leonov¹² investigated the process of the vulcanization using both the oscillating disk rheometer (ODR) and differential scanning calorimetry but the DSC data were found to be unfitting with the cure meter test, because the isothermal reaction peak was too small and broad to be determined accurately. In this work, the effect of the temperature on the kinetics of vulcanization of natural rubber with the sulfur donor agent dipentamethylene thiuram tetrasulphide was investigated by means of both the oscillatory disk rheometer and DSC under dynamic and isothermal conditions. In addition, the activation energy of the vulcanization process was also calculated by means of both techniques.

EXPERIMENTAL

Materials

The natural rubber was based on standardized NR (NR SMR) provided by Malaysian Rubber Board (Kuala Lumpur, Malaysia). The crosslink was made by using dipentamethylene thiuram tetrasulphide (DPTT) provided by Flexsys (Brussels, Belgium). The Zinc oxide used were extra pure grade provided by Lanxess (Germany) and the stearic acid were 95% pure provided by Aldrich (Germany).

PROCEDURES

Blending and curing

Rubber compounds were prepared in an open two-roll mill at a temperature of 40–50°C. The optimized DPTT proportion was three parts per hundred of rubber (phr) and the proportion of the other ingredients were: 5.0 phr for the zinc oxide and 1.0 phr for the stearic acid. Cure measurements were conducted using a Monsanto Moving Die Rheometer, model MDR 2000E. The gum mixes were characterized at 10 temperatures from 90 to 170°C by means of the torque curves in a Monsanto MDR 2000 rheometer. From each of these curves some characteristic parameters as the torque maximum S_H and the minimum torque S_L , ΔS ($S_H - S_L$) and t_{97} were obtained.

The crosslink decomposition was evaluated from the reversion degree (R), according to the equation:

$$R(\%) = \frac{(S_H - S_{H+30})}{S_H} \times 100 \quad (5)$$

where S_H is the maximum torque and S_{H+30} is the torque after 30 min from the maximum torque.

Determination of crosslink density

Equilibrium swelling in toluene (~ 3 days at 30°C) was used to determine the crosslink density of the different compounds vulcanized at their respective cure time t_{97} in the moving die rheometer. The volume fraction of polymer in the swollen sample (V_r) was calculated using the following equation:

$$V_r = \frac{V_{\text{rubber}}}{V_{\text{rubber}} + V_{\text{solvent}}} \quad (6)$$

where V_{rubber} is the volume of the compound minus the volume of the oxide zinc, and V_{solvent} is calculated by the following expression:

$$V_{\text{solvent}} = \frac{W_s - W_d}{\rho} \quad (7)$$

where W_s is the swollen weight of the compound, W_d is the dry weight of the compound, and ρ is the solvent density.

Cured compounds crosslink density was obtained by using the Flory-Rehner equation²¹:

$$v = -\frac{1}{2V_i} \times \frac{\ln(1 - V_r) + V_r + \chi V_r^2}{V_r^{1/3} - V_r/2} \quad (8)$$

where V_i is the solvent molar volume and χ is the polymer-solvent interaction parameter (0.393).

DSC experiments

The DSC experiments were carried out in a Mettler Toledo differential scanning calorimeter (DSC 822^e) in a nitrogen atmosphere. The temperature and heat flow calibration was performed against standard samples of indium ($T_{\text{melt}} = 156.6^\circ\text{C}$; $\Delta H_{\text{spec}} = 28.4419 \text{ J/g}$) and Zn ($T_{\text{melt}} = 419.6^\circ\text{C}$). The mass of the sample under study was $\sim 20 \text{ mg}$. Under isothermal conditions, the sample was heated to the preset temperature at a heating rate of $80^\circ\text{C}/\text{min}$ then, isotherms were recorded. The time during which the thermal stability was attained was $\sim 1.1 \text{ min}$. The DSC isotherms were recorded at temperatures from 120 to 170°C . At lower temperatures the peaks of the reactions of crosslink are too small. Under no isothermal conditions, the samples were heated at a rate of 5, 10, 15, and $20^\circ\text{C}/\text{min}$. The temperature dependences were obtained at $25\text{--}300^\circ\text{C}$. Weight losses of the samples after the experiments were insignificant—no more than 0.5% of the initial sample mass. The amount of heat released was determined from the peak area between the DSC curve and baseline. The accuracy of measurements was $>1^\circ\text{C}$ for the temperature and $\sim 3\%$ for the heat of crosslink.

RESULTS AND DISCUSSION

Theory

Today there is no evidence to fully support any one cure mechanism. Consequently, the controversy on the nature of the action of the active sulphurating agent remains without clarity.¹ In absence or presence of zinc oxide, a free-radical mechanism,^{22–26} in which the active sulphurating agent is an accelerator polysulphide as shown in the Scheme 1, seems to fit the experimental results best.

The thermal scission of DPTT is proposed to take place through homolytic cleavage to produce radical species as shown in eq. (1). The unsymmetrical cleavage is also possible; however, it is not so likely, since it requires breaking of the more stable C–S bond.

A variety of exchange reactions can occur in the early stages of vulcanization. Gradwell and McGill²⁷ suggest exchange reactions between the radical species indicated in eq. (1) with DPTT to obtain radicals of higher sulfur rank, as shown in eq. (2). In general,

for these reactions occurring is necessary that the intermediate free-radical have sufficient stability for it can diffuse in the matrix and react to form species with higher sulfur rank. The stability of this radical species is due to resonance stabilization and formation of a three-electron bond between the two thermal sulfur atoms.^{28–30}

The thiocarbonyl radical indicated in eq. (1) or others obtained via recombination of radical species, can abstract a hydrogen atom of the rubber to form the crosslink precursor or sulphurating agent. This species subsequently reacts with another rubber molecule through the same free-radical pathway to form a crosslink. Two macroradicals could also form a crosslink via recombination but it is less probably because of the limited diffusional mobility of two macroradicals. This active sulphurating species can also be transformed into a crosslink via disproportionation. In this case, two crosslink precursors form one crosslink an accelerator polysulphide.

With the reaction of disproportionation, it is possible to obtain also the formation of crosslink of higher lengths. However, the reaction cannot account for the formation of monosulphidic crosslinks.

Another objection comes from the consideration of the low diffusional mobility, as we are dealing with bulky molecules which must diffuse in a highly viscous rubber matrix. The formation of crosslinks by this mechanism is probably not very important. Another possible mechanism of formation of crosslinks is by direct reaction of the crosslink precursor with an allylic moiety of a near rubber chain,^{13,14,31} as shown in eq. (8).

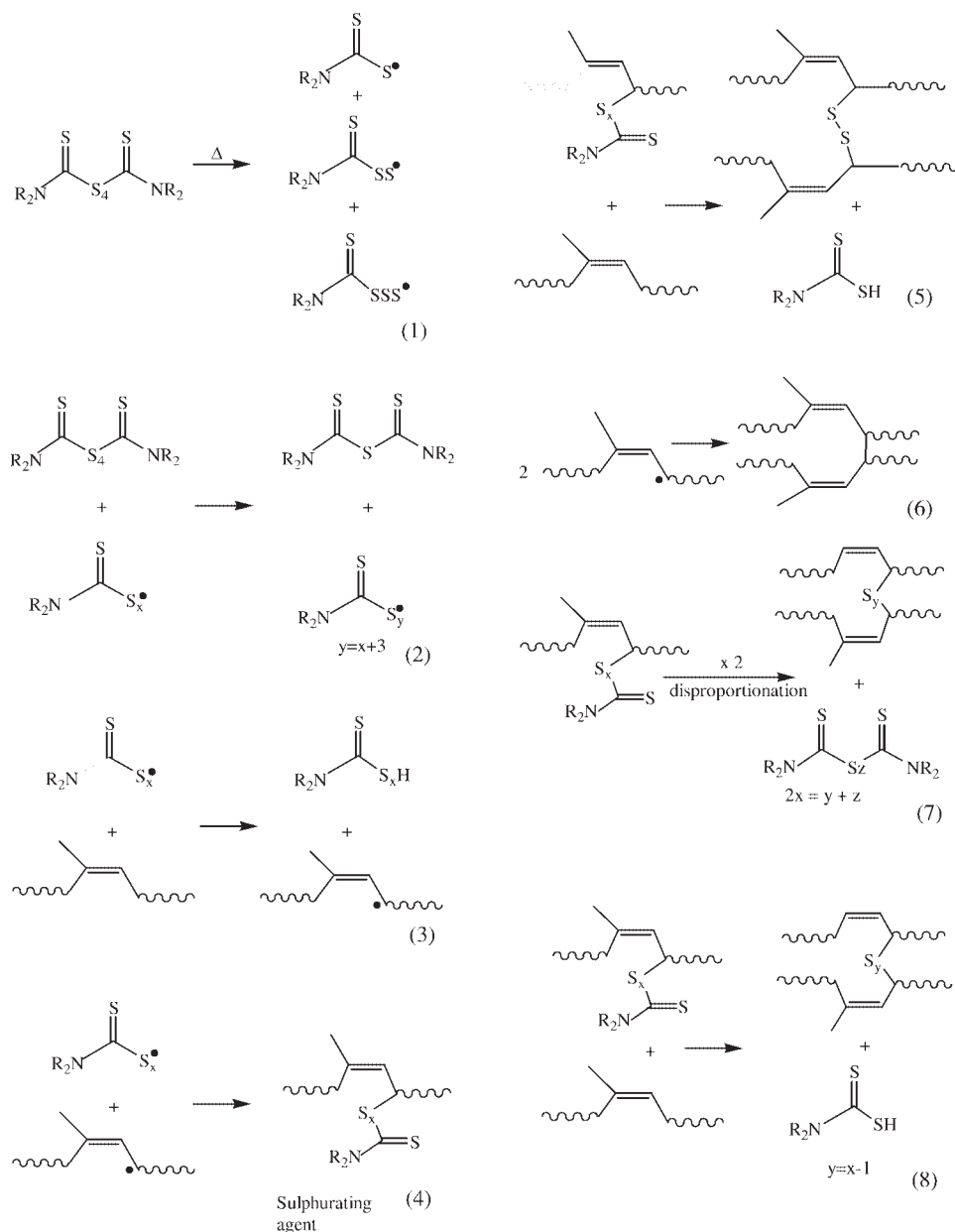
The free-radical intermediates produced by the different accelerator species in the absence of sulfur must have sufficient stability so that they can diffuse and react to form the polysulphidic species. Evidence of the existence of radical species is provided by EPR spectroscopy.^{23,32} It is possible to conclude that the rubber vulcanization proceed via radical intermediates, however, a mixed radical and polar mechanism results upon addition of zinc oxide to system.

A simplified kinetic scheme for accelerated sulfur vulcanization is according to Coran¹⁵ is shown in the Scheme 2.

Where A is the accelerator, in this case, the sulfur donor and/or its reaction products that is, the active sulphurating agent (see (4) of the Scheme 1); B is the crosslink precursor; B* is an activated form of B, for example a polythiyl radical; V_u is the crosslink; α and β are adjustable stoichiometric parameters.

Theory of the vulcanization kinetic from rheometer

It was shown that the increase in the rheometer torque is directly related to the crosslink density.¹⁹



Scheme 1 Free-radical mechanism for the accelerated sulfur vulcanization.

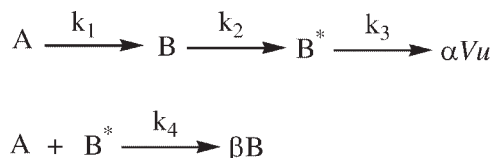
Assuming that the vulcanization follows first-order kinetics, to determine the constant k_2 , the torque variation is plotted against time, as follows eq. (9):

$$\ln\left(1 - \frac{\Delta S_t}{\Delta S}\right) = k_2 t \quad (9)$$

where ΔS corresponds to the difference between maximum (S_H) and minimum torques (S_L) and ΔS_t corresponds to the difference between the torque at a particular time and the minimum torque.

Figure 2 shows this plot. The velocity constant k_2 corresponds to the negative slope of the straight line portion of the curve after the induction period, that

is, the conversion range that follows the first-order kinetics, assuming the formation of V_u to be first order in B.¹³ The first-order nature of the crosslink formation is not achieved immediately upon the onset of crosslink formation. The time required for



Scheme 2 Kinetic scheme for accelerated sulfur vulcanization.

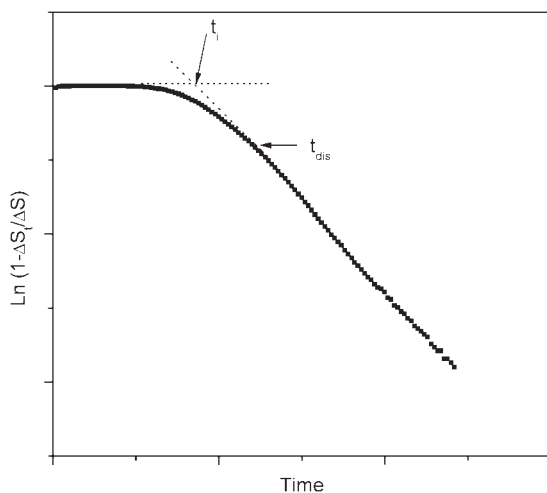


Figure 2 Typical curve of $\ln(1 - \Delta S_i/\Delta S)$ versus time, according to Coran model.

crosslink to become an unperturbed first-order reaction is assumed to be the time t_{dis} ¹¹ required for the curvature in the log plot to disappear. The time t_i corresponds to the intersection of the two regions of the log plot and is considered as the induction period.

Coran has also proposed the determination of the constant, k_1 , from a mathematical treatment, taking into consideration the rate of disappearance of species A.¹³ The following expression was proposed in the Coran model:

$$k_1 t_{\text{dis}} - \ln k_1 = k_2 t_{\text{dis}} - \ln k_2 \quad (10)$$

For the solution of this equation, Coran assumed that $k_1/k_2 = Z$, and

$$k_2 t_{\text{dis}} = -\ln\left(\frac{Z}{1-Z}\right) \quad (11)$$

Coran has calculated values of $k_2 t_{\text{dis}}$ for various values of Z and plotted them against one another. From the $k_2 t_{\text{dis}}$ values obtained from rheometer traces, the Z values and consequently k_1 were obtained.¹³

The Arrhenius equation was used to calculate the activation energy of the mixes:

$$k_i = k_{i0} \exp(-E_i/RT) \quad (12)$$

where k_{i0} , E_i , and R are the pre-exponential constant, activation energy and gas constant, respectively.

A plot of $-\ln k_i$ versus $1/T$ gives a straight line for the sulfur donors system. The activation energy (E_i) can be calculated from the slope of this line.

Theory of the vulcanization kinetics using DSC

A DSC thermogram is the net result of all reactions occurring within the temperature range of interest. When a rubber compound is heated, many reactions occur competitively; thus, is very difficult to measure the enthalpy for a specific reaction.¹⁹ The DSC principal assumption²⁰ is that chemical reaction rate at any given moment is directly proportional to the rate of heat release:

$$\frac{d\alpha}{dt} = \left(\frac{1}{\Delta H_0}\right) \frac{dH}{dt} \quad (13)$$

where $d\alpha/dt$ is the reaction rate, dH/dt is the heat released per unit time or the heat flow, and ΔH_0 is the reaction heat determined from the peak area between the DSC curve and the baseline.

The degree of conversion (crosslink) at the moment t is determined as a ratio between the heat released at this moment and the total heat of the reaction:

$$\alpha = \frac{\Delta H_t}{\Delta H_0} \quad (14)$$

Vulcanization kinetic from the rheometer

The curing characteristics, expressed in terms of S_H , S_L , ΔS , optimum cure time (t_{97}), and % R (reversion) for the studied material are reported in Table I. The effect of temperature on the rheometer curves with the sulfur donor DPTT, are shown in Figure 3. Over the temperature range from 90 to 130°C, the compound displays a flat plateau indicating that at these temperatures the formed crosslinks are thermally stables. The maximum torque is shown at the temperature of 130°C which is an indication of increased

TABLE I

Cure parameters	T (°C)								
	90	100	110	120	130	140	150	160	170
S_H (dNm)	7.97	8.36	7.86	7.80	9.04	7.85	7.77	7.44	7.30
S_L (dNm)	1.09	0.95	0.75	0.63	0.55	0.45	0.41	0.38	0.43
ΔS	6.88	7.41	7.11	7.17	8.49	7.4	7.36	7.06	6.87
t_{97} (min)	479.84	164.2	59.39	22.98	14.78	5.44	3.14	1.69	1.09
% R	–	–	0.13	0.64	2.54	2.93	6.56	11.16	16.44

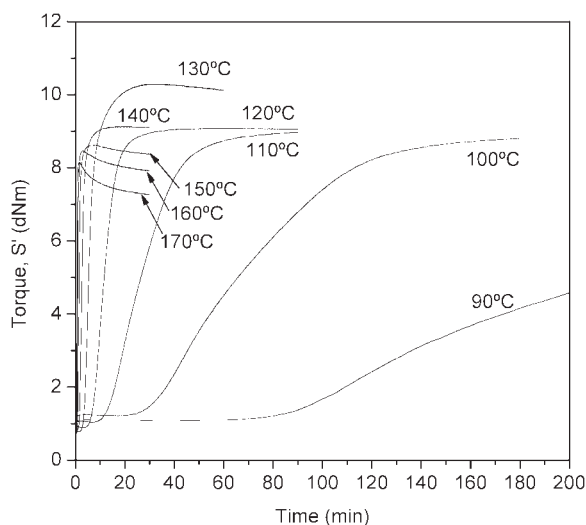


Figure 3 Torque versus time curves of NR/DPTT at the different temperatures.

crosslink density. When cure temperature increases, thermal stability slightly decreases. Blends present the three different crosslink structures: polysulphidic, disulphidic, and monosulphidic; and the most abundant species are the polysulphidic structures around 70%, as previously reported.^{1,33} At the temperature increase, due to the cleavage of the polysulphidic crosslinks, that have low thermal stability, an increased tendency towards reversion in the compounds was observed.

The formation of polysulphidic structures suggests²⁴ that the reaction between the radical species obtained with the thermal cleavage of DPTT given in the literature³⁴ to obtain species with higher sulfur rank,¹ and also by the route of disproportionation seems to be present.

Table II shows the changes in V_r (volume fraction of rubber), crosslink density and M_c (molecular weight between crosslinks) of the vulcanized at the different temperatures and their optimum cures times, measured by equilibrium swelling in toluene and calculated by the Flory-Rehner equation. The maximum values of V_r , and v is shown at the 130°C temperature. These results are in agreement to the

TABLE II

T (°C)	V_r	v (mol/cm ³) × 10 ⁻⁵	M_c
100	0.1906	6.4593	7122
110	0.1890	6.3306	7266
120	0.1924	6.5963	6974
130	0.1979	7.0377	6536
140	0.1949	6.7947	6770
150	0.1925	6.5096	7066
160	0.1916	6.5307	7044
170	0.1914	6.5197	7055

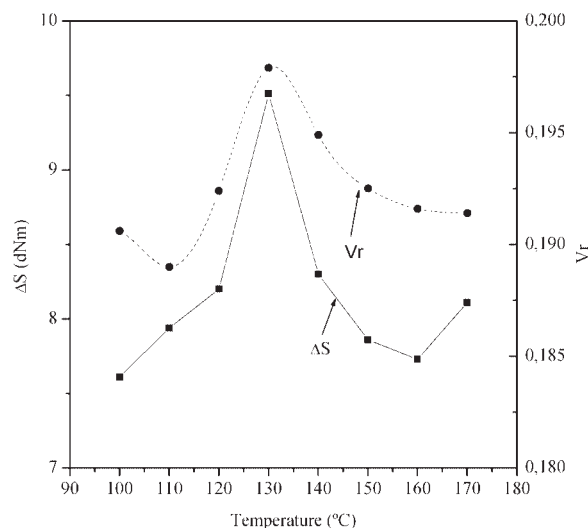


Figure 4 Changes to the temperature, in the torque increment and rubber volume fraction.

results obtained to the rheometer curves as it is shown in Figure 4.

To study the influence of the temperature on the kinetic vulcanization with the sulfur donor DPTT, we used the Coran simplified model, previously described in the introduction. Figure 3 describes the dependence of torque variation against time. From these curves the kinetic parameters were calculated, as summarized in Table III. The k_1 values were calculated from a mathematical relationship proposed by Coran¹³ as summarized in the introduction part of this work. As observed in Figures 5 and 6, the time t_{dis} required for crosslink to become an unperturbed first-order reaction was reduced when increasing the temperature. These results corresponded to an increase of k_1 values at increasing the temperature as it observed in the Table III. The parameter k_1 ¹² is temperature dependent and mainly determines the induction time. Larger values of k_1 result in a shorter induction time. The values of k_1 are lower than the values of k_2 at every temperatures studied.

TABLE III

T (°C)	t_{dis} (min)	t_i (min)	k_1 (min ⁻¹)	k_2 (min ⁻¹)	E_{a1} (KJ/mol)	E_{a2} (kJ/mol)
90	284.74	177.05	0.00115	0.0114	100.7	101.9
100	97.58	68.58	0.00320	0.0383		
110	36.40	26.90	0.00796	0.1120		
120	10.79	8.70	0.03654	0.2462		
130	7.18	1.92	0.07295	0.2746		
140	3.19	1.53	0.11533	0.8955		
150	1.99	0.82	0.17311	1.5382		
160	1.18	0.69	0.23648	3.6043		
170	0.59	0.51	0.52034	6.4687		

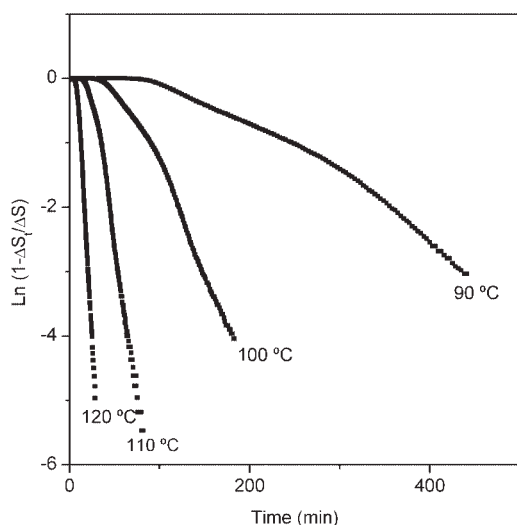


Figure 5 $\text{Ln}(1 - \Delta S_t/\Delta S)$ versus time from 170°C to 130°C.

The parameter k_2^{12} is a function of temperature and controls the rate of cure, especially in the late stage of the curing period. Higher values of k_2 indicate a faster rate of cure. As observed in Figures 5 and 6, after the time t_{dis} , the curing period of natural rubber vulcanization with the sulfur donor (DPTT) consists of two stages, just as Pal et al.^{15,16} proposed that the curing period could be treated as two stages expressed in two first-order kinetics equations with different rate constants. Wang et al.¹⁰ proposed that the curing period of natural rubber vulcanization consists of two stages: stage I follows first-order kinetics and stage II has values of reaction order in a range of 0.68–0.74, the stage II is near the end stage of curing period. They explain these two different stages accepted that the initially formed networks undergo reaction of crosslink shortening, crosslink

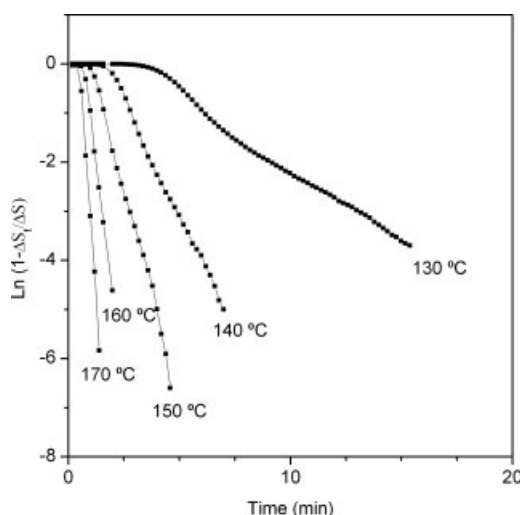


Figure 6 $\text{Ln}(1 - \Delta S_t/\Delta S)$ versus time from 120°C to 90°C.

destruction and S–S bond interchange. Thus, the change of reaction order from $n = 1$ in stage I to $n \neq 1$ in stage II could be considered as a reflection of the effect of aging on crosslink.

The 120°C rheogram shows a large plateau and in this case it can be inferred that every useful sulfur atoms of DPTT molecule (there are two useful sulfur atoms per DPTT molecule) were totally consumed in the different crosslink types, mono-, di-, and polysulphide species. When the temperature was elevated at 130°C the rheogram presented also a flat response, but in this case, with a higher torque, indicating a decrease in the contents of polysulphide species. This phenomenon allows the increase of the crosslink density in a network formed with less sulfur atoms per link. When the temperature continued increasing the polysulphide species underwent crosslink shortening and crosslink destruction reactions of polysulphide species as it is shown by the decrease in the maximum torque.

Over the temperature range studied, there is no difference between the activation energy for the formation of the sulphurating agent (B) and the later active sulphurating agent form (B*) and the obtained values are similar to the values found in the literature.¹⁹

Vulcanization kinetics from DSC

Because of when a rubber compound is heated in the DSC, many reactions occur competitively; thus, is very difficult to measure the enthalpy for a specific reaction.¹⁹ The DSC curves of samples obtained at various heating rates are shown in Figure 7. Every DSC curves showed at least two (possibly three) closely situated thermal events. The DSC curve

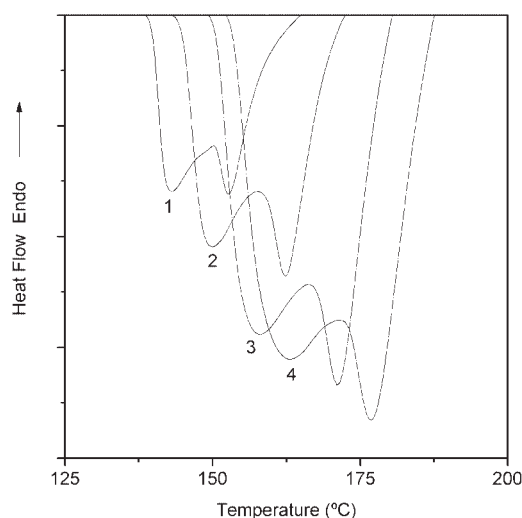


Figure 7 DSC thermograms of crosslink NR for various scan rates: 5°C/min (1), 10°C/min (2), 15°C/min (3), 20°C/min (4).

TABLE IV

β ($^{\circ}\text{C}/\text{min}$)	T_{init} ($^{\circ}\text{C}$)	T_{max} ($^{\circ}\text{C}$)	ΔH_0 (J/g)	E_a (KJ/mol)				
				Ozawa		Kissinger		
				$T_p(1)$	$T_p(2)$	$T_p(1)$	$T_p(2)$	
5	139	144	152	0.62	101.3	91.4	94.2	84.1
10	143	150	162	4.84				
15	149	158	170	3.24				
20	153	164	176	4.98				

of the DPTT pure and the polymer were made too but the changes enthalpies were insignificance in comparison with the enthalpy of the crosslink reaction.

It is evident from Figure 7 that an increase in the scanning rate results in shifting the peak of crosslink to the region of higher temperatures.²⁰ The vulcanization stage is initiated at the temperature (T_{init}) of completion of the induction period; this in agreement with the concept about the mechanism of vulcanization. From the thermograms obtained, the temperature of initiation (T_{init}) and the maximums rate (T_{max}) of the two thermal events as well as the heat effect of the reaction at different scanning rates were determined. Total heat was calculated by the formula including the rate of heating of the sample where β is the heating rate according to the equation:

$$\Delta H_0 = \frac{1}{\beta} \int_{T_1}^{T_2} \frac{dH}{dt} dT \quad (15)$$

The temperature and total heat of NR crosslink at various scanning rate are listed in Table IV. The reaction heat must be increased as the scanning rate is increased.²⁰ At $15^{\circ}\text{C}/\text{min}$, the heat reaction of crosslink decreases; the effect may be caused by other secondary reactions that contribute to the total heat effects of the process.

The shift in the temperature of the second peak crosslink of rubber to the region of higher temperatures with increasing heating rate may be attributed to the influence of the molecular mobility in the chemical process. At a low heating rate,²⁰ there is enough time for the chains to reach the states favorable for crosslink. At a high heating rate, these states are attained later, at higher temperatures.

The E_a of the curing process was estimated by means of both the Ozawa and Kissinger equations^{35,36}:

$$E_a = -2.3R \left[\frac{(d \log \beta)}{(d(1/T_p))} \right] \quad (16)$$

$$E_a = -2.3R \left[\frac{(d \log (\beta/T_p^2))}{(d(1/T_p))} \right] \quad (17)$$

where T_p is the temperature of the exothermic peak and β is the heating rate.

The results obtained by both expressions are summarized in Table IV. The result of the Energy of activation close to the literature data^{19,35,36} and rheometer results correspond to the E_a calculated with the Ozawa equation for the maximum of the peak 1.

From the temperatures dependences of NR crosslink proceeding under isothermal conditions at various temperatures (Fig. 8), it is evident that the higher the temperature is, the sooner the crosslink is initiated.²⁰ Because of the time of induction of the compound at 170°C is lower than the time to stabilize the temperature in the DSC, the beginning of the exotherm peak is not recorded. When the temperature decrease, it is observed that two exotherm peaks due to the crosslink are recorded at the curing period of natural rubber vulcanization with the sulfur donor (DPTT). This is in agreement with the rheometer results where it is observed that in the curing period there are two stages. The stage II¹⁰ is

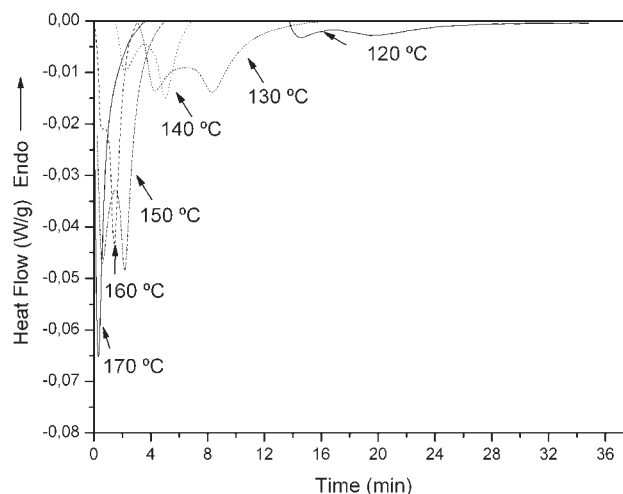


Figure 8 Isothermal DSC curves of crosslink NR from 170 to 120°C .

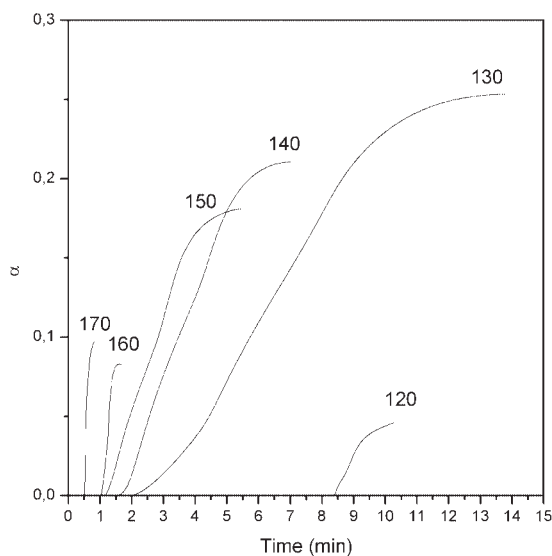


Figure 9 Kinetic curves of crosslink NR at 170°C (1), 160°C (2), 150°C (3), 140°C (4), 130°C (5) and 120°C (6).

near the end stage of curing period where the initially formed networks undergo reaction of crosslink shortening, crosslink destruction and S—S bond interchange and the crosslinks follows formed network, the DSC is capable to record these two thermal events.

The degree of crosslink achieved by the time t was determined as $\alpha = \Delta H_t / \Delta H_0$, where ΔH_0 is the heat of rubber crosslink under nonisothermal conditions at a heating rate of 5°C/min. Figure 9 shows the kinetic curves of the NR vulcanization proceeding under isothermal conditions from 170 to 120°C. In all cases, we observe a drastic increase in the crosslink rate after the end of the induction period. The induction period (the absence of a recordable heat effect) involves melting and interactions of the vulcanizing group components; these processes are associated with an insignificant total heat effect. The quasy-stationary segment of the kinetic curve corresponds to the period of formation of crosslinks between macromolecules. From the kinetic curves, we determined the maximum rate and the effective energy of activation of NR crosslink with the vulcanizing group chosen and the obtained value was 79 KJ/mol is slightly lower than the obtained from the rheometer results.

Due to all useful sulfur atoms of DPTT molecule were totally consumed in the different crosslink types, mono-, di-, and polysulphide species, a small degree of crosslink is showed at the 120°C kinetic curve. When the temperature was elevated at 130°C the kinetic curve presented also a flat response, but in this case, with a higher degree of crosslink, indicating a decrease in the contents of polysulphide species. These results are in agreement to the results obtained to the rheometer curves, and the swollen

measurements as it is shown in Figures 3 and 4. When the temperature continued increasing the polysulphide species underwent crosslink shortening and crosslink destruction endothermic reactions of polysulphide species that they are consuming energy from the exothermic crosslink reaction leading to a less degree of crosslink.

The formation of polysulphidic structures suggests²⁴ that the reaction between the radical species obtained with the thermal cleavage of DPTT given in the literature³⁴ to obtain species with higher sulfur rank,¹ and also by the route of disproportionation seems to be present.

CONCLUSIONS

The effect of the temperature on the kinetics of vulcanization of natural rubber with the sulfur donor agent dipentamethylene thiuram tetrasulphide was investigated by means of both the oscillatory disk rheometer and DSC under dynamic and isothermal conditions.

The gum mixes were characterized from 90 to 170°C by means of the torque behavior in a Monsanto MDR 2000 rheometer. The Coran's model was applied to set the kinetic constants within each distinct step of the vulcanization process using the obtained values of the rheometer curves. The values of k_1 and k_2 increase when the temperature increase and the values of t_{dis} and t_i decrease when the temperature increase. During the curing period it was observed that there were two stages. Either the torque increment (ΔS) or the crosslink density arise a maximum value at 130°C.

Differential scanning calorimetry is a rapid and convenient method of studying the whole process of sulfur donor's vulcanization system including the induction period. The kinetic parameters obtained by DSC measurements, duration of the induction period, vulcanization rate and effective activation energy, are consistent with both, literature data and the results obtained by the other procedures studied: rheometer curves and swollen measurements.

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