

Effect of 2-Mercaptobenzothiazole Level on Kinetics of Natural Rubber Vulcanization

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ABSTRACT: The kinetics of natural rubber vulcanization were investigated by use of a vulcameter. The vulcanization process before t_{dis} (the time when the accelerators and/or intermediates react to depletion) was expressed in an equation as $\ln(M_H - M_t) = \ln A - k_1(t - t_0)^\alpha$, which is different from the famous equation of $Vu_t = -[\alpha(k_3/k_4)]\ln[(k_2e^{k_1t} - k_1e^{k_2t})/(k_2 - k_1)]$ deduced by Coran. It was found that the rate constants of two vulcanization processes with different reaction mechanisms before and after t_{dis} increase and their activation energies decreased with an increase in 2-mercaptobenzothiazole (MBT) level. The consid-

erable effect of MBT level on the activation energies of the vulcanization process before t_{dis} and the obvious temperature dependency of the reaction rate of vulcanization process after t_{dis} were observed. The time t_{dis} was shortened with an increase in MBT level, whereas the degree of vulcanization at t_{dis} remained unchanged. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 3260–3265, 2004

Key words: activation energy; kinetics; 2-mercaptobenzothiazole (MBT); natural rubber; vulcanization

INTRODUCTION

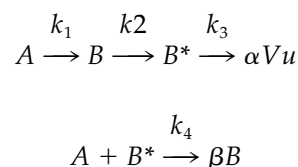
The concept of vulcanization intermediates or crosslink precursors formed in the initial stage of natural rubber vulcanization is generally accepted and confirmed experimentally.^{1–4} The formation of crosslink precursors is somewhat analogous to that of molecular chain branching with respect to increased rubber viscoelasticity. The formation of crosslink network in the main stage of natural rubber vulcanization brings about an increase in rubber elasticity. The values of vulcameter torque during the course of rubber vulcanization will increase irrespective of whether the viscoelasticity or elasticity increases. Hence it is convenient to investigate the kinetics of rubber vulcanization by using a vulcameter. The rate equation of rubber vulcanization can be expressed in the velocity V of the change of vulcameter torque as

$$V = -d(M_H - M_t)/dt = K(M_H - M_t)^n$$

For a first-order reaction, the kinetic equation can be written as

$$\ln(M_H - M_t) = \ln B - Kt$$

With respect to natural rubber vulcanization a typical curve is generally obtained by plotting $\ln(M_H - M_t)$ against t , as shown in Figure 1, where t_{dis} is the time when the accelerators and/or intermediates react to depletion.⁵ Doubtless the vulcanization process after t_{dis} is a first-order reaction. Coran^{5,6} suggested a model to explain the vulcanization process before t_{dis} , expressed as **Scheme 1**:



Scheme 1

where A is the accelerator and/or its reaction products (with sulfur, Zn^{++} , etc); B is a precursor to crosslinking, probably polymeric; B^* is an activated form of B , such as a polymeric polythiyl radical; Vu is a crosslink; and α and β are adjustable stoichiometric parameters. It was considered that if the reaction through k_4 is much faster than that through k_3 , the immediate crosslink precursors B^* are rapidly quenched, and crosslink formation would be impeded until A is substantially depleted. It is also considered that k_4 and k_3 are much greater than k_1 and k_2 . Based on this scheme and assumptions, Coran deduced an equation of $Vu_t = -[\alpha(k_3/k_4)]\ln[(k_2e^{k_1t} - k_1e^{k_2t})/(k_2 - k_1)]$ to describe

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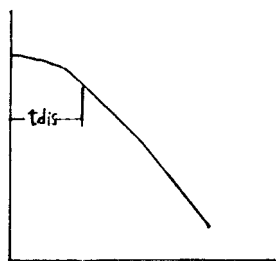
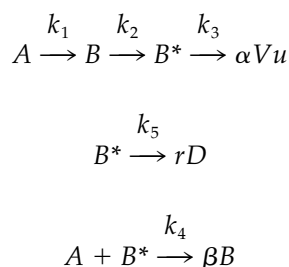


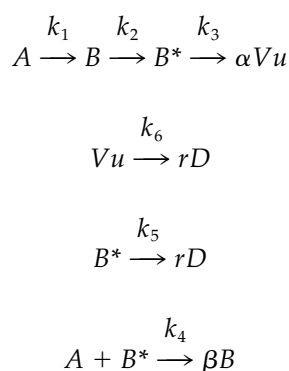
Figure 1 Relation between $\ln(M_H - M_t)$ (vertical axis) and t (horizontal axis).

the vulcanization process before t_{dis} . **Scheme 1** also serves to describe the curing and overcure (with equilibrium character) periods. For styrene-butadiene rubber showing a change of equilibrium modulus with temperature, Ding⁷ suggested a modified **Scheme 1**, expressed as **Scheme 2**:



Scheme 2

where D represents inactive side products and r is an adjustable stoichiometric parameter. **Scheme 2** introduces a competition between main reactions and side reactions and describes styrene-butadiene rubber vulcanization process with equilibrium overcure. For natural rubber (NR) with reversion in the overcure period, Ding⁸ suggested another modified scheme, expressed as **Scheme 3**:



Scheme 3

where the reaction through k_6 produces inactive species such as pendant sulfur branches and/or cyclic

sulfur in rubber backbones. In our previous work⁹ it was found that the time t_p , when the change of vulcanometer torque during the course of vulcanization reaches the maximum velocity, V_m , is nearly the same as t_{dis} . An equation of $\ln(M_H - M_t) = \ln A - k(t - t_0)^\alpha$ can be used to express the vulcanization process before t_{dis} and the value of $k_1^{1/\alpha}$ as a rate constant to calculate the activation energy of the vulcanization process before t_{dis} according to an Arrhenius equation.

2-Mercaptobenzothiazole (MBT) is an accelerator commonly used in rubber compounds. During the vulcanization process, according to **Scheme 3**, MBT would react (in the presence of zinc oxide and stearic acid) to produce a complex and the complex would react with a molecular sulfur to form a sulfuring agent. In turn the sulfuring agent would react with rubber chains to form a crosslinking precursor that subsequently would form polysulfidic crosslinks.^{10,11} At the same time some side reactions described in **Scheme 3** would occur.

This work continues the research begun in our previous work.⁹ The effect of MBT level on the kinetics of natural rubber vulcanized with sulfur in the presence of zinc oxide and stearic acid was investigated by using a vulcameter. It was observed that the increase of vulcameter torque value with vulcanization time does not follow first-order kinetics when the value of vulcameter torque increases, approaching maximum torque. In our opinion the change of kinetics in the vulcanization process is probably attributable to the effect of degradation, desulfuration, and S-S bond interchange on crosslink density, an area of investigation that will be discussed in a future article. Thus, the discussions in this article are limited to the range of scorch delay or induction period and crosslink period following first-order kinetics.

EXPERIMENTAL

Materials

The natural rubber was commercial standard Chinese rubber #5. Other materials were of industrial grade and were not purified.

Preparation and testing of samples

The test samples were prepared according to the following formulation (in parts per hundred of rubber): natural rubber, 100.0; sulfur, 3.0; zinc oxide, 5.0; stearic acid, 0.5; and 2-mercaptobenzothiazole, (MBT) variable.

The stocks were compounded according to Chinese Standard GB6038-93.

The curves of vulcanization were obtained by using an LHY-II vulcameter at 140, 150, 160, and 170°C,

TABLE I
Values of α , $k_1^{1/\alpha}$, k_2 , A , and B

MBT level	Parameter	140°C	150°C	160°C	170°C
0.7 (part)	α	2.2	2.0	2.0	2.1
	$k_1^{1/\alpha}$	0.1709	0.2506	0.3557	0.4904
	k_2	0.1380	0.2322	0.4187	0.7080
	A	2.5163	2.5625	2.4500	1.9931
	B	3.0465	3.2018	3.4914	3.4639
	r_1^a	0.9999	0.9999	0.9999	0.9999
1.0 (part)	r_2^b	0.9999	0.9989	0.9996	0.9994
	α	2.3	2.3	2.3	2.6
	$k_1^{1/\alpha}$	0.2517	0.3429	0.4909	0.6472
	k_2	0.2045	0.3546	0.6238	1.0215
	A	2.6928	2.6496	2.6266	2.5800
	B	3.3468	3.7652	4.1525	5.2857
1.3 (part)	r_1^a	0.9999	0.9999	0.9999	0.9999
	r_2^b	0.9998	0.9986	0.9999	0.9996
	α	2.3	2.3	2.4	2.5
	$k_1^{1/\alpha}$	0.3229	0.4236	0.5460	0.7081
	k_2	0.2579	0.4398	0.7079	1.1906
	A	2.7199	2.7153	2.6496	2.5953
1.6 (part)	B	3.3228	3.8286	4.4004	5.6718
	r_1^a	0.9999	0.9999	0.9999	0.9999
	r_2^b	0.9997	0.9993	0.9997	0.9999
	α	2.3	2.4	2.4	2.6
	$k_1^{1/\alpha}$	0.3441	0.4475	0.5604	0.6818
	k_2	0.2871	0.4769	0.7116	1.2956
	A	2.7475	2.7254	2.6078	2.5948
	B	3.4130	3.9020	4.1829	6.9130
	r_1^a	0.9999	0.9996	0.9995	0.9997
	r_2^b	0.9999	0.9988	0.9991	0.9999

^a r_1 , correlated coefficients of α and $k_1^{1/\alpha}$ calculated according to eq. (1).
^b r_2 , correlated coefficients of k_2 calculated according to eq. (2).

respectively, according to Chinese Standard GB9869-88.

The time t_0 was determined from the time at which the minimum torque M_L just began to increase.

RESULTS AND DISCUSSION

Calculations of kinetic parameters

The rate constant $k_1^{1/\alpha}$ of the vulcanization process before t_{dis} was calculated according to the following equation⁹:

$$\ln(M_H - M_t) = \ln A - k_1(t - t_0)^\alpha \quad (1)$$

where M_H is maximum torque, M_t is torque at vulcanization time t , t is vulcanization time, t_0 is the time at which minimum torque M_L begins to increase, A is a constant, k_1 is a constant, and α is a modified coefficient.

The rate constant k_2 of the vulcanization process after t_{dis} was calculated according to the following equation⁹:

TABLE II
Values of t_0 , t_{dis} , Σ^* , and P

MBT level	Parameter ^a	140°C	150°C	160°C	170°C
0.7 (part)	t_0 (min)	2.3	1.5	1.2	0.8
	t_{dis} (min)	2.54	1.85	1.65	1.45
	Σ^*	0.0000	0.0081	0.0077	0.0149
	P (%)	14.71	19.01	28.74	38.21
1.0 (part)	t_0 (min)	2.0	1.4	0.9	0.6
	t_{dis} (min)	1.78	1.58	1.29	1.13
	Σ^*	0.0112	0.0354	0.0030	0.0062
1.3 (part)	P (%)	14.14	20.39	29.47	35.67
	t_0 (min)	1.8	1.2	0.8	0.6
	t_{dis} (min)	1.37	1.28	1.18	1.08
	Σ^*	0.0001	0.0254	0.0201	0.0074
1.6 (part)	P (%)	14.19	20.79	28.88	39.88
	t_0 (min)	1.6	1.1	0.8	0.5
	t_{dis} (min)	1.33	1.25	1.13	1.21
	Σ^*	0.0008	0.0108	0.0024	0.0186
	P (%)	15.12	21.68	28.43	45.20

^a Σ^* : $\Sigma = [\ln B - k_2(t - t_0)] - [\ln A - k_1(t - t_0)^\alpha]$ when $t - t_0 = t_{dis}$.

$$\ln(M_H - M_t) = \ln B - k_2(t - t_0) \quad (2)$$

where B is a constant and k_2 is a rate constant. Values of A , B , α , $k_1^{1/\alpha}$, and k_2 , calculated according to eqs. (1) and (2), are listed in Table I.

The time t_{dis} corresponding to the tangent point of the curve and the straight line in Figure 1 was obtained from the solution of eqs. (1) and (2):

$$\ln(M_H - M_t) = \ln A - k_1(t - t_0)^\alpha$$

$$\ln(M_H - M_t) = \ln B - k_2(t - t_0)$$

The calculated values of t_{dis} are listed in Table II.

The degree of vulcanization P at t_{dis} was obtained from the equation

$$P = \left(1 - \frac{M_H - M_t}{M_H - M_L} \right) \times 100\% \quad (3)$$

TABLE III
Values of E_1 and E_2

MBT level (part)	E_1 (kJ/mol)	E_2 (kJ/mol)	r_1^a	r_2^b
0.7	53.412	83.488	0.9998	0.9995
1.0	48.522	81.938	0.9992	0.9999
1.3	39.653	76.959	0.9999	0.9997
1.6	34.631	74.690	0.9990	0.9960

^a r_1 , correlated coefficients of E_1 calculated according to Arrhenius equation.

^b r_2 , correlated coefficients of E_2 calculated according to Arrhenius equation.

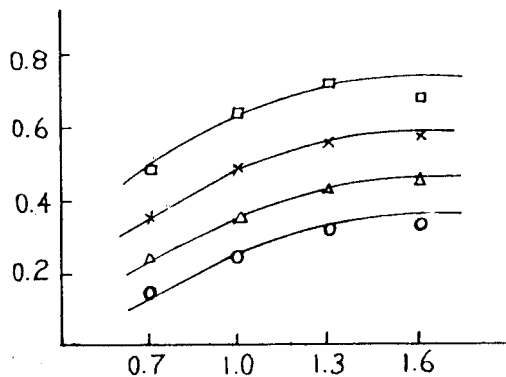


Figure 2 Relation between $k_1^{1/\alpha}$ (vertical axis, in min^{-1}) and MBT level (horizontal axis, in part). \circ , 140°C; \triangle , 150°C; \times , 160°C; \square , 170°C.

where M_L is the minimum torque. The calculated values of P are listed in Table II.

The activation energy was calculated according to the Arrhenius equation

$$\ln K = \ln Z - E/RT \quad (4)$$

The values of activation energies E_1 and E_2 , corresponding to those of the vulcanization process before and after t_{dis} , are listed in Table III

Rate of reaction

With an increase in MBT level the rising trends for $k_1^{1/\alpha}$ and k_2 and the decreasing trends for t_0 and t_{dis} are obvious, as shown in Figures 2, 3, 4, and 5, respectively. The decreasing trends of t_0 indicate that an increase in MBT level brings about a shorter time for initial formation of crosslink precursors. With respect

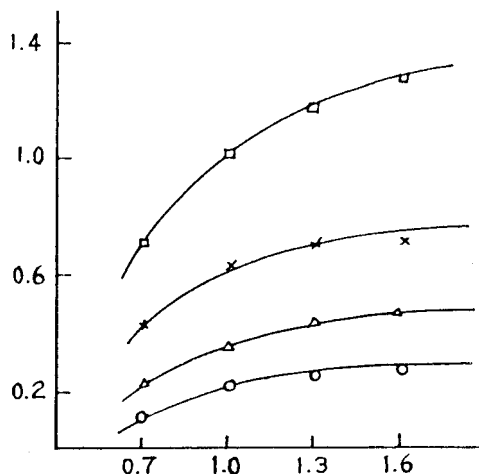


Figure 3 Relation between k_2 (vertical axis, in min^{-1}) and MBT level (horizontal axis, in part). \circ , 140°C; \triangle , 150°C; \times , 160°C; \square , 170°C.

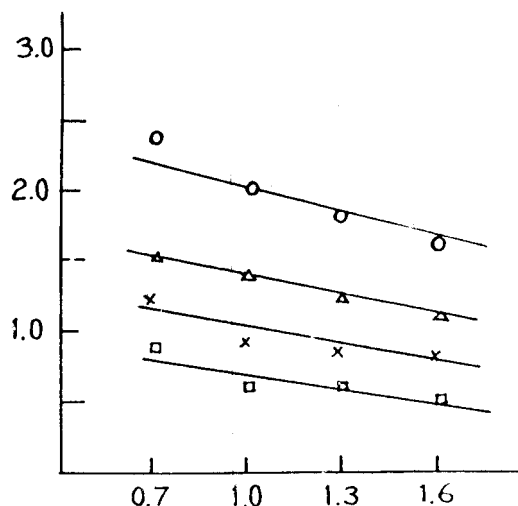


Figure 4 Relation between t_0 (vertical axis, in min) and MBT level (horizontal axis, in part). \circ , 140°C; \triangle , 150°C; \times , 160°C; \square , 170°C.

to t_{dis} it is clear that a rising MBT level brings about a decrease in the time not only for intermediates to be depleted but also for first-order crosslinking to occur. It is evident from Figures 2 and 3 that the formations of crosslink precursors and crosslink networks proceed rapidly with a rising MBT level, although the increments of $k_1^{1/\alpha}$ and k_2 are not linearly related to the MBT level. In our work, $k_1^{1/\alpha}$ is defined as an apparent rate constant of all reactions in the vulcanization process before t_{dis} . Although $k_1^{1/\alpha}$ is somewhat different from the k_1 defined by Coran and Ding in physical meaning, the effect of $k_1^{1/\alpha}$ on induction period is the same as that of k_1 . The temperature dependency of $k_1^{1/\alpha}$ is similar to that of k_1 , as is also evident from Figure 2.

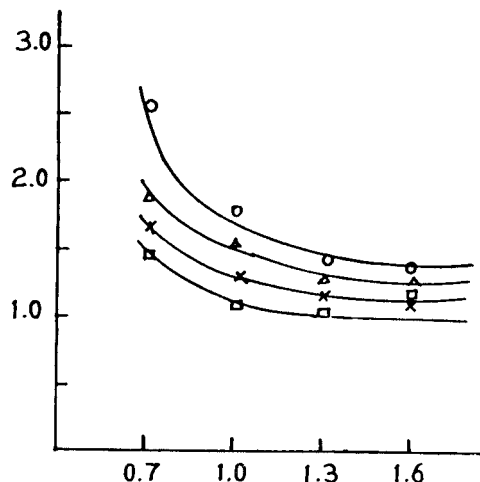


Figure 5 Relation between t_{dis} (vertical axis, in min) and MBT level (horizontal axis, in part). \circ , 140°C; \triangle , 150°C; \times , 160°C; \square , 170°C.

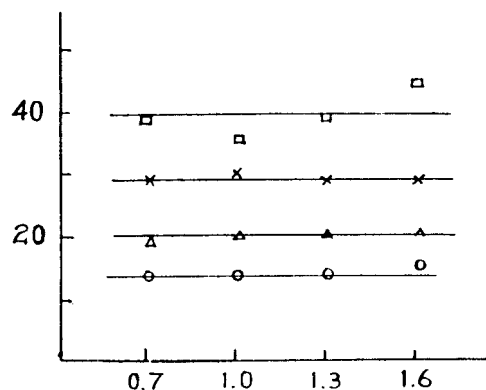


Figure 6 Relation between degree of vulcanization P at t_{dis} (vertical axis, in %) and MBT level (horizontal axis, in part). \circ , 140°C; \triangle , 150°C; \times , 160°C; \square , 170°C.

Degree of vulcanization at t_{dis}

It is surprising from Figure 6 that the degree of vulcanization at t_{dis} remains unchanged even though the time t_{dis} became shorter with a rising MBT level, except the abnormal result for the compound containing MBT 1.6 part at 170°C. The time t_{dis} in Figure 1 is the termination and starting point for the vulcanization processes involving different reaction mechanisms. The increase of vulcameter torque in the vulcanization process before t_{dis} is largely attributed to the increasing viscoelasticity because of the formation of crosslink precursors, whereas the increase of vulcameter torque in the vulcanization process after t_{dis} is mainly ascribed to the increasing elasticity because of the formation of crosslink networks,¹²⁻¹⁴ which means from the evidence of the degree of vulcanization that the concentration of crosslink precursors formed when the first-order crosslink reaction is just beginning to occur does not increase, although the time t_{dis} decreases with a rising MBT level. In the vulcanization process before t_{dis} , a possible structure of the complex formed from MBT, zinc oxide, and stearic acid is shown in Figure 7.¹⁵ In this structure each molecular

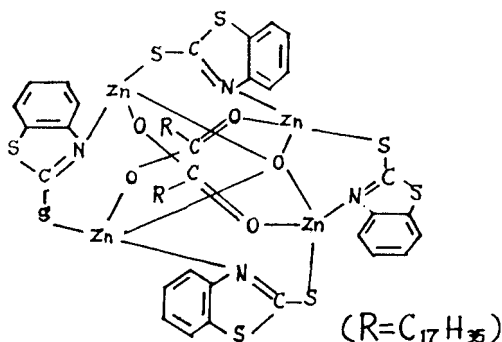


Figure 7 A possible structure of complex formed from MBT, zinc oxide, and stearic acid.

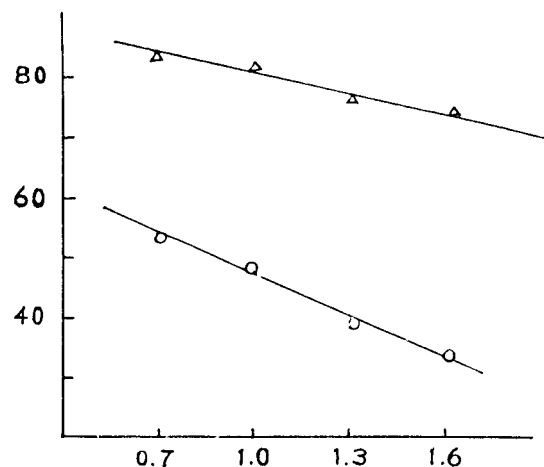


Figure 8 Relation between activation energy E (vertical axis, in kJ/mol) and MBT level (horizontal axis, in part). \circ , E_1 ; \triangle , E_2 .

complex consists of 4 mol of MBT and 2 mol of stearic acid. In our test the molar ratios of MBT and stearic acid contained in the compounds were 2.38 : 1, 3.55 : 1, 4.42 : 1, and 5.44 : 1, respectively. The excess of MBT in the compounds means that the concentration of complex formed in the vulcanization process before t_{dis} would not increase unless additional stearic acid is incorporated. In the case of the test compounds containing a constant level of stearic acid it may be assumed that the concentration of crosslink precursor does not increase. However, the effect of temperature on the degree of vulcanization at t_{dis} is striking, in that the degree increases from about 14–15% to more than 35% when the temperature increases from 140 to 170°C.

Activation energy

The activation energies of both vulcanization processes before and after t_{dis} decrease with an increase in MBT level, as shown in Figure 8. The activation energy E_1 of the vulcanization process before t_{dis} decreases from 54.413 to 34.631 kJ/mol, whereas the activation energy E_2 decreases from 83.488 to 74.690 kJ/mol, with respect to the vulcanization process after t_{dis} . It is obvious that the increments in MBT level have a significant impact on the activation energy of the vulcanization process before t_{dis} . Consideration of the high activation energy E_2 at any MBT level for the vulcanization process after t_{dis} indicates that the rate of first-order crosslink shows significant temperature dependency.

CONCLUSIONS

1. The rate constants of both vulcanization process before and after t_{dis} increase concomitantly with an increase of MBT level, but t_0 and t_{dis} decrease.

2. In a compound containing an excess level of MBT, the degree of vulcanization process at t_{dis} changes, not with the increase of MBT level, but with the increase of temperature.
3. The activation energies of both vulcanization processes before and after t_{dis} decrease with an increase of MBT level. The effect of MBT on the activation energy of the vulcanization process before t_{dis} is substantial. The rate of first-order crosslink provides evidence of significant temperature dependency.

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