Premature Vulcanization Behaviors of Rubber Compounds under High Shear Rates Processing

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ABSTRACT: The premature vulcanization behaviors of six kinds of common rubber (NR, BR, SBR, NBR, CR, and EPDM) compounds containing curing agents were studied in a wide processing temperature range (100–140°C) and rotor speed range (30–70 rpm) using a Brabender torque rheometer, which can supply the rubber compounds a high shear rates processing condition. After comparison with the Mooney scorch time (MSt$_5$), it is shown that Mooney scorch time cannot predict the premature vulcanization time under high shear rate processing. Six models were put forward based on the data obtained from the Brabender mixing head. The regression analysis and variance analysis showed that these models could simulate the premature vulcanization time very well. An explanation was given based on the reactivity and of rubber chain segments: the increasing reactivity and the impact probability of reactive rubber chain segment under high shear rate is the main reason of shorter scorch time of rubber compounds under high shear rate internal mixing. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 5414–5420, 2006

Key words: high shear rates; internal mixing; premature vulcanization; rubber compounds

INTRODUCTION

Scorch is the premature vulcanization in which the rubber compound becomes partly vulcanized before the product turns to its final form and is ready for vulcanization. The period before vulcanization starts is referred to as ''scorch time,'' which is one of the most important parameters on rubber processing control.[1–5] Previous studies considered that scorching time is the result of both the temperature reached during processing and the amount of time the compound is exposed to elevated temperatures.[3–5] Normally, Mooney shearing viscometer and vulcameter are used to evaluate the scorch properties of rubber compounds. Mooney scorch time (MSt$_5$) and curing index (Δt_{30}) are measured using viscometer in a low temperature (100 or 120°C) and very low shear rate (about 1.6 s^{-1}), while scorch time (t_{10}) and plateau cure time (t_{90}) are measured using vulcameter under the curing temperature and also low shear rate (about 2 s^{-1}). However, there are much difference between the shear rates adopted in these apparatus and the shear rates used in the actual rubber processing. For both Mooney shearing viscometer and vulcameter, the shear rates adopted in the testing equipment are much lower than that used in actual rubber processing such as internal mixing, extruding and injecting, etc.[1,2,6,7] There are very few articles on the scorch time, simulating the real processing conditions. It is necessary to propose a testing method that can consider both temperature and shear rate to evaluate the premature vulcanization behaviors of rubber compounds. Zhijie and Guishao[2] presented a method to simulate the scorch properties of NR compounds in different temperatures and shear rates using a Brabender torque rheometer, and some relational quadratic equations were proposed to simulate the relationship between scorch time and temperature or shear rate. But no explanations were given, and their study did not consider the interaction between temperature and shear rate, also lack of the comprehensive analysis of temperature and shear rate. Lee and Poh[3] and Sadequl et al.[5] studied the temperature dependence of Mooney scorch time of NR and epoxidized NR rubber compounds, but they did not consider the shear rate during rubber processing. Nakajima and coworkers[8,9] studied the Mooney viscosity of SBR using variable speed Mooney rheometer under different rotor speeds (0.5–

20 rpm), but the shear rate (0.4–16 s^{-1}) used were still much lower than that used in actual rubber processing, and the Mooney scorch properties were not discussed.

This study presents the effect of temperature and shear rate on scorch properties of rubber compounds during high shear rate processing using a Brabender torque rheometer,[2,10] and some relational models were proposed to evaluate the scorch behaviors and processing safety in rubber processing.[11,12]

According to the studies of Nielsen[7] and Nakajima and Harrel,[8] the shear rate in an internal mixing head can be calculated as follows:

$$\gamma = R\omega_r/e \qquad (1)$$

where γ is the shear rate (s^{-1}), R, the radius of rotor (mm), ω_r, the angular velocity of the rotor (rad s^{-1}), and e is the distance between the rotor nog and chamber (mm). The shear rate was linear with the rotor speed for a given mixing head, so rotor speed (ω) was chosen to represent shear rate in this study.

For the mixing head (model MB30H, attached to Brabender) used in this study, as shown in Figure 1, $R = 21.0$ mm, $e = 2.0$ mm, and $\omega_r = 2\pi\omega/60$, thus relation (1) can be expressed mathematically as follows:

$$\gamma = 1.10\omega \qquad (2)$$

where ω is the rotor speed (rpm).

For the rotor speed chosen (30–70 rpm) in the research, the Brabender mixing head can supply a shear rate in the range of 33–77 s^{-1}, which is consistent with the shear rate range of rubber processing under high shear rate, such as internal mixing and extruding.
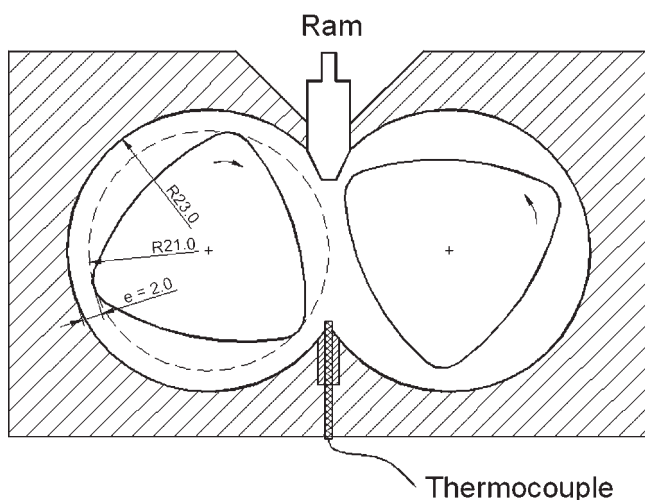
Figure 1 The sketch map of MB30H mixing head attached to Brabender Plasticorder.

EXPERIMENTAL

Materials

Natural rubber (grade SMR20), made in Malaysia, was supplied by Guangdong Guangtaihe Rubber. Butadiene rubber (BR, grade BR9000) and styrene butadiene rubber (SBR, grade SBR1502) were supplied by Jilin Chemical Industry (China). Ethylene–propylene–diene monomer rubber (EPDM, grade Keltan514) was supplied by DSM, Heerlen, Netherlands. Butadiene–nitrile rubber (NBR, grade N230S) was supplied by Zeon (Japan). Chloroprene rubber (CR, GN type, grade CR1211) was supplied by Chongqing Changshou Chemical Industry (China). Others materials are commercially available and were used as purchased.

Sample preparation

The rubber compounds was mixed in a two-roll (XK-160, Zhanjiang Chemical Machinery, China) mill according to the standard test recipes and methods described by the related standards listed in Table I, and the storage period for all the blends is 24 h under room temperature before testing.

Measurements

Mooney scorch properties

The Mooney scorch time (MSt$_5$), Mooney curing time (MSt$_{35}$), and Mooney curing index (Δt_{30}) of the six compounds were determined using Monsanto Mooney MV2000 (Monsanto, St. Louis) viscometer, according to the test procedures described in ASTM D 1646-04.

Premature vulcanization time (T_v)

To distinguish from Mooney scorch properties, the scorch time, curing time, and curing index measured under high shear rate in Brabender mixing head are named as premature vulcanization time (T_v), dynamic curing time (T_{10}), and dynamic curing index (ΔT), respectively.

The premature vulcanization time (T_v) and dynamic curing index (ΔT) were determined with a two shaft internal roller mixer (model MB30H, capacity 25 mL) fitted to a Brabender Plasticorder (PLE 651, Brabender OHG, Duisburg, Germany), according to DIN 53764.[10] Delta (triangular) rotors are used in the internal roller mixer. A schematic diagram of the design of an internal mixing head MB30H is given in Figure 1.

Generally, the torque versus time curves measured using MB30H mixing head can evaluate the premature vulcanization behavior of rubber compounds under high shear rate processing.[1,10] The amount loaded

TABLE I
Recipe for Rubber Compound[a]

Ingredients	Content					
	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
NR	100	–	–	–	–	–
BR	–	100	–	–	–	–
SBR	–	–	100	–	–	–
NBR	–	–	–	100	–	–
CR	–	–	–	–	100	–
EPDM	–	–	–	–	–	100
Zinc oxide	5.0	3.0	3.0	3.0	5.0	5.0
Magnesium oxide	–	–	–	–	4.0	–
Stearic acid	2.0	1.0	2.0	1.0	0.5	1.0
Carbon black[b]	35	60	50	40	–	–
Accelerator NS[c]	0.7	0.9	1.0	0.7	–	–
Sulfur	2.25	1.50	1.75	1.5	–	–
DCP[d]	–	–	–	–	–	3.0
Reference standard	ASTM D3192-02	ASTM D3189-99	ASTM D3186-02	ASTM D3187-00	ASTM D3190-00	ASTM D3568-03

[a] Concentrations in parts per hundred parts of rubber (phr).
[b] High abrasion furnace black (HAF, grade N330).
[c] N-oxydiethylene-2-benzonthiazole sulfonamide.
[d] Dicumyl peroxide.

(20 ± 1 cm^3) was determined according to the capacity of the mixing head. The mixing chamber, heated by circulating oil, is fitted with a thermocouple at the bottom of the chamber to measure the material's temperature, as shown in Figure 1. The ram pressure was supplied by a heavy piston of 5.0 kg, which supplies the ram pressure of about maximum 0.6 MPa to the mixture by means of a lever arm.

The measurement was done as follows: when the mixer chamber reached the desired temperature, the rubber compound prepared by two-roll mill was cut to strips and charged into the chamber and mixed at a given rotor speed until the torque rises 10 N m from the minimum torque, as shown in Figure 2. All the data were recorded and timing started after the ram forced down. The effect of temperature in the range of 100–140°C and rotor speed in the range of 30–70 rpm were studied in this research. Identical instrumental settings were maintained throughout all the experiments and torque versus time data were recorded for each test.

Since the mixing chamber were not full-filled by the rubber blend, it would roll and flow irregularly in the chamber, the torque data recorded by Brabender are undulant; thus, the torque data were processed using the method of median, and all the data processing were based on the heavy line calculated using the method of median, as shown in Figure 2.

According to DIN 53764,[10] the premature vulcanization T_v is defined as the time required for an increase of 3 N m above the minimum torque from the ram forced down, and the dynamic curing index (ΔT) is defined as the difference on time required for an increase of 10 N m (T_{10}) above the minimum tor-

que over that for an increase of 3 N m (T_v) above the minimum torque, as plotted in Figure 2, i.e.,

$$\Delta T = T_{10} - T_v \quad (3)$$

The premature vulcanization time T_v defines the real scorch time under high shear rate processing such as internal mixing. The dynamic curing index (ΔT) defines the overall rate or speed of dynamic cure under high shear rate processing.

The batch temperature was recorded using the thermocouple fitted at the button of the mixing chamber (shown in Fig. 1); the difference between chamber temperature and batch temperature at the time of T_v was defined as "batch temperature build-up" (ΔT_{emp}) (shown in Fig. 2). It was found that the batch temperature was just a very slowly and slightly shift during the mixing, from 1 to 4°C for varied mixing condi-
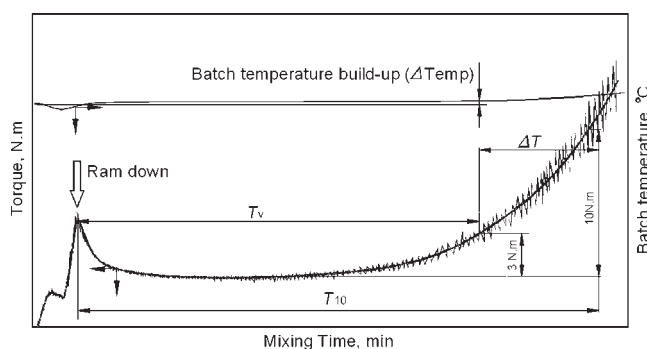

Figure 2 The sketch map of premature vulcanization time (T_v) and dynamic curing index (ΔT).

tions, so the batch temperature can be considered to be approximately constant during the mixing.

RESULTS AND DISCUSSION

The effect of temperature on Mooney scorch properties

According to Lee and Poh,[3] the exponential decrease in scorch time with increasing temperature can be expressed mathematically as

$$t_5 = Ae^{-f(T)} \tag{4}$$

where t_5 and T are the Mooney scorch time and temperature, respectively. The shorter Mooney scorch time observed as the temperature increases can be accounted for by the availability of sufficient thermal energy to affect faster curing at higher temperatures. Also, the mobility of the rubber chain is increased, which increases the probability for crosslinking to occur.

As the representative of the six kinds of common rubbers, CR was chosen to measure the Mooney scorch properties.[13] The Mooney scorch properties of CR compounds were measured under different temperatures. The results were shown in Figure 3, which shows that the Mooney scorch time (MSt$_5$) and curing index (Δt_{30}) versus temperature (T) curves of CR compounds can match relation (4), and the curves can be fitted to the following two relational expressions:

$$\text{MSt}_5 = 5686e^{-0.046T} \tag{5}$$

$$\Delta t_{30} = 12,546e^{-0.0582T} \tag{6}$$

where the correlation coefficient r of relational expressions (5) and (6) are 0.9927 and 0.9937, respec-
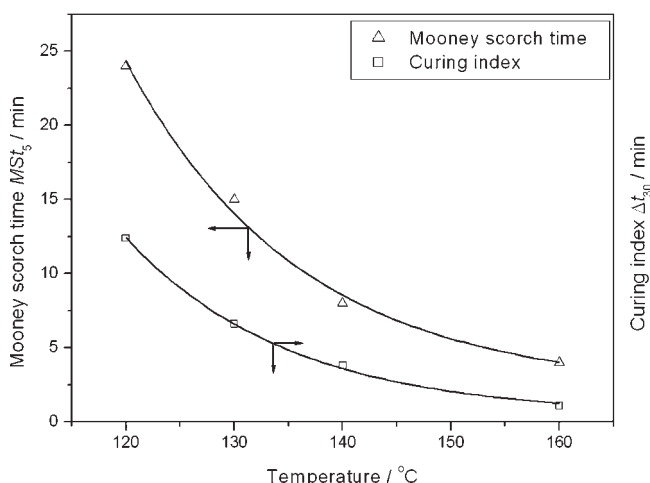
Figure 3 Temperature dependence of Mooney scorch time and curing index for CR compound.

tively, which shows good correlation of the two equations.

### Effect of temperature and rotor speed on premature vulcanization properties

Mooney viscometer determines the scorch behavior of rubber compounds under low shear rate (about 1.6 s^{-1}), but it does not consider the influence of high shear rate. Since most rubber processing is carried out under high shear rate (up to 50 s^{-1} or more),[1,2,6,7] the Mooney viscometer cannot estimate the scorch properties of rubber compounds accurately and actually under high shear rate processing, such as internal mixing and extruding. For example, for a typical Banbury type F270 internal mixer, the maximum shear rate that act on rubber blends is about 70–100 s^{-1}.

As discussed above, the Brabender mixing head can supply a testing condition of different temperatures and shear rates. To evaluate the processing safety of rubber compound more comprehensively and accurately, measurement of premature vulcanization properties under different temperatures and shear rates (i.e., rotor speeds) is necessary.

The three-dimensional figure of premature vulcanization time (T_v) versus temperature (T) and rotor speeds (ω) of six kinds of common rubbers (NR, BR, SBR, NBR, CR, EPDM) compounds are presented in Figure 4(a)–(f), respectively. The test data were listed in Table III. As shown in Figure 4, the premature vulcanization time T_v is decline exponentially with the shifting of temperature and rotor speed. Since Mooney scorch time under different temperature agrees with the relational expression (4), we can assume that the relation between premature vulcanization time T_v and rotor speed ω, i.e., shear rate, can be expressed as the following relational expression:

$$T_v = Ae^{-f(T, \omega, T \cdot \omega)} \tag{7}$$

where T and ω are mixing temperature and rotor speed, while $T \cdot \omega$ represents the interaction of mixing temperature and rotor speed. In other words, T_v is affected by three possible factors: temperature T, rotor speed ω, and the interaction of mixing temperature and rotor speed $T \cdot \omega$. Since not all factors are significant for each rubber compounds, multivariate regression analysis and stepwise regression analysis were performed to match and analysis the test data. All the programs were executed within the SAS software (Statistical Analysis System, release 8.1), and all results were given by SAS. While handling the data using stepwise regression analysis, the level of leading variable (α) is 0.05, which means the variables leaded are all fully significant. The relational expressions were listed in Tables II and III.
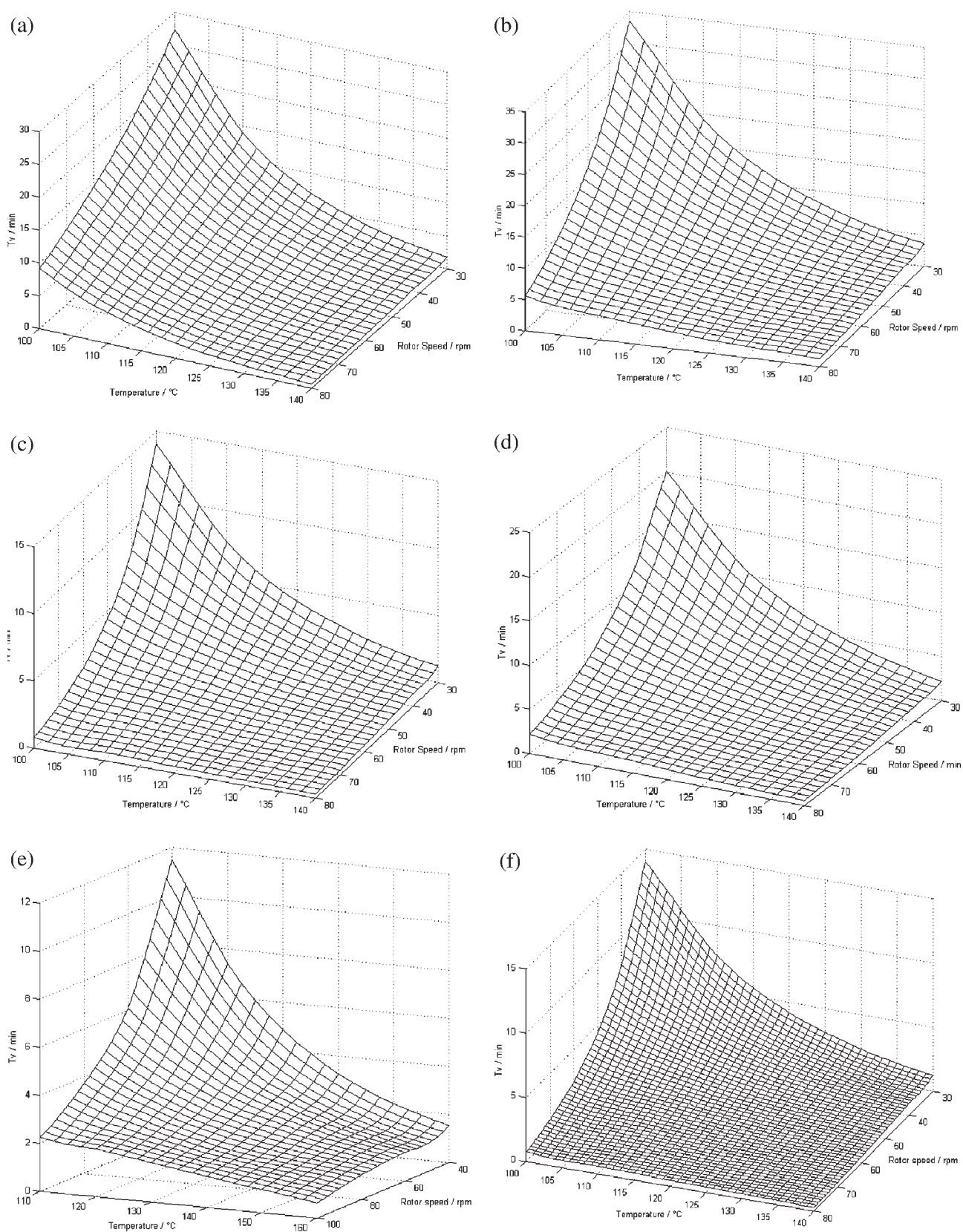
Figure 4 The relation-model of premature vulcanization time (T_v) on rotor speeds and temperatures for (a) NR, (b) BR, (c) SBR, (d) NBR, (e) CR, (f) EPDM compound.

TABLE II
The Relational Models of $T_v - (T, \omega)$

Rubber type	Relational expression of $T_v - (T, \omega)$	RMSE	R^2	$\|Pr > F\|$
NR	$T_v = 46{,}723.4e^{-0.0679T - 0.0217\omega}$	1.10	0.9987	<0.0001
BR	$T_v = 72{,}330.4e^{-0.0661T - 0.0706\omega + 0.000350T\,\omega}$	1.04	0.9981	<0.0001
SBR	$T_v = 6173.4e^{-0.0494T - 0.0323\omega}$	1.18	0.9680	<0.0001
NBR	$T_v = 64{,}990.7e^{-0.0675T - 0.0865\omega + 0.000421T\omega}$	1.10	0.9911	<0.0001
CR	$T_v = 5767.3e^{-0.0679T - 0.0217\omega}$	1.08	0.9925	<0.0001
EPDM	$T_v = 323{,}327.2e^{-0.0679T - 0.0217\omega}$	1.21	0.9668	<0.0001

RMSE in Tables II and III represents root mean square error, which is calculated as the square root of the mean square error. R^2 indicates the proportion of the corrected total variation attributed to the fit. "$\|Pr > F\|$," represents the p-value, also referred to as the probability value or observed significance level, is the probability of obtaining (by chance alone) an F statistic greater than the computed F statistic when the null hypothesis is true. The smaller the p-value, the stronger is the evidence against the null hypothesis. In F statistic test, if "$\|Pr > F\|$" value was smaller than 0.01, it means the model obtained was fully significant.

Table III shows the comparison of the values predicted by the relational models listed in Table II and the measured values. To prove these six models better, 3 additional samples (100°C and 80 rpm, 110°C and 30 rpm, 140°C and 20 rpm) were tested and the measured values were listed in Table III, numbered B1–B3. The results of comparison given in Table III showed that in the experimental ranges studied, the six relational models presented in this study can predict the premature vulcanization time very well.

The scorching properties of rubber blends containing curing agents is a complex chemical and physico-chemical process, at least two factors were involved in this process: batch temperature and shear rate.

The batch temperature has two parts: chamber temperature and batch temperature build-up, as discussed in Premature Vulcanization Time section, the batch temperature build-up (ΔT_{emp}) was less than 4°C under different mixing condition, and ΔT_{emp} would be higher with faster rotor speed. As ΔT_{emp} is so small, its influence can be ignored, and the main influence of temperature was by the circulating oil.

The later can be explained by analyzing the reactivity of rubber chain segments[11,12] with the increase in the rotor speed. Normally, the reactivity of rubber chain segment includes two parts, reaction reactivity and impact reactivity. The reaction reactivity is determined by both temperature and the activation energy of the reaction, and the impact reactivity is affected by the impact probability of the reactive rubber chain segment, i.e., the active sites. For internal mixing processing, the larger the shear rates the higher the impact probability of reactive rubber chain segment. We noticed that scorch is the primary stage of rubber curing, so the reaction model of scorch can also match the Arrhenius equation, which means scorch time is decreasing exponentially with the increasing of temperature, as have been proved in eq. (5). While under the same temperature, the increasing of shear rates enhances the impact probability of reactive rubber chain segment, which directly results in the increasing

TABLE III
The Comparison of the T_v Values Predicted by the Relational Models and the Measured Value

			T_v (min)									
			NR		SBR		BR		NBR		EPDM	
No.	T (°C)	ω (rpm)	Measured value	Predict value	Measured value	Predict value	Measured value	Predict value	Measured value	Predict value	Measured value	Predict value
A1	100	40	25.80	22.03	12.50	12.08	24.30	23.44	12.05	12.86	9.10	7.87
A2	100	60	15.80	14.28	8.50	6.33	11.30	11.52	6.15	6.39	2.20	2.48
A3	110	50	7.30	8.99	4.30	5.33	10.10	10.11	6.10	6.18	2.00	2.78
A4	110	70	5.55	5.83	2.30	2.80	5.40	5.33	2.10	2.32	1.15	1.01
A5	120	30	6.35	7.03	6.50	6.21	10.80	10.99	7.10	6.69	4.70	4.20
A6	120	70	2.85	2.96	1.75	1.71	3.55	3.52	1.55	1.59	0.85	0.73
A7	130	30	3.50	3.57	3.50	3.79	6.20	6.30	3.70	3.86	2.15	2.30
A8	130	50	2.35	2.31	2.00	1.98	3.60	3.82	1.95	2.05	1.15	1.10
A9	140	40	1.57	1.46	1.80	1.67	3.10	2.92	1.70	1.69	1.00	0.93
A10	140	60	1.00	0.94	0.92	0.88	1.90	1.90	1.05	0.98	0.45	0.51
B1	100	80	7.00	9.26	2.60	3.32	6.20	5.66	2.85	2.18	1.30	0.78
B2	110	30	13.95	13.88	10.70	10.18	18.15	19.17	11.80	11.58	9.80	7.67
B3	140	20	2.35	2.25	3.10	3.19	4.80	4.48	3.40	2.94	2.15	1.69

of the reaction reactivity and probability of reactive chain segment. Thus the shifting of rotor speed can promote the crosslinking reaction of rubber chains, and shorter the scorching time of rubber blends containing curing agents. Zhijie and Guishao's study[2] also showed that the tendencies of premature vulcanization properties on temperature and shear rate agree with this explanation.

CONCLUSIONS

Premature vulcanization time of rubber compounds changes with the change of mixing temperature and shear rate (i.e., rotor speed), and an explanation based on the reactivity of rubber chain segments was presented in this study, which can explain the tendencies appropriately. The results showed that the six relational models presented in the study could simulate and predict the experimental results very well.

The scorch time of rubber mixing under high shear rates is shorter than that of Mooney scorch time measured under very low shear rates. It is necessary to study the premature vulcanization properties of rubber compounds containing curing agents under simulated actual processing conditions, such as tempera-

ture, shear rate, pressure, etc. This research will contribute to understand the processing safety more comprehensively and accurately.

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