

# Temperature Dependence of Mooney Scorch Time of Rubber Compounds

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## Synopsis

A study of the temperature dependence of Mooney scorch time was carried out by using two grades of natural rubber, *Hevea Brasiliensis* (SMR L and SMR 10), and on synthetic rubber, styrene-butadiene rubber (SBR), in the temperature range of 100–180°C. Results show that the scorch time for SBR system is greater than that of the other grades of natural rubber. This is attributed to the lower degree of unsaturation in SBR. Effects of 2-mercaptobenzothiazole (MBT) and other types of accelerators on the scorch properties were also investigated and discussed. One black-filled compound was used to study the dependence of carbon black on the scorch property, and data indicate that the effect is more evident for temperature lower than 100°C.

## INTRODUCTION

Scorch is premature vulcanization in which the rubber compound becomes partly vulcanized before the product is in its final form and ready for vulcanization.<sup>1</sup> It reduces the plastic properties of the compound so that it can no longer be processed. Scorching is the result of both the temperature reached during processing and the amount of time the compound is exposed to elevated temperatures. The period of time before vulcanization starts is referred to as "scorch time."

Scorching is possible as soon as all the necessary vulcanizing ingredients have been added to the mix. Vulcanization is accelerated by an increase in temperature, and so the danger of scorching is enhanced when a completed mix is processed at an elevated temperature. Processing safety with desirable changes in the vulcanization behavior is the prime importance in all compounded rubber stocks.

Many studies on the scorch properties have been reported.<sup>2-7</sup> Duchacek<sup>6</sup> suggested the possibility that the inhibition effect of accelerator (2-mercaptobenzothiazole) is attributable to the formation of a complex with zinc dimethyldithiocarbamate which decreases the reaction rate in the initial steps of the sulfur-free thiuram vulcanization and thus causes the scorch delay. The formation of a MBT intermediate during the cure delay period was suggested by Campbell and Wise.<sup>7</sup> This intermediate appears to be a crosslinking precursor since MBT is released during crosslinking. Several mechanisms for the delay action of sulfur vulcanization of rubbers were proposed.<sup>8-11</sup>

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TABLE I  
Specification of SMR 10 and SMR L

	SMR 10	SMR L
Dirt (max % wt)	0.10	0.03
Ash (max % wt)	0.75	0.50
Nitrogen (max % wt)	0.60	0.60
Volatile matter (max % wt)	0.80	0.80
Plasticity retention index (min %)	50	60

In view of the importance of scorching in rubber compounds, it is thus the aim of this paper to discuss some of the findings obtained on scorch data which were determined by the use of Mooney Shearing Viscometer.

## EXPERIMENTAL

### Materials

Two SMR grades natural rubber, belonging to the *Hevea Brasiliensis* species and one synthetic SBR (Buna Hüls, 1502), were used as the elastomers. Technical specifications of the two SMR grades are as shown in Table I.<sup>12</sup>

Buna Hüls 1502 supplied by Bayer has 33.5% by weight of target bound styrene. The density, ash content, Mooney viscosity, and volatile matter are 0.9 g/cc, 0.5%, 50, and 0.2%, respectively. Details of accelerators used are tabulated in Table II. Oil furnace black (HAF grade having a surface area of about 65–70 m<sup>2</sup>/g), obtained from RRIM, was used as the filler for the black-filled compound. The other compounding ingredients were zinc oxide, stearic acid, and sulfur. They were of commercial grades and the composition of which were kept constant in the formulation.

### Compounding<sup>13</sup>

The recipe for the preparation of test sample is given in Table III. The mixing procedure was done in accordance to the American Society for Testing and Materials (ASTM)—Designation D 3184-80.<sup>13</sup> Mixing was done on the two-roll mill maintained around 70°C. Total time taken to complete one mixing cycle is 18 min for the gum stock and 29 min for the black-filled

TABLE II  
Specification of Accelerators Used in This Study

Abbreviation	Chemical name	mp (°C)	Supplier
MBT	2-Mercaptobenzothiazole	172	Behn Meyer
TMTD	Tetramethylthiuram disulfide	140	Behn Meyer
TBBS	<i>N</i> - <i>tert</i> -butyl-2-benzothiazyl sulfenamide	103	Texchem
CBS	<i>N</i> -Cyclohexyl-2-benzothiazyl sulfenamide	96	Bayer
ZDMC	Zinc dimethyldithiocarbamate	250	Monsanto

TABLE III

Ingredients	Gum stock (phr) <sup>a</sup>	Black-filled stock (phr) <sup>a</sup>
Rubber	100	100
Zinc oxide	6.00	5.00
Sulfur	3.50	2.25
Stearic acid	0.50	2.00
Accelerator	variable	0.70
Oil furnace black	—	variable

<sup>a</sup> Parts per hundred parts of rubber.

compound. The batch mass for the compound was checked and recorded. If they differed from the theoretical value by more than 0.5%, they were rejected. The sheeted stock was then conditioned for 24 h at a temperature of  $23 \pm 3^\circ\text{C}$  in a closed container before testing.

### Testing Procedure

Mooney Shearing Disk Viscometer with dies and rotor (biconical types) having uniform shearing rate of 2 rev/min was used. The combined mass of the two pieces of test samples was  $27 \pm 3$  g. Testing procedure was carried out in accordance with the method described in ASTM D 1646-81.<sup>14</sup> The Mooney scorch time is defined as the time required for an increase of

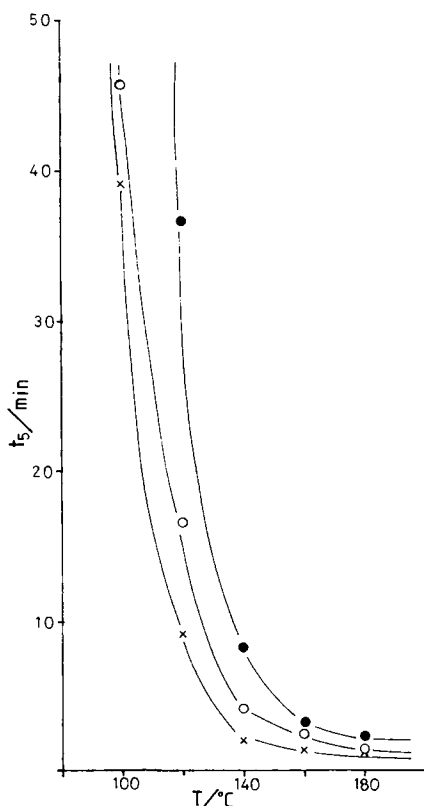


Fig. 1. Temperature dependence of Mooney scorch time for the various types of rubbers studied. MBT = 0.50 phr. (○) SMR L; (X) SMR 10; (●) SBR.

5 units above the minimum viscosity as determined from a plot of Mooney viscosity versus time. For the cure index ( $\Delta t_L$ ), it is defined as the difference in time required for an increase of 35 units ( $t_{35}$ ) above the minimum viscosity over that for an increase of 5 units ( $t_5$ ) above the minimum viscosity, i.e.,

$$\Delta t_L = t_{35} - t_5$$

The cure index defines the overall rate or speed of cure.

## RESULTS AND DISCUSSION

Results obtained from this study are discussed with respect to the variation of rubber, accelerator, and oil furnace black on the scorch properties.

### Rubber Types

The Mooney scorch time vs. temperature for the different types of rubber studied are presented in Figure 1. For the three types of rubber studied, scorch time increases exponentially with decreasing temperature. There is a marked difference in scorch time between SBR and the other two SMR grades. However, the difference decreases as temperature is increased. This observation can be explained by the fact that, in SBR, the degree of unsaturation is lower than that in natural rubber where the repeating unit is the isoprene monomer. Thus, we would expect slower rate of cure in SBR compared to natural rubber. This is clearly shown by the cure index vs. temperature plot as shown in Figure 2. As temperature of curing is increased, there is sufficient thermal energy to cause faster curing. Also, the

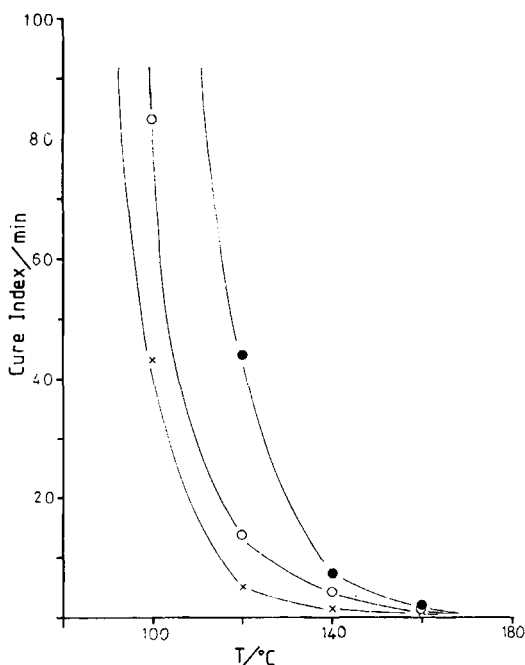
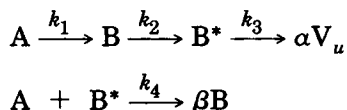


Fig. 2. A plot of cure index vs. temperature for various types of rubber. MBT = 0.50 phr. Symbols as in Figure 1.

mobility of rubber chain is increased, and this would mean that the probability for crosslinking is increased. The small difference observed in the scorch and cure behavior between SMR L and SMR 10 can be attributed to higher dirt and ash content in SMR 10 as illustrated in Table I. The higher ash content, which are essentially inorganic matter naturally present in the rubber, enhance faster rate of curing. Thus, shorter scorch time is observed. The presence of these naturally occurring matters also accounts for the difference in scorch behavior between synthetic SBR and natural rubber.

For a particular type of rubber used, the dependence of scorch time on temperature can be explained by using Coran's kinetic scheme for scorch delay.<sup>3</sup> Basically, the scheme can be represented as follows:



where A = accelerator/its reaction product, B = precursor to crosslinks, B\* = activated form of B,  $V_u$  = a crosslink, and  $\alpha$ ,  $\beta$  are stoichiometric constants.

Rubber is not used in the scheme since it is considered to be in excess and of constant concentration throughout the process.

If the reaction through  $k_4$  is much faster than that through  $k_3$ , i.e., at low temperature, very little crosslink formation can occur until A is essentially depleted. However, if the temperature is increased, the rate  $k_3$  is assumed to increase much more rapidly, hence reducing the ratio  $k_4/k_3$  (the quenching ratio), thereby giving rise to crosslink formation and consequently shorter scorch time. It is also assumed that the reaction through  $k_4$  and  $k_3$  is much faster than the reaction through  $k_2$ . In other words,  $k_2$  is the rate controlling step for crosslink formation after A is essentially depleted. Since an increase in temperature is followed by an increase in  $k_2$ , this means that a faster cure; hence faster crosslink formation is possible. Since the rate of reaction is exponentially dependent on temperature as given by the Arrhenius equation,

$$k = A_0 e^{-E/RT}$$

we would thus expect an exponential dependence of scorch time with temperature, or, expressed mathematically,

$$t = f(1/T) e^{-\lambda T}$$

where  $t$  and  $T$  are the scorch time and temperature, respectively.

### Types of Accelerators

When sulfur is the vulcanizing agent, accelerators are used to increase the rate of cure and to improve the physical properties and age resistance of the vulcanizate. Results obtained on the effect of the various accelerators studied toward scorch behavior are shown in Figure 3. From the plot, we

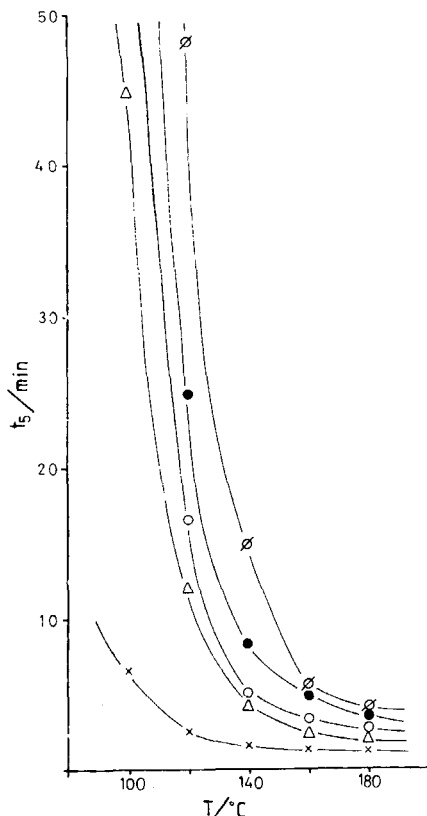


Fig. 3. Temperature dependence of Mooney scorch time for various types of accelerators. Concentration of accelerator is 0.50 phr. SMR L. (∅) TBBS; (●) CBS; (○) TMTD; (△) MBT; (X) ZDMC.

can conclude that TBBS exhibits the longest scorch time. Qualitatively, the accelerators can be arranged in the order of decreasing scorch time as follows:



At temperature lower than 140°C, there is a greater difference in the scorch properties between the various accelerators.

Both TBBS and CBS show typical behavior of a sulfenamide accelerator where long scorch time is observed. This is desirable especially in the processing of rubber compounds because greater processing safety is assured. TBBS, in particular, shows a very steep drop in scorch time with increasing temperature. On the other hand, scorch time for the ZDMC system exhibits a gentler dependence on temperature. The long delay period encountered by TBBS and CBS may be due to a slower rate of disappearance of the accelerator and its apparent immediate reaction product with sulfur. Crosslink formation appears to occur in a first order fashion, only after the nearly complete disappearance of the accelerator and its apparent immediate reaction products with sulfur.<sup>3</sup> Hence the time required for the disappearance of these species is long, probably due to higher energy of activation. Thus, the sulfenamide accelerators give longer scorch time. On the contrary,

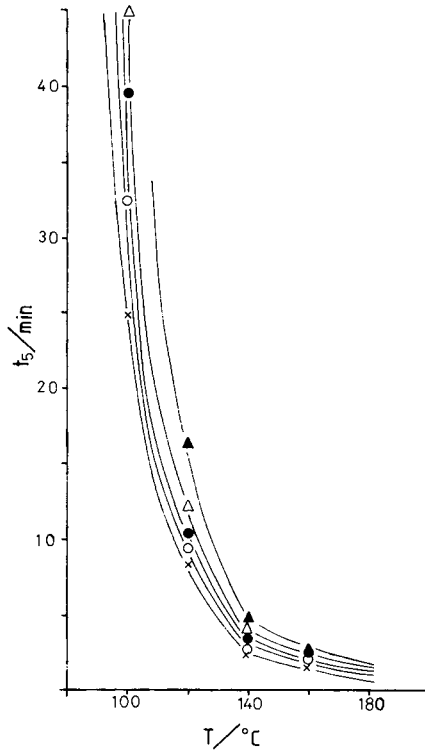


Fig. 4. Temperature dependence of Mooney scorch time for various loadings of MBT. SMR-L. (▲) 0.25; (△) 0.50 (●) 0.75; (○) 1.00; (X) 1.25.

ZDMC mixes show a tendency of early scorch. This is because the accelerator belongs to a class of accelerators known as "ultraaccelerators," which are more active than the rest. Apart from its direct function as the catalyst for producing the initial polysulfides, the accelerator also involves itself specifically in the formation of monosulfides.<sup>15</sup>

However, as temperature is increased, the difference in scorch time for the various accelerator systems narrows down. At temperature greater than 160°C, the scorch time for each accelerator system tends to a limiting value, i.e., does not depend greatly on temperature. Most probably, this observation can be explained by the fact that, at temperature greater than 160°C, the activation energy is lower compared to that at temperature less than 160°C (as discussed above). This means that the scorch time is practically independent on the type of accelerator used at high temperature of curing.

#### Accelerator Concentration

MBT was chosen as the accelerator to study the effect of accelerator concentration on scorch property. The reason is that MBT is one of the most commonly used accelerator in rubber vulcanization. As revealed in Figures 4 and 5, as the concentration of MBT is increased, scorch time decreases. The effect of MBT concentration is more obvious especially at temperature lower than 120°C. However, for temperature greater than 120°C, it seems that scorch time is not sensitive to the variation of accel-

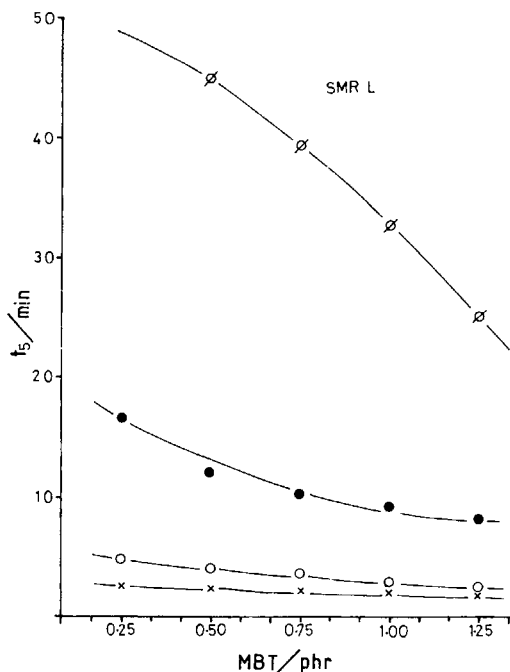
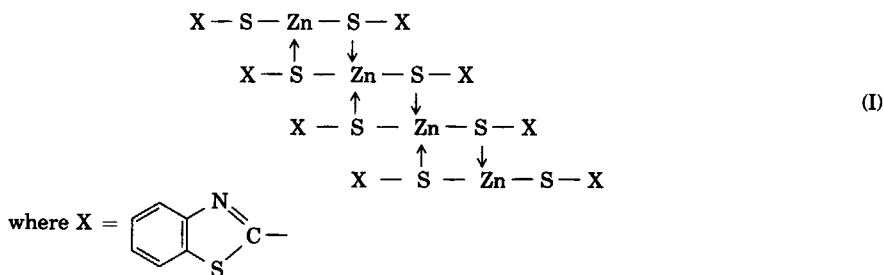
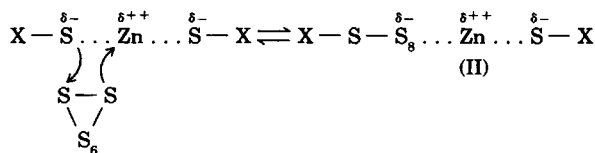


Fig. 5. Variation of Mooney scorch time with MBT loadings for different temperatures of curing. SMR L. (∅) 100°C; (●) 120°C; (○) 140°C; (X) 160°C.

erator concentration. MBT influences the scorch time by involving itself directly in the interaction with molecular sulfur in order to produce intermediates which are active sulfurating reagents.<sup>15</sup> Initially, MBT will react with zinc oxide to form the zinc benzothiazolyl mercaptide complexes (I):

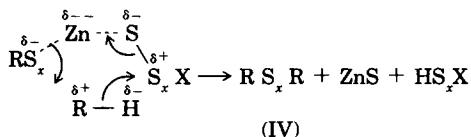
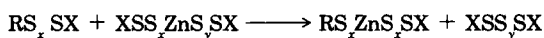
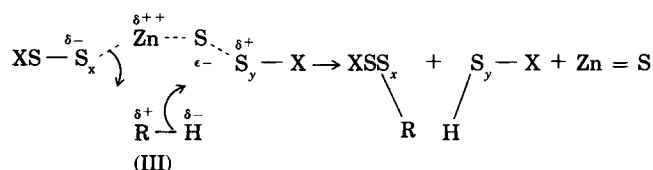
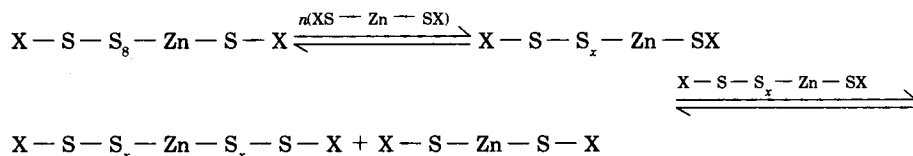


The complexes then will react with molecular sulfur,  $\text{S}_8$ , to form the active sulfurating reagent (II):





The sulfurating complexes in turn will react with other accelerator molecules to yield a spectrum of sulfurating complexes of varying sulfur chain length. This is followed by reaction with rubber molecules (III) giving rise to crosslinking (IV):



Hence for higher MBT content, more sulfurating complexes (II) are formed which will enhance more crosslinking; thus shorter scorch delay is observed.

### Effect of Oil Furnace Black

The effect of carbon black (oil furnace black—high abrasion furnace grade) on scorch time is illustrated in Figure 6. It can be clearly seen that the addition of carbon black will decrease the scorch delay. The higher the amount of carbon black added, the shorter the scorch time. Just as in the case of accelerator concentration in the rubber mixes, the effect is more significant at low temperature of curing (less than 100°C in this case). Similarly, at higher temperature, the scorch time does not depend greatly on the carbon black concentration.

Most sulfur-containing vulcanizing systems can be activated by trace amounts of hydrogen sulfide. When sulfur and rubber are heated at vulcanizing temperatures, hydrogen sulfide formation is extremely slow. Carbon black promotes this hydrogen sulfide formation by promoting dehydrogenation of rubber by sulfur.<sup>16</sup> With delayed action accelerators of the sulfenamide type, it is necessary to break the S—N bond before the accelerator becomes active. Carbon black causes this rupture of the S—N linkage when heated with sulfenamides in rubber, either in the presence or absence of other compounding ingredients.<sup>16</sup> Thus, the presence of carbon black will make an accelerated sulfur compound more scorchy.

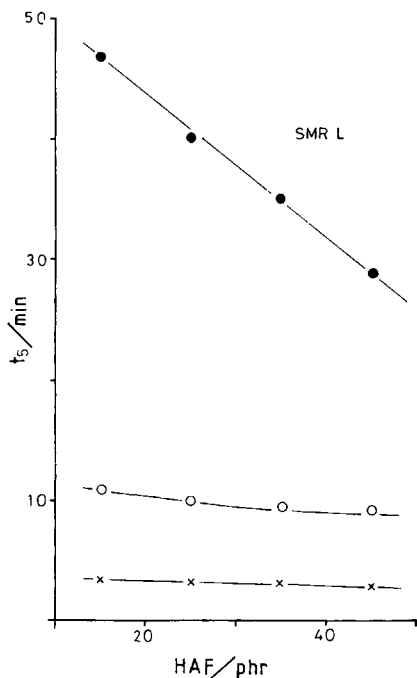


Fig. 6. Variation of Mooney scorch time with HAF loadings for different temperatures of curing. SMR L. (●) 120°C; (○) 140°C; (X) 160°C.

### CONCLUSION

From this study, the following important conclusions can be drawn:

1. Scorch time increases in an exponential manner with a decrease in temperature for the various types of rubber studied. The scorch time for SBR system is always longer than SMR rubbers, and this is attributed to the lower degree of unsaturation in the former.

2. For the different types of accelerators investigated, Mooney scorch time decreases in the order shown below. TBBS > CBS > TMTD > MBT > ZDMC

3. Concentration studies on MBT reveals that as the accelerator concentration is increased, the scorch time is decreased, the effect being more evident at lower temperature of curing. It is suggested that, for higher MBT content, more sulfuring complexes, which will enhance faster crosslinking, are formed.

4. The higher the amount of oil furnace black used, the more scorchy is the compound. This is attributed to the catalytic action of the black to promote the formation of hydrogen sulfide by promoting dehydrogenation of rubber by sulfur. For sulfenamide type of accelerator, e.g., TBBS, it helps in the rupture of the S—N linkage, thus easing early crosslinking.

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