

Dependence of Mooney Scorch Time of SMR L, ENR 25, and ENR 50 on Concentration and Types of Antioxidants

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ABSTRACT: The effect of concentration of antioxidants on the Mooney scorch time of two grades of epoxidized natural rubbers (ENR 25 and ENR 50) and one grade of natural rubber (SMR L) was studied using a Monsanto automatic Mooney viscometer (MV 2000). Three types of antioxidants, viz., 2,2'-methylene-bis(4-methyl, 6-tertbutylphenol) (AO 2246), *N*-isopropyl-*N'*-phenyl-*p*-phenylenediamine (IPPD) and poly-2,2,4-trimethyl-1,2-dihydroquinoline (TMQ) were used, and the concentration range was varied from 0 to 5 phr. The conventional vulcanization system with 2-mercaptobenzothiazole (MBT) as the accelerator was used throughout the study. Results show that increasing the phenol-based antioxidant (AO 2246) concentration will increase the scorch time of ENR at a lower temperature of vulcanization while its effect on SMR L is not significant. This retardation effect is attributed to the "solvation" of epoxide group by the phenolic group in AO 2246, thus reducing the activation of adjacent double bond in ENR. The scorch time, however, is shortened by the amine-based antioxidants (IPPD and TMQ) for the three rubbers studied, a phenomenon associated with the ability of the amine group to enhance the formation of more active sulfurating agent and subsequently increases the cure rate as the concentration of the amine-based antioxidants is increased. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 2940–2946, 1999

Key words: scorch; concentration; cure; rubber; antioxidant

INTRODUCTION

Recently, we have conducted several studies involving the scorch behavior of epoxidized natural rubber (ENR). It is found that the scorch time of ENR is shorter than that of natural rubber due to the activation of double bond by the adjacent epoxide group in ENR.¹ A study on the effect of stearic acid on the scorch behavior of ENR² shows that scorch time increases with stearic acid loading, the rate of increase being fastest in ENR 50, followed by ENR 25 and SMR L. The Mooney scorch time of unaccelerated sulfur vulcanization of ENR has also been reported.³ A strong exponential dependence of Mooney scorch time of ENR

on sulfur loading for temperature below 120°C is observed, but for higher temperature it is virtually independent of sulfur concentration. The effect of accelerator/sulfur ratio, i.e., various vulcanization systems, on the scorch time of ENR was systematically studied using five common accelerators.⁴ We have also extended the scorch study to ENR blends⁵ involving ENR 50/SMR L and ENR 50/SBR blends. A negative deviation of scorch time from the interpolated value is obtained, an observation attributed to the induction effect of ENR 50 in the blend. However, with regard to the effect of antioxidants on the scorch behavior of ENR, no systematic investigation is reported so far. In view of the technological importance of scorch time during rubber processing coupled with the use of antioxidants in diene-based rubbers to prevent oxidation of rubber products during service, we have carried out a

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Table I Recipes Used in the Rubber Formulation

Ingredient	phr ^a
Rubber	100
Zinc oxide	6
Sulfur	3.5
Stearic acid	0.5
MBT	0.5
Antioxidant	Variable

^a Parts per hundred parts of rubber.

study on the effect of three commonly used antioxidants on the Mooney scorch time of ENR 25 and ENR 50 as well as one grade of natural rubber (SMR L).

EXPERIMENTAL

Materials

One grade of unmodified natural rubber (SMR L) and two grades of epoxidized natural rubber (ENR 25 and ENR 50) having 0, 25, and 50 mol % of epoxidation respectively were used as the elastomers. SMR L was supplied by Rubber Research Institute of Malaysia, whereas ENR 25 and ENR 50 were purchased from Guthrie Co., Malaysia. The respective technical specifications of the rubbers used were given in our previous papers.^{1,6} Three antioxidants, viz., 2,2'-methylene-bis(4-methyl, 6-tertbutylphenol) (AO 2246), *N*-isopropyl-*N'*-phenyl-*p*-phenylenediamine (IPPD), and poly-2,2,4-trimethyl-1,2-dihydroquinoline (TMQ) were freshly supplied by Bayer Co., Malaysia. Other compounding ingredients such as zinc oxide, stearic acid, sulfur, and 2-mercaptobenzothiazole (MBT) were of commercial grades and used as supplied.

Compounding and Testing

The formulation and compounding procedure was carried out in accordance with the method described by ASTM D 3184–89.⁷ A typical recipe for the gum compound is shown in Table I.

Mixing was carried out by using a two-roll mill at a temperature of $70 \pm 5^\circ\text{C}$ and the total time taken to complete one mixing cycle was 18 min. The sheeted compound was conditioned at 23°C for 24 h in a closed container before testing. A Monsanto Automatic Mooney Viscometer (MV 2000) was used

to determine the Mooney scorch time (t_5)—time required for an increase of 5 units above the minimum viscosity—according to the testing procedure described in ASTM D 1646–96a.⁸

RESULTS AND DISCUSSION

The effect of concentration of AO 2246 on the Mooney scorch time for SMR L, ENR 25, and ENR 50 is shown in Figures 1–3 respectively for the various temperatures studied. Figure 1 indicates that scorch time is virtually independent on antioxidant concentration for the temperature range investigated. This means that the presence of AO 2246—a phenol-type antioxidant—does not affect significantly the curing characteristics of SMR L. The scorch time at 120°C is much higher than the other temperatures studied because the thermal energy supplied at 120°C is smaller and not enough to overcome the activation energy of vulcanization. However, the difference in scorch time narrows down as temperature is increased as more thermal energy is available to overcome the activation energy of vulcanization. Contrary to SMR L, the effect of antioxidant concentration on the scorch time is more significant for ENR 25 and ENR 50, as shown in Figures 2 and 3, respectively, especially at lower temperatures of vulcanization. This increase in scorch time with increase in antioxidant loading may be attributed to the interaction of the phenolic group in AO 2246 and the epoxide group of ENR, the effect being more pronounced as the % epoxidation is increased as reflected by the stronger dependence on AO 2246 concentration in the ENR 50 system. This interaction results in the “solvation” of the epoxide group in ENR, an effect that reduces the activation of the adjacent double bonds and hence slows down the rate of vulcanization, as discussed in our previous paper on the concentration effect of stearic acid on scorch behavior of ENR.² As in the case of SMR L, scorch time at 120°C exhibits higher values compared to that above 120°C due to the availability of thermal energy at higher temperatures of vulcanization. In fact, at 180°C , the scorch time is virtually independent on AO 2246 concentration, indicating that the abundant supply of thermal energy has eclipsed the effect of solvation of epoxide group in ENR, even as the AO 2246 concentration is increased. The role of solvation however, diminishes as temperature is increased. The effect of solvation is not observed in SMR L since there is no epoxide group in SMR L.

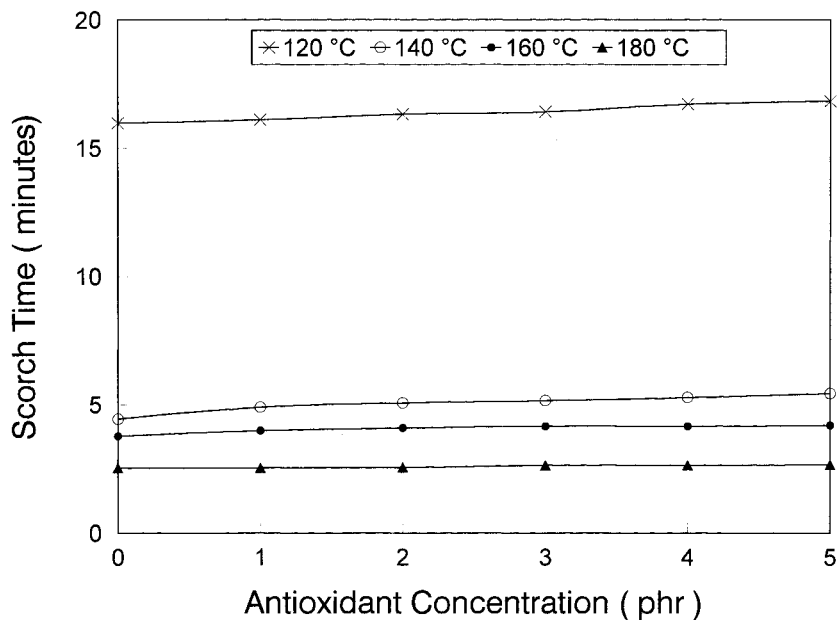


Figure 1 Variation of Mooney scorch time with AO 2246 concentration for SMR L at various temperatures of vulcanization.

The slight increase in scorch time at 120°C for SMR L may be associated with the steric hindrance of the bulky groups of AO 2246, which results in the reduction in vulcanization rate. This steric effect is easily overcome by the elevation of the temperature of vulcanization, as reflected by the independence of scorch time on AO

2246 concentration for temperatures greater than 120°C.

In order to understand better the concentration effect of antioxidant, the effect of other commonly used amine-based antioxidants such as IPPD and TMQ was plotted together with AO 2246, a phenol-based antioxidant. Figures 4–6

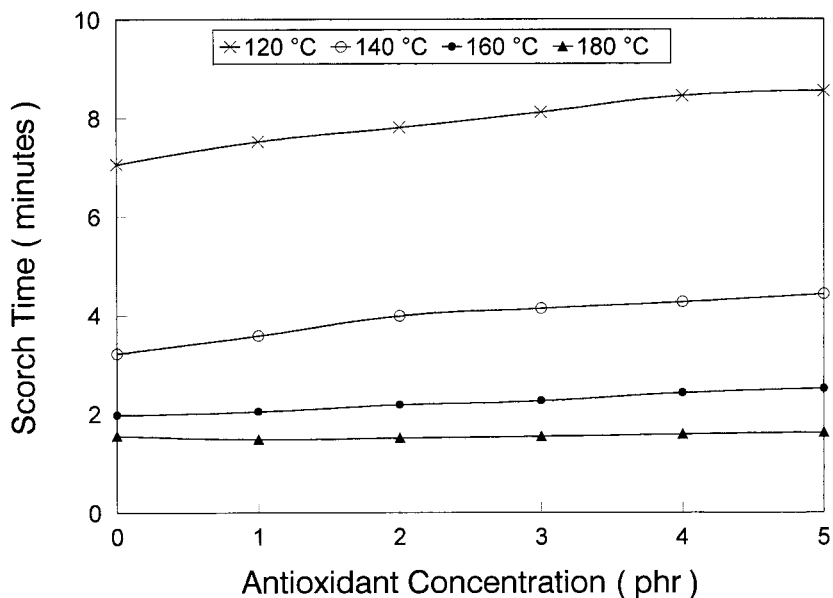


Figure 2 Variation of Mooney scorch time with AO 2246 concentration for ENR 25 at various temperatures of vulcanization.

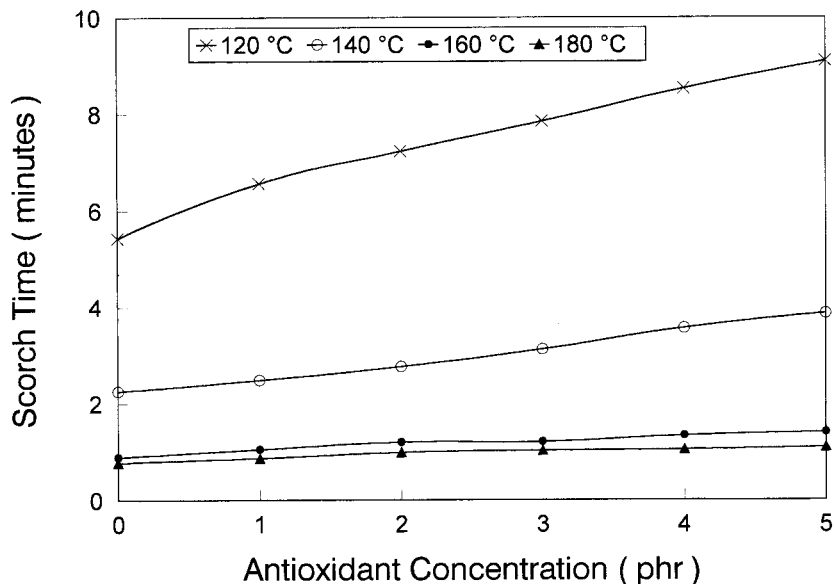


Figure 3 Variation of Mooney scorch time with AO 2246 concentration for ENR 50 at various temperatures of vulcanization.

show such plots for SMR L, ENR 25, and ENR 50, respectively, at 120°C only since scorch time does not depend significantly on antioxidant concentration at higher temperatures of vulcanization. One interesting observation is that for the amine-based antioxidants, scorch time decreases with increasing antioxidant concentration for the three rubbers studied. This finding is contrary to that

observed for AO 2246, a phenol-based antioxidant. The catalytic effect shown by the amine-based antioxidant may be attributed to the ability of the amine group in the antioxidant to act as ligands by occupying the vacant zinc orbitals and weaken the Zn-S binding, increasing the nucleophilicity of the mercaptide sulfur atoms in the complexes,—and hence facilitating the formation

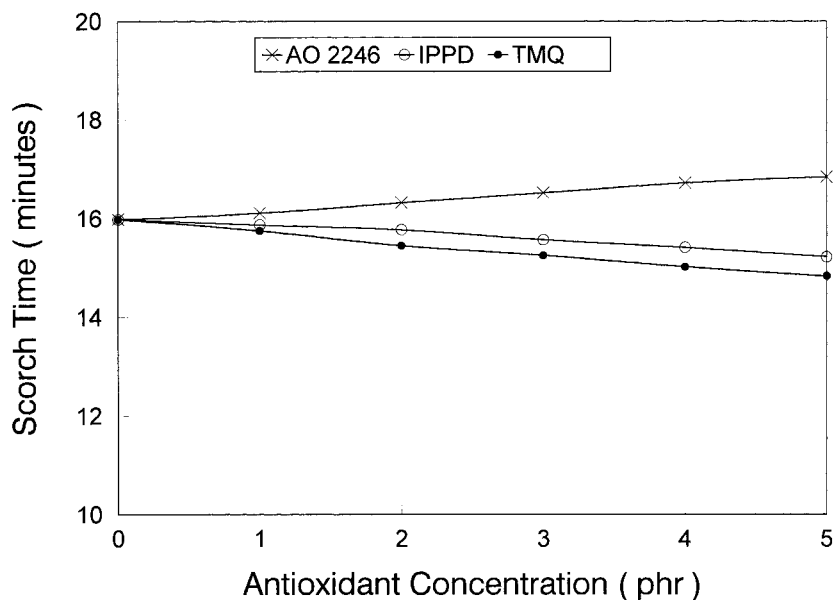


Figure 4 A comparison of the effect of various antioxidants on Mooney scorch time at 120°C for SMR L.

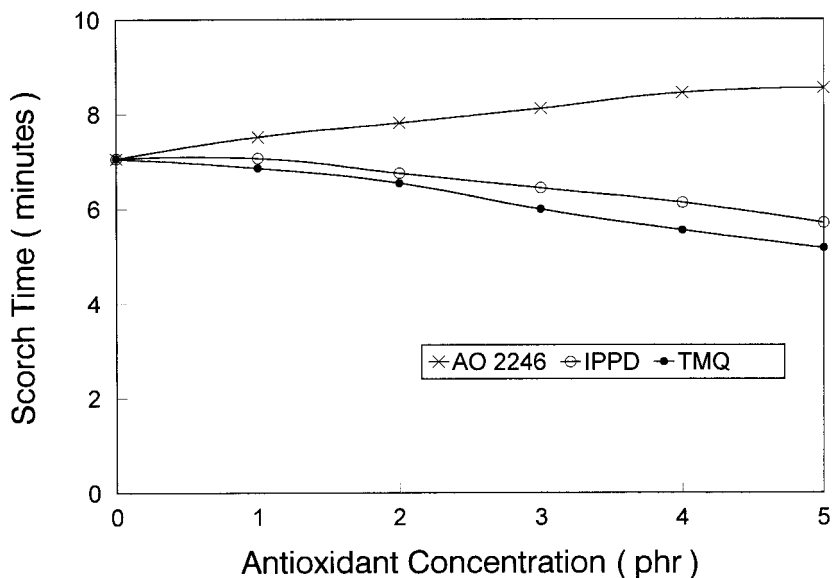


Figure 5 A comparison of the effect of various antioxidants on Mooney scorch time at 120°C for ENR 25.

of active sulfurating reagent⁹ necessary for the accelerated sulfur vulcanization of rubbers. The external ligands also aid in the solubilization of insoluble zinc mercaptides in rubber, thus increasing the cure rate. As the concentration of the amine-based antioxidant is increased, the rate of formation of active sulfurating reagents is correspondingly increased, and thus increases the rate of vulcanization as shown by the shorter scorch

time as the concentration of the amine-based antioxidants is increased. From this study, TMQ is slightly more efficient than IPPD in the enhancement of cure, as indicated by the shorter scorch time in the former for the three rubbers investigated. The scorch time for the amine-based antioxidants drops essentially in a linear manner, especially for SMR L (Fig. 4) with antioxidant concentration indicating that the number of ac-

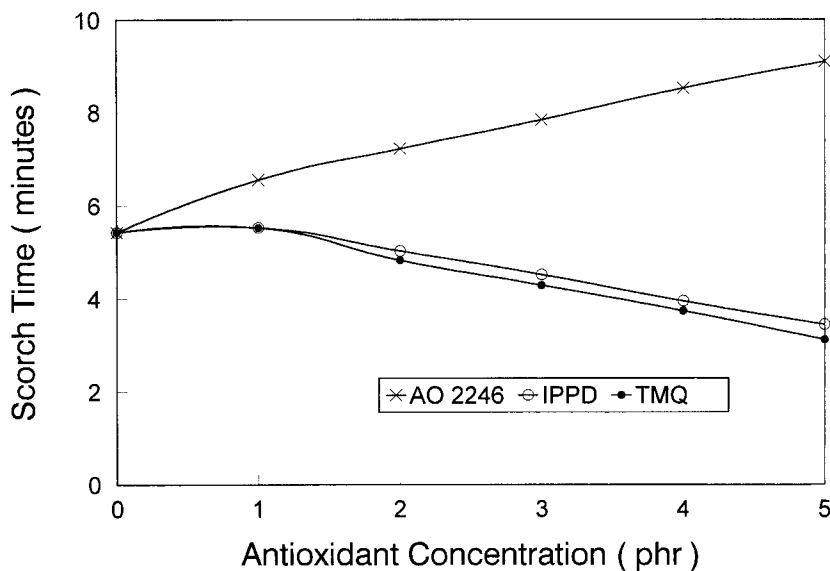


Figure 6 A comparison of the effect of various antioxidants on Mooney scorch time at 120°C for ENR 50.

Table II Δt_5 (min/phr) for the Three Antioxidants Studied at 120°C

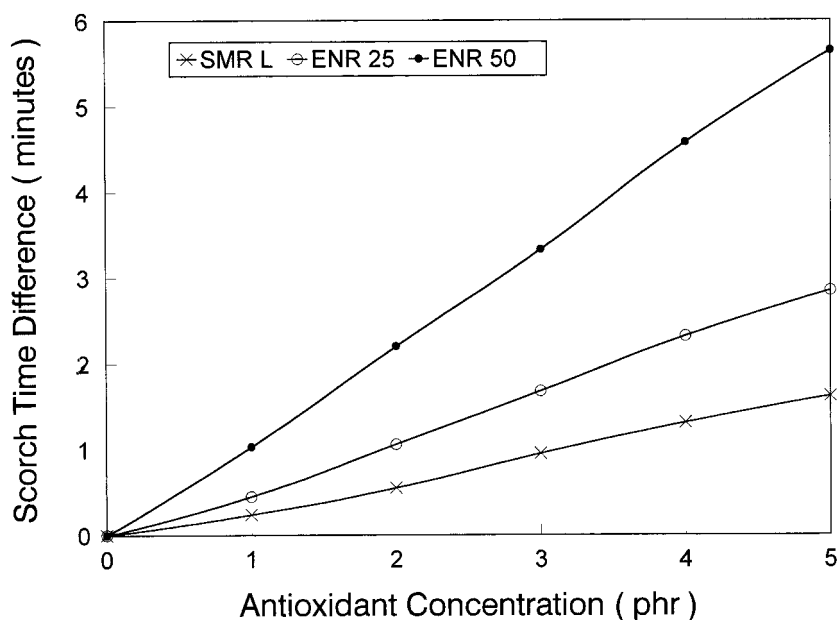
	AO 2246	IPPD	TMQ
SMR L	0.17	-0.15	-0.23
ENR 25	0.30	-0.27	-0.38
ENR 50	0.73	-0.40	-0.46

tive sulfurating reagents formed is directly proportional to the antioxidant concentration. The average change of scorch time per unit concentration of antioxidant (Δt_5) is shown in Table II. For AO 2246, Δt_5 increases with degree of epoxidation, whereas for IPPD and TMQ the reverse behavior is observed, with TMQ giving more significant drop than IPPD. For the three rubbers studied, the order of decreasing Δt_5 is

$$\text{AO 2246} > \text{IPPD} > \text{TMQ}$$

At lower antioxidant concentration, i.e., below 1 phr, there is insignificant difference in scorch time between the three antioxidants used. However, as the antioxidant loading is increased, the difference in scorch time between the phenol- and amine-based antioxidants widens, suggesting the increasing role of antioxidant concentration on the scorch time of SMR L, ENR 25, and ENR 50 at

higher loading of antioxidants, as shown in Figures 4–6. Figure 7 shows the scorch time difference between AO 2246 and IPPD ($t_{5, \text{AO 2246}} - t_{5, \text{IPPD}}$) for the three rubbers studied at 120°C. The plot shows that ENR 50 gives the greatest difference, especially at higher antioxidant concentration. This is due to the presence of more epoxide groups in ENR 50, which experiences the greatest solvation effect by the phenol-based antioxidant (AO 2246). Therefore, cure retardation is greatest in ENR 50, followed by ENR 25 and SMR L, and the effect becomes more pronounced at higher antioxidant concentration. Figure 8 compares the scorch behavior of SMR L, ENR 25, and ENR 50 for the three types of antioxidants at 3 phr concentration and at 120°C. For each antioxidant used, SMR L consistently indicates higher scorch time than ENR, an observation similar to that reported in our previous study¹ for a gum stock without antioxidant. As explained previously, ENR 50, which has more epoxide groups, experiences greater activation of adjacent double bonds and thus gives shorter scorch time than ENR 25 and SMR L. For the AO 2246 system, the scorch time difference between ENR 25 and ENR 50 is smaller compared to that of IPPD and TMQ systems. This observation is again explained by the higher solvation in ENR 50 by the phenol-based antioxidant, which retards vulcanization, an effect similar to that reported for the presence

**Figure 7** Scorch time difference ($t_{5, \text{AO 2246}} - t_{5, \text{IPPD}}$) vs antioxidant concentration for the rubbers studied at 120°C.

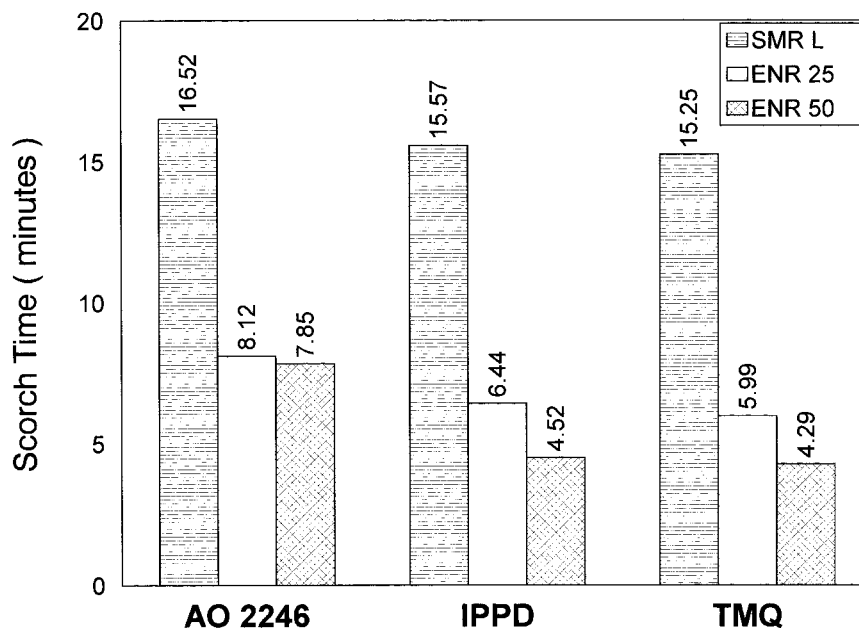


Figure 8 A comparison of Mooney scorch time for the rubbers studied at 120°C and 3 phr of antioxidants.

of excess stearic acid in rubber compound where the rate of increase in scorch time is fastest in ENR 50, followed by ENR 25 and SMR L.² On the other hand, the amine-based antioxidants, i.e., IPPD and TMQ, which do not solvate ENR, catalyze equally the vulcanization reaction to all the rubbers studied, as shown by the progressive drop in scorch time corresponding to the increase in degree of epoxidation.

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