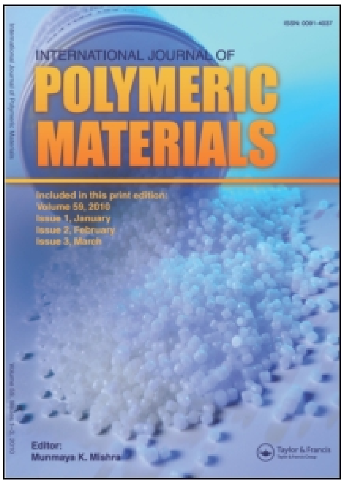

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The Effects of High Styrene Resin on the Mooney Viscosity, Scorch Time, Cure Time and Physical Properties of Rubber Vulcanizates

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The effects of high styrene (HS) resin on the Mooney viscosity, scorch time, cure time and physical properties of rubber vulcanizates were evaluated. The Mooney viscosity decreased with increasing HS composition up to 20% after which it started to increase. The incorporation of HS was found to increase the scorch and cure times of the rubber vulcanizates. Physical properties *i.e.*, hardness, tensile modulus (M100) and resilience also increased with increasing HS composition. However the opposite trend was observed in the case of crosslink density.

Keywords: High styrene resin; Mooney viscosity; processability; physical properties

1. INTRODUCTION

In our previous work [1], the effect of various combinations of accelerators on the physical properties of rubber vulcanizates was studied. A combination of 2-mercapthobenzothiazol (MBT), dibenzothiazyl disulfide (MBTS), tetramethyl thiuram monosulfide (TMTM) and diphenylguanidine (DPG) and sulfur was found to be synergistically contributive in crosslink density. As a result, there was a synergistic relationship between the tensile modulus, hardness and resilience

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of the rubber vulcanizates with the various combination of the above accelerator ratios. In this work, one combination of these accelerators was used, *i.e.*, MBT/MBTS : TMTM in a ratio of 1.5 : 1.5. For this selected combination, the effects of high styrene resin on the Mooney viscosity, scorch time, cure time and physical properties of rubber vulcanizates were evaluated.

2. EXPERIMENTAL

2.1. Materials and Chemicals

Table I shows the materials, their manufacturers and level used in the preparation of masterbatch. The formulation was based on the semi-efficient vulcanization system (semi-EV). All materials were used as supplied. Table II shows the percentage variation of high styrene resin and master batch used in this study.

TABLE I The materials, manufacturers and level of various ingredients used in the masterbatch

Materials	*Manufacturer*	*Formulation (phr)*
Natural rubber (SMR-L)	RRIM[a]	62.69
SBR-1502	Bayer (M) Ltd	37.31
Zinc oxide	Bayer (M) Ltd	7.84
Stearic acid	Nipol (M) Ltd	1.49
Sulphur	Nipol (M) Ltd	3.59
Silica (Tokusil URT)	Nipol (M) Ltd	31.34
Napthenic Oil (Shell Flex)	Bayer (M) Ltd	12.51
MBT/MBTS	Bayer (M) Ltd	2.63
TMTM	Bayer (M) Ltd	2.63
Pigment (BHT)	Bayer (M) Ltd	0.63

[a] Rubber Research Institute of Malaysia.

TABLE II Percentage of high styrene (HS) and the masterbatch

Mix	1	2	3	4	5	6
Masterbatch	100	90	80	70	60	50
High Styrene (HS)* resin	0	10	20	30	40	50

* High styrene resin-HS82 was supplied by Nipol (M) Bhd.

2.2. Sample Preparation

The mixing procedure was carried out according to the American Society for Testing and Materials (ASTM-Designation D 3184-89). Mixing was done a two-roll mill with temperature maintained at 70 ± 5°C. Total time taken to complete one mixing cycle was 29 minutes. The batch mass was checked and recorded. If it differed from the theoretical value by more than 0.5%, the batch was rejected. The sheeted compound was conditioned at a temperature of 25 ± 2°C for 24 hours in a closed container before assessment by using a Monsanto Rheometer (MR 100) at 150°C to determine the optimum cure time. The Mooney viscosity was determined by using Mooney Viscometer MV 2000 at 120°C.

2.3. Measurement of Physical Properties

The tensile properties of the rubber vulcanizates were measured on an Instron Universal Testing Machine, Model 114, according to BS 903: Part A3. The cross-head speed was set at $500\,\text{mm}\,\text{min}^{-1}$. The test for hardness was carried out by using a Shore A Durometer according to ASTM 2240. Resilience test was done by using a Wallace Tripsometer Dunlop according to BS 903: Part A8. The angle of rebound was measured and resilience calculated using the equation below:

$$R = \frac{1 - \cos(\text{angle of rebound}) \times 100}{1 - \cos(\text{angle of fall})}$$

All tests were performed at room temperature (25°C). Thermo-oxidative ageing studies were done according to BS 7646. The tensile samples were placed in an air oven and aged at 70°C for 3 days.

2.4. Crosslink Density Measurement [2]

Crosslink density measurement was carried out based on Mooney-Rivlin plot, *i.e.*,

$$\frac{\partial}{2(\lambda\ 1/\lambda^2)} = C_2\lambda^{-1} + C_1$$

where

λ = extension ratio
∂ = tensile stress
C_1 and C_2 = constant

Stress data at 10%, 15%, 20%, 40%, 60%, 80%, 100%, 300% and 500% were recorded and $\partial/2(\lambda\ 1/\lambda^2)$ calculated. $\partial/2(\lambda\ 1/\lambda^2)$ was plotted against $1/\lambda$ and the slope of the graph gives C_2. The graph also cross the vertical axis to give $C_1 = v_{\mathrm{Rev}}$ = crosslink density.

3. RESULTS AND DISCUSSION

3.1. The Effect on High Styrene (HS) Resin on Mooney Viscosity

Figure 1 shows the effect of HS on Mooney viscosity of the compounds. It can be seen that the Mooney viscosity decreases with the addition of 10 and 20% of HS. The minimum viscosity occurred at 20% of HS and further addition of HS increases the Mooney viscosity.

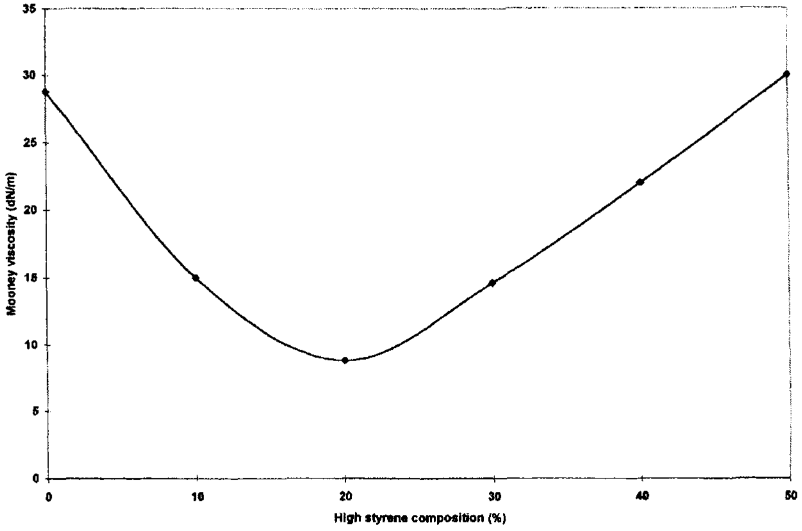

FIGURE 1 The effect of high styrene composition on the Mooney viscosity.

Morphology of blends is influenced by various factors such as viscosity ratio of both blend components [3], relative elasticity, original individual morphologies of components, compatibility and solubility factors, mechanical processes imposed during blending which inherently affect microscopic orientation, composition of components, and other microrheology factors [4].

Under high temperature and pressure condition, the lower percentage of HS tend to form a small domain which is dispersed in elastomer phase. This is due to shear friction of rotor which creates energy to viscous polymer, internal slipping friction, lower thermal conductivity of polymer and internal heat generation. When the blend temperature increased and at lower HS resin composition ($<20\%$), solubility of HS in elastomer increased. Consequently, slipping friction and elastic deformation of elastomer phase decreased because the shear force of rotor is focussed on the lower viscosity of HS component [5]. However, the minimum viscosity at 20% of the HS indicates that there was a critical composition, above which, more than this percentage, the solubility of HS component in elastomer starts to decrease so that the blend morphology tend to form a big HS phase domain which is dispersed in the continuous elastomer phase and consequently increased the Mooney viscosity.

3.2. The Effect of High Styrene (HS) Resin on Cure Time, t_{90} and Scorch Time, t_5

Table III shows the effect of HS resin on t_{90} and t_5. It can be seen that both properties increase with increasing the percentage of HS.

HS resin has a low degree of unsaturation with only 20% of butadiena component. In addition, the vulcanizing agents proportion decreases with increasing HS resin composition. Consequently, t_{90} and t_5 decrease

TABLE III The effect of HS resin addition at different composition on t_{90} and t_5

Mix	t_5 *(min)*	t_{90} *(min)*
1 (0% HS)	2.3	9.0
2 (10% HS)	2.5	9.7
3 (20% HS)	2.8	10.9
4 (30% HS)	3.2	13.0
5 (40% HS)	4.6	17.0
6 (50% HS)	5.4	21.0

with increasing percentage of HS due to lower degree of cross link density. However, the minimum Mooney viscosity at 20% HS composition might be due to low incremental rate of scorch time at this composition (the effect of HS solubility in elastomer which varied with temperature and the dominant composition of HS as discussed in previous section). The reason could be due to the initial presence of trapped elastomer coated by the layer of HS domain which subsequently resulted in some of the additive being involved in vulcanization within the HS phase and eventually reducing the crosslink density rate or vulcanization process. When the HS proportion increases further, the two distinct insoluble continuous phases formed resulted in the lower interphasial surface as compared to HS volume. Consequently, the true additives taking part in vulcanization is effectively reduced in content due to overall reduction of interphase surface area of HS and elastomer. In addition, the trapped additive in HS phase further reduce the vulcanization rate because of low unsaturation of HS resin. So t_5 and t_{90} increase with increasing HS composition.

3.3. The Effect of High Styrene Resin on Physical Properties

3.3.1. The Effect on Hardness

Figures 2 – 3 show the effect of HS addition on crosslink density and hardness of the vulcanizates. Theoretically the reduction of crosslink density should be followed by the decrease in hardness. However the reverse trend can be seen in Figure 3. The increase in hardness and also Young Modulus [2, 6] might be due to the presence of insoluble, hence filler like, HS resin domain, albeit in low composition condition. Conversely at higher HS composition phase reversal occur, in that the elastomer domain is insoluble and takes over as a filler.

At higher composition of HS, HS is a continuous phase whereas elastomer form as a dispersed domain. HS phase is hard and stiff at room temperature due to it's high softening point (95°C). Higher forces is needed for indentor penetration during hardness test with the increasing HS composition in the vulcanizates.

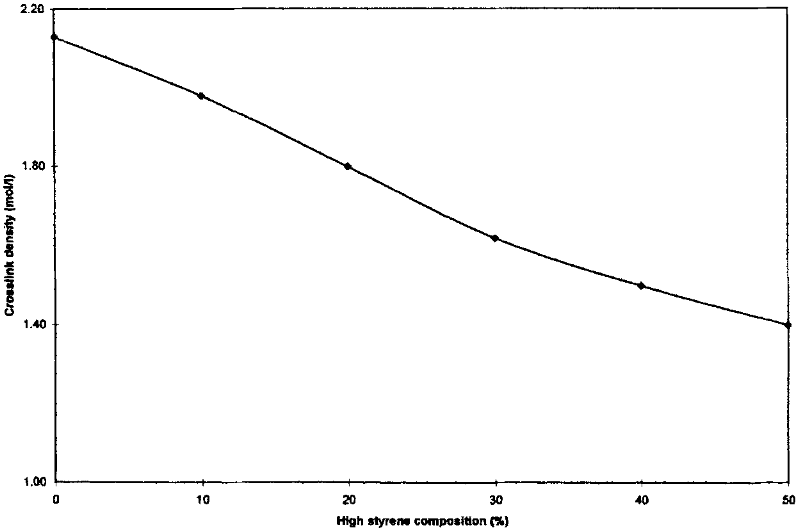

FIGURE 2 The effect of high styrene composition on the crosslink density.

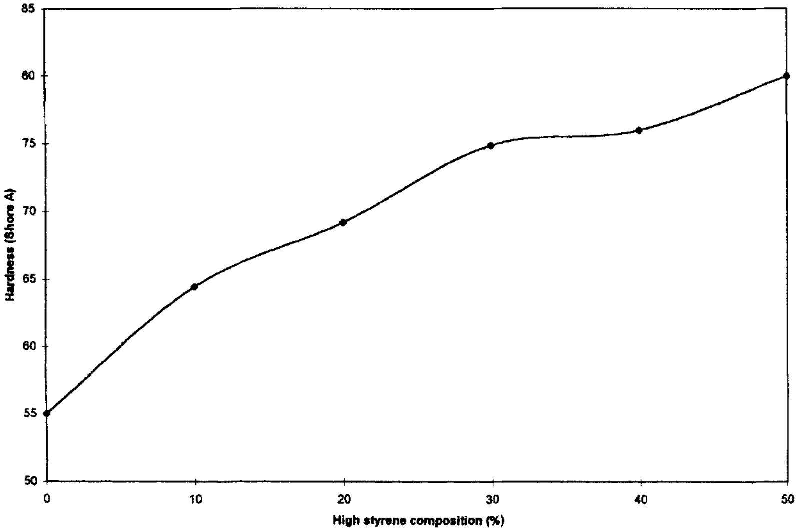

FIGURE 3 The relationship between high styrene composition and hardness of the rubber vulcanizates.

3.3.2. The Effect on Tensile Modulus, M100

The effect of HS resin composition on tensile modulus, M100 (before ageing) is shown in Figure 4. Tensile modulus for rubber vulcanizates at low elongation or M100 is an empirical approximation of crosslink density [8]. However M100 also depend on blend composition, non-linearity stress-strain relationship, effect of time, pressure, strain rate, morphological factors *etc*. As discussed before the addition of HS resin at room temperature and low concentration creates HS domain in continuous elastomer phase. At higher composition, the opposite situation occurred where elastomer become the continuous phase and HS domain acted as a filler in the blend. This of course will increase the M100.

3.3.3. Ageing Effect on M100

The increase in modulus during the early periods of ageing is due to the increase in the crosslink density [8]. These include the de-

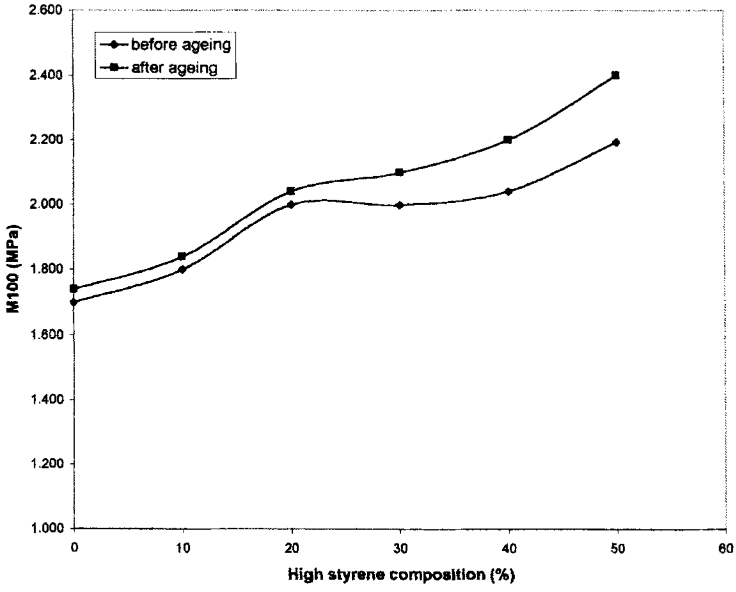

FIGURE 4 The effect of high styrene composition on the M100 before and after ageing.

sulphurization process which produce new active sulphuration complex which caused additional crosslink, crosslink by unbounded free sulphur and also by oxidative crosslinking. Hence, more free sulphur available in the vulcanizate for further crosslink (see Fig. 4).

3.3.4. The Effect on Resilience

Figure 5 shows the effect of HS resin on resilience. It can be seen that resilience decreases with increasing HS composition. The increment in chain segment stiffness in free elastomer phase due to the filling of HS domain at lower HS composition caused higher forces is needed to deform the chain segment [9]. But the energy supplement at a higher rate in the form of impact resulted in permanent deformation. This is due to the reduction of chain flexibility and the energy lost from the system as a result of the chain slippery, entanglement slippery, the broken of unstable secondary bonds or weak polysulphidic and others energy absorption mechanism. At higher HS composition, HS phase become dominant. Since at room temperature, the HS is stiffer than elastomer, so during impact the elastomer chain segments could not

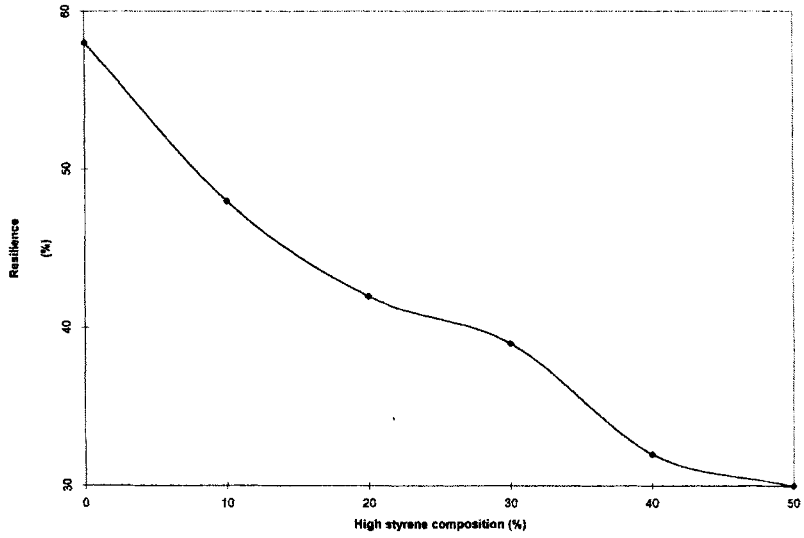

FIGURE 5 The relationship between high styrene composition and resilience of the rubber vulcanizates.

react effectively. HS might behaves like perfect elastic materials where main deformation mechanism is stretching, bending, compression and rotation of covalent bonds. However since the test involve the use of energy at higher rate the probability of chain fracture due to linear deformation or permanent deformation due to friction slippery, might occurred because of chain flexibility of HS copolymer. This flexibility was due to weaker intermolecular forces to cause permanent deformation where in this case, time to elastic respond is not enough especially because of lower HS chain flexibility. Moreover, energy transfer rate at interphase decrease due to the breakage of secondary bonds and HS-elastomer interphases which increase the energy lost mechanism from the system. So the energy return to the system as external work decreases and the hysteresis component increases.

3.3.5. The Effect on Crosslink Density

As shown in Figure 2, the crosslink density decreases with increasing HS concentration. This observation might be due to four factors:

(i) The reduction of overall vulcanizations additives in vulcanizates is responsible for the lower crosslink density.

(ii) At high temperature test, the solubility of elastomer-HS probably increases. But there is also probability that their solubility decreases again at higher temperature. Consequently, at vulcanization temperature, *i.e.*, 150°C, this probability might separate the additive which is situated in HS phase from elastomer. t_{90} measurement with Rheometer MDR 2000 was based on elastomer phase which form continuous phase and due to higher unsaturation on HS. This is because elastomer phase is cured faster than HS phase whereas some of the additive situated in HS phase. So before HS phase cured completely, elastomer phase has achieved its steady state in curing process.

(iii) The reverse condition might occurred where elastomer domain was formed and HS resin was the continuous phase. In this case the crosslink rate of continuous phase was very slow. Also, reduction of additive content in continuous phase would further reduced the crosslink density. Table III shows the effect of factors (ii) and (iii) on t_{90} and t_5.

(iv) Not like other fillers such as carbon black, HS domain is long chain copolymers and hence the heat transfer rate to occluded rubber is low. This would reduced the crosslink contribution between the rubber phase outside and inside domain to the measured crosslink density.

3.3.6. Processability

Processability depend on Mooney viscosity and scorch time. From Table III, it can be seen that scorch time, t_5 increased with increasing HS concentration. This means that HS can be used to overcome the scorch phenomenon in the rubber vulcanizates.

Mooney viscosity is minimum at 20% HS composition (see Fig. 1). The lower Mooney viscosity means a better flow characteristics of the compounds in the cavity during vulcanization. This characteristics enable the perfect formation of specimen in cavity before cured. The viscous flow is more dominant than elastic property of the melting sample and hence the ability of the chain mix and flow through each other is easier.

4. CONCLUSION

The incorporation of HS resin in the rubber vulcanizates was found to have beneficial effects by prolonged the scorch time and improved physical properties such as hardness and tensile modulus. However from processability aspect of view, 20% of HS composition is the optimum concentration where the rubber compounds exhibit the minimum Mooney viscosity.

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