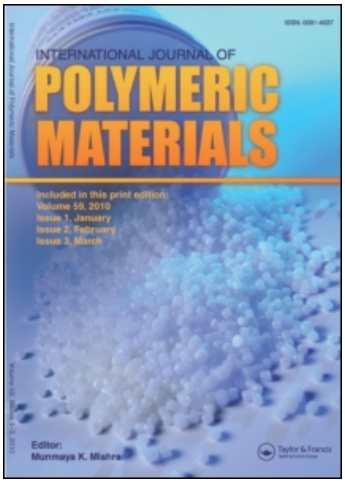

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The Effect of Various Combinations of Accelerators on the Physical Properties of Rubber Vulcanizates

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Systems of combined accelerators comprising 2-mercaptobenzothiazol (MBT), dibenzothiazyl disulfide (MBTS), tetramethyl thiuram monosulfide (TMTM) and diphenyl guanidine (DPG) were used to study the physical properties of rubber vulcanizates. The study was conducted by divisioning the work into 3 sets; namely set 1, set 2 and set 3 whereby the combinations of the accelerators were carried out in such a way that only the ratios were subject to changes. We found that there was a synergistic effect on the vulcanizates properties leading to, higher or lower property values from the normally expected ones demonstrating the role of crosslink on tensile modulus, hardness and resilience.

Keywords: Accelerators; rubber vulcanizates; physical properties; crosslink density

1. INTRODUCTION

Vulcanization systems using two or more accelerators finds wide technological application. Such systems generally possess an increased activity over that obtained with the individual components [1]. Many types of synergism between various accelerators have been reported by previous researchers [1–3]. Krymowski and Taylor [4] observed that combinations of thiocarbamysulfenamides and benzothiazylsulfenamides give higher states of cure, less reversion, and higher percentages

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of monosulfidic crosslinks than either vulcanization accelerator alone could give. In the present investigation, we have studied the effect of various combinations of accelerators on the physical properties of rubber vulcanizates. Four types of accelerators were used, *i.e.*, 2-mercaptobenzothiazol (MBT), dibenzothiazyl disulfide (MBTS), tetramethyl thiuram monosulfide (TMTM) and diphenylguanidine (DPG).

2. EXPERIMENTAL

2.1. Materials and Chemicals

Table I shows the materials, their manufactures and levels used in this study. The formulation was based on the semi-efficient vulcanization system (semi-EV). Four different sets of accelerator ratios were prepared as follows:

Set 1: MBT/MBTS: TMTM accelerator ratio (in phr) was changed. The total of other ingredients and accelerator (in phr) maintained.

Set 2: MBT/MBTS: DPG accelerator ratio (in phr) was changed. The total of other ingredients and accelerator (in phr) maintained.

Set 3: MBT: MBTS accelerator ratio (in phr) was changed. The total of other ingredients and accelerator (in phr) maintained.

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

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
Calcium Carbonate	Nipol (M) Ltd	168.66
Napthenic Oil (Shell Flex)	Bayer (M) Ltd	12.51
Accelerator [b]	Bayer (M) Ltd	5.26
Pigment (BHT)	Bayer (M) Ltd	0.63

[a] Rubber Research Institute of Malaysia;
[b] Different accelerator ratios were used (see Tab. II).

For each sets 1–3, accelerator ratios were changed from 3:0 to 0:3 as shown in Tables II–IV.

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 on a two-roll mill with temperature maintained at $70 \pm 5°C$. Total time taken to complete one mixing cycle was 29 minutes. The batch mass was checked and recorded. If it differed from the theoritical value by more than 0.5%, the batch was rejected. The sheeted compound was conditioned at a temperature of $25 \pm 2°C$ 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.

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:

TABLE II Accelerator ratios for set 1

Accelerator (phr)	I	II	III	IV	V
MBT/MBTS	5.26	3.51	2.6	1.75	–
TMTM	–	1.75	2.6	3.51	5.26
MBT/MBTS:TMTM	3:0	2:1	1.5:1.5	1:2	0:3

TABLE III Accelerator ratios for set 2

Accelerator (phr)	I	II	III	IV	V
MBT/MBTS	5.26	3.51	2.6	1.75	–
DPG	–	1.75	2.6	3.51	5.26
MBT/MBTS:DPG	3:0	2:1	1.5:1.5	1:2	0:3

TABLE IV Accelerator ratios for set 3

Accelerator (phr)	I	II	III	IV	V
MBT	5.26	3.51	2.6	1.75	–
MBTS	–	1.75	2.6	3.51	5.26
MBT:MBTS	3:0	2:1	1.5:1.5	1:2	0:3

Part A3. The cross-head speed was set at 500 mm 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 [5]

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

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

where λ = extension ratio, σ = tensile stress, C_1 and C_2 = constant.

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

3. RESULTS AND DISCUSSION

3.1. The Effect of Crosslink Density

Figures 1–3 show the relationship between crosslink density and accelerator ratio for all the three sets studied. It can be seen that the crosslink density obtained deviates from the expected crosslink density as shown by the broken line. This means synesgistic increase in crosslink density efficiency of the system occurred. Since the amount of sulphur was constant, this phenomenon might be due to the shorter crosslink with the increasing TMTM, DPG and MBT level in the accelerator ratios for sets 1–3.

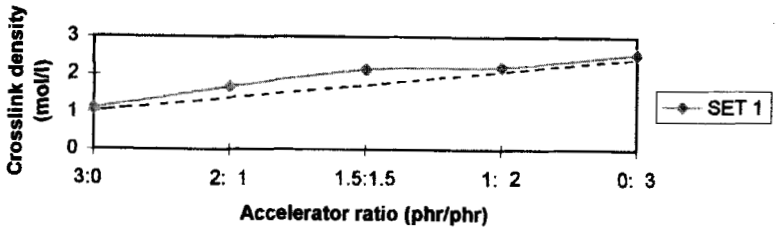

FIGURE 1 The effect of various MBT/MBTS: TMTM accelerator ratio on crosslink density.

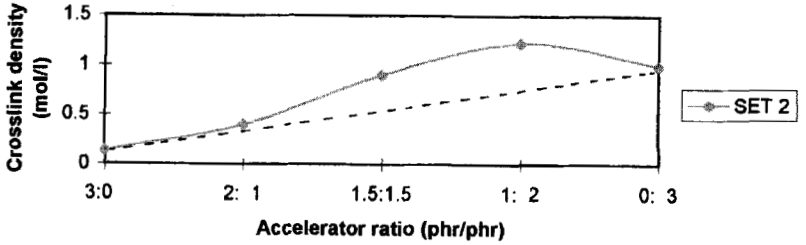

FIGURE 2 The effect of various MBT/MBTS: DPG accelerator ratio on crosslink density.

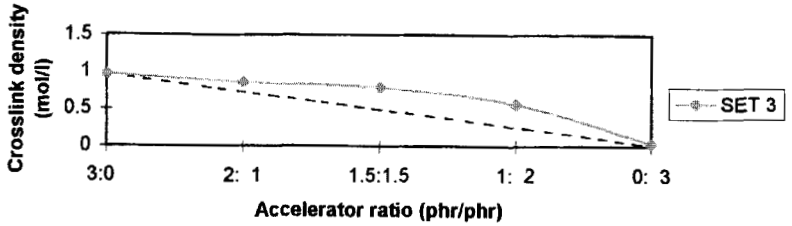

FIGURE 3 The effect of various MBT : MBTS accelerator ratio on crosslink density.

According to Coran [6–7], the kinetics associated with the accelerated sulfur vulcanization of unsaturated elastomers, wherein long density periods are encountered is given by the basic scheme as follows:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} B^* \xrightarrow{k_3} \alpha Vu$$

$$A + B^* \xrightarrow{k_4} \beta B$$

Where A is the accelerator and/or its reaction products (with sulfur, Zn^{++}, *etc.*); B is a precursor to crosslinks probably polymeric; B^* is an activitated form of B, such as a polymeric polythiyl radical; Vu is a crosslink; and α and β adjust stoichiometry.

If the reaction through k_4 is much faster than that through k_3, very little crosslink formation can occur until A is essentially depleted. Both the reaction through k_4 and that through k_3 are assumed to be much faster than the reaction through k_2. Hence, the reaction through k_2 is the rate controlling crosslink formation after the depletion of A is almost completed. The plots of dx/dt against vulcanization time for a range of times between ts_2 and t_{90} in the rheograph obtained from MR 100 rheometer are shown in Figures 4–6. It can be seen that the reaction rate, k_2 as shown in the scheme proposed by Coran for any accelerator combination for sets 1–3 is higher compared to accelerator ratios at 3:0 and 0:3. This might be due to the formation of an active sulphur complex with different amount of bounded sulphur which in itself depend on the formation type of the complex and its inherent characteristics.

Layer [8] in his studies on synergism between thiocarbamyl (OTOS) and 2-benzothiazyl sulfenamide (OBTS) accelerators found that the accelarator complex at certain accelerator ratio showed distinctly different structures. In this study of the OTOS–OBTS system, the

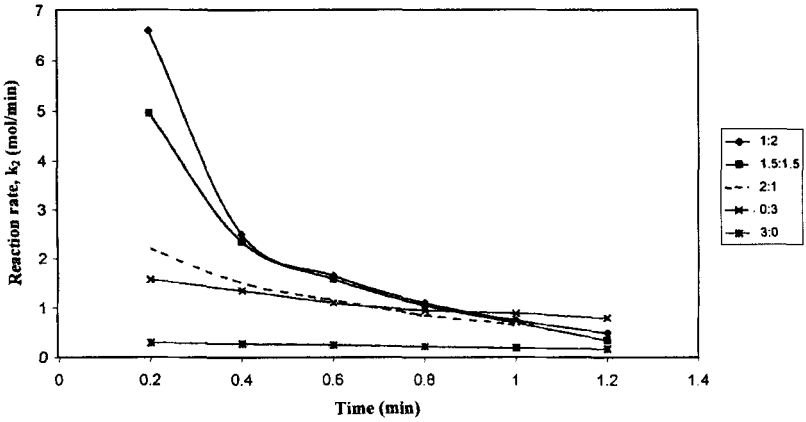

FIGURE 4 The effect of various MBT/MBTS: TMTM accelerator ratio on reaction ratio, k_2.

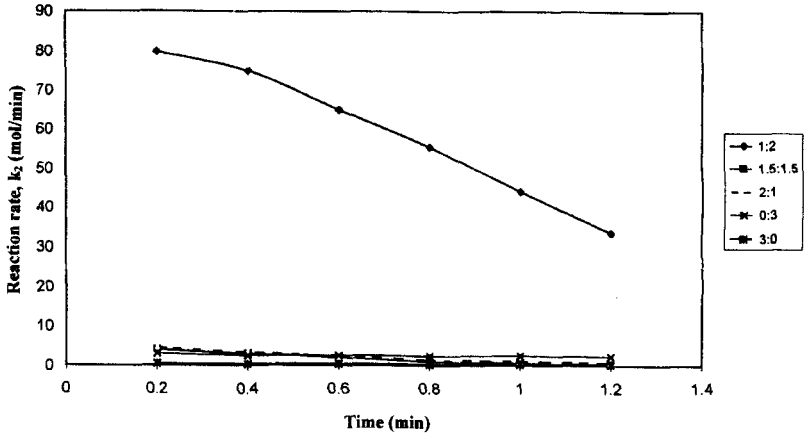

FIGURE 5 The effect of various MBT : MBTS : DPG accelerator ratio on reaction rate, k_2.

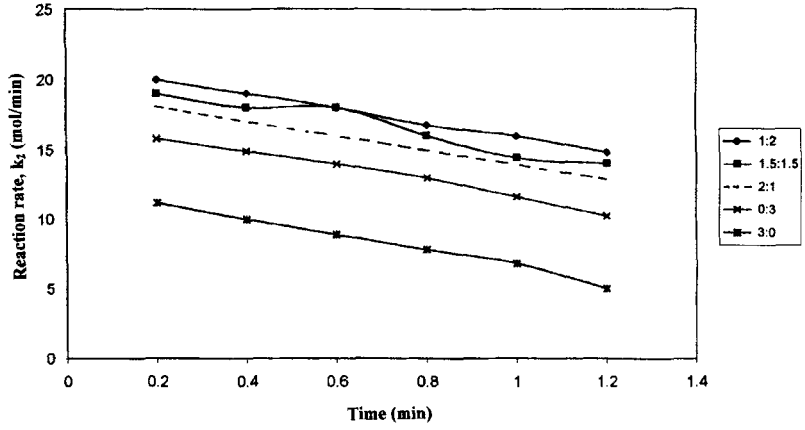

FIGURE 6 The effect of various MBT : MBTS accelerator ratio on reaction rate, k_2.

strength of the Zn—S was affected by the active sulphur complex. Consequently the formation of system complexes for sets 1–3 would affect the number of sulphur atom bound in the complex, which in the end could determine the vulcanization efficiency and whether any synergistic effect could take place. However, the increase in crosslink density might also occur due to increment or without changing in the

degree of polysulphides [9–10]. If the increment occurred, it might be due to the more usage of sulphur during vulcanization and the lower quantity of unbounded sulphur at the end of vulcanization (t_{90}). This observation is reported by Layer [8] with OTOS/OBTS system.

3.2. The Effect on Tensile Modulus, M100

Figures 7–9 show the effect of accelerator ratios on the modulus at 100% extension (M100) for MBT/MBTS: TMTM, MBT/MBTS: DPG and MBT:MBTS before and after ageing. All figures show synergistic relationship whereas different combination of accelerator ratios show M100 higher than the expected value (broken line). As discussed before, this is due to the increase in crosslink density. This result is consistent with the reported theory [11] that tensile modulus at low elongation is an empirical approximation of crosslink density. Correlation between the M100 and crosslink density support our

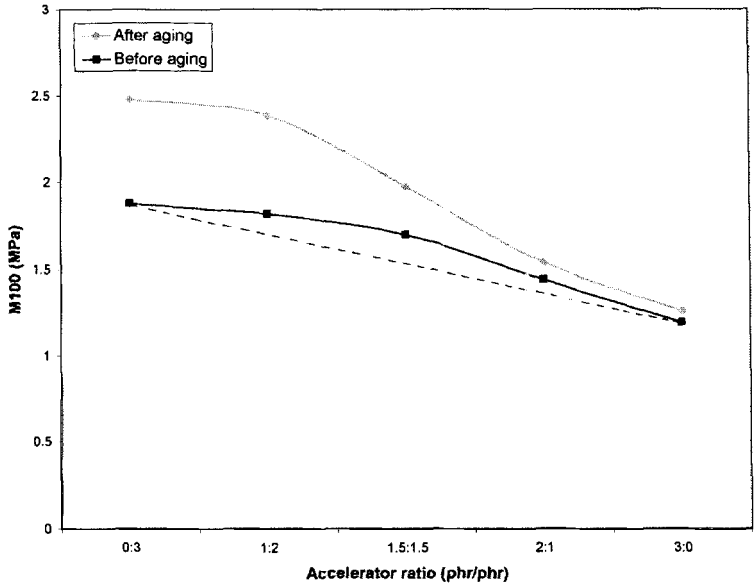

FIGURE 7 The effect of various MBT/MBTS:TMTM accelerator ratio on M100 before and after ageing.

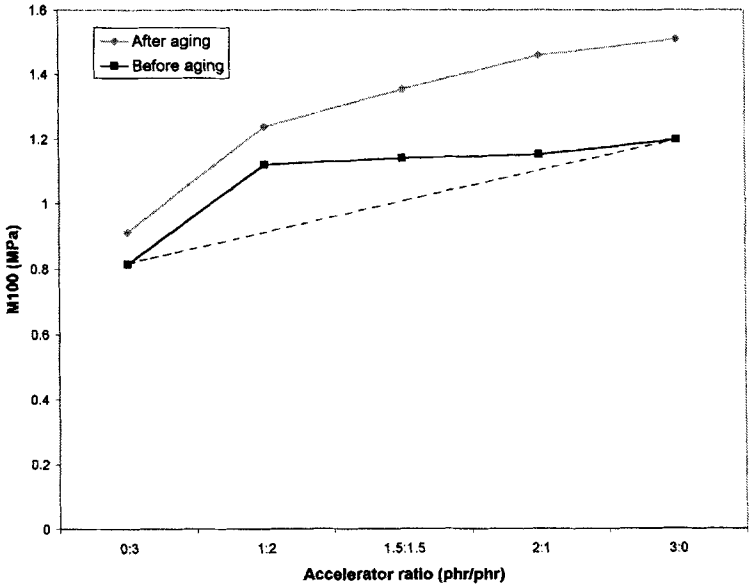

FIGURE 8 The effect of various MBT/MBTS:DPG accelerator ratio on M100 before and after ageing.

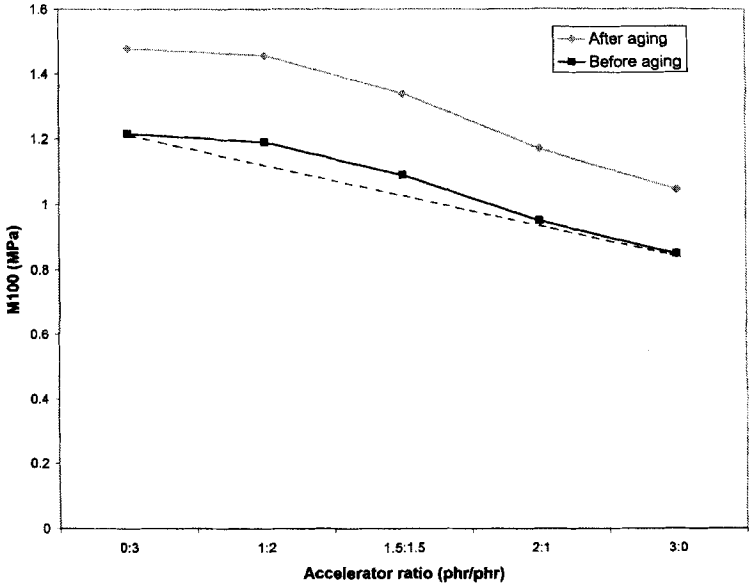

FIGURE 9 The effect of various MBT:MBTS accelerator ratio on M100 before and after ageing.

proposal that there was a complex reacting in favourably synergisitc way in the vulcanizates during vulcanization process.

3.3. Ageing Effect on M100

It can be seen in Figures 7–9 that the M100 increased when the rubber vulcanizates were exposed to thermo-oxidative ageing. According to Mathew and De [12] the increase in modulus during the early periods of ageing is due to the increase in the crosslink density. The increase in crosslink density during ageing is contributed by both the oxidative crosslinking and the post-curing reactions.

3.4. The Effect on Hardness

From Figures 10–12, it can be seen that the hardness increased synergistically as for M100 and crosslink density. The mode of the hardness test also measure the stress at certain strain by indentor

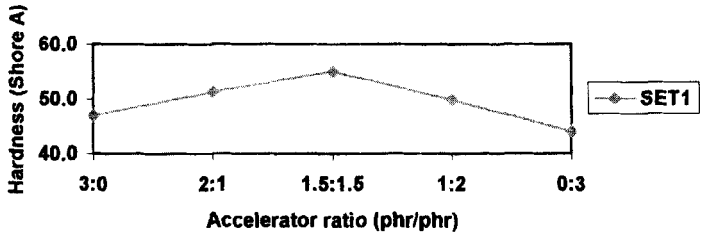

FIGURE 10 The effect of various MBT/MBTS:TMTM accelerator ratio on hardness.

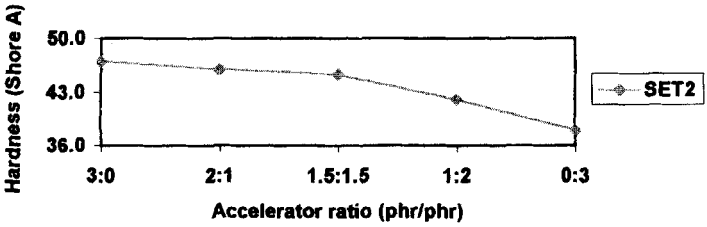

FIGURE 11 The effect of various MBT/MBTS:DPG accelerator ratio on hardness.

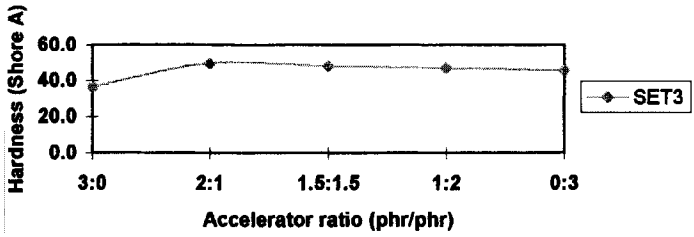

FIGURE 12 The effect of various MBT:MBTS accelerator ratio on hardness.

penetration on the samples – a good correlation exist between M100 and hardness. Sets 1 and 3 give higher hardness value at accelerator ratio 2:1, 1.5:1.5 and 1:2 which shows synergistic relationship compared to accelerator ratio at 3:0 and 0:3. However, this observation is absent in M100 and crosslink density measurement.

The increased in crosslink density (in previous section), caused immobility of the chain segments between the crosslinks to be further increased. This means that higher force is needed for deformation [13] and the indentor penetration for small deformation is also decreased. Consequently the hardness in shore A increased. However the measurement of tensile modulus at 100% elongation was done at cross head speed of 500 mm/min with higher application of force compared to hardness test by indentor. So the behaviour of the chain segments between the crosslink for the two tests was different. In addition, the test mode for M100 is tensile stress at large deformation in relation to overall sample whereas hardness test is carried out at small deformation in compression mode and only on the sample surface.

3.5. The Effect on Resilience

Figures 13–15 for sets 1–3 give similar relationship, *i.e.*, resilience for accelerator ratios of 2:1, 1.5:1.5 and 1:2 are higher compared to accelerator ratios of 3:0 and 0:3.

An elastomer is predominantly viscoelastic but it's vulcanizates did not show perfect elasticity characteristics [14], as we would have expected. The deviation from the ideal elastic state can be obtained

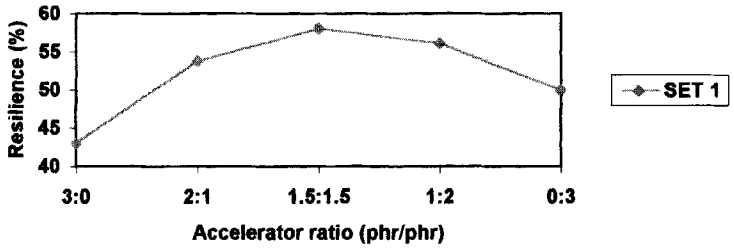

FIGURE 13 The effect of various MBT/MBTS:TMTM accelerator ratio on resilience.

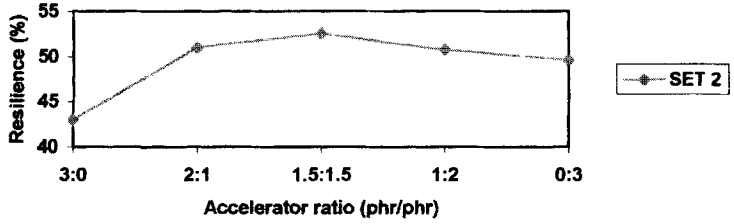

FIGURE 14 The effect of various MBT/MBTS:DPG accelerator ratio on resilience.

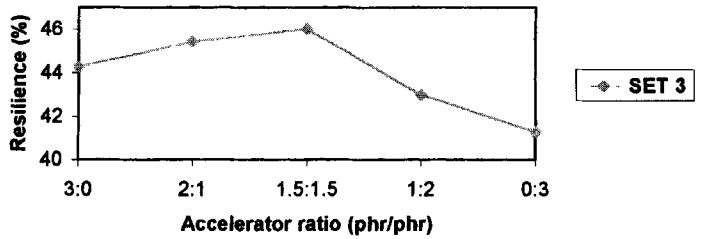

FIGURE 15 The effect of various MBT:MBTS accelerator ratio on resilience.

from resilience test which is given by the following equation [15].

$$R = \left(\frac{\text{Energy returned by vulcanizate}}{\text{Energy supplied by vulcanizate}} \right) \cdot 100\%$$

where R is the resilience percentage. So, hysteresis (H) can be obtained from;

$$H = 100 - R$$

This means that, resilience test is a test for elastomer viscoelasticity [14]. The increase in crosslink density (synergistically obtained) would either increase or decrease entropic elasticity. This may be due to:

(a) The increase in crosslink density would increase the immobility of the chain segments between the crosslinks and a higher force is needed to deform this chain segments [13]. However at higher rate of energy supply *i.e.*, under pendulum impact condition, the decrease in flexibility resulted in permanent deformation due to the inability of the chain segments to react and also due to the magnitude of the energy. In contrast to plastics [16], at higher deformation rate the lower force between the elastomer molecules resulted in permanent deformation due to the increase in chain immobility. Consequently the original condition of the chains was altered permanently. At the same time, the unstable secondary bond might be broken [17] and the permanent deformation could increase.

(b) At the same time, the increase in crosslink density initiated reduction in the internal friction [18] by chain segments slippage, chain entanglement, the effect of the force between chain ends *etc.* For example the slippage of the chain entanglements would form more free elastic energy [19]. The permanent slippage was actually decreased due to the more returnable energy. The increase in resilience shows that factor (b) is more dominant. However there is also energy lost to the system from factor (a) [20] due to the viscoelasticity system and the rearrangement of the chain segments. Some of the energy is converted to heat which increase the vulcanizates temperature whilst the remaining energy is return as external work. The lost energy is called hysteresis.

CONCLUSION

A combination of 2-mercaptobenzothiazol (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 of

the rubber vulcanizates with the various combination of the above accelerator ratios.

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