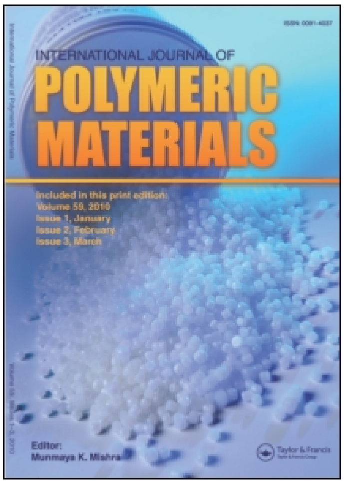

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The Fatigue and Hysteresis Behaviour of Filled Epoxidized Natural Rubber Compounds

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The paper reports on the fatigue behaviour of white rice husk ash (WRHA), silica and carbon black-filled ENR 50 vulcanizates. The properties investigated include the stress-strain behaviour, effect of coupling agent and hysteresis. Carbon black filled vulcanizates showed the highest stress-strain behaviour followed by silica and WRHA. This observation was supported by the plot of accumulated strain energy versus extension ratio. Carbon black showed the highest value followed by silica and WRHA. The incorporation of silane coupling agent has improved the fatigue life of WRH-filled vulcanizates. Hysteresis studies showed that as the filler loading increased there was an increase in hysteresis and carbon black filled vulcanizate exhibited the highest hysteresis i.e. the most sensitive towards changes in strain energy.

Keywords: Fatigue behaviour; hysteresis; epoxidized natural rubber; filler; curing characteristics; coupling agent

1. INTRODUCTION

Epoxidized natural rubber (ENR) is a chemically modified natural rubber. Numerous studies have reported on ENR-filler interaction and reinforcement [1–3]. Nasir and Choo [4] studied the cure characteristics and mechanical properties of carbon black filled styrene-butadiene rubber and epoxidized natural rubber blends. Recently Hanafi *et al.* [5–7] reported the use of rice husk ash as a filler in ENR compounds. However all these reports involve short term properties i.e. tensile strength, tear strength and hardness. Fatigue being one of the important long term test methods has been used extensively for various rubbers [8–10]. In our previous report [11] we studied the fatigue behaviour of filled ENR compounds. The fatigue behaviour of white rice husk ash (WRHA) filled ENR-50 compounds was compared with those of silica (Vulcasil-S) and carbon black (N-330) filled compounds. The increase in filler loadings resulted in the reduction of the fatigue life. The fatigue behaviour of ENR-50 vulcanizates was observed to be strain dependent. At a similar filler loading, silica filled vulcanizates showed the highest fatigue life followed by those of WRHA and carbon black. In this work, we report further on the fatigue behaviour of filled epoxidised natural rubber compounds particularly the stress-strain behaviour, effect of coupling agent and hysteresis.

2. EXPERIMENTAL

2.1. Materials and Chemicals

Table I shows the typical semi-efficient (semi-EV) vulcanization system of ENR 50 compounds used in this study. Epoxidized natural rubber (grade ENR-50) was obtained from Kumpulan Guthrie Sdn. Bhd., Seremban, Malaysia. White rice husk ash (WRHA) was supplied by Plastic Technology Centre, S.I.R.I.M, Malaysia. Table II shows the

TABLE I Formulations of ENR-50 filled compounds

Materials	*phr*
ENR-50	100
Sulphur	1.6
Zinc oxide	2.0
Stearic acid	1.5
CBS[a]	1.9
TMTD[b]	0.9
IPPD[c]	2.0
Fillers[d]	0, 10, 20, 30, 40, 50

[a]N-cyclohexyl-2-benzothiazole-2-sulphanamide.
[b]Tetramethylthiuram disulphide.
[c]N-isopropyl-N-phenylenediamine.
[d]WRHA, carbon black (N 330) or silica (Vulcasil-S).

TABLE II Chemical composition of WRHA [5]

Properties	*Value*
Chemical composition (%)	
CaO	0.1
MgO	0.4
Fe_2O	0.1
K_2O	1.6
Na_2O	0.1
Al_2O_3	trace
P_2O_5	trace
SiO_5	96.2
Lost on ignition (LOI)	1.6
Physical properties	
Mean particle size (μm)	5.4
Surface are (m^2/g)	1.4
Density (g/m^3)	2.2

chemical properties of WRHA [5]. Precipitated silica (grade Vulcasil-S), carbon black (grade N 330) and other additives such as zinc oxide, sulphur, stearic acid, antioxidant and accelerator were purchased from Bayer (M) Ltd.

2.2. Mixing and Cure Characteristic Determination

Mixing was carried out on a laboratory size (160 mm × 320 mm) two roll mill. The total mixing time has been kept to a minimum to avoid sticking of the rubber compound to the mill rolls. Care was taken to ensure that the mill-roll temperature was not too high, i.e. exceeding the set temperature, to avoid premature crosslinking during mixing. This has been achieved by using cooling water. The cure times at 140°C as indicated by the respective t_{90} were then determined using a Monsanto Rheometer, model MDR 2000. 2% w/w on filler of γ-mercaptopropyltrimethoxysilane (A-189) was applied for the modification of the filler surface. The coupling agent was premixed with the fillers prior to compounding on the two roll mill.

2.3. Measurement of Fatigue Life

The rubber compounds were compression moulded at 140°C according to their respective t_{90}, into rectangular sheet (22.9 cm × 7.6 cm ×

0.15 cm) with beaded edges. Individuals dumbbell samples were cut at right angles to the grain using a BS type E dumbbell cutter. Fatigue tests of the vulcanizates were then carried out on a Monsanto Fatigue To Failure Tester (FTFT). The samples were subjected to repeated cyclic strain at 100 cpm. The extension ratio used ranged from 1.6 to 2.4. Six specimens were used for each test. The number of cycles were recorded automatically. The fatigue life in kilocycles (kc) for each sample was computed as the J.I.S. average, which was obtained from the four highest values recorded using the formula:

$$\text{J.I.S. average} = 0.5\,A + 0.3\,B + 0.1\,(C + D)$$

where A is the highest value followed by B, C and D.

2.4. Strain-Energy Measurement

The equipment used consists of a stand incorporating upper clamp, pan incorporating lower clamp (weight 50 g) plus various weights (1 × 1 kg; 2 × 500 g; 1 × 200 g; 1 × 50 g; 2 × 100 g) was supplied with Monsanto Fatigue To Failure Tester.

2.4.1. Method

Strain-energy values were obtained from the stress-strain curve of a sample which has been cycled for more than 30 cycles by machine at the maximum extension ratio used in determining the fatigue curve. The width and thickness of the linear region of the sample were measured by a dial gauge. Horizontal chalk lines were drawn on the sample in the linear region, when fully extended. The pan was then detached and the unloaded distance between the marks measured. Distances were also measured by replacing the pan with 50 gm. weight, followed by successive additional loadings of 200 gm at one minute intervals, until an extension ratio of ca. 2.5 was attained.

2.4.2. Strain-Energy Calculation

Manual calculation consists of plotting the calculated load/area vs. extension ratio curve and reading off stress values (*h*) from this curve at intervals of 0.1 extension ratio ranging from 1.0 to 2.5. Strain-energy values are obtained by applying Simpson's Rule to sets of three consecutive results to give the areas (A) of sections of the curve and subsequently the total area of the curve at extension ratio increments of 0.2 (see Equation 1).

$$\text{Area} = \frac{1}{3}a[h_X + 4h_{(X-1)} + h_{(X+2)}] \tag{1}$$

where $a = 0.1$ (strain interval).

3. RESULTS AND DISCUSSION

3.1. Stress-Strain Behaviour and Strain Energy

Figure 1 shows the stress-strain behaviour of ENR 50 vulcanizates filled with WRHA, N 330 carbon black and silica (Vulcasil-S) fillers at

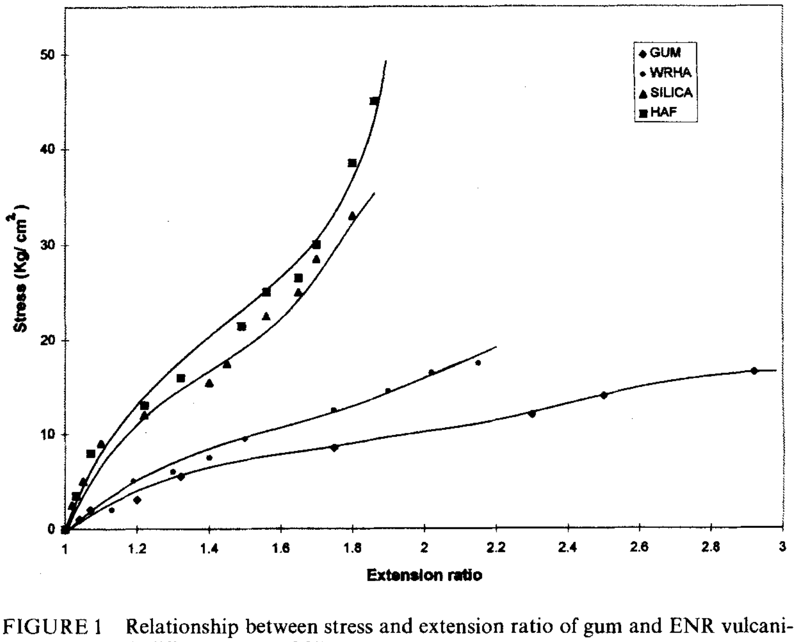

FIGURE 1 Relationship between stress and extension ratio of gum and ENR vulcanizates filled with different types of filler.

50 phr and ENR 50 gum vulcanizate. It can be seen that carbon black (N330) filled vulcanizate exhibits the highest stress at any extension ratio followed by silica (Vulcasil-S) then WRHA. This result is in agreement with an earlier work by Baker *et al.* [12] who reported that Vulcasil-S filled rubber compound without coupling agent has mechanical properties similar to that of HAF black (N 300). The incorporation of 50 phr WRHA has also moved the gum stock curve up albeit not as high as HAF black and Vulcasil-S. This may be due to poor interaction between WRHA and the rubber matrix compared to the two other fillers. This observation is further supported by the plot of accumulated strain energy versus extension ratio shown in Figure 2. It obvious that the work required to deform the rubber specimen is highest for N 330 carbon black followed by Vulcasil-S and WRHA. The difference between the accumulated strain energy of carbon black and silica is small especially at extension ratios below 1.8. As reported in our previous work [6] the tensile strength of WRHA-filled vulcanizates is inferior to those of N 330 carbon black and Vulcasil-S.

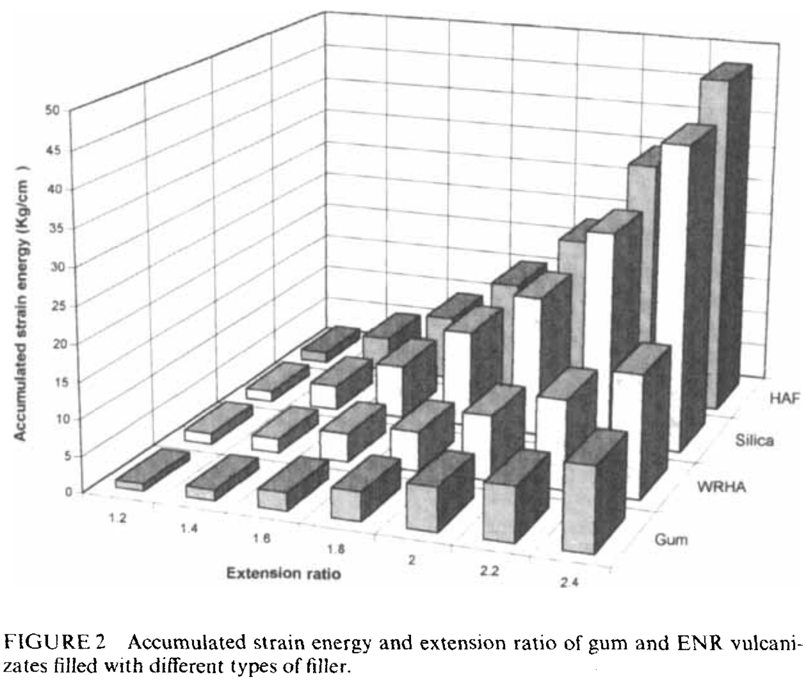

FIGURE 2 Accumulated strain energy and extension ratio of gum and ENR vulcanizates filled with different types of filler.

WRHA has larger particle sizes compared to the two commercial fillers (see Tab. III). Patterman [13] and Mark [14] have reported that significant reinforcement is only attainable when the particle size of the filler is of the order of 0.02–0.05 μm. Nasir and Choo [4] and Parkinson [15] found that decreasing the particle size of silica and carbon black fillers generally enhanced mechanical properties such as tensile and tear strength. An earlier study by Haxo and Mehta [16] who investigated the utilization of RHA in EPDM and SBR also reported that ground RHA is only a moderate reinforcing filler.

3.2. Effect of Coupling Agent on Fatigue Life

Figure 3 shows that A-189 silane coupling agent increased the fatigue life of WRHA-filled ENR 50 vulcanizates. This effect is expected as silane coupling agents are known to improve the interaction between the rubber matrix and filler [2, 17]. According to Wagner [17] the chemical and/or physical bridges help to reduce the amount of heat build up during the dynamic deformation and consequently reduce the incidence of chain scission. This further enhances the fatigue life of the vulcanizates. Nasir *et al.* [2] reported that the mechanical properties of Vulcasil-S-filled ENR 50 compounds were enhanced by the incorporation of A-189 silane coupling agent. They found that the optimum level of this coupling agent was 2% based on phr of silica used.

The enhancement in fatigue life with the addition of A-189 coupling agent might be due to the reaction of the coupling agent with both the rubber matrix and filler. According to Wagner [17] the silane which has an alkoxysilyl group can react with silanol groups on the silica surface (main composition in WRHA) to form a stable siloxane linkage while its organic functionality participates in reactions and cause

TABLE III Physical Properties of WRHA, Silica (Vulcasil-S) and Carbon Black (N 330)

	WRHA	*Silica*	*Carbon black*
Mean particle size (μm)	5.4	0.011–0.019	0.026–0.030
Surface area (m^2/g)	1.4	170	98.9
Density (g/cm^3)	2.2	2.2	1.8

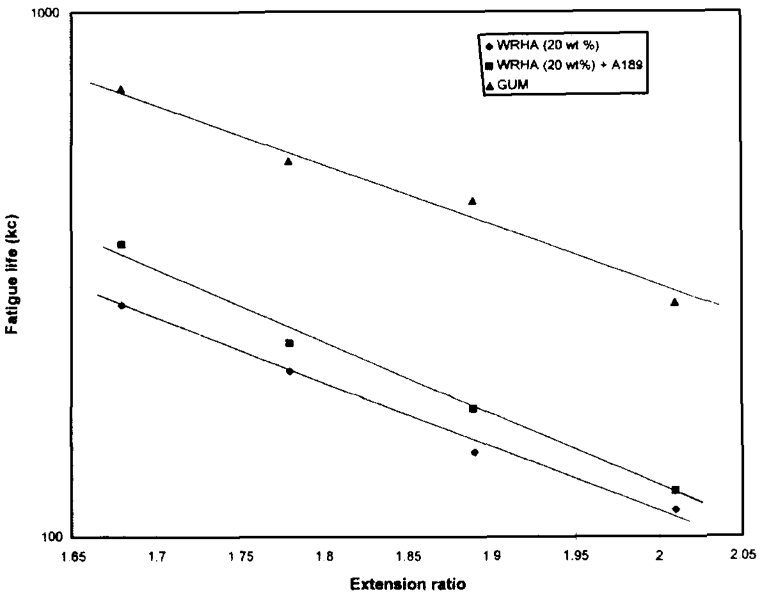

FIGURE 3 The effect of silane coupling on the fatigue life of WRHA-filled ENR vulcanizates.

linkages with the rubber. Voet *et al.* [18] studied the reinforcement of elastomer by silica and found that the improvement in mechanical properties in the presence of mercaptosilane was not only caused by improved filler–elastomer adherence but also by a better dispersion. This would improved the wettability of silica by the matrix and thus account for the enhancement in mechanical properties, i.e. fatigue life of the vulcanizate. The presence of filler agglomeration in matrix should be avoided since it has a tendency to cause stress concentration point which will results in premature fatigue failure. From their work on silica-filled natural rubber containing mercaptosilane, Cameron *et al.* [19] obtained a considerable evidence for chemical interaction leading to significantly enhanced physical properties. It was proposed that when using silane with silica fillers, a stable Si—O—Si bond was formed between the silane and the filler particle surface.

Figure 3 also shows that the effect of A-189 silane coupling agent in WRHA filled ENR compounds is better at lower extension ratio where enhancement in fatigue life is higher. This indicates that linkages form between rubber matrix-coupling agent – WRHA can function more effectively at lower extension ratio than higher extension ratio.

3.3. Hysteresis Effect on Fatigue Property

Figure 4 shows the fatigue life of ENR 50 vulcanizates filled with 20 phr of fillers at different extension ratio. It is shown that the differences in fatigue life for silica (Vulcasil-S), HAF 300 and WRHA become more significant with increasing extension ratio. The highest fatigue life is obtained for Vulcasil-S followed by WRHA and HAF 330 carbon black. However a different trend is observed when 50 phr of fillers used. There is no significant differences in fatigue life at various extension ratio (see Fig. 5). This effect may be due to heat generation which occurred when vulcanizate was subjected to cyclic strain. For ENR 50 vulcanizates filled with 50 phr of fillers, it was

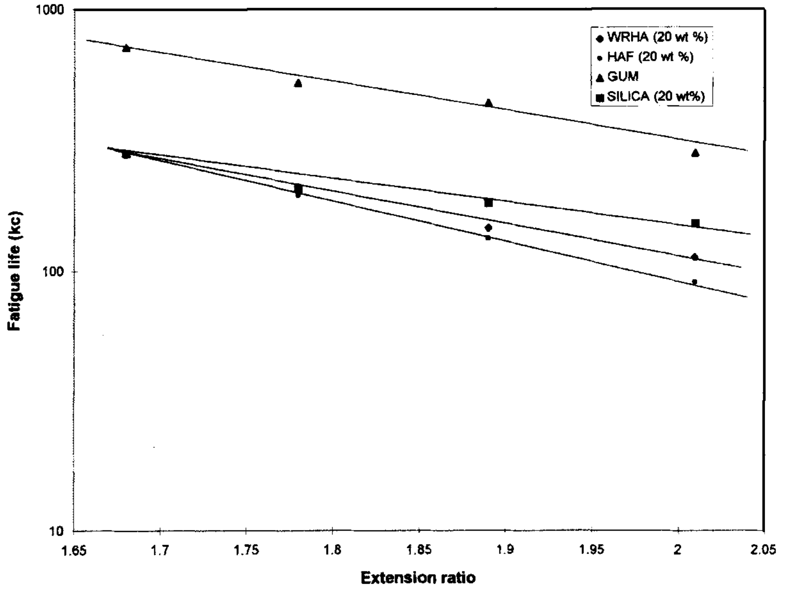

FIGURE 4 Fatigue life and extension ratio of gum and ENR vulcanizates filled with different types of filler at 20 phr.

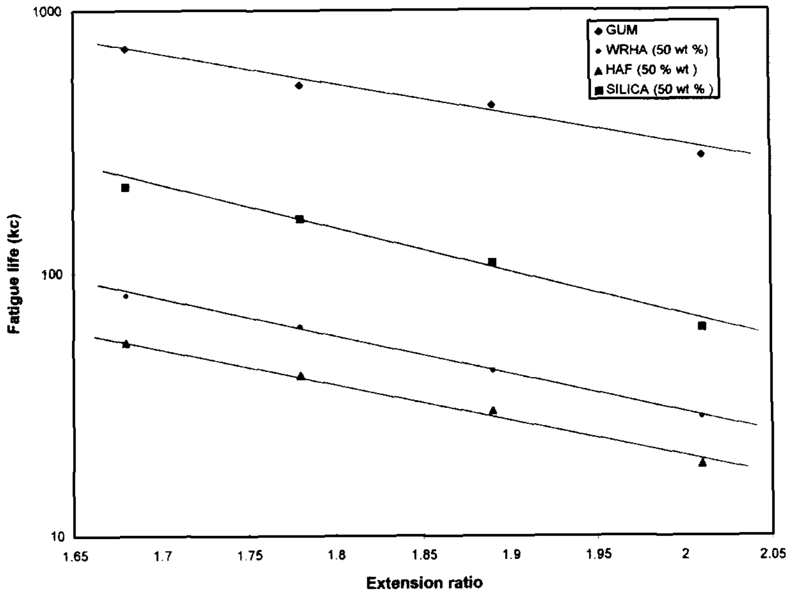

FIGURE 5 Fatigue life and extension ratio of gum and ENR vulcanizates filled with different types of filler at 50 phr.

found that the specimen failure was due to cyclic stress applied and heat generation in specimen. While for vulcanizates filled with 20 phr of fillers and at lower extension ratio, the effect of heat generation may not be significant and the specimen was fractured by cyclic strain only. Consequently, the fatigue life at lower extension ratio was not much different.

The better fatigue life of the lower filler loading vulcanizates (i.e. 20 phr) may also be attributed to the improved filler dispersion. Consequently, better wetting by rubber matrix on fillers can be expected. Higher amount of filler (i.e. 50 phr) might have produced filler agglomeration in the matrix and the interaction between filler and rubber matrix become less efficient. This will eventually creates stress concentration area which encourage premature failure.

Figure 6 show the plot of fatigue life versus strain energy for WRHA, silica and carbon black-filled vulcanizates at 50 phr loading. The hysteresis value which is indicated by the strain exponent (n) can be obtained from the slope of such plots according to the following

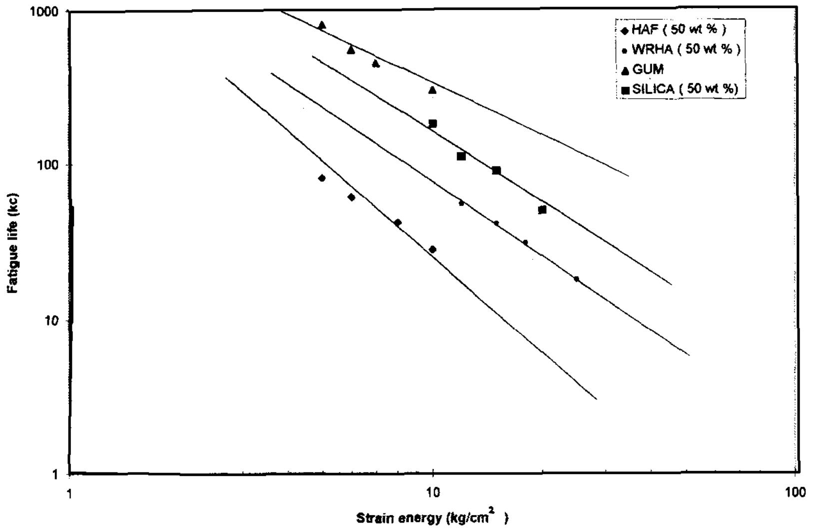

FIGURE 6 Relationship between fatigue life and strain energy of gum and ENR vulcanizates filled with different types of filler.

equation [20]:

$$N = \frac{G'}{(n-1)W^n} \cdot \frac{1}{C_0^{n-1}}$$

where N is the number of cycles to failure, G' the modified cut growth constant, C_0 the effective critical flaw size and W the strain energy per unit volume. The higher the value of n, the greater is the sensitivity of fatigue life towards changes in strain energy as exhibited by the highest filled vulcanizates. The higher hysteresis shown by the n values gives an indication of the extent of energy loss, hence the heat build up during the cyclic deformation process.

Table IV shows the values of strain exponent (n) for WRHA, silica and carbon black-filled ENR 50 vulcanizates. From the values of n obtained, it can be inferred that carbon black filled vulcanizate is the most sensitive towards changes in strain energy hence exhibited the highest hysteresis. This is followed by WRHA and Vulcasil-S. Over previous report [11] on the fatigue life of the similar vulcanizates also showed that the carbon black has the lowest fatigue life.

TABLE IV Strain exponent values (n) for ENR 50 vulcanizates filled with various fillers

Filler type	*n value* Filler Loading (phr)	
	20	50
WRHA	1.26	1.47
HAF 330	1.56	1.75
Vulcasil-S	0.55	1.67

CONCLUSIONS

Carbon black filled ENR 50 vulcanizates has the highest stress-strain behaviour followed by silica and WRHA. The lowest stress-strain behaviour for WRHA may be due to the poor interaction between WRHA and rubber matrix as compared to carbon black and silica. This suggestion is supported by the plot of accumulated strain energy versus extension ratio which showed a similar trend. Incorporation of the silane coupling agent has resulted in the improvement of fatigue life in all vulcanizates. Hysteresis studies showed that the carbon black filled vulcanizate is the most sensitive towards changes in strain energy hence exhibited the highest hysteresis. This trend is in agreement with the values of fatigue life of the respective vulcanizates.

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References

[1] Hashim, A. S. and Kojiya, S. (1993). *Kautsch. Gummi. Kunstst.*, **3**, 208.
[2] Nasir, M., Poh, B. T. and Ng, P. S. (1989). *Eur. Polym. J.*, **25**, 267.
[3] Medalia, A. I. (1987). *Rubb. Chem. Technol.*, **60**, 45.
[4] Nasir, M. and Choo, C. H. (1989). *Eur. Polym. J.*, **25**, 355.
[5] Hanafi Ismail, Ishiaku, U. S., Arinab, A. R. and Mohd Ishak, Z. A. (1997). *Intern. J. Polymeric Mater.*, **36**, 39.
[6] Hanafi Ismail, Ishiaku, U. S., Arinab, A. R. and Mohd Ishak, Z. A., *Polym. Plast. Technol. Eng.*, in press.
[7] Hanafi Ismail, Ishiaku, U. S., Arinab, A. R. and Mohd Ishak, Z. A., *J. Elast. Plast.*, in press.

[8] Beatty, J. R. (1984). *Rubb. Chem. Technol.*, **37**, 1341.
[9] Lake, G. J. and Lindley, P. B. (1964). *J. Appl. Polym. Sci.*, **8**, 707.
[10] Young, D. G. (1986). *Rubb. Chem. Technol.*, **59**, 809.
[11] Hanafi Ismail, Ishiaku, U. S., Lu, E. S. and Mohd Ishak, Z. A., *Intern., J. Polymeric Mater.*, in press.
[12] Baker, C. S. L., Gelling, I. R. and Newell, R. (1985). *Rubb. Chem. Technol.*, **58**, 67.
[13] Patterman, M. Q. (1986). *Rubb. World*, **194**, 38.
[14] Mark, H. F. (1964). *Encyclopedia of Polymer Sciences and Technology*, **12**, p. 42. Interscience, New York.
[15] Parkinson, D. (1957). Reinforcement of Rubbers, p. 12. Lakeman & Co., London.
[16] Haxo, H. E. and Mehta, P. K. (1975). *Rubb. Chem. Technol.*, **48**, 71.
[17] Wagner, M. P. (1976). *Rubb. Chem. Technol.*, **49**, 703.
[18] Voet, A., Morawski, J. C. and Donnet, J. B. (1977). *Rubb. Chem. Technol.*, **50**, 342.
[19] Cameron, G. M., Ranney, M. W. and Sollman, K. J. (1974). *Eur. Rubb. J.*, **3**, 38.
[20] Payne, A. R. and Whittaker, R. E. (1971). *J. Appl. Polym. Sci.*, **15**, 1941.