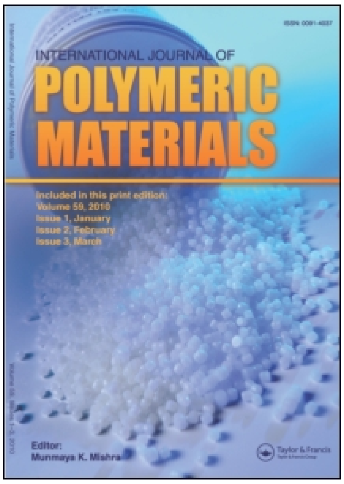


**International Journal of Polymeric Materials**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

# The Fatigue Behaviour of Filled Epoxidized Natural Rubber Compounds

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**To cite this Article** Ismail, Hanafi , Ishiaku, U. S. , Lu, E. S. and Ishak, Z. A. Mohd(1997) 'The Fatigue Behaviour of Filled Epoxidized Natural Rubber Compounds', International Journal of Polymeric Materials, 38: 3, 275 — 289
**To link to this Article: DOI:** 10.1080/00914039708041023
**URL:** http://dx.doi.org/10.1080/00914039708041023

*Intern. J. Polymeric Mater.*, 1997, Vol. 38, pp. 275–289
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# The Fatigue Behaviour of Filled Epoxidized Natural Rubber Compounds

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*(Received 16 January 1997)*

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 effect of WRHA loading on scorch time and Mooney viscosity was also studied. The incorporation of WRHA in ENR-50 compounds reduced the scorch time but increased the Mooney viscosity. The increment in filler loadings has 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.

*Keywords:* Fatigue behaviour; epoxidized natural rubber; filler; fracture surface; curing characteristics

## 1. INTRODUCTION

Epoxidized natural rubber (ENR) is a relatively new polymer, having properties resembling those of synthetic rubbers rather than natural rubber (NR) [1–2]. It can offer unique properties such as reduced air permeability, decreased resilience, improved wet grip and rolling resistance, coupled with high strength. The epoxidation increased the polarity which brought about an improved resistance towards hydrocarbon oil [3–4]. In our previous report [5], the mechanical properties viz tensile and tear strength were enhanced by the addition of white rice husk ash (WRHA) in ENR compounds. The optimum level of WRHA to obtain maximum mechanical properties was achieved at

20 phr. The presence of silane coupling agent, γ-mercaptopropyl trimethoxy silane (A-189) increased the effectiveness of WRHA as a filler for ENR compounds. While the previous study has been focused on short term properties, the present work will report on one of the important long term properties, i.e. fatigue behaviour of filled ENR compounds. The work was carried out to achieve the following objectives:

(a) The effect of WRHA loading on scorch time and Mooney viscosity.
(b) The effect of WRHA loading on fatigue life of ENR vulcanizates.
(c) The fatigue life of ENR compounds filled with different types of commercial fillers.

The mode of failures of the various filled ENR compounds will also be investigated.



## 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 Center, S.I.R.I.M, Malaysia. Table II shows the chemical properties of WRHA [5]. Precipitated silica (grade Vulcasil

TABLE I Formulation 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-sulphenamide.
[b] Tetrametylthiuram 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 area ($m^2/g$) | 1.4 |
| Density ($g/m^3$) | 2.2 |



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 x 320 mm) two roll mill. 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 any crosslinking during mixing. This has been achieved by using cooling water. The respective cure times at 140°C as measured by $t_{90}$ were then determined using a Monsanto Rheometer, model MDR 2000. The scorch characteristic was determined by using Mooney Viscometer MV 2000 at 120°C.

## 2.3. Measurement of Fatigue Life

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

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

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



### 2.4. Scanning Electron Microscopy

Examination of the fracture surface was carried out using a Scanning electron microscope (SEM) model Leica Cambridge S-360. The fracture ends of the fatigue specimens were mounted on aluminum stubs and sputter coated with a thin layer of gold to avoid electrical charging during examination.

## 3. RESULTS AND DISCUSSION

### 3.1. The Effect of WRHA Loading on Scorch Time and Mooney Viscosity

The results from Mooney viscometer MV 2000 at 120°C (Fig. 1) shows that as the WRHA loadings in ENR compound increased, the scorch time decreased, i.e. it shows enhancement in cure rate. According to Miles [6], silica reacts with zinc oxide and deactivates the activation system in natural rubber vulcanizates, consequently increasing the scorch time. Wagner [7] also found that the most frequently used accelerator systems were severely deactivated by silicas. As a result, both the optimum cure and the state of cure are reduced substantially.

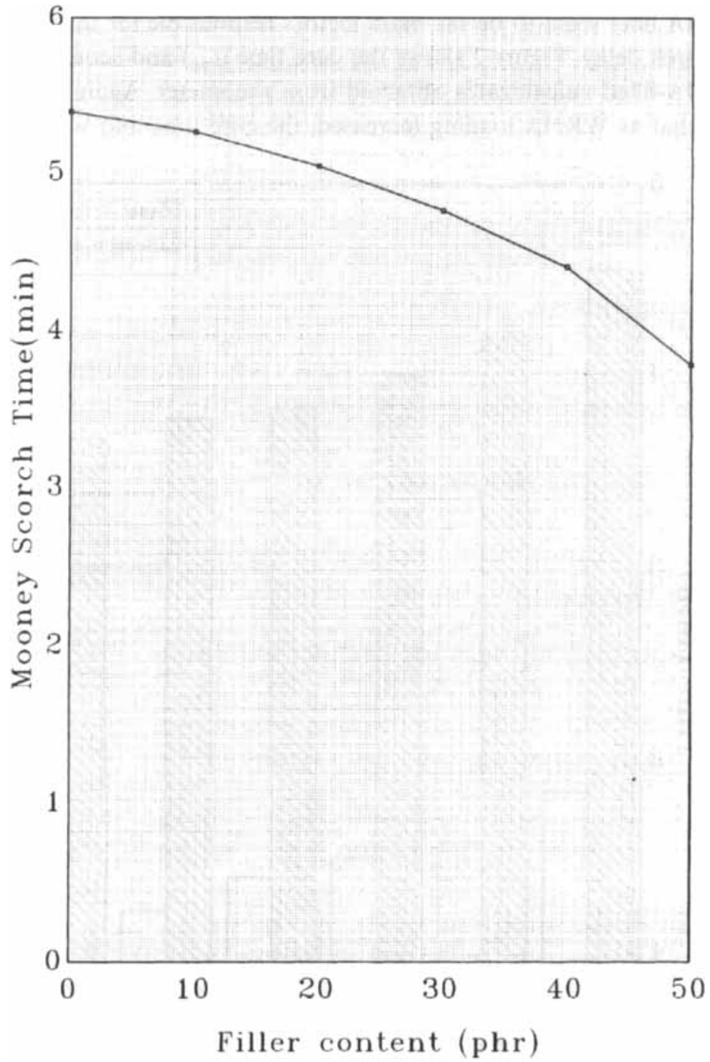


FIGURE 1 The effect of filler loading on Mooney scorch time of WRHA-filled ENR vulcanizates.

However, the fast cure rate displayed by WRHA is rather unexpected. In spite of having 96.2% silica content (see Tab. II), it does not behave like commerical silica. Perhaps the lower surface area, relatively higher metal oxide content and the presence of other impurities in the

WRHA filler seem to be the main factors responsible for the decrease in scorch delay. Figure 2 shows the cure time ($t_{90}$) and scorch time of WRHA-filled vulcanizates obtained from rheometer. Again it can be seen that as WRHA loading increased, the cure time and scorch time

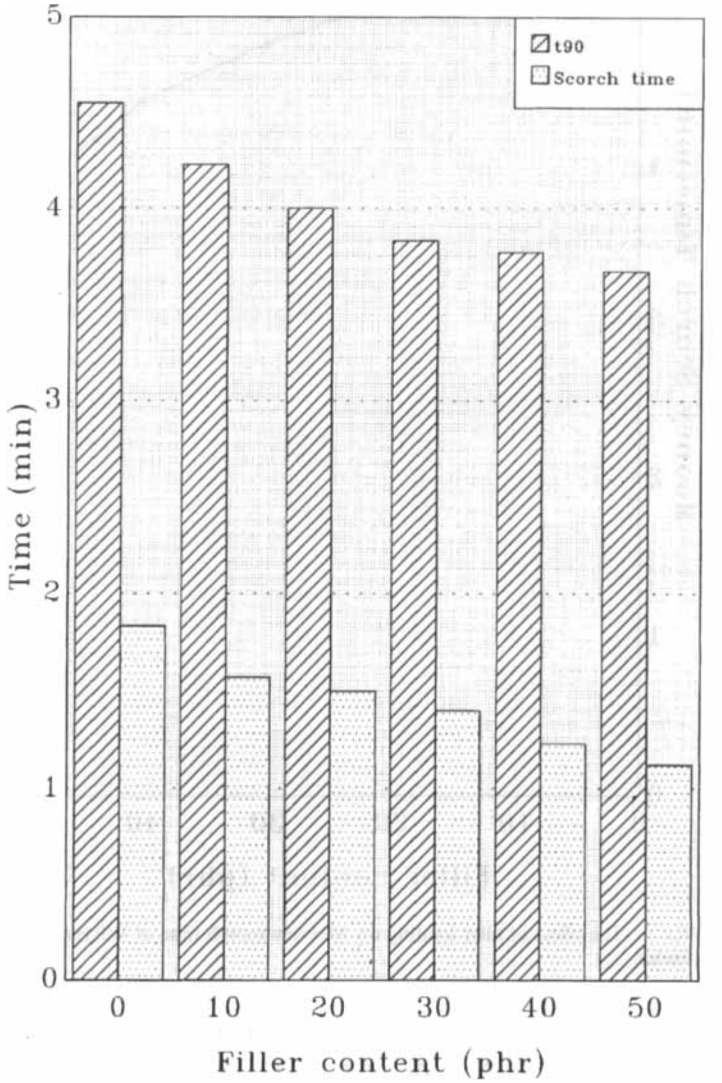


FIGURE 2 The effect of filler loading on $t_{90}$ and scorch time of WRHA-filled ENR vulcanizates.

decreased. Mehta and Pitt [8] also reported that rice husk ash has a faster cure rate compared to carbon black.

Figure 3 shows that Mooney viscosity increases with increasing WRHA content in ENR-50 compounds. The presence of WRHA in

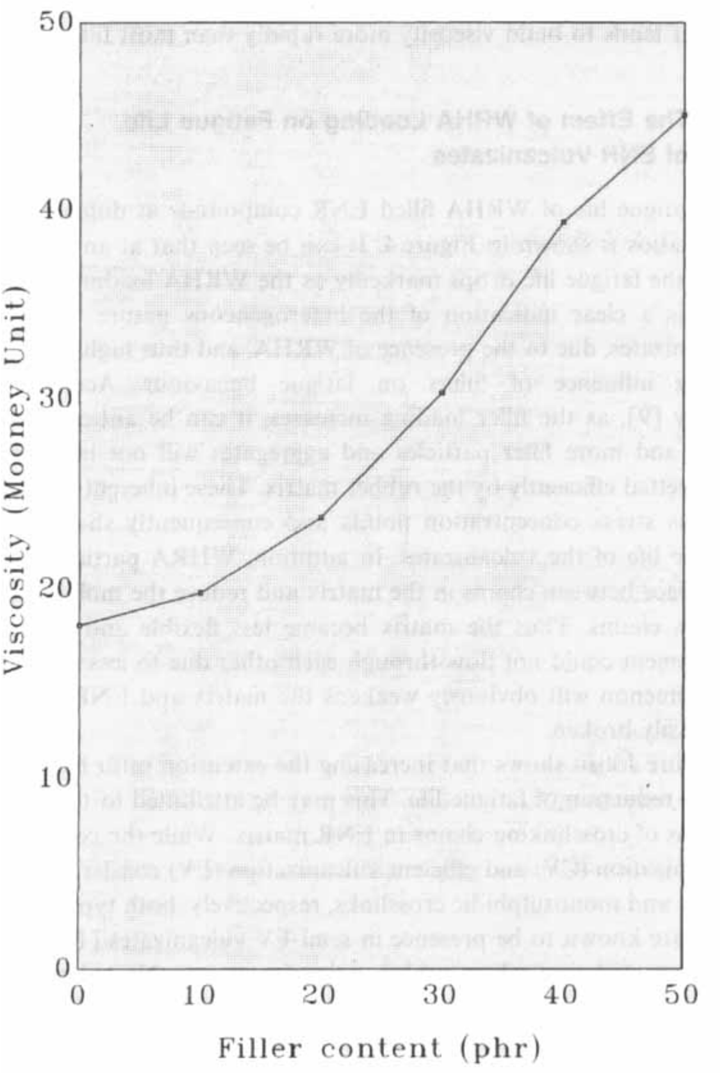


FIGURE 3 The effect of filler loading on viscosity of WRHA-filled ENR vulcanizates.

the rubber matrix has reduced the mobility of the macromolecular chains of the rubber. In addition, the presence of 96.2% silica in WRHA may give rise to complex filler-filler and filler-matrix interactions. Baker *et al.* [3] found that silica has good interaction with ENR and showed similar mechanical properties compared to carbon black filled ENR compounds. According to Wagner [7], adding silica to rubber tends to build viscosity more rapidly than most fillers.

### 3.2. The Effect of WRHA Loading on Fatigue Life of ENR Vulcanizates

The fatigue life of WRHA filled ENR compounds at different extension ratios is shown in Figure 4. It can be seen that at any extension ratio the fatigue life drops markedly as the WRHA loading increases. This is a clear indication of the heterogeneous nature of ENR-50 vulcanizates, due to the presence of WRHA, and thus highlighting the strong influence of fillers on fatigue behaviour. According to Beatty [9], as the filler loading increases, it can be anticipated that more and more filler particles and aggregates will not be dispersed and wetted efficiently by the rubber matrix. These inherent defects can acts as stress concentration points and consequently shortened the fatigue life of the vulcanizates. In addition, WHRA particles occupy the space between chains in the matrix and reduce the mobility of the matrix chains. Thus the matrix became less flexible and chains entanglement could not flow through each other due to less space. This phenomenon will obviously weakens the matrix and ENR-50 chains are easily broken.

Figure 4 also shows that increasing the extension ratio has resulted in the reduction of fatigue life. This may be attributed to the different lengths of crosslinking chains in ENR matrix. While the conventional vulcanization (CV) and efficient vulcanization (EV) consist of polysulphidic and monosulphidic crosslinks, respectively, both types of crosslinks are known to be presence in semi-EV vulcanizates [10]. Thus it can expected that when rubber vulcanizates is subjected to fatigue deformation, these different types of crosslinks will respond differently in terms of their ability to stabilise the stress distribution in the samples. At smaller extension ratio, the shorter crosslinking chains would be able to withstand the fatigue deformation. However, when

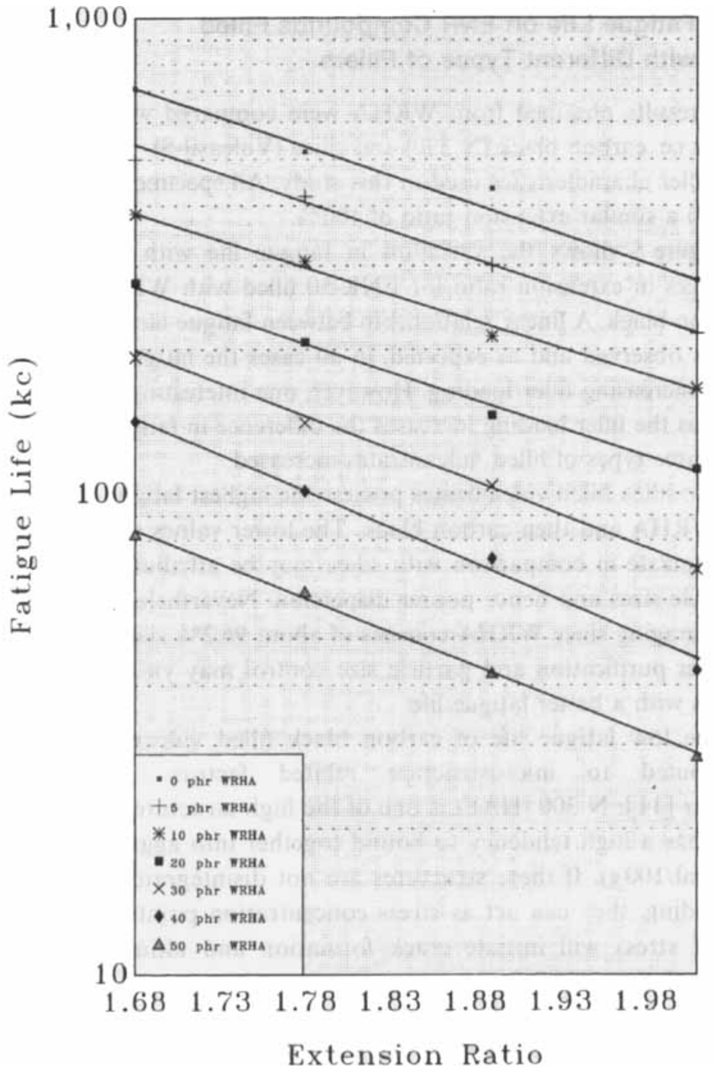


FIGURE 4 Relationship between fatigue properties and filler loading of WRHA-filled ENR vulcanizates.

higher extension ratios were used, these shorter chains could no longer resists the deformation and are not capable of relieving the dynamic stresses imposed on the samples. The earlier fatigue failure occurs at higher extension ratios.

### 3.3. Fatigue Life on ENR Compounds Filled with Different Types of Fillers

The results obtained from WRHA were compared with commercial fillers i.e. carbon black (N 330) and silica (Vulcasil-S). Table III shows the filler characteristics used in this study. All specimens were subjected to a similar extension ratio of 100%.

Figure 5 shows the variation in fatigue life with respect to the changes in extension ratio for ENR-50 filled with WRHA, silica and carbon black. A linear relationship between fatigue life and filler loading is observed and as expected, in all cases the fatigue life decreases with increasing filler loading. However, one interesting observation is that as the filler loading increases the difference in fatigue life between the three types of filled vulcanizates increased.

The silica filled vulcanizates possess the highest fatigue life followed by WRHA and then carbon black. The lower values of WRHA filled vulcanizate in comparison with silica may be attributed to the large particle sizes and hence poorer dispersion. Nevertheless, this result is encouraging since WRHA consists of about 96.2% silica and perhaps further purification and particle size control may yield filled vulcanizates with a better fatigue life.

The low fatigue life of carbon black filled vulcanizates may be attributed to microstructure related factors. According to Kraus [11], N 300 (HAF) is one of the high structure carbon blacks and has a high tendency to bound together into aggregates (CTAB, 102 ml/100 g). If these structures are not disintegrated during compounding, they can act as stress concentration points which during cyclic stress will initiate crack formation and ultimately leads to earlier fatigue failure.

Cox and Parks [12] reported that fatigue life is related to chain flexibility in the vulcanizates. The more flexible rubber chains are, the

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 |

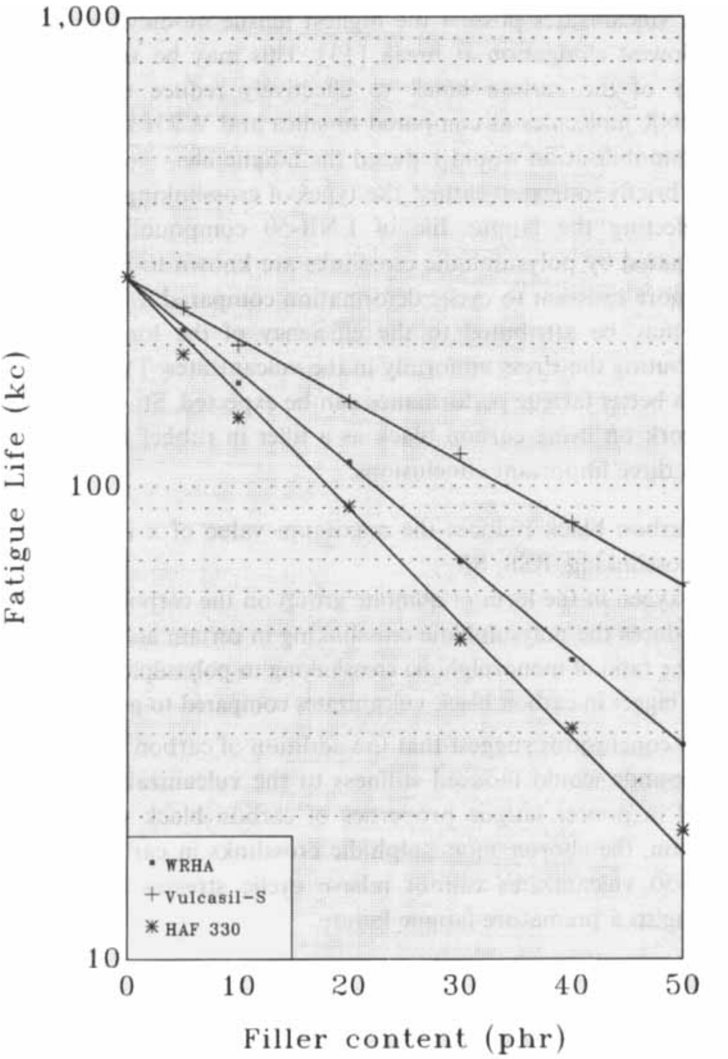


FIGURE 5 The effect of filler loading on fatigue life of WRHA-filled ENR vulcanizates.

higher the resilience it has towards cyclic deformation, hence higher fatigue life.

In a previous study on WRHA, silica and carbon black filled ENR-50 compounds using semi-EV system, it was reported that carbon black vulcanizates possess the highest tensile modulus and hardness and lowest elongation at break [13]. This may be attributed to the ability of the carbon black to effectively reduce the mobility of the ENR molecules as compared to silica and WRHA. Consequently, the immobilisation would reduced the fatigue life.

As briefly indicated earlier, the types of crosslinking is also capable of affecting the fatigue life of ENR-50 compounds. Vulcanizates dominated by polysulphidic crosslinks are known to be more flexible and more resistant to cyclic deformation compared to monosulphidic. This may be attributed to the efficiency of the long crosslinks in distributing the stress uniformly in the vulcanizates. Thus vulcanizates with a better fatigue performance can be expected. Studebaker [14] in his work on using carbon black as a filler in rubber compounds has made three important conclusions:

i) Carbon black reduces the maximum value of $x$ in polysulphidic crosslinking, $RSS_x SR$.
ii) Oxygen in the form of quinone group on the carbon black surfaces reduces the polysulphidic crosslinking in certain accelerated curing.
iii) The ratio of monosulphidic crosslinking to polysulphidic crosslinking is bigger in carbon black vulcanizates compared to gum vulcanizates.

These conclusions suggest that the addition of carbon black in rubber compounds would induced stiffness to the vulcanizates and thus resulted in poorer fatigue properties of carbon black vulcanizates. In addition, the shorter monosulphidic crosslinks in carbon black filled ENR-50 vulcanizates cannot relieve cyclic stresses efficiently, thus leading to a premature fatigue failure.

## 3.4. Mode of Fracture

Scanning electron microscopy (SEM) was employed to study the fatigue fracture surfaces of WRHA filled ENR 50 vulcanizates. The objective is to get some information regarding filler dispersion, mode of failure and bonding quality between filler and matrix.

Examination of the fracture surface revealed that the filled vulcanizates exhibited two failure zones, indicated as zones I and II in the schematic diagram (Fig. 6) and supported by SEM micrographs (Fig. 7). The rugged nature of the fracture surface shown by the micro-

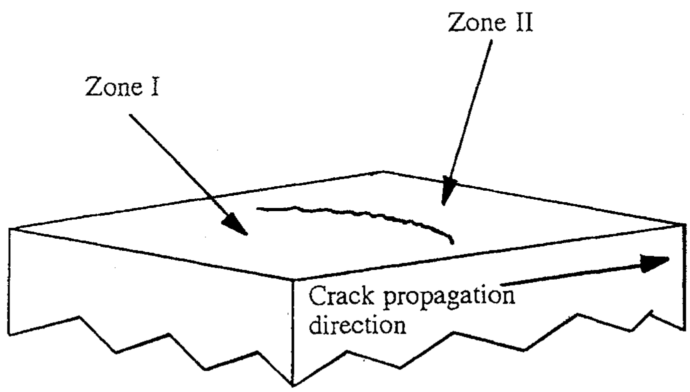


FIGURE 6 Schematic diagram showing the direction of crack propagation and the failure zones.



graph in Figure 7a provides a clear indication that the fracture process in zone I is relatively slower than zone II (micrograph shown in Fig. 7b). Thus the crack growth in zone I allows matrix tearing to takes place. However, as the fracture propagates into zone II, there is a significant change in the mode of failure. The relatively faster and unstable crack propagation which arises as a result of non-uniform stress distribution in the vulcanizates is believed to occur. This catastropic fracture which inhibit matrix tearing has resulted in the formation of relatively smoother fracture surface. Similar mode of fractures have been observed for silica and carbon black filled vulcanizates [15]. This observation also agrees well with earlier investigation reported by Dizon *et al.* [16] and Gent *et al.* [17] for cut growth from flaws on die-stamped dumbell test pieces subjected to dynamic tests.

## CONCLUSIONS

The following conclusions can be drawn on the scorch time, Mooney viscosity and fatigue life of ENR compounds filled with different types of fillers:

a) The incorporation of WRHA in ENR-50 compounds reduced the scorch time but increased the Mooney viscosity. This observation

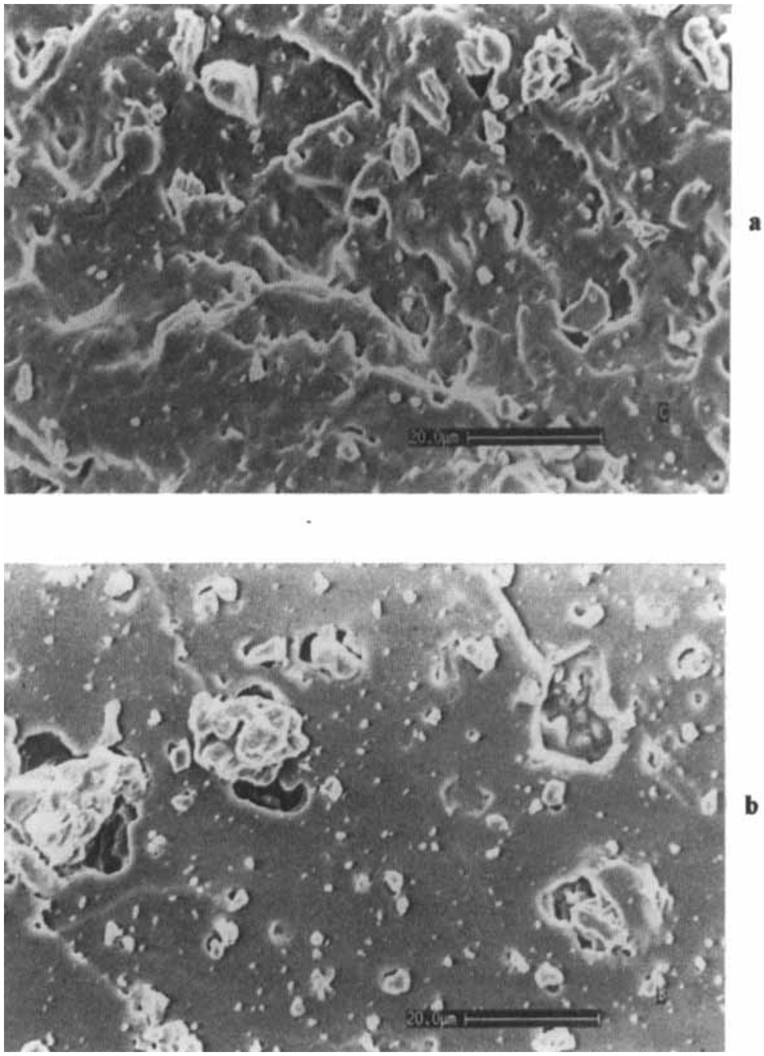


FIGURE 7 SEM micrograph of the fatigue failure surface of WRHA-filled ENR vulcanizates at 20 phr filler loading (a) fracture surface in zone I (b) fracture surface in zone II.

suggests that as the loading of WRHA increases, the processing characteristics become more difficult and a retarder should be used to overcome the shorter scorch time.

b) The fatigue life of WRHA-filled ENR-50 vulcanizates decreased with increasing extension ratio. This shows that fatigue life in ENR-50 vulcanizates is strain dependent.
c) The incorporation of WRHA into ENR 50 matrix has resulted in the reduction of the fatigue life of the vulcanizates. A similar trend was observed for carbon black and silica-filled compounds.
d) *At any filler loading, the fatigue life of all fillers studied follows the* same trend i.e.

Silica (Vulcasil-S) > WRHA > carbon black (N 300).

Thus, it could be concluded that the fatigue behaviour of ENR-50 vulcanizates is strongly controlled by filler related characteristics such as filler type, particle size and their distribution in rubber matrix.



## *Acknowledgement*

The author wish to express their thanks to Universiti Sains Malaysia (USM) and the Malaysian Government for the financial support.

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