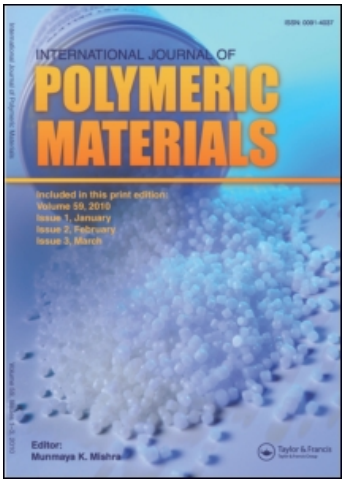

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Effect of Filler Loading on the Mechanical Properties of Epoxidized Natural Rubber (ENR 25) Compared with Natural Rubber (SMR L)

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The mechanical properties *viz.*, tensile strength, elongation at break, tear strength and fatigue life of epoxidized natural rubber (ENR 25) was studied using a semi-efficient vulcanization system. Carbon black and calcium carbonate were chosen as the fillers with loading up to 60 phr. SMR L grade natural rubber was used for comparison purposes. Tensile property, tear strength and fatigue life were determined by using a Monsanto Tensometer T10, Instron Universal Tensile Tester and Fatigue To Failure Tester respectively. Results indicate that the tensile property increases with filler loading up to a maximum value after which it drops with further loading of filler. This observation is attributed to the dilution effect of filler after the maximum level of reinforcement. However, the fatigue life decreases steadily with increasing filler content, a finding which is associated with the chain immobility with increasing filler concentration. Carbon black and calcium carbonate show varying effects on the properties investigated whereas SMR L exhibits better tensile properties but poorer fatigue life than ENR 25. Scanning electron microscopy was used to support the observed trends in mechanical properties.

Keywords: Epoxidized natural rubber; filler; mechanical properties

INTRODUCTION

Epoxidized natural rubber (ENR) is a chemically modified form of natural rubber (cis 1, 4 – polyisoprene) in which some of the unsatura-

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tion is converted into epoxide groups which are randomly distributed along the polymer chain [1, 2]. ENR has been the subject of recent research interest after the realization that the chemically modified natural rubber possesses physical properties similar to those of synthetic rubbers [3, 4]. Several studies on the curing behavior and aging properties of ENR have been reported [4 – 10]. A few studies on the physical properties were also reported [4, 11 – 13], including the possible use of rice husk ash (RHA) as a filler for ENR vulcanizates [14, 15]. However, with regard to the comparison study of mechanical properties between ENR and natural rubber, there is no systematic investigation reported so far. It is thus the aim of this paper to report some of our findings on the mechanical properties of ENR and natural rubber, with and without fillers.

EXPERIMENTAL

Materials

ENR 25 having 25 mol% of epoxidation was used in this study while one- grade of unmodified natural rubber (SMR L) was used as a control. The rubbers were freshly supplied by Guthrie Sdn. Bhd. and their respective technical specification is shown in Table I.

Sulfur and 2-mercaptobenzothiazole (MBT) were used as the vulcanizing agent and accelerator respectively throughout the study. Other standard rubber chemicals such as zinc oxide, stearic acid and fillers were also used. All these chemicals were of commercial grades and used without further purification. The base formulation of the rubber compound was rubber, 100; zinc oxide, 6; stearic acid, 2; MBT, 2; sulfur, 2; filler, variable. Carbon black (N 300) and calcium carbonate having a surface area of $70\,m^2/g$ and $22\,m^2/g$ respectively were chosen as the fillers, with loading ranged from 0 – 60 phr.

TABLE I Technical specification of SMR L and ENR 25

	SMR L	*ENR 25*
Glass Transition Temperature (°C)	−72	−45
Specific gravity	0.92	0.97
Mooney viscosity, $M_{L,1+4}$(100°C)	78	110

Compounding

The mixing procedure was done in accordance to the American Society for Testing and Materials (ASTM)-Designation D 3184–89 [16]. Mixing was done on the two-roll mill, with the temperature maintained at 70°C ± 5°C and the total time taken to complete one mixing cycle was 18 minutes for the gum stock and 29 minutes for the filled stock. The batch mass for the compound was checked and recorded. If it differed from the theoretical value by more than 0.5% the batch was rejected. The sheeted compound was then conditioned at a temperature of 23 ± 2°C for 24 hours before testing.

Testing

The various rubber compounds were compression molded into test specimen sheets at 140°C according to their respective optimum cure times determined by a Monsanto Moving Die Rheometer (MDR 2000). Tensile, tear and fatigue properties were studied at room temperature (25 ± 3°C). The respective testing procedures are described below:

Tensile Strength and Elongation at Break

Tensile strength was determined on a Monsanto Tensometer (Model T10). Dumbbell shaped specimens were cut from a 2 mm thick molded sheet. The gauge length and width of the dumbbell sample was 33 ± 2 mm and 6.3 ± 0.1 mm respectively. Tensile testing was carried out according to ISO 37: Type III. A crosshead speed of 50 cm/min was used. The Tensometer displays the stress/strain responses directly. These were recorded on the digital display windows. The tensile strength and % elongation at break were read off from the digital displays at the end of each test.

Tear Strength

Tear strength was determined on the Instron Universal Testing Machine (Model 1114). Trouser shaped specimens were cut from a

2 mm thick molded sheet. The length and width of the sample was 100 mm and 15 mm respectively and with a 40 mm center cut. Tear strength tests were carried out according to ISO 34: Type III. A crosshead speed of 10 cm/min was used and the two 'trouser legs' were fixed to the jaws of the tensile machine. An average force calculated from the peaks and valleys within the plateau region was divided by the specimen thickness to obtain the tear strength from the equation:

$$\text{Tear Strength} = 2F/T$$

where F is the tearing force and T is the thickness of the sample.

Fatigue to Failure Test

The fatigue tests were carried out on a Monsanto Fatigue to Failure Tester (FTFT). Dumbbell samples were cut from rectangular sheets ($22.9 \times 7.6 \times 0.15$ cm) with beaded edges at right angles to the grain using a BS type E dumbbell cutter. The samples were subjected to repeated cyclic strain at 100 cpm at an extension ratio of 1.6. Six specimens were used for each test. The number of cycles needed for failure was 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:

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

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

Scanning Electron Microscopy (SEM)

Examination of the fracture surface of the samples subjected to fatigue tests was carried out using a scanning electron microscope (SEM) model Leica Cambridge S-360. The objective was to get more idea on the mode of fracture, the bonding quality between the matrix and filler surfaces and filler dispersion. All the surfaces were examined after first

sputter coating with gold to avoid electrostatic charging and poor image resolution.

RESULTS AND DISCUSSION

The results obtained from this study is discussed with respect to the tensile strength, elongation at break, tear strength and fatigue properties of SMR L and ENR 25.

Tensile Strength

The effect of carbon black and calcium carbonate on tensile strength of SMR L and ENR 25 is shown in Figure 1. For carbon black, increasing the filler content increases the tensile strength until a maximum value is reached at about 30% filler loading. Further increase in filler content reduces the tensile strength. As the filler loading is increased, more surface area is available for intermolecular interaction between filler particles and rubber molecules, hence reinforcement increases with an increase in filler loading. However, maximum reinforcement level is reached eventually at about 30 phr of filler loading after which dilution effect occurs as filler content is further increased [17]. The filler particles or aggregates were no longer adequately dispersed or wetted by the rubber phase, thus a reduction in tensile strength is observed. Similar observations have also been reported [13, 15, 18]. Figure 1 also shows that the tensile strength of calcium carbonate-filled SMR L and ENR 25 vulcanizates indicates a lower tensile strength compared to that of carbon black-filled vulcanizates. Although there is an increase in tensile strength (albeit small) with increase in filler loading, a more or less constant value is maintained at higher loading. This may be attributed to the larger particle size of calcium carbonate which gives rise to a weaker interaction between the filler and rubber matrix and thus a non-reinforcing filler. Figure 2 compares the tensile strength between SMR L and ENR 25 at 30 phr of filler loading. The slightly higher tensile strength exhibited by SMR L is attributed to the higher strain-induced crystallization of the rubber compared to ENR 25 where a reduction in crystallinity occurs with epoxidation of natural rubber [1].

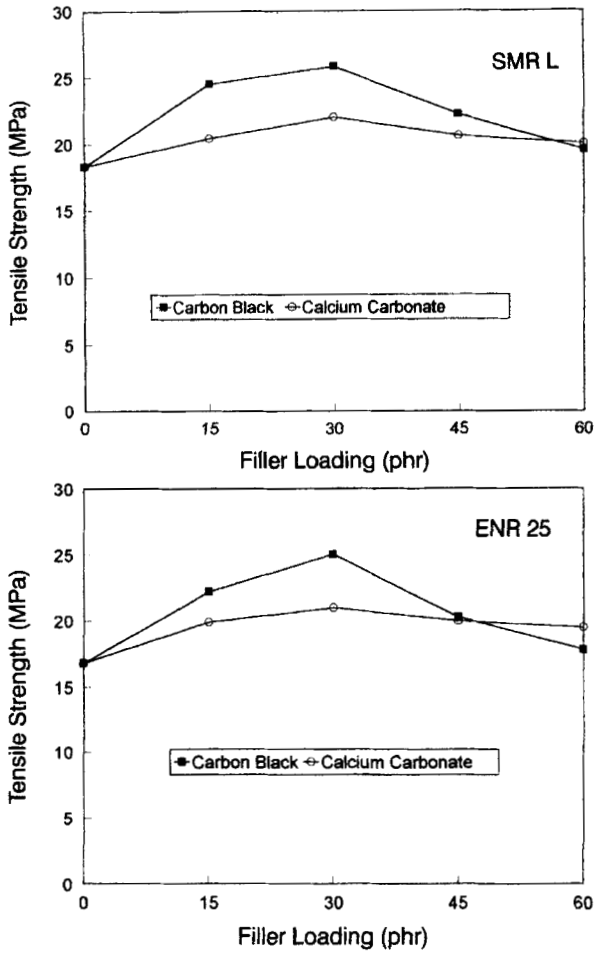

FIGURE 1 Effect of filler loading on the tensile strength of SMR L and ENR 25.

Elongation at Break

Elongation at break for the two rubbers studied is shown in Figure 3. As in the case of tensile strength, both rubbers exhibit an increasing trend with increasing carbon black content until a maximum value is reached. Further increase in carbon black content reduces the elongation at break. Initially, as the filler loading is increased, intermolecular interaction between carbon black particles and rubber

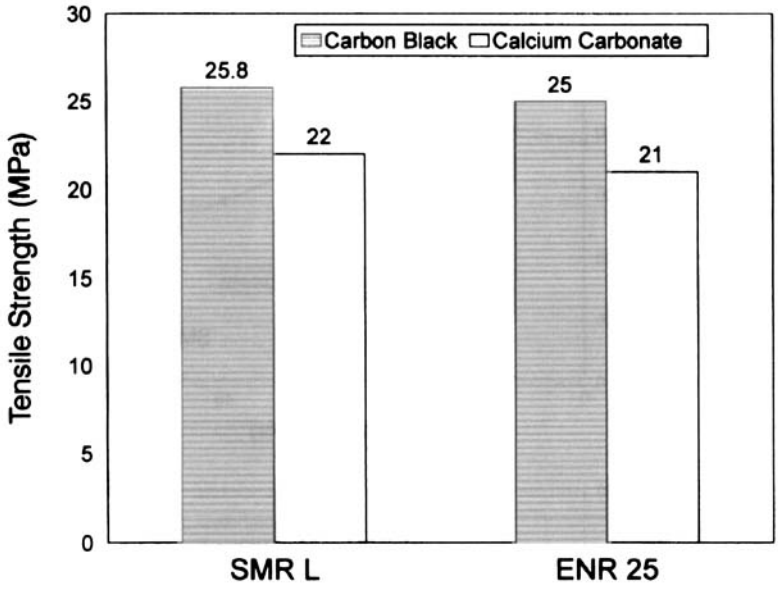

FIGURE 2 Comparison of tensile strength of SMR L and ENR 25 at 30 phr of filler loading.

matrix increases correspondingly, thus resulting in the increase in elongation at break. However, further increase in carbon black loading beyond its maximum level will reduce the filler-rubber interaction, *i.e.*, dilution effect occurs. Once the rubber-filler interaction or the bonding quality is decreased, the applied stress can no longer be transferred efficiently from rubber to filler. Thus, after the optimum loading the elongation at break decreases with the filler loading, an observation similar to that reported by Hanafi *et al.* [15]. On the contrary, ENR 25 and SMR L do not show such sensitivity towards calcium carbonate loading. Much higher loading of calcium carbonate can be accommodated without an adverse effect on the values of elongation at break. This again depicts the non-reinforcing property of calcium carbonate *i.e.*, it does not have much influence on mechanical properties, a property which it makes it suitable as a cheapener. In this study, calcium carbonate gives the highest elongation at break than carbon black. This may be attributed to the larger particle size of the former which results in a poorer interaction between the filler and rubber matrix. The elongation at

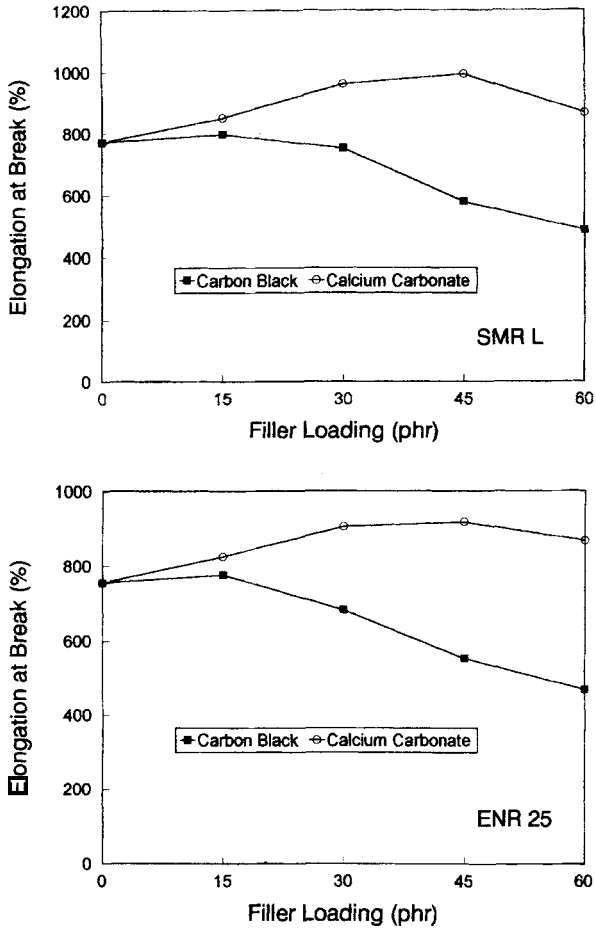

FIGURE 3 Effect of filler loading on the elongation at break (%) of SMR L and ENR 25.

break decreases with decreasing particle size or increasing structure of filler [19]. Carbon black filled vulcanizates show lower elongation at break which may be attributed to the ability of the carbon black to effectively reduce the mobility of the rubber chains due to its smaller particle size, thus increasing the degree of rubber reinforcement. This immobilisation will then induce stiffness in the vulcanizates [15]. Comparison of elongation at break between SMR L and ENR 25 is shown in Figure 4. SMR L indicates higher values than ENR 25 for

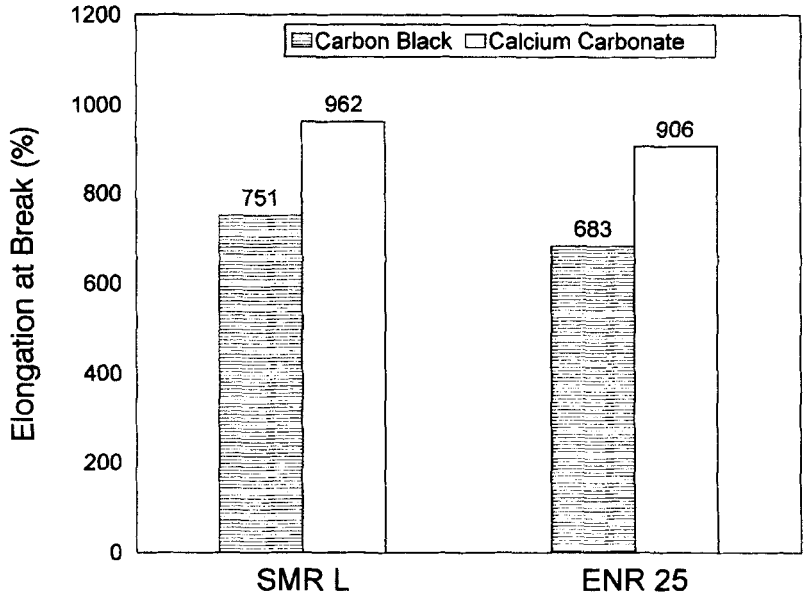

FIGURE 4 Comparison of elongation at break (%) of SMR L and ENR 25 at 30 phr of filler loading.

both fillers studied. This observation, again, is associated with the higher crystallinity in the former upon stretching.

Tear Strength

The effect of carbon black and calcium carbonate on tear strength of SMR L and ENR 25 is shown in Figure 5. For both rubbers, the tear strength increases with carbon black content until maximum values are reached. Further filler loading reduces the tear strength. This observation is very similar to that of tensile strength discussed earlier, *i.e.*, the dilution effect of filler increases with increasing filler loading after a maximum value is reached, thus resulting in the reduction in tear strength. Figure 5 shows that the tear strength of calcium carbonate-filled SMR L and ENR 25 vulcanizates show inferior to those of carbon black-filled counterparts. While carbon black-filled vulcanizates show a value, calcium carbonate-filled ones do not, instead they maintain a more or less constant value. This may be due to the poor reinforcement nature of calcium carbonate which has a smaller surface area than that of carbon black, hence giving rise to a

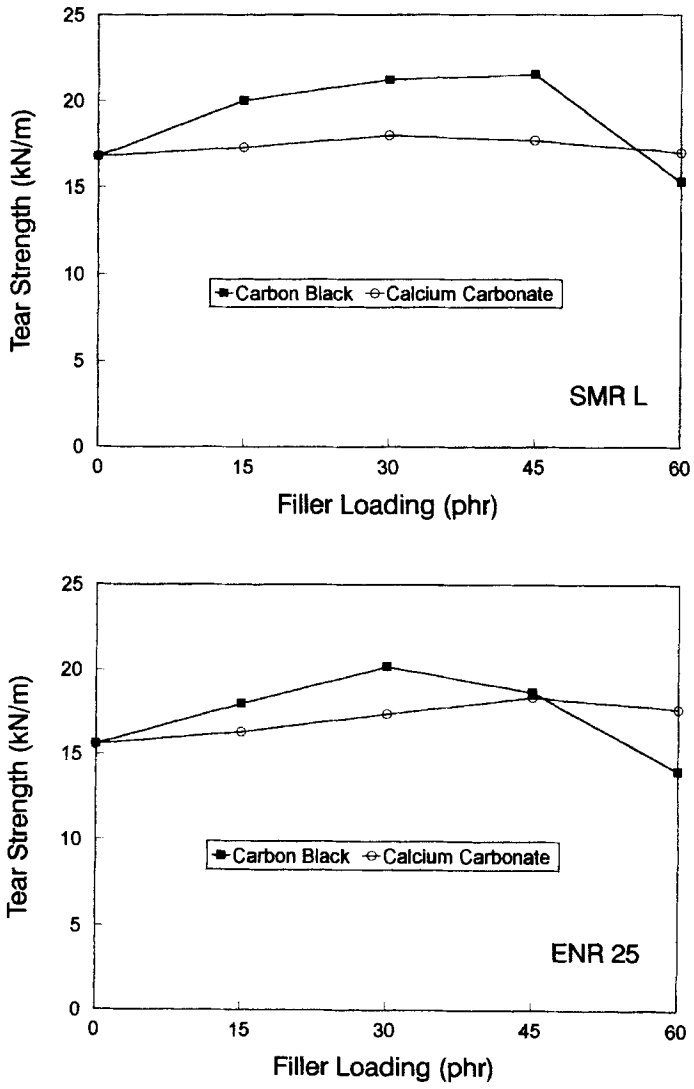

FIGURE 5 Effect of filler loading on the tear strength of SMR L and ENR 25.

weaker intermolecular interaction in the former. The tear strength increases with increasing surface area or decreasing particle size of the filler [20]. The tear strength of SMR L and ENR 25 is compared in Figure 6. As in the case of tensile strength, the tear strength of SMR L

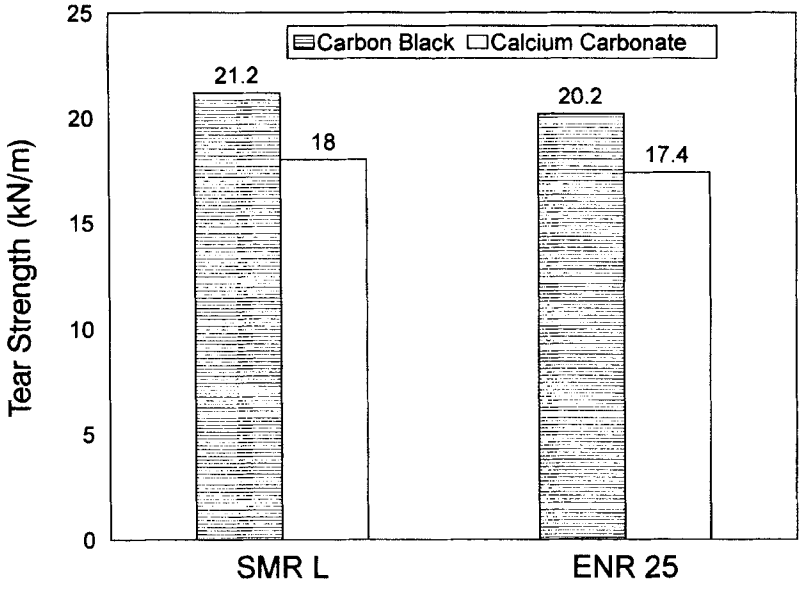

FIGURE 6 Comparison of tear strength of SMR L and ENR 25 at 30 phr of filler loading.

is slightly higher than that of ENR 25 for the two fillers studied, an observation resulting from the higher strain-induced crystallization of SMR L upon tearing.

Fatigue

The fatigue life of carbon black and calcium carbonate-filled SMR L and ENR 25 vulcanizates is illustrated in Figure 7. It decreases with increasing filler loading. This observation indicates that the heterogeneous nature of these vulcanizates, thus, the filler particles are not dispersed and wetted efficiently by the rubber matrix [21] as a result of increased filler concentration. These inherent defects can cause fatigue failure. The higher the filler loading, the higher is the heterogeneous defects as reflected by the drop in fatigue life as the filler content is increased. From Figure 7, it can be seen that calcium carbonate-filled vulcanizate possesses higher fatigue life than that of carbon black. This finding suggests that calcium carbonate, being a poor reinforcing filler, creates more free volume in the vulcanizate, hence enhances the

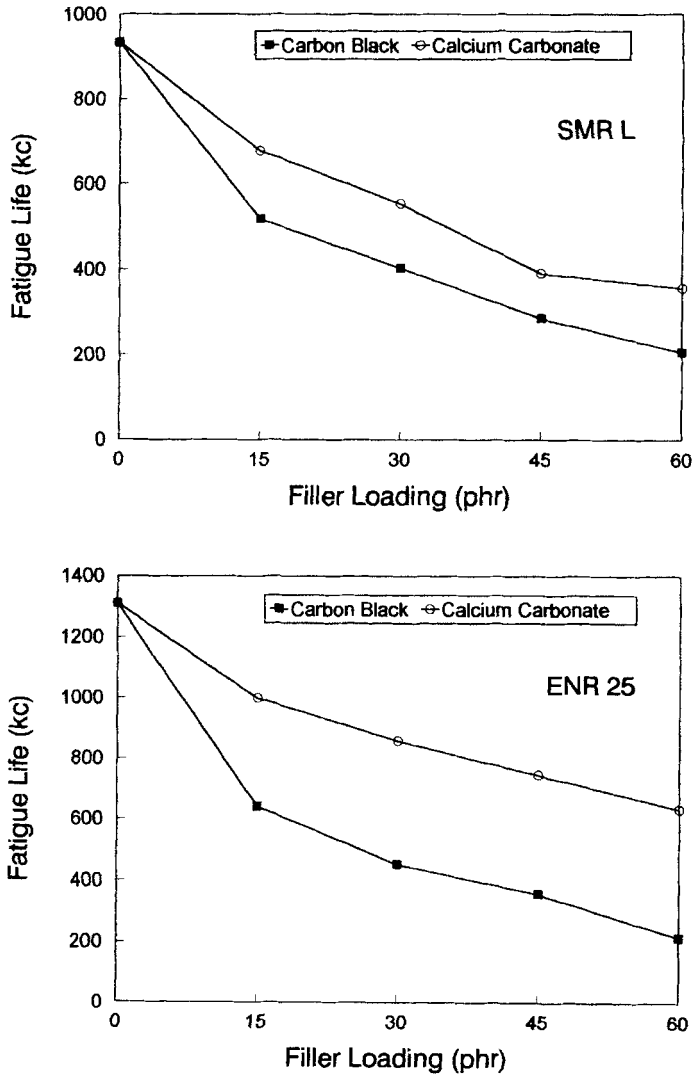

FIGURE 7 Effect of filler loading on the fatigue life of SMR L and ENR 25.

mobility of rubber chains. This means that cyclic stresses developed during fatigue testing will be relieved more easily by the mobile rubber chains, thus higher fatigue life is obtained. On the other hand, carbon black particles are bound together in aggregates and if these structures

do not disintegrate during compounding, they can act as stress concentration points in the vulcanizates. Obviously, during cyclic deformation such inhomogeneity will initiate crack formation which finally leads to failure. Secondly, it has been shown that fatigue life is related to the stiffness of the rubber chain in the vulcanizates [22]. The more flexible the chain is, the higher is the resilience towards cyclic deformation, hence higher fatigue life. From Figure 8, ENR 25 shows higher fatigue life than SMR L for all the filled vulcanizates, an observation which is consistent with earlier results reported by Baker *et al.* [23]. The difference in fatigue behavior between SMR L and ENR 25 may be due to the higher degree of saturation and hysteresis in the latter. Since ENR 25 contains less double bonds than SMR L, less oxidation and ozone attack occurs in ENR 25, thus higher fatigue life is obtained. Also, higher hysteresis in ENR 25 resulting from its higher glass transition temperature, attributes to the higher fatigue life of the rubber.

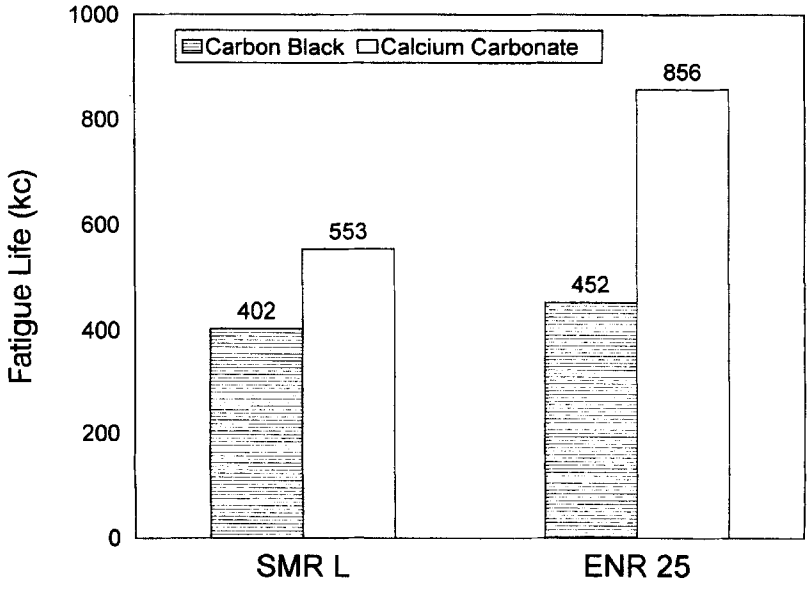

FIGURE 8 Comparison of fatigue life of SMR L and ENR 25 at 30 phr of filler loading.

Scanning Electron Microscopy (SEM)

The scanning electron micrographs presented in Figures 9 and 10 depict two distinct phenomena, *i.e.*, filler particle sizes and their distribution as well as the failure mode of the samples. Under similar loading, it is obvious that carbon black is better dispersed and less aggregated (Fig. 9). This accounts for the observed reinforcement and hence improved mechanical properties. Calcium carbonate, on the other hand, (Fig. 10), shows agglomeration and poor dispersion which accounts for the non-reinforcing properties. During fatigue testing, a stage is reached at which the cyclic deformation will result in the propagation of cracks within the samples. The portions marked (a) indicate the initial stages of crack propagation which can be said to be dutile. The rough nature of the surface is an indication that the fracture process is relatively slower. As such, it allows some matrix tearing to occur. However, as the failure progresses, the stress distribution in the vulcanizate in no longer uniform and the samples cannot obviously resist the crack propagation. Thus, fast and unstable crack propagation is believed to have occurred, leading to catastrophic failure. This results in the formation of a relatively smoother failure surface marked (b). The overall picture of crack propagation can be seen in Figures 9(c) and 10(c) for carbon black and calcium carbonate respectively. Based on the scanning electron micrographs, and also various other filler concentrations in both rubbers [24], it can be inferred that crack initiation occurs anywhere in the sample.

CONCLUSION

From this study, the following conclusions can be drawn.

1. Tensile strength and tear strength of SMR L and ENR 25 increases with carbon black and calcium carbonate loading up to about 30 phr of the filler. The increase is attributed to the increasing reinforcing effect of filler which is more significant in the case of carbon black. The drop in tensile properties after the maximum value is associated

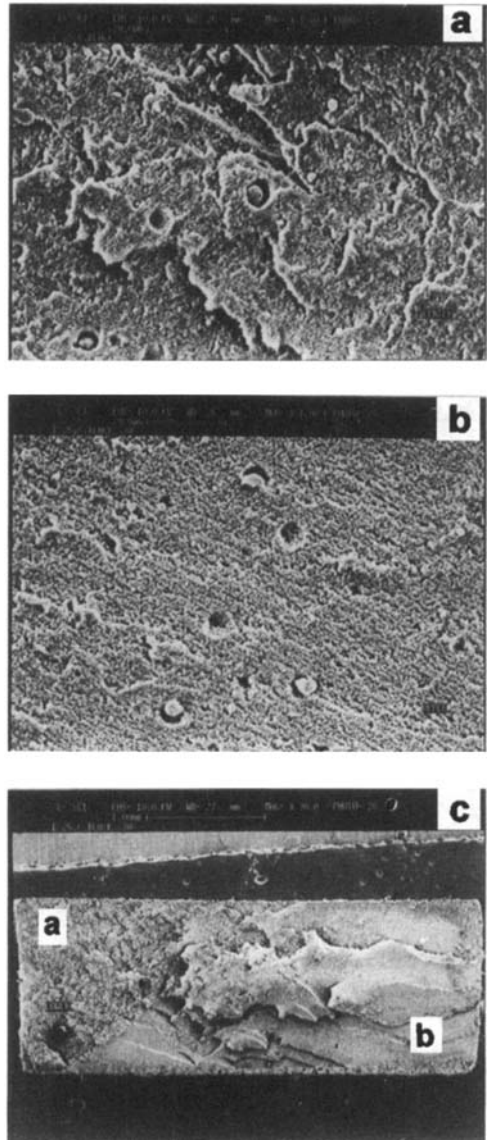

FIGURE 9 SEM micrographs of carbon black filled (30 phr) ENR 25 showing the fracture surface after fatigue failure: (a) dutile failure, (b) catastrophic failure, (c) whole surface indicating the failure zones.

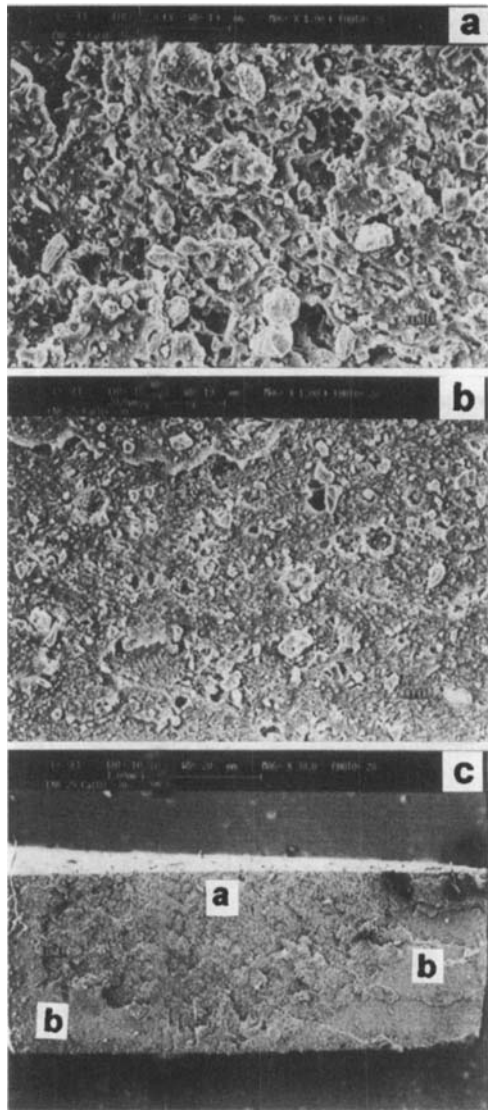

FIGURE 10 SEM micrographs of calcium carbonate filled (30 phr) ENR 25 showing the fracture surface after fatigue failure: (a) dutile failure, (b) catastrophic failure, (c) whole surface indicating the failure zones.

with the dilution effect of filler as the filler loading is further increased. SMR L which experiences higher degree of strain-induced crystallization exhibits higher tensile values than ENR 25.

2. For the elongation at break, both rubbers also show an increasing trend with increasing filler loading up to a maximum value. However, in this case, calcium carbonate gives a consistently higher elongation at break than carbon black due to the larger particle size of the former which results in poorer intermolecular rubber-filler interaction. This effect leads to a greater chain mobility, thus higher elongation at break is observed in calcium carbonate-filled vulcanizate.
3. The fatigue life for both rubbers decreases steadily with an increase in filler loadings. Calcium-carbonate-filled vulcanizate indicates better fatigue property than that of carbon black. This observation is attributed to the creation of more free volume in the vulcanizate by calcium carbonate which is a poor reinforcing filler due to its larger particle size, thus enabling greater chain mobility and consequently, cyclic stressess can be relieved more easily during fatigue testing. On the other hand, carbon black which is a good reinforcing filler, binds so tightly to the rubber chains that chain mobility is restricted, hence fatigue failure occurs earlier due to the inability of rubber chains to relieve stresses during cyclic deformation. For the both fillers studied, ENR 25 shows higher fatigue life than SMR L because of higher degree of saturation and hysteresis in the former.
4. Based on scanning electron microscopy studies, an indication of better dispersion and less aggregation of carbon black filler particles as compared to the calcium carbonate accounts for the reinforcement which has resulted in improved mechanical properties for the carbon black filled vulcanizates. The fact that failure is initially slow followed by a rapid catastrophic failure can also be deduced from the scanning electron microscopy studies.

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