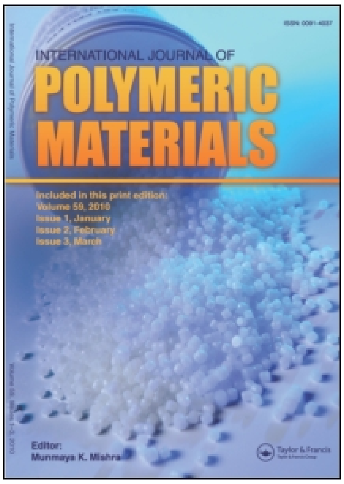


International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

The Effect of Feldspar Loading on Curing Characteristics, Mechanical Properties, Swelling Behavior and Morphology of Natural Rubber Vulcanizates

Hanafi Ismail[a]; Hakimah Osman[a]; Azlan Ariffin[a]
[a] School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia, Nibong Tebal, Penang, Malaysia

To cite this Article Ismail, Hanafi , Osman, Hakimah and Ariffin, Azlan(2005) 'The Effect of Feldspar Loading on Curing Characteristics, Mechanical Properties, Swelling Behavior and Morphology of Natural Rubber Vulcanizates', International Journal of Polymeric Materials, 54: 1, 43 — 62

To link to this Article: DOI: 10.1080/00914030390245929

URL: http://dx.doi.org/10.1080/00914030390245929

International Journal of Polymeric Materials, 54:43–62, 2005

ISSN: 0091-4037 print/1543-5253 online
DOI: 10.1080/00914030390245929

THE EFFECT OF FELDSPAR LOADING ON CURING CHARACTERISTICS, MECHANICAL PROPERTIES, SWELLING BEHAVIOR AND MORPHOLOGY OF NATURAL RUBBER VULCANIZATES

Hanafi Ismail
Hakimah Osman
Azlan Ariffin
School of Materials and Mineral Resources Engineering,
Universiti Sains Malaysia, Nibong Tebal, Penang, Malaysia

Feldspar is being used herein as a filler in natural rubber vulcanizates. Two different types of natural rubber, SMR L and ENR 50 having 0 and 50 mol% of epoxide groups and semi-efficient vulcanization were used. The scorch time, (t_2) and cure time, (t_{90}) of both rubber vulcanizates slightly increased with increasing feldspar loading. At a similar feldspar loading, the ENR 50 vulcanizates showed shorter t_2 and t_{90} than SMR L vulcanizates. Besides t_2 and t_{90}, maximum torque, (M_{HR}) and torque difference ($M_{HR} - M_L$) were also investigated. Results indicate that M_{HR} and $M_{HR} - M_L$ increase for both rubbers with increasing feldspar loading. Swelling test results showed a reduction in the swelling percentage for both rubbers with increasing feldspar loading. At a similar filler loading, SMR L vulcanizates showed lower swelling percentage than ENR 50 vulcanizates. The mechanical properties such as tensile strength (up to certain filler loading), tensile modulus and hardness increased with increasing feldspar loading for both rubbers. However, at a similar feldspar loading, the mechanical properties of SMR L vulcanizates are higher than ENR 50 vulcanizates.

Keywords: feldspar, natural rubber, curing characteristics, mechanical properties, swelling behavior

INTRODUCTION

Natural rubbers in vulcanized form are frequently used to produce various rubber products such as mechanical goods, tyre treads, hoses,

Received 28 May 2003; in final form 8 June 2003.
Address correspondence to Hanafi Ismail, School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia, 143000 Nibong Tebal, Penang, Malaysia. E-mail: hanafi@eng.usm.my

soles, seals, v-belts, gaskets, and so on. In the vulcanization of rubber, carbon black and silica are often used among the compounding ingredients as reinforcing fillers. In spite of being well known for their capabilities; that is, they impart strength and stiffness to the vulcanized rubber, these fillers are relatively expensive [1]. Therefore, further research is being carried out to reduce the cost of rubber products while maintaining their desired properties.

Feldspar is a mineral filler, obtained from white granite by quarrying the rock, crushing and grinding. It is anhydrous, alkali, alumino silicates, in coarse to medium particles sizes and rather versatile. The use of feldspar in polymer appears to improve the mechanical properties of the polymer by having high silica contents [2]. This improvement occurs because the incorporation of silica into polymer imparts good strength, stiffness, hardness, and high resilience to the polymer matrix [3]. Moreover, when added to a thermoplastic feldspar can improve chemical, weather, and abrasion resistance, ease wetting, dispersion, and deairing, and it has little to no effect on promoter, accelerator, or additive activity, and so on [4].

The objective of this study is to develop a new type of filler in natural rubber compound because feldspar has been used as a filler in thermoplastic, materials except rubber [4]. In this study, the curing characteristics, mechanical properties, and swelling behavior of feldspar-filled SMR L and ENR 50 vulcanizates were investigated. Scanning electron microscopy (SEM) studies were also conducted to examine the tensile fracture surfaces of the vulcanizates.

EXPERIMENTAL

Compounding Ingredients and Formulation

Table 1 shows the formulation used in this study. Natural rubber (SMR L) was obtained from Rubber Research Institute of Malaysia (RRIM) while epoxidized natural rubber (ENR 50) was obtained from Kumpulan Guthrie Sdn. Bhd. (M). Feldspar (grade KM 325) was supplied by Commercial Minerals Sdn. Bhd. (M). The chemical and physical properties of feldspar are given in Table 2. Other ingredients, such as sulphur, zinc oxide, stearic acid, N′−phenyl−p−phenylene diamine (IPPD) and N−cyclohexyl−benzothiazole-2-sulphenamide (CBS) were obtained from Bayer (M) Ltd. All materials were used as received.

Sample Preparation

Mixing was carried out on a laboratory size ($160 \times 320\,\text{mm}$) two-roll mixing mill (model XK−160) in accordance to the method described

TABLE 1 Formulation of Feldspar-Filled Natural Rubber Compounds

Materials	phr
SMR L/ENR 50	100
Sulphur	1.6
Zinc oxide	1.5
Stearic acid	1.5
CBS	1.9
IPPD	2.0
Feldspar	0, 10, 20, 30, 40

by ASTM D 3184-80. The mixes were conditioned at a temperature of $23 \pm 2^\circ C$ for 24 h in a closed container, before cure assessment. The respective cure times at 150°C as measured by t_{90} were then determined using a Monsanto Rheometer, model MDR 2000 (Moving Die Rheometer). The scorch times, torque, elastic modulus, and so on were also determined from the rheograph.

Measurement of Tensile, Hardness, and Resilience Properties

The rubber compounds were compression molded at 150°C, according to their respective t_{90}, into sheets. Tensile tests were carried

TABLE 2 Chemical and Physical Properties of Feldspar

Properties	Value
Chemical composition (%)	
SiO_2	67.0
Al_2O_3	19.0
CaO	0.11
Na_2O	2.3
P_2O_5	0.18
SO_3	0.028
K_2O	11.0
Fe_2O_3	0.12
NiO	0.025
Rb_2O	0.28
Ignition loss	0.2
Physical properties	
Mean particle size (μm)	13.6
Surface area (m^2/g)	0.73
Density (g/cm^3)	2.0

out according to ASTM D 412–92 on a Monsanto Tensometer T10. 2 mm thick dumb-bell specimens were cut out from the molded sheets with a Wallace Die Cutter. For tensile tests, a crosshead speed of 500 mm/min was used. Hardness of the rubber vulcanizates was determined according to ASTM D 1415–88 whereas resiliences were measured using a Rebound Pendulum, according to ASTM D 1054–91. All tests were conducted at room temperature (23 ± 2°C).

Measurement of Swelling Behavior

Determination of the swelling percentage of vulcanizates was carried out according to ASTM D 471. Cured test pieces of vulcanizates of dimension $30 \times 5 \times 2$ mm were weighed using an electrical balance and this was considered to be the original weight (W_1). The test pieces were immersed in toluene at room temperature (23 ± 2°C) for 48 h. The test pieces were then patted dry and weighed (W_t). The swelling percentage of the vulcanizates was then calculated as follows:

$$\text{Swelling percentage} = \frac{W_t - W_i}{W_i} \times 100$$

The sample was then reimmersed in the toluene and the process was repeated for 48 h at room temperature.

Scanning Electron Microscopy

Scanning electron microscopy (SEM) model Leica Cambridge S-360 was used to study the tensile fracture surfaces of the feldspar-filled natural compounds. All the surfaces were examined by SEM after first sputter coating with gold to avoid electrostatic charging and poor resolution.

Fourier Transmission Infra Red Spectroscopy (FTIR) Analysis

Fourier Transmission Infra Red Spectroscopy (FTIR) analysis on feldspar was carried out by using a Perkin-Elmer spectrometer model 2000 FT-IR. At first, the sample was ground to obtain fine particles. KBr pellet was then prepared by pressing these particles at 10 ton pressure. The pellet was scanned for each spectrum and recorded in transmittance.

RESULTS AND DISCUSSION

The Effects of Feldspar Loading on Curing Characteristics of Rubber Vulcanizates

Figures 1 and 2 show the scorch time, t_2 and cure time, t_{90} for SMR L and ENR 50 vulcanizates, respectively. It can be seen that the t_2 and t_{90} for both rubbers slightly increase with increasing filler loading. Table 2 shows that feldspar has high silica content, that is, about 67%. Figure 3 shows the IR spectrum of feldspar exhibiting six peaks that correspond to the Si–O stretching (1008.77 cm^{-1}), Si–$(CH_3)_x$ stretching (769.67 and 727.46 cm^{-1}), SiH_3 stretching (648.22 and 680.3 cm^{-1}) and Si–O_2 stretching (536.12 cm^{-1}). The band at 3456.97 cm^{-1} is assigned to the OH groups. Apart from that, the silica can interact with accelerators such as MBT and activators such as ZnO during compounding, leading to cure retardation [5]. Therefore, as feldspar loading increases, this interference becomes more significant and the vulcanization process slows.

However at a similar feldspar loading, ENR 50 vulcanizates possessed shorter t_2 than SMR L vulcanizates. This is due to the activation of an adjacent double bond by the epoxide groups, which was observed by a previous study [6]. The activation increases with the % mole of epoxidation. Although ENR 50 contains less double bonds than SMR L, the activation of an adjacent double bond by the epoxide

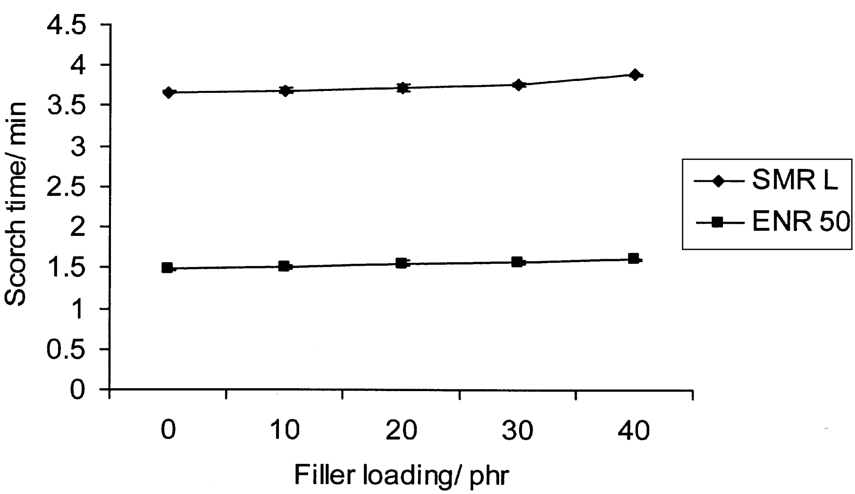


FIGURE 1 The effect of feldspar loading on the scorch time of natural rubber vulcanizates.

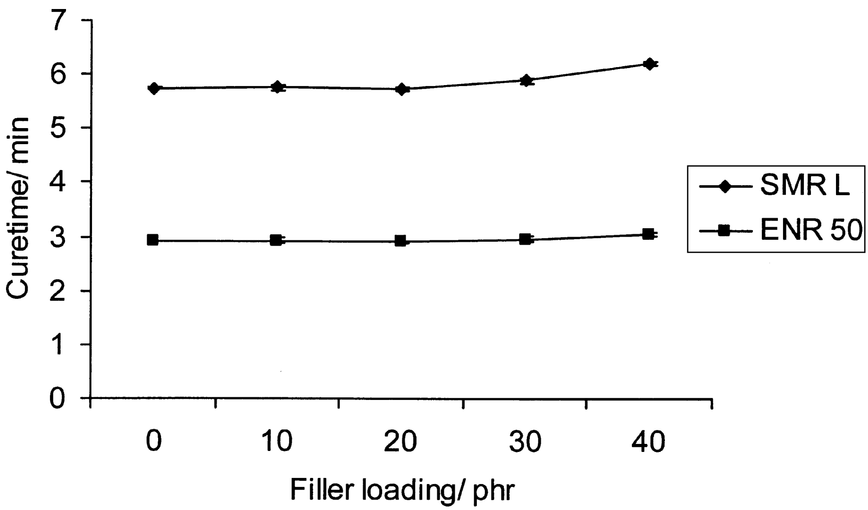


FIGURE 2 The effect of feldspar loading on the cure time of natural rubber vulcanizates.

groups increases the rate of crosslinking and subsequently shortens the scorch time [7]. A similar trend is also observed for the t_{90} as shown in Figure 2.

There is a significant increase in M_H for both rubbers with increasing feldspar loading (Figure 4.) The marked increment in the M_H with

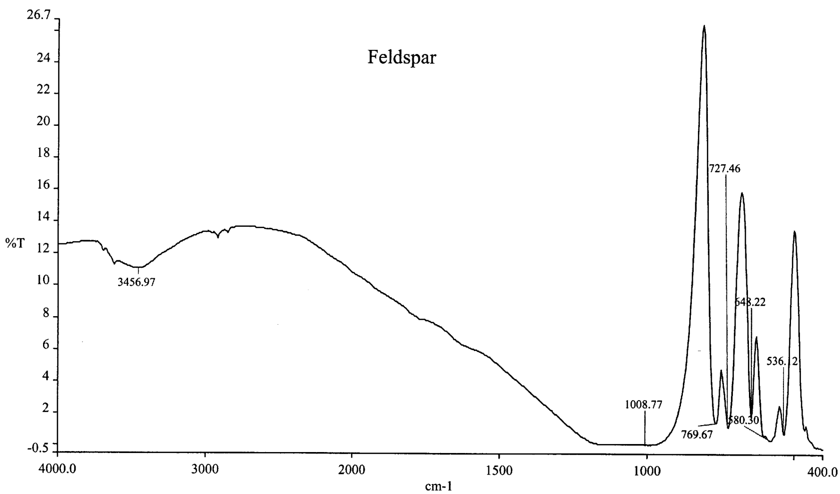


FIGURE 3 FTIR spectrum of feldspar.

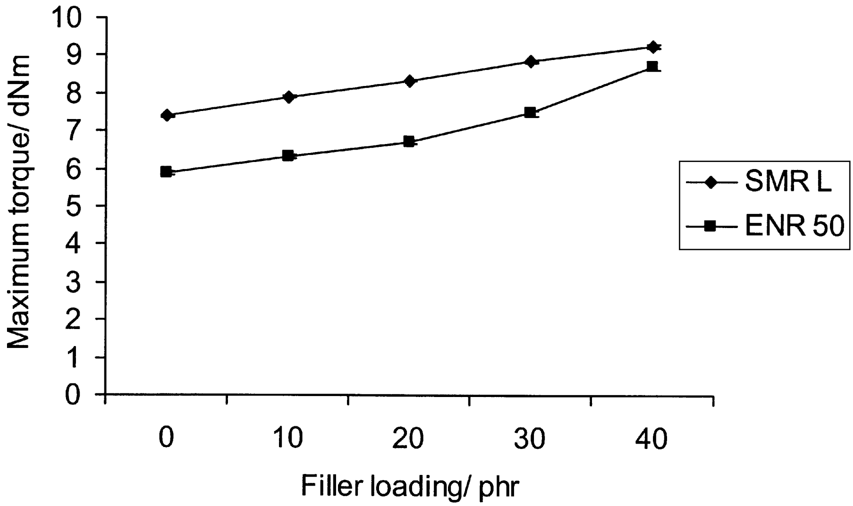


FIGURE 4 The effect of feldspar loading on the maximum torque of natural rubber vulcanizates.

increasing feldspar loading indicates that the presence of feldspar in the rubber matrix has reduced the macromolecular mobility and consequently increased the torque of the feldspar-filled vulcanizates. At a similar feldspar loading, M_H for SMR L vulcanizates is higher compared to ENR 50 vulcanizates. According to Johnson and Thomas [8], the maximum torque (M_H) is a direct measure of the crosslink density in the sample. The higher M_H of SMR L vulcanizates over ENR 50 vulcanizates is mainly due to the high unsaturation of SMR L whereas ENR 50 comprised 60% by weight of epoxide groups. Only these groups (epoxide groups) are capable of reacting with sulphur in a crosslinking reaction because they posses double bonds, whereas in SMR L every isoprene group can take part in the crosslinking process.

Figure 5 shows the torque difference (Maximum torque-Minimum torque), M_H-M_L for SMR L and ENR 50 vulcanizates, respectively. It can be seen that M_H-M_L for both rubbers increased with increasing feldspar loading. From theory, it is known that the torque difference showed shear dynamic modulus, which indirectly related to the crosslink density of the compound [9]. Therefore, it can be concluded that incorporation of feldspar in the rubber matrix has contributed to better crosslinking. It can be seen also that the increment in M_H-M_L is higher for SMR L vulcanizates than ENR 50 vulcanizates.

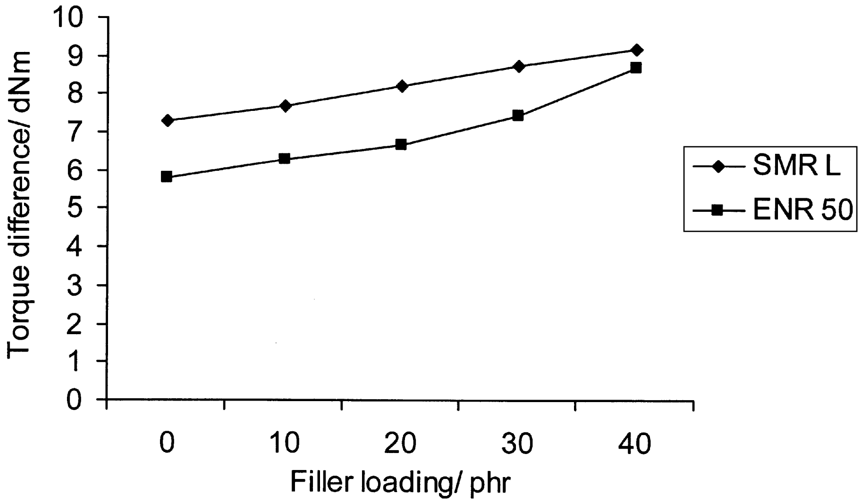


FIGURE 5 The effect of feldspar loading on the torque difference of natural rubber vulcanizates.

The Effects of Feldspar Loading on Mechanical Properties of Rubber Vulcanizates

Figure 6 shows that incorporation of feldspar to SMR L and ENR 50 vulcanizates increases the tensile strength up to a certain level, after which there is a gradual deterioration of properties. For SMR L, the tensile strength increased up to 10 phr of feldspar loading and then decreased with further increasing of feldspar loading. However, the tensile strength of ENR 50 vulcanizates increased up to 20 phr of feldspar loading and then decreased with further increase of feldspar loading. The improvement in tensile strength (up to 10 phr for SMR L and up to 20 phr for ENR 50) is attributed to the improvement in feldspar dispersion and feldspar-rubber interactions in the rubber matrix. Ismail and Chung [10] reported that stronger rubber-filler interaction would increase the effectiveness of the stress transfer from rubber matrix to filler particles and consequently enhance the tensile strength. The reduction in strength after optimum loading may be due to the poor feldspar dispersion and thus reduce the filler-rubber interaction. According to Figure 7, the particles of feldspar are neither of irregular shape nor size. This can decrease the vulcanizates' strength due to the inability of the filler to support stress transferred from the polymer matrix [1]. Furthermore, the reduction occurs because of the agglomeration of the filler particles to form domains

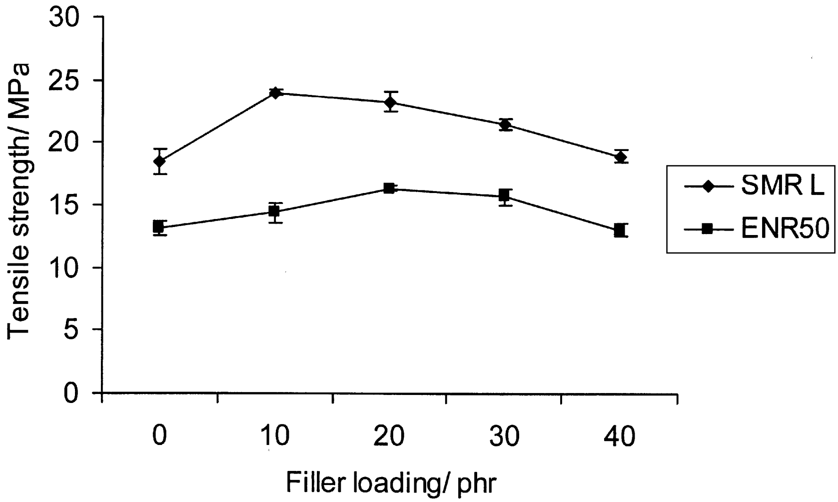


FIGURE 6 The effect of feldspar loading on the tensile strength of natural rubber vulcanizates.

that act like foreign bodies or is simply the tensile result of physical contact between adjacent aggregates [11]. As expected the tensile strength of SMR L vulcanizates showed higher values than ENR 50

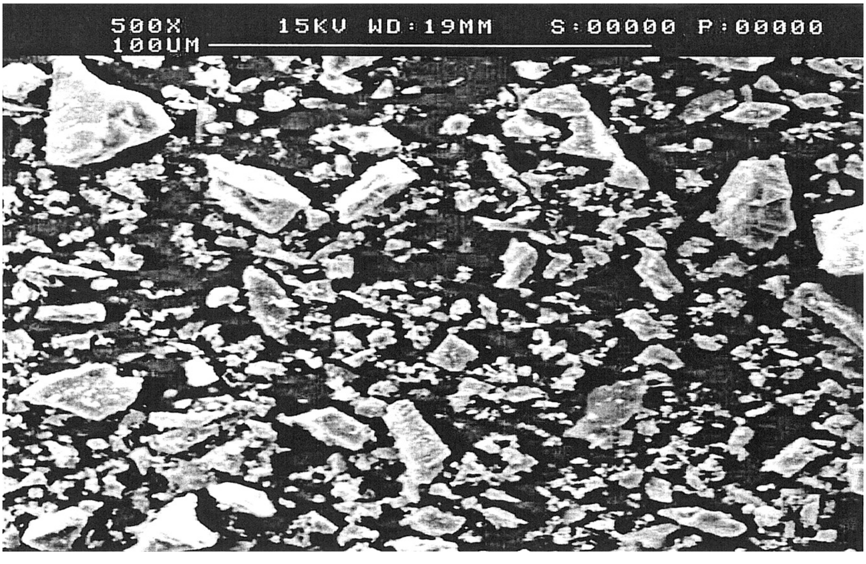


FIGURE 7 SEM micrograph of feldspar (magnification 500×).

vulcanizates due to the reduction in strain crystallization of NR by epoxidation [8].

The incorporation of feldspar into the SMR L and ENR 50 vulcanizates decreased the elongation at break, E_B (Figure 8). Also, with increased feldspar loading, the stiffness and brittleness of the vulcanizates increased gradually. According to Zaini et al. [12], the increased filler content will eventually result in the reduction of the deformability of a rigid interface between the filler and rubber matrix. In other words, the addition of more feldspar tends to impose extra resistance to flow and lead to lower value of E_B. However, it is observed that the E_B for SMR L vulcanizates is higher than ENR 50 vulcanizates. As discussed before, this is due to the lower strain crystallization of ENR 50 as compared to SMR L.

Figures 9 and 10 show the effect of feldspar loading on stress at 100% elongation (M100) and 300% elongation (M300), respectively. It can be seen that increases in both tensile modulus occur with increased feldspar loading. According to Medallia [13], the reduction of tensile strength after its maximum values is consistent with the expected change in modulus. This is because the incorporation of filler in the rubber matrix can improve the stiffness of the natural rubber vulcanizates [14]. Furthermore, this may be attributed to the improvement in the filler-matrix bonding, which leads to an increase in the efficiency of stress transfer from the matrix to the filler. As can be seen from Figures 9 and 10, the tensile modulus values are higher for

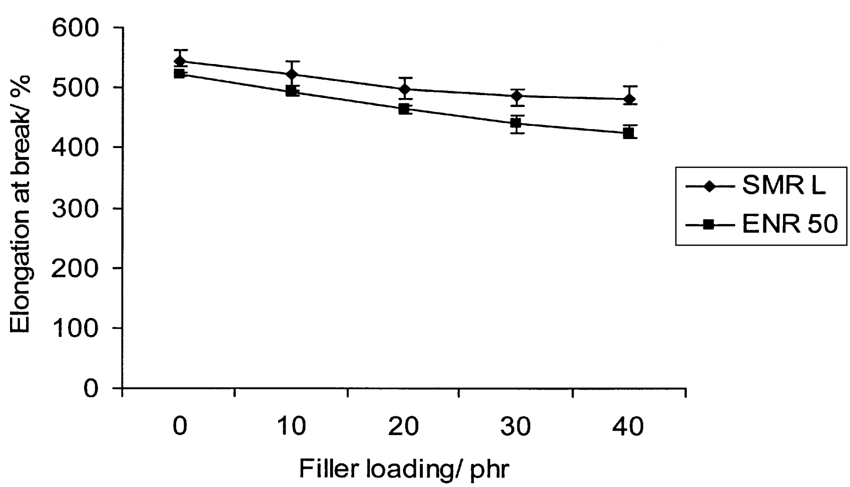


FIGURE 8 The effect of feldspar loading on the elongation at break of natural rubber vulcanizates.

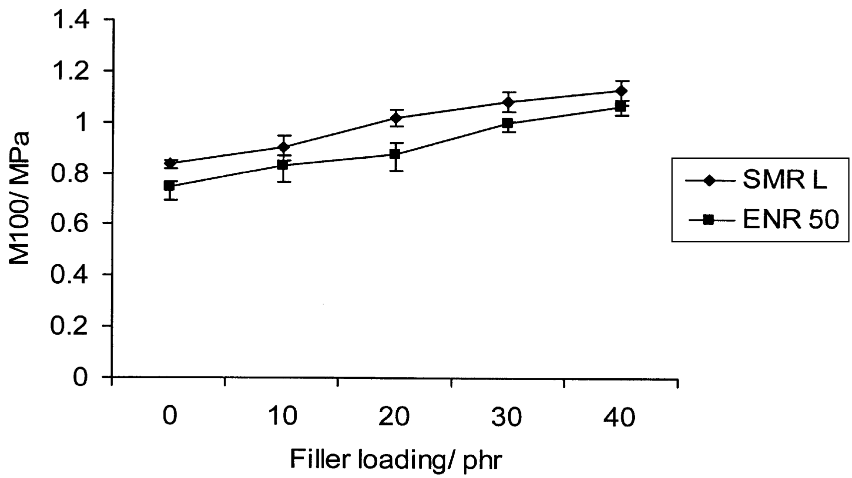


FIGURE 9 The effect of feldspar loading on the stress at 100% elongation of natural rubber vulcanizates.

SMR L vulcanizates than ENR 50 vulcanizates. At higher strains, because the strain crystallizing nature of NR (SMR L) is prominent compared to ENR 50, the modulus values for NR is greater than ENR 50 [8]. Again, this is due to better crosslink density of feldspar-filled SMR L than ENR 50 vulcanizates.

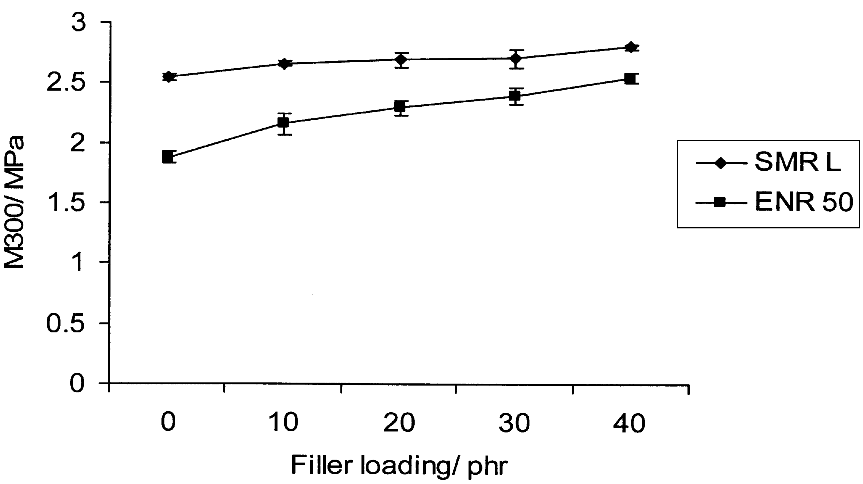


FIGURE 10 The effect of feldspar loading on the stress at 300% elongation of natural rubber vulcanizates.

The effect of feldspar loading on hardness of both rubber vulcanizates is shown in Figure 11. Hardness showed a significant increase with increasing feldspar loading. This result indicates that as more feldspar is incorporated into the rubber matrix, the mobility of the rubber chain is reduced, resulting in more rigid rubber vulcanizates [11]. It can be seen also that the hardness of the SMR L vulcanizates is higher than ENR 50 vulcanizates due to better crosslink density in the SMR L vulcanizates.

Figure 12 shows the resilience of the feldspar-filled SMR L and ENR 50 vulcanizates. According to Morton [15], resilience is the ratio of energy given up on recovery from deformation to the energy required to produce the deformation. From the results, it can be seen that decrease in resilience occurs with increasing filler loading. This indicates that the incorporation of feldspar in the rubber matrix reduced the mobility of the rubber chain, thus the rubber vulcanizates become more rigid. Thus, there is not enough energy to recover the deformation of the rubber vulcanizates. As more filler loading is added to the rubber matrix, the SMR L vulcanizates show better resilience compared to ENR 50 vulcanizates.

The Effects of Feldspar Loading on Swelling Behaviour of Rubber Vulcanizates

The effect of feldspar loading on the swelling behavior of rubber vulcanizates is clearly manifested in Figures 13(a) and (b). It can be seen

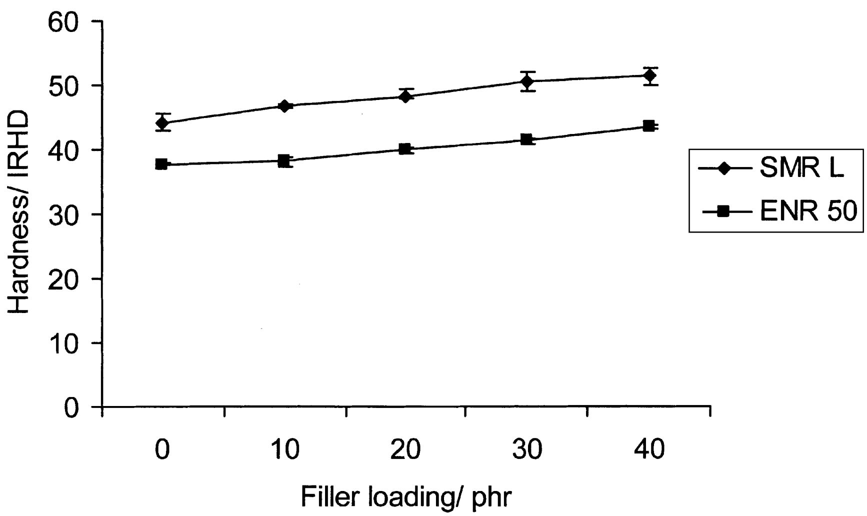


FIGURE 11 The effect of feldspar loading on the hardness of natural rubber vulcanizates.

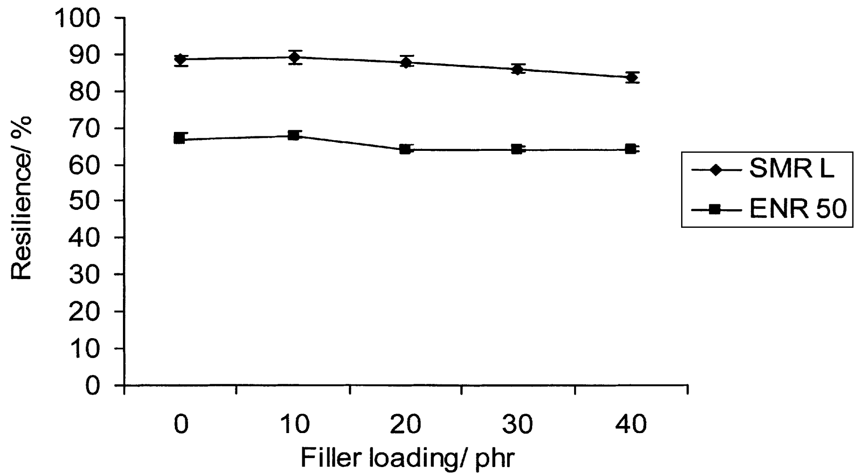


FIGURE 12 The effect of feldspar loading on the resilience of natural rubber vulcanizates.

that the percentage of swelling increases with increasing time up to about 5 hours for both rubbers. However, at the equilibrium state, say, from 10 hours on, the percentage of swelling of both rubber vulcanizates decreases with increasing feldspar loading (Figure 13c). The lower value of toluene uptake is mainly due to the increase in feldspar content in the rubber matrix, lowering the volume fraction of rubber and restricting the molecular movement of the rubber. However at a similar feldspar loading, the swelling percentage of feldspar-filled SMR L vulcanizates is lower than ENR 50 vulcanizates. As shown in Figure 5, feldspar-filled SMR L vulcanizates have higher crosslink density (M_H-M_L) than ENR 50 vulcanizates.

Morphological Study

Figures 14(a) and (b) show the tensile fracture surfaces of gum vulcanizates (control vulcanizates) for both rubbers. This exhibits a good rubber compounding of both rubbers where the rubber is a continuous rubber phase. A comparison of tensile fracture surfaces between SMR L vulcanizates and ENR 50 vulcanizates at certain feldspar loading was made (Figures 14(c)–(f)). From the figures, it is clear that at 40 phr of feldspar loading (Figures 14(e) and (f)) both rubbers showed poorer filler dispersion and weaker rubber-feldspar interaction rubber compounds than

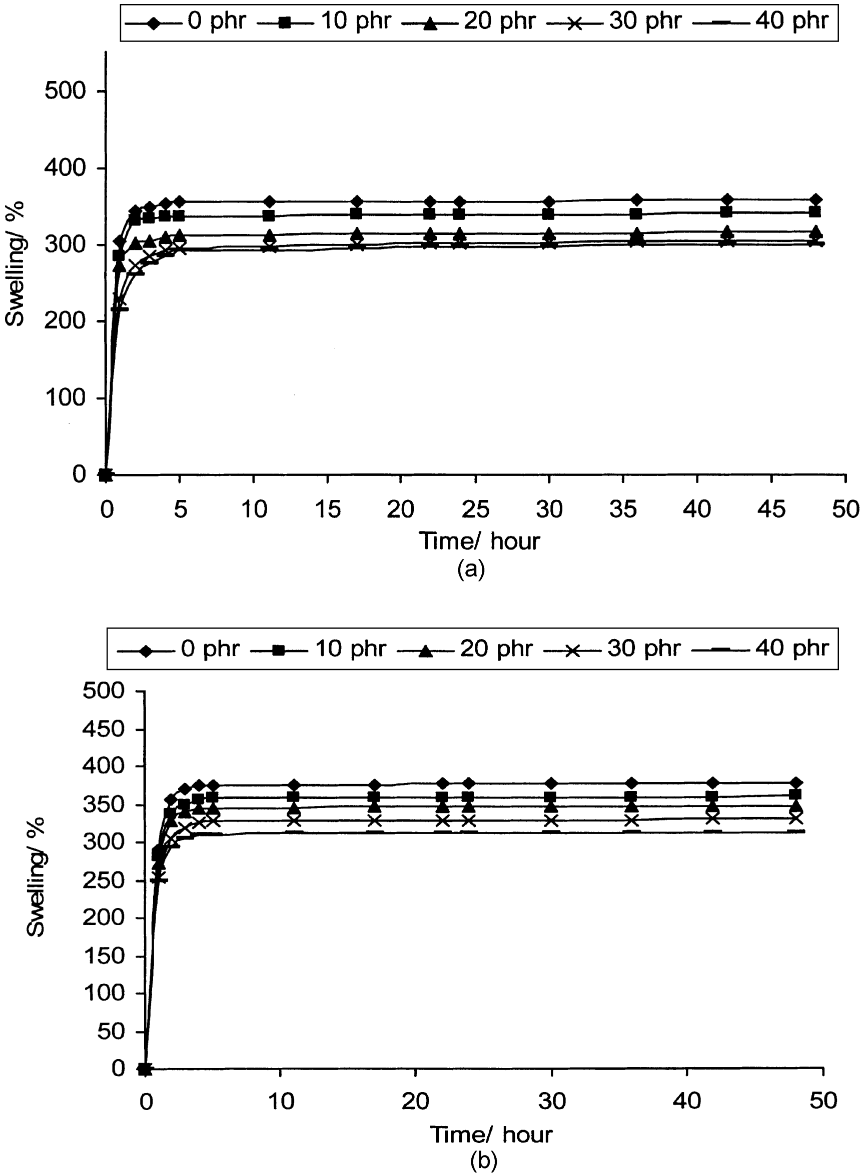
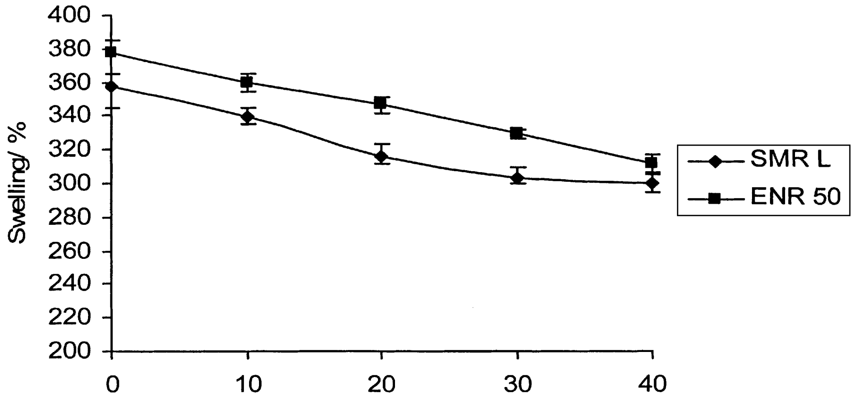


FIGURE 13 (a) The relationship between percentage of swelling and time of SMR L vulcanizates. (b) The relationship between percentage of swelling and time of ENR 50 vulcanizates. (c) The effect of feldspar loading on the percentage of swelling at equilibrium stage of natural rubber vulcanizates.



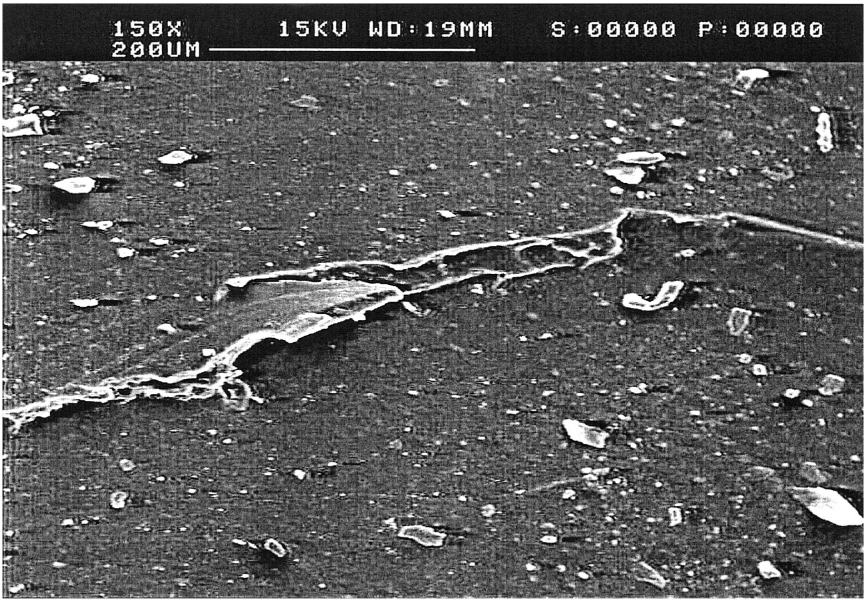
(c)

FIGURE 13 (Continued).

at 20 phr of feldspar loading (Figures 14(e) and (f)) for both rubbers because there are many holes left after the fillers were pulled out from the matrix when the stress was applied and the failure occurred at the weak feldspar and rubber interface. This happened because of poor dispersion and unwetted feldspar agglomerates in the rubber matrix with increasing feldspar loading up to 40 phr. The comparison between the tensile fracture surfaces of ENR 50 and SMR L vulcanizates indicates that ENR 50 vulcanizates showed poorer dispersion and unwetted feldspar agglomerates in the rubber matrix. This is consistent with the results of tensile strength whereby the SMR L vulcanizates showed higher tensile strength than ENR 50 vulcanizates. According to Ismail et al. [14], poorer dispersion of fillers give rise to certain detrimental effects such as reduced product life, poor performance in service, poor product appearances, poor processing characteristics, and so on.

CONCLUSIONS

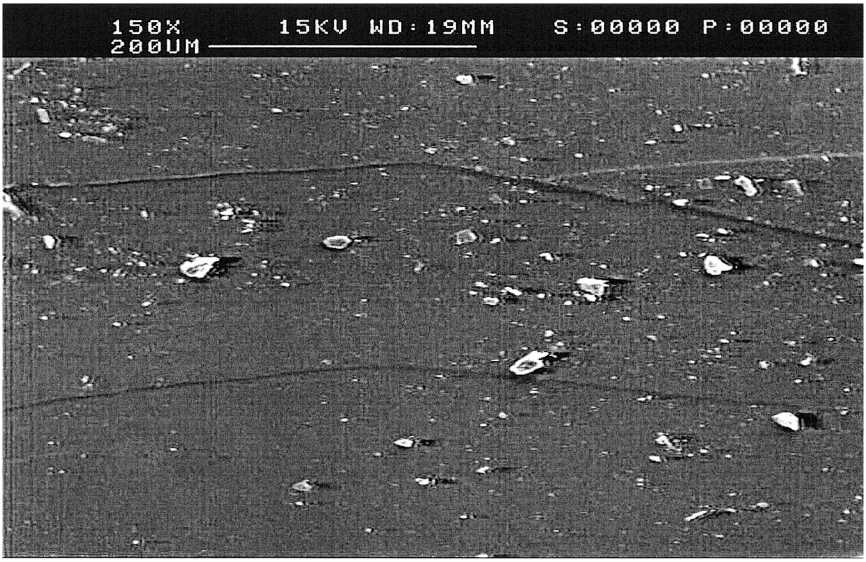
1. Incorporation of feldspar in both rubbers gradually increases the scorch time, t_2 and cure time, t_{90}. For maximum torque, M_{HR} and torque difference, M_{HR}-M_L, the values significantly increase with increasing feldspar loading for both rubbers. At a similar feldspar loading, ENR 50 vulcanizates have shorter t_2 and t_{90} but lower values of M_{HR} and M_{HR}-M_L than SMR L vulcanizates. This indicates that the epoxidation in natural rubber play a major role in determining the cure characteristics of the rubber vulcanizates.



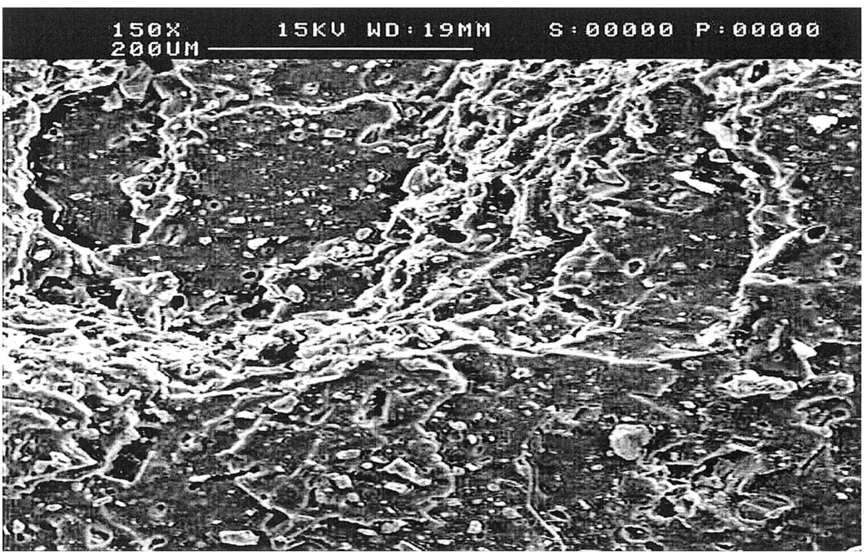
(a)

FIGURE 14 (a) SEM micrograph of the tensile fracture surfaces of SMR L gum vulcanizates. (b) SEM micrograph of the tensile fracture surfaces of ENR gum vulcanizates. (c) SEM micrograph of the tensile fracture surfaces of 20 phr of feldspar–filled SMR L volcanizates. (d) SEM micrograph of the tensile fracture surfaces of 20 phr of feldspar-filled ENR 50 vulcanizates. (e) SEM micrograph of the tensile fracture surfaces of 40 phr of feldspar-filled SMR L vulcanizates. (f) SEM micrograph of the tensile fracture surfaces of 40 phr of feldspar-filled ENR 50 vulcanizates (All magnifications 150×.)

2. In all rubbers studied, the mechanical properties, such as tensile strength (up to certain filler loading), tensile modulus, and hardness, increased with increasing feldspar loading for both rubbers whereas elongation at break, resilience, and percentage of swelling show an opposite trend. However, at similar feldspar loading, the mechanical properties of SMR L vulcanizates are higher than ENR 50 vulcanizates.
3. The percentage of swelling decreases with increasing feldspar loading for both rubbers. However, at a similar feldspar loading, feldspar-filled SMR L vulcanizates exhibit lower percentage of swelling than ENR 50 vulcanizates.
4. SEM studies show that the enhancement in tensile strength is due to a better filler dispersion at lower feldspar loading. However, at

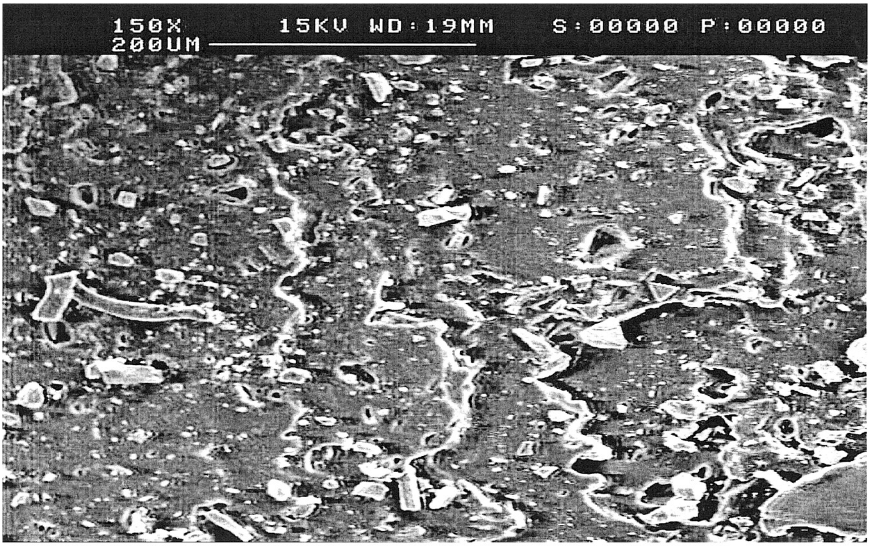


(b)

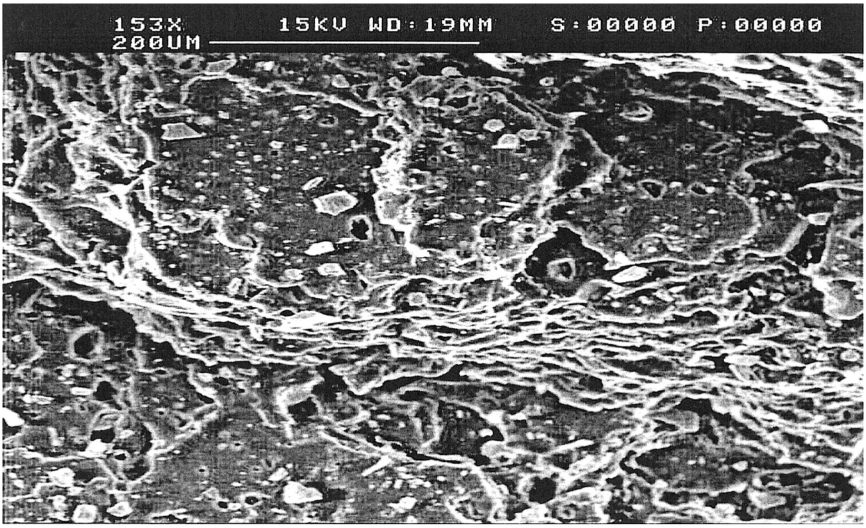


(c)

FIGURE 14 (Continued).

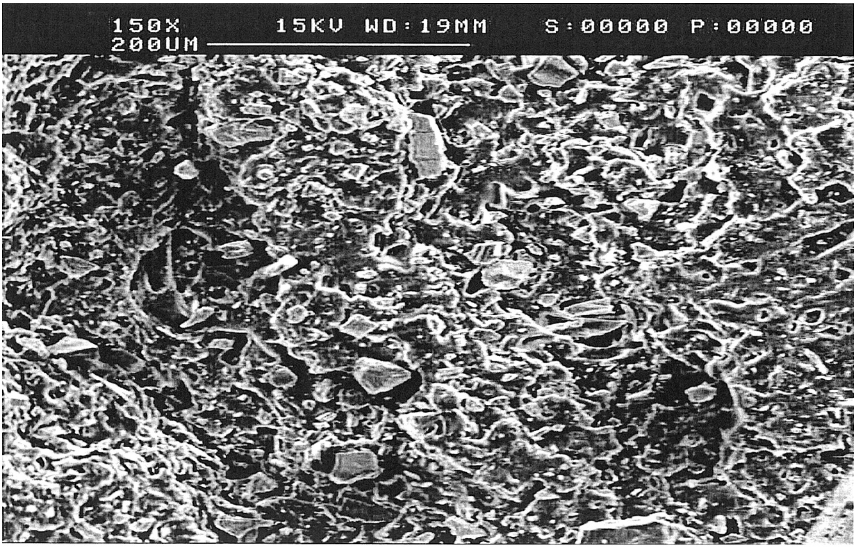


(d)



(e)

FIGURE 14 (Continued).



(f)

FIGURE 14 (Continued).

higher feldspar loading, the agglomeration of feldspar and weak rubber-filler interaction has resulted in reduction of tensile strength.

REFERENCES

[1] Ismail, H., Rozman, H. D., Jaffri, R. M., and Mohd. Ishak, Z. A., *Eur. Polym. J.*, **33**, 1627 (1997).
[2] Poh, B. T. and Ng, C. C., *Eur. Polym. J.*, **34**, 975 (1998).
[3] Furtado, C. R. G., Leblanc, J. L., and Nunes, R. C. R., *Eur. Polym. J.*, **36**, 1717 (2000).
[4] Harry DuBois, J. (1987). *Handbook of Fillers for Plastics*, Van Nostrand Reinhold Com., New York.
[5] Bachmann, J. H., Sellers, J. W., Wagner, M. P., and Wolf, R. F., *Rubb. Chem. Technol.*, **32**, 1286 (1959).
[6] Ismail, H. and Khalil, H. P. S., *Polym. Testing* **20**, 33 (2001).
[7] Sadequl, A. M., Ishiaku, U. S., Ismail, H., and Poh, B. T., *Eur. Polym. J.*, **34**, 51 (1998).
[8] Johnson, T. and Thomas, S., *Polymer* **41**, 7511 (2000).
[9] Ismail, H., Freakley, P. K., Sutherland, I., and Sheng, E., *Eur. Polym. J.*, **31**, 1109 (1995).
[10] Ismail, H. and Chung, F. L., *Iranian Polym. J.*, **7**, 255 (1998).
[11] Ismail, H., Nasaruddin, M. N., and Rozman, H. D., *Euro. Polym. J.*, **35**, 1429 (1999).

[12] Zaini, M. J., Fuad, M. Y. A., Ismail, Z., Mansor, M. S., and Mustafah, J., *Polym. Int.*, **40**, 51 (1996).
[13] Medallia, A. F., *Rubb. Chem. Technol.*, **60**, 45 (1987).
[14] Ismail, H., Nizam, J. M., and Abdul Khalil, H. P. S., *Polym. Testing* **20**, 125 (2001).
[15] Morton, M. (1973). *Rubber Technology* , 2nd ed, Van Nostrand Reinhold Com., New York.