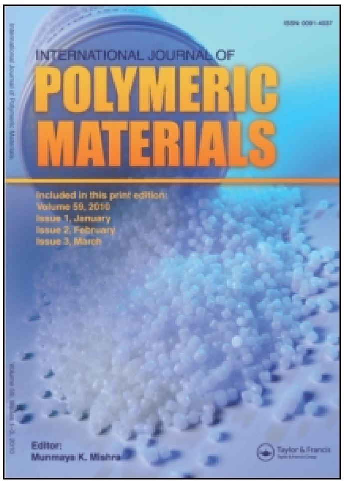

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The Effect of Prolonged Thermo-oxidative Ageing on the Mechanical Properties of Dynamically Vulcanized Poly(Vinyl Chloride)/Nitrile Butadiene Rubber Thermoplastic Elastomers

A. Mousa[a]; U. S. Ishiaku[b]; Z. A. Mohd Ishak[c]
[a] Faculty of Engineering, Department of Materials and Metallurgical Engineering, Al-Balqa Applied University, Salt, Jordan [b] Advanced Fibro-Science, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto, Japan [c] School of Materials and Mineral Resource Engineering, Engineering Campus, Universiti Sains Malaysia, Penang, Malaysia

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A. Mousa
Faculty of Engineering, Department of Materials and Metallurgical Engineering, Al-Balqa Applied University, Salt, Jordan

U. S. Ishiaku
Advanced Fibro-Science, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto, Japan

Z. A. Mohd Ishak
School of Materials and Mineral Resource Engineering, Engineering Campus, Universiti Sains Malaysia, Penang, Malaysia

Plasticized poly(vinyl chloride)/nitrile butadiene rubber (PVC/NBR) thermoplastic elastomers (TPEs) were dynamically vulcanized in the melt stage with the incorporation of a semi-efficient vulcanizing system using a Brabender Plasticorder at 150°C and 50 rpm rotor speed. Curative concentration was progressively increased from 0 to 1 part per hundred (phr) NBR in order to study the effect of dynamic curing on the plasticized blend. The mechanical properties investigated include tensile strength, elongation at break (%EB), modulus at 100% elongation (M100), tear strength, and hardness. The effect of thermo-oxidative ageing (TOA) on the mechanical properties was investigated by exposing the PVC/NBR TPEs in an air oven at 100°C for 3, 7, 14, and 21 days. It was found that tensile and tear strength passed through a maximum value, whereas, hardness and M100 increased steadily with the sulfur content and ageing time. On the contrary, the elongation at break reduced gradually with ageing time until it reaches a minimum value. The increase in crosslink density as well as the steady reduction in swelling index with increasing concentration of curatives provided an excellent evidence for the significant increase in crosslink density with ageing time. The changes in physical and mechanical properties of the TPEs is believed to be closely related to some microstructural changes taking place as a result of the formation of new crosslinks due to prolonged thermo-oxidative environment.

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Address correspondence to A. Mousa, Faculty of Engineering, Department of Materials and Metallurgical Engineering, Al-Balqa Applied University, Salt 19117, Jordan. E-mail: mousa1@bau.edu.jo

Keywords: thermoplastic elastomers, dynamic vulcanization, ageing, tensile strength

INTRODUCTION

Thermoplastic elastomers from blends of rubber and thermoplastics continue to represent a field of intensive research. One of the most common blends in modern science is that of poly(vinyl chloride) with nitrile butadiene rubber [1]. Nitrile butadiene rubber acts as a permanent plasticizer for poly(vinyl chloride) in applications such as wire and cable insulation as well as food containers and many other applications. On the other hand poly(vinyl chloride) enhances ozone, thermal ageing, and chemical resistance of nitrile butadiene rubber in applications such as feed hose covers, gaskets, and conveyor belt covers. Remember that poly(vinyl chloride) vastly improves abrasion resistance, tear strength, as well as tensile properties of the elastomers. It also adds gloss, improves finishing of the extruded articles, and imparts flame retardancy. NBR/PVC blend can be conventionally milled, extruded, or compression molded using traditional processing equipments for natural and synthetic rubbers [2]. Due to the miscible nature of PVC/NBR blend, as evidenced from its single glass transition temperature (T_g), the soft blend of PVC/NBR can be categorized as a thermoplastic elastomer (TPE) and, more specifically, as a melt processable rubber (MPR) [3–5]. Another novelty in TPE technology is dynamic vulcanization to produce thermoplastic vulcanizates (TPVs). TPVs constitute a class of TPEs of rubber/plastic polymer blends in which the rubber is fully vulcanized. Vulcanization confers increased, tensile strength and modulus, pronounced decrease in set, and considerable reduction in swelling by oils [6]. The vulcanization of the rubber phase also enhances retention of the properties at elevated temperatures. Such products look, feel, and perform like elastomers [7]. In this regard the oil resistance behavior of the dynamically cured PVC/NBR TPEs as well as the fatigue behavior were reported by the authors [8–9]. The effect of thermo-oxidative ageing on the mechanical properties at 80°C for 168 h has been reported, and no sign of degradation was observed; on the contrary, further increase in the tensile properties was obtained [10]. Thus, in this article the effect of prolonged thermo-oxidative ageing, up to the degradation point of the dynamically vulcanized PVC/NBR TPEs is reported.

EXPERIMENTAL

Materials

Suspension polymerized poly(vinyl chloride) (PVC) in powder form, with a K-value of 65 and a degree of polymerization of 920-1060,

TABLE 1 Recipe Used to Produce PVC/NBR

Component	(phr)
PVC	70
NBR	30
DOP	50 phr/PVC
Stearic acid	1.5 phr/NBR
ZnO	3 phr/NBR
Sulfur	X
MBTS	X
TMTD	1/3X

X is the amount of sulfur which was varied from 0–1 phr NBR.

was supplied by Malayan Electro Chemical Industry Sdn Bhd, Penang, Malaysia. Nitrile butadiene rubber with 34 mole % acrylonitrile (NBR-34%) was obtained from Bayer AG, Germany. Lead stabilizer $Pb(St)_2$ was obtained from Komita Sdn Bhd. Di-2-ethylhexylphthalate (DOP), sulfur, tetramethylthiuram disulfide (TMTD), 2,2-dithiobisbenzothiazole (MBTS), zinc oxide, and stearic acid were supplied by Bayer (M) Sdn Bhd, Penang, Malaysia. The recipes used to produce the PVC/NBR elastomers are shown in Table 1.

Melt Mixing

PVC was initially premixed with the lead stabilizer in a Jankel IKA Labotehnik Model RE 162/P mixer for 10 min at 30°C. Melt mixing was performed using a Brabender Plasticorder Model PLE 331 coupled with mixer/measuring head (W50H). Mixing was carried out at 150°C and a rotor speed of 50 rpm [8–10]. The NBR was charged into the mixing chamber to equilibrate, followed by PVC and other related additives. Mixing was allowed to proceed for 8 min after which the curatives were added to the compound [8–10]. Mixing was then continued until a constant torque was obtained. The compound was then removed from the mixer and sheeted on a cold two roll mill. It was passed once through the nip to produce approximately a 1 mm thick sheet. The sheets were cut into strips and again subjected to Brabender mixing at 150°C and 50 rpm for 2 min after which the product was again sheeted out prior to compression molding. Sheets of 2 mm thickness were molded with a KAO Tieh compression molding machine with a force of 10 MPa at 150°C.

CHARACTERIZATION AND TESTING

Tensile Tests

Tensile tests were carried out according to ASTM D638 on a Monsanto Tensometer Model T10. Dumb-bell specimens of 2 mm thick were cut from molded sheets with a Wallace Die cutter (S/6/1/4). A crosshead speed of 50 cm/min was used and the tests were performed at 25°C ± 2. Three specimens were used and the average was calculated in each case.

Crosslink Density

The load-extension curves derived from the Monsanto Testometer Model T10 were used to estimate the crosslink density according to the Mooney-Rivlin equation as follows:

$$\frac{f}{A \times \left(\lambda - \lambda^{-2}\right)} = 2C_1 + 2C_2\lambda^{-1} \tag{1}$$

where λ = extension ratio, C_1, C_2 = Elastic constants, f = force, A = cross-sectional area of the specimen. A plot of $f/A \times \left(\lambda - \lambda^{-2}\right)$ vs. λ^{-1} has an intercept of $2C_1$ and the slope is $2C_2$, where:

$$2C_1 = \mathrm{NKT} = \frac{\rho RT}{M_c} \tag{2}$$

N, K, R, M_c and T are avagadro's number, Boltzman constant, universal gas constant, molecular weight, and absolute temperature, respectively. The M_c is related to the crosslink density by $(2M_c)^{-2}$.

Swelling Measurements

A disc of dimensions 25 mm × 5 mm was cut and immersed in a suitable solvent, such as xylene, for a period of 12 h. The diameter/length of the swollen sample were determined and the swelling index was calculated as follow:

$$Swelling\ Ratio = \frac{Swollen\ Mass}{Initial\ Mass} \times 100 \tag{3}$$

Tear Tests

Tear tests were carried out according to ISO 34 Type III using the crescent shape specimens. Monsanto Tensometer Model T10 was used at a crosshead speed of 50 cm/min. Five specimens were used and the average value was calculated.

Hardness Test

A Wallace Dead Load hardness tester was used to measure the hardness in an international rubber hardness degree (IRHD) according to ISO 48 (1979).

Thermo-Oxidative Ageing

Thermo-oxidative ageing studies were performed according to the BS 7646. The samples were placed in an air oven and aged at 100°C for 3, 7, 14, and 21 days. Retention in the properties was calculated as:

$$Retention(\%) = \frac{Value\ after\ ageing}{Value\ before\ ageing} \times 100 \tag{4}$$

Volatile Loss

Volatile loss was carried out to indicate plasticizer migration. Samples of 1 mm thickness were weighed and mounted in an air oven at 100°C for 3, 7, 14, and 21 days. The volatile loss was calculated according to ASTM D 4571 as follows:

$$volatile\ loss(\%) = \frac{initial\ weight - final\ weight}{initial\ weight} \times 100 \tag{5}$$

RESULTS AND DISCUSSION

The Effect of Prolonged Ageing on the Mechanical and Physical Properties

Tensile Properties

Figure 1 illustrates the effect of thermo-oxidative ageing on the tensile strength of the uncured and cured PVC/NBR TPEs at 100°C as a function of ageing time. In all cases, it can be seen that the tensile strength of the TPEs passed through a maximum before it peaked off. This implies that the strength of the materials have increased before rupture. In other words, the breaking stress has increased and the ability of the formulations to stretch has decreased. This behavior is illustrated in Figure 2, which was utilized to estimate the cross link density according to Mooney-Rivlin equation. With reference to Figure 1, it can be seen that both the uncured and cured PVC/NBR TPEs displayed the same behavior although the cured blend obtained higher tensile strength values. In the case of the cured blend, the scenario should be related to the increase in crosslink density from the post curing effect during the ageing process [11]. The increase in tensile

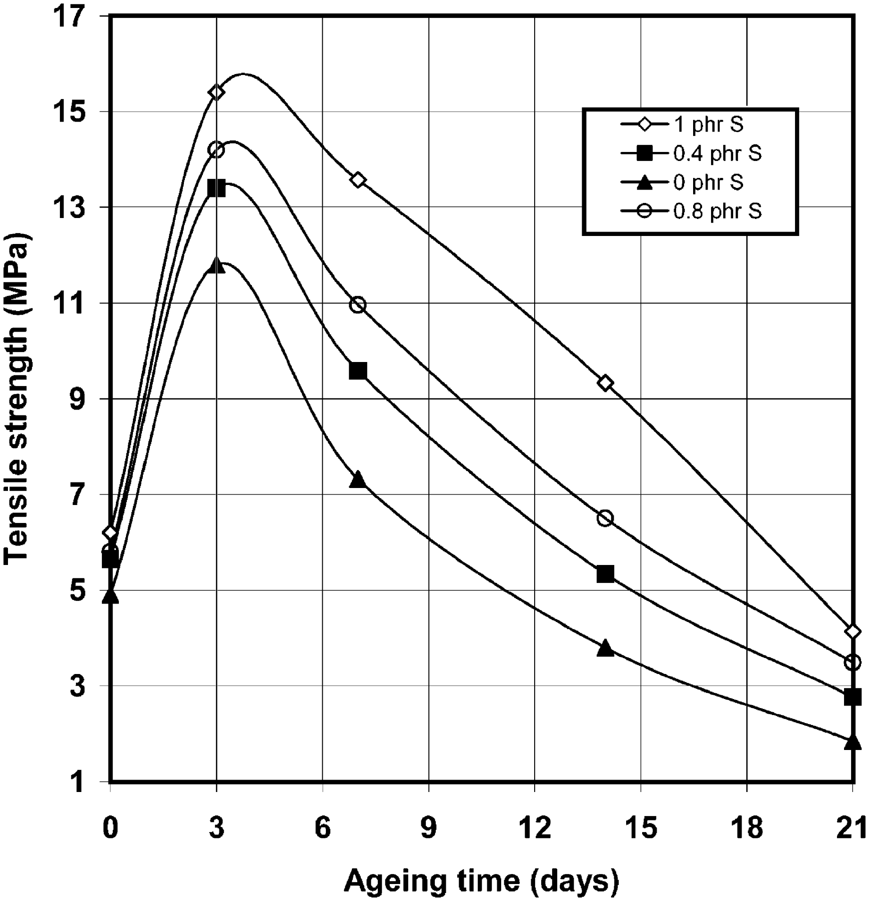

FIGURE 1 The effect of prolonged TOA on the tensile strength of PVC/NBR TPEs.

strength was accompanied with an increase in crosslink density as well as reduction in swelling ratio with ageing time, as shown in Figures 3 and 4, respectively. Because the crosslink density of the thermoplastic vulcanizates is not likely to decrease with ageing, it is clear that changes in crosslink density alone cannot explain the fall in tensile strength of the vulcanizates after prolonged ageing periods. This suggests that overcure occurred and the network structure had deteriorated as a result of prolonged thermal ageing. This is in agreement with previous findings on natural rubber/styrene butadiene rubber (NR/SBR) blends [12]. According to Morell [13], the deterioration in

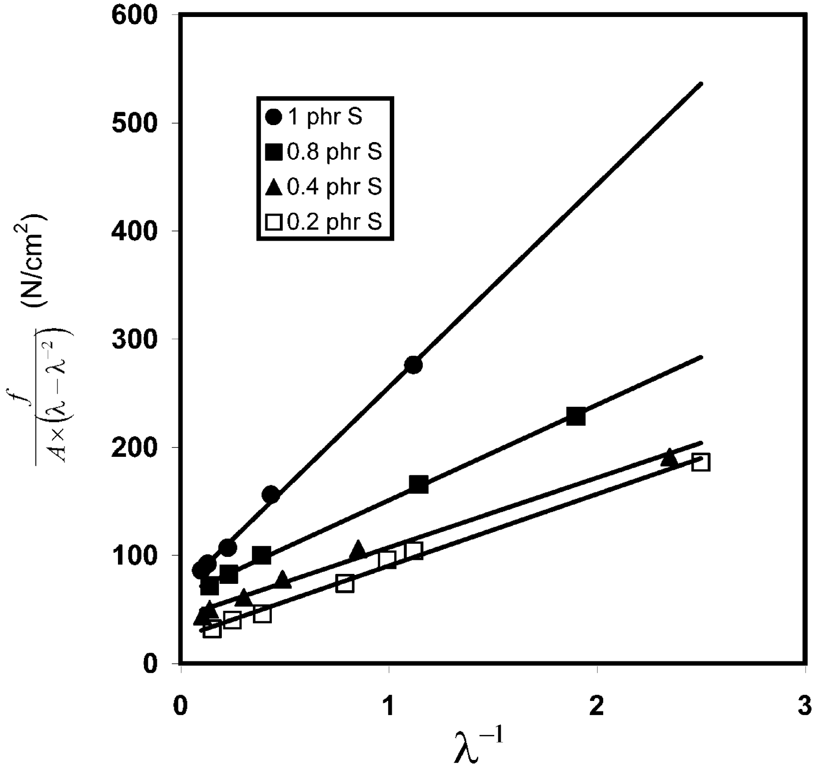

FIGURE 2 Stress – λ^{-1} curves of 3-days aged PVC/NBR TPEs at various sulfur loadings.

tensile strength may principally be due to main chain scission. The chain scission could be related to oxidative reaction that had been initiated by oxygen that propagates autocatalytically [14]. The increase in crosslink density with ageing time is reflected in an increase in sample density, as shown in Table 2. This increase in crosslink density, accompanied by falling tensile strength, may suggest that the thermal stability of the intermolecular network has been reduced. Thus, there seem to be an optimum crosslink density where the retention in tensile strength is maximal. In order to study the effect of the plasticizer migration on the observed trend in Figure 1, especially for the uncured formulations, volatile loss studies were carried out in two ways. First, the volatile loss of the aged PVC/NBR was determined according to ASTM D 4571. Figure 5 illustrates the effect of ageing time on the volatile loss of the PVC/NBR TPEs at various sulfur loadings. It is obvious that volatile loss decreases substantially

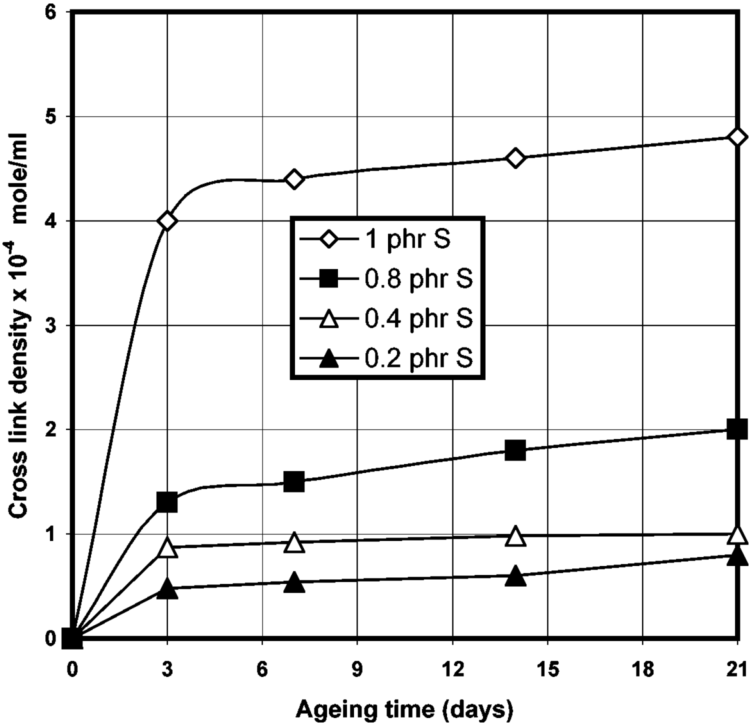

FIGURE 3 The effect of prolonged TOA on crosslink density of PVC/NBR TPEs.

with increasing sulfur loading and reached the minimum value at 1 phr sulfur concentration. This can be related to the fact that the crosslink formation has slowed down the volatile loss of the plasticizer and produced an intermolecular network structure that conferred microstructural changes on the PVC/NBR TPEs. This is in agreement with a related study on poly(vinyl chloride)/epoxidized natural rubber (PVC/ENR) TPEs by Mousa et al. [15]. This suggests that the rate at which the plasticizer molecules traveled through the PVC matrix and evaporated through the surface has been curbed significantly with increasing sulfur content. This may be attributed to the crosslinked rubber particles that are dispersed in the PVC matrix and may have acted as a filler. Thus, it is expected to reduce the diffusion coefficient of the plasticizer in accordance to the theory proposed by Maxwell [16]. This suggests that the presence of the crosslinked rubber particles has increased the effective distance that the plasticizer has to travel to penetrate and subsequently evaporate from the PVC matrix. This

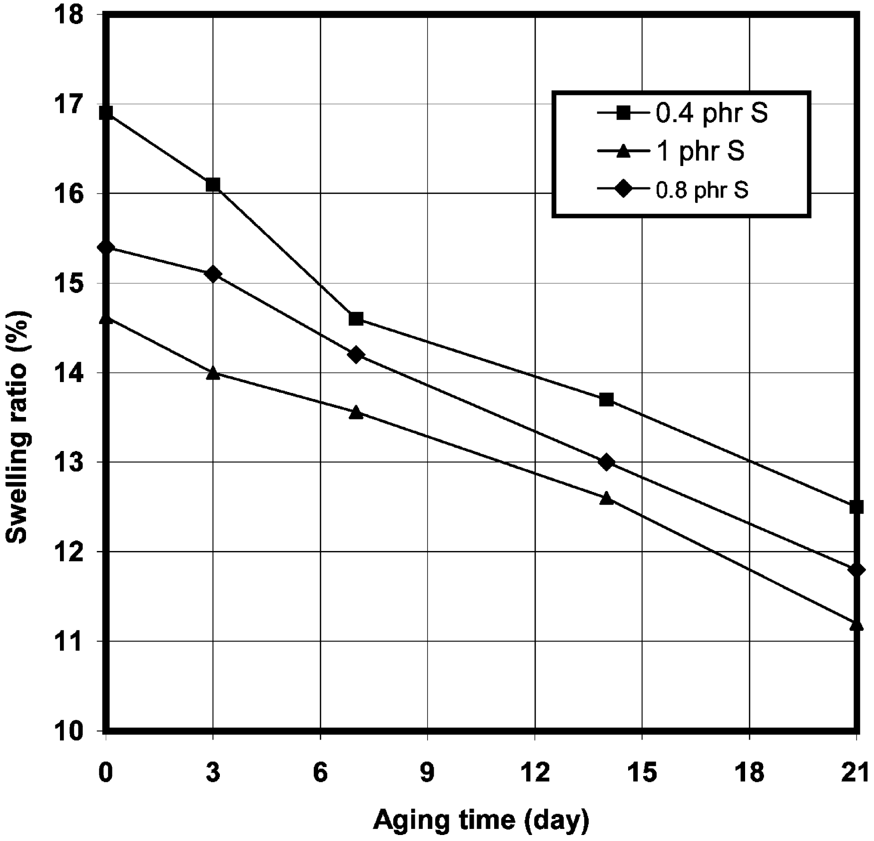

FIGURE 4 The effect of prolonged TOA on swelling ratio of PVC/NBR TPEs.

TABLE 2 The Density of the PVC/NBR TPEs at Various Sulfur Loadings

	Density (g/ml)		
Ageing time (days)	0.4 phr S	0.8 phr S	1 phr S
0	0.99	1.03	1.05
3	1.04	1.08	1.10
7	1.08	1.10	1.15
14	1.10	1.13	1.20
21	1.13	1.17	1.23

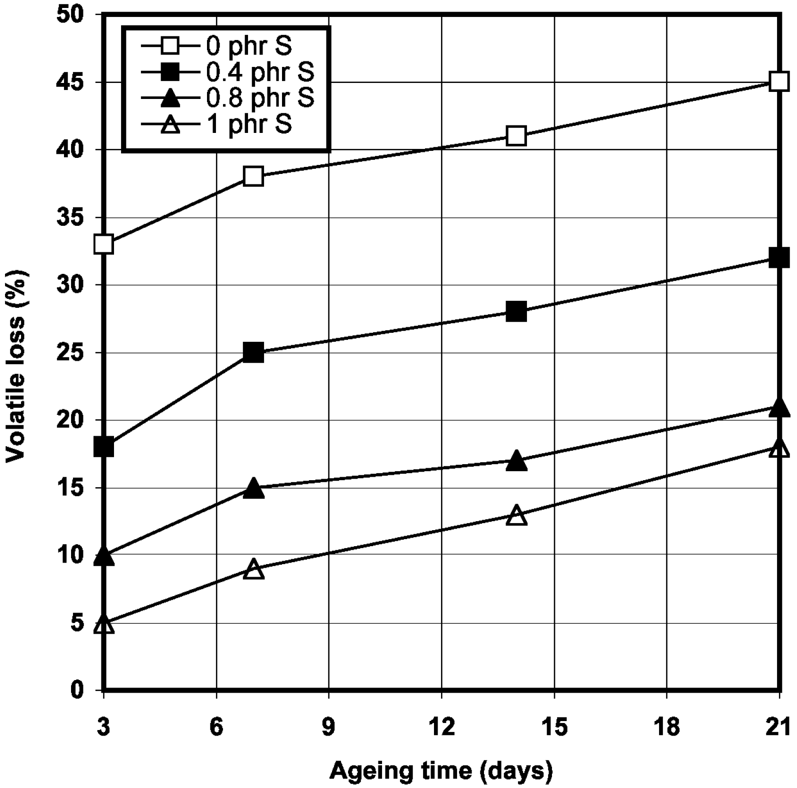

FIGURE 5 The effect of sulfur loading on volatile loss of PVC/NBR TPEs.

subject has been extensively reviewed by Buszard [17]. Thus, lower volatile loss was obtained with increased sulfur concentration as shown in Figure 5. Secondly, the effect of volatile loss after TOA process on the retention of tensile strength and elongation at break was studied, the related data are presented in Figure 6. After thermo-oxidative aging, retention in tensile strength also increases for both the uncrosslinked and crosslinked PVC/NBR TPEs. In the former, the volatile loss was around 30% (Figure 5). This is expected to impart some stiffness to the PVC/NBR TPEs and as a result the tensile strength of the aged sample supersedes that of the unaged counterpart, as shown in Figure 1. This is in agreement with an earlier observation reported on dynamically cured poly(vinyl chloride)/epoxidized natural rubber (PVC/ENR) blends [15]. On the other hand, the retention in the tensile strength of the cured PVC/NBR TPEs, presented in Figure 6, is higher than that of the uncrosslinked counterpart, even

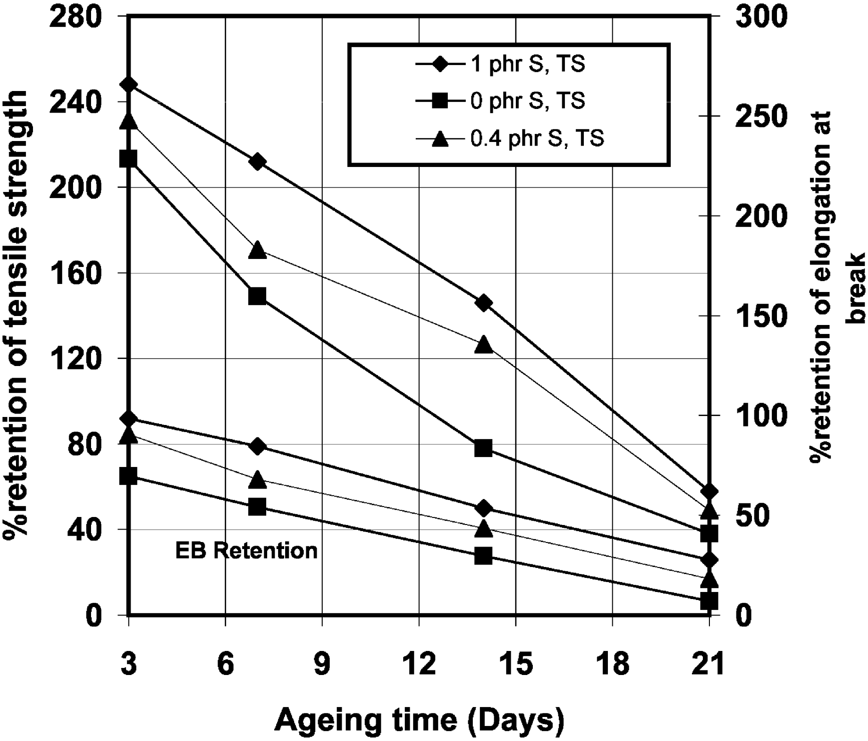

FIGURE 6 The effect of prolonged TOA on the retention of the tensile strength and elongation at break of PVC/NBR TPEs at various sulfur loadings.

though the volatile loss is much lower. This could be related to the effect of thermo-oxidative ageing (TOA), which is expected to produce further crosslinks as a result of the post curing phenomenon, thus increasing the stiffness of the material. This suggests that the crosslinking plays a dominant role in determining the tensile strength of the cured samples. Thus, it can be believed that the same factors are responsible for the trend observed in the case of other mechanical properties, as will be elaborated later. Figure 6 also shows that the retention of % elongation at break for the uncured PVC/NBR TPEs is higher than that of the cured system. This may be due to the effect of crosslinking, which is known to harden the PVC/NBR compounds as a result of shortening of the polythioether bridges after the TOA process. Thus, the samples will not be able to be stretched to a higher extent. In the case of the uncured PVC/NBR TPEs the slight reduction in the % elongation at break after the TOA process may be attributed to the stiffening of the polymer chain resulting from the relatively high volatile loss. This is in agreement with the trend observed by Penn [18] in the case of the volatile loss of plasticized PVC compounds. Higher volatile loss is known to impart embrittlement and stiffening to the aged uncured samples. In the crosslinked system the increase in crosslink density could be responsible for the hardening of the samples. Based on this, and judging from the mechanical and physical behavior of the uncrosslinked system as well as the effect of dynamic vulcanization on the volatile loss, it can be inferred that the increase in the mechanical and physical properties after the TOA of the PVC/NBR TPEs could not be attributed solely to volatile loss. Instead, the increase in crosslink formation is believed to be the main factor contributing to the enhancement in the mechanical and physical properties of cured PVC/NBR TPEs. The effect of ageing time on the modulus at 100% elongation (M100) for various sulfur loading is depicted in Figure 7. The continuous increase in M100 with ageing time may be again attributed to the increase in crosslink density. Because modulus at 100% elongation is a direct function of crosslinks formed [12], the data provides a suitable means for assessing the increase in crosslink density with ageing time. Figure 8 shows the effect of prolonged TOA on the elongation at break of PVC/NBR formulations. It can be seen that the elongation at break decreases with ageing time at any particular sulfur concentration. The deterioration in % elongation at break might be related to an excessive crosslink formation that reduces the chain mobility and confers rigidity to the intermolecular network structure. These materials, with short polythioether crosslinks, are expected to be less flexible due to the ageing process, as indicated in Figure 8. Hence, this may explain the marked reduction in the % elongation at break with ageing time for the various compositions shown in Figure 8. The trend observed in Figure 8 agrees quite well with the load-extension curve in Figure 9. From Figure 9 it is clear that thermo-oxidative ageing has converted the materials to brittle materials with a limited extent for stretching, the extent of which increases with sulfur content. On the other hand, the uncrosslinked counterpart displayed less brittle mode although higher plasticizer migration was recorded, which should be due to the absence of crosslinks.

Tear Strength

Figure 10 shows the effect of prolonged ageing on the tear strength of PVC/NBR TPEs with various sulfur loadings. As expected, with ageing time tear strength passed through a maximum. The profound

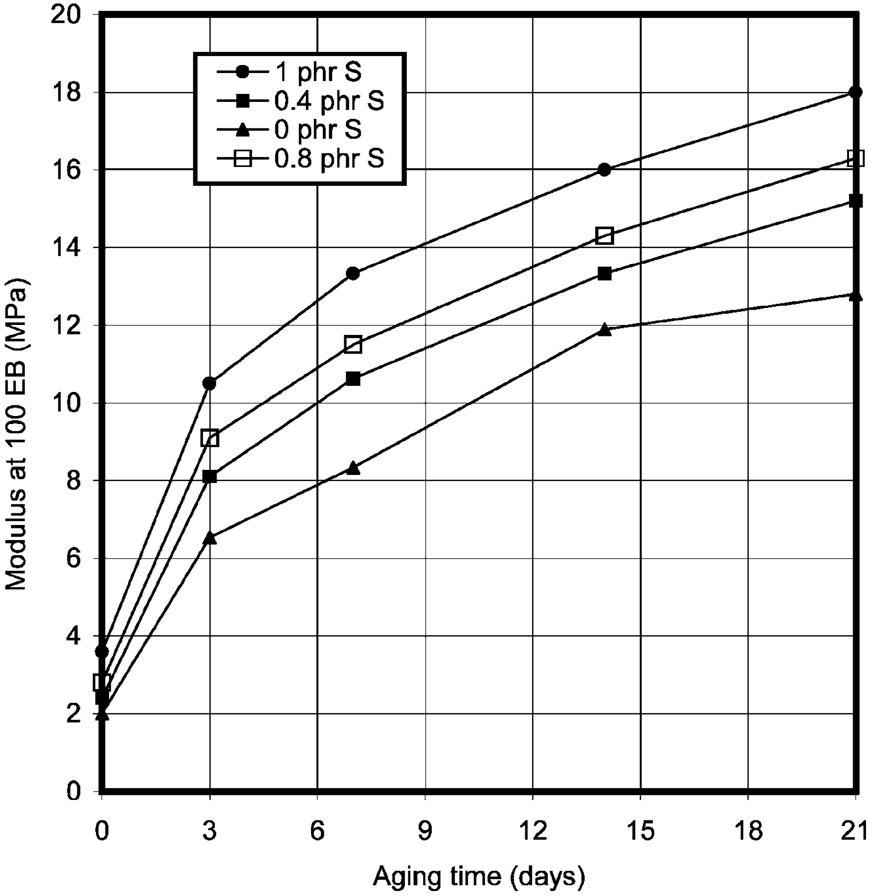

FIGURE 7 The effect of prolonged TOA on modulus at 100% elongation of PVC/NBR TPEs at various sulfur loadings.

increase in tear strength after ageing for 3 days is expected to be related to the excessive crosslink formation that is due to the post-curing effect. The reduction in the tear strength of the PVC/NBR TPEs shown in Figure 10 may be related to the deterioration of the intermolecular network after the prolonged ageing time. The trend observed here is similar to that of the tensile strength. Thus, it can be inferred that some microstructural changes have taken place as a result of prolonged ageing. These changes indicate the formation of excessive crosslinks. The increase in crosslink density after the prolonged thermo-oxidative ageing process markedly accelerates the drop

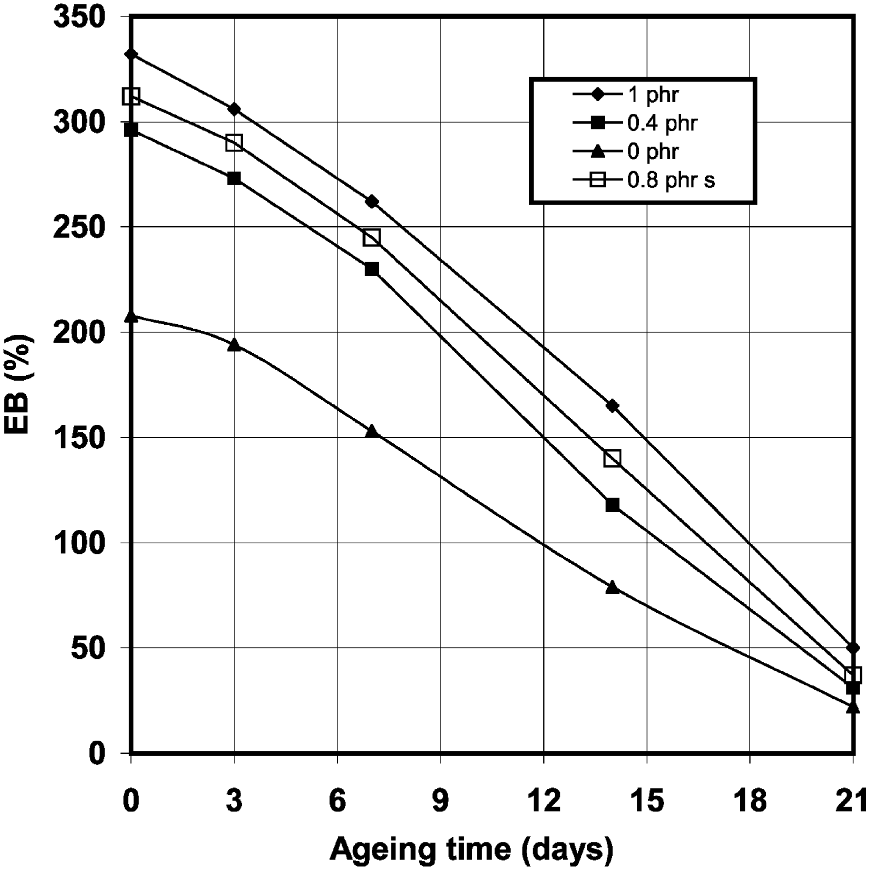

FIGURE 8 The effect of prolonged TOA on the % elongation at break of PVC/NBR TPEs.

in elastic properties of the PVC/NBR TPEs as indicated from the increase in modulus at 100% elongation. This may help in accounting for the observed trends displayed by the samples throughout the prolonged ageing process.

Hardness

Figure 11 depicts the effect of ageing time on the hardness of PVC/NBR TPEs with various sulfur contents. It can be seen that hardness increased with ageing time at all sulfur dosages. This could be related to the increase in crosslink density as well as the swelling ratio data mentioned earlier. This agrees well with the increase in

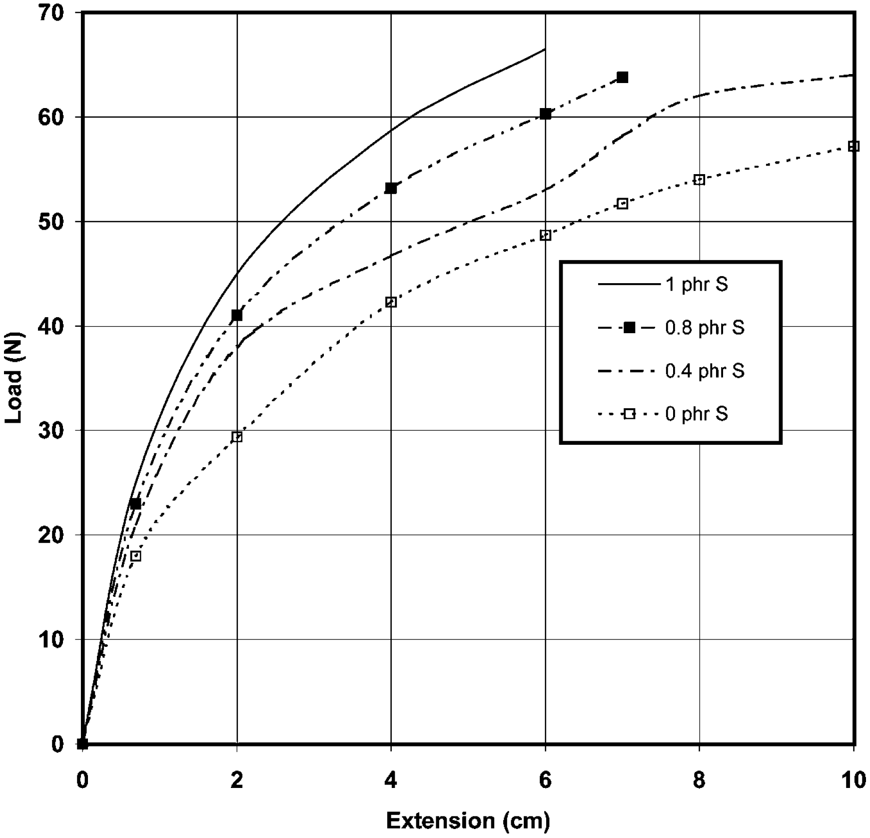

FIGURE 9 Load-extension ratio of PVC/NBR TPEs, aged for three days at various sulfur loadings.

M100 after the thermo-oxidative ageing process shown in Figure 7. The excessive formation of the crosslinks with ageing time leads not only to the hardening but also to the embrittlement of the TPEs, which is a significant sign of degradation.

Failure Mode

Figure 12 presents SEM micrographs of the fracture surface of PVC/NBR TPEs with and without sulfur. The micrographs reveal that the morphology of the control recipe differs from that of the cured blend. The relatively smooth fracture plane of the uncured blend presented in Figure 12a is a good indication that the sample failure

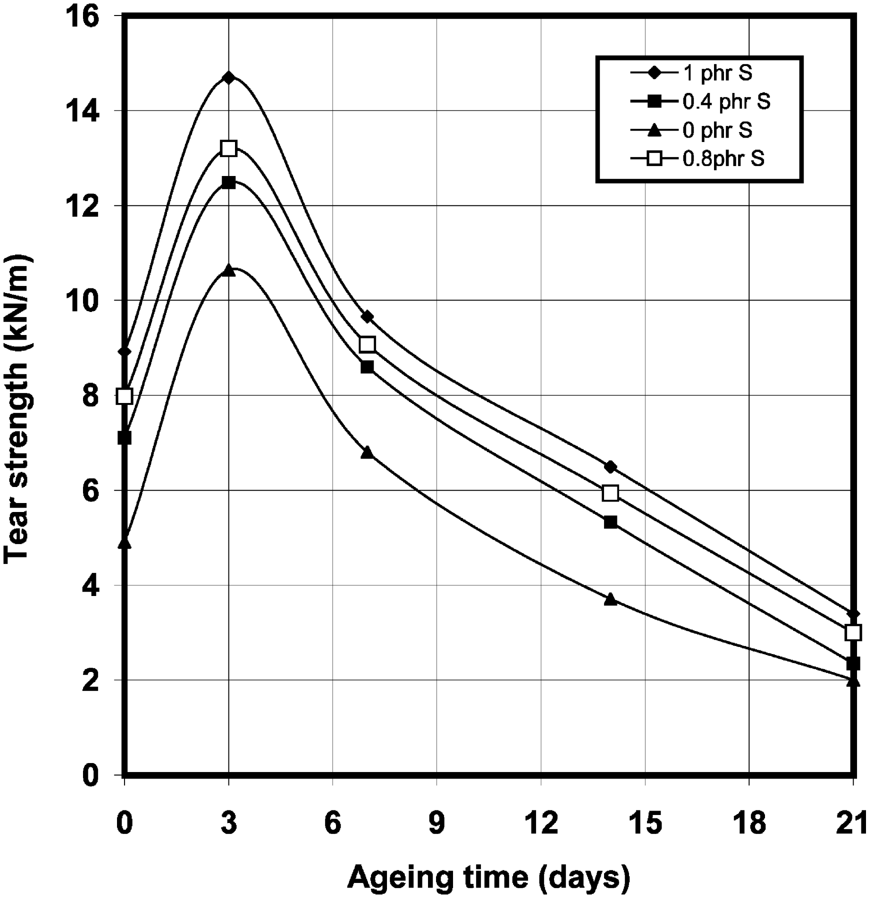

FIGURE 10 The effect of prolonged TOA on the tear strength of PVC/NBR TPEs.

was initiated in several planes before the formation of major crack. In contrast, the presence of sulfur has transformed the fracture surface into a rugged plane with extensive matrix tearing and without signs of secondary cracking. This can be considered as a manifestation of a high degree of curing. The absence of secondary cracks in Figure 12b suggests that this composition is not notch sensitive, which would be a plausible explanation for the superior elastomeric properties of the cured TPEs. This may provide some explanation for the differences in the physical and mechanical properties profile, that is, tensile strength, modulus, tear strength, and crosslink density of the cured blend as compared to the uncured blend. A similar observation on

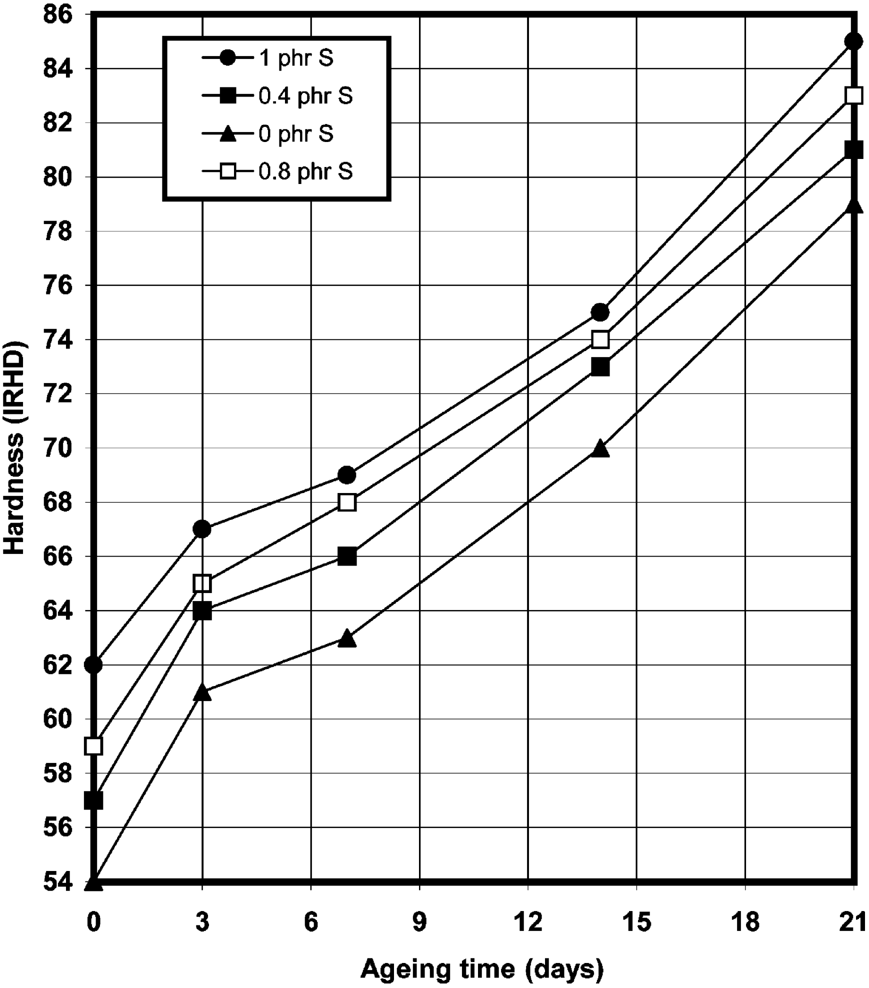

FIGURE 11 The effect of prolonged TOA on the hardness of PVC/NBR TPEs.

PVC/NBR and PVC/ENR blends was reported earlier [15,19]. Figure 12c shows the micrograph of aged cured PVC/NBR TPE at 1 phr sulfur loading. It can be seen that thermo-oxidative aging process has transformed the appearance of the fracture surface of the TPEs. The rather smooth fracture plane with limited extent of matrix tearing, provides a good indication that the samples fractured in a more brittle manner as compared to that of the unaged crosslinked counterpart shown in Figure 12b. This perhaps explains the lower elongation at break observed in the aged cured PVC/NBR TPEs shown in Figure 8.

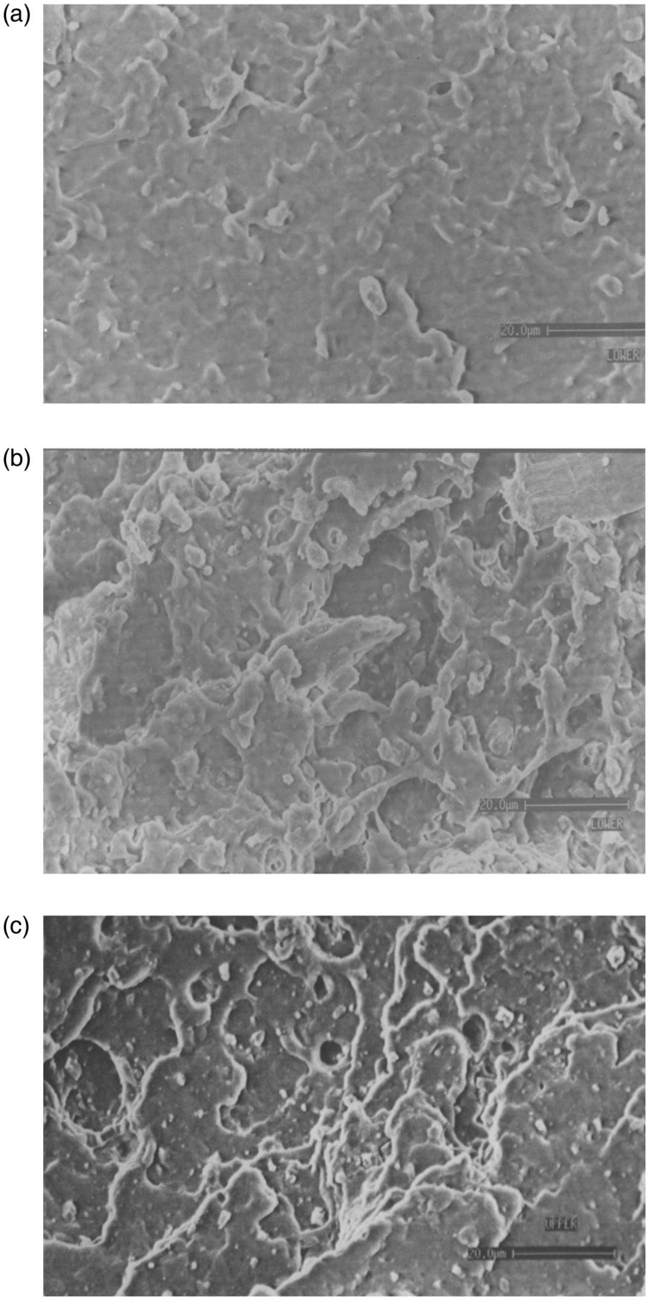

FIGURE 12 SEM micrographs of (a) uncrosslinked, (b) unaged, crosslinked PVC/NBR TPEs, (c) aged, crosslinked PVC/NBR TPEs.

CONCLUSIONS

The prolonged exposure of cured samples at elevated temperature has resulted in increases in mechanical properties until they pass through a maximum and reversion happens. This is related to an increase in crosslink density with ageing time, as indicated from the crosslink density and swelling ratio data, that is, overcure, which accounts for the deterioration of the intermolecular network structure. The volatile loss has been found to decrease with increase in sulfur loading. As for the uncured formulations, the plasticizer migration was cited to justify the increase in mechanical properties prior to failure. SEM micrographs reveal that some microstructural changes have occurred due to the thermo-oxidative ageing.

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