Ranking of Rubber Vulcanizates Used as Seals Based on Effect of Accelerated Aging

V. SUBRAHMANIAN,[1] S. GANAPATHY[2]

[1] Division of Rubber Technology, MIT Campus, Chromepet, Chennai 600 044, India

[2] Anna University, Chennai 600 025, India

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ABSTRACT: Technical properties such as hardness, tensile strength, ultimate elongation, and rebound resilience are popular in quality control, but the trend in these properties shows a generalized picture of the structure–property relations. Test specimens were aged in hot air by systematically varying the time and temperature from 24 to 96 h at 70 to 100°C. For an effective comparison the observed values were plotted as a function of time, temperature, and formulations. The data thus obtained were correlated with shelf-aging in particular cases, and it was observed that aging at 100°C for 24 h could be used for such formulations. A "sulfur donor" system cured nitrile-butadiene rubber (NBR) vulcanizate and an ethylene-propylene-diene (EPDM) vulcanizate showed the best retention of properties. Although the SEM micrograph of the NBR was in agreement with this observation, the EPDM was not. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 2500–2510, 2000

Key words: rubber seals; formulations; aging; technical properties

INTRODUCTION

Tensile properties often are listed in rubber formulations used as seals. Even though these properties have more value in quality control purposes such as the state of cure and process control, the structural changes due to aging can be understood from the trends of these properties. Such an approach based on rebound resilience, stress relaxation, and so forth were discussed in our earlier article.[1] In another article the tensile stress–strain properties were used to deduce Mooney–Rivlin plots and the corresponding constants under nonequilibrium conditions.[2] In the present article a systematic approach of aging is used and the results are discussed. An SEM study and correlation with shelf-aging data in specific cases are also discussed.

EXPERIMENTAL

The formulations are given in Table I. These formulations were studied previously.[1] For the present study, the compound N_3 was replaced by NC. The compound N_3 was replaced by a blend of acrylonitrile-butadiene rubber (NBR) and polychloroprene rubber (NC). The standard test specimens were prepared and tested as discussed in our earlier work.[1] In addition, the specimens were subjected to aging at 70–100°C for durations of 24–96 h. To represent the observed data in place of tabulated values and for better clarity in respect to the trends in the experimental values, graphical illustrations are used. Grapher version

Correspondence to: V. Subrahmanian (vsubbu@mail.mitindia.edu).

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Table I Compound Formulations (phr)

Ingredient	N_1	N_2	N_3	N_4	EPDM	NC
NBR 34.50[a]	100.0	100.0	100.0	100.0	0	50.0
Herlene 502[b]	0	0	0	0	100.0	0
Neoprene W[c]	0	0	0	0	0	50.0
Sulfur	0.5	0.2	1.0	0	1.2	0.3
Zinc oxide	5.0	5.0	5.0	4.0	5.0	3.0
LC MgO	0	0	0	0	0	4.0
Stearic acid	1.0	1.0	1.0	0.5	1.0	0
SP oil	0	1.0	0	0	0	0
CI resin	3.0	5.0	5.0	3.0	0	0
HAF	0	70.0	0	55.0	70.0	0
SRF	50.0	0	40.0	0	0	35.0
DOP or DBP	10.0	15.0	10.0	8.0	0	3.0
Naphthenic oil	0	0	0	0	20.0	0
Antioxidant A[d]	0	0	1.0	1.0	0	1.0
Asbestos fiber pulp[e]	20.0	0	0	0	0	0
MBT	0.5	1.0	2.5	0	1.5	0
TMTD	1.5	2.5	0	3.5	1.0	2.0

[a] Acrylonitrile butadiene rubber; 34% ACN, 50 ML (1 + 4) 100°C.
[b] Ethylene-propylene-diene rubber; ENB = 4, ML (1 + 4), 125°C = 54 and E/P = 67/33.
[c] Polychloroprene rubber; ML 100°C (2.5′), 45–54.
[d] Mixed aryl *p*-phenylene diamine.
[e] Rubber grade.

3.00 and Plot version 2.01 were employed. The SEM was obtained on tensile fractured specimens using a Hitachi S-450 SE microscope operated at 10 kV. The samples were coated with gold to a thickness of 150 Å, an amount adequate to make them conductive using a Hitachi HUS-50B vacuum evaporator. The areas showing the typical characteristics were photographed.

RESULTS AND DISCUSSION

Hardness and Unaged Properties

Figure 1 shows that NC retains ulmost unchanged hardness, irrespective of the aging duration and temperature. Ethylene-propylene-diene (EPDM) and N_4 follow NC in that order. The N_2 shows a considerable increase in hardness, and it is less preferred. Hardness, which is a measure of the state of cure, is well under control in the NC, probably because of the benefit from the polychloroprene rubber being present.

The attempt to optimize the formulations in respect to original tensile strength, ultimate elongation, and resilience (Fig. 2) resulted in the ranking (1) EPDM, (2) N_4, (3) N_2, (4) NC, and (5) N_1. This was applicable to ambient conditions (here unaged). The criteria of this ranking were moderate tensile strength and elongation and high resilience. The figure also shows that the HAF present in N_2 and N_4 imparts high tensile strength, which is normally expected in an amorphous rubber.

Tensile Strength

Figures 3 and 4 show that N_4 is the best choice to ensure better retention of the tensile strength, irrespective of aging time and temperature. It is followed by NC, N_1, EPDM, and N_2 in that order. As recommended, the above conclusions were drawn based on four sets of data.[3]

The following conclusions could be drawn from Figure 5. Figure 5(A) indicates that the method of representing the aging by the percent change in a given property is a good indicator. The inherent quality of the individual formulations of this nature is also clearly evident from the trend.

The relative merits of the formulations are well illustrated at a high temperature of aging. It implies that aging at high temperatures is dependent upon the type of mix.

Figure 5(D) shows that under a given set of conditions, N_4 undergoes the least variation, be-

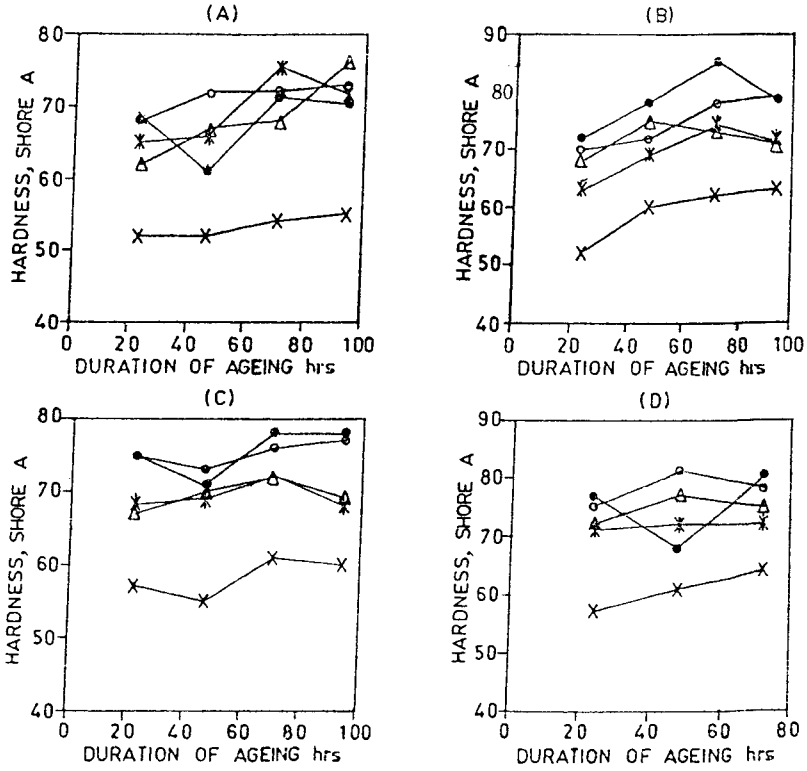

Figure 1 The duration of air aging vs the hardness at (A) 70, (B) 80, (C) 90, and (D) 100°C.

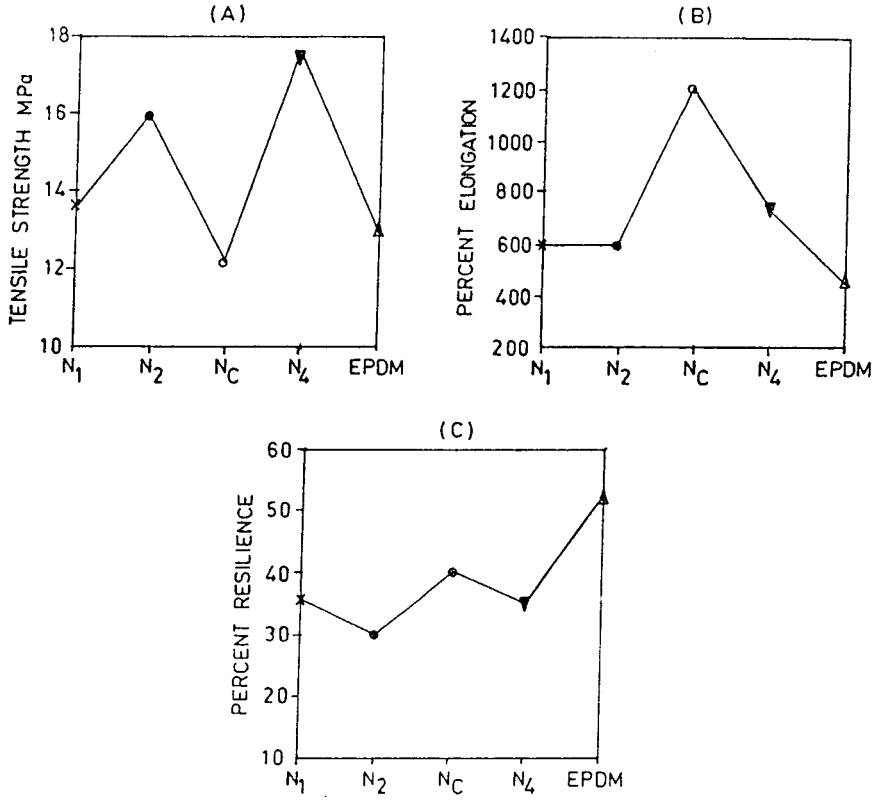

Figure 2 The properties before aging (original): (A) tensile strength (MPa), (B) ultimate elongation, and (C) rebound resilience.

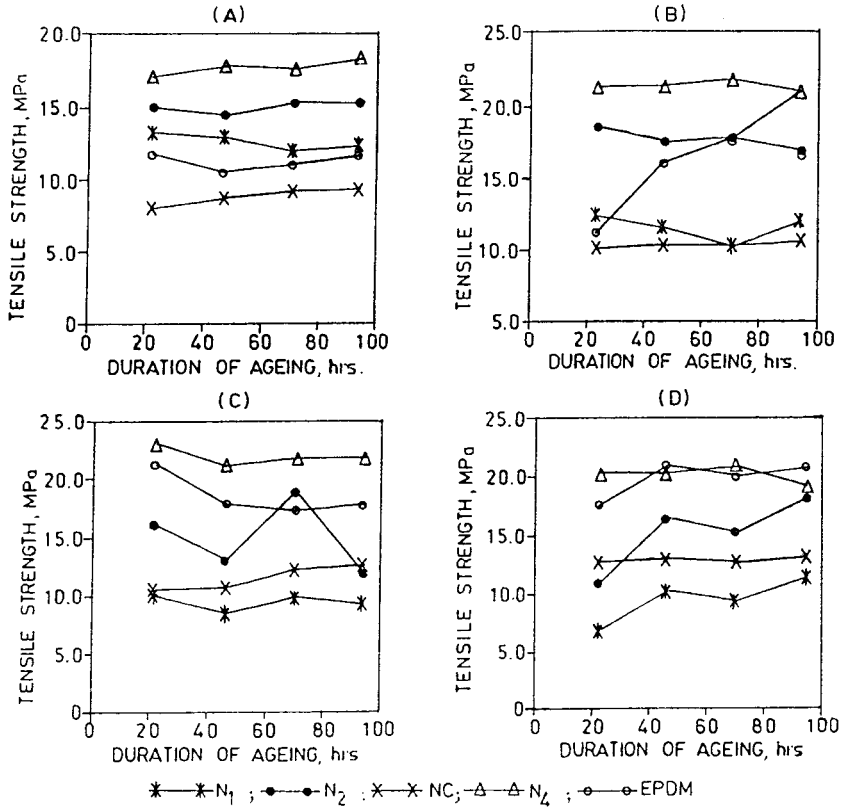

Figure 3 The duration of air aging vs the tensile strength at (A) 70, (B) 80, (C) 90, and (D) 100°C.

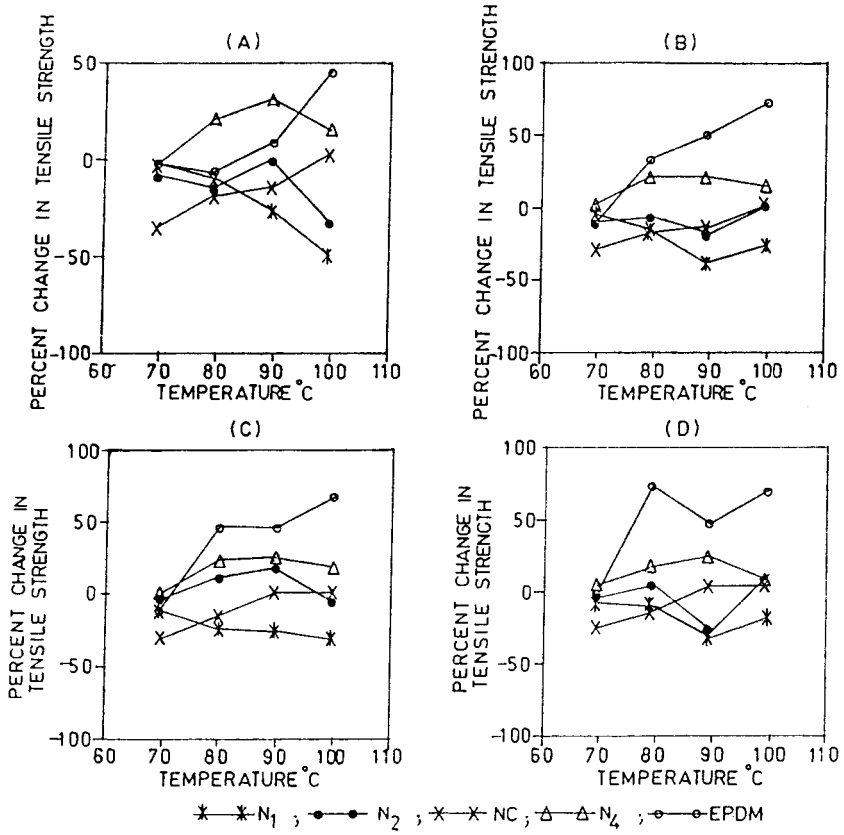

Figure 4 The temperature of aging vs the percent change of the tensile strength for (A) 24, (B) 48, (C) 72, and (D) 96 h.

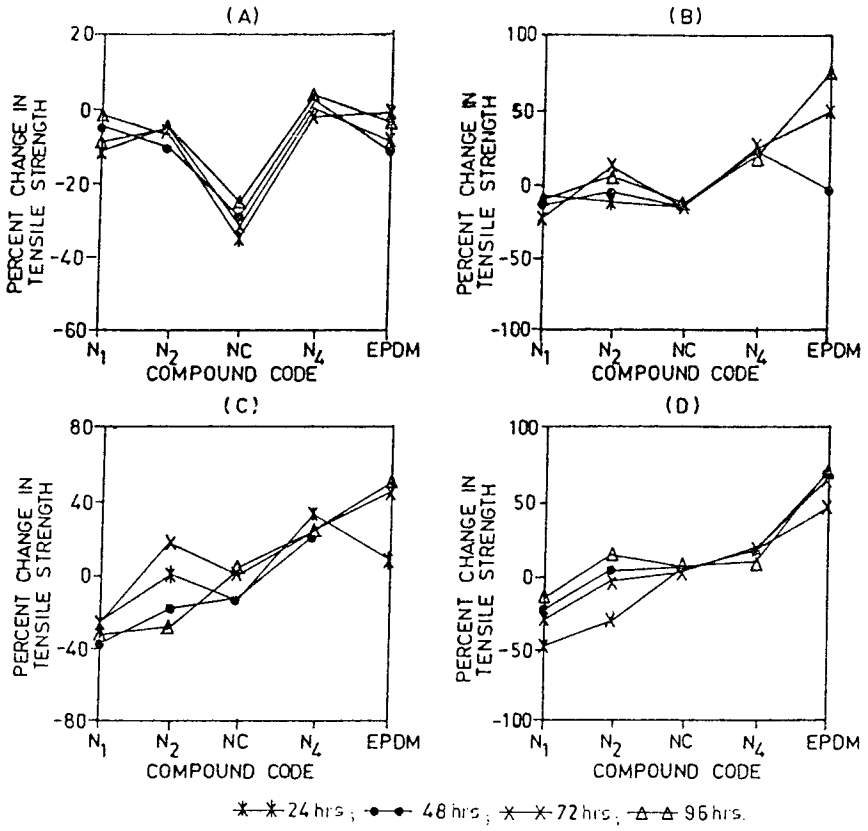

Figure 5 The formulation vs the change in the tensile strength for aging at (A) 70, (B) 80, (C) 90, and (D) 100°C.

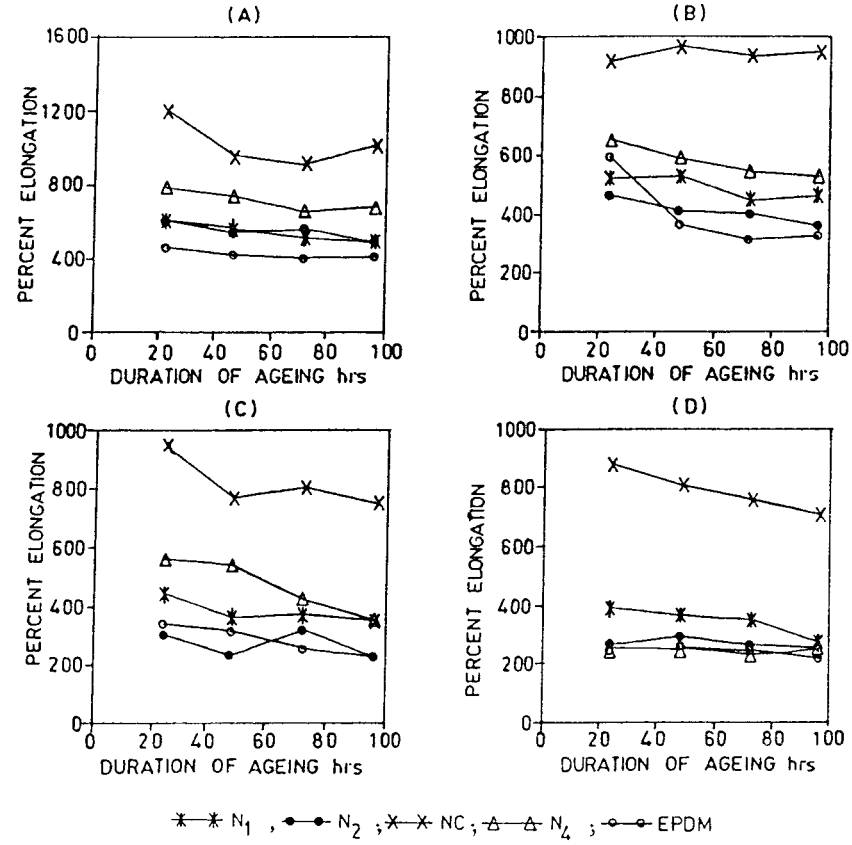

Figure 6 The duration of air aging vs the ultimate elongation at (A) 70, (B) 80, (C) 90, and (D) 100°C.

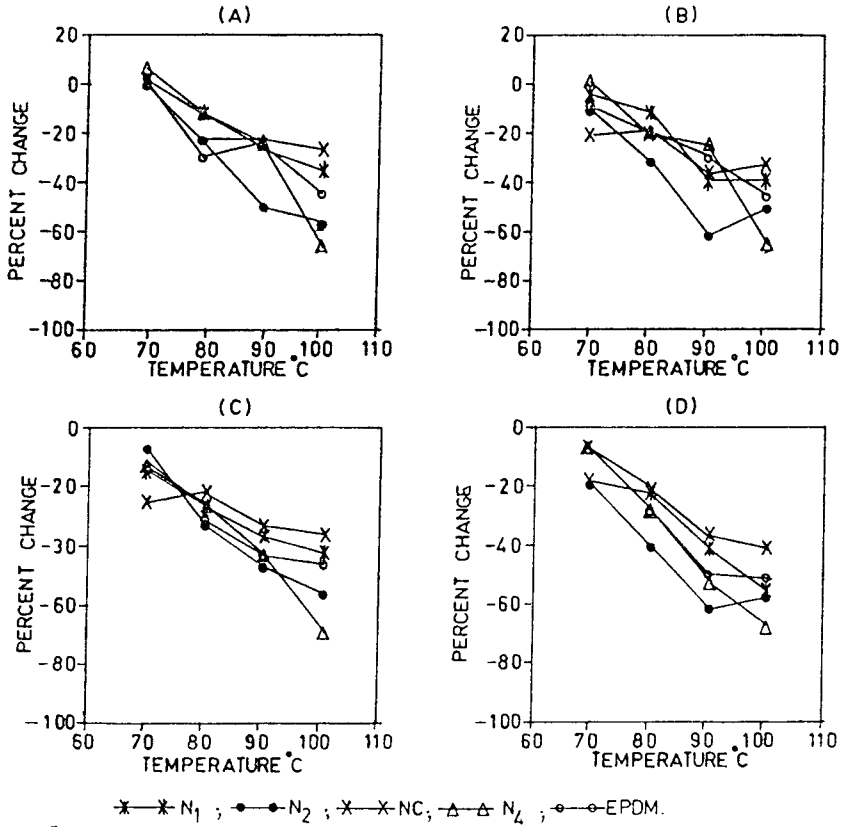

Figure 7 The temperature of aging vs the percent change of the ultimate elongation for (A) 24, (B) 48, (C) 72, and (D) 96 h.

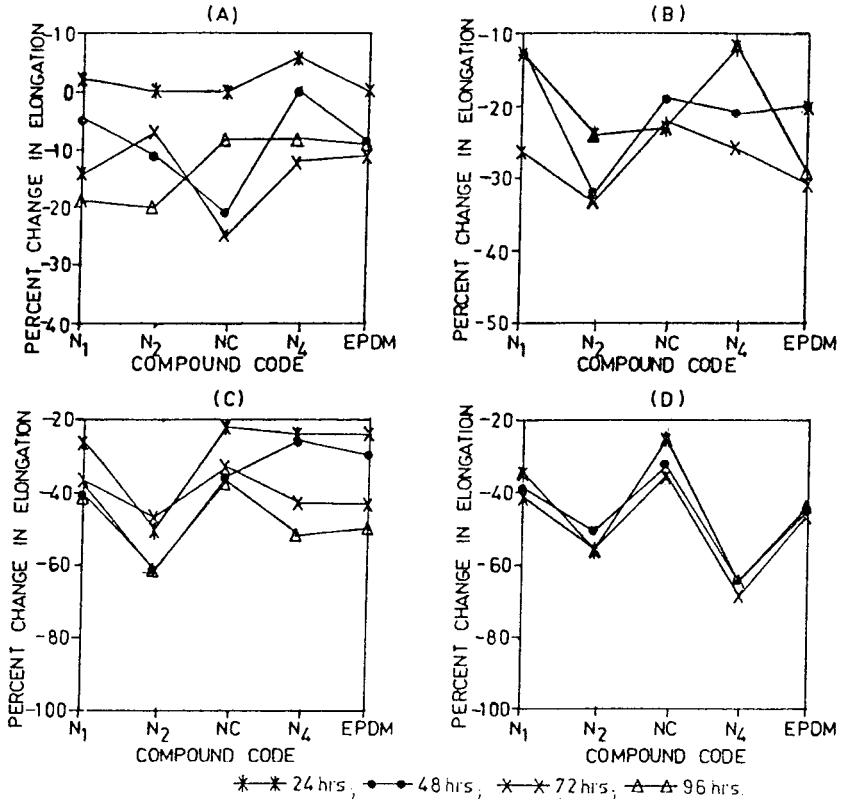

Figure 8 The formulation vs the change in the ultimate elongation for aging at (A) 70, (B) 80, (C) 90, and (D) 100°C.

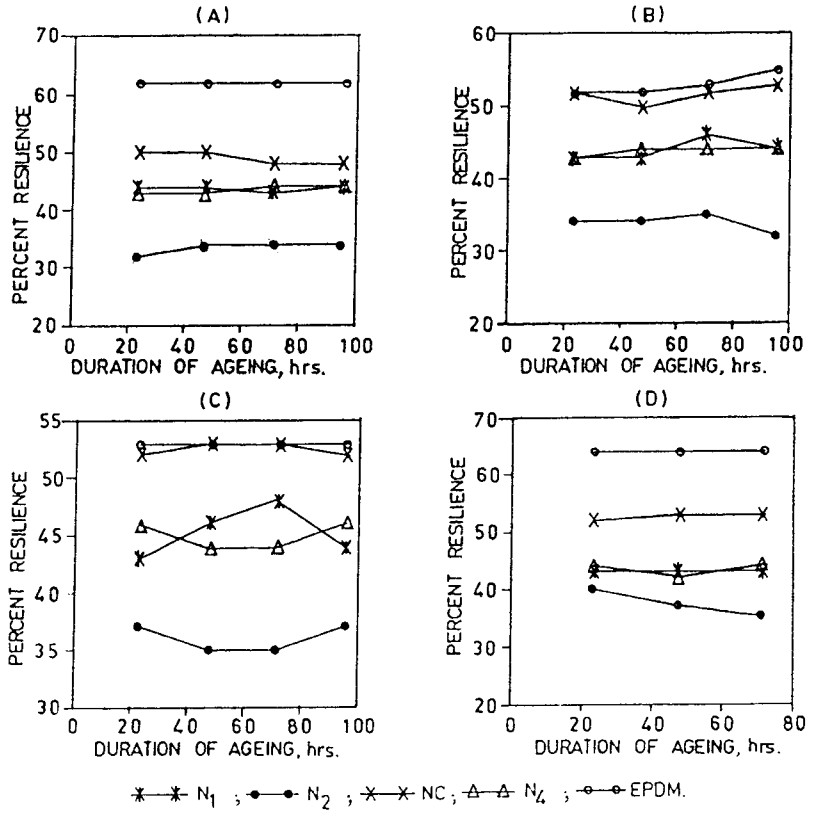

Figure 9 The duration of air aging vs the resilience at (A) 70, (B) 80, (C) 90, and (D) 100°C.

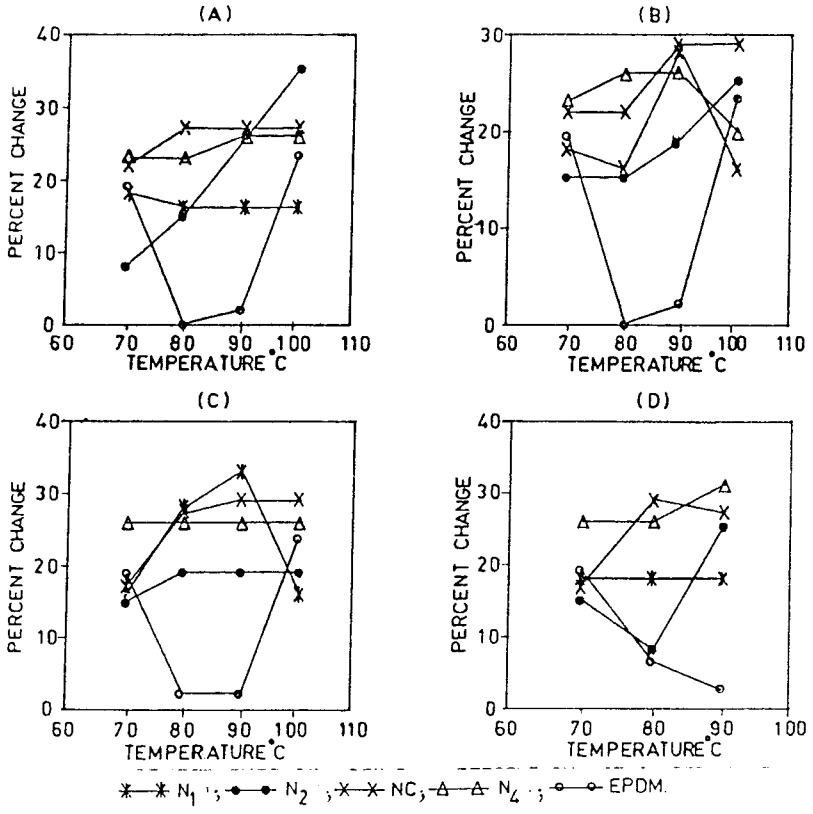

Figure 10 The temperature of aging vs the percent change of resilience for (A) 24, (B) 48, (C) 72, and (D) 96 h.

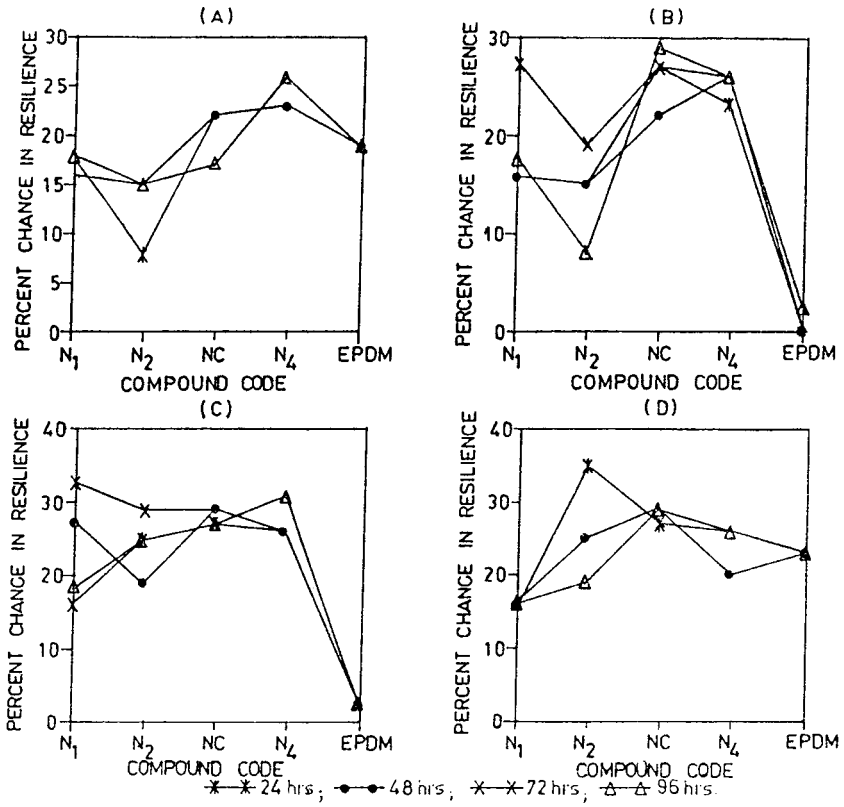

Figure 11 The formulation vs the change in the rebound resilience for aging, at (A) 70, (B) 80, (C) 90, and (D) 100°C.

cause it is based on a "sulfur donor only" curing system. This proposition is further confirmed by the ductile fracture as shown by the SEM micrographs (see discussion that follows).

Ultimate Elongation

Figure 6 shows that, unlike the tensile strength, there is no abnormal fall in elongation if the values are represented as shown. However, in case a minimum of 500% is demanded, then NC, N_1, and N_4 would pass but not N_2.

Figure 7, which is similar to Figure 5, is useful in its own respect. All test formulations show a decline in elongation, irrespective of temperature and time. Here is another clear case of a better illustration of hardening. A high degree of crosslinking leads to low elongation because of interference with the chain alignments and uniform load distribution.[4]

A wide variation of individual formulations is noted in Figure 8(A–C). This trend is in contrast to what is observed for the tensile strength (Fig. 5). However, here aging at 100°C also gives a good picture of the relative merit of the individual formulations. Further, it may be noted that any mix other than N_4 is preferred for conditions that demand little change in elongation.

In sum, it may be concluded that tensile strength and elongation give a good picture of the aging process in their own respect. Because each one is expected to be a function of different molecular features, they need not necessarily show identical results. It is further supported by the lack of correlation between these two properties. Only in some cases (N_1 and N_2) was a positive correlation at around 0.99 noticed in this study.

Rebound Resilience

The resilience data shown in Figure 9 reveal that each mix maintains constant resilience, irrespective of aging time and temperature.

Based on the percentage change of resilience (Fig. 10), N_1 is seen to be an ideal choice. But the retention values (fig. 4.10 in Ref. 1) indicate that N_1 is less preferable. The deviation is probably

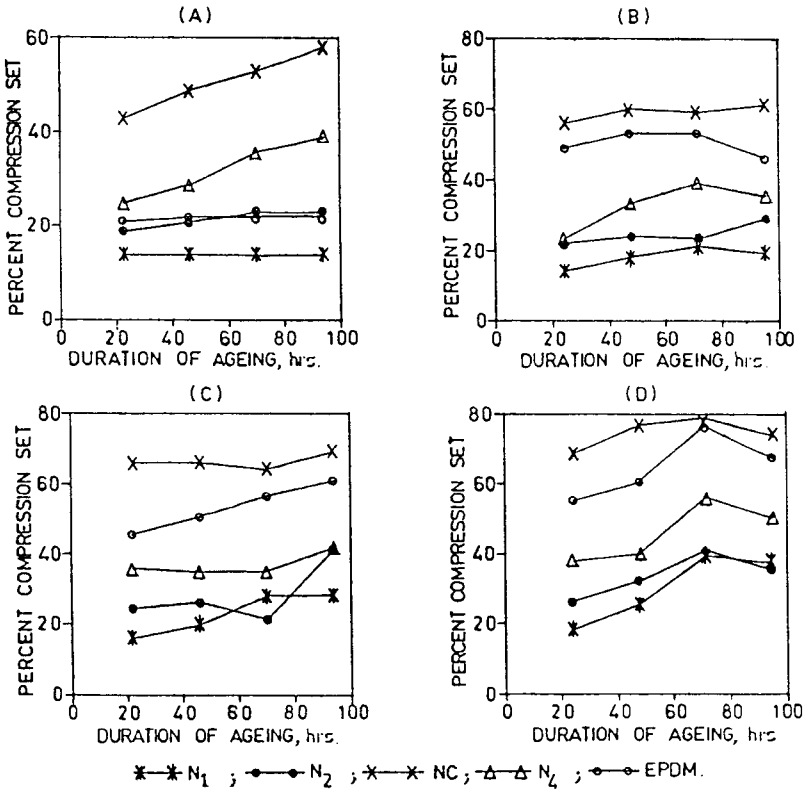

Figure 12 The duration of air aging vs the compression set at (A) 70, (B) 80, (C) 90, and (D) 100°C.

due to the difference in the intensities of aging and hence a generalized conclusion is unlikely.

Figure 11 probably gives a better picture. Similar to Figures 9 and 10, a better distinction of the formulations is possible for aging at 100°C [Fig. 11(D)]. Another noticeable observation is that the aging duration has a similar effect on all compounds. So, for service conditions equal to the aging process for 24–96 h of aging at 70, 80, and 90°C, follow-up of resilience is useful. Similar to elongation (Fig. 8), Figure 11 shows that the least preferred is the N_4. The most preferred is either EPDM or N_2. This observation concurs with the view that ethylidene-norbornene–EPDM has good retention of properties[5] when aged at 100–180°C for 24–72 h.

Compression Set

The behavior of vulcanizates in the compression set test was expected to be different from other properties because of the additional influence from the imposed mechanical stress. This is in spite of the fact that lab testing is generally dominated by thermooxidative degradation.[6] From the Figure 12 it is seen that the change in set value due to duration of aging at 70–100°C is the least for NC. A similar conclusion was drawn for the hardness and elongation.

Correlation to Shelf-Aging

Unpublished data of N_1 and N_4 aging for periods of 2.5 and 13 years show an interesting trend in the tensile strength and ultimate elongation [Fig. 13(A, B)]. If comparison is made with unaged values, maxima are seen for the tensile strength of N_1 and the ultimate elongation of N_4 while minima are seen for the elongation of N_1 and the tensile strength of N_4. The retention values and percentage change from the unaged values show similar trends.

From these figures the following can be seen over the period of 13 years: the N_1 reduction in tensile strength is 44% and the N_4 reduction in elongation is 53%.

The following conclusions were drawn by correlating the data with accelerated aging. The accelerated aging conditions that cause a reduction in tensile strength by 44% in the N_1 and the

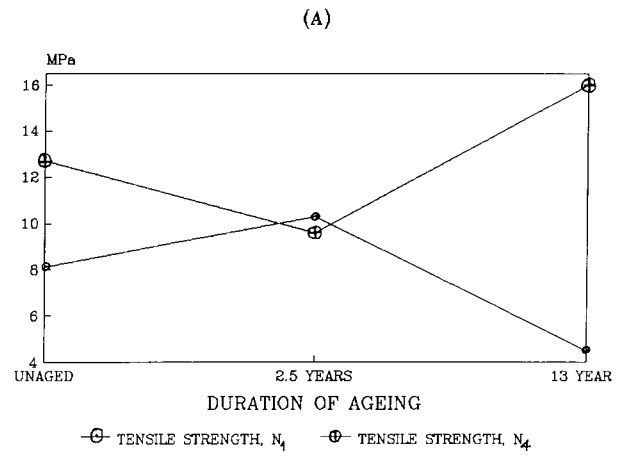

Figure 13 Shelf-aging data of N_1 and N_4 for the (A) tensile strength and (B) ultimate elongation.

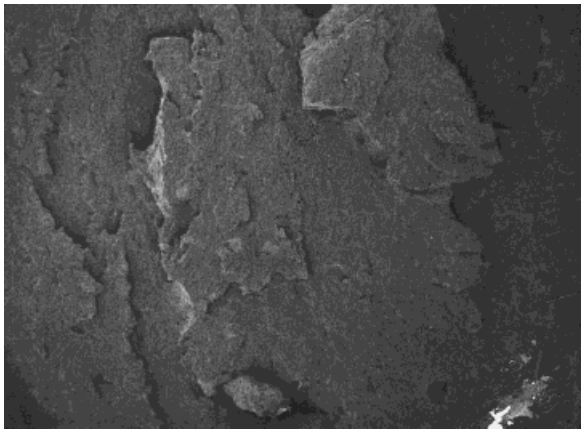

Figure 15 SEM fractography of a tensile fractured specimen of N_4 after aging at 100°C (original magnification ×100).

ultimate elongation by 53% in the N_4 could be equated to 13 years of shelf-aging in respective cases. This trend agrees with the reported observation on shelf-aging of similar vulcanizates.[7] Accelerated aging at 100°C for 24 h (minimum) for N_4 (Fig. 5) and at 100°C for 24 h for N_1 (Fig. 8) indicate that these tests correspond to shelf-aging of 13 years of similar formulations.

SEM Fractography of Tensile Specimens and Role of Aging

Due to inherent heterogeneities and flaws present in the rubber vulcanizates, it is often difficult to corroborate the technical properties with SEM features. However, the SEM fractographs that

Figure 14 SEM fractography of a tensile fractured specimen of N_1 after aging at 100°C (original magnification ×100).

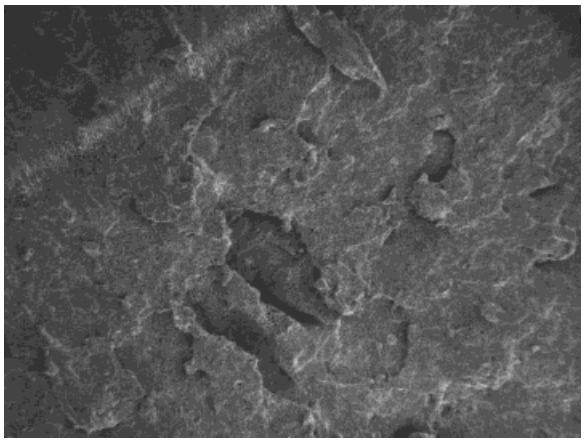

Figure 16 SEM fractography of a tensile fractured specimen of N_4 after aging at 100°C (original magnification ×500).

Figure 17 SEM fractography of tensile fractured specimen of EPDM after aging at 100°C (original magnification ×500).

provide understanding of the properties are presented here based on literature references.[8,9] Further, it was expected that 96 h of accelerated aging imparts greater and permanent variations in the micrographs and they are discussed here.

Aging of N_1

Aging at 100°C (Fig. 14) results in permanent cracks and holes. This kind of observation can be attributed to the lack of molecular cohesion resulting in poor sealing ability of weak sites and the brittle fracture. The contributions from both are likely, because the base polymer lacks cohesive strength and there is a loss of elongation as seen in Figure 8.

Aging of N_4

Figure 15 is of the unaged case and shows a highly rough surface and the marked presence of flow lines along the failure direction. Such features are not apparent in the preceding mixes.

A clear case of ductile fracture even after aging at 100°C is seen in Figure 16. This concurs with Figure 5. There is no sign of cracks or delamination. The presence of pits perhaps indicates the inherent nature of the vulcanizate, namely, its limited cohesive strength.

Aging of EPDM

The lack of molecular cohesion and the limited scope of compression molding in improving it are apparent in this mix as also seen in Figure 17. However, distinct features of embrittlement such as cracks and tear lines due to aging are not evident. This is in spite of the fact that all of the pictures were taken at higher original magnifications (200× or 500×) as compared to other formulations.

At the same time, the physical properties discussed so far (at least in the ultimate elongation and tensile strength) show the clear trend of this mix that it has good retention of unaged values.

Therefore, a logical conclusion in the aging of EPDM is that the application of the SEM study requires that the vulcanizates be prepared in injection molding. This is likely to remove the uncertainties such as poor molecular cohesion and so forth.

CONCLUSION

The graphically represented accelerated aging data present a clear trend for the rubber seal formulations based on the percentage change and retention values. Only in some cases of the tensile fractured specimens could there be a correlation between the structure–property of the vulcanizates. Shelf-aging data did not produce identical trends in tensile strength and elongation values; such observations were not clearly made in the accelerated aging data.

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