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ROLE OF PNB ANTIOXYDANT ON MECHANICAL PROPERTIES AND NETWORK STRUCTURE OF AGED TYRE TREAD RUBBER

INTRODUCTION

All services which require rubber impose specific requirements for mechanical properties. During service number products are subjected to either cyclic mechanical strain as in the case of running tyre or high ambient temperature, which accelerates oxidative degradation of rubber and results in the deterioration of its properties.

Many authors [1 - 5] have investigated the influence of aging on the physical properties of natural rubber. However, dynamic mechanical properties of aged rubber have not been investigated in details. Thermo-oxidative aging of rubber is believed to occur in two ways, either via main chain scission [6 - 9] or crosslink scission [10, 11]. This may affect the structure of the network. In order to control the effects of rubber aging, either wax or chemical stabilizer is added. Wax film are inadequate in dynamic application due to film breakage. In contrast, chemical stabilizers are more effective and can be used in dynamic applications. Many compounds have been claimed as chemical antioxydants and nearly all are nitrogen containing materials.

The objective of the present study is correlate the changes in tensile properties, tear and fatigue resistance, heat build-up, tangent delta, elastic modulus and abrasion resistance of natural rubber (NR) vulcanizates during aging with the changes in their network structure. The parameters included in this study are the effect of antioxydant and the effect of reinforcing carbon black.

EXPERIMENTAL

Four vulcanizates were prepared from a single bale of NR (ISNR-5) according to the formulations given in Table 1. Mixing was done in the two-roll laboratory mill. Curing characteristics of composites were eva-

luated by a Monsanto Rheometer (R 100) at 150°C. Vulcanization was carried out at 150°C in an electrically heated press for their respective optimum cure times. Test specimens for heat build-up measurements were cured 5 min. longer to take care of the thickness. Mouldings were

Table 1

Formulation of the Mixes and Curing Characteristics

Formation	G_0	G_1	F_0	F_1
NR[a]	100	100	100	100
Zinc oxide	5	5	5	5
Stearic acid	2	2	2	2
PBN[b]	–	1	–	1
N 330, HAF black	–	–	50	50
Process oil	–	–	5	5
CBS[c]	1	1	1	1
Sulphur	2.5	2.5	2.5	2.5
Maximum cure, (dN-m)	8.0	7.9	4.6	4.6
Optimum cure, (dN-m)	7.3	7.2	4.2	4.1
Optimum cure time t_{90}, (min)	12.5	12.0	8.5	7.5
Reversion time, (min)	11.0	12.5	8.5	9.0

[a] Crumb rubber ISNR-5 grade, obtained from the Rubber Research Institute of India, Kottayam.
[b] Phenyl-2-naphtylamine (Accinox DN) Alkali and Chemical Corporation of India Ltd., Rishra.
[c] N-cyclohexyl-benzothiazyl sulphamide (Accicure HBS) – Alkali and Chemical Corporation of India Ltd., Rishra.

quenched quickly in water at the end of the curing cycle and after a conditioning period of 24 h, tensile and tear test specimens were cut from the 2.0+0.1 mm thick sheets along the grain direction.

Aging of vulcanizates

Unstrained vulcanizates were aged in hot air oven at 100°C according to ASTM 573-67 and ISO 188. The test pieces were withdrawn from the oven at different intervals and after conditioning for 24 h, were tested for physico-mechanical and chemical properties.

Determination of technical properties

Tensile properties were determined according to ASTM D412-80 using the C-type dumb-bells. Tear resistance was evaluated according to ASTM D624-81 using the 90° angled tear test pieces (die C). Both the tensile and tear tests were carried out using a Zwick UTM 1445 tensile testing machine. The speed of extension of the specimen was adjusted to 500 mm/min and the temperature of testing was 20°C.

Fatigue to failure test was done using the Monsanto Fatigue to Failure tester. Dumb-bell samples were subjected to a repeated strain cycle by extension (100% elongation) and cycle frequency was 100 rpm.

Compression fatigue test was carried out using the Goodrich Flexometer according to ASTM 623-81. The cylindrical samples of 2.5 cm height and 1.8 cm in diameter was preconditioned at the oven temperature at 50° for 20 minutes. After measurement of heat build-up of the test specimen the sample was taken out, cooled to room temperature and the thickness measured after one hour. The temperature rise ($^{\Delta}T$) at the end of 20 minutes stroke was taken as the heat build-up.

Dynamic mechanical properties

The dynamic mechanical properties of the samples were measured by using an automatic dynamic viscoelastometer, Rheovibron, model DDV-III-EP. The test were carried out from −100°C to +100°C. Moulded samples of dimensions 50×10×4.3 mm were used for testing at a strain amplitude of 0.025 mm and at frequencies of 11 Hz. The heating rate was 2°C/min.

Abrasion resistance was evaluated according to BS 903 Pt. 49 1957, Method C by the Croydon-Acron abrasion tester. The angle between the test specimen and the abrasive wheel was kept constant at 20°C.

Determination of concentration of chemical crosslinks

Vulcanizate samples weighing 0.2—0.3 g were allowed to stand in an excess of benzene for 48 h at 35°C. The swollen samples were weighed; the solvent was removed in vacuo and the sample weighed again. Values of V_r, the volume fraction of rubber in the swollen vulcanizate was calculated from the above measurements using the relations [12].

$$V_r = \frac{(D-FT)\varphi_r - 1}{(D-FT)\varphi_r - 1 + A_s o \varphi_s - 1} \quad (1)$$

where, T is the sample weight, F — the weight fraction of the insoluble components in the system, A_s — the weight of the absorbed solvent corrected for the swelling increment. φ_r and φ_s are the densities of rubber and solvent respectively $\varphi_r = 0.92$ g/cm³ for NR, $\varphi_s = 0874$ g/cm³ for benzene.

The values of V_r were converted into V_{ro} by means of the following equation for carbon black filled samples, which was derived from the data of Porter [13]

$$V_{ro}/V_r = 0.56 \exp(-Z) + 0.44 \quad (2)$$

where, Z is weight fraction of carbon black in the vulcanizate.

The elastic constant C_1 was then caluclated from the relation [14, 15].

$$\{1n(1-V_{ro}) + V_{ro} + XV_{ro}^2\} = 2GV_s(V_{ro} - V_{ro}/2)/RT \quad (3)$$

where X is a parameter characteristic of interaction between the rubber network at the swelling agent, V_s the volume of the swelling agent, R, the gas constant and T, the absolute temperature. X was assumed to the unaffected by the carbon black and probe treatments, and can be correlated to V_{ro} according to the relation [16].

$$Y = X_o + \beta V_{ro} \quad (4)$$

where $X_o = 0.44$ and $\beta = 0.18$ for NR benzene system. The C_1 value so obtained was converted into concentration of chemical crosslinks (2Mc, chem)$^{-1}$ using Mullins equation [17], which accounts for the contribution of chain and physical entanglements in the natural rubber vulcanizates.

$$C_1 = (\varphi RT(2Mc, chem)^{-1} + 0.78 \times 10^6) (1 - 2, 3 (Mc, chem) Mn^{-1}) \quad (5)$$

where φ is the density of the rubber network and Mn is the number average molecular weight of the rubber before vulcanization.

Determination of concentration of polysulfide crosslinks

Vulcanizate samples weighing 0.2 - 0.3 g were treated with a solution of 0.4 M propane — 2 — thiol and 0.4 M piperidine in n-heptane for 2 h at room temperature under nitrogen. The samples were then washed with petroleum ether (bp 40 - 60°C) and dried in vacuo. The polysulfidic crosslink were then obtained by difference from the values of total crosslink concentration (measured by volume swelling) before and after treatment [15].

Determination of amount of free sulphur, sulphide sulphur, and combined sulphur (Sc)

Free sulphur was determined iodometerically by converting it to sodium thiosulpnate acording to ASTM D297-72A. Sulphide sulphur was determined iodometrically from the formation of cadmium sulphide as described in BS902 Pt. 1310 - 1958.

The amount of combined sulphur (Sc) in the vulcanizate samples was obtained from the total sulphur content minus the amount of zinc sulphide sulphur and free sulphur [18].

RESULTS AND DISCUSSION

The physical properties of gum and filled vulkanizates for various aged samples with respect to the period of aging are given in Figures 1 - 10.

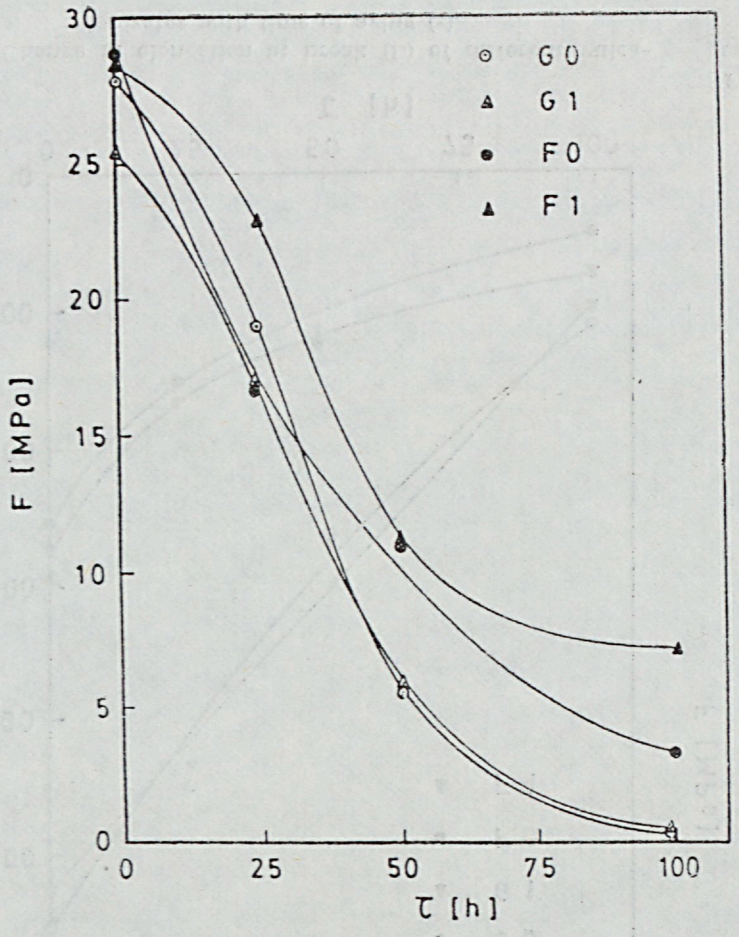


Figure 1. Change in tensile strength (F) of different vulcanizates with time of aging (τ)

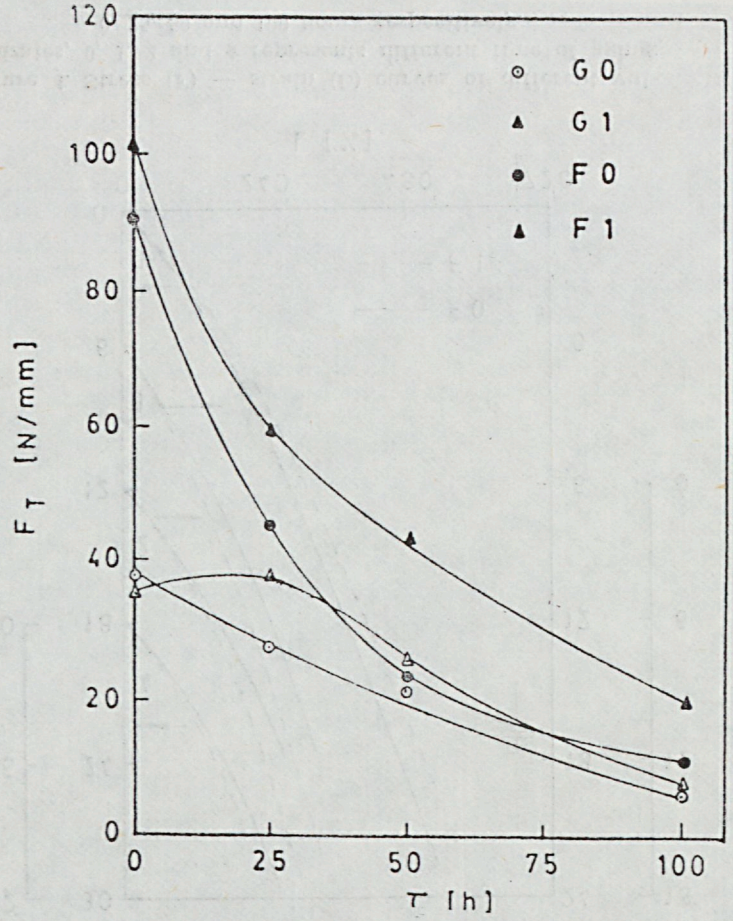


Figure 2. Change in tear ressistance (F_r) of different vulcanizates with time of aging (τ).

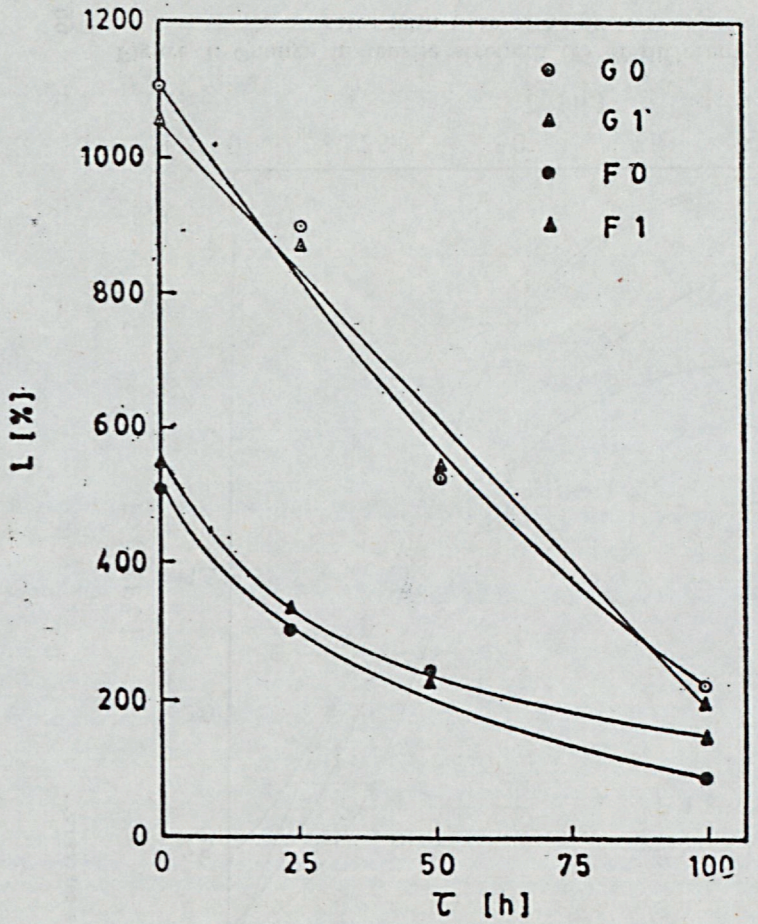


Figure 3. Change in elongation at break (L) of different vulcanizates with time of aging (τ).

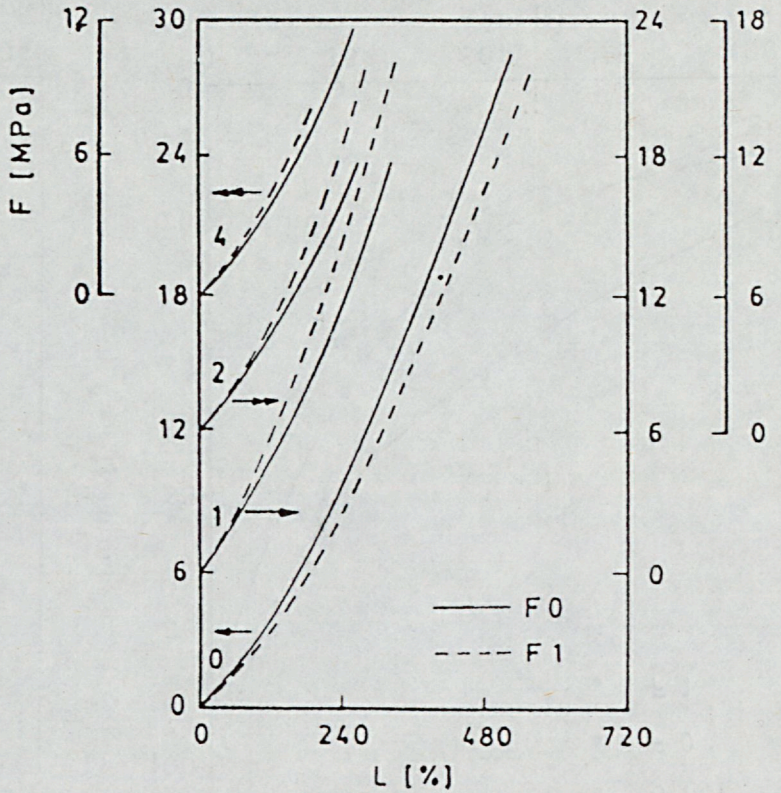


Figure 4. Stress (F) — strain (L) curves of different vulcanizates, 0, 1, 2 and 4 represents different time of aging: 0, 25, 50 and 100 hours respecitively.

Before aging, the vulcanizates without antioxydant have marginally higher tensile strength than those with stabilizer and the tensile strength of filled vulcanizates is higher than that of unfilled ones, as expected due to reinforcement by carbon black (Figure 1). Similarly the stabilizer and the carbon black increase the tear resistance of the rubber (Figure 2).

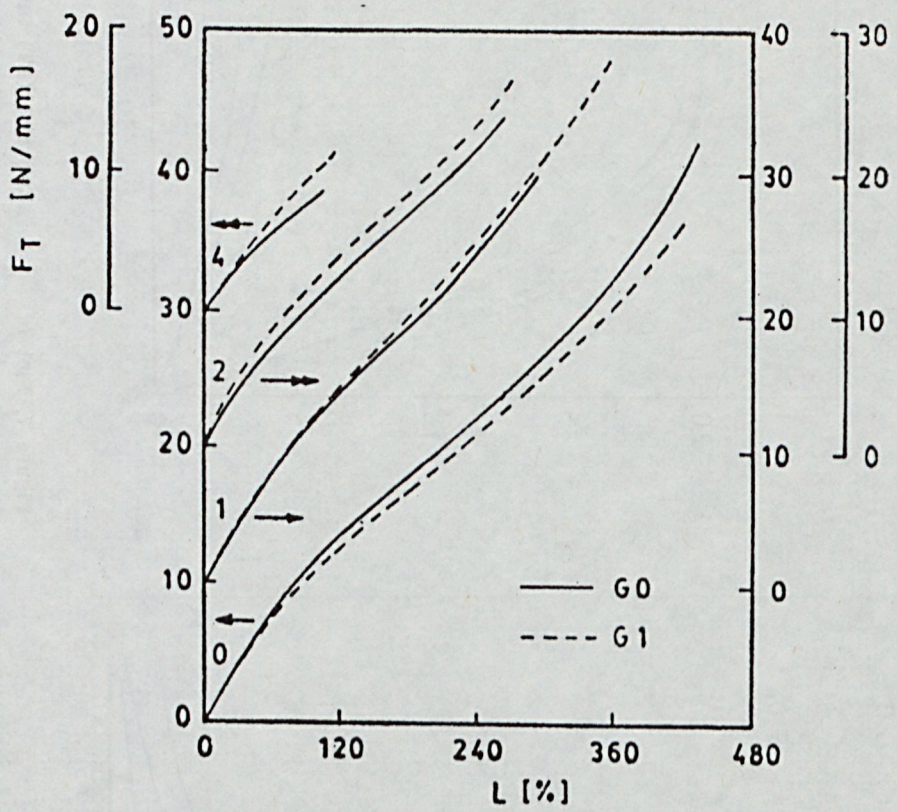


Figure 5. Plot of tear resistance (F_T) versus elongation (L) different vulcanizates. 0, 1, 2, and 4 represents different time of aging: 0, 25, 50 and 100 hours respectively.

With aging the tensile strength decreases and the decrease is less for vulcanizates with antioxydant. Carbon black filled compound shows pronounced effect. Similar results are observed for tear resistance. After 100 h of aging of samples without stabilizers the tear resistance of filled and unfilled samples were almost similar but the vulcanizates with PBN stabilizer have better resistance at all aging periods.

Plot of elongation at break vs. aging times (Figure 3) shows that the changes are also very marked. The rate of changes of elongation at break during aging is higher for gum vulcanizates as compared to the filled

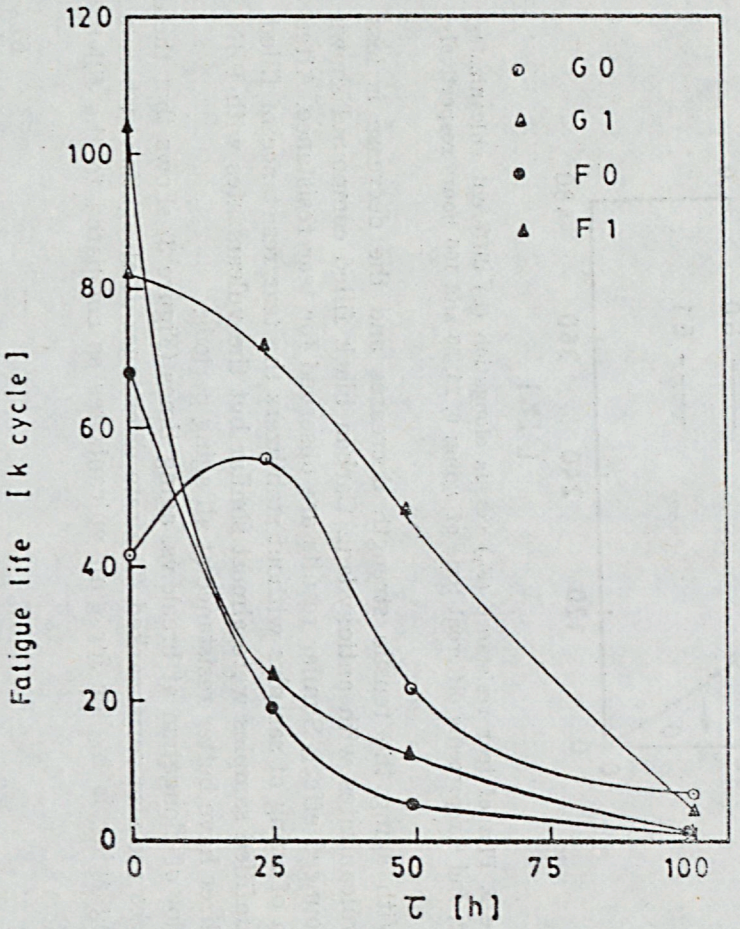


Figure 6. Change in fatigue life of different vulcanizates with time of aging (τ).

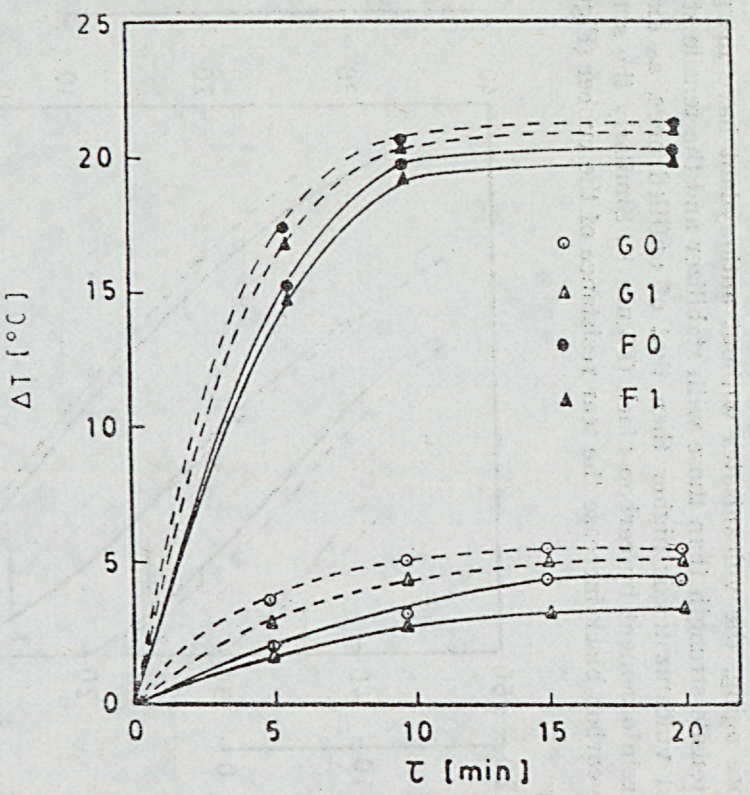


Figure 7. Plot of temperature rise (ΔT) in different vulcanizates versus time of heat build-up experiment (τ) : (——) unaged samples, (– – – –) samples aged for 100 hours.

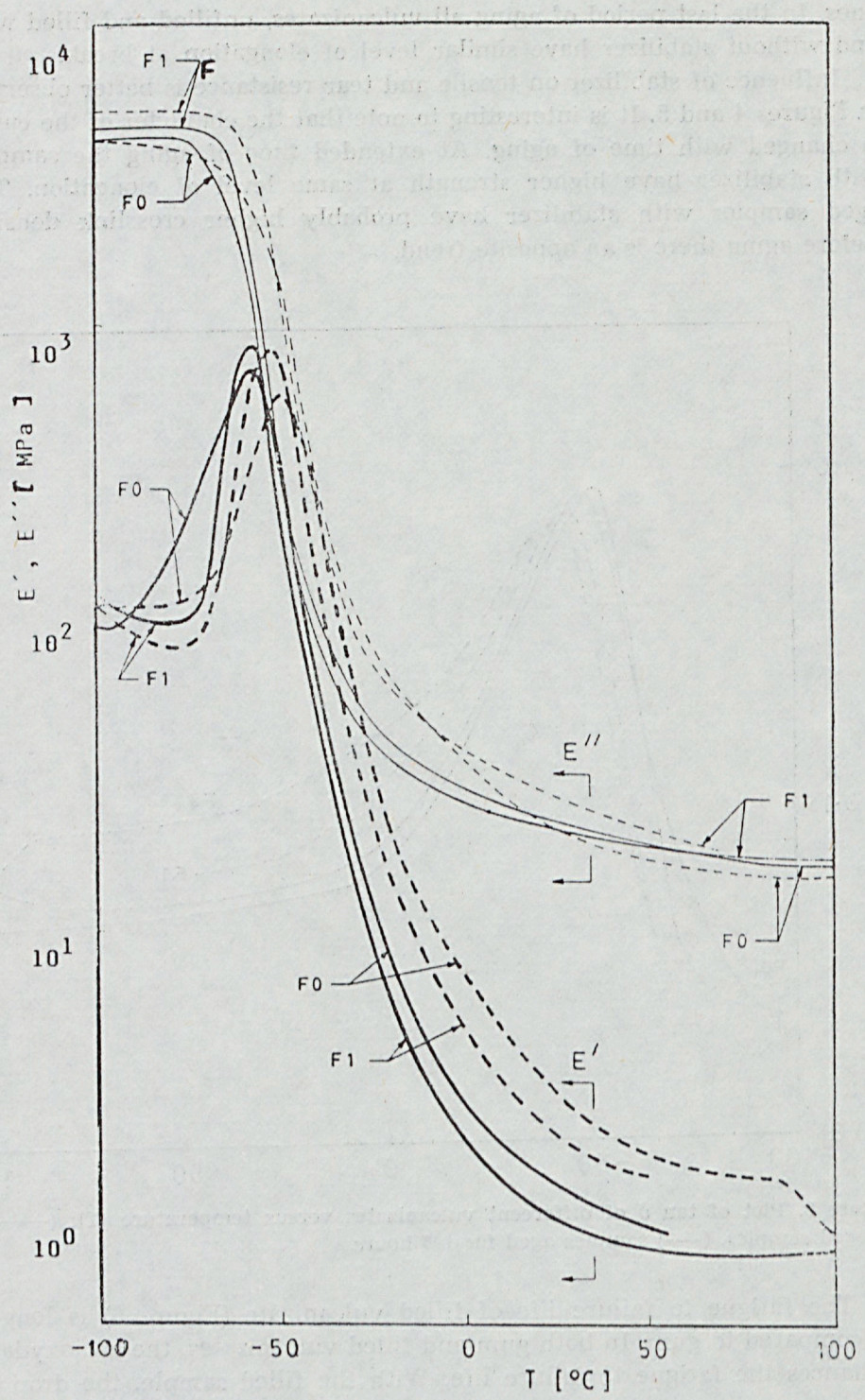


Figure 8. Plot of modulus E′ and E″ of different vulcanizates versus temperature (T): (———) unaged samples, (----) samples aged for 100 hours.

ones. In the last period of aging all vulcanizates, unfilled and filled with and without stabilizer have similar level of elongation at break.

Influence of stabilizer on tensile and tear resistance is better observed in Figures 4 and 5. It is interesting to note that the character of the curve is changed with time of aging. At extended time of aging the samples with stabilizer have higher strength at same level of elongation. The aged samples with stabilizer have probably higher crosslink density. Before aging there is an opposite trend.

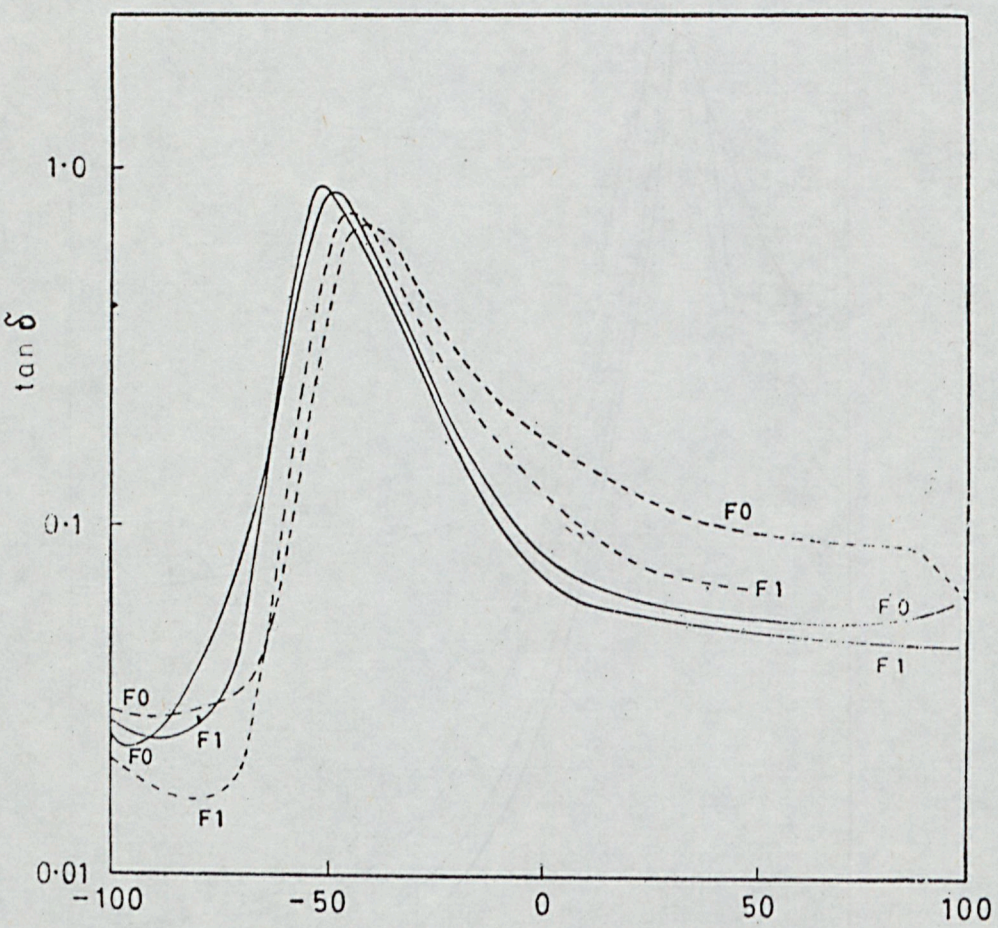


Figure 9. Plot of tan δ of differeent vulcanizates versus temperature (T): (———) unaged samples, (----) samples aged for 100 hours.

The fatigue to failure life of filled vulcanizate (Figure 6) is longer as compared to gum. In both gum and filled vulcanizates, the antioxydant enhances the fatigue to failure life. With the filled sample, the drop in

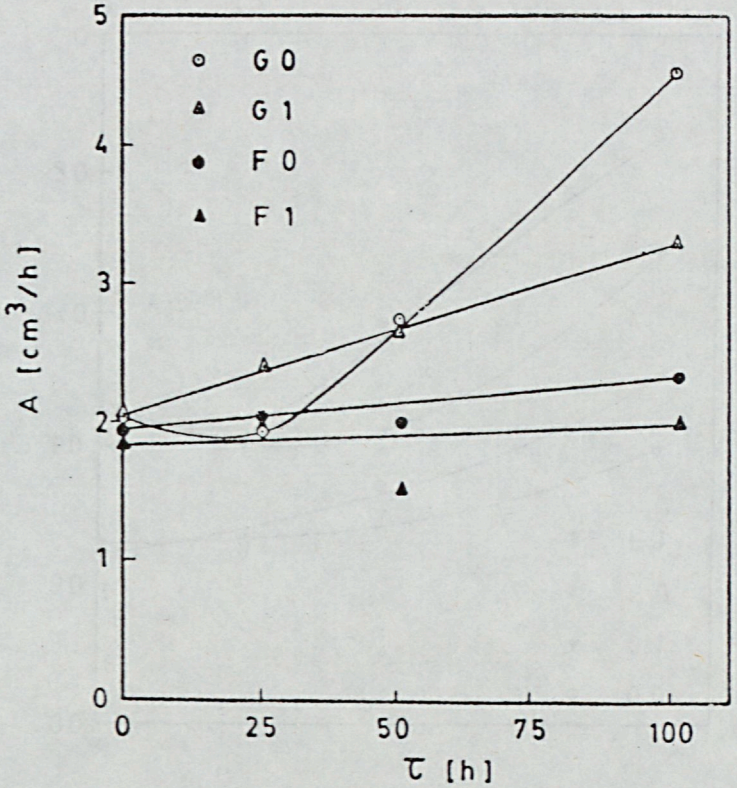


Figure 11. Change in crosslink density (Mc, Chem.)$^{-1}$ of different vulcanizates with time of aging (τ).

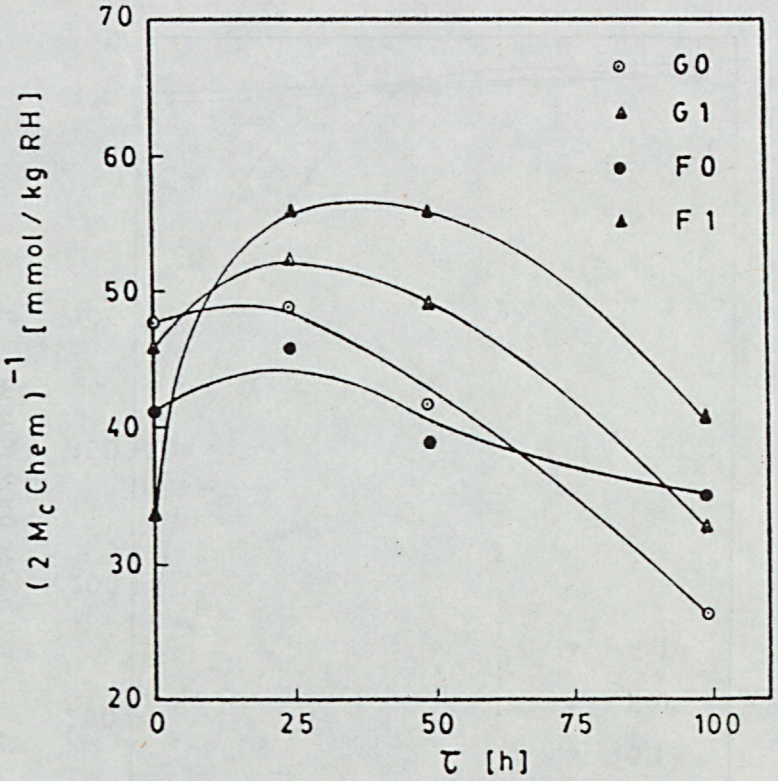


Figure 10. Change in loss of abrasion (A) of different vulcanizates with time of aging (τ).

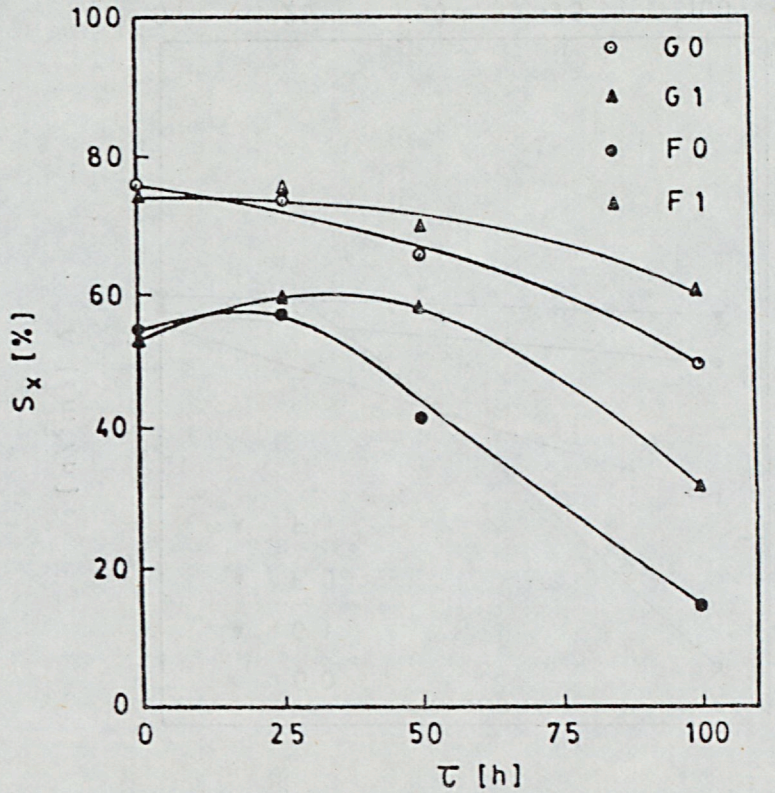


Figure 13. Change in amount of free sulphur (S) in different vulcanizates with time of aging (τ).

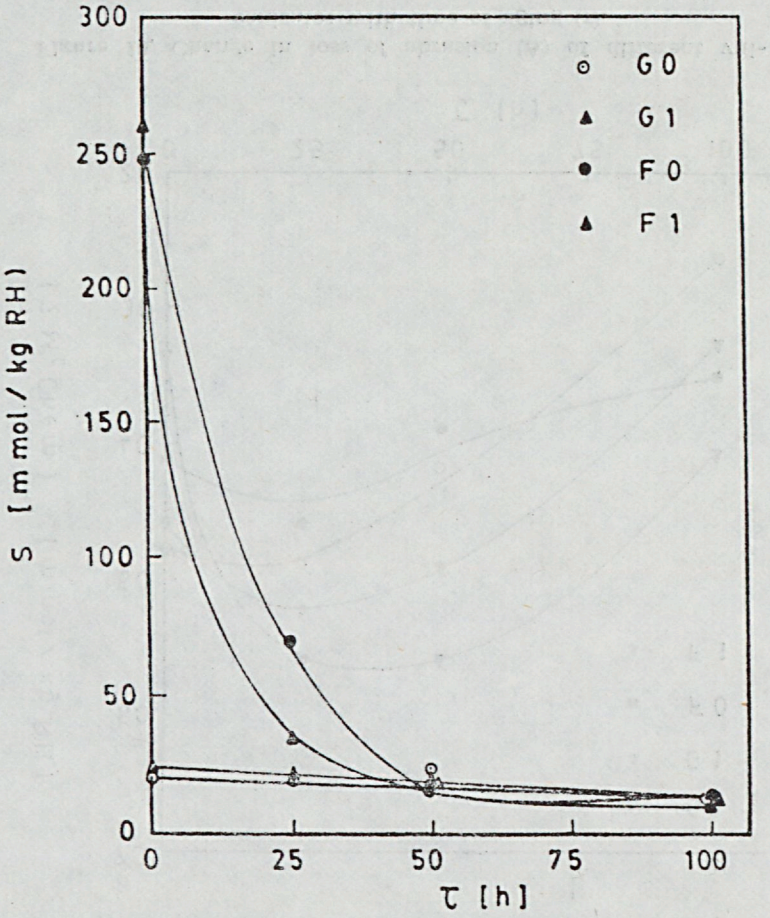


Figure 12. Change in polysulphidic crosslinks (Sx) in different vulcanizates with time of aging (τ).

failure properties is more drastic. The effect of antioxydant is however, more pronounced with gum samples. The drop in properties with aging time is due to the changes in the network structure and rubber-filler interactions for filled samples.

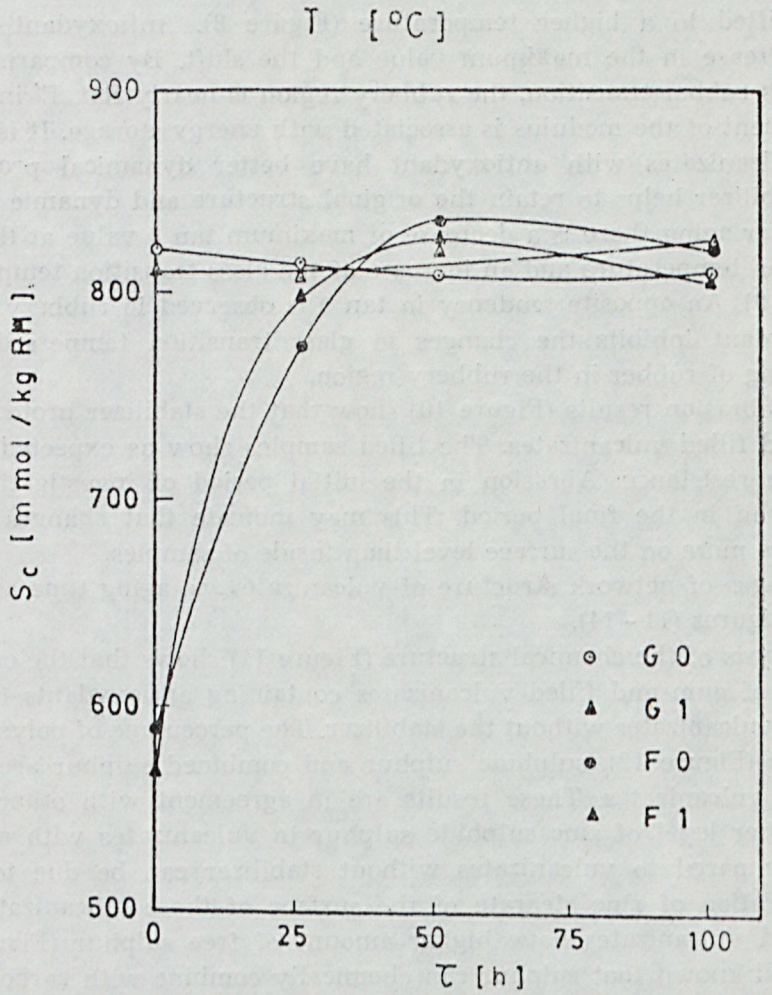


Figure 14. Change in amount of combined sulphur (Sc) in different vulcanizates with time of aging (τ).

The heat build-up results for various aged samples are plotted in Figure 7. Carbon filled vulcanizates show higher heat build-up and higher deformation after flexing compared to gum vulcanizates. The antioxydant has marginal effect over the time of the experiment carried out. However, the aged samples show more heat build-up which is commensurate with the changes in the network structure discussed later.

Dynamic measurements are very important for many of applications of rubber. The out-of-phase component of the modulus E″ increases to a maximum in the region of glass transition where E′ is changed most rapidly. The loss modulus is directly related to the hysteresis of the rubber. With aging the maximum value of loss modulus decreases and also shifted to a higher temperature (Figure 8). Antioxydant retards this decrease in the maximum value and the shift. By comparing with the glass-rubber transition, the rubbery region is nearly flat. E′ in-phase--component of the modulus is associated with energy storage. It is shown that vulcanizates with antioxydant have better dynamical properties. The stabilizer helps to retain the original structure and dynamic properties. After aging there is a decrease of maximum tan δ value at the glass transition temperature and an increase of the glass transition temperature (Figure 9). An opposite tendency in tan δ is observed in rubbery region. Antioxydant inhibits the changes in glass transition temperature and hardening of rubber in the rubbery region.

The abrasion results (Figure 10) show that the stabilizer protects both gum and filled vulcanizates. The filled samples show as expected, better abrasion resistance. Abrasion in the initial period of investigation was more than in the final period. This may indicate that changes during aging are more on the surface level than inside of samples.

Changes of network structure of vulcanizates vs. aging time are plotted in Figures (11 - 14).

Analysis of the chemical structure (Figure 11) shows that the crosslink density of gum and filled vulcanizates containing antioxydants is lower than of vulcanizates without the stabilizer. The percentage of polysulphide linkages (Figure 12), sulphide sulphur and combined sulphur are higher in gum vulcanizates. These results are in agreement with other report [3]. Higher level of zinc sulphide sulphur in vulcanizates with antioxydant compared to vulcanizates without stabilizer can be due to lower concentration of zinc stearate of the surface of those vulcanizates [19].

Filled vulcanizates have higher amount of free sulphur (Figure 13). It is well known that sulphur can chemically combine with carbon black and does not cause crosslinking of rubber. With aging time the free sulphur in gum and filled vulcanizates decreases and an adequate increase is observed in combined sulphur (Figuree 14). It is connected also with initial increase of the crosslink density (Figure 11). However with longer time of aging the crosslink density decreases. The properties dependent on the network structure and polysulphidic crosslink also decrease with time of aging as discussed earlier in this paper. In both cases the antioxydant retards the degradation. Changes in physical properties could be correlated with the changes in the chemical structure of the vulcani-

zates. For example, PBN stabilizer influences the decrease of crosslink density and decrease of tensile strength before aging. Deterioration of physical properties and crosslink density is more pronounced for vulcanizates without antioxydant. There is decrease in polysulphidic crosslink and total crosslink density at longer aging times. Accordingly, the tensile strength, tear, resistance, abrasion resistance, fatigue to failure life and dynamic properties decrease and the heat build-up increases. This is in line with earlier observations [20, 22].

CONCLUSIONS

The fall in physical properties like tensile strength, elongation at break, tear strength, abrasion and fatigue to failure resistance unfilled and filled rubber vulcanizates with aging time is attributed mainly to crossling breakage. There is also an increase in heat build-up which is more pronounced for samples without antioxydant. The antioxydant inhibits the deterioration in technical properties and network structure. Tangent delta at the glass transition temperature decreases with aging time and the glass transition temperature increases after aging. In rubbery region tan δ increases with aging time. The antioxydant retards the shifting of these curves. In longer period of aging the vulcanizates with stabilizer have higher crosslink density and higher percent of polysulphidic crosslinks than those without stabilizer.

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WPŁYW ANTYUTLENIACZA PBN NA WŁAŚCIWOŚCI DYNAMICZNO-MECHANICZNE I STRUKTURĘ SIECI PRZESTRZENNEJ STARZONYCH WULKANIZATÓW PRZEZNACZONYCH NA BIEŻNIKI OPON

Streszczenie

Badano zmiany struktury sieci i właściwości dynamiczno-mechaniczne napełnionych i nienapełnionych wulkanizatów kauczuku naturalnego podczas starzenia w powietrzu o temperaturze 100°C. Określono wpływ fenylo-2-naftyloaminy jako antyutleniacza na te właściwości.

Spadek właściwości mechanicznych, jak: wytrzymałość na rozciąganie, wydłużenie przy zerwaniu, wytrzymałość na rozdzieranie, ścieralność i wytrzymałość na zmęczenie jest głównie związany z pękaniem wiązań łańcucha i pękaniem sieci. Zmiany modułu stratności i tangensa δ po starzeniu wskazują na spadek maksimum krzywej tg δ i wzrost temperatury przemiany stanu szklistego. Antyutleniacz opóźnia degradację pod wpływem tlenu i wzrost twardości wulkanizatów w wyższej temperaturze. Ilość wytworzonego ciepła podczas wielokrotnego ściskania jest większa dla próbek bez antyutleniacza, szczególnie w dłuższych okresach badania.

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ВЛИЯНИЕ АНТИОКИСЛИТЕЛЯ РВН НА ДИНАМИКО-МЕХАНИЧЕСКИЕ СВОЙСТВА И СТРУКТУРУ ПРОСТРАНСТВЕННОЙ СЕТИ ВУЛКАНИЗАТОВ ПОДВЕРГШИХСЯ СТАРЕНИЮ ПРЕДНАЗНАЧЕННЫХ НА ПРОТЕКТОРЫ ПОКРЫШЕК

Содержание

Исследовано изменения структуры сети и динамико-механические свойства наполненных и ненаполненных вулканизатов натурального каучука во время старения в воздухе в температуре 100°C. Определено влияние фенило-2-нафтиламина как антиокислителя на эти свойства.

Уменьшение механических свойств, как: сопротивляемость на растяжение, удлинение при разрыве, устойчивость на раздирание, стирание и устойчивость на усталость главным образом связано с разрывом цепи и разрывом сети. Изменения модуля потерь и тангенса δ после старения указывают на падение максимум кривой тг δ и рост температуры изменения стекловидного состояния. Антиокислитель замедляет деградацию под влиянием кислорода и рост твёрдости вулканизатов в высшей температуре. Количество образованного тепла во время многократного сжатия больше дла проб без антиокислителя, особенно в длительных периодах исследования.