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Degradation Studies of Natural Rubber Cured by Accelerated Low-Sulphur and Urethane Crosslinking Systems

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Abstract

Changes in molecular level network structure have been investigated for natural rubber cured by low sulphur system and Novor$^{(R)}$ *system by measurement of continuous and intermittent stress relaxation. These measurements indicate that, Natural Rubber (NR) cured by Novor*$^{(R)}$ *system, shows more crosslinking and scission reactions at temperatures between 100 and 130° C, whereas at higher temperatures between 150 and 160 °C, shows lower crosslinking and scission reactions compared to NR cured by low sulphur system. At temperatures between 100 and 130 °C, NR vulcanised by low sulphur system shows a lower permanent set, and at temperatures between 150 and 160 °C, shows a higher permanent set as compared with NR vulcanised by Novor*$^{(R)}$ *system. The ageing of Novor*$^{(R)}$ *cured natural rubber, perhaps results in the occurrence of intermolecular interactions such as hydrogen bonding. A lower value of activation energy of stress relaxation shown by Novor*$^{(R)}$ *cured NR, indicate that its machanism of degradation is not identical to that of low sulphur cured NR.*

INTRODUCTION

The study of decay of stress at constant elongation and temperature was used as a physical index of chemical deterioration of rubber[1]. When natural rubber is exposed to elevated temperatures simultaneous crosslinking and scission reactions take place due to interaction with molecular oxygen[2,3]. It is known that these crosslinking and scission reactions are responsible for the permanent set which occurs in rubber samples that are deformed and then released after a definite period of time. Andrews Tobolsky and Hanson [4] had proposed a molecular theory of permanent set for rubber during stress relaxation at elevated temperature. The permanent set was also related to the creep phenomena observed in elastomers[5]. The occurrence of permanent set is a serious limitation on the performance of rubber products in service. The molecular level changes of network structure which account for the permanent set has important implications in the wearing and cracking of rubber articles, such as gaskets seals etc. at elevated temperatures.

Conventionally the efficient vulcanisation system (EV) has been used for samples requiring good resistance to high temperature. Later on an entirely different class of vulcanising agents[6-8] based on the reaction products of nitrosophenols with diisocyanates was introduced for application to high temperatures. The crosslinks produced by these chemicals afforded excellent ageing and reversion resistance. Natural rubber vulcanised with conventional sulphur systems has very good fatigue resistance but deteriorate after ageing at high temperature. The EV system has comparatively low fatigue resistance, but it does not deteriorate on ageing at 100°C. Novor$^{(R)}$ system shows an initial fatigue resistance similar to EV system but exhibits a far improved fatigue resistance after ageing at 100°C for 7 days with no change in modulus or hardness.The retention of stiffness with improved fatigue resistance exhibited by Novor$^{(R)}$ cured samples is extremely useful in many engineering applications of rubber. An attempt is made to understand the changes in molecular level network structure that occur in natural rubber vulcanised using the low sulphur (EV) and the urethane system (Novor$^{(R)}$), by studying continuous and intermittent stress relaxation at elevated temperatures. By these studies it is possible to separate the degradative process into crosslinking and scission reactions[3]. For a homogeneous network in which all network chains are at equilibrium at length, 1, the equation relating stress and elongation to attain length 1u in terms of concentration of network chains in rubber is given by

$f = skT \quad [(l/lu)^2 - (1u/l)]$ ----------(1)

where f is the stress per unit attained cross sectional area , s is the number of network chains per unit volume of rubber, k is Boltzmann's constant and T is the absolute temperature. Thus at a fixed extension and constant temperature the stress produced is entirely due to the load sharing of rubber chains. Hence if network chains break then the stress would decay. Hence at any time, t

$f(t) \alpha \ s(t)$

$f(t)/f(0) = s(t)/s(0)$ --------------(2)

f(o) and s(o) denote the corresponding values at time =0

It is possible that, if any new chains are produced, then some will bear the load and some may not. Hence in a rubber sample maintained at a fixed extension there will be two types of network. One type of network that is in equilibrium with the unstretched condition and the other type of network which is in equilibrium with the stretched condition.If the unstretched and stretched lengths are denoted by 1u and 1x respectively and the final length or set length by 1s, then we may write for two sets of networks the following two equations.

$f_u = s_u kT \, [(1s/lu)^2 - (lu/ls)]$ ------ --(3)

$f_x = s_x kT \, [(ls/lx)^2 - (1x/ls)]$ -------(4)

where f_u is the stress per unit attained cross sectional area which have their equilibrium at unstretched length and su the number of those chains. f_x and s_x are the corresponding stress and number of chains which are in equilibrium at the extended length.

For equilibrium at permanent set,

$f_u = -f_x$ ---------------(5)

Substituting (3) and (4) in (5) and by simplification we get

$s_u lx^2/s_x lu^2 = lx^3 - ls^3/lx^3 - lu^3$ ----------(6)

---— (6

%Permanent set=(1s-1u)/(lx-lu)x100 —(7)

= (1s/lu - 1)/(lx/lu -1) x 100 -------(8)

From simplification of equ. (6) we get

$ls/lu = [\{(lx/lu)^3 - 1/(s_u/s_x)(lx/lu)^2 + 1)\} + 1]^{1/3}$

---------------(9)

Substituting eqn (9) in eqn (8) we get

%permanant set = $[\{(C_1/((s_u/s_x)C_2+1)) + 1\}^{1/3} - 1]$

C_3 -------- (10)

The stress value given by continuous curve is proportional to su and that given by intermittent curve is proportional to su + sx.

If f/fo values given by continuous curve is designated as U and the difference in f/fo values of the intermittent and continuous curves as X, then

$s_u / s_x = U/X$ --------------(11)

%Permanent set= $[\{C_1 / ((U/X)C_2 + 1) + 1\}^{13} - 1]$

C_3 ---- ---- (12)

where C_1, C_2 and C_3 are constants.

$C_1 = (lx/lu)^3 - 1$

$C_2 = (lx - lu)^2$

$C_3 = 100 / (lx/lu) - 1$

MATERIALS AND METHODS

The Novor$^{(R)}$ 950 vulcanising system was obtained from Malaysian Rubber Producers Research Association (MRPRA) UK.. The formulation of the mixes are shown below.

Table 1 : Formulation of the Mixes

	E	N
Natural Rubber	100	100
Zinc Oxide	5	5
Stearic Acid	1	1
IPPD[1]	2	2
Novor $^{(R)}$ 950[2]	-	7.3
ZDC[3]	-	2
Sulphur	0.2	-
CBS[4]	5.0	-

1. N-Phenyl-N^1-1, 3 dimethylpropyl -p-phenylenediamine
2. Reaction product of nitrosophenol and diisocyanate
3. Zinc diethyldithiocarbamate
4. N-Cyclohexyl-2-benzothiazolesulphenamide

The formulations were adjusted so as to have the same extent of crosslinking as obtained from rheometric torque. The rheographs of the mixes are shown in Figure1. The mixes were prepared in a laboratory size 2 roll mixing mill. Sheets of about 1mm thickness were moulded at 180°C for the optimum cure time. Stress relaxation experiments were carried out in an Instron (model 3111) Universal testing machine. The rate of separation of the grips was 50 mm/min. Dynamic mechanical properties were determined using a Perkin Elmer (model DMA7) dynamic mechanical thermal analyser.

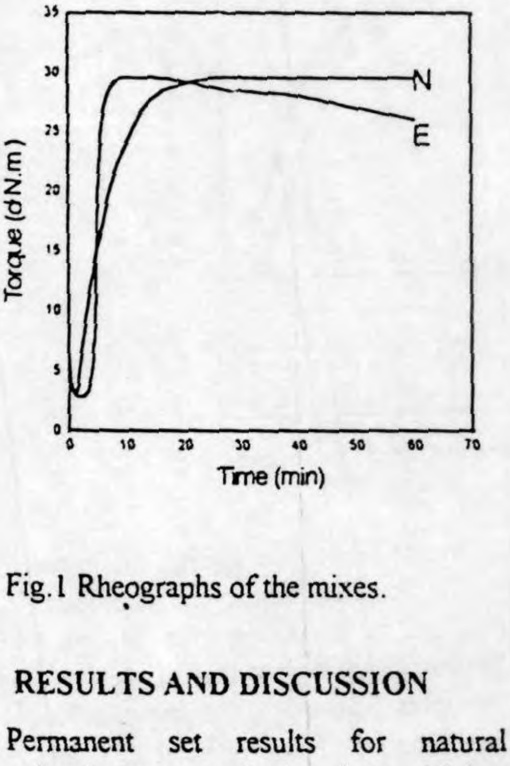


Fig.1 Rheographs of the mixes.

RESULTS AND DISCUSSION

Permanent set results for natural rubber vulcanisates cured by low sulphur system (Table1) at 100°C and 100% strain are shown in Figure 2.

Experimental permanent set values obtained from separate samples are marked in circles. The permanent set values calculated from permanent set theory developed by Tobolsky et al^3 are shown by continuous lines. The permanent set values are quite low and there is good agreement between theoretical and experimental values. The stress relaxation behaviour and permanent set values of NR vulcanisates cured by Novor$^{(R)}$ system at 100°C and 100% strain are shown in Figure3.

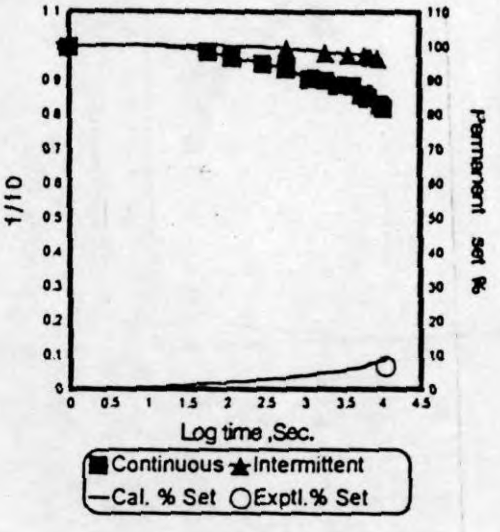


Fig.2 Permanent set of low sulphur cured NR at 100°C

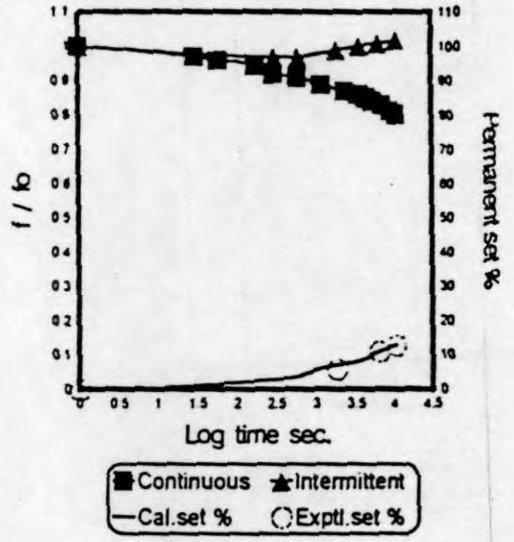


Fig.3 Permanent set of Novor cured NR at 100°C

The permanent set values are comparatively higher than that of NR vulcanisates vulcanised by EV system. There is an increase in the intermittent value of stress relaxation at larger times at 100°C for Novor$^{(R)}$ vulcanised NR showing that at this temperature, compared to EV system, NR cured by Novor$^{(R)}$. system has more crosslinking reaction. Since Novor$^{(R)}$ system has urethane linkages, the isocyanates formed during ageing can form hydrogen bond.

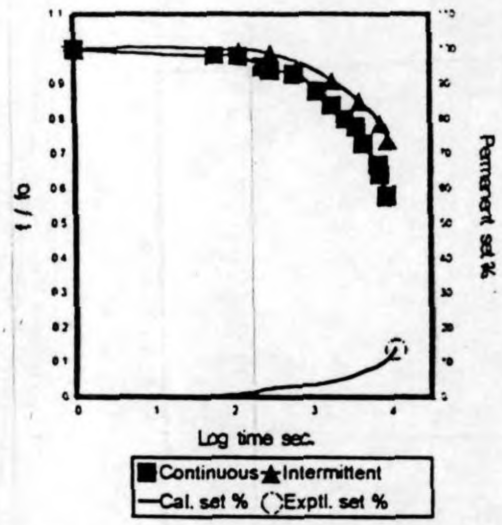


Fig. 4 Permanent set of low sulphur cured NR at 130°C

The decay of stress at 130°C and 100% strain for the NR cured by EV system is shown in Figure 4 and the corresponding curves for NR cured by Novor$^{(R)}$ system are shown in figure5

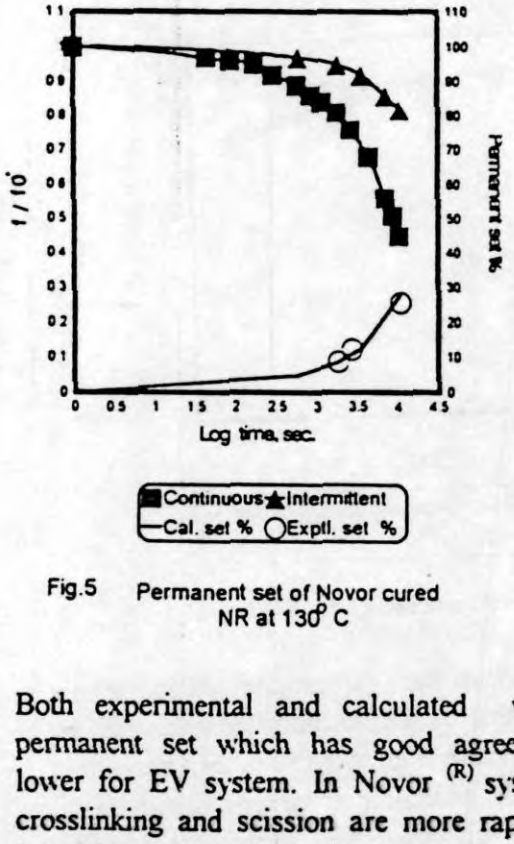


Fig.5 Permanent set of Novor cured NR at 130° C

Both experimental and calculated values of permanent set which has good agreement are lower for EV system. In Novor $^{(R)}$ system both crosslinking and scission are more rapid as the intermittent curve shows less stress decay and the continuous curve a more stress decay than the corresponding curves of EV system. This results in a higher permanent set for the Novor$^{(R)}$ system, similar to its behaviour at 100°C.

The intermittent and continuous stress relaxation data along with permanent set values for EV system at 150°C and 100% strain is shown in Figure 6 and the corresponding values for the Novor$^{(R)}$ system are shown in Figure 7.

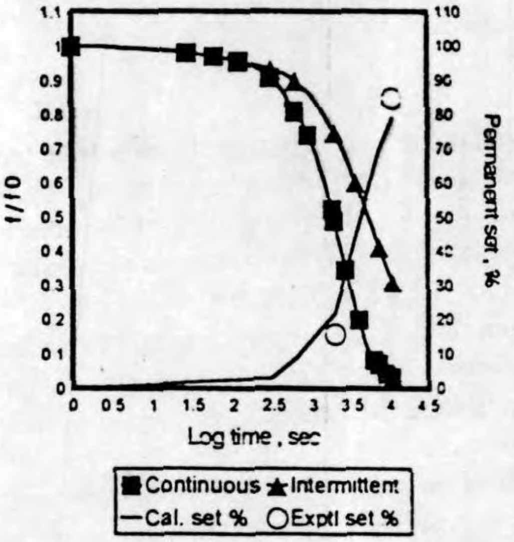


Fig. 6 Permanent set of low sulphur cured NR at 150° C

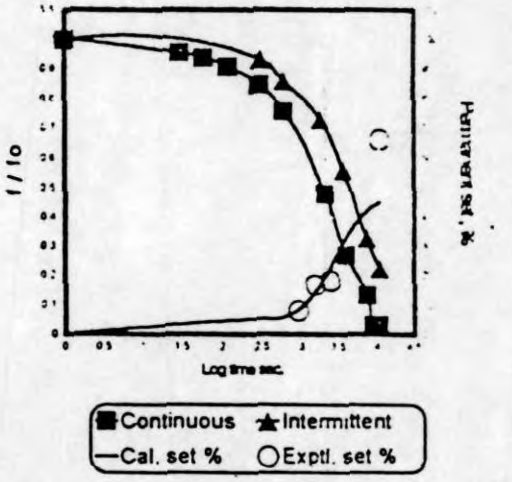


Fig.7 Permanent set of Novor curec NR at 150°C

In continuous stress relaxation, though the initial stress decay of efficiently vulcanised samples is small, after about an hour, the rate of stress relaxation, becomes higher than that of Novor $^{(R)}$ vulcanised samples. During intermittent stress relaxation contrary to the behaviour at 100°C and 130°C, efficiently vulcanized samples show a lower stress decay at higher temperatures. This results in a higher permanent set for efficiently vulcanised samples at 150°C. At lower times the efficiently vulcanised system shows a lower permanent set, whereas at higher duration of time, Novor $^{(R)}$ vulcanised system shows lower permanent set. Thus it appears that in EV system

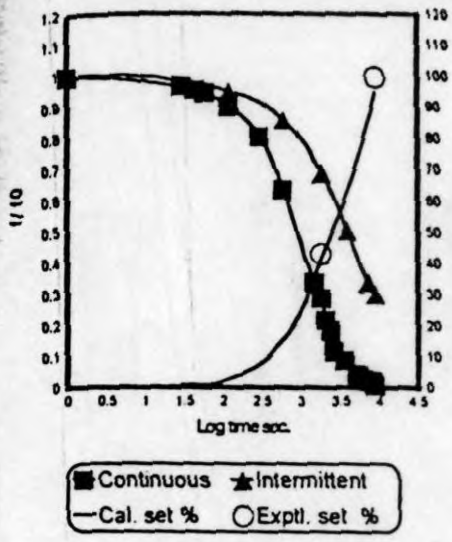


Fig.8 Permanent set of low sulphur cured NR at 160 °C

more crosslinking and more scission reactions take place compared to Novor$^{(R)}$ system, at 150°C.

The stress relaxation characteristics at 160°C for efficiently vulcanised samples is shown in Figure 8 and that of Novor$^{(R)}$ vulcanised samples in Figure 9.

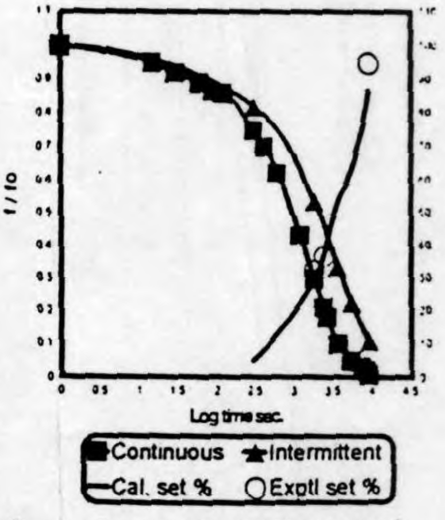


Fig. 9 Permanent set of Novor cured NR at 160 °C

The behaviour of samples is similar to that at 150°C. After about half an hour, the efficiently vulcanised samples show a greater stress decay than the Novor$^{(R)}$ cured samples. A higher permanent set is also seen for the efficiently vulcanised samples.

Figure 10 shows the continuous relaxation curves at two different strain of 100% and 166% for the Novor$^{(R)}$ vulcanised sample at four different temperatures.

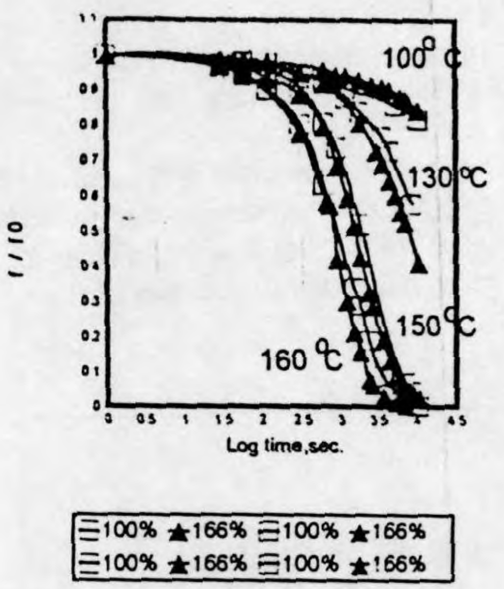


Fig. 10 Effect of strain on stress relaxation of low sulphur cured NR at 100 °C, 130 °C, 150°C and 160°C

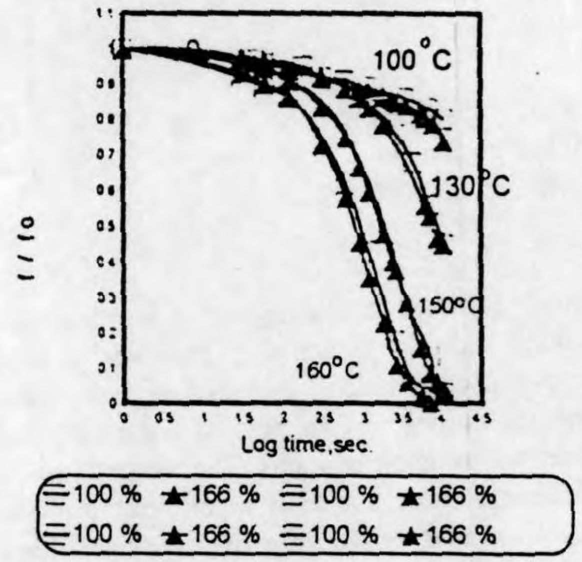


Fig. 11 Effect of strain on stress relaxation of Novor cured NR at 100 °C, 130°C, 150 °C and 160 °C

Figure 11 shows the effect of strain on stress decay for the low sulphur cured system. The stress decay is highly temperature dependent but varies only marginally with strain. This is similar to the observation noted earlier[4] that decay of stress was independent of the strain. The marginal difference for decay of stress could be due to the higher thickness of the test samples which were around 1.2 - 1.4mm.

The activation energy (ΔE) for stress relaxation for Novor$^{(R)}$ system is 23.16 Kcal/mole . The ΔE for EV system is 30.75 Kcal/mole which is very close to the theoretical value (30.4 ± 2 kcal/mole) reported[2]. This shows that the mechanisms controlling degradation are not exactly the same, in NR vulcanisates cured by EV and Novor (R) systems. This is contrary to the earlier investigations [1,2].

The viscoelastic behaviour of NR cured by EV system and Novor (R) system, under isothermal conditions at 180° C is shown in Figure 12. In the early stages of degradation the low sulphur cured vulcanisate, shows a higher elastic modulus and a lower damping. However, at later stages of degradation, the viscous component increases as shown by an increase in damping and a decrease in elastic modulus. The Novor (R) cured vulcanisate does not show much change in the elastic modulus or damping over the time range studied. So the EV cured vulcanisates show a higher extent of scission,than Novor (R) cured vulcanisates at higher temperatures.

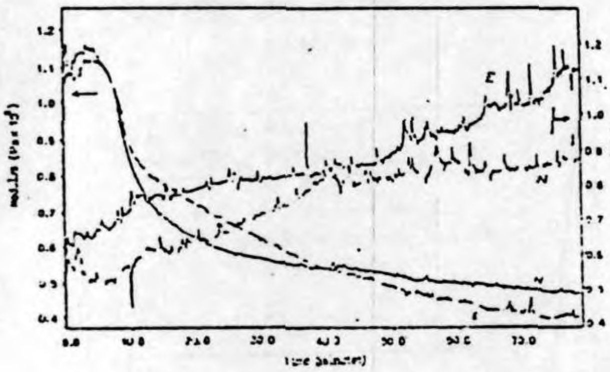
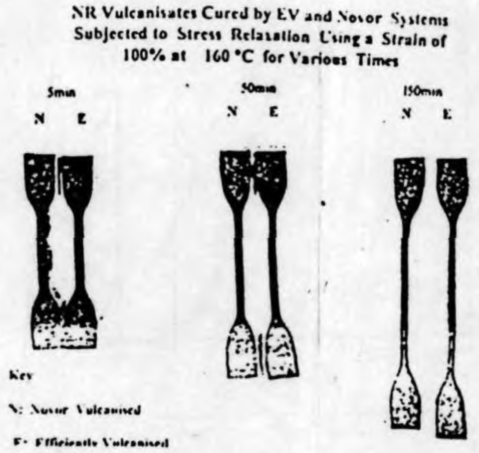
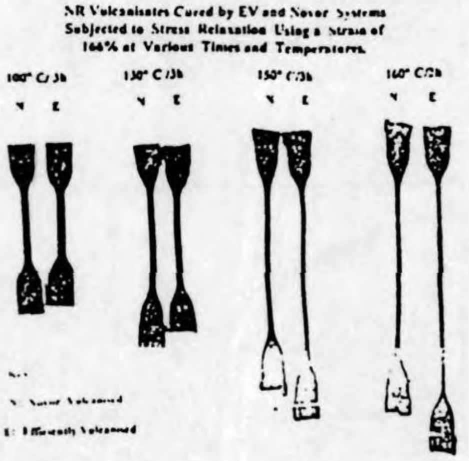


Fig. 12 Viscoelastic behaviour of NR cured by EV system and Novor (R) system, under isothermal conditions at 180°C

Photograph 1 shows the samples subjected to stress relaxation at 100% strain for different times at 160°C. After 5 minutes the low sulphur vulcanised sample shows a lower permanent set while at longer time the Novor (R) vulcanised sample shows a lower set. Photograph 2 shows the samples subjected to stress relaxation at different temperatures and times at a strain of 166%. At temperatures of 100°C and 130°C the efficiently vulcanised system shows a lower permanent set value whereas at higher temperatures the Novor(R) vulcanised sample shows a lower permanent set.



Photograph 1



Photograph 2

It has been shown earlier that as a result of interaction with molecular oxygen, the primary bonds were getting ruptured. The bonds could be the double bond , the carbon atom in the α position of the double bond or the crosslinking bond. In the Novor^R vulcanisation crosslinking involves a diurethane structure which is more flexible compared to EV system which involves either -C-C bond or -C-S-C bond. Novor * cured samples showed a Tg of - 60° C while EV cured sample showed a Tg of -58 ° C. The urethane can change to an isocyanate at high temperature[9]. If isocyanates react with urethanes it will lead to increased branching.The crosslinking reactions of EV system does not lead to increased branching.

CONCLUSION

When deformed and maintained at constant temperature, at higher temperatures between 150°C and 160°C natural rubber cured by Novor $^{(R)}$ system shows a lower permanent set than NR cured by low sulphur system, due to lesser crosslinking and scission reactions. On deformation at lower temperature between 100 and 130°C the low sulphur system shows a lower permanent set due to lesser crosslinking and scission reactions. On ageing at 100°C, NR cured by Novor$^{(R)}$ system shows a higher modulus, possibly due to intermolecular interactions like hydrogen bond.

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