Thermal Oxidative Ageing of Epoxidised Natural Rubber

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Retention in tensile property of epoxidised natural rubber (ENR) vulcanisate obtained after being subjected to thermal oxidative ageing is determined by the net result of the softening and hardening effects. These softening and hardening phenomena occur during the ageing process.

Three types of fillers, namely HAF black, local clay and silica were investigated to observe the differences in the extent of hardening imparted by these fillers after ageing for three days at 100°C. Of the three fillers investigated, silica-filled ENR-50 (ENR with 50 mole per cent epoxidation) vulcanisates gave the highest extent of hardening compared to those of HAF black and local clay. Retention in tensile strength of above 90% could be obtained from vulcanisates with three different reinforcing systems.

The investigation on the effectiveness of antioxidants in retaining the tensile strength of ENR-50 after ageing at 125° C was confined to five amine and phenolic antioxidants. The effectiveness of these antioxidants in retaining the tensile strength was deduced as follows: Santoflex 13 > IPPD > Permanax TQ > Permanax WSL > Vulkanox KB. The most effective antioxidant, Santoflex 13, required a low concentration (i.e. 0.2 p.h.r.) in order to give maximum retention in tensile strength and this can be an advantage in terms of reducing compound cost.

Thermal oxidative degradation of an unsaturated rubber generally results in deterioration of its physical properties as well as the service performance properties. Thus, it is desirable to protect the rubber against degradation by using antioxidants or by other means.

The thermal oxidative ageing of ENR has been discussed in various papers¹⁻⁴. Gelling *et al.*² believe that the poor ageing of sulphurcured ENR vulcanisate is attributable to the formation of sulphur acids during the oxidative process. These sulphur acids can catalyse ringopening of epoxide groups, thus causing crosslinking *via* ether groups. If the extent of crosslinking formed is substantial, the aged vulcanisate can be severely hardened.

It has been demonstrated that a low sulphur vulcanisation system with a high level of sodium carbonate is preferred for improvement in the ageing performance of ENR, in particular $ENR-50^4$.

This paper is an extension of the work done earlier⁴. In this work, factors other than those discussed in the earlier papers¹⁻⁴ were investigated.

EXPERIMENTAL

Materials

Rubbers. ENR-50 prepared from field latex was obtained from the Rubber Research Institute of Malaysia pilot plant using the method of Gelling⁵. The NR used was SMR 5.

Compounding ingredients. The compounding ingredients used were of the recommended grades for rubber. Anhydrous sodium carbonate (98%) was obtained from Fluka AG,

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Switzerland. The chemical names of abbreviations used in this paper are given in *Appendix A*.

Procedure

Mixes were prepared on a 30.5×15.2 cm two-roll mill. The formulation used in this study is as shown in *Table 1* and the following mixing schedules were adopted:

For HAF Black and Local Clay Mixes

- 1. Rubber and sodium carbonate
- 2. Zinc oxide, stearic acid and Permanax TQ
- 3. Filler and oil
- 4. Curatives.

For Silica Mixes

- 1. Rubber, silica, DEG, oil and sodium carbonate
- 2. Stearic acid and Permanax TQ
- 3. Zinc oxide
- 4. Curatives.

Mixing cycle of 20 min was adopted for all the mixes. The mixes were cured to optimum at 150°C. The tensile properties were determined from dumb-bell test pieces cut from the 12.7 \times 15.2 \times 0.2 cm vulcanised sheets. Vulcanisate properties were tested using the Monsanto Tensometer 500. Accelerated ageing tests were carried on the dumb-bell test-pieces using the Wallace Multicell ageing oven. British Standards (BS 903 Part A2, 1971 and BS 903 Part A 19, 1975) were followed, except the ageing resistance was expressed in terms of per cent retention in the property as shown below:

Per cent retention in property	Aged value of the			
	=	property		100
		Unaged value of the property	9	

RESULTS AND DISCUSSION

Fillers

The results presented in *Figure 1* show the effect of using different types of filler namely HAF black, silica and local clay on the extent

Compound	GAU			
compound	Bh	2 . 91	3	4
ENR-50	100	100	5 100	100
HAF black (N 330)	40	· · ·		40
Silica (VN 3)	• =	50	•	_
Local clay	-		50	_
Dutrex 737 MB	34	I FIM - CA	2 _	4
Dutrex 63	to an	4 0	4	_
DEG	Sin	2.5		_
Zinc oxide	5	RUBBE	5	5
Stearic acid	2	2	2	2
Permanax TQ	2	2	2	_
DPG	_	0.5	0.5	_
MOR	1.5	1.5	1.5	3.0
PVI	0.3	_		0.3
Sulphur	Variable	Variable	Variable	0.5
Sodium carbonate	Variable	Variable	Variable	3.0
Antioxidant	-	_		Variable
	1			

TABLE 1. FORMULATIONS USED IN THE STUDY

of hardening (as shown by the increase in per cent retention in modulus at 100% strain, M100) of ENR-50 vulcanisates after being subjected to three days ageing at 100°C. As illustrated by the results, the silica-filled ENR-50 vulcanisates gave the highest extent of hardening compared to those of HAF black and local clay.

The degree of hardening shown by the three types of fillers differentiates the ability of each filler to promote crosslinking during the ageing



Figure 1. Per cent retention in M100 (3 days/100°C)

process. The enhancement of the formation of crosslinks shown by silica is also reflected by the earlier observation⁶ whereby silica gave good reinforcement to ENR-50 without the use of coupling agents. The increased hardening during ageing of ENR-50 silica-filled vulcani-

sates could be due to ENR-50/silica reaction during ageing.

As shown in *Figures 2-4*, the silica-filled ENR-50 vulcanisate gave the highest extent of hardening. This increase in crosslink density



Figure 2. Effect of concentrations of sulphur and sodium carbonate on per cent retention in tensile strength (3 days/100°C) — silica-filled ENR-50,



Figure 3. Effect of concentrations of sulphur and sodium carbonate on per cent retention $_{-}$ in tensile strength (3 days/100°C) — clay-filled ENR-50.

was not substantial enough to result in a decrease in tensile strength as shown in *Figure 2*. However, the increase in the crosslink density was sufficient to result in lower elongation at break as shown in *Figure 5*. For both HAF black and clay-filled vulcanisates, retention in elongation at break of above 80% could be obtained by using formulations with appro-

priate levels of sodium carbonate and sulphur as shown in Figures 6 and 7.

Level of Unsaturation

During the ageing of NR and ENR vulcanisates at 125°C, a severe softening effect of either NR^{7,8} or ENR-25⁴ vulcanisate could



Figure 4. Effect of concentrations of sulphur and sodium carbonate on per cent retention in tensile strength (3 days/100°C) — HAF black-filled ENR-50.

occur while in the case of ENR-50³, hardening of the vulcanisate was observed. This softening effect is presumably due to main-chain scissions occurring at exceptionally high temperature. Since both NR and ENR-25 contain a higher level of unsaturation compared to ENR-50, a higher extent of main-chain scissions would be expected for both NR and ENR-25. However, if the ageing of either $NR^{7,8}$ or $ENR-25^1$ is carried out at 100°C, the main-chain scissions occurring are presumably not substantial and thus improvement in the ageing performance of those rubbers can be obtained by the use of an efficient vulcanisation (EV) system with antioxidants for NR or EV system with bases and antioxidants for ENR-25.



Figure 5. Effect of concentrations of sulphur and sodium carbonate on per cent retention in elongation at break (3 days/100°C) — silica-filled ENR-50.

Antioxidants

Antioxidants are known to inhibit mainchain scissions occurring during the ageing of NR. Thus it would be interesting to observe the effect of various antioxidants in minimising the main-chain scissions occurring in ENR, in particular ENR-50. The results shown in *Figure 8* illustrate the effect of some commercially available antioxidants on the per cent retention in M100 of ENR-50 vulcanisates based on a EV system with 3 p.h.r. of sodium carbonate. The results shown in *Figures 8-10* were based on *Formulation 4* of *Table 1*. As shown in *Figure 8*, the per cent retention in M100 of the vulcani-



Figure 6. Effect of concentrations of sulphur and sodium carbonate on per cent retention in elongation at break (3 days/100°C) — clay-filled ENR-50.

sate depends on the concentrations and the types of the antioxidant. In the absence of any antioxidant, the retention in M100 was 89%, and this is presumably due to the predominant effect of the main-chain scissions as discussed earlier. The per cent retention in M100 of the vulcanisate increased with increasing concentration of antioxidant. Amine-type antioxidants

(*i.e.* Santoflex 13, IPPD and Permanax TQ) were found to be more effective compared to the phenolic type antioxidants in inhibiting the softening of the vulcanisate.

In the ageing process of ENR-50 black-filled vulcanisate based on the EV system, two main reactions are presumably taking place: cross-



Figure 7. Effect of concentrations of sulphur and sodium carbonate on per cent retention in elongation at break (3 days/100°C) — HAF black-filled ENR-50.

linking reactions due to the presence of acid and the main-chain scissions. The degree of crosslinking could be controlled by the levels of the base, sulphur and accelerator added while the extent of the main-chain scissions could be minimised by the level and the type of antioxidant present. Thus the net effect of these two reactions will eventually determine the modulus of the aged vulcanisate, and consequently the tensile strength and the elongation at break of the vulcanisate.

The effectiveness of the various investigated antioxidants in retaining the tensile strength after ageing can be deduced as follows: Santoflex 13 > IPPD > Permanax TQ > Permanax



Figure 8. Effect of antioxidants on per cent retention in M100 (S/MOR/sodium carbonate: 0.5/3.0/3.0).

WSL > Vulkanox KB. For the most effective antioxidant (Santoflex 13) the maximum per cent retention in tensile strength could be obtained at a low concentration of the antioxidant (*i.e.* 0.2 p.h.r.) This can be an advantage in terms of reducing the compound cost. The effect of types and concentrations of the antioxidants on the retention in elongation at break is shown in *Figure 10*. Both amine-type antioxidants (*i.e.* Santoflex 13 and IPPD) gave significant decrease in aged elongation at break at high concentrations of the antioxidants.



Figure 9. Effect of antioxidants on per cent retention in tensile strength (S/MOR/sodium carbonate: 0.5/3.0/3.0).

The mechanism developed by Bolland⁹ to account for amine and phenolic antioxidant activity is illustrated in *Figure 11*. Reactions involving *Steps 3* and 6 are the most important for antioxidant action and these reactions remove the free radical functionality from the rubber so that normal oxidative degradation of the rubber is halted. The differences in the activities of the amine and phenolic antioxidants in these reactions explain the results observed earlier, *i.e.* the amine antioxidants were more effective than the phenolic antioxidants. If reactions involving *Steps 2* and *4* become important, enhanced oxidative degradation of the rubber can occur. Thus, it is important that the level of antioxidant be kept at the optimum since excess antioxidant can result in a pro-oxidant effect¹⁰. As shown in the earlier results, the optimum level required in retaining tensile strength after ageing with Santoflex 13, IPPD and Permanax TQ were found to be 0.2, 0.8 and 1.0 p.h.r. respectively.



Figure 10. Effect of antioxidants on per cent retention in elongation at break (S/MOR/ sodium carbonate: 0.5/3.0/3.0,

It is also possible that the main-chain scissions or softening effect are minimised at higher levels of antioxidant and consequently the tensile strength which depends on the net result of both softening and hardening effects is affected by the level of antioxidant added.

Initiation

1. 2.	ROOH AH + O ₂	→ →	RO• + •OH AOOH	
<u>Tr</u>	ansfer			
3. 4.	RO• / RO ₂ • + A• + RH	→ →	ROH / ROOH + A AH + R•	
Te	rmination			
5.	2 ROO+) Stabla	
6.	2 A•	-) products	
7.	A• + ROO•	+) products	

Figure 11. Mechanism of amine and phenolic antioxidant activity (AH refers to the antioxidant).

CONCLUSIONS

Apart from the factors which have been discussed in the previous papers, this study showed that both fillers and antioxidants influenced the ageing performance of ENR-50 vulcanisates. Of the three fillers investigated, silica gave the highest extent of hardening to ENR-50 on ageing. In the case of antioxidants, their concentrations and types were found to be critical in determining the tensile properties of the aged ENR-50 vulcanisates.

ACKNOWLEDGEMENT

The authors thank Dr A. Subramaniam for useful discussion and suggestions. The able assistance of Encik Ab'llah Che Ha, Mr P. Ramasamy, Cik Noriah Abdullah and the staff of RRIM Physical Testing Laboratory is greatly appreciated.

REFERENCES

 ABU BIN AMU AND SIDEK BIN DULNGALI (1984) Scorch and Ageing Properties of Epoxidised Natural Rubber. Proc. Int. Rubb. Conf. Sri Lanka, 1984.

- GELLING, I.R. AND MORRISON, N.J. (1985) Sulphur Vulcanisation and Oxidative Ageing of Epoxidised Natural Rubber. *Rubb. Chem. Technol.*, 58(2), 243.
- ABU BIN AMU, KU ABDUL RAHMAN BIN KU ISMAIL AND SIDEK BIN DULNGALI (1985) Some Aspects on Processing and Ageing of Epoxidised Natural Rubber. Proc. Int. Rubb. Conf. Kuala Lumpur 1985, 2, 289.
- ABU BIN AMU, SIDEK BIN DULNGALI AND GELLING, I.R. (1986) Latest Developments in Epoxidised Natural Rubber. Proc. Rubberplas Singapore, 1986.
- 5. GELLING, I.R. (1981) Epoxidised Natural Rubber. Br. Pat. No. 2113692.
- BAKER, C.S.L., GELLING, I.R. AND NEWELL, R. (1985) Epoxidised Natural Rubber, *Rubb, Chem. Technol.*, 58(1), 67.
- MALAYSIAN RUBBER PRODUCERS RESEARCH ASSOCIATION (1984) The Natural Rubber Formulary and Property Index.
- MALAYSIAN RUBBER PRODUCERS RESEARCH ASSOCIATION (1979) Natural Rubber Technical Information Sheet D, 74.
- SHELTON, J.R. AND COX, W.L. (1954) Oxidation and Antioxidant Action in Rubber Vulcanisates. *Ind. Engng Chem.*, 46, 816.

APPENDIX A

DEG	Diethylene glycol
DPG	Diphenylguanidine
MOR	N-oxydiethylene benzothiazole-2-sulphenamide
PVI	N-(cyclohexylthio)pththalimide
IPPD	N-isopropyl-N'-phenyl-p-phenylenediamine
Santoflex 13	N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine
Permanax TQ	Poly-(2,2,4-trimethyl-l,2-dihydroquinoline)
Permanax WSL	Methylcyclohexylxylenol
Vulkanox KB	2,6-Di-(tert-butyl)-p-cresol
Dutrex 737 MB	Aromatic processing oil
Dutrex 63	Naphthenic processing oil