J. nat. Rubb. Res., 12(1), 1–10

# Effect of Aerobic Ageing at Elevated Temperatures on Dynamic Mechanical Properties of Certain Natural Rubber Vulcanisates

I.R. GOODCHILD* AND T.J. POND*#

*Dynamic modulus and damping properties have been determined over a range of temperatures from five different natural rubber vulcanisates aerobically aged at elevated temperatures for periods up to 150 days. Overall, aerobic ageing is found to increase the modulus but decrease the damping of the vulcanisates. The rate of change of properties caused by ageing, though initially relatively small, may increase after longer times if antioxidant material becomes depleted. Results at longer ageing times indicate the modulus may, depending upon the vulcanisates' ingredients, pass through a maximum; however the modulus remains greater than for unaged material. Aerobic ageing is also shown to alter the glass transition temperature of a vulcanisate.*

Like other elastomers, the mechanical properties of natural rubber may alter as a result of ageing. Aerobic ageing is normally caused by oxygen diffusing into the rubber and producing chemical reactions with the medium[1]. The oxidative reactions produce crosslinking, scission of the rubber chains and the attachment of polar oxygen-containing groups to the rubber molecules[2]. Such changes to the structure of the rubber can alter its modulus and damping.

The modulus of natural rubber vulcanisates aerobically aged at elevated temperatures has been studied by a number of workers[3–7]. The results have shown that, overall, the modulus tends to increase with aerobic ageing although not always in a monotonic manner. The majority of ageing studies have examined quasi-static stress-strain behaviour with only limited measurements of dynamic properties such as modulus and damping. Bjork and Stenburg[8] have conducted dynamic measurements on two natural rubber vulcanisates which show that the complex modulus and damping both increase after aerobic ageing at 100°C. Their finding that the damping increases with ageing is perhaps surprising since an increase in the modulus of the rubber might be expected to produce a fall in the damping of the material.

The purpose of the present study is to further investigate dynamic modulus and damping properties in aerobically aged natural rubber vulcanisates. The aerobic ageing conditions have been chosen to provide extensively oxidised samples in order to quantify and

* Tun Abdul Razak Research Centre, Brickendonbury, Hertford SG13 8NL, United Kingdom
# Corresponding author

characterise the change in modulus and damping of these materials. The extent of the oxidation in the test samples studied is much greater than that present under lower operating temperatures and the measurements should not be considered representative of normal ambient conditions where the magnitude of the change in properties will be very much smaller.

## EXPERIMENTAL

Natural rubber sheets were manufactured from five different compounds. The composition of each compound and the vulcanisation conditions are shown in *Table 1*. The rubber sheets (220 × 220 × 0.7 mm in thickness) were aged in circulating air ovens at a temperature of 90, 100, 125 or 150°C for various periods of time up to 150 days. After ageing, rectangular test pieces (35 × 10.6 × 0.7 mm) were cut from each sheet away from the edge, and the dynamic modulus ($E'$) and damping (tan $\delta$) were determined by using a dynamic mechanical thermal analyser (DMTA) test machine. The deformation geometry was dual cantilever.

All the measurements were conducted at a frequency of 1 Hz over a temperature range of –60°C to +30°C and at a strain of 0.002%. A very small test-strain is necessary to measure the modulus of highly oxidised rubber since the value of elongation at break is very small due to the glassy and brittle nature of this material. Dynamic test data were also obtained from unaged test pieces of each vulcanisate for comparison with the aged material. Tests were repeated to study the reproducibility of the data which was found to be good.

The weight of unreacted antioxidant (*Santoflex 6PPD*) and rubber-bound nitrogen were determined from test pieces of compound number five after various times of ageing at a temperature of 90°C. Antioxidant levels were determined by extracting each sample in acetone and analysing on a high performance liquid chromatography machine which for these experimental conditions has a low detection limit of 0.001%. The levels of rubber-bound nitrogen were measured using the Kjeldahl method in the usual manner.

## RESULTS AND DISCUSSION

Results of dynamic mechanical testing are given in *Figures1–10*. Aerobic ageing increases the dynamic moduli of all the vulcanisates. A material which is extensively oxidised has a much greater modulus than an unaged material at temperatures greater than about –55°C as illustrated in *Figures 1* and *3*; however, the modulus at –60°C where the rubber behaves like glass is unaltered. The increase in the modulus of a particular vulcanisate is determined by the time and the temperature of ageing. The modulus may increase by a factor of about 100 when the rubber is extensively oxidised. In similar vulcanisates which undergo less extensive oxidation, such as a vulcanisate subjected to ageing temperatures approaching ambient, the increase in modulus is much smaller, typically of the order of 10% to 40%[7]. In extensively oxidised rubber as shown in *Figures 1* and *3*, the material is somewhat brittle and glass-like at ambient temperatures and the normal glass transition temperature is not apparent.

The rate of increase in the modulus of a vulcanisate is not constant with ageing time but typically is quite small during the initial ageing period. At longer ageing times the rate of change of the modulus tends to increase as illustrated in *Figures 3, 5* and *6*. Such a change

TABLE 1. COMPOSITION OF COMPOUNDS AND VULCANISATION CONDITIONS

| Compound ingredients | Compound (p.p.h.r.) | | | | |
|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 |
| Natural rubbers (SMR CV 60) | 100 | 100 | 100 | 100 | 100 |
| Zinc oxide | 5 | 5 | 5 | 5 | 5 |
| Stearic acid | 2 | | | 2 | 2 |
| Sulphur | 2.5 | 0.7 | 0.7 | 2.5 | 1.0 |
| CBS[1] | 0.6 | | | 0.6 | 0.75 |
| *Santoflex 6PPD* | 3 | 3 | 3 | 3 | 3 |
| *Antilux 600* | 3 | 3 | 3 | 3 | 3 |
| Carbon black N220 | | | 50 | 50 | 60 |
| ZE[2] | | 1.0 | 1.0 | | |
| OBS[3] | | 1.7 | 1.7 | | |
| TBTD[4] | | 0.7 | 0.7 | | |
| *Dutrex 729* | | | | | 18 |
| Vulcanisation time (min) | 11 | 12 | 8 | 9 | 8 |
| Vulcanisation temperature (°C) | 160 | 160 | 160 | 160 | 160 |

[1]N-cyclohexylbenzothiazole-2-sulphenamide
[2]Zinc-2-ethylhexanoate
[3]N-oxydiethylenebenzothiazole-2-sulphenamide
[4]Tetrabutylthiuram disulphide

in the modulus can be influenced by the presence of carbon black filler as well as curative ingredients as indicated in *Figure 6*. The ageing time required to reach the point when the modulus significantly increases becomes longer with a fall in the ageing temperature. For vulcanisate number 5 (*Figure 5*) such a point occurs after about 60 days ageing at a temperature of 90°C. From rheometry measurements it is estimated that this ageing condition is approximately equivalent to 700 years ageing at a temperature of 20°C. At long ageing times the modulus may fall according to the compound ingredients as shown in *Figure 6* but remains greater than unaged material. The significant change in the rate of increase of the modulus is believed to be caused by the depletion of antioxidant material within the test pieces.

A comparison of the concentration of unreacted antioxidant remaining in samples of compound five after ageing at 90°C (*Table 2*), with that of the modulus shown in *Figure 5* indicates that unreacted antioxidant levels have fallen to less than 0.001% after 60 days ageing. Such a small concentration of unreacted antioxidant is also present between 28 days and 60 days of ageing and alone could not be expected to provide effective protection of the rubber. Measurements of the nitrogen concentration, which remain unchanged, indicate that the antioxidants are not being significantly volatilised at the ageing

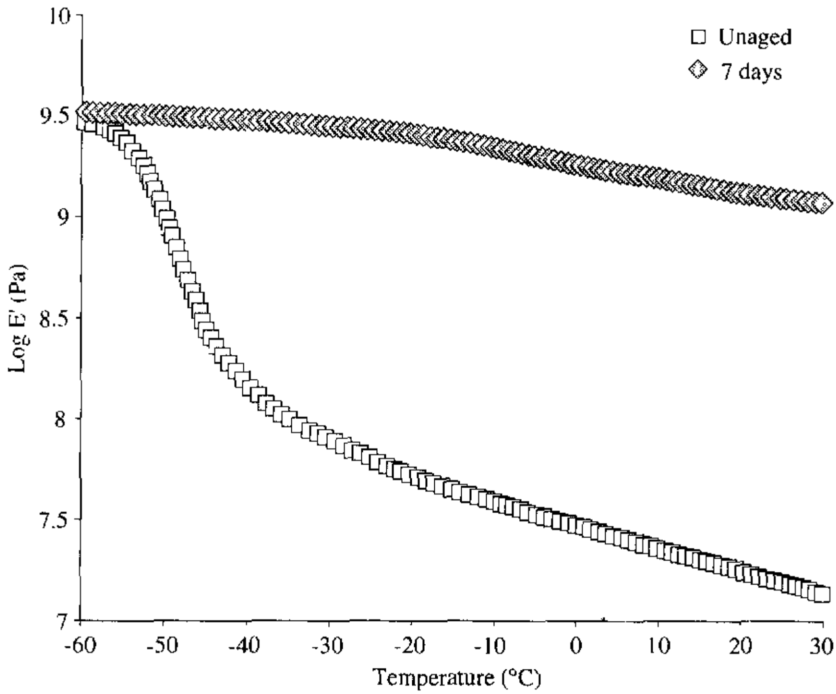


*Figure 1. Data points showing the modulus of an unaged test piece and a test piece after ageing for 7 days at 150°C as a function of temperature (Compound 5).*

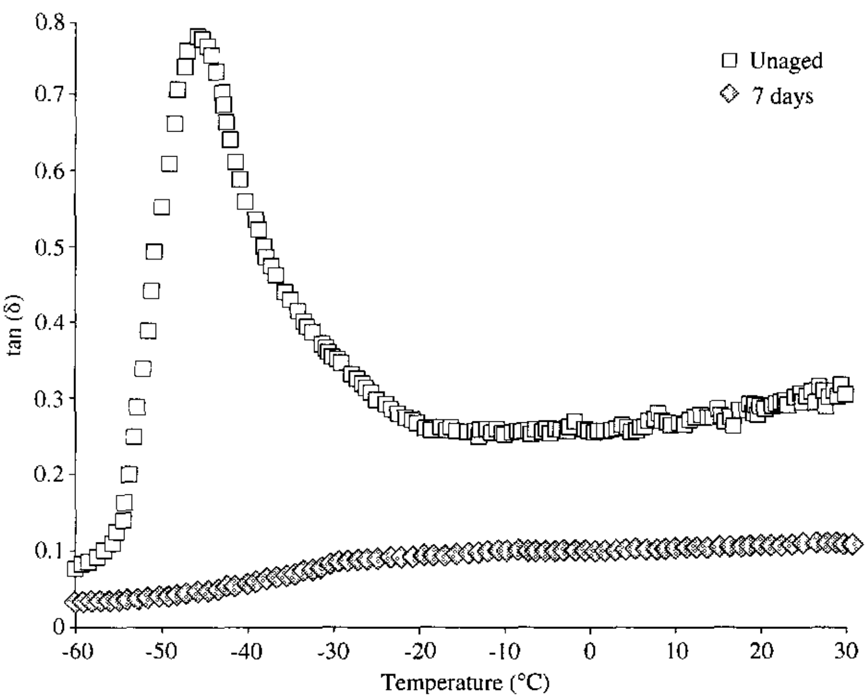


*Figure 2. The damping (tan δ ) of a test piece aged for 7 days at 150°C and an unaged test piece* versus *temperature (Compound 5).*

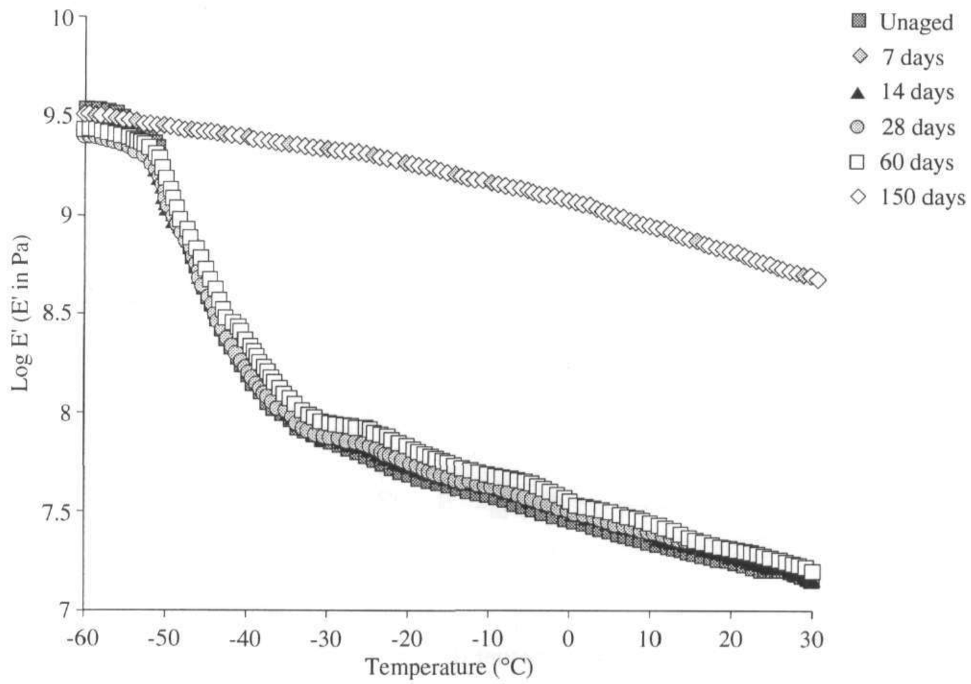


*Figure 3. The moduli of test pieces aged for different times at a temperature of 90°C and an unaged test piece* versus *temperature (Compound 5).*

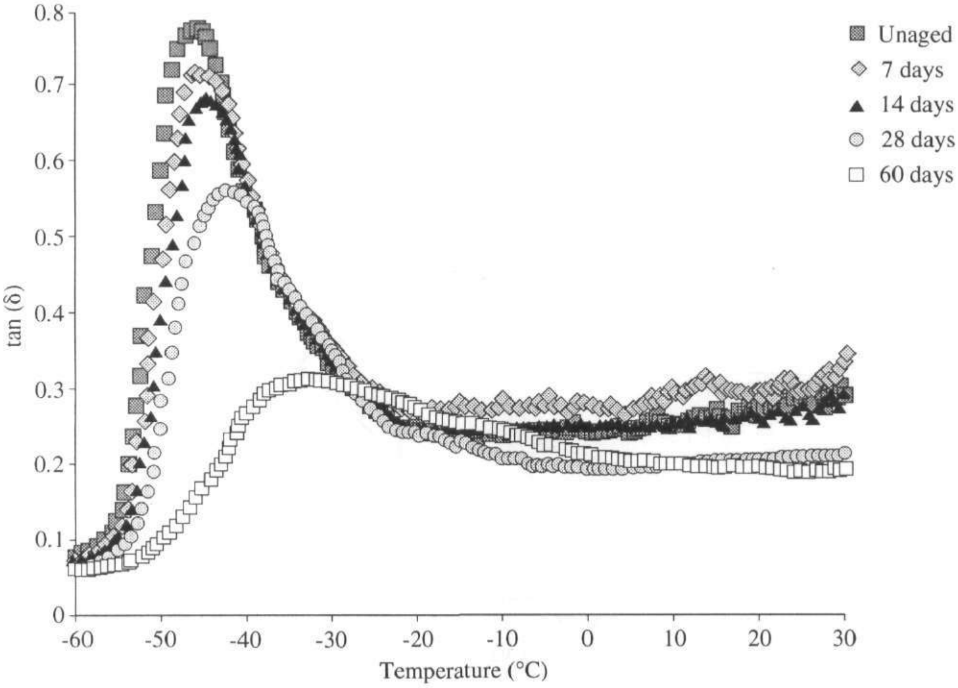


*Figure 4. The damping of test pieces aged for different times at a temperature of 100°C and an unaged test piece* versus *temperature (Compound 5).*

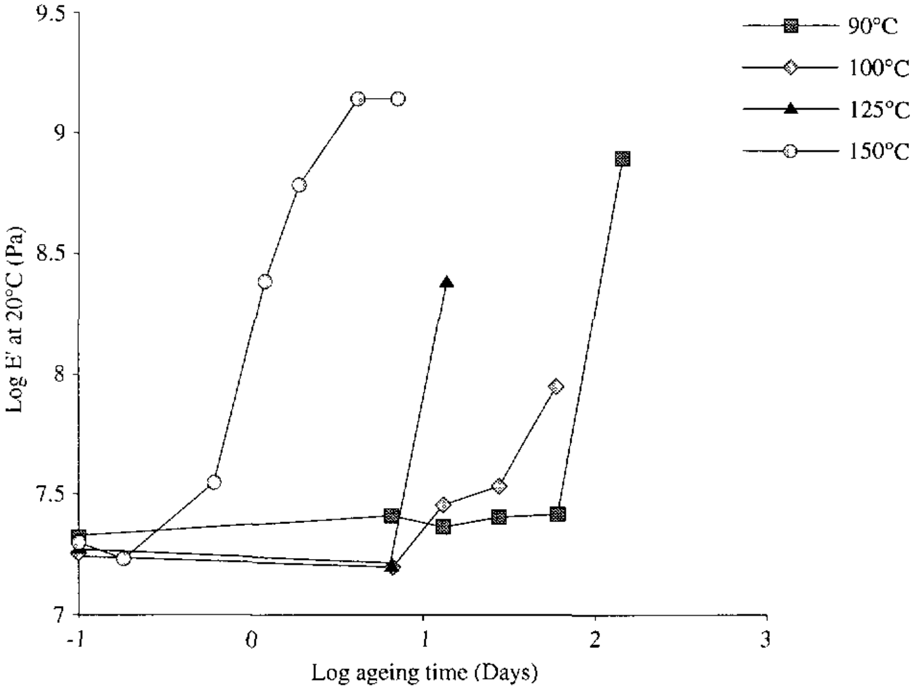


*Figure 5. The moduli of test pieces at a temperature of 20$^{0}$C after ageing at different temperatures between 90$^{0}$C and 150$^{0}$C* versus *ageing time (Compound 5).*

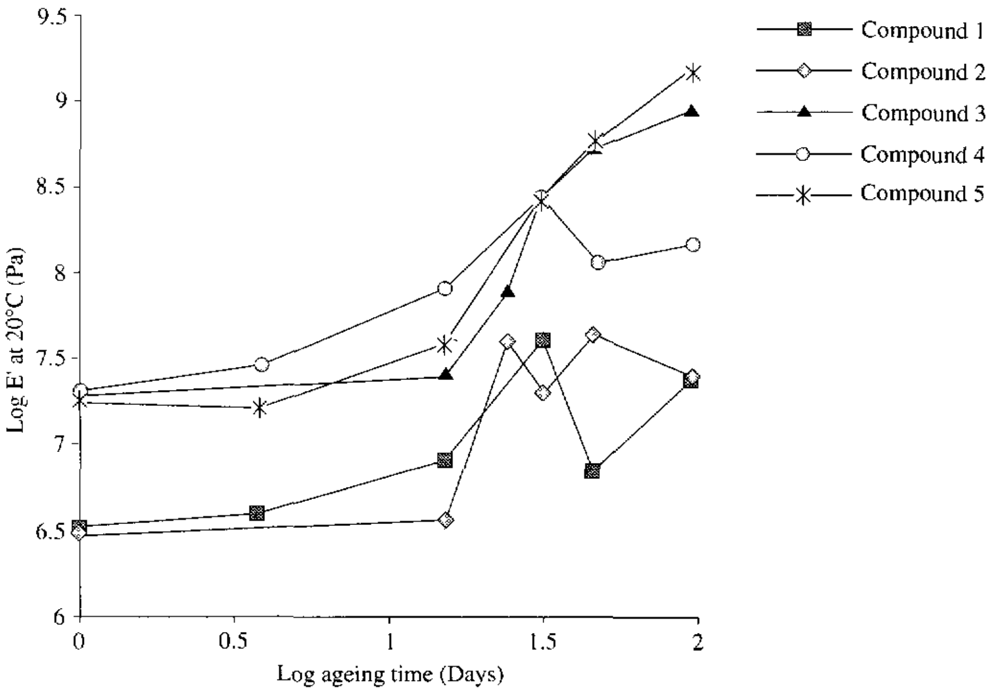


*Figure 6. The moduli of test pieces at a temperature of 20$^{0}$C* versus *ageing time. Ageing temperature: 150$^{0}$C (Compounds 1 to 5).*

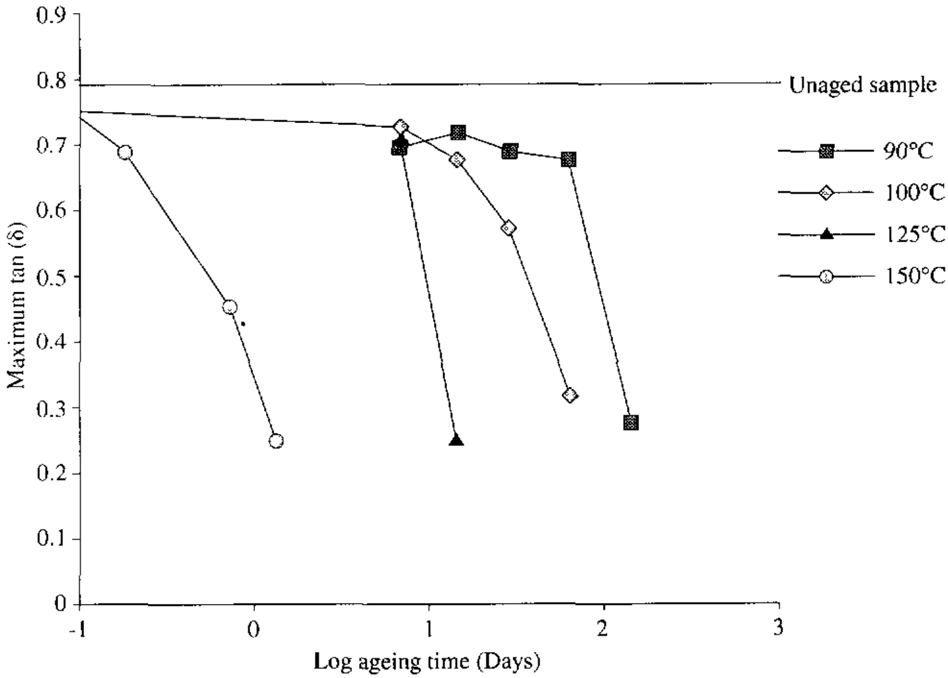


*Figure 7. The maximum value of tan δ from test pieces at a temperature of 20°C after ageing at different temperatures between 90°C and 150°C* versus *ageing time (Compound 5).*

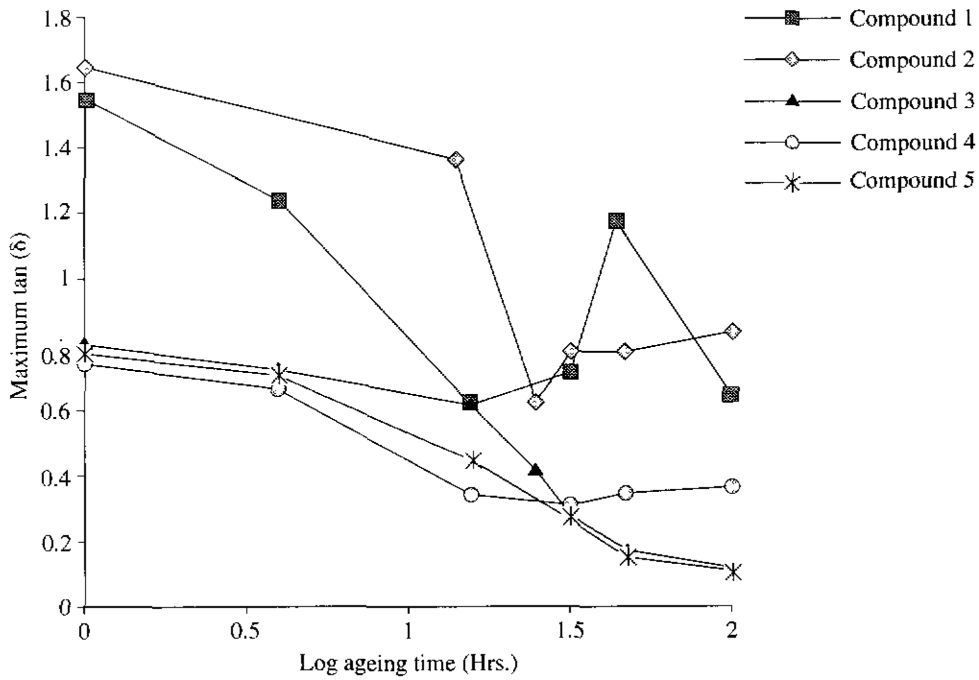


*Figure 8. The maximum value of tan δ from test pieces at a temperature of 20°C* versus *ageing time. Ageing temperature: 150°C (Compounds 1 to 5).*

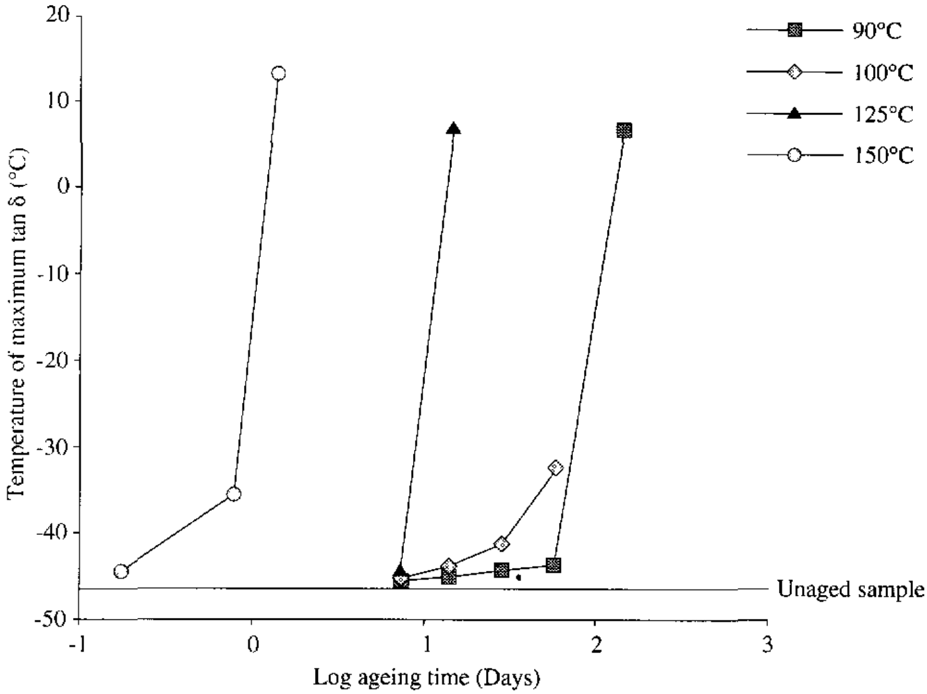


*Figure 9. The temperature at which the maximum value of tan δ occurs from test pieces aged at different temperatures between 90°C and 150°C* versus *ageing time (Compound 5).*

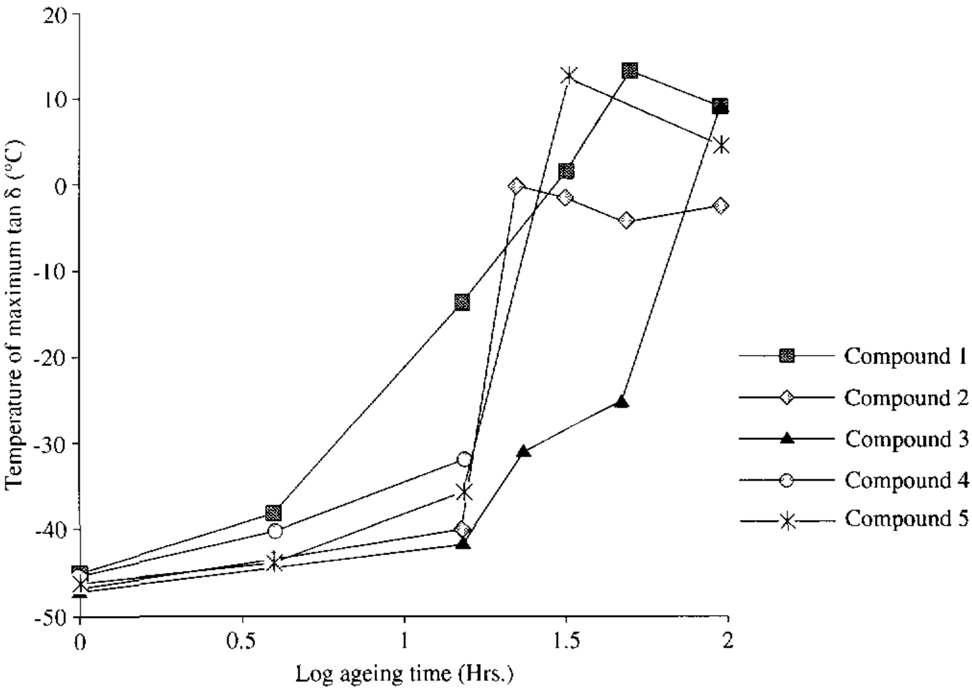


*Figure 10. The temperature at which the maximum value of tan δ occurs* versus *ageing time. Ageing temperature: 150°C (Compounds 1 to 5).*

TABLE 2 THE WEIGHT OF UNREACTED ANTIOXIDANT (*SANTOFLEX 6PPD*) AND NITROGEN IN TEST PIECES AEROBICALLY AGED FOR DIFFERENT TIMES AT A TEMPERATURE OF 90°C

| Ageing time (days) | Compound 5 Antioxidant weight (%) | Nitrogen weight (%) |
|---|---|---|
| Unaged | 0 948 | 0 32 |
| 7 | 0 136 | 0 32 |
| 14 | 0 016 | 0 32 |
| 28 | < 0 001 | 0 32 |
| 60 | < 0.001 | 0 33 |
| 150 | < 0 001 | 0 33 |

The lower detection limit for the antioxidant is 0 001%

temperature of 90°C and that the antioxidant remains in the rubber, being converted to a reacted form. A reason why the modulus increases sharply after 60 days ageing and not just after 28 days when the unreacted antioxidant is virtually depleted could be that the reacted antioxidant material can continue to provide a measure of protection to the rubber even after the unreacted antioxidant is depleted[9].

Material which is extensively oxidised has a different damping characteristic from that of unaged material as illustrated in the damping profiles shown in *Figure 2* The damping peak may be completely removed with ageing resulting in a flat curve with low tan δ values. The damping of aged material at ambient temperature can fall to about one third that of unaged material.

The temperature of the peak damping (tan δ) is termed the glass transition temperature. Ageing tends to lower the value of the damping peak and simultaneously raise the glass transition temperature as illustrated in *Figure 4*. The rate of fall of the peak damping value does not remain constant with ageing. The damping peak initially falls only slightly but is followed by a greater rate of fall at longer ageing times, as indicated by *Figures 7* and *8* At longer ageing times the peak damping can rise as well as fall depending upon the compound ingredients. Such behaviour reflects that of the modulus characteristics. Ageing can raise the glass transition temperature of a vulcanisate to about 0°C or perhaps a little higher as illustrated in *Figures 9* and *10*. It is not possible accurately to determine the glass transition temperature in extensively aged vulcanisates due to the flat nature of the damping profile.

## CONCLUSIONS

Aerobic ageing can significantly alter the dynamic modulus and damping of a vulcanisate Ageing tends to increase the modulus and glass transition temperature of a vulcanisate but it decreases the damping Depletion of antioxidant material in such vulcanisates by ageing is associated with increases in the rate of change of their properties. However, one notes that, after depletion of antioxidant, reaction products remain. These appear to continue to give some protection.

ACKNOWLEDGEMENTS

Thanks are due to Dr D. Campbell and Mr P. Lewis for helpful discussion of chemical reactions.

*Date of receipt: September 1996*
*Date of acceptance: August 1997*

REFERENCES

1. VAN AMERONGEN, G.J. (1964) Diffusion in Elastomers. *Rubb. Chem. Technol.* **37(5)**, 1065.

2. BARNARD, D. AND LEWIS, P.M. (1988) Natural Rubber Science and Technology. Oxford: University Press, 621.

3. LINDLEY, P.B. AND TEO, S.C. (1977) High Temperature Ageing of Rubber Blocks. *Plastics and Rubber Materials and Applications*, **2**, 82.

4. KNIGHT, G.T. AND LIM, H.S. (1975) Factors Influencing High Temperature Ageing of Large Natural Rubber Components. *Proc. Int. Rubb. Conf. Kuala Lumpur, 1975*, **5**, 57.

5. FUJITA, T. *et al.* (1993) Study for the Prediction of the Long-term Durability of Seismic Isolators. *ACS Rubber Division Meeting, Orlando, Florida, Parts I and II. Paper 96.*

6. MALEK, K. AND STEVENSON, A. (1992) A 100 Year Case Study of the Life Prediction of Natural Rubber for an Engineering Application. *J. nat. Rubb. Res.*, **7(2)**, 126.

7. FULLER, K.N.G. AND POND, T.J. (1995) The Long Term Performance of High-damping Natural Rubber Seismic Bearings. *European Seismic Design Practice: Research and Applications (Elnashai, A.S., ed.)*, 15.3, 585. Rotterdam: Balkema.

8. BJORK, F. AND STENBERG, B. (1985) Influence of the Formation of an Oxidized Layer on the Dynamic-mechanical Properties of Natural Rubber. *Polymer Testing*, **5**, 245.

9. LORENZ, O. AND PARKS, C.R. (1961) Antioxidant Efficiency of P-phenylene-diamines in Natural Rubber Vulcanizates. *Rubb. Chem. Technol.*, **34**, 816.