

## ***A 100-year Case Study of the Life Prediction of Natural Rubber for an Engineering Application***

KAMARUDIN AB. MALEK\* AND A. STEVENSON\*\*

*A thick rubber block was obtained after ninety-six years' ageing in air. The rubber was analysed for its formulation. Thick rubber blocks were prepared using this formulation and they were subjected to different periods of ageing and different temperatures. Puncture tests were performed on these aged samples and a characteristic time  $t_a$  was obtained for different ageing temperatures. Arrhenius plots of characteristic times of samples aged up to ten years and from that of the ninety-six-year-old sample were found to be linear.*

Rubber engineering components are frequently bulky and include thick layers of rubber. These components are sometimes expected to last for a very long time – e.g. over 100 years for civil engineering applications. Therefore, it is necessary to have some method of assessing the probable life-time of these rubber components at the design stage. This paper describes the use of a puncture test<sup>1,2,3</sup> to investigate changes in thick rubber blocks subjected to elevated temperatures and long-term ageing. The test consists of indentation and rupture of the surface of a rubber block by a cylindrical indenter as shown schematically in *Figure 1*.

The strength of rubber can be seriously affected by oxidation and the effect becomes worse when the rubber is subjected to high temperatures. It is known that a small amount of oxygen (ca. 1%) absorbed by a natural or synthetic rubber can have a deleterious effect on its physical properties<sup>4</sup>. Much research has been concerned with the mechanisms of the basic oxidation processes, namely the interaction between elemental oxygen and rubbers. The understanding of these chemical processes

has been derived largely from the work on model systems and generally, on thin sheets of vulcanisate<sup>5</sup>.

From an engineering point of view, the chemistry of oxidation has not yet answered the question of how long a bulky rubber component will last in service conditions, especially at elevated temperatures. Conventional ageing tests use thin test-pieces to characterise mechanical properties such as stiffness and strength. The properties are usually measured after oven-ageing for a specific time at a specific temperature. The ageing behaviour of thin rubber test-pieces may not represent that of thick blocks or indeed even that of the surface of thick blocks. This is because of the inhomogeneous nature of high temperature ageing of thick rubber blocks affecting mainly the surface<sup>3,6</sup>. The difference in strength between the surface and the bulk rubber can be easily evaluated by using the puncture test. Moreover, this technique permits the determination of the change in strength of thick rubber components which are subjected to different periods of ageing and different temperatures.

---

\*Rubber Research Institute of Malaysia, P.O. Box 10150, 50908 Kuala Lumpur, Malaysia

\*\*Materials Engineering Research Laboratory Ltd, Hertford SG 13 7OG, United Kingdom

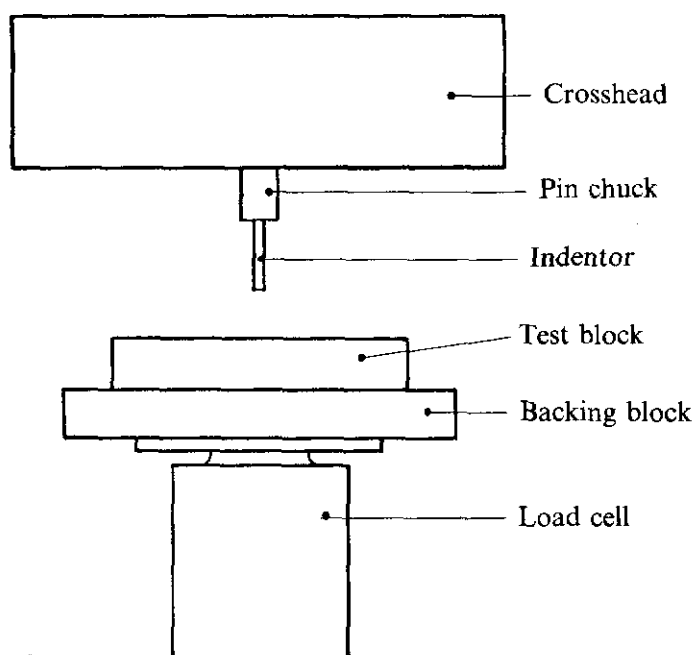


Figure 1. Schematic diagram of a puncture test.

In 1974, an engineering company provided Tun Abdul Razak Laboratory in Hertford, England, with a rubber sample from a ninety-six-year-old rubber bearing from a viaduct in Melbourne, Australia. This rubber was analysed and re-formulated to allow the ageing behaviour of thick rubber blocks to be studied at various times up to and including ninety-six years.

#### EXPERIMENTAL METHOD

The formulation of the ninety-six-year-old rubber was determined using thermogravimetric analysis (TGA) and thin layer chromatography (TLC) techniques<sup>7</sup>. The analyses suggest the following composition in parts per hundred of rubber (p.p.h.r.) by weight:

Natural rubber	100
Calcium carbonate	70
Ferric oxide	10
Sulphur	11

About 2.5 parts of other material, possibly dirt, were also present. The amount of free sulphur was less than 0.1%, indicating that the rubber was fully cured. The analysis also showed no evidence of curing residues or synthetic antioxidants. This is not surprising, because curing systems other than of sulphur plus metal oxide did not come into use until 1906, and synthetic antioxidants were not used until the 1940s.

A fresh natural rubber (RSS 3) compound was prepared using the above formulation and 5 parts of pine tar oil were added to the formulation to aid mixing. The rubber blocks were direct-compression-moulded for 3 h at 140°C to dimensions of 23 × 23 × 2.54 cm. The rubber blocks were then cut with a sharp knife into 2.5 cm test-cubes.

Ten-year-old samples of similar rubber prepared according to the above formulation by the late Dr Lindley of the Tun

Abdul Razak Laboratory, were also evaluated.

All the samples were aged for various times in an air-circulating oven at selected temperatures up to 200°C. One block was used for each combination of ageing time and temperature. After removal from the ovens, the blocks were allowed to cool at 23°C before being tested at room temperature. The blocks were cut open with a razor blade, and several puncture tests were carried out on both the exterior surface and the cut surfaces of the bulk rubber. Puncture tests were carried out using a 0.5 mm diameter indenter with 5  $\mu$ m corner radius. Puncture tearing energies were subsequently obtained for each puncture test using the equation<sup>1</sup>  $T_c = F(1 - \lambda_c)/2 \pi r_o$ , where  $F$  is the puncture force at rupture,  $\lambda_c$  is compression ratio and  $r_o$  is the surface crack radius after puncture as shown in Figure 2. The determination of  $\lambda_c$  was discussed in Kamarudin<sup>1</sup> and it is equal to  $\frac{1}{\lambda^2}$ , where  $\lambda$  is given by:

$$\frac{\text{Radius of the indenter}}{\text{Radius of puncture crack } (r_o)}$$

It has been shown that oxidative degradation in rubber is accompanied by an increase in oxygen content<sup>8</sup>. Thus measurement of oxygen uptake provides a simple and quick way of evaluating the degree of degradation that has taken place in the rubber. Therefore, it would be of interest to find out the variation of oxygen content in the surface and in the bulk of the aged rubber blocks previously used for the determination of puncture energy. The instrument used was a Perkin-Elmer 240 Elemental Analyser which can give the value of the oxygen content to an accuracy of  $\pm 0.3\%$ . The method consisted of pyrolysing the sample in a stream of helium at 975°C over carbon, when the resulting oxygen was converted to carbon monoxide. The carbon monoxide was then passed through copper oxide at 670°C, where it was converted to carbon dioxide which was measured. The machine sub-

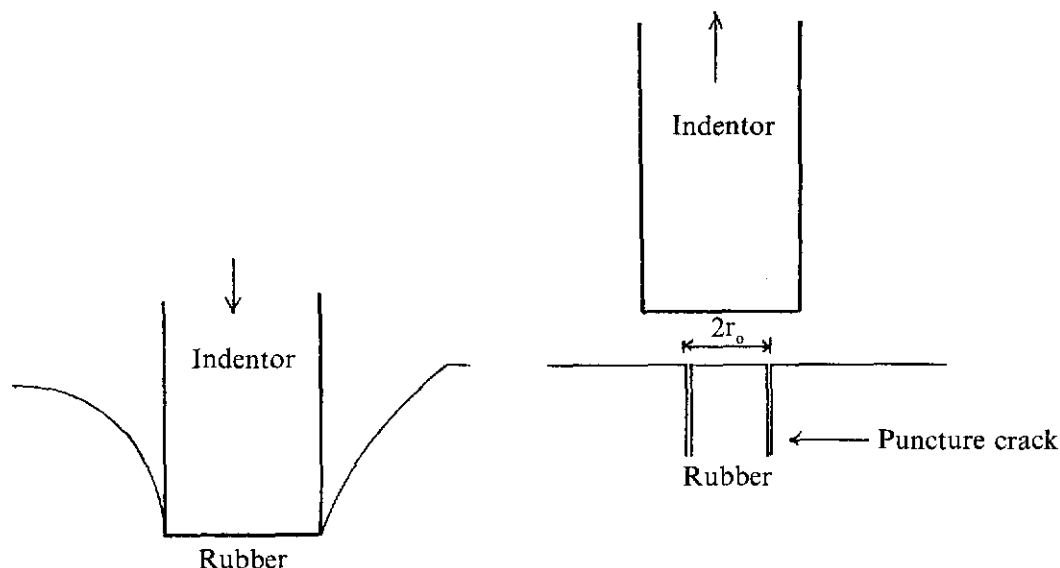


Figure 2. Schematic diagram of an indentation and puncture of rubber.

sequently gave the oxygen content in weight % (% w/w), i.e. as gramme of oxygen per 100 g of rubber vulcanisate.

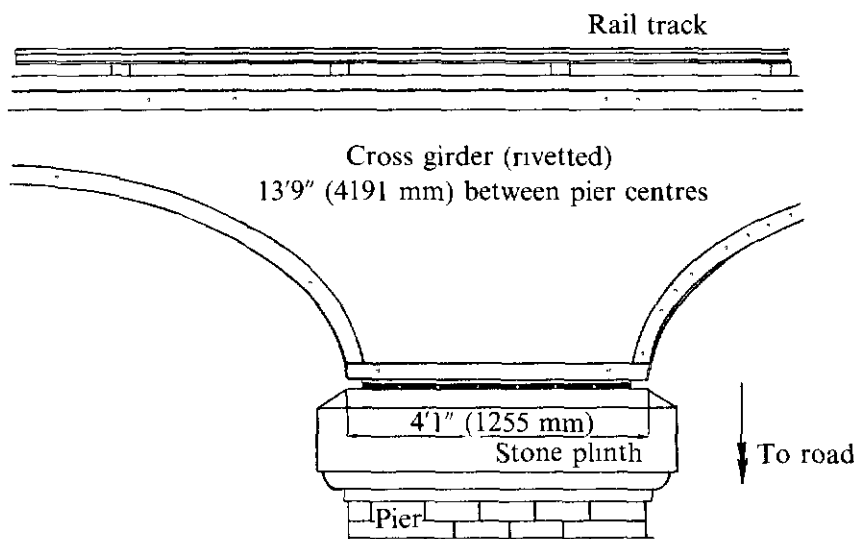
## RESULTS

### **Conditions of Natural Rubber Pad after Ninety-six Years' Service**

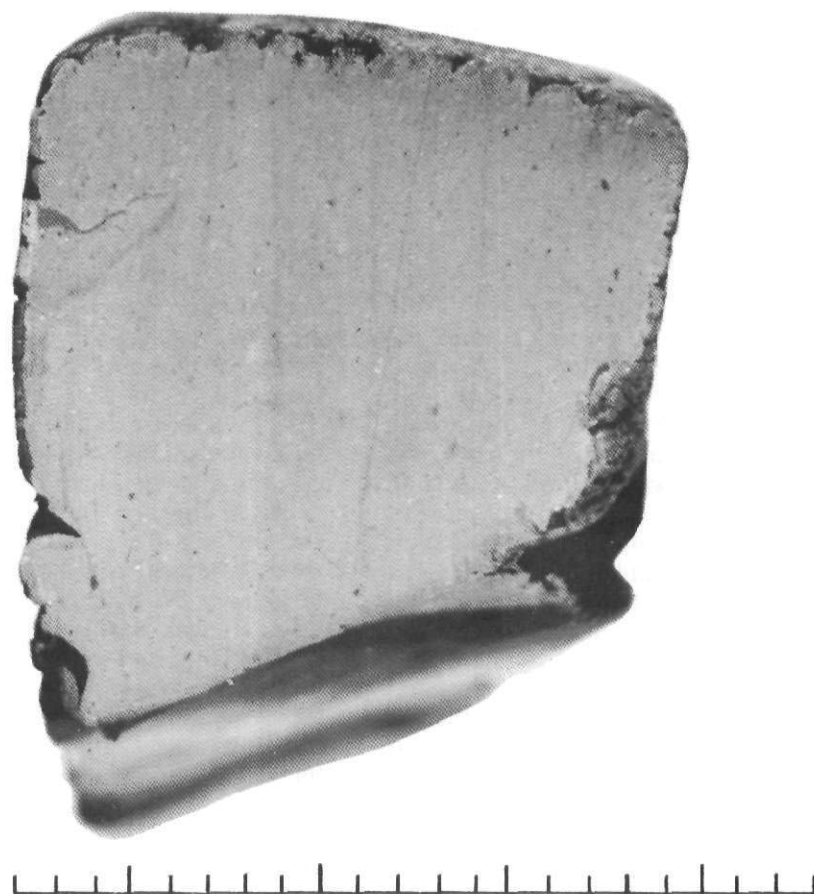
The rubber pads were about 2.5 cm thick and *Figure 3* shows the locations of the pads between the steel structures and the supporting piers of the viaduct. *Figure 4* shows a clean-cut section through the sample to illustrate the depth of any ageing of the rubber. The surface of the rubber is hard and shows evidence of oxidation. Below a depth of about 1.5 mm, however, the rubber is free from such degradation and was there, found still to have a hardness of only 63 IRHD. There was no evidence of significant deterioration of the rubber below this depth and in the centre of the pad. This provides convincing evidence of the fact that the weathering of natural rubber in normal conditions is limited to the surface.

### **Variation of Puncture Energy with Time of Ageing**

These tests were carried out on 2.5 cm cubes aged in air at 23°C, 40°C, 70°C, 100°C, 125°C, 150°C, 175°C and 200°C. The variations of puncture energy of the surface and bulk with time of ageing are shown in *Figures 5 – 12*. The puncture energy scales are linear and the time of ageing scale is logarithmic. *Figure 4* shows the results of air-ageing at 23°C. The ninety-six years' point was obtained from the original rubber from the Melbourne viaduct rubber pad. The puncture energies of the surface and bulk were similar within the first six months of ageing time. Then, the puncture energy dropped sharply. In the case of rubber at the surface, the puncture energy dropped sharply between six months and four years of ageing. With further ageing, it showed little change, but with the limited data available there is an indication of a minimum at about ten years with a subsequent small rise between ten and ninety-six years. In addition, the hardness (80 IRHD) of the surface of the ninety-six-



*Figure 3. Drawing of Melbourne Railway Viaduct incorporating natural rubber pads in 1889 (traced from: N<sup>o</sup> 715, Railway Department, Melbourne, May 1883).*



*Figure 4. Cut section through ninety-six-year-old rubber pad showing that degradation was limited to an outer skin.*

year-old rubber is higher than the hardness of the surface of the ten-year-old rubber (42 IRHD). In the case of the rubber in the bulk, the minimum puncture energy was not observed – the puncture energy obtained from the ninety-six-year-old sample was about 10.0 kJ/m.

For the rubber aged at 40°C (*Figure 6*), a minimum puncture energy was not observed for either the surface or the bulk. This is probably due to insufficient ageing time because a minimum puncture energy could be seen when the rubber was aged at 70°C (*Figure 7*). In this case, the

puncture energies of both the surface and the bulk showed minima. Moreover, at the minimum puncture energy, the surface of the rubber was soft, and with increasing ageing time, the surface became hard. The increase in puncture energy corresponded to the formation of a thin layer of hard skin as shown in *Figure 13*. This rubber was aged at 70°C for 181 days.

*Figures 8 – 12* show the results of ageing at 100°C to 200°C. It can be seen that in all cases, there was no minimum puncture energy for both the surface and the bulk of the rubber. The puncture energy of the

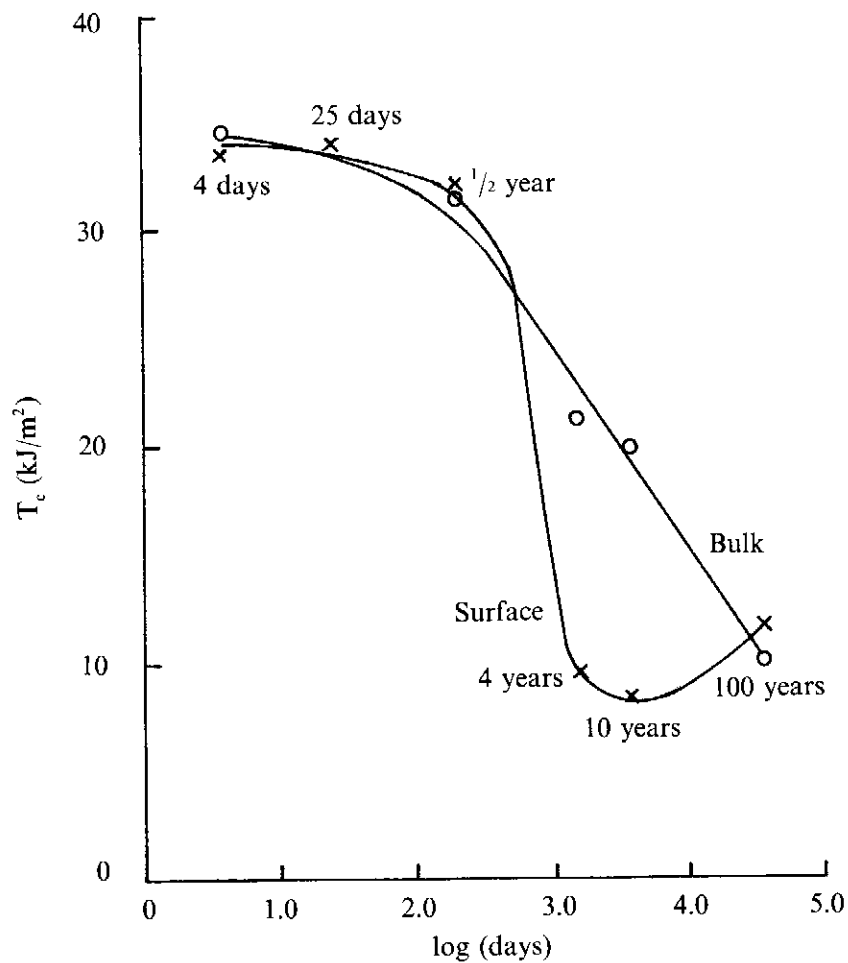


Figure 5. Variation of puncture energy of the surface and bulk of rubber with time of ageing in air at 23°C.

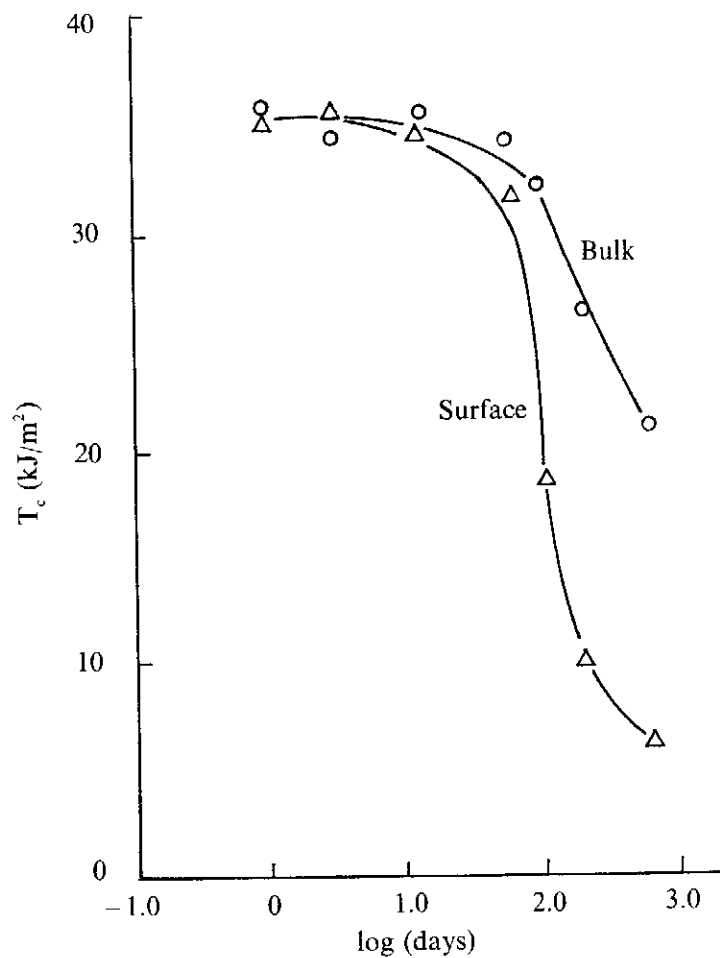


Figure 6. Variation of puncture energy of the surface and bulk of rubber with time of ageing at 40°C.

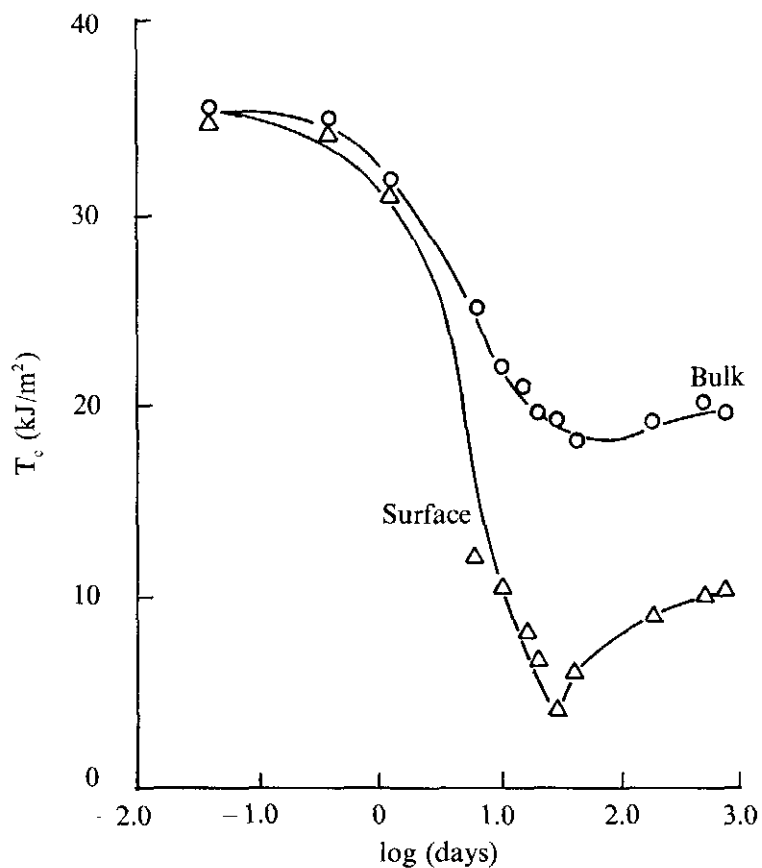


Figure 7. Variation of puncture energy of the surface and bulk of rubber with time of ageing at 70°C.

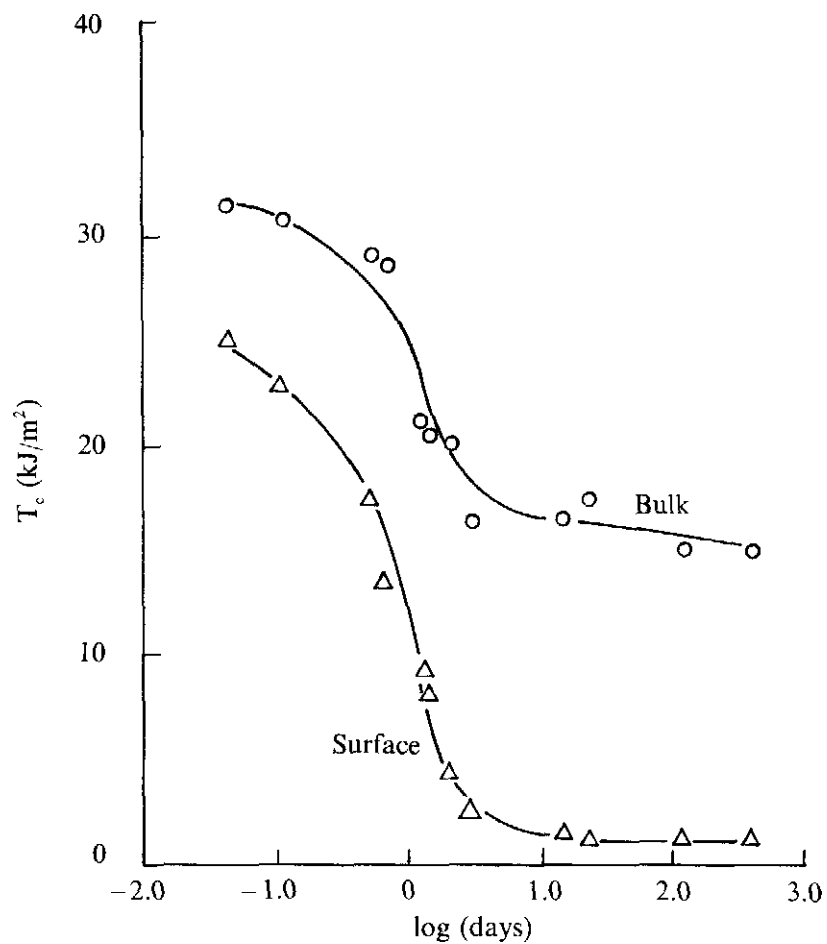


Figure 8. Variation of puncture energy of the surface and bulk of rubber with time of ageing at 100°C

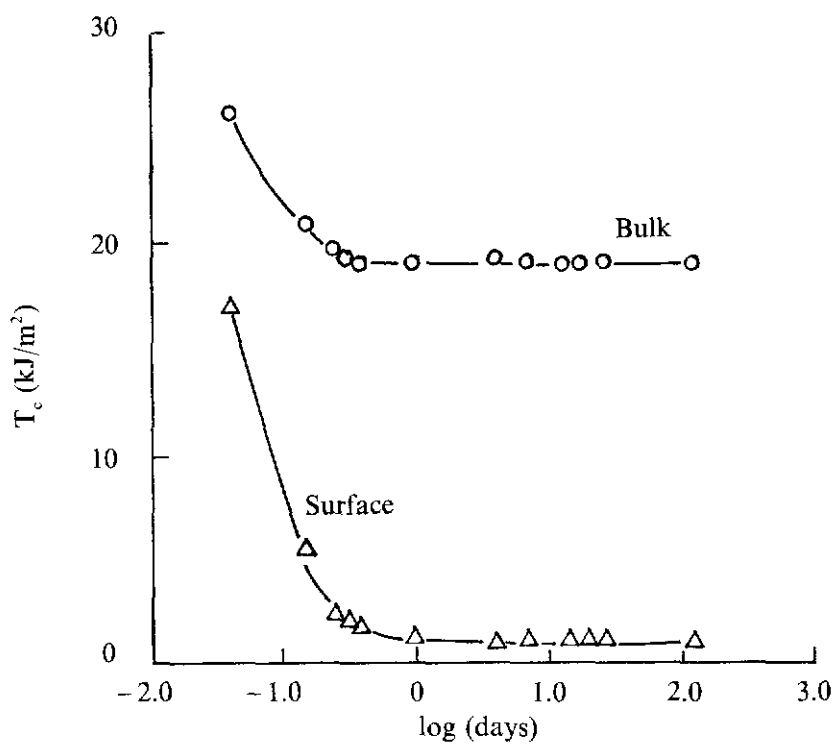


Figure 9. Variation of puncture energy of the surface and bulk of rubber with time of ageing at 125°C.

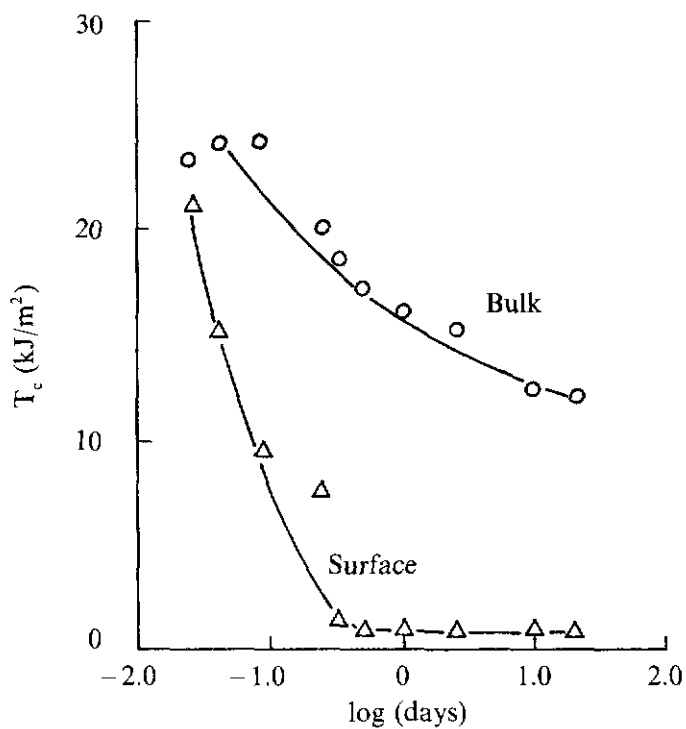


Figure 10. Variation of puncture energy of the surface and bulk of rubber with time of ageing in air ovens at 150°C.



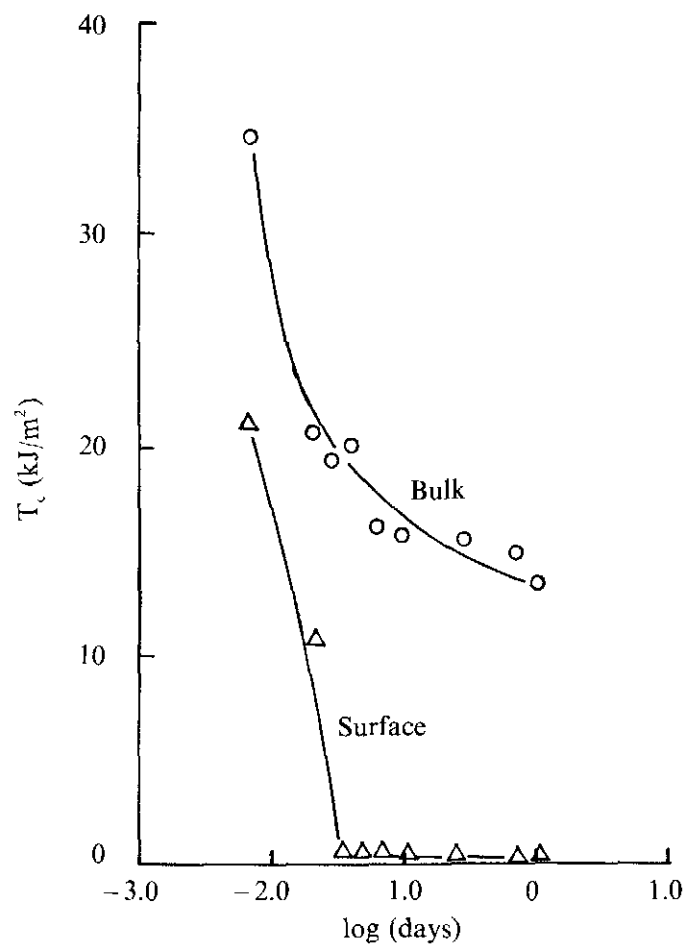


Figure 11. Variation of puncture energy of the surface and bulk of rubber with time of ageing in air oven at  $175^\circ\text{C}$ .

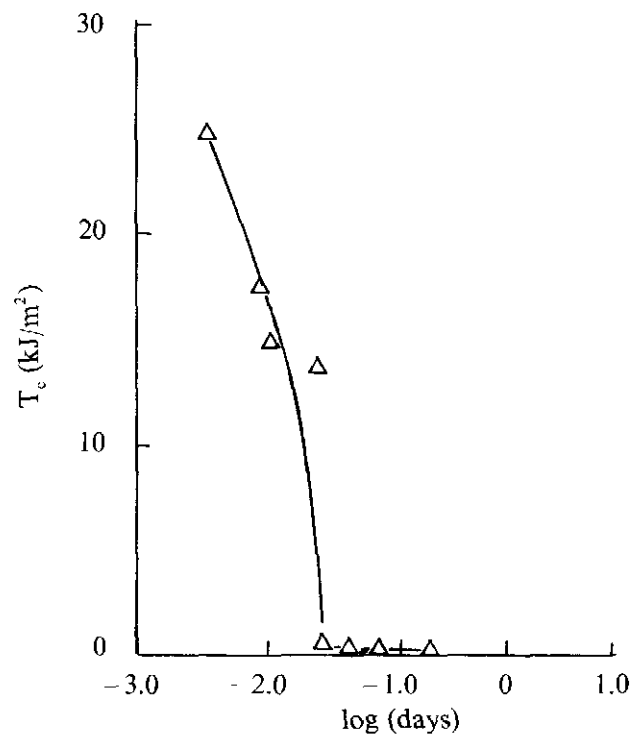


Figure 12. Variation of puncture energy of the surface of rubber ageing in an air oven at  $200^\circ\text{C}$ .

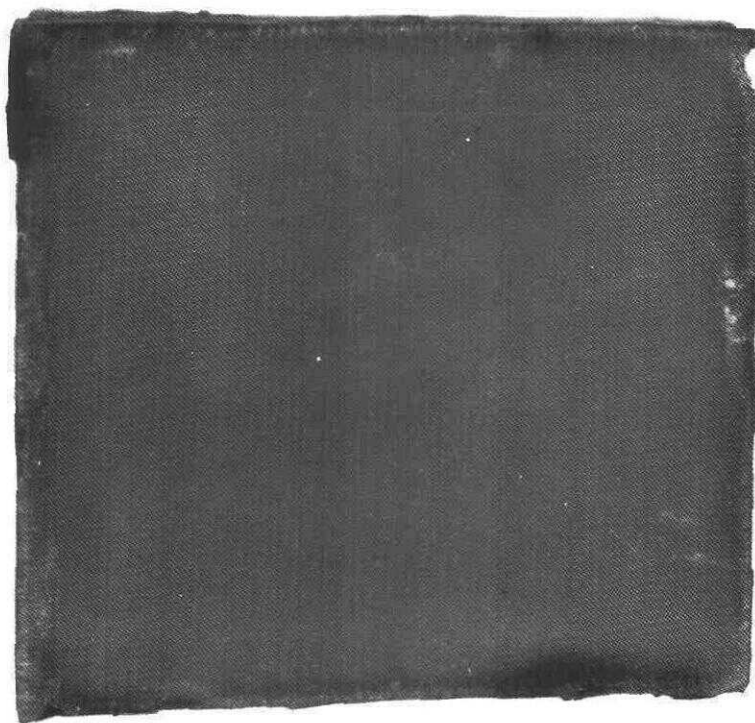


Figure 13. A hard skin on a rubber block aged at 70°C for 181 days.

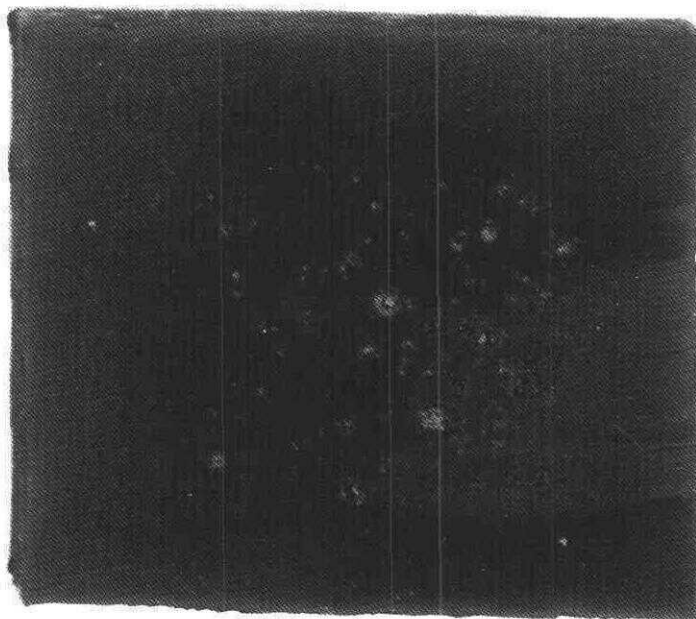
surface rubber decreased with increasing ageing time, and at characteristic time  $t_a$  attained the lowest puncture energy value and remained at this value with increasing ageing times. The time  $t_a$  decreased with increasing temperature. In addition, the lowest puncture energy attained decreased with increasing temperature, for example, at 100°C and 200°C, the lowest puncture energies were 1.25 kJ/m<sup>2</sup> and 0.25 kJ/m<sup>2</sup> respectively. The formation of a thin skin could be observed after ageing time  $t_a$ , but the skin was soft and sticky at 175°C and 200°C.

The puncture energy in the bulk rubber aged at 100°C and 125°C was reduced to the lowest value and it appeared that the puncture energy did not subsequently vary with increasing ageing time. However, at 150°C and 175°C, the puncture energy showed a gradual reduction with in-

creasing ageing time and did not show a constant value. The puncture energy could not be obtained with rubber blocks aged at 200°C because in the bulk of the rubber, there were small holes (Figure 14) which interfered with the puncture test. This provides an interesting example of the limitations of elevated temperature tests as accelerated ageing of room temperature behaviour.

### **Uptake of Oxygen**

Figure 15 shows the variation with time of ageing at 23°C of the oxygen content of the surface and the bulk rubber. The results also include the oxygen content of the ninety-six-year-old rubber. It can be seen that at 23°C for rubbers prepared and aged up to four years, the bulk rubber did not increase in oxygen content. For the



*Figure 14. Holes in the rubber bulk aged at 200°C.*

ten-year-old sample, the oxygen content of the bulk rubber was quite similar to that aged up to four years. The oxygen content in the bulk of the ninety-six-year-old sample was higher by about 4%. However, the increase in the oxygen content was more pronounced in the surface. The total oxygen content in the surface of the ninety-six-year-old sample was 10% higher than that in the four-year-old sample. *Figure 16* shows the increase in the oxygen content in the bulk of rubbers aged at different temperatures and times. Except for the 4% increase for the ninety-six-year-old rubber, the increases in the oxygen content in all other cases were less than 2%. The increase in the oxygen content was much higher in the surfaces of the rubbers, as shown in *Figure 17*. Most of the increase was about 10%. It can also be seen that the increase in the oxygen content was much quicker at higher temperatures than at 70°C or 23°C.

#### DISCUSSION

In general terms, puncture energy decreases with ageing. At very long ageing time near ambient temperature (as represented by the Melbourne bridge sample), there is some indications of a slight rise in puncture energy of the surface. Further evidence for a puncture energy minimum is obtained for ageing at 70°C in both the bulk and the skin. Measurements at 40°C may not have been continued long enough to reveal the minimum. At 100°C and above, the minimum is not observed. For the surface, the puncture energy decreases progressively to a very low level and then remains approximately constant.

A characteristic time  $t_a$  can be defined for each ageing temperature which represents the time to reach either the minimum in the puncture energy curve or the time to attain the low level of puncture energy

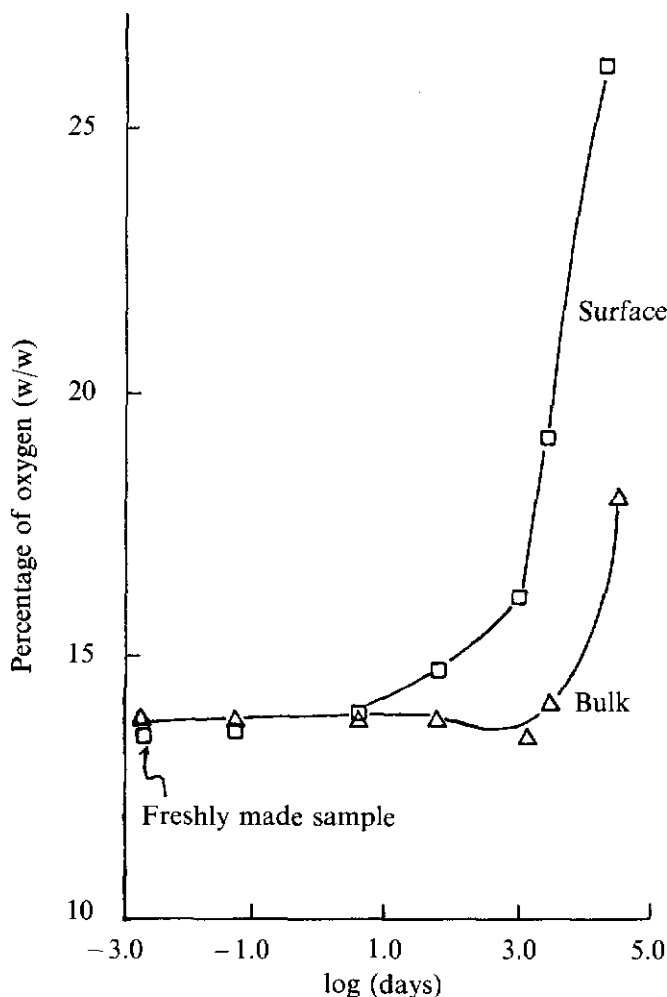


Figure 15. Variation of oxygen content with ageing time at 23°C.

characteristic of long-term ageing. At the higher temperatures ( $>70^{\circ}\text{C}$ ), this time has been taken as the time to the first puncture energy value which lies clearly with the group of nearly constant energies.

The time  $t_a$  can be considered as a measure of the rate of the ageing process. A plot of  $\log(t_a)$  versus reciprocal absolute temperature (Figure 18) is approximately linear and an Arrhenius activation energy<sup>3</sup> of 78.5 kJ/mole can be evaluated from its slope. This activation energy agrees well

with a value of 80 kJ/mole reported by Lindley and Teo<sup>3</sup> for the chemical reaction relating to the skin formation during ageing of a modern accelerated efficient vulcanisate system. The network structure of the efficient vulcanising system consists of mainly monosulphidic crosslinks<sup>9</sup>, whereas the vulcanisate studied here is based on metal oxide/sulphur system and therefore would give different crosslinking network structure. The two vulcanisate structures have different long-term maturing characteristics. The similarity in the

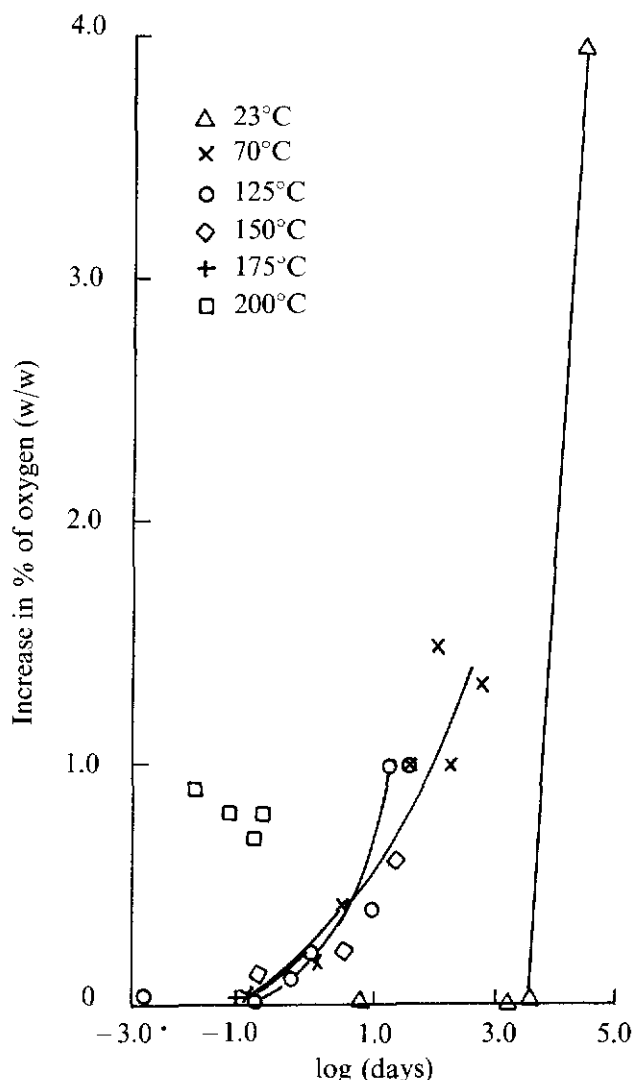


Figure 16. Increase in percentage of oxygen in the bulk of the rubber with ageing time.

activation energies for the ageing of the two materials suggests that this ageing is primarily the effect of oxidation rather than maturing reactions.

Evidence to oxidation is clearly provided by the change in the oxygen content of the samples. The change is more pronounced in the surface than in the bulk of the sample, and the pattern parallels the

puncture energy data from surface and bulk measurements. The observations support the proposal made by Van Amerongen<sup>10</sup> and Stenberg *et al.*<sup>11,12,13</sup> that the surface skin acts as a protective barrier for the bulk of the sample. An important feature of the present results is that the effects of this surface skin can be detected even at quite modest ageing temperatures.

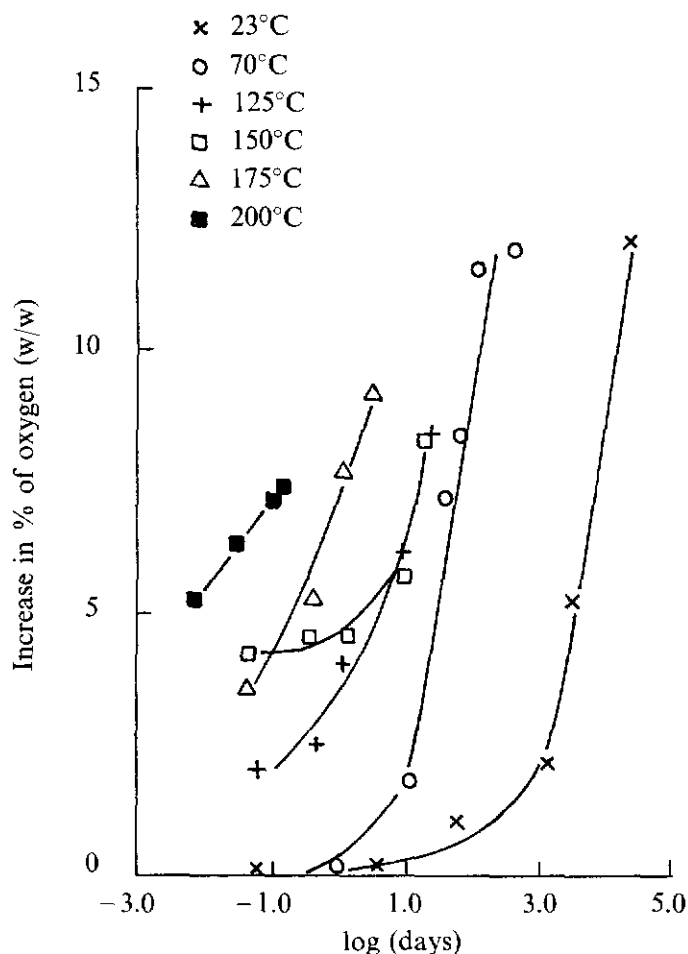


Figure 17. Increase in percentage of oxygen in the surface of the rubber with ageing time.

Puncture energy therefore bears a general relationship to oxidative ageing for the specific case of the metal oxide/sulphur vulcanisate system studied here. The study has taken specific advantage of the availability of the ninety-six-year-old sample which has been exposed to natural air ageing conditions and the results for this sample have been shown to be consistent with the shorter term, accelerated ageing results based on the newly prepared samples of the same formulation. Notwithstanding the fact that the formulation analysed may not be exactly the same 100 years ago, but nevertheless a technique has been developed

here using the puncture test to characterise long-term ageing of thick rubber blocks.

The increase in the puncture energy after the minimum is obviously advantageous to rubber components, but the reason for the increase is not obvious. Two competing processes during ageing, namely chain scission and crosslinking, influence the puncture energy of the rubber.

Initially, the puncture energy is reduced due to oxidative chain scission as observed. With prolonged ageing, a stage will be reached where most of the rubber at the

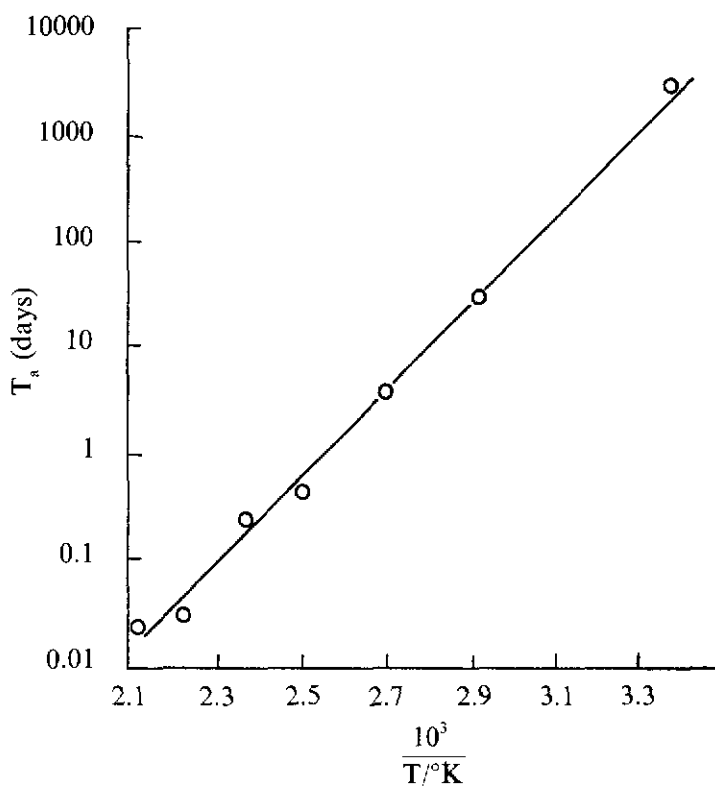


Figure 18. Arrhenius plot of the logarithm of the time  $t_a$  against reciprocal temperature.

surface has reacted with oxygen and forms an oxidised skin thus preventing further penetration of oxygen. In this situation, it is probable that the crosslinking becomes dominant. The rubber used in this investigation contained no accelerator ingredient to increase the rate of crosslinking and to increase the efficiency of utilisation of sulphur in forming the crosslinks. Thus, the initial degree of crosslinking formed after vulcanisation is low<sup>14</sup> even though 11 parts of sulphur per 100 parts of rubber were used. Smith *et al.*<sup>15</sup> showed that a slow crosslinking reaction takes place over long reaction times which gradually increase the number of crosslinks. However, the increase in the number of crosslinks will not be limited by the inefficiency of the rubber vulcanising system. It has been shown<sup>16</sup> that the strength of rubber passes through a maximum as the degree for crosslinking is

increased. Therefore, the apparent increase in the puncture energy with increasing ageing time may be caused by a small increase in the number of crosslinks. A large increase in the number of crosslinks would have reduced the puncture energy.

However, the increase in the puncture energy after the initial drop was not observed when the rubbers were aged at 100°C or higher. This may be explained by the fact that at high temperatures, the crosslinks are thermally unstable<sup>17</sup>. At temperatures around 200°C, the main polyisoprene chains themselves become susceptible to decomposition<sup>18</sup>. At the surface, where oxygen is available, the situation is worse as the unstable crosslinks and the main chains can readily undergo oxidative ageing.

## CONCLUSION

The puncture test was used to study the strength of thick rubber blocks which had been exposed to long-term ageing and high temperatures. A surface skin was observed on the ninety-six-year-old rubber pad which was found to be in good condition and still functioning. Such longevity is believed to be due to the formation of a hard surface skin, which is impervious to penetration by oxygen and thus protects the rubber underneath. A characteristic time  $t_a$  was obtained using a puncture test. Arrhenius plots of the characteristic times up to ten years and that of ninety-six years were shown to be linear. The activation energy was found to be 78.5 kJ/mole.

## ACKNOWLEDGEMENT

This work was carried out at the Malaysian Rubber Producers' Research Association and the authors wish to thank the Analytical Laboratory for chemical analyses and oxygen content measurements. Thanks are also due to Dr Ong Eng Long for helpful comments on the manuscript and to Dr D.S. Campbell for useful discussions.

*Date of receipt: January 1992*

*Date of acceptance: February 1992*

## REFERENCES

1. KAMARUDIN AB. MALEK (1987) On the Puncture Strength of Rubber. Ph.D Thesis, CNA, UK
2. AB. MALEK, K. AND STEVENSON, A. (1984) On the Lubrication and Wear of Metal by Rubber. *J. Mater. Sci.*, **19**, 585.
3. LINDLEY, P.B. AND TEO, S.C. (1977) High-temperature Ageing of Rubber Blocks. *Plast. Rubb. Mat. Appl.*, **2**, 82.
4. McDONEL, E.T. AND SHELTON, J.R. (1959) Effect of Curing System on Rubber Oxidation and Physical Degradation. *J. Chem. Eng. Data*, **4**, 360.
5. BARNARD, D., BATEMAN, L., CUNNEEN, J.I. AND SMITH, J.F. (1963) *The Chemistry and Physics of Rubber-like Substances*, (Bateman, L. ed.). Chap 17. London: Maclaren and Son Ltd.
6. KNIGHT, G.T. AND LIM, H.S. (1975) Factors Influencing High Temperature Ageing of Large Natural Rubber Components. *Proc. Int. Rubb. Conf. Kuala Lumpur*, **5**, 57.
7. TIDD, B.K. (1977) Chemical Analysis of Rubber Vulcanizates. *Plast. Rubb. Mat. Appl.*, **2**, 100.
8. WAKE, W.C., TIDD, B.K. AND LOADMAN, M.J.R. (1983) *Analysis of Rubber and Rubber-like Polymers*, Chap. 6. Applied Science Publishers
9. ELLIOTT, D.J. AND TIDD, B.K. (1974) Development in Curing Systems for Natural Rubber. *Progress of Rubber Technology*, **34**, 83. London: Institution of Rubber Industry.
10. VAN AMERONGEN, G.J. (1964) Diffusion in Elastomers. *Rubb. Chem. Technol.*, **37**, 1065
11. STENBERG, B., SHUR, Y.I. AND JANSSON, J.F. (1979) Hypothesis for the Compression Relaxation of a Natural Rubber. *J. Appl. Polym. Sci., App. Polym. Symp.* **35**, 511.
12. STENBERG, B. AND DICKMAN, O. (1984) The Influence of Antioxidant on Stress Relaxation in Rubber Sample of Different Thicknesses. *Plast. Rubb. Processing and Applications*, **4**, 337.
13. STENBERG, B. AND BJORK, F. (1985) Influence of the Formation of an Oxidized Layer on the Dynamic-mechanical Properties of Natural Rubber. *Polymer Testing*, **5**, 245.
14. GLAZER, J. AND COTTON, F.H. (1961) *The Applied Science of Rubber*, (Naunton, W.J.S., ed.), Chap. 12. London: Arnold.
15. SMITH, D.A., RUSSEL, R. AND WELDING, G.N. (1962) Kinetics of Thiazole-accelerated Sulphur Vulcanization of Natural Rubber, *Proc. Fourth Rubb Technol. Conf., London*.
16. THOMAS, A.G., MULLINS, L. AND GREEN-SMITH, H.W. (1963) *The Chemistry and Physics of Rubber-like Substances* (Bateman, L. ed.), Chap 10. London: Maclaren and Sons Ltd.
17. MORRISON, N.J. AND PORTER, M. (1983) Temperature Effects on Structure and Properties during Vulcanization and Service of Sulphur-crosslinked Rubbers. *Plast. Rubb. Processing and Applications*, **3**, 295.
18. BARNARD, D. (1984) *The Ageing of Natural Rubber*, 75 Years of Rubber Research International Conference held in Colombo, September, 1984.