JOURNAL OF MATERIALS SCIENCE **21** (1986) 147–154

The effect of 42 year immersion in sea-water on natural rubber

K. AB-MALEK, A. STEVENSON
Malaysian Rubber Producers' Research Association, Hertford, Hertfordshire SG13 8NL, UK

A study has been made of the physical condition of vulcanized natural rubber retrieved after 42 yr exposure to sea-water at a water depth of 80 ft (24.3 m). Drying experiments show the maximum amount of water absorbed in the 42 yr period to have been less than 5% of the dry rubber mass. No effect of marine life was observed and the physical properties of the rubber were found to be as good as for new rubber moulded to a similar formation.

1. Introduction

There have been several laboratory studies of the absorption of water by rubbers [1–3], but relatively few reports of the effect of long-term exposure at offshore sites. Sea-water trials of up to 14 yr have been reported [4, 5] on plastics and rubbers used for cable covers. Exposure was in shallow water sites chosen for an abundance of marine growth (Florida and Carolina, USA). Some materials, especially silicone rubber, were reported to be damaged by marine borers (e.g. pholads) burrowing into the surface. However, nitrile rubber (NBR), styrene butadiene rubber (SBR) and polychloroprene (PC) suffered only slight damage after 7 yr, no damage at all being reported for natural rubber (NR) at that time. After 14 yr exposure no reductions in tensile strength greater than 20% were recorded for NR or PC, whereas that for SBR and NBR deteriorated by 30 and 40% respectively. Silicone rubber showed a 70% tensile strength reduction in this period. Muraoka [6] reported no deterioration of NR, BR or PC after 3 yr exposure at a deepwater Pacific site (2 to $\times 10^3$ ft water depth) but confirmed some deterioration of SBR and severe deterioration of silicone rubber. Cumberland [7] has reported on the exposure of four different compounds of PC to sea water in a lagoon in Panama. Modulus increases of between 104 and 245% were recorded after 10 yr, with decreases in the elongation at break of between 62 and 78%. Although these are large changes, similar changes were observed in control testpieces stored in air, so the changes reported cannot be attributed to the presence of sea-water but are simpy due to the poor long-term ageing resistance of these PC compounds.

The present study has investigated the condition of natural rubber tyres and inner tubes recovered from the deck of a sunken vessel resting in 80 to 100 ft (24 .3 to 30.5 m) of water off the NW Coast of Scotland. An account of their discovery has been given elsewhere [8]. The tyres and inner tubes were part of a consignment of military equipment bound for India on the Royal Navy Ship *S.S. Breda* which was sunk in 1941. The first rubber articles were recovered in 1982 [8], then in 1983 a second set of tyres and inner tubes was recovered under more controlled conditions. The tests on the condition of the rubber refer to articles recovered in 1983.

2. Experimental methods

A team of divers recovered the tyres and inner tubes, bringing them to the surface with the aid of a flotation collar. Once at the surface they were immediately transferred to large polythene drums filled with sea-water on-site, and sealed for transportation back to the laboratory. The purpose of this procedure was to prevent any evaporation of water prior to controlled laboratory tests. The divers also collected samples of sea-water from the site at the depth that the tyres were found and at the surface, and also of silt which had settled near to the tyres. All recovered articles were returned to the laboratory and tests commenced on them within 24 h of recovery. Tests are reported here on one inner tube and one tyre.

The inner tube, 1.5 m diameter, consisted of 2.5 mm thick sheeting and so was easy to cut into strips for the performance of physical tests in the laboratory. The tyre was more difficult to prepare for investigation of the rubber condition. It was first cut radially into four segments on-site before sealing into the sea-water tanks for transportation. Then, in the laboratory, shorter segments were cut out which permitted puncture tests to be performed on the cut rubber surface. These tests consist in driving a small cylindrical indenter into the rubber surface under controlled conditions (on a test machine) to provide information about the local strength and modulus of the rubber. This test has been described in detail elsewhere [9, 10]. Other sections were cut into layers and ground smooth to 2 mm thickness. Standard* tensile testpieces were then cut from the layers in the normal way. Since this latter procedure was time consuming and could not be done under water, only dried testpieces were prepared in this way.

Wet samples from both the tyre and the inner tube were weighed (after removal of surface water) using a

---

*British Standard 903.

0022–2461/86 $03.00 + .12

Figure 1 General view of tyre during recovery after 42 yr immersion in sea-water.

Figure 3 General view of truck inner tube after 42 yr immersion in sea-water — shown inflated in the laboratory.

chemical balance and carefully dried in a controlled laboratory atmosphere (23° C and 50% r.h.), weighing being repeated at regular intervals. Physical tests were performed to determine the hardness, tensile strength (TS), elongation at break (EB), tensile strength and compression set of rubber samples. Chemical analysis was performed to determine the main ingredients of the rubber compound and permit preparation of new rubber samples using the likely formulation of the tyre and inner tube. Further chemical tests provided information on the degree of crosslinking in the rubber. Finally sections through rubber samples from the tyre were studied with the aid of a scanning electron microscope to investigate the existence of any surface skin effects.

3. Results and discussion

3.1. Visual appearance

Both tyre (Fig. 1) and the inner tube (Fig. 3) appeared to be in excellent condition on removal from the sea. Neither showed any evidence of attack by marine organisms. The tyre tread was still clear and sharp (Fig. 2) and the inner tube was still capable of inflation, although leakage through the valve area caused it to remain inflated only for 1 day. Markings on the tyre sidewall were still clear enough to read that it had been manufactured by Dunlop in Great Britain. When radial cuts were made through the tyre to cut it into segments, the steel beading thus revealed was bright and completely free from corrosion (Fig. 4) although it was then easy to pull it away form the tyre wall, suggesting poor rubber/metal bonding.

Figure 2 Enlarged view of the tread ot the tyre shown in Fig. 1. Tread pattern is still clear and tread depth is 10 mm

3.2. Composition of tyre and inner tube

Samples of rubber from both the tyre and the inner tube were subjected to acetone extraction followed by thin layer chromatography of the extent and thermogravimetric analysis of the residue. This showed the

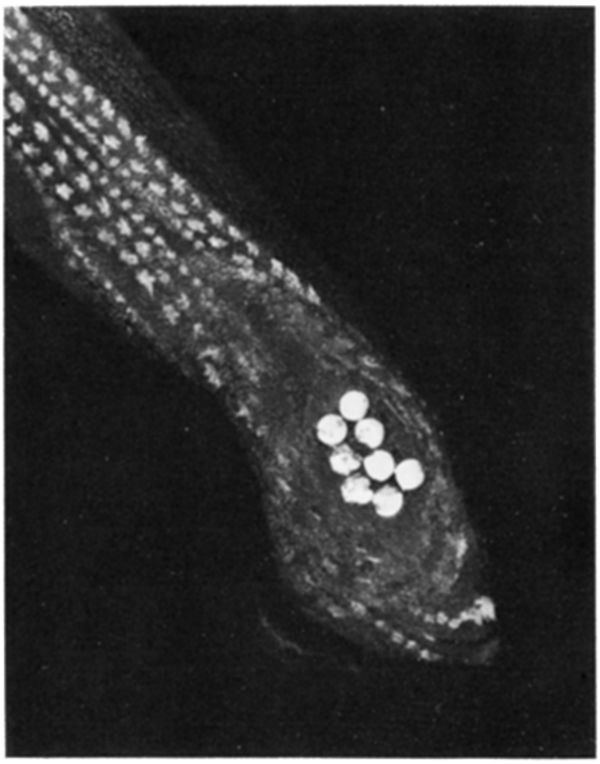


Figure 4 Section cut through tyre showing steel beading still uncorroded after 42 yr sea-water immersion.

TABLE I Composition of 42 yr old tyre and inner tube

Ingredient	Tyre (phr)	Inner tube (phr)
Natural rubber	100	100
Carbon black filler (grade: N330; 26 to 30 nm particle size)	40	–
$CaCO_3$ filler (grade: 2.7 μm mean particle size)	–	20
Sulphur	2.5	3.0
ZnO	5.5	17
Mercaptobenzothiazole	0.75	0.5–1
Stearic acid	2.0	2.0

TABLE II Composition of sea-water from recovery site (80 ft water depth)

Element	Concentration ($g l^{-1}$)
Sodium	12.3
Magnesium	1.9
Potassium	0.59
Calcium	0.41
Strontium	0.009
Iron	0.83×10^{-3}
Lead	0.44×10^{-3}
Manganese	0.12×10^{-3}
Copper	0.11×10^{-3}
Zinc	0.07×10^{-3}

composition to be as given by Table I, where all amounts are expressed in terms of parts per hundred of rubber by weight (phr). The quantity and grade of filler can be difficult to determine accurately and should be regarded as only within 10% of the true figure.

Some traces of antioxidant/antiozonant materials were detected, but it was not possible to make any definitive statements concerning quantity. No polymer other than natural rubber was detected from any part of either the tyre or the inner tube. Separate analyses were performed on rubber taken from three locations, illustrated in Fig. 5: the tread (A), from the shoulder beneath the tread (B), and from the tyre sidewall (C). However, no difference in composition could be detected between any of these three regions.

Analysis was also carried out of the metal beading around the rim of the tyre (see Fig. 4). This was found to be predominantly iron, with traces of aluminium, manganese and silicone. The analysis suggested the beading composition to be typical for ordinary mild carbon steel.

3.3. Composition of sea-water environment

Samples of sea-water were sealed by the divers at 80 ft water depth near to where the tyres were discovered. Atomic absorption spectrophotometry was used to quantify the elements shown in Table II. Ion chromatography determined the chloride content as 1.5% and the sulphate content as 0.2%.

The water temperature was measured as 8° C at 80 ft and 13° C at the surface. The pH of water samples both from the surface and at depth was 7.8. Measurements were also made of the dissolved oxygen levels. Water samples from 80 ft depth showed 8.77 (± 0.05) $mg l^{-1}$ of dissolved oxygen whereas samples from the surface showed 9.70 (± 0.05) $mg l^{-1}$. By way of comparison, laboratory tap water, tested at the same time, showed 10.95 (± 0.05) $mg l^{-1}$ of dissolved oxygen. The level of dissolved oxygen at the 80 ft depth of the recovery site is thus relatively high, consistent with a drainage of cold oxygenated water from nearby mountanious regions. Other laboratory experiments for

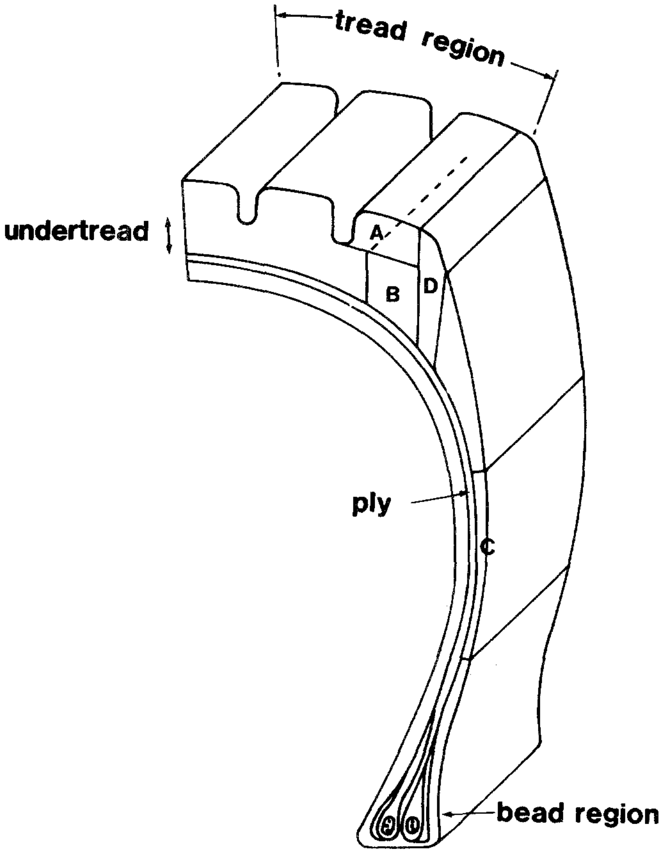


Figure 5 Schematic view of tyre section showing location of regions A (tyre tread), B (shoulders under tread) C (tyre sidewall) and D (tread plus shoulder) from which rubber samples were taked for analysis.

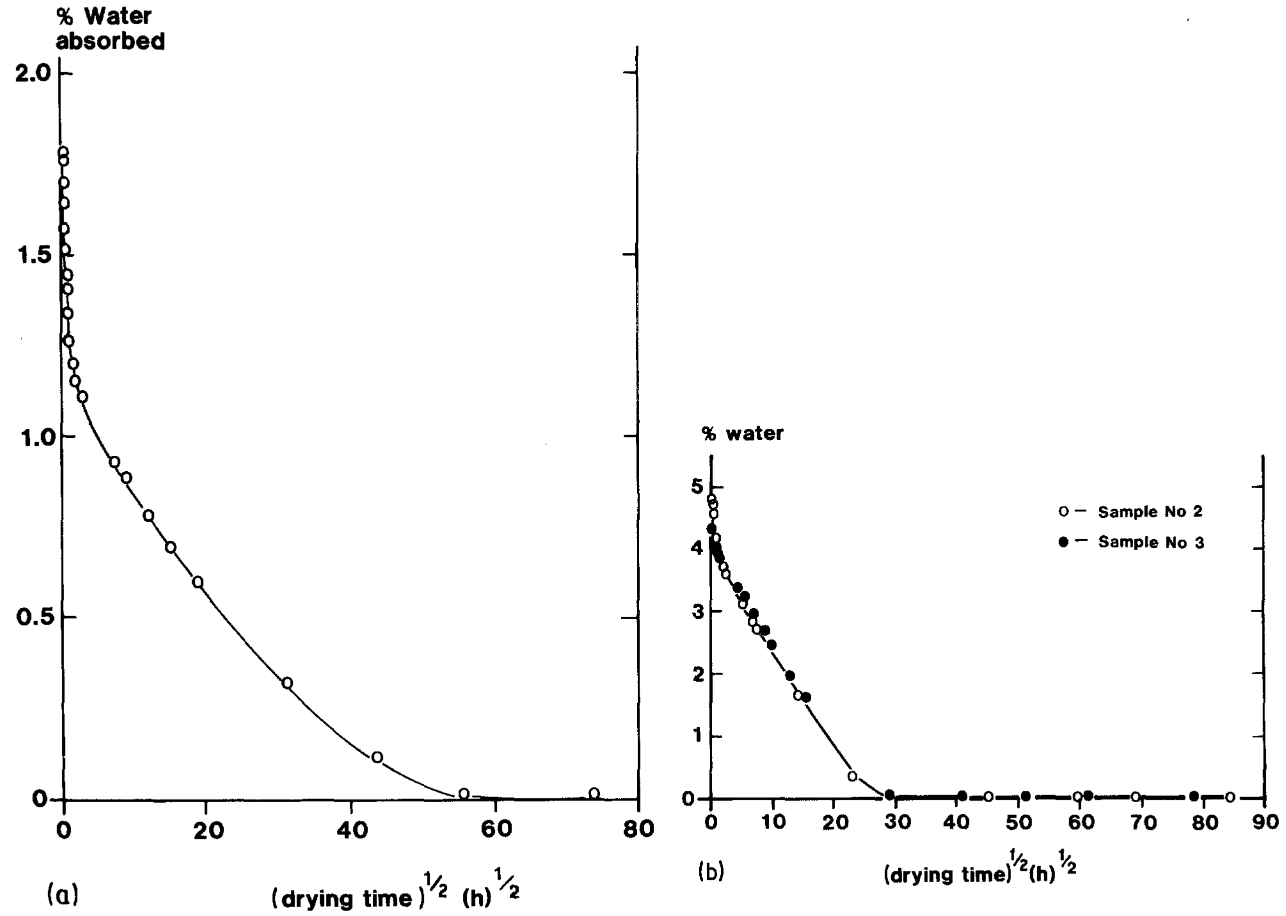


Figure 6 Drying curves showing per cent residual water in the rubbers plotted against square root of drying time. Residual water is expressed as a percentage of final dry weight of rubber, (a) for sample cut from tyre tread, (b) for two samples from inner tube.

example, with sealed tanks containing corroding metal (which uses up available dissolved oxygen) have lead to measurements as low as 1.0 mg l^{-1}. The value recorded is thus high enough for very significant corrosion of steel to occur and this was indeed observed. Extensive corrosion of exposed steelwork on the vessel may have caused the relatively high iron contents measured in both insoluble form in the silt on the deck and as dissolved ions in the sea-water itself.

The tyre that was recovered was taken from a stack of tyres resting on the ship's lower deck. The floor of the deck and the sea bed near to the sunken ship were covered by a carpet of silt, that the divers observed to be easily disturbed. Samples were therefore also taken of the silt and analysis carried out of its composition. The insoluble content of the silt was found to consist mainly of iron, magnesium, aluminium, silicon, potassium and sulphur with some titanium and a very low level of barium. All silt particles were seen, using scanning electron microscopy, to be highly irregular in nature, with sharp edges and corners.

3.3. Water absorption by rubber samples after 42 yr sea-water immersion

Samples of rubber from both the tyre and the inner tube were dried under controlled laboratory conditions immediately following removal from sealed sea-water containers. Weighing at time intervals up to about 300 days produced values of mass loss as a function of drying time in air. The results are shown in Figs. 6a (tyre) and b (inner tube) where mass loss has been plotted against the square root of the drying time. Mass loss is expressed as a percentage of the final dry weight and thus represents the amount of water in the rubber. The tyre samples showed an initial amount of water of 1.8% which reached equilibrium "final" dry weight after about 135 days drying. The inner tube samples showed an initial amount of water of 4.7% and reached final dry weight after about 33 days drying. All drying experiments were continued for 300 days, but no further changes were observed beyond the above times. In both cases at least the initial stages of drying were approximately linear with the square root of time as would be expected from the usual diffusion theory. The tyre sample geometry was 10 mm × 10 mm × 7 mm whereas the inner tube samples were 50 mm × 50 mm × 2.5 mm. The shortest path length for water evaporation for the tyre sample was thus twice that of the inner tube samples. The four-fold longer drying time is thus also explained by standard diffusion theory. Less easy to understand is the significantly lower level of water uptake observed in the tyre samples.

Laboratory experiments [11] with natural rubber strips of similar composition to that of the tyre have shown at this temperature about 2.5% water uptake after 1 yr exposure to synthetic sea-water of similar composition to that given in Table II. In the laboratory tests the strips were of 1 mm thickness whereas the tyre minimum thickness was 6 mm. Quasi-equilibrium was reached in the laboratory after 1 yr, and so this is expected for the tyre after about 49 yr. Thus available equilibrium water uptake should have been very nearly reached in the 42 yr tyre sample tested, and this is

TABLE III Physical properties of inner tube after 42 yr sea-water immersion

Test	Inner tube, wet	Inner tube, dry	New rubber sheet of similar formuation
Tensile strength (MPa)	21	22	23
Tensile modulus (M300) (MPa)	3.2	4.9	2.2
Elongation at break (%)	619%	593%	730%
Trouser tear strength ($N\,mm^{-1}$)	13.7	11.5	9.5

expected to exceed 2.5%, only 1.8% was measured. It may be that the longer time approach to equilibrium permitted some form of surface ageing such that a thin skin was formed on the outer tyre tread surface, inhibiting water absorption. Some evidence for this is presented in Section 3.5.

The inner tube was found to have absorbed 4.7% water, which is a little higher than expected from laboratory tests assuming a "classical" approach to a true equilibrium [2]. There is evidence, however, even from relatively short term (2 yr) laboratory tests [11] that in fact there is an approach to a lower, secondary, diffusion rate in the long term and no true equilibrium. Thus a figure of 4.7% after 42 yr exposure is perhaps reasonable in the circumstances. Moreover, the inner tube samples were found to have been filled with $CaCO_3$ which may be slightly more hydrophilic when bound into the vulcanized rubber than the carbon black used elsewhere.

3.4. Physical properties of rubber samples

Standard tensile and tear testpieces were cut from strips of the inner tube both before and after drying experiments. This provided some comparative data on the properties of the rubber with (wet) and without (dry) the 4.7% measured water absorption. In addition a new sheet of rubber was made to the formulation of what the inner tube was thought to be. This inevitably involves some guesswork and the compound may not be exactly the same, but does provide a general indication of the sort of physical properties that are expected when the rubber was new. The results are summarized in Table III. Each result is the mean of at least three separate testpieces. The physical properties show the rubber to be in very good condition – certainly exceeding any normal test requirements for newly vulcanized rubber. There was a slight difference between sections of the tube tested wet and dry. Wet and dry, the tear strengths were identical, while the elongation at break was slightly higher wet than dry and the modulus was lower wet than after drying. This could be associated with some plasticizing type effect of the absorbed water. The small difference in tear strengths is too small to be significant. Correction was made for slightly different initial dry dimensions when testpieces are cut wet (i.e. swollen to 4.7% by water). There was also no significant difference between tensile and tear strengths of the new (dry) vulcanizate and the dry samples from the 42 yr old inner tube. The modulus was, however, lower for the new rubber and the elongation at break higher – suggesting that in fact the "guessed" formulation used for the new vulcanizate contained too little filler or too coarse a grade of particle size. With a higher filler level the results are likely to have been indistinguishable from those of the inner tube. The alternative explanation, of some overall age-hardening is inconsistent with the trouser tear strength being, in fact, slightly higher for the 42 yr old samples than for the new testpieces. These results lead to the overall conclusion that 42 yr sea-water immersion has had no serious effect on the mechanical properties of the rubber from the inner tube.

TABLE IV Physical properties of tyre after 42 yr sea-water immersion

Test	Tyre (dry) (region B)	New rubber sheet of similar formulation
Tensile strength (MPa)	29	30
Tensile modulus (M300) (MPa)	13.5	11
Elongation at break (%)	512	600
Trouser tear strength ($N\,mm^{-1}$)	9	9
Hardness (IRHD)	71	61
Compression set (%)	26	38

"Wet" testpieces could not be prepared from the tyre since a more elaborate preparation procedure was required due to the rubber not being in sheet form. The thicker tread, however, enabled compression set and hardness discs to be prepared, not possible from the thin inner tube sheet. The results are summarized in Table IV.

Very similar comments apply to the results for the tyre as for the inner tube. The general level of physical properties is very good and exceeds any normal specifications for new rubber of this type. It again looks as if the amount of filler in the new simulated compound was slightly too low or the grade too coarse. Otherwise there is little significant difference in physical condition between rubber taken from the tyre after 42 yr sea-water immersion and new rubber.

In addition to standard physical tests, a series of puncture tests was performed on a section cut through the tyre. This test [9] enables a large number of values for puncture load to be collected over the whole surface by performing successive indentation/punctures at 2 mm intervals. A contour map of the resulting puncture loads is shown in Fig. 7. This test is more sensitive in detecting local differences in strength than any of the standard physical tests. Indeed the results show higher puncture loads over part of the tread region than deeper towards the carcass. Similar tests on a flat moulded block of the new vulcanizate over a similar area yielded values of 20 (±2)N. The difference is just large enough to be significant and may indicate some ageing towards the outer tread surface. Alternatively, the difference could have been caused

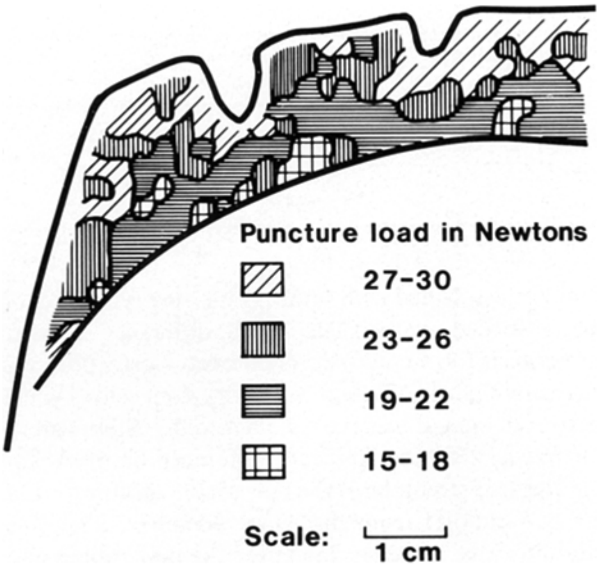


Figure 7 Contour map of puncture strength across a section through the tyre.

by different processing methods being used for the tread and the carcass of the tyre. Modern tyres even use different rubber compounds for these regions – so comparisons cannot easily be made with a new tyre.

For one tyre segment, puncture tests were performed wet (before drying) and then at timed intervals, together with corresponding weight measurements as the segment was dried in a controlled laboratory environment. Thus puncture load and modulus could be plotted as a function of the amount of adsorbed water. The results, shown in Fig. 8, do not suggest any substantial effect. There may be a slight tendency towards higher puncture loads and higher modulus values with increasing amounts of absorbed water – but the difference is barely significant.

3.5. Chemical analysis of rubber condition

The crosslink network in this type of rubber is formed by means of monosulphidic and polysulphidic linkages.

TABLE V State of cure in tyre samples

	Tread surface, *A* (phr)	Under-tread region, *B* (phr)
Natural rubber	100	100
Combined sulphur (S_c)	2.71	2.40
Sulphide (S^{2-})	0.68	0.34
$S^{2-}/(S_c - S^{2-})$	0.33	0.17

An indication of the state of cure of rubber in the tyre was obtained by sulphur analysis. No free sulphur was found in samples from any of the three locations A, B or C (see Fig. 5) indicating the rubber to be everywhere fully cured. Analysis of sulphide content (S^{2-}) and combined sulphur (S_c) may be used [12] to provide information concerning the state of cure by consideration of the ratio $S^{2-}/(S_c - S^2)$. The results are presented in Table V.

The generally low values of $S^{2-}/(S_c - S^{2-})$ suggest that a good state of cure exists throughout the tyre. However, this ratio is higher for A than for B suggesting that some polysulphidic crosslinks in the tread region may have degenerated into sulphides. This could be an ageing process due to the proximity of the tread to the external environment, or it could again reflect initial differences in processing methods between the tread and under-tread regions.

Analyses were also carried out of the oxygen content in the rubber from segment D of Fig. 5: (i) at the tread surface (ii) just below the tread surface, and (iii) in the centre of the tyre segment D. The results were (i) 3.7, (ii) 3.6 and (iii) 4.0% w/w[†], respectively indicating no significant difference in oxygen content throughout the tyre. Tests on new rubber discs yielded oxygen contents of 2.1 to 2.3% w/w 3 h after moulding, rising to 2.5 to 2.6% w/w after 38 day in air. Extensively oxidized rubber, produced for example by air ageing at elevated temperatures, can typically show an increase greater than 10% O_2 w/w. These results thus

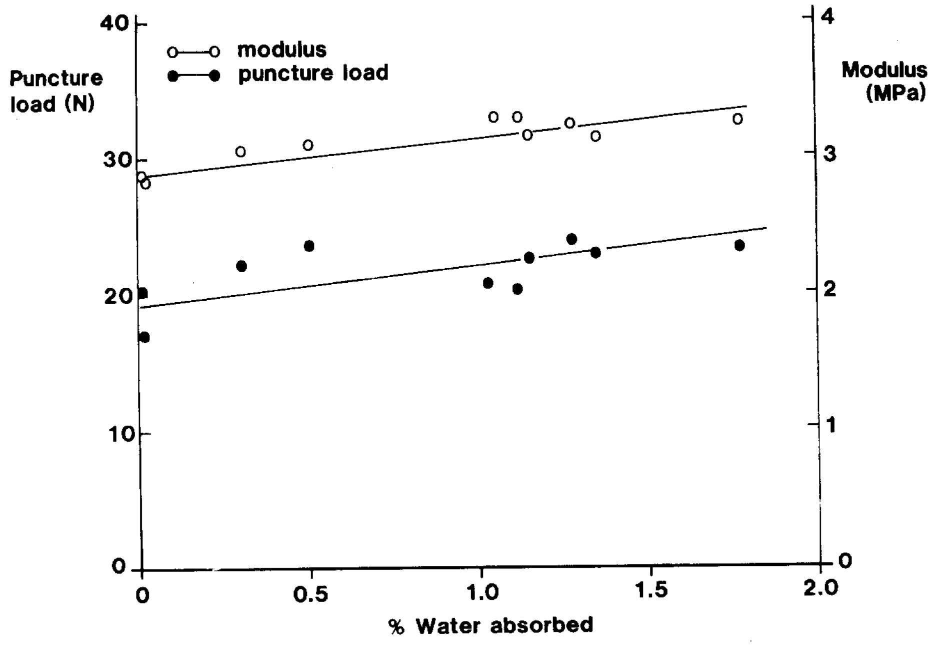
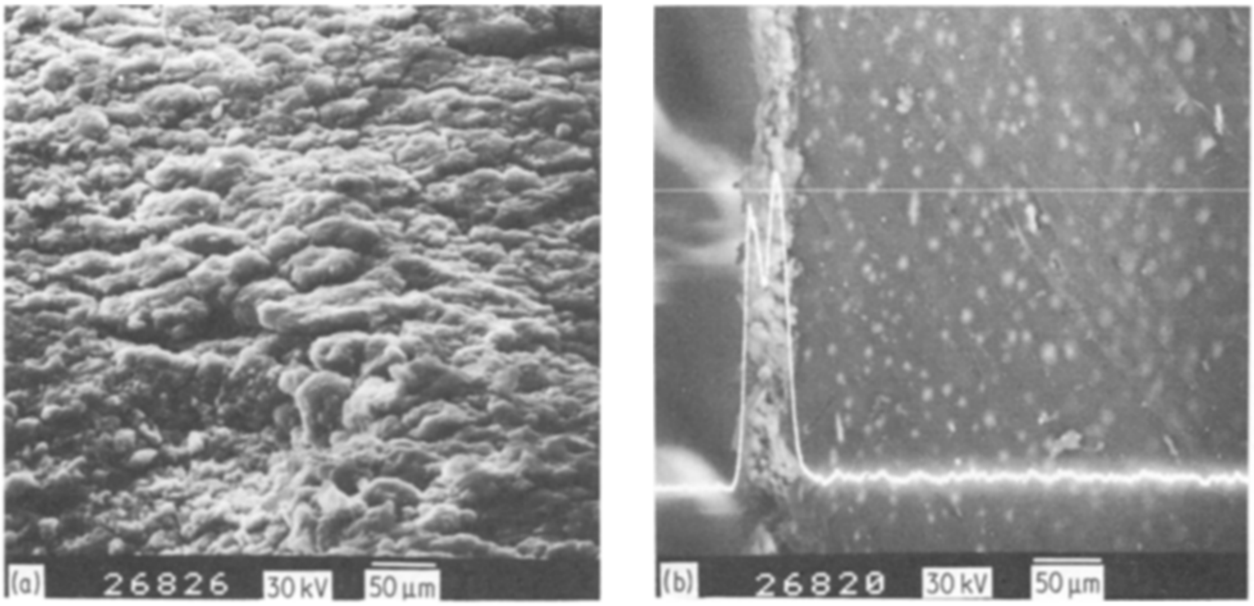


Figure 8 Puncture load and modulus as a function of the percentage of water absorbed by the rubber tyre.

[†] 1% w/w indicates 1 g of O_2/100 g polymer.



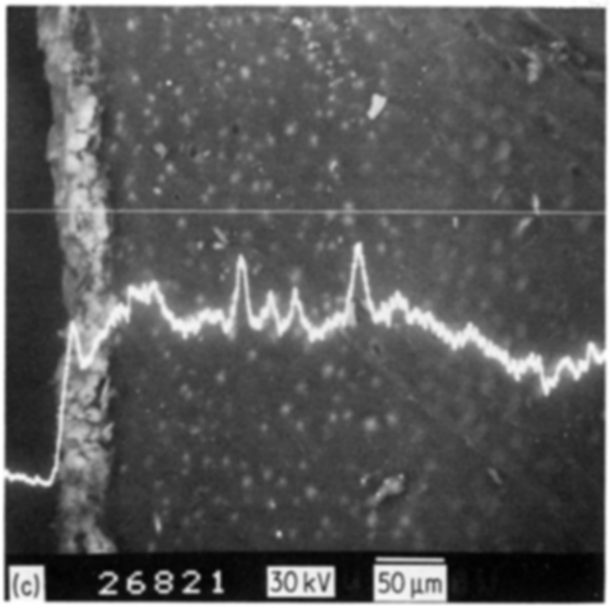


Figure 9 Scanning electron micrographs of tyre tread (region A). (a) Outer tread suface with particulate "crust" (b) Profile of section through the tread segment showing outer layer of particulate material of maximum thickness 50 μm. The superimposed line scan for iron shows the outer layer to be of different composition from the underlying rubber. (c) Similar micrograph to (b) with line scan for sulphur.

suggest that no significant oxidation ageing or oxygen retention had occurred during the 42 yr life of the tyre.

A section through the tyre tread was also examined by scanning electron microscopy. The tread surface appeared highly particulate in character (see Fig. 9a) and most unlike that of a degraded rubber surface although the surface texture was not dissimilar to some recent new tyre tread surfaces. Examination of the section revealed a layer of aggregated particulate material with a maximum thickness of 50 μm (Fig. 9b). Electron probe analysis of both the tread surface and the "bulk" rubber beneath the surface showed normal levels of sulphur in each case but an increased amount of aluminium in the tread surface. In addition the tread surface sample showed a strong presence of iron which was not detected at all in the bulk rubber. A scan for iron is shown superimposed on Fig. 9b. The full element scan for samples from each region are shown in Fig. 10. There may also have been a slightly reduced level of zinc in the tread surface sample. Fig. 9c shows a section through the sample with a coincidental plot of sulphur content as measured by the intensity of the appropriate K_α X-ray peak. There is clearly no significant difference between the surface layer and the "bulk" rubber. The corresponding photograph with iron content (Fig. 9b) clearly shows a strong presence of iron only in the surface layer.

There was no trace of iron in the analysis of the rubber compound itself and indeed no reason for it to be there. There was, however, a strong presence of iron in the silt-like material recovered from the deck of the vessel from which the tyres were obtained. The most likely explanation of the surface layer is then that there was a sediment over the years of iron oxide from corrosion products of the vessel structure. This formed a fine layer which interacted slightly with the rubber surface to form a very thin skin of some 0.05 mm thickness. This skin then seems to have had some protective value and even (as discussed in Section 3.3) have retarded the absorption of water by the rubber. Because of the topography of the surface it is difficult to say from the evidence whether this fine surface layer is purely the result of accretions of extraneous matter or whether some mild chemical degradation of the rubber surface may also have occurred. The unchanged sulphur content in this layer is not instructive since sulphur was also detected in silt samples at similar concentrations. In any case if there is some degradation it has been restricted to a very thin surface layer of maximum thickness 0.05 mm.

There was no similar skin on rubber from the inner tubes – these were, however, reported to have been recovered from a section of the vessel less exposed to silt and corrosion products from the steel.

4. Conclusions

A detailed investigation of rubber samples has shown no serious deterioration in rubber condition after 42 yr

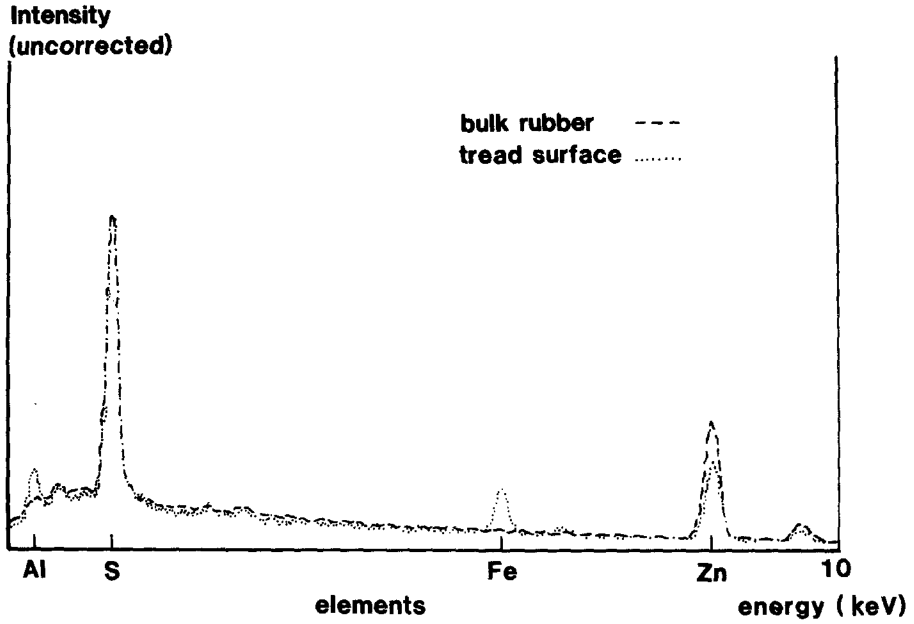


Figure 10 Element scans for tread surface (including surface "crust") and bulk rubber (no "crust") under tread. Obtained using a Hitachi S500 scanning electron microscope with a Link energy dispersive spectrometer.

exposure to sea water. There was no attack by any marine organisms, although many varieties were known to inhabit the area. The maximum amount of water absorbed by the rubber after 42 yr was 4.7% and this had no adverse effect on properties. The presence of a thin rubber layer over ordinary mild steel beading in the tyre was sufficient to prevent corrosion in spite of the water being relatively highly oxygenated. A very thin (0.05 mm) surface layer of iron-based material was found to have formed a skin on the surface of the tyre which seemed to have some beneficial effect in inhibiting the absorption of water. Extensive tests on the rubber showed it generally still to possess physical properties which were as good as would normally be expected of a new rubber of this type.

Acknowledgements

The authors would like to thank the Board of the Malaysian Rubber Producers' Research Association for permission to publish this paper; B. Batley and colleagues of Sub-C Divers for recovering the tyre and inner tube; M. J. Loadman and colleagues of MRPRA for the analytical data and A. J. Cobbold of MRPRA for the scanning electron microscopy.

References

1. J. A. BARRIE, D. MACHIN and A. NUNN, *Polymer* **16** (1975) 811.
2. E. SOUTHERN and A. G. THOMAS, *ACS Symp. Series* **127** (1980) 375.
3. P. E. CASSIDY and T. M. AMINABHARI, *Rubb. Chem. Technol. Rev.* **56** (1983) 594.
4. L. R. SNOKE, *Bell System J.* **36** (1957) 1095.
5. R. A. CONNOLLY, *J. Mater.* **5** (1970) 339.
6. J. S. MURAOKA, US Naval Civil Engineering Technical Reports R329, R393, R428 and R445 (1966).
7. D. W. CUMBERALAND, "Panama Weathering Study", Dupont Technical Report 5D-EL6, 515, 225 (1983).
8. B. BATLEY, *Rubb. Devel.* **36** (1983) 22.
9. K. AB-MALEK and A. STEVENSON, *J. Mater. Sci.* **19** (1984) 585.
10. P. B. LINDLEY and S. C. TEO, *Plast. Rubb. Mater. Appl.* **2** (1977) 820.
11. A. STEVENSON (ed), in "Rubber in Offshore Engineering", (Adam Hilger, 1984) Ch. 2.
12. W.C.WAKE, B. K. TIDD and M. J. R. LOADMAN, in "Analysis of Rubber and Rubberlike Polymers" (Applied Science, 1983) Ch. 2.

*Received 30 January
and accepted 8 March 1985*