

Ageing Resistance and Network Structures of Some Commercial Natural Rubber Gloves

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Three methods were used to compare the effect of ageing on some commercial natural rubber gloves. Tensile testing and oxygen absorption measurements were carried out on the gloves and a network visualisation technique using transmission electron microscopy (TEM) was utilised to study rubber microstructure. The ageing resistance of natural rubber gloves was shown to be affected by the nature of surface treatment or modification employed. Gloves that had been chlorinated were found to lose tensile strength on ageing to a greater degree than the other polymer-coated gloves investigated. The TEM images revealed that the reduction in tensile properties was accompanied by some visible changes in the rubber network structure. However in this work, the oxygen absorption of the gloves was shown not to correlate with ageing resistance.

Key words: transmission electron microscopy (TEM); microstructure; ageing resistance; natural rubber gloves; tensile strength; network structure; oxygen absorption; chlorinated gloves

Natural rubber (NR) gloves are generally categorised into pre-powdered and powder-free. The powder-free NR gloves are usually obtained by means of surface treatment such as chlorination or surface coating in order to reduce surface tackiness and facilitate donning. Powdered gloves are prepared by applying lubricating powder onto the surfaces of the gloves. In the context of glove consumption, there exist a tendency to shift towards powder-free gloves^{1,2}. Therefore, an understanding of the effect conferred by surface treatments on NR gloves properties is deemed necessary.

One of the important properties of NR gloves is ageing resistance, which is normally characterised by accelerated heat ageing and tensile testing. In NR gloves manufacturing, accelerated heat ageing tests are conducted as a quality control measure in accordance with various available standards. One instance is that the NR examination gloves should retain a tensile strength of at least 14 MPa after ageing at 70°C for seven days to meet the physical requirement specified in the *ASTM* standard³. Reduced level of tensile retention on ageing in chlorinated powder-free NR gloves is a commonly observed phenomenon. Lai *et al.*⁴

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reported in a survey of commercial NR gloves that powder-free chlorinated gloves exhibited lower tensile retention values on ageing compared to powder-free polymer-coated gloves.

This study reports some effects of ageing on chlorinated and polymer-coated powder-free gloves using measurements of tensile strength and oxygen absorption. Changes in the network structure of the differently treated gloves after ageing were studied using the network visualisation technique described by Cook *et al.*⁵, which has proven to be a useful tool in analysing the microstructure of different crosslink densities in NR prevulcanised latex film⁶.

MATERIALS AND METHODS

Four different brands of powder-free NR gloves, *i.e.* a brand of chlorinated glove, two brands of polymer-coated gloves, and a brand of hydrogel-coated glove were studied. These gloves were used as received unless otherwise specified.

FTIR-ATR analysis (Germanium trapezoidal crystal, fixed at 60° angle, 128 scans) was conducted initially to determine which of the gloves that were indeed chlorinated. The FTIR-ATR spectra of the hydrogel-coated and chlorinated gloves were compared with the bands associated with chlorine^{7,8}: at the 915 cm⁻¹ – 910 cm⁻¹; 800 cm⁻¹ – 750 cm⁻¹, and 730 cm⁻¹ corresponding to Cl stretching on Cl – C – C, Cl_n – C, and Cl-Cl-H, respectively. The results obtained (*Figure 1*) indicated that the hydrogel-coated glove was in fact chlorinated.

Preparation of Samples for Network Visualisation

Small portions of the gloves (unaged and aged) were cut from the palm region and

prepared for acetone extraction and styrene swelling as described elsewhere⁹.

Transmission Electron Microscopy (TEM)

The sample sectioning and visualisation under the electron microscope were carried out as follows. Ultra-thin sections (approximately 100 nm – 150 nm) were cut from the swollen embedded samples at –110°C (except for the aged samples) with an RMC MT-7000 Ultramicrotome using 45° freshly cleaved glass knives set at a shallow clearance angle. (The sectioning of the aged glove samples was carried out at 25°C. This was done because sectioning at –110°C was found to produce too many knife marks across the sections). The sections obtained were placed on grids that had previously been dipped in ethanol in order to aid sample collection. The sections were then stained with osmium tetroxide for an hour. The stained sections were examined using a Philips EM 300 Transmission Electron Microscope operating at 100 kV.

Ageing and Tensile Testing

Ageing was conducted at 70°C for 21 days. Tensile strength measurements were done according to ISO 37 for unaged and aged samples.

Oxygen Absorption

Oxygen absorption measurements were carried out using a manometric type apparatus (*Figure 2*) at 70°C for 21 days. A strip of 1 cm × 10 cm of each glove was taken. The weights of each of the strips were then recorded. Prior to measurements, the apparatus dead volume (V_d), apparatus volume (V_a) and the apparatus

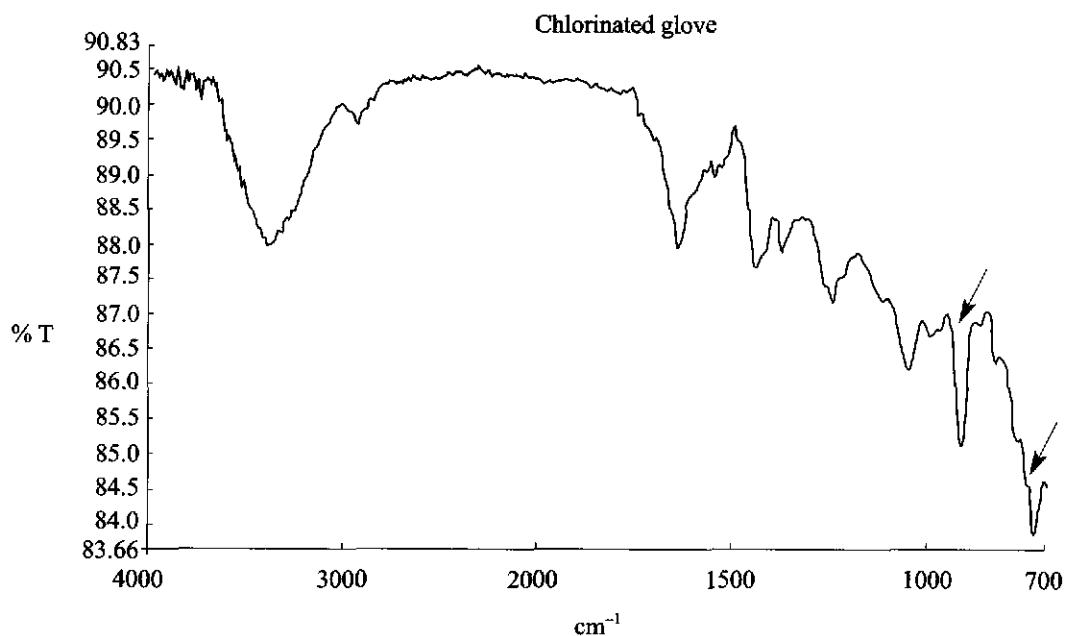
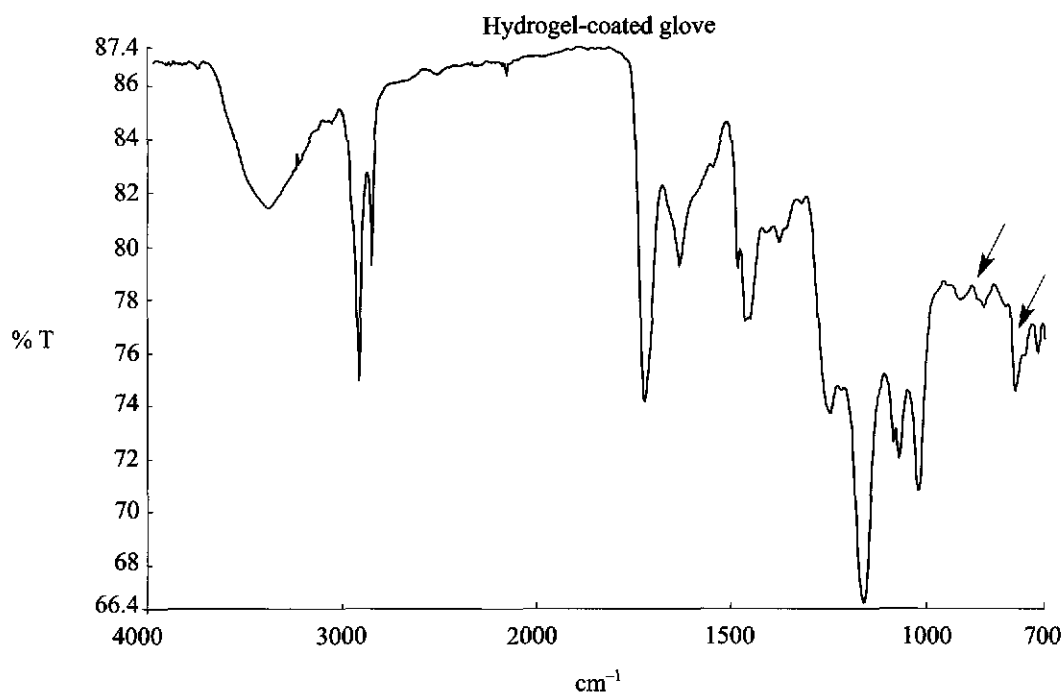


Figure 1. FTIR-ATR spectra of hydrogel-coated and chlorinated gloves. Shown are the band assignments related to chlorine: 915 cm^{-1} – 910 cm^{-1} , 800 cm^{-1} – 750 cm^{-1} and 730 cm^{-1} .

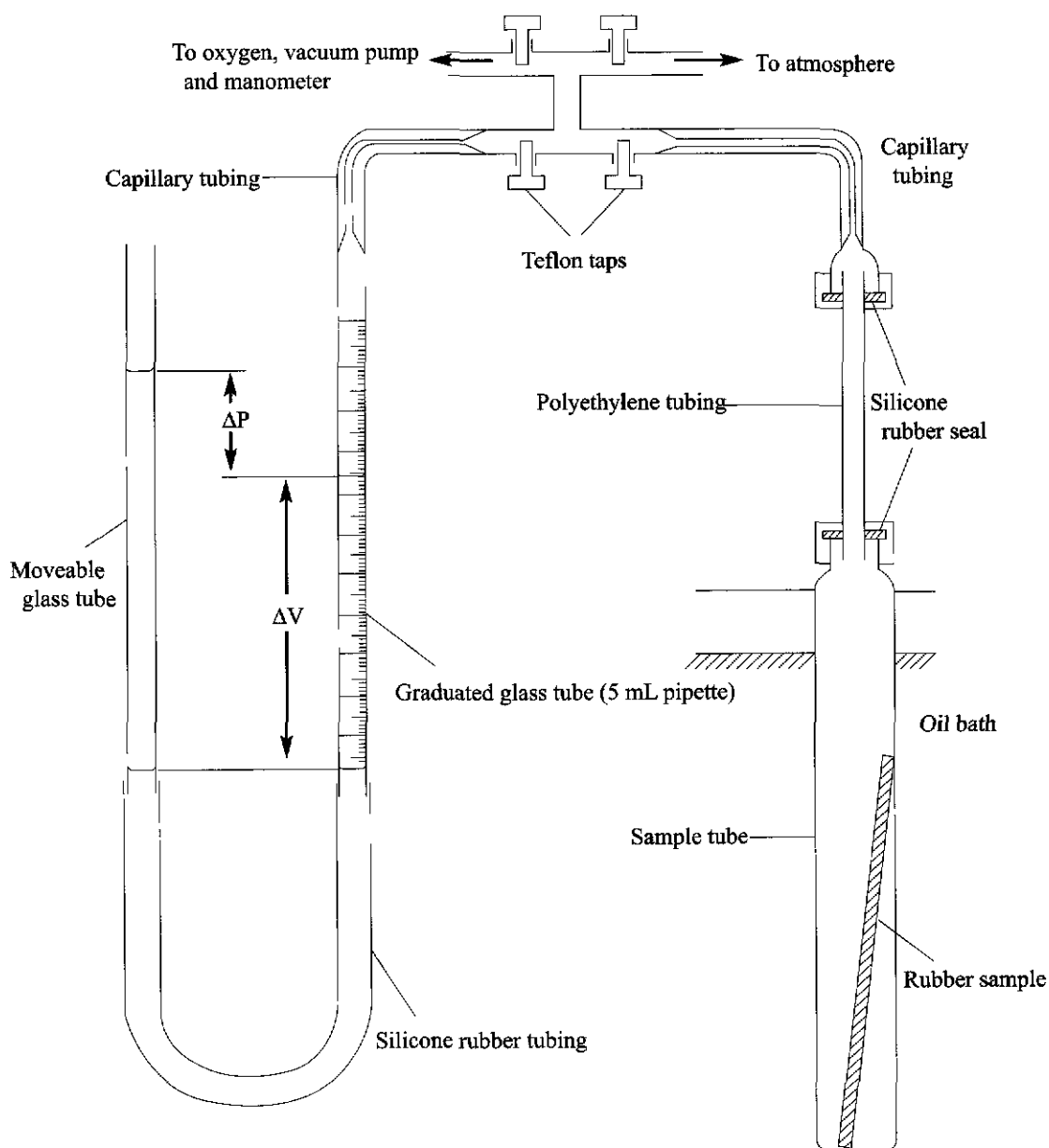


Figure 2. Schematic representation of the oxygen absorption apparatus.

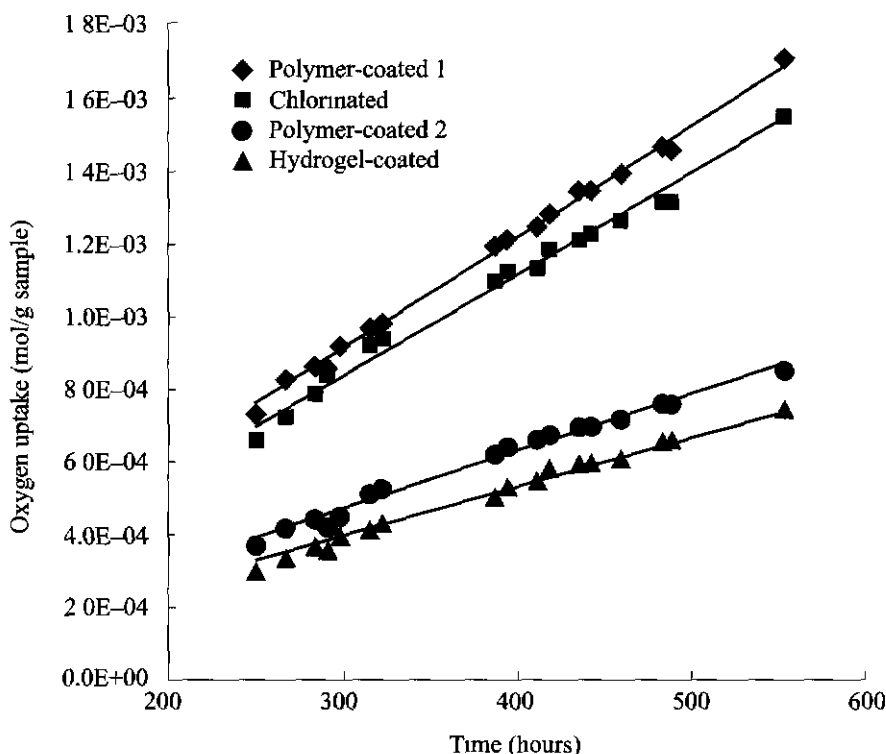


Figure 3 Oxygen absorption of NR gloves

leakage under internal pressure were determined. The strips were then placed inside the sample tube. The apparatus was then filled with oxygen. The filling, evacuation and refilling was done more than twice to ensure only oxygen was present inside the apparatus.

The initial atmospheric temperature (T_o , °C), atmospheric pressure (P_o , mmHg) and the volume reading (V_o , mL) in the manometer arm of the apparatus were recorded. Volume measurements were then carried out at specific time intervals at constant pressure inside the apparatus. The constant pressure was achieved by raising or lowering the moveable tube such that, $\Delta P \text{ mmHg} = (P_o - P) \times 13.97 \text{ mm silicone}$

oil, where P is the current atmospheric pressure in mmHg.

The volume change, $\Delta V = V_o - V$ was corrected for the change expected due to change in temperature to give $\Delta V_c = (V_d + V_o)(T/T_o - 1) + \Delta V$. The oxygen uptake of sample was derived from the equation: Oxygen uptake (moles/g) = $[(P_o \Delta V_c)/(RT \times 760)]/\text{sample weight}$.

Antioxidant Level Determination

An approximate weight of 2 g of each glove was extracted in hot dichloromethane

overnight. The extracted solutions were then made up to 10 mL using a 9:1 v/v mixture of isopropyl alcohol and chloroform. 1 mL aliquots of the prepared solutions were then taken for thin layer chromatography (TLC) analysis using petroleum ether and diethyl ether (60:40) as the mobile phase. Subsequent analysis *via* reverse-phase HPLC using acetonitrile as the mobile phase was carried out to quantify the level of antioxidant present in the gloves.

RESULTS AND DISCUSSION

Tensile Properties, Antioxidant Level and Oxygen Absorption

The results of the tensile properties (*Table 1*) demonstrated that the polymer-coated NR gloves were relatively better in terms of ageing

resistance, with tensile retention of more than 50%, compared to the chlorinated and the hydrogel-coated gloves. Nevertheless, the resistance of these gloves to ageing could be strongly influenced by the presence and level of antioxidant. Thus, the type and level of antioxidant present in the gloves were measured chromatographically prior to ageing to determine whether the differences in retention of tensile properties were simply a result of differing levels of antioxidant.

It was found that all four gloves contained the polymeric hindered phenol type of antioxidant Wingstay-L®. They contained similar amounts of this antioxidant, with the exception of the hydrogel-coated glove that had approximately 30% more than the other gloves (*Table 2*). This showed that the poorer ageing resistance of the chlorinated and hydrogel-coated gloves was not mainly due to the different levels of antioxidant

TABLE 1. TENSILE PROPERTIES OF THE UNAGED AND AGED NR GLOVES

Gloves	Tensile strength (MPa)		Tensile retention (%)	Elongation at break (%)		M300% (MPa)		M500% (MPa)	
	U	A		U	A	U	A	U	A
Chlorinated	28.50	14.50	50.88	850	900	1.65	1.20	3.30	1.95
Polymer-coated 1	17.00	14.50	82.29	700	750	1.50	1.50	3.50	3.00
Polymer-coated 2	20.50	20.20	98.54	750	800	1.50	1.20	3.80	2.90
Hydrogel-coated	23.00	11.00	47.83	850	700	1.40	1.20	2.60	2.10

U: unaged; A: aged at 70°C for 21 days

TABLE 2. ANTIOXIDANT LEVEL

Gloves	% antioxidant identified as Wingstay-L®
Chlorinated	0.64
Polymer-coated 1	0.64
Polymer-coated 2	0.63
Hydrogel-coated	0.80

in the gloves investigated. Evidently, the hydrogel-coated glove was subjected to chlorination in their manufacture and it is likely that the gloves previous history of surface treatment is responsible for the reduction in ageing resistance. However, the actual nature of the interactions and mechanism of ageing that occurred is not clearly understood. This is particularly due to the complexity of the propriety coating systems utilized. The elucidation of the complexity is further envisaged in the results obtained for oxygen absorption measurements on ageing.

As illustrated in *Figure 3*, the chlorinated glove exhibited appreciable oxygen absorption, corresponding with poor ageing resistance. The destructive role of available oxygen is well known to be significant¹⁰ and as low as 1% by weight of oxygen absorbed can cause the loss of elastomeric properties¹¹. Adequate work was done in showing the effect of chlorination of latex gloves and films^{7,12}; it demonstrates the susceptibility of chlorinated NR films to thermal oxidative chain scission and consequently, reduction in physical properties. The occurrence is likely due to the hydrolysis⁷ and dehydrochlorination¹³ of the chlorinated rubber, with the introduction of conjugated double bond structures that are highly prone to oxidative chain scission at elevated temperature.

On the other hand, similar trend of oxygen absorption was not observed in the polymer-coated gloves. In spite of similar oxygen absorption to the chlorinated glove, polymer-coated *Glove 1* displayed considerably better ageing resistance. Likewise, the hydrogel-coated glove, which exhibited poor retention of tensile properties on ageing, showed relatively low oxygen absorption. Whether surface treatment, in particular surface coating, influences the propensity of the sample to absorb oxygen and could this be related to the resistance of the

gloves to ageing at this temperature is yet to be discovered. At a glimpse, these results may indicate that the utilisation of oxygen for oxidative scission of the rubber molecules (scission efficiency) varies between the samples and this may be dependent upon the nature of the surface treatment.

Network Structure Visualisation

Unaged gloves. Osmium tetroxide preferentially stains carbon-carbon double bonds so the NR in the sample appears darker than the polystyrene. The individual styrene-swollen latex particles were clearly visible in all the micrographs. Inside the latex particles a dark network of rubber is seen against the unstained background of polymerised styrene. The pale regions between the rubber particles and beyond the edge of the rubber surface are also polystyrene.

Some parts of the inside surface of the chlorinated glove possessed a very distinctive layer which was noticeably paler (less stained) than the latex particles on some areas on the surface (*Figure 4*). This distinctive layer is likely to be the effect of chlorination, as chlorine attacks the carbon-carbon double bonds and therefore causes the rubber to take up less of the osmium tetroxide stain. The chlorinated layer is discontinuous and lacks the mesh structure observed for the underlying latex film. The outside surface has a similar appearance but these chlorinated regions appeared to be thinner and less continuous than those on the inside surface. This observation would lead to the notion that the glove was chlorinated on-line (and then everted during stripping). It is believed that in the on-line process the glove is chlorinated whilst still in a slightly stretched state on the former resulting in an increased level of chlorine penetration.

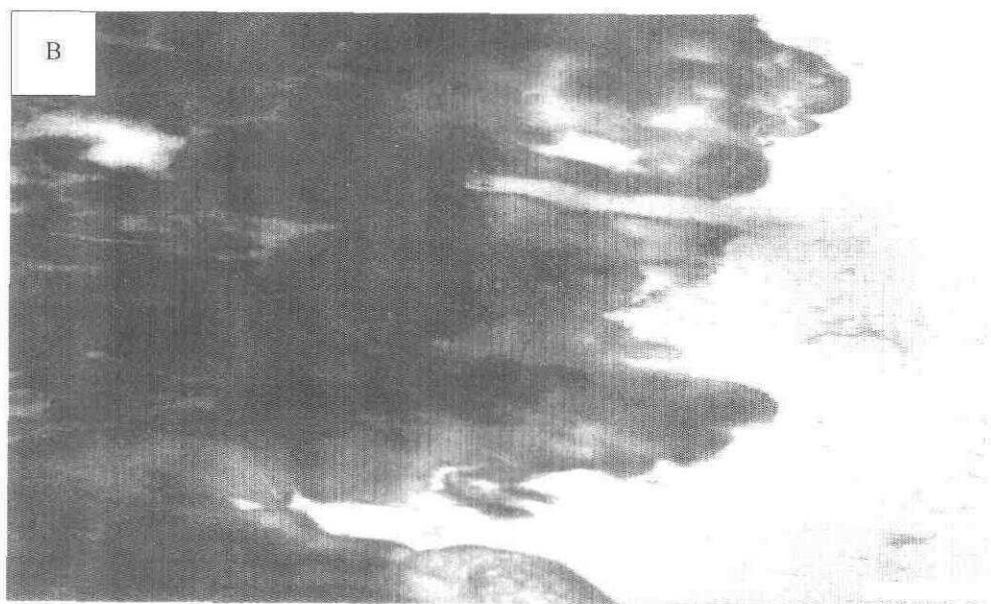
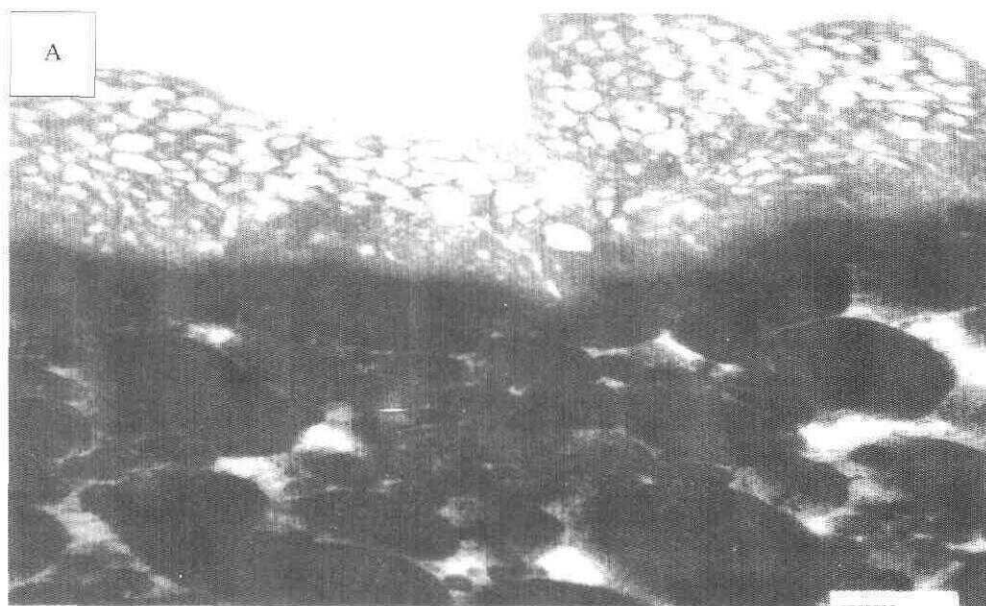


Figure 4. TEM Micrographs of the unaged chlorinated glove: inside surface (A) and outside surface (B). Bars = 0.5 μ m.

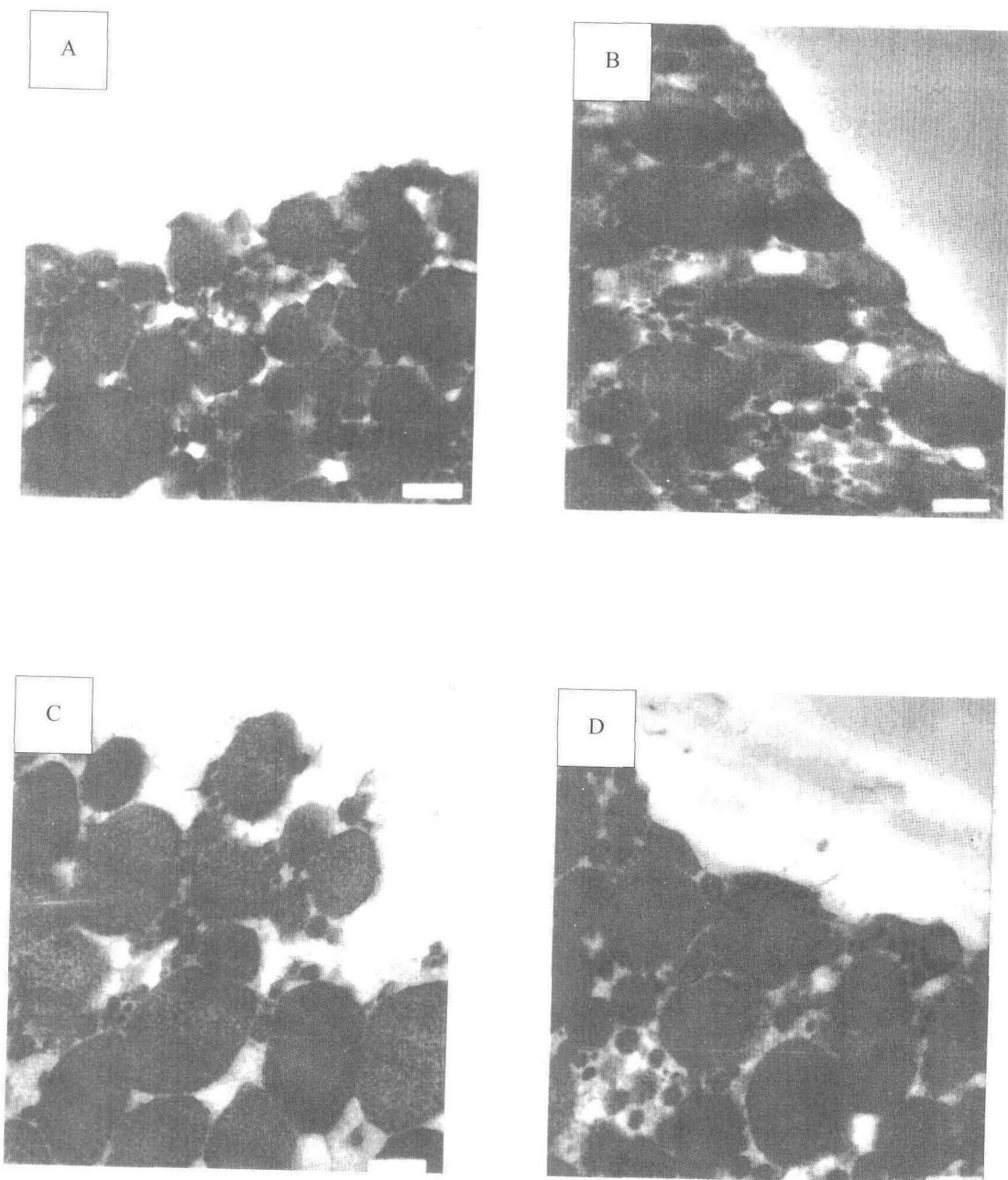


Figure 5. TEM micrographs of the unaged polymer-coated gloves. These show the outside and inside surfaces of the unaged polymer coated gloves: PC 1 inside (A); outside (B); PC 2 inside (C) and outside (D). Bars = 0.5 μm .

The network structures of the polymer-coated gloves appeared to be similar to those of the chlorinated one (Figure 5). Apart from a few possible traces, signs of a polymer layer on either surface of polymer-coated *Gloves 1* and *2* were not observed. The integrity of the coating materials is presumably disrupted either during the acetone extraction or the styrene swelling process. These observations indicate that the coating process involved did not chemically bond the coating material to the underlying latex film.

Conversely, the inside surface of the hydrogel-coated glove displayed intact pieces of coating material having a 'droplet-like' shape. These are mostly unstained by the osmium tetroxide and therefore exhibited a very pale appearance (Figure 6). This is presumably hydrogel polymer, which has remained bonded to the latex film. The outside surface of this glove showed the pale grey structures, which are characteristic of the outside surface of the chlorinated glove.

Aged gloves. The results obtained for the polymer coated gloves were fairly similar to the equivalent unaged gloves, though it was noticed that the latex particles were generally in closer contact with each other compared to the unaged gloves (Figure 7). The cause of this effect remains unclear. None of the major disruption or changes in network structure has been observed. The physical properties of the rubber have to be quite severely reduced before changes can be clearly observed in the network distribution and this observation could be attributed to the high degree of ageing resistance.

The latex particles within the chlorinated and the hydrogel-coated gloves exhibited a lower network structure and distribution

(Figure 8) than those in the equivalent unaged gloves. A looser network between the latex particles in the aged samples was also observed. Apparently, in these two gloves, the reduction in physical properties of the rubber has been accompanied by breakdown in the rubber network distribution.

CONCLUSIONS

This work confirms the findings of Lai *et al.*³ that exhibited reduced ageing resistance of chlorinated NR gloves in comparison to polymer-coated gloves. It was shown that the process of chlorination could bring about a significant reduction in tensile properties on ageing, irrespective of whether the gloves were formerly coated with hydrogel. The gloves that were surface treated by means of polymer coating only, displayed better ageing resistance than the other two gloves which had been exposed to chlorination. The reduced ageing resistance as indicated by a drop in tensile strength on ageing that was observed for the gloves that had been chlorinated was associated with some reduction in the network structure of the rubber, as revealed by the TEM analysis of styrene-swollen samples. The technique also revealed the effect of chlorination on the rubber surface and the presence of hydrogel layers. In this work, the reduced retention of tensile properties on ageing of NR gloves could not be correlated to the level of oxygen absorption.

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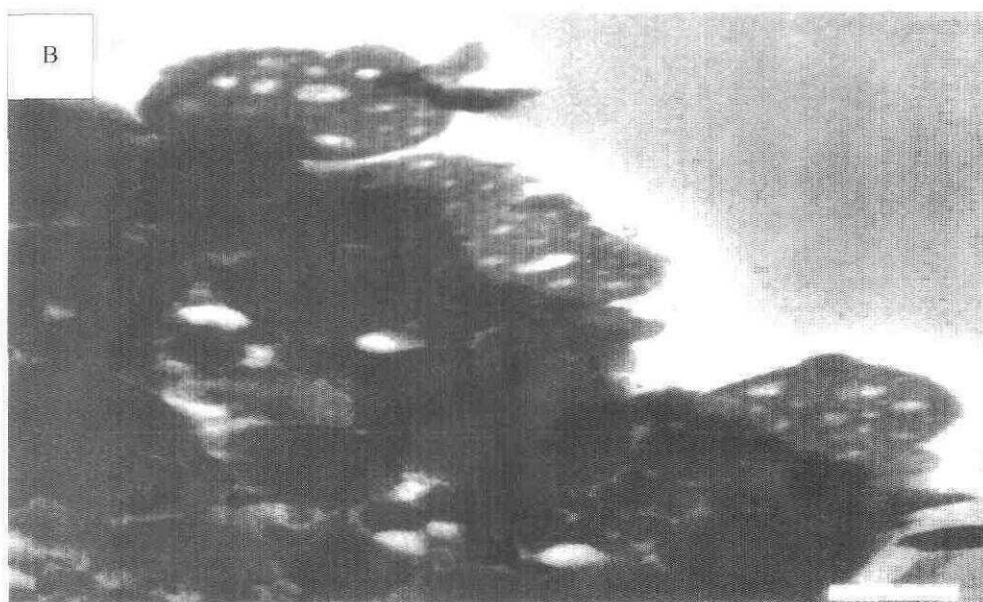
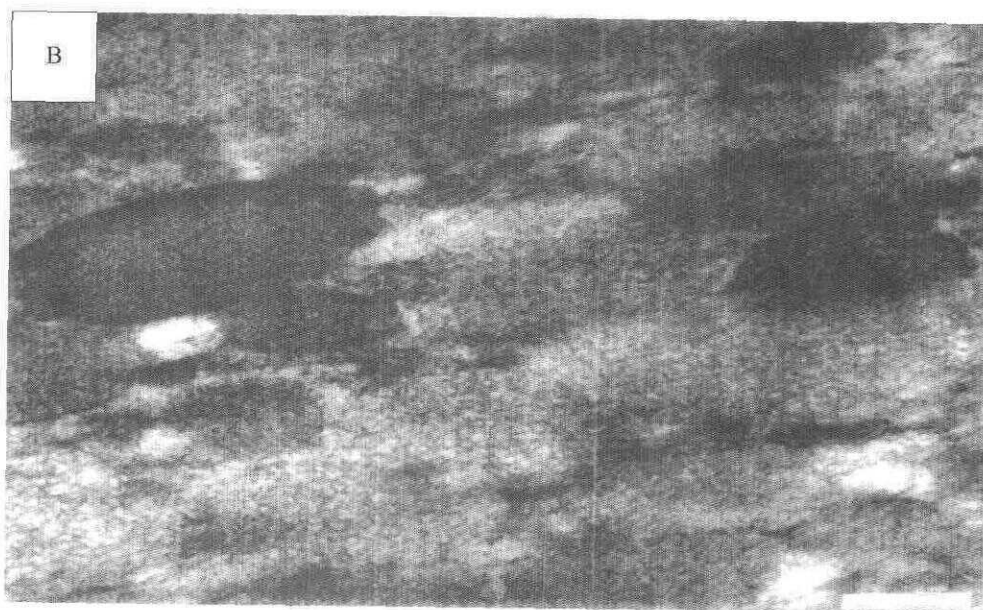
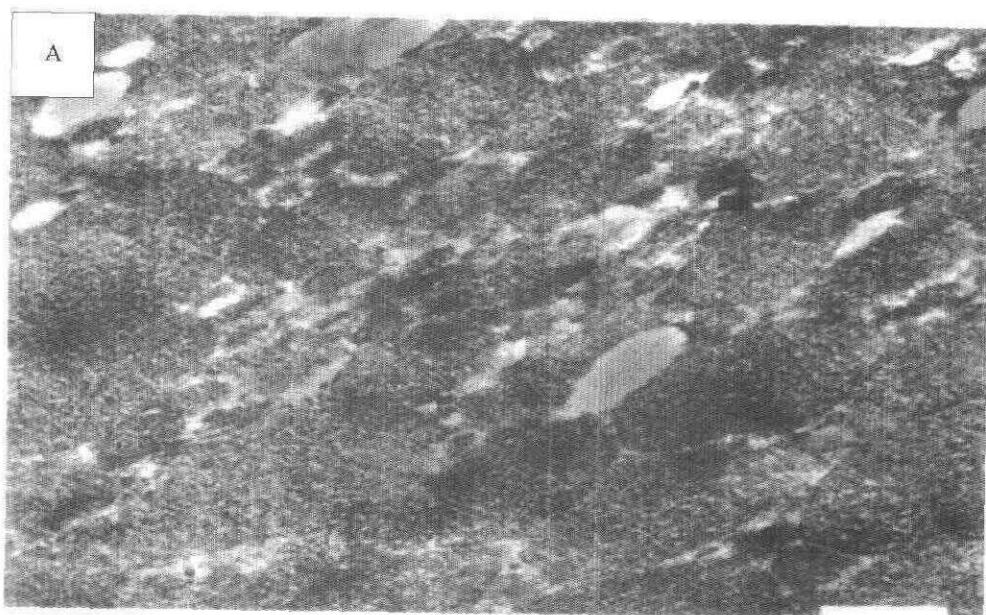


Figure 6. TEM micrographs of the unaged hydrogel-coated glove: inside surface (A) and outside surface (B). Bars = 0.5 μ m.



*Figure 7. TEM micrograph of aged polymer coated gloves:
PC 1 (A) and PC 2 (B). Bars = 0.5 μ m.*

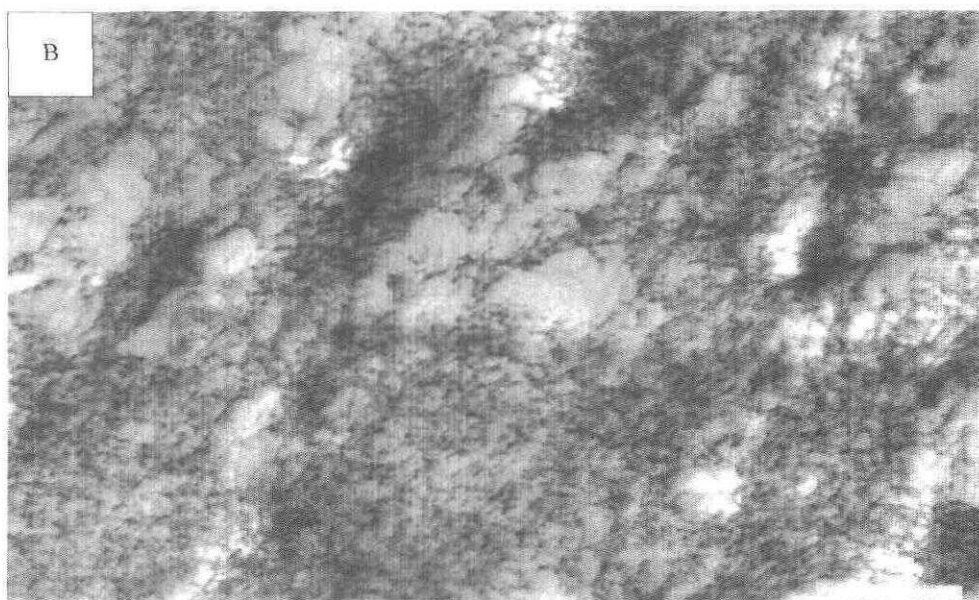


Figure 8. TEM micrograph of aged chlorinated and hydrogel coated gloves. Shown is the reduction in rubber network distribution: chlorinated (A) and hydrogel (B). Bars = 0,5 μm .

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