Electron Microscopy of Partially Dried Sheet Rubber

W. A. SOUTHORN

Electron micrographs of sections taken through the thickness of partially dried sheet rubber show differences in micro-structure in different regions of the sheet and give direct evidence of a barrier to diffusion.

In the drying of sheet rubber there is at first a rapid reduction of water content to around 10% followed by a relatively slow rate of drying. From consideration of drying rates for different thicknesses of sheets, PIDDLESDEN (1937) concluded that the slow drying phase was controlled by a diffusion process. The work of GALE (1959) and others supports this view, which is now generally accepted.

These changes in drying rate are accompanied by changes in the visual appearance of the sheet. Whereas the wet sheet is white and opaque, the dry sheet is translucent. The translucent region first appears at the outer exposed surfaces of the sheet and travels inwards as drying progresses, so that over most of the slow-drying phase a section of the sheet has the appearance of a sandwich of opaque white material enclosed within two translucent layers. Water diffusing from the interior of the sheet under these conditions must cross these translucent layers, so that the permeability or otherwise of the translucent material is of interest. It has been suggested by STEVENS (1948) that the machining operation may be detrimental in so far as it may reduce porosity. Investigations by GALE (1959) indicate that the effect of machining is complex and must affect the micro-structure of the sheet. Stresses are set up by this operation which are relaxed in the early stages of drying and influence the release of water by syneresis. Dimensional changes due to stress relaxation are greater in the direction of machining than they are at right angles to it. Other factors affecting the internal structure of the sheet during drying are the plastic flow of rubber under its own weight when the sheet is hung over the berotie, and the flow of rubber into space previously occupied by water as the latter is removed.

In view of the importance of these questions for an understanding of the diffusion phase of drying, it would be of value to have more direct information on the actual micro-structure of the partially dried machined sheet. Optical microscopy does not permit sufficiently high resolution for significant conclusions. Electron microscopy is a more powerful method but presents some preparational problems since very thin sections are required and rubber is notoriously difficult to cut.

EXPERIMENTAL

One day's collection of latex (38% d.r.c.) from the Institute's smallholding at Ulu Klang was processed in the normal manner by dilution to 15% and coagulation with formic acid. The following morning the coagulum was sheeted, giving ribbed sheets which were left to drip on beroties for 24 hours at room temperature before transfer to the drying chamber at 120°F. After 24 hours in the drying chamber the sheets were sampled by clipping out small pieces with scissors near the centre of the half sheet, i.e. the edges and the region near the berotie were avoided. At this stage the mean thickness of the sheet was 3.3 mm, it contained 4.5% water and a section through the thickness of the sheet showed translucent material at the surfaces exposed in

COMMUNICATION 366

the drying chamber, with opaque white material between these surfaces.

The samples were dropped into dry-ice/alcohol freezing mixture and initial sections were cut from the frozen block at approximately 100 μ intervals through the thickness of the sheet. These initial sections were then fixed in 1% osmic acid at 0°C. Preliminary experiments showed that osmic acid rapidly cross-links rubber particles, preserving their shape and rendering them resistant to attack by the reagents used in later stages of the preparation. Sheet specimens fixed with osmium alone proved to have rather poor cutting properties, and for this reason a further treatment was given (after osmium fixation) with bromine water to harden the rubber. The fixed brominated sections were subsectioned by hand under the dissecting microscope to give small blocks approximately 400×400×100 μ from selected regions of the initial sheet section (see *Figure 1*) and dehydrated through alcohol.

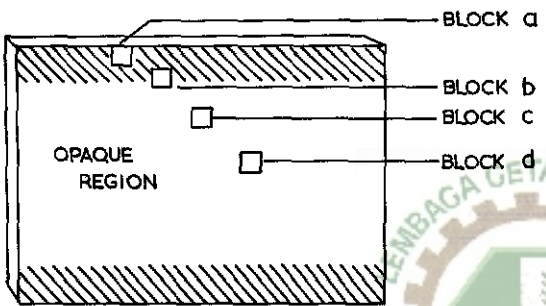

Figure 1. Method for subsectioning from initial section

These small blocks were embedded in partially polymerised butyl/methyl methacrylate, great care being taken to preserve their identity and orientation. After full polymerisation by ultraviolet light the plastic impregnated blocks were further trimmed by hand and then cut on a Porter Blum microtome at approximately 800 Å thickness using glass knives, to give electron microscope sections which were mounted on carbon coated grids, and examined on a Philips 100 B electron microscope at 80 K.V. The results are shown in *Figure 2.*

DISCUSSION

The innermost portion of the sheet (micrograph *d*) shows numerous small pockets of serum entrapped by partial fusion of rubber particles. Whereas latex is in broad terms a rubber in serum dispersion, the sheet interior is now phase inverted and may be regarded as a serum in rubber dispersion. It is of interest that there are still residual traces of the original rubber particle shapes.

The outermost portion of the sheet (micrograph *a*) shows a very different picture. Here the rubber has almost entirely merged together and must present a very formidable barrier to diffusion. The dark streaks in this region are considered to be discontinuities containing non-rubber material. They are oriented in the direction of machining and probably arise from the collapse of cavities originally filled with serum. Micrographs *b* and *c* show intermediate conditions. In micrograph *c* most of the cavities have collapsed and the rubber has fused together with loss of residual particulate structure. The remains of cavities can be seen but they are not strongly oriented, indicating that the influence of machining on micro-structure diminishes from the surface inwards.

The inhomogeneity of the sheet is of interest. At least some of the non-rubbers are deposited in discrete regions dispersed through the mass. These are likely sites for gas formation under suitable conditions. They are also regions where water could be re-absorbed when, for example, a dry sheet is immersed in water. This would occur by diffusion of water into the interior of the sheet and would be assisted if, as is likely, the residual non-rubbers are hydrophilic. Apart from any effect which such material could have on the maintenance of a vapour pressure gradient, it would provide weak points where complete fusion of the rubber was inhibited. Such regions could readily swell up again into cavities filled with aqueous medium. The

COPYRIGHT © MALAYSIAN RUBBER BOARD

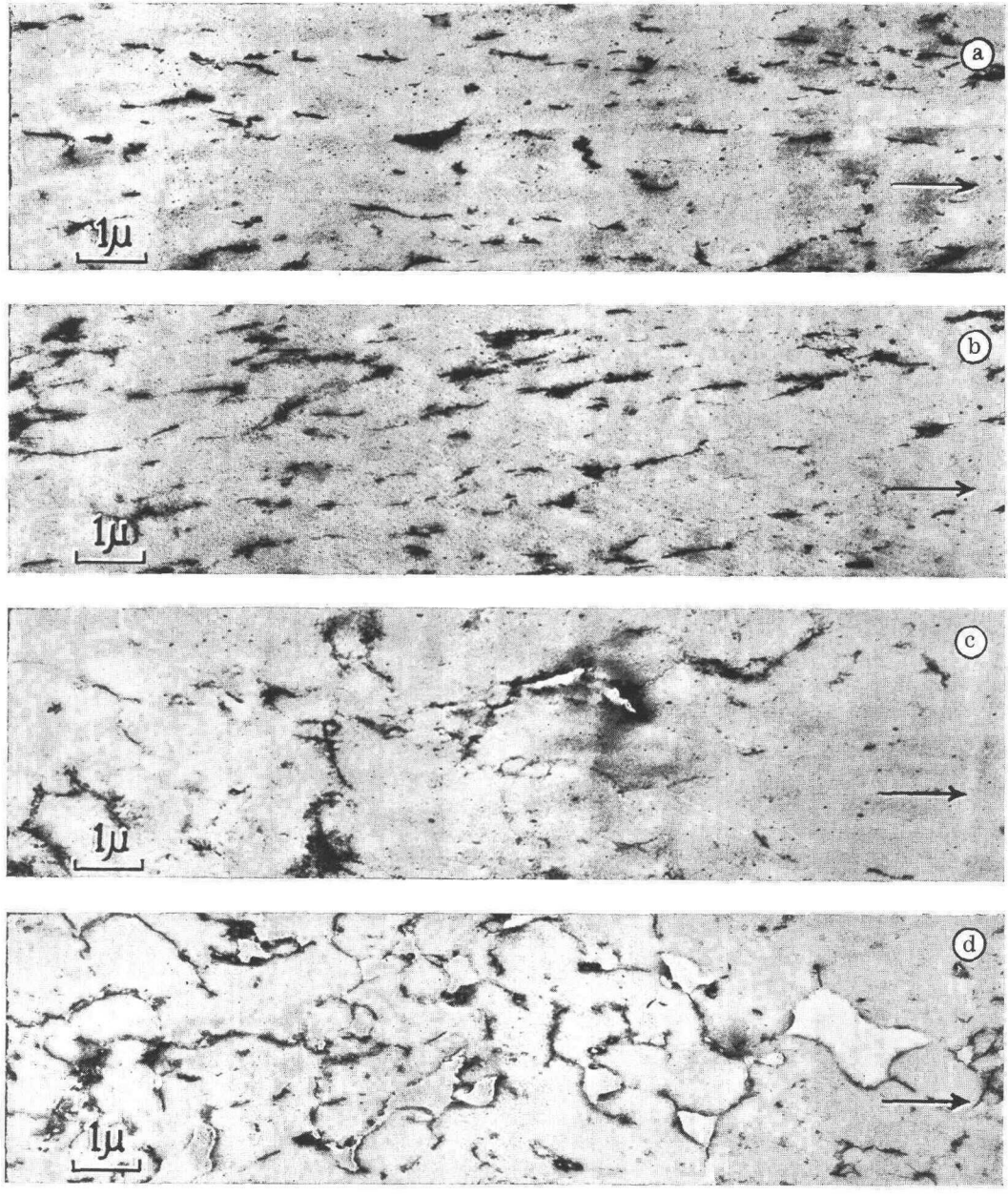

Figure 2. Electron micrographs of sections through partially dried rubber sheet. Micrographs (a)—(d) correspond to blocks (a)—(d) of Figure 1. Micrograph (a) shows the surface condition, (d) the centre, (b) and (c) are at intermediate locations. The arrow shows the direction of machining.

rehydration of dry rubber is of course well known but its interpretation in terms of micro-structure has presented certain difficulties (SCHOON, 1953).

The present results give direct evidence for the first time of the micro-structure of partially dry sheet.

ACKNOWLEDGEMENTS

The experimental assistance of the staff of the Colloid and Electron Microscope section of Chemical Division is gratefully acknowledged, particularly that of Mr Yee Shin Meng and Miss Ho Lai Har.

Chemical Division
Rubber Research Institute of Malaya
Kuala Lumpur *October 1963*

REFERENCES

GALE, R. S. (1959) A survey of factors involved in an experimental study of the drying of sheet rubber. *J. Rubb. Res. Inst. Malaya* **16**, 38.

PIDDLESDEN, J. H. (1937) The drying of rubber. *J. Rubb. Res. Inst. Malaya* **7**, 117.

SCHOON, T. H. C. F. (1953) Hydrogel of rubber. *Arch. Rubbercult.* Extra Number 2, October p. 1

STEVENS, H. P. (1948) Continuous coagulation. *India Rubb. J.* **114**, No. 14, 437.