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Electron Microprobe Investigation into the Diffusion of Ions Through Polymers

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The objective of this investigation is to study the mechanism of ion diffusion through polymeric films and coatings. A better understanding of this phenomenon should aid progress with problems such as corrosion protection and desalination membranes. The authors wish to report some preliminary results obtained by means of electron microprobe analysis.

Salt diffusion through polymeric materials have been studied by several methods, e.g. chemical analysis [1], radioactive tracer techniques [2], and neutron activation analysis [3]. Although such methods yield useful information about average diffusion parameters, they provide no insight into details of diffusion on a localised and microscopic scale. The electron microprobe, on the other hand, can be used to determine the presence of specific ions in a volume element as small as 1 μm in diameter. Therefore, microprobe analysis should be useful in determining local concentrations of diffusing ions and in examining the details of the diffusion process in polymers.

1. Experimental Method and Results

Samples of neoprene, and EPDM (ethylene-propylene-diene-terpolymer) rubbers (2 × 2 × $\frac{1}{16}$ in.), were immersed in a 10% aqueous magnesium sulphate solution for different periods of time at room temperature. After soaking, the samples were freeze-dried, and sliced parallel to the diffusion direction. The sections produced by this technique were then mounted between two brass plates for microprobe analysis.

The microprobe was used to look at two different aspects of the problem of ion diffusion in polymers. First of all, the location of a high concentration of a particular ion was determined. This was accomplished by using X-ray area scans for Mg_{K_α} and S_{K_α} and sample current scans on exposed and unexposed samples. All data were taken at a probe operating voltage of 20 kV, a sample current of 0.05 μA, and at a magnification of 1000. Figs. 1a-c show a sample current picture, as well as the distribution of magnesium and sulphur ions in the same area for unexposed neoprene. The lighter areas on the sample current pictures (fig. 1a) show the pores which are present at the surface of the prepared sample. The pore sizes in neoprene average about 10 μm in their longest dimension. A comparison of figs. 1a and b indicates that a few of the pores contain Mg even in the unexposed condition. Figs. 2a-c show the sample current scans and the Mg and S X-ray scans for a neoprene sample exposed for 20 min. In this sample one can see almost a one to one correlation between the indicated presence of a pore and a high Mg concentration. The Mg ions therefore diffuse along short circuiting paths (pores). The sulphur X-ray scan shows an even distribution of sulphur in the polymer. As discussed later, S apparently does not readily diffuse in neoprene.

The second type of analysis was to determine the average concentration of a particular ion in localised areas throughout the polymer. Since the ions are distributed on a very fine scale, we decided that a microprobe-chemical analysis of 100 μm^2 area would be quite suitable to define each localised area. This type of information permits one to determine profiles of ion concentration versus distance from the edge of the sample in an entirely analogous fashion to those profiles measured for metals and ceramics. This analysis was accomplished by determining the count rate at 100 second intervals from X-ray area scans,

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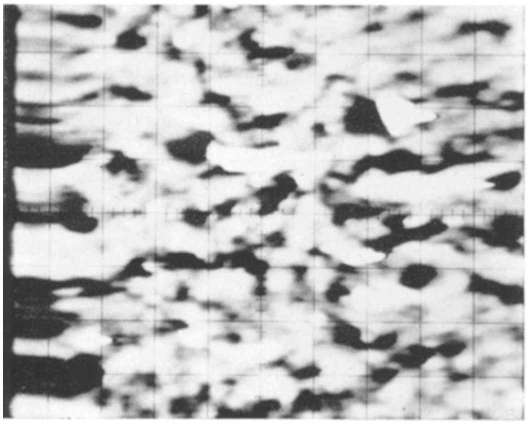

Figure 1a Sample current picture for unexposed neoprene.

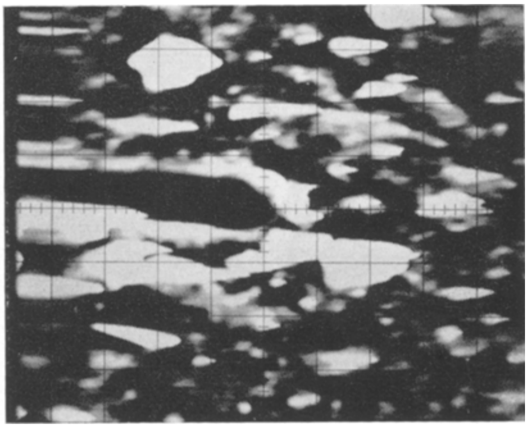

Figure 2a Sample current picture for neoprene exposed to 10% magnesium sulphate solution for 20 min.

Figure 1b Magnesium X-ray scan for unexposed neoprene.

Figure 2b Magnesium X-ray scan for neoprene exposed to 10% magnesium sulphate solution for 20 min.

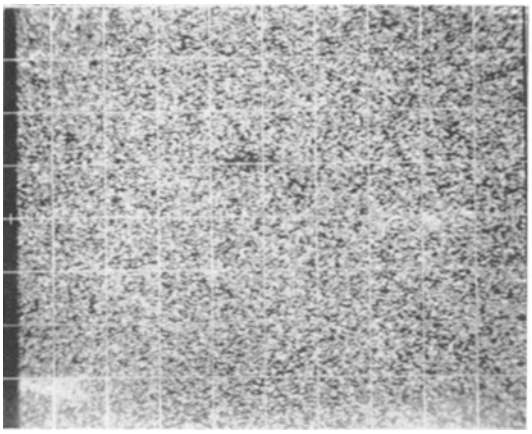

Figure 1c Sulphur X-ray scan for unexposed neoprene.

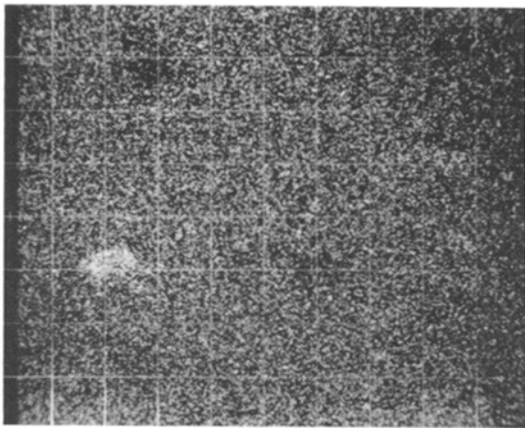

Figure 2c Sulphur X-ray scan for neoprene exposed to 10% magnesium sulphate solution for 20 min.

100 μm^2 in area, at various positions in the sample. Background radiation due to the continuum X-rays was measured for Mg and S by moving the X-ray spectrometer off the peak position. These backgrounds were subtracted from the Mg and S X-ray counts obtained from the exposed, and unexposed rubbers. Pure Mg was used for the Mg standard, and the mineral FeS_2 was used for the S standard. In this manner, we can detect an increase of 0.05 wt % Mg or S above their respective X-ray backgrounds.

The measured sulphur and magnesium contents of the unexposed neoprene were 1.9 and 0.5 wt %, and of EPDM, 1.8 and 0.05 wt %, respectively. The X-ray area-scan type of analysis showed that the sulphur contents in the centre of neoprene and EPDM samples were constant within ± 0.1 wt % for all samples exposed to $MgSO_4$ and were also within ± 0·1 wt % of the values for unexposed samples. On the other hand, the magnesium content increased by as much as 0.1 wt % after 1 h of exposure and by 0.5 wt % after 2 h of exposure. Since sulphur does not accumulate in the centres of the neoprene sample, it is selectively prevented from diffusing through the material. The magnesium content, however, does increase with increasing soaking time for both samples. The average concentration of the Mg ions does not vary in an orderly fashion from edge to centre to edge of the sample. This is probably due to the fact that diffusion in these polymers is controlled by pore, rather than bulk, diffusion.

2. Discussion

The magnesium ion concentration in several of the pores or holes was measured by using a static beam. We found that the Mg content was higher than in magnesium sulphate. Apparently only magnesium as an ion can diffuse in the polymer. It probably accumulates as magnesium hydroxide. It is possible that neoprene behaves as though it is negatively charged with its electronegativity arising from the presence of residual sulphate groups introduced during polymerisation or processing. Such electronegativity has been proposed by Glass and Smith [4], and by Kumins and London [5].

In conclusion, microprobe analysis shows promise as a technique for probing morphological details at the micron level, and for determining local ion concentrations. Experiments are in progress with other membranes as well in order to determine the concentration profile, and to correlate microprobe analysis with overall diffusion measured by other methods.

Acknowledgement

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