SHORT NOTE

A RAPID PREPARATION TECHNIQUE FOR STUDYING HIGHLY WATER-SWOLLEN MEMBRANES WITH A SCANNING ELECTRON MICROSCOPE (SEM) SUPPLIED WITH A CRYO-UNIT

H.D.W. ROESINK, J.M. KOENHEN, M.A. DEJONGH and C.A. SMOLDERS
Twente University of Technology, Dept. of Chemical Engineering, Enschede, The Netherlands

Received 26 June 1978

In this study the cryo-unit is introduced as a new and useful instrument to investigate water-containing specimens with the SEM. Often water-containing biological specimens are studied, but in our case we used water-swollen polymer membranes. The results show that application of a cryo-unit permits the study of this material at low temperatures up to magnifications of about 10 000 times, while other techniques failed to give reproducible results.

1. Introduction

In our laboratory we are studying phase-separation phenomena of polymer solutions in contact with non-solvents. As is known from the literature [1], these phenomena play an important role during the formation of asymmetric membranes. These membranes consist of an extremely thin selective layer (0.1-0.2 µm) backed by a porous support structure. The waterflux of these membranes is relatively high, while a good rejection of dissolved materials (e.g. salts) is maintained [2]. In our case we used highly water-swollen membranes. Cross-sections of water-containing polymer membranes are usually studied with a SEM using sample preparation techniques such as freeze-drying and solvent substitution [3,4]. These techniques, however, are rather time-consuming. In addition we have found that artifacts can be introduced when, after the freeze-drying step, the sample in its dry state is brought to room temperature.

In this study we investigate the use of a cryo-unit (freeze-shock, followed by cryogenic breaking and observing the specimen at low temperatures) and the effect of defrosting treatments on the SEM results.

2. Apparatus

The SEM (JEOL, JSM-U3) is equipped with a cryo-unit (JEOL, CRU). The normal pre-evacuation chamber is exchanged by a longer one, with a liquid nitrogen-cooled specimen table. In this pre-evacuation chamber there is a knife for producing a fresh specimen surface (figs. 1 and 2). There is also a defroster, a heating element (30 W) to remove the ice grown on the specimen surface. The specimen stage in the microscope can also be cooled with liquid nitrogen.

Fig. 1. Cryo-unit. (1) defrosting heater, (2) specimen fracturing knife, (3) specimen fracturing pin, (4) specimen exchange chamber cold stage, (5) refrigerant tank.
3. Sample preparation

Sample preparation is very simple and takes only a few minutes; the wet specimen is put into the specimen holder, and then put into liquid nitrogen to freeze the specimen immediately (a so-called freeze-shock). As soon as possible the specimen is brought into the cooled pre-evacuation chamber, where a fresh cross-section is obtained. The image of the specimen now shows a very iced surface (fig. 3). There are two methods for removing this ice:

- by sublimation in the microscope; this takes three to four hours.
- by using the defroster in the pre-evacuation chamber; since structural damage might occur, the rate and intensity of defrost must be determined experimentally for the specimen under study.

4. Results

In this work we used highly water-swollen, partially ionic modifications of styrene-isoprene-styrene (SIS) membranes. SIS is a thermoplastic rubber, consisting of glass-like domains of polystyrene ($T_g \approx$
100°C) embedded in a rubber-like matrix of polyisoprene \(T_g \approx -100°C\). Modification of the polyisoprene middle block, to introduce ionic groups, will not destroy this rubber-like character at room temperature. In water this ionic membrane will be rather swollen \([5]\), producing a certain swelling tension in the polymer as a whole.

To study specimens with a SEM it is necessary to remove the water, without damaging the swollen structure in which the water prevents the relaxation of the tension. All water can be removed by freeze-drying; that is, by sublimation of the ice at \(-130°C\) in a high vacuum. However, to prevent charging up of the sample in the microscope, coating with a charge-conducting layer (carbon/gold) is required. To apply this layer it is necessary to bring the specimen to room temperature; the structure may then collapse partly and may therefore have a denser appearance. The results are seen in figs. 4 and 5.

Another method is air-drying. Now relaxation of the tension in the rubber network and additional capillary forces cause a dense structure without any pores remaining in the substructure (see fig. 6). The reason is that when the temperature is kept low \((\approx -100°C)\) during the electron microscopic investigation, the polymer remains below its glass-transition point, and the “wet structure” will be retained. When the temperature rises above the glass-transition point of polyisoprene, the tension in the structure can relax, producing a denser structure or a collapse of the structure.

Fig. 4. Structure after freeze-drying (coal/gold, 15 kV).

Fig. 5. Structure after freeze-drying (coal/gold, 25 kV).

Fig. 6. Structure after air-drying (10 kV).
The cryo-unit offers the possibility of studying the specimen at low temperatures (≈ −130°C); at these temperatures the structure is not damaged and is comparable with the “wet structure”. A further advantage of this method is that no coating of a charge-conducting layer is necessary, since the ice in the porous support structure prevents charging up of the specimen at low voltages (6–10 kV). The top layer of the ice can be removed easily by the defroster.

5. Conclusions

For highly swollen rubber-like structures there is no alternative way of handling than keeping the specimen at temperatures below −100°C. In comparison with freeze-drying we conclude that use of the cryo-unit means an enormous gain of time. When using the defroster for a short period (15–30 s) to free the surface from ice, no effect on the structure can be found.

References