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A preparation technique for examination of wet-spun polymer fibers in a scanning electron microscope

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With 8 figures

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1. Introduction

In the investigation of morphological structures by a scanning electron microscope (SEM) the factors which effect the resolution power and magnification can be devided into two groups. Those factors connected with the design of the instrument will depend on the specification provided by the manufacturer. On the other hand, sample properties, sample preparation and conditions during examination in the microscope form a group of very important variables. Therefore with the instrument available, much attention should be paid to the last group of variables.

In our laboratory we are studying coagulation phenomena of polymer solutions in contact with non-solvents.

Especially the changes in morphology during coagulation of the polymer phase are relevant to polymer membrane and fiber structure and properties.

In order to study the morphology during all stages of coagulation of a spinning fiber, we tried to use the freeze-shock and freeze-etching technique in combination with transmission electron microscopy (1). Difficulties in obtaining a satisfactory cleavage surface with the freeze ultramicrotome for several polymer species, forced us to look for a different method. The present study of morphological structures makes use of the large depth of field of the SEM. Sample preparation consists essentially of cryogenic breaking of a wet-spun fiber, followed by a low temperature and low pressure freeze drying (or etching) treatment.

To prevent charging up of the sample in the microscope a coating is given with a charge conducting layer.

2. Sample preparation

Previously (2, 3, 4) methods have been developed for the examination of external fiber surfaces and fatigue broken fiber ends by scanning electron microscopy. Attention was paid to coating techniques, by vapour deposition of carbon and metals like Ag, Au and Pt.

A cryogenic breaking technique has also been employed earlier, for the investigation of dry polymer membranes (5) and biological materials (6).

In the present work excellent fracture surfaces of freshly coagulated wet-spun fibers have been obtained through breaking under liquid nitrogen or liquid propane. To reveal the coagulation structure of the polymer, the specimen is then freeze-dried (or etched) at low

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temperature and pressure in special equipment (Leybold Hereaus EPA–100). Either the whole specimen or only a part of it can be freed from solvents in this way. We will describe here procedures for preparing samples which are completely coagulated during wet-spinning, or which are only partly coagulated.

Coating and further handling of these small fiber samples is described also.

A. Completely coagulated fibers

The morphological structure of wet spun fibers depends strongly on the composition of the polymer solution (polymer content) and of the coagulation bath (solvent/non-solvent ratio).

To prevent modifications of the final structure which has been obtained in the coagulation bath (e.g. after 24 hours equilibration) the remaining solvent in the fiber should be exchanged for non-solvent as completely as possible. This procedure is necessary since during drying of the fiber the relative content of a high boiling solvent could increase, with the result that the polymer might redissolve and the structure might be distorted or even collapse.

In the case of polyurethane/DMF solutions spun to equilibrium in coagulation baths of different ratios of DMF/water, the fiber was equilibrated during successive periods of 24 hrs. in mixtures of DMF/water with increasing water content, up to pure water.

The fiber was then cooled rapidly in liquid nitrogen and cryofractured with the help of two tweezers. Two alternative ways of drying these samples completely have been followed.

A 1. Low temperature drying

The frozen fiber sample is transferred directly to the freeze-drying apparatus (EPA–100), then at −50 °C and at a pressure of 10^{-5} Torr the specimen is dried completely, which takes several hours.

The fiber is then coated with a thin charge-conducting layer and subsequently placed, at normal T, on a SEM-disk (see section C).

A 2. Room temperature drying

The fiber specimen is brought to room temperature, placed on a SEM-disk (section C) and transferred to the freeze-drying apparatus, where at normal temperatures and at moderately lowered pressures the fiber is dried.

This takes only several minutes. Subsequently the fiber is coated with carbon and gold.

It is clear that this last method can only be applied for fibers which have enough mechanical strength, to withstand the capillary forces operative in porous structures during drying. For the fibers investigated in this study (polyurethane and nylon-6) both drying procedures gave identical structures.

After breaking and drying, the specimen has to be coated with a thin (200–300 Å) charge conducting layer. Carbon and gold are here applied by vapour deposition. During coating, the samples were kept at low temperature (cooling finger of the EPA–100) in order to prevent heat damage to the fiber structure.

B. Intermediate stages of coagulation

In order to study early stages in coagulation the spinning fiber was picked up from the coagulation bath using two tweezers coupled at fixed distance and the sample was put into liquid nitrogen immediately.

Knowing the spinning speed (cm^3/sec), the diameter of the fiber and taking samples at different distances from the spinneret, the time of coagulation can be varied. The fiber is broken under liquid nitrogen, put in a special clip and transferred directly at low temperature to the EPA–100.

Since solvent is always present in this case and since (like for DMF/water) the solvent may have a higher sublimation point than the non-solvent, it is not possible here to dry the specimen completely.

In the case of DMF, with a freezing point of −60 °C one should stay at a low enough temperature during etching to prevent redissolution of the polymer in the eutectic melt of the DMF/water system. Therefore the specimen was freeze-etched for a limited time (a few hours) at −100 ° C and at a pressure of 10^{-5} Torr, so that enough solvent/non-solvent could have sublimated to reveal the structure of a sufficiently deep surface layer at the cleavage plane.

Subsequently the deeply cooled sample was coated with a relatively thick (about 400 Å) layer of carbon, to preserve the morphological

structure features of the etched surface. A thin layer of gold was applied to provide surface conductance.

The sample was then brought at room temperature and normal pressure and the remaining DMF and water in the fiber were carefully removed in the EPA–100 apparatus at moderately lowered pressures, or the polymer was coagulated completely by placing the fiber in DMF/water mixtures of increasing water content up to pure water and dried thereafter.

The fiber specimen could then be placed on a SEM-disk (section C).

C. Fiber handling for microscopy

Examination of fracture surfaces of fibers in the SEM raises the question how to keep the fiber vertically under the electron beam. A simple solution was found to this by adhering the fiber specimen at one end in a vertical position to a disk of the SEM, using a charge conducting paint (Dotite silver paint).

The intimate contact between the coated fiber and the silver provides a better means of charge flow than squeezing the fiber between stages manipulated with a screw.

Good results are obtained when the fiber specimen is not longer than about 3 mm. With longer fibers bending over of the fiber might give problems and also possible discontinuities in the coating layer might accumulate to give limited charge dissipation.

Results

The microscope used in this study was a JEOL–JSM.U3 scanning electron microscope, operated at an acceleration voltage of 25 kV.

The fibers were spun from spinnerets with diameters of 0.2–0.5 mm. This produces relatively thick fibers, which facilitates the handling of the fiber.

Fig. 1 shows a fiber which was spun from a 25% polyurethane solution in DMF in pure water. The fiber was prepared further with the technique described under A1, (low temperature drying). A similar fiber prepared as described under A2, (room temperature drying) is shown in fig. 2.

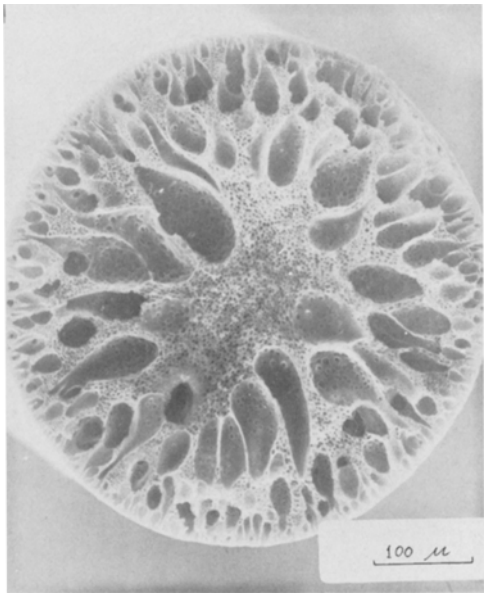

Fig. 1. Wet spun polyurethane fiber: 25% PU in DMF spun in pure water; sample preparation by low temperature drying

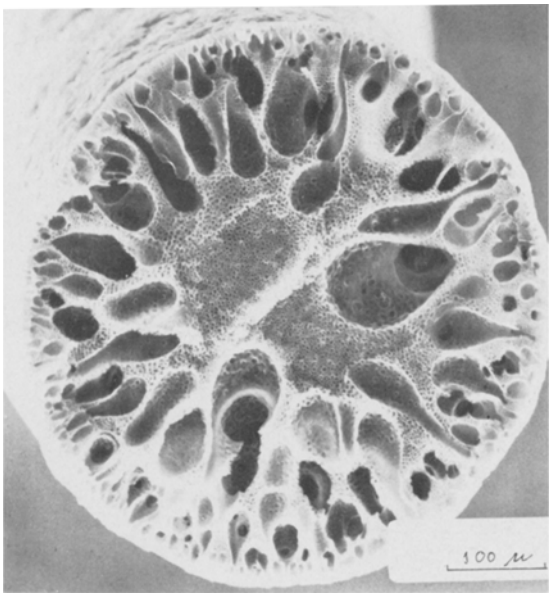

Fig. 2. Wet spun polyurethane fiber: 25% PU in DMF, spun in pure water; sample preparation by room temperature drying

In fig. 3 a fiber is shown, which was spun in a coagulation bath of 20% DMF/80% H_2O from a 25% polyurethane solution in DMF. The preparation technique used after complete exchange of DMF for water was according to A2.

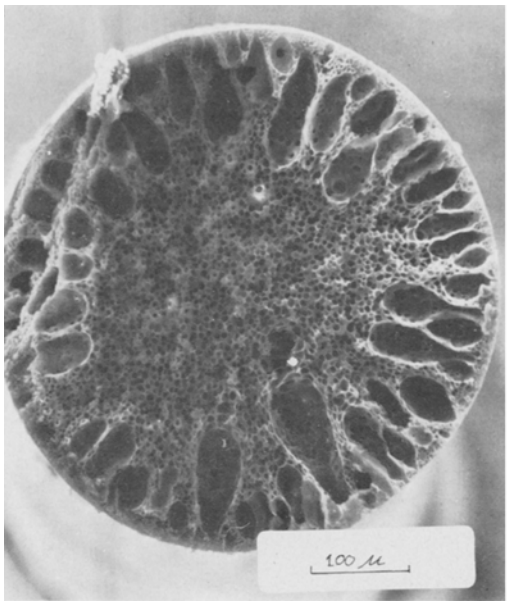

Fig. 3. Wet spun polyurethane fiber: 25% PU in DMF spun in a coagulation bath containing 20% DMF/80% water. Sample preparation by room temperature drying

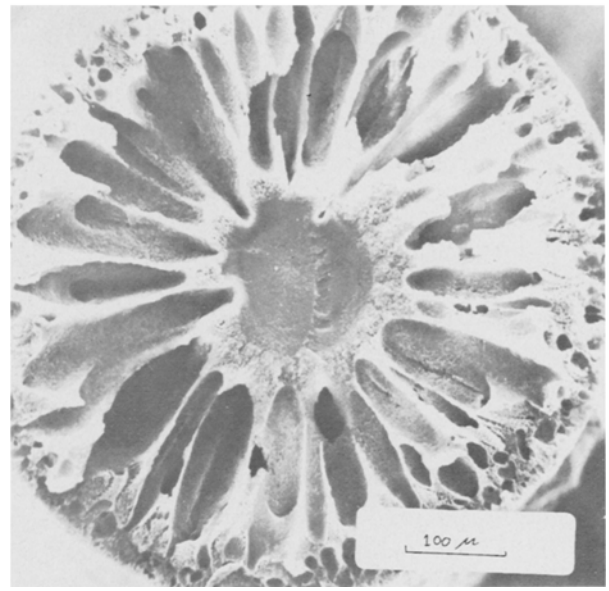

Fig. 5. Polyurethane fiber (20% PU in DMF spun in pure water) in intermediate stage of coagulation

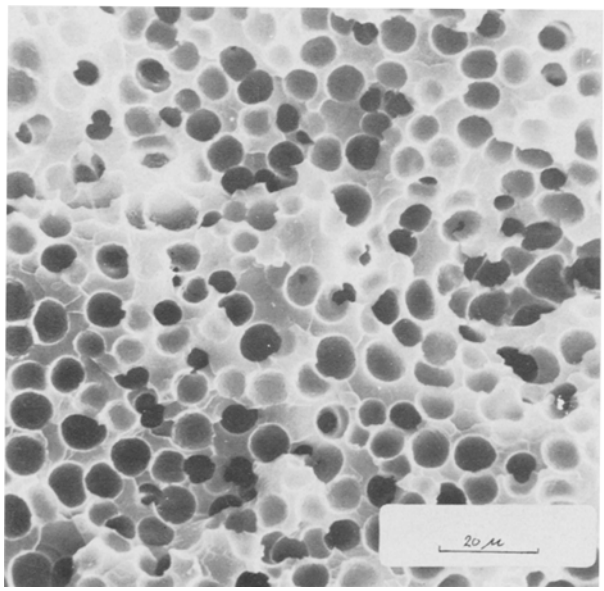

Fig. 4. Core structure of the fiber from fig. 3 at five times higher magnification

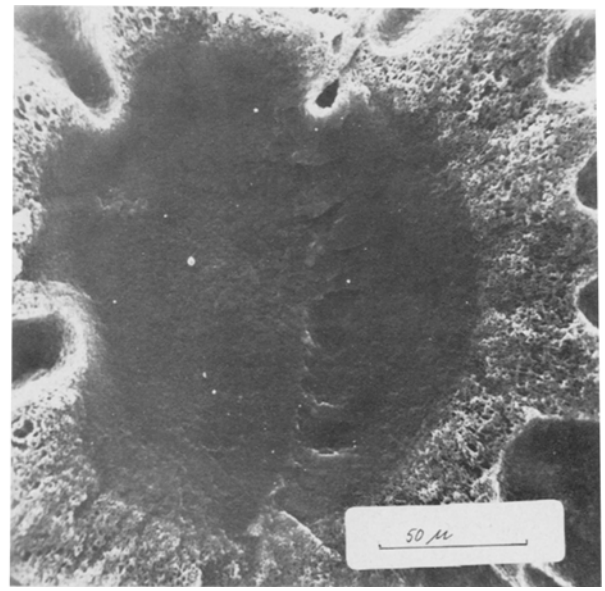

Fig. 6. Core structure of the fiber shown in fig. 5

In fig. 4 a higher magnification is shown of the structure which is present in the core of the previously described fibers. The magnification values of the carbon and gold coated specimens could easily reach 30.000 times, with good sharpness and contrast. However, in these pictures there was no additional detail in comparison with pictures with magnification factors of about 1000.

Fig. 5. shows a fiber spun from a 20% polyurethane solution in DMF, which had been in contact with the coagulation bath

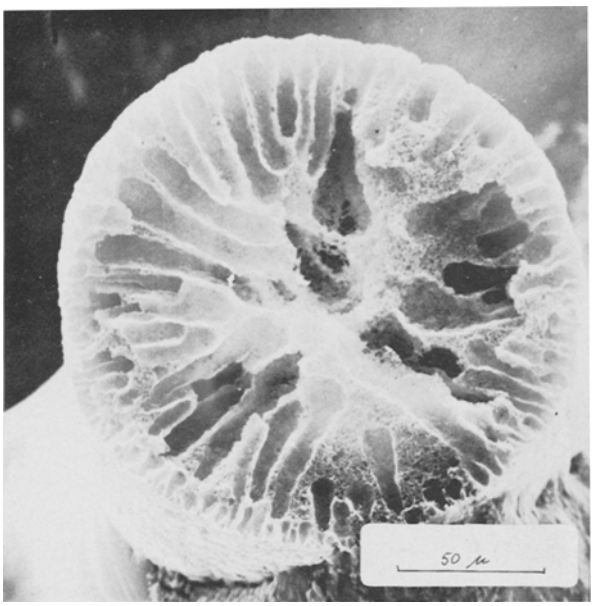

Fig. 7. Nylon-6 wet spun fiber

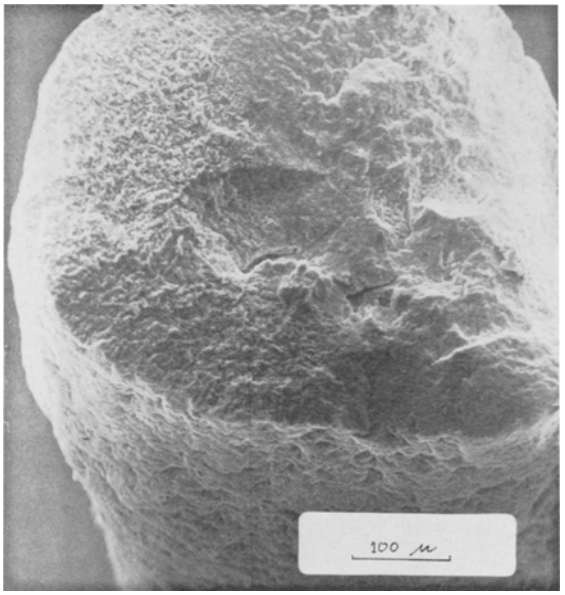

Fig. 8. Incorrectly treated wet spun polyurethane fiber

(pure water) during only 5 seconds and which was not entirely coagulated at the moment of freeze-shock; the fiber sample was treated according to method B (freeze-etching at low T). A higher magnification of the core structure of this fiber is given in fig. 6.

In fig. 7 the structure of a wet spun nylon-6 fiber is shown (10% nylon-6 in methanol-$CaCl_2$ spun in water). This fiber sample was prepared by method A2.

An example of an incorrect treatment of the cryofractured fiber where removal of DMF and water in a partly coagulated polyurethane fiber has been performed at too high temperatures is given in fig. 8.

Discussion

The most secure procedure for the preservation of the morphological structure in completely coagulated fibers is the method where freeze-drying of the fiber at low temperatures is followed. For the polymers employed in this study, the fiber structures revealed by room temperature drying do not differ perceptibly from those for which freeze drying has been employed. We can conclude that these polymers have enough mechanical strength to withstand capillary forces of the remaining non-solvent during drying at room temperature, at least down to the pore radii which are most abundant in wet spun fibers (1–5 μ).

From fig. 1–4 we can see that the core of the fibers is build up from a spongy polymer structure.

The walls between the spherically shaped holes are sometimes perforated so that these holes are interconnected. This gives rise to a more or less penetrable porous structure. This type of information is not easily obtainable by conventional techniques in transmission electron microscopy.

In fig. 5 and 6 we can see the development of the structure in the fiber. The outer part of the fiber is already coagulated, while the inner part is still homogeneous on this scale.

The relatively thick layer of coal employed here acts as a rigid support, which remains intact when the contents of this native fiber becomes fluid again at normal temperatures. Thin coating layers in most cases were not stable enough to allow after-treatment at room temperature.

We conclude that much information about morphologies of fibers can be obtained with the preparation methods described in this paper, even when the fibers are not completely coagulated.

Zusammenfassung

In diesem Beitrag wird eine Methode zum Präparieren von Proben naß-gesponnener Polymerfasern, die noch nicht weiter bearbeitet sind, zwecks Untersuchung mit einem Raster-Elektronenmikroskop, besprochen.

Bei dieser Methode werden die Fasern kryogen gebrochen, gefolgt durch Gefriertrocknen oder Gefrierätzen der Fasern, wonach die Fasern mit einer gut leitenden Schicht überdeckt werden.

Diese Methode kann auch angewendet werden für die Untersuchung von Zwischenstrukturen der Fasern während des Spinnprozesses.

Ergebnisse werden besprochen für Nylon-6 und Polyurethane-naß-gesponnene Fasern.

Summary

In this paper the technique is discussed of sample preparation for freshly wet-spun polymer fibers, to be examined by scanning electron microscopy.

It makes use of cryogenic breaking of the samples, followed by freeze drying or freeze-etching of the specimen and coating it with a charge conducting layer.

The method can also be adapted to the investigation of intermediate coagulation structures of the spinning fiber. Results are discussed for nylon-6 and polyurethane wet-spun fibers.

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