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Effect of Additives on the Cross Section of PAN Fibers

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ABSTRACT

Additives are generally added to spin dope in wet spinning to facilitate mechanical operations, increase solid content, and effect gelation to precede phase separation. Besides these advantages, they have an effect on the cross section of PAN fibers. Organic compounds (hydrochlorides of aryl, alkyl secondary amines, etc.) change the cross section to a bean shape, whereas a nonsolvent (water) and inorganic compounds (calcium salts, borax, boric acid, etc.) retain the circular cross section of PAN fibers. The change in cross section can be attributed to the change in skin and core effects at different pH values of the spin dope in the presence of the additives.

The parameters that control the cross-sectional shape of polymeric fiber in the wet spinning process are the temperature of the coagulation bath [1, 2], the polymer content in the spinning dope [3], and the pH of the coagulation bath [4].

Generally the nonround shape of the fiber cross section is explained

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in terms of the solvent-nonsolvent fluxes [5] and the mechanical behavior of the skin formed in the coagulation process.

Additives are sometimes added to the spin dope to reduce viscosity, to facilitate many technical operations (such as dissolution, filtration, and deaeration), and to effect gelation.

Some organic additives [6] are reported to reduce viscosity and increase solid content of the dope. Addition of nonsolvent is also known to reduce viscosity and hasten the gelation of the polymer. It is reported in the literature that additives such as congo red [7], borax, and boric acid [8] stimulate gelation and make gelation precede phase separation for the production of fibers of good mechanical properties.

This communication deals with the effect of some additives on the cross-sectional shape of PAN fibers.

Additives of the kind that reduce viscosity and effect gelation have been chosen for the study.

EXPERIMENTAL

Polyacrylonitrile-co-methyl acrylate (6%) was prepared in the laboratory at 69-70°C using a redox catalyst system.

Dimethylformamide (DMF) was used as a solvent for making the spin solution, and DMF-H_2O (55-45%) was used as the coagulation bath.

Organic additives such as the hydrochlorides of aryl and alkyl secondary amines of analar grade were used at 0.5 to 5%. They were added to DMF while the spin solution was being made.

Such inorganic additives as calcium salts, borax, and boric acid were used in the concentration range of 0.05 to 0.2%. One-half to 1.5% of distilled water was used as the nonsolvent in the preparation of the dope solution. The compositions of the spinning solution and the coagulation bath, as well as the temperature, were the same for all the experiments performed.

The pH values of the salts in the DMF solvent were measured by a digital pH meter.

Because the polymer content throughout was the same, any change in pH of the DMF is due only to the additives. A Fourne Laboratory model wet spinning assembly with 48 holes of 0.025 mm diameter was used to spin PAN fibers. Such spinning parameters as the volume rate flow, the temperature, the composition of the stretch baths, and the stretch ratios were kept constant through all the experiments. The fibers obtained in each experiment were embedded in a polymer matrix and examined under a transmission microscope. Their cross-sections have been photographed.

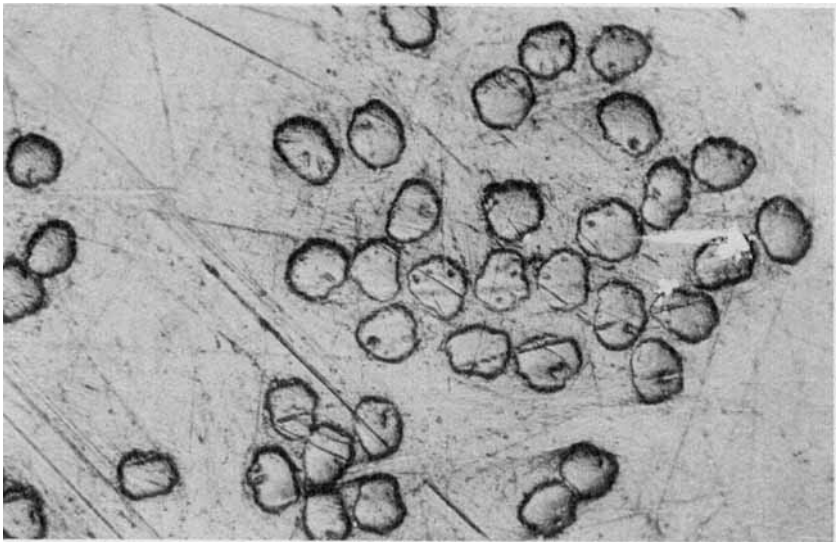

FIG. 1. PAN fiber cross section without any added additive.

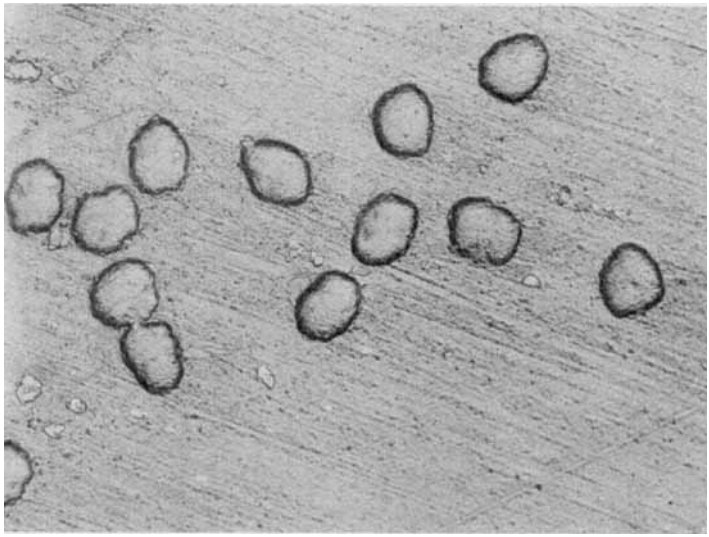

FIG. 2. PAN fiber cross section in the presence of an inorganic additive.

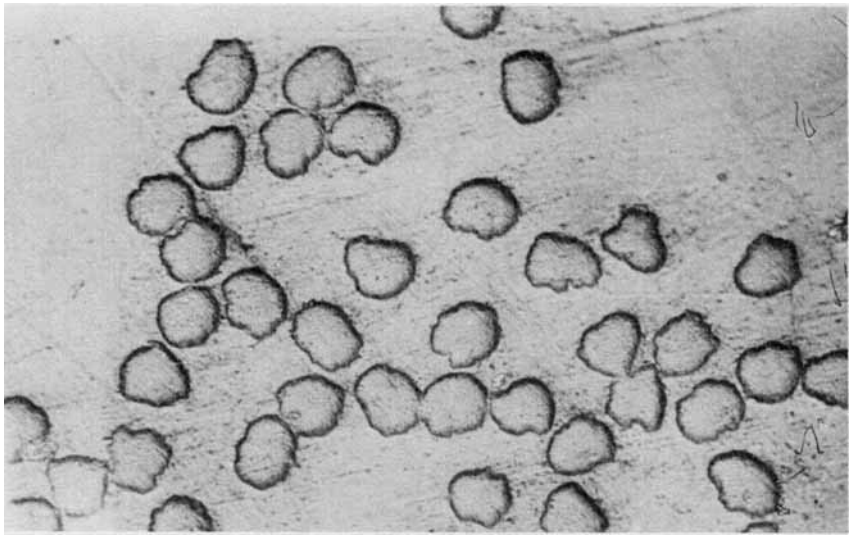

FIG. 3. PAN fiber cross section in the presence of a nonsolvent.

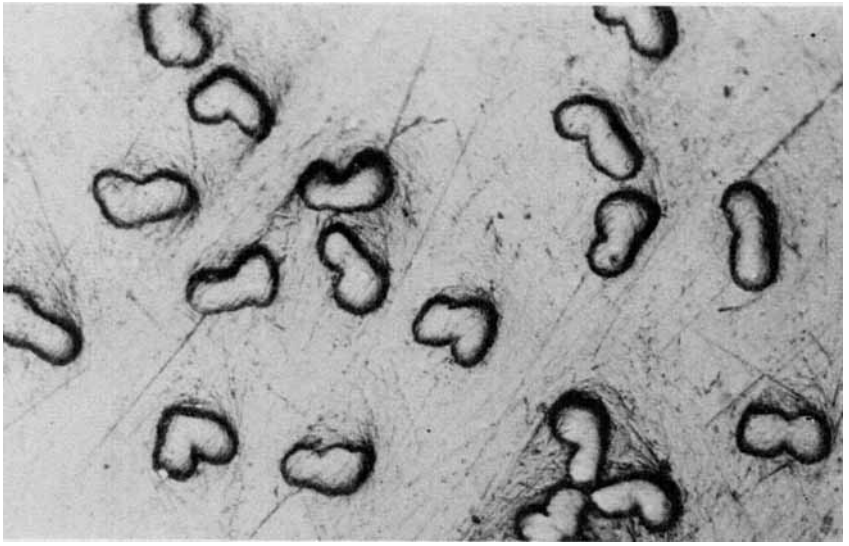

FIG. 4. PAN fiber cross section in the presence of an organic additive.

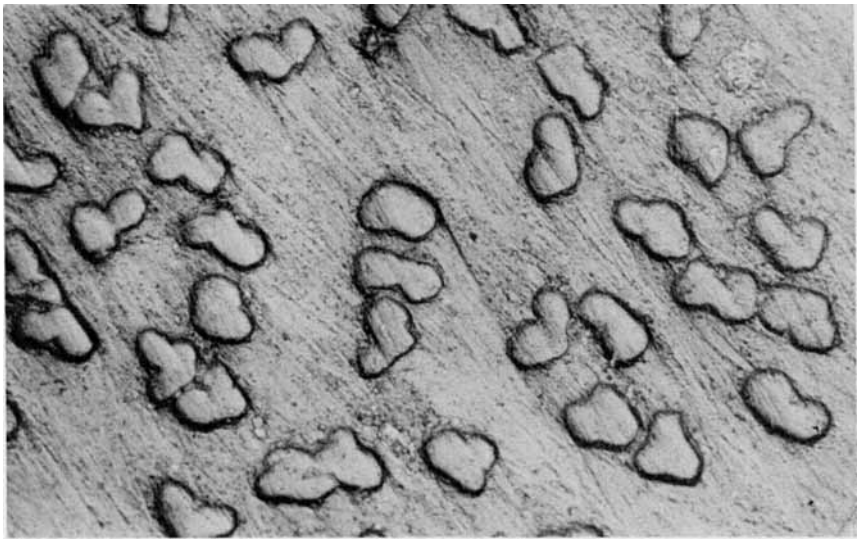

FIG. 5. PAN fiber cross section in the presence of nonsolvent, inorganic, and organic additives.

RESULTS AND DISCUSSION

Figures 1, 2, and 3 show the cross sections of PAN fibers with no additive, with an inorganic additive, and with a nonsolvent added to the dope solution. Interestingly, the cross section of the fibers with the above additives is round while with an organic additive (Fig. 4) and a mixture of the above additives (Fig. 5) the cross section is bean shaped.

The nonround shape of the fibers is due to the difference in the diffusion of solvent or nonsolvent in the polymer solution and the rate at which the polymer coagulates on the surface. This is also true when the temperature of the coagulation is reduced [1, 2].

Grobe and Gieseke [4] reported the change in fiber cross section from round to bean structure on the addition of HCl, HOAC, or oxalic acid to the coagulation bath. This has been explained in terms of a change in pH of the coagulation bath, with the bean shape at $pH < 3$ and the round shape at $pH > 6$.

It is worthwhile to note that the dope in the present experiments, and not the coagulation bath, contained the additive. We expect a pH change to take place in the coagulation bath after extrusion of dope into the bath.

Turbidimetric titrations were performed and the titer value of the

coagulant (DMF-H_2O) for 25 mL, 1% PAN (DMF additive, organic non-solvent, and inorganic) solution varied from 6.7 to 8.15 mL in the pH range of 4.2 to 13.6.

The change in cross section may be due to the strong dope solution creating a very strong skin on the fiber. The core must remain fluid for a longer time because the process will be governed by osmosis rather than by diffusion. Complete removal of solvent may become exceedingly difficult under such circumstances.

The disproportion between the rate of diffusion of solvent or non-solvent in the polymer solution or gel on one side and the rate at which the polymer is coagulated or dried at the filament surface on the other also leads to deformation of the cylindrical form of fibers.

Detailed studies on the cross-sectional shape of fibers are under way and the results will be discussed in subsequent publications.

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