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Effect of Spinning Bath Liquids on the Properties of Acrylic Fibers

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Synopsis

Fibers of an acrylonitrile copolymer spun from dimethylformamide solution into nonsolvent spinning baths are found to have tensile and contraction properties which correlate with the aggregating power of the bath.

Detailed investigation of the dependence of fiber properties on spinning conditions have been made for polyacrylonitrile (PAN) and acrylonitrile (AN) copolymers by several groups of workers, notably Takahashi,[1] Kambara,[2] and Okamura.[3] The nature and temperature of the coagulating bath for polymer spun from dimethylformamide (DMF) or dimethyl sulfoxide solution have received careful attention. Systematic variation of the coagulating properties of the spin bath have been achieved by using DMF-water mixtures and have shown, for example, that the tensile strength of the drawn fiber increases rapidly when the spin bath contains more than 80% DMF. Increasing the solvent component of the bath delays the onset of coagulation so that the disorientation effects at the jet face arising from the viscoelastic properties of the polymer solution can be overcome. These considerations will, of course, be affected by the extrusion and draw-off rates, jet hole diameter, and the respective diffusion coefficients factors which, as far as possible, need to be kept constant.

Takahashi and Watanabe[1] have also investigated the effect of other nonsolvents, both as the bath liquid and as a replacement for water in the DMF mixtures. Spinnability of the polymer solution can be measured by the ratio winding speed/extrusion speed which passes through a minimum value as the concentration of DMF in the spin bath is increased. Data obtained by Takahashi and Watanabe[1] for an AN + MA copolymer (96 mole-% AN) are given in Table I, where C_{min} is the per cent weight concentration of nonsolvent at the point of minimum spinnability. There is a clear correlation with turbidometric titrations. Coagulation values (z) for PAN[4] are also in close agreement. No similar trend can be detected in their tensile strength results; this may partly be ascribed to the voids present in fibers produced in strong coagulating baths.

Climie and White[5] have shown that aggregation effects occur in PAN

TABLE I
Data of Takahashi and Watanabe[1] for AN–MA Copolymer Spun from DMF into DMF–Nonsolvent Mixtures

Spin bath	Spinnability C_{min}[a]	Turbidity[a]	Coagulation z[b]
DMF–CCl_4	81	44	
DMF–xylene	71	42	
DMF–ethylene glycol	59	30	26
DMF–butanol	45	28	
DMF–water	24	12	12

[a] % w/w.
[b] % v/v.

and AN copolymer solutions. On addition of nonsolvent to a DMF solution of polymer, a critical region is reached after which the turbidity of the solution increases rapidly. This is distinct from phase separation. It is in general found: (*a*) for a common nonsolvent this critical concentration (or aggregation point, *P*) is directly proportional to the mole fraction AN in a random copolymer and independent of the comonomer; (*b*) for a given copolymer, *P* is characteristic of the nonsolvent. Because of the time-dependent nature of the aggregation process, *P* is arbitrarily defined[5] but is significant to $\pm 1\%$. Aggregation occurs through the formation of intermolecular links which are here associated with the AN residues. Doty, Wagner, and Singer[6] postulate a spectrum of secondary bond strengths for the similar case of poly(vinyl chloride)–dioxane solutions, but such bonds in acrylic copolymers may be CN dipolar or more probably hydrogen-bond forces. Aggregates are in effect regions of microcrystalline order and so must be advantageous in respect of the mechanical properties of the fiber.

Filaments of approximately 2 den. were prepared from DMF solution (15% w/v) of an AN copolymer, similar in composition to that of Takahashi and Watanabe,[1] by spinning under constant conditions into spin baths of different aggregating properties. A stretch of about 700% was then given to produce almost maximum extensibility.[7] Lengths of fibers were afterwards allowed to relax freely in boiling water, sufficient time being allowed for this process to be completed.[8] Microbalance weighings were used to determine fiber denier both before and after relaxation. Stress–strain diagrams were obtained using a Cambridge tensile extensometer (55% R.H., 18°C.) operated at a constant rate of elongation of 43%/min.

Results given in Table II show both the tenacity and extensibility to be dependent on aggregation point particularly following relaxation treatment. Tenacity is reduced, whereas extensibility is at least doubled by relaxation in water at 100°C. A toluene spin bath gives the most useful improvement in fiber properties, and these conditions have been utilized to prepare PAN fibers which show particularly well oriented x-ray diagrams.

TABLE II

	Initial				Final				
Spin bath	Tenacity, g./den.	Extensibility, %	Denier	Contraction, %	Tenacity g./den.	Extensibility, %	Denier	P[a]	z[b]
Toluene	4.4	10	2.2	25	3.9	34	2.5	38	
Benzene	4.6	14	2.0	27	2.8	31	2.3	37	66
Benzyl alcohol	3.5	12	2.2	27	3.6	34	2.5	33	
Ethanol	4.0	11	2.0	22	2.4	23	2.3	17	
Water	3.9	9	1.8	19	2.4	18	2.2	8	12

[a] % w/w.
[b] % v/v.

A large contraction occurs on relaxation which shows some dependence on P and agrees with results of Takahashi and Watanabe[1] and Klimenkov and Kargin,[8] who also examined the rate of shrinkage in PAN fibers. Farrow[9] has determined the length changes in a wide variety of textile filaments brought about by hot water treatment. Whereas no change was found for the AN copolymer fibers (Orlon and Acrilan), poly(vinyl chloride) (Rhovyl, Fibravyl), vinyl chloride–vinylidene chloride copolymer (Tygan), and vinyl chloride–vinyl acetate copolymers do show contractions comparable with the present observations. Filaments which show the largest contraction effect (Table II) are those produced with the use of nonsolvents for which the aggregation and coagulation points are well separated thus offering the greatest chance for aggregates to form.

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Résumé

Des fibres d'un copolymère de l'acrylonitrile, filées au départ d'une solution dans le diméthylformamide injectée dans des bains non-solvants et tournants, révèlent avoir des propriétés à la traction et la contraction qui sont en relation avec la puissance d'aggrégation du bain.

Zusammenfassung

Fasern aus einem Acrylnitrilcopolymeren, die aus Dimethylformamidlösung in ein Fällungsmittel- Spinnbad gesponnen wurden, besassen Zug-und Kontraktionseigenschaften, welche zum Aggregierungsvermögen des Bades in Korrelation standen.

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