Properties of Fiber from Acrylonitrile–Vinyl Chloride Alternating Copolymer

INTRODUCTION

In recent years, the subject of alternating copolymerization has received considerable attention. Although there have been many papers dealing with polymer preparation or polymerization mechanism, very little has been disclosed concerning the effects of alternating structure on copolymer properties. Furukawa has reported properties of rubber prepared from acrylonitrile–butadiene alternating copolymer[1,2]; and the patent literature presents general claims of utility for a number of alternating copolymers.[3,4] In the present communication, the preparation of wet-spun fiber from acrylonitrile (AN)–vinyl chloride (VCl) alternating copolymer is described, and the effects of alternating structure on fiber properties are discussed.

EXPERIMENTAL

Alternating AN–VCl copolymer with η_{sp} = 0.11 (measured in dimethylformamide, 25°C, 0.1 g/dl) was prepared in the presence of ethylaluminum dichloride, following procedures described previously.[5] A 33 wt-% solution of the polymer in dimethylacetamide was extruded through a 25-hole, 0.003-in. spinnerette into a spin bath containing ethylene glycol at 60°C. The resulting fiber was given a sevenfold orientation stretch in water at 75°C and dried under tension. In a similar manner, fiber from equimolar AN–VCl random copolymer with η_{sp} = 0.14 (measured in dimethylformamide, 25°C, 0.1 g/dl) was prepared by extruding a 26 wt-% solution of the polymer in dimethylacetamide into ethylene glycol.

Fiber tensile properties were determined using an Instron Model TT tensile tester; dry-heat, free-shrinkage measurements were made using a modified Fisher-Johns melting point apparatus. Sonic modulus determinations were made using a PPM-5 Dynamic modulus tester.

RESULTS AND DISCUSSION

The AN–VCl system is one of the very few which allow a study of the effects of alternating copolymer structure on fiber properties. Most alternating copolymers containing AN are relatively insoluble in the hydrocarbon media in which they are prepared, a phenomenon which is thought to be responsible for the low polymer molecular weights observed.[6] On the other hand, alternating copolymer compositions which maintain sufficient solubility to allow for extensive chain growth (e.g., AN–butadiene, methyl acrylate–propylene) are not, in general, of a type expected to form fiber having useful properties. For AN–VCl alternating copolymer, solution viscosities (η_{sp}, 0.1 g/dl) in the range 0.09–0.13 have been reported,[5,7] values which make this polymer an acceptable fiber-forming candidate.

Two AN–VCl fibers were prepared, one from an alternating copolymer and one from a random copolymer of the same composition. Fiber tensile properties are shown in Table I. Properties of the random copolymer fiber lie in the typical modacrylic range. The alternating copolymer fiber, however, has properties more typical of vinyon [poly(vinyl chloride)] fibers,[8] in spite of the presence of 50 mole-% AN.

Dry-heat shrinkage is an important property used in assessing the utility of most modacrylic (35–85 wt-% AN) fibers. Polyacrylonitrile (PAN) fibers undergo very little distortion when heated, whereas poly(vinyl chloride) (PVC) fibers shrink extensively at relatively modest temperatures.[9] It is to be expected that AN–VCl fibers would fall somewhere in between these two extremes, and this is in fact the case, as shown in Figure 1. Interestingly, dry-heat shrinkage performance of the random copolymer fiber is markedly

TABLE I
Properties of AN–VCl Fibers

	Tenacity, g/denier	Elongation at break, %	Young's modulus, g/denier	Sonic modulus, g/denier
Random	4.09	22	50	100
Alternating	2.19	15	54	95

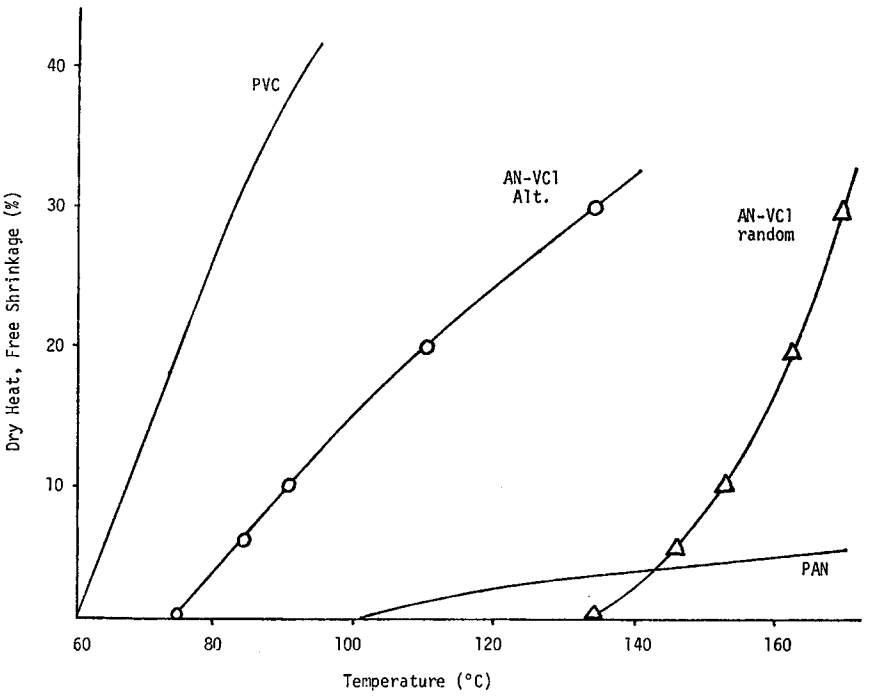

Fig. 1. Diagram showing that alternating copolymer structure is detrimental to dry-heat shrinkage properties of AN–VCl fibers.

superior to that of the alternating copolymer fiber, even though the two fibers have approximately the same degree of orientation, as indicated[10] by values of the sonic modulus (Table I).

We conclude that the beneficial effect on fiber properties of some AN blocking in a random copolymer structure more than counterbalances the effect of concomitant VCl blocking.

References

1. J. Furukawa, Y. Iseda, K. Haga, N. Kataoko, T. Yoshimoto, T. Imamura, Y. Shido, A. Miyagi, K. Tanaka, and K. Sakamoto, *J. Polym. Sci. B*, **7**, 561 (1969).
2. J. Furukawa and A. Nishioka, *J. Appl. Polym. Sci.*, **15**, 1407 (1971).
3. Sumitomo Chemical Co., Ltd., Brit. Pat. 1,056,236 (January 25, 1967).
4. Sumitomo Chemical Co., Ltd., Brit. Pat. 1,107,137 (March 20, 1968).
5. G. Wentworth and J. R. Sechrist, *J. Polym. Sci. B*, **9**, 539 (1971).

6. G. Wentworth and J. R. Sechrist, *J. Polym. Sci. B*, **9**, 205 (1971).
7. J. Furukawa, E. Kobayashi, and J. Yamauchi, *Polym. J.*, **2**(3), 407 (1971).
8. *Man-Made Fiber Fact Book*, Man-Made Fiber Producers Association, Inc., New York, 1971, p. 10.
9. G. H. Fremon, in *Technology of Synthetic Fibers*, ed. by S. B. McFarlane, Fairchild Publications, New York, 1953, p. 172.
10. W. W. Moseley, Jr., *J. Appl. Polym. Sci.*, **3**, 266 (1960).

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