Influence of Drawing and Molecular Weight on Structural-Mechanical Properties of Acrylic Fibers

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Synopsis

The influence of drawing and molecular weight in a narrow range on the several structural-mechanical properties of acrylic fibers have been investigated. Drawing of fibers ($\lambda = 3x–6,5x$) leads to a considerable increase of tenacity. These data were explained with the orientation and perfection of structure. It was found that the molecular weight in closer range influences the density, perfection of structure, and the stability of fibers to repetitive deformation. The results show that the diversions of the average molecular weight, in the manufacture of commercial acrylic fibers, must be negligible.

INTRODUCTION

The influence of drawing and molecular weight of polymers on the structure and properties of acrylic fibers has been investigated[1–5] in very wide ranges. For example Dobretsov et al.[5] prepared fibers with molecular weight 3×10^5 and 3×10^6 and draw ratio $I – 20x$.

Polymers with molecular weight 40,000–100,000 (refs. 6 and 7) are used in the manufacture of commercial acrylic fibers. However, in certain cases negligible diversions of the average molecular weight are observed. Taking this into consideration, we realize the importance of studies on the influence of drawing and molecular weight in a narrow range on the behavior of the acrylic fibers.

The purpose of this paper is to investigate the influence of drawing (in the region $\lambda = 3x–6.5x$) and the molecular weight (in the region 45,000–56,000, corresponding to $\eta_{sp}^{0.5} = 0.740–0.950$) on the structural-mechanical properties of acrylic fibers.

EXPERIMENTAL

Preparation of Samples

The polymer used was a copolymer of acrylonitrile, methyl methacrylate, and a small amount of a sulfonated dyestuff acceptor. The copolymer was produced by polymerization in water with a redox catalyst of ammonium persulfate and sodium bisulfite. The molecular weight of copolymer varied by the amount of the catalyst.

The fibers were prepared by the wet-spinning process (Table I) by using copolymers with molecular weights, respectively, of 45,000, 49,000, 53,000, and 56,000. In all cases the viscosity of spinning solutions was equal.

After coagulation the fibers were washed with water and stretched at 100°C. The samples produced in this manner were treated in the presence of steam at about 100°C and dried at 120–125°C.

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TABLE I

Spinning Conditions

Dope solids:	
molecular weight 45,000	27.5%
molecular weight 49,000	26.5%
molecular weight 53,000	25.0%
molecular weight 56,000	24.2%
Coagulation bath composition	50% DMF:50% H_2O
Coagulation bath temperature	25°C
pH of coagulation bath	3.0
Jet stretch	0.45x

To preserve the structure of the protofibers, they were washed and dried under high vacuum at liquid-nitrogen temperature (24 hr).

Measurements

The molecular weight was determined by viscometry (Oswald) using the formula

$$[\eta] = 2.83 \times 10^{-6} M$$

X-ray data were collected in transmission on a diffractometer (TUR M 62) using Ni-filtered Cu $K\alpha$ radiation with fixed count techniques. The signal was exhibited on a chart recorder. The samples were wound on a suitable holder and rotated. A 2θ scan was made from 4° to 40°.

The width at half-maximum intensity of the peak at $2\theta = 17°$ was used to (approximately) determine the perfection ($B°$) of the structure.[5]

The x-ray orientation was measured from the azimuthal scanning at $2\theta = 17°$. The width at half-maximum intensity ($H° = I_{1/2}$) was used as an index of orientation which may be used to calculate the parallelism of the crystalline part of structure by equation[8,9]
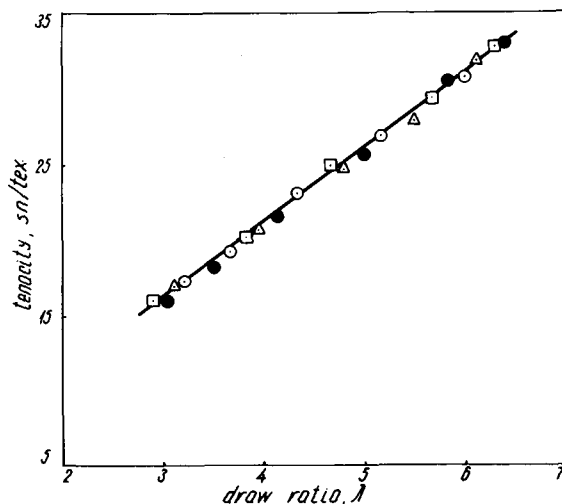
$$P = \frac{90 - H/2}{90} \times 100\%$$

Fig. 1. Effect of draw ratio on the tenacity of fibers produced by polymer with molecular weights: (○) 45,000; (●) 49,000; (△) 53,000; (□) 56,000.

The tenacity was measured on a Fafegraph-IV. All measurements were carried out in a laboratory maintained at 22°C and 65% relative humidity. Measurements were made on 150 single filaments for each sample. Specimens of filaments, 10 mm, were used and stretched at 12 mm/min.

The density was measured by immersion in a wetting mixture (carbon tetrachloride-n-heptane) and in a nonwetting liquid (mercury). The porosity was calculated by

$$\text{porosity} = 100 \ (1 - \rho_{Hg}/\rho_{CCl4})\%$$

The stability of fibers to repetitive deformation was measured by using apparatus "Sinus" after 50,000 cycle and under load 2 g. The change in tenacity after testing was used as an index for stability of fibers to repetitive deformation.

Apparatus type ZT-10 was used for measurement of relaxation of fiber tension (at constant elongation).

RESULTS AND DISCUSSION

Structure formed during coagulation has an effect on the properties of acrylic fibers. In our study the coagulation conditions were held constant, but molecular weight and dope solids were valued. Table II shows some protofiber structure parameters and tenacity. The increase in molecular weight leads to a slight positive influence on the density and perfection of the fiber structure. This could be explained with an increase in conformational changes of the longer molecules, resulting in increased protofiber density. The slight influence in molecular weight on protofiber structure and tenacity is due to a great extent to the close values of molecular weight on the identical viscosity of spinning solutions, and to the low jet stretch.

The tenacity of protofibers is very small and does not depend on the molecular weight (Table II). The increase in tenacity (Fig. 1) with a corresponding increase in draw ratio is related to the structural reorganization in the direction of the stretch (Fig. 2). The orientation is strongly related to draw ratio $\lambda \approx 5x$. However, the tenacity also increases (Fig. 1) after $\lambda = 5x$. The irregularity of the structure influences the tenacity of the fibers. For instance, the probability for appearance of defects in the structure increases with fewer stretched fibers. There is a continuous perfection of structure during an increase in draw ratio (in the studied region) (Fig. 3). On this basis, it is logical to make the assumption that the tenacity increases after $\lambda = 5x$. It is necessary to point out that this data refers to comparatively low values of draw ratio ($\lambda = 3x$–$6.5x$).

The orientation and tenacity of the fibers produced from polymers with different molecular weights are the same (Figs. 1 and 2). On the other hand, there are differences in perfection of the structure depending on molecular weight, particularly in the region of draw ratio $3.5x$–$5.5x$ (Fig. 3). The stability of fibers to repetitive deformation depends in great extent on molecular weight (Table III). The stability to repetitive deformation of fibers is strongly sensitive to the continuity of the fibrillar network. The relaxation in tension is higher with fibers produced from polymers with lower molecular weight. In these fibers the mobility of the structure elements is larger, probably due to the lower forces between the fibrils in the three-dimensional network. The shorter molecules cause a decrease in tenacity after repetitive deformation.

TABLE II
Effect of Molecular Weight on Protofiber Properties

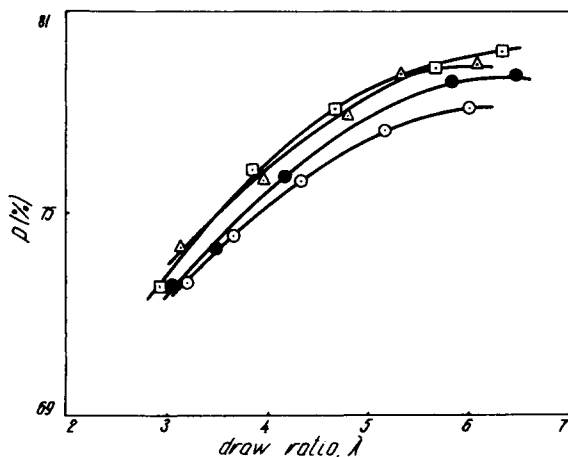| Molecular weight	Mercury density, g/cm^3	Carbon tetrachloride density, g/cm^3	Porosity, %	X-ray orientation, H^0	Perfection of structure, B^0	Tenacity sn/tex
45,000	0.32	1.14	72	N_0	1.74	3.5
49,000	0.37	1.14	68	measurable	1.69	3.6
53,000	0.36	1.14	69	orientation	1.69	3.6
56,000	0.37	1.14	68		1.68	3.6

Fig. 2. Relationship between parallelism and draw ratio. Molecular weight of the polymer: (O) 45,000; (●) 49,000; (△) 53,000; (□) 56,000.

CONCLUSION

The changes in orientation, tenacity, and stability to repetitive deformation and perfection of structure of acrylic fibers, depending on molecular weight of polymer (45,000–56,000) and drawing ($\lambda = 3x$–$6.5x$) were discussed.
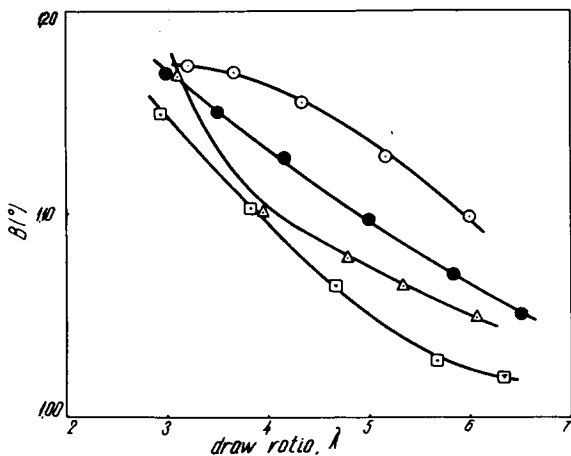

Fig. 3. Relationship between the perfection of structure and draw ratio. Molecular weight of the polymer: (O) 45,000; (●) 49,000; (△) 53,000; (□) 56,000.

TABLE III
Effect of Molecular Weight on Porosity, Stability to Repetitive Deformation, and Relaxation of Tension of Finished Fibers

Molecular weight	Porosity, %	Reduction in tenacity in percent after repetitive deformation	Residual tension after 160 min, kg/mm^2
45,000	59	21.4	1.45
49,000	53	20.8	1.90
53,000	50	14.1	2.50
56,000	50	12.6	2.65

Small changes in molecular weight do not influence the tenacity of proto- and finished-fibers. However, molecular weight does influence the density, perfection of structure and stability of fibers to repetitive deformation. The effect of molecular weight on the density and perfection of structure are displayed in greater extent after the stretching process. The results obtained during variations of molecular weight in closer ranges confirm the results obtained by Craig et al.[10] and Knudsen,[11] that the protofibers structure and properties are responsible for the finished fibers properties.

It is possible that the observed changes may be due to the molecular-weight distribution of the polymer. Each change in molecular weight is closely connected with the change in the rheology properties of the spinning solution. The regulating factor is the polymer concentration in the spinning solution. However, this requires changes in the drawing step for production of fiber with equal thickness (titer). It may be concluded, therefore, that the production of acrylic fibers with constant properties requires minimum changes in molecular weight ($\Delta M < 2000$).

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