

## Rheological Behavior of Some Acrylic Fibers Dissolved and Spun in the $\text{ZnCl}_2$ System

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### Synopsis

Concentrated solutions of Acrilan 16 and 1656, Creslan 58 and 61, Orlon 42, and several experimental acrylic copolymers were prepared by dissolution of the staple fibers in 60%  $\text{ZnCl}_2$ . The solutions were investigated rheologically. It was shown that a 3.5-power relationship between the log of the Newtonian viscosity and the log of the molecular weight held for these solutions. Their elastic behavior as exhibited by the Barus effect was shown to be a function of shear stress and independent of molecular weight or composition. The  $\text{ZnCl}_2$  solutions of the acrylic fibers were spun under a harsh and a mild condition of coagulation. On physical and bending properties of the fibers, mild coagulation has an effect similar to an increase in the content of the minor component of the copolymer. The loop properties and shrinkage of Turbo-stretched fibers are shown to be mainly functions of their composition.

### INTRODUCTION

The preparation of synthetic fibers by the wet spinning process involves extruding a polymer solution through small orifices into a coagulation bath. Coagulation occurs either by chemical reaction or by an interchange of solvent and nonsolvent between the extruded filament and the coagulation medium. The coagulated filaments, at this stage, have a very cheesy structure from which the remaining solvent is easily removed. Although the wet gel has significant properties, on drying, it becomes very brittle and unsuited for textile applications. To render the fibers useful two processes are necessary, orientation and compactness. Orientation is achieved by stretching, usually in boiling water; compactness of structure occurs during drying when the wet gel collapses.

Due to the complexities of the fiber spinning process it is advisable to restrict oneself to an investigation of only a few variables at a time. In this report the effect of polymer composition on the polymer solution properties and on the initial fiber structure in the polyacrylonitrile (PAN)- $\text{ZnCl}_2$  wet spinning system, will be discussed.

The initial fiber structure of PAN has been studied as a function of solvent (*N,N*-dimethylacetamide, sodium thiocyanate, 60%  $\text{ZnCl}_2$ ) and technique (wet and dry spinning) by Craig et al.,<sup>1</sup> as a function of coagulation variables in the DMAc system by Knudsen,<sup>2</sup> and as a function of copolymer composition in the DMSO system by Takeda et al.<sup>3</sup>

This communication reports the results of an investigation of solution properties of some commercial and experimental acrylic polymers in the  $\text{ZnCl}_2$  system as well as the properties of fibers spun from these polymers.

### DISSOLUTION OF ACRYLIC FIBERS IN 60% $\text{ZnCl}_2$

The dissolution of stretched acrylic fibers in 60%  $\text{ZnCl}_2$  has to be undertaken with caution. On heating a concentrated solution of  $\text{ZnCl}_2$ , one

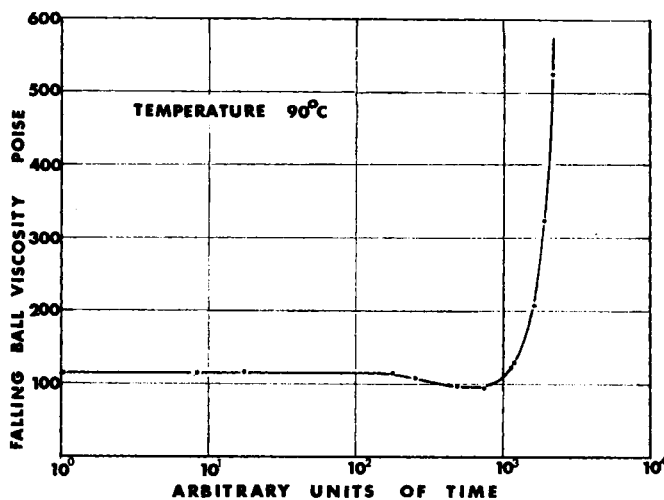


Fig. 1. Hydrolysis of PAN in 60%  $\text{ZnCl}_2$ .

increases the content of  $\text{ZnO}$ , which greatly accelerates the rate of hydrolysis of the nitrile groups of the PAN polymer. As indicated by Nakajima,<sup>4</sup> the rate of the hydrolysis can be controlled by adjusting the pH of the solution. Figure 1 shows the effect of hydrolysis on viscosity of the PAN poly-

TABLE I  
Composition of Some Commercial Acrylic Fibers

Acrylic fiber	Composition <sup>a</sup>		Mole fraction of VCN
PAN homopolymer	100%	PAN	1.00
PAN copolymer #1	95%	" -5% MA	0.969
Orlon 42 <sup>b</sup>	94%	" -6% MA	0.962
Acrilan 16 <sup>b</sup>	92.5%	" -7.5% VA	0.953
PAN copolymer #2	91.7%	" -8.3% MA	0.947
Creslan 61 <sup>b</sup>	90%	" -10% MMA	0.944
Acrilan 1656	88.2%	" -5% VA-6.8% MVP	0.936
Creslan 58	87%	" -5.9% VA-6.4% MVP	0.932

<sup>a</sup> MA = methyl acrylate; MMA = methyl methacrylate; VA = vinyl acetate; MVP = 2-methyl 5-vinylpyridine.

<sup>b</sup> The presence of any dye receptor monomers were ignored in this analysis.

mer dissolved in 60%  $\text{ZnCl}_2$  acidified with HCl to pH of 2.7.\* Conversion of the nitrile group to an amide cannot be detected by viscosity measurements up to about 8% amide. The sharp increase in viscosity in Figure 1 is attributed to crosslinking.

To minimize hydrolysis and prevent formation of gels, the dissolution was started at  $-20^\circ\text{C}$ . and allowed to reach room temperature in 2 hr. The solutions were blended for an additional 2 hr. at temperatures never exceeding  $50^\circ\text{C}$ .

Table I shows the composition, determined by infrared analysis of the acrylic fibers investigated. After dissolution and spinning in the  $\text{ZnCl}_2$  system the composition showed no significant change from the original fibers. Hydrolysis as indicated by per cent amide was negligible, never exceeding 1% by weight.

### RHEOLOGY OF ACRYLIC POLYMERS IN 60% $\text{ZnCl}_2$

Figures 2 and 3 show the shear stress at the wall versus apparent shear rate data, obtained with a capillary viscometer, for the acrylic polymer solutions investigated. The concentrated polymer solutions, whose solids content was controlled to 0.1% by weight, were prepared from staple fibers scoured free of finish and dissolved in 60%  $\text{ZnCl}_2$  acidified to a pH of 2.7.

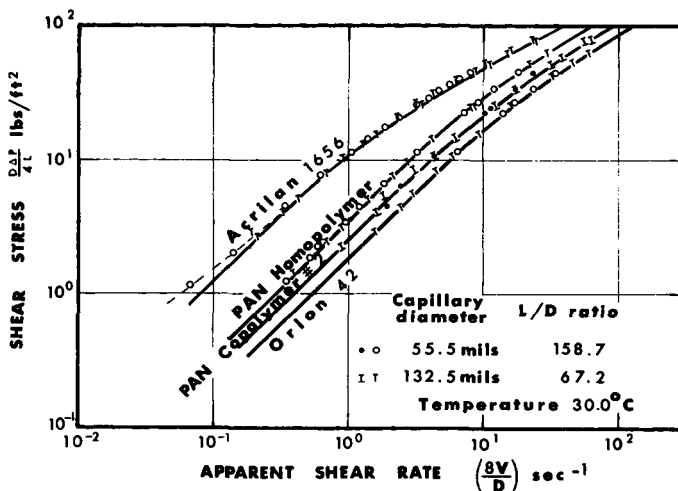


Fig. 2. Flow curves of acrylic fibers dissolved in 60%  $\text{ZnCl}_2$ .

Because the data from the two capillary tubes of different length-to-diameter ratios fell on a single line it was not necessary to correct the data.<sup>5</sup> The two flow lines for Creslan 58 represent two different fiber lots.

The data for Acrilan 1656 show a deviation from Newtonian flow at low shear stresses. The transition from Newtonian to non-Newtonian flow can be seen much better in Figure 4, which shows the apparent viscosity as a

\* pH of 2.7 is recorded after a 10:1 dilution of 60%  $\text{ZnCl}_2$  in water.

function of shear stress. The transition is not a function of viscosity but of molecular weight. PAN homopolymer at 0°C., although higher in viscosity than Acrilan 1656, has a transition point at a higher stress, identical to the curve for homopolymer at 30°C.

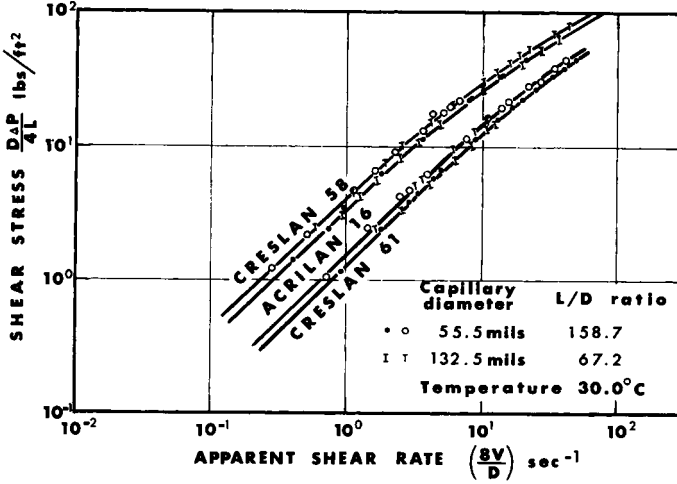


Fig. 3. Flow curves of acrylic fibers dissolved in 60% ZnCl<sub>2</sub>.

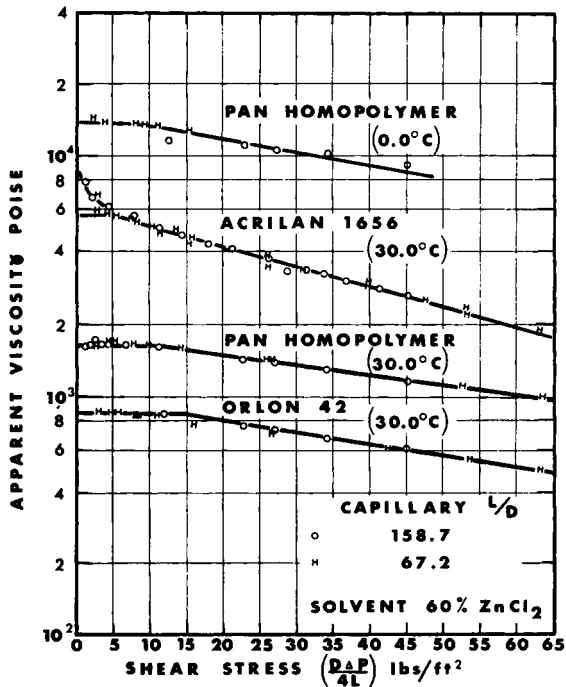


Fig. 4. Viscosity as a function of shear stress for acrylic polymers.

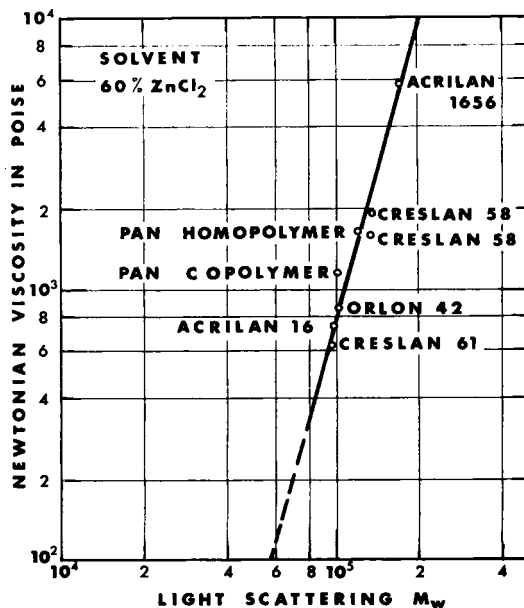


Fig. 5. Viscosity-molecular weight relationship of acrylic polymers.

The upturn in viscosity of Acrilan 1956 at low shear stress indicates the presence of a yield point, which is probably due to gelation. This phenomenon, which has not been observed in PAN solution previously, might be due to high molecular weight of the sample. The molecular weight of the sample was also responsible for the high viscosity, which made it very difficult to obtain a uniform solution without blending it at an elevated temperature for a considerable time. The tendency of Acrilan 1656 to hydrolyze rather quickly at elevated temperatures made it impossible to convert the solution into amide-free fibers.

Figure 5 shows a log plot of the Newtonian viscosity obtained from Figures 2 and 3 versus molecular weight. The molecular weight was determined in DMF by light scattering. The relationship is in good agreement with theory and experimental data of Porter and Johnson<sup>6</sup> and numerous other investigators of various polymer systems. The slope of 3.5 between the viscosity and molecular weight in Figure 5 not only indicates that the  $ZnCl_2$ -acrylic polymer system conforms to the general theory but also that the dissolution of oriented fibers was successful.

### ELASTICITY OF THE POLYMER SOLUTIONS

In wet spinning the elastic properties of the solution are important insofar as they exhibit the phenomenon of bulbing (Barus effect) upon emergence from the spinneret hole. The coagulation bath stretch defined as the ratio of the areas of the undisturbed bulb to that of the filament as it leaves the coagulation bath can significantly affect the fiber properties under

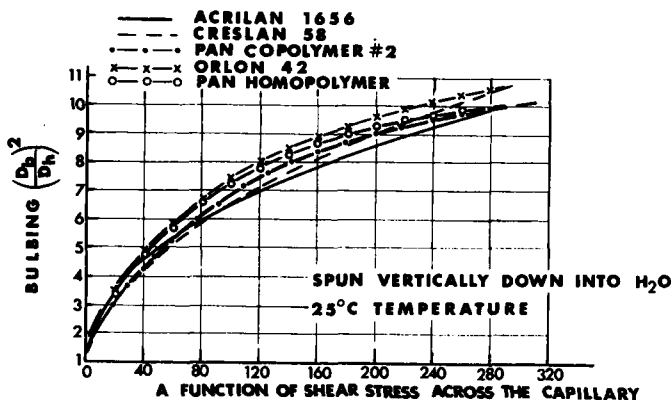


Fig. 6. Bulbing as a function of stress for acrylic polymers in  $\text{ZnCl}_2$ .

certain conditions of coagulation. For correct identification of the coagulation conditions it is necessary to determine the bulb diameter as a function of some flow variable through the spinneret hole.

Bulbing was investigated by means of a single-hole spinneret of 8-mil diameter, 4 mils long, with an approach angle of  $30^\circ$ . All measurements were made spinning down into water at room temperature.

Figure 6 shows bulbing as a function of shear stress across the capillary for Acrilan 1656, Creslan 58, Orlon 42, and PAN homopolymer and copolymers. Although one might be tempted to predict that bulbing is a function of stress and molecular weight, the reproducibility of the data will not allow it. The accuracy of the data is only within  $\pm 1/2$  bulbing units. Until more accurate data are available, it has to be concluded that bulbing is a function of shear stress only and independent of polymer composition, (1.0–0.93 mole fraction of VCN), molecular weight (80,000–200,000), temperature (0.0– $50^\circ\text{C}$ .), or surrounding medium (water, air, concentrated  $\text{ZnCl}_2$  solution).

## SPINNING

### Coagulation

The polymer solutions were spun by means of a spinneret with  $100\times 3.3$ -mil diameter holes into a coagulation bath under two conditions: (1) mild coagulation (39.0%  $\text{ZnCl}_2$ ,  $15.0^\circ\text{C}$ .) and (2) harsh coagulation (32.0%  $\text{ZnCl}_2$ ,  $30.0^\circ\text{C}$ .). All other conditions, (including boiling water stretch,  $16.0\times$  in two pans; final speed, 120 ft./min.; drying,  $135^\circ\text{C}$ . dry bulb; denier, 5 den./filament) were held constant.

Figure 7 shows schematically the laboratory-scale wet-spinning unit used. The concentration of the coagulation bath liquor was maintained constant by circulation and addition of water. The dried fibers from the oven were wound on a spool for further experimentation.

Small differences in total stretch and denier were accounted for by cor-

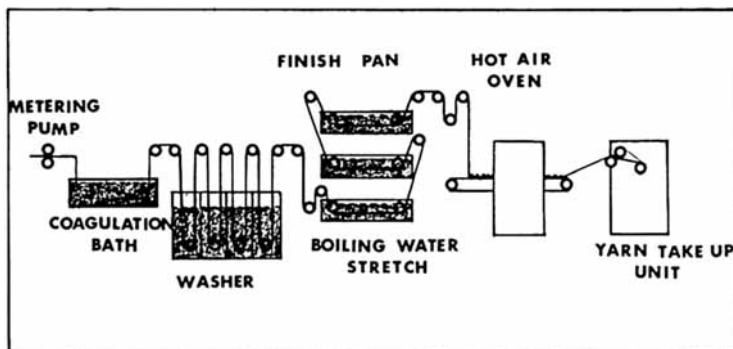


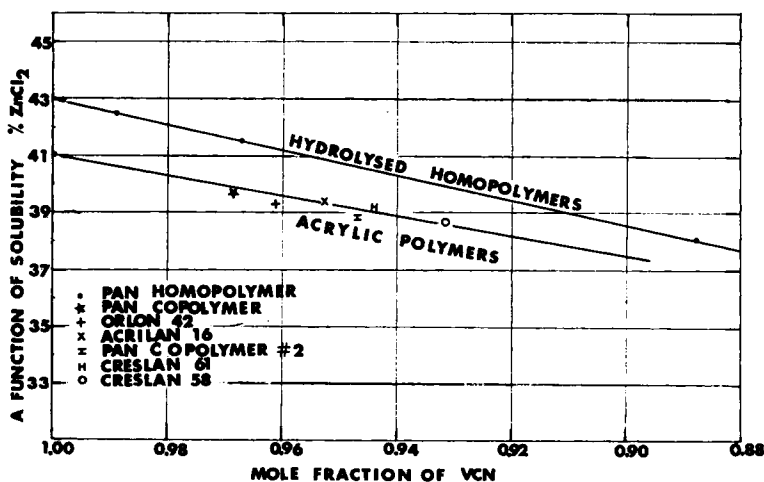
Fig. 7. Laboratory wet spinning unit.

recting the physical properties of the fibers from relationships developed in this laboratory between denier, stretch, and physical properties. In no case did these corrections account for more than 10% of the experimental value, and no trends were changed due to corrections.

### Solubility

In the  $ZnCl_2$  spinning system, maximum coagulation bath stretch is a complicated function of the concentration gradient and the bulb size. At high concentrations of  $ZnCl_2$  one can use the coagulation bath stretch as a measure of the solubility of the polymer in the solvent. This route of determining the solubility is necessary because of the difficulty of determining accurately the gel point of highly viscous polymer solutions.

One measure of solubility would be the concentration of solvent at which a freshly coagulated gel would dissolve; this is a convenient method and can be used to good advantage. Another method which is used in this

Fig. 8. Solubility of acrylic polymers in the  $ZnCl_2$  system.

study and is reproducible to within  $\pm 0.2\%$  of the actual concentration is to determine the  $\text{ZnCl}_2$  concentration at which a wet gel in the coagulation bath cannot be stretched above some arbitrary number ( $1.5\times$  in this study). To obtain this concentration one has to slowly increase the bath concentration by addition of concentrated solution of  $\text{ZnCl}_2$ .

For the acrylic polymers investigated this concentration is plotted in Figure 8 as a function of the mole fraction of VCN. The decrease in the concentration at which the arbitrary stretchability occurs is attributed to an increased solubility of the polymer solution. This conclusion is reinforced by the upper curve in Figure 8, which is for a homopolymer solution whose VCN content was decreased by hydrolysis. An increase in hydrolysis will make a polymer more soluble if there is no crosslinking. The differences in intercepts between the curves are due to different spinning techniques. For the hydrolyzed polymer an 8-mil hole spinneret was used, while the others were spun through a 3.3-mil hole spinneret.

### PHYSICAL PROPERTIES

Figure 9 shows the tenacity and elongation of fibers produced from the polymer solutions prepared by dissolution of the acrylic fibers indicated on the abscissa. From left to right the polymers are arranged in order of decreasing mole fraction of VCN.

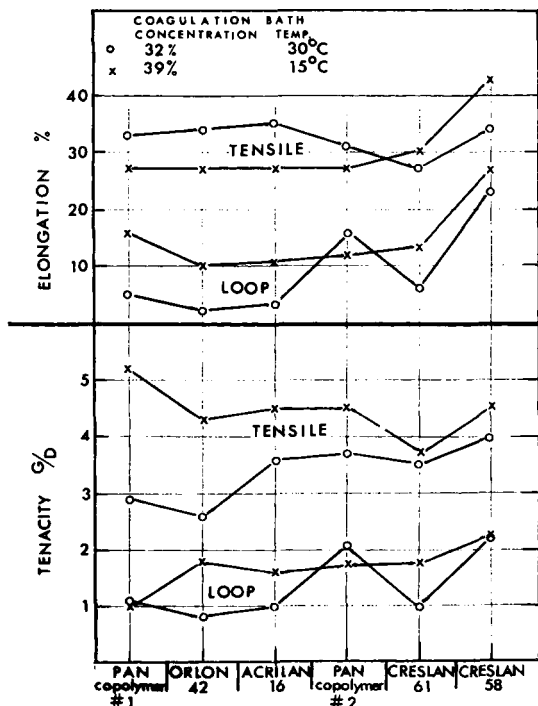


Fig. 9. Properties of acrylic fibers spun in the  $\text{ZnCl}_2$  system.



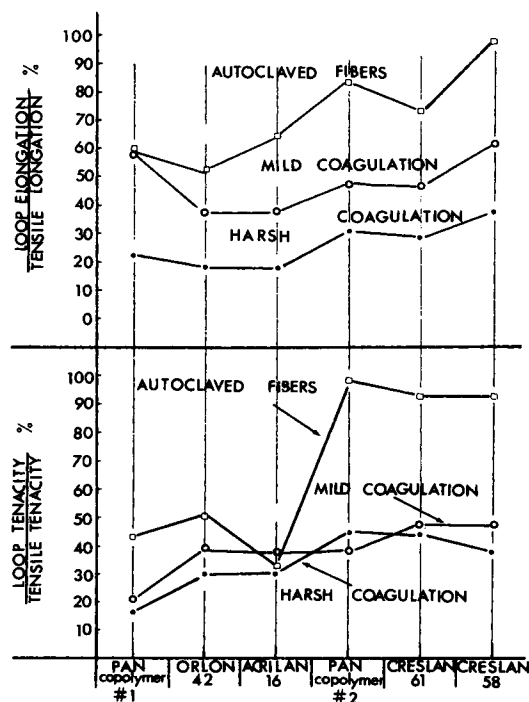


Fig. 10. Loop efficiencies of acrylic fibers in the  $ZnCl_2$  system.

Two trends can be observed. (1) Harsh coagulation produces a fiber that has a high elongation but low tenacity when compared to a fiber coagulated at a mild condition. (2) Under harsh coagulation a decrease in the mole fraction of VCN in a polymer increases its tenacity.

These effects can be explained on the basis of the Von Wieman theory of gels,<sup>7</sup> which states that

$$n = kP/L$$

where  $n$  is the number of crystallization points,  $k$  is a factor involving the viscosity,  $P$  is the degree of supersaturation, and  $L$  = the solubility of the solid which precipitates.

Harsh coagulation, which is characterized by a large concentration difference between the coagulation bath and the gel (a high degree of supersaturation  $P$ ), will tend to produce many small crystallization centers and thus a fine structure. This type of structure tends to produce weak gels of high elongation.

An increase in the solubility of the polymer with a decrease in the mole fraction of VCN, on the other hand will decrease  $n$  and thus produce a gel that is stronger due to larger crystals. In the preceding sentence the term crystal is not used in the strict sense of the word, but is meant to convey the idea of network junctions. In a sense, the number of crystals or junctions would be inversely proportional to pore size as characterized by Craig.<sup>1</sup>

For loop properties\* there is no inverse relationship between tenacity and elongation. Tenacity becomes dependent on elongation as one approaches small diameters for a brittle polymer like PAN. The loop test measures the breaking extension of the bent fiber rather than its tenacity. Lower tensile elongation of fibers coagulated at a mild condition produces higher loop elongations indicating a lower brittleness. Both loop elongation and tenacity of fibers increase with an increase in solubility of the polymer in the coagulant.

A decrease in brittleness of the fibers with increasing content of comonomers is better seen in Figure 10, where loop efficiencies are shown for polymers investigated. Loop efficiencies are simple ratios of loop to tensile, tenacity, and elongation. Fibers coagulated under a mild condition at an equal denier have a higher tensile and elongation efficiency and thus by definition lower brittleness. On autoclaving, the loop efficiencies of these fibers can be increased to almost 100% for polymers with a high content of comonomers. Autoclaving can thus be assumed to consolidate small crystals into large ones or to create larger fibrils.

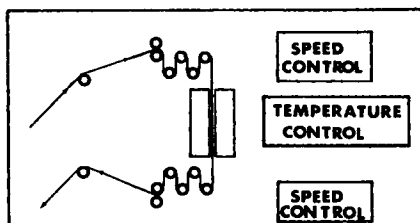


Fig. 11. Laboratory hot stretch unit.

At first the foregoing argument seems to be inconsistent because it is well known that steaming decreases the tenacity and increases the elongation of the fibers. It should be remembered that a steamed fiber loses some of its orientation by increasing in diameter. Thus, a valid comparison between steamed and unsteamed fibers should be made at some constant orientation.

### TURBO STRETCHING

Stretching of a tow at an elevated temperature on a commercial Turbo machine to produce high bulk fibers is commonly referred to as Turbo stretching. On the laboratory scale this process was approximated by stretching the fibers on the apparatus shown in Figure 11.

The speed of the two cluster rolls can be controlled independently, and fibers can be heated in the stretch zone by means of electrical heaters. During experimentation the heater plates were held at 300° F.

\* The loop test determines at a constant rate of extension the tenacity and elongations of a pair of fibers looped together. The breaking tenacity is found by dividing the total tenacities by two. The extension is the elongation at break.

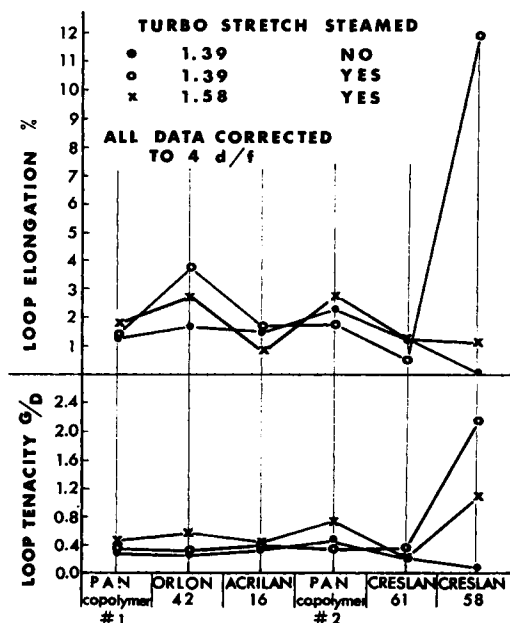


Fig. 12. Loop properties of Turbo-stretched acrylic fibers spun in the  $ZnCl_2$  system.

In Figure 12 the loop properties of unsteamed fibers are very low, indicating that  $1.39\times$  stretch ratio was too high for every sample. For the steamed fibers, Creslan 58 having the lowest mole fraction of VCN of all the fibers investigated, has high loop properties. The steamed fibers, when stretched to  $1.58\times$ , have low loop properties. If high loop properties are a desirable feature for Turbo stretched fibers, then it becomes important not only to have the right composition but also to select carefully the stretch ratio. In Figure 12 no significance is attributed to differences of  $\pm 2\%$  in loop elongation and  $\pm 0.2$  g./den. in loop tenacity. The fiber tester used was not sensitive to small differences on the low end of the scale.

### SHRINKAGE OF ACRYLIC FIBERS

Shrinkage of stretched acrylic gels is sensitive to coagulation variables, composition, and orientation stretch. During drying, coagulation variables play the major role. Harsh coagulation produces a fine structure which shrinks more than the coarse structure produced under mild coagulation (Fig. 13). On the other hand, compositional differences play a major part during autoclaving of dried fibers. The incorporation of comonomers lowers the glass transition temperature of the polymer, thus allowing the fibers to shrink during autoclaving. The autoclaving temperature used was enough to affect the shrinkage of polymers containing more than 0.95 mole fraction of VCN. Orientation stretch was not a variable in this experiment.

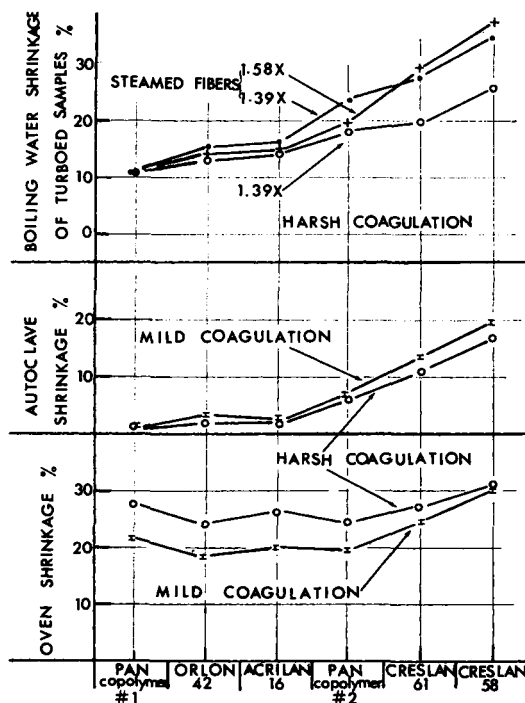


Fig. 13. Shrinkage as a function of process variables.

The boiling water shrinkage of Turbo-stretched acrylic fibers increases sharply with the decrease in the mole fraction of VCN. On stretching the steamed fibers, the trend becomes even more pronounced. When the fibers are overstretched\* as they are for the PAN copolymers, Orlon 42, and Acrilan 16 at a stretch ratio of 1.58 $\times$  then the resulting shrinkage in boiling water is less than at a lower stretch ratio of 1.39 $\times$ . Only for the two Creslans is shrinkage increased by an increase in Turbo stretch. Both Creslans have by weight more than 10% comonomers.

## CONCLUSIONS

The mole fraction of VCN (in the range of 1.0–0.93) in polyacrylonitrile copolymer system does not affect either the flow or elastic characteristics of  $ZnCl_2$  solutions. On the other hand, a decrease in the mole fraction of VCN in a copolymer of VCN with VA, MA, MMA, or MVP increases its solubility in  $ZnCl_2$  solutions, which in turn changes the structure of the wet gel.

The increase in the content of the comonomers seem to produce an effect similar to a decrease in harshness of the coagulation. In both cases the result is less brittle fibers.

\* By overstretching is meant stretching the fibers to a point where they have insignificant loop properties.

Although undoubtedly the effect of chemical properties of the individual comonomers will have an important bearing on some fiber properties, on physical, loop, and shrinkage properties, their effects are minor if not negligible.

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### Résumé

Les solutions concentrées d'acrilan 16 et 1656, Creslan 58 et 61, orlon 42 et de nombreux copolymères acryliques expérimentaux ont été préparés par dissolution de la fibre dans du chlorure de zinc à 60%. Les solutions ont été étudiées rhéologiquement. On a montré qu'il existe une relation à la puissance 3,5 entre le log de la viscosité Newtonienne et le log du poids moléculaire pour ces solutions. Leur comportement élastique tel qu'il est manifesté par l'effet de Barus était une fonction de la tension de cisaillement et était indépendante du poids moléculaire moyen en poids ou de la composition. Les solutions dans le chlorure de Zinc et des fibres acryliques ont été tissées et coagulées dans des conditions douces. Du point de vue des propriétés physiques des fibres, une coagulation douce à un effet similaire à une augmentation de la teneur en composants mineurs. Les propriétés au noeud et de retrécissement des fibres Turbo étirées sont fonctions principalement de leur composition.

### Zusammenfassung

Konzentrierte Lösungen von Acrilan 16 und 1656, Creslan 58 und 61, Orlon 42 und einigen experimentellen Akrylnitrilpolymeren wurden durch Auflösung der Stapelfasern in 60%  $ZnCl_2$  hergestellt. Die Lösungen wurden rheologisch untersucht. Es wurde gezeigt, dass bei diesen Lösungen eine 3,5-Potenzbeziehung zwischen dem log der Newton-Viskosität und dem log des Molekulargewichts besteht. Ihr elastisches Verhalten, wie es sich im Barus-Effekt zeigt, erwies sich als Funktion der Schubspannung und als unabhängig von Molekulargewicht und Zusammensetzung. Die  $ZnCl_2$ -Lösungen der Acrylfasern wurden unter scharfen und milden Koagulationsbedingungen versponnen. Auf die physikalischen und Biegeeigenschaften der Fasern hatte die milde Koagulation einen ähnlichen Einfluss wie eine Erhöhung des Gehalts der in geringerer Menge vorhandene Komponente des Copolymeren. Die mechanischen Schlingeneigenschaften und die Schrumpfung von Turbo-gestreckten Fasern sind in der Hauptsache eine Funktion ihrer Zusammensetzung.

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