

## Structural Modification and Molding of Polyacrylonitrile

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### Synopsis

Polyacrylonitrile can be compression-molded with conventional equipment if the inherent polymer particle structure is modified. With normal polymerization methods, a circumferential orientation in the polymer particle is obtained. This structure can be changed under the effects of shear to yield highly ordered, laminar particles with planar orientations. In this form, PAN can be compression-molded into tough, clear, chemically resistant articles with retention of the laminar structure. The polymer has been characterized by its x-ray diffraction and infrared spectrum which, in combination, distinguish it from previously observed forms of PAN.

### INTRODUCTION

Within the past few years, two methods have been devised for the preparation of shaped, transparent articles from polyacrylonitrile (PAN). Both of these processes utilize acrylonitrile monomer with free-radical initiators, but differ in technique and cycle time. The first process, discovered by workers at the Weizmann Institute<sup>1-3</sup> and improved at the American Cyanamid Company,<sup>4,5</sup> involves a slow polymerization of monomer around insoluble preformed polymer (or polymer formed *in situ*) at a rate sufficient to allow monomer to diffuse into voids caused by the monomer-to-polymer contraction. The reaction rate must also be slow enough to permit dissipation of the heat of polymerization. For a molding equivalent to that in the second process described below, the polymerization requires 18 days. The second process, developed in this laboratory,<sup>6</sup> involves a rapid free-radical polymerization of acrylonitrile around preformed polymer which is insoluble in the monomer. In this case heat and pressure are applied to the system in order to (1) increase the monomer diffusion rate and (2) contain the monomer at temperatures well above its boiling point. Cycle times of  $1/2$  hr or less are sufficient for the polymerization.

Although both of these processes lead to articles exhibiting interesting physical properties, the requirement that initiated monomer be present is inconvenient. This paper describes a new method of fabricating PAN into molded objects in which no additional materials need be involved. The process utilizes conventional presses and leads to articles showing greatly improved physical properties, especially impact resistance. The change in

physical properties and molding process is based on changing the inherent structure of PAN particles.

## EXPERIMENTAL

### Polymer Preparation

In this work a change in structure was created through the combined effects of mechanical and thermal energy. A differential-speed rubber mill heated to 250–375°F was used with roll speeds set at 24 and 34 rpm. With a nip of approximately 1/100 in., transparent sheets could be formed from PAN powder on the first pass. Further milling leads to a matted, translucent sheet. After 1–2 min of milling with the nip being opened to about 0.1 in., a tough sheet was formed. The material was cut into small pieces with shears and pulverized to a coarse (about 0.1 in.) powder with a Waring Blendor. This material was further pulverized to a fine powder on a Wiley mill.

As would be expected, a molecular weight change occurs during milling. Emulsion-polymerized feed polymer of 682,000 molecular weight (viscosity average<sup>7</sup>) leads to 301,000 molecular weight sheared polymer while feed of 126,000 molecular weight is reduced to 118,000. As the feed polymer molecular weight is decreased, this effect, of course, becomes negligible.

The polymer used in this work was prepared by emulsion polymerization although the same results are obtained with bulk- or suspension-polymerized PAN.

### Molding Method

Test bars measuring  $5 \times \frac{1}{2} \times \frac{1}{8}$  in. were prepared in conventional molds using a hydraulic press equipped with heated platens and having provisions for water cooling. For convenience, a temperature "sweep" was generally used in which the cold mold was heated under pressure to a predetermined mold temperature and then cooled. As a rule, the maximum mold temperatures employed were between 140 and 230°C, while pressures were normally between 2000 and 7000 psi. Bars prepared in this manner without added stabilizer were transparent and ranged in color from light yellow to orange as the molding temperature was increased. The material could be easily machined without danger of fracture, unlike both the PAN-AN molding and casting process described above.

### Polymer Characterization

Sheared PAN was distinguished from other forms of the polymer by its infrared spectrum using a Perkin-Elmer 521 spectrophotometer and by its x-ray diffraction with nickel-filtered  $\text{CuK}\alpha$  radiation.

## RESULTS AND DISCUSSION

### Physical Properties

When PAN is prepared by suspension, emulsion, or bulk polymerization, the polymer particles exhibit an inherent order under x-ray examination. An internal order of approximately 33% is found from x-ray diffraction and is independent of the method of polymerization. This order is generated during the polymerization when the polymer particle size grows by the deposition of and/or growth of propagating chains on the particle surface to form a pearlike structure having a circumferential orientation. During this work, this order was found to occur even in polymer precipitated from dimethylformamide solution, although to a lesser extent. Considering the pearlike structure and lack of flow properties, it is not surprising that PAN cannot be conventionally molded. If a circumferentially oriented particle that is in contact with other such particles is considered, it is evident that, in the absence of bulk flow, a polymer chain on the surface of a given particle will remain attached to that surface unless the polymer is at a point of contact with an adjacent sphere. Only at points of particle contact will this sintering (or partial fusion) occur. The polymer chains within the spheres remain relatively unaffected, so that the overall orientation remains essentially constant ( $\sim 33\%$ ). The resultant sintered mass would be expected to exhibit poor tensile strength and impact resistance. Typical values for sintered PAN are shown in Table I, Column 1. In the PAN-AN molding techniques mentioned above, the polymerizing monomer effectively increases the particle-particle contact area by filling voids between polymer spheres, although in this case the orientation as measured by x-ray diffraction decreases in proportion to the monomer concentration. If the particle structure is changed from a circumferential orientation to a laminar, planar form, the fusible polymer concentration is increased due to the increase in useful particle surface area. This is to say that the concentration of chains or chain segments capable of particle-particle bonding is increased. In addition to an increase in number of chains capable of particle-particle bonding, an increase in internal order is observed. The x-ray diffraction indicates an average internal orientation of approximately 57% with orientations in all three dimensions which is greater than the 33% observed in untreated PAN. This internal order is present before and after molding. The particle transformation described may be accomplished by shearing.

On the basis of the above discussion, physical property improvements based on increased bonding between particles would be expected to increase in the order: sintered PAN (no pretreatment, conventional polymer); molded PAN-AN<sup>6</sup> (monomer-polymer mixture); molded PAN (sheared) (roll-milled polymer); molded PAN (sheared)-AN (monomer-milled polymer mixture). Typical physical properties are shown in Table I and may be compared with those of poly(methyl methacrylate) which are also given in Table I. It should be stressed that these values are typical, not

TABLE I  
Physical Properties of Polyacrylonitrile

ASTM test	Property	Sintered		Cast		Molded		Sheared		PMMA <sup>c</sup>
		PAN	PAN-AN <sup>a</sup>	PAN-AN <sup>a</sup>	PAN-AN <sup>b</sup>	PAN	PAN-AN	PAN-AN	PMMA <sup>c</sup>	
D-648-264 psi	Deflection temperature, °C	100-108	90	92-94	92-111	92	96			
D-790	Flex strength $\times 10^{-3}$ , psi	7	4.9	9	12	16	16			
D-790	Flex modulus $\times 10^{-6}$ , psi	6	6.7	7	10	10	4.5			
D-638	Tensile strength $\times 10^{-3}$ , psi	2-4 <sup>e</sup>	5.1	6 <sup>d</sup>	8 <sup>d</sup>	9 <sup>d</sup>	9-11			
D-256	Izod impact, ft-lb/in. of notch	0.2	0.2	0.2	1.7-2.0	2.0	0.4			
D-1505	Rockwell hardness (M scale)	108	111	110	106	106	93			
D-192-50	Specific gravity	—	—	1.18	1.18	—	1.19			

<sup>a</sup> Method of Pellon et al.<sup>5</sup>

<sup>b</sup> Method of Griffith.<sup>6</sup>

<sup>c</sup> Data of Rohm & Haas.<sup>8</sup>

<sup>d</sup> Tensile strength test bars conform to the dimensions given in D-1822, Type S.

maximum. Improvements in a given physical property at the sacrifice of others can be obtained through variations in molding conditions.

Comparison of sintered PAN (Table I) with molded PAN-AN shows an increase in all the measured physical properties due to increased bonding, with the exception of the deflection temperature and impact strength. This reduction in deflection temperature, mentioned previously,<sup>6</sup> is caused by the low molecular weight PAN formed *in situ* during the PAN-AN molding process. In the case of molded sheared PAN, the deflection temperature rises to and above that of sintered PAN due to both the lack of low molecular weight material and improved bonding. A range of values are shown since the deflection temperature depends on the maximum mold temperature. This improvement in bonding and increased internal order or orientation is also noticeable in the increased flexural and tensile values. The increase in Izod impact by a factor of 10 for sheared PAN is probably due to more than increased bonding and internal order. In this case, a glassy fracture is not encountered, since the growing crack must propagate around rather than through the polymer particles. Since PAN is not capable of thermally induced bulk flow or major displacement of polymer chains, the initial polymer particle structure is retained. This retention of structure can be seen by microscopic examination of test bars after rupture. The laminar polymer particles are clearly visible at the fracture site.

A further increase in most of the physical properties is obtained by molding sheared PAN in the presence of initiated acrylonitrile (Table I). The deflection temperature is lower, however, for the reason described above. As in the case with PAN-AN molding,<sup>6</sup> a decrease in orientation as measured by x-ray diffraction is observed in direct proportion to the amount of acrylonitrile consumed. Apparently the monomer undergoes polymerization in such a way that the polymer formed *in situ* is essentially amorphous.

It has been previously observed<sup>5</sup> that PAN-AN castings became opaque on heating to 150°C. During this work, it has been found that if the mold is removed from the press while hot (above 100°C), the test bar is opaque and appears unfused due to myriads of irregular cracks. This effect is noted regardless of the molding material, i.e. PAN-AN, sheared PAN or sheared PAN-AN. Since similar molding conditions followed by cooling under pressure leads to clear test bars, the crazing observed when the mold is removed while hot appears to be caused by the formation of thermal stresses. Enough fusion is present, however, to give physical properties superior to those obtained with monomer-polymer molding<sup>6</sup> and the monomer-polymer casting technique.<sup>4,5</sup> The crazed test bars show heat distortion temperatures of 93-110°C, while the flexural strength and modulus values range between  $6-8 \times 10^3$  and  $5.5-6 \times 10^5$  psi, respectively. The notched Izod was near 2 ft-lb/in. notch while the tensile strength values were  $8 \times 10^3$  psi. This strength in a crazed glassy polymer is quite remarkable and emphasizes the fact that the extent of particle to particle bonding is low in PAN molded or shaped by any reported technique. Large increases in most physical properties would be expected for a truly homo-

geneous PAN where the initial polymer particles no longer retain their identity.

### Characterization of the Sheared PAN

Polyacrylonitrile fibers and films exhibit only two-dimensional order as normally prepared.<sup>9-11</sup> Under certain conditions, however, spherulites<sup>11</sup> or single crystals<sup>12</sup> may be prepared, but these differ from drawn or oriented material in their x-ray,<sup>12</sup> optical (birefringence),<sup>11</sup> and infrared<sup>13</sup> characteristics. Examination of different forms of polyacrylonitrile by x-ray diffraction using nickel filtered  $\text{CuK}\alpha$  radiation give typical values of orientation, or order, as shown in Table II. These values were estimated from the ratio of the peak area above the amorphous region to the total area of the diffractogram.

When PAN is subjected to shear at elevated temperatures, a significant increase in overall orientation occurs. The x-ray examination of this material shows the normal 5.3 Å diffraction maxima and the onset of a peak at 3.38 Å. Stefani<sup>18</sup> has previously reported this 3.38 Å maximum but attributed it to isotactic spacings. No 5.1 Å maximum or line splitting is

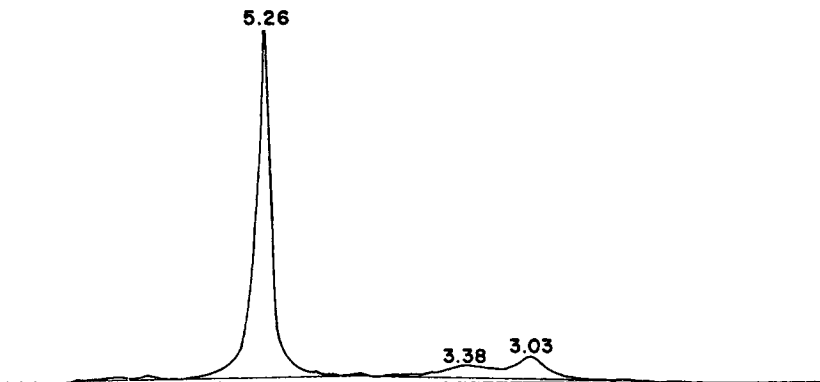


Fig. 1a. X-Ray diffraction pattern of a sheared PAN sheet (top surface).

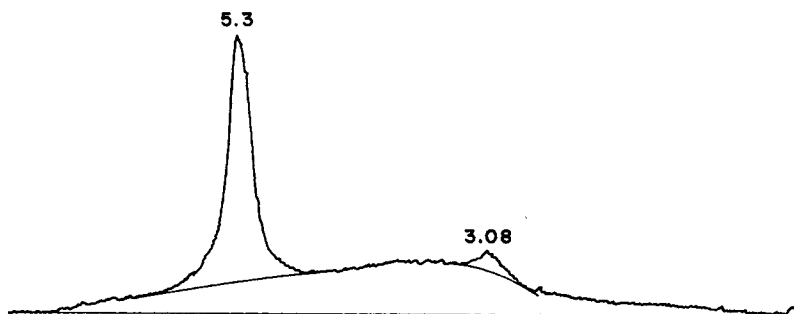


Fig. 1b. X-Ray diffraction pattern of unsheared PAN powder.

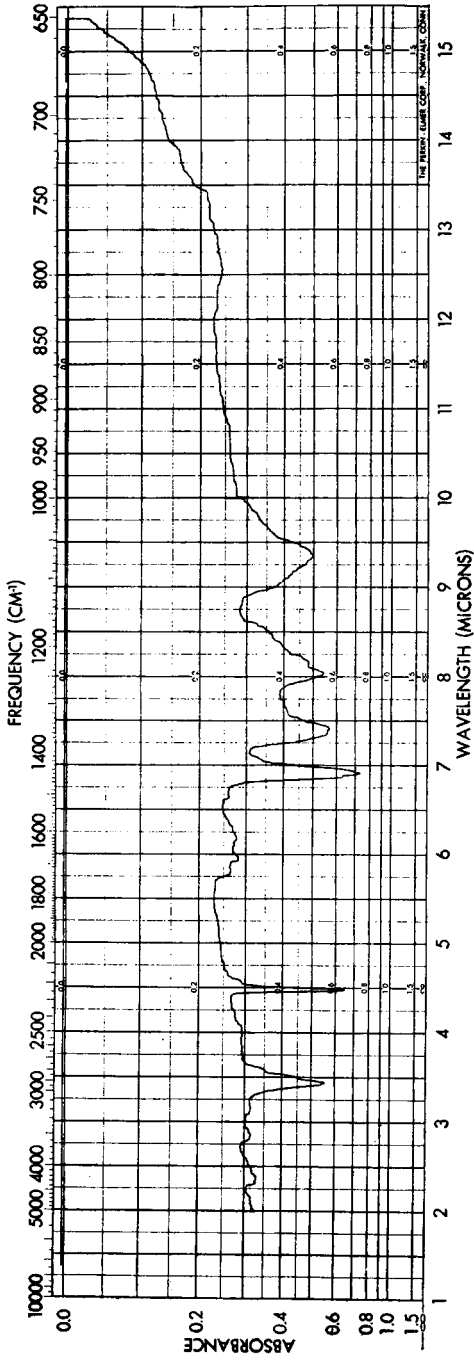


Fig. 2. Infrared spectrum of a sheared PAN film.

TABLE II  
 Orientation in Pan

	Orientation, %			
	Top	Side	End	Average
PAN powder (emulsion)	—	—	—	33
PAN powder (bulk)	—	—	—	32
Orlon fiber (type 42)	—	—	—	43
Cast film <sup>a</sup>	24	33	32	30
Sheared PAN	73	57	40	57

<sup>a</sup> The films were cast from dimethylformamide in the usual manner<sup>14-17</sup> then dried to a DMF content of less than 1%.

observed as in the case of PAN prepared in isobutyraldehyde<sup>19</sup> or crystalline PAN.<sup>20</sup> The x-ray diffraction pattern of the sheared PAN sheet is shown in Figure 1a and may be compared with the diffraction pattern obtained prior to shearing (Fig. 1b). The crystalline spacings are not observed at 5.1, 2.9, and 2.6 Å as reported by Holland et al.<sup>12</sup> for PAN spherulites. Table II (bottom line) shows the increased orientation in three dimensions. The infrared spectrum of this material (Fig. 2) was identical to that of untreated PAN but differed significantly from both PAN prepared in isobutyraldehyde<sup>19</sup> and crystalline PAN.<sup>13</sup> Of particular interest is the lack of strong absorption in the 800 cm<sup>-1</sup> region. Although the reasons for variations in this region are not yet clear, it has been suggested<sup>13</sup> that this absorption is associated with a form of regularity. It is of interest to note that the intensity of absorption in this region is inversely proportional to the polymer density. PAN prepared in isobutyraldehyde having a density of 1.15 g/cm<sup>3</sup> shows strong absorption at 795 cm<sup>-1</sup>.<sup>19</sup> Untreated emulsion polymerized PAN or dimethylformamide cast films (density of 1.17 g/cm<sup>3</sup>) show medium absorption while the sheared PAN (density of 1.18 g/cm<sup>3</sup>) exhibits only broad, weak absorption. Whether these changes in absorption are due to variations in order or crystallinity as yet remains to be determined.

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