

Molding of Polyacrylonitrile

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Synopsis

A method has been devised whereby clear, chemically resistant, compression-molded articles of polyacrylonitrile are prepared within minutes. The molding powder consists of preformed polyacrylonitrile, acrylonitrile, and initiator. The effects of process variables on the physical properties are discussed.

INTRODUCTION

The use of polyacrylonitrile has been limited by the fact that clear, inherent, bulky objects could not be prepared by conventional techniques. Polyacrylonitrile, for example, cannot be melt-cast into sheets and until recently could not be bulk-polymerized in a mold to give a clear strong object because the polymer is insoluble in the monomer and precipitates as a white flocculent mass during the polymerization. At reasonable polymerization rates, the polyacrylonitrile precipitate leads to local superheating due to the decreased thermal conductivity of the system. This is generally followed by an uncontrollable exotherm. At very low rates of polymerization, however, the heat of reaction can be dissipated, and an opaque white mass is formed consisting of polyacrylonitrile and voids caused by the monomer-to-polymer contraction.

Workers at the Weizmann Institute^{1,2} found that if a slow polymerization was conducted and acrylonitrile was continuously added to the system, a transparent lower layer of polyacrylonitrile could be formed. This process provided the first means of obtaining shaped articles of polyacrylonitrile without the use of solvents. The process was, however, slow and required polymerization times up to a month. Workers at the American Cyanamid Company^{3,4} have greatly improved the process to the point where transparent sheets can be prepared in a few days.

This paper describes a process whereby molded transparent articles of polyacrylonitrile can be obtained within minutes. Strong, clear test bars have been prepared having physical properties equal or superior to the cast polyacrylonitrile.

APPARATUS AND MOLDING COMPOUND

Apparatus

Molded bars measuring 1/2 in. × 5 in. by about 1/8 in. were prepared in standard compression molds by using a hydraulic press having heated platens and provisions for water cooling. Typical molding pressures were 4000–8000 psi. Molding times of 15–30 min were employed at temperatures in the range of 80–150°C.

Molding Compound

The preferred process consists of mixing preformed polyacrylonitrile with acrylonitrile containing a free-radical initiator and molding the seemingly dry, free-flowing powder. The acrylonitrile content ranges from about 30 to 50 wt-% of the molding compound. These values, however, are not limiting, as the tightness of the mold and the polymer particle size have an effect on the optimum amount of polyacrylonitrile involved. The polymer used for this study was obtained by emulsion polymerization of acrylonitrile to a viscosity-average molecular weight⁵ in the 100000–130000 range with an average particle size near 0.015 mm.

MOLDING PROCESS

Successful fusion of the molding compound is based on the interaction of two separate processes: (1) the pressure-induced monomer diffusion into and/or around the preformed polymer, and (2) monomer polymerization. A definite balance must be maintained for optimum physical properties. If either of the two variables is significantly altered, fusion does not occur. Low pressure (insufficient diffusion) or a low monomer content leads to an opaque, brittle material. Insufficient initiation or low temperatures (incomplete polymerization) give similar results.

Diffusion of monomer into polymer may be controlled by variations in (1) the acrylonitrile content, (2) the initiator half life, (3) the molding pressure, or (4) the temperature.

TABLE I
Deflection Temperature as a Function of Initial Acrylonitrile Content^a

AN, wt-% ^b	Deflection temperature, °C	Residual acrylonitrile, % ^c
28.5	83	0
34.8	84	1.2
48.3	92	1.1
51.6	80	1.6
61.6	76	—

^a At 264 psi; azobisisobutyronitrile (AIBN) was used as the initiator.

^b Based on the molding compound.

^c Determined by vapor chromatography of DMSO solutions.

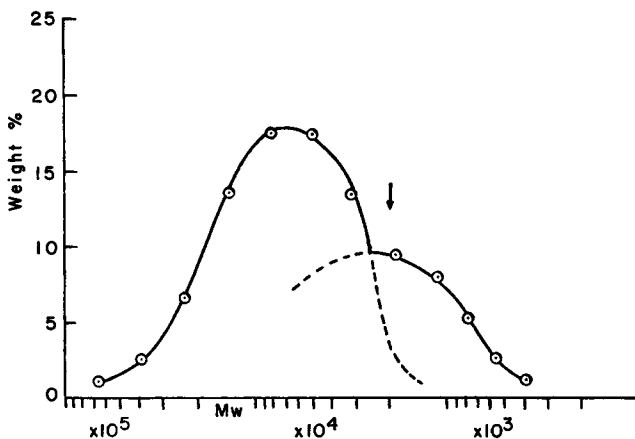


Fig. 1. Molecular weight distribution: arrow shows polymer formed *in situ*.

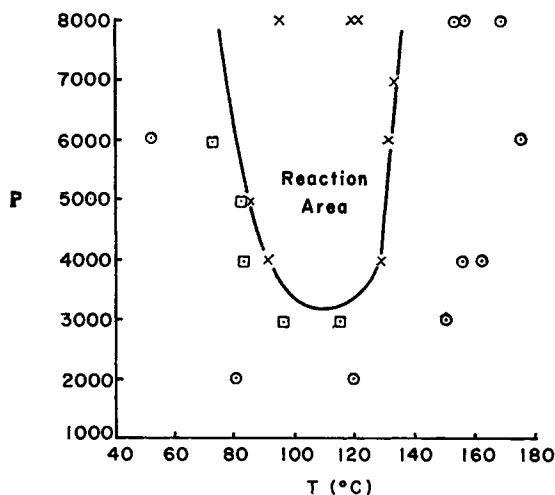


Fig. 2. Mold pressure (psig) vs. molding temperature: (X) complete fusion; (□) 25% unfused; (⊙) no fusion.

Table I shows the effect of acrylonitrile concentration in the molding compound on the deflection temperature measured at 264 psi.

At low levels of acrylonitrile, insufficient diffusion results leading to poor fusion as reflected by the low deflection temperature. The decrease in the deflection temperature value at high initial acrylonitrile charges is believed to be due to both free acrylonitrile and an increase in low molecular weight PAN formed *in situ*. Figure 1 shows a gel permeation chromatograph representation of the final polymer. The shoulder at a (weight-average) molecular weight of about 20000 is absent in the preformed polymer used.

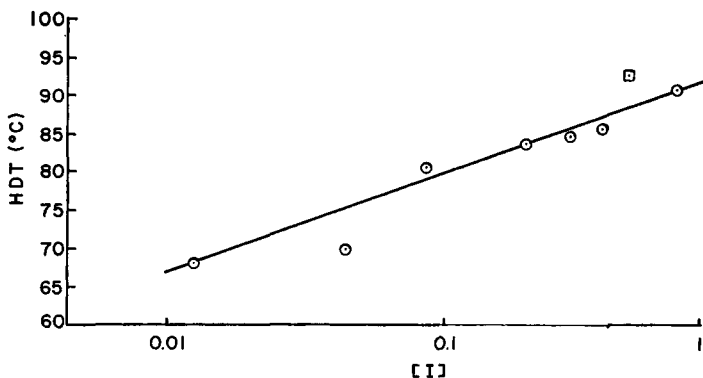


Fig. 3. Deflection temperature vs. initiator concentration: (○) parts of AIBN/100 parts AN; (◻) parts benzoyl peroxide/100 parts AN.

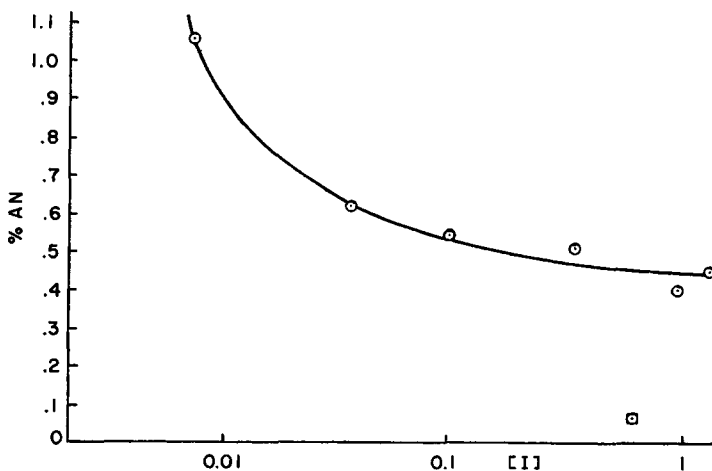


Fig. 4. Weight per cent residual acrylonitrile vs. initiator concentration: (○) parts of AIBN/100 parts AN; (◻) parts benzoyl peroxide/100 parts AN.

The balance between diffusion and polymerization can also be seen in the shape of a pressure-temperature plot (Fig. 2). The data were obtained by molding a powder consisting of 10 parts polyacrylonitrile, 5.3 parts of acrylonitrile, and 0.1 part of azobisisobutyronitrile (AIBN) in a preheated press that was thermostated at the indicated temperature.

Since the diffusion phenomenon is dependent on both temperature and pressure, a curve tending to asymptote at both high pressures and high temperatures would be expected. The polymerization, on the other hand, should be independent of pressure (as a first approximation) but should follow an exponential curve similar to the decomposition curve of the initiator. The region of fusion in a temperature-pressure plot should, in short, be within the area formed by the two exponential curves of opposite

sense. Since a pressure-temperature plot is a function of the initiator used, the minimum in the curve will vary with the catalyst.

Figure 3 shows the initiator concentration effect on the deflection temperature. The gradual increase is a reflection of the decreasing acrylonitrile content, as can be seen in Figure 4. By using benzoyl peroxide the residual monomer content is reduced to an insignificant level. The specific gravity at 25°C was similarly found to be slightly higher with benzoyl peroxide (1.179) than that obtained with the use of AIBN (1.174).

PHYSICAL PROPERTIES OF MOLDED PAN

Typical physical property values are listed in Table II and compared with those of poly(methyl methacrylate).

TABLE II
Physical Properties of Molded PAN

Property	Molded PAN	Poly(methyl methacrylate) ^a
Deflection temperature, °C	94	96
Tensile strength $\times 10^{-3}$ psi	6-10	9-11
Flexural strength $\times 10^{-3}$ psi	6-9	14-16
Flexural modulus $\times 10^{-5}$ psi	6-8	4-4.5
Notched Izod, ft-lb/in. notch	0.2	0.4
Rockwell (M)	112	93
Specific gravity	1.18	1.19
Scratch resistance, g	100	—

^a Data of Rohm & Haas.⁶

These results are similar to those obtained with annealed, cast PAN sheets.^{3,4}

Monomer Content

The amount of acrylonitrile used in the molding powder has no observable effect on the flexural strength or modulus within the range studied (28-52

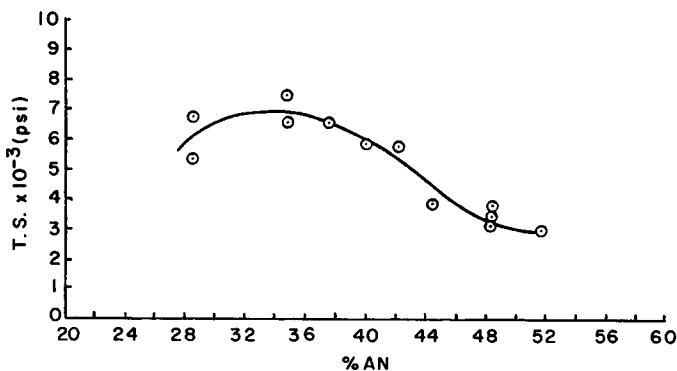


Fig. 5. Tensile strength vs. weight per cent acrylonitrile used in the molding compound.

wt-% acrylonitrile). A maximum is obtained, however, in the tensile strength curve (Fig. 5). The reason for this maximum is that at low acrylonitrile contents, insufficient diffusion provides a poor sample, while at high monomer levels a large amount of low molecular weight polymer is formed.

Time and Temperature

The relationship between the molding time and the physical properties is of major commercial significance. This relationship for molded PAN is illustrated in Figure 6, where flexural strength and modulus are plotted against molding times. A temperature sweep was used, where the cold molds were placed between press platens at room temperature, heated to 138°C, then held at this temperature for a predetermined time before

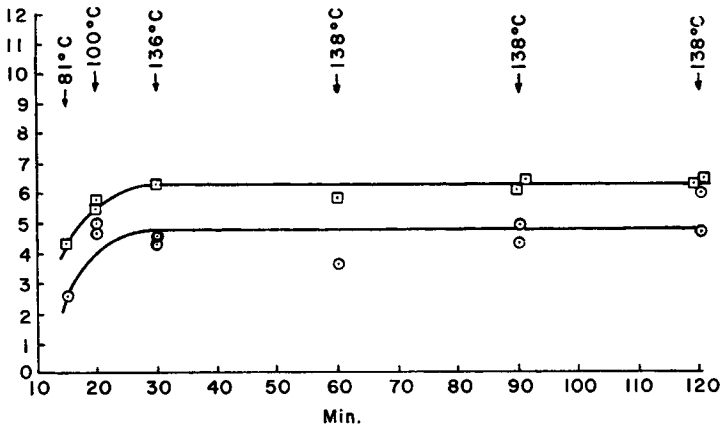


Fig. 6. Molding time vs. (○) flexural strength × 10³ psi and (□) flexural modulus (× 10⁵ psi).

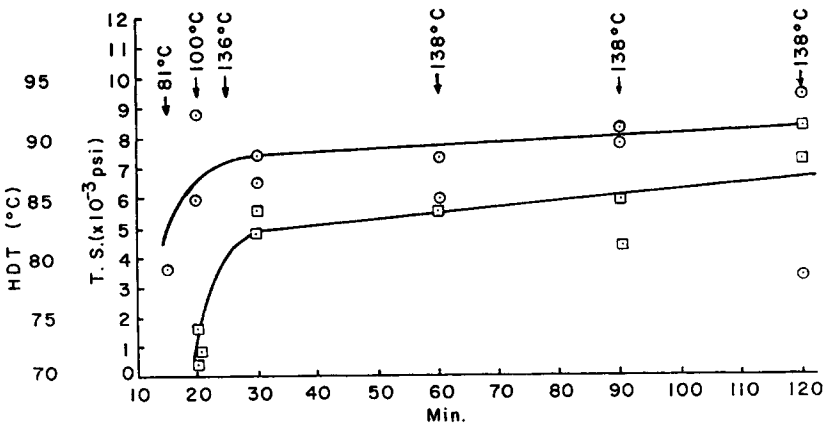


Fig. 7. Molding time vs. (○) tensile strength × 10³ psi and (□) deflection temperature.

cooling to investigate possible degradation effects. Figure 7 shows the tensile strength and distortion temperature curves under these conditions.

It would appear from the above that the polymerization is complete either within 30 min or by the time the mold temperature has reached about 136°C. As will be shown below, the mold temperature is the most important variable. In fact, the reaction time is so short that it cannot be determined due to the thermal lag involved with compression molds. Some indication of the reaction time required may be obtained, however, by considering the initiator half life at the molding temperatures shown in Table III.

TABLE III
Azobisisobutyronitrile Half Life

Temperature, °C	Time, min
100	7
120	1
135	0.25
150	0.0185

Since the molding temperature is in excess of 135°C and since the initiator concentration is relatively high, it would not be unreasonable to expect essentially complete reaction within 1 min.

The final mold temperature has little effect on the properties of flexural strength and modulus over the range 100–150°C, but decreases at either extreme. The deflection temperature increases monotonically to a maximum near 150°C, then decreases due to polymer degradation.

Initiator and initiator concentration effects: The initiator concentration has surprisingly little effect on the flexural strength and modulus over the range of 0.03–3.0 parts initiator (AIBN) per 100 parts acrylonitrile. The values show only a slight increase. The deflection temperature (Fig. 3) and tensile strength values, however, increase with increasing initiator. A far larger effect is noted with the use of different initiators (Table IV).

TABLE IV
Physical Properties of Molded PAN as a Function of Initiator*

Initiator	Flexural strength $\times 10^{-3}$ psi	Flexural modulus $\times 10^{-5}$ psi	Tensile strength $\times 10^{-3}$ psi
<i>tert</i> -Butyl peroxyphthalate	5.5–6.0	7.0–7.9	2.5–2.6
Azobisisobutyronitrile	4.5–4.8	6.0–6.7	5.7
Benzoyl peroxide	5.0–5.5	6.6–6.8	4.0
<i>p</i> -Methane hydroperoxide	—	—	4.7–4.9

* Conditions: 10 parts PAN, 5.3 parts AN, 0.1 part initiator; molding time, 30 min; molding temperature, 135 ± 3°C; pressure, 2400 psi.

DISCUSSION

Within the past few years,¹⁻⁴ the concept of preparing clear, solvent-free articles from polyacrylonitrile has been confirmed. The work described here brings the fabrication of this polymer into clear, compression-molded articles within the realm of commercial feasibility.

The process involves a post-polymerization reaction wherein the spherical particles of preformed PAN are bonded together by a layer of low molecular weight polyacrylonitrile formed *in situ*. Since PAN is not capable of flow under heat and pressure, the monomer mobility is required for proper dispersion of the low molecular weight polymer.

Although an optically homogeneous molding is obtained in this process, electron micrographs of fracture surfaces show inhomogeneity caused by retention of the preformed polymer particle structure. In addition to retention of structure, the initial polymer particles appear to be unaffected by the molding process in that no crosslinking or chain scission can be detected. In view of the lability of the PAN α -hydrogen atom crosslinking or chain scission would be anticipated. Lack of polymer modification of this type indicates that diffusion of monomer into the preformed polymer particles is either very limited or does not occur at all.

Although this report has been concerned with polyacrylonitrile, the simultaneous diffusion and polymerization described are applicable to other heterogeneous systems and afford a convenient path to polymer blends. While there are problems involved in the monomer-polymer molding with conventional compression-molding equipment, the useful qualities of polyacrylonitrile such as hardness, solvent resistance, gas and water vapor barrier properties can more than compensate for the processing difficulties involved.

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