

Cast Polyacrylonitrile. II. Properties

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Synopsis

Polyacrylonitrile sheet cast by a novel method described in Part I is clear, colorless, chemically resistant, brittle, and rather weak. It undergoes irreversible thermal changes above about 80°C., but if heated quickly, it can be oriented to give greater strength parallel to the direction of orientation. Some improvement in strength can be achieved by the use of fibrous fillers. Certain copolymers are stronger than the homopolymer but have lower softening temperatures.

INTRODUCTION

In Part I¹ we described the preparation of clear, cast polyacrylonitrile sheets. The casting method was an extension of work at the Weizmann Institute, Israel.^{2,3} Since sheets of this type had never been available before, it was of interest to examine their general physical properties. This paper lists physical test results and describes the changes in properties brought about by heat treatment, by orientation, by fibrous reinforcement, and by copolymerization.

PROPERTIES OF CAST SHEETS

General Properties

Physical properties were determined on $\frac{3}{16}$ in. sheets cast as described in Part I.¹ Results are listed in Table I for sheets cast with the use of each of the initiators, *p*-toluenesulfonic acid-H₂O₂ (TSA) and azobisisobutyronitrile (AIBN). Comparative data are given for commercial cast poly(methyl methacrylate).

The data of Table I show that cast polyacrylonitrile (PAN) is relatively weak and brittle. Compressive strength of a sample similar to those of Table I was 10,000 psi, about the same as that of poly(methyl methacrylate). Cast PAN and cast poly(methyl methacrylate) were judged similar in their resistance to mild surface abrasion. Micro testing of small rods cast in Israel² yielded results very similar to those of Table I. Thus these figures are regarded as descriptive of cast PAN.

At room temperature, cast PAN is resistant to 0.5*N* HCl, 0.5*N* NaOH, hexane, chloroform, ethanol, and 5% soap solution. These reagents produce mild yellowing during a one hour period of boiling.

TABLE I
Physical Properties of Cast PAN Sheets

ASTM test	Property	Cast PAN		
		AIBN initiator	TSA initiator	Poly-(methyl methacrylate)
D-1505	Density, g./cc.	1.162	1.162	1.19
D-785	Rockwell hardness (M scale)	78	79	93
D-648-264 psi	Deflection temperature, °C.	64	59	96
D-1525	Vicat temperature, °C.	>260	>202	—
D-256	Izod impact, notched ft.-lb./in.	0.13	0.15	0.4
D-256	Izod impact, unnotched, ft.-lb./in.	—	0.25	—
D-790	Flexural strength, psi. $\times 10^{-3}$	7.7	5.4	16.0
D-790	Flexural modulus, psi $\times 10^{-6}$	0.52	0.45	0.45

Cast PAN burns with formation of a heavy char. Its rate of burning is considerably less than that of poly(methyl methacrylate). Color and clarity of PAN as cast is comparable in the best instances to poly(methyl methacrylate), but some yellowing occurs on heating or on long exposure to light.

Thermal behavior of cast PAN is complex. Irreversible chemical changes occur on heating above 80°C.; in addition, there are changes due to relief of strain and loss of residual monomer. Any measured softening point depends on the rate of heating and the thermal history of the sample. Thermogravimetric analysis of one specimen gave the results shown in Table II.

TABLE II

	In air	In nitrogen
First loss (T_i)	305°C.	315°C.
10% loss (T_{10})	380°C.	330°C.

Heat Treatment

Some sheets made with TSA initiator were post-cured to reduce residual monomer and also to consolidate the structure. In each case, this treatment reduced the unpolymerized acrylonitrile content from about 5% to less than 0.3%. Post-curing increased the heat distortion temperature and hardness but produced no significant improvement in strength. Table III summarizes the data. Similar results were obtained on post-curing castings made with AIBN initiator. Castings post-cured at 80°C. sometimes became opaque if they were heated subsequently to 150°C. The structure may have compacted enough at the lower temperature to become impermeable to volatiles formed at the higher temperature and as a consequence become crazed.

TABLE III
Properties of Cast Sheets as Affected by Post Curing

ASTM test	Property	Cast specimen		
		As cast	After 26 hr., 80°C.	After 20 hr., 140-150°C.
D-790	Flexural strength, psi $\times 10^{-3}$	5.9	5.8	6.8
D-790	Flexural modulus, psi $\times 10^{-6}$	0.47	0.63	0.61
D-638	Tensile strength, psi $\times 10^{-3}$	4.5	—	4.9
D-256	Izod impact, notched, ft.-lb./in.	0.17	—	0.18
D-785	Rockwell hardness (M scale)	79	110	111
D-648	Distortion temperature under 264 lb. load, °C.	65	83	99
D-1525	Modified Vicat temperature, °C.	82	106	186
D-1505	Density, g./cc.	1.15	1.18	1.18

Orientation

A number of years ago it was noted in this laboratory that polyacrylonitrile compression-molded from powdered polymer is comparatively weak, but that pieces molded from chopped, oriented acrylic fibers are strong in flexure and impact. Very little flow is observed during molding (typically 160–200°C. at 2000–5000 psi), and although the molded pieces are fairly clear, it appears that they retain to a large extent the substructure of the material from which they were pressed. On this basis, it was thought that the strength of cast PAN might be increased substantially by orientation.

Some degree of orientation was achieved without much thermal degradation by heating samples rapidly in a high frequency dielectric heater, then pressing them in a hot press or passing them through hot squeeze rolls. Table IV lists results on sheets cast with TSA initiator. The increases in strength are attributed to consolidation and orientation. Al-

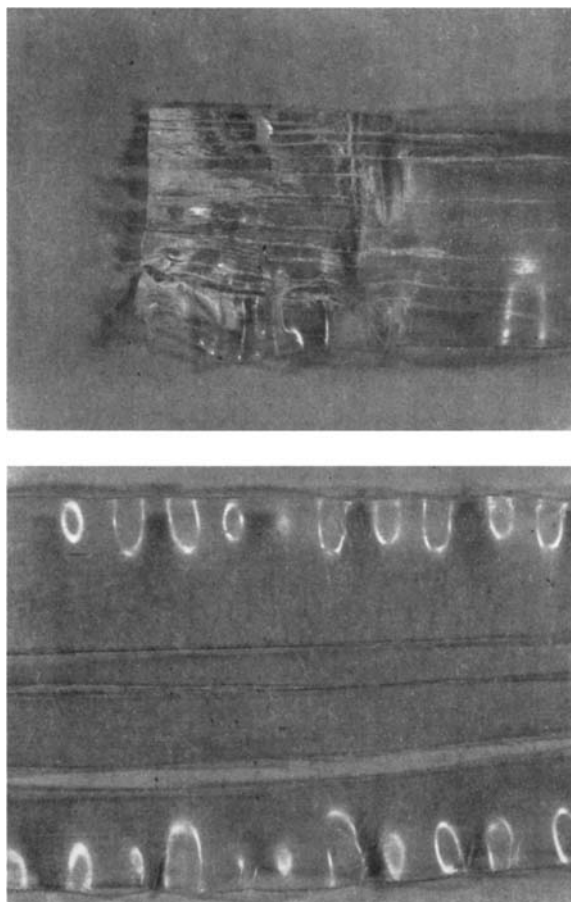


Fig. 1. Cast PAN sheets after hot milling (see Table IV). Two sections are shown.

TABLE IV
 Properties on Post-Formed PAN

Sample treatment	Sheet thickness, in.	Flexural strength, psi $\times 10^{-3}$	Tensile strength, psi $\times 10^{-3}$	Appearance
None	0.150	4.0-8.0	2.0-5.0	Clear, water-white
Preheat, compress at 160°C.	0.132	6.8	—	Clear, water-white
Preheat, compress at 200°C.	0.098	12.9	—	Partially opaque, light yellow
Preheat, mill at 180°C.	0.064	—	15.9 ^a	Translucent, water-white

^a Tensile strength measured parallel to the direction of extension during milling.

though decrease in thickness during pressing is not sufficient evidence for orientation, there was no doubt that the milled sample was highly oriented. The strip fibrillated easily, and its strength perpendicular to the direction of milling was very low (Fig. 1).

Similar results were obtained by molding powdered polymer (made by conventional polymerization in water), heating in the dielectric heater, and then pressing or milling as with cast sheets. To make the original molding step easier, a copolymer with 11% methyl methacrylate was used in these tests. The similarity of results suggest that the degree of consolidation and orientation of the cast product is low, comparable to that of compression-molded polymer powder.

Reinforcement

Castings could be made with fibrous fillers by supporting a piece of mat or fabric in the cell prior to introducing monomer. This step added new problems to an already difficult casting operation. These difficulties included entrapment of gases, poor bonding, changes in polymerization rates and uneven placement of the reinforcing sheet. Table V lists results with a commercial acrylic mat (Orlon acrylic fiber, DuPont) and Fiberglas mat

 TABLE V
 Properties of Reinforced Sheets

ASTM test	Property	Filler		
		None	Acrylic mat	Glass mat
D-790	Flexural strength, psi $\times 10^{-3}$	5.8	5.5	5.0
D-790	Flexural modulus, psi $\times 10^{-6}$	0.63	0.59	0.64
D-638	Tensile strength, psi $\times 10^{-3}$	5.2	4.6	4.7
D-638	Tensile modulus, psi $\times 10^{-6}$	0.24	0.71	0.92
D-256	Izod impact, notched, ft.-lb./in.	0.14	0.13	1.4
D-1525	Modified Vicat temperature, °C.	214	>260	>260
—	Deflection temperature, °C.	83	97	154

(Corning). Although the glass filler improved impact strength and both fillers raised the softening temperature, the results were not encouraging.

Copolymerization

General information on copolymerization is given in Part I, and the preparation of a typical cast sheet is described.¹ Table VI compares

TABLE VI
Physical Properties of Cast Copolymers

	Cast PAN	6% Ethyl acry- late	12% Ethyl acry- late	6% Methyl meth- acrylate	12% Methyl meth- acrylate	12% Allyl meth- acrylate
Flexural strength, psi $\times 10^{-3}$	4.9	10.2	16.9	10.7	12.3	9.7
Flexural modulus, psi $\times 10^{-6}$	0.67	0.59	0.65	0.64	0.53	0.37
Tensile strength, psi $\times 10^{-3}$	5.1	6.4	10.2	6.8	10.0	5.8
Elongation at break, %	1.5	2.9	4.6	3.0	4.1	4.2
Izod impact, notched, ft.-lb./in.	0.16	0.16	0.17	0.18	0.17	0.19
DTL distortion tem- perature under load, °C.	90	74	69	95	71	49
Vicat temperature, °C.	>260	168	131	192	159	>260
Modified Vicat tem- perature, °C.	125	90	82	—	80	64
Rockwell hardness (M scale)	111	101	103	111	101	52
Density, g./cc.	1.174	1.170	1.170	1.176	1.172	1.136

properties of five copolymers with those of cast PAN. Substantial improvements in flexural and tensile strengths were accompanied by a drop in softening temperature. The changes in strength are probably associated with better bonding of the polymer particles due to enhanced compatibility, whereas the lower softening temperatures reflect the expected behavior of copolymers.

DISCUSSION

Results of this work can be rationalized on the basis of the following picture of the casting process. During the first half of the reaction polymer precipitates as unswollen, roughly spherical particles. These particles pack themselves to give a rather weak but coherent cake. During the second half of the reaction, polymerization continues with monomer from above the cake flowing into the interstices and polymerizing. Shrinkage during polymerization requires that none of the pores be closed prematurely

or voids will be formed. Bonding among particles is due primarily to surface adhesion rather than to interpenetration. About 5% monomer remains in the cake.

Rapid heating discharges residual monomer and provides transient plasticity during which period the sheet can be oriented and some consolidation of structure can be achieved. Higher strength can be obtained in this way, but uniaxial orientation produces weak lateral bonding and fibrillation. Further heating produces irreversible changes resulting in a stiff, discolored, and sometimes opaque sheet.

Copolymerization with selected monomers improves the strength of the cast sheet, possibly due to an increase in interparticle bonding. Incorporating a filler in the casting is feasible but difficult and has been only moderately successful.

Physical tests were conducted under the direction of Mr. F. L. Graves and Mr. W. C. Wikstrand. Mr. R. L. Webb supervised microtesting of samples cast in Israel and Dr. M. L. Miller provided the information on chemical resistance.

References

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Résumé

Une feuille de polyacrylonitrile coulée par la nouvelle méthode décrite dans la partie I est claire, incolore, résistant chimiquement, fragile et plutôt faible. Elle subit des changements thermiques irréversibles à environ 80°C, mais si elle est chauffée rapidement, elle peut être orientée et donner une force plus élevée parallèlement à la direction d'orientation. Certaines améliorations de la force peuvent être obtenues en utilisant des charges fibreuses. Certains copolymères sont plus forts que leur homopolymère mais ont des températures de ramollissement plus basses.

Zusammenfassung

Die nach einer neuen, in Teil I beschriebenen Methode hergestellte Polyacrylnitrilfolie ist klar, farblos, chemisch beständig, spröde und von geringer Festigkeit. Oberhalb etwa 80°C erleidet sie irreversible thermische Veränderungen, bei rascher Erhitzung kann sie jedoch orientiert werden, und erhält eine grössere Festigkeit parallel zur Orientierungsrichtung. Ein gewisse Verbesserung der Festigkeit kann durch die Verwendung faserartiger Füllstoff erreicht werden. Gewisse Copolymere besitzen eine grössere Festigkeit als das Homopolymere, jedoch eine niedrigere Erweichungstemperatur.

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