

HIGH PERFORMANCE PLASTICS



NATIONAL TECHNICAL CONFERENCE
Society of Plastic Engineers
October 5-7, 1976
Cleveland, Ohio

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SECTION I

STRUCTURE AND PROPERTIES - I
 "HIGH PERFORMANCE PLASTICS"

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ENGINEERING PROPERTIES AND PERFORMANCE OF HIGH ACRYLONITRILE/STYRENE POLYMER SYSTEMS

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I. INTRODUCTION

Copolymers of styrene (S)-acrylonitrile (AN) near azeotropic compositions (75% S/25% AN) have long been commercially available. In recent years, high nitrile resins greater than 50% AN have been developed with excellent physical and chemical properties. In this paper, their properties and suggested end-use applications are discussed.

II. POLYMERIZATION

Since the discovery of the dramatic reduction of water and gas permeabilities of high nitrile polymers (1, 2), intensive efforts have been made in the development of barrier packaging resin systems. The high nitrile resins not only offer excellent barrier properties (3, 4) but also good physical and chemical properties.

Copolymerization of S and AN can be accomplished by the four well-known methods, namely, emulsion, suspension, mass and solution. The chemistry of free radical polymerization has been well documented and it is beyond the scope of this paper. Preferably, the polymerization reaction is carried out to achieve homogeneity of composition. This is standard practice in most copolymer polymerizations and means for achieving homogeneity are well known. Composition drift should be controlled within $\pm 2\%$ of target values. Molau (5) discussed phase separations in heterogeneous AN/S systems. In cases where water is used as the carrier, the AN water solubility must be considered. Smith (6) and Mino (7) conducted systematic studies on AN/S polymerization systems. Our studies showed solubility of AN in water for the high AN polymerization systems followed the same pattern.

III. HIGH AN/S COPOLYMER PERFORMANCE & APPLICATIONS

Rigid, high AN/S copolymers (ANS) have been tailor-made for specific evaluations. These copolymers can be injection molded, blow molded, extruded and thermoformed or cast, for end-use applications where good barrier, chemical resistance, rigidity, clarity and weatherability properties are required.

1. Thermal Stability and Melt Viscosity

The thermal stability and the melt viscosity of the ANS, like their barrier properties, are AN concentration dependent. The higher the AN content, the lower the resin thermal stability (Figure 1). We determined the resin stability by the resistance to change the viscoelastic melt to crosslinked resin at an elevated temperature. The time for this change is defined as the "critical time". The apparent melt viscosities of samples of different AN content of the same molecular weight (MW) were measured. The viscosity data (Figure 2) shows its AN dependency. Along with barrier properties, we believe the 60-70%

AN copolymers offer a balanced property map for many film, sheet, and molding applications.

2. General Polymer Properties

A model resin of 63% AN and medium MW was selected for the following property evaluation on injection molded specimens.

Property	Unit	Value
Specific Gravity		1.10
Tensile Strength		
at Yield, 0°F	psi	16,000
73°F		11,700
150°F		8,000
at Fail, 73°F		8,400
Ultimate Elongation, 73°F (D-638)	%	25
Tensile Modulus	psi	6.0×10^5
Flexural Strength	psi	19,500 ⁵
Flexural Modulus	psi	6.1×10^5
Rockwell Hardness	R	124
	M	98
Taber Scratch Resistance	Gms.	60
Equilibrium Moisture (50% RH, 20°C)	%	1.5
Coeff. of Linear Thermal Expansion	in./in./°C	5.5×10^{-5}
HDTUL, Unannealed		
64 psi	°F	221
264 psi		212

IV. SPECIFIC APPLICATIONS AND PROPERTIES

1. Oriented Film and Sheet Properties

Due to its composition and molecular structure, ANS is readily orientable, producing tough films and sheet. This approach has many recognizable advantages versus the rubber modified polyblends, which include optical clarity, insensitivity to temperature of both optical and physical properties, absence of crease whitening, greater rigidity and barrier properties. The following are typical oriented film and sheet properties. These, of course, depend on the degree of orientation imparted to the polymer.

Property	Unit	Film (1 Mil)	Sheet (5 Mil)
Tensile, Yield	psi	13,000	13,000
Elong. @ Fail	%	15	15
Elmendorf, Tear	G./mil	15	28
Dart Drop (D1922)	Gm.	45	370
Area Factor	in. ² /lb./mil	25,600	5,120

The Elmendorf tear strength of blown film varies significantly as a function of AN content. For example, the 50% AN film provides 6.5 gm./mil, while

a 63% film gives 15 gm./mil. The dimensional stability of the ANS film against moisture is comparable to polystyrene and far superior to cellophane. These properties would suggest uses where cellophane is now used but where improvements in dimensional stability are needed.

2. Melt Flow

Due to its high glass transition temperature, ANS is relatively stiff flowing but still readily processable in standard molding and extrusion equipment. Viscosity comparisons between the ANS and other commonly known high performance thermoplastics are as follows:

Melt Viscosity, Kp (450°F)

	100 Sec. ⁻¹	1000 Sec. ⁻¹
ANS (63% AN)	16	4.0
ANS (69% AN, Low MW)	18	4.4
ANS (69% AN, High MW)	26	5.0
Typical SAN	9	1.7
Acrylic	13	3.1
Rigid PVC, @ 400°F	63	5.2

3. Chemical Resistance for Packaging

ANS resins are highly chemically resistant as compared to polystyrene, PSAN, and ABS resins. They are unaffected by most acids, alkalis, alcohols, oil, aromatic and aliphatic hydrocarbons. Acetone, dimethyl formamide, and propylene carbonate are excellent solvents.

In environmental stress cracking tests as measured by their critical strains, polymers with different AN levels were tested in the cotton seed oil/oleic acid solution. Data in Figure 3 demonstrates the superiority of the ANS systems. Static creep resistance of the same series of resins was measured at 3,000 psi. The static load of short duration in the presence of the same chemical environment produced gross differences (Figure 4) in mechanical behavior of these resins. The excellent properties would suggest packaging or molding applications where good chemical resistance is needed.

4. UV Resistance and Outdoor Weathering

The unique combination of weather and chemical resistance suggests evaluation of ANS for applications which must maintain high property levels after extended exposure outdoors. In an accelerated lab UVA test, ANS show excellent retention of original properties. The AN level has the greatest effect in reducing color change during UV exposure. AN levels above 60% show no advantage in improving color change (Figure 5). The 63% AN copolymer UV exposure properties were compared with an acrylic resin with the following results:

Exposure, (Hrs.)	Retention* of Tensile Strength		Retention* of Ultimate Elongation	
	ANS	Acrylic	ANS	Acrylic
0	100	100	100	100
500	100	61	56	36
1000	88	59	40	32
2000	76	56	20	20

* Percent of original value, stabilized specimen.

Based on this data, ANS appears to be comparable to PMMA for appearance and weather resistance for outdoor applications such as shutters, siding, glazing, signs or patio furniture. Its superior strength, HDTUL and a lower thermal coefficient of expansion versus PMMA makes ANS even more attractive.

5. Permeability Transfer of Gases and Water Vapor

ANS offers a good balance of low gas and water vapor transmission (Figure 6), being superior to commonly used packaging resins such as polyethylene, polypropylene and PVC. The following data illustrates these differences:

	Permeation Rates		
	Gases		Water Vapor
	73°F		100°F
	O ₂	CO ₂	100% R.H.
ANS (63% AN)	3.3	6.4	7.0
ANS (69% AN)	1.8	4.0	5.0
SAN	70	280	16
HDPE	110	300	0.5
PP	150	450	0.5
PVC (Rigid)	15	30	3

The combination of low permeation rates with good physical and chemical properties makes ANS unique for food and non-food packaging applications where retention of content properties are required.

V. CONCLUSION

Copolymers of 60-70% acrylonitrile with styrene have been synthesized. They offer a unique combination of optical, barrier, mechanical, chemical and weatherability properties. These properties make them well suited for many diverse applications such as food and non-food packaging, film overwraps, containers, glazing, signs, siding, shutters, exterior appliance housings and outdoor furniture.

VI. ACKNOWLEDGEMENTS

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VII. BIBLIOGRAPHY

1. Trementozzi, Q. A., U.S.P. 3,451,538 (1969), 3,540,577 (1970).
2. Hughes, E. C., Idle, J. P. et al., J. Appl. Polym. Sci., 13 2567-77 (1969).
3. Nemphos, S. P. and Lee, Y. C., Appl. Poly. Symp., #25, 285-292 (1974).
4. Salame, M. and Temple, E. J., Adv. in Chem. Series, Am. Chem. Soc., #135, pp. 61-76 (1974).
5. Molau, G. E., J. Poly. Sci., Vol. 3, 1007-1015 (1965).
6. Smith, W. V., J.A.C.S., 70, 2177 (1948).
7. Mino, G., J. Polym. Sci., Vol. 22, pp. 369-383 (1956).
8. Ott, J. B., Inter-Company Report.

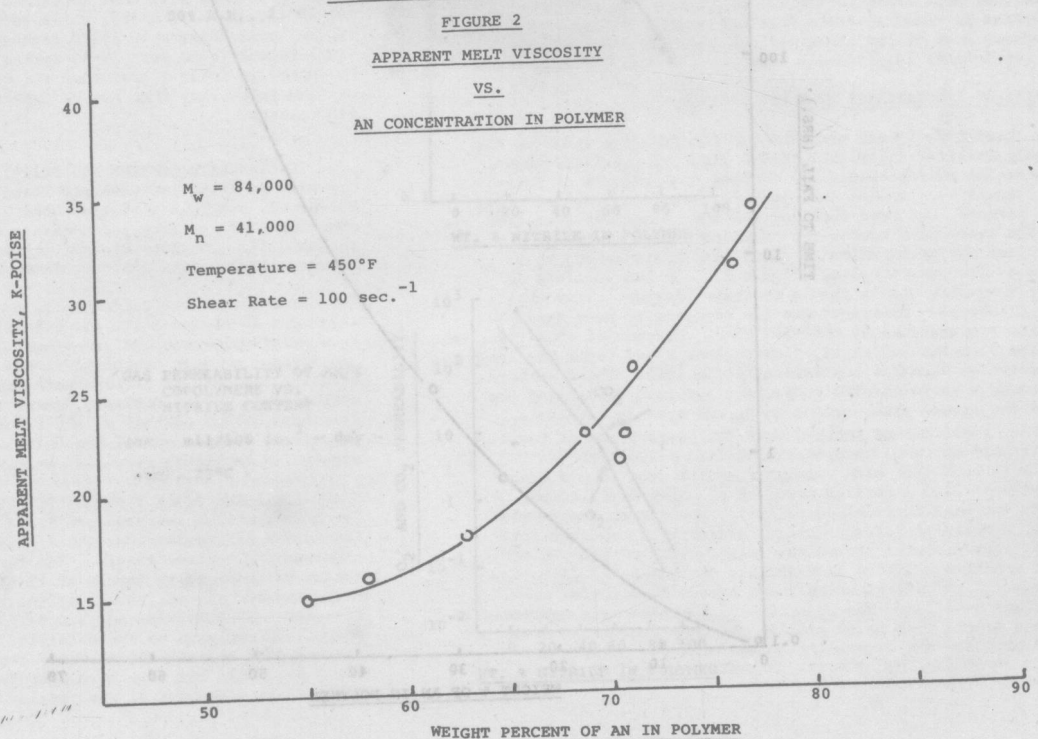
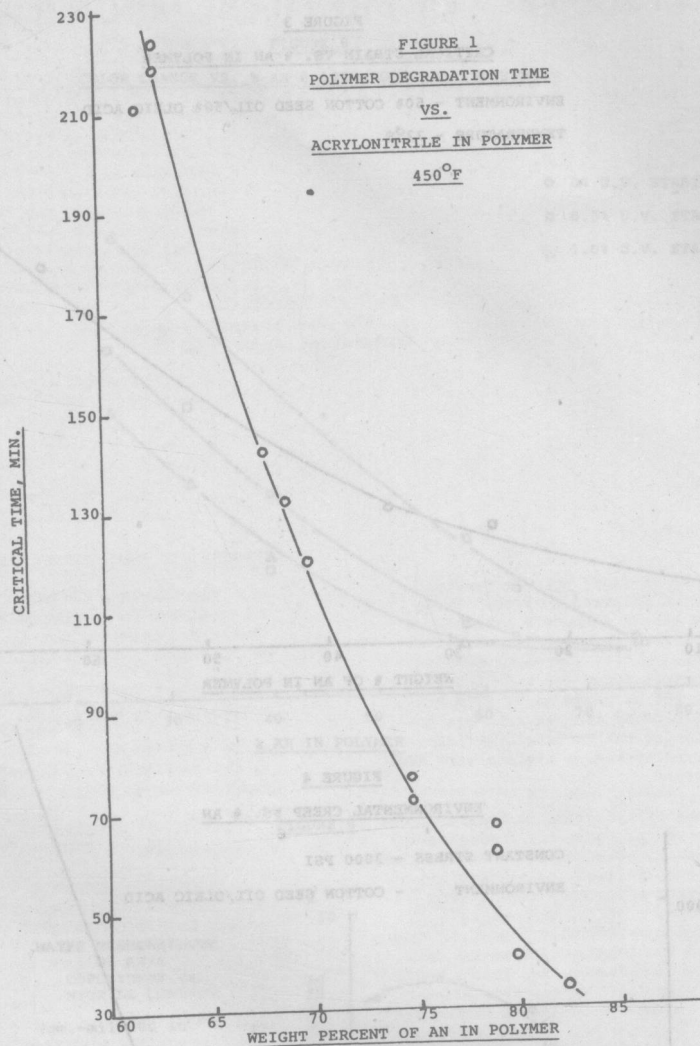


FIGURE 3

CRITICAL STRAIN VS. % AN IN POLYMER

ENVIRONMENT - 50% COTTON SEED OIL/50% OLEIC ACID

TEMPERATURE - 72°F

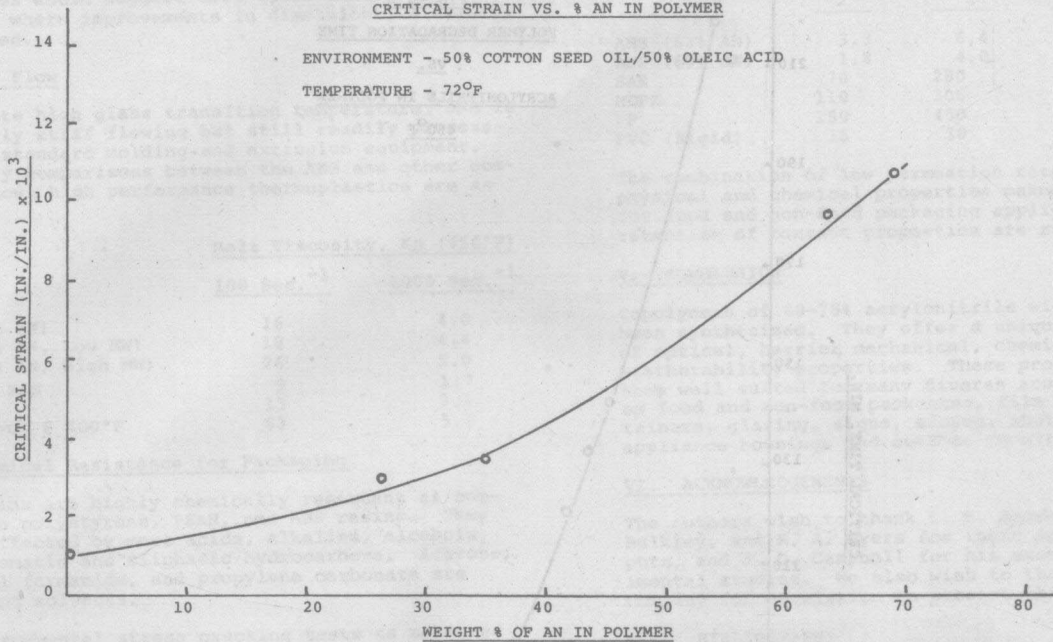
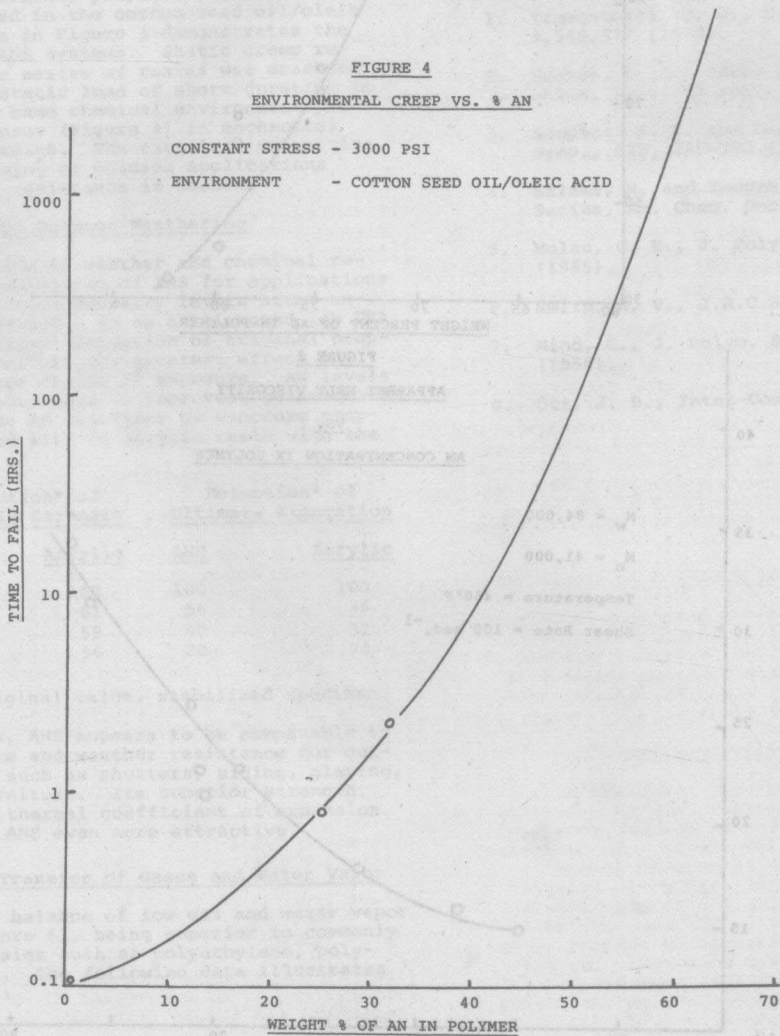


FIGURE 4

ENVIRONMENTAL CREEP VS. % AN

CONSTANT STRESS - 3000 PSI

ENVIRONMENT - COTTON SEED OIL/OLEIC ACID



THE EFFECT OF URETHANE MODIFICATION ON THE EFFECTS OF

FIGURE 5
COLOR CHANGE VS. % AN @ 1000 HOUR UVA EXPOSURE

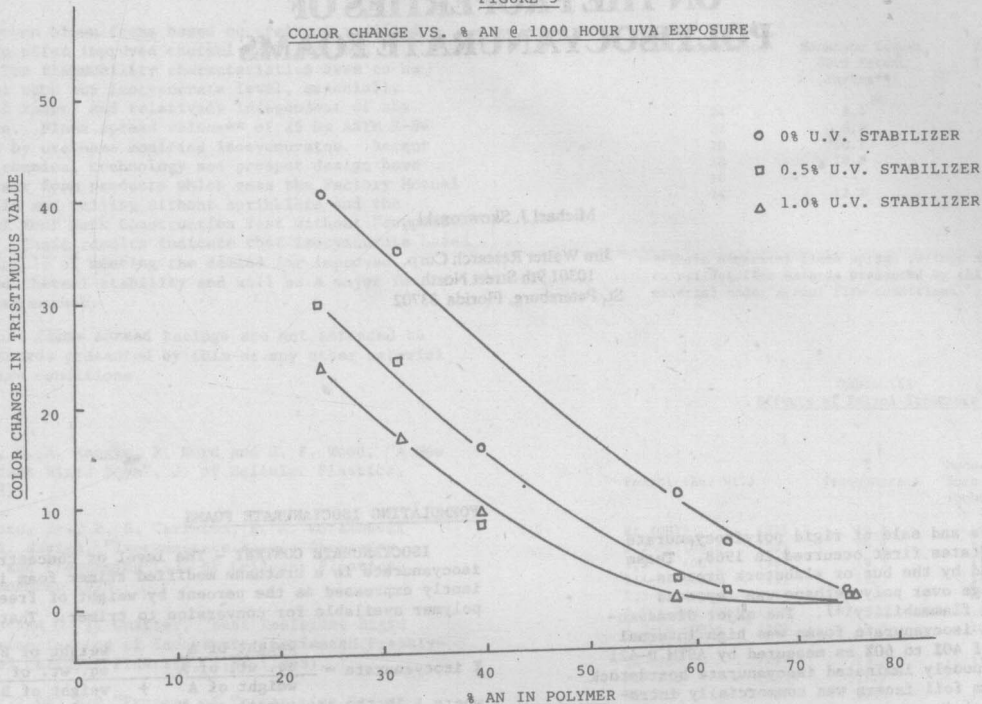
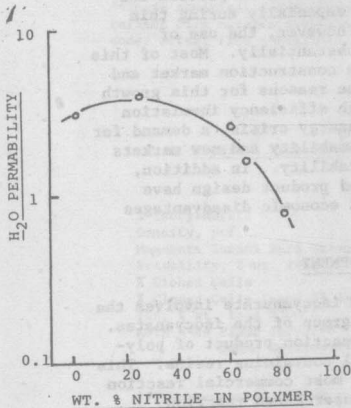


FIGURE 6



GAS PERMEABILITY OF AN/S COPOLYMERS VS. NITRILE CONTENT
 (cc - mil/100 in.² - day - atm), 23°C

