Transparent Barrier Resins with High Nitrile Content

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Synopsis

The effect of 30–49 wt-% nitrile group content on the properties of copolymers is demonstrated. The nitrile is furnished by either acrylonitrile or methacrylonitrile. The exceptional resistance of such high nitrile content resins to the passage of gases and of solvents is shown and variations therein demonstrated for different comonomers. Transparent, tough, grafted polymers of good color are described which retain these properties. These qualities, combined with low second-order transition temperatures and adequate heat deflection temperatures, provide polymers of interest wherever containment and barrier are desired. Bottles, thermoformed containers, etc., could benefit from the use of some of the polymers described.

INTRODUCTION

Nitrile polymers have long played a useful role in all of the main applications of polymers. Rubbers, rigid plastics, and latex coatings containing up to 35% acrylonitrile find substantial outlets because of their extraordinary resistance to solvents, chemicals, and liquid fuels.[1,2]

Acrylonitrile–α-olefin polymers of even higher acrylonitrile content, prepared by free radical polymerization, have been shown to have potential value in molding resins, films, surface coatings, and flexible sheeting. The α-methyl-substituted olefins appear particularly promising, with resin strength decreasing and heat deflection temperature increasing with increasing molecular weight of the olefin used.[3]

It has also been known for some time that films formed from polymers containing more than about 80% acrylonitrile exhibited exceptional gas barrier properties. For example, it was observed that a film of polyacrylonitrile has an O_2 transmission rate of 0.03 cc-mil/100 in.^{2}/1 atm per day, and that N_2, CO_2, and H_2O have comparable values respectively of 0.02, 0.04, and 0.30 at ambient temperature ($23° \pm 2°C$). Transmission rates for O_2, N_2, and CO_2 through polyethylene decrease when increasing amounts of acrylonitrile are grafted onto the olefin backbone.[4] This imperviousness has been ascribed to the dipole interaction (packing) of the nitrile groups.[5,6]

Polyacrylonitrile contains 49.1 wt-% nitrile group. While it has been reported to have a T_g of 140°C,[7,8] it cannot be melt-processed because of inter- and intramolecular reactions to yield ladder and crosslinked prod-

ucts.[9,10] The high T_g also results in brittle copolymers in the high acrylonitrile-content region. However, polymethacrylonitrile has a T_g of 120°C[11,12] and is stable enough for melt forming. Transparency in molding resins is excellent and stability to sunlight has often been remarked, particularly for acrylonitrile fibers.[1]

PROCEDURE

It was of interest to determine means for providing substantial concentrations of nitrile groups in polymers which would not only provide these barrier qualities and transparency, but also be "tough" enough to be of value in packaging and to be formable in typical commercial equipment.

A series of copolymers with acrylonitrile (AN) or methacrylonitrile (MAN) was made by free radical polymerization as typified by the following procedure, wherein the nitrile groups were provided by MAN: 80-100 Parts MAN, 0-20 parts methyl methacrylate, 225 parts demineralized water, 3 parts emulsifier, anionic, 0.05 parts chelating agent, 0.5 parts n-octyl mercaptan, 0.5 parts tetradecyl or n-dodecyl mercaptan,* 0.1 parts potassium persulfate, pH adjusted to 7. Polymerization goes to 95%-98% conversion in 6-8 hr at 77°C, under nitrogen.

GRAFT RESULTS

AN and MAN grafted polymers have also been made in the presence of nitrile rubbers. Typical preparations employed 5%-20% of rubber in latex form; the procedure was otherwise similar to the above.

Results of the grafting reaction are quite sensitive to the percentage of AN in the rubber. Figure 1 shows this relationship for two of the copolymers with a sharp maximum for notched Izod impact in the 27 ± 3% range of AN. Figure 2 shows the effect of rubber concentration in two typical copolymers. The shape of these curves is typical of grafting technology and shows that important "toughening" was achieved in the range of 5%-25% of rubber. The copolymer examples cited in the figures had nitrile group contents in the approximate range of 34-36 wt-%.

The reality of the improvement in impact properties has been demonstrated by dropping filled bottles made from many of these resins. Resins with Izod impact strengths as low as 1-2 ft-lb/in. notch result in drop heights (ASTM D-2436-65T) of 6-10 feet. These resins exhibit good clarity. For example, a 2.5 mil-thick disk, compression molded from a rubber-modified AN/methyl acrylate (MA) polymer (about 36 wt-% CN) had a 92% light transmission, 7% haze (ASTM D-1003-61) and a yellowness index of 0.9 (ASTM D-1925-62T). Some other typical properties of this particular resin composition are flexural strength 14,000 psi, flexural modulus 490,000 psi, tensile strength 9,500 psi, and Izod impact 1.5 ft-lb/in. notch. An unusual property of this resin is that it remains clear and transparent even at liquid nitrogen temperature.
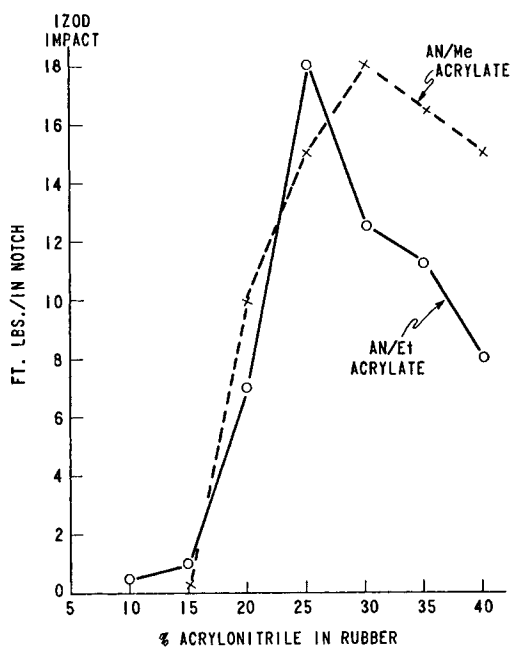
* Type and amount of mercaptan variable.

Fig. 1. Effect of acrylonitrile content of BD/AN rubber on impact strength.
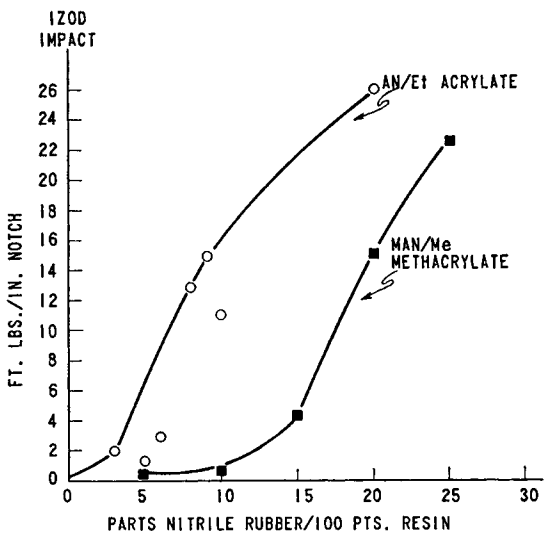

Fig. 2. Effect of amount of rubber on impact strength of graft resin.

BARRIER PROPERTIES

The nitrile content is the most important compositional variable relating to barrier qualities as is shown by Figures 3, 4, and 5. However, distinct differences may be introduced by the choice of comonomers. In Figure 3, the WVTRs (water vapor transmission rates) of polymers are related to CN-group content. For example, at a level of 38.8% CN-group, the WVTR varied from 1.5 to 6 g-mil/100 in.^{2} per 24 hr. The lowest was that of an MAN polymer. The other values represent copolymers of AN, which increase in water vapor transmission rate according to the following co-monomer series: MA or isooctyl acrylamide (OAA) < n-butyl acrylate < ethyl acrylate (EA) or methyl methacrylate (MMA) < styrene. All of these resins are clear glasses with low notched Izods.

Figure 4 covers some of the same copolymers grafted to nitrile rubbers to provide higher notched Izod suitable for break-resistant container usage. Many of these high nitrile resins are readily processable, with molecular weights of around 100,000. The rubber addition reduces the WVTR by a small amount; for example, at 37% nitrile content the addition of 10% rubber to an AN–MA copolymer reduces WVTR from 4.9 to 4.4. The rubber-modified copolymers organize themselves in the same way as did the unmodified copolymers in the prior figure, i.e., MAN (with MMA or MA) < MA–AN < EA–AN. The range of interest can be indicated by the fact
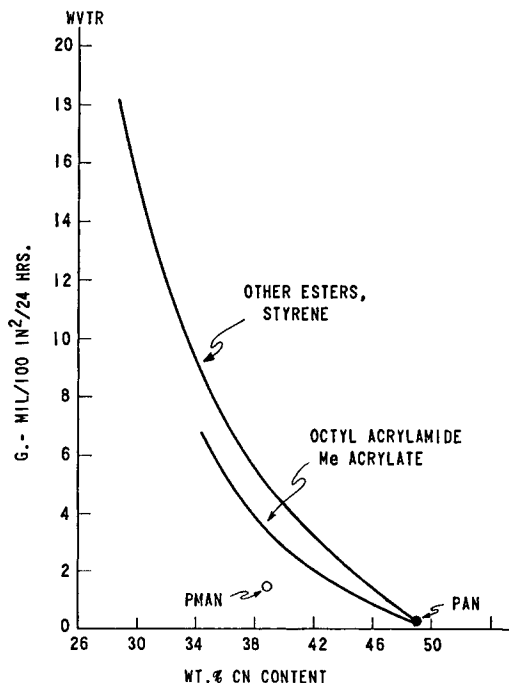

Fig. 3. Effect of CN content on water vapor transmission rate in acrylonitrile copolymers.
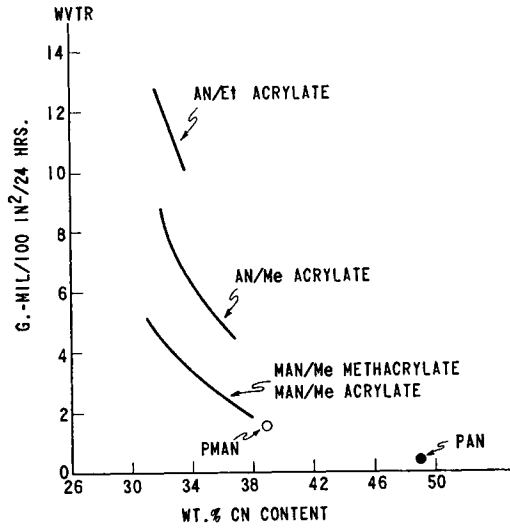
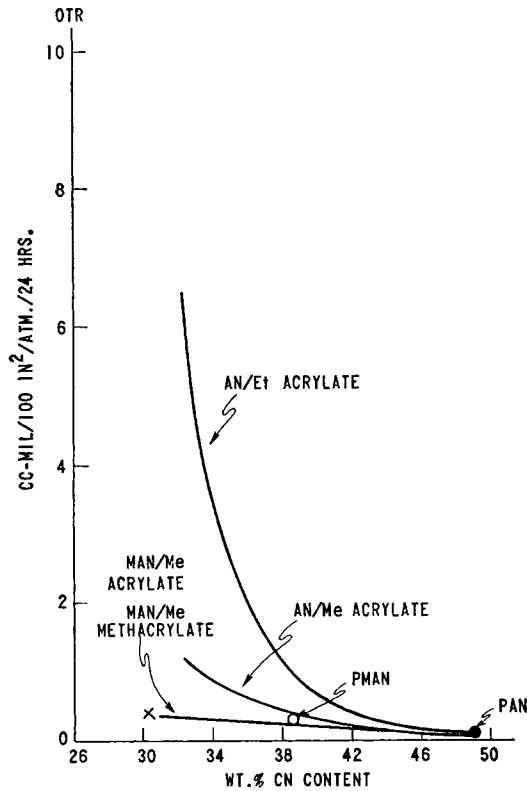Fig. 4. Effect of CN content on WVTR of rubber-modified copolymers.

Fig. 5. Effect of CN content on oxygen transmission rate (with and without rubber).

that the WVTRs of bottle-grade PVCs [poly(vinyl chloride)] are a little above the lower levels.

The differences are not solely due to ester linkage content as shown by the fact that EA is inferior as a barrier comonomer to MA, although the latter introduces a higher percentage of ester at equal CN.   Packing may account for some of the difference.

Figure 5 shows the unusual control which CN exerts on OTR (oxygen transmission rate).   For comparison, PVC shows an OTR of about 8 and HDPE (high density polyethylene), about 185.   Processable copolymers in the range of 33%–37% nitrile concentration varied from 0.25 to 4 cc-mil/100 in.^{2}/atm per 24 hr.   The polymer in which nitrile was furnished by MAN had the lowest rate.   The use of MA with AN again resulted in much lower O_2 transmission than EA.   The impact MA copolymer had a value of only 0.16 for CO_2 and 0.24 for N_2.

RHEOLOGY

The HDT (heat deflection temperature) of PAN is about 86°–87°C and that of PMAN is 100°C.   The HDT in each copolymer system can be correlated also to the nitrile content, as shown in Figure 6.   Large differences can be achieved in these barrier polymers by choice of comonomer and per cent nitrile.   An unexpected result was shown by the OAA–AN (non-grafted) resin.   Both this resin and the impact 95 MAN–5 MMA resin had HDTs in the range of 98 ± 2°C.   The other resins line up in the manner
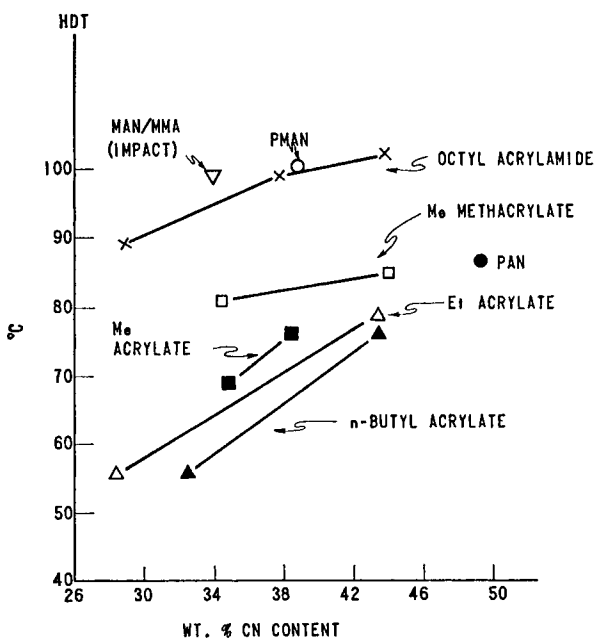

Fig. 6. Effect of CN content on heat deflection temperatures of AN copolymers.

predictable from the T_g or HDT of the comonomers, i.e., for AN comonomers, OAA > MAN > MMA > MA > EA > n-butyl acrylate. Within the interesting barrier range provided by 33%–37% nitrile, HDTs from 56°C to 100°C can be selected.

These polymers become readily processable in the various container-forming machines at molecular weights of 90,000–130,000 as shown in
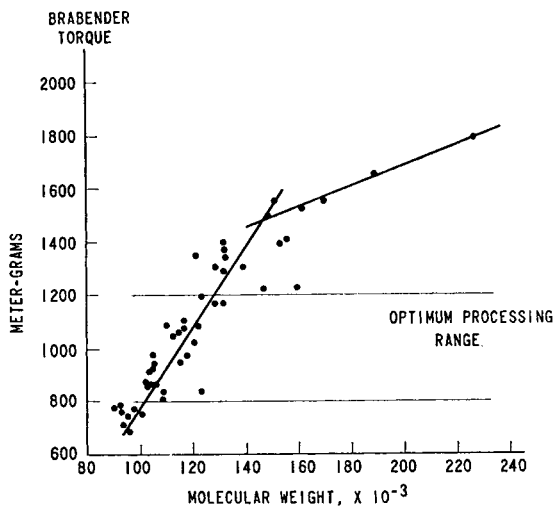

Fig. 7. Effect of molecular weight on Brabender torque in MAN resins.
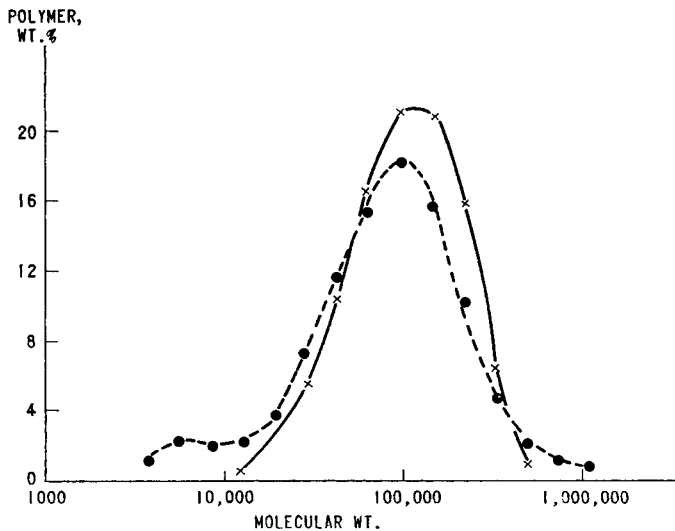

Fig. 8. Molecular weight distributions for rubber-modified methacrylonitrile resins of 125,000 mol wt: (●) Brabender torque 1000, $M_w/M_n = 3$; (×) Brabender torque 1500, $M_w/M_n = 2$.

Figure 7. Figure 8 shows differences in rheology, as measured by the Brabender torque, depending upon molecular weight distribution at a constant weight-average molecular weight.
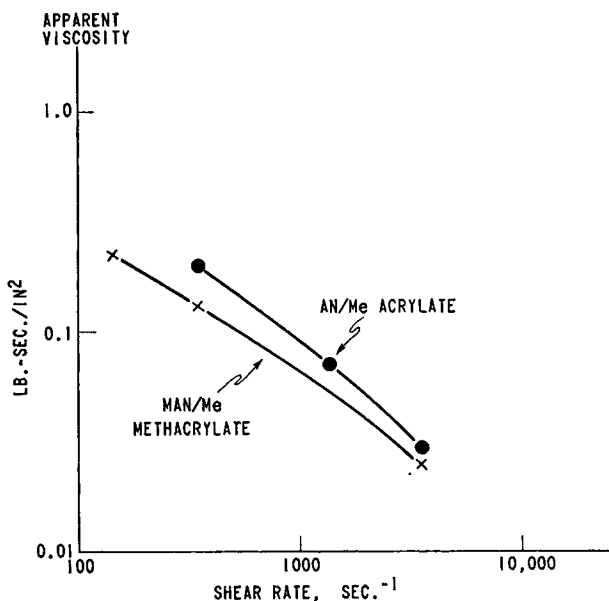

Fig. 9. Instron rheometer curves for rubber-modified resin at 200°C.

Figure 9 compares two impact systems as to apparent viscosity versus shear rate. It indicates that no difficulties would be found in operating extruders, etc., in this 100,000 mol wt range. For comparison, a typical high VC (vinyl chloride) content PVC copolymer would be described by a curve above those of Figure 9.

OTHER PROPERTIES

Table I shows standard solvency tests which indicate that the usual resistance of the nitrile group is accentuated by its high content (approximate range of 34–36 wt-%) in these polymers. Of particular note is the comparative resistance of the AN polymer to ethyl acetate and of the MAN resins—which contain little or no comonomer—to aromatic and chlorinated hydrocarbons.

Two transitions which are observed in the impact resins are shown in Table II; however, two additional transitions have been found by differential thermal analysis (DTA), as shown in Figure 10. The transitions shown in Table II relate to the T_g of the nonimpact resins and the impact modifier, respectively. The latter is low enough so that impact properties are observed in the temperature ranges in which resins are commonly used.

TABLE I
Chemical Resistance[a]

	Weight change, %		
	Impact AN/MA copolymer	Impact MAN/MMA copolymer	Impact PVC
Water, distilled	2.1	0.4[c]	0.3
Acetic acid, glacial	− 0.02	1.1[c]	4.6
Ammonia, conc.	0.5	0.3[c]	0.6
Methanol	5.1	2.7	0.9
Hexane	− 0.4	0.1	− 0.02
Benzene	3.8[b]	0.7[c]	77
Carbon tetrachloride	8.4[b]	0.2[c]	11
Acetone	55[b]	highly swollen	specimen distintegrated
Ethyl acetate	7[b]	8	277

[a] Conditions: complete immersion at room temperature for 72 hr except where noted.
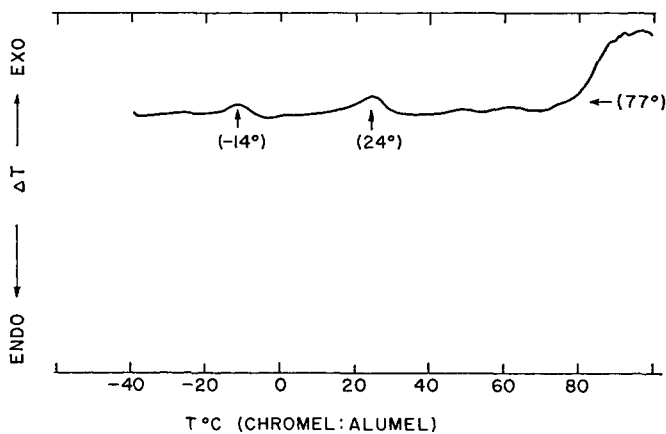[b] 336 hours.
[c] 144 hours.

Fig. 10. Transition temperature in AN/methyl acrylate impact resin (du Pont 900 thermoanalyzer).

TABLE II
Transition Temperatures for Nitrile Copolymers

Polymer composition	Transition temperatures, °C	
	DTA	TP[a]
75/25 AN/MA	83	—
·Impact 75/25 AN/MA	77	−30
95/5 MAN/MMA	108	—
·Impact 95/5 MAN/MMA	107	−30

[a] Torsion pendulum (PLAS-TECH).

APPLICATION

The polymer chemistry reported in this paper has been applied to a new barrier polymer for food packaging, Barex* bottle resin. The gas permeation rates for Barex resins compared with typical values for PVC and acrylic multipolymer are listed in Table III. Selected physical properties of Barex

TABLE III
Gas Permeation Rates of Polymers[a]

	Barex	PVC[b]	Acrylic multipolymer[b]
Oxygen	0.80	8	18.7
Carbon dioxide	0.24	9	11.0
Nitrogen	0.16	–	7.9
Water vapor	7.0	3	10.7

[a] Gases, cc-mil/100 in.^{2}/atm per 24 hr at 73°F; water vapor gm-mil/100 in.^{2} per 24 hr at 100°F/90% RH.
[b] Average or typical values from manufacturer's bulletins, including copolymers.

TABLE IV
Properties of a typical copolymer containing more than 70% acrylonitrile[a]

Property	Value
Specific gravity	1.15 gm/cc
Tensile at yield	9,500 psi
Elongation at yield	5.0 %
Flexural modulus	490,000 psi
Flexural strength	14,000 psi
Izod impact	1.5 ft-lb/in.
Drop height to break	8 ft
Heat deflection at 66 psi	165 °F
Melt index	4.0 gm/10 min
Brabender Plasti-Corder torque	1,300 m-g

[a] A resin undergoing field trials under the registered trademark of Barex by the Vistron Corporation.

resins are listed in Table IV. Food packaging end uses for which Barex resin containers show promise are those which require gas barrier, toughness, and disposability by incineration.

CONCLUSIONS

A series of high nitrile resins was prepared and correlations were made on the basis of the nitrile content. An impact-toughened group of transparent solvent- and gas-resistant resins of HDT between about 60°C and 100°C has also been described in this framework. Of particular note is the role of methacrylonitrile in copolymers for combining high HDT with uncommon

* Registered trademark of Vistron Corporation, a subsidiary of The Standard Oil Company, Ohio.

barrier qualities. Graft copolymers of acrylonitrile are shown also to have useful impact-resistant and barrier qualities. Furthermore, the rheology properties are equal to or better than those of commonly used resins, although polymers of acrylonitrile have long been known for their brittleness and difficulty of processing. The barrier to oxygen and carbon dioxide, so exceptional in 100% polyacrylonitrile, was found to extend in these polymers to a valuable degree.

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