ETHYLENE-ACRYLIC ELASTOMERS

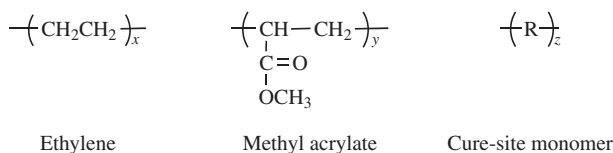## 1. Introduction

Ethylene−acrylic is a term used to describe a family of acrylic elastomers that was first introduced commercially in 1975 under the trademark Vamac by DuPont. The original elastomer was the result of an intensive research effort to develop an oil-resistant polymer with greater heat resistance than that of

nitrile or polychloroprene rubbers, at a moderate cost well below that of silicones and fluoroelastomers. Ethylene–acrylic elastomers are best known for their excellent heat and oil resistance, but they also possess a good balance of compression set resistance, flex resistance, physical strength, low temperature flexibility, and weathering resistance. Special compounded attributes include uniquely temperature-stable vibrational dampening properties and the ability to produce flame-resistant compounds with combustion products having an exceptionally low order of smoke density, toxicity, and corrosiveness. Because of this balance of properties, ethylene–acrylic elastomers have found ready acceptance in many high performance applications, especially in the automotive market (1–4).

2. Polymer Properties

2.1. Polymer Composition. Ethylene–acrylic elastomer terpolymers are manufactured by the addition copolymerization of ethylene [74-85-1] and methyl acrylate [96-33-3], in the presence of a small amount of an alkenoic acid to provide sites for cross-linking with diamines (5).

$$-\left(CH_2CH_2\right)_x \qquad -\left(\underset{\underset{OCH_3}{\overset{\displaystyle|}{\underset{|}{C=O}}}}{\overset{|}{CH}}-CH_2\right)_y \qquad -\left(R\right)_z$$

Ethylene   Methyl acrylate   Cure-site monomer

In the early 1990s, DuPont commercialized a new family of copolymers of just ethylene and methyl acrylate, which do not include a cure-site monomer. These dipolymers are cured with peroxides.

The polymerization process yields a random, amorphous terpolymer or a random, amorphous dipolymer (no cure-site monomer). The polymer backbone is fully saturated, making it highly resistant to ozone attack even in the absence of antiozonant additives. The fluid resistance and low temperature properties of ethylene–acrylic elastomers are largely a function of the methyl acrylate to ethylene ratio. As the methyl acrylate level increases, the polymer becomes more polar and has better fluid resistance to aliphatic hydrocarbon oils. Also, as the methyl acrylate level increases, the glass-transition temperature (T_g) of the polymer increases slightly. There is a trade-off between oil resistance and low temperature performance.

2.2. Commercial Forms. Four different base polymers of Vamac ethylene–acrylic elastomers are commercially available (Table 1). Until 1990, existing grades of ethylene–acrylic elastomers were based on a single-gum polymer, Vamac G, defined as a terpolymer of methyl acrylate, ethylene, and a cure-site monomer (6). In 1991, a higher methyl acrylate terpolymer, Vamac GLS, was introduced. The composition of this polymer was specifically chosen because it significantly increased the oil resistance of the polymer while minimizing the loss in low temperature flexibility (7).

A new family of peroxide-cured dipolymers was introduced in 1991. The peroxide cure provides copolymers that cure faster and exhibit good compression set properties without a post-cure. The removal of the cure-site monomer has

Table 1. **Vamac Ethylene–Acrylic Elastomer Polymers**

Commercial designation	Monomers[a]	Methyl acrylate level	Type of cure system
Vamac G	E/MA/CS	average	amine
Vamac HVG	E/MA/CS	average	amine
Vamac GLS	E/MA/CS	high	amine
Vamac DP	E/MA	average	peroxide

[a] E is ethylene; MA, methyl acrylate; and CS, proprietary cure-site monomer.

made the polymer less susceptible to attack from amine-based additives. By varying the methyl acrylate level in the dipolymer, two offerings in this family have been synthesized, Vamac D and its more oil-resistant counterpart, Vamac DLS (7).

2.3. Curing. Carboxyl cure sites are incorporated in the ethylene–acrylic terpolymer to permit cross-linking with primary diamines (1,8). Guanidines are added to accelerate the cure. If faster cure is desired for the terpolymers, one can use the combination of diamine and peroxide to approximately double the cure rate (9,10) as measured by tc (90). Dipolymers are cured only with peroxides.

2.4. Heat Resistance and Aging Properties. The main features of ethylene–acrylic elastomers are heat (175°C by ASTM D2000) and oil resistance. At elevated temperatures, ethylene–acrylic elastomers age by an oxidative cross-linking mechanism, resulting in eventual embrittlement, rather than reversion. A general heat resistance profile is shown in Table 2.

As shown, ethylene–acrylic elastomers will function for more than 24 months at 121°C, or 6 weeks at 171°C continuous service. Exposures up to 190–200°C can be tolerated, although service life at these temperatures is measured in days rather than weeks. When immersed in service fluids, the oxidative process is often slowed down leading to longer actual service life.

Ethylene–acrylic elastomers are highly resistant to the damaging aspects of weather, ie, sun, water, oxygen, and ozone. Vulcanizates have shown little change in tensile properties and no visible signs of surface deterioration after exposure to the elements in Florida for 10 years. Samples under 20% tensile strain (static) displayed no cracks after one week's exposure to 100 ppm ozone in air, a concentration 100 times greater than is usually specified in qualifying tests.

Table 2. **Heat Resistance Profile**

Temperature of continuous exposure, °C	Approximate useful life of >50% absolute elongation
121	24 months
149	6 months
171	6 weeks
177	4 weeks
191	10 days
200	7 days

Table 3. **Fluid Resistance**

		Volume swell, %	
Medium	Time, h/Temp, °C	Vamac G	Vamac GLS
ASTM #1 oil	70/150	+5	+2
ASTM #2 oil	70/150	+24	+10
IRM 903 oil	70/150	+50	+25
Service fluid 105	1008/150	+22	+10
Motor oil-5W/30	168/150	+19	+9
Motor oil-5W/30	1008/150	+20	+10
Synthetic motor oil-5W/30	1008/150	+10	+4
ATF fluid	168/150	+25	+14
ATF fluid	3000/150	+32	+20
power steering fluid	168/150	+15	+5
Fuel B	168/23	+73	+57
kerosene	168/23	+31	
unleaded gasoline	168/23	+68	
water	504/100	+6	
ethylene glycol	504/100	+4	

2.5. Fluid Resistance.   Ethylene–acrylic elastomers are well suited for applications requiring continuous exposure to hot aliphatic hydrocarbons, a class that includes most lubricants derived from petroleum (11). Volume swell data in Table 3 illustrate the good resistance of ethylene–acrylic elastomers to most common automotive lubricants and hydraulic fluids and to ASTM oils at elevated temperatures. The higher methyl acrylate polymer, Vamac GLS, exhibits approximately one-half the volume swell in these fluids of Vamac G. Low swell in motor oils and transmission fluids indicates usefulness for service as various seals, gaskets, and cooler hoses for transmission and engine oil and seals for wheel and crankshaft bearings. Recently, the synthetic motor oil is gaining attention because of its significantly longer service life between oil changes. Both Vamac G and Vamac GLS exhibit low volume swell and excellent retention of properties in the synthetic oils. Although resistance to water and glycol is excellent, some antifreeze-additive packages can cause excessive stiffening of the terpolymer vulcanizates. Ethylene–acrylic elastomers should not be selected for service in continuous contact with gasoline, brake fluid, highly aromatic fluids, or polar solvents such as esters and ketones.

2.6. Mechanical Properties.   Typical properties of ethylene–acrylic elastomers, like those of other compounded rubbers, vary widely with formulation and also polymer grade. Among compounding ingredients, reinforcing fillers and plasticizers as well as type and amount of curing agents exert the greatest influence. A typical compound based on Vamac G and Vamac GLS with pertinent vulcanizate properties is shown in Table 4. Note that while Vamac GLS has improved oil resistance versus Vamac G, its low temperature flexibility is about 2–5°C higher than that of the Vamac G compound.

2.7. Low Temperature Properties.   Medium hardness compounds of average methyl acrylate, ie, Vamac G, without a plasticizer typically survive

Table 4. **Vulcanizate Properties of Vamac G and Vamac GLS in Black Loaded Compound**[a,b]

Property	Vamac G	Vamac GLS
Physical properties at RT		
100% modulus, MPa[c]	5.3	6.2
tensile strength, MPa[c]	15.1	16.0
elongation at break, %	290	273
hardness, Durometer A	67	66
tear die C, kN/m[d]	34	32
Low temperature properties		
glass-transition by dsc, °C	−35	−33
fluid resistance, 168 h at 150°C		
volume change, %		
in ASTM #1 oil	2	−1
in SF 105	23	10
in Dexron III	28	13
compression set, method B, plied		
70 h at 150°C	14	16
168 h at 150°C	19	14

[a] Compound parts: polymer, 100; Naugard 445 (substituted diphenylamine), 2; Armeen 18D (octadecylamine), 0.5; stearic acid, 1.5; Vanfre VAM (complex organic alkyl acid), 1.0; FEF Carbon Black (N550), 60; DIAK #1 (hexamethylenediamine carbamate), 1.5; and DOTG, 4.
[b] Press cure is 5 min at 177°C. Post-cure is 4 h at 175°C.
[c] To convert MPa to psi, multiply by 145.
[d] To convert kN/m to ppi, divide by 0.175.

180° flex test at −40°C. This type of performance is good for a heat-resistant polymer. Low temperature properties can be greatly enhanced by the use of ester plasticizers (12). Careful selection of the plasticizer is necessary to preserve the heat resistance performance of the polymer. At equivalent plasticizer levels, compounds made from the high methyl acrylate grades lose a few degree celsius in flexibility, compared to compounds made with the average methyl acrylate levels.

2.8. Flame Resistance and Smoke Suppression. Ethylene−acrylic elastomers are not inherently resistant to burning. Through compounding, the rate of burning can be retarded and the amount of smoke generated can be suppressed. An important feature of ethylene−acrylic elastomers is their ability to respond to the addition of hydrated alumina (13). This polymer/filler combination provides vulcanizates with good flame resistance, freedom from corrosive gases, and most importantly in many judgments, an unusually low smoke density.

2.9. Dynamic Mechanical Properties. Ethylene−acrylic elastomers have a high capacity for dampening that is uniquely insensitive to temperature changes between −10 and 160°C. Damping characteristics at room temperature, as indicated by loss tangent (tan δ), are similar to those of butyl rubber, which is noted for its damping properties. Ethylene−acrylic elastomers differ from butyl and other elastomers, however, by their ability to maintain a high loss tangent as temperature is raised to 160°C. This loss tangent remains virtually unchanged

after six months aging in air at 150°C. Damping properties of ethylene–acrylic elastomers are also relatively insensitive to compound variations (14,15).

3. Processing

3.1. Mixing. Ethylene–acrylic elastomers are processed in either an internal mixer with an upside down process for large-scale production or a rubber mill for smaller scales. In either case, it is important to keep the compound as cool as possible and to avoid overmixing. Ethylene–acrylic elastomers require no breakdown period prior to addition of ingredients. Mixing cycles for a one-pass mix are short, typically 2.5–3.5 min. When compounds are mixed in a rubber mill, care should be taken to add the processing aids up front with additives. Normal mill mixing procedures are followed otherwise.

3.2. Extrusion and Calendering. Most compounds of ethylene–acrylic elastomers have low nerve and yield smooth extrusions or calendered sheets. To improve collapse resistance in hoses, compounding techniques should be used to maximize compound viscosity. This includes using a higher viscosity terpolymer, a higher structure carbon black, or fumed silica. The extruder temperatures should be kept quite low. A suggested starting temperature gradient would go from 50 to 65°C, with 75°C at the die. Extruded hose is usually vulcanized by exposure to high pressure steam in an autoclave. Other applications, such as wire insulation and jacketing, are subjected to fast, continuous, high pressure steam vulcanization. Vulcanization at atmospheric pressure produces highly porous vulcanizates and is not recommended.

3.3. Molding. Parts can be produced from ethylene–acrylic elastomers using compression, transfer, or injection-molding techniques. Because the viscosity of these polymers is usually lower than the typical rubber used in the industry, compounds of ethylene–acrylic elastomers have a tendency to trap air during molding, especially in a compression mold. This situation can be avoided with adequate venting of the mold, the use of an effective mold lubricant, the use of compounding techniques to maximize compound viscosity, good preforming techniques, and proper mold temperatures. The low viscosity of ethylene–acrylic elastomers makes them especially good for injection molding.

Mold temperatures vary between 150 and 200°C, depending on the molding methods and part size. Parts can be molded in 1.5–10 min depending on the configuration and thickness of the part, the mold temperature, and the desired state of cure at demolding. Since most ethylene–acrylic parts are post-cured, it is sometimes possible to demold partly cured articles and complete vulcanization in the post-curing oven.

3.4. Post-Curing. Whenever production techniques or economics permit, it is recommended that compounds based on terpolymer grades be post-cured for optimum properties. Relatively short press cures can be continued with an oven cure in order to develop full physical properties and maximum resistance to compression set. Various combinations of time and temperature may be used, but a cycle of 4 h at 175°C is the most common. The post-cure step increases modulus, greatly improves compression set performance, and stabilizes the initial stress–strain properties. During the post-cure step, the

chemical cross-link is converted from an amide linkage to a more stable imide linkage. Peroxide-cured dipolymer compounds need not be post-cured.

3.5. Adhesion.   Commercially available one- or two-coat adhesive systems produce cohesive rubber failure in bonds between ethylene–acrylic elastomer and metal (16). Adhesion to nylon, polyester, or aramid fiber cord or fabric is greatest when the cord or fabric have been treated with carboxylated nitrile rubber latex.

Additional information on processing compounds of ethylene–acrylic elastomers can be found in References 17,18–19.

4. Economic Aspects

The market for ethylene–acrylic elastomers was greater than 5000 t/year in 2000. The growth rate for ethylene–acrylic elastomers has been greater than 10% in the 1990s. Over 50% of ethylene–acrylic elastomers are sold in Europe.

Several new products are under development (10), including a more flex resistant polymer and a lower T_g polymer. These new products, when commercialized, will expand the serviceability of the ethylene–acrylic elastomers and also improve their processability.

5. Uses

The favorable balance of properties of ethylene–acrylic elastomers has gained commercial acceptance for these elastomers in a number of demanding applications, especially in the automotive industry and in wire and cable jacketing.

Approximately 80% of ethylene–acrylic elastomers are used in automotive applications with hose and tubing as the single largest end use. The recent steady increases in automobile operating temperatures make ethylene–acrylic a prime candidate for under-the-hood applications. Applications include oil and transmission seals, O-rings and gaskets, high velocity CVJ boots, spark plug boots, torsional dampers, and extruded sponges (20,21). Hose applications include transmission and engine oil cooler hoses, air conditioning hose, power steering hose, and turbo charger hose.

Industrial applications include pipe seals, hydraulic system seals, dampers for machinery and high speed printers, and motor lead wire insulation. The fact that the polymer contains no halogens along with certain unique compounding techniques for flame resistance prompts the selection of ethylene–acrylic as jacketing material on certain transportation/military electrical cables, and in floor tiles.

BIBLIOGRAPHY

"Acrylic Elastomers" under "Elastomers, Synthetic" in *ECT* 3rd ed., Vol. 8, pp. 459–469, by T. M. Vial, American Cyanamid Co.; "Ethylene–Acrylic Elastomers" in *ECT* (online), posting date: December 4, 2000, by Theresa M. Dobel, Du Pont Chemical Company.

1. J. F. Hagman, and co-workers, *Rubber Age* **108**(5), 29, (1976).
2. R. G. Peck, *Ethylene/Acrylic Elastomer—Meeting the Challenges of a Demanding Market*, Bulletin EA-020.0185, DuPont Polymers, Stow, Ohio, Jan. 24, 1985.
3. T. M. Dobel, *Auto. Polym. Des.* **9**(6), 26, (1990).
4. H. J. Barager and L. C. Muschiatti, *Vamac*® Ethylene Acrylic Elastomers for Demanding Automotive Applications, Paper No. 189, American Chemical Society Rubber Division, Orlando, Fla., Sept. 1999.
5. U.S. Pat. 3883472 (May 13, 1975), R. N. Greene and K. J. Lewis (to E. I. du Pont de Nemours & Co., Inc.).
6. J. F. Hagman, *Vamac G Gum Ethylene/Acrylic Elastomer*, Bulletin E-52096, DuPont Polymers, Stow, Ohio, Sept. 1978.
7. T. M. Dobel, *New Development in Ethylene/Acrylic Elastomers*, Paper No. 28, American Chemical Society Rubber Division, Detroit, Mich., Oct. 1991.
8. U.S. Pat. 3904588 (Sept. 4, 1975), R. N. Greene (to E. I. du Pont de Nemours & Co., Inc.).
9. J. F. Hagman, *Curing Mechanisms of Vamac*, Bulletin EA-030.0684, DuPont Polymers, Stow, Ohio, 1980.
10. H. J. Barager, K. Kammerer, E. McBride, L. C. Muschiatti, and Y. T. Wu, *Increased Cure Rates of Vamac*® *(AEM) Dipolymers and Terpolymers using Peroxides*, American Chemical Society Rubber Division, Cincinnati, Ohio, Oct. 2000.
11. W. M. Stahl, *Fluid Resistance of Vamac*, Bulletin H-02366, DuPont Polymers, Stow, Ohio, Aug. 1988.
12. J. F. Hagman, *Compounding Vamac For Low-Temperature Performance*, Bulletin E-10770, DuPont Polymers, Stow, Ohio, Sept. 1978.
13. R. J. Boyce, *Flame Retardance in Mineral-Filled Compounds of Vamac*, Bulletin E-17762, DuPont Polymers, Stow, Ohio, Jan. 1978.
14. A. E. Hirsch and R. J. Boyce, *Dynamic Properties of Ethylene/Acrylic Elastomers: A New Heat Resistant Rubber*, Bulletin EA-530.604, DuPont Polymers, Stow, Ohio, May 1977.
15. A. E. Hirsch, *Dynamic Characteristics of Fluoroelastomers and Ethylene/Acrylic Copolymers*, Bulletin EA-530.602, DuPont Polymers, Stow, Ohio, 1980.
16. J. F. Hagman, *Bonding Systems for Vamac*, Bulletin E-36062, DuPont Polymers, Stow, Ohio, July 1980.
17. J. F. Hagman, *Processing Vamac*, Bulletin E-10755, DuPont Polymers, Stow, Ohio, Aug. 1976.
18. C. Williams, *Vamac Ethylene/Acrylic Elastomer, A Survey of Properties, Compounding and Processing*, Bulletin H-34753, DuPont Polymers, Stow, Ohio, Jan. 1992.
19. J. W. Crary, *Ethylene/Acrylic Elastomer—Basic Principles of Compounding and Processing*, Bulletin EA-030.0482, DuPont Polymers, Stow, Ohio, Apr. 1982.
20. R. G. Peck, *Auto. Eng.* **95**(7), 37 (1987).
21. R. E. Vaiden, *Elastomeric Materials for Engine and Transmission Gaskets*, Paper No. 920132, Society of Automotive Engineers, Detroit, Mich., Feb. 1992.

YUN-TAI WU
EDWARD MCBRIDE
E.I. du Pont de Nemours & Company, Inc.