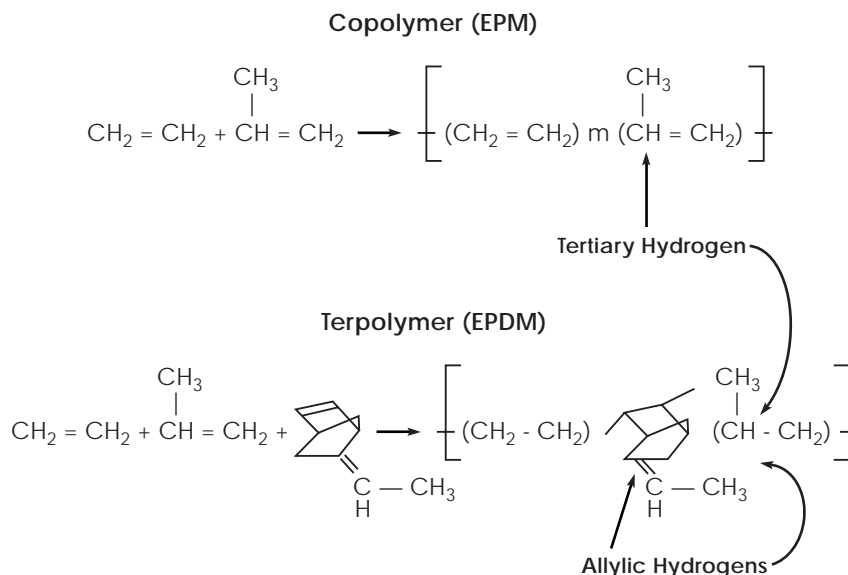


## Vulcanization of Vistalon Polymers

Vulcanization (also called cure) is primarily a crosslinking process in which chemical bonds or bridges are formed between adjacent polymer chains. The nature of the resulting three-dimensional network is characteristic of the cure system employed. This irreversible process enhances the strength and elastic properties of the compound and imparts greater dimensional stability and reduced set or creep over a wide temperature range. The elastomeric material becomes less plastic and more resistant to swelling in organic fluids. However, once the vulcanization process



is complete, the rubber compound cannot be recycled in the usual sense, unlike a thermoplastic material.

Ethylene and propylene are the basic monomeric units of EP(D)M elastomers and the structures are shown in the figure below.

These chemical formulas are oversimplified; not shown are the probable distributions of ethylene and propylene units which are determined by the ratio of the monomers employed, the catalyst system and the polymerization and reactor conditions. Thus, among the EP(D)M producers, many grades are significantly different, despite commonality of Mooney viscosity and E/P comonomer ratio.

### Vulcanization of Vistalon EPM

Vistalon EPM copolymer is crosslinked exclusively via a free radical mechanism. This is usually accomplished via the decomposition of organic peroxides, although vulcanization using electron beam radiation is also possible. The secondary hydrogen on the copolymer main chain is abstracted by a peroxy radical to form a polymer radical (see figure above).

This subsequently combines with adjacent polymer radicals to complete the crosslink. In general, free radical vulcanization is enhanced by utilizing polyfunctional coagents such as ethylene dimethacrylate, triallyl cyanurate, and the like. These reagents increase the crosslinking efficiency of the peroxide, overcome steric-hindrance effects, and minimize undesirable side reactions which detract from obtaining a good state of cure. However, the decomposition rate of the peroxide, which is a function of temperature, is not altered.

Recommended levels of polyfunctional coagents and other free-radical chemicals that enhance vulcanization and physical property performance are shown in the table below.

### Chemicals for Enhanced EPM Free Radical Vulcanization

Coagent		Function
Sulfur	0.3 phr	Improves the efficiency of vulcanization and reduces chain scission
EDMA*	1.0 phr	
TMPT(SR-350)*	1.5 phr	
TAC	1.5 phr	
1,2 PBD	1.3 phr	
MPBM (HVA-2)	1.2 phr	

Coupling/Wetting Agents (0.5 to 2.0 phr)	Function
Vinyl silane	Enhanced stress-strain properties with mineral fillers
Acrylic silane	
Polyethylene glycol	

\*Also used in radiation cures.

Acidic compounding ingredients such as stearic acid promote ionic breakdown of peroxides and should be avoided. Calcium stearate can be employed in place of stearic acid with peroxide cures. Aluminum silicate based clays which are widely used in mineral filled compounds are also acidic in nature; Agerite Resin D or equivalent reagents would be included in the compound to insure that the peroxide decomposes radically rather than ionically.

One undesirable side reaction with free-radical vulcanization is the competing chain breakdown at the tertiary hydrogen site. For this reason, higher ethylene grades of EPM, which have fewer sites, are preferred for vulcanization, whenever rheological or end-use considerations permit. The nature and quantity of vulcanizing agents for Vistalon EPM can be adjusted to meet individual needs for scorch safety, cure development, and compound properties.

### Vulcanization of Vistalon Polymers

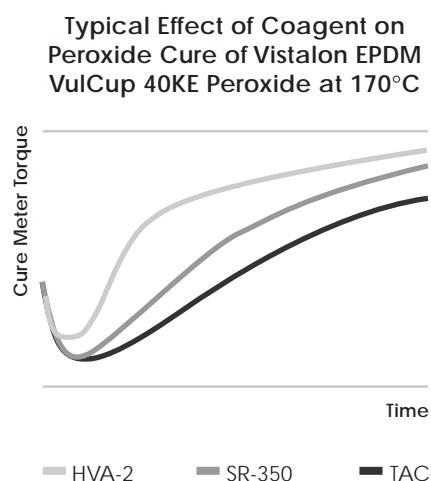
The peroxide cure system can also be used with EPDM; the principal site for crosslinking is at or near the side chain double bond on the diene (see figure on previous page).

Reactivity rates are significantly greater for EPDM terpolymers due to the presence of allylic hydrogen on the diene. Peroxides are used with EPDM when the ultimate in heat resistance and

lowest compression set is required. Generally these are high quality compounds in which the process oil level is minimized to avoid interference of the active free-radical with the polymer network.

If higher plasticizer levels are needed, additional peroxide can be added to compensate for free-radicals consumed by the hydrocarbon oil.

The peroxide decomposition rate, which is a function of temperature, is a key factor in cure development. The next figure is a cure meter plot showing the rate of cure with three different peroxides in a Vistalon EPDM compound.



The onset or initiation of crosslinking and development of the network are dependent on the rate of free radical generation (half life of peroxide) as well as the structure of a given peroxide. Likewise, the effect of different coagents on peroxide cure is shown in this figure. Each coagent has different reactivity in the crosslinking process which results in the diverse range of cure state in the final product. It was previously noted that the pendant carbon-carbon double bond in the terpolymer provides additional reactivity through the allylic hydrogens. With ENB as the non-conjugated diene, the peroxide radical will preferentially react via hydrogen abstraction at the allylic site. Since there are five allylic hydrogens available, there is a higher probability that crosslinking will occur at one of these positions.

## Sulfur Vulcanization

Sulfur vulcanization through the diene is used in the majority of EPDM applications. The type of crosslink is related to the specific cure system used. High sulfur systems favor the formation of a polysulfidic bond. These vulcanizates offer high stress-strain properties and good flexibility, but thermal stability is marginal compared to systems generating monosulfide bonds. Vulcanization rate is related to the amount and type of diene present in the polymer, as well as to the cure system. When properly boosted with ultra accelerators, a nominal 5 weight percent ENB grade can be vulcanized in fast cure cycles. However, the amount of diene is not the only controlling factor; narrow MWD polymers attain a higher cure rate and state than do broad MWD polymers.

Basic sulfur cure systems for EPDM consist of:

- Crosslinking Agents
  - Sulfur
  - Sulfur donor
- Primary Accelerator
  - Thiazole
- Ultra Accelerators
  - Thiuram
  - Dithiocarbamate

### **Vulcanization Modes**

Ethylene-propylene rubber is compatible with all methods used to achieve the desired state of cure.

In compression molding the uncured stock is placed directly in the mold cavity. The mold is then assembled and placed in the hydraulic press. The press closes the mold and causes the stock to fill the cavity. When cure is complete, the mold is removed from the press, disassembled, and the rubber parts removed.

Transfer molding is a refinement of the compression molding process in which the mold is tightly closed before the cavity is filled. Stock is “transferred” from a holding pot to the cavity under pressure.

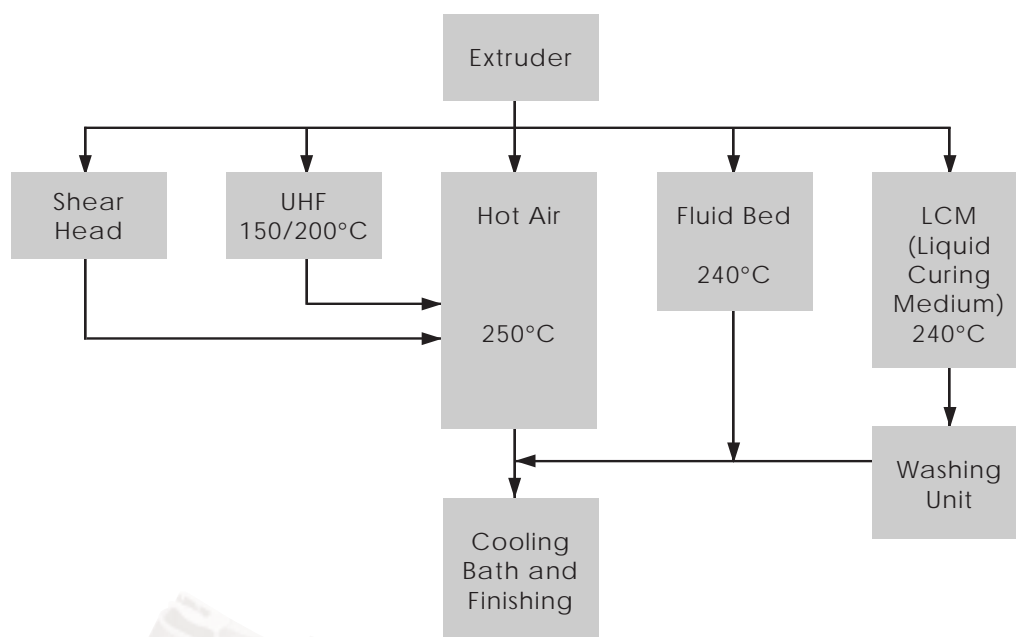
Injection molding is similar to transfer molding except that the stock is metered into the mold cavities through runners fed by an injection head. On some machines one injection head may serve several presses and molds. This higher degree of automation permits short, high temperature cures with short change times.

Open steam in an autoclave has long been used to cure extruded products. With this method, the article may be in direct contact with the steam or wrapped with fabric tape.

Continuous vulcanization has the advantage of combining processing and curing steps into one continuous operation on many extruded profiles. Traditionally, extruded profiles and hoses have been separately processed and vulcanized. During the processing step, the profile is extruded in a continuous operation, but the extrudate is accumulated for later batch vulcanization, in a steam autoclave for example. Basically there are four stages to the continuous vulcanization process:

1. Formation of the profile
2. Heating to cure temperature
3. Curing
4. Cooling

#### Continuous Vulcanization Process Installations



Heat may be generated inside the extrudate by dielectric heating (Ultra High Frequency, UHF), by friction (Shear Head), or by heat transfer from the outside (Hot Air, Fluid Bed, Liquid Curing Media (LCM)). Curing is achieved by maintaining the temperature for the time needed to fully crosslink the rubber. Typically, some of these operations may be combined. For example, shear head of UHF heating may be followed by one or more heat air curing stages.

Recently, jet air heating systems have been introduced. These are generally positioned immediately after the extruder, and generate a high velocity flow of very hot air (450-500°C). Jet air systems maximize heat transfer and improve surface aspect in sponge.

Ethylene-propylene rubber itself is non-polar and does not respond to UHF heating, but common

compounding ingredients increase microwave receptivity. Extrusion grade carbon blacks, N660 GPF and N550 FEF, are good as are polar materials such as polyethylene glycol.

Collapse resistance is important in continuous vulcanization because of the high temperatures and the buoyancy pressures of the solid and liquid media. High molecular weight and very high diene Vistalon grades are preferred for maximum collapse resistance. Both types of polymers also resist the development of porosity at the high cure temperatures, preventing deterioration of quality and giving higher output.

More recently, Electron Beam Radiation has attracted some attention. Work at our technology labs indicates that ENB, the diene most often used in Vistalon EPDM, is more reactive than 1.4-hexadiene or cyclopentadiene. A high molecular weight, high ethylene content, and narrow MWD grade shows particularly good cure response to this method. A typical Vistalon product formulation designed for electron beam radiation is displayed in the table below.

**Cure by Electron Beam Radiation** **phr**

Component	
Vistalon Elastomer	100
Hydrated Aluminum Oxide (Hydral 710)	100
Process Oil Type 104B (Sunpar 2280)	50
Vinyl Silane (A-172 Drimix)	3
TMPT (75%)	3
Antioxidant (Aminox)	1
Vulkanox ZMB-2	2

**Original Physical Properties, 10 Mrad Dosage**

Hardness, Shore A	66
100% Modulus, MPa	1.8
300% Modulus, MPa	3.3
Tensile Strength, MPa	7.0
Elongation, %	790

**Aged Physical Properties, Air Oven, 168 hr at 150°C**

Tensile Change, %	-11
Elongation change, %	-1