

PERP Program – 04/05S2, EPDM New Report Alert

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Nexant's *ChemSystems* Process Evaluation/Research Planning program has published a new report, *EPDM (04/05S2)*. To view the table of contents or order this report, please click on the link below: http://www.nexant.com/products/csreports/index.asp?body=http://www.chemsystems.com/reports/show_cat.cfm?catID=2

Introduction

Ethylene propylene rubber (EPR) includes both the copolymer EPM (ethylene-propylene monomers) and the terpolymer EPDM (ethylene-propylene-diene monomer). For this analysis, the term EPDM will be used to constitute both the copolymer and terpolymer, unless otherwise noted.

EPDM is a relatively new rubber that was commercially developed in the early 1960s. By comparison, SBR (styrene-butadiene rubber) and NBR (acrylonitrile-butadiene rubber) were the first synthetic rubbers developed in the late 1930s. Unlike SBR, which was developed as an inexpensive replacement for natural rubber in tires, EPDM's higher performance and cost relegate it primarily to non-tire applications. EPDM has a fully saturated molecular backbone that provides excellent ozone resistance, weatherability, and heat resistance properties, as well as very good dielectric performance and low temperature flexibility. Its major disadvantage is its propensity to absorb oil, which eliminates its use in oil environments. However, this also becomes an advantage, since EPDM compounds can be extended with oil and filler and made less costly. EPDM is produced by solution polymerization based on Ziegler-Natta or metallocene catalysis. Thus, it is more expensive than rubbers produced by emulsion polymerization.

EPDM is a highly versatile rubber. The copolymer and terpolymer can be used uncured in polymer blends as an impact modifier for other polyolefins. The copolymer can also be crosslinked (cured) using organic peroxides for wire and cable insulation, polymer blends, and lubricant oil viscosity improver. The terpolymer is most often vulcanized (sulfur cured) for various types of molded and extruded rubber goods. It is estimated that copolymer demand is about 20 percent of the total EPDM market consisting primarily of automotive end uses, wire and cable, and oil viscosity improver applications.

Each EPDM end-use application has its performance requirements, which can be satisfied by manipulating four basic parameters in the production process:

• Molecular weight (MW) can be varied to achieve target viscosities. Lower MWs provide lower viscosity grades that are easy to process and are often used for non-oil filled compounds such as lubricant oil additives and some extruded products. Higher MW (higher viscosity) grades provide tougher physical performance, such as improved tensile strength,



and are often highly extended with oil and/or filler to reduce compound costs and improve processability.

- Molecular weight distribution (MWD) is variable. Wide MWD provides easier processability and mixing and improved hot green strength but sacrifices toughness due to the low MW components. At equal viscosities, a more narrow MWD provides better physical properties and sometimes faster extrusion rates.
- The ethylene:propylene ratio can be controlled most commercial grades fall within the ethylene range of 50-75 percent, averaging 60 percent. Grades with lower ethylene content tend to be amorphous and easier to process (more rubberlike). Higher ethylene content creates more crystallinity and tougher grades with better cold green strength, allowing for higher oil or filler extended compounds.
- The type and amount of termonomer (diene) will affect rubber properties:
 - Dicyclopentadiene (DCPD) results in a slow cure rate and a foul odor, but is inexpensive
 - Ethylidene norbornene (ENB) provides very fast cure rates but is expensive
 - Hexadiene (HD) provides a moderate cure rate and somewhat better heat stability

Average diene content is 1.5 to 7.0 percent with faster cure rates achieved by increasing the diene to as much as 11 percent. The most popular diene, by far, is ENB, which supports the trend to develop faster curing grades to reduce fabrication costs.

Figure 1 summarizes the variability of EPDM grades and the resulting performance attributes. Table 1 shows a typical EPDM grade slate comparison.

In EPDM, properties such as compression set and aging depend largely on the cross-linking agent. Carbon-carbon bonds, as provided by peroxides or radiation, provide the best heat resistance although they are more expensive than sulfur-based systems. Sulfur-based systems are also less affected by the presence of oil extenders. Polysulfide linkages provide higher strength, while monosulfide links provide better aging properties and stability.

In 1998/1999, DuPont Dow Elastomers introduced EPDM produced in a solution process, but made with a metallocene catalyst. On a molecular level, these EPDM grades have a very defined molecular architecture providing improved lot-to-lot consistency, and more uniform co-monomer incorporation. Also, since metallocene catalysts are more efficient than Ziegler-Natta ones, there are fewer catalyst residuals in the polymer. Hence, a cleaner resin is produced. These resins are also produced and shipped as pellets, as opposed to bales for most traditional EPDMs, thus affording easier handling in some end-uses.



	HIGH	 C₂ (L)/ENB(H) Very fast cure rate Superior roll processability and flow 	C ₂ (M)/ENB(H) • Very fast cure rate • High temperature, short period continuous vulcanization	C ₂ (H)/ENB(H)	Ethylene content, wt% LOW: 40-50 MEDIUM: 50-60 HIGH: Above 60
ENB CONTENT	MEDIUM	 C₂ (L)/ENB(M) Superior low- temperature characteristics High cure rate 	C ₂ (M)/ENB(M) General EPDM High cure rate Good low-temperature characteristics Balanced processability	C ₂ (H)/ENB(M) • High green strength • Better extrudability • High loading properties • High cure rate • High molecular weight	ENB content, iodine vaue LOW: 5-10 MEDIUM: 12-19 HIGH: Above 20
	LOW	C ₂ (L)/ENB(L)	C ₂ (M)/ENB(L) • Low/medium cure rate • Better heat resistance	C ₂ (H)/ENB(L)	
		LOW	MEDIUM	HIGH	

Figure 1 Grade Characteristics by Ethylene/ENB Content

ETHYLENE CONTENT

A few years later, DuPont Dow Elastomers commercialized EPDM metallocene grades produced in a gas-phase reactor. Since the EPDM is never in solution in this process, there are fewer viscosity limitations and hence a higher molecular weight EPDM can be produced.

Chemistry

Linear polyethylene is highly crystalline, and the formation of several irregularities along the polymer chain (by addition of propylene, for instance) leads to an amorphous compound. In general, elastomeric behavior appears when the propylene content of the macromolecule is between 30 and 80 weight percent.

Ethylene and propylene (EP) can be copolymerized with certain coordination catalysts (e.g. Ziegler-Natta), and when the ethylene:propylene ratio is in a suitable range, an amorphous elastomer polymer is formed. Incorporating unsaturation into side-chains provides sites for cross-linking (curing). Note that the unsaturation is not added in the polymer backbone as that detracts from ozone and oxidation resistance.



Ethylene/Dronylene/	Manufacturing	EPDM Grade Differences	Parformance Differences Over
Diene Content	Process		Base Grade
60/40/0	Solution	Bumper/polymer blends impact modifier, viscosity improver	-
51/47/2	Solution	Construction roofing membrane	Good low temperature characteristics, low cure rate, better overall temperature characteristics
60/35.5/4.5	Solution	General purpose extrusion, mechanical goods, wire and cable	Fast cure, high green strength
70/25.5/4.5	Solution	Wire and cable, hose, impact modifier for TPO	Fast cure, high green strength
50/43/7	Solution	Automotive sponge tire applications	Very fast cure, low temperature resistance, superior covulcanization with other diene rubbers (sponge)

Table 1

Stereoregular placements are most desired and the normal propylene addition with vanadium catalysts results in a combination of isotactic and syndiotactic placements.

The products made from ethylene and propylene are saturated and cannot be sulfur cured, but require a peroxide (e.g., dicumyl peroxide or ditertiary-butyl peroxide). The incorporation of a third diolefinic monomer such as dicyclopentadiene, ethylidene-5-norbornene-2 (ENB), or trans-1,4hexadiene adds unsaturation and permits the conventional type of sulfur cure.





R contains one unsaturated linkage

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Effect of Diene Selection

ENB is now the preferred diene among the world's EPDM producers, and over 90 percent of all EPDM produced uses ENB. In the United States, Uniroyal (Crompton) is the only producer that uses both dicyclopentadiene (DCPD) and ENB. In Western Europe, only DSM uses both DCPD and ENB. In the Far East, all producers use ENB and some, at times, substitute DCPD. Sumitomo produces its own ENB for captive use.

The nonconjugated, straight-chain diolefin 1,4-hexadiene and cyclic dicyclopentadiene and ethylidene norbornene have the following in common:

- They contain at least two olefin units, one of which is polymerizable, the other suitable for vulcanization
- They are relatively uniformly distributed along the main chain
- They exhibit a high copolymerization rate while not interfering with the polymerization of ethylene and propylene. The reactivity of each diene's double bonds with respect to polymerization is different. The cyclic dienes readily enter the polymer with much higher polymerization efficiency than 1,4-HD.

A summary of EPDM characteristics based on diene type is presented in Table 2.

Diene	Characteristics	Branching
ENB	Fast cure rate Good tensile strength Good set	Some
1,4-HD	Best compression set Normal cure rate Scorch-safe	None
DCPD	Slow cure rate Good set Odor	High

Table 2EPDM Diene Characteristics

All EPDM elastomers are distinguished by having at least five double bonds per 1,000 carbon atoms. Five bonds is the limit for HD-derived EPDM. ENB-based EPDM can be produced with 9 to 12 double bonds due to the higher relative reactivity of ENB. Final properties are influenced by the degree of unsaturation. The higher the unsaturation, the higher the maximum crosslink density attained. Terpolymers with a higher degree of unsaturation cure faster and yield vulcanizates with a lower compression set. However, compression set also depends on crosslink type. ENB-containing EPDM can attain a higher degree of unsaturation for a higher fraction of monosulfidic crosslinks than less-unsaturated diene EPDMs, producing improved compression sets.



The major disadvantage of DCPD and HD-based EPDM is the slower cure rate attainable where fast cure characteristics are needed. HD-based EPDM requires about 1.5 parts sulfur per hundred parts resin to vulcanize as compared to 1.0 part sulfur per hundred for ENB formulations, resulting in higher processing costs to the end user.

Economics

Economics were developed for a 70:25:5 weight percent ethylene/propylene/diene EPDM product. The economics include a minimal level of additives, notably an anti-oxidant additive package; the costs of extender oils, fillers and the like are not included.

Cases evaluated include:

- Slurry EPDM
- Zeigler-Natta Solution EPDM
- Metallocene Solution EPDM
- Metallocene Gas-Phase EPDM
- Metallocene Solution POE (polyolefin elastomer)

In order to provide comparable figures, the economics for gas-phase EPDM were prepared on a 100 percent polymer basis. Therefore, the 30 percent or so of carbon black (weight basis of final product) or other inert fluidizing agent that is used in the process and passes through to the final product is not included in the economics.

The economics include propylene and diene recovery for all EPDM lines. However, ethylene recovery is only included in the gas-phase and metallocene solution processes. The Ziegler-Natta and slurry processes have very high first pass ethylene conversion rates, and thus ethylene is not typically recovered from the off-gases.

The economics for polyolefin elastomer have also been included as a comparison, though the product lacks EPDM's cross-linking ability, and thus cannot achieve the same level of elastomeric properties as crosslinked EPDM. However, POEs have been successful in replacing EPDM in less demanding applications.

This economic analysis suggests that metallocene EPDM enjoys a cost advantage over Ziegler-Natta EPDM processes of about 30 percent in terms of total cost including capital charges. Such a cost advantage is very significant, and would suggest that no additional Ziegler-Natta solution plants will be built – new plants will be metallocene solution technology. Note that the slurry process also enjoys a cost advantage over the Ziegler-Natta process. This is interesting in that the slurry process is out of favor in deference to the solution processes, suggesting that the product performance deficiencies of slurry-process EPDM are quite substantial.



Supply/Demand

Globally, EPDM demand was an estimated 935,000 tons in 2004. Demand is forecast to increase at an average annual rate of 3.5 percent for 2004-2009, reaching 1,110 tons in 2009.

A break-down of global EPDM demand by end-use segment is illustrated in Figure 2. The importance of the "automotive" sector is apparent, as this sector accounts for about 42 percent of EPDM demand directly, and a sizeable proportion of indirect EPDM demand included in the "polymer modification" and "all other" segments. "Roofing" is a small segment, important mainly in North America and other developed countries.

On a regional basis, demand outside North America, Western Europe, and Japan will be an increasingly important component of the EPDM business.

Annual demand is provided for these regions over the 2001-2009 period, along with global capacity, production, and operating rate data.



Figure 2 Global EPDM Demand by End-use Segment, 2004

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