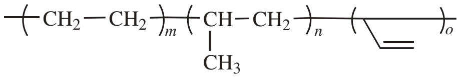
ETHYLENE–PROPYLENE POLYMERS

1. Introduction

Copolymers of ethylene and propylene (EPM) and terpolymers of ethylene, propylene, and a diene (EPDM) as manufactured today are rubbers based on the early work of G. Natta and co-workers (1). A generic formula for EPM and EPDM may be given as follows, where $m = \sim 1500$ (~ 60 mol%), $n = \sim 975$ (~ 39 mol%), $o = 25$ for EPDM (~ 1 mol%), and zero for EPM in an average amorphous molecule, and the comonomers are preferably statistically distributed along the molecular chain.



(1)

EPM can be vulcanized radically by means of peroxides. A small amount of built-in third nonconjugated diene monomer in EPDM permits conventional vulcanization with sulfur at the allylic carbon atoms relative to the pendent sites of carbon–carbon unsaturation.

Among the variety of synthetic rubbers, EPM and EPDM are particularly known for their excellent ozone resistance in comparison with natural rubber (*cis*-1,4-polyisoprene) and its synthetic counterparts IR (isoprene rubber), SBR (styrene–butadiene rubber), and BR (butadiene rubber). Further, EPDM–rubber can be extended with fillers and plasticizers to a very high level in comparison with the other elastomers mentioned, and still give good processability and properties in end articles. This leads to an attractive price/ performance ratio for these polymers.

Even though EPM– and EPDM–rubbers have been commercially available for >40 years, the technology concerning these products, both their production and their applications, is still very much under development.

2. Polymer Properties

The properties of EPM–copolymers are dependent on a number of structural parameters of the copolymer chains: the relative content of comonomer units in the copolymer chain, the way the comonomers are distributed in the chain (more or less randomly), the variation in the comonomer composition of different chains, average molecular weight, and molecular weight distribution. In the case of EPDM–terpolymers, there are additional structural features to be considered: amount and type of unsaturation introduced by the third monomer, the way the third monomer is distributed (more of less randomly) along the chain, and long-chain branching. These structural parameters can be regulated via the operating conditions during polymerization and the chemical composition of the catalyst.

Although the rubbery properties of ethylene–propylene copolymers are exhibited over a broad range of compositions, weight percentages of commercial products generally range from 45:55 to 80:20 ethylene/propylene. On the high propylene side, the polymer fails on thermal and ozone stability, because of the lower oxidative stability of the propylene units relative to ethylene units; on the high ethylene side, the polymer is too highly crystalline and looses its rubbery character. Depending on the catalyst system and polymerization conditions used, the ethylene units may tend to group together to form blocky or sequential structures. This tendency is the more pronounced, the higher the ethylene/propylene ratio. These ethylene sequences impart a level of crystallinity to the EP(D)M rubbers of $<1\%$ at room temperature for 50:50 ethylene/propylene ratio—also designated as amorphous EP(D)M rubber—till $>10\%$ for the high ethylene/propylene ratio—also called semicrystalline or sequential EP(D)M. Crystallinity renders the EP(D)M rubber a certain green strength:tensile strength in the unvulcanized state, making the polymer easier to handle and to store. Moreover, it adds to the strength of EP(D)M vulcanizates in those cases, where carbon blacks cannot be used as reinforcing fillers and only less reinforcing light colored fillers can be applied. On the other side, these blocky structures or crystallinity have a detrimental effect on the rubbery properties of the polymer, particularly at subambient temperatures. They enhance the thermoplastic nature of the polymer.

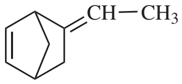
In addition to the ethylene/propylene ratio, the average molecular weight of the rubber is controlled by polymerization variables. Whereas the polymer chemist generally measures the average molecular weight by gel permeation chromatography or intrinsic viscosity, the rubber compounder uses Mooney viscosity for practical purposes. The ethylene–propylene rubbers are controlled within a range of raw polymer Mooney viscosities that has been found to fit the various processing and applications requirements of the rubber industry and includes most other commercial synthetic rubbers. Mooney viscosity of EPM and EPDM is preferably measured 4 min after a 1-min warm-up at 125°C (2). The measurement is expressed as ML $(1+4)$ at 125°C and ranges between $\sim$10 and 90. Grades with higher molecular weight are also produced, but are generally extended with either paraffinic or sometimes naphthenic oil to reduce the Mooney viscosity for processing purposes.

The structure of EPM shows it to be a saturated synthetic rubber. There are no double bonds in the polymer chain as there are in the case of natural rubber and most of the common commercial synthetic rubbers. The main-chain unsaturation in these latter materials introduces points of weakness. When exposed to the degrading influences of light, heat, oxygen, and ozone, the unsaturated rubbers tend to degrade through mechanisms of chain scission and cross-linking at the points of carbon–carbon unsaturation. Since EPM does not contain any carbon–carbon unsaturation, it demonstrates an inherently higher resistance to degradation by heat, light, oxygen, and, in particular ozone.

The double bonds in natural rubber and the common polydiene synthetic rubbers are essential to their curing. They are commonly vulcanized into useful rubber products by using conventional chemical accelerators and sulfur. As a saturated elastomer, EPM cannot be cured or cross-linked using these chemicals pertinent to the unsaturated rubbers, but can be vulcanized using peroxides.

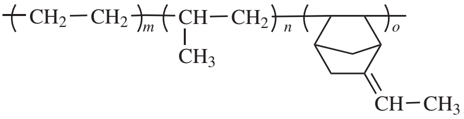
EPDM is a more commercially attractive product that retains the outstanding performance features, of heat, oxygen, and ozone resistance. It includes some carbon–carbon unsaturation—pendent to the main chain—from a small amount of an appropriate third nonconjugated diene monomer to accommodate it to conventional sulfur vulcanization chemistry. A great variety of dienes were investigated in the past as third monomers (3), of which only two are used commercially at present in significant quantities. A characteristic of the structure of commercially used third monomers is that the two double bonds are nonconjugated. They are cyclic and bicyclic dienes with a bridged ring system.

The most commonly used third monomer is 5-ethylidene-2-norbornene [16219-75-3], or ENB (**2**).



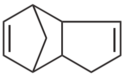
(**2**)

which is polymerized into the ethylene–propylene chain to give poly(ethylene-*co*-propylene-*co*-ENB) [25038-36-2] (**3**). The norbornene double bond in the bridged, or strained, ring is the more active with respect to polymerization and the five-membered ring with its double bond is left as a pendent substituent to the main polymer chain.



(**3**)

Less commonly used as third monomer is dicyclopentadiene [77-73-6], or DCPD, for which, due to its symmetrical shape, the tendency of the second double bond to take part in the polymerization process is more pronounced than for ENB. This is one of the reasons for the formation of long-chain branches. The resulting product is poly(ethylene-*co*-propylene-*co*-DCPD) [25034-71-3] (**4**).



(**4**)

Formerly, one manufacturer of EPDM used a noncyclic diene: 1,4-hexadiene [592-45-0], but this was displaced by ENB because of the latter's superior performance both in incorporation during polymerization and in vulcanization. EPDM containing hexadiene is not commercially available anymore.

Recently, the development of commercial EPDMs with 5-vinyl-2-norbornene [3048-64-4], or VNB, a precursor in the synthesis of ENB, as third monomer has been reported, aiming at a higher vulcanization yield with peroxide

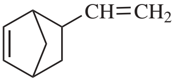
Table 1. **Properties of Raw Ethylene–Propylene–Diene Co- and Terpolymers**

Property	Value
specific gravity	0.86–0.88
appearance	glassy-white
ethylene/propylene ratio by wt	
amorphous types	45/55
crystalline or sequential types	80/20
onset of crystallinity,°C	
amorphous types °C[a]	Below −50
crystalline types	below ∼30
glass transition temperature, °C[a]	−45 to −60
heat capacity, kJ/(kg · K)	2.18
thermal conductivity, W/(m · K)	0.335
thermal diffusivity, m/s	1.9×10^{-5}
thermal coefficient of linear expansion per°C	1.8×10^{-4}
Mooney viscosity, ML (1 + +4) 125°C [b]	10–90

[a] Dependent on third monomer content.

[b] Oil extended grades, when viscosity >100 for the raw polymer.

curatives, relative to ENB- or DCPD-containing EPDMs (4):



(5)

Also other third monomers are being proposed for better or faster vulcanization with sulfur or peroxide curatives, but have not reached commercial status yet (5).

Combinations of more than one-third monomer are also applied. The amount of third monomer in general purpose grades is ∼1 mol% or ∼4 wt%. For faster curing grades, this amount may be as high as 2 mol% or ∼8 wt%, and there is a tendency to go to even higher amounts. At equal amounts of a third monomer (in mol%) DCPD as a third monomer leads to polymers that require about twice as long a curing time for sulfur vulcanization than ENB (6). Because of the consequent economic benefits in processing, ENB is mostly preferred as the third monomer.

As EPM, EPDM shows outstanding resistance to heat, light, oxygen, and ozone because one double bond is lost when the diene enters the polymer and the remaining double bond is not in the polymer backbone but is external to it. Properties of typical EPDM rubbers are shown in Table 1.

3. Manufacture

The two principal raw materials for EPM and EPDM, ethylene [74-85-1] and propylene [115-07-1], both of which are gases, are available in abundance at high purity. Propylene is commonly stored and transported as a liquid under pressure. Although ethylene can also be handled as a liquid, usually at cryogenic temperatures, it is generally transported in pipelines as a gas. Of the third monomers, DCPD is also available in large quantities (see CYCLOPENTADIENE AND DICYCLOPENTADIENE). ENB is produced in a two-step process: a Diels-Alder reaction of cyclopentadiene (in equilibrium with DCPD) and butadiene; the resulting product VNB is rearranged to ENB via proprietary processes.

EPM and EPDM rubbers are produced in continuous processes. All EPDM manufacturing processes are highly proprietary and differ greatly between various suppliers. A great series of patents covers the many details of various processes.

3.1. Solution Process. Most widely used are solution processes, in which the polymer produced is in the dissolved state in a hydrocarbon solvent (eg, hexane). The choice of catalyst system is determined, among other things, by the nature of the third monomer and factors such as the width of the molecular weight distribution to be realized in the product. A number of articles review the influence of catalyst systems on the structural features of the products obtained (3,7–9). The catalyst comprises two main components: first, a transition metal halide, such as $TiCl_4$, VCl_4, $VOCl_3$, etc, of which $VOCl_3$ is the most widely used; second, a metal alkyl component such as $(C_2H_5)_2AlCl$ diethylaluminum chloride, or monoethylaluminum dichloride, $(C_2H_5)AlCl_2$, or most commonly a mixture of the two, ie, ethylaluminum sesquichloride, $(C_2H_5)_3Al_2Cl_3$.

Under polymerization conditions, the active center of the transition-metal halide is progressively reduced to a lower valence state, ultimately to V^{2+}, which is unable to polymerize monomers other than ethylene. The ratio V^{3+}/V^{2+}, in particular, under reactor conditions is a measure for catalyst activity to produce EPM and EPDM species. This ratio V^{3+}/V^{2+} can be upgraded by adding a promoter to the reaction mixture, that causes oxidation of V^{2+} to V^{3+}. Examples of promoters in the earlier literature were carbon tetrachloride, hexachlorocyclopentadiene, trichloroacetic ester, and benzotrichloride (10). Later, butyl perchlorocrotonate and other proprietary compounds were introduced (11–13).

For EPDM, long-chain branching and gel can be introduced during the polymerization. This may happen by at least two mechanisms; by Ziegler polymerization through both double bonds of the diene third monomer or through cationic coupling of pendent double bonds (14,15). For Ziegler polymerization to occur through both double bonds, both must be accessible to the polymerization catalyst. The strained five-membered ring in the norbornene structures is highly reactive and is rapidly incorporated in the polymer chain. Reaction of the second double bond results in a tetra-functional branch point in the EPDM backbone. The ethylidene double bond in ENB is so sterically hindered that Ziegler polymerization of the second double bond is not possible under the production conditions for EPDM. Conversely, the use of a diene, such as vinyl-norbornene and to a lesser extent dicyclopentadiene, can result in substantial amounts of branching due to the accessibility of the vinyl group in VNB to the polymerization catalyst and the second five-membered ring in DCPD.

During Ziegler polymerization it is also possible to couple the chains cationically through pendent olefinic groups (14). The extent of this reaction strongly depends on the Lewis acidity of the catalyst components. In general, the amount of cationic coupling decreases as the aluminum alkyl cocatalyst is varied from $(C_2H_5)AlCl_2$ through $(C_2H_5)_2AlCl$ to triethyl aluminum. Particularly, ENB tends to cationically couple with another ENB molecule built into another polymer chain, thereby creating another form of long-chain branches. In the presence of Lewis bases, this amount of branching is markedly reduced. By the same mechanism, the coordination Ziegler-Natta catalysts are extremely sensitive to water and other polar materials, as they decompose the catalyst to Lewis acids. Only a few parts per million of water are allowed in any of the feed streams. Extended forms of long-chain branching finally lead to gel formation, which damage the processability of the products in the final application.

In the solution process making use of Ziegler-Natta catalysis, dry solvent, ethylene, propylene, diene, and catalyst and cocatalyst solutions are continuously and proportionately fed to one or a series of polymerization vessels. Polymerization of individual molecules, or chains, is extremely fast, and a few seconds at most is the average life of a single growing polymer molecule from initiation to termination. The polymerization is highly exothermic. The heat must be removed, since the polymerization temperature (∼35°C) has to be kept within narrow limits to ensure a product with the desired average molecular weight and molecular weight distribution. Therefore, these processes can be grouped into those in which the reactor is completely filled with the liquid phase, and those in which the reactor contents consist partly of gas and partly of a liquid phase. In the first case, the heat of reaction (∼2500 kJ/kg EPDM) is removed by means of cooling systems, either external cooling of the reactor wall or deep cooling of the reactor feed, or combinations. In the second case, the evaporation heat from unreacted monomers also removes most of the heat of reaction. Most commonly, hydrogen is used as the chain-transfer agent to regulate the average molecular weight.

As the polymer molecules form and dissociate from the catalyst, they remain in solution. The viscosity of the solution increases with increasing polymer concentration. As the EPDM polymerization is a continuous process run in stirred reactor(s) at high conversion and rubber solids concentration, the practical upper limit of solution viscosity is dictated by considerations of heat transfer, mass transfer, and fluid flow. At a rubber solids concentration of 5–10%, depending on the molecular weight of the polymer produced, a further increase in the solution viscosity becomes impractical, and the polymerization is stopped by killing the catalyst. This is usually done by vigorously stirring the solution with water. If this is not done quickly, the unkilled catalyst continues to react, leading to above described uncontrolled side reactions, resulting in an increase in Mooney viscosity called Mooney Jumping.

The reactivity of ethylene is high, whereas that of propylene is low and the various dienes have different polymerization reactivities. The viscous rubber solution contains some unpolymerized ethylene, propylene, unpolymerized diene, and ∼5–10% EPDM, all in homogeneous solution. This solution is passed continuously into a flash tank, where reduced pressure causes most of the unpolymerized monomers to escape as gases, which are collected and recycled.

Catalyst residues, particularly vanadium and aluminum, have to be removed as soluble salts in a water-washing and decanting operation. Vanadium residues, and to a lesser extent chlorine residues in the finished products are kept to a few parts per million (ppm), because these may have a strong negative influence on the ageing characteristics of the EPDM. If oil-extended EPDM is the product, a metered flow of oil is added at this point. In addition, antioxidant, typically of the hindered phenol type, is added at this point.

The rubber is then separated from its solvent by steam stripping. The viscous cement is pumped into a violently agitated vessel partly full of boiling water. The hexane flashes off and, together with water vapor, passes overhead to a condenser and to a decanter for recovery and reuse after drying. Residual unpolymerized ethylene and propylene appear at the hexane condenser as noncondensibles, and are recovered for reuse after drying. Unreacted diene may be recovered with the solvent and further fractionated for purification and recycling. The polymer, freed from its carrier solvent, falls into the water in the form of crumb.

The rubber crumb, now a slurry in hot water, is pumped over a shaker screen to remove excess water. The dewatered crumb is fed to the first stage of a mechanical-screw dewatering and drying press. Here, in an action similar to a rubber extruder, all but 3–6% of the water is expressed as the rubber is pushed through a perforated plate by the action of the screw. The cohesive, essentially dry rubber then passes into the second-stage press. This is similar to the first-stage dewatering machine, except that the mechanical action of the screw causes the rubber in the barrel to heat up to temperatures as high as 150°C. This rubber is extruded through a perforated die plate at the end of the machine, the small amount of remaining water is flashed off as a vapor, and the nearly dry rubber crumb is finally subjected to air-drying in a fluid bed or tunnel drier at temperatures of $\sim$110°C to reduce the level of remaining volatile matter to <0.7, preferably <0.3 wt%. This EPDM crumb is then continuously weighed, pressed into bales, and packaged for storage and shipment. Highly crystalline or sequential types are sufficiently form-stable to be produced in the form of pellets by a direct extruder operation, if necessary with application of a small amount of a separating or partitioning agent.

3.2. Slurry Process. In this process, a nonsolvent diluent and an operating temperature are used so that the monomers are soluble, but the polymer is not. The diluent must also be inert with respect to the catalyst components. As the diluent the monomer propylene is used. It is of course not an inert substance, but its conversion level is low enough to allow for its use as a nonsolvent diluent.

The advantages of this process reside in the low viscosity of the dispersion of precipitated crumby EPDM particles in the low viscosity propylene medium. This bears on heat transfer, solvent recycle capacity, and slurry transport problems. For example, temperature control of the reactor can more readily be effected by controlled evaporation of the propylene and to a lesser extent ethylene. Another advantage lies in much higher production rates due to higher slurry concentrations (20–40%) compared to the solution process. The slurry process also allows for higher molecular weight EPDMs, because a viscosity rise of the solution does not apply in this case. Another advantage is the lower catalyst level needed in comparison with the solution process, because of the great abundance of propylene as the monomer being the diluent at the same time.

The disadvantage of the slurry process lies in the problems related to the removal of catalyst residues. Catalyst tends to become occluded in the precipitated EPDM. Although the slurry process has lower catalyst consumption, the problem with removing catalyst residues leads to higher catalyst residues in the final polymer. These catalyst residues then have the tendency to become involved in intermolecular branching reactions of the type described above, which increases the probability of premature cross-linking reactions (= gelation) during the killing step and during storage. Further, these catalyst residues contribute significantly to the degradation of rubber vulcanizate properties upon heat ageing.

The greatest benefit of this technology is achieved if the steam-stripping operation is replaced by a progressive series of degassing operations, vessels, and extruders, for cost reasons and to do away with water in the whole operation (16).

3.3. Gas-Phase Process. Another noteworthy development in the field of EPDM manufacture is the so-called gas-phase process, as an extension of the well-known gas-phase processes for polyethylene and polypropylene (17). The process uses a fluid-bed reaction vessel to which gaseous ethylene, propylene, and third monomer ENB are fed. The reaction heat is removed through circulation of the gas, which serves to fluidize the polymer bed as well as to act as the raw material for the polymerization. In fact, this process can be pictured as a continuous percolating fountain of small EPDM granules, coated *in situ* with a steady stream of fluidization aid in order to prevent sticking together of the granules. As fluidization aid finely ground furnace carbon black is being used up till quantities of ~16 wt% or 20 phr (parts per hundred rubber) (18). This carbon black remains in the EPDM. The gas-phase technology is solvent- or diluent-free, so no stripping is required. The nonconverted monomers are recovered by purging and are recycled. Drying and finishing is therefore not applicable to gas-phase produced EPDM as no water is involved in the process. The product is delivered in granular form, as directly recovered from the reactor.

Also, this process offers the possibility of greatly reduced finishing operations and consequent cost savings. The gas-phase process does not permit catalyst removal. This is both an advantage in cost and a disadvantage in terms of catalyst residue. These polymers will have a high catalyst residue as long as conventional Ziegler-Natta catalysts are used. It may be possible to lower catalyst residue if metallocene catalysts can be adapted for this process (see next section). Note that removal of unreacted ENB from the gas-phase product is not a trivial matter. An additional purging step is needed to remove the third monomer (19). The question applies, whether this technology will offer a comparable flexibility in due course to make the wide variety of EPDM molecular structures that have been designed over the years to comply with market requirements for the various applications of EPDM rubber.

3.4. New Catalysis Technologies Using Metallocenes. In past years, a very rapid development of single-site metallocene catalysts has taken place, primarily for polyethylene and polypropylene, but with spin-offs to EPDM-manufacture (20–23). In combination with methylaluminoxane or boron-fluorine compounds as the cocatalysts, these metallocene catalysts show an enormous increase in activity relative to the traditional Ziegler-Natta

Table 2. **EPM/EPDM Rubber Production Capacities**[a]

Manufacturer	Country	Capacity, t/yr
Bayer/Polysar	U.S. and Germany	110,000
DSM Elastomers	U.S., the Netherlands, Brazil, Japan	216,000
Du Pont Dow	U.S.	90,000
EniChem Elastomeri	Italy	85,000
ExxonMobil Chemical	U.S., France	174,000
Herdilia	India	10,000
Japan Synthetic Rubber	Japan	65,000
Korea Polychem	South Korea	40,000
Mitsui Petrochemcial	Japan	60,000
Sumitomo Chemical	Japan	35,000
Union Carbide	U.S.	90,000
Uniroyal Chemical Co.	U.S.	93,000
Others		30,000

[a] Ref. 24.

catalysts. They show a greatly increased catalyst activity for higher alpha-olefins. In addition, they keep their activity at higher polymerization temperatures than commonly employed for Ziegler-Natta catalysts. Metallocene catalysts usually give a different comonomer distribution than traditional Ziegler-Natta catalysts.

Various advantages are claimed for metallocene catalyst technology: such a low catalyst consumption that catalyst residues do not need to be removed from the polymer after deactivation. Further, the higher operating temperature of the catalyst allows for a higher temperature regime of the total process, resulting in a reduction of cooling operations. It also allows for higher solution concentrations with consequent lower stripping energies involved, particularly if this technology is combined with an older technology where the steam stripping operation is replaced by the water-free finishing mentioned before (16).

In spite of the many advantages claimed for this technology, note that many of these are offset by various countereffects: the need for higher pressure operations and consequent additional investments if the increased temperature regime of this technology is to be exploited; the need for highly purified raw materials, because metallocene catalysts are much more sensitive to poisoning by adverse compounds than the traditional Ziegler-Natta catalysts. Metallocene technology is still at its early beginning in the industrial production of EPDM. Much has still to be developed in the field of metallocene catalysis in order to fully exploit the possibilities to produce the wide variety of EPDM molecular structures, which are dictated by the market requirements.

3.5. Production Capacities. Production capacities of EPM/EPDM of the largest manufacturers are listed in Table 2 (24).

4. Compounding

EPM/EPDM grades have to be compounded with reinforcing fillers if high levels of mechanical properties are required. The EPM/EPDM grades with a high

Mooney viscosity and a high ethylene content are particularly capable of accepting high loadings of filler, eg, 200–400 parts per hundred parts rubber (phr), and plasticizer, eg, 100–200 phr, and still giving useful vulcanizates.

Carbon blacks are usually used as fillers. The semireinforcing types, such as FEF (fast extrusion furnace) and SRF (semi-reinforcing furnace) give the best performance (see CARBON, CARBON BLACK). To lower the cost and improve the processibility of light colored compounds, or to lower the cost of black compounds, calcined clay or fine-particle-size calcium carbonates are used.

The most widely used plasticizers are paraffinic oils. For applications that specify high use temperatures, or for peroxide cures, paraffinic oils of low volatility are definitely recommended. Because paraffinic oils may tend to exudation at low temperatures from EPDM vulcanizates, or from high ethylene EPDMs, they are sometimes blended with naphthenic oils. On the other hand, naphthenic oils interfere with peroxide cures. Aromatic oils reduce the mechanical properties of vulcanizates, and also interfere with peroxide cures. Therefore, they are generally not recommended for EPM/EPDM.

Although EPM can only be cross-linked with peroxides, peroxide, or sulfur plus accelerators, even other vulcanization systems like resins can be used for EPDM. The choice of chemicals used in an EPDM vulcanizate depends on many factors, such as mixing equipment, mechanical properties, cost, safety, and compatibility. In sulfur vulcanization, ENB-containing EPDM is about twice as fast as DCPD-containing EPDM at the same level of diene unsaturation. If peroxide cures are required for better heat stability, DCPD-containing EPDM gives higher cure states than EPM. The reactivity of ENB–EPDM is a little lower in peroxide cures. For peroxide cures of EPM and to a lesser degree of DCPD–EPDM, activators, also called coagents, such as a small amount of sulfur, acrylates, allyl-cyanurates, or maleimides are also needed to increase the cross-link density.

Because of the low level of C=C unsaturation in the polymer compared to, eg, natural rubber and SBR, EPDM needs high levels of highly active accelerators for sulfur vulcanization (see RUBBER CHEMICALS; RUBBER COMPOUNDING). Usually, combinations of benzothiazole derivatives or sulfenamides with so-called ultraaccelerators like thiuram compounds or dithiocarbamates are used. Because of the limited solubility of these various accelerators in EPDM vs the large quantities needed to obtain a sufficient level of vulcanization, an EPDM compound often contains four or more accelerators next to elemental sulfur; every accelerator obeys its own maximum dosage related to its solubility limit. Modern legislation puts much emphasis on the prevention of the formation of carcinogenic secondary *N*-nitrosamines as by-products of sulfur vulcanization. This limits the choice of possible accelerators to those that have no secondary amine groups embedded in their chemical structure or may contain residual secondary amines dating back to their synthesis: Usually the ultraaccelerators mentioned above. In such cases, it is exceptionally difficult to develop a proper vulcanization system. New ultraaccelerator systems like dibenzyl dithiocarbamate or tetrabenzyl thiuramdisulfide may be used in such cases, where the dibenzyl-amine embedded in these compounds is an exception in that it does not generate *N*-nitrosamines carcinogenic to human beings.

In Table 3, a few examples are given of typical EPDM recipes with pertinent cured properties.

Table 3. **Typical EPM/EPDM Compounding Recipes for a 60° Shore A Solid Application**

Components	Sulfur cure[a]	Low nitrosamine sulfur cure[a]	Peroxide cure[b]
EPDM, 4 wt% ENB, Keltan[c] 4802	100	100	
EPDM, 4 wt% DCPD, Keltan[c] 720			100
zinc oxide	5	5	
stearic acid	1	2	0.5
carbon black, N 683	105		
carbon black, N 765		95	
carbon black, N 550			110
$CaCO_3$ whiting	50		80
oil, Sunpar[d] 2280	70	50	–
oil, Sunpar[d] 150			75
CaO, 75% paste	8	6	6
poly(ethylene glycol) 4000			2
N-cyclohexylbenzothiazole-2-sulfenamide, 70%	2.1		
zinc dibutyldithiocarbamate, 80%	2.5		
ethylthiurea	1.0		
tellurium diethyl dithiocarbamate, 75%	0.63		
tetramethylthiuram disulfide, 50%	1.0		
zinc dialkyl dithiophosphate, 67%		2.5	
dithiodiacaprolactam, 80%		1.0	
zinc dibenzyldithiocarbamate, 70%		1.0	
2-mercaptobenzothiazole, 80%		1.9	
sulfur	1.5	1.5	
1,3-bis(*tert*-butylperoxy-isopropyl)-benzene, 40%			6
1,1-di-*tert*-butylperoxy-3,3,5-trimethylcyclohexane, 40%			3
trimethylolpropane trimethacrylate			1
	Properties		
compound Mooney[e] ML (1 + 4) 100°C	83	92	44
profile vulcanization	UHF/hot air	UHF/hot air	LCM
temperature,°C/time, s	250/160	250/215	240/60
hardness[f], IRHD	64	60	61
tensile strength[g], N/mm^2	10.0	13.7	7.7
elongation at break[g], %	400	460	330
compression set[h], 22h/70°C, %	13	19	
compression set[h], 22h/100°C, %			16

[a] Automotive profile, phr.
[b] Building profile, phr.
[c] Keltan is a registered trademark of DSM Elastomers.
[d] Sunpar is a registered trademark of Sun-Oil Co.
[e] ISO 289.
[f] ISO 48.
[g] ISO 37.
[h] ISO 815.

5. Processing

Only compounds of low Mooney EPM or EPDM grades can be mixed on open mills. EPM/EPDM compounds are therefore almost exclusively mixed in internal mixers. In the latter case, the cycles and dump temperatures are about the same as would be used for SBR. The mechanisms involved in the mixing of EPM/EPDM as a function of molecular structural parameters, in particular molecular weight, molecular weight distribution (25,26), and long-chain branching (27,28), have been studied in great detail. It turns out that the speed of carbon black dispersion is greatly dependent on these parameters within practical mixing cycles. The molecular weight distribution and the level of long-chain branching of the EPM/EPDM rubber should be suitably chosen, depending on the desired degree of carbon black dispersion in the application concerned: a narrow distribution for average carbon black dispersions, and a broad distribution for applications requiring excellent carbon black dispersions. The EPDMs with controlled long-chain branching, combining a narrow molecular weight distribution with a high level of long-chain branching, or with bimodal molecular weight distributions have proven to be particularly beneficial for ease of processing, quality of carbon black dispersion, production consistency, and good mechanical properties as a result of this (24,26,29).

For EPM/EPDM grades with high ethylene contents, the disintegration of the bales is a dominating factor. If the polymer is in the form of a compact bale, it is difficult to disintegrate the rubber sufficiently to form a fine dispersion with the other compounding ingredients, so that the shearing action of the mixer can disperse the ingredients evenly. In such cases, particulate forms of the rubber such as crumbs, pellets, and friable bales shorten the mixing cycle considerably.

In general, EPM/EPDM compounds can be extruded easily on all commercial rubber extruders. Also, for extrusion purposes, both long-chain branching and broad molecular weight distribution have a positive effect (30). The higher shear thinning character of these polymers permits higher extrusion speeds, while the presence of branched molecules or molecules with very high molecular weight increase resistance to collapse via chain entanglements, ie, the tendency of extruded profiles of complicated shape to deform under the influence of gravity between the extruder exit and the vulcanization line and during the early stages of vulcanization. Furthermore, EPDM compounds can be calendered both as unsupported sheeting and onto a cloth substrate.

EPM/EPDM compounds are cured on all of the common rubber-factory equipment: compression molding, transfer molding, steam cure, hot-air cure, and injection molding are all practical. Where profile extrusion is the most important shaping technique, molten-salt (LCM) cure, and ultra high frequency (UHF) electromagnetic heating followed by hot air are the most common vulcanization techniques. UHF heating, however, is only applicable for black-filled compounds. Further, in the case of peroxide curing, open-air vulcanization in the presence of free oxygen in UHF and hot air is problematic, because of surface degradation due to peroxide radicals in combination with oxygen taken from the air. This, however, is an intrinsic problem of curing with peroxides, occurring with all other rubbers as well.

6. Properties of EPM and EPDM Vulcanizates

Mechanical properties depend considerably on the structural characteristics of the EPM/EPDM and the type and amount of fillers in the compound. A wide range of hardnesses can be obtained with EPM/EPDM vulcanizates. The elastic properties are by far superior to those of many other synthetic rubber vulcanizates, particularly of butyl rubber, but they do not reach the level obtained with NR or SBR vulcanizates. The resistance to compression set is surprisingly good, in particular for EPDM with a high ENB content and cross-link density or when cured with peroxide.

The resistance to heat and aging of optimized EPM/EPDM vulcanizates is better than that of SBR and NR. Peroxide-cured EPM can, eg, be exposed to 150°C for 1000 h without significant hardening. Particularly noteworthy is the ozone resistance of EPM/EPDM vulcanizates. Even after exposure for many months to ozone-rich air of 100 pphm, the vulcanizates will not be seriously harmed. EPM/EPDM vulcanizates have an excellent resistance to chemicals, such as dilute acids, alkalis, alcohol, etc, which is in contrast to the resistance to aliphatic, aromatic, or chlorinated hydrocarbons. EPM/EPDM vulcanizates swell considerably in these nonpolar media.

The electrical-insulating and dielectric properties of the pure EPM/EPDM are excellent, but in compounds they are also strongly dependent on the proper choice of fillers and their dispersion. The electrical properties of vulcanizates are also good at high temperatures and after heat aging. Because EPM/EPDM vulcanizates absorb little moisture, their good electrical properties suffer minimally when they are submerged in water.

7. Health and Safety Factors

EP(D)M is not classified as a hazardous material. It is not considered carcinogenic according to Occupational Safety and Healthy Administration (OSHA) Hazard Communications Standard and IARC Monographs. Commonly used paraffinic extender oils contain <0.1 wt% polynuclear aromatic compounds (PNAs).

In handling EPM/EPDM, normal industrial hygienic procedures should be followed. It is advisable to minimize skin contact. The use of EPM/EPDM is permitted for food contact under the conditions given in the respective FDA paragraphs: §177.1520 for olefin polymers, and §177.2600 for rubber articles intended for repeated contact with food.

8. Uses

Expressed as percentages of total annual synthetic rubber consumption worldwide, EPM and EPDM have increased from 0% in 1964 to 8.9% in 2000, as shown in Table 4. Both EPM and EPDM have still showed a steady growth over the years. Part of this growth comes from replacement of the general purpose rubbers such as NR and SBR, by virtue of their better ozone and thermal resistance.

The main uses of EPM and EPDM are in automotive applications such as weatherstrip profiles, (radiator) hoses, and seals; in building and construction as sealing profiles, roofing foil, and seals; in cable and wire as cable insulation and jacketing; and in appliances as a wide variety of mostly molded articles.

Table 4. **Worldwide EPM and EPDM Consumption as Percentage of Total Rubber Consumption**[a]

Year	EPM/EPDM, t/yr	EPM/EPDM consumption, %[b]
1964		0.0
1970	89,000	
1980	328,000	
1990	609,000	
2000	919,000	8.9

[a] Ref. 24.

[b] Of total synthetic rubber consumption.

Another application for EPDM is in blends with general purpose rubbers. Ozone resistance is thus provided, with the host rubber comprising the principal portion of the blend. This technique has been applied in enhancing the ozone and weathering resistance of tire sidewalls and cover strips. This use accounts for essentially all EPDM consumption in tires, as the dynamic and wear properties of EPDM do not favor its use for the carcass and tread parts of the tire. EPDM compounds are, moreover, nontacky, whereas tackiness is a prerequisite for building tires. Although this can be solved to some extent, there are no all-EPDM tires currently being produced. Economic factors favor the use of natural and general purpose synthetic rubbers in tires.

Considerable amounts of EPM and EPDM are also used in blends with thermoplastics, eg, as impact modifier in quantities up to ~25% wt/wt for polyamides, polystyrenes, and particularly polypropylene. The latter products are used in many exterior automotive applications such as bumpers and body panels. In blends with polypropylene, wherein the EPDM component may be increased to become the larger portion, a thermoplastic elastomer is obtained, provided the EPDM phase is vulcanized during the mixing with polypropylene (dynamic vulcanization) to suppress the flow of the EPDM phase and give the end product sufficient set (31).

One of the more interesting uses of EPM is as an additive to lubricating oils. The addition of relatively small quantities of EPM to lubricating oil raises the viscosity of the solution to an overall less temperature-dependent level. Due to the thinning character of its molecular chains with decreasing temperature, the natural increase of oil viscosity with decreasing temperature is thereby largely compensated. The leading polymer for this application is EPM because of its excellent heat and shear stability under the operating conditions of automobile engines (32).

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