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 Natta and co-workers (1). A generic formula for EPM and EPDM may be given as follows, where $m = \sim 1500$ ($\sim 60$ mol%), $n = \sim 975$ ($\sim 39$ mol%), $o = \sim 25$ for EPDM ($\sim 1$ mol%) and 0 for EPM in an average amorphous molecule, and the comonomers are preferably statistically distributed along the molecular chain.

\[
\left( -\text{CH}_2\text{CH}_2 \right)_m \left( -\text{CH} - \text{CH}_2 \right)_n \left( -\text{CH}_3 \right)_o
\]

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). Secondly, 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 more than 40 years, the technology concerning these products, both their production and their applications, is still very much under development.

**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 or 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 wt% 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 loses 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. The higher the ethylene/propylene ratio, the more pronounced is this tendency. These ethylene sequences impart a level of crystallinity to the EP(D)M rubbers of less than 1% at room temperature for 50:50 ethylene/propylene ratio—also designated as amorphous EP(D)M rubber—till above 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. While 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 (2,3). The measurement is expressed as ML (1+4) at 125°C and ranges between ca 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, or also commonly called vulcanization into useful rubber products 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. It can be vulcanized using peroxides. EPDM is a more commercially attractive product that retains the outstanding performance features, ie, heat, oxygen, and ozone resistance. It includes some carbon–carbon unsaturation—pendent to the main chain—from a small amount of an appropriate nonconjugated diene monomer to accommodate it to conventional sulfur vulcanization chemistry. A great variety of dienes were investigated in the past as third monomers (4), 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] [2], or ENB:

\[
\text{CH} = \text{CH}_3
\]

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.

\[
\left(\text{CH}_2 = \text{CH}_2\right)_m \left(\text{CH} = \text{CH}_2\right)_n \left(\text{CH} = \text{CH}_3\right)_o
\]

Less commonly used as third monomer is dicyclopentadiene [77-73-6] [4], or DCPD, for which, because of 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].

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] (5), a precursor in the synthesis of ENB, as third monomers has been reported, aiming at a higher vulcanization yield with peroxide curatives, relative to ENB- or DCPD-containing EPDMs (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 (6).

Combinations of more than 1 third monomer are also applied. The amount of third monomer in general-purpose grades is about 1 mol% or ca 4 wt%. For faster curing grades this amount may be as high as 2 mol% or ca 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 which require about twice as long a curing time for sulfur vulcanization than ENB (7). Because of the consequent economic benefits in processing, ENB is mostly preferred as the third monomer.

Both EPDM and EPM show 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 external to it. Properties of typical EPDM rubbers are shown in Table 1.

**Manufacture**

The two principal raw materials for EPM and EPDM, ethylene [74-85-1] and propylene [115-07-1], both 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
Table 1. Properties of Raw Ethylene–Propylene–Diene Co- and Terpolymers

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity</td>
<td>0.86–0.87</td>
</tr>
<tr>
<td>Appearance</td>
<td>Glassy–white</td>
</tr>
<tr>
<td>Ethylene/propylene ratio by wt</td>
<td></td>
</tr>
<tr>
<td>Amorphous types</td>
<td>50/50</td>
</tr>
<tr>
<td>Crystalline or sequential types</td>
<td>75/25</td>
</tr>
<tr>
<td>Onset of crystallinity, °C</td>
<td></td>
</tr>
<tr>
<td>Amorphous types</td>
<td>Below −50</td>
</tr>
<tr>
<td>Crystalline types</td>
<td>Below ca 30</td>
</tr>
<tr>
<td>Glass-transition temperature, a °C</td>
<td>−45 to −60</td>
</tr>
<tr>
<td>Heat capacity, kJ/(kg·K)</td>
<td>2.18</td>
</tr>
<tr>
<td>Thermal conductivity, W/(m·K)</td>
<td>0.335</td>
</tr>
<tr>
<td>Thermal diffusivity, m/s</td>
<td>$1.9 \times 10^{-5}$</td>
</tr>
<tr>
<td>Thermal coefficient of linear expansion per °C</td>
<td>$1.8 \times 10^{-4}$</td>
</tr>
<tr>
<td>Mooney viscosity, ML (1 + 4) 125 °C b</td>
<td>10–90</td>
</tr>
</tbody>
</table>

a Dependent on third monomer content.
b Oil extended grades, when viscosity > 100 for the raw polymer.

also available in large quantities. ENB is produced in a two-step process: a Diels–Alder reaction of cyclopentadiene (in equilibrium with DCPD) and butadiene; the resulting product vinyl-norbornene (VNB) is rearranged to ethylidene norbornene 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.

**Solution Process.** Most widely used are solution processes, in which the polymer produced is in the dissolved state in a hydrocarbon solvent (e.g., 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 (4,8–10). The catalyst comprises two main components: first, a transition metal halide, such as TiCl₄, VCl₄, VOCl₃, of which VOCl₃ is the most widely used; second, a metal alkyl component such as diethylaluminum chloride, (C₂H₅)₂AlCl, or monoethylaluminum dichloride, (C₂H₅)AlCl₂, or most commonly a mixture of the two, i.e., ethylaluminum sesquichloride, (C₂H₅)₃Al₂Cl₃.

Under polymerization conditions, the active center of the transition-metal halide is progressively reduced to a lower valance state, ultimately to V²⁺, 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 to the reaction mixture a promoter, which causes oxidation of V²⁺ to V³⁺. Examples of promoters in the earlier literature were carbon tetrachloride, hexachlorocyclopentadiene, trichloroacetic ester, and benzotrichloride (11). Later, butyl perchlorocrotonate and other proprietary compounds were introduced (12–14).
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 (15,16). For Ziegler polymerization to occur through both double bonds, both must be accessible to the polymerization catalyst. The strained five-member 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 tetrafunctional 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 VNB and to a lesser extent DCPD, can result in substantial amounts of branching because of the accessibility of the vinyl group in VNB to the polymerization catalyst and the second five-member ring in DCPD (see ZIEGLER–NATTA CATALYSTS).

During Ziegler polymerization it is also possible to couple the chains cationically through pendent olefinic groups (15). 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 (C₂H₅)₂AlCl₂ through (C₂H₅)₃AlCl 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 damages 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 (ca 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 (ca 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 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 un killed 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 about 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 and chlorine, 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, 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 ca 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.

**Slurry Process.** In this process a nonsolvent diluent and an operating temperature are used so that the monomers are soluble, but not the polymer. The diluent must also be inert with respect to the catalyst components.
As 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 levels needed in comparison with the solution process, because the great abundance of propylene as monomer being 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 vulcanizates 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 (17).

**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 (18). 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 about 16 wt% or 20 phr (parts per hundred rubber) (19). This carbon black remains in the EPDM. The gas-phase technology is solvent- or diluent-free, and 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). It should also be noted 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 (20). The question applies, whether this technology will offer a comparable flexibility in due course to make the wide variety of EPDM molecular structures, which have been designed over the years to comply with market requirements for the various applications of EPDM rubber.

**New Catalysis Technologies Using Metallocenes.** Through the last 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 (21–24). In combination with methylaluminoxane as the cocatalyst, these metallocene catalysts show an enormous increase in activity relative to the traditional Ziegler–Natta catalysts. They show a greatly increased catalyst activity for higher alpha-olefins, like the third monomers. In addition, they keep their activity at higher polymerization temperatures than commonly employed for Ziegler–Natta catalysts. Metallocene catalysts (qv) usually give a different comonomer distribution than traditional Ziegler–Natta catalysts (qv).

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 (17).

In spite of the many advantages claimed for this technology, it has to be noted 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 these catalysts are much more sensitive to poisoning by adverse compounds than the traditional Ziegler–Natta catalysts; the question whether this technology will have a comparable flexibility in order to make the wide variety of EPDM molecular structures, which have been designed over the years as dictated by the market requirements.

**Production Capacities.** Production capacities of EPM/EPDM of the largest manufacturers are listed in Table 2 (25).

### Compounding

EPM/EPDM grades have to be compounded with reinforcing fillers if high levels of mechanical properties are required. 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 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 (semireinforcing furnace), give the best performance. To lower the cost and improve the processability of light colored
Table 2. EPM/EPDM Rubber Production Capacities

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Country</th>
<th>Capacity, t/year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bayer/Polysar</td>
<td>United States and Germany</td>
<td>110,000</td>
</tr>
<tr>
<td>DSM Elastomers</td>
<td>United States, the Netherlands, and Brasil, Japan</td>
<td>216,000</td>
</tr>
<tr>
<td>DuPont Dow</td>
<td>United States</td>
<td>90,000</td>
</tr>
<tr>
<td>EniChem Elastomeri</td>
<td>Italy</td>
<td>85,000</td>
</tr>
<tr>
<td>ExxonMobil Chemical</td>
<td>United States and France</td>
<td>174,000</td>
</tr>
<tr>
<td>Herdilia</td>
<td>India</td>
<td>10,000</td>
</tr>
<tr>
<td>Japan Synthetic Rubber</td>
<td>Japan</td>
<td>65,000</td>
</tr>
<tr>
<td>Korea Polychem</td>
<td>South Korea</td>
<td>40,000</td>
</tr>
<tr>
<td>Mitsui Petrochemical</td>
<td>Japan</td>
<td>60,000</td>
</tr>
<tr>
<td>Sumitomo Chemical</td>
<td>Japan</td>
<td>35,000</td>
</tr>
<tr>
<td>Union Carbide</td>
<td>United States</td>
<td>90,000</td>
</tr>
<tr>
<td>Uniroyal Chemical Co.</td>
<td>United States</td>
<td>93,000</td>
</tr>
<tr>
<td>Others</td>
<td></td>
<td>30,000</td>
</tr>
</tbody>
</table>

*Ref. 20.*

compounds, or to reduce 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 they 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 or even other vulcanization systems like resol 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. 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 such as small amounts of sulfur, acrylates, or maleimides are also needed. The chemistry involved in sulfur and resol resin curing of ENB-containing EPDM has been investigated in detail by several authors (26–29).

Because of the low level of C=C unsaturation in the polymer compared to, eg, natural rubber (NR) and SBR, EPDM needs significant amounts of highly active accelerators for sulfur vulcanization. Usually, combinations of benzothiazole derivatives or sulfenamides with so-called ultra-accelerators like thiuram compounds or dithiocarbamates are used. Because of the limited solubility of these various accelerators in EPDM versus 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 (30). This limits the choice of possible accelerators to those which have no secondary amine groups embedded in their chemical structure or may contain residual secondary amines dating back to their synthesis: usually the ultra-accelerators mentioned above. In such cases it is extra difficult to develop a proper vulcanization system. New ultra-accelerator systems like dibenzyl dithiocarbamate or tetrabenzyl thiuram disulfide may be used in such cases, where the dibenzyamine embedded in these compounds is an exception in that it does not generate $N$-nitrosamines carcinogenic to human beings (31).

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

### Processing

The larger part of EPM and EPDM rubber finds applications in continuous extruded profiles or calendered sheets for automotive and building sealing applications. A smaller part is being used for a diversity of applications, from molded goods till viscosity modifiers for lubricant oils. The processing of EPM and EPDM rubbers must be viewed in relationship to the sort of application envisaged.

**Mixing.** Compounds of low Mooney EPM or EPDM grades can be mixed on open mills. For most applications EPM and EPDM compounds are almost exclusively mixed in internal mixers. The mechanisms involved in the mixing of EPM/EPDM as a function of molecular structural parameters, in particular molecular weight, molecular weight distribution (32–34), and long-chain branching (35,36), have been studied in great detail. It turns out that the speed of carbon black dispersion is greatly dependent on these parameters for practical mixing cycles. The molecular weight distribution and 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. A pronounced high molecular weight fraction within the molecular weight distribution—often called bimodality or tailored molecular weight—has a beneficial effect on mixing behavior by raising the shear toughness of the EPDM: it allows for higher shear forces exerted by the mixer and consequently a better dispersion of the reinforcing filler: the better dispersed filler is somewhat less reinforcing, which generally results in a lower viscosity of the mixed compound (32–34). On the other hand, a more pronounced fraction of low molecular weight material acts like a plasticizer and also has a decreasing effect on the viscosity of the mixed compound. The concept of controlled long-chain branching, combining a narrow molecular weight distribution with a high level of long-chain branching, has proven to be particularly beneficial for ease of processing and good mechanical properties as a result of this (36).

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
Table 3. Typical EPM/EPDM Compounding Recipes for a 60° IRHD Hardness Solid Application

<table>
<thead>
<tr>
<th>Components</th>
<th>Sulfur cure&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Low nitrosamine sulfur cure&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Peroxide&lt;sup&gt;b&lt;/sup&gt; cure&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPDM, 4 wt% ENB, Keltan&lt;sup&gt;c&lt;/sup&gt; 4802</td>
<td>100</td>
<td>100</td>
<td>—</td>
</tr>
<tr>
<td>EPDM, 4 wt% DCPD, Keltan&lt;sup&gt;c&lt;/sup&gt; 720</td>
<td>—</td>
<td>—</td>
<td>100</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>5</td>
<td>5</td>
<td>—</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>1</td>
<td>2</td>
<td>0.5</td>
</tr>
<tr>
<td>Carbon black, N 683</td>
<td>105</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Carbon black, N 765</td>
<td>—</td>
<td>95</td>
<td>—</td>
</tr>
<tr>
<td>Carbon black, N 550</td>
<td>—</td>
<td>—</td>
<td>110</td>
</tr>
<tr>
<td>CaCO&lt;sub&gt;3&lt;/sub&gt; whiting</td>
<td>50</td>
<td>—</td>
<td>80</td>
</tr>
<tr>
<td>Oil, Sunpar&lt;sup&gt;d&lt;/sup&gt; 2280</td>
<td>70</td>
<td>50</td>
<td>—</td>
</tr>
<tr>
<td>Oil, Sunpar&lt;sup&gt;d&lt;/sup&gt; 150</td>
<td>—</td>
<td>—</td>
<td>75</td>
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<tr>
<td>CaO, 75% paste</td>
<td>8</td>
<td>6</td>
<td>6</td>
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<tr>
<td>Poly(ethylene glycol) 4000</td>
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<td>—</td>
<td>2</td>
</tr>
<tr>
<td>N-Cyclohexylbenzothiazole-2-sulfenamide, 70%</td>
<td>2.1</td>
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<td>—</td>
</tr>
<tr>
<td>Zinc dibutylidithiocarbamate, 80%</td>
<td>2.5</td>
<td>—</td>
<td>—</td>
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<tr>
<td>Ethylthiurea</td>
<td>1.0</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Tellurium diethyl dithiocarbamate, 75%</td>
<td>0.63</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Tetramethyldiisulfur disulfide, 50%</td>
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<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Zinc dialkyl dithiophosphate, 67%</td>
<td>—</td>
<td>2.5</td>
<td>—</td>
</tr>
<tr>
<td>Dithiodiacaprolactam, 80%</td>
<td>—</td>
<td>1.0</td>
<td>—</td>
</tr>
<tr>
<td>Zinc dibenzylidithiocarbamate, 70%</td>
<td>—</td>
<td>1.0</td>
<td>—</td>
</tr>
<tr>
<td>2-Mercaptobenzothiazole, 80%</td>
<td>—</td>
<td>1.9</td>
<td>—</td>
</tr>
<tr>
<td>Sulfur</td>
<td>1.5</td>
<td>1.5</td>
<td>—</td>
</tr>
<tr>
<td>1,3-Bis(t-butylperoxy-isopropyl)benzene, 40%</td>
<td>—</td>
<td>—</td>
<td>6</td>
</tr>
<tr>
<td>1,1-Di-t-butylperoxy-3,3,5-trimethylcyclohexane, 40%</td>
<td>—</td>
<td>—</td>
<td>3</td>
</tr>
<tr>
<td>Trimethylolpropane trimethacrylate</td>
<td>—</td>
<td>—</td>
<td>1</td>
</tr>
</tbody>
</table>

Properties

| Compound Mooney<sup>e</sup> 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<sup>f</sup> IRHD         | 64           | 60           | 61           |
| Tensile strength<sup>g</sup> N/mm²   | 10.0        | 13.7         | 7.7          |
| Elongation at break<sup>g</sup> %   | 400          | 460          | 330          |
| Compression set<sup>h</sup> 22 h/70 °C, % | 13       | 19           | —            |
| Compression set<sup>h</sup> 22 h/100 °C, % | —       | —            | 16           |

<sup>a</sup>Automotive profile, phr.
<sup>b</sup>Building profile, phr.
<sup>c</sup>Keltan is a registered trademark of DSM Elastomers.
<sup>d</sup>Sunpar is a registered trademark of Sun-Oil Co.
<sup>e</sup>ISO 289.
<sup>f</sup>ISO 48.
<sup>g</sup>ISO 37.
<sup>h</sup>ISO 815.
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 may shorten the mixing cycle considerably.

**Extrusion.** For automotive and building sealing profiles, extrusion is the common shaping technology. In general, EPM/EPDM compounds can be extruded on all commercial rubber extruders. The extrusion behavior of EPM and EPDM compounds must be seen in relation to the compound quality, as achieved during mixing and influenced by the same molecular structural parameters as quoted above (34,37–40).

Also for extrusion purposes long-chain branching has a particularly positive effect (40): it increases extrusion speed and the resistance against collapse: the tendency of extruded profiles of complicated shapes to deform under the influence of gravity between the extruder and the vulcanization line.

**Curing.** EPM/EPDM compounds are cured on all of the common rubber-factory equipment: press cure, transfer molding, steam cure, hot-air cure, and injection molding are all practical. Where profile extrusion is the shaping technique, hot-air tunnel curing and ultrahigh frequency (UHF) electromagnetic heating followed by a hot-air tunnel or molten-salt bath (LCM) cure are the most common vulcanization techniques (41).

Many hot-air lines are homemade and differ substantially in quality and efficiency. It is a cheap curing technique and therefore often favored. A wide variety of air temperatures and tunnel lengths are directly related to the production speed, which can be achieved with a particular line. Air speed is another important factor. The heat transfer from the hot air to the EPDM rubber profile is poor compared to the other techniques, dictating much longer hot-air lines than, eg, LCM or UHF lines to achieve the same states of cure.

UHF heating is the continuous curing technique most commonly applied. The purpose of the UHF unit is a fast and homogeneous heating of even very complex shaped profiles, within a short distance. The following hot-air tunnel then serves to keep the profile at the curing temperature. Much milder hot-air conditions and shorter lines can be used than for hot air alone.

In spite of the somewhat old-fashioned nature and environmental problems of this curing technique, LCM curing is still the second most important continuous curing technique for EPDM sealing profiles. A major reason why this technique still survives or rather revives relative to the others is that this is the only continuous curing technique which allows for peroxide vulcanization. Peroxide vulcanization with free access of oxygen from the air—like in hot-air curing—leads to an intricate interaction between the oxygen molecules and peroxy radicals, which results in surface degradation instead of vulcanization and a consequent stickiness of the profile surface. This is an intrinsic problem of curing with peroxides, occurring with all other rubbers as well. The molten salt effectively shields the profile surface from this free oxygen. Another reason for the LCM revival is that this curing technique in general leads to the smoothest surface finish of extruded EPDM sponge profiles (see below).

**Sponge Processing.** Extrusion sponge represents a part of EPDM application technology, which requires the highest level of know-how, and consequently
includes all aspects of EPDM-compounding and EPDM-processing technology (42). In line with major automotive requirements calling for improved comfort and luxury, automotive body seals and profiles are becoming increasingly complex and numerous. Sponge plays a major role in this context. On a weight basis it represents a minor part of the profile technology, but because of the fact that sponge in most cases is coextruded with solid/dense profiles it represents about 50% of the sealing profiles on a volume basis. This combination with solid/dense extrusions calls for an integrated approach (43).

In summary the requirements on sponge converge on finding a good compromise between what could be called “the Magic Triangle” in EPDM-sponge technology:

- Smooth surface
- Good (dynamic) elastic properties
- Processability

Many, if not all, of these performance aspects can directly or indirectly be influenced by

1. the seal cross-sectional design and dimensions;
2. the sponge density, which must be adjusted by a proper balance between the amount of blowing agent and the curing accelerator package: to vary between 0.2 g/cm³ till completely solid;
3. closed vs open cell structure: a phenomenon difficult to quantify or adjust, but of major influence on the closed surface skin and the tendency of the sponge profile to absorb water.

With the great variety of curing techniques as described previously, it is not possible to come forward with “general” compounding rules for sponge. Every curing technique in combination with the vulcanization system requires its own set of compounding rules to obtain the best results. In summary a series of requirements can be formulated which generally apply:

1. The Mooney viscosity of the sponge compound is generally adjusted to such a level, that the blowing agent can expand the compound to the required density, before being arrested by the curing: compound Mooney ML(1 + 4) 100°C typically between 30 and 45 (but not limiting).
2. Compound viscosity variations should be kept to a minimum to guarantee a reproducible and constant amount of blowing and curing from batch to batch: compound Mooney typically ±2 Mooney units.
3. A homogeneous and very fine dispersion of ingredients to guarantee a homogeneous blowing.
(4) Blowing agents are most often used in combinations and occasionally with activators. The selection and use of a proper blowing agent depends on many factors and is a difficult matter. They are activated by numerous compounding ingredients, generally reducing the decomposition temperature of the blowing agents. The reader is referred to the pertinent literature (44,45) for details.

(5) Carbon black loading alone tends to create a coarse cell structure and irregular sponge surface. Hence sponge compounds are often modified by the addition of mineral fillers such as whiting, calcined clay, and platy talcum: they serve as nucleating agents for the blowing agents, resulting in a fine and homogeneous cell structure and smooth surface finish.

(6) The choice of the vulcanization system in combination with the blowing agent(s) to produce smooth weatherstrip sponge is another difficult aspect. Commonly, highly active cure systems are applied with a variety of vulcanization accelerators added to their maximum solubility level in the compound, in order to raise the vulcanization speed and reduce scorch time. To achieve the right dimensions of the sponge profile at the right density, the expanding foam needs to be arrested by scorch just at the right moment. Many attempts were made to simulate this mutual interaction of blowing and curing in laboratory simulations (46–48), but it still is the experience and craftsmanship of the compounder which determines the chance of a quick success: the result of many iterative trials.

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 superior to those of many other synthetic rubber vulcanizates, particularly of butyl rubber, but they do not reach the level obtained with NR of SBR vulcanizates. The resistance to compression set is surprisingly good, in particular for EPDM with a high ENB content or when cured with peroxide.

The resistance to heat and ageing of optimized EPM/EPDM vulcanizates is better than that of SBR and NR. Peroxide-cured EPM can, for instance, 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, and alcohol. This 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. The electrical properties of vulcanizates are also good at high temperatures and after heat-ageing. Because EPM/EPDM vulcanizates absorb little moisture, their good electrical properties suffer minimally when they are submerged in water.
Health and Safety Factors

EP(D)M is not classified as a hazardous material. It is not considered carcinogenic according to OSHA Hazard Communications Standard and IARC Monographs. Commonly used paraffinic extender oils contain less than 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.

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. EPM and EPDM still show a steady growth over the years.

The main uses of EPM and EPDM are in automotive applications as weatherstrip profiles, automotive coolant hoses, air-conditioning and brake hoses, and seals. In building and construction EPDM is used in sealing profiles, roofing foil, and seals; in cable and wire as cable insulation and jacketing; and in appliances in a wide variety of mostly molded articles.

With respect to automotive coolant hoses, the ever-increasing temperatures under the hood, combined with a performance requirement of 10 years or 200,000 km, have led to significantly more stringent testing conditions. Temperatures commonly occurring under the hood in the area of the radiator hose are 110–125°C, with peak temperatures as high as 140°C locally. Sulfur-cured EPDM has established itself as the most preferred elastomer for radiator coolant hoses under these conditions. The newer automotive standards request for higher temperature resistance: typical operating temperatures between 125 and 150°C continuous use, with peaks as high as 175°C. Further, new metal alloys containing aluminum and magnesium are used for the car engines. These new metals as well as the higher temperatures dictate appropriate changes in the compositions of the cooling liquids, in particular the stabilization packages against metal corrosion. These lead to an increased tendency to form deposits with zinc and accelerator remnants leached out of sulfur-cured EPDM. The deposits tend to block the cooling capillaries in the engine and the radiator, reducing heat transfer and eventually

<table>
<thead>
<tr>
<th>Year</th>
<th>EPM/EPDM, t/year</th>
<th>EPM/EPDM consumption, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1964</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1970</td>
<td>89,000</td>
<td></td>
</tr>
<tr>
<td>1980</td>
<td>328,000</td>
<td></td>
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<tr>
<td>1990</td>
<td>609,000</td>
<td></td>
</tr>
<tr>
<td>2000</td>
<td>919,000</td>
<td>8.9</td>
</tr>
</tbody>
</table>

*Ref. 20.
*Of total synthetic rubber consumption.
leading to engine break down. In these cases, where zinc is not acceptable in EPDM compounds, as well as for those cases where the temperature requirements surpass the ageing performance commonly achieved with sulfur cure, the alternative of peroxide curing of EPDM is the preferred method (49,50).

For the same reason of increased temperatures under the hood, the use of EPDM for dynamic applications is gaining importance as a replacement of NR, the natural choice for such applications because of its excellent fatigue resistance and low hysteresis. Applications envisaged are automotive engine mounts, vibration mountings, and muffler mounts. By a proper selection of EPDM characteristics—very high molecular weight, narrow molecular weight distribution, in combination with a relatively low amount of fillers added during compounding, EPDM practically matches the dynamic performance of NR in these applications. Its temperature resistance can even be improved by choosing peroxide rather than sulfur for the vulcanization, although the dynamic properties of peroxide cured compounds are generally somewhat reduced in comparison with sulfur cures (51).

The use of EPDM in low and medium voltage wire and cable applications has made steady progress, as a result of its superior electrical treeing retardancy. EPDM rubber insulated cables are more stable under wet conditions than cross-linked polyethylene insulation. The choice among various EPDM grades in designing insulation compounds is governed by the service requirements such as low electric loss, extrudates free of surface defects, high extrusion output, and good heat ageing properties (52). Also for this application long-chain branching has shown to be particularly beneficial for overall optimum performance (53).

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 about 25 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, it gives the end product good set properties (54).

Substantial amounts of EPM are also used as viscosity modifiers in lubrication oils. Molecular weight, molecular weight distribution, ethylene propylene ratio and in particular sequence distribution are important parameters to meet the desired performance. They markedly influence the thickening efficiency, low temperature properties, temporary and permanent viscosity loss due to shear, and engine performance as a whole. Much work aims at modification of the EPM
backbone as a post-polymerization step with polar groupings: eg, by grafting maleic anhydride onto the EPM chain, followed by a reaction with a variety of polar groupings such as amines (55,56).

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DSM Elastomers, R&D

**EXTRUSION.**  See Volume 2.