

The Chemistry of Ethylene Propylene Insulation, Part I

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Introduction

Crosslinked polyethylene (XLPE) and ethylene propylene rubber (EPR) are the primary extruded dielectrics used today in medium and high-voltage power cables. An earlier article* reviewed XLPE. Here EPR is covered on the 30-year anniversary of its plant-scale commercialization. (*Editor's note: This is the first of a two-part series. The second part of this article will appear in the November/December issue.*)

History

Karl Ziegler of Germany discovered in 1951 a new class of catalysts that polymerized alpha olefin monomers by an anionic mechanism in a non-aqueous solvent. These catalysts were a combination of a transition metal halide and an organometallic reducing agent, such as an aluminum alkyl. They were first used in the manufacture of low-pressure, linear high-density polyethylene (HDPE).

In Italy, Giulio Natta found that these catalysts could be used to make polypropylene. This was the second commercial crystalline plastic developed from the new catalyst technology. Natta extended the technology further by discovering that certain selected Ziegler catalysts brought about the irregular or random copolymerization of ethylene and propylene to yield an amorphous material with elastic or rubbery properties.

Polymer Structure

This polymer chain formed by the reaction of ethylene and propylene is called EPR. At room temperature and atmospheric pressure, both ethylene and propylene are gaseous hydrocarbons obtained by cracking natural gas liquids or naphtha from petroleum. Both are composed of carbon and hydrogen atoms, as shown by the structures in Fig. 1. The olefin sites or carbon-carbon double bond unsaturation in both molecules can react under certain conditions, for example, in the presence

*A. Barlow, IEEE Electrical Insulation Magazine, Vol. 7, No. 1, 8 (January/February 1991).

The history, polymeric structure and properties of EPR are covered on the 30-year anniversary of its plant-scale commercialization.

of a Ziegler-Natta catalyst to form long chains of linked carbon atoms. Each ethylene molecule may react with itself or a propylene molecule. Likewise, the propylene may join with itself or an ethylene molecule. The EPR polymer chain formed is not flat, as indicated by Fig. 2, but rather is three-dimensional with hydrogen atoms and methyl groups from propylene arranged along a zigzag chain of carbon atoms extending above and below the plane. The arrangement of the ethylene and propylene molecules to one another is random so that the resulting polymer structure is neither alternating nor very blocky. Statistics of the ethylene/propylene monomer feed ratio, selectivity of the Ziegler-Natta catalyst, and the polymerization conditions determine the blockiness of the EPR and whether it is completely amorphous or contains some crystalline content.

Diene

Some manufacturers polymerize a diene monomer with ethylene and propylene to form a terpolymer. Incorporation of the diene allows curing with sulfur, the conventional cure system in the rubber industry for polymers with carbon-carbon unsaturation. This is the

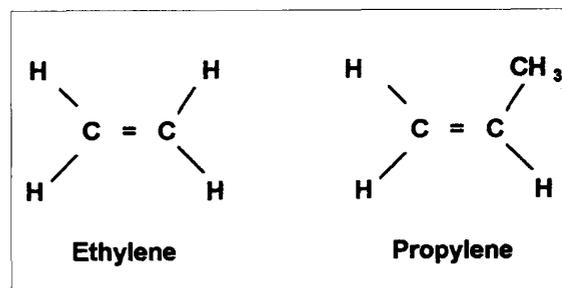


Fig. 1. Structures of Ethylene and Propylene

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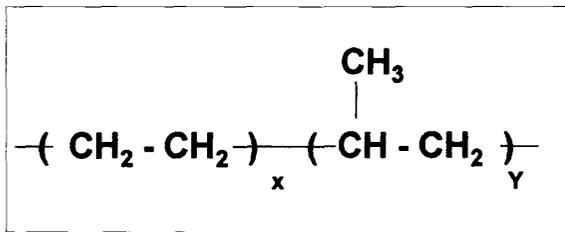


Fig. 2. Structures of Ethylene Propylene Rubber

NAME	ABBREVIATION	STRUCTURE
5-Ethylidene-2-norbornene	ENB	
1,4-Hexadiene	HD	$\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_3$
Dicyclopentadiene	DCPD	

* Polymerizable Double Bond

Fig. 3. Dienes in EPDM

classical sulfur vulcanization of unsaturated rubber developed by Charles Goodyear in 1839.

The three primary dienes used commercially, typically at levels of 3-7 wt. %, are listed in Fig. 3. ENB is manufactured by the Diels-Alder dimerization of butadiene and cyclopentadiene. HD is prepared by rhodium-catalyzed dimerization of ethylene and butadiene. DCPD is a petroleum refinery product.

All three contain non-conjugated double bonds that readily polymerize with ethylene and propylene preferentially at the carbon-double bond starred in Fig. 3. The remaining double bond then is pendant to the ethylene propylene rubber chain and available for sulfur curing. The structures for polymer incorporating ENB and HD are shown in Fig. 4.

These three cure site monomers show distinct differences in sulfur cures for cure rate, scorch safety, and physical properties. ENB is the fastest curing, DCPD the slowest, and HD is intermediate. ENB is used at concentrations of around 10 wt. % to provide very fast sulfur-curing polymers.

In the electrical industry, all medium and high voltage insulation is cured with peroxide because better electrical properties are realized compared with sulfur cures. Olefinic sites improve the curing response with peroxides, but differences between diene-containing terpolymers and copolymers in end-use properties are relatively minor, especially when peroxide coagents are used with the copolymers to enhance cure. Both diene-containing terpolymers and copolymers are suitable for electrical insulation.

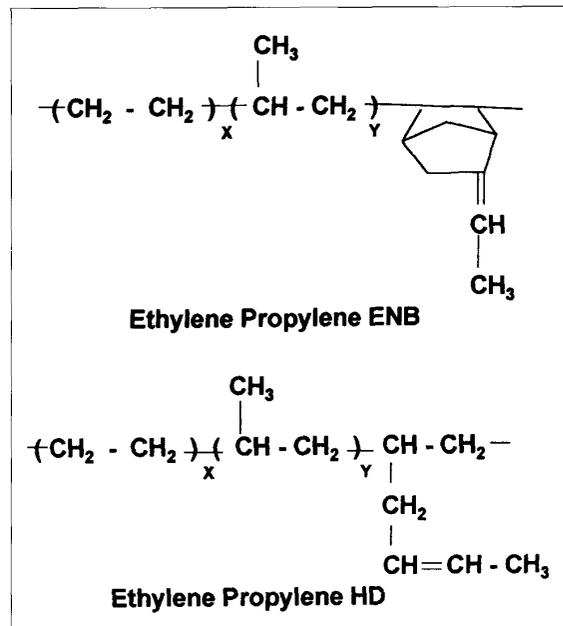


Fig. 4. ENB and HD in EPDM

Nomenclature

Ethylene propylene copolymers are denoted EPM and ethylene propylene diene terpolymers are labeled EPDM by ASTM nomenclature. In EPDM, the "E" stands for ethylene, the "P" for propylene, the "D" for diene, and the "M" for the repeating CH₂ units of the saturated polymer backbone. The term EPR is used in the electrical industry to refer to all ethylene propylene rubbers whether or not they contain a diene monomer. The term EP rubber is used likewise.

Polymer Variables

Crystallinity, molecular weight (MW)/molecular weight distribution (MWD), branching, and diene type/level are the major variables that can be manipulated to define the variety of commercial polymers currently available.

Crystallinity — Ordered and regularly repeating arrangements of atoms or groups of atoms can result in crystallinity. Crystallinity occurs in EPR when ordered blocks of ethylene groups form crystallites with ordered blocks of adjacent polymer chains. Propylene groups are not stereoregular enough or of sufficient block length to make them a factor in EPR crystallinity [1]. Ethylene blocks are too short in a random polymer to give significant crystallinity and an amorphous polymer results (Fig. 5). As block lengths become longer, crystalline melting points in the range of 30° to 60°C are possible. Block length and crystal perfection define the

melting point. Although the blocks in crystalline EPR are formed of ethylene segments, they are considerably shorter than the ethylene blocks in low-density polyethylene, which has a melting point of about 110°C.

The composition of commercial EPR polymers is approximately 50 to more than 75 wt. % ethylene. At around 60 wt. % ethylene, crystallinity typically begins to be observed. Although Fig. 5 of [2] shows a rough relation of crystallinity to ethylene content, it does not follow that ethylene content uniquely defines crystallinity. Variations in crystallinity at the same ethylene content are significant and are the result of differences in catalyst and polymerization conditions used for each discrete grade.

Differential scanning calorimetry (DSC) is the common method used today to measure crystallinity. It provides a fingerprint for the polymer in a rapid, inexpensive, and automated method that traces heat capacity vs. temperature. Heat capacity shows large and rapid changes, such as melting.

Amorphous EPR is soft and easy to process and generally has lower physical properties than a crystalline counterpart. As crystallinity is introduced, the polymer can be pelletized. It becomes tougher and does not mix as easily, especially when high molecular weight and physical properties such as modulus and tensile strength increase along with hardness. Low temperature set, elastic recovery, and flex resistance are poorer. In addition, crystalline EPR shows increased cold green strength and higher filler/oil loading capability, which translates to lower cost (Fig. 6) [3]. Cold green strength is the strength of the uncured polymer at ambient temperature.

Molecular Weight/Molecular Weight Distribution

— Ethylene and propylene monomer each have a finite molecular weight based on the total weight of the carbon and hydrogen atoms in each molecule. Polymerization fastens these monomers together to form an ethylene propylene polymer chain with a much higher molecular weight. Since the chains are not all the same length, each polymer molecule is not exactly the same molecular weight. The longer chains have higher molecular weight than the shorter chains. The average molecular weight is the mean of these weights.

Molecular weight distribution (MWD) provides information about the distribution of the higher and lower molecular weights around the average. The MWD is narrow if the EPR is made up of polymer chains whose molecular weights are close to the average. Polymers with a broad MWD have a wide range of molecular weights from the average. Narrow and broad MWD are depicted in Fig. 7. In this hypothetical case, both polymers have the same average molecular weight of 10^5 but different distributions of molecular weights. Molecular weight distribution for EPR polymers typi-

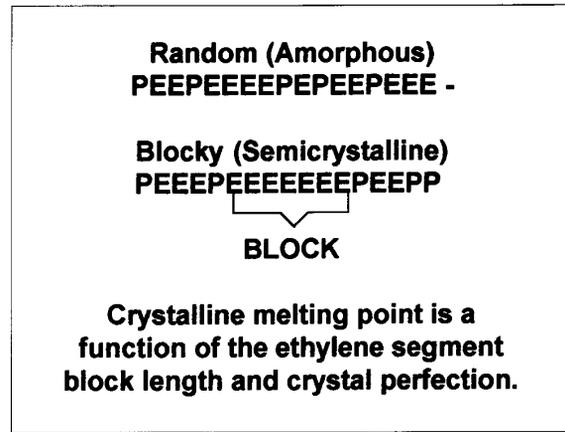


Fig. 5. Crystallinity

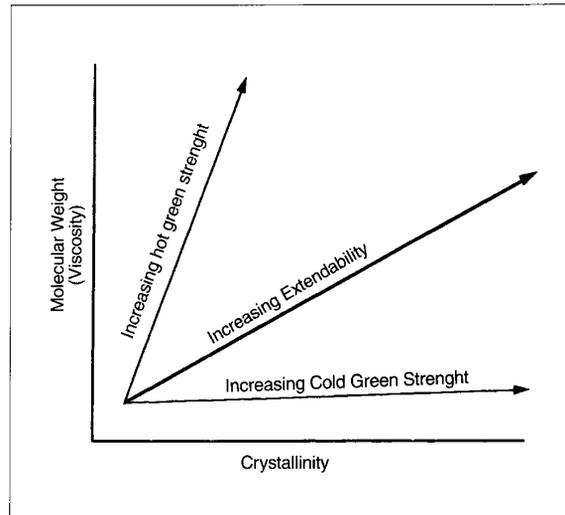


Fig. 6. Effect of MW and Crystallinity

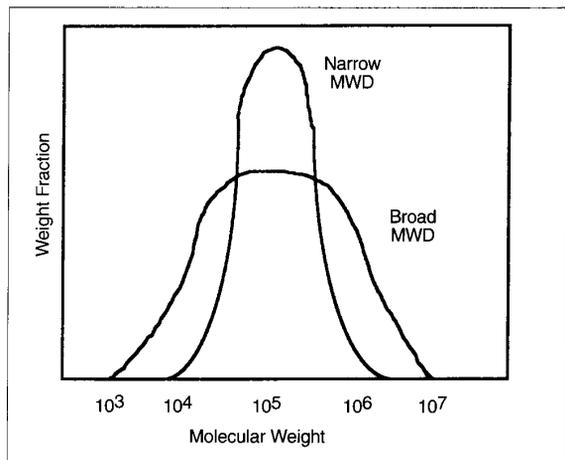


Fig. 7. Molecular Weight Distribution

cally is not symmetrical as in Fig. 7, but rather is skewed because of contributions from low or high molecular weight fractions. Polymer molecular weight and MWD are generally measured by gel permeation chromatography.

Mooney viscosity is the bulk viscosity measurement in a shearing disk rheometer used by the rubber industry to classify polymers. Mooney viscosity corresponds roughly to polymer molecular weight but provides no indication of MWD. Polymer hot green strength increases with increasing molecular weight or viscosity (Fig. 6). Higher molecular weight polymers accept more filler and oil for lower compound cost and have better physical properties, such as increased tensile and tear strength, but tend to extrude more slowly and generally process with more difficulty.

Polymer MWD chiefly affects processing characteristics. EPR with a broad MWD shows improved mill mixing, higher hot green strength [4], and generally better surface appearance on extrusion [5]. But extrusion speed, cure rate, and cure state tend to be lower. Physical properties tend to be lower, also. In general, broader MWD polymers have better processing but poorer cure characteristics than their narrow MWD counterparts.

Branching — EPR may be branched under certain polymerization conditions. When this occurs, repeating CH₂ units form a side chain from the main polymer backbone. Long-chain branching modifies polymer rheological characteristics. For example, polymer cold flow on storage is reduced with branching. EPDM is more likely to be branched than EPM, particularly at higher molecular weight. In general, DCPD is most prone to branching, HD least, and ENB lies in between. Long-chain branching leads to broadening of MWD and in the extreme to eventual polymer gelation. Gels are cross-linked inhomogeneous polymer particles that don't disperse well during compounding.

Long-chain branching is being used by polymer manufacturers to enhance EPR rheological properties. Branching lowers polymer viscosity at higher shear rates to provide improved extrusion characteristics. Various techniques are available to distinguish between branched and linear polymers [6]. As branching increases, Mooney viscosity, a bulk viscosity characteristic, increases. Inherent viscosity, a solution measurement, remains about the same.

Polymer Properties

Both EPM and EPDM have outstanding resistance to ozone and oxygen, excellent weathering and heat resistance, low temperature flexibility, and excellent electrical properties. The saturated polymer backbone of EPR is the key to its superb oxidative stability and excellent

weathering resistance. Non-conjugated dienes, such as those in Fig. 3, introduce the unsaturation pendant to the EPDM polymer backbone. In contrast, conjugated dienes, such as butadiene, introduce unsaturated olefinic sites along the polymer chain. Thus, oxidative attack by oxygen or ozone on the olefinic site in EPDM does not result in cleavage of the backbone. Weatherability can be achieved without antioxidants or antioxidants.

EPR is suitable for continuous service up to 150°C with excursions up to 175°C and higher. This excellent heat resistance is again the result of the saturated polymer backbone. Loss of elongation is usually the limiting factor on high temperature ageing.

The non-polar hydrocarbon nature of EPR results in its excellent electrical properties, which approach those for XLPE. The dielectric constant for unfilled EPR is 2.4, while its power factor is 0.06%. Chemical resistance to polar materials, such as acids, alkalis, oxygenated solvents, water, and steam, is excellent. Resistance to non-polar hydrocarbon solvents, such as toluene and gasoline, is poor. Excellent electrical properties and water resistance are keys to making EPR so useful in electrical applications.

Low temperature flexibility is excellent with glass transition temperatures approaching -60°C. The low specific gravity for EPR of 0.86 g/cc can result in reduced costs for finished products [7].

Next issue: The manufacturing and applications of EPR will be discussed, along with its compounding, curing, processing and performance.

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