THE CHEMISTRY OF
POLYETHYLENE IHSULATION

Extruded dielectrics, cable jackets, and semi-conductive compounds are common expressions in the field of medium and high voltage cables; but what are they, what are they made of, why are some pliable and other tough and stiff? They are all polymers or apolymers or polyethylene. So what is the difference between them?

The two major subdivisions of the large and still growing family of plastics-thermosets and therrnoplastics-are based on their behavior toward heat.

Thermosets, or thermosetting plastics, soften only once under heat and do not soften again on subsequent heating. Thermoplastics, on the other hand, can time and again be softened by heating and made rigid by cooling. Polyethylene is a member of a series of related chemical compounds called polyolefins and is a thermoplastic This article is mainly concerned with polyethylene and its copolymers.

The physical properties of a polyethylene resin are mainly though not exclusively dependent on basic molecular properties such as short chain branching, average molecular weight and molecular weight distribution. These basic properties in turn are controlled by the size, structure and uniformity of the polyethylene molecules. Ethylene is a gaseous hydrocarbon composed of two carbon atoms and four hydrogen atoms, C2H4, arranged as indicated in Fig. 1.

The two carbon atoms in the ethylene molecule are held together by a strong bond characteristic for some hydrocarbons Under certain conditions, however, this bond will "open' as shown in Fig. 2. This enables an ethylene molecule to join with others to form a chain in which all the carbon atoms are linked Such a chain of ethylene molecules is called polyethylene Polyethylene chains are not flat or two-dimensional as Fig. 3 appears to indicate. They have a three-dimensional shape, the hydrogen atoms being arranged along an inner zigzag chain of carbon atoms. Polyethylene chains may be rather short or enormously long and consist of many thousands of atoms. In fact, the polymerization of ethylene creates a mixture of chains of unequal length; some of them may be very short, about 12 molecules or less, while others are giants containing several hundred thousand ethylene units.

There is no commercial polyethylene that is built up exclusively of chains as simple as the one presented in Fig. 3 The molecular structure of most commercial low density polyethylene resins is far more complicated. Laboratory examination has revealed that for every 100 ethylene units in the molecular chain there are roughly 1 - 10 branches (some of them other than ethylene) growing from the chain. The molecule therefore is not a straight chain but one with a great number of short and long side branches. Figure 4 shows a schematic picture of such a side branching chain; the branches radiate three-dimensionally, just as the branches of a tree point in all directions from various places along the trunk.

The presence of such side branches is a reason for variations in a number of important physical properties (such as density, hardness, flexibility and melt viscosity) which distinguish polyethylene resins. Chain branches also become points in the molecular network where oxidation may take place. Chain branching is not the only complication in the molecular structure, crosslinking (Fig. 5) is another. Such linking takes place between carbon atoms in neighboring chains A network of crosslinked molecular chains may be compared to a number of heavily branched trees joined together somewhere along their branches - a highly intricate, three-dimensional molecular structure.

Intentionally crosslinked polyethylene or polyethylene copolymer resins are useful for wire and cable coating.
Resins of this type may be compounded with a very high content of carbon black or other fillers. Controlled crosslinking results in a resin with outstanding physical and heat resistant properties without impairing other essential properties.
However, by crosslinking the polyethylene molecules, the polymer is changed from a thermoplastic to a thermoset and thus cannot be softened and reused. Polyethylene can be crosslinked by adding a peroxide and subjecting the mixture to heat and pressure or by irradiating the end product with electrons or gamma rays Both of these are free radical processes. An alternative method is to graft into the polymer chain a silane substituent which will undergo a number of reactions, resulting in a crosslink when exposed to moisture. These various crosslinking mechanisms are discussed later.

ORDER AND DISORDER IN POLYETHYLEHE

Polyethylene molecules are not all arranged parallel to each other. In some areas of the plastic mass the molecular chains, though branched, are closely packed and lined up parallel in an orderly crystalline fashion. In other areas, the chains are randomly arranged liked boiled spaghetti. This structure is what the chemist calls amorphous. Above its melting point, polyethylene is always an amorphous mass.

A polyethylene that remains totally amorphous at room temperature would be soft and greasy and thus useless for extrusion or molding applications. A totally crystalline polyethylene, on the other hand, would probably be too hard and brittle to be useful. The right mixture of crystalline and amorphous regions is what the processor needs to make good end products. Figure 6 shows schematically the distribution of crystalline and amorphous areas. Low and medium density polyethylenes made by the high-pressure process generally have crystallinities ranging from 40 to 609a. High density polyethylene resins consist of molecular chains with only a few occasional branches. Therefore, the chains can be packed more closely The result is higher crystallinity, up to 80%.

An increase in crystallinity has a decided influence on some essential properties. The higher the degree of crystallinir/, the denser the resin Densir/, in turn, favorably influences a host of end product properties One of these effects is easy to understand; since there is less space between the more closely packed molecular chains, articles made of more highly crystalline or more dense polyethylene are less permeable to gases and moisture. Gases and moisture penetrate more readily through the amorphous areas.

Perhaps equally as important as the amount of crystallinir/ are the size and size distribution of the crystalline regions. Although information in this area of polymer chemistry is still limited, it is known that changes in size and size distribution of crystalline regions in polyethylene will affect stress crack resistance, brittleness and other properties.
Generally speaking, it has been found that for a given amount of crystallinity in a polyethylene, a uniform distribution of small crystalline areas will result in the most favorable properties for most applications.

BASIC MOLECULAR PROPERTIES AFFECT RESIH AND END PRODUCT PROPERTIES

Three basic molecular properties - short chain branching, average molecular weight, and molecular weight distribution - affect most of the mechanical and thermal properties essential for processing polyethylene and obtaining good end products. Small variations in the molecular structure may improve or impair some of these properties considerably. The electrical properties of a polyethylene resin, on the other hand, are only slightly affected by these three basic molecular factors. Polyethylene resins are currently available across a broad range of densities, about 0.88 g/cc to 0 96 g/cc. A classification dividing polyethylene resins into five ranges of density is generally used by the ASTM. These ranges are shown in Table 1. The earliest polyethylene resins, e.g. LDPE, also knovm as high pressure polyethylene or conventional polyethylene, had densities in the range 0.910 to 0.926 g/cc. Chronologically, these were followed by the high density polyethylenes (HDPE), also known as linear polyethylene or low pressure polyethylene, which exhibit densities between 0 940 and 0.965 g/cc. In the early 1980's, techniques for manufacturing linear low density polyethylene were introduced and, more recently, the very low densir/ polyethylenes (i.e. those with a density less than 0 910 glee) were added to the family of polyethylene resins.

LOW DENSITY POLYETHYLENE

LDPE is made at high pressure (20,000 psi to 40,000 psi) and temperature (300°F to 575°F), in either autoclave or tubular reactors. The reaction is initiated with a peroxide which generates free radicals, causing the double bonds of the ethylene molecule to open and one molecule to add to another. However, under the extreme conditions used, the molecules do not add linearly, and the growing polymer chain undergoes complex reactions which lead to the formation of short side chains. It is these side chains which inhibit the polymer molecules from crystallizing perfectly, and lead to the observed densir/ range given in Table 1. In addition. The free radicals may abstract a hydrogen atom from a polymer chain, and another polymer chain can grow from this site attached to the old polymer. This structure is known as long chain branching, and has a significant influence on the melt flow properties of the polymer. Employing the vast data base generated over the past 50 years, today's manufacturers of low density polyethylene are able to tailor these polymers to provide desired combinations of densir/ and melt how characteristics