Polyvinyl

By *Martin Batiuk**, *C. A. Clark*†, *A. F. Korney*†, *J. R. Russell*†, *G. A. Small*† and *D. E. Witenhafer**

One of the most important and diversified groups of thermoplastics is that made up of vinyl polymers and copolymers. They are available in a variety of chemical types such as polyvinyl chloride (PVC) and copolymers, *chlorinated PVC*, *polyvinyl acetate* used in paint and adhesives, polyvinylidene chloride used in packaging films and coatings, polyvinylidene fluoride, polyvinyl alcohol and polyvinyl butyral used as a laminate in safety glass.

*Development Consultant, †Senior Development Scientists, and **Development Scientist, B.F. Goodrich Chemical Co., 6100 Oak Tree Blvd., Cleveland, Ohio 44131.

Some of the newer copolymers, such as ethylene-vinyl-acetate or the olefins as comonomers with vinyl chloride, have attained some commercialization in the past several years because of their contributions to *ease of processing or impact improvement*.

The polyvinyl chloride family of homopolymers and copolymers has by far the largest commercial utilization. This is mainly because PVC can be compounded to produce a wide spectrum of physical properties. Cellular PVC can be rigid or flexible and density can be varied widely. The impact resistance of PVC can be modified by compounding and various fillers, processing aids and stabilizers can be added to reduce cost, increase production speed and to reduce the effects of heat and sunlight.

Thus polyvinyl chloride fills a wide variety of needs from rugged extruded pipe and building products to the demanding and sensitive requirements of very thin, flexible surgeon's inspection gloves.

Vinyl chloride polymerizes easily. Rapid polymerization is obtained with many free-radical initiators at 140° F.

 Published - October 1973

(60° C.). The molecular weight can be varied over a wide range by changing the polymerization temperature.

There are three main processes for polymerizing PVC. In the *suspension process* droplets of monomer are dispersed in water and polymerized to yield porous particles about 100 microns in diameter. In the *mass process* special agitation is used to polymerize liquid monomer without water present. This yields particles similar to suspension resin. Vinyl chloride polymerizes well in an *emulsion system* to yield a colloidal water dispersion, or latex, of PVC particles with about ½ micron diameter. Emulsion polymers can be purchased as a latex or as a very fine, spray-dried powder resin used mainly in making plastisols and organosols. A relatively small volume of PVC is polymerized by the costlier solution process to produce a resin with a minimal amount of gel.

Polyvinyl chloride is sold as a free-flowing resin (without additives), as a compound (with additives) or as latex.

Regardless of end-use or method of fabrication, compounding ingredients must be added to PVC resins. These materials can be classified as stabilizers, plasticizers, lubricants, fillers, impact modifiers and processing aids. All compounds do not contain all the groups of compounding materials. For example, rigid compounds contain no plasticizers; flexible compounds contain no impact modifiers; and transparent compounds contain no fillers.

Stabilizers prevent heat degradation during processing and for many applications extend service life. While they have little influence on most structural properties, they have a gross effect on such properties as electrical and outdoor weathering. (See article on stabilizers on p. 242.)

Plasticizers impart flexibility to PVC. (See "Plasticizers," p. 254.)

Lubricants aid flow during PVC processing. The correct types and amounts of lubricants are important for the best extrusion rate and to prevent plateout during calendering. Also, the choice of lubricant can affect electrical properties, outdoor weathering and other characteristics.

Fillers reduce the cost of PVC formulations. Fillers in rigid compounds are used at low levels. (For details on fillers, see p. 216.)

Impact modifiers and processing aids improve impact and melt processibility of rigid PVC compounds. Typical impact modifiers are methyl methacrylate butadiene styrene, acrylonitrile butadiene styrene (ABS) and chlorinated polyethylene. Common processing aids are methyl mathacrylate and styrene acrylonitrile. Other materials such as color pigments, flame retardants and fungicides may be added for specific requirements.

Types of PVC

Rigid vinyl is a hard, tough thermoplastic material. It can be compounded to achieve a wide range of structural properties and it can also be modified for processing by a multitude of different techniques.

Rigid vinyls provide such significant properties as corrosion resistance, thermal and electrical insulation, weather resistance and a wide range of opaque colors or outstanding clarity.

For a quarter of a century rigid vinyls have been successfully employed for industrial pipe, duct systems, fume hoods, tanks, water supply and sanitary systems, many installations of which have been subjected to a wide range of environmental exposure. Based on the experience gained from these applications, the merits of properly formulated rigid PVC are now used in building products, including house siding, window sash, building panels, gutters and downspouts, flashing, conduit and electrical raceways.

Cellular rigid vinyl has found a ready market for decorative molding and trim and this is considered a major breakthrough as an economical wood substitute. Parts made by extrusion provide a close duplicate for prefinished wood in density, feel and appearance. In addition, its superior toughness, nailability, crack resistance, smoothness, ease of fabrication, unlimited lengths and maintenance-free characteristics have allowed cellular vinyl to overcome acceptance problems associated with previous wood substitutes.

Rigid vinyl sheet and film materials are well suited for making shapes that can be formed by vacuum, drape, cold forming or by variations of these methods. Bubble or "blister" packaging with clear, thin, rigid PVC film provides visual appeal and protection as well as economy.

Injection-molded vinyl parts are produced using in-line screw-preplasticizing equipment. Products include automotive and appliance parts, electrical and pipe fittings, all of which are well known for their durability, attractive appearance and fidelity of surface reproduction.

Rigid vinyl's excellent dimensional stability, chemical inertness, high impact resistance and exceptional clarity permit its use by the packaging industry for lightweight blow-molded containers.

Chlorinated PVC extends the many useful characteristics of opaque rigid PVC to higher temperatures. As the degree of chlorination increases, properties such as density and heat distortion temperature are improved, while other properties are maintained or improved. Products include hot and cold water piping, automotive under-the-hood applications, roof exhausts and electrical housings.

Flexible vinyls contain plasticizers in sufficient quantity (20 to 100 or more parts/100 of resin) to impart flexibility. Compounds with lower levels of plasticizer (20 to 40 phr) are often termed semi-rigids. Flexible compounds find use in wire and cable, insulation, automotive parts, toys and packaging.

Flexible compounds can be fabricated by several means. Sheet materials are either calendered or extruded, while tubing, profiles and wire insulation are extruded. Many other shapes that cannot be made by these processes are injection molded.

The wire and cable industry uses large volumes of flexible PVC. Excellent electrical and physical properties, flame retardance, along with low cost and flexibility over a wide temperature range are the primary properties responsible for the continued growth of this market. New resins and other compounding ingredients continue to make new applications for this material possible.

Flexible film and sheet is a well established area for PVC. Wall coverings, packaging film, shower curtains, upholstery and clothing fabrics are typical products. These products were made by calendering but in recent years large volumes have been made by extrusion. Each application requires a compound formulated to meet specific requirements. For example, food-grade packaging film for meat and produce must be based on FDA-sanctioned ingredients, must have good low-temperature properties and be transparent. Baby pants formulations must have excellent soapy water resistance.

Various types of gasketing and weatherstripping are made from flexible PVC. By the proper choice of plasticizer and stabilizer, compounds can be made for a range of applications from refrigerator gasket to outdoor weatherstrip.

Each year the automotive industry continues to use larger volumes of flexible PVC. Applications include wire insulation, injection-molded knobs, upholstery, trim and bumper strips. Besides the usual properties that make flexible vinyl desirable, its availability in a wide range of colors makes it especially desirable for use in the automotive industry.

Melt processing

The most common method of converting compounded polymer is by the *melt* process.

In extrusion, processing on single-screw extruders is done at basically two melt viscosity levels. High-viscosity, low-temperature systems are associated with low production rates but they maintain dimensional precision of a product. Low-viscosity, high-temperature melts usually are identified with powder compounds because of the high shear rates required to convert powder to a melt on a single-screw extruder; these conditions, however, favor substantially higher output rates. Multiple-screw extruders, using powder compounds, now claim a large share of the pipe and architectural markets. They can extrude at moderate temperatures (370 to 390° F.) maintaining substantial output rates. The lower extrudate temperatures provide a significant advantage in thermal stability, especially when large inventory dies are used, as in large-diameter, thick-walled pipe.

Injection molding of PVC, especially rigids, became practical with the advent of screw injection molding machines. High-shear screws generate low-viscosity melts that flow more freely into the furthermost sections of the mold cavity.

In blow molding, programming of the

Continued on page 113

parison is coming into wider use to reduce costs by providing more uniform wall thickness. There not only is a saving in material, but time cycles also are reduced because thick-wall, slow-cooling sections are eliminated.

In calendering, it is necessary to provide a means of fluxing the compound at a rate to match the capacity of the calender. A Banbury-mill combination is normally used. A short-barreled extruder downstream of the mixing equipment is desirable to strain out any foreign materials that might damage the costly calender rolls.

Liquid processing

Special fine-particle-size PVC resins termed dispersion resins are dispersed in plasticizers, usually by low shear, stir-in techniques, to produce remarkably versatile liquid systems. The plasticizers have little effect on the resin at room temperature, providing liquids with viscosity stability over a long period of time. Heating the system to about 177° C. (350° F.) causes fusion (mutual solubilization of resin and plasticizer) to occur. Cooling the melt to below 60° C. (140° F.) provides a tough, flexible vinyl product. In ease of formability vinyl dispersions are the quintessential plastics material, since the force of gravity alone is often sufficient to produce the desired shape and surface contour.

Plastisols are vinyl dispersions containing little or no volatile liquids and thus are essentially 100% solids. Organosols are similar in composition to plastisols except for the presence of volatile liquids used to extend the liquid phase and thus reduce viscosity. Heat, without pressure or shear, is all that is required to convert these dispersions to flexible solid materials quite similar in physical and chemical properties to vinyl products prepared by melt processing of solid compounds.

Polyvinyl chloride for plastisols and organosols is polymerized in emulsion systems that provide colloidal water dispersions containing ultimate particles of approximately 0.2 to 2.0 microns in size. Spray drying of the water dispersion produces the commercial product, a dry powder of approximately 2 microns average particle size, with some particles as large as 15 to 20 microns. About 10% of the PVC used in the U.S. is dispersion grade.

Formulating vinyl dispersion resins is similar to that of melt processed vinyl resins, except that the compounding ingredients must be selected to keep the rheological properties of the liquid system within the limits imposed by the processing method. In addition to the compounding ingredients mentioned, certain large particle size, suspension polymerized PVC resins, designated blending resins, are often used to replace part of the dispersion resin to reduce cost or adjust flow properties.

Most vinyl dispersion resins find use in the two broad areas of coating and moldings. Roll coating, spraying and dipping are all employed to coat a variety of substrates. Fabrics, coil metal, paper and roll goods flooring are usually processed by knife or roll coating. Spray coating is often used on stamped metal and dipped coatings may be applied to racks as well as to formed metal parts.

Rotational casting of plastisols is used to mold open or closed hollow objects such as dolls, balls and automotive upholstery parts such as arm rests. Open hollow parts such as boots and traffic cones can be efficiently produced by slush molding plastisols. Cloth supported and unsupported gloves are typical examples of dip molded products.

Organosols are used to produce thin films of higher hardness than can generally be obtained from plastisols. Greater hardness is made possible through the use of volatile dispersants and diluents and low concentrations of plasticizer. Dispersants are polar ketones and esters that aid in dispersion and fusion of the resin, while diluents are nonpolar solvents that adjust flow properties and reduce the solvating effect of the dispersant.

Vinyl solutions. Polyvinyl chloride and copolymers with vinyl acetate and vinylidene chloride can be dissolved by electron-donor solvents. Viscosity depends upon composition and molecular weight of the polymer and the total solids of the solution. A wide range can be obtained, which allows the processor to deposit polymer films by most common methods. Some of the copolymers contain carboxyl and hydroxyl groups for improved adhesion and reactivity with isocyanate, methylol and epoxy resins. Solution technology allows deposition of hard, high-molecular-weight polymers at room temperature or thin films of 1 mil or less.

Latex liquid systems of vinyl chloride homopolymers and copolymers are also available. These systems are colloidal dispersions in water. The average particle size is usually less than 0.3 micron. Polyvinyl chloride latexes form film as a result of the enormous capillary forces that are exerted as the last amounts of water volatilize from the wet film.

Latexes are effectively used to coat, impregnate or saturate fabrics, paper and leather with polymeric dispersions of lower viscosity than most plastisols. Latexes are also used as tie coats on fabric or paper to bond plastisols, organosols or calendered film to these substrates. In end uses where flame retardancy is a requirement, latexes can be used in conjunction with antimony oxide, phosphates or chlorinated paraffins. Latexes are applied by most of the common coating methods including knife, roll, spray and curtain.

Vinyls are an established plastics family with broad uses throughout industry and in consumer products. At the same time, new varieties of vinyl materials and improved processing methods and compounding ingredients are continually developing. These advances account for the steady expansion of the uses of vinyl materials.

Additional information related to vinyls may be found as follows: Charts in the Data Bank (p. 533) give technical information. Processing methods appear in two sections: Primary Processing (p. 273) and Fabricating and Finishing (p. 479). Index of Classified Advertisers (p. 889) lists advertiser page references. Free product literature available from suppliers appears on p. 877. And for additional sources of supply, see p. 773.