

Polyvinyl and vinyl copolymers

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Vinyl polymers and copolymers comprise one of the most important groups of thermoplastics. The characteristic common to the members of this group is their derivation from vinyl chloride ($\text{CH}_2 = \text{CHCl}$), vinyl acetate ($\text{CH}_2 = \text{CHOCOCH}_3$), or vinylidene chloride ($\text{CH}_2 = \text{CCl}_2$). These thermoplastic polymers include polyvinyl chloride (PVC) and copolymers, chlorinated PVC, polyvinyl acetate, polyvinylidene chloride, polyvinylidene fluoride, polyvinyl alcohol, and polyvinyl butyrate.

PVC and copolymers comprise 84% of the total polyvinyls produced and are therefore the largest family in the group. One of the primary reasons for this large use level is the wide range of properties possible for PVC by compounding with various lubricants, plasticizers, processing aids, stabilizers, impact modifiers, and other additives. These properties allow the production of a wide variety of products from rigid pipe to flexible thin film.

PVC manufacturing processes

All four basic manufacturing processes involve the polymerization of the monomer(s) in pressure vessels equipped with agitators and heat-removal systems. Polymerization is initiated by free radicals produced by the thermal decomposition of peroxides and peroxydicarbonates and proceeds exothermically at temperatures of 40 to 70° C. Reaction temperature, agitation characteristics, and reactor ingredients are the primary determinants affecting polymer properties.

In the most widely used process, suspension polymerization, monomer drop-

lets are suspended in an aqueous medium by a combination of agitation and protective colloids such as methyl cellulose, gelatin, or partially hydrolyzed polyvinyl alcohol. Average PVC particle diameter is typically 100 to 125 microns. The resultant resin slurry is stripped to remove residual monomer, then is centrifuged and dried.

In the mass polymerization process, the monomer is converted to PVC in the absence of water in two specifically designed reactors. This two-step polymerization process involves partial conversion in a vertical reactor followed by final conversion in a horizontal reactor. After stripping the residual monomer, the product is ready for use.

The emulsion polymerization process is similar to the suspension process except that a colloidal dispersion of monomer(s) is maintained with the addition of emulsifying agents. Water-soluble free radical initiators are used to produce particles which average 0.5 micron in diameter. This latex is stripped to remove residual monomer and used directly or spray-dried to produce a powder for use in plastisols and organosols.

In the least widely used process, solution polymerization, monomer(s) is first dissolved in an organic solvent, then polymerized. The resultant polymer is precipitated from the solution followed by a solvent removal step. The process is used primarily to produce specialty copolymers for coating and adhesive applications.

Types of PVC

PVC homopolymer resins are produced with various characteristics to meet specific end-use requirements. The primary differences between homopolymers are their molecular weight, surface characteristics and porosity,

and particle size. High-molecular-weight resins generally have better physical properties while lower-molecular-weight resins are easier processing. Surface characteristics and porosity are important determinants in the compounding process, especially if plasticizers are involved. Particle size is important in distinguishing between emulsion resins and suspension or mass resins.

Homopolymers are used in the majority of PVC applications but copolymers are favored in some applications. Vinyl chloride-vinyl acetate copolymers are used in solution coatings because of their greater solubility, and in vinyl asbestos floor tile because of their higher melt flow and pigment binding ability. Post chlorination of PVC homopolymers improves the heat deflection temperature sufficiently to allow CPVC pipe to be used in hot-water applications.

PVC compounding

PVC by itself is not a commercially useful polymer. To achieve processability and performance, various compounding ingredients must be added. The one additive common to all PVC compounds is a thermal stabilizer. PVC is a thermodegradable polymer and requires stabilization to prevent degradation during processing. Depending upon type and level used, the stabilizer may also contribute to extending the service life of the end product.

In addition to thermal stabilizers, major additives may also include lubricants, plasticizers, impact modifiers, process aids, fillers, and primary pigments. Minor additives, used for specific purposes, include UV stabilizers, antioxidants, blowing agents, flame retardants, fungicides, antistatic agents, and antiblocking agents.

Depending upon the type of PVC and

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the processing method, PVC compounds can be powders, pellets, or liquids. Powder compounds are made by ribbon blending or high-intensity mixing of the PVC with all of the desired additives present. These powders are then processed directly. Pellets are powder compounds which have been put through a mastication procedure and die-face cut or cubed to provide ease of shipment, handling, processing, and, in some cases, to provide preliminary work input into the compound to improve end-product properties such as clarity and absence of gels. Liquid systems are plastisols (emulsion resins/plasticizers and other additives) and organosols (emulsion resin/plasticizers/solvents and other additives). Both can be mixed on low-shear planetary mixers or medium-shear, high-speed blade-type mixers.

Thermal stabilizers. The most common stabilizers for use with PVC are organometallic salts—usually tin, lead, barium, cadmium, calcium, and zinc compounds. Epoxides, phosphite chelators, antioxidants, etc., also are commonly used. While thermal stabilizers usually have little influence on most structural properties, they have a gross effect on such properties as electrical and outdoor weathering.

Plasticizers impart flexibility to PVC. Properties of plasticized PVC depend greatly on the type and amount of plasticizers used. The level of plasticizer used may vary from 10 parts per hundred of resin (p.h.r.) in semirigid compounds to 100 p.h.r. in very soft compounds. Phthalate esters are the most widely used types, but other organic acid esters, such as adipates, azelates, etc., and organic phosphate esters and epoxidized oils also are commonly used. Mixtures of various types of plasticizers often are used to obtain desirable cost-performance characteristics. End-use properties such as low migration, low-temperature flexibility, flame retardance, and enhanced thermal stability are major considerations in determining the use of one or a blend of plasticizers.

Lubricants. The primary lubricants used in the processing of PVC are waxes, fatty esters, and metallic soaps of fatty acids. Lubricants facilitate the melt flow and processing characteristics of PVC.

Lubricants are classified as internal, external, or both, depending on chemical structure and compatibility. The correct types and amounts of lubricants are important for optimum processing and development of maximum physical properties. The choice of lubricants is also important to clarity, electrical properties, outdoor weathering and other characteristics.

Processing aids such as methyl methacrylate copolymers or styrene-acrylonitrile copolymers frequently are used in rigid PVC compounds. They increase homogeneity and hot-melt strength during processing.

Impact modifiers are used most often with unplasticized rigid PVC compounds to improve impact resistance. Typical

impact modifiers are elastomeric polymers such as MBS, ABS, EVA, and CPB. Depending upon the degree of impact resistance desired, use levels vary in the 5 to 15 p.h.r. range. At levels of 15 p.h.r. or higher these elastomeric modifiers have significant effects on other physical properties, e.g., tensile, modulus, specific gravity, heat deflection temperature, etc.

Fillers, by definition, are used primarily to lower the raw material cost of PVC compounds. Calcium carbonate is the most common filler used.

Significant changes in finished product physical properties can be expected depending upon the filler particle size, surface treatment, and use level in the compound.

Primary pigments are used to impart color, opacity, and weatherability to PVC compounds. Both organic and inorganic pigments can be used. Cost and end requirements are the determining factors in the types and use levels of pigments.

PVC processing

The most common methods of converting PVC compounds are by melt and liquid processing.

Rigid and flexible PVC compounds in solid form, either powder or pellets, are converted by *melt processing*. The melting process is accomplished by internal (shear) and external heating in combination with pressure via several different types of processing equipment.

In *extrusion*, both single and multiple screw extruders are used. Compounds run the range from rigid and semirigid to full flexible compounds. Essentially any continuous shape, irregular or symmetrical in cross-section, can be produced by the extrusion process. Some examples of products are profiles, pipe, blown film sheet, tubing, etc. Both rigid and flexible cellular vinyls also are processed by extrusion.

Injection molding of flexible vinyl compounds is relatively easy. Injection molding of rigid vinyl has become practical with the development of reciprocating-screw injection molding machines. High-shear screws and lower-molecular-weight vinyl resins make it possible to generate low-viscosity melts which have acceptable thermal stability and can flow into the outermost parts of the mold cavity. Injection molding is used to produce discrete parts varying in shape from very simple to very complex.

In *blow molding*, extruded tubular parisons are clamped in molds and air-blown to conform to the mold. Programmed control of the parison provides a more uniform wall thickness and has helped significantly to reduce costs in blow molding operations. Blow molding is used extensively in the manufacture of PVC bottles or other containers. Injection molding of parisons, particularly for small containers, allows lower scrap generation and more efficient utilization of compound.

Calendering produces a product similar to that made by flat-die extrusion of

film and sheet. It is a large-volume processing method requiring high capital equipment investment compared with the extrusion process. Calendering requires prefluxing of the compound on Banbury/roll mill equipment at a rate matching the calender's capacity. Sometimes, in conjunction with the Banbury/roll mill equipment, a short-barreled extruder is used to feed the calender rolls. Calendering produces flexible and rigid vinyl sheeting in the 3 to 25 mil thickness range. Production rates are high and the process is particularly good for thin-film applications.

Powder coating is another method which has been recently applied to both flexible and rigid vinyl powder compounds. The principal application techniques are electrostatic spray, fluidized bed, and electrostatic fluid bed coating. Both rigid and flexible compounds can be applied as 100% solid coatings on metal and other substrates. This technology is efficient and avoids problems associated with solvent-based coatings.

In the *liquid processing* of PVC resins there are usually three basic types: plastisols and organosols, solution coatings, and latexes. In liquid processing, fine particle size resins (0.2 to 2 microns), known as dispersion or emulsion resins, are dispersed in liquid plasticizers by low- to medium-shear agitation. The resin/plasticizer interaction must be minimized to obtain low viscosity which remains stable for an extended storage time at ambient temperatures.

Formulating vinyl dispersion resins is similar to that for melt processed resins, except that all additives must be carefully chosen to obtain the desired rheological properties. Small-particle-size suspension resins (blending resins) often are used to replace part of the dispersion resin to reduce cost and/or to adjust flow properties. If these dispersions contain little or no volatile ingredients, they are referred to as plastisols. Volatile solvents, nonpolar diluents, and/or more polar dispersants, are sometimes added to reduce viscosity and/or permit reduced plasticizer levels, increasing hardness. In this case, the resultant dispersion is known as an organosol.

Heat without pressure or shear is all that is required to convert plastisols and organosols to flexible solid or cellular materials quite similar in physical and chemical properties to flexible vinyl products prepared by the melt process. Heating these dispersions to about 177° C. (350° F.) causes mutual solubilization of the resin and plasticizer, resulting in a homogeneous melt. No working of the hot melt is required, as is the case with melt processing. Simply cooling the melt to below 60° C. (140° F.) produces a tough, flexible vinyl product.

Dispersion resin compounds are used for coatings and cast moldings. Roll casting, spraying, and dipping are all employed to coat a variety of substrates. Fabrics, coil metal, paper, and roll goods flooring usually are processed by knife or roll coating. Spray coating is

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used on stamped or preformed metal. Racks, other complex parts, and supported and unsupported gloves are produced by dip coating. Rotational casting of plastisols is used to mold open or closed hollow objects such as dolls, balls, and automotive arm rests. Slush molding is used to efficiently produce open hollow parts such as boots and traffic cones.

Organosols are used to produce thin films of higher hardness than can generally be obtained from plastisols. The higher hardness is possible due to the use of volatile solvents and low concentrations of plasticizers. Organosols most commonly are processed by spray and roll coating.

Foamed plastisols account for a significant portion of overall dispersion resin consumption. Foamed dispersions are made by mechanical or chemical expansion of plastisol before fusion, or by chemical expansion of fused melts. When pressure molded, vinyl foam is completely closed-cell and useful for thermal insulation and flotation applications.

PVC and copolymers with vinyl acetate and vinylidene chloride can be dissolved by electron donor solvents to produce vinyl solutions. Viscosity depends upon the composition and molecular weight of the resin and the type and concentration of solvents. Some of the copolymers contain polar groups such as hydroxyl or carbonyl for improved adhesion to metal, and for crosslinking reactivity with epoxy, isocyanate, and methylol-type polymers. All common liquid coating methods of application can be used. Solution technology permits production of hard thin films of 1 mil or less at room temperatures. It does, however, impose some ecological problems as a result of the solvents used.

PVC and copolymers also are available in latex form. This class of vinyls represents a relatively small part of the overall vinyl market. Latexes are true colloidal aqueous dispersions of vinyl resin which have particles of usually 0.2 micron or smaller average diameter. They are used for coating, impregnating, or saturating paper, fabrics, and leather. All common liquid-coating methods—knife, roll, spray, brush, and curtain—can be used.

PVC applications

PVC homopolymers and copolymers are used in two basic compounded forms which become rigid or flexible vinyl products.

Rigid vinyls are unplasticized thermoplastic materials that are hard and stiff. They can be transformed into transparent, high-clarity film, sheet, and containers for packaging. A larger use is as opaque colored compounds used to make pipe, fittings, conduit, house siding, and a variety of profiles for the automotive, construction, and appliance areas.

Flexible vinyls are thermoplastic materials that contain plasticizers that impart flexibility. Flexible vinyls result in packaging films with good clarity, wire and cable coverings with good electrical properties, refrigeration gaskets with

good low-temperature properties, and upholstery material with softness and a wide range of colors.

Packaging applications consume a large portion of the extruded and calendered film and sheet. Rigid clear sheet is used in blister packs and box lids. Highly plasticized extruded films are used in the packaging of food products. PVC bottles are used to contain cooking oil, cosmetics, and liquid detergents. Growth of PVC bottles was slowed when trace amounts of vinyl chloride monomer (VCM) were found in certain bottle contents. Since then, producers have lowered the residual VCM levels in the bottles so that VCM migration cannot reasonably be expected to occur. Growth in this area is expected to return.

Household uses and consumer goods require large quantities of PVC. Furniture upholstery and wall coverings are the major household uses; however, shower curtains, garden hoses, and small-appliance components are important products. Phonograph records are the largest PVC consumer product followed by footwear. Other consumer goods are toys, sporting goods, and outerwear.

Transportation uses for PVC include upholstery, vinyl car tops, floor mats, and trim. Other PVC uses include medical tubing, credit cards, and a variety of miscellaneous items.

Other polyvinyls

Other polyvinyls with commercial utility include polyvinyl acetate (PVAc) homopolymer, and copolymers of vinyl acetate with acrylates, maleates, and ethylene. These are used primarily in emulsion or latex form for paints, adhesives, textile sizing and coating, and pigment binders and coatings for paper. Special homopolymers and copolymers are used as chewing gum bases. Chemical derivatives of polyvinyl acetate include polyvinyl alcohols, polyvinyl formal and polyvinyl butyral.

Polyvinyl alcohols are manufactured

in different molecular weights and acetate contents. PVA resins usually are used as aqueous solutions. In the textile industry, PVA is used as a warp size and as a finishing resin to impart stiffness. It is useful for paper coatings, where it imparts oil and grease resistance, ink blot out, and solvent resistance. PVA solutions are good adhesives for wood and paper.

Major applications for PVA are for moistenable adhesives for envelopes, labels and for water-resistant adhesives in food and beverage cartons. PVA films also are used for mold release in polyester fabrication processes and for polarizing optics. Cold water-soluble films are used for disposables such as hospital laundry bags and detergent packages.

Polyvinyl acetals are resins derived from the reaction of PVA with aldehydes. Only polyvinyl formals and polyvinyl butyrals have any commercial importance.

Polyvinyl formal is used primarily in the manufacture of enamels for heat-resistant wire insulation, usually in combination with phenolics. Polyvinyl butyral has an important use in varnishes for marine applications; but serves mainly as an adhesive interlayer in safety glass, where clarity, impact resistance, and weathering stability are critical properties.

Polyvinylidene chloride and copolymers with vinyl chloride, alkyl acrylates, and acrylonitrile are soft, flexible plastics. They are used mainly for film and coating applications in the packaging industry and for fibers. Resistance to oils, fat, oxygen, and water vapor are their primary advantages. These polymers may be used alone, usually as biaxially oriented, unsupported films, or may be combined with other substrates such as cellophane, PE, PVC, paper and paperboard, either in lamination or coating techniques.

Extruded monofilaments are used in household and automotive upholstery, drapery fabrics, filter cloths, insect screening, and venetian blind tapes.