

tones. These polymers, therefore, resist hydrolysis and aqueous acid and alkaline environments.

Properties

Short-time mechanical test results are shown in the *Plastics Properties Chart*, p. 142. Polysulfone has high tensile strength—10,200 p.s.i. at yield—and stress-strain behavior typical for rigid, ductile materials.

Flexural modulus of elasticity is high—nearly 400,000 p.s.i. at room temperature. With increase in temperature, flexural modulus stays above 300,000 p.s.i. to about 320° F.

Chemical and solvent resistance. Polysulfone is highly resistant to mineral acid, alkali, and salt solutions. Resistance to detergents, oils, and alcohols is good even at elevated temperatures under moderate levels of stress. For example, specimens have withstood 500 hr. in 2% detergent solution at 140° F. and 1500 p.s.i. stress.

Polysulfone will be attacked by such polar organic solvents as ketones, chlorinated hydrocarbons, and aromatic hydrocarbons.

Electrical properties. Polysulfone's electrical properties are retained over a wide temperature range, up to 350° F., and after immersion in water or exposure to high humidity. Comparison of electrical properties of polysulfone, polycarbonates, and polyacetals indicate two areas of significant difference. First, the dissipation factor of polyacetals is higher by a factor of 10, compared to polysulfone and polycarbonates. Second, good electrical properties are retained up to 350 to 375° F. for polysulfone, 275 to 300° for polycarbonates, and 210 to 250° for polyacetals.

Long-term performance. The value of polysulfone as an engineering material is best measured by its performance under physical stress, at room and elevated temperatures, and over comparatively long periods of time. Creep or elongation under load is a useful measure of such performance. In a comparison of the creep of polysulfone with that of polycarbonate, heat-resistant ABS, and polyacetal at room temperature for 10,000 hr. (over a year) at 3000 p.s.i., polysulfone is slightly better than polycarbonate, showing about 1% total strain after a year. Both of these materials exhibit less than half the creep of polyacetal. At 210° F., the creep of polysulfone at 3000 p.s.i. is higher than at room temperature, but total strain is still well under 2% after a full year of such exposure. Polysulfone has a great advantage over polycarbonate at this stress and temperature, whereas polyacetal and ABS do not approach these values.

For design use, it is helpful to convert stress-strain information into creep modulus values. These are sometimes referred to as "apparent" modulus values, and can be used directly in conventional design equations to estimate deflections. A plot of creep modulus as a function of time at 72, 210, and 300° F. indicates that creep modulus is essentially independent of stress up to stress levels of 4000, 3000, and 1000 p.s.i., respectively.

As for long-term performance, polysulfone at 300° F. shows about a 10% increase in strength and modulus values, 90% retention of electrical properties, and 70% retention of impact strength. Changes take place within the first two to three months, after which the values remain substantially constant for the

remainder of the two-year test period. Polysulfone is recommended for continuous use in air at temperatures up to 340° F.

Changing environmental conditions produce exceptionally small dimensional changes in polysulfone. Equilibrium conditions are reached in all cases where such changes take place, except in thermal cycling tests. The very small dimensional changes, coupled with a low mold shrinkage of 0.007 in./in., mean that close tolerances can be maintained with polysulfone.

Applications

Present commercial use of polysulfone encompasses a wide variety of application areas. In the electrical and electronic area, integrated circuit carriers, connectors, coil bobbins, housings for meters, switches, and electronic components, and light-fixture sockets and shades are produced from polysulfone. It finds automotive uses in under-the-hood switch and relay bases, as well as electroplated dome-light bezels.

The aerospace industry is currently using polysulfone for aircraft-cabin interior parts because of its self-extinguishing and low smoke-density characteristics. It is also being used for face shields for astronauts because of heat and radiation resistance.

Polysulfone is used in appliances in parts for coffeemakers, humidifiers, high-intensity lamps, hot shaving-lather and hot-chocolate dispensers, color-TV sets, and kitchen-range hardware. Other applications include shower heads, film for transparencies, and toy-oven windows. It resists the aggressive environments encountered by alkaline battery cases and fuel cell components.

Polyvinyls

By R. J. Abramowitz*, L. J. Friedmant, and R. V. Lucke**

Vinyl polymers as a class constitute approximately one quarter of all plastics resins in use in the U.S. Vinyl chloride homopolymers and multipolymers form the largest subgroup, and hold greater than 80% of the markets for the vinyl family.

Worthy of mention are the polyvinyl acetate, alcohol, and formal groups. The latter two find application in solution coatings. The polyvinyl acetate family finds its heaviest applications in the coatings, adhesives, and paper industries, where these polymers are used in water-based form. The acetates gained several of their markets on the basis of specific property superiority over the previously entrenched styrene-butadiene

polymers. The polyvinyl alcohols find unique use as water-soluble temporary coatings, soluble films, and as protective colloids in latex manufacture and in paper coating slips.

The acetate copolymers and their hydrolyzed alcohol copolymer derivatives, with vinyl chloride particularly, extend the usefulness of the basic polymer. The acetates and the alcohols are useful respectively in modifying the processing and adhesion characteristics of PVC.

Vinyl chloride polymers have developed a broad spectrum of market applications through property modification. Such modification can be accomplished through the polymerization route, chain modification with comonomers and termonomers, or by compounding.

Among the major products produced from polyvinyl chloride are pipe, packaging film and bottles, flooring, textile-supported and unsupported sheets and

films for apparel, automotive, home furnishings, wire coatings, and records. Rigid PVC has shown the highest growth rates in recent years, and in 1971 pipe and conduit had an outstanding record in the face of an otherwise slow industry.

Supply-demand

For the near term, vinyl chloride polymer will be kept in reasonable balance with demand, with some de-bottlenecking types of expansion expected in 1972-1973 before any major new capacity commitments. A continued high growth rate in pipe and favorable rulings on the ecology scene for rigid bottles could tighten the supply situation in late 1972 or in 1973.

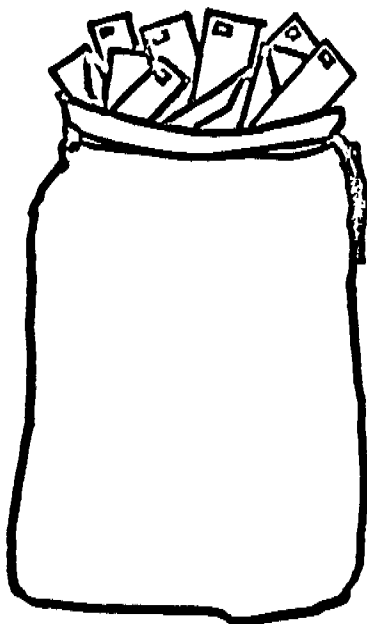
Two major additions were made to vinyl chloride monomer capacity, and a new process has appeared on the horizon, to potentially rival the oxychlorination route to monomer. Called the Transcat process, vinyl chloride monomer is made directly from ethane, chlo-

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For property data on vinyls, see the *Plastics Properties Chart*, p. 142.

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rine, and air. The process projects at least 1¢ lower materials cost/lb. of product, and has no byproducts, or byproduct disposal problems. Commercial viability, however, has yet to be demonstrated.

PVC processes

Vinyl chloride polymers are produced by four commercial routes:

Suspension polymerization. Monomer droplets are suspended in water and agitated under carefully controlled temperature and pressure. The polymerized resin is subsequently dried, blended, and prepared for shipment. The suspension process is used to produce a general-purpose grade of PVC normally ranging in particle size from 90 to 130 microns. However, finer particle size resins are also produced for specialty applications. Major uses of suspension polymerized PVC are in calendered film; extruded film, wire coatings, pipe and profile; and molded products.

Emulsion polymerization. A colloidal dispersion of PVC particles in an aqueous phase is produced in this process. These particles, approximately 0.5 microns in size, can be utilized directly from the dispersion, or latex, either plasticized or unplasticized, or they can be spray dried to a powder for use in plastisols, rigidols, plastigels, or organosols. Processes utilizing PVC dispersion resins include slush molding, casting, dipping, spray coating, roll and knife coating, and rotational molding.

Bulk polymerization. A more recently developed process is carried out in specially designed reactors in the absence of water and suspension additives. Because bulk resins are polymerized in a monomer matrix, the unused portion of which is recycled, they in no way contribute processing residues to the environment as pollutants. While capable of producing both general-purpose and specialty types of PVC, the bulk or mass polymerization process can also produce very porous PVC, the structure of which differs considerably from resins polymerized via suspension. Because PVC particles polymerized in bulk are free of additives used in suspension and emulsion polymerization, they lack membranous coatings. The absence of these pericellular membranes permits bulk PVC particles to fuse very rapidly in minimum work processing situations. Similarly, the excellent clarity inherent in bulk resins has made them preferred in many transparent product markets, including packaging film, bottles, and coatings.

Solution polymerization. A process of lesser commercial importance than the others discussed has been utilized in preparing specialty copolymers and terpolymers of vinyl chloride. Polymerization occurs in an organic solvent which then must be usually removed and recovered. The solution polymers are generally higher priced and used in product applications such as coatings and adhesives.

Almost always PVC requires com-

pounding before processing, but this step permits an unusual range of properties. It is this ability to vary properties so widely that has contributed to several rebirths of growth in the PVC industry. The additives used in PVC compounds may include stabilizers, plasticizers, lubricants, impact modifiers, processing aids, fillers, pigments, UV absorbers, and viscosity depressants.

While compounds of PVC differ with respect to product application requirements, they also differ in additive make-up to meet these requirements. Thus, a flexible garden hose will require a plasticizer for flexibility, whereas a rigid pipe will not. A PVC bottle will call for impact modifier, while a slush molded boot will not. Clear PVC packaging film will, of course, contain no fillers or pigments.

Each additive is selected for a specific purpose.

Stabilizers keep PVC from degrading while exposed to heat during processing, and protect the polymer against degradation in use resulting from heat, light, oxygen, etc. Stabilizers are usually composed of organo metallic salts, primarily tin, lead, barium, cadmium, calcium, and zinc compounds used in conjunction with epoxides, chelators, antioxidants, etc. Generally rigid PVC is formulated with tin and, occasionally, with lead compounds. Flexible PVC compounds are frequently stabilized with liquid or solid barium-cadmium systems. Nontoxic products are usually stabilized with dioctyl tin or calcium-zinc stabilizers.

Plasticizers are added to PVC to impart flexibility to finished products. Phthalate esters are considered to be the workhorse plasticizers. There are many suitable plasticizers, and special types may fulfill specific functions such as improving the rate of fusion, improving low temperature strength, resisting extraction by soapy water or other chemicals, and improving flame resistance properties. Epoxidized soybean, linseed, and tallate oils serve as PVC stabilizers as well as plasticizers. Usually more than one plasticizer is used in compounding PVC when properties in addition to flexibility are required in the finished product.

Lubricants, processing aids, and impact modifiers are used in PVC to improve specific properties. Lubricants such as waxes, esters, and metallic stearates are generally compounded with PVC to facilitate melt flow during processing. Internal lubricants compatible with PVC reduce intermolecular forces between polymer chains, while external lubricants such as polyethylene or mineral oil migrate to the surface of the PVC compound and improve slippage between the compound and the metallic surfaces of processing equipment. Processing aids similarly improve melt flow and increase homogeneity within the resin additive package. Impact modifiers such as chlorinated polyethylene, ABS, and MBS reduce the brittleness of unmodified rigid PVC.

Fillers are used in PVC primarily to

Continued on page 100

lower the cost of the compound. In some products fillers perform additional functions. Both glass and synthetic fibers will raise the impact strength of rigid PVC. Asbestos is reinforcing, and reduces shrinkage in floor tiles. Clay gives good electrical properties in wire compounds. Some fillers are abrasive and tend to scrub metallic surfaces during processing of pipe and profile compounds. Several of the most popular fillers include calcium carbonate, talc, clay, wollastonite, mica, asbestos, and glass beads and fibers.

As a possible substitute for all or some of the compounding normally done, one producer is preparing pipe compounds in situ during polymerization. All of the compounding additives are reportedly being introduced into the PVC reactor or slurry tank. This brings about a uniform distribution of materials previously only obtainable through high-shear, intensive mixing. Cost savings appear probable through elimination of additional preparation steps, equipment, and labor. Bulk handling, blending, and storage are facilitated by the process. Success of this approach could have important effects on processing equipment needs.

Processing

Calendering of PVC film and sheet continues to be the most popular route to large volumes of this product form. Ribbon blenders customarily mix the compound, which is subsequently fed from a Banbury mill to a short barrelled extruder and then to the calender. Production rates are high. Aside from homogenizing the molten compound, the extruder screens out foreign matter that might damage the costly calender rolls. Thin gauge nontoxic rigid packaging film is calendered as the preferred route for high quality end uses. Vinyl wall covering prepared by calendering has shown continued market strength.

In extrusion, compounds based on pellets or powder are being used in flexible, semirigid, and rigid applications. Twin- and four-screw extruders of recent vintage are currently producing large volumes of pipe and conduit from powder. New high efficiency tin stabilizers have made the economics of multi-screw extrusion more attractive. Single screw, 24 L/D machines are still used in producing blown film and flat sheet via a slot die. Rigid PVC foam profile is being extruded for campers and mobile homes. Similarly, foam molding strip is moving into other areas.

Injection molding of PVC has seen growth in both rigid and flexible products. Reciprocating screw injection molding machines are turning out shoe soles, door jams, and decorative parts for appliances. Uses of PVC have continued to grow, particularly in the area of injection molded pipe fittings in sizes as great as 10 in. in diameter. Telephone hand sets have been made of high impact grades of rigid PVC. Improved compounds and resins coupled with increased demand for flame retardancy are beginning



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to quicken application development in this area.

Blow molding equipment of comparative recent development has improved the competitiveness of PVC as a packaging material. There are now a number of suitable machines to choose from. While some fear of unfounded ecological emotional reaction persists, favorable product protection and consumer acceptance data have encouraged growth in the rigid bottle field. Improvements in res-

ins, compounds, stabilizers, and processing aids have paralleled equipment development.

New developments

Producers of PVC continue to predict major future promise in construction for rigid applications, like rain systems and siding, and also in carpet backing, powder coatings, and foamed profile. New offerings were made in each area during the past year.

Rallye 350 with a coating which color matches the rest of the car.

During the past year, growth in urethane coatings has been propelled by developments in the following areas:

Light stable isocyanates. Light-stable isocyanates are finding their way into commercial products which claim 1000 hours of fadeometer resistance to discoloration.

Fire retardancy. Several halogenated diols have appeared within the past few months which are designed for incorporation into urethane formulations. The government has developed a fire-retardant paint that is claimed to retain its ability to intumesce for more than 18 months. Flame-spread rating of surfaces coated with this paint is 25.

Improved hydrolytic stability. Once the bane of many polyester based urethane coatings, hydrolytic stability has been greatly improved because of a greater understanding of the factors contributing to hydrolytic instability and to use of test procedures which more clearly reflect in-use conditions.

Solventless coatings. Based on short and moderate chain length polyols, solventless coating formulations have been commercially applied in seamless flooring and fabric coating. The ecological and economic advantages of this approach are self-evident.

Emulsions and water soluble lacquers. These materials also have ecological and economic advantages. The emulsions can be prepared by inverting an isocyanate free, solvent based system to the water phase. Water soluble urethanes can be prepared by introducing hydrophilic groups into the polymer molecule. Textile and leather finishes are common applications for such products. They are also being evaluated for electrostatic coatings.

Urethane hybrids. The combination of urethanes and other polymers offers unlimited possibilities. Work has been reported on polyisocyanate cured hydroxylated acrylic resins, urethane-melamine copolymers and urethane-epoxy copolymers.

Urethane coatings, especially the light stable ones, are relatively high in price. Within a short time, however, the availability of new isocyanates will make light stable coatings available at prices approximating that of current TDI based systems. Such developments will insure a high growth rate for urethane coatings.

Urethane elastomers*

Urethane elastomers compose a relatively minor portion of the urethane market compared with urethane foam materials. While their growth has been less spectacular, development has progressed steadily and a wide range of materials, fabrication processes, and applications are available.

Basically, urethane elastomers are the reaction products of polyesters or poly-

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Polyurethane

Urethane polymers can take many forms—coatings, adhesives, elastomers, castings, foams, and spandex fibers—yet, they all have one thing in common: they contain urethane linkages, formed by reacting an isocyanate with a compound containing hydroxyl groups.

Among the areas in which significant growth has developed for polyurethane are coatings and elastomers. As protective coatings, urethane is versatile of application and has excellent physical properties. The elastomers are replacing natural and synthetic rubber, plastics and even metals, where their superior toughness, abrasion resistance and elastic modulus can be used to great advantage.

Urethane coatings*

The growth of urethane coatings has been impressive. In 1960, an estimated 6 million lb. of urethane coatings were consumed. Ten years later, polyurethane consumption was almost ten times that amount and growing steadily at an estimated rate of 12 to 15% per year. Table I gives a recent breakdown of urethane coating consumption according to various markets. Also shown is the anticipated growth within these markets projected to 1975. This impressive growth, both past and future, is due to the versatility of the urethane reaction and to the ease and rapidity with which it takes place. Urethane coatings can be tailored to meet the most demanding requirements of a customer.

Urethane coatings are classified according to the scheme shown in Table II. The oil modified urethane was the early leader in volume growth and still accounts for the largest volume among the five types. However, it is generally conceded that moisture cured and polyol cured prepolymers, Types 2 and 5, are growing fastest and will probably outdistance the oil modifieds because of their better properties.

Within the last few years, a sixth type

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For property data on polyurethane, see the Plastics Properties Chart, p. 142.

of urethane coating has appeared which seems destined for tremendous growth. This is the thermoplastic urethane lacquer which, unlike the other five types, does not depend on an isocyanate curing reaction to develop maximum properties but rather on hydrogen bonding phenomena. These secondary bonding forces are so great that the physical properties of these films surpass those of most true vulcanizates. At the same time these materials can be processed like any thermoplastic and can be dissolved, heat sealed, calendared or extruded. They are finding wide use as adhesives, fabric coatings, elastomer overcoatings and industrial films. By coating a nonwoven in a special way in production, an artificial suede which is virtually indistinguishable from genuine suede can be produced. Another use is to overcoat the urethane bumper on the Oldsmobile

Table I. Urethane coating consumption (millions of lb.)

	1970	1975
Trade sales (clear wood finishes)	21.5	27.0
Industrial maintenance, including flooring	19.5	24.0
Wire coating	2.5	4.0
Leather finishes	3.5	5.0
Fabric coatings	3.0	25.0
Other	5.0	6.0
Total	55.0	91.0

Table II. Polyurethane coating types

One package	Two package
ASTM-1, oil modified	ASTM-4, catalyzed prepolymer
ASTM-2, moisture cure	ASTM-5, polyol-prepolymer cure
ASTM-3, blocked isocyanate	Prepolymer-curable
Thermoplastics	
Hybrids	