VINYL CHLORIDE POLYMERS

Poly(vinyl chloride) [9002-86-2] (PVC), commanding large and broad uses in commerce, is second in volume only to polyethylene. In 2002 of 27×10^6 t of PVC were produced worldwide, with an approximate value of $\$19 \times 10^9$ (1). This large volume produced can be attributed to several unique properties. Vinyl compounds usually contain close to 50% chlorine, which not only provides no fuel, but acts to inhibit combustion in the gas phase, thus supplying the vinyl with a high level of combustion resistance, useful in many building as well as electrical housings and electrical insulation applications.

PVC has a unique ability to be compounded with a wide variety of additives, making it possible to produce materials that range from flexible elastomers to rigid compounds, that are virtually unbreakable with a notched Izod impact greater than 0.5 J/mm at −40°C, that are weatherable with good property retention for over 30 years, as well as compounds that have stiff melts and little elastic recovery for outstanding dimensional control in profile extrusion, and also low viscosity melts for thin-walled injection molding.

Produced by free radical polymerization, PVC has the structure of

$$\mathrm{-\!\!\left(CH_2CHCl\right)\!\!-}_n$$

where the degree of polymerization, n, ranges from 500 to 3500. The first discovery of PVC was in 1872, when it was found that exposure of vinyl chloride to sunlight produced a white solid that resisted attack by potassium hydroxide or water and melted with degradation at above 130°C (2,3). From 1912 to 1926, German workers at Chemische Fabrik Griesheim-Electron tried but failed to build machinery that could process PVC and overcome its instability (3). In 1926, a researcher at BFGoodrich, while looking for an adhesive to bond rubber to metal for tank liners, found that boiling PVC in tricresyl phosphate or dibutyl phthalate made it highly elastic (3), thus inventing the first thermoplastic elastomer.

1. Physical Properties

1.1. Morphology as Polymerized.

The principal type of polymerization of PVC is the suspension polymerization route. The morphology formed during polymerization strongly influences the processibility and physical properties. Mass-polymerized PVC has a similar morphology to suspension PVC.

In the suspension polymerization of PVC, droplets of monomer 30–150 μm in diameter are dispersed in water by agitation. A thin membrane is formed at the water–monomer interface by dispersants such as poly(vinyl alcohol) or methyl cellulose. This membrane, isolated by dissolving the PVC in tetrahydrofuran and measured at 0.01–0.02-μm thick, has been found to be a graft copolymer of polyvinyl chloride and poly(vinyl alcohol) (4,5). Early in the polymerization, particles of PVC deposit onto the membrane from both the monomer and the water sides, forming a skin 0.5–5-μm thick that can be observed on grains sectioned after polymerization (4,6). Primary particles, 1 μm in diameter, deposit onto the membrane from the monomer side (Fig. 1), whereas water-phase polymer, 0.1 μm in diameter, deposits onto the skin from the water side of the membrane (Fig. 2) (4). These domain-sized water-phase particles may be one source of the observed domain structure (7).

Mass-polymerized PVC also has a skin of compacted PVC primary particles very similar in thickness and appearance to the suspension-polymerized PVC skin, compared in Figure 3. However, mass PVC does not contain the thin-block copolymer membrane (7).

In suspension PVC polymerization, droplets of polymerizing PVC, 30–150-μm dia agglomerate to form grains at 100–200-μm dia (8). With one droplet per grain, the shape is quite spherical. With several droplets making up the grain, the shape can be quite irregular and knobby (9). The grain shape plays an important role in determining grain packing and bulk density of a powder (9).

For both suspension and mass polymerizations at less than 2% conversion, PVC precipitates from its monomer as stable primary particles, slightly below 1-μm dia (4,10–12). These primary particles are stabilized by a negative chloride charge (4,13). Above 2% conversion, these primary particles agglomerate. Sectioning the PVC grains of either suspension or mass resins readily shows the skins: primary particles at 1-μm dia, and agglomerates of primary particles at 3–10-μm dia (4,7,8,14).

These primary particles also contain smaller internal structures. Electron microscopy reveals a domain structure at about 0.1-μm dia (8,15,16). The origin and consequences of this structure is not well understood. PVC polymerized in the water phase and deposited on the skin may be the source of some of the domain-sized structures. Also, domain-sized flow units may be generated by certain unusual and severe processing conditions, such as high temperature melting at 205°C followed by lower temperature mechanical work at 140–150°C (17), which break down the primary particles further.

On an even smaller scale is the microdomain structure at 0.01-μm spacing. Small-angle x-ray scattering reveals a scattering peak (Fig. 4) corresponding to density fluctuations spaced at about 0.01 μm (18–20). When PVC is swelled by plasticizer or with a poor solvent such as acetone, swelling reaches a limit after which the PVC can no longer absorb plasticizer or acetone (21). This data suggest a structure where the crystallites of about 0.01-μm spacing are tied together by molecules in the amorphous regions. Plasticizer or acetone only swells the amorphous regions without dissolving the crystallites. Also, electron microscopy shows a spacing in plasticized PVC of 0.01 μm (22).

1.2. Hierarchical Structure of PVC. PVC has structure that is built upon structure which is, in turn, built upon even more structure. These many layers of structure are all important to performance and are interrelated. A summary of these structures is listed in Table 1; Figure 5 examines a model of these hierarchies on three scales.

1.3. Morphology during Processing. The first step in processing is usually powder mixing in a high speed, intensive mixer. PVC resin, stabilizers, plasticizers, lubricants, processing aids, fillers, and pigments are added to the powder blend for distributive mixing. For both suspension and mass PVC resins, intensive mixing above the glass-transition temperature results in a progressive increase in apparent bulk density as mixing temperature rises (23). This increase in apparent bulk density results from the smoothing and rounding of the irregular surface. However, the grains of PVC are largely unchanged; they are neither grossly deformed nor broken down to smaller particles (23).

In plasticized PVC, liquid plasticizers first fill the voids or pores in the PVC grains fairly rapidly during powder mixing. If a large amount of plasticizer is added, the excess plasticizer beyond the capacity of the pores initially remains on the surface of the grains, making the powder somewhat wet and sticky. Continued heating increases the diffusion rate of plasticizer into the PVC mass where the excess liquid is eventually absorbed and the powder dries.

PVC powder compounds are heated, sheared, and deformed during melt processing. During this process, the grains of PVC are broken down. First the skin is torn, exposing the PVC grain's internal structures (24). Subsequently the grains are broken down to agglomerates of primary particles, then to primary particles as the melt flow units. The primary particles seem to be persistent and fairly stable structures in the melt (25–32). This processing window of stable primary particles exists even with continued melt processing. The primary particle is about a billion molecules of PVC held together by a structure of crystallites and tie molecules (21).

The PVC crystallites are small, average 0.7 nm (3 monomer units), in the PVC chain direction, and are packed laterally to a somewhat greater extent (4.1 nm) (21,33). A model of the crystallite is shown in Figure 6. The crystalline structure of PVC is found to be an orthorhombic system, made of syndiotactic structures, having two monomer units per unit cell and 1.44–1.53 specific gravity (34–37).

1.4. PVC Fusion (Gelation). The PVC primary particle flow units (billion molecule bundles) can partially melt, freeing some molecules of PVC that can entangle at the flow unit boundary. These entangled molecules can recrystallize upon cooling, forming secondary crystallites, and tie the flow units together into a large three-dimensional structure (21,38). This process is known as fusion or gelation.

The strength created by the fusion process is strongly dependent on the previous processing temperature and the molecular weight of the PVC (38–44). The degree of fusion or gelation is measured in several ways. The entrance pressure in capillary rheometry is often used as a measure of the fusion strength (40,42,45–63). Differential scanning calorimetry is also often used as an indication of previous melt temperature and the amount of crystallinity melted and reformed as secondary crystallinity (54,55). X-ray diffraction has been used to measure gelation (55). Acetone or methylene chloride swelling and observation of structural breakdown is widely used as a qualitative measure of fusion (44,56–59). Sometimes the acetone-swollen specimens are sheared between glass slides to further establish the strength of the three-dimensional structure (59). Fusion has also been assessed based on scanning electron microscopy of fractured surfaces (29,30,46), and inverse gas chromatographic measurements have also been useful in accessing the degree of fusion of PVC (60).

The strength of this large three-dimensional fused (gelled) structure has been shown to be critical in determining Izod impact, creep rupture strength, and even flow in rigid injection molding. In these cases, both the melt temperature during processing and the PVC molecular weight play a large role in the Izod and creep rupture (38–41). In plasticized PVC, this large three-dimensional structure, which is also dependent on molecular weight and previous processing temperature, determines tensile strength, creep, and cut resistance. A model for accounting for molecular weight effects and processing temperature effects on PVC fusion is presented in Figure 7.

PVC normally improves in properties with increasing fusion (or increasing melt temperature); however, some observations show a falling off in impact properties with higher melt temperatures (42,56). This has been shown to be caused by melt fracture, when PVC fuses and flows as large melt flow units of multiple primary particles (61). These flow units of fused multiple primary particles can lead to surface roughness during extrusion, in both rigid and plasticized PVC (44,56,62); they can also be responsible for roughness when improperly handling regrind (63).

1.5. Plasticized PVC Morphology. Although most of the discussion has been on rigid PVC, plasticized PVC has the same structures as rigid PVC, except that plasticizer enters the amorphous phase of PVC and makes the tie molecules elastomeric. The grains break down to 1-μm primary particles which become the melt flow units (44). The crystallites are not destroyed by plasticizer (21). Partial melting allows entanglement at the flow unit boundaries, followed by recrystallization upon cooling to form a strong three-dimensional elastomeric structure (38,45). Table 2 provides a list of the PVC physical parameters.

2. Chemical Properties

2.1. Molecular Structure and Monomer Addition Orientation. The addition of vinyl monomer to a growing PVC chain can be considered to add in a head-to-tail fashion, resulting in a chlorine atom on every other carbon atom, ie,

$$-\!\!\left(CH_2CHClCH_2CHClCH_2CHClCH_2CHCl \right)\!\!_n-$$

or in a head-to-head, tail-to-tail fashion, resulting in chlorine atoms on adjacent carbon atoms, ie,

$$-\!\!\left(CH_2CHClCHClCH_2CH_2CHClCHClCH_2 \right)\!\!_n-$$

Dechlorination of head-to-head, tail-to-tail structure can be expected to go to 100% completion. If dechlorination of head-to-tail structure starts at random positions, then 13.5% of the chlorine should remain at the end of reaction. Dilute solutions of PVC treated with zinc removes 87% of the chlorine, proving the head-to-tail structure of PVC (71).

2.2. End Groups and Branching. Both saturated and unsaturated end groups can be formed during polymerization by chain transfer to monomer or polymer and by disproportionation. Some of the possible chain end groups are

$-CH_3$
$-CH_2Cl$
$-CHCl_2$
$-CH_2CHClCH{=}CHCl$
$-CH_2CHClCCl{=}CH_2$
$-CH_2CHClCH{=}CH_2$

PVC polymerization has a high chain-transfer activity to monomer; about 60% of the chains have unsaturated chain ends (72) and the percentage of chain ends containing initiator fragments is low (73). Chain transfer to polymer leads to branching. Branching in PVC has been measured by hydrogenating PVC, removing chlorine with lithium aluminum hydride. The ratio of methyl to methylene groups is measured by infrared spectroscopy using bands at 1378 and 1350, or 1370 and 1386/cm. Conventional PVC resins, made by mass or suspension polymerization at 50–90°C, contain 0.2 to 2 branches per 100 carbon atoms (65,73).

2.3. Stereoregularity. The addition of monomer fixes the tacticity of the previous monomer unit. Syndiotactic structure has the adjacent chlorine atoms oriented to opposite sides of the carbon–carbon–carbon plane, whereas isotactic structure has the adjacent chlorine atoms oriented to same side of the carbon–carbon–carbon plane. The potential energy for syndiotactic conformation is 4.2–8.4 kJ/mol (1–2 kcal/mol) lower than for isotactic conformation (74,75). Thus the ratio of propagation rates for syndiotactic to isotactic, k_s/k_i, must increase with decreasing temperature. Consequently, with decreasing polymerization temperature, the degree of syndiotacticity in PVC should increase. Measured amounts of syndiotacticity are illustrated in Figure 8 (76,77).

2.4. Polymerization Kinetics of Mass and Suspension PVC. The polymerization kinetics of mass and suspension PVC are considered together because a droplet of monomer in suspension polymerization can be considered to be a mass polymerization in a very tiny reactor. During polymerization, the polymer precipitates from the monomer when the chain size reaches 10–20 monomer units. The precipitated polymer remains swollen with monomer, but has a reduced radical termination rate. This leads to a higher concentration of radicals in the polymer gel and an increased polymerization rate at higher polymerization conversion.

Reactions in the liquid phase proceed as follows:

$$\textit{Initiation} \quad M \xrightarrow{k_i} M^{\cdot}$$

$$\textit{Propagation} \quad R^{\cdot} + M \xrightarrow{k_p} R\ (M)^{\cdot}$$

$$\textit{Chain transfer to monomer} \quad R^{\cdot} + M \rightarrow P + M^{\cdot}$$

$$\textit{Termination} \quad R^{\cdot} + R^{\cdot} \xrightarrow{k_t} P$$

and reactions in the polymer gel are

$$\begin{aligned}&\textit{Propagation}\quad (R^{\cdot}) + M \rightarrow (R\ (M)^{\cdot})\\&\textit{Chain transfer to monomer}\quad (R^{\cdot}) + M \rightarrow (P) + M^{\cdot}\\&\textit{Termination}\quad (R^{\cdot}) + (R^{\cdot}) \rightarrow (P)\end{aligned}$$

where $R^{\cdot}$ is a polymer chain radical in liquid monomer; $(R^{\cdot})$, a polymer chain radical in the polymer gel phase; M, a monomer molecule; (M), a monomer molecule in the polymer gel phase; P, polymer in monomer; (P), polymer gel; and k_i, k_p, and k_t are reaction rate coefficients for initiation, propagation, and termination, respectively. Values for k_p and k_t at 60°C are 1.23×10^5 and 2.3×10^{10} L/(mol·s), respectively (78).

Polymerization in two phases, the liquid monomer phase and the swollen polymer gel phase, forms the basis for kinetic descriptions of PVC polymerization (79–81). The polymerization rate is slower in the liquid monomer phase than in the swollen polymer gel phase on account of the greater mobility in liquid monomer, which allows for greater termination efficiency. The lack of mobility in the polymer gel phase reduces termination and creates a higher concentration of radicals, thus creating a higher polymerization rate. Thus the polymerization rate increases with conversion to polymer.

Chain transfer to monomer is the main reaction controlling molecular weight and molecular weight distribution. The chain-transfer constant to monomer, C_{m}, is the ratio of the rate coefficient for transfer to monomer to that of chain propagation. This constant has a value of 6.25×10^{-4} at 30°C and 2.38×10^{-3} at 70°C and a general expression of $5.78\,e^{-2768/\mathrm{T}}$. At 30°C, chain transfer to monomer happens once in every 1600 monomer propagation reactions; at 70°C, chain transfer happens once every 420 monomer additions (80,82–84). Thus temperature of polymerization strongly influences PVC molecular weight, ie, the molecular weight increases with lower polymerization temperature (Fig. 9).

PVC molecular weights are usually determined in the United States using inherent viscosity or relative viscosity measured according to ASTM D1243: 0.2 g/100 mL of cyclohexanone at 30°C. In Europe, K values are used, measured at 0.5% in cyclohexanone. The relationship among inherent viscosity, K value, number-average molecular weight (M_n), and weight-average molecular weight (M_w) for commercial grades of PVC is shown in Table 3.

3. PVC Resin Manufacturing Processes

3.1. Mass Polymerization. Mass or bulk polymerization of PVC is normally difficult. At high conversions the mixture becomes extremely viscous, impeding agitation and heat removal, causing a high polymerization temperature and broad molecular weight distribution (86). A two-stage process that overcomes these problems was originally developed by Saint Gobain (France). The first stage of the process, which forms a skeleton seed grain for polymerization in a second stage, is carried out in a prepolymerizer with flat blade agitator and baffles to about 7–10% conversion. The number of grains remain constant throughout this polymerization (87).

In the second-stage polymerizer, a larger horizontal vessel and more monomer and initiator are added. This vessel is equipped with a slow-moving agitator blade running close to the vessel wall. The reaction proceeds through the liquid stage and at about 25% conversion becomes a powder. Heat removal is achieved, 30% by the jacket, 60% by a condenser, and 10% by the cooled agitator shaft (88). Unreacted monomer is removed by vacuum. Although the mass process saves drying energy, it has remained a minor process when compared to the suspension process.

3.2. Suspension Polymerization.

Suspension polymerization is carried out in small droplets of monomer suspended in water. The monomer is first finely dispersed in water by vigorous agitation. Suspension stabilizers act to minimize coalescence of droplets by forming a coating at the monomer–water interface. The hydrophobic–hydrophilic properties of the suspension stabilizers are key to resin properties and grain agglomeration (89).

Kinetics of suspension PVC are identical to the kinetics of mass PVC, both increasing in rate with conversion (90). After polymerization to about 80–90% conversion, excess monomer is recovered, the slurry is steam-stripped in a column to a residual monomer level of about 0.0001% (10 ppm), excess water is centrifuged off, and the resin is dried with hot air.

3.3. Emulsion Polymerization.

Emulsion polymerization takes place in a soap micelle where a small amount of monomer dissolves in the micelle. The initiator is water-soluble. Polymerization takes place when the radical enters the monomer-swollen micelle (91,92). Additional monomer is supplied by diffusion through the water phase. Termination takes place in the growing micelle by the usual radical–radical interactions. A theory for true emulsion polymerization postulates that the rate is proportional to the number of particles $[N]$. N depends on the 0.6 power of the soap concentration $[S]$ and the 0.4 power of initiator concentration $[I]$; the average number of radicals per particle is 0.5 (93).

However, the kinetics of PVC emulsion does not follow the above theory. The rate shows the same increasing behavior with conversion as mass polymerization (94,95). $[N]$ depends on $[S]$, but the relationship varies with the emulsifier type (96,97). However, the rate is nearly independent of $[N]$ (95). The average number of radicals per particle is low, 0.0005 to 0.1 (95). The high solubility of vinyl chloride in water, 0.6 wt %, accounts for a strong deviation from true emulsion behavior. Also, PVC's insolubility in its own monomer accounts for such behavior as a rate dependence on conversion.

Emulsions of up to 0.2-μm dia are sold in liquid form for water-based paints, printing inks, Printing inks and finishes for paper and fabric. Other versions, 0.3–10-μm dia and dried by spray-drying or coagulation, are used as plastisol resins. Plastisols are dispersions of PVC in plasticizer. Heat allows fast diffusion of plasticizer into the PVC particle, followed by fusion (gelation), to produce a physically cross-linked elastomer, where the physical cross-links are PVC crystallites.

3.4. Microsuspension Polymerization.

Whereas emulsion polymerization uses a water-soluble initiator, microsuspension polymerization uses a monomer-soluble initiator. The monomer is homogenized in water along with emulsifiers or suspending agents to control the particle sizes. Microsuspension paste resins at 0.3–1-μm dia are used to make plastisols for flooring, seals, barriers, etc. These plastisols are also dispersions of PVC in liquid plasticizer and are cured by heating. Heating allows plasticizer to diffuse uniformly into the PVC particles; at higher temperatures, the plasticized particles fuse. Microsuspension blending resins at 10–100-μm dia are used as extenders to paste resins in plastisols (98).

3.5. Solution Polymerization. In solution polymerization, a solvent for the monomer is often used to obtain very uniform copolymers. Polymerization rates are normally slower than those for suspension or emulsion PVC. For example, vinyl chloride, vinyl acetate, and sometimes maleic acid are polymerized in a solvent where the resulting polymer is insoluble in the solvent. This makes a uniform copolymer, free of suspending agents, that is used in solution coatings (99).

3.6. Copolymerization. Vinyl chloride can be copolymerized with a variety of monomers. Vinyl acetate [9003-22-9], the most important commercial comonomer, is used to reduce crystallinity, which aids fusion and allows lower processing temperatures. Copolymers are used in flooring and coatings. This copolymer sometimes contains maleic acid or vinyl alcohol (hydrolyzed from the poly(vinyl acetate)) to improve the coating's adhesion to other materials, including metals. Copolymers with vinylidene chloride are used as barrier films and coatings. Copolymers of vinyl chloride with maleates or fumerates are used to raise heat deflection temperature. Copolymers of vinyl chloride with acrylic esters in latex form are used as film formers in paint, nonwoven fabric binders, adhesives, and coatings. Copolymers with olefins improve thermal stability and melt flow, but at some loss of heat-deflection temperature (100). Copolymerization parameters are listed in Table 4.

4. Compounding

The additives found in PVC help make it one of the most versatile, cost-efficient materials in the world. Without additives, literally hundreds of commonly used PVC products would not exist. Many materials are useless until they undergo a similar modification process. Steel, for instance, contains among other things chromium, nickel, and molybdenum. PVCs are tailored to the requirements using sophisticated additives technology.

4.1. Stabilizers. Lead stabilizers, particularly tribasic lead sulfate, is commonly used in plasticized wire and cable compounds because of its good nonconducting electrical properties (122).

Organotin stabilizers are commonly used for rigid PVC, including pipe, fittings, windows, siding profiles, packaging, and injection-molded parts. These repair unstable sites on PVC, removing unstable chlorine and replacing it with a ligand from the tin stabilizer molecule (123–125). This produces stability at least an order of magnitude better than without stabilizer. Examples of effective tin compounds are dialkyl tin dilaurate and mono- and dialkyl tin diisooctylthioglycolate. Certain grades of methyl tins and octyl tins are used in food contact applications.

Antimony tris(isooctylthioglycolate) has found use in pipe formulations at low levels. Its disadvantage is that it cross-stains with sulfide-based tin stabilizers (122). Barium–zinc stabilizers have found use in plasticized compounds, replacing barium–cadmium stabilizers. These are used in moldings, profiles, and wire coatings. Cadmium use has decreased because of environmental concerns surrounding certain heavy metals.

Calcium–zinc stabilizers are used in both plasticized PVC and rigid PVC for food contact where it is desired to minimize taste and odor characteristics. Applications include meat wrap, water bottles, and medical uses.

Many stabilizers require costabilizers. Several organic costabilizers are quite useful with barium–zinc and calcium–zinc stabilizers, eg, β-diketones, epoxies, organophosphites, hindered phenols, and polyols (122).

4.2. Impact Modifiers. In the early days of plastics, many unplasticized PVC products were brittle. This gave plastics a cheap reputation. It was therefore quite desirable to develop technology to produce tough plastics. In the early 1950s, The Geon company (then a part of BFGoodrich) began adding rubbery polymers to PVC to improve toughness (126). Rubbery particles act as stress concentrators or multiple weak points, leading to crazing or shear-banding under impact load (127). This can result in cavitation and/or cold drawing, thus allowing the PVC to absorb large amounts of energy. Impact modifier choices are listed in Table 5.

4.3. Processing Aids. PVC often flows in the form of billions of molecule primary particles. Processing aids glue these particles together before the PVC melts, thus acting as a fusion promoter. Processing aids also modify melt rheology by increasing melt elasticity and die swell; some by reducing melt viscosity and melt fracture. Some processing aids affect dispersion of fillers, impact modifiers, and pigments (129); others lubricate to reduce PVC sticking to metal. The most common processing aids are high molecular weight acrylics based primarily on polymethylmethacrylate copolymers.

4.4. Lubricants. Lubricants are often classified as internal or external (130–134). Internal lubricants were considered either to be soluble in PVC, to have little effect on fusion, or to be capable of reducing melt viscosity; external lubricants were considered to retard fusion or to promote metal release (see LUBRICATION AND LUBRICANTS). This system of classifying lubricants has too many conflicting measurements to be consistent and useful. Others have shown classifications based on synergy between various lubricants (135,136) but did not explain the nature of that synergy. A model for the lubrication mechanism has been developed that explains synergy between certain lubricants (62). This model treats lubricants as surface-active agents. Thus, some lubricants have polar ends that are attracted to other polar ends and to polar PVC flow units and to polar metal surfaces. These also have nonpolar ends that are repelled by the polar groups. Synergy happens when nonpolar lubricants are added, which are attracted to the nonpolar ends and act as a slip layer. This model is shown in Figure 10.

4.5. Plasticizers. It was found in 1926 that solutions of PVC, prepared at elevated temperatures with high boiling solvents, possessed unusual elastic properties when cooled to room temperature (137). Such solutions are flexible, elastic, and exhibit a high degree of chemical inertness and solvent resistance.

This unusual behavior results from unsolvated crystalline regions in the PVC that act as physical cross-links. These allow the PVC to accept large amounts of solvent (plasticizers) in the amorphous regions, lowering its T_g to well below room temperature, thus making it rubbery. PVC was, as a result, the first thermoplastic elastomer (TPE). This rubber-like material has stable properties over a wide temperature range (32,138–140).

A few plasticizers impart specific properties for particular applications. For example, citrate esters are used in food contact applications, benzoates are used for stain resistance, and chlorinated hydrocarbons impart flame resistance and good electrical properties. Aliphatic diesters offer good low temperature flexibility; linear alcohol-based phthalates offer good low temperature flexibility and also have reduced volatility; phosphates improve flame resistance; trimellitates have low volatility, are used for high temperature applications, and also have good low temperature properties. Polymeric plasticizers do not migrate easily but suffer from poor low temperature flexibility. Epoxy plasticizers are also good plasticizers that have low volatility and act as costabilizers, improving the thermal stability of PVC. Commonly used PVC plasticizers are listed in Table 6.

Plasticizers and stabilizers in particular have been researched at length to determine their potential impact on human health and the environment. DEHP (di-2-ethylhexylphthalate) has been used worldwide in applications such as blood bags, saline solutions, meat wraps, and other highly credible uses. However, there has been much debate over that impact because of the differing methods used to evaluate them. Although the U.S. National Toxicology Program and the International Agency for Research on Cancer have classified the plasticizer DEHP as a possible human carcinogen, their methodologies have been criticized for potentially inaccurately ascribing results obtained with rodents to humans (141,142). Mechanistic studies indicate that the carcinogenic response which DEHP produces in rodents is directly related to physiologic and metabolic changes that are specific to that species. Because the evidence indicates the response is an artifact to that species and not a true indication of human hazard, a number of regulatory bodies do not consider DEHP to pose a hazard to humans. The Specialized Experts Working Group of the European Commission, for instance, has concluded that there is no evidence to warrant the classification of DEHP as a carcinogen (143). DEHP is not regulated as a carcinogen by the U.S. Food and Drug Administration, which has long governed the plasticizer's use in medical devices and in food contact applications. DEHP-plasticized PVC is used in medical applications like blood bags where it is known to protect red blood cells from deterioration. Flexible PVC film is considered the most desirable material for wrapping meats, because it is oxygen-permeable, maintains the bright red color needed to make meats salable to consumers, and extends the shelf life of meats.

4.6. Fillers. Fillers are used to improve strength and stiffness, to lower cost, and to control gloss. The most common filler is calcium carbonate, which ranges in size from 0.07 to well over 50 μm. Some forms are treated with a stearic acid coating. Clay fillers, such as calcined clay, improve electrical properties. Glass fibers, talc, and mica improve tensile strength and stiffness, but at a loss in ductility.

4.7. Pigments. A variety of pigments are added to PVC to give color, including titanium dioxide and carbon black.

4.8. Ultraviolet Light Stabilizers. One form of stabilization is to absorb the ultraviolet light. Both titanium dioxide and carbon black are strong ultraviolet light absorbers and effective in protecting the PVC. Carbon black is a stronger absorber than titanium dioxide and can therefore be used at lower levels in PVC for protection. For ultraviolet light absorption in transparent PVC or for improvement of pigmented systems, various derivatives of benzotriazole are used, such as 2-(2′-hydroxy-3′,5′-(di-*t*-butyl)phenyl)benzotriazole. Where tin carboxylate stabilizers are used instead of tin mercaptide stabilizers, hindered amine light stabilizers, particularly with ultraviolet absorbers, are effective (144).

4.9. Biocides. Although PVC itself and rigid PVC compounds are resistant to attack by microorganisms, plasticized PVC, in specific applications such as flashing and sealing boots on roofs, shower curtains, and swimming pools, may need protection. Many biocides, often containing arsenic compounds, are available for a balance of stability, compatibility, weatherability, and biocidal effectiveness.

4.10. Flame Retardants. Because PVC contains nearly half its weight of chlorine, it is inherently flame-retardant. Not only is chlorine not a fuel, but it acts chemically to inhibit the fast oxidation in the gas phase in a flame. When PVC is diluted with combustible materials, the compound combustibility is also increased. For example, plasticized PVC with $>30\%$ plasticizer may require a flame retardant such as antimony oxide, a phosphate-type plasticizer, or chlorinated or brominated hydrocarbons (145,146).

4.11. Foaming or Blowing Agents. Cellular PVC can be made by a variety of techniques, such as whipping air into a plastisol, incorporating a gas under pressure, incorporating a physical blowing agent into the melt, or using a chemical blowing agent which releases a gas when it decomposes with heat.

The most common chemical blowing agent is 1,1′-azobisdicarbonamide, which decomposes with heat to release nitrogen gas. Typically, the closed-cell foams of rigid PVC range down to a density of 0.4 g/cc. Physical blowing agents, such as chlorofluorocarbons, which volatilize without changes in the chemical bonds, are capable of producing foams at down to 0.03 g/cc when used with a copolymer PVC. Because of the damage to the ozone layer in the stratosphere, not all chlorofluorocarbons are acceptable. Newer types of physical blowing agents are becoming available that can minimize ozone depletion.

5. Economic Aspects

Poly(vinyl chloride) is the second largest commodity thermoplastic produced in the world, after polyethylenes. In 2002, nearly 27×10^6 t of PVC were produced worldwide valued at $\$19 \times 10^9$ (1).

PVC is a global product, manufactured by roughly 150 companies in approximately 50 countries. It is likely that additions to PVC capacity will be in Asia, especially China, and in Eastern Europe and the Middle East. Expansion in the United States is expected to be incremental. Investments in new PVC capacity in Western Europe and Japan will be minimal.

More than 90% of the PVC produced in North America is by the suspension route. Table 7 lists the North American producers of PVC and their capacities for 2003 (147).

Demand for PVC is expected to be about 15.66×10^9 pounds up from 14.02×10^9 pounds in 2002. The growth rate is expected at the rate of 2.8% through 2006 (147).

The construction industry accounts for 70% of PVC demand, thus, growth or decline depends on the construction industry. After decline in demand in 2000–2001, the U.S. PVC market revived and this revival has carried forward to the present. Stricter water management regulations will drive higher demand for pipe in the U.S. PVC's continuous development in new grades and novel compounding gives PVC good opportunities in the pipe market. The market remains under pressure, however, from high energy and feedstock costs.

6. Health and Safety Factors and Toxicology

There are no significant health hazards arising from exposure to poly(vinyl chloride) at ambient temperature (149–152). However, a British study has found a small decrease in breathing capacity for workers who smoked and were exposed to vinyl resin dust (153). This decrease was about one-seventh of that caused by normal aging and about equal to that expected with a one-pack-a-day cigarette smoker.

Because routine inhalation of dust of any kind should be avoided, reduction of exposure to poly(vinyl chloride) dust may be accomplished through the utilization of care when dumping bags, sweeping, mixing, or performing other tasks that can create dust. The use of an approved dust respirator is recommended where adequate ventilation may be unavailable.

At processing temperatures, most polymers emit fumes and vapors that may be irritating to the respiratory tract. This is also true for PVC and its additives. Such irritation may extend to the skin and eyes of sensitive people. Processing emissions exposure can also be greatly reduced or eliminated by the use of properly designed and maintained exhaust ventilation.

Decomposition of plastics, eg, through greatly elevated temperatures above normal operating temperatures, can result in personnel exposure to decomposition or combustion products. In the case of PVC compounds, such decomposition involves hydrogen chloride, which causes irritation of the respiratory tract, eyes, and skin. Depending on the severity of exposure, physiological response can be coughing, pain, or inflammation of the respiratory tract. Fortunately, the pungent odor of hydrogen chloride provides an excellent warning signal, causing exposed personnel to be driven from the area which prohibits long-term exposure. The odor of hydrogen chloride is detectable as low as 1–5 ppm.

6.1. Fire and Explosion. Poly(vinyl chloride) resin has a flash point of approximately 391°C (735°F) and a self-ignition temperature of approximately 454°C (850°F) (ASTM D1929). In general, PVC burns with difficulty because a substantial amount of energy is required to break down the polymer into smaller fragments that can sustain combustion in the gas phase, principally as a consequence of the action of the halogen content of the material. Consequently, PVC is difficult to ignite. Fires tend to extinguish naturally in the absence of a substantial external source of heat or flame. Because hydrogen chloride is generated during combustion, this action serves as a flame-quencher in the vapor phase. Poly(vinyl chloride) releases less heat than many other combustible materials. Precautions should be taken similar to those for other combustible materials, eg, wood or other plastics.

Poly(vinyl chloride) powder has a very low tendency to explode. The minimum ignition energy for explosion is much higher than that of natural materials such as corn starch and flour and also exceeds those of other plastic materials. However, as with any powder materials, care should be taken in addressing ignition sources in working and handling areas if dusting should occur. In addition, walkways and floors should be cleared of PVC dust to prevent slippery footing.

In firefighting where PVC is involved, water, ABC dry chemical, or protein-type air foams should be used as extinguishing media. Carbon dioxide may be ineffective on larger fires because of lack of cooling capacity, which may result in reignition. Firefighters should utilize a self-contained breathing apparatus (SCBA) in positive-pressure mode. In addition, for an enclosed or poorly ventilated area, an SCBA should be worn during cleanup immediately after a fire as well as during the attack phase of firefighting operations.

PVC should not be melt-mixed with acetal polymers. These polymers are chemically incompatible; mixing could cause rapid decomposition and gas evolution.

6.2. Toxicology. Toxicology studies have shown poly(vinyl chloride) to be equivocally tumorigenic through oral and implant studies. The International Agency for Research on Cancer (IARC) shows inadequate evidence that poly(vinyl chloride) is carcinogenic in animals or humans and has an overall evaluation of 3 (not classifiable). The United States has no occupational exposure limits for PVC except as particulates not otherwise classified (PNOC). For PNOCs, the American Conference of Governmental Industrial Hygienists (ACGIH) has a threshold limit value (TLV) of 10 mg/m^3 for inhalable and 3 mg/m^3 for respirable, whereas the Occupational Safety and Health Act (OSHA) permissible exposure limits (PELs) are 15 mg/m^3 for total dust and 5 mg/m^3 for the respirable fraction.

Poly(vinyl chloride) is listed on the TSCA inventory and the Canadian Domestic Substances List (DSL) as ethene, chloro-, homopolymer [9002-86-2]. Because polymers do not appear on the European Community Commercial Chemical Substances listing or EINECS, poly(vinyl chloride) is listed through its monomer, vinyl chloride [75-01-4]. In the United States, poly(vinyl chloride) is an EPA hazardous air pollutant under the Clean Air Act Section 112 (40 CFR 61) and is covered under the New Jersey Community Right-to-Know Survey: N.J. Environmental Hazardous Substances (EHS) List as “chloroethylene, polymer” with a reporting threshold of 225 kg (500 lb).

7. Environmental Considerations and Recycling

7.1. Chlorine. Chlorine, the material used to make PVC, is the 20th most common element on earth, found virtually everywhere, in rocks, oceans, plants, animals, and human bodies. It is also essential to human life. Free chlorine is produced geothermally within the earth, and occasionally finds its way to the earth's surface in its elemental state. More usually, however, it reacts with water vapor to form hydrochloric acid. Hydrochloric acid reacts quickly with other elements and compounds, forming stable compounds (usually chloride) such as sodium chloride (common salt), magnesium chloride, and potassium chloride, all found in large quantities in seawater.

The chlorides found in common salt water are an essential element in all body fluids and, in this form, make up about 0.15% of total body weight. A large number of complex organic chlorides and organochlorines are naturally produced chemicals, widely present in nature, and play many essential roles (154–157). Chlorine is also an essential element of naturally occurring antibacterial and antifungal agents such as chlortetracycline, chloramphenicol, and griseofulvin, which have revolutionized the treatment of human bacterial and fungal infections.

Even more complex cyclic organochlorines, including dioxins and furans, are produced from burning wood and other vegetable matter, and are natural by-products of forest fires (158,159). Chlorine-based chemicals are everywhere, and have been so since before the existence of mankind. Both dioxins and furans have been found in lake sediments dating back to 1860 (160), and samples taken from ice cores in Greenland dating back to 1869 showed definite spikes in chlorine content correlating with volcanic activity (161). Given the fact that chlorine compounds are naturally produced in such vast quantities, and so widely distributed in the natural world, banning production of chlorine to keep chlorine compounds out of the environment would be futile, extremely costly, and would deprive the world of hundreds of products critical to society's health and well-being. Also, the environment would be worse off.

Over 30% of the chlorine produced on a global basis goes to make PVC. Not only is chlorine essential to the chemical composition of PVC, it provides a number of unique properties that give this versatile plastic a distinct advantage in product applications and the marketplace. It makes PVC inherently flame-retardant. PVC is the world's leading electrical material, with over 250×10^3 t (500×10^6 lb) used annually for wire and cable insulation and sheathing, electrical conduit, boxes, and components. PVC is over 50% chlorine and, as a result, one of the most energy-efficient polymers. Chlorine makes PVC far more environmentally acceptable than other materials that are totally dependent on petrochemical feedstocks. In addition, recycling PVC is easier because the chlorine in PVC acts as a marker, enabling automated equipment to sort PVC containers from other plastics in the waste stream (162).

7.2. Vinyl Solid Waste and Recycling. Although vinyl is the world's second most widely used plastic, less than one-half percent by weight is found in the municipal solid waste stream. Most of that consists of vinyl packaging, bottles, blister packaging, and flexible film. This is because most vinyl applications are long-term uses, such as pipe and house siding, and are not disposed of quickly. Vinyl wastes are handled by all conventional disposal methods, ie, recycling, landfilling, and incineration (including waste-to-energy).

All types of vinyl products can be recycled and reprocessed into second-generation products. According to a 1999 study by Principia Partners (163), more than 1×10^9 pounds of vinyl were recovered and recycled into useful products in North America in 1997. About 18×10^6 pounds of that was post-consumer vinyl diverted from landfills and recycled into second-generation products. Overall, more than 99% of all manufactured vinyl compound ends up in a finished product, due to widespread post-industrial recycling (163).

Vinyl containers or rigid blister packaging can be identified by the “3” symbol as specified by The Society of the Plastics Industry coding system, now law in 39 states. A vinyl container can also be identified by the “smile” or “slash” mark found on its bottom side. These markings can be used by consumers to easily sort plastics for curbside collection.

The vinyl industry has taken the lead in developing automated sorting technology that large-scale recycling operations can use to separate different plastics from each other more efficiently. These include systems developed by National Recovery Technologies, Nashville, Tenn.; ASOMA Instruments, Austin, Texas; and Magnetic Separation Systems, Nashville, Tenn. The vinyl industry has also sponsored pilot recycling programs to evaluate the success of these systems and to test the feasibility of expanded recycling of vinyl.

Once recycled, vinyl can be reused in such applications as packaging, pipe, siding, parking stops, floor files, notebook covers, traffic cones and more. A study conducted by the University of Toledo in 1989 identified nearly 100 potential applications for recycled vinyl.

In landfills, vinyl wastes, like all plastics, are extremely resistant to decomposition. In fact, high technology landfills are often lined with thick-gauge vinyl and use PVC pipe to handle liquid leachate and methane gas for environmental protection. A method and apparatus for recovery of PVC from waste has been reported (164).

Vinyl compares favorably to other packaging materials. In 1992, a lifecycle assessment comparison of specific packages made from glass, paperboard, paper, and selected plastics concluded that vinyl was the material that has the lowest production energy and carbon dioxide emissions, as well as the lowest fossil fuel and raw material requirements of the plastics studied (165).

7.3. Incinerating PVC Wastes. A study (166) sponsored by the American Society of Mechanical Engineers (ASME), involving the analysis of over 1700 test results from 155 large-scale, commercial incinerator facilities throughout the world, found no relationship between the chlorine content of waste and dioxin emissions from combustion processes. Instead, the study stated, the scientific literature is clear that the operating conditions of combustors are the critical factor in dioxin generation. This work includes and confirms a number of other studies, most notably, the work conducted in 1987 by the New York Energy Research and Development Authority (167). Those tests revealed that the presence or absence of PVC had no effect on the amount of dioxin produced during the incineration process.

Incinerator scrubbing systems can remove about 99% of the hydrogen chloride generated by incinerating vinyl plastics and other chlorine-containing compounds and materials (168). New requirements from the U.S. Environmental Protection Agency make scrubbers mandatory on all incinerators so that they can neutralize a range of acid gases, including sulfur dioxide and nitrogen oxide, which are produced by a variety of materials. Because acid generated in incinerators comes from a variety of sources, including table salt and paper products, scrubbers are necessary whether or not PVC is present in the waste feed (169). A more recent study, conducted by Midwest Research Institute and published by the ASME, concluded that removing vinyl from the waste stream would not eliminate the need for air pollution control devices and monitoring equipment, nor would it influence the choice of incineration equipment (170).

Municipal incinerators are often targeted as a primary cause of acid rain. In fact, power plants burning fossil fuels, which produce sulfur dioxide and nitrogen oxide, are actually the leading cause of acid rain, along with automotive exhaust (171). In Europe and Japan, studies show that only about 0.02% of all acid rain can be traced to incineration of PVC (172).

There are many common misconceptions about vinyl. For example, the idea that vinyl is not recycled is untrue. Industrial scrap vinyl has been recycled for years, but in more recent years, post-consumer vinyl recycling is growing too. When the Council for Solid Waste Solutions (now the American Plastics Council) conducted a nationwide survey in 1991, it found that there were an estimated 1100 municipal recycling programs in place or planned in the United States that include vinyl.

Nor is it true that there is no market for recycled vinyl. In 1989, the University of Toledo identified nearly 100 uses for recycled vinyl. Overall, the potential demand for recycled vinyl is estimated to be over twice the potential supply of all vinyl bottles produced in the United States each year (247×10^3 tons needed vs 103.5×10^3 tons available via recycling of bottles). A more recent directory published by the Vinyl Institute lists nearly 50 companies that make commercial products out of recycled vinyl (173).

It is not true either that vinyl is the problem in municipal recycling because it contaminates other resins. Contamination occurs whether or not vinyl is present. Other resins are just as much a contamination problem as vinyl. Except for commingled plastics applications, different plastic materials cannot be mixed successfully in most recycled products applications. This is why it is crucial to separate efficiently one plastic from another. Because of the chlorine that is present in it, vinyl lends itself very well to automated sorting technology.

Nor is it true that poly(ethylene terephthalate) (PET) and high density polyethylene (HDPE) packaging are listed as 1 and 2 in the Society of the Plastics Industry (SPI) recycling coding system because they are the most recyclable. The numbers assigned to each plastic in the SPI coding system are purely arbitrary and do not reflect the material's recyclability.

The misconception that vinyl gives off dioxin when it is incinerated is misleading. A study conducted by ASME in 1995 (156) found that the presence, or absence, of chlorine-containing wastes in incinerators had no effect on the levels of dioxin produced. Rather, it was found that incinerator operating conditions (primarily temperature) were the key to controlling dioxin formation. More recently, German officials examined the issue of incinerating vinyl waste and decided there was no cause for concern (174).

Misleading also is the idea that vinyl should be banned from incinerators because it contains heavy-metal additives. This is an evolving issue. Most vinyl products do not contain heavy metals and vinyl is a small fraction in feed to incinerators. Reformulation to replace heavy metals is in progress but some use is likely to continue. Banning vinyl from incinerators does not eliminate this problem. Rather, regulations should specify that incinerator residues (ash) be disposed of appropriately.

Furthermore, it is not true that European packagers, grocery stores, and regulators have banned vinyl. There is only one ban on vinyl packaging in Europe, and that is on the use of vinyl-bottled mineral water in Switzerland, a commercial ploy to block the sale of French mineral water in that country. There is a voluntary agreement in Denmark by industry to substitute alternatives to vinyl packaging when feasible. Some municipalities in Germany have restricted the use of certain vinyl products in municipally funded building projects. Industry is working to change those restrictions with several notable reversals, including Berlin and Bielefeld. Government studies on PVC in Belgium and the Netherlands have concluded that there should be no bias against the use of PVC (175–177). Elsewhere in Europe, vinyl packaging continues to be widely used. In Britain, one of the leading retailers, Marks & Spencer, has chosen vinyl over other materials as the chain's most environmentally friendly polymer. In Switzerland, retailer Migros has stated that its whole attitude toward vinyl will change when incinerator scrubber technology is fully employed. The late-1990s trend in Europe, led by the Germans, is to take a comprehensive look at waste reduction and make industry a partner in that process. This involves all industries, not just the vinyl industry. Overall, Europe remains a larger consumer of vinyl packaging than the United States.

It is also not true that vinyl plastics decompose in landfills and give off vinyl chloride monomer, because like all plastics, vinyl is an extremely stable landfill material. It resists chemical attack and degradation, and is so resistant to the conditions present in landfills that it is often used to make landfill liners. On those occasions when vinyl chloride monomer is detected in landfills, it typically can be traced to the presence of other chemicals and solvents.

Furthermore, it is not true that other plastics are more environmentally friendly than vinyl. A more recent study compared vinyl to a number of other packaging materials and found that vinyl consumed the least amount of energy, used the lowest level of fossil fuels, consumed the least amount of raw materials, and produced the lowest levels of carbon dioxide of any of the plastics studied (178). In fact, the Norwegian environmental group Bellona has concluded that a generally reduced use of vinyl plastics can lead to a worsening of the environmental situation (179).

Lastly, it is not true that in a fire, vinyl is unusually hazardous and damaging. The real hazards in a fire are carbon monoxide and heat; these are especially a problem with other materials that readily burn. Because vinyl products contain chlorine, they are inherently flame-retardant and resist ignition. When it does burn, however, vinyl produces carbon monoxide, carbon dioxide, and hydrogen chloride. Of these, the most hazardous is carbon monoxide.

Hydrogen chloride is an irritant gas that can be lethal at extremely high levels. However, research indicates that those levels are never reached or even approached in real fires. All organic materials, when burned, release a lengthy list of chemical by-products. For instance, when wood burns, as many as 175 different fire gases may be produced, including benzene and acrolein (180). Burning wool produces hydrogen cyanide. Even the simple act of barbecuing a steak or smoking a cigarette can produce dioxin (181). More importantly, virtually all burning materials produce carbon monoxide, which is by far considered the greatest toxic hazard in fires because of the abundant levels produced and the low levels that can cause death (182).

The fire death rate in the United States is decreasing, dropping from a rate of 76 per million in the 1940s, when most construction and decorative products were made of natural materials, to 29 per million in the 1980s, by which time, PVC had replaced natural materials in numerous applications (183). This downward trend can be attributed in large part to improved building codes and the broader use of sprinkler systems and smoke detectors. However, the increased use of more fire-resistant materials, such as PVC, deserves part of the credit for this improvement.

Hydrogen chloride is produced when PVC burns. A series of tests for the Federal Aviation Administration studied this issue. In those studies, test animals were able to survive exposures to hydrogen chloride reaching 10,000 ppm (184). More recent studies indicate less of a potential for delayed effects on lung function than expected (185). In a typical fire, hydrogen chloride levels rarely exceed 300 ppm, a fact confirmed by the Boston Fire Department and Harvard University (186). In hundreds of autopsies conducted on fire victims in the United States, not one death has been linked to the presence of PVC.

Bell Laboratories studied wire and cable compounds made of PVC or other halogen-based compounds vs halogen-free compounds and found that neither type of material presented a clearcut advantage in a fire, and that the halogenated compounds sometimes outperformed the nonhalogenated products in terms of creating less corrosion (187).

8. Uses

Numerous specifications and standards are used to define PVC resins and compounds. Table 8 summarizes a few of these standards.

PVC is so versatile that it can be compounded for a wide range of properties and used in a wide variety of markets. Most of the products are durable goods and have long life spans. Its use in short-term, one-time-use products is limited.

Use of PVC in 2003 breaks down as follows: construction, 74% (includes pipe and tubing, 46%; siding, 14%; windows and doors, 6%; other including flooring, 8%); consumer goods, 9%; packaging, 6%; electrical fittings and wire and cable coatings, 5%; transportation, 2%; home furnishings, 2%; miscellaneous, 2% (147).

8.1. Pipe and Fittings.

Pipe and fittings, a principal market for PVC, are a prime example of PVC as an engineering thermoplastic. These applications are designed with PVC for long-term satisfactory performance and are highly optimized for efficient production at high rates and minimal costs. Pipe manufacturing uses powder compounds, twin-screw extruders, and vacuum sizing/cooling. Because of the volume of products, the process is highly developed. The products, designed to meet appropriate ASTM standards, include pressure pipe of various sizes and drain, waste, and vent applications.

Chlorinated PVC (CPVC) is used in higher temperature applications such as hot-water piping. Because of its superior creep resistance, CPVC is also used in automated fire-safety sprinkler systems.

8.2. Weatherable Siding, Windows, and Doors. PVC is accepted commercially as an excellent weathering material. Plastic materials are damaged by the sun, particularly by ultraviolet light. PVC's chemical response to weathering is well understood so that compounds and products can be designed for satisfactory outdoor performance. The mechanism of degradation starts by absorbing the sun's damaging ultraviolet light. Because this absorption is affected by PVC's previous thermal degradation during processing (188,189), it is important to avoid thermal damage to PVC during processing. The absorbed light breaks bonds and forms free radicals, which leads to loss of hydrogen chloride, yellowing, and, at the same time, oxidative bleaching (removal of yellowing). With a proper level of titanium dioxide to protect the PVC from the absorption of ultraviolet light (190), the right choice of the type of titanium dioxide to control the rate of the oxidation and bleaching process, and a correct use of other weather-stable ingredients, a well-designed PVC formulation can be very durable to the weather.

As with pipe, siding manufacturing is highly optimized for efficient production at high rates and minimal costs. Siding uses powder compounds, twin-screw extruders, and vacuum sizing/cooling.

Other products, such as windows, may or may not use the powder compound, twin-screw extruder, and vacuum-sizing approach. For windows, this is a much more complex operation than for pipe, requiring large investments to develop and operate the process. Cubed compound, where the PVC grains are already broken down, can be run faster on simpler single-screw extruders because lower melt temperatures are typical. Because elastic swell is reduced at lower melt temperatures, die design is simpler. Either vacuum sizing or air sizing/cooling is possible. The products are designed to meet appropriate ASTM standards. Products include siding, soffits, gutters and down spouts, windows (including all-vinyl windows and vinyl-protected wood windows), and door-glazing applications and garage doors.

8.3. Profiles. Complex profiles require specialty manufacturing skills to build, maintain, and operate extrusion dies as well as cooling and sizing equipment to deliver the exact dimensions required. Cubed compound, where the PVC grains are already broken down, can be run faster on simple single-screw extruders on account of the typical low melt temperatures. Because elastic swell is reduced at lower melt temperatures, die design is simpler and is often the same dimensions as the desired profile. Either vacuum sizing or air sizing/cooling is possible.

The low elastic swell, unique to PVC, results from the presence of the billion molecule flow units. Other plastics have higher die swell, which increases at lower melt temperatures (191). These plastics thus pose much more difficulty in designing dies and in maintaining a process to hold dimensions.

8.4. Wire and Cable.

PVC has been used in wire and cable applications since World War II, when the U.S. Navy demanded lower combustibility materials in construction. These products are manufactured by cross-head extrusion, usually from pellet compounds on single-screw extruders. Some line speeds are 1524 m (5000 ft) per minute (60 mph). The compounds are optimized for the requirements, including low temperature flexibility, high use temperature, especially low combustibility, weatherability, and high resistance to cutthrough.

8.5. Injection-Molded Products.

Numerous housings, electrical enclosures, and cabinets are injection-molded from rigid PVC. These take advantage of PVC's outstanding UL flammability ratings and easy molding into thin-walled parts. PVC has developed melt flow capabilities to the point where it competes with essentially any other flame-retarded engineering thermoplastic and molds easier than most.

Pipe fittings require quite high tensile and creep resistance; they are thus molded from compounds that have less melt flow than for thin-walled housings. Plasticized compounds are injection-molded into a variety of parts requiring elastomeric properties.

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Table 1. **Summary of Poly(vinyl chloride) Morphology**

Feature	Size	Description
droplets	30–150 μm dia	dispersed monomer during suspension polymerization
membranes	0.01–0.02 μm thick	membrane at monomer–water interface in suspension PVC (usually graft copolymer of PVC and dispersant, such as poly(vinyl alcohol))
grains	100–200 μm dia	after polymerization, free-flowing powder usually made up of agglomerated droplets; in mass polymerization, it is free-flowing powder
skins	0.5–5 μm thick	shell on grains made up of PVC deposited onto membrane during suspension polymerization; in mass polymerization, it is PVC compacted on grain surface
primary particles	1 μm dia	formed as single polymerization site in both suspension and mass polymerization by precipitation of polymer from monomer; made up of over a billion molecules, it is often melt flow unit established during melt processing (in emulsion polymerization, it is emulsion particle)
agglomerates of primary particles	3–10 μm dia	formed during polymerization by merging of primary particles
domains	0.1 μm dia	formed under special conditions such as high temperature melting (205°C) followed by lower temperature mechanical work (140–150°C); water-phase polymerization also produces domain-sized structure
microdomains	0.01 μm spacing	crystallite spacing
secondary crystallinity	0.01 μm spacing	crystallinity reformed from amorphous melt and responsible for fusion (gelation)

Table 2. **PVC Physical Parameters**

PVC property	Value			Reference
crystallographic data	orthorhombic, two monomer units/cell			
	a	*b*	*c*	
commercial PVC, nm	1.06	0.54	0.51	34
single crystal, nm	1.024	0.524	0.508	37
crystallinity, %				
as polymerized		19		
from melt		4.9		64
density (uncompounded), g/cc				
whole		1.39		65
crystallites		1.53		37
oxygen permeability, cc/(cm·s)cm^2 cm Hg		$238\, e^{-13.3/\mathrm{RT}}$		66
Poisson ratio (rigid PVC)		0.41		
refractive index		1.54		67
glass-transition temperature, °C		83		
coefficient of linear thermal expansion (unplasticized), °C		7×10^{-5}		
specific heat rigid PVC	temp, °C	value, J/g °C[a]		
	23	0.92		68
	50	1.05		
	80	1.45		
	120	1.63		
plasticized PVC (50 phr DOP)	23	1.54		68
	50	1.67		
	80	1.75		
	120	1.88		
thermal conductivity (unplasticized), J/(cm·s)°C		17.5×10^{-4}		69
dielectric strength				
kV/mil		0.5		
kV/mm		20		
solubility parameter, (J/cm^3)$^{0.5}$		40.7 (av)		70

[a] To convert J to cal, divide by 4.184.

Table 3. **Commercial PVC Molecular Weights**[a]

Inherent viscosity, ASTM D1234	Relative viscosity, ASTM D1234	K value, (DIN 53726)	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$
0.42	1.09	45.0	15.0	30.0
0.47	1.10	47.1	18.0	36.0
0.52	1.11	49.3	20.0	40.0
0.57	1.12	51.3	22.5	45.0
0.62	1.13	53.6	25.0	50.0
0.67	1.14	56.1	27.5	55.0
0.73	1.16	58.2	30.5	61.0
0.78	1.17	60.5	33.0	67.0
0.83	1.18	62.9	36.0	72.0
0.88	1.19	64.9	38.5	78.0
0.92	1.20	67.1	41.0	82.5
0.98	1.22	69.2	44.0	89.5
1.03	1.23	71.5	47.0	95.0
1.08	1.24	73.3	50.0	101.0
1.13	1.25	74.9	52.5	107.5
1.21	1.27	77.5	57.0	117.0
1.30	1.30	80.7	62.5	128.5
1.40	1.32	83.8	68.5	141.0
1.60	1.38	90.8	81.0	168.0
1.80	1.43	96.7	93.5	195.0

[a] Ref. 85.

Table 4. **Copolymerization Parameters of Vinyl Chloride**

M_2	r_1	r_2	e	Q	Temperature, °C	Ref.
acrylic acid	0.107	6.8	0.77	1.15	60°C	101
acrylonitrile	0.04	2.7	1.20	0.60	60°C	102
butadiene	0.035	8.8	−1.05	2.39	50°C	103
butene	3.4	0.21				104
n-butyl acrylate	0.07	4.4	1.06	0.50	45°C	(101,105)
diethyl fumarate	0.12	0.47	1.25	0.61	60°C	106
dimethyl itaconate	0.053	5.0	1.34	1.03	50°C	107
diethyl maleate	0.77	0.009				104
ethylene	3.21	0.21	−0.20	0.015	50°C	108
ethylhexyl acrylate	0.16	4.15				104
isobutylene	2.05	0.08	−0.96	0.033	60°C	(109,110)
isoprene			−1.22	3.33		
maleic anhydride	0.296	0.008	2.25	0.23	75°C	111
methacrylic acid	0.034	23.8	0.65	2.34	60°C	101
methacrylonitrile			0.68	0.86	60°C	112
methyl acrylate	0.12	4.4	0.60	0.42	50°C	113
methyl methacrylate	0.1	10	0.4	0.74	68°C	114
octyl acrylate	0.12	4.8	1.07	0.35	45°C	105
propylene	2.27	0.3	−0.78	0.002		(115,110)
styrene	0.02	17	−0.80	1.0	60°C	116
vinyl acetate	1.68	0.23	−0.22	0.026	60°C	117
N-vinylcarbazole	0.17	4.8	−1.40	0.41	50°C	118
vinyl chloride			0.20	0.044		
vinyl laurate	7.4	0.2				104
vinylidene chloride	0.3	3.3	0.36	0.22	60°C	119
vinyl isobutyl ether	2.0	0.02			50°C	120
N-vinylpyrrolidone	0.53	0.38	−1.14	0.14	50°C	121

Table 5. **Impact Modifiers Used for PVC Applications**[a,b]

Use	acr	m-acr	ABS	CPE	EVA	MBS	MABS
siding	+	+		+	+		
windows	+	+		+	+		
gutters	+	+		+	+		
pipe and conduit	+	+	+	+	+	+	+
irrigation pipe	+	+		+	+		
fittings	+	+	+	+	+	+	+
interior trim	+	+	+	+	+	+	+
foam	+						
interior profiles	+	+	+	+	+	+	+
clear film			+			+	+
clear bottles			+			+	+
credit cards	+	+	+	+	+	+	+
furniture	+	+		+	+		
appliances	+		+			+	
housings	+		+			+	

[a] Ref. 128.

[b] acr = all acrylic; m-acr = modified acrylic; ABS = acrylonitrile–butadiene–styrene; CPE = chlorinated polyethylene; EVA = ethylene–vinyl acetate; MBS = methyl methacrylate–butadiene–styrene; and MABS = methacrylate–acrylonitrile–butadiene–styrene.

Table 6. **Commonly Used PVC Plasticizers**

Plasticizer	Abbreviation
aliphatic ester	
di(2-ethylhexyl) adipate	DOA
di(2-ethylhexyl) azelate	
di(2-ethylhexyl) sebacate	
phthalate	
di(2-ethylhexyl)	DOP or DEHP
diisooctyl	DIOP
diisodecyl	DIDP
butylbenzyl	BBP
butyloctyl	BOP
diisononyl	DINP
ditridecyl	DTDP
diundecyl	DUP
linear C7-C11	711 phthalate
di(2-ethylhexyl) terephthalate	DOTP
phosphates	
trioctyl	TOP
cresyl diphenyl	CDP
tricresyl	TCP
triphenyl	
tri(2-ethylhexyl)	TEHP
trimellitates	
tris(2-ethylhexyl)	TOTM
triisooctyl	TIOTM
epoxies	
epoxidized soybean oil	ESO
epoxidized linseed oil	
epoxy stearate	
2-ethylhexyl epoxytallate	

Table 7. **North American Producers of PVC and Their Capacities,** × **10^3 t**[a]

Producer	Location	Capacity
	United States	
Certain Teed	Lake Charles, La.	215.4
Colorite Polymers	Burlington, N.J.	54.4
Dow Chemical	Texas City, Tex.	63.5
Formosa Plastics	Baton Rouge, La.	449
	Delaware City, Del.	65.8
	Illiopolis, Ill.	147.4
	Point Comfort, Tex.	623.7
Geismar Vinyls Company	Geismar, La.	260.8
Georgia Gulf	Aberdeen, Miss.	453.6
	Oklahoma City, Okla.	222.3
	Plaquemine, La.	557.9
Occidental Chemical	Pottstown, Pa.	99.9
OxyVinyls	Deer Park, Tex.	308.4
	Louisville, Ky.	265.4
	Pasadena, Tex.	934.4
	Pedricktown, N.J.	158.7
PolyOne	Henry, Ill.	52.2
	Pedricktown, N.J.	59
Shintech	Addis, La.	272.2
	Freeport, Tex.	1360.8
	Plaquemine, La.	590
Westlake PVC	Calvert City, Ky.	362.9
U.S. Total		*7577.4*
	Canada	
OxyVinyls	Fort Saskatchewan, Alberta	158.8
	Niagara Falls, Ontario	260.8
Royal Group, Technologies	Sarnia, Ontario	215.5
Canada Total		*635*
North America Total		*8212.4*

[a] Ref. 147.

Table 8. **Specifications and Standards for PVC Resins and Compounds**

Standard	Description
ASTM D1755	PVC resin cell classification
ASTM D1784	PVC rigid compound cell classification
ASTM D1785	PVC pipe, schedule 40, 80, 120
ASTM D2287	PVC nonrigid (plasticized) compound cell classification
ASTM D2464	PVC THR fittings
ASTM D2466	PVC socket fittings, schedule 40
ASTM D2467	PVC socket fittings, schedule 80
ASTM D2665	DWV pipe and fittings
ASTM D2729	PVC sewer pipe and fittings
ASTM D2740	PVC tubing
ASTM D2846	CPVC hot water distribution system
ASTM D2949	PVC DWV 7.62 cm (3 in.) thin wall
ASTM D3033	PVC PSP sewer pipe and fittings
ASTM D3034	PVC PSM sewer pipe and fittings
ASTM D4216	PVC rigid building products compounds
NSF 14	PVC potable water, fittings
UL 62	PVC wire insulation
UL 83	PVC T, TW, THW, THWN, THHN wire insulation
UL 444	PVC telecommunications wire insulation jacket
UL 719	PVC NM jacket
UL 758	PVC AWM wire insulation
UL 1272	PVC TC cable jacket

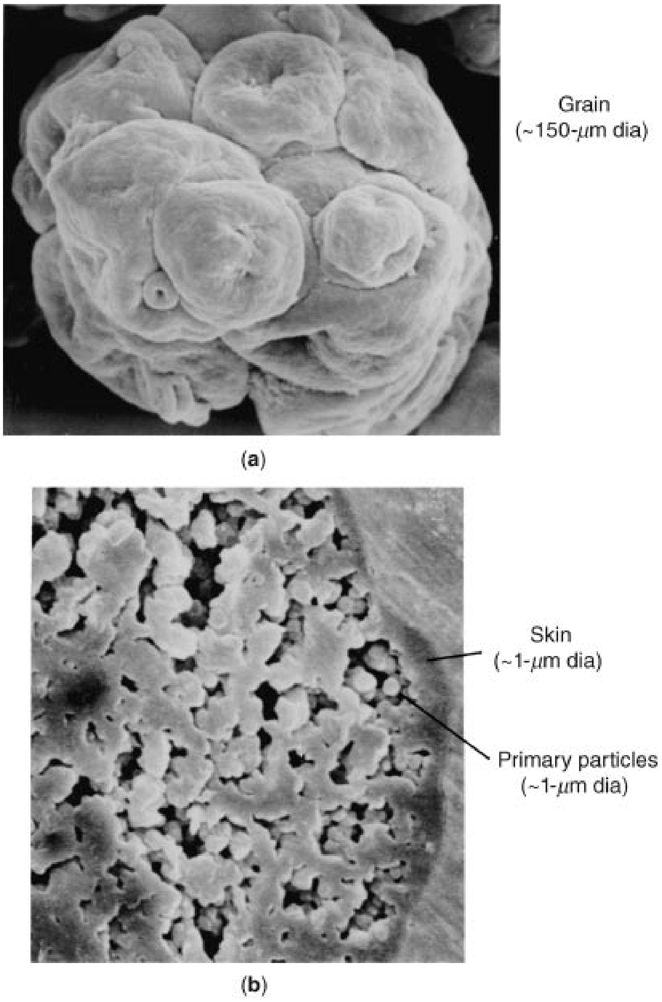


Fig. 1. A grain of (**a**) suspension PVC and (**b**) its cross-section showing the skin and primary particles.

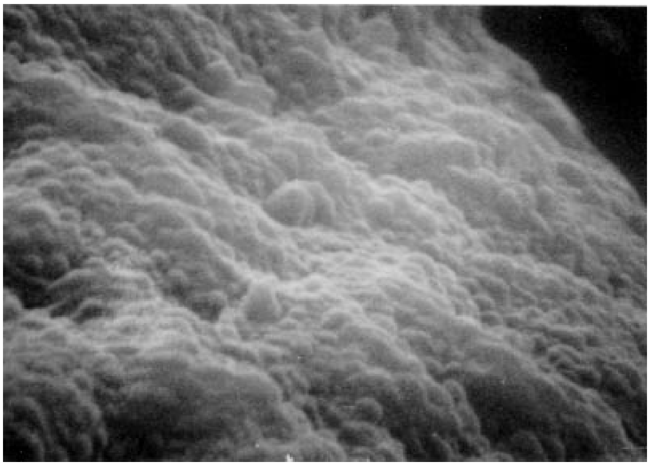
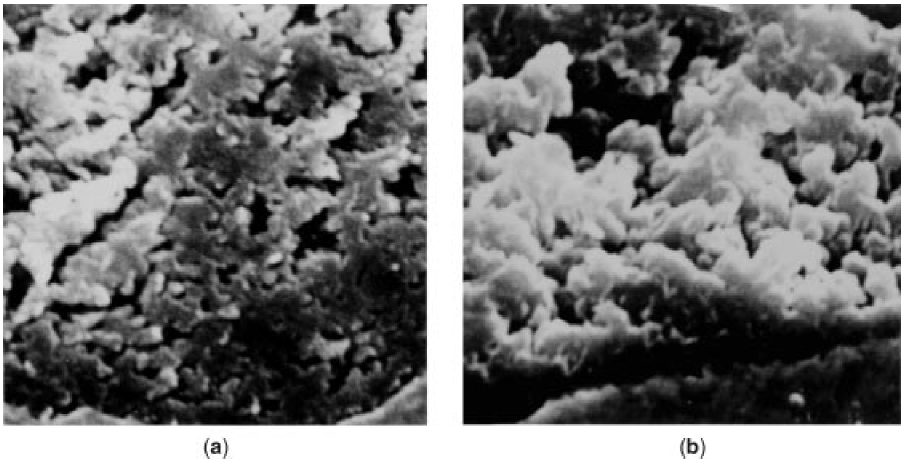


Fig. 2. Skin of a suspension PVC grain showing 0.1-μm dia particles deposited from the water phase.



(a) (b)

Fig. 3. Cross-sections of PVC grains from (**a**) suspension and (**b**) mass PVC grains showing similar morphologies.

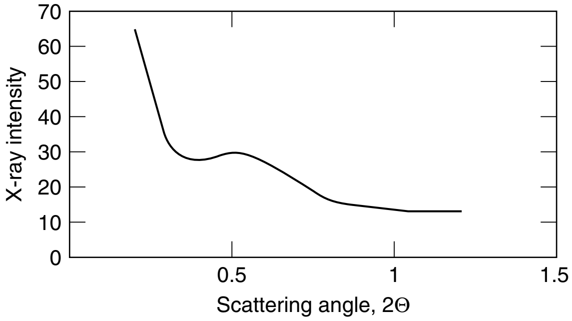


Fig. 4. Small-angle x-ray scattering pattern from PVC plasticized with 20 parts per hundred resin of dioctyl phthalate (18).

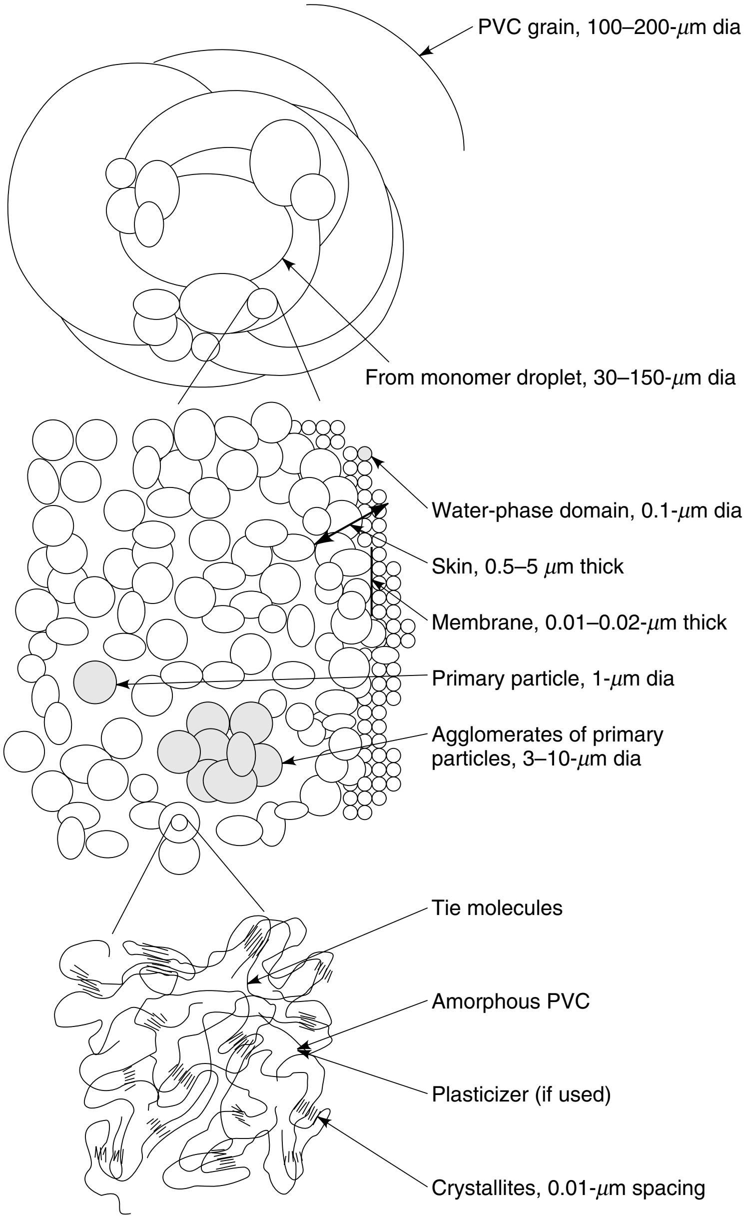


Fig. 5. The hierarchical structure of PVC.

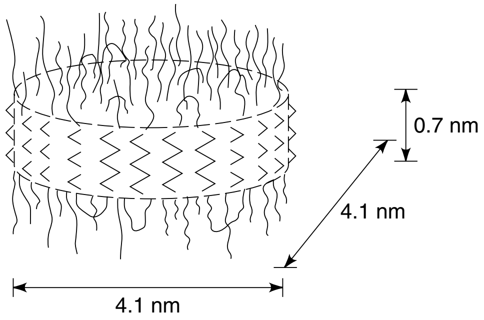


Fig. 6. The crystallite structure of PVC.

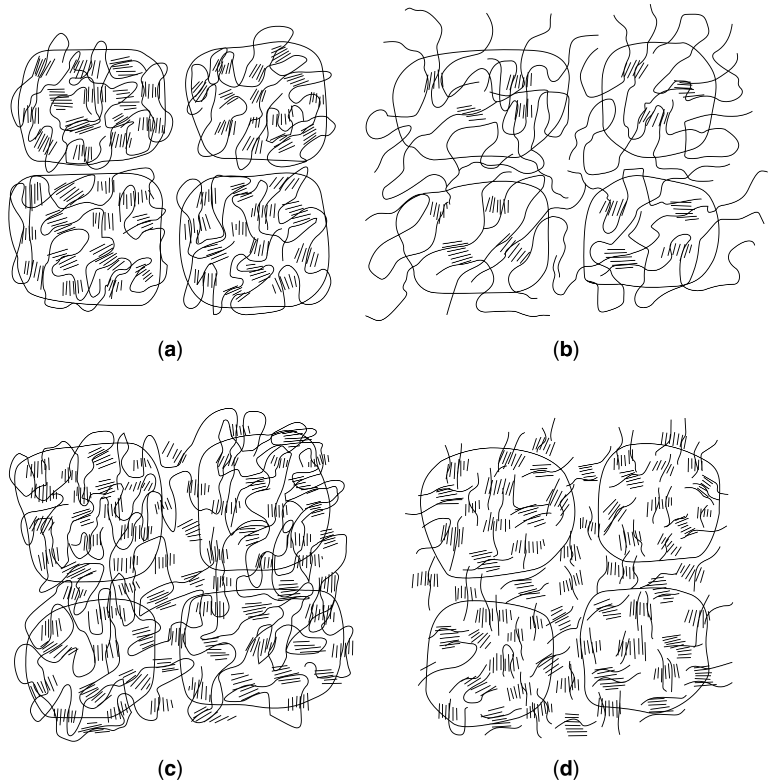


Fig. 7. Model for PVC fusion, accounting for molecular weight effects and processing temperature effects: (**a**) unfused PVC primary particles; (**b**) partially melted PVC primary particles; (**c**) partially melted then recrystallized high molecular weight PVC, showing strong three-dimensional structure; and (**d**) partially melted then recrystallized low molecular weight PVC, showing weak three-dimensional structure.

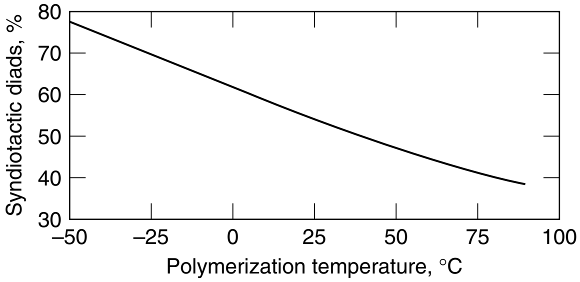


Fig. 8. The syndiotactic structure of PVC (76,77).

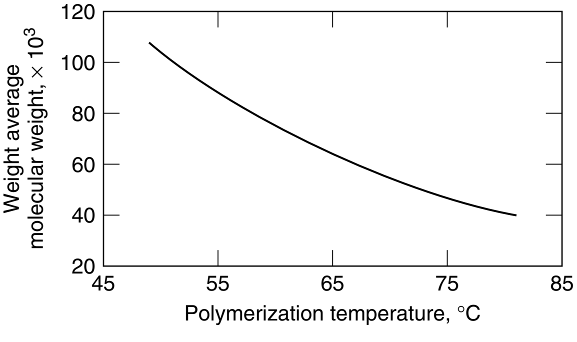


Fig. 9. PVC molecular weight as influenced by polymerization temperature.

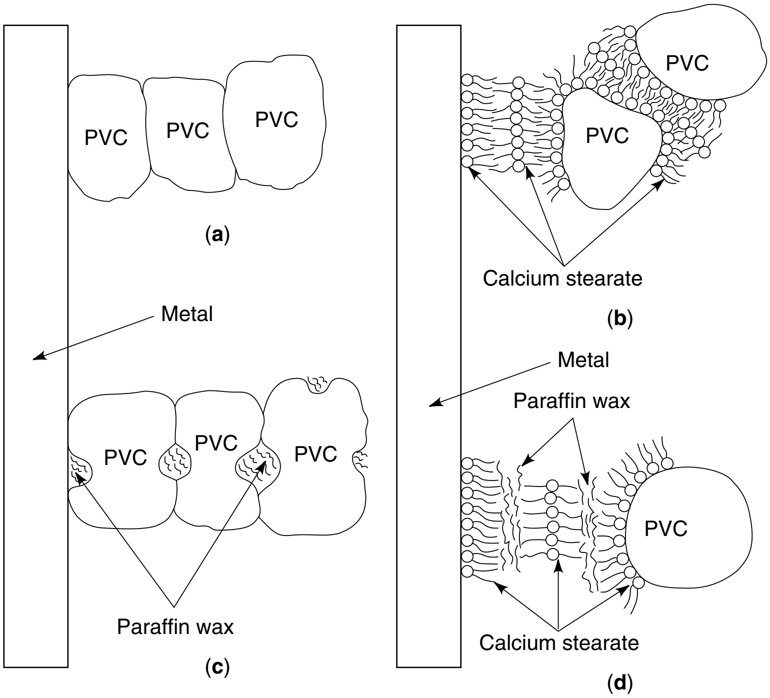


Fig. 10. A model of PVC lubrication mechanism showing (**a**) PVC adhesion to metal without lubricant; (**b**) surface activity of calcium stearate; (**c**) nonmetal releasing character of paraffin only; and (**d**) synergy between calcium stearate and paraffin (62).