MODERN CHEMICAL TECHNOLOGY

PART 16

Polymerization of Vinyl Chloride

Suspension, emulsion, bulk and solvent techniques convert vinyl chloride monomer into polyvinyl chlorides. Initiating the reaction and controlling polymer size, length and molecular weight depend to a large extent on the chemistry and on the type of multiple-phase relations that occur during the course of polymerization.

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Polyvinyl chloride polymers (commonly called PVC polymers) are the second largest family of high polymers in the U.S., based on the amount produced. In 1966, production was over 2 billion lb., or over 17% of all plastics. The term "PVC polymers" as used here will include materials produced by polymerizing pure vinyl chloride (VC), or mixtures of comonomers that are predominantly vinyl chloride.

PVC polymers are by far the most important member of the family of vinyl polymers,* which normally includes polyvinyl chloride, polyvinyl acetate, polyvinyl alcohol, polyvinyl acetals and polyvinylidene chloride.

Production of PVC polymers since 1955 has grown almost 15%/yr. in the U.S.[11, 17] This rate is expected to remain at this level for the next five years. In many parts of the world, production has increased even more rapidly than in the U.S. In 1946, the U.S. produced 80% of all PVC, but it only makes about 25% currently. The amount of PVC produced in Common Market countries now surpasses that in this country, and Japanese output is over half of that in the U.S.

Part of the major increase for PVC production in the rest of the world is caused by delays in getting adequate production of other thermoplastic polymers, including polyethylene. When other polymers are produced abroad in larger quantities, they may displace PVC for certain uses. Nevertheless, the average annual growth rate for PVC polymers is estimated to be substantial in most countries, and to vary between 12 and 14% for the Common Market from 1965 to 1970.

Increased production of PVC during the last few years has been caused in part by a steady and significant decrease in the selling price. Present prices for the general-purpose grade PVC are 15¢/lb., or much lower for quantity purchases. Projections based on recent process improvements (particularly those for vinyl chloride manufacture) indicate that PVC will sell for less than 10¢/lb. (based on 1965 dollars) by 1970.[11] At least 23 companies in the U.S. presently produce and sell PVC resins.

The uses for PVC are many and varied, as indicated in Table I.[26] Extremely wide variations in the physical properties are possible because of several major modifications that include plasticized polymers or copolymers produced primarily from vinyl chloride. PVC producers are spending large amounts of money in an effort to find new uses and to develop improved products. They have high hopes for:

1. Developing clear PVC polymers that can be used

End-uses for polyvinyl chloride polymers and copolymers during 1965 in the U.S.—Table I

Flexible polyvinyl chlorides	
Coatings for cables	12%
Films and sheets	18%
Flooring	17%
Coatings	15%
Miscellaneous extruded products	14%
Miscellaneous uses	14%
	90%
Rigid polyvinyl chlorides	
Tubes and fittings	5%
Bottles, records, etc.	3%
Films and sheets	2%
	10%

Data calculated from Glover.[27]

To meet the author, see *Chem. Eng.*, Feb. 13, 1967, p. 164

* Some authors use the term "vinyl polymers" differently. For example, Billmeyer uses it to refer to all polymers in which the repeating unit of the polymer has the formula $-CH_2-CHX-$, where X is any atom except hydrogen, or R is a group of atoms

The Chemistry of Vinyl Chloride Polymerization

Vinyl chloride or mixtures of comonomers that are predominantly vinyl chloride are polymerized commercially by free-radical chain reactions that are quite similar in the basic steps to those of high-pressure polymerization of ethylene.* The basic steps and kinetics for vinyl chloride polymerization follow.

Initiation is normally accomplished with a compound that forms free radicals at relatively low temperatures. Initiators in large-scale use for vinyl chloride polymerization are lauroyl peroxide, isopropyl percarbonate, and azo-*bis*-isobutyronitrile.[1] About 30% of all peroxide initiators (for polymerization of various polymers) are used for vinyl polymers, including polyvinyl acetate. Consumption of peroxide initiators totals about 13 to 14 million lb. yr. Chemical steps that occur during initiation are:

$$\mathrm{I} \xrightarrow{k_d} 2\mathrm{R}\bullet \qquad (1)$$

$$\mathrm{R}\bullet + \mathrm{CH_2{=}CHCl} \rightarrow \mathrm{R{-}CH_2{-}\dot{C}HCl} \qquad (2)$$

where R• is a free radical obtained from the initiator I, and k_d is the rate constant for Eq. (1). The initiator fragment R• becomes incorporated in the free radical formed in Eq. (2).

The rate of decomposition of I is:

$$-d(\mathrm{I})/dt = k_d(\mathrm{I}) \qquad (3)$$

where the parentheses around I in Eq. (3) indicate concentration of I in the solution. [Parentheses will be used similarly in other kinetic equations in this article.]

Since two free-radicals R• are formed from each decomposition of an initiator molecule, and since only a fraction f of R• reacts via Eq. (2):

$$d(\mathrm{M}\bullet)/dt = 2k_d f(\mathrm{I}) \qquad (4)$$

where M• is the free radical formed after the addition of a vinyl chloride molecule to a free radical such as R•.

Propagation involves addition of vinyl chloride to free radical at the end of a growing chain.

$$-\mathrm{R(-CH_2{-}CHCl)_n{-}CH_2{-}\dot{C}HCl} + \mathrm{CH_2{=}CHCl} \xrightarrow{k_p} \mathrm{R(-CH_2{-}CHCl)_{n+1}{-}CH_2{-}\dot{C}HCl} \qquad (5)$$

where n varies from zero to a very large number. The reaction-rate constant k_p for the propagation steps is considered to be independent of chain length, i.e., the value of n. Such an assumption has been verified for many types of free-radical polymerizations. The kinetic equation for Eq. (5) is then:

$$-d(\mathrm{CH_2{=}CHCl})/dt = k_p(\mathrm{M}\bullet)\,(\mathrm{CH_2{=}CHCl}) \qquad (6)$$

where M• is, in this case, the concentration of:

$$\mathrm{R(-CH_2{-}CHCl)_n{-}CH_2{-}\dot{C}HCl}$$

Termination steps, in which the concentration of free radicals decreases, often involve the reaction between two growing chains M•. Coupling is essentially the combination of $(\mathrm{M}\bullet)_n$ and $(\mathrm{M}\bullet)_m$ to form M_{n+m}, where n and m refer to the number of $(-\mathrm{CH_2{-}CHCl}-)$ groups in each chain. Disproportionation results in two polymer molecules, M_n and M_m; one of the molecules is saturated, and the other has a double bond at one end. The rate equation is:

$$-d(\mathrm{M}\bullet)/dt = 2k_t(\mathrm{M}\bullet)^2 \qquad (7)$$

where k_t is the rate constant for termination by both coupling and disproportionation. The integer, 2, is required, since two free-radicals are destroyed by each termination reaction.

The steady-state approximation is often applicable to free-radical polymerizations, including those of vinyl chloride. This approximation says that $d(\mathrm{M}\bullet)/dt$ approaches and remains equal to zero for most of the polymerization. Therefore, the sum of Eqs. (4) and (7) is zero, and hence:

$$(\mathrm{M}\bullet) = \left(\frac{k_d f}{k_t}\right)^{1/2} (\mathrm{I})^{1/2} \qquad (8)$$

Substituting Eq. (8) into Eq. (6) yields:

$$-\frac{d(\mathrm{CH_2{=}CHCl})}{dt} = \left(\frac{k_d f}{k_t}\right)^{1/2} k_p\,(\mathrm{CH_2{=}CHCl})\,(\mathrm{I})^{1/2} \qquad (9)$$

If f has a low value, it is then essentially directly proportional to $(\mathrm{M}\bullet)$. In this case, the rate of vinyl chloride polymerization is proportional to $(\mathrm{CH_2{=}CHCl})^{3/2}$.

Since (I) and $(\mathrm{CH_2{=}CHCl})$ vary with time, Eq. (9) or its modifications has frequently been used only for determining initial rates of polymerization—in which case, the quantities (I) and $(\mathrm{CH_2{=}CHCl})$ refer to the initial concentrations. Eq. (9) has been found to represent the kinetic data for some polymerizations of vinyl chloride that occur in dilute solutions. This evidence tends to substantiate the proposed model for the reaction. However, when concentrated solutions or undiluted vinyl chlorides are used, the equation does not fit the data. In suspension polymerization, which is of major industrial importance, vinyl chloride is present in an undiluted state.

Chain-transfer steps are methods of terminating the growth of a free-radical chain; but, in the process, the radical is transferred to another molecule. The net result is that there is no decrease in the concentration of free radicals. Chain transfer can occur with vinyl chloride as follows:

$$\mathrm{R(-CH_2{-}CHCl)_n{-}CH_2{-}\dot{C}HCl} + \mathrm{CH_2{=}CHCl} \longrightarrow \mathrm{R(-CH_2{-}CHCl)_n{-}CH_2CHCl_2} + \mathrm{CH_2{=}\dot{C}H}$$

Vinyl chloride can add to the radical $\mathrm{CH_2{=}\dot{C}H}$ to form another growing chain. However, some of these radicals act to terminate and destroy other free radicals.[2] For example:

$$2\mathrm{CH_2{=}\dot{C}H} \rightarrow \underset{\text{(Butadiene)}}{\mathrm{CH_2{=}CH{-}CH{=}CH_2}}$$

Butadiene acts as a chain terminator. When it adds to a growing chain, an unreactive resonance-stabilized allyl radical is formed.

Chain transfer can also occur with the initiator or PVC polymer molecule. With the latter, a long-chain branch will form. Chain-transfer steps in which another active radical is formed do not affect the over-all rate of polymerization. Usually, the molecular weight of the polymer is decreased when transfer is with vinyl chloride or with the initiator; but it is not decreased when transfer is with a polymer molecule.

Operating conditions during polymerization affect the characteristics of PVC molecules. As a rule, increased temperature and increased concentrations of initiator decrease the molecular weight of the PVC polymer. Chain branching becomes of increased importance when the concentration of polymer builds up, i.e. at high degree of polymerization. Various additives such as those used in suspension and emulsion polymerization may result in chain-transfer steps.

*These steps were described in an earlier article of this series, *Chem. Engr.*, Dec. 19, 1966, p. 114.

for food packaging. At present, PVC film has found wide acceptance as a meat-wrap, and some believe that it will dominate this field by 1968. Suitable plasticizers that can get clearance from the Food and Drug Administration are not always available for other types of film, or blow-molded bottles. Reynolds Metals has publicized some features of its process to form a heat-shrinkable PVC film that is plasticized with an epoxidized soybean oil, or similar material.[2] This latter film is proposed for irregularly shaped articles such as fruits, vegetables or frankfurters. Recently Air Reduction Co. has announced a propylene-modified PVC that is clear and has received FDA clearance.[6]

2. Increasing use of PVC polymers in buildings.[3, 5] An effort is being made to develop suitable polymers for siding, window frames, conduits, gutters and tiling. In many cases, it is necessary to have archaic building codes changed to allow use of these plastics for building components.

Polymerization Fundamentals

More than one phase exists during polymerizations of vinyl chloride. This is particularly true in suspension or emulsion polymerization—presently the two most common commercial methods. In both methods, at least two phases are always present, namely the discontinuous organic phase and the continuous water phase. However, as polymerization progresses, there is both a vinyl chloride phase and a PVC phase also present. Mass transfer is then of importance during the polymerization reaction.

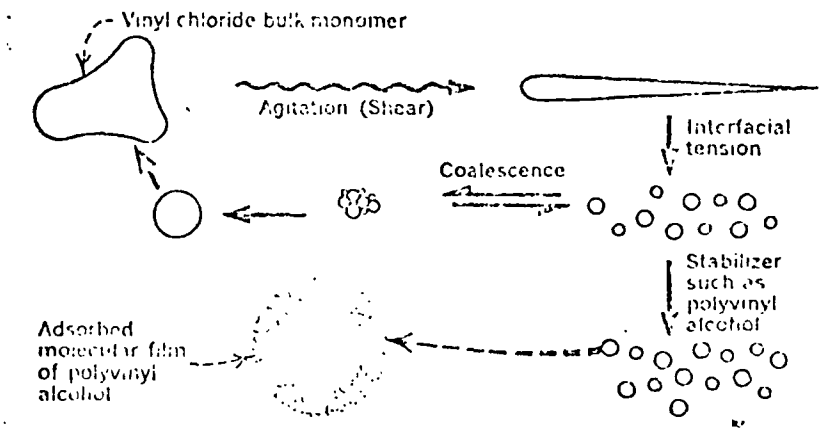
Suspension Polymerization

Winslow and Matreyek[7] have presented a schematic diagram of the states of dispersion of vinyl chloride for suspension polymerization. This is shown in Fig. 1. The dispersed vinyl chloride droplets suspended throughout the water phase are subjected to shear by means of mechanical agitation. As a result, the larger unstabilized droplets are broken up into smaller ones that tend to coalesce and reform into larger droplets. A dynamic equilibrium between dispersion and coalescence then occurs. The degree and type of dispersion-coalescence is important in terms of the porosity and bulk density of the final polymer product.

Protective colloids such as starch, proteinaceous materials or, frequently, polyvinyl alcohol (as indicated in Fig. 1) are added to stabilize the vinyl chloride droplets and help prevent agglomeration of the PVC droplets. These colloids are soluble in water but insoluble in vinyl chloride. One of their important properties is that they can increase the viscosity of the water layer, and hence delay the process of coalescence.[23] Inorganic materials are sometimes added to help prevent or regulate coalescence. Materials such as kaolin, barium sulfate, magnesium carbonate, talcum, neutral phosphates, and bentonite clay have been found effective. These inorganic particles are quite insoluble in either phase, and concentrate at the interface between the water and organic phases.

The initiator that starts polymerization is soluble in vinyl chloride. Viscosity of the organic phase increases as polymerization occurs, and polymer molecules form throughout the droplets, which become syrupy. Agglomeration of particles is a problem during this phase of polymerization. Since PVC is quite insoluble in vinyl chloride, a "PVC phase" is produced in the dispersed organic droplets. When this phase occurs, auto-acceleration is noted by an increase in the rate of polymerization instead of the decrease that is expected as vinyl chloride concentration decreases.

Auto-acceleration has been explained by a decrease in the rate of termination steps for the over-all reaction. Evidence has been obtained to indicate that polymerization occurs in both the vinyl chloride and PVC phases. Polymerization in the PVC phase occurs as vinyl chloride diffuses to the active sites of that phase.[15] These active sites tend to be located close to the surface of the semisolid PVC phase. Due to their limited mobility in the PVC phase, the active sites cannot easily react with each other to cause coupling or disproportionation reactions that destroy free radicals. When auto-acceleration occurs, the degree of polymerization also increases—thus supporting the



SUSPENSION POLYMERIZATION occurs with a suitable stabilizer in a series of steps, as illustrated schematically. The type and degree of coalescence is important relative to the bulk density and porosity of the final polyvinyl chloride particles.—Fig. 1

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hypothesis that there is a decreased possibility of chain-terminating steps.

Emulsion Polymerization

The theory of emulsion polymerization is not yet completely understood. Although the general concept as outlined by Harkins[14] is widely accepted, the mechanism may not be entirely applicable to all types of emulsion polymerization of vinyl chloride. For example, Peggion and others[15] report data for some polymerizations, which do not agree with the earlier mechanism.

At least four components are involved in emulsion polymerization—water, vinyl chloride, initiators, and an emulsifying agent. Water is the continuous phase; vinyl chloride is the discontinuous phase. The initiators are water soluble, and the emulsifying agent stabilizes the emulsion formed when the system is agitated. Emulsifiers, either anionic or cationic, behave as essentially normal electrolytes at low concentrations. When the emulsifier concentration is increased, surface tension decreases between phases, and conductivity of the mixture increases. Eventually a critical concentration is achieved. Above this concentration, surface tension and conductivity change less rapidly. The emulsifier that was previously distributed uniformly begins to agglomerate into groups (called micelles) that contain 20 to 30 molecules.[14]

The initiator in the water phase forms a free radical that migrates to the micelle. Here the radical reacts with vinyl chloride to initiate the polymer chain, as shown in Eq. (2).

Propagation reactions occur as additional vinyl chloride molecules combine with the growing free radical, as shown in Eq. (5). A polymer particle starts to form, and the emulsifier collects at the surface. Vinyl chloride molecules then diffuse from the dispersed droplets of vinyl chloride through the water phase and through the emulsifier to the growing chain. As polymerization progresses, and as the other polymer particles grow in size, more emulsifier is needed at the surface of the particles. In some cases when 12 to 20% conversion is reached during emulsion polymerization, the emulsifier micelles have disappeared and the emulsifier is all located at the surface of the particles.[14] At higher conversions (perhaps 60%), all of the monomer is in the polymer phase.

The number of polymer particles formed and hence their size seems to be controlled in the early stages of polymerization. Initially, there is competition between growing polymer particles and micelles for each vinyl chloride molecule that is transferred. If a growing polymer chain forms in most micelles, there will then be many particles, but each will be small because the molecules of vinyl chloride will be limited. In some cases, the number of polymer particles remains almost constant after the micelles disappear.[16] Evidently, polymerizations cannot easily be initiated in dispersed vinyl chloride droplets.

Auto-acceleration sometimes occurs in emulsion polymerization,[17] and apparently both monomer and polymer phases exist in the polymer particles. After all of the emulsifier has been transferred to the polymer phase, and as the polymer particles grow, a lesser and lesser amount of emulsifier is available for a given surface area.

The amount of emulsifier affects the stability of the emulsion[18]; the number of micelles, and hence the number of polymer particles produced; and, in some cases, the rate of polymerization. The results of Peggion[15] differ from those of Harkins[14] relative to the effect of some of the operating variables. Peggion suggests that in the early stages of polymerization some vinyl chloride is polymerized while it is dissolved in the water. He points out that a rather appreciable amount (0.6% by weight) of vinyl chloride is soluble in water at 50 C. After the polymer groups formed by initiation in the micelle grow, and after the micelles disappear, polymer formed in solution coagulates and precipitates on other polymer particles. Peggion indicates that the mechanism for polymerizing vinyl chloride may be quite different than that for less-soluble monomers.

Termination steps involving coupling or disproportionation are rare in emulsion polymerization because the number of PVC polymer chains for each particle is small. Hence, PVC polymers produced by emulsion polymerization tend to have high molecular weights. Occasionally, a second free radical enters the polymer particle and causes termination, or initiates another polymer chain.

There is still a need for considerably more investigation of emulsion polymerization. Many operating variables are of importance, and each has complex effects on the final reaction and on the character of the emulsion. There is evidence that no sharp line of difference exists between emulsion and suspension polymerization.

Bulk Polymerization

The characteristics of bulk polymerization are essentially identical to those of suspension polymerization if the temperature can be adequately controlled. Methods of temperature control are quite different, and will be discussed in a later article that will describe a commercial bulk-polymerization process.

Solvent Polymerization

The kinetics and mechanism of solvent polymerization have been thoroughly discussed by Mickley, Michaels and Moore.[15] A solid PVC phase often forms as polymerization progresses, and some solvents are better for solubilizing PVC than others. When a solid PVC phase occurs, auto-acceleration also occurs. The reaction mechanism is in many respects similar to that of suspension polymerization.

Characteristics of PVC Molecules

Vinyl chloride monomers can combine in several ways during propagation. In most cases, vinyl chloride molecules react to form a head-to-tail arrangement of

Effect of molecular weight on unplasticized PVC and blends of PVC and ABS polymers—Table II

	Vygen 65*	Vygen 85*	Vygen 120*	Vygen 85/ABS†	Vygen 120/ABS‡
Molecular weight of PVC	62,000	74,000	107,000	74,000	107,000
Solution viscosity	0.70	0.80	1.18	.....	.....
Tensile strength, psi	7,750	7,775	7,850	6,150	6,250
Flexural strength, psi	11,750	12,000	12,500	9,225	9,600
Flexural modulus, psi	420,000	420,000	440,000	330,000	360,000
Notched Izod at 77 F., ft.-lb./in.	0.44	0.50	0.80	14.0	18.0
Heat distortion (264 psi.) for:					
10-mil deflection, °C.	69	69	75	66	72
60-mil deflection, °C.	75	76	80	74	78

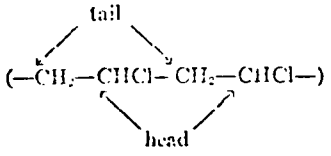
* Product of General Tire & Rubber Co.
† Blend contains 70 parts Vygen 85 and 30 parts ABS
‡ Blend contains 70 parts Vygen 120, and 30 parts ABS.

Effect of molecular weight on plasticized PVC—Table III

	Vygen 85*	Vygen 105*	Vygen 110*	Vygen 120*
Molecular weight	74,000	83,000	93,000	107,200
Solution viscosity	0.80	0.93	1.03	1.18
Tensile strength, psi	2,160	2,490	2,730	2,890
Ultimate elongation, %	230	300	340	350
Tensile strength at 100% elongation, psi	1,290	1,400	1,420	1,460

* Product of General Tire & Rubber Co. The formulation for the plasticized PVC (Vygen) is: 100 parts resin, 50 parts plasticizer (dioctyl phthalate), and 2 parts of Ba Cd stabilizer.

the repeating units (—CH_2—CHCl—) in the chain[12]:



Occasionally, a few tail-to-tail and head-to-head arrangements occur:

(—CHCl—CH_2—CH_2—CHCl—)

(—CH_2—CHCl—CHCl—CH_2—)

Crystallinity Factors

The carbon atom to which the chlorine atom is attached is asymmetric. As a result, PVC polymers can occur in various stereospecific arrangements*—namely, atactic, syndiotactic and isotactic.[1, 24, 25] Commercial PVC has been reported to be primarily syndiotactic in nature but is said to have considerable amounts of atactic regions.[1, 25] Some polymer experts believe that PVC is primarily atactic. In any case, commercial PVC is only slightly crystalline—perhaps being as high as 10 to 15%.[24, 25] Crystallinity varies with the method of polymerization. The polymer macromolecule is thought to be screw-shaped.

Attempts have been made to produce isotactic PVC, and partial success seems to have been realized. The following points must be considered to determine whether isotactic PVC would have important commercial interest:

1. The unplasticized product would presumably be quite crystalline, having increased density and tensile strength. These improved properties would be of definite interest.

2. The unplasticized product would presumably have a higher softening temperature.[21] A problem with presently available PVC is a high softening temperature that is almost as high as its decomposition temperature. This is especially true of high-molecular-weight PVC. The decomposition problem with isotactic PVC would likely be accentuated, perhaps to an unreasonable extent. If so, conventional methods of extrusion and injection molding might not be applicable with the unplasticized product. Further, modification of these molding methods would likely be expensive.

* The importance of these stereospecific arrangements of the repeating units of a polymer is dramatically demonstrated by polypropylene. Atactic polypropylene is so mechanically weak that it is of no commercial importance as a plastic. Isotactic polypropylene has found extensive uses both as a plastic and a synthetic fiber. The atactic form of the polymer because of the random d- and l- arrangements of the repeating units of the polymer does not pack as well. Either the all d- or all l- arrangement of the isotactic polymer, the syndiotactic form that has an alternating d- and l- arrangement is presumably intermediate in packing ability to the atactic and isotactic forms.

3. If isotactic PVC were plasticized to destroy its improved packing and crystallinity, it is questionable whether the material would have any significantly improved properties as compared with presently available plasticized materials.

Molecular Weight of PVC Polymers

Commercial PVC polymers have number-average molecular weights that vary from about 50,000 to 150,000.[24, 25] Routine laboratory tests for PVC generally involve the measurement of solution viscosity of the polymer rather than the direct measurement of molecular weight. The relationship between solution viscosity η and molecular weight M for a specific polymer is: $\eta = KM^a$ where K and a are constants for a given polymer-solvent combination.

The higher-molecular-weight PVC resins are plasticized and used for flexible tubing, welting, electrical components, garden hose and calendered film. These products are obtained by extrusion, and the resin is subjected to elevated process conditions for only a short period of time.[9] Intermediate-molecular-weight resins are used in film and sheet, coated fabrics and rigid products. Low-molecular-weight resins are used in fluidized-bed coatings, phonograph records and injection-molded parts.

Tables II and III indicate the effect of molecular weight on the physical properties of unplasticized and plasticized PVC polymers.[9] Molecular weight has a significant effect on the impact resistance of unplasticized polymers, and on the elongation and tensile strength at 100% elongation of plasticized products. Even better impact strength is obtained for rigid polymers (containing little or no plasticizers) by blending nitrile rubber or ABS polymers* with PVC polymers. As indicated in Table II, a blend of 70% PVC and 30% ABS produces impact strengths up to 20 times greater than pure PVC. Tensile and flexural strengths of the blends are somewhat lower.

Chemical Factors Affecting Stability

PVC polymers are relatively unstable with regard to temperature (especially 200 C., or higher) and light.[5] Hydrogen chloride is then evolved. Some of the double bonds thus formed are attacked by oxygen or enter into cross-linking reactions. Severe degradation of physical properties and appearance may result, depending on the plasticizer. Although all factors affecting stability are not known, several features of the polymer molecule contribute to this instability. (Hence, variations in the techniques of polymerization that minimize these features are important.)

The end-groups of PVC molecules are often the weak point at which decomposition reactions begin. Such an end-group is, $-CHCl-CH_2-CCl-CH_2$. A free-radical mechanism can easily begin at the double bond. Additional double bonds are produced during dehydrochlorination, allowing additional decomposition reactions to occur on a given polymer chain. Evidence supporting these facts is:

1. The rate of dehydrochlorination increases as molecular weight decreases, i.e. the rate is essentially proportional to the number of end-groups.

2. Chlorination of the double bonds decreases the rate of dehydrochlorination.

Initiator fragments on the end of PVC polymer molecules may also be the starting point for decomposition reactions. Chain branching, which occurs to only a relatively small extent, also decreases the stability of the polymer because tertiary carbon atoms exist with chlorine atoms attached. Such chlorine atoms are much easier to abstract than those attached to secondary carbon atoms. If any head-to-head arrangement occurred, the polymer molecule would be relatively unstable at the point where the two chlorine atoms were adjacent.

The exact mechanism for dehydrochlorination is not completely understood but depends on the presence or absence of oxygen. Inorganic stabilizers are added to most PVC resins.

Quality Control Tests

The following tests are generally made on batches of the finished polymer before shipment to the consumer: (a) solution viscosity in order to determine average molecular weight, (b) bulk density, (c) plasticizer takeup, (d) irreversible plasticizer takeup, (e) moisture content, (f) mill stability, (g) clarity, (h) "fish eyes" or gel particles, (i) foreign particles such as dirt, (j) particle-size distribution, and (k) press stability. For electrical-grade PVC, the following additional tests are made: conductivity and pH. Plasticizer takeup is of interest since it indicates the rate at which the plasticizer and PVC resin mix, and hence the rate at which extrusion or injection molding can be done. Careful control of quality is therefore essential in order to produce suitable polymers.

Compounding of PVC Polymers

The polymers of vinyl chloride are often compounded (i.e., blended) with plasticizers and stabilizers. Lubricants and pigments are sometimes added.

Hard, hornlike PVC is converted to a softer and rather flexible material by compounding it with a plasticizer. Generally, plasticizers decrease the tensile strength of the polymer, decrease the processing time for extrusion or molding operations, increase the allowable elongation of the polymer, and increase the impact strength and the low-temperature flexibility.[10, 18] The exact role of the plasticizer in PVC is not known, but it acts to partially solvate the polymer chains. As a result, separation of the chain is increased and, hence, the otherwise strong intermolecular forces between the chains are decreased. Any crystallinity originally present in PVC polymers is destroyed by the plasticizer.

Table IV gives one example of the relationship among the various degrees of plasticization and im-

* Terpolymers of acrylonitrile (A), butadiene (B), and styrene (S).

per ties physical properties. Desired properties for the plasticizer include:

1. Adequate compatibility with the PVC resin—that is, the degree to which PVC resin is solvated by the plasticizer. With high compatibility, a more or less true solution is formed. With lower compatibility, there may be a phase separation. For example, at higher temperatures such as are used in extrusion or molding, a single phase may be present. As the mixture is cooled, a PVC-continuous phase forms and a plasticizer-discontinuous phase is also present. The degree of compatibility has an important effect on the properties of the final product. In addition, and especially with low compatibility, the plasticizer may slowly diffuse out of the final product. Hence the physical properties could change significantly with time.
2. Low volatility, in order to minimize loss of plasticizer from the product and to minimize odor.
3. Good stability—particularly in regard to heat and light, or other forms of radiation.
4. Nonflammability.
5. Nontoxicity.
6. Satisfactory low-temperature properties.
7. Reasonable cost.

No plasticizer meets all of these characteristics, and selection of the plasticizer or mixture of plasticizers involves a compromise.

Several classifications have been given to plasticizers. External plasticizers are those additives that are mixed physically with the PVC resin, whereas internal plasticizers react chemically and are incorporated into the polymer chain. The following discussion pertains to external plasticizers that are divided into primary and secondary ones. Primary plasticizers are highly compatible with the resin, but secondary ones are only of intermediate compatibility.

Plasticizers are commonly organic esters with a high molecular weight, about 300 to 1,500. In 1965, phthalic anhydride esters amounting to 679 million lb. were produced as plasticizers, of which di-(2-ethylhexyl) phthalate was the major one.[7] Other phthalate esters include various C_1 to C_{10} alkyl phthalates. Esters of sebacic, adipic, azelaic and phosphoric acids are also good plasticizers. Alcohols for these esters are frequently obtained by using the Oxo process. Straight-chain alcohols such as produced by Continental Oil Co.'s Alfol process may have certain advantages as compared with branched-chain alcohols.[8]

Epoxidized oils and esters, polymeric esters having molecular weights ranging from about 2,000 to 5,000, chlorinated polyethylene, and other polymers such as ABS resins (see Table II) have been used commercially as plasticizers or as special blending materials.[9]

Stabilizers

Certain stabilizers have been found useful in minimizing decomposition reactions caused by heat, light or ultraviolet radiation. Heat is always a factor in the extrusion or molding operations of the polymer. Most stabilizers are metal salts. Coprecipitated barium and cadmium laurates, sometimes with zinc laurate, are used in most PVC resins as stabilizers against heat oxidation.[9] By making an opaque plastic, stabilization against ultraviolet or visible light is accomplished. With transparent PVC, several stabilizers have now been found to be quite successful. In general, the stabilizers are used in relatively low concentrations, frequently less than 1 to 2% in the final polymeric material. A detailed analysis of the complicated problem of stabilization, and available stabilizers is given by Chevassus and deBroutelles.[6]

Other Additives

Fillers, pigments or dyes, lubricants, and fungicides or pesticides are sometimes added, depending on the final use of the plastic. The fillers are generally cheap extenders such as clays used for certain electrical-grade PVC resins. The clays absorb free acid and other polar compounds. Asbestos fillers are used in certain floor-tile products.

Copolymers

Copolymers prepared from a mixture of comonomers containing 60%, or more, of vinyl chloride, with the remainder being primarily vinyl acetate, are of commercial importance.[10] Copolymers account for perhaps 25% of the production capacity of vinyl chloride polymers. Copolymers tend to improve two important physical properties of the homopolymer of vinyl chloride, namely flexibility, and limited solubility in solvents. External plasticizers may provide one method for increasing flexibility, but such plasticizers are not always adequate for solubility requirements.

Effect of plasticizing with dioctyl phthalate—Table IV

	Parts of dioctyl phthalate per 100 parts of Vygen 120*					
	0	30	40	50	60	70
Tensile strength, psi	7,750	3,550	3,200	2,850	2,500	2,100
Elongation, %	5 to 25†	265	295	345	370	410
Shore A hardness, 10 sec	115	98	92	86	79	72

*Vygen 120 (a product of General Tire & Rubber Co.) has an intrinsic viscosity of 1.11 and a molecular weight [illegible]
†Estimated from Plastics Properties Chart in "Modern Plastics Encyclopedia 1965," McGraw Hill, New York, 1964

Properties of rigid press-polished sheets of vinyl chloride/vinyl acetate copolymers—Table V

Property	Vinyl Acetate Content 3%	15%
Mill roll temperature for softening, ° F.	340	250
Hardness, Rockwell M	60	50
Notched impact, ft-lb./in.	0.65	0.20
Abrasion loss in 2,000 cycles, %	0.02	0.13
Heat distortion (66 psi.), ° C.	67	57
Tensile strength, psi	8,200	8,500
Yield stress in flexure, psi	12,800	12,200

In one sense, copolymers are internal plasticizers. Certain comonomers such as vinyl stearate or long-chain esters of maleic anhydride are sometimes copolymerized into the final product. In such a case, the plasticizer is chemically bonded into the polymer chain and hence is a true internal plasticizer.

Vinyl Chloride/Vinyl Acetate Copolymers

The properties of copolymers of vinyl chloride and vinyl acetate are dependent on the relative ratio of the two comonomers that have reacted, assuming that the final polymer molecules have the same molecular weights. Copolymers containing less than 10% vinyl acetate have physical properties quite similar to those of the homopolymer of vinyl chloride, except for the lower temperatures required for compounding. Differences in mechanical properties tend to increase rapidly as concentrations of vinyl acetate increase above 10%. Table V gives the properties of two copolymers containing 3% and 15% vinyl acetate.[13]

Copolymers containing 15%, or more, of vinyl acetate and having relatively low molecular weights are used for protective and decorative coatings, flexible film, floor tiles, and compression moldings where exceptionally good flow characteristics are required.[13] Phonograph records are one example in which precise duplication, and hence excellent flow characteristics, are needed. A vinyl chloride/vinyl acetate ratio of 87/13 for the copolymer has been used. If the heat stability problem can be solved, relatively low molecular weight homopolymers can be used as an alternative solution.[21] Copolymers containing less than 13% vinyl acetate and having relatively high molecular weights are used for rigid sheeting, extruded rods and calendered articles.

When the copolymer is to be used for protective or decorative coatings, a small amount of maleic anhydride or other polymerizable carboxyl hydrocarbon is sometimes copolymerized with the vinyl chloride and vinyl acetate.[13] Carboxyl groups improve the adhesion properties of the coatings. In other cases, a portion of the acetate groups on the polymer chain is removed by hydrolysis to produce hydroxyl groups that also improve adhesion.

Vinyl chloride/vinyl acetate copolymers are produced by batch polymerizations. Hence, the relative ratios of vinyl chloride and vinyl acetate that react tend to vary with the time of the run, unless vinyl chloride (the more reactive comonomer) is added in order to maintain a constant ratio of comonomers for the reaction.[13]

Vinyl chloride is also copolymerized commercially in significant amounts with acrylonitrile and vinylidene chloride.[22] Other types of copolymers have been reported, but their commercial importance is small.

A copolymer of vinyl chloride and propylene has recently been announced by Air Reduction Co. The properties announced for this copolymer are such that it will likely find important uses—especially since it has received clearance from the Food and Drug Administration for "clear" food containers.[6]

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Key Concepts for This Article

Active (8)	Passive (9)	Input/Feedstock (1)	Output/Product (2)
Reactions:	Processes*	Monomers*	Plastics*
	Chemistry*	Vinyl chloride*	Polymers*
	Polymerization*	Vinyl acetate*	Copolymers*
	Polymers*	Plasticizers*	Polyvinyl chloride*
		Stabilizers*	

(Words in bold are role indicators; numbers correspond to CPC-AIChE system except for Role 8 modification. Asterisks mark key concepts suggested for indexing. Others are added to improve reading as an abstract. Indexing is described in *Chem. Eng.*, Oct. 11, 1965, p. 187, or you may order Key Concept reprint, 50¢, use Reader Service Postcard.)