Kirk-Othmer Encyclopedia of Chemical Technology.

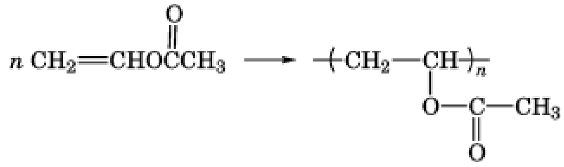
VINYL ACETATE POLYMERS

1. Introduction

Vinyl acetate [108-05-4] (VAc), $CH_2{=}CHOOCCH_3$, the ethenyl ester of acetic acid, is primarily used for the manufacture of poly(vinyl acetate) [9003-20-7] (PVAc) and vinyl acetate copolymers. Poly(vinyl acetate) homo- and copolymers are found as components in coatings, paints and sealants, binders (adhesives, nonwovens, construction products, and carpet-backing), and miscellaneous uses such as chewing gum and tablet coatings. Applications have grown over the years in a number of areas (1,2,3,4).

Vinyl acetate is a colorless, flammable liquid having an initially pleasant odor which quickly becomes sharp and irritating. Table 1 lists the physical properties of the monomer. Information on properties, safety, and handling of vinyl acetate has been published (5,6,7,8,9). The vapor pressure, heat of vaporization, vapor heat capacity, liquid heat capacity, liquid density, vapor viscosity, liquid viscosity, surface tension, vapor thermal conductivity, and liquid thermal conductivity profile over temperature ranges have also been published (10). Table 2 (11) lists the solubility information for vinyl acetate. Unlike monomers such as styrene, vinyl acetate has a significant level of solubility in water which contributes to unique polymerization behavior. Vinyl acetate forms azeotropic mixtures (Table 3) (12).

The most important chemical reaction of vinyl acetate is free-radical polymerization (13,14). The reaction is summarized as follows:



$$n\,CH_2{=}CHO\overset{O}{\overset{\|}{C}}CH_3 \longrightarrow -\!\!\left(CH_2-\underset{O-\underset{\underset{O}{\|}}{C}-CH_3}{\underset{|}{CH}}\right)_{\!n}$$

Polymerization can be initiated by organic and inorganic peroxides, azo compounds, redox systems, light, and high energy radiation. Polymerization is inhibited or strongly retarded by aromatic hydroxyl, nitro or amine compounds, and by oxygen, quinone, crotonaldehyde, copper salts, sulfur, conjugated polyolefins, and enynes. Tabulations of quantitative information, eg, polymerization-rate constants, chain-transfer constants, and activation energies for the polymerization reactions of vinyl acetate, are available (13,14). Vinyl acetate has been polymerized by bulk, suspension, solution, and emulsion methods. It copolymerizes readily with some monomers but not with others. Some reactivity ratios are presented in Table 4 for common comonomers. The ***Q*** (monomer reactivity factor) and *e* (electronic factor) values are 0.026 and −0.22, respectively (14).

Hydrolysis of vinyl acetate is catalyzed by acidic and basic catalysts to form acetic acid and vinyl alcohol which rapidly tautomerizes to acetaldehyde. This rate of hydrolysis of vinyl acetate is 1000 times that of its saturated analogue, ethyl acetate, in alkaline media (15). The rate of hydrolysis is minimal at pH 4.44 (16). Other

Table 1. Properties and Characteristics of Vinyl Acetate

Property	Value
formula weight	86.09
physical state	liquid
flammable limits in air (101.3 kPa[a]), vol %	LEL 2.6, UEL 13.4
flash point, °C	
Tag closed cup (ASTM D56)	−8
Tag open cup (ASTM D1310)	−4
autoignition temperature, °C	426.9
boiling point at 101.3 kPa[a], °C	72.7
relative evaporation rate (*n*–butyl acetate = 1)	8.9
vapor pressure, kPa[a]	
at 60°C	64.9
40°C	29.5
20°C	11.8
Antoine equation coefficients	logP = A − [B/(T + C)]
log = base10, *T* = °C, *P* = kPa[a]	range = 10–83°C
A	7.51868
B	1452.058
C	240.588
critical temperature, °C	246
critical pressure, kPa[b]	3950
color	Clear and colorless
specific gravity, 20/20°C	0.934
vapor density (air = 1.00)	2.97
viscosity at 20°C	0.43 cps
freezing point, °C	−92.8
heat of combustion at 25°C	−495.0 kcal/mol
heat of vaporization (1 atm)	87.6 cal/g
heat of formation (liquid at 25°C), kJ/mol[c]	−349.4
heat of polarization, kJ/mol[c]	89.1
specific heat at 20°C (liquid)	0.46 cal/g °C
odor	not unpleasant, sweetish smell in small quantities
reactivity	reactive with self and variety of other chemicals; stable when property stored and inhibited
light sensitivity	light promotes polymerization
electrical conductivity at 23°C	2.6 × 104 pS/m (1 S = 1 mho)
refractive index, n^{20}_{D}	1.3953
surface tension at 20°C, mN/m(= dyn/cm)	23.6
coefficient of cubical expansion	0.00137/°C at 20°C

[a] To convert kPa to mm Hg, multiply by 7.5.
[b] To convert kPa to atm, divide by 101.3.
[c] To convert kJ/mol to kcal/mol, divide by 4.184.

Table 2. Solubilities of Vinyl Acetate[a]

Solubility of	Temperature, °C	Concentration, %
water in vinyl acetate	20	2.0–2.4
	50	2.1–2.5
vinyl acetate in water	20	0.9–1.0
	50	2
2.0 wt% solution of sodium lauryl sulfate	30	4.0
organic liquids		soluble

[a] Ref. 11.

Table 3. Azeotropes of Vinyl Acetate[a]

Second component	Azeotropic boiling point, °C	Vinyl acetate, wt%
water	66.0	92.7
methanol	58.9	63.4
2-propanol	70.8	77.6
cyclohexane	67.4	61.3
heptane	72.0	83.5

[a] Ref. 12.

Table 4. Copolymerization Parameters of Vinyl Acetate (M_1) and Comonomers (M_2)

Comonomer (M_2)	r_1	r_2	Temperature, °C
acrylamide	0.07	7.5	50
acrylic acid	0.01 ± 0.003	10.0 ± 1	70
n-butyl acrylate	0.388	5.529	50
crotonic acid	0.33 ± 0.05	0.01 ± 0.01	68
diethyl maleate	0.17 ± 0.01	0.043 ± 0.005	60
ethylene	1.02 ± 0.02	0.97 ± 0.02	120
2-ethylhexyl acrylate	0.04	7.5	60
maleic anhydride	0.072	0.010	
methyl acrylate	0.029 ± 0.011	6.7 ± 2.2	60
sodium acrylate	0.01	2.0	70
styrene	0.01 ± 0.01	55 ± 10	60
vinyl benzoate	0.6	1.3	60
vinyl chloride	0.6 ± 0.2	1.8 ± 0.6	40
vinylidene chloride	0.0 ± 0.03	3.6 ± 0.5	60
vinylidene cyanide	0.0054	0.11	45
vinyl formate	1.41	0.68	50
vinyl laurate	1.4	0.7	60
vinyl pivalate	0.75 ± 0.04	0.43 ± 0.05	60
N-vinylpyrrolidinone	0.205 ± 0.015	3.30 ± 0.15	50
vinyl stearate	0.90	0.73	70
vinyl versatate VV9	0.93	0.90	60
vinyl versatate VV10	0.99	0.92	60

chemical reactions which vinyl acetate may undergo are addition across the double bond, transesterification to other vinyl esters, and oxidation (15,16,17,18,19,20,21).

World production of vinyl acetate monomer was 4×10^6 t in 1999. This represented 84% of the total capacity. In 2002, North American companies produced 1654×10^3 t of vinyl acetate. See Table 5 for producers and their capacities (22). The dominant method of production in North America is by the reaction of ethylene with acetic acid and oxygen in the presence of palladium catalyst. New construction in recent years has been focused in southeast asia, although European and North American producers have expanded their plants.

Vinyl acetate's main use is as a monomer. Consumption patterns vary by world area, however. In the United States, consumption in 2002 was as follows: 82%, poly(vinyl acetates) including poly(vinyl alcohol); 8%, ethylene vinyl acetate; 6%, ethylene–vinyl alcohol; 1%, vinyl chloride/vinyl acetate copolymer; 3%, miscellaneous. In Japan and China the major final consumption is for poly(vinyl alcohol). Half of Western Europe's consumption of vinyl acetate goes to producing poly(vinyl acetate).

Most of the applications for vinyl acetate are mature. The strongest growth areas are in ethylene–vinyl alcohol, poly(vinyl butyral), and vinyl acetate–ethylene resins. Growth of use for ethylene–vinyl alcohol is expected at 10–15%/year through 2004. Poly(vinyl butyral) is used in safety glass in automobile windshields.

Table 5. North American Producers of Poly(vinyl acetate) and their Capacities, 10^3 t[a]

Producer	Location	Capacity
Celanese Mexicana	Cangrejera, Mexico	109
Celanese	Bay City, Tex.	288
Celanese	Clear Lake, Tex.	265
Dow Chemical	Texas City, Tex.	340
DuPont	LaPorte, Tex.	272
Millennium Petrochemicals	LaPorte, Tex.	381
Total		1654

[a] (Ref. 22).

Table 6. Typical Manufacturers' Specifications for Vinyl Acetate

Specification	Value
Vinyl acetate, wt%, min	99.8
Boiling point, °C	72.0–73.0
Acidity as acetic acid, wt%, max	0.007
Carbonyls as acetaldehyde, wt%, max	0.013
Water, wt%, max	0.04
Color, APHA system	0.5
Suspended matter	none

The U.S. market is mature for this use, but has a potential as a replacement for tempered glass in Europe. A potential market exists for side and rear automobile windows worldwide (23).

Overall growth in consumption through 2004 is forecasted as follows: United States, 3%/year; Western Europe, 2.8%/year; and Japan, 1–2% (23).

Vinyl acetate monomer is supplied in three grades, which differ in the amount of inhibitor they contain but otherwise have identical specifications. A low *p*-hydroquinone grade, containing 3–7 ppm *p*-hydroquinone, is preferred if it is expected to be used within two months of delivery. For monomer stored up to four months before polymerization, the grade containing 12–17 ppm *p*-hydroquinone is used. When indefinite storage is anticipated, a grade containing 200–300 ppm diphenylamine is supplied. Typical manufacturers' specifications are given in Table 6 (5,6,7,8,9).

In storage, vinyl acetate should be kept away from ignition sources. It should be stored in a cool environment away from heat, direct sunlight, oxidizing materials, and free-radical generating chemicals to avoid rapid uncontrolled polymerization. Bulk storage should be blanketed with dry nitrogen. The monomer is actually more stable at a lower oxygen concentration (24). In the presence of oxygen, there is a tendency to form polyperoxides which could lead to polymerization. Using dry gas helps avoid the potential for hydrolysis to acetic acid and acetaldehyde. Additional information concerning the safe handling and transportation of vinyl acetate is provided in the Material Safety Data Sheet (MSDS) for vinyl acetate (5,25).

Gas chromatography is an excellent method to determine vinyl acetate and its volatile contaminants. If wet chemical techniques are used, vinyl acetate is assayed by adding excess bromide to an aliquot of material, followed by addition of excess potassium iodide and titration with standard sodium thiosulfate. Acidity is determined by direct titration in methanol solution with a standard caustic solution, aldehydes are determined by the addition of excess sodium bisulfite followed by titration with standard iodine solution, and water is determined by the Karl Fischer method. *p*-Hydroquinone and diphenylamine can be determined by standard titration techniques, or spectrophotometrically in the UV region after evaporation of vinyl acetate. Several companies describe in their product brochures empirical procedures for determining the polymerization activity of the monomer. In these tests, a given amount of monomer is polymerized under standard conditions and the rate of temperature increase or volume shrinkage and induction period are measured. Appropriate ASTM specifications and test procedures are D2190, D2191, D2193, and D2083.

The National Institute for Occupational Safety and Health (NIOSH) recommends a ceiling limit of 4 ppm for 15 min of exposure to vinyl acetate vapor. The American Conference of Governmental Industrial Hygienists (ACGIH) recommends an 8-h TLV Time Weighted Average of 10 ppm and a 15-min. short-term exposure limit of 15 ppm to its vapor. Vinyl acetate is a severe eye and skin irritant, forming blisters on the skin, and redness, swelling, or corneal burns on the eyes. The vapor is irritating to the nose and throat, and high levels of exposure may result in pulmonary edema. Nausea, headache, or weakness may result with inhalation of mists. Good industrial hygiene practices should be followed and adequate ventilation provided. Repeated or prolonged exposure should be avoided. The ACGIH has designated vinyl acetate as an A3 Animal Carcinogen. This designation refers to an agent which is carcinogenic in experimental animals at a relatively high dose. The International Agency for Research on Cancer (IARC) has evaluated vinyl acetate as a Group 2B material (26). This evaluates VAc as probably carcinogenic to humans on the basis of the sufficient evidence of the carcinogenicity of acetaldehyde in experimental animals. Both VAc and acetaldehyde were found to induce nasal tumors in rats on inhalation. VAc was also found to be genotoxic to human cells *in vitro* and to animal cells *in vivo*.

Vinyl acetate has moderate acute toxicity if ingested. The LD_{50} for oral ingestion in rats is 2.9 g/kg body weight; for absorption through the skin, the LD_{50} in rats is more than 5 mL/kg in 24 h. First-aid procedures to be followed in the event of overexposure to vinyl acetate are as follows:

Type of exposure	Treatment
Ingestion	Do not induce vomiting; drink large quantities of milk
Inhalation	Provide fresh air; keep victim warm and quiet; apply artifical respiration if necessary
Skin contact	Wash with water
Eye contact	Flush with water for 15 min; contact physician immediately

2. Vinyl Acetate Polymers

2.1. Properties

Poly(vinyl acetate) (PVAc) polymer resins are manufactured in a variety of molecular weights. Some physical properties of the polymer are listed in Table 7 (27,28,29). With increasing molecular weight, properties vary from viscous liquids to low melting solids to tough, horny materials. They are neutral, water-white to stray-colored, tasteless, odorless, and nontoxic. The resins have no sharply defined melting points but become softer with increasing temperature. Because of their solubility parameter, they are soluble in organic solvents, eg, esters, ketones, aromatics, halogenated hydrocarbons, carboxylic acids, etc, but are insoluble in the lower alcohols (excluding methanol), glycols, water, and nonpolar liquids such as ether, carbon disulfide, aliphatic hydrocarbons, oils, and fats. Alcohols, eg, ethyl, propyl, and butyl, containing 5–10 wt% water dissolve PVAc; butyl alcohol or xylene, both of which only swell the polymer at normal temperatures, dissolve it when heated. The electrical properties are strongly affected by the ability of poly(vinyl acetate) to absorb water. Whereas dried resin has a dielectric constant ϵ of 3.3 and a loss factor ϵ' of 0.08 ± 0.02 at 35°C and 60 Hz, after exposure to 100% relative humidity the numbers become 10 and 0.7, respectively (30,31).

Table 7. Physical Constants for Poly(vinyl acetate)

Property	Value
absorption of water at 20°C for 24–144 h, %	3–6
coefficient of thermal expansion, K^{-1}	
cubic	6.7×10^{-4}
linear, below T_g	7×10^{-5}
above T_g	22×10^{-5}
cohesive energy density, $(\mathrm{MJ/m^3})^{1/2}$[a]	18.6–19.09
compressibility, $\mathrm{cm^3/(g \cdot kPa)}$[b]	17.8×10^{-6}
decomposition temperature, °C	150
density, $\mathrm{g/cm^3}$	
at 20°C	1.191
25°C	1.19
50°C	1.17
120°C	1.11
200°C	1.05
dielectric constant at 2 MHz	
at 50°C	3.5
150°C	8.3
dielectric dissipation factor, at 2 MHz, tan δ	
at 50°C	150
120°C	260
dielectric strength, V/L	
at 30°C	0.394
6°C	0.307
dipole moment, $\mathrm{C \cdot m}$[c] per monomer unit	
at 20°C	2.30
150°C	1.77
dynamic mechanical loss peak at 100 Hz, °C	70
elongation at break, at 20°C and 0% rh, %	10–20
glass-transition temperature, T_g, °C	28–31
pressure dependence, °C/100 MPa[d]	0.22
hardness, at 20°C, Shore units	80–85
heat capacity, at 30°C, J/g[a]	1.465
heat distortion point, °C	50
heat of polymerization, kJ/mol[a]	87.5
refraction index, n_D	
at 20.7°C	1.4669
30.8°C	1.4657
52.1°C	1.4600
80°C	1.4800
142°C	
interfacial tension, mN/m (= dyn/cm)	
at 20°C with polyethylene	14.5
20°C with polydimethylsiloxane	8.4
20°C with polyisobutylene	9.9
20°C with polystyrene	4.2
internal pressure, $\mathrm{MJ/m^3}$ [a]	
at 0°C	255
28°C	397.8
60°C	418.7
20°C	284.7
40°C	431.3

Table 7. *Continued*

Property	Value
modulus of elasticity, GPa[d]	1.275–2.256
notched impact strength, J/m[e]	102.4
softening temperature, °C	35–50
specific volume, L/kg	
at $t = 100–200°C$	$0.823 + (6.4 \times 10^{-4}\,t)$
$t = 28°C$ (T_g)	0.84
surface resistance (Ω/cm)	5×10^{11}
surface tension, mN/m(= dyn/cm))	
at 20°C	36.5
140°C	28.6
180°C	25.9
tensile strength, MPa[d]	29.4–49.0
thermal conductivity, mW/(m · K)	159
Young's modulus, MPa[d]	600

[a] To convert J to cal, divide by 4.184.
[b] To convert kPa to atm, divide by 101.3.
[c] To convert C · m to debye, divide by 3.336×10^{-30}.
[d] To convert MPa to psi, multiply by 145; GPa to psi, multiply by 145,000.
[e] To convert J/m to lbf/in., divide by 53.38.

As with many thermoplastic resins, strength properties increase with molecular weight; tensile strengths up to 50.3 MPa (7300 psi) may be obtained. The softening point, as determined by the ring-and-ball method or by the Kraemer and Sarnow method, also increases with molecular weight, as shown in Table 8 (32,33). Poly(vinyl acetate) resin is commercially available in pure, dry form as beads, granules, or lumps and is graded according to viscosity at 20°C of a 1 *M* solution in benzene (86.09 g or 1 *M* of repeating units of the resin dissolved in benzene to make 1 L). In Europe, the Fikentscher *K* value, also derived from viscosity measurements, is used to characterize commercial resins.

On cooling below room temperature, poly(vinyl acetate)s become brittle. The brittle point may be lowered by plasticization or copolymerization. When heated above room temperature and above the polymer glass-transition temperature (30°C), all viscosity grades become very flexible, and at 50°C become limp. The glass-transition temperature of PVAc is depressed by the incorporation of moisture causing the polymer to be more flexible under humid conditions. Poly(vinyl acetate) can be heated at 125°C for hours without changing, but at 150°C it gradually darkens, and at over 225°C it liberates acetic acid forming a brown insoluble resin which carbonizes at a much higher temperature. The products of thermal decomposition of PVAc are at 150–200°C acetic acid, and at 300–350°C aromatic compounds, ie, benzene, toluene, naphthalene, etc (34). PVAc resists oxidation and degradation by UV and visible radiation; therefore its aging qualities are excellent.

The NMR spectrum of PVAc in carbon tetrachloride solution at 110°C shows absorptions at 4.86δ (pentad) of the methine proton; 1.78δ (triad) of the methylene group; and 1.98δ, 1.96δ, and 1.94δ, which are the resonances of the acetate methyls in isotactic, heterotactic, and syndiotactic triads, respectively. Poly(vinyl acetate) produced by normal free-radical polymerization is completely atactic and noncrystalline. The NMR spectra of ethylene vinyl acetate copolymers have also been obtained (35). The IR spectra of the copolymers of vinyl acetate differ from that of the homopolymer depending on the identity of the comonomers and their proportion.

The chemical properties of PVAc are those of an aliphatic ester. Thus, acidic or basic hydrolysis produces poly(vinyl alcohol) and acetic acid or the acetate of the basic cation. Industrially, poly(vinyl alcohol) is produced by a base-catalyzed ester interchange with methanol, where methyl acetate forms in addition to the polymeric product. The chemical properties of PVAc can be modified by copolymerization. When a comonomer having a carboxylic acid group or a sulfuric acid group is used, the copolymer becomes soluble in dilute aqueous alkali or ammonia. These copolymers also adhere better to metals than homopolymers or neutral copolymers because of

Table 8. Softening Points and Molecular Weights of Commercial Poly(vinyl acetate)[a, b]

		Softening point, °C		
Grade viscosity, mPa · s (= cP)	Fikentsher *K* value	Kraemer and Sarnow	Ring-and-ball	Mol weight
1.5	13	65	75	11,000
2.5	19	81	90	18,000
7	32	106	116	45,000
15	42	131	139	90,000
25	38	153	163	140,000
60	58	196		300,000
100	62	230		500,000
800	79			1,500,000

[a] (Refs. 32 and 33).
[b] A 1 *M* solution in benzene at 20°C.

the interaction between the acid groups and the metal surface. Copolymerization with monomers such as butyl acrylate can improve flexibility and provide specific adhesion to surfaces. Monomers such as *n*-methylol acrylamide copolymerized with vinyl acetate provide sites for cross-linking either during polymerization reaction or in use. Other comonomers such as vinyl Versatate (vinyl neodecanoate) reduce the potential for hydrolytic breakdown of the polymer chain by shielding the VAc group from attack.

In poly(vinyl acetate) copolymer emulsions, the properties are significantly affected by the composition of the aqueous phase and by the stabilizers and buffers used in the preparation of these materials, along with the process conditions (eg, monomer concentrations, pH, agitation, and temperature). The emulsions are milk-white liquids containing ca 55 wt% PVAc, the balance being water and small quantities of wetting agents or protective colloids. The use of poly(vinyl acetate) or copolymer emulsions eliminates the need for expensive, flammable, odorous, or toxic solvents and the need for the recovery of such solvents. They are easy to apply and the equipment is easy to clean with water, if done promptly. Emulsions also offer the advantage of high solids content with fluidity, since the viscosity of emulsions are independent of the molecular weight of the resin in the particles.

The specific gravity at 20°C for all poly(vinyl acetate) emulsions is about 1.1. There generally is a slight odor of residual monomer in standard materials, but if this is removed by some means, such as steam stripping or further reaction, the emulsions are virtually odorless. Traces of acetic acid can be neutralized with a base, eg, ammonia, sodium bicarbonate, or triethanolamine, and when the free monomer has been removed, the pH of the resulting emulsion can be adjusted to remain constant at ca 7. The product developer can choose from ingredient and process options to develop properties for the intended end use. These properties include particle size and molecular weight distributions, pH, emulsion viscosity, particle charge, environmental resistance (solvent, moisture, temperature, and UV), film characteristics (modulus, elongation, toughness), and stability to storage, freezing, dilution, mechanical action, and compounding.

Poly(vinyl acetate) polymer and copolymer properties may be modified through the addition of plasticizers and fillers. Cross-linking agents react with copolymers of vinyl acetate containing a cross-linkable group. The material properties can be altered to allow improved flow, rigidity, and toughness. Various resins, plasticizers, thickening agents, solvents, pigments, extenders, and some dyes may be added. Plasticizers are often added to provide increased flexibility to the dried film, but these usually are not incorporated before the final formulation is made because their presence may adversely affect stability, particularly in cold weather.

When the emulsion is applied to a surface, water is lost by evaporation and absorption if the surface is porous. The particles stick together and eventually coalesce to form a tough and somewhat clear continuous coating. Clarity is often improved by the presence of plasticizer, which also enhances the film's resistance to water. This may be due to the improvement in coalescence of the films. Films from most emulsions containing poly(vinyl alcohol) as the protective colloid are likely to re-emulsify on contact with water, unless they contain relatively large quantities of plasticizer or solvent, or are costabilized with a surfactant which helps plasticize the polymer. The films are unaffected by light, oxygen, chlorine in moderation, and dilute solutions of acids, alkalies, and salts. The films are also inert to oils, fats, waxes, and greases, unless these are mostly aromatic. Some solvents, namely acetone, alcohol, ethyl acetate, benzene, and toluene, dissolve or at least swell the film. The extent of dissolution depends on the branching in the chain.

Poly(vinyl acetate) emulsion films adhere well to most surfaces that have relatively high surface energy, (eg, wood, paper, glass, and metal), and have good binding capacity for pigments (qv) and fillers. The ability to bond to other surfaces may be enhanced with the use of comonomers. Ethylene copolymers have shown good adhesion to PVC. Elasticized films are strong and flexible at ordinary temperatures.

An important property of a PVAc film is its permeability to water vapor. The permeability to saturated water vapor at 40°C is 2.1 $g/(h{\cdot}m^2)$ for a film 0.025 mm thick. This allows the film to be laid down on a damp surface with trapped moisture gradually passing through the film without lifting or blistering it.

Poly(vinyl acetate) polymers are environmentally friendly because they easily biodegrade. Poly(vinyl acetate) may be hydrolyzed to poly(vinyl alcohol) which is then assimilated by naturally occurring organisms. In the use of emulsion polymers, the associated components (stabilizers, initiators, etc) should be scrutinized for their effect on the environment. Poly(vinyl acetate) is nontoxic and is approved by the U.S. Food and Drug Administration (FDA) for food applications (CFR 176.170, 175.105). Components in the emulsion polymer system which may migrate from the film into the food may impact the approval of the total package. In food applications the impact on odor and taste of residual low molecular weight components may be important in the selection of a product for use.

2.2. Polymerization Processes

Vinyl acetate has been polymerized industrially by bulk, solution, suspension, and emulsion processes (36). Perhaps 90% of the material identified as poly(vinyl acetate) or copolymers that are predominantly vinyl acetate are made by emulsion techniques. Detailed information is in patent and scientific literature and in procedures available in the brochures from monomer producing companies (15,36).

2.3. Emulsion Polymerization

Poly(vinyl acetate)-based emulsion polymers are produced by the polymerization of an emulsified monomer through free radicals generated by an initiator system. Descriptions of the technology may be found in several references (37,38,39,40,41) (see Heterophase Polymerization).

2.3.1. Recipe

An emulsion recipe, in general, contains monomer, water, protective colloid or surfactant, initiator, buffer, and perhaps a molecular weight regulator. The recipe may contain 30–70% monomer, but most commercially available emulsions contain ca 55 wt% solids, although copolymer emulsions have been commercially introduced which have greater than 70% solids content. Several monomers are copolymerized commercially with vinyl acetate in emulsion polymerization and numerous others have been copolymerized on a laboratory scale. Among the comonomers most commonly used industrially in emulsion copolymerization with vinyl acetate are ethylene, dibutyl maleate, bis(2-ethylhexyl) maleate, ethyl-, butyl-, and 2-ethylhexyl acrylates, vinyl laurate, and vinyl neodecanoate (13,15). Vinyl hydrogen maleate and vinyl hydrogen fumarate have also been used as comonomers, as have acrylic acid, maleic anhydride, and sodium ethylenesulfonate, in order to incorporate an acidic or ionic group in the polymer. The neutral comonomers are added primarily to decrease the brittle temperature of the polymer below commonly encountered ambient temperatures, since many uses of PVAc require some degree of flexibility in service. They may also improve the compatibility of the polymer with surfaces of different compositions and energies. The monomers that contain acidic groups are added primarily to make the copolymer soluble in basic media, eg, aqueous ammonia. They also help improve adhesion to metallic surfaces. Copolymerization with monomers which lower the glass-transition temperature, gives a polymer which is innately and permanently flexible. In comparison, the lowering of the brittle point accomplished by addition of plasticizers such as dibutyl phthalate, tricresyl phosphate, etc, to the preformed polymer may be lost with the migration of the plasticizer out of the film. The most efficient plasticizing comonomer on a weight or price basis is ethylene. Copolymerization of vinyl acetate with ethylene is the most significant in the adhesive market (42).

Many different combinations of surfactant and protective colloid are used in emulsion polymerizations of vinyl acetate as stabilizers. The properties of the emulsion and the polymeric film depend to a large extent on the identity and quantity of the stabilizers. The choice of stabilizer affects the mean and distribution of particle size, which affects the rheology and film formation. The stabilizer system also impacts the stability of the emulsion to mechanical shear, temperature change, and compounding. Characteristics of the coalesced resin affected by the stabilizer include tack, smoothness, opacity, water resistance, and film strength (43,44).

Poly(vinyl acetate) emulsions can be made with a surfactant alone or with a protective colloid alone, but the usual practice is to use a combination of the two. Normally, up to 3 wt% stabilizers may be included in the recipe, but when water sensitivity or tack of the wet film is desired, as in some adhesives, more may be included. The most commonly used surfactants are the anionic sulfates and sulfonates, but cationic emulsifiers and nonionics are also suitable. Indeed, some emulsion compounding formulas require the use of cationic or nonionic surfactants for stable formulations. The most commonly used protective colloids are poly(vinyl alcohol) and hydroxyethyl cellulose, but there are many others, natural and synthetic, which are usable if not preferable for a given application.

Issues to be considered in selecting the best stabilizing system are polymeric chain branching which increases with high temperature and the presence of some stabilizers, polydispersity of the particles produced, and grafting copolymerization, which may occur because of the reaction of vinyl acetate with emulsifiers such as poly(vinyl alcohol) (45,46).

In general, the greater the quantity of stabilizers in a recipe, the smaller the particle size of the emulsion. At the higher emulsifier levels ($\geq$1 wt%) used for emulsion polymerization, the polymer forms tiny particles that do not settle but remain indefinitely suspended. Particle sizes resulting from high surface active agent to low protective colloid ratios may be 0.005–1 μm; such emulsions contain lower solids and have lower viscosities. Commercial poly(vinyl acetate) emulsions used in adhesives usually are made with higher ratios of protective colloids in the recipes and usually contain ca 55 wt% solids. Average particle sizes are 0.2–10 μm and the viscosity of the emulsion is 400–5000 mPas (= cP). These latter compositions, ie, with higher ratios of protective colloids, are occasionally described as stable dispersions rather than true emulsions (47,48,49,50,51). The term *latex* is also used to denote these products, particularly those with small, ie, $<$0.2 μm, particle size.

The initiators used in vinyl acetate polymerizations are the familiar free-radical types, eg, hydrogen peroxide, peroxysulfates, benzoyl peroxide, *tert*-butyl hydroperoxide, lauryl peroxide, and redox combinations. In redox combinations, reducing agents such as sodium metabisulfite, sodium formaldehyde sulfoxylate, and ascorbic acid are among those commonly used along with transition-metal salts such as ferrous sulfate. Emulsion polymerizations are usually conducted with water-soluble initiators; benzoyl peroxide has been used in emulsion polymerizations with water-soluble initiators, especially where monomer has been added continuously during the reaction. Radiation-induced initiation has been explored because the activation energy is lower (29 kJ/mol), allowing polymerization to take place at lower temperatures (52).

Buffers are frequently added to emulsion recipes and serve two main purposes. The rate of hydrolysis of vinyl acetate and some comonomers is pH-sensitive. Hydrolysis of monomer produces acetic acid, which can affect the initiator, and acetaldehyde which as a chain-transfer agent may lower the molecular weight of the polymer undesirably. The rates of decomposition of some initiators are affected by pH and the buffer is added to stabilize those rates, since decomposition of the initiator frequently changes the pH in an unbuffered system. Vinyl acetate emulsion polymerization recipes are usually buffered to pH 4–5, eg, with phosphate or acetate, but buffering at neutral pH with bicarbonate also gives excellent results. The pH of most commercially available emulsions is 4–6.

Often a chain-transfer agent is added to vinyl acetate polymerizations, whether emulsion, suspension, solution, or bulk, to control the polymer molecular weight. Aldehydes, thiols, carbon tetrachloride, etc, have been added. Some emulsion procedures call for the recipe to include a quantity of preformed PVAc emulsion, and sometimes antifoamers must be added (see Vinyl Alcohol Polymers).

2.3.2. Process

A polymerization process may consist of simply charging all ingredients to the reactor, heating to reflux, and stirring until the reaction is over while controlling the heat removal at the reaction temperature using cooling systems. However, this simple procedure is seldom followed. Typically, only a portion of the monomer and catalyst is initially charged and the remainder is added during the course of the reaction. Better control of the rate of polymerization can be maintained in this fashion, which is particularly important in industrial-scale operations where large quantities of material are involved and heat-transfer capacity may be limited. Continuous monomer addition in emulsion polymerization usually leads to smaller particle size and a more stable dispersion. On the molecular level, monomer fed over the course of the reaction results in more branches in the polymer chain, if the monomer content of the reaction mix is held low. Consequently, the rate of monomer addition has an effect on final film properties. Copolymerizations usually must be conducted with a continuous monomer feed to obtain homogeneous polymer compositions, especially if there is a significant disparity in the reactivities of the two monomers. Emulsifiers may also be added in increments to help stabilize growing particle populations. In a Kuraray comparison of batch to semicontinuous systems (53), films from emulsions made batchwise were found to have better tensile strength than films made from semicontinuous emulsions.

Various finishing techniques are used to reduce the residual monomer in the emulsion polymer. These include raising the temperature, adding a more concentrated initiator, or using mechanical means, such as stripping. Industrially, polymerizations are carried out to over 99% conversion, and thus there is no need to reduce the unreacted monomer unless very low levels are required to meet regulatory, product, or workplace requirements. Most poly(vinyl acetate) emulsions contain less than 0.5 wt% unreacted vinyl acetate, which minimizes development of acetic acid and acetaldehyde by monomer hydrolysis on long storage. Rohm and Haas has patented an ultrafiltration process for recovering and recycling polymer emulsions from dilute wastewater (54).

All of these processes are operated in conventional glass-lined or stainless steel kettles or reactors. The pressure rating of the reactors depends on the volatility of the monomers used. In the homopolymerization of the vinyl acetate and its copolymerization with monomers of low vapor pressure, the use of vessels with a pressure rating close to atmospheric pressure is sufficient. The ethylene–vinyl acetate copolymer (EVA) processes must of necessity be operated under high pressure (42). Agitation design in these systems is important, taking into consideration the need to blend all the ingredients without zones of high concentration and remove the heat from the reaction mass while avoiding subjecting the reaction mixture to conditions of high shear which could destabilize the material. Heat removal in atmospheric pressure reactions, especially those carried out close to or higher than the boiling point of the vinyl acetate, uses reflux condensers. In vinyl acetate polymerizations where low temperatures are maintained to avoid chain transfer, which results in lowering the average molecular weight, internal coils, jackets on the reactors, and external heat exchangers are used.

Control of the process is important to ensure reproducibility of the product. Methods have been developed to control the composition of copolymers and their molecular weight (55,56). Calorimetric methods have been described to estimate conversion and provide the basis for control of the reaction. Other properties such as density and particle size can also be monitored to gauge the reaction progress and development of the product properties (57,58,59). Agitator design is important in controlling particle size and can influence the kinetics, molecular weight, and coagulum formation (60).

Continuous emulsion copolymerization processes for vinyl acetate and vinyl acetate–ethylene copolymer have been reported (61,62,63,64,65,66). Cyclic variations in the number of particles, conversion, and particle-size distribution have been studied. Control of these variations based on on-line measurements and the use of preformed latex seed particles have been discussed (63,64).

Continuous polymerization systems offer the possibility of several advantages including better heat transfer and cooling capacity, reduction in downtime, more uniform products, and less raw material handling (61,62). In some continuous emulsion homopolymerization processes, materials are added continuously to a first kettle and partially polymerized, then passed into a second reactor where, with additional initiator, the reaction is concluded. Continuous emulsion copolymerizations of vinyl acetate with ethylene have been described (63,64,65,66). Recirculating loop reactors which have high heat-transfer rates have found use for the manufacture of latexes for paint applications (61).

Mini-emulsion processes have been developed where the monomer is emulsified under high energy with either a long-chain alcohol or a polymer producing very small droplets. The long-chain alcohol retards the diffusion of the monomer out of the droplets (67). Polymerization takes place primarily in the droplets, allowing the development of fine, narrow particle-size distributions (68). The proceedings of a symposium on the emulsion polymerization of vinyl acetate is available (69).

2.4. Bulk Polymerizations

In the bulk polymerization of vinyl acetate, the viscosity increases significantly as the polymer forms, making it difficult to remove heat from the process. Low molecular weight polymers have been made in this fashion. Continuous processes are known to be used for bulk polymerizations (70).

2.5. Suspension Polymerization

At very low levels of stabilizer, eg, 0.1 wt%, the polymer does not form a creamy dispersion that stays indefinitely suspended in the aqueous phase but forms small beads that settle and may be easily separated by filtration (71). This suspension or pearl polymerization process has been used to prepare polymers for adhesive and coating applications and for conversion to poly(vinyl alcohol). Products in bead form are available from several commercial suppliers of PVAc resins. Suspension polymerizations are carried out with monomer-soluble initiators predominantly, with low levels of stabilizers. Suspension copolymerization processes for the production of vinyl acetate–ethylene bead products have been described, and the properties of the copolymers determined (72). Continuous tubular polymerization of vinyl acetate in suspension (73,74) yields stable dispersions of beads with narrow particle-size distributions at high yields.

2.6. Solution Polymerization

Solution polymerization of vinyl acetate is carried out mainly as an intermediate step to the manufacture of poly(vinyl alcohol) (see). A small amount of solution-polymerized vinyl acetate is prepared for the merchant market. When solution polymerization is carried out, the solvent acts as a chain-transfer agent and, depending on its transfer constant, has an effect on the molecular weight of the product. The rate of polymerization is also affected by the solvent but not in the same way as the degree of polymerization. The reactivity of the solvent-derived radical plays an important part. Chain-transfer constants for solvents in vinyl acetate polymerizations have been tabulated (13). Continuous solution polymers of poly(vinyl acetate) in tubular reactors have been prepared at high yield and throughput (75,76).

2.7. Mechanisms

Because of its considerable industrial importance as well as its intrinsic interest, emulsion polymerization of vinyl acetate in the presence of surfactants has been extensively studied (77,78,79). The Smith-Ewart theory, which describes emulsion polymerization of monomers such as styrene, does not apply to vinyl acetate. Reasons for this are the substantial water solubility of vinyl acetate monomer, and the different reactivities of the vinyl acetate and styrene radicals; the chain transfer to monomer is much higher for vinyl acetate. The kinetics of the polymerization of vinyl acetate has been studied and mechanisms have been proposed (80,81,82,83,84).

2.8. Initiation

Radicals formed from the initiator species, or generated by chain transfer, initiate the dissolved monomer in the water phase as well as in the micelles (aggregates of stabilizer molecules). Homogeneous nucleation applies to moderately soluble monomers like vinyl acetate (75,79,85). In homogeneous nucleation, oligomers grow from monomers in the water phase. After reaching the solubility limit, they precipitate and partially stabilized primary particles are formed. The particles grow by absorbing and converting monomer to polymer and also by coagulation. Where PVOH is used as a protective colloid, grafting may occur onto the PVOH backbone and the growing polymer may maintain its solubility in water to a higher degree of polymerization (86). The efficiency of the initiator system may be dependent on the stabilizer used. The presence of oxygen may be inhibitory in nature, probably due to the high chain-transfer constant of the oxygen–vinyl acetate adduct (Table 9). pH is also important as the initiator efficiency may be affected, especially in redox systems.

Table 9. Chain-Transfer Constants

Compound	$C_s \times 10^4$	°C
n-heptane	17.0	50
toluene	20.75	60
methanol	6	60
ethanol	25	60
tert-butyl alcohol	1.3	60
acetone	1.5	60
acetaldehyde	530	45
propionaldehyde	1000	60
crotonaldehyde	1800	60
methyl acetate	2.5	60
n-butyl mercaptan	$(48 \pm 14) \times 10^4$	60
acetic acid	10	60
lauroyl peroxide	1.0×10^3	60
oxygen–vinyl acetate adduct	2.6×10^3	60
poly(vinyl alcohol)	3.5×10^{-3}	60
poly(vinyl chloride)	2.1×10^{-1}	60
polystyrene	1.5×10^{-3}	60
	1.9×10^{-3}	75
poly(methyl methacrylate)	2.1×10^{-3}	60
	2.6×10^{-3}	75
poly(vinyl acetate)	1.5×10^{-4}	60

2.9. Propagation

The rate of emulsion polymerization has been found to depend on initiator, monomer, and emulsifier concentrations. In a system of vinyl acetate, sodium lauryl sulfate, and potassium persulfate, the following relationship for the rate of polymerization has been suggested (87):

$$R_p = k_p[M]_0^{0.34}[E]_0^{0.5}[I]_0^{0.5}$$

where R_p is in g/(cm^3 of H_2O) in seconds, $[M_0]$ is the monomer concentration, $[E_0]$ the emulsifier concentration, and $[I_0]$ the initiator concentration. The polymerization rate is constant during the period when monomer conversion is between 15 and 80%. The number of particles per unit volume of aqueous phase is given by the following equation:

$$N_p = [E]_0^{0.094}[I]_0^{0.04}$$

The Smith–Ewart theory predicts $R_p = K[I]^{0.4}$. The rate of polymerization of vinyl acetate is virtually independent of emulsifier concentration, depending on the study, whereas the Smith–Ewart theory predicts the rate to be proportional to the 0.6th power of the emulsifier concentration for monomers such as styrene. This may be due to the high chain transfer to the vinyl acetate monomer. The resulting small radical size has higher mobility, allowing diffusion out of the particle into the aqueous phase and causing reinitiation there. This has a significant effect in lowering the molecular weight of the polymer and increasing the overall rate. At high conversions where monomer concentrations are low (due to either a low feed rate of monomer or in later stages of the reaction), the transfer to polymer becomes important, leading to branched chains. Transfer can also occur to the stabilizing species resulting in permanent incorporation into the polymer matrix. An assessment of the best values of the rate constants for propagation and termination is given below (21):

$$\text{Propagation } k_p \ [L/(\text{mol}\cdot s)] = 3.2\times10^7\exp(-3150/T)$$

$$\text{Termination } k_t \ [L/(\text{mol}\cdot s)] = 3.7\times10^9\exp(-1600/T)$$

For example, at 60°C, $k_p = 2300$ and $k_t = 2.9 \times 10^7$. An estimate of kinetic chain lifetime, ie, the time from initiation to termination by reaction with another radical, is 1–2 s at 50°C and 4% per hour rate of polymerization. If there are five chain-transfer steps in the course of the kinetic chain, then a PVAc molecule forms in 0.2–0.4 s. Faster rates of conversion give shorter kinetic chain lifetimes in inverse proportion, but an increased percentage of conversion leads to longer chain lifetimes. At 75% conversion and at 60°C, the radical lifetime is ca 10 s.

Vinyl acetate polymerizes chiefly in the usual head-to-tail fashion, but some of the monomers orient head-to-head and tail-to-tail as the chain grows. The fraction of heat-to-head addition increases with temperature. For example, a 1.15 mol% head-to-head structure and a 1.86 mol% structure were determined at 15°C and 110°C, respectively (88).

In vinyl acetate polymerizations, the molecular weights of the products increase with the extent of conversion: the ratio of weight to number-average degree of polymerization also changes, becoming larger at higher conversions (89,90). The dilute solution viscosity of poly(vinyl acetate) can be related to the molecular weight by the following equations (30):

$$[\eta] = 0.0102M^{0.72}\text{d}L/\text{g in acetone solvent at } 30^\circ C$$

$$[\eta] = 0.314M^{0.60}\text{d}L/\text{g in methanol solvent at } 30^\circ C$$

These equations apply to linear polymers of $M_w/M_n = 2.0$.

2.10. Chain Transfer

At the molecular scale, vinyl acetate polymerizations are generally understood as free-radical polymerizations, but are characterized in particular by a relatively large amount of chain transfer (13). This high reactivity of the PVAc growing chain radical is attributed to its low degree of resonance stabilization. The high reactivity of the vinyl acetate radical also contributes to the high rate constant for propagation in vinyl acetate polymerization compared to styrene, the acrylates, and the methacrylates. Chain transfer to monomer is an extremely important factor controlling the molecular weight (13). Several determinations of the transfer constant to monomer C_m, ie, the ratio of rate constants of the transfer reaction and the propagation step k_{tr}/k_p, show that C_m increases from 1×10^4 to 3×10^4 from 0 to 75°C (13,91,92).

Chain transfer to monomer and to other small molecules leads to lower molecular weight products, but when polymerization occurs in the relative absence of monomer and other transfer agents, such as solvents, chain transfer to polymer becomes more important. As a result, toward the end of batch-suspension or batch-emulsion polymerization reactions, branched polymer chains tend to form. In suspension and emulsion processes where monomer is fed continuously, the products tend to be more branched than when polymerizations are carried out in the presence of a plentiful supply of monomer.

Chain transfer also occurs to the emulsifying agents, leading to their permanent incorporation into the product. Chain transfer to aldehydes, which may be formed as a result of the hydrolysis of the vinyl acetate monomer, tends to lower the molecular weight and slow the polymerization rate because of the lower activity of the radical that is formed. Thus, the presence of acetaldehyde condensates as a poly(vinyl alcohol) impurity strongly retards polymerization (93). Some of the initiators such as lauryl peroxide are also chain-transfer agents and lower the molecular weight of the product.

Investigation has shown that chain transfer to polymer occurs predominantly on the acetate methyl group in preference to the chain backbone; one estimate of the magnitude of the predominance is 40-fold (94,95). The number of branches per molecule of poly(vinyl acetate) polymerized at 60°C is ca 3, at 80% conversion. It rises rapidly thereafter and is ca 15 at 95% conversion and $1\text{–}2 \times 10^4$ number-average degrees of polymerization.

2.11. Grafting and Stabilizers

The degree of grafting of poly(vinyl acetate) (PVAc) on poly(vinyl alcohol) (PVA) and other stabilizers during emulsion polymerization strongly affects latex properties such as viscosity, rheology, and polymer solubility (96). The composition and structure of poly(vinyl alcohol) significantly affects the emulsion polymerization of vinyl acetate. The chain distribution of residual acetate groups in poly(vinyl alcohol) is important to successful vinyl acetate emulsion polymerization. A block-like distribution is preferred over a random distribution (97,98,99, 100). The structure of poly(vinyl acetate-*co*-vinyl alcohol) emulsion particles has been determined by electron microscopy. The latex particle is formed of a great many smaller particles packed together by flocculation processes (101,102).

An extensive series of papers (103,104,105,106,107,108,109,110,111) have been published on the grafting of vinyl acetate and styrene on poly(vinyl alcohol) studying the effects of type and concentration of the poly(vinyl alcohol), initiator, and reaction temperature. The partially acetylated poly(vinyl alcohol) was the superior grafting base because of the attachment of the poly(vinyl acetate) segments to the polymerizing particle. The resulting latices with the anchored poly(vinyl alcohol) chains had superior stability. The methine hydrogen atom of the poly(vinyl alcohol) was proposed to be a grafting site in all cases as opposed to the acetyl groups. In mixed systems of poly(vinyl alcohol) and ethoxylated cetyl alcohol both benzene-soluble and water-soluble fractions of graft copolymer were identified, with their ratio dependent on the ratio of initially charged-to-delay fed stabilizer and the stirring speed (112).

Emulsion polymerizations of vinyl acetate in the presence of ethylene oxide- or propylene oxide-based surfactants and protective colloids also are characterized by the formation of graft copolymers of vinyl acetate on these materials. This was also observed in mixed systems of hydroxyethyl cellulose and nonylphenol ethoxylates. The oxyethylene chain groups supply the specific site of transfer (113). The concentration of insoluble (grafted) polymer decreases with increase in surfactant ratio, and R_p (max) is observed at an ethoxylation degree of 8 (114).

Porous membranes with selective permeability to organic solvents have been prepared by the extraction of latex films prepared with moderate ratios of PVA–PVAc graft copolymer fractions. The extracted films are made up of a composite of spherical cells of PVA, PVAc microgel, and PVA–PVAc graft copolymers (115).

Poly(vinyl acetate) chains are also stabilized as aqueous-soluble anionic species by complexation with a surfactant. The charge on the water-soluble species prevents their absorption into the particle (116).

The kinetics of vinyl acetate emulsion polymerization in the presence of alkyl phenyl ethoxylate surfactants of various chain lengths indicates that part of the emulsion polymerization occurs in the aqueous phase and part in the particles (117). A study of the emulsion polymerization of vinyl acetate in the presence of sodium lauryl sulfate reveals that a water-soluble poly(vinyl acetate)–sodium dodecyl sulfate polyelectrolyte complex forms, and that latex stability, polymer hydrolysis, and molecular weight are controlled by this phenomenon (118).

Problems with grafting and morphological changes in the particles are reviewed (119). Vinyl acetate has been grafted onto atactic polypropylene (120) and casein (121).

2.12. Copolymers

The effects of emulsion polymerization process type or latex and polymer properties have been studied. Vinyl acetate copolymerizes easily with a few monomers, eg, ethylene, vinyl chloride, and vinyl neodecanoate, which have reactivity ratios close to its own (see Table 4). The kinetics and the effect of process parameters on the copolymerization of vinyl acetate with ethylene have been studied (122,123). With some monomers, eg, maleic anhydride, it tends to form alternating copolymers. Other monomers with high r_2 and low r_1, eg, alkyl acrylates, tend to form copolymers much leaner in vinyl acetate than the initial charge composition with near homopolymer formed by the faster reacting comonomer. A process is required in which the faster reacting monomer is kept at a low concentration relative to the vinyl acetate, preferably by adding it over the course of the reaction. Studies have been carried out to design processes that result in copolymers which have narrow composition distributions (55,56). The morphology of the polymer particle depends on the monomer characteristic and the process. Thus, emulsion copolymerization of vinyl acetate–butyl acrylate comonomer systems by a delayed monomer addition process yields a core-shell structure particle, in which poly(butyl acrylate)-rich copolymer forms the core and vinyl acetate-rich copolymers form the shell (124).

Block copolymers of vinyl acetate with methyl methacrylate, acrylic acid, acrylonitrile, and vinyl pyrrolidinone have been prepared by copolymerization in viscous conditions, with solvents that are poor solvents for the vinyl acetate macroradical (125). Similarly, the copolymerization of vinyl acetate with methyl methacrylate is enhanced by the solvents acetonitrile and acetone and is decreased by propanol (126). Copolymers of vinyl acetate containing cyclic functional groups in the polymer chain have been prepared by copolymerization of vinyl acetate with *N*,*N*-diallylcyanamide and *N*,*N*-diallylamine (127,128).

Alternating equimolar copolymers of vinyl acetate and ethylene and alternating copolymers of vinyl acetate and acrylonitrile have been reported (129,130). Vinyl acetate and certain copolymers can be produced directly as films on certain metallic substrates by electroinitiation processes in which the substrate functions as one electrode (131).

New terpolymers of vinyl acetate with ethylene and carbon monoxide have been prepared and their uses as additives to improve the curing and flexibility of coating resins, eg, nitrocellulose, asphalt, phenolics, and polystyrene, have been described (132,133,134). Vinyl acetate and vinylidene cyanide form highly alternating copolymers.

The low vinyl acetate ethylene–vinyl acetate copolymers, ie, those containing 10–40 wt% vinyl acetate, are made by processes similar to those used to make low density polyethylene for which pressures are usually >103 MPa (15,000 psi). A medium, ie, 45 wt% vinyl acetate copolymer with rubber-like properties, is made by solution polymerization in *tert*-butyl alcohol at 34.5 MPa (5000 psi). The 70–95 wt% vinyl acetate emulsion copolymers are made in emulsion processes under ethylene pressures of 2.07–10.4 MPa (300–1500 psi).

2.13. Blends

Latex film properties are commonly modified through the blending of latexes, eg, a "soft" polymer is made slightly harder by blending with a "hard" latex.

Poly(ethyl methacrylate) (PEMA) yields truly compatible blends with poly(vinyl acetate) up to 20% PEMA concentration (135). Synergistic improvement in material properties was observed. Poly(ethylene oxide) forms compatible homogeneous blends with poly(vinyl acetate) (136). The T_g of the blends and the crystallizability of the PEO depend on the composition. The miscibility window of poly(vinyl acetate) and its copolymers with alkyl acrylates can be broadened through the incorporation of acrylic acid as a third component (137). A description of compatible and incompatible blends of poly(vinyl acetate) and other copolymers has been compiled (138). Blends of poly(vinyl acetate) copolymers with urethanes can provide improved heat resistance to the product providing reduced creep rates in adhesives used for vinyl laminating (139).

2.14. Economic Aspects

In 2000, approximately 1.4×10^6 t of poly(vinyl acetate) emulsions and resins (dry content, including copolymers) were produced in North America, Western Europe, and Japan. The United States accounted for 50% of production, Western Europe accounted for 39%, Japan accounted for ca 9%, and the remainder was attributed to Canada and Mexico (140).

In general, poly(vinyl acetate) production is located close to end use industries (textile mills, adhesive plants, etc). In the United States, small-volume captive producers also contribute to the market.

In the United States, poly(vinyl acetate) consumption will follow general economic growth. Adhesives for use in packaging and construction will exhibit the largest growth. Demand for paper coatings will grow at less than GDP. Demand for PVAc copolymers for use in latex paint formulations will also grow. These formulations replace solvent-based paints that government regulations are limiting because of solvent emissions from the coatings.

Western European consumption of poly(vinyl acetate) and its copolymers is forecasted to grow at the rate of 1.5%/year. PVAc homopolymers will grow at the rate of 1%/year. Copolymers with ethylene are expected to grow at the rate of 3.4% through 2005. Redispersible powers will show the most dynamic growth increasing at the rate of 5%/year. Paint and coatings demand will decline because of substitution by acrylic-based emulsions. Japanese demand for poly(vinyl acetate) emulsions and resins should grow at the rate of 2%/year. Adhesives will be the biggest market (140).

2.15. Specifications and Standards

Typical specifications of the commercially available emulsions are tabulated in Table 10. However, there are exceptions to the ranges given. For example, most emulsions contain 55–56 wt% solids, but some are available at 46–47 wt% with viscosities of 10–15 $\text{mPa}\cdot\text{s}$ ($=$cP), and others at 59 wt% solids with viscosities of 200–4500 $\text{m}\cdot\text{s}$. Specialty copolymer emulsions are available containing 72 wt% solids and viscosities under $2000\text{mPa}\cdot\text{s}$ (141).

Borax stability is an important property in adhesives, paper additives and resins, and textile applications where borax is a frequently encountered substance. This is a function of poly(vinyl alcohol) used for stabilization

Table 10. Poly(vinyl acetate) Emulsion Specifications

Property	Range	Method
solids, wt%	4–72	moisture balance or oven
viscosity, mPa · s (= cP)	200–4500	viscometer
pH	4	pH meter
residual monomer, % max	0.5	titration or gas chromatography
particle size	0.1–3.0	
particle charge	neutral or negative	
density at 25°C, g/cm^3	0.92	pyknometer
borax stability	Stable or unstable	stable to borax addition
mechanical stability	Good or excellent	maintain stability for set period in high speed high shear blender
freeze–thaw stability	Passes 0–5 cycles	remains fluid after multiple cycles of freezing and thawing
accelerated sedimentation, %	<4	sediment after centrifuging diluted sample
coagulum	<50 GMs on 100-mesh screen	filter through a screen or stacked screens
T_g (glass-transition temperature), °C		DS calorimetry

of the product. Other emulsion properties tabulated by manufacturers include tolerance to specific solvents, surface tension, minimum film-forming temperature, dilution stability, freeze–thaw stability, percent soluble polymer, and molecular weight. Properties of films cast from the emulsions are also sometimes listed, including clarity, gloss, light stability, water resistance, flexibility, heat-sealing temperature, specific gravity, and bond strength. Homopolymer resin specifications usually include viscosity grade (1.0 molar solution in toluene at 20°C), 1.5–800 mPa · s (= cP) ~ 10%; volatiles, 1–2 wt%; acidity as acetic acid, 0.1–0.3 wt%; and softening point. Data are also given on heat-sealing temperature, tensile strength, elongation, and abrasion resistance. For alkali-soluble resins, the solubility in ammonia and its viscosity are listed (see Table 10).

Poly(vinyl acetate) and its copolymers with ethylene are available as spray-dried emulsion solids with average particle sizes of 2–20 μm; the product can be reconstituted to an emulsion by addition of water, or it can be added directly to formulations, eg, concrete. The powders may be used to raise solids of a lower solids latex. Solutions of resin in methyl and ethyl alcohol at 2–50 wt% solids are also available.

Emulsions are shipped in 19-L pails, 209-L drums, 11.0–18.9-m^3 (3000–5000 gal) tank trucks, and 38–76-m^3 (10,000–20,000 gal) railroad tank cars. During storage and handling, care should be taken not to destabilize or otherwise alter the character of the product. Storage tanks must be maintained clean and free from microbial contamination. Latices must not be put into a tank which contains a material with which it is incompatible. Routine cleaning is scheduled to remove skins or other accumulations of dried latex. Some of the large particle size latices may settle if stored for a long time and may need to be agitated to retain consistency. Latices corrode ordinary steel (qv) and must be stored in tanks with stainless steel, glass, plastic, or coated surfaces. Suitable coatings are baked phenolic, epoxy phenolic, or PVC. Storage should be at around room temperature, because excessive exposure to high or low temperatures may cause phase separation. Large shipments are insulated against cold. Precautions should be taken to avoid the formation of foam during unloading. If containers are not full during shipment, foam may be generated because of sloshing. Containers should be closed to prevent evaporation of water, which leads to skin formation. Diaphragm pumps and screw pumps are preferred to centrifugal pumps (qv). High shear pumps such as centrifugal pumps may destabilize the latex causing the formation of grit or coagulum. In the case of colloid-protected latices, an irreversible reduction of viscosity may occur. Latices are susceptible to biocontamination, largely due to the stabilizer systems. In handling the latices, care should be taken to avoid exposure to microbial sources. Producers add microbicidal agents to protect the material against a moderate level of incident contamination. Biocontamination can result in the generation of foul odor, discoloration, and destabilization of the latex. Dry resins should be stored at or below room temperature to prevent caking.

2.16. Uses

2.16.1. Adhesives

The uses of poly(vinyl acetate) adhesive are packaging and wood gluing (142,143). Table 11 (144) lists characteristics of poly(vinyl acetate) (PVAc) emulsions important to adhesive applications. PVAc copolymer adhesives are finding application in more diverse areas such as construction and adhesion to more difficult-to-bond surfaces because of the range of adhesion and the flexibility that may be built into the polymer. The emulsion form of PVAc is especially suitable for adhesives because of several properties that are peculiar to emulsion systems. The stability of PVAc emulsions allows them to accept many types of modifying additives without being damaged. For example, solvents, plasticizers, tackifying resins, and fillers can be added directly to homopolymer and copolymer emulsions without requiring pre-emulsification, unlike the elastomeric adhesive latexes. Homopolymer emulsions containing partially hydrolyzed poly(vinyl acetate) as a protective colloid can accept greater amounts of these modifying additives than any other type of emulsion without coagulating.

Table 11. Characterization of Emulsion Polymers[a]

Compound	Properties
emulsion	surface tension foaming tendency stability (dilution, mechanical, shear, freeze–thaw, heat, bacterial) compatibility (plasticizers, thickeners, pigments, extenders, coalescing agents) rheological character
polymer	T_g molecular weight distribution rheological behavior solubility infrared spectra
film	blocking flex tensile/elongation hardness water and chemical resistance
adhesive	heat seal temperature bond strength (miscellaneous substrates) tack peel creep

[a] (Ref. 144).

The stability of the emulsions further permits them to be compounded in simple liquid-blending vessels by means of agitators, eg, marine-type propellers, paddles, or turbines. The adhesives can be adapted to any type of machine application, ie, from spray guns to rollers to extruder-type devices. Different applicators are fairly specific in their viscosity requirements, as are the various substrates receiving the adhesive.

Poly(vinyl acetate) emulsions can be used in high speed gluing equipment. In contrast to aqueous solutions of natural or synthetic products which lose water slowly, the emulsions quickly lose water and invert and set rapidly into a bond.

Poly(vinyl acetate) homopolymers adhere well to porous or cellulosic surfaces, eg, wood, paper, cloth, leather, and ceramics. Homopolymer films tend to creep less than copolymer or terpolymer films. They are especially suitable in adhesives for high speed packaging operations.

Copolymers wet and adhere well to nonporous surfaces, such as plastics and metals. They form soft, flexible films, in contrast to the tough, horny films formed by homopolymers, and are more water-resistant. As the ratio of comonomer to vinyl acetate increases, the variety of plastics to which the copolymer adheres also increases. Comonomers containing functional groups often adhere to specific surfaces; for example, carboxyl-containing polymers adhere well to metals.

Plasticization, whether internal (by copolymerization) or external (with additives), is also extremely important for proper performance at the time of application. The ease of coalescence and the wetting characteristics of the polymer emulsion particles are related to their softness and the chemical nature of the plasticizer.

New vinyl acetate–acrylate (VAA) emulsion copolymers stabilized with poly(vinyl alcohol) have been developed. The acrylic component of the VAAs contributes to improved compatibility with tackifiers (145).

Cross-linked polymer emulsions accept water-miscible solvents better than straight-chain emulsions. In the film state, the former resist water and organic solvents better and tend to have higher heat-sealing temperatures, which signify a greater resistance to blocking and cold flow. Straight-chain polymers can have high molecular weights, which contribute to high heat-sealing temperatures. Varying the conditions of polymerization results in either straight-chain or cross-linked polymer emulsions. The incorporation of functional monomers such as *n*-methylol acrylamide or acrylic acid into the polymer provides the ability to cross-link the product in the application either through heat, catalysis, or by a curing agent. In these cases, the polymer flows onto the substrate surface, then develops its strength on curing. Wood glues which can withstand boiling water immersion have been prepared in this fashion (146).

Tack enables an adhesive to form an immediate bond between contacting surfaces when they are brought together. It permits the alignment of an assembly and prevents the adherends from separating before the adhesive sets. Tack is differentiated into two types: (*1*) wet tack, also called grab or initial tack, is the tack of an adhesive before the liquid carrier, ie, organic solvent or water, has fully evaporated; (*2*) dry tack, also called residual tack or pressure sensitivity, is the tack remaining after the liquid carrier has evaporated. Wet tack is often necessary in paper-converting operations. Applicators with little or no pressure on the combining section require emulsion adhesives with enough wet tack to bond strongly at the slightest touch. Emulsions containing poly(vinyl alcohol) as a protective colloid have stronger wet tack than those protected with a cellulose derivative. If more wet tack is required of the poly(vinyl alcohol)-protected adhesive, both a solvent and a plasticizer can be added and the solids content can be increased. Dry tack is needed where two nonporous surfaces are to be bonded. The nature of the adherends does not permit the water in the adhesive to escape by penetration or evaporation, and so the adhesive must dry before the adherends are joined, yet still retain enough tack to form a permanent bond. Film-to-film and film-to-foil laminations are good examples of applications requiring dry tack.

The *setting speed of an adhesive* is the time during which the bond formed by the adhesive becomes permanent. Before the setting of an emulsion adhesive can occur, inversion of the emulsion must take place; that is, it must change from a dispersion of discrete polymer particles in an aqueous continuous phase to a continuous polymer film containing discrete particles of water. The point at which the adhesive has actually set is that point at which an assembly, whether joint or lamination, can no longer be disassembled without damaging one or more of the adherends. Rapid setting speeds are necessary in many types of packaging adhesives intended for use with high speed gluing equipment. The rapid inversion possible with PVAc emulsions and their low viscosities allow them to be compounded into adhesives that not only set rapidly but also machine easily at high speeds. This machinability permits their application by practically any means, including glue guns, rollers, and spray guns.

Increases in setting speed can be achieved by increasing the dispersed phase content; that is, by increasing the amount of water-insoluble substances contained in the emulsions. This crowds the aqueous phase of the emulsion, hastening inversion and setting. Adding tackifying resins is one way to crowd the emulsion; adding plasticizers and solvents is another, but these additives mainly increase the setting speed by softening the polymer particles and hastening their coalescence. Surface-active agents also increase setting speed by helping the water in an adhesive to penetrate porous surfaces more rapidly; they can also retard it by stabilizing the emulsion. The usual way to prepare a high speed adhesive is to add both a solvent and a plasticizer to the base emulsion.

Poly(vinyl acetate) emulsions are excellent bases for water-resistant paper adhesives destined for use in manufacturing bags, tubes, and cartons. Glue-lap adhesives, which require moderate-to-high resistance to water, exemplify this type. When routine water resistance is required, a homopolymer vinyl acetate emulsion containing a cellulosic protective colloid is effective for most purposes. Next effective are emulsions containing fully hydrolyzed poly(vinyl alcohol) as a protective colloid, followed by those containing partially hydrolyzed poly(vinyl acetate).

When more than routine water resistance is required, a copolymer vinyl acetate emulsion can be used. The plasticizing comonomer in the polymer particles increases their intrinsic coalescing ability; thus, they can coalesce more readily than homopolymer particles to a film that has a higher resistance to water. This resistance to water does not extend to the organic solvents, however, which are better resisted by homopolymer films. The soft copolymers have lower solubility parameters than homopolymers and are more readily attacked by solvents of low polarity, eg, hydrocarbons.

Despite their high resistance to water, copolymer emulsions are seldom chosen to bond paper to paper, as the less expensive homopolymer emulsions are effective enough. When copolymers are used in paper adhesives, it is done so chiefly to join coated or uncoated papers to films so as to take advantage of the lower critical surface tension required for wetting the copolymers. Because most packaging adhesives must be able to form strong paper-to-paper bonds, homopolymer vinyl acetate emulsions containing cellulosic protective colloids are always the first choice. The water resistance of any emulsion can be increased by improving its coalescence into a film either by adding solvents and plasticizers to it or by adding specific coalescing agents, eg, diethylene glycol monoethyl ether or diethylene glycol monoethyl ether acetate. Emulsions containing completely hydrolyzed poly(vinyl alcohol) can also be incorporated with cross-linking agents, which further insolubilize them. Cross-linking agents, however, can make a formulation unstable, so that it must often be used within a few hours after it has been compounded.

For any adhesive to be effective, it must first thoroughly wet the surface to be bonded; hence, it must be fluid at the time it is applied. Fluidity is not a problem with emulsion adhesives; wetting, however, can be problematic, especially when slick or coated surfaces are to be joined. An example is the manufacture of high gloss, clay-coated cartons, or the adhering of waxed papers. Copolymer emulsions tend to wet slick surfaces better than homopolymer emulsions because of the extra mobility and softness given to the polymer particles by the plasticizing comonomer. Their dried films also tend to conform better with this type of substrate. Homopolymer emulsions containing poly(vinyl alcohol) as a protective colloid wet paper surfaces well and are the first choice for paper-to-paper packaging adhesives. The setting ability of these emulsions can be increased by incorporating either nonionic wetting agents or partially hydrolyzed poly(vinyl acetate), or both. Small amounts of partially hydrolyzed poly(vinyl acetate) present in an adhesive also help it to wet lightly waxed papers.

The viscosity of an adhesive directly influences its penetration into a substrate; as the viscosity increases, the penetrating power decreases. It also determines the amount of mileage or spread that can be obtained. An optimum viscosity exists for each substrate and each set of machine conditions and must be achieved in order to manufacture an efficient adhesive. Poly(vinyl acetate) emulsions are frequently too low in viscosity to be metered efficiently or to perform well as adhesives by themselves. They must be bodied to working viscosities, eg, by adding thickeners.

Blocking and cold flow are undesirable properties. Blocking refers to dried adhesive surfaces that become sticky, causing unwanted bonding. Cold flow occurs with a polymer having a low softening point; if the temperature of the adhesive assembly warms to the softening range of the polymer, the bond slips. The temperature at which a dried adhesive film forms an instantaneous bond between two surfaces when heat is applied is its *heat-sealing temperature*. This property is closely related to the blocking temperature and to the temperature at which cold flow or creep can occur.

The heat-sealing temperature of an emulsion is related to the thermoplasticity of the poly(vinyl acetate) particles dispersed in it. Thermoplastic polymers are softened by heat; those of relatively high molecular weight or those that are cross-linked soften at higher temperatures than those of low molecular weight. In addition, poly(vinyl acetate) homopolymers soften at higher temperatures than do copolymers (with monomers that lower the glass-transition temperature) which have similar molecular weight. Another factor which affects the heat-sealing temperature of an emulsion is the amount of poly(vinyl alcohol) in it, if any, since poly(vinyl alcohol) has a high melting point. High heat-sealing temperatures, which are desirable in an emulsion adhesive because they indicate resistance to blocking and cold flow, are usually attainable with emulsions containing large amounts of poly(vinyl alcohol) as a protective colloid.

Fillers are added to emulsion adhesives to build the total solids content, to reduce penetration into a porous substrate, and to lower costs. Plasticizers are added to emulsion adhesives to modify several properties of both the emulsion and the finished adhesive film. By softening the polymer particles dispersed in the emulsion and increasing their mobility, plasticizers cause them to flow together more easily. This usually increases the viscosity of the emulsion and tends to destabilize it for faster breaking and setting speeds at the time it is applied. In addition, the increased softness and mobility help the emulsion to wet smooth, nonporous surfaces, eg, films, foils, and coated papers, thereby increasing its adhesion to them. Also, the softened polymer particles coalesce more rapidly and at a lower temperature than is possible with the unplasticized emulsion. This improved coalescence increases the water resistance of the adhesive film. Plasticizers are usually high boiling esters, eg, phthalates. Phosphate esters are useful as fire-retardant plasticizers.

Solvents are frequently used to perform several functions in emulsion adhesives. Solvents promote adhesion to solvent-sensitive surfaces, they increase the viscosity of the emulsion and intensify the tack of the wet adhesive, and they improve the coalescing properties of the film. Low boiling solvents impart only wet tack to the adhesive film, whereas high boiling solvents confer both dry and wet tack and lower the heat-sealing temperature. The solvent can impart the necessary speed to the wet adhesive but, because it evaporates, it does not cause the dried bond to creep, which often happens with a plasticized film that ages under stress. Solvents promote adhesion to solvent-sensitive adherends by softening and partially dissolving them, thus allowing the adhesive to wet or penetrate the surface or both. Because of the increasing regulatory pressure on solvent emissions, there is a need to develop these properties without volatile materials.

Tackifiers are used to increase the tackiness and the setting speed of adhesives. They increase tackiness by softening the poly(vinyl acetate) polymer in the wet and the dry adhesive film. Tackifiers are usually rosin or its derivatives or phenolic resins. Other additives frequently needed for specific application and service conditions are antifoams, biocides, wetting agents, and humectants.

Specialized copolymer latices, which are inherently and permanently tacky, are available as pressure-sensitive emulsions. They are mechanically stable and have excellent machinability. They are compatible with many other PVAc latices and, therefore, can be easily blended with other resins for modification of surface tack, peel strength, and creep.

Poly(vinyl acetate) dry resins and ethylene–vinyl acetate (EVA) copolymers are used in solvent adhesives, which can be applied by total industrial techniques, eg, brushing, knife-coating, roller-coating, spraying, or dipping. Proper allowances must be made for evaporation of solvent during or before bonding. Poly(vinyl acetate) resins and EVA copolymers containing 21–30 wt% vinyl acetate are widely used in hot-melt adhesive applications. Homopolymers are compounded with 25–35 wt% plasticizer and 25–30 wt% extender resins. These additives increase fluidity and adhesion as well as reduce cost. Ethylene–vinyl acetate resins are mixed with waxes, rubbers, and resin to make the hot-melt adhesive compound. Hot-melt adhesive application processes may be extremely rapid both in application and setting speed, cause no problems resulting from solvent or water evaporation, and provide bonds of high water resistance. The adhesive materials have indefinite shelf lives. Hot-melts are largely used in packaging, laminating, and bookbinding. For the last application, alkali-soluble copolymers are frequently used to facilitate the reclamation of scrap paper.

Film and foil adhesives based on internally plasticized copolymer adhesives have been suggested. For instance, vinyl acetate–ethylene or vinyl acetate–acrylate copolymers may be used for adhesion of films to porous surfaces. For metallic foil adhesion, copolymers containing carboxylate functionality are suggested.

Spray-dried powders find application in adhesives to build solids, increase viscosity, improve tack, and decrease drying time (147). A primary use is in joint compounds with other applications in mastics and grouts, and patching compounds (148).

2.16.2. Paints

Paints prepared from poly(vinyl acetate) and its copolymers form flexible, durable films with good adhesion to clean surfaces, including wood, plaster, concrete, stone, brick, cinder blocks, asbestos board, asphalt, tar paper, wallboards, aluminum, and galvanized iron (149). Adherence is also good on painted surfaces if the surfaces are free from dirt, grease, and rust. Developments in emulsion polymerization for paint latices have been reviewed (150).

Poly(vinyl acetate) latex paints are the first choice for interior use (151). Their ability to protect and decorate is reinforced by several advantages belonging exclusively to latex paints: they do not contain solvents so that physiological harm and fire hazards are eliminated; they are odorless; they are easy to apply with spray gun, roller-coater, or brush; and they dry rapidly. The paint can be thinned with water, and brushes or coaters can be cleaned with soap and tepid water. The paint is usually dry in 20 min to 2 h, and two coats may be applied the same day.

Poly(vinyl acetate) latex paints are also widely used as exterior paints. Their durability, particularly their resistance to chalking, far surpasses that of any conventional oleoresinous paints, which chalk soon after application. The good nonchalking properties of PVAc paints result from their resistance to degradation by UV light. Latex paints that are correctly formulated from quality PVAc latices develop little or no chalk, thus giving maximum tint retention, and they last a long time before repainting becomes necessary. The blister resistance of PVAc paints is another important advantage for their exterior use. Latex paint films are permeable enough to permit water vapor to penetrate them, which prevents blistering and peeling. Their film formation is not impaired if they are painted on damp surfaces or are applied under very humid conditions.

Several types of plasticizing comonomers can be copolymerized with vinyl acetate to produce latices suitable for manufacturing paints. The older, less common comonomers are the alkyl maleates and fumarates, eg, dibutyl maleate and dibutyl fumarate. Acrylic esters, eg, butyl acrylate and 2-ethylhexyl acrylate, as well as ethylene, are the most widely used comonomers in the 1990s. The chief reason for using a comonomer in vinyl acetate polymers is to increase the deformability of the paint film permanently, thus permitting it to expand and contract as the dimensions of the substrate change with changes in temperature. The plasticizing comonomer also softens the polymer particles. For a film to form from a latex paint, the polymer particles must deform and fuse to form a continuous film. This coalescing ability is directly related to the amount of comonomer present. In both interior and exterior paints, the improvement in coalescence that is obtainable by using high comonomer levels results in a general improvement in all the properties necessary for interior and exterior paints. High levels of comonomers, such as ethylene or butyl acrylate, must be added with care. If high comonomer levels are used with low molecular weight polymers, the resulting paint film suffers from excessive dirt pickup at high temperatures because it becomes soft and tacky. It is required, therefore, that high molecular weight polymers be prepared, because only with these is a sufficient amount of comonomer incorporated to give the tint retention without dirt pickup required in exterior paints.

The strength of a polymer increases with its molecular weight; consequently, the toughest paint films are formed from latex polymers having the highest molecular weights. For exterior paints, there is a federal specification of a minimum intrinsic viscosity of 0.45 dL/g. The minimum intrinsic viscosity of commercial paint polymers usually is 0.60–1.0 dL//g and above.

Special vinyl acetate copolymer paints have been developed with greatly improved resistance to blistering or peeling when immersed in water. This property allows better cleaning and use in very humid environments. These lattices exhibit the water resistance of higher priced acrylic resins (152). VAc, vinyl chloride–ethylene terpolymers have been developed which provide the exterior resistance properties of vinyl chloride with the flexibility of the ethylene for exterior paint vehicles (153).

The critical pigment volume concentration (CPVC) of vinyl acetate paints is 48–60%. Generally, the smaller and softer the polymer particles, the higher the CPVC and the greater the pigment-binding capacity of the latex. The most widely used white pigment is titanium dioxide in the form of rutile or of anastase. The color pigments used in latex paints are of two types: the organic pigments (see), which are usually hydrophobic, and the inorganic pigments (see), which are usually hydrophilic. The hydrophilic pigments are relatively easy to incorporate into water-base paints. The hydrophobic pigments are more difficult to incorporate, but this can be overcome by choosing the correct blend of surfactants for a particular pigment. The organic colorants commonly used are toluidine red, Hansa yellow, phthalocyanine blue and green, pigment green B, and carbon black, among others. Examples of acceptable inorganic colorants are iron oxide red, brown, yellow, black, and chrome oxide green. Colorants that should not be used are those that are reactive, partially water-soluble, or sensitive to pH changes.

In addition to latex and pigment, paint formulations contain dispersants and wetting agents (both surfactants), defoamers, thickeners and protective colloids, freeze–thaw stabilizers, coalescing agents, and biocides. The coalescing agents used in the paint formulations tend to be volatile. In order to reduce the odor levels and reduce solvent emissions, some paint producers are researching latex bases which require less or no solvent to aid in coalescence and yet provide a durable, glossy surface (154). Copolymers are potentially useful in meeting this requirement (155,156).

2.16.3. Paper

Poly(vinyl acetate) emulsions and resins have been used as the binder in coatings for paper and paperboard since 1955 (157,158,159). The coatings may be clear, colored, or pigmented, and are glossy, odorless, tasteless, greaseproof, nonyellowing, and heat-sealable. Conventional paper-coating equipment is used; formulations normally contain 60–65 wt% solids with a pigment-to-binder ratio of 1:5. Printing quality and ink-pick resistance are excellent. In papermaking, emulsions applied as wet-end additions to the furnish improve the strength and durability of the final product. Plasticized emulsions may be used to give the product toughness and flexibility.

Emulsions used in paper coatings must meet special requirements: the particle size must be small (ca 0.1 μm) and its distribution rather narrow. These properties provide good pigment binding efficiency and high gloss. They must have exceptionally good mechanical stability and freedom from off-sized latex particles or grit, and must exhibit no trace of dilatant flow in a pigment slurry. These properties are required for modern high speed paper-coating applications. They should also be compatible with starch and alginate natural resins frequently used as cobinders (160).

2.16.4. Nonwoven Binders and Textiles

The use of vinyl acetate copolymers as binding agents for nonwoven fabrics has grown rapidly. Vinyl acetate–ethylene copolymer latices have been particularly successful in part because of their low cost but also because of their excellent adhesion to a wide range of substrates, their water and alkali resistance, and their low flammability (161,162,163,164). Products made from these binders include paper towels, wipes, and personal hygiene articles. Self-cross-linking polymers are available as are polymers requiring external curing agents. Many of the self-cross-linking polymers release formaldehyde (qv) as part of the reaction. Because formaldehyde has been listed as a potential carcinogen, alternative chemistries have been developed to reduce or eliminate formaldehyde content in the products.

Poly(vinyl acetate) emulsions are widely used as textile finishes because of their low cost and good adhesion to natural and synthetic fibers. In textile piece goods finishing, dispersions diluted with water to 1–3 wt% resin are most often used to obtain a stiff or crisp hand on woven cotton fabrics. Concentrations of 2–20 wt% emulsion are recommended for bodying, stiffening, and bonding. Principal applications include the stiffening of felts. Finishes to improve snag resistance and body or hand of nylon hosiery are based on PVAc emulsions.

Poly(vinyl acetate) emulsions are used to prime-coat fabrics to improve the adhesion of subsequent coatings or to make them adhere better to plastic film. Plasticized emulsions are applied, generally by roller-coating, to the backs of finished rugs and carpets to bind the tufts in place and to impart stiffness and hand. For upholstery fabrics woven from colored yarns, PVAc emulsions may be used to bind the tufts of pile fabrics or to prevent slippage of synthetic yarns.

The emulsion formulations are generally applied to cloth by padding from a bath and squeezing off the excess. Modifying a formulation in the pad box, eg, to increase or decrease firmness, can be easily done by adding an emulsion or softener. The alkali-soluble vinyl acetate copolymers previously mentioned can be used as warp sizes during weaving.

2.16.5. Concrete Additives

Poly(vinyl acetate) was first used in concrete in the 1940s as a thermoplastic polymer to strengthen the concrete matrix. In contrast to other polymers, the resistance to water permeation is low due to the hydrolysis of the poly(vinyl acetate) (165,166). Ethylene copolymers have been developed which have improved water resistance and waterproofness. The polymer can be used in the latex form or in a spray-dried form which can be preblended in with the cement (qv) in the proper proportion. The compressive and tensile strength of concrete is improved by addition of PVAc emulsions to the water before mixing. A polymer solids to total solids ratio of ca 10:90 is best. The emulsions also aid adhesion between new and old concrete when patching or resurfacing.

2.16.6. Other

Vinyl acetate resins are useful as antishrinking agents for glass fiber reinforced polyester molding resins (167). Poly(vinyl acetate)s are also used as binders for numerous materials, eg, fibers, leather (qv), asbestos, sawdust, sand, clay, etc, to form compositions that can be shaped with heat and pressure. Joint cements, taping compounds, caulks, and fillers are other uses.

Emulsions containing added poly(vinyl alcohol) and dichromate are used to make light-sensitive stencil screens for textile printing and ceramic decoration. The resins are used in printing inks, nitrocellulose lacquers, and special high gloss coatings. Inks made with PVAc and metallic pigments look like foil because the formulations have a high leafing power, do not induce tarnish, and contribute no unwanted color or aging.

Vinyl acetate polymers have long been used as chewing gum bases. They have been studied as controlled release agents for programmed administration of drugs and as a base for antifouling marine paints (168,169).

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