Kirk-Othmer Encyclopedia of Chemical Technology.

VINYL ALCOHOL POLYMERS

1. Introduction

Poly(vinyl alcohol) (PVA), a polyhydroxy polymer, is the largest volume, synthetic water-soluble resin produced in the world. It is commercially manufactured by the hydrolysis of poly(vinyl acetate), because monomeric vinyl alcohol cannot be obtained in quantities and purity that makes polymerization to PVA feasible (1–3).

Poly(vinyl alcohol) was discovered by Haehnel and Herrmann who, through the addition of alkali to a clear alcoholic solution of poly(vinyl acetate), were able to obtain the ivory-colored PVA (4). The first scientific reports on PVA were published in 1927 (5,6).

The excellent chemical resistance and physical properties of PVA resins have resulted in broad industrial use. The polymer is an excellent adhesive and possesses solvent, oil, and grease resistance, properties matched by few other polymers. Poly(vinyl alcohol) films exhibit high tensile strength, abrasion resistance, and oxygen barrier properties which under dry conditions are superior to those of most polymers. The polymer's low surface tension provides for excellent emulsification and protective colloid properties.

The main uses of PVA are in textile sizing, adhesives, protective colloids for emulsion polymerization, fibers, production of poly(vinyl butyral), and paper sizing. Significant volumes are also used in the production of concrete additives and joint cements for building construction and water-soluble films for containment bags for hospital laundry, pesticides, herbicides, and fertilizers. Smaller volumes are consumed as emulsifiers for cosmetics, temporary protective film coatings, soil binding to control erosion, and photoprinting plates.

2. Physical Properties

The physical properties of PVA are highly correlated with the method of preparation. The final properties are affected by the polymerization conditions of the parent poly(vinyl acetate), the hydrolysis conditions, drying, and grinding. Further, the term PVA refers to an array of products that can be considered to be copolymers of vinyl acetate and vinyl alcohol.

The effect of hydrolysis and molecular weight is illustrated in Figure 1. The variations in properties with molecular weight are for a constant degree of hydrolysis (mol%) (7), and the effect of hydrolysis is at a constant molecular weight. Representative properties are shown in Table 1.

2.1. Crystallization and Melting Point

The ability of PVA to crystallize is the single most important physical property of PVA as it controls water solubility, water sensitivity, tensile strength, oxygen barrier properties, and thermoplastic properties. Thus, this feature has been and continues to be the focal point of academic and industrial research (8–37). The

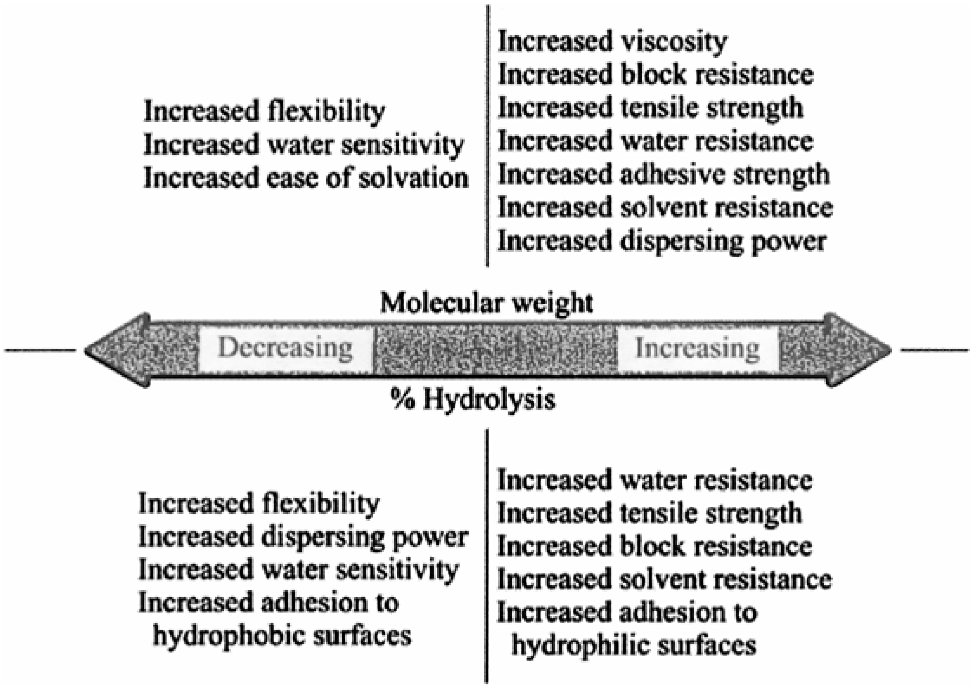


Fig. 1. Effect of molecular weight and hydrolysis on the properties of PVA (7).

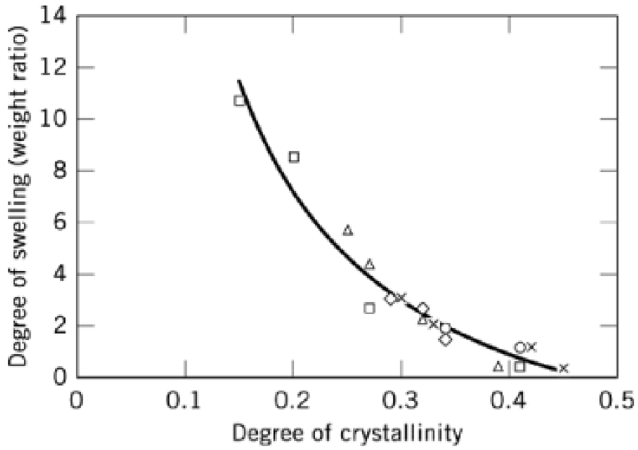


Fig. 2. Relationship between swelling and crystallinity. □, DP 304; △, DP 708; ○, DP 1288; ◇, DP 2317; ×, DP 4570.

degree of crystallinity as measured by x-ray diffraction can be directly correlated to the products density or the swelling characteristic of the insoluble part (Fig. 2).

The size of the crystals determines the melting point. Reported values for the melting point of PVA range between 220 and 267°C for fully hydrolyzed PVA (38–42). Exact determination of the crystalline melting point using normal data techniques is difficult as decomposition takes place above 140°C. The divergence in melting point may be ascribed to decomposition or prior treatment history. The melting point of PVA containing an

Table 1. Physical Properties of Poly(vinyl alcohol)

Property	Value	Remarks
Appearance	White to ivory white granular powder	
Specific gravity	1.27–1.31	Increases with degree of crystallinity
Tensile strength, MPa[a](98–99% hydrolyzed)	67–110	Increases with degree of crystallinity (heat treatment), and molecular weight, decreases with increasing humidity
Tensile strength, MPa (87–89% hydrolyzed)	24–79	Increases with molecular weight and decreases with increasing humidity
Elongation, %	0–300	Increases with increasing humidity
Thermal coefficient of expansion per °C	$7–12 \times 10^{-5}$	
Specific heat, J/(g·K)[b]	1.67	
Thermal conductivity, W/(m·K)	0.2	
Glass-transition temperature, K	358	98–99% hydrolyzed
	331	87–89% hydrolyzed
Melting point, K	503	98–99% hydrolyzed
	453	87–89% hydrolyzed
Electrical resistivity, Ω·cm	$(3.1–3.8) \times 10^7$	
Thermal stability	Gradual discoloration above 100°C; darkens rapidly above 150°C; rapid decomposition above 200°C	
Refractive index n_D(20°C)	1.55	
Degree of crystallinity	0–0.54	Increases with heat treatment and degree of hydrolysis
Storage stability (solid)	Indefinite when protected from moisture	
Flammability	Burns similarly to paper	
Stability in sunlight	Excellent	

[a] To convert MPa to psi, multiply by 145.
[b] To convert J to cal, divide by 4.184.

appropriate amount of diluent or comonomer is less influenced by decomposition. Thus, the melting point of fully hydrolyzed PVA can be determined by the extrapolation of the measured values to 0% diluent. A more reliable melting point is obtained in this manner. The melting points determined by the diluent method are 255–267°C for commercial superhydrolyzed PVA (greater than 99% hydrolysis). The melting point determined by melting point depression caused by noncrystallizing comonomer units assumes as a first approximation that the vinyl acetate units are randomly distributed. This assumption usually does not apply to commercial PVA. The extrapolated values of heat of fusion and melting point obtained with this method are therefore highly dependent on the manufacturing method and the resulting blockiness (Fig. 3). The heat of fusion, determined by either of the above methods, has been calculated as 6.82 ± 2.1 kJ/mol (43–45).

2.2. Glass-Transition Temperatures

The glass-transition temperature of fully hydrolyzed PVA has been determined to be 85°C for high molecular weight material. The glass transition in case of 87–89% hydrolyzed PVA varies according to the shown formula (46):

$$T_g = 58 - (2.0 \times 10^{-3}/\mathrm{DP}[^\circ C] \qquad (1)$$

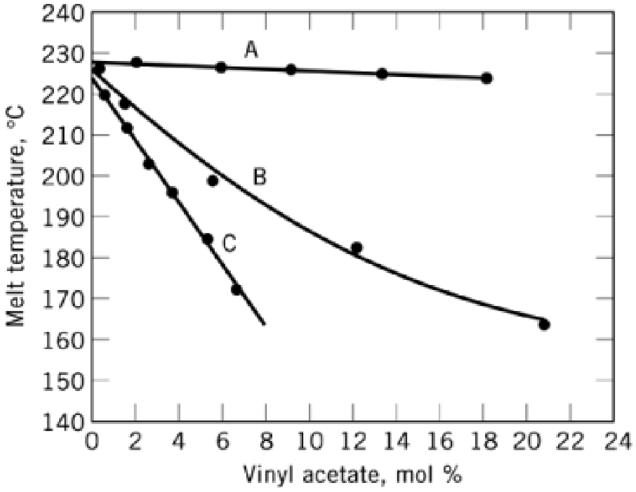


Fig. 3. Influence of vinyl alcohol–vinyl acetate copolymer composition on melting temperature (44), where A represents block copolymers; B, block copolymers; and C, random copolymers.

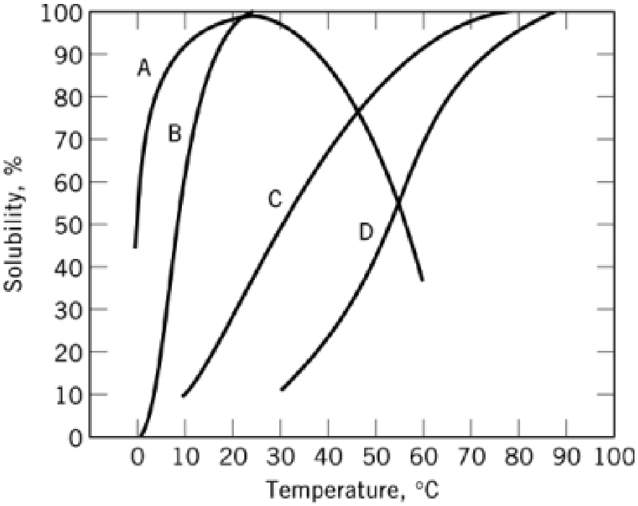


Fig. 4. Water solubility of PVA grades: A, 78–81 mol% hydrolyzed, DP = 2000–2100; B, 87–89 mol% hydrolyzed, DP = 500–600; C, 98–99 mol% hydrolyzed, DP = 500–600; D, 98–99 mol% hydrolyzed, DP = 1700–1800 (47).

2.3. Solubility

Poly(vinyl alcohol) is only soluble in highly polar solvents, such as water, dimethyl sulfoxide, acetamide, glycols, and dimethylformamide. The solubility in water is a function of the degree of polymerization (DP) and hydrolysis (Fig. 4). Fully hydrolyzed PVA is only completely soluble in hot to boiling water. Partially hydrolyzed grades are soluble at room temperature, although grades with a hydrolysis of 70–80% are only soluble at water temperatures of 10–40°C. Above 40°C the solution first becomes cloudy (cloud point), followed by precipitation of PVA.

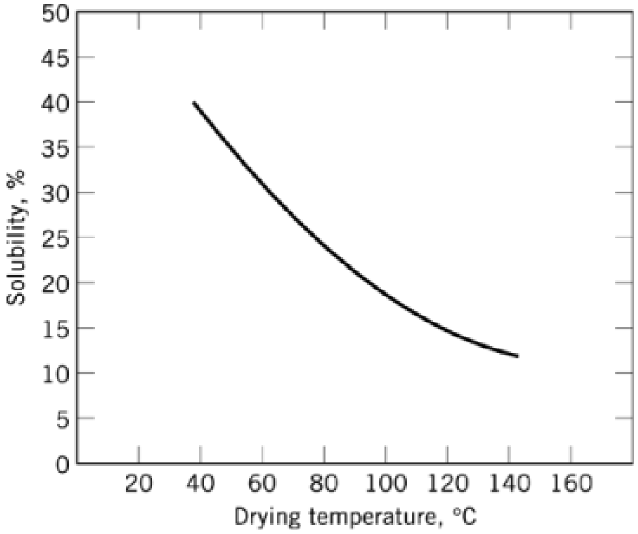


Fig. 5. Influence of heat treatment on solubility at 40°C; DP = 1700, 98–99 mol% hydrolyzed.

The hydroxyl groups in PVA contribute to strong hydrogen bonding both intra- and intermolecularly, which reduces solubility in water. The presence of residual acetate groups in partially hydrolyzed PVA weakens these hydrogen bonds and allows solubility at lower temperatures.

The hydrophobic nature of the acetate groups results in a negative heat of solution (48–50), which increases as the number of acetate groups is increased. This means that the critical θ temperature is lower, ie, the solubility decreases as the temperature is increased.

Heat treatment or drying of a few minutes increases crystallinity and greatly reduces the solubility and water sensitivity (Fig. 5). Prolonged heat treatment does not further increase crystallinity. The heat treatment melts the smaller crystals, allowing for diffusion and reformation of crystals with a melting point higher than that of the treatment temperature. The presence of acetate groups reduces the extent of crystallinity; thus, heat treatment has little or no influence on low hydrolysis grades. The influence of heat treatment is desirable in some applications such as adhesives and paper coatings where a greater degree of water resistance is needed, but is highly undesirable in textile warp sizing where the polymer must be removed after a drying cycle.

Poly(vinyl alcohol) solutions also exhibit high tolerance toward many electrolytes (Table 2).

2.4. Solution Viscosity

The viscosities of PVA solutions are mainly dependent on molecular weight and solution concentration (Fig. 6). The viscosity increases with increasing degree of hydrolysis and decreases with increasing temperature. Materials with a high degree of hydrolysis tend to show an increase in viscosity on standing and may even gel (47,51–55). The rate of increase depends upon dissolution temperature, concentration, and storage temperature. The lower the storage and dissolution temperatures and the higher the concentration, the higher is the rate of the viscosity increase (Fig. 7). Viscosity can be stabilized to a certain degree by adding small amounts of lower molecular weight aliphatic alcohols (56), urea, or salts such as thiocyanates. The solution viscosity of partially hydrolyzed PVA grades exhibit a greater degree of stability.

Table 2. Minimum Salt Concentration for Precipitation of a 5% Poly(vinyl alcohol) Solution[a, b]

Salt	Concentration, g/L
$(NH_4)_2SO_4$	66
Na_2SO_4	50
KSO_4	61
$ZnSO_4$	113
$CaSO_4$	112
$Fe_2(SO_4)_3$	105
$MgSO_4$	60
$Al_2(SO_4)_3$	57
$KAl(SO_4)_2$	58
NH_4NO_3	490
$NaNO_3$	324
KNO_3	264
$Al(NO_3)_3$	255
NaCl	210
KCl	194
Na_3PO_4	77
K_2CrO_4	136

[a] Ref. (47).
[b] 98% hydrolyzed, DP = 1700–1800.

3. Mechanical Properties

The tensile strength of unplasticized PVA depends on degree of hydrolysis, molecular weight, and relative humidity (Fig. 8). Heat treatment and molecular alignment resulting from drawing increase the tensile strength; plasticizers reduce tensile strength disproportionately because of increased water sensitivity.

Tensile elongation of PVA is extremely sensitive to humidity and ranges from $<10\%$ when completely dry to 300–400% at 80% rh. Addition of plasticizer can double these values. Elongation is independent of degree of hydrolysis but proportional to the molecular weight. Tear strength increases with increasing relative humidity or with the addition of small amounts of plasticizer.

3.1. Solvent Resistance

Poly(vinyl alcohol) is virtually unaffected by hydrocarbons, chlorinated hydrocarbons, carboxylic acid esters, greases, and animal or vegetable oils. Resistance to organic solvents increases with increasing hydrolysis. This resistance has promoted the use of PVA in the manufacture of gloves for use when handling organic solvents (57).

3.2. Gas-Barrier Properties

The oxygen-barrier properties of PVA at low humidity are excellent. However, barrier performance deteriorates above 60% rh (Fig. 9). No additives or chemical modifiers are known that can effectively reduce moisture sensitivity. The gas-barrier performance is affected by the degree of hydrolysis and rapidly diminishes as the hydrolysis is decreased below 98%.

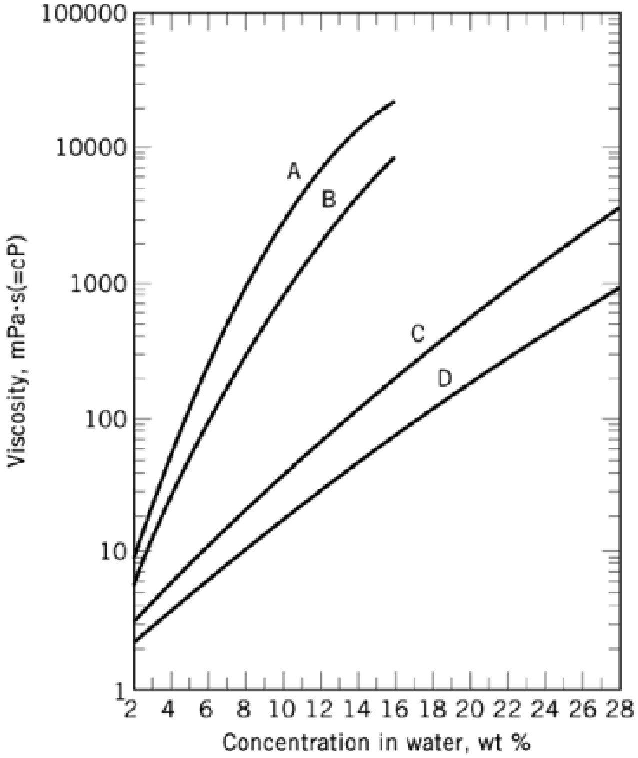


Fig. 6. Solution viscosity of 87–89 mol% hydrolyzed PVA at 20°C. DP: A, 2200; B, 1500; C, 550; D, 220.

3.3. Surface Tension

The surface tension of aqueous solution of PVA varies with concentration (Fig. 10), temperature, degree of hydrolysis, and acetate distribution on the PVA backbone. Random distribution of acetyl groups in the polymer results in solutions having higher surface tension compared to those of polymers in which the blocks of acetyl groups are present (58–61). The surface tension decreases slightly as the molecular weight is reduced (Fig. 11).

3.4. Intrinsic Viscosity and Molecular Weights

The relationship between the intrinsic viscosity and molecular weight changes with degree of hydrolysis of the polymer (Table 3). Methods for determining molecular weight and molecular weight distribution using gpc and low angle laser light scattering detection have been developed and utilized (63,64). These methods show a polydispersity of 2.0 or less, which indicates the presence of few long-chain branches. No long-chain branches are found in PVA samples that have a degree of hydrolysis higher than 80 mol%. The number of short-chain branches is identical to the mole percent of short-chain branches generated during the formation of the poly(vinyl acetate) in the range of 0.12–0.17 mol% (65).

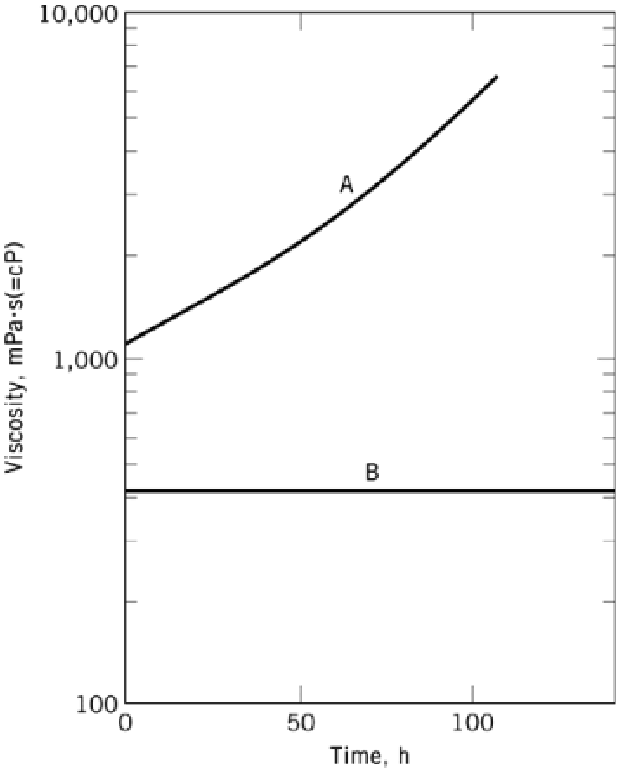


Fig. 7. Effect of aging on solution viscosity of PVA (47): A, DP = 1500, degree of hydrolysis, 98–99 mol%; B, DP = 1500, degree of hydrolysis, 87–89 mol%.

Table 3. Intrinsic Viscosity–Viscosity-Average Molecular Weight Relationship as a Function of Hydrolysis [a]

Hydrolysis, mol%	$[\eta]$
86.8	$(8.0 \times 10^{-4})\, M_v^{0.58}$
93.5	$(7.4 \times 10^{-4})\, M_v^{0.60}$
96.4	$(6.9 \times 10^{-4})\, M_v^{0.61}$
100.0	$(5.95 \times 10^{-4})\, M_v^{0.63}$

[a] Ref. (62).

4. Chemical Properties

Poly(vinyl alcohol) participates in chemical reactions in a manner similar to other secondary polyhydric alcohols (66–68). Of greatest commercial importance are reactions with aldehydes to form acetals, such as poly(vinyl butyral) and poly(vinyl formal).

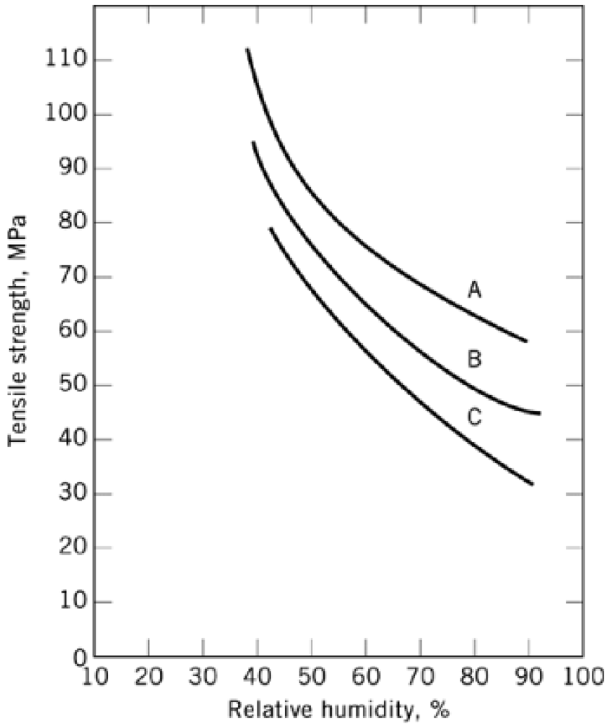
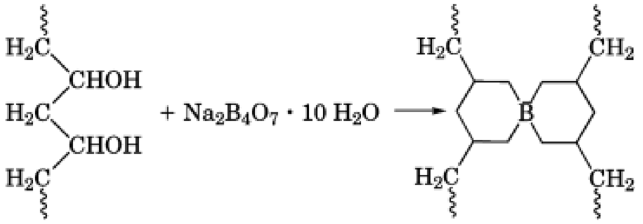


Fig. 8. Tensile strength as a function of relative humidity for fully hydrolyzed PVA films. A, DP = 2400; B, DP = 1700; C, DP = 500 (47). Reproduced by permission of John Wiley & Sons, Ltd. To convert MPa to psi, multiply by 145.

4.1. Esterification

4.1.1. Inorganic Esters

Boric acid and borax form cyclic esters with PVA (69–76). The reaction is markedly sensitive to pH, boric acid concentration, and the cation-to-boron ratio. An insoluble gel is formed at a pH above 4.5–5.0.



Similar complexes are formed between PVA and titanium lactate (72,77), titanyl sulfate (78), or vanadyl compounds (79).

Poly(vinyl nitrate) has been prepared and studied for use in explosives and rocket fuel (80,81). Poly(vinyl alcohol) and sulfur trioxide react to produce poly(vinyl sulfate) (82–86). Poly(vinyl alkane sulfonate)s have been prepared from PVA and alkanesulfonyl chlorides (87,88). In the presence of urea, PVA and phosphorus pentoxide (89) or phosphoric acid (90) yield poly(vinyl phosphate)s.

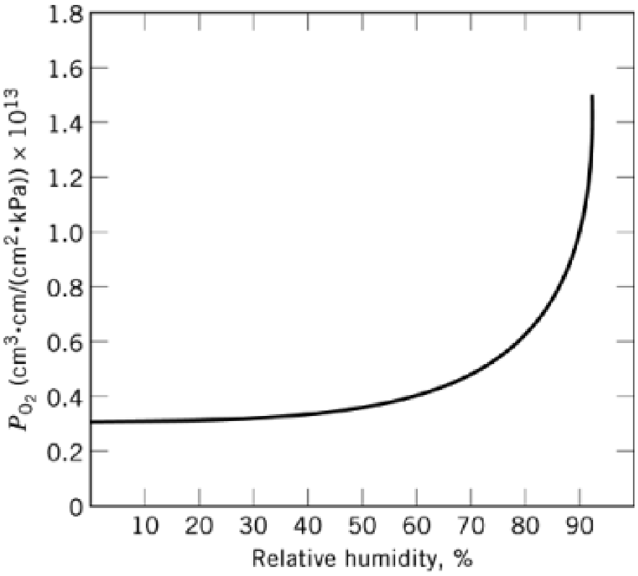


Fig. 9. Oxygen permeability of PVA as a function of humidity; degree of hydrolysis, 99.9 mol%, DP = 1750 (47).

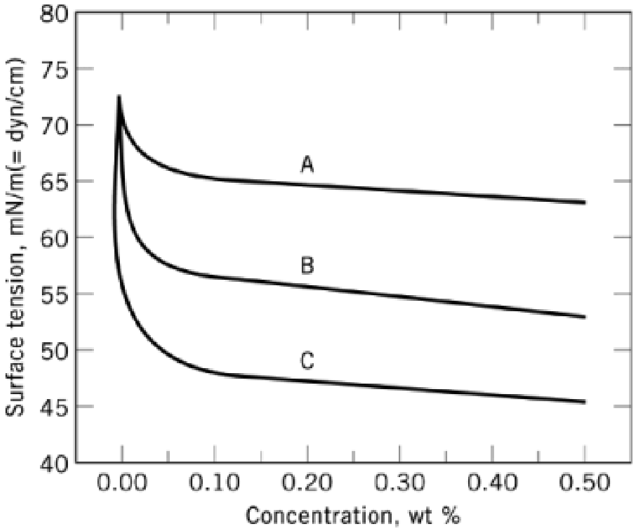


Fig. 10. Surface tension of aqueous PVA solutions at 20°C, DP = 1700. A, 98–99 mol% hydrolyzed; B, 87–89 mol% hydrolyzed; C, 78–81 mol% hydrolyzed.

4.1.2. Organic Esters

An unlimited number of organic esters can be prepared by reactions of PVA employing standard synthesis (66,68). Chloroformate esters react with PVA to yield poly(vinyl carbonates) (91).

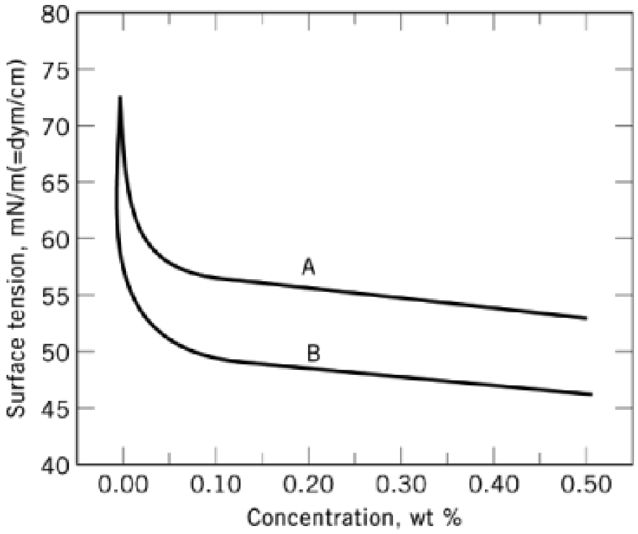
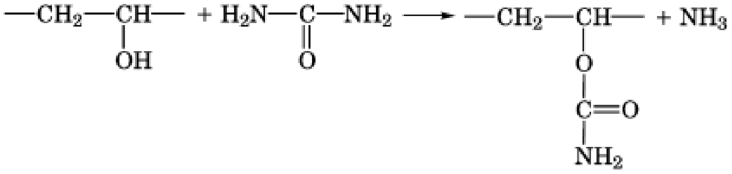


Fig. 11. Surface tension dependence on molecular weight at 20°C, degree of hydrolysis 87–89 mol%. DP: A, 1700; B, 550.

$$-CH_2-\underset{\substack{|\\ OH}}{CH}- + ClCOOR \xrightarrow{\text{base}} -CH_2-\underset{\substack{|\\ O\underset{\substack{\|\\ O}}{C}OR}}{CH}- + HCl$$

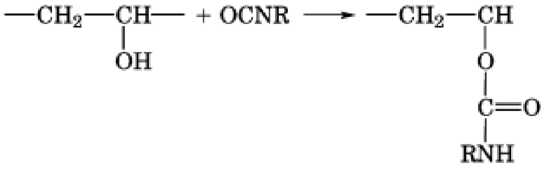
Poly(acrylic acid), poly(methacrylic acid), and maleic anhydride containing polymers react with PVA to form insoluble gels (92–94) useful as absorbents for water, blood, urine, etc.

Urea and PVA form a polymeric carbamate ester (95–98):



$$-CH_2-\underset{\substack{|\\ OH}}{CH}- + H_2N-\underset{\substack{\|\\ O}}{C}-NH_2 \longrightarrow -CH_2-\underset{\substack{|\\ O\\ |\\ C=O\\ |\\ NH_2}}{CH}- + NH_3$$

Reaction between PVA and isocyanates yields substituted carbamate esters (99–103):



$$-CH_2-\underset{\substack{|\\ OH}}{CH}- + OCNR \longrightarrow -CH_2-\underset{\substack{|\\ O\\ |\\ C=O\\ |\\ RNH}}{CH}$$

4.2. Etherification

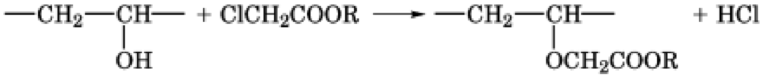
Ethers of PVA are easily formed. Insoluble internal ethers are formed by the elimination of water, a reaction catalyzed by mineral acids and alkali.

Ethylene oxide reacts with PVA under normal ethoxylation conditions (104–110). The resulting products have properties which make them useful as cold water-soluble films.

Cationic PVA has been prepared by the reaction of *N*-(3-chloro-2-hydroxypropyl)-*N*,*N*,*N*-trimethylammonium chloride and PVA and sodium hydroxide (111). Reactions between alkylidene epoxide and PVA in particulate, free-flowing form in an alkaline environment have been reported (112).

Poly(vinyl alcohol) undergoes Michaels addition with compounds containing activated double bonds, including acrylonitrile (115–117), acrylamide (118–120), *N*-methylolacrylamide (121–123), methyl vinyl ketone (124,125), acrolein (124), and sodium 2-acrylamido-2-methylpropanesulfonate (126). The reactions have been carried out under conditions spanning homogeneous reactions in solvent to heterogeneous reactions in the swollen powder or fiber.

Poly(vinyl alcohol) also reacts with monochloroacetates to yield glycolic acid ethers (127).

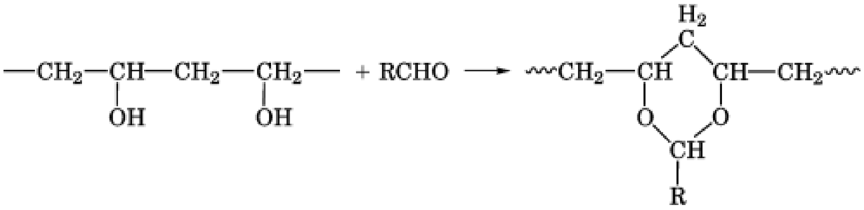


$$-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}- + ClCH_2COOR \longrightarrow -CH_2-\underset{\displaystyle OCH_2COOR}{\underset{|}{CH}}- + HCl$$

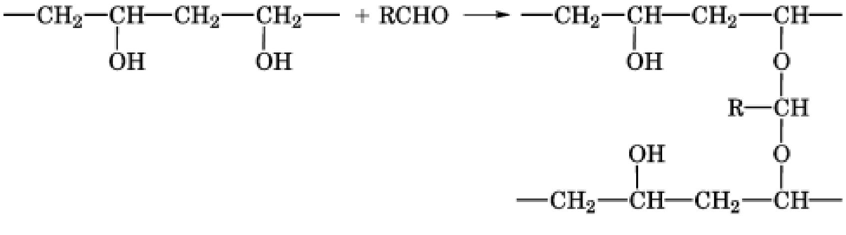
4.3. Acetalization

Poly(vinyl alcohol) and aldehydes form compounds of industrial importance.

Intramolecular acetalization



Intermolecular acetalization



Poly(vinyl butyral) prepared by reacting PVA with *n*-butyraldehyde finds wide application as the interlayer in safety glass and as an adhesive for hydrophilic surfaces (128). Another example is the reaction of PVA with formaldehyde to form poly(vinyl formal), used in the production of synthetic fibers and sponges (129).

Poly(vinyl alcohol) is readily cross-linked with low molecular weight dialdehydes such as glutaraldehyde or glyoxal (130). Alkanol sulfonic acid and PVA yield a sulfonic acid modified product (131).

4.4. Other Reactions

Poly(vinyl alcohol) forms complexes with copper in neutral or slightly basic solutions (132). Sodium hydroxide or potassium hydroxide forms an intermolecular complex with PVA (132,133) causing gelation of the aqueous solution.

Certain organic compounds form reversible gels with PVA. Congo red, for example, yields a red gel that melts sharply at about 40°C. Other organic compounds that form a temperature reversible complex with PVA include azo dyes, resorcinol, catechol, and gallic acid (133,134)

Fully hydrolyzed PVA and iodine forms a complex that exhibits a characteristic blue color similar to that formed by iodine and starch (135–137). The color of the complex can be enhanced by the addition of boric acid to the solution consisting of iodine and potassium iodide. This affords a good calorimetric method for the determination of PVA. Color intensity of the complex is effected by molecular weight, degree of hydrolysis, extent of branching, stereoregularity, 1,2-glycol content, and reagent composition. The higher the 1,2-glycol content and the lower the molecular weight, the weaker the color (138–140). Partially hydrolyzed PVA and iodine forms a red complex, which is sensitive to the sequence distribution of the remaining acetate groups. The color intensity increases with increasing blockiness (141–148).

4.5. Cross-linking

Poly(vinyl alcohol) can be readily cross-linked using a multifunctional compound that reacts with hydroxyl groups. These types of reactions are of significant industrial importance as they provide ways to obtain improved water resistance of the PVA or to increase the viscosity rapidly. The most commonly used cross-linking agents include glyoxal, glutaraldehyde, urea–formaldehyde, melamine–formaldehyde, trimethylolmelamine sodium borate or boric acid, and isocyanates. Most of the reactions are either acid- or base-catalyzed.

The study of hydrogel formation and their properties is a field of active academic research (76,149–151). The PVA molecule is loosely cross-linked, using standard cross-linking agents as mentioned above, which prevents solubility but allows for swelling. Application areas of interest range from enhanced oil recovery to drug delivery.

Strongly chelating metal salts of copper and nickel, eg, cupric ammonium complexes, chromium complexes, and organic titanates and dichromates, can be effective insolubilizers for PVA. Heat treatment during drying of the PVA film or coating is generally sufficient to accomplish the cross-linking reaction. The dichromate reaction is catalyzed by ultraviolet light.

Poly(vinyl alcohol), even when insolubilized by cross-linking, swells in water and loses strength on extended exposure. Complete water insensitivity cannot be achieved.

4.6. Thermal Decomposition

The thermal decomposition of PVA in the absence of oxygen occurs in two stages. The first stage begins at about 200°C and is mainly dehydration, accompanied by the formation of volatile products (152–158). The residue is predominantly macromolecules of polyene structure (152,159,160). Further heating to 400–500°C yields carbon and hydrocarbons (152,158). The available data on the nature of the decomposition products show some disagreement (152–157). Differences in manufacturing conditions of the PVA can significantly impact the thermal stability of the PVA as both molecular structure and the presence of catalyst residues are known sources for decreased thermal stability. The most common decomposition products of vinyl alcohol–vinyl acetate copolymers are shown in Table 4. The formation rate of volatile vapors from PVA pyrolyzed at 185–350°C can be described using a first-order rate equation (159).

The thermal degradation of PVA in the presence of oxygen can be described by the same decomposition scheme as in the absence of oxygen with one modification. Oxidation of the unsaturated polymeric residue

Table 4. Thermal Decomposition Products of Vinyl Alcohol–Vinyl Acetate Copolymers, %[a]

	Hydrolysis, mol%						
Product	0	33	50	68	75	84	98
Water	14.10	16	20.30	43.57	60.24	59.98	73.88
Methanol	1.05	2.0	2.20	7.53	3.80	1.32	0.56
Acetone	4.20	2.1	8.90	4.35	2.62	2.62	0.85
Ethanol	7.00	6	2.30	1.13	0.43	0.61	1.25
n-Propanol	1.10	1.40	1.50	1.0	0.48	1.39	traces
Cotonaldehyde	–	3.05	2.30	traces	traces	0.67	traces
Acetic acid	74.00	79.00	59.03	35.13	26.30	26.68	6.98
Unidentified compounds	–	1.98	3.01	1.6	1.83	traces	8.03
Benzene	5	traces	–	–	–	–	–

[a] Ref. 142.

from the dehydration introduces ketone groups in the polymer chain. These groups promote the dehydration of the neighboring units, producing conjugated unsaturated ketone structures (161). Cross-linking under these conditions has also been observed (162). The first-stage degradation is similar to that obtained during vacuum pyrolysis (160). Above 250°C in the presence of oxygen, induced decomposition with self-ignition may take place (163).

4.7. Biodegradation

Poly(vinyl alcohol) is one of the few truly biodegradable synthetic polymers with the degradation products being water and carbon dioxide. At least 55 species or varieties of microorganisms have been shown to degrade or take an active role in the degradation of PVA (164). Poly(vinyl alcohol) degrading organisms consist not only of 20 different genera of bacteria, but molds, yeast, and fungi as well. The microorganisms which degrade PVA exist in most environments including activated sludge, facultative ponds, anaerobic digesters, septic systems, compost, aquatic systems, soil, and landfills. The time period for PVA to degrade is dependent upon the physical properties of the polymer, the form in which the product exists and the environment in which it is degraded. PVA is rapidly degraded by activated sludge especially if the sludge has already been adapted to the PVA molecule (164–168). Many of the microorganisms which degrade PVA can be isolated from soil (169–173).

The mechanism of PVA degradation consists of a random oxidation of a hydroxyl group to a ketone through the influence of a secondary alcohol oxidize. The random oxidation is continued until a β-diketone is formed. This group is cleaved by a extracellular hydrolase, leading to a reduction in molecular weight and the formation of a carboxylic end group and a methyl ketone end group. Continued degradation eventually leads to the formation of acetic acid, which in turn is converted into carbon dioxide and water. The degradation is normally accomplished by means of symbiotic organisms. Symbiotic bacterial pairs known to degrade PVA include, for Type I, *Pseudomonas putida* VM 15A, *P. vesicularas* Va., *P. porolyticus* PH, and *P. alkaligenes*; and for Type II, *P. Sp.* VM15C, *P. vesicularis* XL, *P. vesicularis* XL, and *P. vesicularis* PD. More recent studies have shown that isotactic blocks in PVA molecule are more readily biodegraded than those having an atactic structure (174,175). The biological oxygen demand for degradation of a 0.1% PVA solution is approximately 5 ppm (170).

5. Manufacture

Poly(vinyl alcohol) can be derived from the hydrolysis of a variety of poly(vinyl esters) such as poly(vinyl acetate), poly(vinyl formate), and poly(vinyl benzoate) and from the hydrolysis of poly(vinyl ethers). However, all commercially produced PVA is manufactured by the hydrolysis of poly(vinyl acetate). The manufacturing process can be viewed as one segment that deals with the polymerization of vinyl acetate and another that handles the hydrolysis of poly(vinyl acetate) to PVA.

5.1. Production of Poly(vinyl acetate)

5.1.1. Chemistry

Vinyl acetate is polymerized commercially using free-radical polymerization in either methanol or, in some circumstances, ethanol. Suitable thermal initiators include organic peroxides such as butyl peroxypivalate, di(2-ethylhexyl) peroxydicarbonate, butyl peroxyneodecanoate, benzoyl peroxide, and lauroyl peroxide, and diazo compounds such as 2,2′-azobisisobutyronitrile (176–179). The temperatures of commercial interest range from 55 to 85°C (176,177).

Propagation of the polymerization occurs nearly exclusively by head-to-tail with only a small fraction of head-to-head reactions. The relative ratio of the two reactions is only a function of temperature and has been found to be independent of molecular weight, polymerization solvent, and method of polymerization. The head-to-head addition yields a 1,2-glycol structure in the resulting PVA, which in turn can influence the degree of crystallinity, strength, solubility, and thermal stability.

Termination reaction with vinyl acetate is nearly exclusively by disproportionation (180), although there are reports that recombination increases in importance at lower temperatures (181). Termination by disproportionation produces a double bond at the end of one molecule and a saturated bond at the other. The presence of the unsaturated bond results in an aldehyde group once the associated acetate group is hydrolyzed (182–184). The resulting aldehyde group decreases the thermal stability of the PVA, because the activation energy for splitting off water is reduced on account of the increased ability for formation of conjugated double bonds. The higher color level, observed in lower molecular weight commercial PVA grades, is a result of this reaction.

Chain transfer to monomer is important during vinyl acetate polymerization (181,185,186). The reaction is an abstraction of the hydrogen on the acetyl group of the vinyl acetate (187–189). The growing radical is transferred to the vinyl acetate monomer, which then reinitiates the polymerization. The reaction results in an unsaturated end group, which is still polymerizable. The inclusion of this terminal end group in a growing chain leads to a trifunctional branch point with the incorporation of the entire polymer molecule as a long-chain branch (185–191).

Chain transfer to polymer is considerable in vinyl acetate polymerization. The intermolecular transfer of a growing radical to a polymer molecule results in a branch point. Several studies have determined the fraction of branch points through the acetate group compared to those generated directly on the main chain (191,193–197). The results reported in the literature have been highly variable, ranging from over 0.95 to less than 0.5 at 60°C. The main distinction between branches generated through the acetoxy group and those connected directly to the main chain is that the first type is cleavable upon hydrolysis, the latter is not.

It has been shown that intramolecular chain transfer to polymer occurs during the polymerization of vinyl acetate, leading to short-chain branching (65,198–201). The number of short-chain branches has been estimated by nmr to be in the range of 0.12–1.7 mol% (65). The number of short-chain branches increases significantly with decreasing monomer concentration.

Chain transfer to low molecular weight alcohols occurs readily. However, the resulting end groups are not known to affect the physical or chemical properties of the resulting PVA. Chain transfer to acetaldehyde results in the incorporation of a ketone end group. Acetaldehyde is formed as a result of the transesterification between vinyl acetate and the added alcohol solvent. A small amount of an acid (2–50 ppm) may be added to the

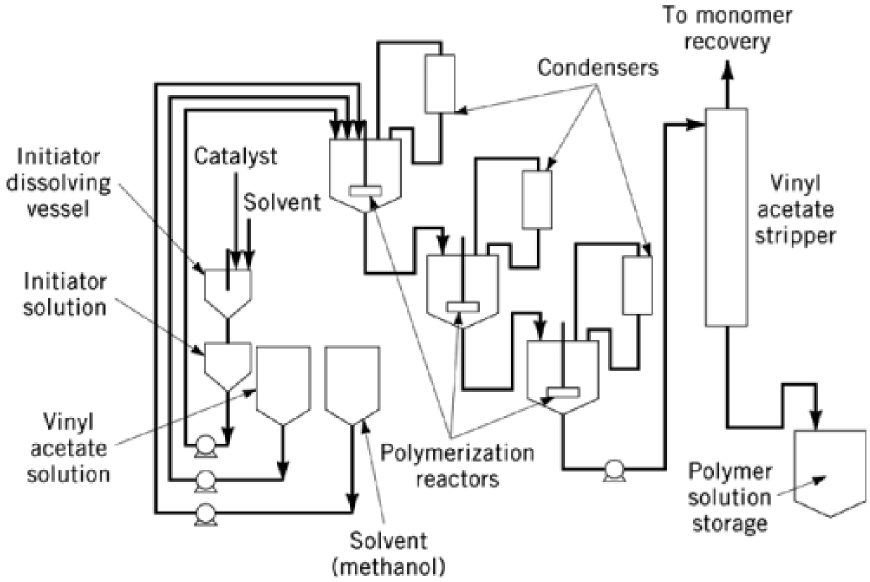


Fig. 12. Typical polymerization flow diagram for the continuous polymerization of vinyl acetate (208).

vinyl acetate in order to limit the transesterification (177,202–207). Suitable acids include phosphorous acid, oxalic acid, citric acid, and tartaric acid. The presence of the ketone end group in the resulting PVA facilitates the formation of conjugated double bonds and leads to color.

5.2. Commercial Manufacturing Processes

5.2.1. Continuous Polymerization

A typical continuous flow diagram for the vinyl acetate polymerization is shown in Figure 12. The vinyl acetate is fed to the first reactor vessel, in which the mixture is purged with an inert gas such as nitrogen. Alternatively, the feed may be purged before being introduced to the reactor (176). A methanol solution containing the free-radical initiator is combined with the above stream and passed directly and continuously into the first reactor from which a stream of the polymerization mixture is continuously withdrawn and passed to subsequent reactors. More initiator can be added to these reactors to further increase the conversion.

The polymerization temperatures can range from 45 to 130°C; the preferred range is 55–85°C, which results in operating pressures of 0.1–0.5 MPa (1–5 atm). The heat of reaction is removed by condensing monomer and solvent vapors. Cooling coils show low efficiency because of the low heat transfer coefficient of the highly viscous material. Viscosity during polymerization can range from 10 to 500 P. Molecular weight is controlled by the residence time in the reactors, monomer feed rate, solvent concentration, initiator concentration, and polymerization temperature.

A stripping column is used to remove unpolymerized vinyl acetate from the poly(vinyl acetate) solution leaving the last reactor (Fig. 13). Methanol vapors are used to strip vinyl acetate from the solution (209,210). An inhibitor such as hydrazine, hydroquinone, sulfur, or quinone can be added to poly(vinyl acetate) solution leaving the reactor in order to prevent further polymerization in the stripping column (176). The overhead fraction from the stripping column consisting of solvent and vinyl acetate may be passed to a recovery system, or directly recycled to the reactor. Vinyl acetate and methanol not recycled to the reactor must be separated

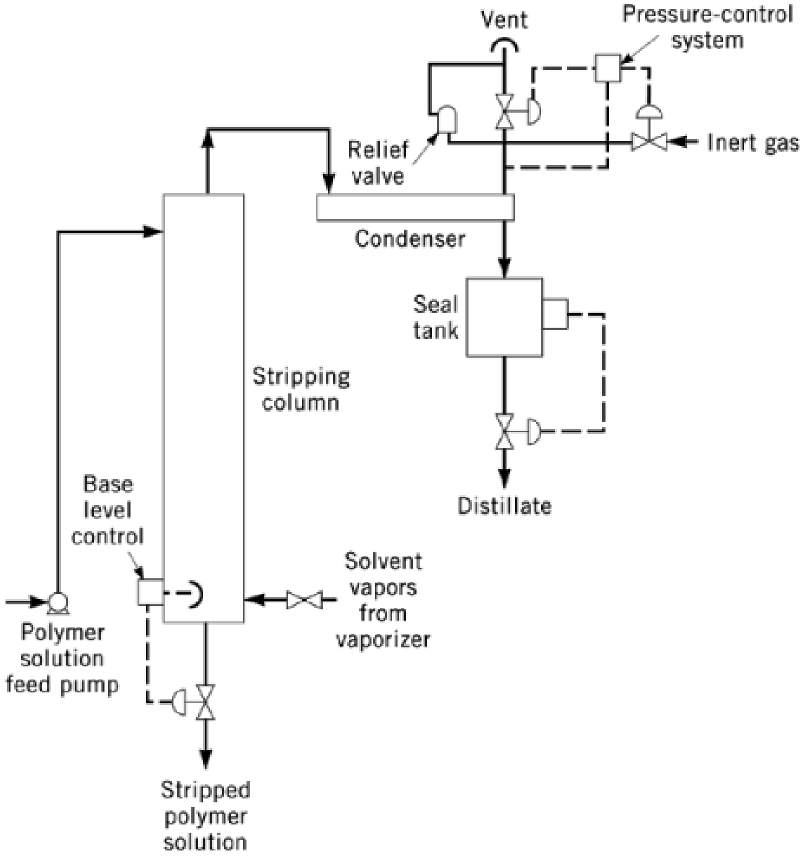


Fig. 13. Typical scheme for monomer stripping (209).

and purified. Extractive distillation is normally used because methanol and vinyl acetate form an azeotrope. Suitable solvents include water and ethylene glycol.

The vinyl acetate content in the bottom effluent from the stripping column is reduced to less than 0.07 wt%. Higher concentrations of vinyl acetate will lead to yellowing because of acetaldehyde formation and subsequent aldol condensation during the hydrolysis reaction.

5.2.2. Batch and Semibatch Polymerization

The reactor is normally operated in a semicontinuous mode by delaying the addition of vinyl acetate, solvent, and initiator. The same reactor can be used for stripping the poly(vinyl acetate) solution, provided that careful addition of methanol is used in order to prevent the viscosity in the reactor from becoming excessive (211). The disadvantages of batch polymerization are the lack of product consistency and unsatisfactory economics in large-scale production. The true batch reaction, where all the reactants are added to the reactor at time zero, yields a product having a very broad molecular weight distribution of limited commercial value.

5.3. Production of PVA

5.3.1. Chemistry

Poly(vinyl acetate) can be converted to PVA by transesterification, hydrolysis, or aminolysis. Industrially, the most important reaction is that of transesterification, where a small amount of acid or base is added in catalytic amounts to promote the ester exchange.

The catalysts most often described in the literature (176,177,212) are sodium or potassium hydroxide, methoxide, or ethoxide. The reported ratio of alkali metal hydroxides or metal alcoholates to that of poly(vinyl acetate) needed for conversion ranges from 0.2 to 4.0 wt% (177). Acid catalysts are normally strong mineral acids such as sulfuric or hydrochloric acid (213). Acid-catalyzed hydrolysis is much slower than that of the alkaline-catalyzed reaction, a fact that has limited the commercial use of these catalysts.

The solution of poly(vinyl acetate) generated during the stripping operation is normally passed directly through to the alcoholysis system. This has limited the available solvents to methanol and ethanol (176,177). Substituting the alcohol used as solvent with the generated ester limits the hydrolysis and greatly affects how the remaining acetyl groups are distributed on the PVA chain (214–216). The distribution is often referred to as the blockiness of the PVA. The higher the methyl acetate concentration, the higher the degree of blockiness.

The presence of catalyst residues, such as alkali hydroxide or alkali acetate, a by-product of the hydrolysis reaction, is known to increase the thermal instability of PVA. Transforming these compounds into more inert compounds or removal through washing are both methods that have been pursued. The use of mineral acids such as sulfuric acid (217), phosphoric acid (218), and *ortho*-phosphoric acid (219) has been reported as means for achieving increased thermal stability of the resulting PVA.

5.3.2. Commercial Hydrolysis Process

The process of converting poly(vinyl acetate) to PVA on a commercial scale is complicated on account of the significant physical changes that accompany the conversion. The viscosity of the poly(vinyl acetate) solution increases rapidly and greatly as the conversion proceeds because the resulting PVA is insoluble in the most common solvents used for the polymerization of vinyl acetate. The outcome is the formation of a gel swollen with the resulting acetic acid ester and the alcohol used to effect the transesterification.

5.3.3. Continuous Saponification

There are several types of continuous systems, each with their own benefits and drawbacks. The basic premise is that continuous mixing is not required after the poly(vinyl acetate) and the caustic is mixed (220). Several designs for the high intensity mixing unit have been suggested in order to obtain efficient mixing and little fouling (221,222).

In the belt process, the mixture is cast onto the belt or conveyer (high temperature polyethylene) (223) where the gelling occurs (220,224). The gel is removed from the surface before syneresis, cut into smaller particles, and passed to a holding or washing tank (Fig. 14). The liquid is removed from the precipitate using common chemical deliquefying methods, and the resulting particles are dried in a continuous dryer.

In the slurry process, the hydrolysis is accomplished using two stirred tank reactors in series (225). Solutions of poly(vinyl acetate) and catalyst are continuously added to the first reactor, where 90% of the conversion occurs, and then transferred to the second reactor to reach full conversion. Alkyl acetate and alcohols are continuously distilled off in order to drive the equilibrium of the reaction. The resulting PVA particles tend to be very fine, resulting in a dusty product. The process has been modified to yield a less dusty product through process changes (226,227) and the use of additives (228). Partially hydrolyzed products having a narrow hydrolysis distribution cannot be prepared by this method.

In the screw conveyer process, solutions of poly(vinyl acetate) and catalyst are mixed in a high intensity mixer and continuously introduced to a screw-type saponification and conveyer system (229). Downstream details are similar to those found in the belt process.

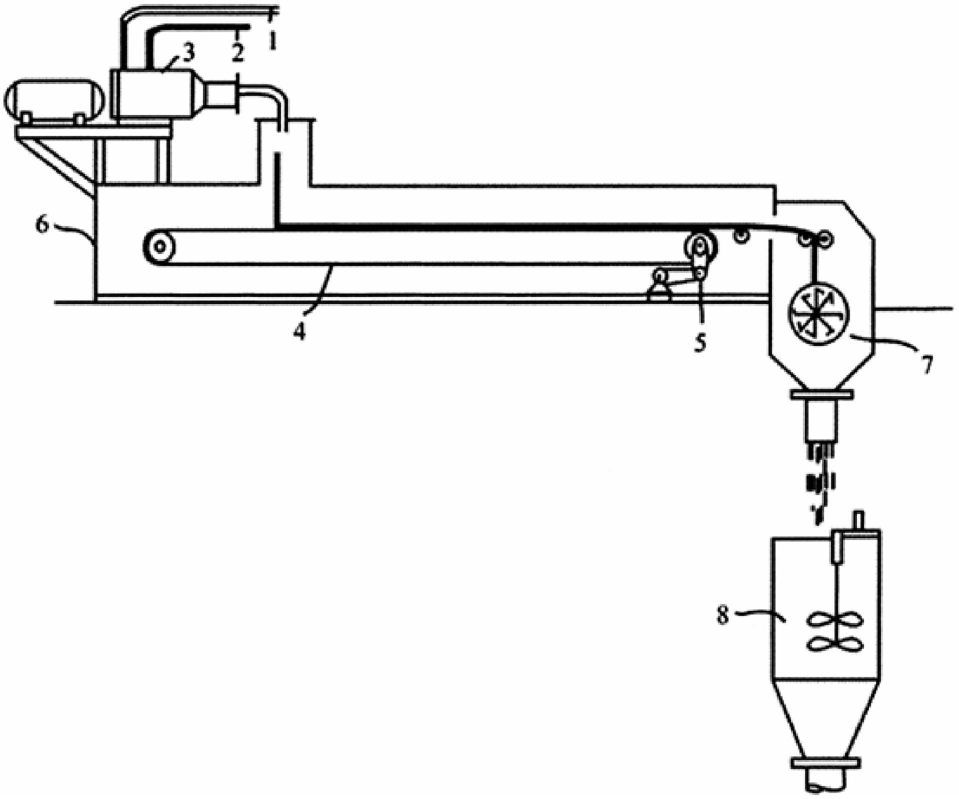


Fig. 14. The belt saponification process as used in the production of PVA (223). 1, Polyvinyl acetate/methanol mixture; 2, catalyst in methanol; 3, mixer; 4, belt; 5, drive; 6, housing; 7, cutter; 8, slurry tank (wash tank).

Other methods also exist for handling the reaction mixture. For instance, an intermeshing, self-wiping, twin-screw extruder process has been proposed (230). The advantages described include higher saponification temperature (less catalyst), increased water solubility, and fewer impurities (231).

5.3.4. Batch Saponification

Batch saponification, the oldest PVA manufacturing method (232), is mainly used for the production of specialty products. The process uses a kneader in which the hydrolysis, washing, and drying operations are performed. This is the simplest method of saponification, but the production rates are low, and producing the product quality needed by many end uses is difficult.

5.4. Drying/Solids Separation

Separation of the polymer gel from the methanol/methyl acetate liquid is an important step, accomplished by using standard pieces of equipment such as filters, screw presses, or centrifuges.

Drying of the PVA is critical both to the color and solubility of the final product. Excessive drying temperatures result in high product color and an increase in the crystallinity, which in turn reduces the solubility of the product. Drying is initially subjected to a flash regime, where the solvent not contained within the particles is flashed off. This first phase is followed by a period where the rate is controlled by the diffusion rate of solvent

Table 5. Principal Poly(vinyl alcohol) Producers

Producer	Trade name	Capacity, t/year
Celanese	Celvol	90, 000
Chang Chun	CCP	75, 000
Chin-Shan Petrochemical		33, 000
DuPont	Elvanol	68, 000
Kuraray	Poval	194, 000
Nippon Goshei	Gohsenol	77, 000
Shi-Shan Vinylon		45, 000

from the PVA particles. Because the diffusion rate falls as the material dries, complete drying is not practical. The polymer is, therefore, generally sold at a specification of 95% solids.

5.5. Solvent Recovery

A mixture of methanol and methyl acetate is obtained after saponification. The methyl acetate can be sold as a solvent or converted back into acetic acid and methanol using a cationic-exchange resin such as a cross-linked styrene–sulphonic acid gel (233–236). The methyl acetate and methanol mixture is separated by extractive distillation using water or ethylene glycol (237–241). Water is preferred if the methyl acetate is to be hydrolyzed to acetic acid. The resulting acetic acid solution is concentrated by extraction or azeotropic distillation.

6. Copolymers

Numerous vinyl alcohol copolymers have been prepared (242). Copolymers with ethylene and methyl methacrylate are the only copolymers that have found sizable commercial utility. Ethylene–vinyl alcohol (EVOH) copolymers containing 20–30 mol% ethylene are used as an oxygen barrier in food packaging. However, a five-layer coextruded structure with polyolefins is needed in order to protect the EVOH from moisture. Vinyl alcohol–methyl methacrylate copolymers are used as sizing agents in the textile industry. The presence of the methacrylate unit disrupts the crystallinity making the product easier to remove during the desizing operation. The product is especially useful as an alkaline-resistant textile size.

7. Economic Aspects

The capacity of PVA in 2001 was greater than 625,000 t. The industry has experienced major changes since 1995, including the sale of the Air Products & Chemicals position to Celanese in September 2000, and the Clariant (formerly Hoechst) position to Kuraray in July 2001. New capacity, 40,000 t, was added by Kuraray and Nippon Gohsei in form of a joint venture, located in Singapore. Incremental expansion projects have also been initiated or completed by several of the current producers.

Approximately two-thirds of capacity is located in Japan, China, and Taiwan, with the remainder in the United States and Europe. Approximately 50,000 t of the Japanese and a large portion of the Chinese production is captively consumed for fiber production. The principal PVA producers in the world (capacity >30,000 t/year) are shown in Table 5.

The PVA process is highly capital-intensive as separate facilities are required for the production of poly(vinyl acetate), its saponification to PVA, the recovery of unreacted monomer, and the production of acetic

Table 6. Degree of Hydrolysis of Commercial Poly(vinyl alcohol) Grades

Grade	Hydrolysis, mol%
Super	99.3+
Fully	98.0–98.8
Intermediate	95.9–97.0
Partially	87.0–89.0
Low	79.0–81.0

Table 7. Viscosity and DP[a] of Principal Commercial Poly(vinyl alcohol) Grades[b]

Grade	Nominal DP	Viscosity of 4% solution, mPa·s (=cP)
Low–low	220	3–4
Low	550	5–7
Intermediate	900	13–16
Medium	1500	28–32
High	2200	55–65

[a] DP = Degree of polymergation.
[b] Grade = molecular range.

acid from the ester formed during alcoholysis. Capital costs are far in excess of those associated with the traditional production of other vinyl resins.

The PVA price has historically reflected the cost of ethylene, acetic acid, and energy. However, recent overcapacity has put strain on the pricing structure and lowered the return on investment. The price rose from \$0.77/kg in 1970 to \$2.20/kg in 1980, \$2.75/kg in 1988, \$2.65/kg in 1995, and \$2.20/kg in 2001 for medium molecular weight fully hydrolyzed grade.

8. Specifications and Standards

The important commercial grades of PVA are distinguished by the degree of hydrolysis and molecular weight. The resins are most often categorized by degree of hydrolysis, ie, mole percent of alcohol groups in the resin (Table 6). Poly(vinyl alcohol)s having other degrees of hydrolysis are also produced, but maintain a much smaller market share than those shown in Table 6.

Poly(vinyl alcohol) is produced mainly in five molecular weight ranges expressed as degree of polymerization (DP) (Table 7). Several other molecular weight resins are available, but their market shares are relatively low. Industry practice expresses the molecular weight of a particular grade in terms of the viscosity of a 4% aqueous solution. An unlimited number of viscosities can be generated by blending the available molecular weights. Products having different degrees of hydrolysis can also be blended to obtain a particular performance characteristic. However, blended products have a broad distribution with respect to molecular weight and in some cases hydrolysis, which may be undesirable in some applications.

PVA is an innocuous material with unlimited storage stability. It is most commonly supplied in 20-, 22.7- (50-lb), and 25-kg bags equipped with a moisture barrier to prevent caking. Poly(vinyl alcohol) is also available in bulk or in super sacks. The FDA regulations governing the use of PVA are shown in Table 8. Poly(vinyl alcohol) maintains an exemption for tolerance from the EPA.

Table 8. FDA Regulations for Poly(vinyl alcohol) in Food Applications

Regulation	Description
181.30	Manufacture of paper and paperboard products used in packaging of fatty foods
175.105	Adhesives, no limitations
176.170	Components of paper and paperboard in contact with aqueous and fatty food; extractive limitations
176.180	Components of paper and paperboard in contact with dry food; no limitations
177.1200	Cellophane coating; no limitations
177.1670	Poly(vinyl alcohol) film
177.2260	Filters, resin-bonded where fiber is cellulose
177.2600	Filters, extractables must be less than 0.08 mg/cm^2
175.200	Resinous and polymeric coating
175.320	Resinous and polymeric coatings for polyolefin films; net extractable less than 0.08 mg/cm^2
177.2800	Textiles and textile fibers; for dry foods only
178.3910	Surface lubricants in the manufacture of metallic articles

9. Analytical and Test Methods

The important analytical test methods are those related to the determination of degree of hydrolysis, pH, viscosity, ash, and volatiles. Percent hydrolysis of the PVA is measured by placing the material in a mixture of water and methanol, adding a predetermined quantity of sodium hydroxide, and boiling under reflux to hydrolyze residual acetate groups. The moles of sodium hydroxide consumed are equivalent to the number of hydrolyzable acetate groups and are determined by back titration with strong acid.

The pH is measured using a 4% aqueous solution. Viscosity is normally measured using a Brookfield viscometer. Alternatively, a capillary viscometer or falling ball such as Hõppler may be employed. The type of viscometer used must always be noted.

Ash is a measure of residual sodium acetate. A simple method consists of dissolving the PVA in water, diluting to a known concentration of about 0.5 wt% and measuring the electrical conductivity of the solution at 30°C. The amount of sodium acetate is established by comparing the result to a calibration curve. A more lengthy method involves the extraction of the PVA with methanol using a Soxhlet extractor. The methanol is evaporated and water is added. The solution is titrated using hydrochloric acid in order to determine the amount of sodium acetate.

Volatiles such as residual methanol, methyl acetate, and water are determined as the loss in mass when the polymer is dried at 105 ± 2°C until constant mass is attained. Higher drying temperatures may cause decomposition and related weight loss.

10. Health and Safety Factors

Poly(vinyl alcohol) is a nonhazardous material according to the American Standard for Precautionary Labeling of Hazardous Industrial Chemicals (ANSI 2129.1-1976). Extensive tests indicate a very low order of toxicity when it is administered orally to laboratory animals (170). No toxicity was detected by oral administration of the maximum amount of 1500 mg/kg of two types of PVA (DP 1400, 99.5% hydrolyzed; and DP 1700, 86.8% hydrolyzed) or by subcutaneous injection of 3000 mg/kg to mice. PVA injected under the skin or into the lungs is not absorbed by the tissue and remains as a foreign body. The increase in growth and weight of mice given 1000 mg/kg every day during a 3-month chronic toxicity test was about the same as that of the control group animals. No histopathologic tensions were observed.

Poly(vinyl alcohol) has a low oral toxicity rating. The oral LD_{50} is higher than 10,000 mg/kg (rats). Concentrations of up to 10,000 mg/L in water were tested for toxicity to bluegill sunfish. No mortality or response indicative of intoxication was observed (243).

Short-term inhalation of PVA dust has no known health significance but can cause discomfort and should be avoided in accordance with industry standards for exposure to nuisance dust. The dust is mildly irritating to the eyes. There are no known dermal effects arising from short-term exposure to either solid PVA or its aqueous solutions.

During transport and handling, granular PVA may form an explosive mixture with air. However, the severity rating is 0.1 (Bureau of Mines Rating) on a scale in which coal dust has a rating of 1.0 (244). The explosive hazard does depend on particle size, and extremely fine dust has a higher explosive rating of 1.0–2.0. Residual methanol and methyl acetate can accumulate in the air space of bulk storage tanks; this is especially true at elevated temperatures. Precautions should be taken to ventilate the air space in large vessels and eliminate spark-producing equipment in the area. The issue of residual organic volatiles has been addressed by a few PVA producers who have proactively implemented manufacturing specifications aimed at obtaining less than 1 wt% organic volatiles in the final product.

11. Processing

Poly(vinyl alcohol) is not considered a thermoplastic polymer because the degradation temperature is below that of the melting point. Thus, industrial applications of PVA are based on and limited by the use of water solutions.

11.1. Solution Preparation and Handling

Poly(vinyl alcohol) should be completely dispersed in water at room temperature, or lower, before heating of the water solution is commenced. Good agitation is important to prevent lumping during the addition of solid PVA to water. A large diameter, low speed agitator is preferred for providing good mixing at the surface without excessive air entrainment. Agitation requirements increase with solution concentration and with decreasing hydrolysis; the latter is associated with greater solubility in cold water and a tendency to lump.

The temperature of the slurry must be increased to 70–90°C in order to solubilize the PVA fully. Ways to increase the temperature includes direct steam injection, jet cooking, or heating with jacket or coil. Aqueous solutions of PVA are stable on storage but must be protected from bacterial growth. An increase in viscosity is commonly observed when storing fully hydrolyzed PVA solutions. Stainless steel or plastic containers are recommended for long-term storage. Many biocides are effective including FDA-approved compounds (245).

Prolonged heating of the PVA solution has negligible effect on its properties. However, the addition of strong acid or base to solutions of partially hydrolyzed PVA can increase the degree of hydrolysis.

11.2. Extrusion

Several attempts to introduce and produce extrudable PVA products have and continue to be made (246–260). However, these types of products have not achieved any significant commercial success. The main obstacles are thermal stability during extrusion and gels in the final product. A wide variety of high boiling water-soluble organic compounds containing hydroxyl groups have been used as plasticizers in order to lower the melt temperature and avoid decomposition. Glycerol and low molecular weight poly(ethylene glycol)s are most widely used. Water is an excellent plasticizer for PVA, although extrusion temperatures below 100°C are required in order to avoid the formation of foam at the extruder outlet.

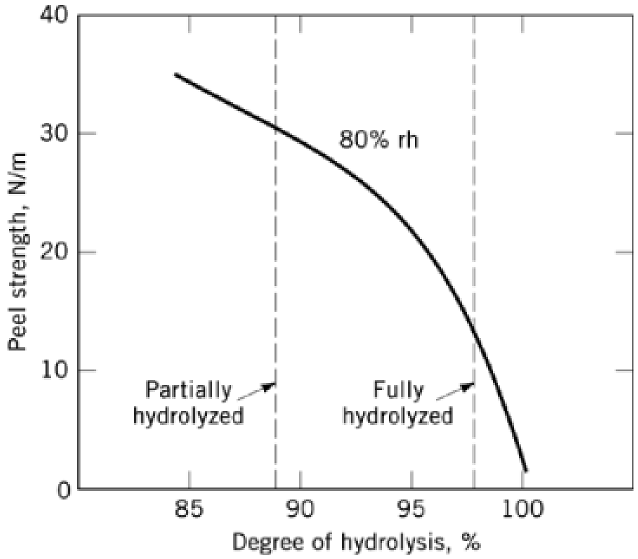


Fig. 15. Adhesion expressed as peel strength of PVA film on polyester film (7). To convert N/m to ppi, divide by 175.

12. Uses

The main applications for PVA are in textile sizing, adhesives, polymerization stabilizers, and paper coating, poly(vinyl butyral), and PVA fibers. In terms of percentage, and omitting the production of PVA not isolated prior to the conversion into poly(vinyl butyral), the principal applications are textile sizes, at 30%; adhesives, including use as a protective colloid, at 25%; fibers, at 15%; paper sizes, at 15%, poly(vinyl butyral), at 10%; and others, at 5%, which includes water-soluble films, nonwoven fabric binders, thickeners, slow release binders for fertilizer, photoprinting plates, sponges for cosmetic, and healthcare applications.

12.1. Textile and Warp Sizing

Warps are sized to obtain increased abrasion resistance and strength in order to avoid breakage when passing through the loom. Yarn breakage during the weaving process reduces weaving efficiency and detracts from the quality of the finished cloth. The sizing material must allow for both easy splitting of the warp yarns after sizing and rapid desizing once the weaving process is complete. The typical sizing process consists of a size application box, squeeze rolls to remove excess size, drying drums, yarn-splitting rods, and beam-winding equipment.

Poly(vinyl alcohol) is an excellent textile warp size because of superior strength, adhesion, flexibility, and film-forming properties. The adhesion of PVA to natural or synthetic fibers or fiber blends depends on the degree of hydrolysis. Adhesion to such hydrophobic fibers as polyester is enhanced as the degree of hydrolysis is reduced (Fig. 15). Fully hydrolyzed grades adhere well to cotton and other hydrophilic fibers and impart the highest tensile strength for equivalent amounts added. However, there continues to be a trend away from fully hydrolyzed PVA because of its poor adhesion to synthetic fibers and the difficulty encountered when desizing heat-set fabric (176,261,262). The best hydrolysis grade for warp sizing is specific to each manufacturing operation and is controlled by factors such as yarn quality, yarn construction, and speed and type of loom.

The highest molecular weight grades provide the best protection at equivalent concentration for spun yarns. However, low solids sizing solutions are needed to maintain manageable viscosity; this increases drying cost and limits production. Desizing of the fabric is difficult because of the lower solubility rate of these grades. Thus, the commonly used warp size grades for spun yarns are the medium to lower molecular weight resins because they provide balance, strength, solution viscosity, and desizing to yield the best possible economics. The best size for filament yarns are those PVA grades that have low degrees of polymerization.

Typical size formulations contain a lubricating wax, starch, and other processing aids. The role of these materials is to provide easy splitting of the yarns after drying, to decrease the sticking tendency of PVA to the drying drums, and to provide lubricity during the weaving process. The additives must to a large degree be incompatible with the dried PVA film to provide the desired function. However, a large degree of incompatibility can result in decreased encapsulation of the yarn and increased shedding during the weaving operation. Poly(vinyl alcohol) is normally used in 3–10-wt% concentrations in the aqueous size solution. Amount of size needed depends on both fabric and loom type, but is usually in the 5–10% range.

The fabric is desized after the weaving operation by passing it through a heated water bath to remove all the size. The rate at which this operation can be accomplished depends to a great degree on solubility rate of the PVA. Difficulties encountered in completely removing the lubricating wax, usually tallow wax, has led to the development of several wax-free size compositions (263–271). The main component contained in these blends is PVA in combination with a small amount of a synthetic water-soluble lubricant.

Poly(vinyl alcohol) can be recovered from the desizing liquid by means of commercial ultrafiltration equipment. Recovery rates and effluent losses are inversely proportional to the PVA solution viscosity and independent of the degree of hydrolysis.

12.2. Adhesives

Poly(vinyl alcohol) is used as a component in a wide variety of general- purpose adhesives to bond cellulosic materials, such as paper and paperboard, wood textiles, some metal foils, and porous ceramic surfaces to each other. It is also an effective binder for pigments and other finely divided powders. Both fully and partially hydrolyzed grades are used. Sensitivity to water increases with decreasing degree of hydrolysis and the addition of plasticizer. Poly(vinyl alcohol) in many applications is employed as an additive to other polymer systems to improve the cohesive strength, film flexibility, moisture resistance, and other properties. It is incorporated into a wide variety of adhesives through its use as a protective colloid in emulsion polymerization.

Adhesives for paper tubes, paperboard, corrugated paperboard, and laminated fiberboard are made from dispersions of clays suspended with fully hydrolyzed PVA. Addition of boric acid improves wet tack and reduces penetration into porous surfaces (73,272). The tackified grades have higher solution viscosity than unmodified PVA and must be maintained at pH 4.6–4.9 for optimum wet adhesion.

Poly(vinyl alcohol) is employed as a modifier of thermosetting resins used as adhesives in plywood and particleboard manufacture (273,274). The polymer is added to urea–formaldehyde or urea–melamine–formaldehyde resins to improve initial grab, increase viscosity, and in general to improve the characteristics of the board.

Poly(vinyl alcohol)s are used as components in vinyl acetate emulsions both as a protective colloid and as a means for improving adhesive properties. Addition of PVA to the resulting emulsions is commonly employed to modify viscosity, flow properties, and the rate of formation of the adhesive bond as well as the quality. High addition rates of partially hydrolyzed PVA can be used to prepare remoistenable adhesive formulations. All PVA grades promote the acceptance of starch and clay fillers into a formulation, which in turn prevents excessive adhesive penetration into porous surfaces. The PVA also offers reactive sites that can be used to cross-link the adhesive and improve the water resistance. Cross-Linking is accomplished by means of either *N*-methylolacrylamide, copolymerized with the vinyl acetate (275,276), or other commonly used cross-linking agents, such as glyoxal. The performance of poly(vinyl acetate)-based wood glues is to a great extent dependent upon the presence of PVA to provide both the cohesive and adhesive properties.

Table 9. Relative Strength of Paper Binders

Binder	Parts for equal strength
Poly(vinyl alcohol)	1
Styrene–butadiene	2–2.5
Poly(vinyl acetate)	2–3
Soy protein	2.5–3
Casein	2.5–3
Starch	3–4

12.3. Emulsion Polymerization

Poly(vinyl acetate) and poly(vinyl acetate) copolymer latices prepared in the presence of PVA find wide applications in adhesives, textile finishes, and coatings. The emulsions show excellent stability to mechanical shear and to the addition of electrolytes, and possess excellent machining characteristics.

Partially hydrolyzed PVA grades are preferred because they have a hydrophobic/hydrophilic balance that make them uniquely suited for emulsion polymerization. The compatibility of the residual acetate units with the poly(vinyl acetate) latex particles partly explains the observed stabilization effect. The amount of PVA employed is normally 4–10% on the weight of vinyl acetate monomer. The viscosity of the resulting latex increases with increasing molecular weight and decreasing hydrolysis of the PVA (277).

12.4. Paper Coating

The unique binding properties of PVA has made it a primary contributor to the development of higher quality, specialized paper products. Its use spans a great variety of grades, including silicone-coated release liners, grease-proof and glassine packaging papers, food-grade boards, carbonless grades, currency and banknote grades, offset printing papers, high brightness printing and writing grades, offset masters, ink-jet and thermal printing papers, and cigarette filter tip papers.

Poly(vinyl alcohol) is utilized principally as a surface-treating agent, as in clear sizing, pigmented sizing, and pigmented coating. Exceptions include its use as a creping aid in tissue and towel manufacturing, in dye encapsulation for carbonless papers, and in some wet-end addition applications. Poly(vinyl alcohol) imparts exceptional strength and outstanding resistance to oils, greases, and organic solvents, and is widely recognized as the strongest paper binder available (Table 9) (278).

The resistance of the polymer to oils and organic solvents can be directly attributed to the hydroxyl functionality and the film-forming properties of the polymer. Treated paper substrates display a significant amount of oil resistance which make them valuable for packing papers and food-grade paperboard containers. This performance improvement is achieved despite the fact that the 1–3 wt% add-on level, typical of size press applications, is too low to provide a continuous PVA film.

The fully and super-hydrolyzed PVA grades are preferred by the paper industry as they provide superior strength, greater adhesion to cellulose, better water resistance, and low foaming. However, the intermediate and partially hydrolyzed grades provide better surface-filming characteristics on many paper and paperboard substrates.

Poly(vinyl alcohol) is widely used on release liners for silicone topcoat holdout. The wide diversity in performance requirements of the various release liners has resulted in recommendation for add-on ranging from 1.5–2.0 (279) to 10 g/m^2. Ultimately, the characteristics of the base paper itself, as well as the level of release required of the finished sheet, determine the best add-on level of the PVA.

The role of PVA in ink-jet printing papers is described in numerous patents. The market has shown fast growth in recent years. Most of the technology has been developed in Japan, which by 1985 had filed 75% of the

400 issued patents (280). Requirements call for a hydrophilic, high porosity surface capable of absorbing ink-jet droplets quickly, with little spreading, wicking, or dye penetration. The coating on the base sheet primarily consists of silica powder using PVA as the binder of choice (281).

12.5. Building Products

Poly(vinyl alcohol) is widely used in connection with spray-drying of emulsions, in particular ethylene–vinyl acetate copolymer emulsions. The PVA is added both as a protective colloid during the polymerization and as a redispersing aid prior to the actual spray drying for a total amount of 2–15 wt% (282–285). The PVA contained in these products greatly enhances the adhesion to cementitious materials, improves water retention, and increases strength. The powder, when added to tile grouts, joint compounds, textured compounds, and cementitious repair mortars, improves the bond strength, abrasion resistance, and flexibility of the final construction.

Poly(vinyl alcohol) is used as an additive to dry-wall joint cements and stucco-finish compounds. Rapid cold water solubility, which can be achieved with finely ground PVA, is important in many dry mixed products. Partially hydrolyzed grades are commercially available in fine particle size. The main purpose of the PVA is to improve adhesion and to act as a water-retention aid.

12.6. Fibers

Poly(vinyl alcohol) fibers possess excellent strength characteristics and provide a pleasant feel in fabrics. The fiber is usually spun by a wet process employing a concentrated aqueous solution of sodium sulfate as the coagulating bath. Water insolubility, even in boiling water, can be obtained by combining stretching, heat treatment, and acetalization with formaldehyde. Super-hydrolyzed PVA is the preferred material for fiber production.

PVA fibers have found widespread industrial use in cement as replacement for asbestos in cement products, reinforcement of rubber material such as conveyer belts, and hydraulic rubber hoses used in cars, ropes, fishing nets, etc. Only a small amount of fibers is used in the production of textiles. Several patents (286–288) have been issued, claiming processes for production of ultrahigh tensile strength PVA fibers, which have tensile strength comparable to that of Kevlar.

12.7. Other Applications

Poly(vinyl alcohol) film can be produced by solution casting or extrusion. Film casting is most common as unplasticized films of all molecular weights and extents of hydrolysis can readily be produced. Water solubility of the film can be controlled by selection of the proper degree of hydrolysis. These films can be made into bags used for packaging of detergents, insecticides, hospital laundry, and numerous other items that are to be placed in water.

Poly(vinyl alcohol) is useful as a temporary protective coating for metals, plastics, and ceramics. The coating reduces damage from mechanical or chemical agents during manufacturing, transport, and storage. The protective film can be removed by peeling or washing with water.

The ultraviolet cross-linking of PVA with dicromates is the basis for its use in photoengraving, screen printing, printed circuit manufacture, and color television tube manufacture.

Partially hydrolyzed grades are used in many cosmetic applications because of their emulsifying, thickening, and film-forming properties. Poly(vinyl alcohol) is also used as a viscosity builder for aqueous solutions and dispersions.

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