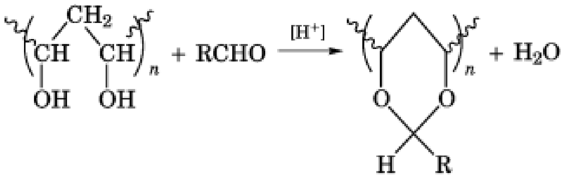
Kirk-Othmer Encyclopedia of Chemical Technology.

VINYL ACETAL POLYMERS

Vinyl acetal polymers are made by the acid-catalyzed acetalization of poly(vinyl alcohol) [9002-89-5] with aldehydes (1).



Analogously, poly(vinyl ketals) can be prepared from ketones, but since poly(vinyl ketals) are not commercially important, they are not discussed here. The acetalization reaction strongly favors formation of the 1,3-dioxane ring, which is a characteristic feature of this class of resins. The first of this family, poly(vinyl benzal), was prepared in 1924 by the reaction of poly(vinyl alcohol) with benzaldehyde in concentrated hydrochloric acid (2). Although many members of this class of resins have been made since then, only poly(vinyl formal) [9003-33-2] (PVF) and poly(vinyl butyral) [63148-65-2] (PVB) continue to be made in significant commercial quantities.

Commercialization of PVF and PVB began during the 1930s and 1940s following development efforts by a number of companies, including Union Carbide, DuPont, Shawinigan Chemicals (now Monsanto Chemical), Wacker-Chemie, and I.G. Farben Industrie (now BASF) (3–12). One incentive for this activity was the discovery that safety windshields made with plasticized PVB interlayer offered significant advantages over windshields made with plasticized cellulose acetate, which was then in general use (13, 14).

PVB accounts for about 90% of the poly(vinyl acetal) resin made in the 1990s. Most PVB is plasticized and made into interlayer for vehicle and architectural safety glass, and the remainder is used as an ingredient in a variety of coating, binding, printing, and adhesive applications. PVF accounts for the remaining 10% of the poly(vinyl acetal) made. PVF's primary use is for wire and cable insulation. In this application, PVF is combined with other reactive resins and cured to form tough, chemical- and abrasion-resistant coatings (see Insulation, electric). Applications for PVF and PVB resins make use of the toughness, resilience, optical clarity, high pigment/filler binding capacity, and high adhesion the resins can provide when appropriately formulated.

The poly(vinyl acetal) prepared from acetaldehyde was developed in the early 1940s by Shawinigan Chemicals, Ltd., of Canada and sold under the trade name Alvar. Early uses included injection-molded articles, coatings for paper and textiles, and replacement for shellac. Production peaked in the early 1950s and then decreased as a result of competition from less expensive resins such as poly(vinyl chloride) (see Vinyl polymers, poly(vinyl chloride)). Alvar is no longer manufactured.

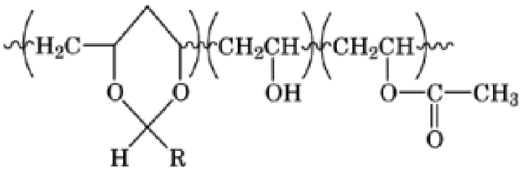
1. Synthesis and Structure

Poly(vinyl alcohol) used to manufacture the poly(vinyl acetal)s is made from poly(vinyl acetate) homopolymer (see Vinyl polymers, vinyl alcohol polymers; Vinyl polymers, vinyl acetate polymers). Hydrolysis of poly(vinyl acetate) homopolymer produces a polyol with predominantly 1,3-glycol units. The polyol also contains up to 2 wt % 1,2-glycol units that come from head-to-head bonding during the polymerization of vinyl acetate monomer. Poly(vinyl acetate) hydrolysis is seldom complete, and for some applications, not desired. For example, commercial PVF resins may contain up to 13 wt % unhydrolyzed poly(vinyl acetate). Residual vinyl acetate units on the polymer help improve resin solubility and processibility (15). On the other hand, the poly(vinyl alcohol) preferred for commercial PVB resins has less than 3 wt % residual poly(vinyl acetate) units on the polymer chain.

Poly(vinyl acetals) are made from poly(vinyl alcohol) and aldehydes by acid-catalyzed addition–dehydration. The mechanism of acetalization has been proposed (16, 17). The degree of acetalization and the conditions used during the reaction significantly affect product properties. Batch and continuous processes in both aqueous and organic media are used during manufacturing. In single-stage batch processes, hydrolysis of poly(vinyl acetate) and acetalization of the poly(vinyl alcohol) hydrolysis product are carried out in the same kettle at the same time. In two-stage batch processes, hydrolysis and acetalization take place in separate kettles.

Assuming that acetalization is irreversible and that both 1,3- and 1,2-glycol units are present in poly(vinyl alcohol), the highest degree of acetalization that can be expected on a statistical basis is 81.6% (18). However, acetalization is reversible (19), and even higher degrees of acetalization are possible (7, 20, 21). For most applications, complete acetalization is not needed, and would be difficult to achieve on a commercial scale without a significant amount of intermolecular acetalization.

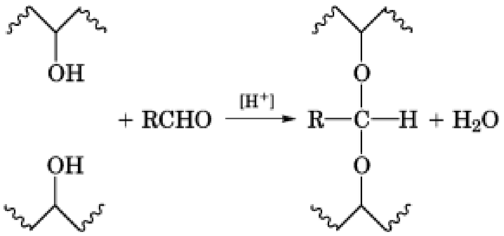
Commercial poly(vinyl acetal)s are terpolymers with varying amounts of vinyl acetate and vinyl alcohol units remaining on the backbone after acetalization. The class can be represented by the following structure, showing acetal (**1**), vinyl alcohol (**2**), and vinyl acetate (**3**) units.



(1) **(2)** **(3)**

The physical properties of the resin can be modified over a wide range of values because resin properties are a function of the relative amounts of the three monomeric units, average molecular weight, molecular weight distribution, aldehyde chain length, and the stereochemistry of the backbone pendent groups, all of which can be manipulated during manufacturing. Aldehyde blends have also been used to achieve unique properties (22).

Both intramolecular and intermolecular acetalization can occur, although intramolecular acetalization predominates during early stages of the reaction. Late in the reaction intermolecular acetalization begins to take place when isolated hydroxyl groups from two different polymer chains form acetal linkages. As the level of intermolecular acetalization increases, the resin becomes more difficult to process and gel particles form as cross-linked networks begin to build.



For commercial applications, a small degree of intermolecular acetalization is tolerated and, to a limited extent, it can be manipulated to control the molecular weight distribution of the resin. This in turn affects the solubility and rheological properties of the resin. Other than the possibility of cross-linking, hydrolysis and acetalization do not significantly alter the resin's chain length. Thus the molecular weight of an acetylated resin is largely determined by that of the poly(vinyl acetate) from which it is derived.

The poly(vinyl alcohol) made for commercial acetalization processes is atactic and a mixture of *cis*- and *trans*-1,3-dioxane stereoisomers is formed during acetalization. The precise cis/trans ratio depends strongly on process kinetics (16, 17) and small quantities of other system components (23). During formylation of poly(vinyl alcohol), for example, *cis*-acetalization is more rapid than *trans*-acetalization (24). In addition, the rate of hydrolysis of the *trans*-acetal is faster than for the *cis*-acetal (25). Because hydrolysis competes with acetalization during acetal synthesis, a high cis/trans ratio is favored. The stereochemistry of PVF and PVB resins has been studied by proton and carbon nmr spectroscopy (26–29).

The resin's unacetalated hydroxyl groups take part in both intramolecular and intermolecular hydrogen bonding. Intermolecular hydrogen bonding helps bind individual polymer molecules together, making it more difficult for polymer chains to untangle and slip by each other. Resin glass-transition temperature (T_g), viscosity, modulus, and tensile strength increase as the hydroxyl level increases. Simultaneously, processibility and resiliency are reduced. Backbone hydroxyl groups also can form hydrogen and covalent bonds to the surface of polar substrates and are largely responsible for the adhesion characteristics of this resin class (30).

2. Physical Properties

The thermal glass-transition temperatures of poly(vinyl acetal)s can be determined by dynamic mechanical analysis, differential scanning calorimetry, and nmr techniques (31). The thermal glass-transition temperature of poly(vinyl acetal) resins prepared from aliphatic aldehydes can be estimated from empirical relationships such as equation 1 where OH and OAc are the weight percent of vinyl alcohol and vinyl acetate units and C is the number of carbons in the chain derived from the aldehyde. The symbols with subscripts are the corresponding values for a standard (s) resin with known parameters (32). The formula accurately predicts that resin T_g increases as vinyl alcohol content increases, and decreases as vinyl acetate content and aldehyde carbon chain length increases.

$$T_g = T_g s + 1.26\,(\mathrm{OH} - \mathrm{O\ H_s}) - 0.6\,(\mathrm{OAc} - \mathrm{OAc_s}) + 46\ln\,(\mathrm{C_s/C}) \qquad (1)$$

Unformulated poly(vinyl acetal) resins form hard, unpliable materials which are difficult to process without using solvents or plasticizers. The solubility parameter ranges for some commercially available PVF and PVB resins are listed in Table 1. Plasticizers not only aid resin processing but also lower the glass-transition temperature, T_g, and can profoundly change other physical properties of the resins. For example, the mechanical glass-transition temperature of a poly(vinyl acetal) plasticized with dibutyl phthalate is reduced by 1.3°C per part of plasticizer added to 100 parts resin (34). Acetalization with longer chain aldehydes (35) and aldehydes

Table 1. Solubility Parameter Ranges for Some Commercial PVF and PVB Resins[a]

Resin	Low hydrogen bonding solvents	Medium hydrogen bonding solvents	High hydrogen bonding solvents
PVF			
low acetate	9.3–10.0	9.7–10.4	9.9–11.8
PVB			
hydroxyl (9–13%)	9.0–9.8	8.4–12.9	9.7–12.9
hydroxyl (17–21%)	[b]	9.9–12.9	9.7–14.3

[a] Ref. 33.
[b] Insoluble.

with polyalkylene oxide chains (36) provides a degree of internal plasticization. Long-chain acetal ends tend to reduce T_g without relying exclusively on liquid plasticizers (37).

Poly(vinyl acetal)s can be formulated with other thermoplastic resins and with a variety of multifunctional cross-linkers. Examples of resins that are at least partially compatible with PVF or PVB resins include some types of polyurethanes (38), polyvinylpyrrolidinone (39), cellulose triacetate (40), nitrocelluloses, poly(vinyl chloride) (41, 42), epoxies, isocyanates, phenolics, silicones, and urea–formaldehyde resins. During the curing step with cross-linkers, which is usually carried out at elevated temperatures, covalent bonds are formed between hydroxyl groups on the poly(vinyl acetal) backbone and the reactive centers on the cross-linker. When cross-linking takes place the resin becomes thermoset. Thermosetting generally increases thermal stability, rigidity, and abrasion resistance, and improves resistance to solvents and to acids and bases. It also severely limits processibility by making the resin insoluble and impossible to extrude.

Although they lack commercial importance, many other poly(vinyl acetal)s have been synthesized. These include acetals made from vinyl acetate copolymerized with ethylene (43–46), propylene (47), isobutylene (47), acrylonitrile (48), acrolein (49), acrylates (50, 47), allyl ether (51), divinyl ether (52), maleates (53, 54), vinyl chloride (55), diallyl phthalate (56), and starch (graft copolymer) (47).

Resins with ionomeric pendent groups have also been prepared by acetalating with an aldehyde containing ionic functionality (57–60). At moderate temperatures the ionic groups cluster to form crystalline-like domains which make the resin stiffer than conventional PVB resins (61). At higher processing temperatures, the crystalline-like domains melt out, resulting in sharper drops in resin viscosity. This reduces stickiness and increases resistance to blocking at ambient temperatures, and lowers melt viscosity and improves flow during higher temperature extrusion and laminating steps compared to conventional PVB resins (62).

3. Health and Safety Factors

Representative unformulated PVB and PVF resins are practically nontoxic orally (rats) and no more than slightly toxic after skin application (rabbits). No mortalities were produced in rats exposed by single inhalation for four hours and no allergic skin reactions were observed in controlled skin contact studies with human volunteers. More specifically, a representative PVB resin is practically nontoxic by single-dose oral ingestion ($LD_{50} > 10.0$ g/kg) or by single dermal applications ($LD_{50} > 7.9$ g/kg), and it is only slightly irritating to the eyes (2.8 on a scale of 0–110) and nonirritating (0 on a scale of 0–8) to the skin of rabbits tested in standard FHSA tests for irritation (63). Unformulated, the resins appear to have no acute toxicological properties that would require special handling other than good hygienic practices. The highest purity grades of PVB can be formulated to meet the extractibility requirements of the FDA, and some can be used in accordance with CFR regulations as ingredients for can enamels, adhesives, and components for paper and paperboard in contact with aqueous and fatty foods (33).

Table 2. Physical Properties of Butvar Resins

Property	Method	B-72	B-74	B-76	B-90	B-98
molecular mass × 10^3 (avg)	[a]	170–250	120–250	90–120	70–100	40–70
viscosity 15 wt %, Pa·s[b]	[c]	7–14	3–7	0.5–1	0.6–1.2	0.2–0.4
viscosity 10 wt %, Pa·s[b]	[d]	1.6–2.5	0.8–1.3	0.2–0.45	0.2–0.4	0.07–0.2
Ostwald soln viscosity, mPa·s[b] (=cP)	[e]	170–260	40–50	18–28	13–17	6–9
specific gravity, 23°C/23°C	ASTM D792-50	1.100	1.100	1.083	1.100	1.100
refractive index	ASTM D542-50	1.490	1.490	1.485	1.490	1.490
vinyl alcohol content, wt %		17–20	17–20	11–13	18–20	18–20
vinyl acetate content, wt %		0–2.5	0–2.5	0–1.5	0–1.5	0–2.5

[a] Determined by size exclusion chromatography in tetrahydrofuran with low angle light scattering.
[b] To convert Pa·s to P, multiply by 10.
[c] Measured in 60:40 toluene:ethanol at 25°C using a Brookfield viscometer.
[d] Measured in 95% ethanol at 25°C using an Ostwald-Cannon-Fenske viscometer.
[e] B-72 in 7.5 wt % anhydrous methanol at 20°C; B-76 and B-79 in 5.0 wt % SD 29 ethanol at 25°C; B-74, B-90, and B-98 in 6.0 wt % anhydrous methanol at 20°C, all using an Ostwald-Cannon-Fenske viscometer.

OSHA and ACGIH have not established specific airborne exposure limits for PVB and PVF resins; however, some products may contain sufficient fines to be considered nuisance dust and present dust explosion potential if sufficient quantities are dispersed in air. Unformulated PVB and PVF resins have flash points above 370°C. The lower explosive limit (lel) for PVB dust in air is about 20 g/m^2.

Many grades of PVB and PVF resins are made, and most are eventually compounded and used as multicomponent products. Individual product MSDSs need to be consulted prior to handling and each product should be handled appropriately and in accordance with good industrial hygiene and safety practices, which include appropriate skin, respiratory, and eye protection.

4. Poly(vinyl butyral)

Monsanto, DuPont, Hoechst, Sekisui, and Wacker Chemie are major manufacturers of PVB resins. Several grades are available that differ primarily in residual vinyl alcohol content and molecular weight. Both variables strongly affect solution viscosity, melt flow characteristics, and other physical properties. The physical, mechanical, and thermal properties of various grades of Monsanto's Butvar resins are listed in Tables 2, 3, 4, respectively. In general, resin melt and solution viscosity increase with increasing molecular weight and vinyl alcohol content, whereas the tensile strength of materials made from PVB increases with vinyl alcohol content for a given molecular weight.

Commercially available PVB resins are generally soluble in lower molecular weight alcohols, glycol ethers, and certain mixtures of polar and nonpolar solvents. A representative list is found in Table 5. Grades with lower vinyl alcohol content are soluble in a wider variety of solvents. A common solvent for all of the Butvar resins is a combination of 60 parts of toluene and 40 parts of ethanol (95%) by weight. pt

PVB resins are also compatible with a limited number of plasticizers and resins. Plasticizers (qv) improve processibility, lower T_g, and increase flexibility and resiliency over a broad temperature range. Useful plasticizers include dibutyl and butyl benzyl phthalates, tricresyl and 2-ethylhexyl diphenyl phosphates, butyl ricinoleate, dibutyl sebacate, dihexyl adipate, triethylene glycol di-2-ethylbutyrate, tetraethylene glycol diheptanoate, castor oil, and others (64–73).

PVB combinations with the thermoplastic resins nitrocellulose or shellac have been used as sealers for wood finishing. In these applications the PVB component adds flexibility and adhesion. Tough, optically

Table 3. Mechanical Properties of Butvar Resins

Property	ASTM method	B-72	B-74	B-76	B-90	B-98
tensile strength, MPa[a]						
yield	D638-58T	47–54	47–54	40–47	43–50	43–50
break		48–55	48–55	32–39	39–46	39–46
elongation, %						
yield	D638-58T	8	8	8	8	8
break		70	75	110	110	110
modulus of elasticity, GPa[b]		2.28–2.34	2.28–2.34	1.93–2.0	2.07–2.14	2.14–2.21
flexural strength yield, MPa[a]	D790-59T	83–90	83–90	72–79	76–83	76–83
hardness, Rockwell						
M	D785-57	115	115	100	115	110
E		20	20	5	20	20
impact strength, J/m[c]	D256-56[d]	58.7	58.7	42.7	48	37.4

[a] To convert MPa to psi, multiply by 145.
[b] To convert GPa to psi, multiply by 145,000.
[c] To convert J/m to ft·lb/in., divide by 53.38.
[d] Notched Izod (1.27×1.27 cm (0.5×0.5 in.)).

Table 4. Thermal Properties of Butvar Resins

Property	Method	B-72	B-74	B-76	B-90	B-98
flow temperature, °C, 6.9 MPa[a]	ASTM D569-59	145–155	135–145	110–115	125–130	105–110
T_g, °C	[b]	72–78	72–78	62–72	72–78	72–78
heat distortion temperature, °C	ASTM D648-56	56–60	56–60	50–54	52–56	45–55
heat sealing temperature, °C	[c]	220	220	200	205	200

[a] 6.9 MPa = 1000 psi.
[b] By differential scanning calorimetry from 30 to 100°C on dried resin.
[c] Dried film (0.025 mm) on paper cast from 10 wt % resin in 60:40 toluene:ethanol; heat sealer dwell time, 1.5 s at 0.4 MPa (60 psi).

clear blends have been made with aliphatic polyurethanes (74). Conducting polyacetylene exhibits enhanced stability under ambient conditions when blended with PVB (75). Thermosets are prepared with cross-linkers that form covalent bonds with hydroxyl groups. Cross-linking resins include select isocyanate, phenolic, and epoxy resins. Lower molecular weight organic cross-linkers include dialdehydes, isocyanates, and etherified melamines. Inorganics that can function as cross-linkers include chromic, boric, and phosphoric acid and their derivatives (76).

4.1. Manufacture

PVBs are manufactured by a variety of two-stage heterogeneous processes. In one of these an alcohol solution of poly(vinyl acetate) and an acid catalyst are heated to 60–80°C with strong agitation. As the poly(vinyl alcohol) forms, it precipitates from solution (77). Ethyl acetate, the principle by-product, is stripped off and sold. The precipitated poly(vinyl alcohol) is washed to remove by-products and excess acid. The poly(vinyl alcohol) is then suspended in a mixture of ethyl alcohol, butyraldehyde, and mineral acid at temperatures above 70°C. As the reaction approaches completion the reactants go into solution. When the reaction is complete, the catalyst is neutralized and the PVB is precipitated from solution with water, washed, centrifuged, and dried. Resin from this process has very low residual vinyl acetate and very low levels of gel from intermolecular acetalization.

Table 5. Solubility of Butvar Resins[a]

Solvent	B-72; B-74[b]	B-76; B-79[c]	B-90; B-98[c]
acetic acid (glacial)	S	S	S
acetone	I	S	SW
butyl acetate	I	S	PS
N-butyl alcohol	S	S	S
butyl cellosolve	S	S	S
cyclohexanone	S	S	S
diacetone alcohol	PS	S	S
diisobutyl ketone	I	SW	I
N,*N*-dimethylacetamide	S	S	S
N,*N*-dimethylformamide	S	S	S
dimethylsulfoxide	S	S	S
ethyl acetate (99%)	I	S	PS
ethyl alcohol (95%; anhydrous)	S	S	S
ethylene dichloride	SW	S	SW
ethylene glycol	I	I	I
isophorone	PS	S	S
isopropyl alcohol (95%; anhydrous)	S	S	S
isopropyl acetate	I	S	I
methyl acetate	I	S	PS
methyl alcohol	S	SW	S
methyl ethyl ketone	SW	S	PS
methylene chloride	PS	S	S
methyl isobutyl ketone	I	S	I
naphtha (light)	I	SW	I
N-methyl-2-pyrrolidinone	S	S	S
propylene dichloride	SW	S	SW
tetrachloroethylene	SW	SW	SW
tetrahydrofuran	S	S	S
toluene	I	PS	SW
toluene:ethanol, 95% (60:40 by wt)	S	S	S
1,1,1-trichloroethane	SW	S	SW
xylene	I	PS	SW

[a] S, soluble; PS, partially soluble; I, insoluble; and SW, swells.
[b] Employed 5% solids mixture agitated for 24 h at ambient temperature.
[c] Employed 10% solids mixture agitated for 24 h at ambient temperature.

In the second stage of a representative aqueous process, an aqueous solution of poly(vinyl alcohol) is heated with butyraldehyde [123-72-8] and an acid catalyst (78, 79). PVB precipitates from solution as it forms. After 2–3 h at a temperature of about 90°C, when the reaction is complete, the acid is neutralized and the resin is washed, filtered, and dried. While the cost of solvent handling is minimal in this process, it is offset somewhat by the need for separate hydrolysis and acetalization facilities. Because PVB resin precipitates early in the reaction there is a tendency toward high levels of intermolecular acetalization. Cross-linking can be minimized by adding emulsifiers to control particle size (80–84) or substances like ammonium thiocyanate (85), or urea (86) to improve the solubility of PVB in the aqueous phase. To increase the average molecular weight of the resin small quantities of a dialdehyde like glutaraldehyde can be added during the acetalization step (87).

4.2. Applications

During 1994, about 68,000 t of unplasticized PVB was manufactured worldwide. Of this, the overwhelming majority, about 66,000 t, was plasticized and extruded into sheet for use in laminated safety glass. Only about 2,300 t of unplasticized PVB was used for noninterlayer applications.

4.2.1. Laminated Glass

About 1.5×10^8 m^2 of safety glazing interlayer was manufactured worldwide in 1994. About 75% of this was used for vehicle windshields and most of the rest was used for laminated architectural glazing (88, 89) and a variety of security glass applications (90). Major producers of interlayer for laminated glass are Monsanto (Saflex), the largest producer, followed by DuPont (Butacite), Sekisui (S'Lec) and Hüls (Trosofoil).

Plasticized PVB is uniquely suited for safety and security glazing applications. It is easily extruded into sheet. The laminated sheet exhibits high adhesion to glass, optical clarity, stability to sunlight, and high tear strength and impact-absorbing characteristics, all of which are demanded for safety glazing use. In windshields, for example, the interlayer serves several potentially life-saving functions. It adheres to glass shards after a glass-breaking impact, thereby helping to reduce injury from flying glass. After the glass is broken during an impact, the interlayer's high tear strength and resiliency acts like a safety net by absorbing enough energy to resist penetration by a projectile or a vehicle occupant's head (91). In addition to its safety features, laminated glass in architectural applications adds sound attenuation, heat insulation, and break-in security, and also blocks uv radiation.

Most laminated safety glazings are glass–PVB–glass trilayer composites, but bullet- and projectile-resistant laminates. Laminates for other specialty uses may be made with more than three layers. In addition to glass, poly(ethylene terephthalate) (PET), acrylic, and polycarbonate structural components (92) are used in specialty laminated glazing products.

Many grades of interlayer are produced to meet specific length, width, adhesion, stiffness, surface roughness, color (93, 94), and other requirements of the laminator and end use. Sheet can be supplied with vinyl alcohol content from 15 to about 23 wt %, depending on the supplier and application. A common interlayer thickness for automobile windshields is 0.76 mm, but interlayer used for architectural or aircraft glazing applications, for example, may be much thinner or thicker. There are also special grades to bond rear-view mirrors to windshields (95, 96) and to adhere the components of solar cells (97, 98). Multilayer coextruded sheet, each component of which provides a separate property not possible in monolithic sheet, can also be made (99–101).

Adhesion of plasticized PVB to clean glass is very high. It is postulated that both hydrogen bonds and silyl alkyl ether covalent bonds are formed between resin hydroxyl groups and silanol groups at the interlayer–glass interface (30) (Fig. 1). However, the surface chemistry of float glass is complex, and both moisture and low concentrations of ionic substances at the interlayer–glass interface affect adhesion. Thus, interlayer–glass adhesive strength depends not only on the interlayer's formulation and moisture content, but also on the type, age, and condition of the surface of the glass. Salts and moisture are thought to reduce adhesion by competing with resin hydroxyls for bonding sites on the glass surface.

Because there is an inverse relationship between interlayer–glass adhesive strength and laminate penetration resistance, adhesion must be carefully controlled in safety glass applications. If adhesion is too low, glass retention during an impact will be sacrificed even though the interlayer is not penetrated. If adhesion is too high, a projectile can easily penetrate the laminate because cracks made in the glass propagate through the interlayer. In order for the interlayer to cushion an impact, enough debonding must take place in the laminate to allow the interlayer to expand after the glass is cracked.

One measure of impact resistance is the laminate's mean break height (MBH) (102). In the standard test, there is a 50% probability that a five-pound (2.27-kg) ball will not fall through a laminate if the ball is dropped at the MBH. Typical MBHs for 12 in. ($\sim$30 cm) square laminates prepared with 30 mil (0.76 mm) thick

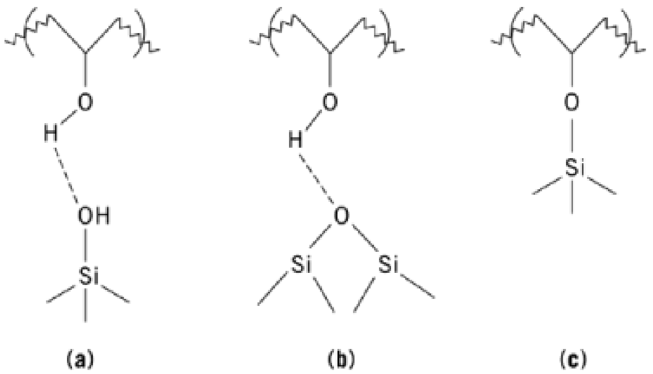


Fig. 1. Hydrogen and covalent bonds can form between the resin's hydroxyl groups and the surface of glass: (**a**) a hydrogen bond to a silanol group; (**b**) a hydrogen bond to a silyl ether oxygen; and (**c**) an ether-type covalent bond.

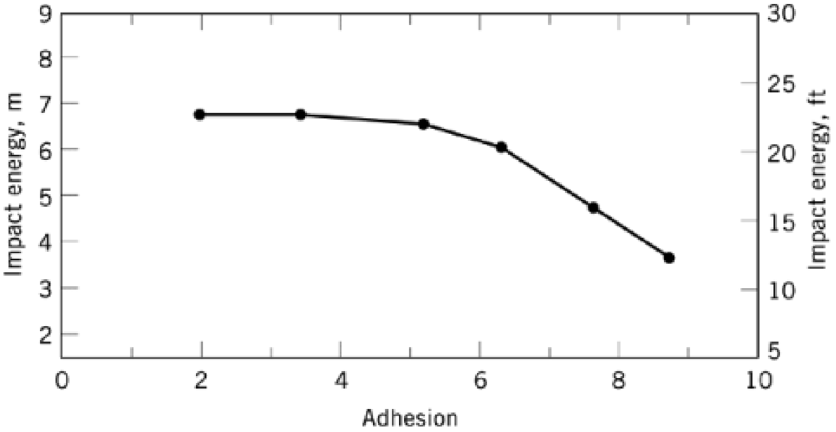


Fig. 2. Typical impact energy vs adhesion (10 is high, 0 is no adhesion) curve obtained from the mean break height test carried out at 21°C with a 2.27 kg ball on 30-cm square laminates. Mean break height dramatically declines when adhesion is at high levels.

interlayer are 10 ft (~3 m) at 0°F (−18°C) and 15 ft (~4.6 m) at 70°F (21°C). Figure 2 shows a relationship between adhesion and falling ball penetration resistance measured at 21°C.

To maximize penetration resistance without danger of delamination during impact or aging, adhesion to glass is reduced from inherently high levels (10, in Fig. 2) to intermediate levels ((3–7), in Fig. 2) by adding parts per million quantities of Group Ia or IIa alkanoate salts (103–113) or surfactants (114) to the resin. It is not clear how these additives influence adhesion, but they also strongly affect the product's moisture sensitivity and some other performance attributes. Often adhesion fine tuning is carried out on the interlayer after it is extruded by adjusting the interlayer moisture level to between 0.2 and 1%.

Plasticized PVB interlayer is hygroscopic. In addition, T_gs are in the neighborhood of 30°C; thus, interlayer tends to adhere to itself, or block, when rolls or stacks of cut blanks are stored at ambient conditions. For these reasons handling and shipping must be carried out under controlled humidity and at temperatures well below the sheet's T_g. Precut interlayer blanks and rolls are usually stored or shipped refrigerated (3–10°C), and when rolls need to be stored or shipped at ambient conditions, the sheet is interleaved with a thin sheet of nonadhering plastic such as polyethylene.

To help prevent air from being trapped between glass and interlayer surfaces during lamination, the interlayer surface is textured during manufacture (115–120). The textured surface provides pathways for air to escape. Several methods are used to de-air during lamination. In one, the sheet is positioned between two pieces of glass and the prelaminate is tacked together by nipping the sheet between large rubber rolls at about 38°C. The sandwich is then heated to about 50–75°C and subjected to an additional nipping step to eliminate most of the remaining air and seal the edges. Excess sheet at the edges is trimmed with a trimming tool. Finally, the laminate is autoclaved at 135–150°C for 30–120 min in pressurized air, 1.3–1.8 MPa (13 to 18 kg/cm^2), or in sealed bags under vacuum (121). During lamination, full adhesion and optical clarity are attained as the softened interlayer flows and wets the glass. Any remaining trapped air dissolves into the sheet.

Interlayer with various widths of gradient color bands are made for automobile windshields (122–124). The band is added by printing the interlayer surface or by coextruding previously mixed dyed or pigmented resin. Before laminating, gradient interlayer is often shaped to accommodate the curvature of the windshield. This is accomplished by differentially stretching sheet heated at about 85–100°C over a tapered shaping drum. The hot sheet is then cooled with cold air, cut into blanks, and stacked prior to laminating.

4.2.2. Noninterlayer Applications

Some categories of nonglazing uses for PVB are as follows:

- Phenolic/adhesives
  - adhesives/sealants/gaskets
  - abrasives and break pad binders
  - printed circuit boards
  - structural composites/laminates

- Metal/glass binders
  - metal oxide binders
  - retroreflective coatings
  - glass optical coatings

- Hard copy printing
  - inks
  - toners
  - photoimaging
  - reprographics

- Coatings/additives
  - wash primers
  - wood coatings
  - paint and varnish additives
  - maintenance, metal, and industrial coatings
  - wire enamels
  - can coatings
  - foil coatings
  - nail polish

- Others
  - pest strips
  - powder coatings
  - miscellaneous

For most of these, the resin serves as a film-forming additive, an adhesive, and/or as a binder for pigments, fillers, metal oxides, ceramics, and other materials. The resin provides toughness and flexibility and adheres strongly to additive particles and to glass or other polar surfaces. For example, PVB binds the glass beads used in retroreflective films for licence plates, decals, and road signs. It also helps bind the retroreflective films to the surfaces of which they are applied. PVB is used to bind metal oxide particles during the fabrication of certain glasses, ceramics (125–127), and superconductors (128). PVB resin is also used to make membranes for fuel cells (129), gas–liquid separators (130), and ultrafiltration devices (131).

PVB is used as a film-forming component in corrosion-inhibiting primers for metals called wash primers or metal conditioners. The primers have good adhesion to ferrous metal surfaces and form a good foundation for various types of topcoats. The primers act by stabilizing the metal oxide surface and by continuously supplying corrosion-inhibiting ions such as chromate (132). Formulations containing nontoxic corrosion-inhibiting ions have also been made (133, 134). Wash primers are used on storage tanks, bridges, ships, highway guard rails, and on submerged structures (76, 135).

Aqueous dispersions of plasticized PVB are used for many coating applications (136, 137). The dispersions are manufactured by intensive kneading of the resin in the presence of a plasticizer, surfactant, and water (138–140). Generally, the dispersions are about 50% solids, including about 40 parts of plasticizer per 100 parts of resin. Cast, air-dried films are tough and transparent and adhere to many materials. They are resistant to water and grease, which makes them useful as coatings for grease-proof washable wallpaper, window shades, and packaging materials. Properly formulated, they can be used for strippable or temporary protective coatings.

PVB dispersions are widely used in the textile industry to impart abrasion resistance, durability, and fiber strength. They have been used for finishing nylon webbing for parachute harnesses and seat belts. They can be applied to textiles by spraying, from a dilute bath by impregnation on a padder, or from a thickened dispersion by coating on spreading equipment. The dried dispersion imparts a soft, full-bodied finish to rayon, cotton, or nylon and helps prevent raveling of filament yarns. PVB dispersions have been used to finish curtain and drapery fabrics and upholstery goods, to join fabric to fabric and other materials, and as a component in transparent rug backings.

5. Poly(vinyl formal)

Estimated worldwide production of poly(vinyl formal) resin was about 2700 t in 1994. PVF resins are currently manufactured by Wacker Chemie (Pioloform F) in Germany and by Chisso (Vinylec) in Japan. Chisso purchased Monsanto's PVF (Formvar) business in 1992. The Vinylec resins are free-flowing white powders with a poly(vinyl formal) content of about 81 wt %. The properties of representative grades are listed in Table 6. Chemical resistance of Vinylec to acids, bases, and aliphatic hydrocarbons is excellent, and chemical resistance to alcohols, aromatic hydrocarbons, esters, and ketones is good; however, chemical resistance to chlorinated solvents is rated poor (141). Residual vinyl acetate and vinyl alcohol component levels are 9–13 wt % and about 5 wt %, respectively. Grades are available with average molecular weights from about 25,000 to 100,000.

Table 6. Properties of Vinylec Poly(vinyl formal) Resins[a]

Property	Value
specific gravity	1.1–1.3
tensile strength, MPa[b]	49–78
flexural strength, MPa[b]	108–127
hardness, Shore	70–80
flow temperature, °C	140–150
heat distortion temperature, °C	84–93
dielectric strength, kV/mm	26–39
dielectric constant, 60 Hz	3.0–3.7
volume resistivity, Ω·cm	10^{14}–10^{16}
dissipation factor, 60 Hz	0.006–0.015

[a] Ref. 141.
[b] To convert MPa to psi, multiply by 145.

In general, PVF resins are soluble in a limited number of solvents and in certain mixtures of alcohols and aromatic hydrocarbons.

The solubility of representative poly(vinyl formal) resins is as follows in single solvents, where S = soluble and I = insoluble:

acetic acid (glacial)	S	chloroform	S
monochloro acetic acid	S	ethylene dichloride	S
benzyl alcohol	S	acetone	I
dioxane	S	carbon disulfide	I
cresol	S	ethyl alcohol	I
tetrahydrofuran	S	ethyl acetate	I
dimethyl sulfoxide	S	butyl acetate	I
methyl benzoate	S	methyl ethyl ketone	I
N,*N*-dimethylformamide	S	cyclohexanone	I
N,*N*-dimethylacetamide	S	nitropropane	I
xylenol	S	hydrocarbons	
furfural	S	aliphatic	I
pyridine	S	aromatic	I

For mixed solvents, PVF is soluble in toluene:ethyl alcohol (95%) (60:40 wt %) and xylene:methyl alcohol (60:40 wt %), but insoluble in toluene:butyl alcohol (60:40 wt %) and xylene:butyl alcohol (60:40 wt %). The solubility of PVF resins in polar solvents increases with increasing proportions of residual vinyl acetate content. Increasing vinyl acetate content also reduces resin stiffness and tensile and impact strength. Solution viscosity increases with increasing vinyl alcohol content and with the average molecular weight of the resin. Although moderate increases in the average molecular weight of the various commercial grades do not substantially affect tensile strength, modulus, and some other physical properties of the unmodified resins, they strongly increase solution viscosity.

PVF resins are generally compatible with phthalate, phosphate, adipate, and dibenzoate plasticizers, and with phenolic, melamine–formaldehyde, urea–formaldehyde, unsaturated polyester, epoxy, polyurethane, and cellulose acetate butylate resins. They are incompatible with polyamide, ethyl cellulose, and poly(vinyl chloride) resins (141).

Commercial PVF is manufactured by a single-stage batch process in acetic acid (142–144). In the single-stage process, hydrolysis and formalization take place concurrently. In one process, poly(vinyl acetate) is dissolved in an aqueous mixture of acetic acid and formaldehyde. Sulfuric acid catalyst is added and the mixture is maintained at 75–85°C for about 6–8 h or until the reactions are completed. The average molecular weight of the product is largely determined by the average molecular weight of the poly(vinyl acetate) charge. The ratio of vinyl acetate and vinyl alcohol components in the acetal product is controlled by the ratio of acetic acid, water, and formaldehyde used. When the reaction is complete, the mineral acid is neutralized. As water is added to the agitated mixture, PVF resin precipitates as fine, off-white granules. Color can be improved by adding antioxidants during formalization (145). The resin is centrifuged and dried after washing with water to remove salt and organic by-products. In this process, hydrolysis of poly(vinyl acetate) is the rate-controlling step.

5.1. Applications

PVF resins are used almost exclusively to make electric and magnetic wire insulation. In these applications the PVF resin component helps provide toughness, as well as abrasion and thermal resistance. The resin is combined with phenolic, epoxy, melamine, or other resins capable of cross-linking with hydroxyl groups in suitable vehicles to produce formulations called wire enamels (146–149). A typical wire enamel consists of 100 parts of PVF and 50 parts of a cresol–formaldehyde resin dissolved in a mixture of cresylic acid and naphtha solvent (150). The enamels are coated on copper or aluminum wire and cured in ovens at elevated temperatures to form thermoset coatings with good thermal stability, insulating properties, and abrasion and chemical resistance (151). Magnetic wire insulation made with PVF wire enamels performs well on high speed motor winding equipment and maintains good insulating properties at the elevated temperatures generated during motor overloads.

PVF resins have also been used in a variety of other applications, including conductive films (152), electrophotographic binders (153), as a component for inks (154), and in membranes (155, 156), photoimaging (157), solder masks (158), and reprographic toners (159).

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