## 3 Polyvinyl Butyral

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### CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1 Historical Development and Commercialization</td>
<td>90</td>
</tr>
<tr>
<td>3.1.1 History</td>
<td>90</td>
</tr>
<tr>
<td>3.1.2 Economic Data</td>
<td>90</td>
</tr>
<tr>
<td>3.2 Polymer Formation</td>
<td>91</td>
</tr>
<tr>
<td>3.2.1 Polymerization</td>
<td>91</td>
</tr>
<tr>
<td>3.2.2 Postpolymerization Chemistry</td>
<td>96</td>
</tr>
<tr>
<td>3.3 Structural and Phase Characteristics</td>
<td>100</td>
</tr>
<tr>
<td>3.3.1 IR Spectroscopy</td>
<td>100</td>
</tr>
<tr>
<td>3.3.2 UV Spectroscopy</td>
<td>100</td>
</tr>
<tr>
<td>3.3.3 $^{13}$C NMR Spectroscopy</td>
<td>100</td>
</tr>
<tr>
<td>3.3.4 $^1$H NMR Spectroscopy</td>
<td>100</td>
</tr>
<tr>
<td>3.3.5 Dosing of Acetate</td>
<td>103</td>
</tr>
<tr>
<td>3.3.6 Glass Transition Temperature</td>
<td>104</td>
</tr>
<tr>
<td>3.3.7 Solvents, Solution Properties, and Molecular Weight Characterization</td>
<td>104</td>
</tr>
<tr>
<td>3.3.8 Thermal Degradation (High Temperature Conditions in Nitrogen)</td>
<td>106</td>
</tr>
<tr>
<td>3.4 Polymer Engineering Properties</td>
<td>106</td>
</tr>
<tr>
<td>3.4.1 Density</td>
<td>106</td>
</tr>
<tr>
<td>3.4.2 Surface Properties</td>
<td>106</td>
</tr>
<tr>
<td>3.4.3 Adhesion Properties</td>
<td>109</td>
</tr>
<tr>
<td>3.4.4 Electrical Properties</td>
<td>110</td>
</tr>
<tr>
<td>3.4.5 Mechanical Properties</td>
<td>111</td>
</tr>
<tr>
<td>3.4.6 Photodegradation and Photoaging</td>
<td>112</td>
</tr>
<tr>
<td>3.4.7 Thermo-Oxidation</td>
<td>114</td>
</tr>
<tr>
<td>3.5 Processing Technologies</td>
<td>115</td>
</tr>
<tr>
<td>3.5.1 Thermal Properties for Processing</td>
<td>115</td>
</tr>
<tr>
<td>3.5.2 Viscoelastic and Rheological Properties</td>
<td>115</td>
</tr>
<tr>
<td>3.5.3 Extrusion of Films</td>
<td>116</td>
</tr>
<tr>
<td>3.6 Additive Effect on Properties and Applications</td>
<td>116</td>
</tr>
<tr>
<td>3.6.1 Plasticizers</td>
<td>116</td>
</tr>
<tr>
<td>3.6.2 Antioxidants</td>
<td>117</td>
</tr>
<tr>
<td>3.6.3 Light and UV Stabilizers</td>
<td>118</td>
</tr>
<tr>
<td>3.6.4 Flame Retardants</td>
<td>118</td>
</tr>
<tr>
<td>3.7 Blends and Composites</td>
<td>118</td>
</tr>
<tr>
<td>3.7.1 Blends</td>
<td>118</td>
</tr>
<tr>
<td>3.7.2 Composites and Nanocomposites</td>
<td>120</td>
</tr>
<tr>
<td>3.8 Applications</td>
<td>122</td>
</tr>
<tr>
<td>3.8.1 Safety Glasses</td>
<td>122</td>
</tr>
<tr>
<td>3.8.2 Module Encapsulation in PV Application</td>
<td>126</td>
</tr>
<tr>
<td>3.8.3 Miscellaneous Applications</td>
<td>128</td>
</tr>
<tr>
<td>3.8.4 Recycling of PVB</td>
<td>129</td>
</tr>
<tr>
<td>References</td>
<td>130</td>
</tr>
</tbody>
</table>
3.1 HISTORICAL DEVELOPMENT AND COMMERCIALIZATION

3.1.1 History

The development of polyvinyl butyral (PVB) has been primarily driven by the car industry and its demand for safety glass. The discovery of the toughening of glass by lamination with a synthetic layer dates back to the beginning of the twentieth century and was the result of the clumsiness of Edouard Benedictus, a French scientist, in his laboratory. He accidentally knocked over a glass flask of cellulose nitrate reagent on the floor and observed that the star-crazed flask did not break. The laminated glass was discovered and given the name Triplex by Benedictus. The process of manufacture of laminated glass was set up 30 years later, but until 1935, the only interlayer to be used was the cellulose nitrate (named Pyralin). It was the only transparent, clear, and sufficiently strong material available to be bonded to glass with a natural resin (Canada balsam).

The discovery of poly(vinyl alcohol) (PVA) in Germany by Haehnel and Herrmann in 1924 (see Ref. [1] for a complete story), subsequent patenting of its acetalization [2,3], and large development efforts by a number of companies during the 1930s and 1940s lead among others to the patenting of PVB by the chemical company Union Carbide and Carbon Corporation in 1935 [4]. The new thermoplastic polymer was successful in replacing the cellulose nitrate in laminated safety glass for automobiles. Though the commercialization of various vinyl acetal polymers had already begun during the early 1930s, PVB prepared from butyraldehyde (BA) was found to be superior to other vinyl acetal polymers owing to its better cold temperature characteristics and toughness over a wide range of temperatures at lower cost.

Since then, the leading manufacturers of PVB have changed their offer of PVB for laminated glass to meet different types of lamination process (degassing or vacuum calendering and vacuum processes with or without autoclave) and the requirements of growth and productivity of automotive (from 1960), building (from 1980), and PV (from 2000) industries. Also, PVB has found other applications as a binder and coating material owing to its adhesion properties related to bonding capability, which in turn is related to the chemistry of the monomeric units. Nevertheless, laminated products remain the leading application, though the PVBs used today are no longer comparable to those of the first generation because their chemical composition has been adjusted and physical performances strongly improved, especially following technological processing innovations. Specialty-grade PVBs (PVB acoustic, solar PVB, structural PVB, PVB PV) meet the emerging needs of different markets. In particular, the manufacturers of PVBs have ignored the PV market in the 1980s, letting ethylene-vinyl acetate (EVA) become the leading material in this area, because of its superior properties for permeability and flexibility without additives [5]. Since then, the market crisis in the automotive and building industries has renewed the development effort toward selected grades meeting the requirements of the solar module industry.

3.1.2 Economic Data

The total world capacity of PVB is not published, but it is estimated to be over 200,000 tons. The main producer of PVB worldwide is Solutia, the former Monsanto, with trademark Saflex. There are two main producers, Solutia and DuPont, both reluctant to reveal their capacity figures. It is estimated that Solutia controls 50% of the world supply of PVB, DuPont controls 30%, and smaller companies such as Sekisui in Japan and the former Hüls plant at Troisdorf control the remaining 20% (see Table 3.1) [6].

In 2011, 89% of PVB was used for the production of construction and automotive industry safety glass, 4% was used in solar PV materials, and the remaining 7% was used in paints, glues, dyes, and other materials [7]. Its main use is in car windshields, which is about 90% in the United States but only 60% in Europe; its application in construction glazing is relatively more important in Europe. In 2008, the global PVB resin consumption was 270,000 tons, with a market size of about US$2200 million. The demand for this product was estimated to increase at an average growth rate of 6%,
leading to a 2015 consumption that will amount to 410,000 tons. Solutia, Sekisui, DuPont, and Kuraray occupy 96% of the market share. The automotive industry is the largest ultimate customer of PVB films since safety glass is mainly used for automotive windshields where industry safety standards are very strict. According to statistics [7], in 2009, the automobile industry PVB films represented a market size of US$818 million with a 6.5% annual growth rate. There is a potential in its use in side windows and rear windows because the movable side window must be very hard, and at present, the majority of movable glass materials used are relatively fragile and not safe enough.

The construction industry is the second largest user of PVB films as an interlayer material embedded in safety glass, being mainly used in office buildings. In 2009, the global construction industry consumption of PVB films amounted to 89,000 tons, with US$614 million in sales revenue. At present, many factors promote the PVB membrane application in the building trade, such as regulation for residential buildings to use safe glass and better noise reduction.

The demand of the PV market is increasing since PVB membrane is used in the PV modules as a sealing material. The PV cell panel is characterized by long service life, generally up to 20 years, and sealing is a means to prolong the life of modules. At present, the PV cell panel sealants are dominated by EVA, with PVB as a thermoplastic material being the second candidate.

### 3.2 POLYMER FORMATION

#### 3.2.1 POLYMERIZATION

Poly(vinyl acetate), which is polymerized from vinyl acetate by suspension or solution polymerization, is the starting material for the production of PVB. First, PVA is obtained from poly(vinyl acetate) by means of transesterification (alcoholysis) usually with methanol and base catalysis (Scheme 3.1).

Hydrolysis of poly(vinyl acetate) produces PVA with predominantly 1,3-glycol units and also 1,2-glycol units that come from head-to-head configuration of vinyl acetate monomers and, depending on the conditions of polymerization, also branches. Second, the well-known reaction between aldehydes and alcohols, where the nucleophilic addition of an alcohol to the carboxylic group of an aldehyde produces a hemiacetal, and unstable hemiacetals further react with another alcohol to yield a stable acetal ring, is used to form acetal under conditions of acid catalysis. Finally, in the net reaction, one molecule of aldehyde reacts with two molecules of alcohol (Scheme 3.2).
SCHEME 3.1 Transesterification of poly(vinyl acetate).
Polyvinyl Butyral

PVA reacts with an aldehyde primarily to form six-membered rings between adjacent, intramolecular hydroxyl groups; to a lesser extent, intermolecular acetals are also formed. This side reaction can lead to branched and eventually cross-linked polymer. The reaction can be used for the making of any vinyl acetal polymer and proceeds on the various units in intramolecular reactions (Schemes 3.3 and 3.4) and, to a lesser extent, in intermolecular reactions (Scheme 3.5).

As a particular case, the reaction of an aqueous PVA solution with butanal (BA) in the presence of small amounts of mineral acid, acting as a catalyst, yields PVB. The hydroxyl groups of PVA react with BA to form 1,3-dioxane rings (acetal rings), and partial or even almost complete exchange of the original functional group for a new one can occur (Scheme 3.6). Detailed mechanisms are given in Ref. [8].

Since not all hydroxyl groups of the PVA react with aldehyde, PVB invariably contains a certain percentage of hydroxyl groups. Moreover, a small percentage of the acetyl groups always remain in the polymer chain from the upstream transesterification during which polyvinyl acetate is converted to PVA (generally less than 2.5 mol%). Therefore, the final product has the character of a terpolymer of vinyl butyral, vinyl alcohol (VA), and vinyl acetate (Scheme 3.7).

From statistical reasons, mainly because the cyclization reaction requires the presence of two adjacent hydroxyl groups on the PVA chain, Flory [9] calculated the theoretical upper limit of the acetalization reaction of PVAs assuming no vinyl acetate unit. The amount of isolated and unreacted

\[
\begin{align*}
\text{Scheme 3.2} & \quad \text{Conversion from aldehyde to acetal.} \\

\text{Scheme 3.3} & \quad \text{Intramolecular acetalization of the 1,3-glycol group.} \\

\text{Scheme 3.4} & \quad \text{Intramolecular acetalization of the 1,2-glycol group.} \\

\text{Scheme 3.5} & \quad \text{Intermolecular acetalization of the 1,3-glycol group.}
\end{align*}
\]
hydroxyl units should be 0.184 mol% for 1,3- and 1,2-glycol containing PVA and 0.135 mol% for pure 1,3-glycol containing PVA if acetalization is irreversible. For acetalization with BA, always assuming no vinyl acetate unit, this corresponds to an unreacted VA content between 12.25 and 8.84 wt% in PVB. Attempts have been made to synthesize polyvinyl acetics with a degree of acetalization exceeding the predicted values [10]. Raghavendrachar and Chanda [11] suggested a possibility of achieving degrees of acetalization above 86.5% while keeping the assumption of irreversibility, but the predicted value has not been significantly exceeded. Indeed, Flory initially assumed that acetalization was an irreversible reaction, but the question of the reversibility of formation of acetal rings was left open. Reversibility of acetalization and interchange can theoretically lead to higher levels of acetalization and can be taken into account in statistical calculations [12]. However, in practice, intermolecular acetalization limits higher levels of acetalization in commercial products to about 82 mol%. Consequently, PVBs always contain at least 7% by weight residual VA units. It is standard to use PVBs with VA contents of 9% to approximately 30% by weight (Table 3.2).

Since the residual acetate content is kept as low as possible (0–2.5 mol%), the balance between residual hydroxyl groups and acetal rings depends on the reaction conditions, and this balance provides distinct properties to the final polymer. The properties are determined mainly by three

**SCHEME 3.6** Acetalization of PVA in the case of BA.

**SCHEME 3.7** Terpolymer structure of PVB.

**TABLE 3.2**

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Trade Name</th>
<th>VA Content (wt%)</th>
<th>VAc Content (wt%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solutia</td>
<td>Butvar</td>
<td>11–20</td>
<td>0–2</td>
<td>[13]</td>
</tr>
<tr>
<td>DuPont</td>
<td>Butacite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kuraray</td>
<td>Mowital</td>
<td>11–27</td>
<td>0–2.5</td>
<td>[14]</td>
</tr>
<tr>
<td>Kuraray</td>
<td>Pioloform</td>
<td>14–18</td>
<td>0–2.5</td>
<td>[14]</td>
</tr>
<tr>
<td>Sekisui</td>
<td>S-Lec</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Polyvinyl Butyral factors: the degree of acetalization, the degree of polymerization, and the used aldehydes, as they determine the polarity and molecular weight of the polymer. For the PVB for safety glass, the reaction of acetalization is stopped at about 75% conversion of the hydroxyl groups so that the residual or unreacted hydroxyl groups provide the required strength and adhesion to glass, since a good bond between the components of the laminate is imperative. Assuming no remaining acetate, the molar composition in VA ($m$ in mol% VA) is deduced from the weight fraction of VA, $w$ in wt% VA, by the following equation:

$$m = \frac{100 \times 142w}{44(100 - w) + (142w)}$$

(3.1)

Special grades of PVB were also obtained by the use of both butanal and ethanal [14] or furfural [15,16], leading to the slightly different structures (Schemes 3.8 and 3.9). Ionomeric PVB can be synthesized by using the sodium salt of $o$-benzaldehyde sulfonic acid in a preliminary step, and then going on the polymerization in the conventional way. Ionomeric PVB containing 3 and 5 mol% of ionomer groups has been used [17]. Grafting of polydimethylsiloxane, polyoxyethylene [18], and also long branches of PVB [19] has been described.

High acetalization reaction can be conducted in homogeneous solution processes. The acetals of PVA are generally prepared by the action of aldehydes on PVA in an aqueous medium. However, because these acetals are nonsoluble in water, the contact time of the reactants is not very long. Theoretically, 100% acetalization of PVA should be possible if the reaction is carried out homogeneously in a non-aqueous nonpolar solvent when hydrogen bonding is the least. It was reported [20] that various acetalizations of PVA, including conversion to PVB, could be carried out until 90–95 mol% in a mixture of DMF/benzene (4:1 v/v) using a catalytic concentration of ethyl nitrate dimethyl sulfoxide ($1.4 \times 10^{-3}$ mol/mol PVA); 93% acetalization was also claimed using $N$-methyl-2-pyrrolidone (NMP) as a solvent for PVA and PVB [21]. The simultaneous methanolysis and butyralization of poly(vinyl acetate) was also conducted via the reaction of methanol and BA with

![Scheme 3.8](image)

**SCHEME 3.8** Poly(vinyl butyral-co-ethanal).

![Scheme 3.9](image)

**SCHEME 3.9** Poly(vinyl butyral-co-furfural).
polyvinyl acetate under batch conditions at temperatures from 70°C to 90°C at the vapor pressure of the reactants [22].

Finally, from the chemical engineering point of view, for the preparation of poly(vinyl acetal), five different processes are known [23–25]:

1. **Precipitation**. An aqueous solution of PVA reacts with the aldehyde until the homogeneous phase reaction changes to a heterogeneous reaction when the acetal precipitates.
2. **Dissolution**. PVA powder is suspended in a suitable nonsolvent that dissolves the aldehyde and the final product. The reaction starts out heterogeneously and is completed homogeneously.
3. **Homogeneous reaction**. The reaction starts in a water solution of PVA. A solvent for the acetal, which can mix with water, is added continuously to prevent precipitation.
4. **Heterogeneous reaction**. PVA in film or fiber form react with the aldehyde.
5. **Direct conversion of poly(vinyl acetate) to poly(vinyl acetal)**. This is also a homogeneous reaction. The poly(vinyl acetate) is dissolved in a suitable solvent and is hydrolyzed by a strong mineral acid and acetalized at the same time.

A detailed list of patents on the ingredients and polymerization of PVB can be found in Ref. [3]. Other details on synthesis can be found in Ref. [26] and in various papers on the subject [18,27,28]. Hydrolysis and acetalization can be conducted either sequentially or concurrently. In practice, only two basic processes with variants are used commercially today, and they are described hereafter. More detailed schemes of the polymerization arrangements, especially concerning the solvent process using sequential hydrolysis and acetalization and the aqueous process, for chemical engineering are described in Ref. [3].

The solution process is carried out in an organic solvent. To limit the undesirable poly(vinyl acetate) content, simultaneous hydrolysis and acetalization cannot be used. Poly(vinyl acetate) is first saponified by transesterification with ethanol and a mineral acid catalyst to produce PVA that precipitates and therefore can be separated from remaining ethanol and ethyl acetate by centrifugation. PVA is then acetalized in a separate operation, after being slurried with ethanol, and heated with BA and the acid catalyst. As the acetalization reaction proceeds in the solvent process, the slurry of PVA dissolves as PVB in the reaction mixture. Upon completion of the acetalization reaction, PVB is precipitated into water, and aqueous neutralization of the acid catalysis occurs. Neutralization, with sodium hydroxide or potassium hydroxide, and washing stages are necessary to remove the acid catalyst and to improve resin thermal stability [29]. By-products can be recovered. Resin has very low levels of gel from intermolecular acetalization.

The aqueous process is carried out in water, where PVA dissolves easily. The acetal is precipitated during the reaction of the aldehyde with an aqueous solution of PVB containing acetic acid and a mineral acid. Acidity is neutralized after completion of the reaction. Precipitated resin in the aqueous acetalization shows higher levels of intermolecular acetalization, which can be avoided by emulsifiers ammonium thiocyanate or urea that improve solubility in water.

To increase the average molecular weight and polydispersity, small quantities of various dialdehyde or trialdehyde can be added during the acetalization to promote a low amount of cross-linking. Other cross-linking agents are cited next.

### 3.2.2 Postpolymerization Chemistry

PVB is a thermoplastic material that is soluble in a large number of organic solvents, but it can be cross-linked with various species owing to OH groups in order to improve solvent, chemical, and thermal resistances. The cross-linking capacity depends on the number of OH groups available. Phenolic (Scheme 3.10), melamine (Scheme 3.11), epoxy (Scheme 3.12), isocyanate (Scheme 3.13), aldehyde (Scheme 3.14), and formaldehyde hydrate can be used [30]. Urea and melamine as well as polyisocyanate enable curing at room temperature with acid catalysts.
SCHEME 3.10  Reaction of PVB with phenolic compounds.
SCHEMA 3.11 Reaction of PVB with melamine.
SCHEME 3.12 Reaction of PVB with epoxy compounds.

SCHEME 3.13 Reaction of PVB with isocyanates.

SCHEME 3.14 Reaction of PVB with aldehydes.
3.3 STRUCTURAL AND PHASE CHARACTERISTICS

Finally, PVB is a random terpolymer composed of vinyl butyral, VA, and vinyl acetate monomeric units. Structure and properties are strongly dependent on the hydroxyl content. For example, it controls the adhesion to surfaces, improves properties of thermoset resin, influences cross-linking behavior, and affects miscibility and morphology of blends. Therefore, much analytical effort has been exerted to develop reliable tools for its characterization [31–33]. PVB is not a hazardous product. PVB used for the process is a colorless and odorless powder. Users still need to protect themselves from the dust, which can irritate throat, eyes, and respiratory system and cause coughing. Under air combustion, PVB will produce carbon dioxide. Butavar and Mowital are nontoxic and suitable for food packaging according to US Food and Drug Administration 21 CFR.

3.3.1 IR SPECTROSCOPY

Fourier transform infrared (FTIR) spectra show typical peaks attributed to PVA, with OH stretching vibration bands at 3490 cm\(^{-1}\), plus absorptions arising from the presence of acetalic functions (in the region between 1050 and 1150 cm\(^{-1}\)). The band at 1740 cm\(^{-1}\) appears because of the acetate group. Figure 3.1 and Table 3.3 give the assignation of the various peaks [21,34].

3.3.2 UV SPECTROSCOPY

Figure 3.2 exhibits the UV absorption spectra of PVB. The UV–vis spectral analysis shows a strong absorption band at around UV at 415 nm and a small shoulder at 390 nm [35]. The absorption band observed for PVB is expected for hydroxyl-containing groups related to n to \(\pi^*\) electronic transition characteristic of oxygen lone pair of electrons due to the OH groups, or of the acetyl C=O and C–O–C cyclic electrons present in the polymer backbone, all functional groups involved in intramolecular and intermolecular hydrogen bonding.

3.3.3 \(^{13}\text{C} \)NMR SPECTROSCOPY

Due to the terpolymer nature of PVB, \(^1\text{H} \) and \(^{13}\text{C} \) nuclear magnetic resonance (NMR) spectroscopy is useful to determine the PVB structure [36]. Since the acetalization degree is reflected in the solubility of PVB in various solvents, spectra of PVB must be obtained in dimethyl sulfoxide (DMSO)-d6 for low acetalization and in CDCl\(_3\) for high acetalization rates. Deuterated methanol (CD\(_3\)OD) was also used [37]. \(^{13}\text{C} \) NMR spectrum of PVB (90 mol% VB) in deuterated chloroform (CDCl\(_3\)) is given in Figure 3.3 with tetramethylsilane (TMS) as the internal standard. The \(^{13}\text{C} \) NMR assignments of peaks and chemical shifts are given in Table 3.4 in correspondence with the figure and the racemic (r) and meso (m) stereostructures [21,26,36]. Indeed, as in any vinyl monomeric unit with asymmetric carbon, acetal ring conformations are due to the rotational isomeric states of meso and racemic diads of parent PVA (Scheme 3.15), also responsible for the meso and racemic peaks of the remaining VA [38]. Of course, the degree of acetalization and the racemic stereostructure fraction of acetal rings are correlated.

3.3.4 \(^1\text{H} \)NMR SPECTROSCOPY

Figure 3.4 gives an example of \(^1\text{H} \) NMR spectrum in DMSO-d6 of PVB with 21–27 wt% VB using TMS as the internal standard. The \(^1\text{H} \) NMR assignments of peaks and chemical shifts are given in Table 3.5. In addition to confirmation of structures, it enables the quantification of the extent of acetalization by the following equation:
FIGURE 3.1 FTIR spectrum of PVB with 24–27 wt% VA.

TABLE 3.3
IR Assignment of Functional Groups

<table>
<thead>
<tr>
<th>Wave (cm(^{-1}))</th>
<th>Groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>3490</td>
<td>OH (VA)</td>
</tr>
<tr>
<td>2850 and 3000</td>
<td>CH(_3), CH(_2), CH</td>
</tr>
<tr>
<td>1400 and 1280</td>
<td>Alkynes</td>
</tr>
<tr>
<td>1740</td>
<td>C=O (VAc)</td>
</tr>
<tr>
<td>1200</td>
<td>Ester</td>
</tr>
<tr>
<td>1100</td>
<td>C–O–C (VB)</td>
</tr>
<tr>
<td>960</td>
<td>Acetal (VB)</td>
</tr>
</tbody>
</table>

FIGURE 3.2 UV absorption spectrum of PVB with 18–20 wt% VA. (From Kalu, E.E. et al., *Int. J. Electrochem. Sci.*, 7, 5297–5313, 2012. © Copyright ESG. Adapted and reproduced with permission.)
FIGURE 3.3 $^{13}$C NMR spectrum of PVB (90 mol% VB) in CDCl$_3$ with TMS as standard. (Adapted from Fernandez, M. et al., *J Appl Polym Sci* 102, 5007–5017, 2006.)

### TABLE 3.4
Assignments of $^{13}$C NMR Peaks

<table>
<thead>
<tr>
<th>Number</th>
<th>Structural Unit</th>
<th>Chemical Shift (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Butyral CH$_3$</td>
<td>13.7–18.1–18.2</td>
</tr>
<tr>
<td>2</td>
<td>Butyral CH$_2$</td>
<td>21.9–22.0</td>
</tr>
<tr>
<td>3</td>
<td>Butyral CH$_2$</td>
<td>41.1–41.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>46.6–46.8</td>
</tr>
<tr>
<td>4m</td>
<td>Meso-butyral O–CH–O</td>
<td>105.5–105.6</td>
</tr>
<tr>
<td>4r</td>
<td>Racemic butyral O–CH–O</td>
<td>98.5–98.6</td>
</tr>
<tr>
<td>5m</td>
<td>Meso butyral CH</td>
<td>76.4–78.8</td>
</tr>
<tr>
<td>5r</td>
<td>Racemic butyral CH</td>
<td>72.4–72.5</td>
</tr>
<tr>
<td>6</td>
<td>Vinyl alcohol–CH$_2$</td>
<td>41.1–41.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>49.3–49.4</td>
</tr>
<tr>
<td>7</td>
<td>Vinyl alcohol–CH</td>
<td>68.0–69.0</td>
</tr>
</tbody>
</table>


SCHEME 3.15  Meso and racemic stereostructures of PVB.
The dioxymethine protons $4m$ and $4r$ could be utilized to determine the fraction of the stereostructure of butyral rings. All resonances in the range 15–50 ppm correspond to methylene and those from 60 to 110 ppm to methines. Other finer interpretations can be found in Ref. [37], which use both proton and carbon NMR techniques coupled to two-dimensional J-resolved spectroscopy for better assignment of the peaks.

### 3.3.5 Dosing of Acetate

According to Ref. [39], the quantity of acetate can be dosed by a simple method. Iodine–iodide solution placed on a PVB sample changes its color in a few seconds. PVB with less than 15% acetate content gives a yellow color, 15–27% produces green, 27–40% gives a bluish-green color, and over 40% produces blue.
Generally, PVB is amorphous, only polymers with a very high VA content (higher than 63.3 wt% VA) are crystallizable, and the melting temperature was found to be between 171°C and 218°C, approaching that of PVA [40]. In all other cases, PVB is amorphous and displays an easily observable glass transition. The effect of the vinyl content on the glass transition of PVB has been studied in detail by varying the VA content [8,21,40], and the glass transition temperature was found to increase upon the VA molar content (Figure 3.5). Butyral groups have a plasticizing effect, and the increase in the content of hydroxyl groups gives rise to an increase in hydrogen bonding, which leads to a significant departure from group additivity. The $T_g$ of PVB with low VA content (10 mol%) is nearly 330 K, that of PVB with 50 mol% is 350 K, whereas that of a PVB with 80 mol% is 358 K. Higher values were reported on unplasticized Butvar PVB (18 wt% VA) at 80°C [41] and by Dhaliwal (74 K) [36].

3.3.7 Solvents, Solution Properties, and Molecular Weight Characterization

The useful relations among molecular weight, intrinsic viscosity $[\eta]$, and specific $\eta_{sp}$ or relative viscosity $\eta_r$ are given in the following (in which all constants are solvent- and temperature-dependent):

The Mark–Houwink relation: $[\eta] = KM^a$  \hspace{1cm} (3.3)

The Huggins and Kramer relation: $\frac{\eta_{sp}}{C} = [\eta] + K_H [\eta]^2 C$  \hspace{1cm} (3.4)

The Kramer relation: $\frac{\ln(\eta_r)}{C} = [\eta] - K_K [\eta]^2 C$  \hspace{1cm} (3.5)

For PVB, the Mark–Houwink exponent ($a$) has been found to be 0.72 in tetrahydrofuran (THF) at 25°C. The $K$ parameter depends on the hydroxyl content being $2.89 \times 10^{-4}$ mL/g for 20 wt% VA and slightly less ($2.52 \times 10^{-4}$ mL/g) for 10 wt% VA [42]. Results in glycol ether [43] showed values of $a = 0.72$, $K_H = 0.41$ g/dL, and $K_K = -0.10$ g/dL for PVB with 22 wt% VA. Virial and refraction
indices increment $dn/dc$ of PVB with 43 mol% VA can be found in Refs. [19,44,45] according to Table 3.6. For methanol and methyl isobutyl ketone, most mixtures are better solvents for PVB than either individual solvent that leads to polymer aggregation.

Most of the industrial PVBs have weight average molecular weights in the range 40,000–250,000 g/mol [13,14]. The molecular weight of PVB can be determined by size-exclusion chromatography (SEC). THF can be used as a solvent to measure the molecular weight of PVB by SEC [46], but hexafluoroisopropanol (HFIP) is required for PVB with VA content higher than 20% [47]. Indeed, HFIP eliminates aggregates and gives better accuracy of molecular weight averages as demonstrated by low-angle laser light scattering (LALLS). Normal-phase gradient polymer elution chromatography (NP-GPEC) was used for determination of molecular weight distribution (MWD) and VA content using dimethylacetamide (DMAc) with 0.5% lithium chloride (LiCl) as the solvent [31].

The solubility parameters have been given by theoretical analysis using the solubility parameter concept and blend miscibility [48]. The dispersion, polar, and hydrogen bonding contributions and the total solubility parameter of the repeating unit $\delta_D$, $\delta_P$, $\delta_H$, and $\delta$ have been found to be 7.72, 2.90, 3.26, and 8.87 MPa$^{1/2}$, respectively, for VB and 7.62, 6.80, 11.54, and 15.41 MPa$^{1/2}$ for VA. Overall, different values were found by using the Hoftyzer–Van Krevelen method of structural groups or other calculation methods (see Table 3.7) [49–51].

### Table 3.6

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Temperature (°C)</th>
<th>$A_2$ (mL mol/g$^2$)</th>
<th>$dn/dc$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol (MeOH)</td>
<td>25</td>
<td>–0.5</td>
<td>0.1562</td>
</tr>
<tr>
<td>Methanol (MeOH)</td>
<td>50</td>
<td>–</td>
<td>0.1676</td>
</tr>
<tr>
<td>Methyl isobutyl ketone (MIBK)</td>
<td>44</td>
<td>–</td>
<td>0.1015</td>
</tr>
<tr>
<td>MIBK/MeOH (3:1 vol)</td>
<td>25</td>
<td>0.00079</td>
<td>0.1120–0.1145</td>
</tr>
<tr>
<td>MIBK/MeOH (1:1 vol)</td>
<td>25</td>
<td>0.00036</td>
<td>0.1284</td>
</tr>
<tr>
<td>MIBK/MeOH (9:1 vol)</td>
<td>25</td>
<td>0.00015</td>
<td>0.1062</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>25</td>
<td>0.00104</td>
<td>0.1173</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>80</td>
<td>–</td>
<td>0.1302</td>
</tr>
<tr>
<td>DMAc–0.5% LiCl</td>
<td>35</td>
<td>0.00139</td>
<td>0.0570</td>
</tr>
</tbody>
</table>


### Table 3.7

<table>
<thead>
<tr>
<th>Name</th>
<th>VA (wt%)</th>
<th>$\delta_D$</th>
<th>$\delta_P$</th>
<th>$\delta_H$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mowital B60H</td>
<td>18–21</td>
<td>15.5</td>
<td>6.5</td>
<td>10.4</td>
<td>[50]</td>
</tr>
<tr>
<td>Mowital B30T</td>
<td>24–27</td>
<td>19.1</td>
<td>9.5</td>
<td>12.2</td>
<td>[51]</td>
</tr>
<tr>
<td>Mowital B30H</td>
<td>18–21</td>
<td>18.6</td>
<td>12.9</td>
<td>10.3</td>
<td>[49]</td>
</tr>
<tr>
<td>Mowital B60H</td>
<td>18–21</td>
<td>20.2</td>
<td>11.2</td>
<td>13.3</td>
<td>[49]</td>
</tr>
<tr>
<td>Butvar B76</td>
<td>11.5–13.5</td>
<td>18.6</td>
<td>4.4</td>
<td>13.0</td>
<td>[49]</td>
</tr>
<tr>
<td>Butvar B-90, B-98</td>
<td>18–20</td>
<td>21.7</td>
<td>7.9</td>
<td>14.6</td>
<td></td>
</tr>
<tr>
<td>Butvar B-72, B-74</td>
<td>17.5–20</td>
<td>21.2</td>
<td>8.7</td>
<td>14.0</td>
<td></td>
</tr>
<tr>
<td>Butvar B-76, B-79</td>
<td>11–13.5</td>
<td>17.7</td>
<td>7.2</td>
<td>12.6</td>
<td></td>
</tr>
</tbody>
</table>
PVB is soluble in the following solvents: acetic acid, acetone, methanol, ethanol, 2-propanol, butanol, 2-butoxyethanol, cyclohexanone, benzyl alcohol, 1-methoxy-propanol-2, butyl glycol, \( n \)-butyl acetate, ethyl acetate, \( N,N \)-dimethylacetamide, \( N,N \)-dimethylformamide, \( N,N \)-dimethyl sulfoxide, NMP, and THF, but solubility is strongly dependent on the composition and especially the VA content. PVB is also resistant to weak and strong acids, and weak and strong bases. Table 3.8 shows the solubility of commercial PVB (Mowital, Pioloform, and Butvar) in various solvents. The VA content is clearly the important parameter, whereas molecular weight has a secondary effect.

### 3.3.8 Thermal Degradation (High Temperature Conditions in Nitrogen)

The thermo-oxidation and thermal degradation of PVB at high temperatures in various atmospheres have been studied by many authors. Indeed, with PVB being used as a binder for ceramics processing, its elimination during the process of sintering is a critical issue for the quality of the final product. Under nitrogen, PVB starts to decompose at 280°C (ramp of 5°C/min) and under air at 200°C. As it relates to the processing properties, thermal degradation in air will be addressed in Section 3.4.7. The main products of degradation are BA, 2-butanal, butanoic acid, acetic acid, 2,5-dihydrofuran, and butanol. Traces of other chemicals such as 1-phenyl ethanone, 3,5-diphenyl, 1,2,4-trioxolane, and 2,4-hexadiene are also detectable. The degradation of PVB takes place in three steps: First, water from the VA copolymer is eliminated between 315°C and 350°C with formation of a small amount of butanal. The second step is the degradation of side groups and main chain scission. In the second step, 85% of the polymer is degraded between 350°C and 445°C. Finally, cross-linked and cyclic compounds are formed above 445°C [52]. Hydroxyl groups have a dramatic effect on the stability of PVB [8,21]. The decomposition of PVB takes place in one step when the percentage of VA unit is less than 80%, and PVB starts to decompose at 280°C with a weight loss between 80% and 90% at 480°C. For higher VA content, decomposition of PVB takes place in two steps with maximum at 316°C and at 382°C and weight loss of 40% and 50%, respectively (Figure 3.6). As has already been indicated in the synthesis part, the addition of bases such as hydroxides increases the stability of PVB, and the starting decomposition temperature can be delayed until 330°C in air [29].

### 3.4 Polymer Engineering Properties

#### 3.4.1 Density

The density of PVB ranges from 1.083 g/cm\(^3\) for PVB with a VA content of 11 wt% (28.5 mol%) to 1.100 g/cm\(^3\) at a VA content of 19 wt% (43.1 mol%) [8,13]. The variation of the specific volume with temperature was given by Wilski for similar VA contents [53] with a value of variation with temperature of \( 2.52 \times 10^{-6} \text{ cm}^3/\text{g}/°\text{C} \) below the glass transition and \( 6.91 \times 10^{-6} \text{ cm}^3/\text{g}/°\text{C} \) above it (Figure 3.7).

#### 3.4.2 Surface Properties

Surface tension of PVB was evaluated by the pendant drop method [54] and found to be \( 36.4 \pm 0.2 \text{ mN/m} \) at 240°C with linear temperature dependence of \(-0.6 \text{ mN/m} \) between 240°C and 260°C. The value of 38 mN/m was calculated with dispersion and polar components of 23.0 and 15.0 mN/m, respectively [51]. Values of the critical surface tension by the Zisman method given at room temperatures (24–25 mN/m [55,56]) for various VA contents show very little influence of OH groups.
### Table 3.8

**Solubility of Commercial PVB in Various Solvents, 10% Solution unless Indicated**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Butvar B76</th>
<th>Butvar B90</th>
<th>Butvar B16H</th>
<th>Mowital B30H</th>
<th>Mowital B45H</th>
<th>Mowital B60H</th>
<th>Mowital B75H</th>
<th>Butvar B72a</th>
<th>Mowital BX860b</th>
<th>Mowital B45M</th>
<th>Mowital B30T</th>
<th>Pioloform BL16c</th>
</tr>
</thead>
<tbody>
<tr>
<td>VA wt%</td>
<td>11.5–13.5</td>
<td>11–14</td>
<td>12–16</td>
<td>18–20</td>
<td>18–21</td>
<td>18–21</td>
<td>18–21</td>
<td>17.5–20</td>
<td>18–21</td>
<td>21–24</td>
<td>24–27</td>
<td>14–18</td>
</tr>
<tr>
<td>Methanol</td>
<td>SW</td>
<td>PS</td>
<td>PS</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>PS</td>
<td>PS</td>
<td>PS</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>Ethanol</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
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<tr>
<td>n-Propanol</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>n-Butanol</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
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<td>S</td>
<td>S</td>
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<td>Diacetone</td>
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<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>PS</td>
<td>S</td>
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<td>S</td>
</tr>
<tr>
<td>alcohol</td>
<td>Tetrahydrofuran</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>Methyl</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>cellulose</td>
<td>Ethyl cellulose</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
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<tr>
<td>Butyl cellulose</td>
<td>S</td>
<td>S</td>
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<td>S</td>
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<td>S</td>
</tr>
<tr>
<td>Methyl acetate</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>PS</td>
<td>PS</td>
<td>PS</td>
<td>PS</td>
<td>I</td>
<td>I</td>
<td>PS</td>
<td>PS</td>
<td>I</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>PS</td>
<td>PS</td>
<td>S</td>
<td>PS</td>
<td>PS</td>
<td>S</td>
<td>I</td>
<td>PS</td>
<td>PS</td>
</tr>
<tr>
<td>Butyl acetate</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>PS</td>
<td>PS</td>
<td>PS</td>
<td>PS</td>
<td>I</td>
<td>I</td>
<td>PS</td>
<td>PS</td>
<td>I</td>
</tr>
<tr>
<td>Acetone</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>SW</td>
<td>PS</td>
<td>PS</td>
<td>PS</td>
<td>I</td>
<td>I</td>
<td>PS</td>
<td>PS</td>
<td>I</td>
</tr>
<tr>
<td>Methyl ethyl ketone</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>PS</td>
<td>S</td>
<td>S</td>
<td>PS</td>
<td>I</td>
<td>SW</td>
<td>PS</td>
<td>PS</td>
<td>S</td>
</tr>
</tbody>
</table>

(Continued)
### TABLE 3.8 (CONTINUED)

**Solubility of Commercial PVB in Various Solvents, 10% Solution unless Indicated**

| Polymer | Butvar B79 | Mowital B30HH | Mowital B60HH | Butvar B98 | Mowital B16H | Mowital B20H | Mowital B30H | Mowital B45H | Mowital B60H | Mowital B75H<sup>a</sup> | Butvar B72<sup>b</sup> | Mowital BX860<sup>b</sup> | Mowital B45M | Mowital B30T | Mowital B60T | Pioloform BL16<sup>c</sup> |
|---------|------------|---------------|---------------|------------|--------------|--------------|--------------|--------------|--------------|----------------|----------------|----------------|-------------|--------------|------------|---------------|---------------------|
|         | Butvar B79 | Mowital B30HH | Mowital B60HH | Butvar B98 | Mowital B16H | Mowital B20H | Mowital B30H | Mowital B45H | Mowital B60H | Mowital B75H<sup>a</sup> | Butvar B72<sup>b</sup> | Mowital BX860<sup>b</sup> | Mowital B45M | Mowital B30T | Mowital B60T | Pioloform BL16<sup>c</sup> |
| Methyl isobutyl ketone | S | S | S | I | PS | S | PS | I | I | I | PS | PS | I | S |
| Cyclohexanone | S | S | S | S | S | S | S | S | S | S | PS | PS | S | S |
| Toluene | PS | P | PS | PS | PS | PS | PS | PS | I | I | I | I | I | PS |
| Xylene | PS | P | PS | PS | PS | PS | PS | PS | I | I | I | I | I | PS |
| Acetic acid | S | S | S | S | S | S | S | S | S | S | S | S | S | S |
| Dimethyl sulfoxide | S | S | S | S | S | S | S | S | S | S | S | S | S | S |


**Note:** I: insoluble; PS: partially soluble; S: soluble; SW: swelling.

<sup>a</sup> 5% solution.

<sup>b</sup> 14–18 wt% acetate.

<sup>c</sup> With ethanal.
3.4.3 Adhesion Properties

The hydroxyl groups of PVB are also responsible for its outstanding adhesion to many substrates, the most important for technological applications being its affinity to glass. Both chemical bonding and hydrogen bonding with glass silanols are involved (Figure 3.8). Figure 3.9 shows the effect of the hydroxyl content on the work of adhesion measured on glass beads [57]. According to measurements on interlayers for laminated glass [58], the activity of hydroxyl depends on the pH and on the water content in PVB sheets. Alkali modification decreases the adhesion of PVB to glass, whereas acidic modification increases it and provides higher stability of adhesion regarding the water content in PVB sheet. Therefore, adhesion depends on the amount of organic acid added and on the provenance of PVB and its plasticizers. Improvements of adhesion by silane coupling have been explored. The mono-alkoxy silanes have weak impact on adhesion when compared to untreated.
glass due to the poor attachment of the mono-alkoxy silane to the mineral surface. Di- and tri-alkoxy silanes enhance adhesion strength due to stability of their bonds to the glass surface and formation of interphases with the polymer [59]. Aminosilanes form acid–base moieties between the hydroxyl groups of PVB and amino groups of aminosilane, and the adhesion strength is controlled by the length of the amino functional group, suggesting that the adhesion promotion is controlled by compatibility and penetration of the silane organo functional group [60].

3.4.4 Electrical Properties

In PVB, two major relaxation processes—one above room temperature, designated the $\beta$ or secondary relaxation, and the other below room temperature, designated the $\alpha$ or primary relaxation—have been detected by dielectric measurements [61–63] and confirm results by thermally stimulated depolarization current spectroscopy [64,65] and mechanical measurements [30] (cf. also Section 3.4.5). Typical dispersion data are shown in Figure 3.10. The $\alpha$ process is attributed to the rotation of dipoles from one quasi-stable position to another. It is possible only at higher temperatures at which the diffusional motion of segments occurs, and it is strongly dependent on the molecular structure of the polymer. In PVB, the activation energy for this relaxation was found to be 63 kJ/mol. It is not a single relaxation process, but rather it has a distribution of relaxations. The $\beta$ process is associated with the deorientation of the aligned dipoles involving the acetate/hydroxyl groups when large-scale...
Polyvinyl Butyral

Conformational rearrangement of the main chain is frozen. The activation energy of this relaxation is lower (33 kJ/mol in PVB), and it becomes quite difficult to observe by conventional dielectric spectroscopy with high-molecular-weight samples. The $\beta$ relaxation is of Debye type with a symmetrical distribution of relaxation times. Thermally stimulated depolarization (TSD) current studies also reveal a relaxation process at high temperatures that has been attributed to the release of trapped space charges. Comparisons of the dielectric behavior and particularly of the $\alpha$ dispersion of various polyacetals reflect the internal plasticization with increasing size of the substituent group (formal to butyral) and the shifting of dispersion to lower temperatures [66]. Typical values of dielectric constant and dissipation factor at room temperature are given for Butvar PVB in Table 3.9 [13].

### 3.4.5 Mechanical Properties

Dynamic mechanical spectroscopy on neat PVB around the glass transition usually displays the $\alpha$ relaxation process [30,63] with a usual decrease of three decades of the storage modulus from the glassy plateau at about $G' = 1$ GPa until a rubbery plateau at $G' = 1.2$ MPa in shear (Figure 3.11). Consistent values in tensile tests, $E' = 2$ GPa in the glass state and a rubbery plateau at $E' = 5$ MPa, were reported in Ref. [63].
Typical tensile properties of various commercial unplasticized PVBs at room temperature are summarized in Table 3.10.

### TABLE 3.10  
Mechanical Properties of Butvar PVB Resins

<table>
<thead>
<tr>
<th>Property</th>
<th>ASTM Standard</th>
<th>Butvar B72–B74</th>
<th>Butvar B76–B79</th>
<th>Butvar B90–98</th>
</tr>
</thead>
<tbody>
<tr>
<td>VA content (wt%)</td>
<td></td>
<td>17.5–20</td>
<td>11.5–13.5</td>
<td>18–20</td>
</tr>
<tr>
<td>Yield stress (MPa)</td>
<td>D638-58T</td>
<td>47–54</td>
<td>40–47</td>
<td>43–50</td>
</tr>
<tr>
<td>Elongation at yield (%)</td>
<td>D638-58T</td>
<td>8</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>D638-58T</td>
<td>70–75</td>
<td>110</td>
<td>100–110</td>
</tr>
<tr>
<td>Tensile modulus (GPa)</td>
<td>D638-58T</td>
<td>2.3–2.4</td>
<td>1.9–2.0</td>
<td>2.1–2.2</td>
</tr>
<tr>
<td>Flexural strength at yield (MPa)</td>
<td>D790-59T</td>
<td>83–90</td>
<td>72–79</td>
<td>76–83</td>
</tr>
<tr>
<td>Hardness, Rockwell M</td>
<td>D785-51</td>
<td>115</td>
<td>100</td>
<td>110–115</td>
</tr>
<tr>
<td>Hardness, Rockwell E</td>
<td>D785-51</td>
<td>20</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>Impact strength notched Izod</td>
<td>D256-56</td>
<td>0.587</td>
<td>0.477</td>
<td>0.374–0.481</td>
</tr>
</tbody>
</table>


#### 3.4.6 Photodegradation and Photoaging

For more than 50 years, PVB has been employed in the repair and preservation of museum objects as an adhesive, an impregnant, a consolidant, or a surface coating. Therefore, the issue of its photodegradability under moderate conditions of exposure has been widely addressed. The studies have shown that the region of short wavelengths is the most detrimental from the point of view of PVB photooxidation. When covering the sheets with glass used for making windshields, the intensities of shorter wavelengths are suppressed, but still relatively long wavelength light remains capable of inducing the photooxidation of PVB, and an additional protection of PVB material in safety glass, by UV stabilizers, may be necessary. The use of PVB in the solar module industry has
renewed the scientific interest for a better understanding of the mechanisms involved and on the manner in which PVB may chain-break, cross-link, or discolor upon exposure principally to near-ultraviolet and visible radiation at various temperatures in quite severe conditions [67]. Although the structure of PVB should not theoretically allow absorption of light from the near-UV region, this polymer is readily degraded by these wavelengths. Commercial PVB, however, contains ketonic carbonyl groups already present in the starting PVA. The tertiary hydrogens present in the PVB structure represent the most likely sites of radical attack, which, in the presence of oxygen, lead eventually to the formation of hydroperoxides. The latter will easily be split, by the action of either light or heat, to give oxygen-centered radicals, which subsequently yield molecular fragments. The process of photooxidation is autocatalytic, which is the key role being played by ketones and hydroperoxide intermediates [68]. It was suggested that the weakest C–H bond is that in the acetal cycle between oxygens [69] followed by that in the VA segment. Influence of the remaining acetate has also been pointed out but only in the case of unusually high acetate contents [63]. In the course of photochemical aging under visible, middle, and near-ultraviolet wavelengths, PVB passes through the usual sequence of events in photoaging (Figure 3.12). At first, during a period of induction, the measured concentration of peroxide rises, passes through a maximum, and then declines to a notably low level. A change in weight follows the same trend, and when the loss reaches 2–3%, brittleness and discoloration occur. The initial gain and subsequent loss in weight are closely associated with the rise and fall of peroxide concentration. The decline in the peroxide content may be attributed to photolysis of hydroperoxides; the larger the butyral group content, the more intense the formation of carbonyl. The detailed mechanism for the deterioration of PVB comprises chain-breaking, growth of carbonyl, and release of low-molecular-weight fragments predominated by BA (butanal) and butyric acid. The release of aldehyde is far more important because it arises simply as a reversal of the initial reaction between aldehyde and PVA involved in the synthesis of the polymer. Nevertheless, both aldehyde and acid can contribute to the decomposition of hydroperoxides that may remove peroxides from the solid polymer after prolonged photooxidation. Volatile peroxides formed by scission reactions in hydroperoxide-containing segments near the ends of the polymer chain or chains, or by recombination of hydroxyl and alkoxy radicals formed by the homolysis of solid-state hydroperoxides, have also been observed [70]. However, in a material that has had some exposure to ultraviolet, PVB surprisingly develops no noticeable yellowness when heated moderately for a substantial length of time [68]. Apparently, the formation of appreciable color, which
is essentially a thermally induced process, tends to occur at a point at which the marked decline in peroxide concentration has taken place and on a polymer having the lower degree of butyral substitution. A further reason why discoloration of PVB has not been a marked feature in many photochemical exposures is that yellowing is observed when the polymer is in the dark, whereas bleaching occurs when it is exposed to light due to the disruption of the bonds in chromophores. Finally, at moderate temperatures below the glass transition temperature, PVB tends to chain-break when exposed to visible and near-ultraviolet wavelengths, and at higher temperatures, cross-linking is expected.

3.4.7 Thermo-Oxidation

Due to its composition, PVB is very sensitive to the degradation and migration of plasticizers. The thermal oxidation of PVB in mild conditions such as those encountered during processing (150–180°C) has been reviewed essentially in view of the stabilization of the polymers and of long-term aging and recycling [71] since it can have an effect on the optical and mechanical properties of the interlayer of safety glasses [39]. Almost all the functional groups characteristic of the polymer being investigated are susceptible to the thermal degradation process [72]. In the case of high acetate contents, the initial point of degradation is the acetate group. In standard PVB, the degradation of the cyclic butyral moiety is important when the temperature reaches 100°C with the production of butanoic acid, butanol, and butanal [52,73], and the reduction of the melt viscosity indicates chain scission rather than cross-linking (Scheme 3.16). Plasticization by water or by added plasticizer has a favorable effect since it decreases the viscosity of the polymer and self-heating during the processing step [74]. In plasticized PVB, the relative thermal stability of commercial PVB samples as measured by thermogravimetry, from mass loss against temperature plots [36], shows that weight loss of 20% and 70% occurs in two distinct regions between 200–300°C and 300–500°C. Below 260°C, the change in mass can be attributed to plasticizer loss by evaporation in the case of dibutyl sebacate. Nevertheless, the loss of plasticizer at common processing temperatures up to 200°C is not significant. PVB decomposes by side group elimination above 260°C. BA, butenal, water, and acetic acid are the major components from these elimination reactions, but benzene and other aromatic products are observed from the decomposition of polyene residues. Instability of PVB can also be attributed to acid materials, or other substances that are easily oxidized into acids, which attack

Scheme 3.16 Degradation pathways during thermo-oxidation of PVB.
the 1,3-dioxane ring and then result in its opening. That is why these acid materials are removed or neutralized by purification or addition of bases like inorganic bases, such as sodium hydroxide, calcium hydroxide, and barium hydroxide, or organic bases, like hexamine, at the end of the synthesis process [29].

3.5 PROCESSING TECHNOLOGIES

3.5.1 THERMAL PROPERTIES FOR PROCESSING

Since thermal, physical, and rheological data are requested in software packages that are useful and nowadays widely used for the modeling of processing techniques and design, a few useful values are proposed hereafter. The heat capacity of unplasticized PVB with 18–22 wt% VA [53] at 20°C is 1.36 J (g K)⁻¹, and the thermal conductivity [41] is 0.236 W (m K)⁻¹. At the glass transition, the variation of the heat capacity is 0.577 J (g K)⁻¹.

3.5.2 VISCOELASTIC AND RHEOLOGICAL PROPERTIES

The linear viscoelastic properties of PVB with 18 wt% VA [75] show a high level of rubbery plateau modulus (1.3 MPa) and a low molecular weight between entanglements $M_e$ (2670 g/mol). Consequently, it displays a rubbery state in a wide temperature range. The onset stress of shark-skin failure is around 0.18 MPa, which is almost identical to that of a conventional polyethylene. This high onset shear stress of the shark-skin failure enables high output rate at extrusion processing. The correlation with roughness during lamination is addressed in Ref. [76]. Other rheological data on a PVB with weight average molecular weight of 143,000 g/mol and glass transition at 15–20°C, both in shear and extension (extensional rate from 0.01 to 0.1 s⁻¹), can be found in Ref. [77] with a value of 1 MPa for the rubbery plateau. Coefficients of William-Landel and Ferry for time–temperature superposition are also given at 105°C ($C_1 = 53$ and $C_2 = 256°C$). Extensional measurements at 105°C show the classical behavior with slight extension thickening behavior at high shear rates (>0.1 s⁻¹) and steady plateau below this value (Figure 3.13). Results on miscible blends with polyethylene glycol (PEG) show that the viscosity fits the Arrhenius model very well in the homogeneous region with an activation energy of 30 kJ/mol [78]. Addition of ionomeric PVB was claimed to improve the flow properties [17].

![Extensional viscosity of PVB at 105°C.](image)

**FIGURE 3.13** Extensional viscosity of PVB at 105°C. (From Juang, Y.-J. et al., *Polym Eng Sci*, 41, 275–292. © Copyright 2001 Society of Plastics Engineers. Adapted and reproduced with permission.)
3.5.3 Extrusion of Films

The extrusion of films is a step that is commonly used for PVB films utilized in laminated safety glasses. The extrusion process of the resin into a film is complex and delicate. The resin, the plasticizer, and the additives are stored in silos and further mixed with appropriate amounts of additives. After homogenization, the mixture is transferred by gravity in the hopper of an extruder. Under the effect of temperature (>200°C) and of the extrusion screw rotation, the mixture melts into a viscous liquid. With PVB, the resin is partially melted before plasticizer addition, and the position of injection of plasticizer is carefully controlled; delayed injection can induce yellowness and surging, while premature injection can cause plugging in the feeding zone. Water must be extracted from the polymer by degassing under vacuum. Filtration of the melt before it flows into the die head of the extruder is necessary to remove mixture impurities such as unmelted solid particles and other contaminants. The die controls the shape and the surface roughness of the PVB interlayer, and its lips are often water-cooled. In close proximity to the exit of the die, the polymer film is cast onto a roll with a specially prepared surface that imparts the desired surface characteristics to one side of the molten polymer. The PVB sheet is mostly manufactured at thicknesses 0.38 mm (for architectural industry) and 0.76 mm (for automotive and architectural use). Special applications require thicknesses of 1.14 and 1.52 mm. The width of the PVB sheet can be up to 3.5 m. Manufactured PVB sheet is rolled and either separated by thin patterned polyethylene sheet or rolled undercooled (15°C) to avoid blocking because the PVB sheet must not be stuck for subsequent use [79].

3.6 Additive Effect on Properties and Applications

3.6.1 Plasticizers

The PVB resins are commonly used with appropriate additives such as antioxidants, anti-UV stabilizers, or inorganic pigments for colored PVB. The choice and amount of plasticizer used in the formulation of the PVB are essential especially concerning the mechanical and rheological properties. The plasticizer must be compatible and soluble with the resin, and this miscibility is greatly influenced by the VA content with some partitioning between rich and depleted zones within the polymer [41]. A priori calculation with the solubility parameters can be used for this purpose [48]. Phthalates have been used, but regulations have restricted the use of these additives; therefore, this class of plasticizers is not addressed in this chapter. An exhaustive list of phthalate-free plasticizers and of the limits for their use is given in Ref. [80]. The best known plasticizers are tetraethylene glycol di-n-heptanoate and triethyleneglycol di-(2-ethyl hexanoate) (3GO or TEGH) [81] and dibutyl sebacate for architectural PVB or automotive [82]; dihexyl adipate (DHA), dioctyl adipate (DOA), hexyl cyclohexyl adipate, or mixtures of heptyl and nonyl adipates for laminated glass in aeronautics and acrylics; whereas PEG is used in cathodes for fuel cells, biphenyl or its derivatives in electrographic photoconductors, and diglycidyl ether of bisphenol A as resin plasticizers in aqueous emulsions. The plasticizer content varies between 15 wt% (structural PVB) and 30 wt% (acoustic PVB). The lightly cross-linked PVB resins can be plasticized with 45 wt%, but 30 wt% is a classical amount for safety glass use with PVBs containing 17–25 wt% VA. Oil-modified sebacid alkyls and mixtures of phosphates, adipates, and polymeric plasticizers are also used in coatings. Plasticizers and PVB can be premixed in a mixer, possibly with an extrusion step in the melt process or within a common solvent in the casting process. PEGs with various molecular weights have also been investigated as plasticizers and for viscosity reduction. Lower-molecular-weight PEG (PEG 400) gives better results, comparable to the efficiency of phthalate plasticizers [83].

The glass transition temperature depends on the percentage and type of plasticizer; the higher the increase in the plasticizer content, the greater the decrease in the glass transition temperature. In a limited range of plasticizer amount, the variation of the glass temperature of the mix follows
the Fox law [36]; however, a limit of miscibility is also observed [51]. Figure 3.14 shows the results for dibutyl sebacate (DBS) in PVB containing 24 wt% VA. In addition to reducing the stiffness of polymers, plasticizers increase strain softening [84] and absorption of impact forces in the case of laminated glass, control adhesion to glass, reduce residual stress in the photoconductive layer of solar modules, affect the processing temperature, sometimes generating undesirable bubbles, and improve film-forming properties or processability especially in high extrusion throughput processes. In glass PVB sheet, plasticizers must not reduce light transmittance and adhesion to glass and must not increase yellowness. The analysis of the plasticizers can be performed by extraction from the polymer either by using organic solvents that are nonsolvents of the polymer such as n-heptane [36], or supercritical fluids, ethylene [85], or ethyl acetate modified supercritical CO₂ [81], followed by FTIR spectroscopy or chromatography [36].

### 3.6.2 Antioxidants

One of the reasons for deterioration of the optical properties of PVB could be the oxidation, which occurs during processing or use of the polymer. To prevent it, thermo- and photostabilizers are added to the polymer. However, these additives, which are soluble at high temperatures in the polymer melt, may become insoluble at low temperatures in the polymer, giving rise to phase separation and clouding. Therefore, as for plasticizers, the limit of solubility is important, and it is also connected to the type and amount of stabilizer; since plasticizers increase the mobility of polymer chains, they affect the solubility and diffusion of additives. Upon small additions of a plasticizer, antioxidant dissolves better than predicted by a sum of its solubilities in polymers and plasticizers. Larger additions of the plasticizer cause a strong polymer–plasticizer interaction, which decreases the antioxidant dissolution. The solubility of antioxidant in DHA and triethylene glycol is lower than its solubility in dibutyl sebacate [82]; 0.1–0.2 wt% of hindered phenols are classically used among various species: methyl ether of 3,5-di-tert-butyl-4-hydroxyphenyl propionic acid, ester of 3,5-di-tert-butyl-4-hydroxyphenyl propionic acid and ethyleneglycol, ester of 3,5-di-tert-butyl-4-hydroxyphenyl propionic acid and pentaerytrite, dimethyl-(3,5-di-tert-butyl-4-hydroxy-benzyl) phosphonate, diphenyl-(3,5-di-tert-butyl-4-hydroxybenzyl) phosphonate, phenyl ether of 2,2-methylene-bis-(4-methyl-6-tert-butylphenyl) phosphoric acid, and tris(2,4-di-tert-butylphenyl) phosphite [86].

![Graph showing variation of the glass transition temperature with the amount of plasticizer](image-url)
3.6.3 LIGHT AND UV STABILIZERS

UV stabilization of PVB may be particularly desirable for long-term strong exposure such as those required for the encapsulation of PV modules. High transparency is also required in the efficient wavelength that yields the highest quantum efficiency for the specific PV materials. The effects of UV radiation can be mitigated by the inclusion of a UV absorber such as a benzotriazole (0.2–0.35 wt%). Finally, combination with antioxidants such as a hindered amine light stabilizer (HALS; 0.1–0.2 wt%) and possibly a phenolic phosphonite can be used to decompose peroxide radicals that may form due to thermal or UV exposure [86]. HALS is not consumed as opposed to the phenolic phosphonite, which is oxidized to produce phosphate and phenols. Benzophenone has shown incompatibility with phenyl phosphonite because they had a significant tendency to form chromophores at least in other polymer systems with acetate groups [87].

3.6.4 FLAME RETARDANTS

Alumina trihydrate (ATH) performed best as a hydrated filler-type flame retardant of plasticized PVB especially in combination with low-level addition of red phosphorus that significantly improved limiting oxygen index (LOI) values. The presence of hydroxyl groups on the polymer backbone had a beneficial effect. Magnesium hydroxide addition had a limited effect on the LOI of plasticized PVB, and addition of red phosphorus made little difference because of the mismatch between the decomposition temperature of Mg(OH)$_2$ and the temperature at which the PVB plasticizer vaporizes [88].

3.7 BLENDS AND COMPOSITES

3.7.1 BLENDS

PVB has been used in various polymer blends as a minor component especially to modify the properties of the matrix polymer. The number of patents and publications in this area is rapidly increasing, essentially because large amounts of recycled PVB of quite good quality and purity become available from the recycling of laminated glass particularly from the automotive industry. Therefore, the polymers are generally blended in the melt using the conventional extrusion blending technique or directly on the injection molding machine. Otherwise, virgin PVB can be found in polymer blends for membranes made by film casting in a common solvent or for coating materials. These later types of blends will be mentioned but not addressed in detail since it is not the aim of the present book and the focus on thermoplastics was preferred. Generally, as in the case of most of high-molecular-weight polymer blends, miscibility is seldom observed between PVB and other polymer species. In particular, due to the terpolymer nature of PVB and to strong variations in the composition, even homologous blends of PVB with variation of chemical compositions can be immiscible [89]. However, ionomeric PVB was used as a viscosity modifier in conventional PVB [17]. PVB is often expected to toughen the semicrystalline polymer matrices especially when plasticized PVB is used. Compatibility can be achieved by hydrogen bonding or interchain reaction between the hydroxyl groups of PVB and the reactive chain ends of polyamides or polyesters; otherwise, the use of compatibilizing agents has been suggested. For example, PVB has been widely reported to be a toughening agent for polyamide 6. Miscibility of PVB and polyamide 6 directly relates to the overall VA content in the blend as demonstrated in both binary and ternary blends of PVB, PVA, and nylon-6. Miscibility window is observed in the range of 55–70 wt% of VA in PVB for binary blends [90] and approximately 40–60 wt% of total VA in the ternary blends [91]. Methylene and amide groups of nylon-6 were observed to interact favorably with VA in the amorphous phase. For lower VA contents, using plasticized PVB from recycled laminated automotive windshields, super-toughened material can be obtained for 40 wt% PVB in the blend [92]. Virgin material can also be used as a toughening additive [93]. Combination with styrene–ethylene/butylene–styrene copolymer (SEBS) as an impact modifier has been used, and the best impact properties are obtained
for PVB contents in the range 20–35 wt% [94,95]. Addition of a maleated SEBS (SEBS-g-MA) is not necessary in PA6 but improves the mechanical properties in polyamide 6-6 [96]. Attempts to use PVB as a compatibilizer between polyamide 6 and polypropylene have failed [97]. On the other hand, the use of compatibilizers in blends of PVB with olefinic polymers such as polypropylene is necessary to overcome the poor affinity between the hydrophobic and hydrophilic species. PP–PVB blends show very little improvement of mechanical properties. However, adding PP as the minor phase and obtaining thermoplastic elastomers after dynamic cross-linking and phase inversion in the melt can be a promising route [93]. Maleic anhydride grafted polypropylene (PP-g-MA) and reactive compatibilization have been used for other blends [40]; but the effect of the compatibilizer remains limited, and in composites, with mica as a filler, little toughening was observed [98]. Polyvinylidene fluoride is a crystalline technical polymer whose hydrophobicity can be modulated by addition of PVB for membrane applications [99]. It is fully miscible with PVB until 30 wt% of PVB [100,101]. Polyesters also belong to a class of crystalline polymers that has been addressed for blending with PVB. In coatings or for improvement of the weathering resistance [102] because of incompatibility, layering of the phase can provide a protective surface layer. Blending in the melt starting from cyclic oligomers and inducing miscibility by grafting during the polymerization have been reported [103]. Biodegradable polyesters such as polycaprolactone (PCL) have been tested in tape casting, green tapes, and ceramics to change the degradability of the substrate [104,105] and also because PVB changes the crystallization behavior of PCL. In particular, addition of a few percent of amorphous PVB strikingly reduces the nucleation frequency of the PCL crystals; therefore, it reduces the nucleation density and allows the spherulites of PCL to grow on the order of centimeters. The morphological changes also include a marked enhancement in the regularity of the lamellar organization in the banded spherulite; the band spacings of PCL spherulites decrease with increasing PVB content, indicating a shortening of the period of lamellar twisting, giving rise to interesting electrical properties in presence of conductive fillers (carbon black [CB]) as, for example, a positive temperature coefficient [97,106–109]. Other biodegradable polyesters coming from biological and agricultural resources have been investigated, especially poly(lactic acid) [110] and poly(3-hydroxybutyrate) [111], the latter showing partial miscibility in PVB with 24–36 wt% VA after melt-blending. Cellulose acetate is miscible with a fraction of PVB lower than 20 wt% and can be used for pervaporation in a membrane field [112]. Other nonpolyester biodegradable polymers from agricultural resources such as thermoplastic starch (TPS) can be blended with PVB by melt extrusion [113]. Polyether of the poly(ethylene-glycol) family can be easily melt-blended to bring some plasticizing effect [83] or viscosity modification [78]. PVB microporous membranes have been prepared via thermally induced phase separation because the PVB/PEG systems show an upper critical solution temperature (UCST) behavior and remain homogeneous at 150°C and 160°C while phase separation occurs at 140°C. Control of the morphology can be tuned by using an emulsifier such as an ethoxylated–propoxylated block copolymer [114–116] or by ternary blends with polystyrene (PS), because PS has better compatibility with PVB than PEG [117]. Combination with poly(ethylene-co-vinyl alcohol) (EVOH) generates both UCST and LCST behaviors. Cycloaliphatic polyether thermoplastic polyurethanes (TPUs) are melt-blended with PVB for improvement of resistance of the PVB interlayer [118], and poly(ethersulfone) (PES) can be used in blends obtained by casting for membranes for ultrafiltration [119].

Though it is expected to toughen rigid semicrystalline thermoplastic, especially when using plasticized PVB owing to its rubbery behavior at room temperature, PVB is also used in blends with amorphous materials. However, in the latter, it may be expected that significant transfer of plasticizers occurs within the amorphous phases, especially when the glass transition of the host polymer is low. Polymethyl methacrylate (PMMA) is not miscible with PVB, but a UCST-type phase behavior was observed in certain blends obtained in the melt. The miscibility range depends on the copolymer composition and on the molecular weight of PMMA with a minimum at 22–33 wt% VA. This is mainly attributed to a copolymer effect in which the unfavorable interaction between PVB and PMMA is minimized at a certain copolymer composition due to the repulsive interaction between
VA and VB units within the PVB chains [120]. The morphology of films obtained by spin-coating has been observed by AFM [121]. Recycled scraps of PVB were also used in blends with excellent optical properties and toughness owing to compatibilization in the melt by the incorporation of a copolymer of methyl methacrylate–butadiene–styrene (MBS) [122]. Blends with polyvinyl chloride (PVC) have been thoroughly studied because of the large amounts of recycled PVB of excellent quality that become available on the market. The cheap recycled and plasticized material can be used as a filler material that may provide interesting additional properties such as toughening [93]. Attention must be paid to the migration and compatibility of the plasticizer of each phase, since PVB can accept only a limited amount of plasticizers in comparison to PVC [51]. PVB was reported to act as a thermal stabilizer of PVC owing to radical substitution of chlorine atoms on PVC chain by PVB, interrupting the dehydrochlorination of PVC and HCl scavenging by acetic acid or butyral moieties [72,123]. Miscibility has been observed for amounts of PVB lower than 10 wt% [124]. Blends with phenolic resins (phenol-formaldehyde) without chemical reaction with the OH groups (but with strong hydrogen bonding) and without catalyst enable the preparation of mesoporous carbon fibers [125,126]. Finally, miscellaneous blends with technical polymers such as polyvinylpyrrolydone (PVP) [127,128] or polyaniline and sulfonated PS [129] are reported for membrane or humidity sensors. A variety of polymer blends with PVB are shown in Table 3.11.

3.7.2 Composites and Nanocomposites

This section will address mostly the particulate composites; indeed laminated glass can be considered as an evident laminated composite material based on the sandwich of glass and PVB, but this will be developed in Section 3.8. Apart from this case, most of the composites with a PVB matrix are nanocomposites. Because of its wide use in the green tape industry for ceramics and sol-gel applications, as a binder, PVB has been used in a great variety of mixtures involving various minerals. In this section also, only the composites and nanocomposites with functional applications other than binding will be addressed. The use of PVB as a binder will also be dealt with in Section 3.8. In fact, most of the work also refers to nanocomposites, and only a few conventional composites are mentioned. Among these, polyamide fibers in combination with silica [130,131] have been used in solvent-casting to generate high mechanical and impact resistance. Leather fibers (30–70 wt%) were mixed with PVB by extrusion and act as a reinforcing material with good distribution and adhesion between matrix and fibers [132]. Glass beads were melt-blended with PVB [59], mostly as a demonstrator for the use of silanes regarding adhesion to glass. Silica aerogel can be mixed at any amount with PVB to lower the thermal conductivity [133].

The other examples are nanocomposites, though unusually large amounts of filler were sometimes used. For example, silica was used at 15 wt% in PVB to prepare nanofibers by electrospinning and to enable modulation of the diameter of the fibers [134]. Nanocomposites with Fe3O4 nanoparticles at contents up to 14.5 vol% were synthesized, spray-dried, and further processed in injection molding, showing well-distributed nanoparticles and reduction of glass transition temperature, magnetic losses, coercivity, and saturation [135]. Barium titanate nanopowder was introduced in PVB in the range 60–90 wt% to change volume resistivity, dielectric constant, and dissipation factor and their variation with temperature [136]. High dielectric constant and low dielectric loss have also been obtained by addition of ferroelectric ceramic lead zirconate titanates (PZTs) at 85 vol% amounts [137]. Nanocomposites with clays of the montmorillonite type (Cloisite with sodium cations) were obtained in the melt with various intercalants such as 3-aminopropyltrimethoxysilane (APS), trimethyl chlorosilane (TMCS), and octyltrimethoxysilane (OTMS) and also using commercially modified montmorillonite (Cloisite 30B) [138]. All nanocomposites until 3 wt% of nanoclay reached a mix of intercalated and exfoliated structures with an increase in the breaking strength and significant changes in the light transmission. Nanocomposites of PVB and titanium oxide (TiO2) were prepared by the sol-gel process in film casting [139]. Pure PVB became stiff and brittle by the addition of TiO2, with more than a twofold increase in the Young’s modulus with 2 wt% of TiO2.
TABLE 3.11
Blends with PVB

<table>
<thead>
<tr>
<th>Blend</th>
<th>Targeted Properties</th>
<th>Process</th>
<th>Reference</th>
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<tbody>
<tr>
<td>PVB-PA6-PVA</td>
<td>Miscibility</td>
<td>Melt</td>
<td>[91]</td>
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<td>PVB-PA6</td>
<td>Miscibility—toughening—tensile properties</td>
<td>Melt-virgin or recycled PVB</td>
<td>[90,92,93]</td>
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<td>PVB-PA6-SEBS</td>
<td>Tensile and impact properties</td>
<td>Melt-recycled PVB</td>
<td>[94,95]</td>
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<tr>
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<td>Tensile and impact properties</td>
<td>Melt-recycled PVB</td>
<td>[96]</td>
</tr>
<tr>
<td>PVB-PA6-PP</td>
<td>Tensile and impact properties</td>
<td>Melt-recycled PVB</td>
<td>[95]</td>
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<tr>
<td>PVB-PP</td>
<td>Tensile and impact properties</td>
<td>Melt</td>
<td>[93]</td>
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<td>Tensile and impact properties</td>
<td>Melt, TPE, dynamic cross-linking</td>
<td>[93]</td>
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<td>[40]</td>
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<td>Tensile and impact properties</td>
<td>Melt</td>
<td>[98]</td>
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<td>Tensile properties, surface properties, hydrophobicity, permeation</td>
<td>Casting</td>
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<td>Dielectric properties, weathering resistance</td>
<td>Melt, casting</td>
<td>[102,103]</td>
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<td>Casting</td>
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<td>[113]</td>
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<td>[119]</td>
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<td>Morphology</td>
<td>Melt-spin coating</td>
<td>[120,121]</td>
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<td>Melt, recycled PVB</td>
<td>[122]</td>
</tr>
<tr>
<td>PVB-PVC</td>
<td>Toughness, tensile properties, thermal stabilizer, permeation, hydrophobicity, surface properties</td>
<td>Melt or casting, Recycled or virgin PVB</td>
<td>[51,72,93,123,124]</td>
</tr>
<tr>
<td>PVB-phenol formaldehyde</td>
<td>Carbon fibers</td>
<td>Melt-pyrolysis</td>
<td>[125,126]</td>
</tr>
<tr>
<td>PVB-PVP</td>
<td>Ultrafiltration</td>
<td>Spin-coating</td>
<td>[127,128]</td>
</tr>
<tr>
<td>PVB-PANI-SO3PS</td>
<td>Humidity sensors</td>
<td>Casting</td>
<td>[129]</td>
</tr>
</tbody>
</table>

Thermal and abrasion resistances were also improved. The solubility and the degree of swelling in ethanol became drastically lower by mixing a small amount of TiO$_2$, and nanocomposites containing 5 wt% were ethanol-selective in permeation. Sol-gel generation of nanoparticles is generally more efficient to generate enhanced properties both with silica or titanium dioxide even when prepared by melt compounding from colloidal sol in comparison to simple mixing of solid particles. Introduction of these nanocomposites within Kevlar/PVB composites showed very high mechanical properties with 5–7 wt% of nanofiller [130] and a glass temperature decrease. Functionalized
mesoporous silica added at amounts until 1.5 wt% in PVB composite films obtained by solution casting films yields thermodependence of the conductivity. Doping of silica was obtained by tripen-teraerythritol [141]. PVB–Al(NO$_3$)$_3$ sol has been reported as a precursor of alumina fibers in composites with PVB [142] owing to the reaction of aluminum nitrate nonahydrate with vinyl acetates and VAs. Carbonaceous materials have been also investigated using various allotropic forms. CB is used in combination with PCL to obtain a positive temperature coefficient of conductivity [97,106–109]; graphene provides improvements of the thermal and mechanical properties inducing toughness and flexibility for cast composites [34]; and oriented graphite modulates the thermal conductivity of composite sheets prepared by tape casting [143].

A wide development of functional nanocomposites is driven by the improvement and generation of new properties in the glass industry particularly in energy-saving glass since nanoparticles enable to keep transparency in the visible spectrum while still strongly interacting with the UV spectrum. Antimony-doped tin oxide (ATO) nanoparticles were employed to fabricate ATO/PVB nanocomposites. UV–Vis–NIR spectra show that the addition of ATO nanoparticles can significantly enhance the thermal insulating efficiency of ATO/PVB nanocomposites. With the increase in the ATO content, the thermal insulating efficiency is increased. UV can be almost fully absorbed. Visible transmittance is over 72.7%, and haze is below 2% when the ATO content is in the range of 0.1–0.5 wt%. The thermal insulating tests indicate a 1–3°C temperature reduction [139].

3.8 APPLICATIONS

PVB fits the checklist for an enormous number of applications, such as safety glasses for architecture and automotive, increasingly for encapsulation of solar modules in PV applications, and as a binder in various coatings, paintings, enamels, adhesives, and inks. All these applications are related to its tremendous adhesion properties on various materials through covalent and hydrogen bonding by the hydroxyl groups.

3.8.1 SAFETY GLASSES

PVB is an essential constituent of lightfast, highly transparent, elastic, and tear-proof films. The manufacture of PVB films for laminated safety glass is one of the most important applications of PVB. The outstanding properties of the PVB films include toughness, good adhesion to glass, good light resistance, and excellent transparency. The films are responsible for the special safety advantages of laminated safety glass. Laminated safety glass is a combination of two or more annealed or tempered glass sheets linked together with one or more films of PVB. Therefore, laminated glass is a composite material combining the properties of the glass and those of the polymer (glass adhesion, elasticity, impact resistance). The synthetic layer plays two roles. On one hand, it dissipates part of the impact energy by viscoplastic deformation and avoids projection of fragments because the glass splinters also adhere to the film minimizing the risk of injury. On the other hand, after impact, it will keep a residual strength ensuring the maintenance of the glazing. The interlayers can improve the mechanical performance of a glass and also, acoustically by attenuation of given frequencies, provide protection from UV and heat control while retaining transparency. Grades of PVB with a high molecular weight are combined with plasticizers to produce safety glass films in a thermoplastic extrusion process. The PVB film is pressed between two glass panels to create fracture-resistant and shatter-proof laminated safety glass used mainly in the building and automotive industries. Though other synthetic materials, resins, or gels can be used [144], PVB is most commonly used for laminated glazing applications because of its high compatibility with glass, due to its high transparency and its remarkable adhesive properties, and finally due to its viscoelastic properties guaranteeing a large deformation before failure and a maximum damping at low frequencies at room temperature [145–147].

The manufacture of laminated glass is performed through several steps including washing, assembly, degassing, autoclaving, and cleaning [148]. After precutting and possible shaping, in a
Washing step, glass products are washed to remove all traces of contamination and dried thoroughly. The assembly is performed in a closed chamber to avoid dust at a relative humidity of 30% and temperature of 18–20°C to avoid premature joining of glass and PVB film. Glass and PVB are stacked depending on the desired composition. Trimming of the laminate can be performed before entry in a preheating furnace. Degassing is the next operation and is critical to eliminate the air trapped between the PVB and glass and to get the proper clarity [76]. Sealing the edges avoids entrance of air during the final step of autoclaving (Figure 3.15). This is done by calendering in a preheating oven with temperature conditions depending on the composition and production speed. If the temperature of the preheating stage is too low, laminated glass cannot seal, while, on the contrary, too high temperature will cause seal edge early, which may stop the exhaust of air trapping large air bubbles in the laminated glass. For curved glass, such as automobile windshields, curvature is accomplished by differentially stretching the sheet heated at about 85–100°C over a tapered shaping drum. Rolls of sheet or precut interlayer blanks are usually stored or shipped refrigerated at 3–10°C, or shipped at ambient conditions with an interleaved thin sheet of plastic such as polyethylene to prevent blocking. The laminated glass is disposed into a vacuum bag or a vacuum rubber ring is put around the glass. Low pressure conditions (0.5–0.8 bar) are used to exhaust air out from the laminated glass before the sealing of the edges. The exhausting has two periods: one with cold air below 25°C during about 15 min, and the second in hot exhausting conditions with a temperature of laminated glass surface between 80°C and 110°C during about 30 min. Comparing the surface transparency of laminated glass through both production ways, the vacuum exhausting method is better than hot rolling exhausting. The final adhesion of the glass and PVB is carried out at a pressure of 12 bars and at temperature of 135–145°C in the autoclaving step, which allows a flow of PVB that fits perfectly onto the glass surface and creates adhesion. Temperature reduction is performed until 45°C under pressure; otherwise the edge of laminated glass will show bubbles. The cycle times depend on the composition of the laminated glass. If possible, a second calendering can be necessary to eliminate the excess of PVB by creep. Checking of humidity, adherence, and impact strength is required to the European standard EN ISO 12543-4. Manufacturing process also allows addition of dyes to be used as a decorative element. For laminated safety glass, the strength of the adhesive bond between the glass and the interlayer must be carefully controlled [58]. If adhesion is too high, a projectile can easily penetrate the laminate because cracks made in the glass propagate through the interlayer. If adhesion is too low, glass retention during an impact will be reduced, even though the interlayer is not penetrated. Alkanoate salts as well as moisture can act to reduce adhesion by competing with resin hydroxyls for bonding sites on the glass surface [3,58].

Typically, safety glass is composed of two or more glass sheets connected to each other by sheets of PVB. The number of leaves can reach up to 18 sheets, the thinnest being two glasses of 2 mm combined with an interlayer of 0.38 mm of PVB. Usually, safety laminated glasses are separated in various types depending on the level of performance and use: protection against injuries, against fall of people, against falling objects, against vandalism and burglary, against gunfire, and against explosions, and also enhanced protection. The composition of the safety glass is often referred to as xxx.y, with xxx indicating the glass panel and y the number of PVB sheets of 0.38 mm thickness. For example, 444.8 means three glass panels of 4 mm each separated by 8 layers of PVB with individual thickness of 0.38 mm. The thickness can be easily calculated by the sum of individual thickness and therefore is the specific weight (in kg/m²) with a glass density of 2.5 g/cm³ and PVB
density of 1 g/cm³. Double- or triple-laminated glasses are used for separation, stairwell, roof, balcony, shop display, and protection against burglary, vandalism, and riot including explosion (Figure 3.16) [149].

In architecture, for protection of, or simple security to protect, people from accidental impact against a glass, the safety glass must withstand shocks of a person falling against a window. If the glass cracks, PVB will hold the glass pieces together and prevent their dangerous dispersion. This uses two glass panels with a minimum of one PVB layer, and it is used for the glass in doors, windows, shower screens, bus shelters, and roof glazing. For protection against injuries with risk of fall, for example, in a tall building, the glass pieces must remain in place and protect the fall. At minimum, two glass panels are laminated with two PVB layers; typical compositions range from 33.2 to 44.6. They are used for balcony railings, banisters, spandrels, balustrades, internal partitions, lift partitions, and façade glazing to the ground level. These compositions are also used for protection from simple burglary that does not use heavy objects. Glasses developed to be used against organized burglary are resistant to destruction of a window by means of a hammer or an ax to make an opening of 400 × 400 mm. Typical compositions are 444.8 to 444.12. Depending on breaking strength requirements, they can be used in private residences, commercial office blocks, urban event locations such as high-risk shop windows. Security against weapons requires the use of asymmetrical laminated glasses such as 3663.6 or a combination with other polymers. PVB composites are layered with a film of poly(ethylene terephthalate), acrylic, or polycarbonate, or metal fabric in addition to glass [150]. The application ranges from counters and glazing in banks, vehicles transporting money, and embassies. A grid of copper that is extremely thin (0.08 mm in diameter) and barely visible can also be introduced between the PVB layers in order to trigger an alarm in case of cutting the thread or to provide radio-frequency shielding from an external source. In addition to security issues, the PVB interlayer has also a significant effect on other functional properties. It enables the blocking of 99% of the UV rays (below 380 nm) of the sun preventing the fading of colors of fabric, furniture, and flooring over time, especially upon addition of particles (Figure 3.17) [151,152] or by use of diffractive holographic elements [153]. Colored films can also be used for visual improvements. Due to its viscoelastic properties and low $T_g$, especially upon addition of a plasticizer, PVB provides also the damping of vibration and sound. To increase damping effectively and to obtain good sound attenuation, laminated glass is used with a viscoelastic plastic interlayer that changes vibration energy into heat energy. Special grades known as acoustic PVB are used in multilayer assemblies. These grades have a low glass transition temperature between 16°C and
18°C, and therefore the relaxation modulus at 20°C at 3 s (which is considered to be representative of a typical wind load) is 10 to 100 times less than that of conventional PVB (Figure 3.18) [154–158]. For example, the use of acoustic PVB yields 10 dB of noise reduction for a 6 mm laminated glass in the 1000–3000 Hz band (Figure 3.19), which is the noise transparency range that lets the most irritating noise through inducing a 50% reduction of perceived sounds [159].

Looking at the history of automotive glazing, laminated glass with a PVB interlayer was first introduced in the United States in 1935 and regulated by law in 1938. In 1964, high penetration resistance laminate was developed for passenger safety. New functions are now required for automotive glazing such as comfort, security, and environmental issues in addition to safety. Modifying
the PVB interlayer is a practical way of adding new functions. Noise reduction is targeted and can be further improved by the use of multilayer films, keeping a high mechanical resistance. Indeed, the acoustic interlayer is inferior to the normal PVB interlayer in terms of mechanical strength and handling because of low elasticity or softness required for damping at ambient temperature. For example, three-layer make-up has a low elasticity PVB layer as a core for maximum acoustic performance and normal PVB resin as outer layers for mechanical strength and handling ease. Damping is particularly increased in the 100–300 Hz band associated to engine noise [160]. Solar control PVB for windshields has also been developed with very high absorbance in UV and IR and 70% transmittance in visible light [142], decreasing air temperature in the vehicle by 1°C in a midday average weather condition in Colorado [161]. An interlayer with gradient color bands is also made for automotive windshields. The band is printed on the interlayer surface or tinted by coextrusion with pigmented resin.

3.8.2 Module Encapsulation in PV Application

Since the 1980s, the experience in lamination and high level of control of these technologies has driven intensive developments toward the use of PVB films for solar module encapsulation, and nowadays, PVB is increasingly assuming a leading role among alternative encapsulation materials for solar cells as EVA copolymers. Reliable and long-term protection of solar cells from external influences is required for solar modules. Transparent plastic encapsulation materials contribute to the durability of PV modules and to the long-term generation of electricity from sunlight. The first manufacturer worldwide to develop a special PVB film for use in solar modules was Kuraray Europe GmbH with Trosifol trademark. Solar modules using PVB films have been successfully undergoing outdoor weathering tests since the beginning of the 1980s. To ensure module durability and long-term power generation, cell encapsulation materials have to display certain important features such as mechanical protection of the cell, protection from weathering, electrical insulation, external impact resistance, barrier to oxygen and water vapor, prevention of cell corrosion, adapted adhesion to other module components (glass, cell, backing film, contact), and obviously high transparency and high UV protection (to prevent degradation of the plastic). There are few plastics that display all of these properties reliably in practice. Classical solar modules using crystalline Si wafers are encapsulated between two layers of PVB (Figure 3.20) and glass. In thin-film PV
Polyvinyl Butyral modules, the semiconductor photoactive layer is applied directly on a glass substrate and separated from the front glass by a PVB film. The few polymer materials suitable as encapsulation products and industrially used today are mainly cross-linked elastomers and thermoplastic materials. The cross-linked elastomer products are EVA, TPU and acrylate encapsulation resins, and two-component silicones that cross-link on exposure to heat and/or UV light to form a rubber-elastic material and thus firmly embed the solar cell. Thermoplastic products melt without cross-linking on exposure to heat, thus retaining their original chemical composition. PVB is the most important encapsulation alternative, particularly for thin-film solar modules, and competes with TPU, ionoplastics, modified polyolefins, and thermoplastic silicones (TSI). The advantage of PVB for PV application is the high transparency [162] of this material in the effective wavelength window of solar modules above 450 nm (Figure 3.21) [163]. However, PV modules must also stand for corrosion and aging, and the major causes are humidity and UV radiation. The encapsulant is important as it stores and disperses water on the one hand and decreases the transparency due to UV radiation on the other hand. The thermoplastic foils (TPU and TSI) show the highest water vapor transmission rate, whereas the ionomer foils show the lowest. The saturation concentration of PVB is the highest, followed by TPU and EVA, while silicone and ionomer store practically no water [164]. Ionomer and PVB offer higher protection from environmental exposure for thin-film modules than

**FIGURE 3.20** Various types of solar module assemblies.

**FIGURE 3.21** Transparency of PVB in the range of maximum yield of silicium solar devices. (From Kuraray, Trosifol—Solar Module Optimisation with PVB Film—Solar Technology in Perfection, Hattersheim am Main, Germany: Kuraray Europe GmbH. Adapted and reproduced with permission.)
EVA, with diffusion being higher in PVB but solubility being higher in EVA. Adhesion of PVB to glass remains a key advantage [165]. The performance and reliability of a PV module can also be affected by the degradation behavior of the polymeric components, especially in hard weathering conditions caused mainly by UV irradiation, temperature, and humidity. High irradiation doses, large temperature gradients between night and day, and high humidity at high temperature may easily impair the components with various kinds of degradation processes, especially discoloration, that lead to transmission losses and delamination. Corrosion of the metallization is less critical with PVB than with EVA that may release acetic acid, but PVB suffers from sensitivity to hydrolysis.

Depending on the type of PV module, PVB can be processed in single-stage vacuum laminators or in the two-stage process using de-airing in a bag or in a calendar with subsequent autoclaving. In vacuum laminators, films are de-aired, pressed, and cooled; the cycle time is 8–20 min for glass/back sheet and 8–25 min for glass/glass modules, depending on glass thickness. On the same principle as laminated safety glass, glass/glass modules can be de-aired in bags made of plastic or rubber and in a vacuum of less than 100 mbar in a hot-air oven. The maximum temperature is about 135°C. The modules are finally laminated in an autoclave at elevated temperature and pressure. Roll laminator permits high machining speeds, even for large-format modules, with short cycle time (1 min).

### 3.8.3 MISCELLANEOUS APPLICATIONS

Many coatings, paintings, enamels, adhesives, and inks are based on PVB due to its excellent adhesive properties in connection to the hydroxyl content and to the flexibility that can be brought to the thermosetting materials. The hydroxyl groups enable good wetting of most substrates and provide reactive sites for chemical combination, self-crosslinking, or cross-linking with phenolics, epoxies, isocyanates, melamines, or ureas. It is used both in powdery and liquid coats.

PVB resins may be used in stoving or wire enamels to overcoat magnet wires so that coils made from that wire can be easily bonded with heat (hot air bonding, oven, resistance, or electric) at moderate temperatures, 110–140°C, or by solvent activation with ethanol or methanol. Such wires are used in stepping motors for quartz watches, sound application coils, sensors, and RFID cards.

PVB is used alone or in combination with a wide variety of resins to give functional surface coating compositions. Films that may be air-dried, baked, or cured at room temperature can be obtained by dip-coating for improved corrosion resistance [102,166,167]. In protective coatings for metal, PVB is used as wash primers to obtain effective corrosion inhibition due to good adhesion to metal and fast drying. It improves coating uniformity, minimizes cratering, improves adhesion, and increases coating toughness and flexibility. It is widely used on metal surfaces: in storage tanks, ships, airplanes, bridges, and dam locks. Wash primer is very effective for inhibition of corrosion in a single treatment. Combination of PVB, chrome pigment, phosphoric acid, and metal complex yields the phosphatizing of the metal surface and acts as a corrosion-inhibiting pigment in an adhering binder also supplying chromate ions to repair pin holes in the phosphate film. Adhesion is improved by stoving at temperatures up to about 140°C. Because of concerns about the toxicity of chromium compounds, systems using zinc borate, phosphate, or molybdates are increasingly used.

Coating metal foil (aluminum, brass, tin, lead, iron) with PVB solution increases moisture-proofness and printability. Application is made by brush, spray, dip, and fluidized bed for drum and can linings, and curing enables to meet the extractability requirements of the US Food and Drug Administration for indirect food additive uses.

PVB is used as a component of wash coats and sealers for wood providing holdout, intercoat adhesion, moisture resistance, flexibility, toughness, and impact resistance to the coating. The wood substrate is protected against discoloration for polyester and polyurethane coatings. Combination with phenolic resins gives excellent barriers to bleeding of terpenes from wood.

PVB combined with nitrocellulose and plasticizer has been used in paint for leather. But generally it is also suitable to coat textiles to give water and stain resistance without affecting appearance,
Polyvinyl Butyral can be applied as a transparent film to practically all common textile materials such as cotton, wool, silk, nylon, viscose rayon, and other synthetics. PVB and aluminum isopropanol were deposed by dip coating on carbon fiber and used as a precursor of a hybrid coating of aluminum oxide and amorphous carbon that improves thermal stability of carbon fiber and its adhesion toward aluminum matrix [168]. Mixtures of PVB and phenolic resin are used as structural adhesives for bonding metal, glass, leather, wood, cloth, paper, and other materials. After the solvent has been completely removed at room temperature, the surfaces are heated and pressed together with curing time and temperature at 160°C for 15–30 min. In printed-circuit board adhesives where peel strength, blister resistance, and dielectric properties are required, such mixtures are used in joining the prepregs of phenolic laminate with copper foil. PVB can also be a base for hot melt adhesives providing a tough, clear film with adhesive strength. PVB binds the glass beads used in retroreflective films for license plates, decals, and road signs.

PVB is used in printing inks because it is soluble in mild solvents such as alcohols and esters, and it improves flexibility, adhesion, and toughness of inks used for gravure, screen, ink jet printing, and flexography. PVB is also soluble in aromatic and fast-drying solvents for high-speed and high-quality printing. Actually, it is used in many printing technology as conductive pastes, printer ribbons, pen inks, and offset printing plates. It also serves as a secondary binder in toners to increase viscosity, to improve film integrity over the fuser roll, and to minimize the level of fine particles [14,162]. Finally, owing to its outstanding binding power and elasticity, PVB is suitable for the manufacture of ceramic slurry and green tape with alumina [169,170], ferrites [171,172], barium titanate [173,174], silica zirconium, titanium, chromium, cerium, yttrium, and nickel [175–177]. Since it combuts with virtually no residue during sintering, it is an ideal temporary binder for the manufacture of high-performance ceramics provided that suitable conditions are used. This was demonstrated by many degradation studies in presence of various inorganics such as SiGe or FeSi2 [178,179], silica, mullite, α-alumina, and γ-alumina [180], glass ceramics and silver [181]. These tapes are used in the manufacture of multilayer electronic devices [182], and even in fuel cells [183], solid polymer electrolytes in dye-sensitized solar cells [184,185], and electrochromic devices (using lithium iodide, lithium thiocyanate, lithium perchlorate, and lithium triflate as dopant salts) [186] or sensors such as radiation dosimeters [187]. Nanofibers with polyaniline were used as humidity sensors [129].

3.8.4 Recycling of PVB

In the last few years, interest in recycling of PVB waste has been raised and it has driven a lot of investigations. Indeed, the total amount of produced PVB sheets including all industrial applications was estimated to be about 120,000 tons/year [79], and at present, PVB is much less recycled than glass, though the price could be half that of virgin PVB. The main issues for the recycling of laminated PVB are the removal of glass from the polymer, the prodegrading life cycle of PVB submitted to UV radiation and heat, and the unavoidable reprocessing step. Recycled PVB is separated into three categories. Category 1 includes transparent PVB (98% of PVB, free of any impurity), category 2 refers to colorless PVB (2% of impurities and 96% of PVB), while category 3 represents colored PVB (70% of PVB and 4% of impurities). PVB is recovered from laminated glass by mechanical peeling. More sophisticated and effective techniques [188] use mechanical cracking in a first stage, followed by chemical separation in alkali water solution at 60°C and final mechanical brushing of glass residues. Separation is efficient, though saponification of plasticizers can be expected. The only problem of this technique is that the saponification can leach plasticizers, and it changes PVB properties if excess of alkali (>0.5%) is used. A method for separation and decoloration of colored PVB sheets using ethyl acetate and decolorization reagent was proposed by Wang et al. [189]. Recovery of PVB with properties close to those of the initial plasticized PVB is possible, including chemical properties, amount of plasticizer, strain at break, tensile strength, fracture energy, and even optical transmittance, provided that the processing temperature is lower than...
260°C and that low amounts of alkaline reagent are used in the separation step [36]. Loss of plasticizers can be expected but the amount can be tuned. Low processing temperatures (below 150°C) were suggested for dry PVB, while PVB with moderate moisture contents (8 wt%) can stand higher temperatures because of a plasticizing effect [71]. Recycled PVB can be used for laminated glass and also as toughening agents in blends with other thermoplastics (see Section 3.7.1).

REFERENCES


