

Effect of Water and Acid-Base Reactants on Adhesive Properties of Various Plasticized Poly(vinyl butyral) Sheets

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ABSTRACT: We study the changes in adhesive properties of poly(vinyl butyral) (PVB) sheets assigned for safety glass preparation. PVB sheets have been produced by various worldwide manufacturers by simple blending methods such as extrusion, thermo-mechanical mixer processes, etc. Some samples were modified either by magnesium acetate or by oligo-functional organic acid to either reduce the adhesion to glass or to increase it. Adhesive measurements were evaluated on the air side and the tin side of the laminated glass. The study deals with a recognition of causes of the PVB adhesion change as a function of adsorbed water content into the polymer matrix. Results describe the influence of hydroxyl group content and amount of added acid-base reactants for adhesion adjustment of every tested PVB sheet. It also describes typical adhesion fluctuation and specific adhesion bonding of PVB sheets to glass in particular conditions. The analysis evaluates the best and the worst blend combinations and their modification on the adhesion change. We focused on adhesion sensitivity to increasing water content and the amount of added adhesion modifier. This work also evaluated the critical range of water content that provides adhesion fluctuation. The evaluation of various types of PVB sheets was performed and the most stable adhesion adjustment was found. Obtained values and comparisons are very important for the PVB sheets industry and for industry dealing with lamination of laminated glasses. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: laminated glass; poly(vinyl butyral); adhesion; acid-base agent

Received 27 July 2010; accepted 29 February 2012; published online 00 Month 2012

DOI: 10.1002/app.37597

INTRODUCTION

The plasticized polyvinyl butyral sheets are extensively used for laminated safety glasses for an automotive and a building industry. At present time, worldwide poly(vinyl butyral) (PVB) manufacturers are Solutia, DuPont, Sekisui, and Kuraray. Generally, polyvinyl materials possess excellent acoustooptical properties, which allow their utilization for acoustooptical modulators.¹ Acoustooptical property relates to the use of ultrasound to modulate or change the direction of light in solids. In particular, plasticized PVB is extensively used as PVB sheet for the production of laminated safety glass. The function of PVB sheet is gluing two or more glass surfaces together, rendering an excellent mechanical resistance to the break of the laminate.^{2–8} The laminate structure is shown in Figure 1. The adhesive bonds

between the glass and the PVB are created during the autoclave process of layered materials production. In this case, the most important characteristics of PVB-laminated glass are high strength and absorbability of mechanical energy at car-crash or another accident. Moreover, PVB interlayer must hold glass fragments on its surface and at the same time must adsorb kinetic energy with help of polymer toughness.^{2,7,9} All these described properties provide exactly adjusted adhesion level of PVB to glass.

In the case of automotive safety glass, it is required that the adhesion level is about 50% of maximal adhesion.^{2,10,11} High adhesion degree causes PVB breakage during the car crash. However, low adhesion degree does not keep the glass on PVB surface after the crash. The laminated glass used in building

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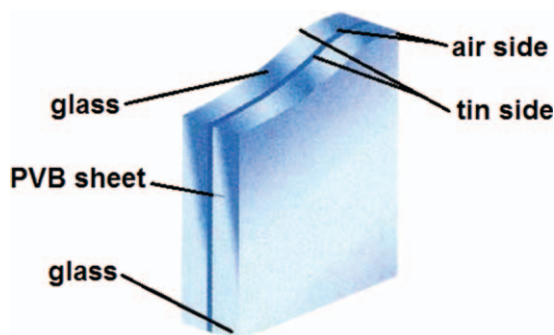


Figure 1. Description of the laminated glass structure. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

industry (safety glass of glazed skyscraper) has the adhesion requirement to be near to the maximal adhesion level.^{2,9}

The adhesive bonding force grows during the two independent steps. The first of them is a transport of PVB macromolecules toward the interface. This is generally described by a diffusion effect.^{3,12} Second part is a generation of Van der Waals interactions between these materials. The bond strength is determined by intermolecular distance and similarity of material polarities. Hence, adhesive force is provided by hydrogen bonding (H-bond) between —OH groups of PVB chain and the —OH groups in the glass.^{2,7,8,13,14} Such adhesive bonding is illustrated in Figure 2. This theory supports that PVB adhesion depends on water content in the polymer matrix.² The water adsorbed into the polymer matrix is bonded to —OH groups of PVB macromolecules.¹⁵ Hence, the measurement has revealed that water content around 2 wt % in PVB caused the saturation of binding sites.^{15,16} Above this level, the adhesive forces decrease and residual adhesion originates only from weak dispersion forces.

Similar hydrogen bonding can be observed in some cases of aggregation of molecules of water, alcohols, or organic acids. Generation of these bonds is reversible and H-bonding stability depends on temperature, molecule solubility, and the amount of dissolved salts, which adjust the polarity and pH of the system.^{2,14} In the case of PVB, it was observed that the adhesion is also reversible. As mentioned above, the PVB adhesion is usually ascribed to H-bonds.^{2,14}

Nowadays, the polymer material must be re-processed because of the increasing amount of the PVB waste.^{3,5,12,15,16} The recyclable PVB is created as waste during sheet manufacturing (material that does not meet quality specifications). The next source of a recyclable PVB material is a trim of the sheet. The trim produced as a waste from glass pre-lamination process is collected and re-processed. The trim and all collected materials are mixed. Unfortunately, the material, which enters to the extruder, has not homogeneous properties, and it is necessary to modify it to obtain the required adhesion grade. Moreover, PVB re-processing degrades polymer that causes changes in the adhesion to the glass.¹⁵ The PVB sheet with an adhesion degree that does not meet quality specifications does not fulfill required safety norms. Therefore, the adhesion adjustment by various reactants must be performed. The next significant technological

problem is the sensitivity of such PVB sheet to water content. Therefore, it is interesting to investigate all these above-mentioned problems.

This article is also focused on the adjustment of primary adhesion during the production of PVB polymer. The polymer made by an acetalization of polyvinyl alcohol has the “virgin adhesion” excessively high for direct use. Above mentioned high adhesion degree is caused by high activity of unacetylated hydroxyl groups in PVB chain (15–23 wt % of —OH groups).^{3,8,17,18} The virgin adhesion is mostly reduced by organic salts of alkali metals and alkaline earth metals added during an extrusion process of plasticized PVB. The most often used substances modifying the adhesion are salts of Na⁺, K⁺, and Mg²⁺ ions in strictly specified ion ratio and their total amounts.^{11,19,20,21,22,23} Moreover, keeping of water content in PVB at a range 0.3–0.5% is necessary for maintaining the required adhesion grade.^{2,18,19,23} This requirement is achieved by venting of water during plasticized PVB extrusion process.^{4,7,10} In the case of lower water content in the PVB sheet, alkali reacting ions are not hydrolyzed. Consequently, ions cannot inhibit active hydroxyl groups in polymer chain and the interaction between the glass and the PVB is not disturbed. However, higher water content in the PVB causes sharp adhesion reduction on “tin side” of the laminated glass. In addition, it is possible to see clearly the non-linear adhesion development on the “air side” of the laminate as a function of the water content in PVB. We have tried to find an explanation of this phenomenon in literature but such study has not been published yet.

With regard to above-mentioned PVB sheet adhesion requirements, the main aim of the work was to study a possibility of PVB adhesion adjustment by varying the water concentration level and also by addition of various reagents.

MATERIALS

PVB is a polyacetal produced by the condensation of polyvinyl alcohol with *n*-butyraldehyde in the presence of an acid

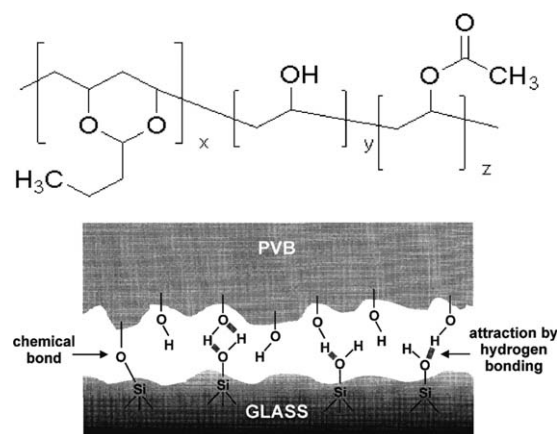


Figure 2. Adhesive hydrogen bonding between the hydroxyl group in a structure of the glass and the hydroxyl group of the PVB chain.² The bonding is present in the case of PVB without modifiers or at water content in PVB matrix up to 0.1%.

Table I. Sources and Description of Virgin, Mixed, and Blended PVB Sheets

Labeling and polymer description	Type of PVB material	Manufacturer modification	Plasticizer type	—OH group content in PVB chain (wt %)
But-3GO-L, M	Virgin, DuPont	No added agents ^a	3GO	18–18.5 ^{11,19,31}
But-3GO-P	Virgin, DuPont	No added agents ^a	3GO	18–18.5 ^{11,19,31}
But-3GO-S, V	Virgin, DuPont	No added agents ^a	3GO	18–18.5 ^{11,19,31}
But-4G7-Z	Virgin, DuPont	No added agents ^a	4G7	22–23 ¹¹
Saflex	Virgin, Solutia	No added agents ^a	3GO	18–18.5 ^{19,27,28}
S-lec	Virgin, Seki-sui	No added agents ^a	3GO	18–18.5 ^{19,27,28}
But-3GO-P +Mg	Alkali modified	Single material + 4 ppm Mg ²⁺	3GO	18–18.5 ^{11,19,31}
But-3GO-S +Mg	Alkali modified	Single material + 14 ppm Mg ²⁺	3GO	18–18.5 ^{11,19,31}
But-3GO-S +OA	Acidic modified	Single material + 7 ppm of organic acid	3GO	18–18.5 ^{11,19,31}
But-3GO-P +OA	Acidic modified	Single material + 35 ppm of organic acid	3GO	18–18.5 ^{11,19,31}
But-4G7-Z +OA	Acidic modified	Single material + 140 ppm of organic acid	4G7	22–23 ¹¹
Saflex + S-lec +OA	Acidic modif., blended	Blended material (3 : 2) + 45 ppm of organic acid	3GO	18–18.5 ^{19,27,28}

^aThe modification ‘no added agents’ labels PVB materials that compound only adjusting adhesion agents added by manufacturer for required adhesion grade.

catalyst.^{8,18,19} The condensation reaction produces 1,3-dioxane rings but the reaction does not run to completion. Residual unreacted hydroxyl groups promote indispensable adhesion to the glass surface during the lamination process.^{2,8,13,14,15} Although polyvinyl alcohol is produced from the hydrolysis of polyvinyl acetate, limited amount of acetate groups is also present. The final structure can be considered to be a random terpolymer of vinyl butyral, vinyl alcohol, and vinyl acetate (Figure 2). This atactic copolymer contains 18–22% of hydroxyl groups (depends on PVB type), less than 2% of acetate and about 76–80% of butyric acid.^{8,9,19} Tested PVB sheets are highly plasticized with the 28% of plasticizers based on branched oligoethylene glycol esters. In past, the different plasticizers were used. The system is differently plasticized and has different polarity. Therefore, different content of hydroxyl groups for better absorbability of applied plasticizer are being used.^{3,9,12,15,17,26,27,28,29} The different hydroxyl group content in polymer chain requires also different modification way and its adhesion stabilization of PVB to glass.

Samples

Virgin plasticized PVB sheets were commercial ones from DuPont (sheet Butacite), Solutia (sheet Saflex), and Sekisui (sheet S-lec). Some of them are suitable either for automotive industry or for building industry laminate glasses. The used materials with or without modification, the type of PVB and plasticizer, the adhesion grade as well as the —OH group content (wt %) in the polymer chain are shown in Table I. The plasticizer label 3GO means chemical composition triethylene glycol bis(2-ethylhexanoate) and the plasticizer label 4G7 means chemical composition tetraethylene glycol bis(heptanoate). Samples mixed with modifiers and blended materials were obtained by extrusion process which is described in the chapter “Methods”.

Precise amount of unacetylated hydroxyl group in polymer chain with used plasticizers is necessary for determination of

stability of polymer system.² Different hydroxyl group content would cause the plasticizer migration out of PVB matrix, especially at higher temperatures.¹⁵ The content of added adhesive adjusting agents (adhesive modifiers) is not available for all PVB sheets. Total amounts of added cations and hydroxyl group content are described in literature.^{11,18,22,23} These values were used for comparison and evaluation described in the article.

METHODS

Material blending and the modification mixing were performed in the single-screw extruder containing screen system with an aperture size up to 60 μm and sheet extrusion die.¹² Because of sheet extrusion to water, the PVB melt retains its shape, thickness, and specific sheet surface, which is necessary for de-aeration at pre-lamination process.³⁰ The consequence adhesion adjustment was achieved by addition of 5% water solution of oligo-functional organic acid or by addition of 15% water solution of magnesium acetate during the extrusion of plasticized PVB. Extruded sheets were conditioned in an air-conditioning cabinet (Weiss, Deutschland) to achieve the required water content in the sheet at 40°C. Conditioned PVB sheets were put between two glasses previously washed with demineralized water; the size of PVB sheets was about 5 mm larger than the size of the glass. Both glasses were oriented with “tin side” facing up. The glass sandwich was pre-laminated in the oven by nip-roll using calender rolls with 0.4 MPa and temperature 130°C. Fixed PVB layered samples were laminated in the autoclave with pressure 1.2 MPa and temperature 140°C for 20 minutes. After that, they were slowly cooled to room temperature.^{9,12,24,25} Finally, samples of laminated glass were cut out to the size 150 × 100 mm². Then water content and adhesion strength by Pummel test were measured.

The float glass used for samples preparation had common chemical composition 71.5% SiO₂, 13.4% Na₂O, 9.2% CaO, 4.15% MgO, 0.7% of Al₂O₃ and also other minor compounds. Float glass was delivered from company AGC Teplice (Czech rep.).

Nowadays, there is only one acceptable way for the float glass production. The float glass is made by the casting of the glass melt on the surface of the melt tin. Because of this fact, float glass has a uniform thickness and absolutely smooth surface that is necessary for the perfect PVB contact with glass during the laminating process. However, extremely thin tin layer remains on the bottom side of the float glass.⁹ This surface is called “tin side”. The tin film causes totally different adhesion response between PVB and glass with increasing water content in a polymer.⁹ The tin side of float glass was detected by UV illumination and all tested glasses were oriented to tin side facing up. It is determined by UV scattering on tin side of the glass and it creates slightly visible white reflexive layer.⁹ Hence, the PVB sheet was in contact with air side of the glass (up side of the laminate) and with tin side of the glass (bottom side of the laminate). The laminated glass contains layers “air side–PVB–tin side”. The complete laminate structure is shown in Figure 1.

The purpose of adhesion Pummel test is to measure the relative bond strength between PVB and glass. This method is described by US Patent.^{2,32} Deep-frozen samples at -18°C undergo repeated hammering with frequency 130 blows per minute of a hammer with weight 450 grams under controlled conditions. The test samples were held at about 5° angles to plane of the Pummel plate, so that only the edge of the unbroken glass contacts the plate. The frozen laminated glass is impacted with an automatic hammer until the glass is pulverized. The strength of the adhesion is subjectively graded visually by comparison to the standards of pummel scale ranging from 0 to 10. The standard for the lowest adhesion was totally exposed to plastic surface and was labeled as degree 0.0 °P; standard for the highest adhesion was plastic surface totally encrusted by the glass splinters and was labeled as degree 10.0 °P.

The water content in PVB sheet laminated between glasses was assessed by adsorption of infrared ray measurement at wavelength $1.92\ \mu\text{m}$ by water (PIER Electronic GmbH). The laboratory equipment was calibrated at room temperature to the standard type Butacite B5 (18% —OH group) at water content 0.16 and 0.75%. Measured glass was placed toward the equipment at angle 60° of detected infrared ray. The measured background was a common mirror.

Evaluation of water content in PVB sheets before lamination was performed by Karl Fischer method. This method is based on conductimetric assessment (at room temperature) of evaporated water out of the sheet (at 100°C) to a special solution of iodine and sulfur dioxide in methanol (Metrohm).

Alkali titer (total alkalinity of the product) of the sheet solution was determined by titration of 0.01 M - HCl with solution of 7.0 g of PVB sheet dissolved in $250\ \text{cm}^3$ of ethanol (ethanol is neutralized by 0.01 M - HCl with bromphenyl blue indicator). The FTIR spectroscopy was used to study the specific PVB adhesion bonds with glass in particular conditions. The measuring equipment Avatar 320 (NICOLET, CZ) with Attenuated Total Reflection (ATR) technique with 64 scans was used. Spectra were collected over the range $4000\text{--}550\ \text{cm}^{-1}$.

RESULTS AND DISCUSSION

PVB Hydrophilicity, the Influence of Water, and Acid–Base Reactants on the Adhesion to the Glass

The adhesion bond causing PVB adhesion to the glass was tested to find the adhesion fluctuation and confirm the

adhesion mechanism. Simultaneously, the adhesion change was estimated as alteration of various physical properties together with chemical reactants. As mentioned, for the comprehension of adhesion mechanism, it was necessary to know the adhesion sensitivity of every PVB sheet and how it is affected by suitable agent with water adsorbed in the polymer matrix. The activity or passivity of added adhesion modifiers is mainly influenced just by low water content (sometimes only 0.1%) that primarily influences the activity of —OH groups in PVB chain. Because of this fact, the water content was very important for final adhesion degree on the air side and on the tin side of the laminate; even without the addition of modifiers.

The influence of the humidity of environment on the water absorption rate in PVB sheets with various plasticizers and with various hydroxyl group content in the polymer chain was observed. PVB sheets Saflex, S-lec, and Butacite (type 3GO) have similar —OH group content and water absorbability. The ability of water to absorb to the PVB sheets is illustrated in Figure 3 by the curve for Butacite 3GO. The first curve describes the PVB with the plasticizer 3GO and the content of —OH groups is 18%; the second curve describes the PVB plasticized by plasticizer 4G7 and it has —OH group content 22%.^{31,32} According to Figure 3, polymer chain with higher content of hydroxyl groups (higher chain polarity) has higher water absorbability.

Obtained result indicates that water plasticizes the PVB matrix. This is manifested also on mechanical properties of PVB sheets; with increasing water content their strength reduces.¹⁵ Accompanying effect was significant whitening of PVB sheets, sharp haze increase and extreme light transmittance decline when the water content was in the range 3.0–5.0% (depending on the manufacturer and the sheet type).¹⁶

Next tests were focused on the influence of water on PVB adhesion change. Sheets were conditioned in a wide range of relative humidity of air. It provided water content in all tested PVB sheets in range 0.1–3.5%. The dissimilarity was observed only in the case of sheet Butacite 4G7, which had water content till 5.8% (Figure 3). Obtained results confirmed indirect dependence of adhesion degree to glass on water content.² However, it was observed only on “tin side” of laminated glass. The

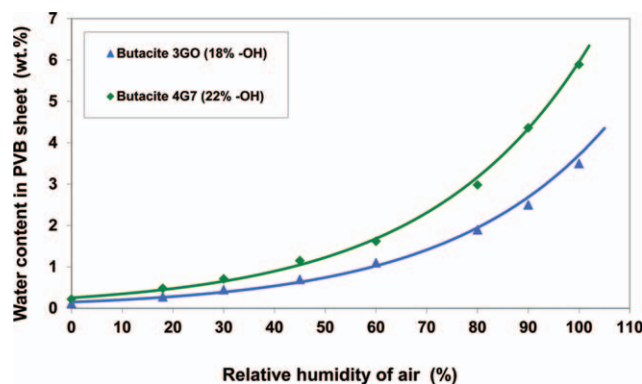


Figure 3. Influence of —OH group amount to absorbability of water. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

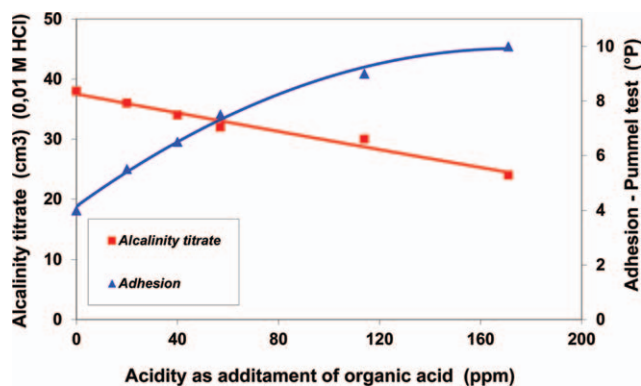


Figure 4. Dependence of alkali titer and adhesion (air side) to organic acid additament to But-3GO-P sheet, at Pummel test was sheet always conditioned to water content 0.5%. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

adhesion of “air side” of the glass provided totally different behavior. Therefore, acceptable reactants and their quantities for required adhesion degree were assessed. Results shown in Figures 4 and 5 confirm suggestions of Fowkes.¹⁴ These authors studied the influence of acid–base agents on the change of the adhesion forces and explained the adhesion mechanism. Results were obtained by modification of Butacite 3GO sheets (types But-3GO-P and But-3GO-V) either by magnesium acetate (MgAc) solution or by oligo-functional organic acid solution (pH = 1.5–2.0). The adhesion grade was assessed from laminated glasses prepared from modified PVB sheet conditioned to water content 0.5%. This water content was chosen because industry manufactured PVB sheets have the same water content and the adhesion on air side and on tin side is the same and this range of water content is easily attainable during manufacturing.

Inhibition of Hydroxyl Groups in PVB Chain

As demonstrated by preliminary tests shown in Figures 4 and 5, magnesium ions interact with hydroxyl groups in polymer chain and as a result of that, they are inhibited.^{2,14} Following adhesion reduction was directly proportional to alkali reacting ion content and to the active –OH group content in PVB chain. According to the results shown in the following sections (Figures 13–15) higher –OH group content in PVB chain needed higher amount of adhesion modifier to get the same adhesion change.

The adhesion modifiers influence the dependence of adhesion on the presence of water. The PVB sheet manufacturers mostly use salts of potassium, sodium, and magnesium for the adhesion reduction. Even though cations are the same; anions are different depending on PVB sheet manufacturer. Unfortunately, amounts of modifiers and their exact chemical structure could not be found in literature, patents contain usually wide ranges and many chemical compounds.²⁴

In addition to the previous observation, reagents with various alkalinities were tested to compare the adhesion reduction ability. It was found that the influence of reactants on adhesion is in the following order: NaOH > KAc > MgAc > H₃BO₃ > NaCl (from the most efficient to the worst). Generally, modifier

with higher pH caused more intensive adhesion reduction, and the water present in PVB matrix multiplied this effect. Most intensive response was observed by NaOH modification. Despite this fact, sodium chloride (neutral salt) did not change the adhesion degree. The boracic acid behaved as slightly alkaline reactant in this case.

The inhibition of polymer –OH group can be explained by alkali ion localization at the PVB–glass interface.² It exhibits a tendency to attract residual moisture from the sheet and eventually leads to clustering of water between the PVB hydroxyl groups and their silanol counterparts. This leads to a weaker adhesive bond. Therefore, alkali reacting ions can interact directly with PVB hydroxyl groups rendering them unavailable for bonding. This process promotes “alkali deactivation” of polar groups that cannot generate intermolecular bonding in mentioned conditions.² However, the active acidic center can be generated. This explanation of adhesion mechanism is described in the chapter “Activation of hydroxyl groups in PVB chain”.

Following tests were focused on the monitoring of adhesion at various water contents in PVB sheets. Several types of Butacite 3GO with various adhesive grades (achieved by various alkali ions content) were tested. The ratio of ions was each time K : Mg = 3 : 1. Depending on alkali ion content in Butacite 3GO sheets, it is possible to label following sheets in the alphabetical order L-M-P-S-V according to increasing PVB adhesion grade. The labeling But-3GO-L belongs to the sheet with the highest alkali modifier amount. For this sample, the lowest adhesion degree was detected (approx. 20% of maximum – measured at 0.5% of water content). However, Butacite labeled as But-3GO-V has the lowest alkali modifier content. The adhesion degree reaches the maximum (100%). It was found that But-L sheet contains approx. three times more of alkali ions than But-3GO-V. Results are shown in Figures 6 and 7.

According to above described behavior, higher alkali ions content causes more intensive adhesion reduction. It was confirmed on “tin side” of the laminates when the adhesion dropped down with increasing water content in every PVB sheet; this behavior was independent on alkali ions content as it is shown on Figure 7. The reason for absence of adhesion fluctuation on the “tin side”

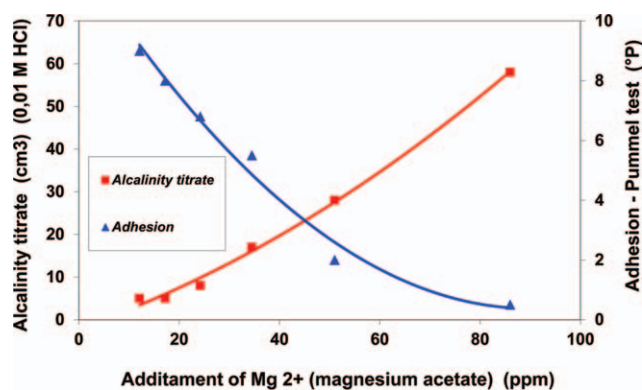


Figure 5. Dependence of alkali titer and adhesion (air side) to magnesium acetate additament to But-3GO-V sheet, at Pummel test was sheet always conditioned to water content 0.5%. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

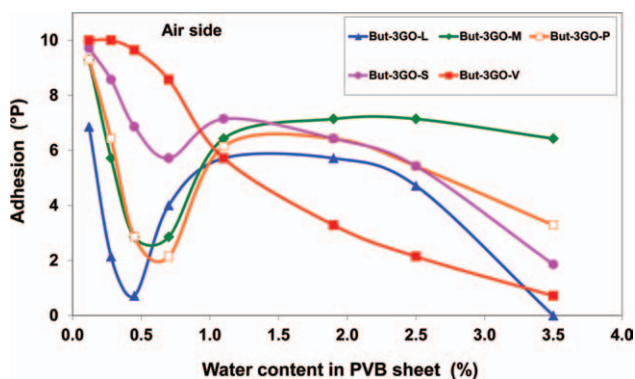


Figure 6. Adhesion behavior of Butacite sheets on water content increasing—air side of the laminate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

could be explained by the hydrolysis of tin nanolayer. The hydrolysis product locates in the interlayer between the PVB and the glass. This product should be complex compound of $[\text{Sn}(\text{OH})_6]^{2-}$ with alkali ion which does not react with free $-\text{OH}$ groups of PVB and the glass and inhibits the adhesion bond.

However, it was found that the common prediction mentioned above is not valid on the “air side” of the laminate at water content above 0.5%. Hence, the “air side” has completely different curve for adhesion with increasing water content in PVB regardless on alkali ions content as it is shown on Figure 6. The shape of the curve is very special in case of higher content of alkali reacting metals ions which is the best observable in case of sample But-3GO-L. Initially, there is a steep decrease in adhesion when the water content is in range 0.2–0.5%; the curve reaches a minimum. Then with increasing water content, the adhesion grows again till about 1.1% of water. When the water content is in range 1.1–2.3%, the adhesion has almost constant level. Finally with still increasing water content (in range 2.3–3.5), the adhesion drops again to 0. In case of lower content of alkali reacting metals ions, the adhesion fluctuation is not so intensive (But-3GO-S and But-3GO-P). The shape of the curves is similar but the fluctuations of adhesion are not so severe. Based on this observation, typical “adhesion fluctuation” in range 0.3–0.8% of

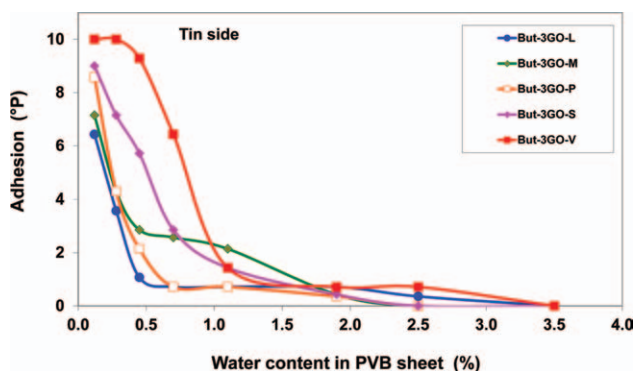


Figure 7. Adhesion behavior of Butacite sheets on water content increasing—tin side of the laminate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

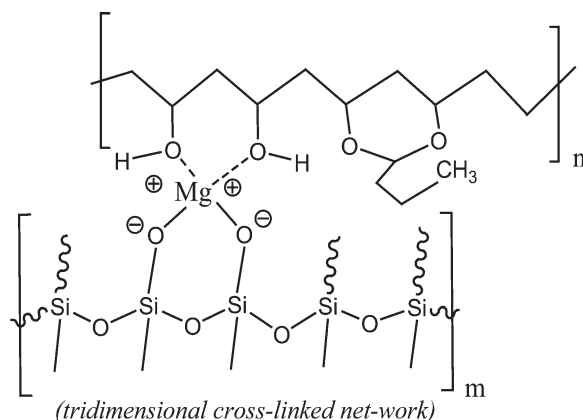


Figure 8. Generation of new adhesion bonding between PVB and glass at present of water content in range 0.8–2.5%.

the adhesion curve as a function of water content in the polymer was determined. Higher alkali ions content caused more intensive curve decrease and then the adhesion extremely grew at water content in the range 0.8–2.5%. This trend was clearly observed for all the PVB sheets (including acid modified materials). Above mentioned abnormality (sharp adhesion increase) was caused by alkali reacting hydrolysis modifiers. Products of the hydrolysis re-activate free $-\text{OH}$ groups of polymer chain and free $-\text{OH}$ groups of the glass. Probable structure of generated chemical compound is shown in Figure 8. Generated strong intermolecular adhesive bonding could be a combination of the Van der Waals and the ionic bonds. This structure was analyzed by FTIR spectroscopy and the results are shown in Figure 9 where there are curves for PVB with water content $<0.3\%$ and the PVB 0.8–2.5% treated with alkali ions. Specific intramolecular and intermolecular $-\text{OH}$ bands mentioned below were detected. As could be seen in Figure 10, changes in $-\text{OH}$ vibration area occurred for sample with water content in range 0.8–2.5%. The intensity of intermolecular $-\text{OH}$ bonds at 3398 cm^{-1} is growing together with peak area. For PVB material (But-3GO-P) with water content smaller than 0.3%, the peak area was 4.97 in region $3769\text{--}3002\text{ cm}^{-1}$. However, for the same PVB material with water content in range 0.8–2.5% treated with alkali ions, it was 11.58. Also new peaks at 3680, 1688, and

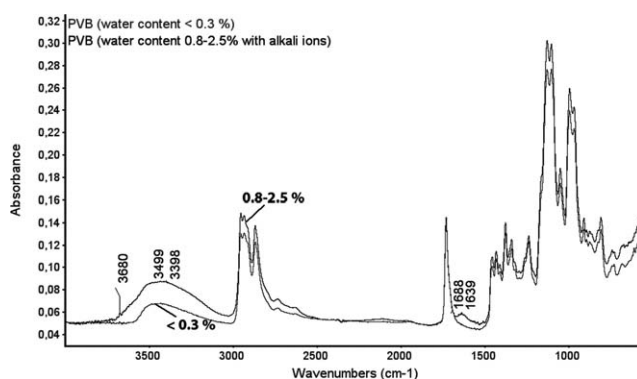


Figure 9. FTIR of PVB treated by alkali ions with different water content.

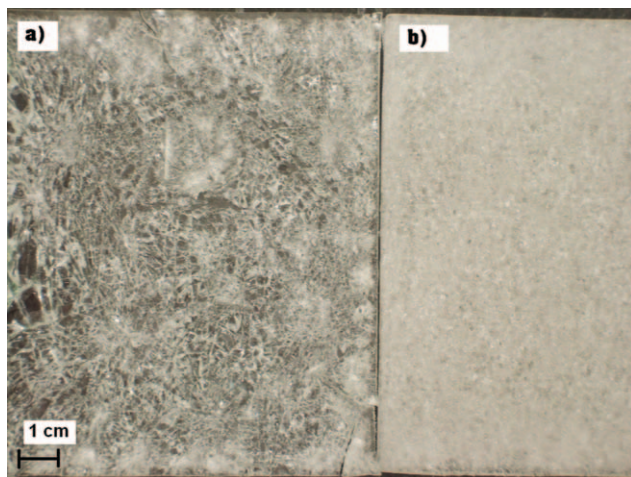


Figure 10. Air side of cracked alkali modified laminates with water content (a) 0.8–2.5% and (b) 0.3–0.6%. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

1639 cm^{-1} were detected. These vibrations are connected with predicted bond shown in Figure 8, and the results indicate that the new adhesion bond between PVB and glass is growing with increasing water content.

However, above-mentioned adhesion bonding (on the air side) disappeared when the water content exceeded 2.5%. In this case, present water generated interlayer that separated the two surfaces.^{11,16} Precise value of such adhesion loss for various types of PVB depends on the amount and a type of added alkali metal ion and its anion acting as adhesion modifier. Comparison of influence of water content on the adhesion of such PVB sheets is described in last chapter “The evaluation of acceptable behavior of adhesion curve”.

Figure 10 shows two different structures of broken glass. In both cases, the alkali modifiers were used but the water content was different. In case of low water content (0.3–0.6%) [Figure 10(b)], the glass fragments had very small dimensions (0.1×0.1 mm) and these small fragments could be broken into the dust. However, in case of higher water content (0.8–2.5%)

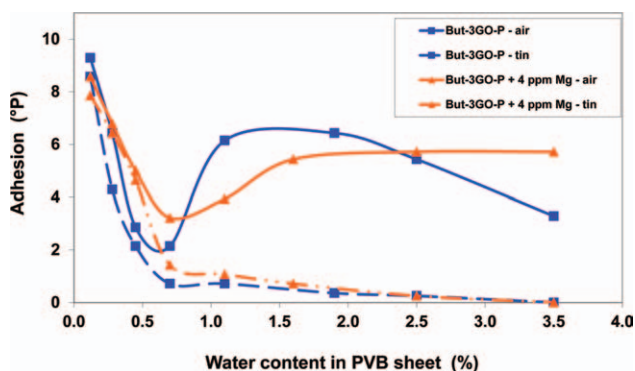


Figure 11. Adhesion behavior of Butacite 3GO, type S (18% —OH groups in PVB chain) and its modifying by 4 ppm of Mg^{2+} ions on water content increasing. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

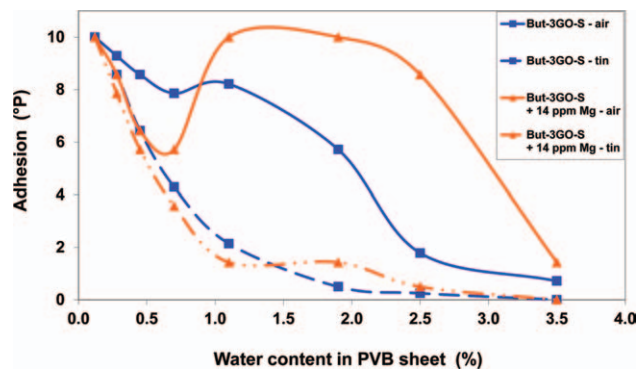


Figure 12. Adhesion behavior of Butacite 3GO, type P (18% —OH groups in PVB chain) and its modifying by 14 ppm of Mg^{2+} ions on water content increasing. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

[Figure 10(a)], the fragmented pieces had much larger size of glass fragments (0.5×0.5 mm). In both cases, the adhesion had high level but the structure of broken glass was quite different.

Following tests were focused on the confirmation of adhesion fluctuation and on comparison of modified and original sheets. PVB sheet But-3GO-P (with low adhesion) and the same polymer material modified by 4 ppm of Mg^{2+} were tested. Similarly, PVB sheet But-3GO-S (intermediate adhesion) and the same PVB material modified by 14 ppm of Mg^{2+} (both added as magnesium acetate) were tested. Resulting adhesion stability in relation to water content in the sheets is illustrated in Figures 11 and 12. Addition of magnesium ions to both Butacite sheets caused only slight adhesion change on tin side. This confirms previous results from adhesion testing of commercial sheets (Figure 7). Moreover, the addition of 4 ppm of Mg^{2+} to material But-3GO-P was too low for generation of any significant adhesion change. However, higher dosage (14 ppm of Mg^{2+}) to material But-3GO-S was sufficient for visible adhesion change when the water content was about 0.5%. Important conclusion of this experiment is that addition of magnesium ions to both Butacite materials evokes more pronounced “adhesion

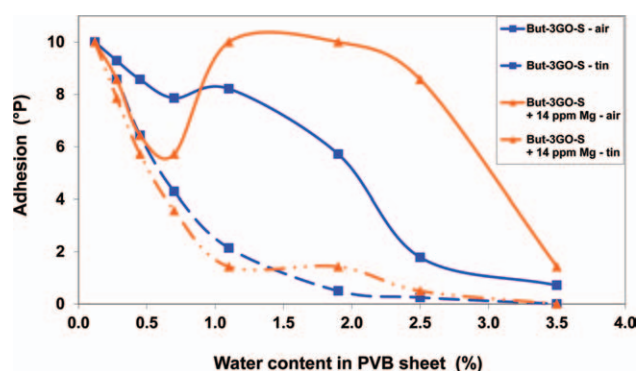


Figure 13. Adhesion behavior of Butacite 3GO, type P (18% —OH groups in PVB chain) and its modifying by 35 ppm of organic acid on water content increasing. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

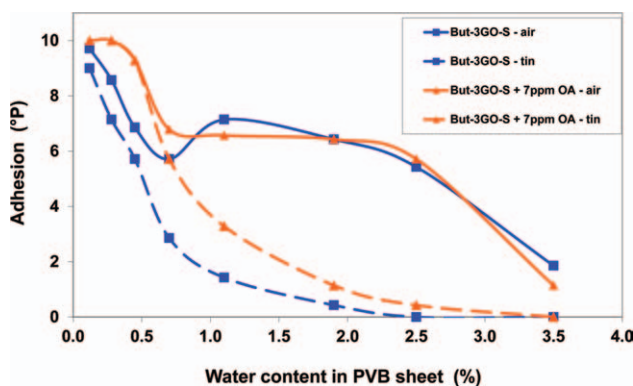


Figure 14. Adhesion behavior of Butacite 3GO, type S (18% —OH groups in PVB chain) and its modifying by 7 ppm of organic acid on water content increasing. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

fluctuation” on the air side of the laminate. It confirms results from the testing of commercial PVB sheets shown previously (Figure 6).

Activation of Hydroxyl Groups in PVB Chain

Successful testing of alkaline PVB modification indicates that acidic reacting agent can cause an adhesion growth. The modification by multifunctional organic acid was tested on PVB sheets from various manufacturers with different types of plasticizers, hydroxyl group content, and adhesion degree. The adhesion increase was directly proportional to the amount of added organic acid as shown on Figures 12–17. The addition of acidic agent neutralized alkali ions present in PVB matrix (that were added by a manufacturer) and thus activates —OH groups in the polymer chain and in the glass. Therefore, cations are not able to inhibit these hydroxyls and the adhesion increase can be observed. As it is shown by our results, higher cation content in PVB matrix or higher hydroxyl group content in polymer chain required higher amount of acid adjusting agents to attain the same adhesion degree. It is perceivable from the results illustrated in Figures 13–15. Generally, the adhesion increase is achieved by protonating of hydroxyl groups and by creation of active centers

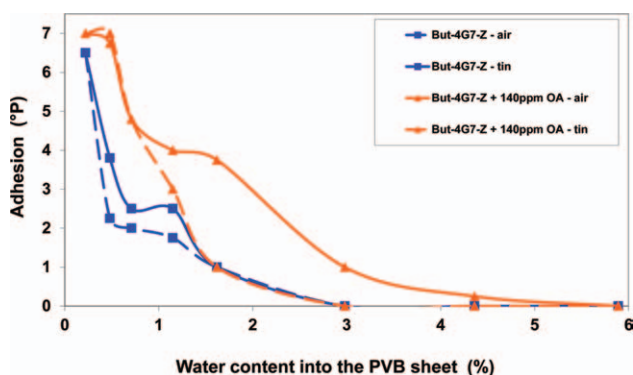


Figure 15. Adhesion behavior of But-4G7-Z (22% —OH groups in PVB chain) and its modifying by 140 ppm of organic acid on water content increasing. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

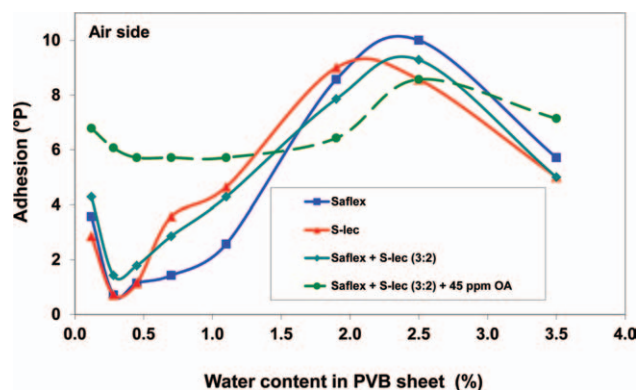


Figure 16. Adhesion behavior of Saflex and S-lec sheets and blended material in ratio 3 : 2 and the blend modified by organic acid on water content increasing—air side of the laminate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

on polymer chain. Acidic modified PVB sheets exhibit several times higher adhesion stability on the air side and on the tin side of the laminate with changing water content; in another words, the adhesion curves had no fluctuation. Thus, the shape of the adhesive curve is quite different compared with the curve of alkali-modified PVB. It is the best visible in case of sample But-3GO-S + 7 ppm organic acid (air side). Initially, there is a slow decrease in adhesion when the water content is in range 0.3–0.8%. When the water content is in range 0.8%, the adhesion has almost constant level. Finally with still increasing water content (above 2.5%), the adhesion gradually decreases again to 0. Generally, the shapes of the curves of acidic-modified PVB sheets are similar; the adhesion fluctuations are suppressed.

Following text describes a comparison of such PVB types before and after acidic modification. Samples contained original amounts of alkali ions (modifier) from the manufacturers; But-3GO-P contains approx. twice more of the alkali ions than But-3GO-S. Because of above-mentioned difference in the amount of alkali ions, we have decided to add five times more organic acid to the material But-3GO-P to achieve the same adhesion degree compared with But-3GO-S. Required adhesion level was expected when the water content was around 0.4–0.5%.

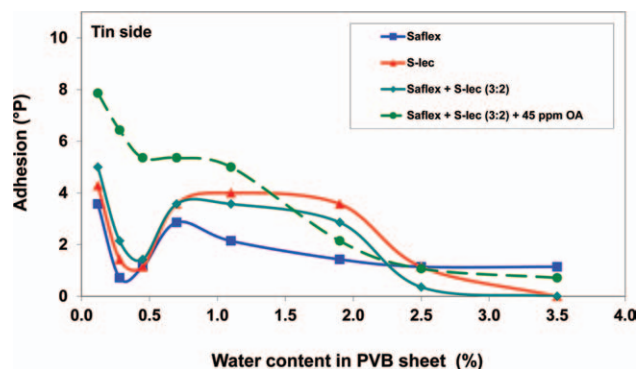


Figure 17. Adhesion behavior of Saflex and S-lec sheets and blended material in ratio 3 : 2 and the blend modified by organic acid on water content increasing—tin side of the laminate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

According to expectation, adhesion level increased proportionally to the amount of added organic acid as it is shown in Figures 13 and 14. Final adhesion curves of both compared materials do not exhibit any adhesion fluctuation. Thus the addition of acidic modifiers decreased the sensitivity of adhesion to water content.

In the case of acidic, non-modified PVB sheets Butacite-3GO, the water content in range of 0.6–0.8% evoked sharp adhesion increase on the air side. Moreover, these sheets exhibit much higher adhesion fluctuation and with water content above 2–3%, the adhesion drops to 0 value (depending on modification degree). However, acidic-modified sheets have much more stable dependence of adhesion to water content and the adhesion was maintained even at higher water content in the sheet (compare Figures 13–17).

Next observations were focused on the comparison of But-4G7-Z and But-3GO-P. Both mentioned Butacite sheets are in the same adhesion grade when the water content is approx. 0.5%. Nevertheless, But-4G7-Z and But-3GO-P sheets are plasticized by different plasticizer and both PVB samples have also different —OH group content (22 vs. 18%). Moreover, these materials have not only dissimilar —OH group content but also they have different adhesion adjusting system. Although But-4G7-Z material is modified only by K^+ ions, the But-3GO-P material is modified by mixture of K^+ and Mg^{2+} ions.^{11,18,33} Moreover, PVB type But-4G7-Z with higher content of —OH groups in polymer chain has to contain approx. five times more of alkali ions to reach the same adhesion degree.¹¹ It is obvious that the amount of added organic acid must be proportional to the hydroxyl group content. Tests demonstrated that higher amount of acidic modifier must be added for activation of higher amount of hydroxyl group in polymer chain to achieve the same adhesion change. The dissimilar hydroxyl group content and the adhesion adjusting system caused higher hygroscopic behavior of polymer system But-4G7-Z, which multiplies the influence of the adhesive centers. As a result of that, the adhesion stability of But-4G7-Z was quite different in the whole range of relative humidity (0–99%). Along with that, it brought higher sensitivity of But-4G7-Z to adhesion change as a function of a change in the water content.

Because the materials from several producers are usually in industry mixed together, following study was focused on the observation of the adhesion behavior of the PVB mixtures as a function of water content. The main differences between the materials were either in —OH group content or in adhesion adjusting system. From these differences comes various adhesion degree and therefore these blends have to be modified. Consequently, virgin materials and their modified blends of common materials from worldwide manufacturers Solutia (sheet Saflex) and Seki-sui (sheet S-lec) were tested to find the adhesion change as a function of water content in PVB. Tests on Saflex and S-lec sheet and its extruded blend in wt ratio 3 : 2 and the same blends modified by 45 ppm of organic acid were performed. This content of organic acid was experimentally found to aim the adhesion of blended sheets to be in the typical range required by automotive glass industry. Increased acidity of the polymer elevated —OH group activation, which appeared as increased adhesion of all tested PVB sheets. The adhesion grew

on both sides of the laminate (the air and the tin side), and it was observed in the whole range of tested water content in PVB sheets as shown on Figures 16 and 17. Comparison of such PVB sheets is described in following chapter.

The Evaluation of Acceptable Behavior of Adhesion Curve (Air and Tin Side)

Generally, very important property of adhesion behavior part is a width of a wave of adhesion fluctuation of such PVB sheet (large drop followed by sharp increase). The curve width describes adhesion stability of the polymer to change of the relative humidity of environment air. Wide adhesion fluctuation means higher stability in a water content range being 0.3–0.6% (range adjusted by the sheet manufacturers). However, narrow adhesion fluctuation changed the PVB adhesion abruptly with a low difference of water content. Because all sheets have to be manufactured with water content being in range 0.3–0.6%, PVB adhesion can be influenced significantly just with very small change in water content, such as 0.1%.

Adhesion behavior on the air side of the laminates of Butacite 3GO, Saflex, and S-lec sheets exhibited similar results. Generally, the adhesion fluctuation was reduced either by addition of small amount of alkali reacting ion or by increased concentration of the acidic modifier. It led to narrowing of the fluctuation until it completely disappeared. Similar trend was observed for But-4G7-Z but with different localization of adhesion fluctuation (different PVB hygroscopic behavior).

Blended PVB sheet Saflex + S-lec has adhesion fluctuation in region 0.3–0.7%. It is necessary to remind that blended sheets were tested pure and also modified by the acidic agent. The activation of hydroxyl groups in PVB chain promotes substantial increase of adhesive curve at all ranges of water content in the sheet. Including above-mentioned facts, the acidity promotes a stability of adhesive humidity curve. Nevertheless, the comparison of blended PVB sheets Saflex+S-lec with acidic addition still points out on the high adhesion degree of these materials. The difference of Saflex material was clear particularly on the air side of the laminate above water content 3.0%. Very high adhesion degree was kept in very high water content level, even up to 7–8%. This abnormality was achieved by different adhesion adjusting system of every PVB sheet manufacturer. Unfortunately, the precise amount and composition of adhesion modifiers added by manufacturer is not available in literature.

All above-mentioned results are very significant for the use of PVB sheets in the industry. For example, sheet stored at relative humidity 80% contains approx. 2% of absorbed water. The lamination of this sheet renders the “safety glass” with absolutely inadequate safety properties.¹⁵ Moreover, water can cause haze that reduces the light transmission.¹⁶ Doubtless, such type of PVB sheet has higher sensitivity to the change of adhesion and optical properties with a change of water content in the sheet. The next significant result is establishment of a fact that the adhesion reduction to 0 value is accessible either by higher water content in the sheet or by the presence of alkali reacting ions. This conclusion could be useful during windshield recycling process. However, recovering of pure PVB without glass contamination has not been solved yet. High alkali solution can

reduce the adhesion to value that could provide separable and re-processable PVB sheet. Research of this recycling technology is a subject of our present work.

CONCLUSIONS

This study confirmed that in case of safety glass the adhesion between PVB and the glass is based on Van der Waals bonds between the —OH groups of polymer chain and the —OH groups in glass. However, these —OH groups should not be chemically or physically inhibited or otherwise this adhesive bond is not created (—OH groups are blocked). It was confirmed that the activity or passivity (inhibition) of —OH groups depends mostly on the pH of the system and on the water content in PVB matrix. Therefore, the measurement of adhesion in the whole range of relative humidity (0–99%) was performed and influence of water content on the adhesion was compared for various PVB sheets. Certain sheets were modified by either alkali or acid modifiers. It was confirmed that alkali modification decreases the adhesion of PVB to glass. However, it was discovered that acidic modification increases the adhesion of the polymer to the glass. Moreover, the acidic modification renders much smaller adhesion fluctuation and thus higher stability of adhesion with regards to water content in PVB sheet.

Obtained results confirmed that the adhesion to glass decreases with increasing water content. However, this phenomenon was detected only on “tin side” of the laminated glass. The adhesion on “air side” had unstable dependence with increasing water content in PVB, an adhesion fluctuation was found. Shape of the fluctuation curve was typical for each type of the sheet and each type of modification (pH influence). Thus this adhesion fluctuation plays important role when the water content is in range of 0.3–0.6% that is just the range set by PVB manufacturers.

Summary of this study can be described by the best and the worst type of the sheet including sheet modifications. The blend of acidic modified sheet Saflex and S-lec in wt. ratio 3 : 2 had the best properties of all tested materials. In this case, increased water content caused only minimal adhesion variation on the air side. Together with that, the tin side was also highly stable; the adhesion did not vary till water content 1.3%. Similar adhesion behavior was not found in any other case of tested sheets. However, absolutely unsuitable PVB sheet was the type But-4G7-Z. To increase the adhesion of this sheet, it was necessary to add approximately five times higher amounts of adhesion modifier compared to Butacite 3GO sheets (18 wt % of —OH groups) to get the same adhesion level. Moreover, But-4G7-Z was highly hygroscopic. Although the others tested sheets had adhesion grade between 4 and 7°P at 80% relative humidity; adhesion of But-4G7-Z dropped down to almost 0 level. These results and comparisons are very important for PVB sheet industry and for industry dealing with lamination of PVB between glasses. Influence of these factors on adhesion and comparison of moisture-adhesion curves for various PVB sheets has not been published yet until now.

ACKNOWLEDGMENTS

This work has been supported by the Ministry of Education of the Czech Republic as a part of the project No. VZ MSM 7088352102 and also with support of Operational Programme Research and Development for Innovations co-funded by the European Regional Development Fund (ERDF) and national budget of Czech Republic within the framework of the Centre of Polymer Systems project (reg. number: CZ.1.05/2.1.00/03.0111).

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