

Influence of Water and Magnesium Ion on the Optical Properties in Various Plasticized Poly(vinyl butyral) Sheets

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ABSTRACT: The study is focused on influences of optical properties change of poly(vinyl butyral) (PVB) sheets determined for safety glass preparing. Optic measurements were evaluated itself and after, the laminated glass was observed. The study deals with a cognizance of causation of the optical properties change in different PVB sheets in dependence on adsorbed water content into the polymer matrix. Results of this work describe the influence of —OH group content on PVB chain and type and amount of additives adjusting adhesion of PVB towards glass. However, the most important discovery of this work is evaluation of critical water content that leads to haze generation. The evaluation of various types of sheets was performed. At the same time the artificial

addition of Mg^{2+} salts of organic acids (with various polarity of the molecule) was evaluated to assess their influence on haze generation. It was found that haze caused by Mg^{2+} salt is possible to eliminate when there is certain water content in PVB. Obtained values and comparisons are very important for PVB sheets industry and for industry dealing with lamination of PVB between glasses. Influence of these factors and comparison of haze generation for various PVB sheets has not been published yet. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 2100–2108, 2010

Key words: laminated glass; poly(vinyl butyral); water absorbability; haze; adhesive agent

INTRODUCTION

Generally, polyvinyl materials possess excellent acouptical properties which allow using them for acouptical modulators.¹ Acouptical property relates to the use of ultrasound to modulate or change the direction of light in solids. In particular, plasticized poly(vinyl butyral) (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.^{2–7} The result of the autoclave process of layered materials is adhesive bond between the glass and the PVB. Laminated “safety” glass is required to have the high PVB adhesion to the glass together with excellent optical properties, which are: high light transmission of visible day-light and “zero haze”. The main requirement of light transmission (LT) of standard virgin PVB sheet in common lami-

nated glass is to be in the range 90.5–90.9%.⁸ It was found that the reprocessing degrades PVB and reduces the light transmission, per every reprocess cycle the LT decreases for about 0.2%. Therefore, companies producing PVB sheets specify a minimal LT value to be 89.5%.⁹ Even if the LT reduces for only several tenths of % it is extremely important for safety glass production. The PVB sheet with lower LT value could result decreased visibility through the laminated glass, in particular in dark environment. For example, darker strip on the top of the safety glass has LT about 80%.

Very important parameter describing laminated glass quality is haze of PVB sheet. Haze is caused by foreign particles, e.g. by poorly homogenized additives, dust, fibers, PVB degradation by-products, or by increased water concentration in the sheet. Most of these foreign particles are caught on the screens in the extruder. However, if the concentration of particles that went through the screens (with dimensions smaller than 50–100 μm) is elevated then the human eye can detect them as a haze with critical value being 0.6%.^{9,10} Moreover, haze growing can be caused by blending process of PVB materials with different content of —OH group in PVB chain.

The specific case of haze generation is increased level of water content (above critical value) in PVB matrix.¹¹ And this work focuses on finding this

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critical value for various commercial materials. Present water causes a milky haze and reduces light transmission. Nevertheless, the most intensive haze is caused by the presence of contaminations with the dimensions around wavelength of visible light (380 to 750 nm). Therefore, the optical properties of PVB matrix is very sensitive to dust particles, presence of water and additives forming coagulate. Nevertheless, different sensitivity of various types of PVB sheets to the change of optical properties by various sources is still not being solved. And therefore, this sensitivity to PVB optical properties change is the reason why this study focuses on the influence of presence of water and other additives in PVB matrix.

Another reason for the study of haze problem in laminated glass is a present technological process for laminated safety glass preparing. The edge of manufactured laminated glass is not sealed and the humidity can diffuse into the PVB sheet in safety glass. The PVB sheet has high water content, which causes very intensive haze in the edge of this laminated glass. Probably, the adhesion agent magnesium 2-ethylbutyrate which has been used in adhesion adjusting in PVB sheets Saflex and S-1ec, eliminates this inconvenient haze.

PVB polymer has to be highly plasticized to achieve required strength and elasticity of the sheet.^{2,12,13–15} Plasticizers for PVB are usually branched ethylene glycol oligo-esters.^{2,14,16–18} In past various plasticizers were used having different polarity and absorbability of water.^{2,17} Different polarity of plasticizer affects water absorbability of PVB sheet. Various PVB sheets with various plasticizers and adhesive adjusting agents can have different sensitivity of optical properties on water content. And therefore this study deals also with these influences.

Commercially produced plasticized PVB has high adhesion and cannot be used for automotive glass lamination. It is necessary to reduce the adhesion to about half of the original value.¹⁹ The adhesion toward glass can be reduced by addition of salts of alkali metals or salts of alkaline-earth metals.^{19,20} To avoid a haze generation it is necessary to apply a combination of anions and cations. The salt must be soluble in water and can be dispersed well into polymer system without aggregate generation. It should be emphasized that Mg^{2+} and Ca^{2+} ions play an important role in the charge transfer. Commonly, PVB sheets are produced with water content 0.4–0.5 wt %.²¹ Thanks to this fact the adhesion is kept at required value and there is no haze problem. Nevertheless, it was discovered that after reaching critical concentration of the adhesion modifier or above critical water content the haze is generated. However, to our best knowledge, until now both of these men-

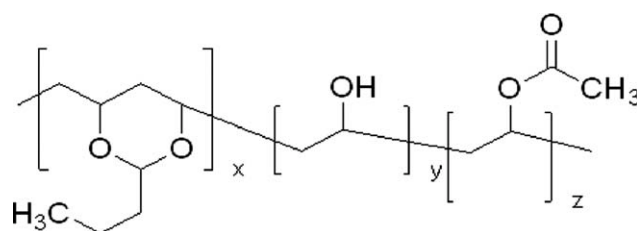


Figure 1 Poly(vinyl butyral) chain structure.

tioned critical concentrations for the haze generation have not been published yet. And therefore this was a subject of this research work, more specifically the influence of water and adhesion modification additives on haze generation and change of light transmission.

MATERIALS AND METHODS

Materials

PVB is a polyacetal produced by the condensation of polyvinyl alcohol with *n*-butyraldehyde in the presence of an acid catalyst.²² The condensation reaction produces 1,3-dioxane rings but the reaction does not run to 100% conversion. Residual unprecipitated hydroxyl groups promote indispensable adhesion to the glass substrate through the lamination. Similarly to the polyvinyl alcohol production (hydrolysis) also in case of PVB some amount of residual —OH groups stays in the PVB chain. The final structure can be considered to be a random ter-polymer of vinyl butyral, vinyl alcohol, and vinyl acetate (Fig. 1). This atactic copolymer structure contains 18–22 wt % of hydroxyl groups (according to PVB type), less than 2 wt % of acetate and the rest is created by butyric groups (around 76–80%).^{2,18} Tested PVB films were highly plasticized with about 28 wt % of plasticizers, mostly branched ethylene glycol esters. PVB sheet Saflex and PVB sheet Butacite produced since 2004 were plasticized with plasticizer type 3GO, which is (triethylene glycol, bis(2-ethylhexanoate)). The applied 3GO plasticizer required unacetalized hydroxyl groups in PVB chain in the content of 18–19 wt %. The older type of PVB Butacite, produced before 2004 was plasticized with more polar plasticizer 4G7, which is (tetraethylene glycol, bis(heptanoate)). Because of this fact commercially produced PVB contain about 22 wt % of unacetalized hydroxyl groups.²³

Samples

Original plasticized PVB sheets were manufactured by DuPont, Solutia and Sekisui as commercial films. Some of them, which contain higher amount of alkali reacting ions were suitable for automotive

TABLE I
Sources and Description of PVB Films

Labeling and polymer description	Type of PVB material	Adhesion grade	Modification	Plasticizer	—OH group content in PVB chain (wt %)
Butacite-L, M	Virgin	Low	No added agents	Type 3GO	18.0–19.0
Butacite-B, P	Virgin	Intermediate	No added agent	Type 3GO	18.0–19.0
Butacite-H, S, V	Virgin	High	No added agents	Type 3GO	18.0–19.0
Butacite-Z	Virgin	Low	no added agents	Type 4G7	22.0
Saflex	Virgin	Intermediate	No added agents	Type 3GO	18.0–19.0
S-lec	Virgin	Low	No added agents	Type 3GO	18.0–19.0
Butacite-H +Mg	Modified	Automotive, intermediate	Single material + 14 ppm Mg ²⁺	Type 3GO	18.0–19.0
Saflex + S-lec	Blended	Automotive, intermediate	Blended material in ratio 7 : 3 and 3 : 2	Blended	18.0–19.0

Note: the modification “no added agents” labels PVB materials which compound only adjusting adhesion agents added by manufacturer for required adhesion grade.

industry. Some of them, which contain only lower amount of alkali reacting ions, were suitable for laminated glasses in building industry. PVB sheet with trade name Butacite B3 (manufacturer DuPont, USA) was made before year 2003 and it was plasticized with plasticizer tetraethylene glycol, bis(heptanoate) (with label 4G7).^{23,24} PVB sheets with trade name Butacite B5 made since year 2003 contain plasticizer triethylene glycol, bis(2-ethylhexanoate) (with label 3GO).²³ The same plasticizer 3GO was present in PVB sheet Saflex (manufacturer Solutia, USA) and in PVB sheet S-lec (manufacturer Seki-sui, Japan).^{12,13}

Unfortunately, the content of added adhesive adjusting agents (alkali reacting ions) was not found in case of PVB sheets Saflex and S-lec. These PVB sheets contain a combination of adhesive agents based on salts of 2-ethylbutyrate and acetate. The amount of mentioned alkali reacting ions also was not published for Butacite 3GO and Butacite 4G7, however, the rate of mentioned ions was found as a sum of added ions and the ratio of added potassium and magnesium ions in Butacite sheets (agents are added in form of acetate salt). Butacite 3GO samples with adhesion type L, M, S, V contain the potassium/magnesium in ratio 3 : 1.

Samples, which were mixed with magnesium additive or blended, were obtained from the manufacturer Retrim (Czech Rep.). The company is reworking PVB trim waste. All tested samples are described in Table I.

Sample preparation

A perfect material blending and the modification mixing were carried out in the single-screw extruder, with screens for filtering with an apertures size up to 60 μm and sheet extrusion head. PVB sheets were conditioned by air-conditioning cabinet

(Weiss, Deutschland) at various relative humidity contents and at 40°C.

Conditioned sheet was placed between two glasses and prelaminated by nip-roll with 0.4 MPa and 130°C. Both glasses were oriented with “tin side” facing down. Fixed PVB layered samples were laminated in the autoclave with pressure 1.2 MPa and temperature 140°C for 20 min. After that it was slowly cooled to temperature 35°C.^{25,26} The cooling by water flow was carried out at a cooling rate 1°C/min and took approximately 120 min. Finally, samples of laminated glass were cut to the size 150 × 100 mm². Water content and optical properties were measured.

Float glasses (AGC Teplice, Czech rep.) were used for laminated samples preparation. Float glass had common chemical composition 71.5% SiO₂, 13.4% Na₂O, 9.2% CaO, 4.15% MgO, 0.7% of Al₂O₃, and other compounds. Optical properties of one lime-soda glass with thickness 2.1 mm could be specified by 91.3% of light transmission and 0.05% of haze.

Methods

Optical properties of the laminate and PVB sheets were evaluated by VIS spectrometer (BYK-Gardner) measuring light transmission in a wavelength range 320–900 nm. All measurements were done at room temperature. The light transmission measurement was carried out as day-light adsorption either through PVB sheet or through PVB glass laminate. Obtained values were read at a wavelength 380–780 nm. The haze intensity was evaluated on the same lab equipment as turbidimetric analysis.

The water content in PVB sheet between glasses (in laminate) was assessed by the measurement of the absorption of infrared ray at a wavelength 1.92 μm (PIER Electronic GmbH). The lab equipment was calibrated to standards of a type Butacite with water

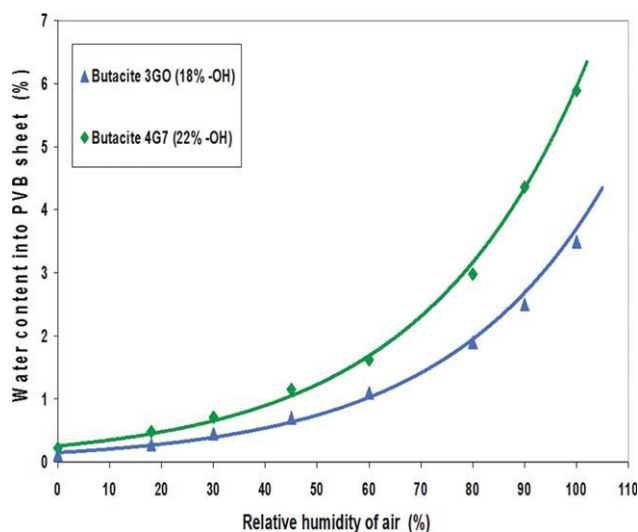


Figure 2 Influence of $-OH$ group content on water absorbability. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

content 0.16 and 0.75%. Angle between the laminate and the ray was 60° , the measurement background was mirror. Mentioned assessment may be bothered by a presence of proteins or compounds with intermolecular hydrogen bonding.

Measurement of water content in PVB sheets was carried out by the method of Karl Fischer. The method is based on conductometric assessment of evaporated water out of the PVB sheet; the water vapor is transported into special solution of iodide and sulfur dioxide in methanol. The analysis may be bothered by a presence of volatile substances, which provide redox chemical reaction with mentioned special solution of agents.

RESULTS AND DISCUSSION

Optic properties changes of PVB sheets with increasing water content

The influence of ambient relative humidity on the water content in PVB sheets with various plasticizers was tested. The measurements were focused on description of PVB sheets optic properties with various hydroxyl group content in the PVB chain; different PVB chain polarity requests dissimilar polarity of used plasticizer. It was found that sheets with higher hydroxyl group content (which means higher chain polarity) have higher water absorbability. Results are shown in Figure 2.

During the measurement of mechanical properties it was also found that with increasing water content the PVB sheet becomes softer. Water probably acts as a plasticizer in PVB sheet.¹³ Accompanying effects are e.g. sheet whitening when the water content is in the range 3–5% (it depends on a sheet manufacturer)

when the light transmission decreases. The change of water concentration in the sheet depends on the sheet thickness, ambient temperature, and relative humidity of ambient atmosphere.

Sheet whitening was used for measurement of water absorbability in PVB. As the sheets did not have smooth surface (various sheets had different roughness) and thus different light scattering measured through the sheet, we could not measure water content by direct turbidity evaluation. And therefore the kinetics of water absorption was measured indirectly by measurements of light transmission. Sheets were immersed in 25°C distilled water and light transmission was measured in certain time intervals. Initially the diffusion of water into PVB is fast (0–2 days) and then it still continues but at slower rate (3–12 days). From the shape of the curves it seems that water absorption continues even after 12 day (but we did not measure that).

In our previous work, we have found that Butacite 3GO sheet after 14 days in water contained 8 wt % of water.¹³ Figure 3 shows very similar curves of light transmission for all types of sheets. Even though in Figure 3 there are sheets Butacite with different $-OH$ group content, the results demonstrate very similar curves of change in light transmission in time in water. According to results shown in Figure 2 one would expect that sheet with higher content of $-OH$ groups (Butacite 4G7) should have faster water absorption into polymer matrix. However, the curves exhibit that for transmittance change the polarity of macromolecule is not the only decisive factor but the presence of adhesion modifying additives is important as well. This theory is confirmed by results shown in Figure 4. Even though all tested PVB sheets have similar change of light transmission in time, the change of optical properties

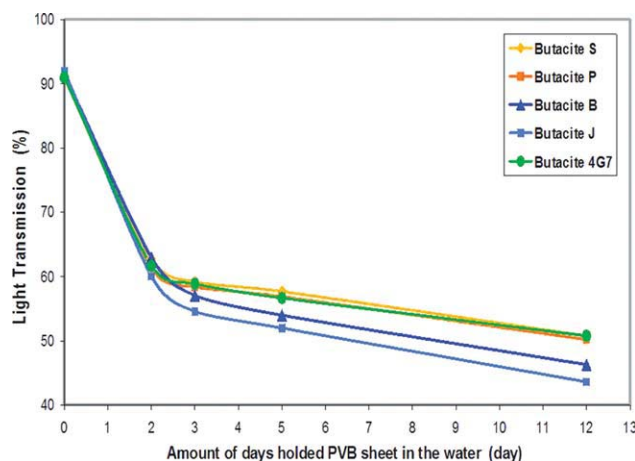


Figure 3 Dependence of light transmission on water content in Butacite sheets. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

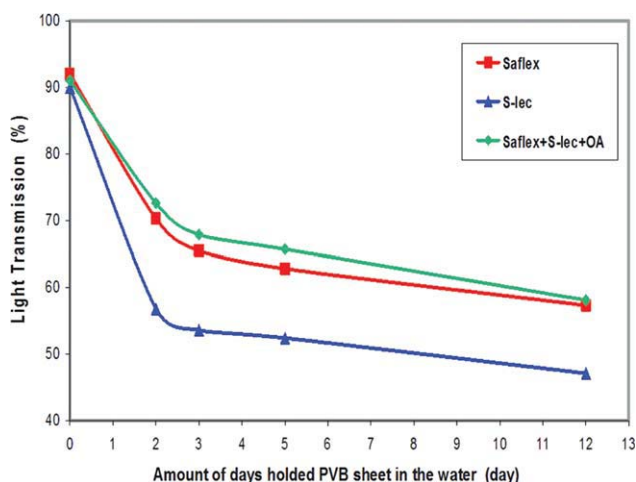


Figure 4 Dependence of light transmission on water content in Saflex, S-lec, and blended sheets. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

of Saflex sheet is very different. Saflex sheet contains the same type of plasticizer like Butacite 3GO. These results imply that Saflex has very different adhesion adjusting system (different additives). This special behavior concerning change in adhesion of PVB towards the glass was described elsewhere.

Together with light transmission change in PVB sheets also haze generation was observed. The haze increased proportionally with water concentration in the sheets up to the maximum level, which was reached after 3 days water immersion when the water content was about 5%. Generated haze was due to presence of water particles, which are immiscible with PVB. Immiscibility is caused by different polarity of PVB and water. All tested samples of PVB contained 18–22% hydroxyl groups. Therefore polymer is soluble in polar solvents such as lower aliphatic alcohols, THF, chlorinated hydrocarbons, etc. Even though PVB is quite polar and therefore hydroscopic it is not water soluble. Water absorption and desorption is reversible, it is possible to remove water completely by drying. After drying the sheet regains back its original optical properties. This reversible phenomenon can be used for recycling of safety glass in wet way, which leads to regaining PVB material with acceptable mechanical, optical, and adhesive properties.

Change of optical properties of PVB sheets measured as component of laminated glass

Following tests were focused on evaluation of optical property changes of conditioned PVB sheets laminated between glasses. The laminated glass preparation was important to reduce extensive light scattering caused by rough PVB sheet surface. Obtained light transmission (LT) was plotted as a

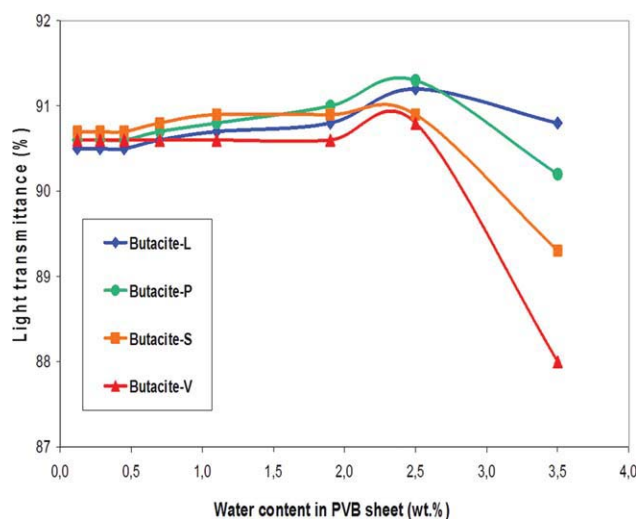


Figure 5 Light transitions on Butacite 3GO sheets—measured through glass laminate. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

function of water content in tested PVB sheets as it is shown in Figures 5 and 6. With increasing water content the LT increases slightly also up to water content 2.0–2.5%. When the concentration increases further (2.5–3.5%) the LT starts to decrease.

While for Butacite-L the decrease is the smallest, for Butacite-V the drop in LT is remarkable (from 90.5 to 88%). Butacite-L has the highest content of adhesion modifying additives while Butacite-V has the lowest one. On the other hand for Saflex, S-lec and their blends and blends with Butacite the decrease of LT at 2.5–3.5% of water is very small. This phenomenon can be explained by filling of

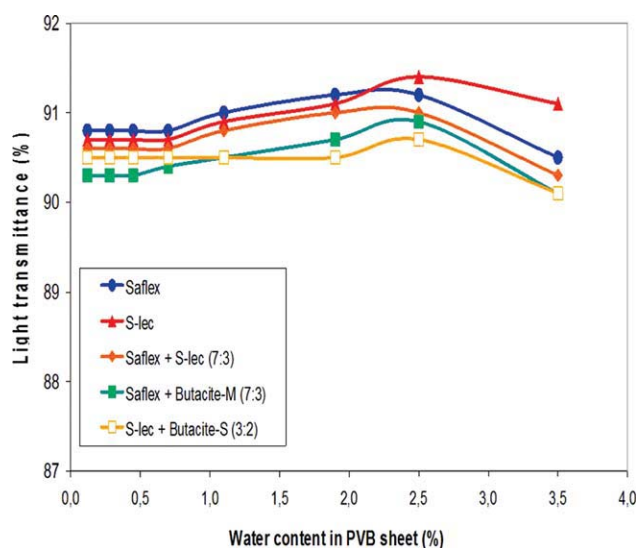


Figure 6 Light transmissions on Saflex, S-lec and its blended sheets—measured through glass laminate. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

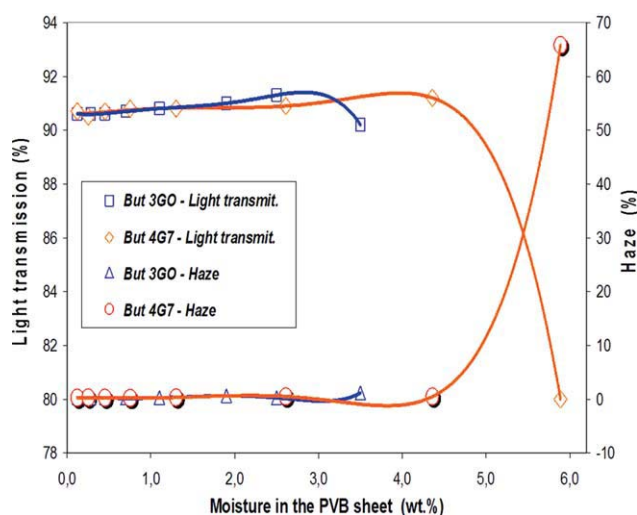


Figure 7 LT dependence on haze detected in Butacite 3GO (type P) and Butacite 4G7—measured through glass laminate. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

intermolecular vacancies (decrease in refractive index) or by increase in solubility adhesion adjusting additives (alkali reaction ions).

Butacite sheets were studied separately. It was found that change of LT with water content above 2% was directly proportional to alkali reaction ions. It is necessary to mention again that Butacite-L contains about three times more of these adhesion modification agents than Butacite-V. As it was already mentioned exact amount of salts adjusting adhesion is not published by manufactures (it is confidential) and in patent it is usually shown a wide range of values.²⁰

Even more distinct drop in LT was found for laminated sheets Butacite 4G7. Comparison with sheet Butacite 3GO (type P, modified to the same degree of adhesion with water content 0.5% as Butacite 4G7) is indicated in Figure 7. Type Butacite 3GO with 18% —OH groups could absorb maximum 3.5% of water at 100% relative humidity of surrounding air. This fact is responsible for smaller changes of optical properties of this sheet. Initially the LT increases from 90.6 to 91.3% (at 2.5% of water content) and then the LT decreases to 90.2% (at 3.5% of water content). From the LT point of view it is acceptable for safety glass manufacturing; however, the haze value was 1.2% that is not acceptable. This shows the importance of measurement of both these values (LT and haze).

In contrast Butacite 4G7 has higher content of hydroxyl groups (22%) and it is also more hydrophilic (Fig. 2). Initially the LT increases from 90.7 to 91.2% (at 4.4% of water content) and then abruptly decreases to 80.0% (at 5.9% of water content). When the relative humidity is 100% and water content

reaches 5.9% this sheet cannot be used to safety glass production. The value of haze at 2.5% water content was 0.5% which is acceptable, however by visual observation she sheet was found to be slightly milky and not acceptable for production.

The light scattering at water content 2.0–3.0% is also caused by higher optical activity of uninhibited —OH groups in PVB chain with water and its generation of intermolecular hydrogen bonding between them. Second reason for haze generation was water microdrops that act as immiscible PVB plasticizer at water content above 3.0%.¹⁰ One can expect interaction mechanism when uninhibited (free) —OH groups generate with water intermolecular hydrogen bonding.¹⁰ This interaction with hydroxyls can create bonds absorbing day-light. Above critical value water can scatter visible light passing through the sheet. It is necessary to mention that LT decrease was mostly caused by light scattering. This is confirmed by obtained results of transmittance and haze generation with increasing water content in Butacite 4G7 and Butacite 3GO sheets. These results are demonstrated in Figures 7 and 8.

On the other hand, the inhibition of haze generation at water content up to about 3.5% is based on the inhibition of free —OH groups in polymer chain due to the presence of alkalic ions. The alkali impact on inhibition of interaction between the polymer and the water is visible in results shown in Figure 8. This inhibition mechanism is observed in the case of decrease of adhesion PVB to glass and also in the case of the inhibition of the haze increase at water content between 2.0–3.5%. Hydroxyl groups in polymer chain are inhibited by alkali ion, the interaction between —OH group and water cannot take place. Butacite-L has about three times more of adhesion

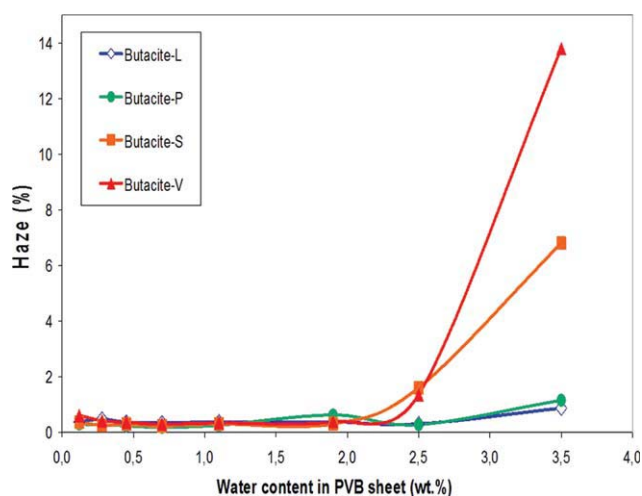


Figure 8 Haze intensity in Butacite sheets—measured through glass laminate. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

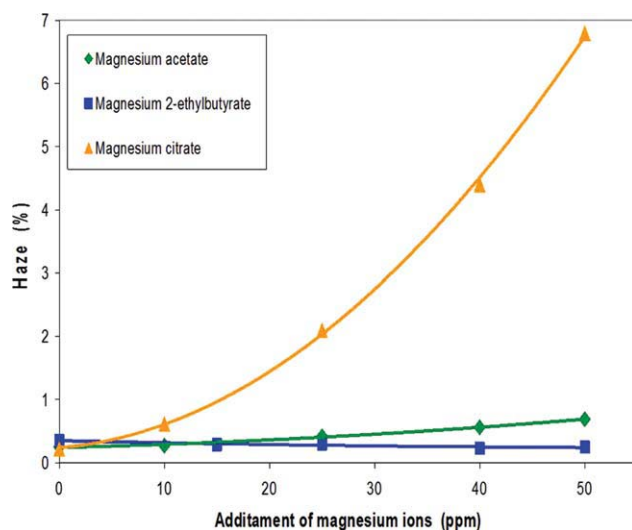


Figure 9 Dependence of haze increasing to modification of Butacite-V material by organic magnesium salts. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

adjusting alkali ions than Butacite-V and the haze of Butacite-L change is very small (similar to LT). In contrast Butacite-V with lower content of alkali ions is much easier susceptible to change of optical properties. This behavior was shown also in Figure 5 as large change of LT in range 2.5–3.5% of water content.

Immiscibility of PVB with water in concentration above 3.5% was observed for all sheets from all manufactures. We observed whitening of all sheets when the concentration was 5–10%. In this case the water molecules were in such high concentration that the system was fully heterogeneous, far from binodale curve of miscibility diagram. The Van der Waals interactions between bound water with free water and PVB were also studied by several authors.¹⁰

Haze increase in PVB sheets caused by the presence of Mg^{2+} ions

Another totally different type of a haze was observed after addition of several magnesium organic acids salts into the system. This type of haze is not visible by human eye but it can be measured instrumentally very well. Moreover, the “magnesium haze” is slightly visible under intensive illumination. Results of haze measurement of virgin and modified PVB sheets are plotted in Figure 9. It is necessary to mention that all sheets were conditioned until water content 0.4–0.5% was reached. The most intensive haze is induced by salt of citric acid. This measurement points out that the haze increase caused by citric anion was caused by highly substituted molecule of citric acid by polar substituent. Free carboxyl or

hydroxyl groups can be in interaction with free hydroxyl groups of polymer chain. It caused haze increase similarly to the case of Butacite haze caused by interaction between —OH polymer groups and the water when the water content was 2.0–3.5%. Listed Butacite sheets were only minimally modified with potassium, sodium or magnesium salt or its combinations as patents describe.^{20,22}

PVB immediately after its production has too high adhesion. In this case, the PVB chain contains high number of free (uninhibited) hydroxyl groups. Because of this, it is necessary do decrease the adhesion by addition of K^+ , Na^+ , Mg^{2+} salts as it is described in these patents.^{20,27–29} The testing was focused on modification of Butacite 3GO sheet (Type H) by various Mg^{2+} organic salts. It is important to mention that Mg^{2+} ion plays an important role in the charge transfer. Modification by Mg salts was chosen because of haze presence in production sheets. Therefore, several Mg salts of organic acid were added to PVB to find out the intensity of haze generation. We found that detected intensity of haze generation was in accordance with decreasing polarity of their Mg salts: citric acid > acetic acid > 2-ethyl-butyric acid. Obtained results can explain haze generation in Butacite sheets. The haze was generated in PVB sheets with higher content of uninhibited —OH groups when the water content was above 2.5%.

Generally, free alkali uninhibited —OH groups of PVB chain interacted either with other —OH groups of PVB chain or with adsorbed water. Moreover, adhesion agents used by worldwide manufacturers of PVB sheets S-lec and Saflex are frequently salts of 2-ethyl-butyric acid.²⁸ 2-ethyl-butyric anion of mentioned salts contains longer hydrocarbonic nonpolar part of organic acid than anion part of acetic acid. Hence, molecule with lower polarity of anion does not show big tendency to interact with other polar groups. Therefore, salts with lower molecular polarity do not interact with hydroxyl groups of polymer and they do not intensify original haze of PVB material with water content around 0.5%.²⁹ This haze is created by aggregation of molecules by intermolecular hydrogen bonds.

The magnesium acetate (MgAc) is commercially used as adhesion modifier of Butacite sheets [X]. And therefore MgAc was tested to find out the dependence of haze generation as a function of water content in Butacite PVB sheet. In commercially produced Butacite sheets with water content 0.4–0.5% usually there is no haze. The reason behind this fact is that the concentration of the Mg agent that could be causing the haze is under the critical value.³⁰ It was verified that the haze was observed at higher concentration of magnesium acetate. Optical properties of PVB sheets were tested for the Butacite 3GO,

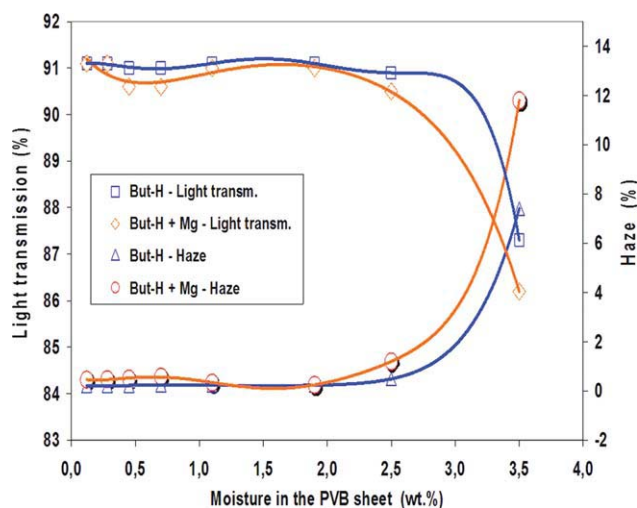


Figure 10 Change of optical properties as a function of increasing water content in Butacite-H material with/without a Mg^{2+} additive. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Type H and its modified material with 50 ppm of Mg^{2+} . Both types of sheet were conditioned to pre-determine water content and laminated between float glasses. The haze, present in common industrially manufactured PVB sheets is usually found in the range 0.1–0.3% (measured as scattered light through laminated 0.76 mm PVB sheet). The haze increasing becomes to be detectable over an added 50 ppm of magnesium acetate.

The addition of 50 ppm of magnesium acetate caused the haze increase to 0.6%. The haze was measurable only on sheets with water content up to 1.0%; it is caused by presence of heterogeneous Mg^{2+} particles with dimensions being in range 0.5–5 μm . Magnesium fragments are slightly visible under intensive illumination of the PVB surface (Tyndale's effect). At the same time the LT changes are observed similarly as in the case of already mentioned haze (Fig. 8). The intensity of transmitted light decreased due to the light scattering caused by presence of micro particles. However, radiation energy of light remained almost the same. This dependency can be also characterized by Lambert-Beer's law, according to an eq. (1):

$$I = I_0 \times \exp(-L \times \tau) \quad (1)$$

Absolute scattered light is influenced by PVB thickness L and turbidity coefficient τ . It depends on magnesium fragments amount 1N in polymer matrix, its pattern and volume which is mentioned as deformability coefficient α and wavelength λ of the light beam landing on the sample in the direction of attenuation. The turbidity coefficient is possible to obtain from Rayleigh's law (2). Already, very small

amount of the heterogeneities in size in order of nanometers (micrometers) is sufficient for the haze generation.³¹

$$\tau = ^1N\alpha^2 \frac{8\pi}{3} \left(\frac{2\pi}{\lambda}\right)^4 \quad (2)$$

The light ray was not diffused by Mg^{2+} insoluble fragments at water content above 1.0% and the haze is reduced to the "virgin value" in PVB without magnesium ions addition. It was observed that this phenomenon is reversible (after drying the haze returned to its original value 0.6%). It is possible to admit that Mg^{2+} aggregates are dissolved by present water. In this case, the haze decrease is affected by a slight decrease of ionic strength and intermolecular interactions between hydroxyl groups and water were inhibited. Additional increment of water content to Butacite sheets above 1.9%, (resp. 2.5% for modified type) was the source of intensive haze and LT decrease as shown in Figures 8 and 10. The water with concentration above about 3.0% has a function of immiscible plasticizer.¹⁰ The change of optical properties with increasing water content in modified and nonmodified Butacite (Type H) material is plotted in Figure 10.

Comparison of light transmission of virgin PVB with PVB modified by Mg^{2+} ions points out that Mg^{2+} ion caused slight light transmission decline in a range 0.4–1.1% of adsorbed water. However, this decrease returned back to its original virgin value at 1.0% of water content in the sheet. A sharp light transmission decrease was detected at water content above 1.9%, resp. 2.5%. Aforementioned light adsorption is caused by the same influences which are the reasons for the haze generation. In this case, LT decline is not produced by true light adsorption in polymer matrix or presence of heterogeneous particles, but the day-light is scattered as it was describes in previous paragraph. Even though optical property change is very small up to water content cca 2.5%, it is still very important in industry for laminated glass production. Generally, the manufacturers of PVB sheet specify minimal value of light transmission to be 90.0% and the haze up to 0.5% of scattered light.⁸ The change of these optical properties even in range of several tenths of percent is very critical parameter for engineering practice. These parameters are often difficult to reach. Change in optical properties can cause serious problems in production. The PVB sheet with low day-light transmission causes reduced visibility through the laminated glass at night. From another point of view the haze is very dangerous in the case of intensive illumination of laminated glass. When the incidence beam hits the particles they get brighter resulting in the laminate's opaqueness.

CONCLUSIONS

This work investigated the cause of the haze generation and the light transmission reduction in various plasticized PVB sheets. Virgin, blended PVB, and modified PVB materials with Mg^{2+} ions were tested. This work focused on discovering causes of change in light transmission and haze generation in various PVB sheets. The testing was focused on influence of water absorbed in PVB on the optical properties change at whole spectrum of relative humidity of air. It was found that when the sheets Saflex and S-lec were conditioned at 0–99% of relative humidity there was no decrease in light transmission and no haze. However for sheet type Butacite with water content 2–3% there was serious milky haze and decrease in light transmission. It was observed that the accurate value of water content is dependence on type and a content of alkali metal ions and alkaline-earth metals. Moreover, this effect becomes stronger with higher content of free hydroxyl groups in PVB chain. Therefore the highest changes in light transmission and haze were observed for sheet Butacite B3 that was softened by 4G7 plasticizer, PVB contained 22% of $-OH$ groups and sheet was modified by high content of alkali ions. The magnification of this effect is probably caused by higher water absorbability of increased macromolecular polarity and by higher concentration of alkali reacting metals in tested PVB sheets.

Simultaneously, another possible cause of haze generation was discovered. This cause is based on the presence of magnesium microfragments that scatter the light. Therefore we tested artificial addition of Mg^{2+} salts of various organic acids with their different polarity of the molecule. It was found that with increasing polarity of the molecule of the additive also haze intensity increases. As magnesium acetate is commonly used for adhesion decrease it was tested for finding a critical concentration causing forbidden haze. This concentration was found to be 50 ppm Mg^{2+} . Also a constant addition of magnesium acetate on haze generation was investigated together with increasing water content. Very important phenomenon was discovered. For sheet Butacite B5 (with plasticizer 3GO and 18% of $-OH$ groups) a serious decrease in haze generation was detected for sheets with water content 1.1%. Modified PVB sheet Butacite-H by Mg^{2+} ions kept the “virgin haze” even up to 2.5% of water content. When the water content was higher than 2.5% sharp increase of haze was observed. Nevertheless, in this case water acts as immiscible plasticizer in PVB sheet.

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