Tomas Bata University in Zlín
Faculty of Technology
Department of Polymer Engineering

English Doctoral Thesis

The study of PVB waste application obtained from recycled windshield

Studium možnosti použití odpadního PVB z recyklovaných automobilních skel

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ABSTRACT

The study deals with describing of water dependence and chemical reactants on the change of optical and adhesive properties of the PVB polymer. The thesis shows very important knowledge about adjusting PVB adhesion to glass and influence of water and adhesion modifiers to the change of PVB properties. Results also describe a possibility increase and degrease the PVB adhesion in various worldwide PVB sheet manufacturers. Due to obtained experiences, 3-steps recycling process of windshields and effective PVB separation from glass was developed. The recycling method was developed for the recycling of windshield containes PVB sheet produced by all worldwide PVB manufacturers.

At last but not least it is necessary to advert that this Doctoral thesis is also focused on PVB re-processing which has been modeled by kneading and rolling in air environment. The PVB was re-processed with different water content; all tests were carried out at different temperatures. The observation and sample analyses allowed to find optimal conditions for re-processing of plasticized PVB waste; i.e. conditions with the lowest polymer degradation.

Key words: poly(vinyl butyral), laminated safety glass, adhesion, recycling, polymer degradation

SOUHRN

Studie se zabývá popisem vlivu vody a chemických činidel na změnu optických a adhezívních vlastností PVB při jeho přepracování. Díky získaným poznatkům práce přináší velmi zajímavé poznatky pro regulaci adheze PVB ke sklu a popisuje vliv vody a modifikátorů adheze na změnu vlastností PVB. Výsledky také popisují citlivost adheze PVB u vybraných fólií světových výrobců PVB a citlivosti změny adheze u modifikovaných fólií. Z dílčích závěrů je navržen technologický postup recyklace bezpečnostního automobilového skla a efektivní separace PVB od skla. Tato metoda recyklace byla vyvinuta pro všechny druhy běžně vyráběných PVB fólií od různých světových výrobců.

V neposlední řadě je třeba zmínit zaměření disertační práce na podmínky přepracování získaného PVB materiálu. To bylo modelováno v laboratorních podmínkách hnětením a válcováním za přístupu vzduchu za odlišných teplotních podmínek a s rozdílným množstvím absorbované vody v PVB matrici. Z pozorování a provedených analýz produktů byly nalezeny optimální podmínky přepracování měkčeného PVB, tedy podmínky s nejnižší degradací tohoto materiálu.

Klíčová slova: polyvinylbutyral, laminované bezpečnostní sklo, adheze, recyklace, degradace polymeru

BACKGROUND

1. PREDOMINANT UTILIZATION OF PVB

The PVB polymer is mostly used in the form of plasticized PVB sheet for preparation of laminated safety glass (LSG). At present time, Solutia, DuPont, Seki sui and Kuraray are worldwide PVB manufacturers. The PVB is the material which can stick together float glasses with holding excellent optical and mechanical properties of the glass laminate [1, 2, 3]. Elasticity, mechanical strength, toughness, high light transmission and the adhesion to glass are the most significant PVB properties. Toughness of PVB sheet is based on high molecular weight of PVB chain. Certainly, the PVB has to be plasticized for achieving high material elasticity [2, 3, 4]. Admittedly, the plasticizer must not reduce light transmittance through the sheet, PVB adhesion to glass, generate haze and yellowness, and migrate out of the polymer matrix [5]. In addition, plasticizer must have perfect compatibility with the polymer and low evaporability during processing conditions.

Worldwide, 65% of all PVB sheets are used in automotive applications [6]. According to data from [7], the worldwide car's production is estimated around 60 millions cars per a year. Regarding to one windshield contains approx. 1 kg of PVB sheet, total amount gives between 60-70 million kg of PVB sheets. In addition to mentioned amount, by-products from PVB sheets manufacturing (5%) and trimmings (< 10%) stems from windshield production must be added [8]. It represents total amount of 80 million kg of automotive PVB sheet waste annually. Total worldwide amount of produced PVB sheet for automotive and architectural industry is estimated around 120 million kg per year.

2. LAMINATED GLASS AND ITS COMPOSITION

2.1. Poly(vinyl butyral)

First labours for improvement of glass resistance to impact and glass breakdown resistance at keeping of required optical properties were already observed in the beginning of the 20th century. Laminated glasses with other transparent polymeric materials (cellulose derivates, methacrylates, etc) were tested for the achievement of increase of the glass resistance to impact [9]. The first patent on laminated safety glass with application of plasticized PVB obtained American company Monsanto in year 1938 *(today it is Solutia).* At progress of a time, companies DuPont, Sekusiu and Kuraray also deal with PVB manufacturing and they are worldwide PVB manufacturers now [10].

The way assigned for PVB production is not easy. Firstly, it is necessary to produce polyvinyl acetate *(PVAc)* by the radical vinyl acetate polymerisation. Consecutive hydrolysis at acidic or basic ambient creates poly(vinyl alcohol) *(PVAl)* which provides poly(vinyl butyral) by acetalization with butyraldehyde at acidic environment. The final structure of high-molecular PVB is used for LSG manufacturing and it is compounded from atactic copolymers 80% of vinyl butyral, 18-23% of vinyl alcohole and up to 1% of vinyl acetate [5, 6, 11, 12, 13]. This chemical structure, viewed in Fig.1, is the same for every manufacturer today. Nevertheless, exact consequence and properties of every PVB sheet depends on every PVB type, manufacturer and PVB sheet composition. The sheet is mostly stabilized by antioxidants and thermal stabilizers in many times [14].

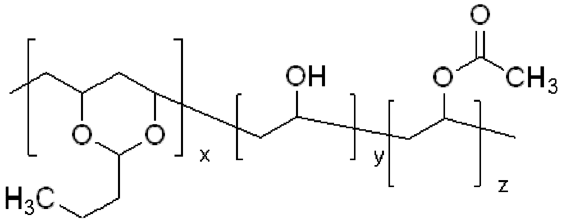


Fig.1: PVB chain structure with composition of functional groups: vinyl butyral 81%, vinyl alcohol 18-23%; vinyl acetate <1%

Final PVB properties are assigned by polymerization degree of input PVAc, distribution curve of molecular weight, PVAl hydrolysis degree, catalyst acid strength, reaction temperature and PVAl conversion degree to PVB. The last one is crucial for final polarity of produced PVB. The PVB polymer is white powder, dissolvable in ethanol, THF, ketones and other semi-polar dissolvents [15]. The PVB solubility depends on –OH group content in the polymer chain and PVB molecular weight [16].

2.2. PVB sheet composition

Certainly, achievement of high PVB toughness must be prove by polymer plasticizing. However, the plasticizer must not considerably reduce light transmittance through the sheet, increase haze and yellowness, reduce PVB adhesion to glass and migrate out of the polymer matrix [4, 10]. The plasticizer also must have perfect compatibility with polymer matrix and its evaporability during the processing is prohibited [10]. Different plasticizers, used in beyong, were for example triethylenglycol-di-2-ethylbutyrate, dibuthylsebacate, tetraethylenglycol-di-heptanoate and dihexyladipate [6, 10]. Mentioned plasticizers have different molecular polarity. Therethrough, due to it was indispensable to produce PVBs with different amount of hydroxyl groups in

PVB chain [6, 11, 17]. The final polymer system has different absordability of the plasticizer and water [18]. At present time, produced PVB sheets assigned for glass lamination are plasticized with 28% of applied plasticizer; mostly triethylenglycole-bis(2-ethylhexanoete), (labeled 3GO) [5, 17, 19, 20].

Due to mentioned sheet physical properties, the most important characteristics of windshield are high mechanical strength and absorbability of kinetic energy during car-crash [3, 4]. However, PVB interlayer must keep glass particles on its surface [2, 3]. All these described properties provide exactly adjusted adhesion grade of PVB to glass. Because the PVB has exceedingly high adhesion degree it cannot be used for automotive glass lamination. Thus, high adhesion degree it is necessary reduced to ½ of the original adhesion value [3, 5, 6, 20]. The virgin adhesion is reduced by addition of organic salts of alkali metals or alkaline-earth metals during an extrusion process of plasticized PVB sheet. This is described in several patents [18, 21, 22, 23, 24, 25]. The mostly used substances modifying the adhesion are organic salts of Na^+, K^+ and Mg^{2+}. Ion ratio and its total amount are strictly specified [18, 20, 21, 22, 23, 24, 25]. Moreover, the water content in PVB sheet has to be in range 0.3-0.5% which is necessary for maintaining the required adhesion grade [3, 5, 21, 25].

2.3. Sheet extrusion and lamination process

Based on the several authors [3, 4, 26, 27, 28], all PVB sheet manufacturing technologies are based on similar principle. Melt plasticized PVB is extruded by sheet extrusion die at temperature 160-210°C into water. The screw placement must be evacuted in case of adjustment of water content in the sheet. The PVB melt retains its shape, thickness and specific sheet surface which are necessary for de-aeration at pre-lamination process [4, 10]. Plasticizer and additives addition runs at mixing equipments before the extruder in many times. The PVB sheet is mostly manufactured in thickness 0.38 mm (LSG for architectonical industry) and 0.76 mm (LSG for automotive and architectonical use). Special applications require thicknesses 1.14 and 1.52 mm. The width of PVB sheet can be up to 3.5 meters. Manufactured PVB sheet is rolled and either separated by thin patterned polyethylene sheet or rolled under-cooled (Tg = 15°C) because PVB sheet must not be glued for following use [4, 10, 14].

Consequently, the PVB sheet must be layered between two (or more) clear shaped glasses with PVB oversize around 5 mm. This multiple-layer sandwich is pre-laminated between two rolls or by vacuum at temperature 90-140°C and pressure 0.2-1.0 MPa. The pre-laminated product still is not transparent at all laminate surface, it also contains a residual air. Oversized PVB is cut near the glass edge and autoclaved at temperature 130-150°C and pressure 0.9-1.5 MPa for several tens of minutes. During the autoclaving process the adhesive bonds are generated. It assures holding glass fragments on PVB sheet after the accident. This is the most important property of PVB sheet [10, 14, 28].

The adhesive bonding strength between the PVB sheet and the glass grows in two independent steps. The first of them is a transport of PVB metage to surface of glass. This is generally described by diffusion effect [6]. Second part is a generation of Van der Waals interaction between materials. The intermolecular distance and similarity of material polarities determinates strength of the adhesion. Therethrough, polar –OH group of PVB provides adhesive hydrogen bridging with free oxygen bond of the glass [3, 12]. The adhesive bonding is depended on temperature and acid-base environment, also on water content in PVB matrix. The water content around 2% in PVB causes saturation of binding sites and the PVB to glass declines. A residuary adhesion value probably corresponds only to dispersion forces [4, 29].

2.4. Float glass utilized for glass lamination

The LSG manufacturing process uses float glass bended to a required shape. Nowadays, there exists only one acceptable way for the float glass preparation. The float glass is made by the casting of the glass melt on the surface of the melt tin. Due to this fact, prepared float glass has the 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 [4]. This bottom surface is called “tin side”. The tin film, which is determinable by UV-rays reflections, causes totally different adhesion response between PVB and glass with increasing moisture in a polymer [4]. Therefore, the laminated glass is layered in following composition in every case: “air side–PVB–tin side”.

Nevetheless, manufactured pair of float glasses must be bended beside layering with PVB sheet. Both glasses are shaped as double glazing unit predetermined for layering with the PVB sheet. Glasses are separated at shaping process by micronized calcium carbonate or silica. The shaping temperature is approx. 600°C and after cooling the separator is washed out [4].

The float glass applied for sample preparing had common chemical constitution 71.5% SiO_2, 13.4% Na_2O, 9.2% CaO, 4.15% MgO, 0.7% of Al_2O_3 and other compounds. Glasses were delivered from company AGC Teplice *(Czech rep.)*. The tin side of float glass was detected by means of UV illumination which creates lightly visible white reflexive layer of UV scattering on tin side of the glass [4]. All tested glasses were oriented to tin side up. Due to it, the PVB sheet is after lamination in contact with the air side of the glass (up side of the laminate) and with the tin side of the glass (down side of the laminate). Optical properties of one lime-soda glass at a thickness 2.1mm were 91.3% of light transmittance and 0.05% of a haze.

3. SOURCES FOR PVB SHEET RECYCLING

3.1. By-product from sheet manufacturing process

This kind of PVB sheet has the best quality for following recycling process. By-product sheets are not contaminated by powder fragments but there may be present some un-homogeneous parts like plasticizer, light and heat stabilizers, adhesion modifiers, pigments and other elements of the system. The reasons why the sheet has to be re-processed are some specificific defects in manufacturing technology (thickness, sheet roughness, edges). In every case, sheet edges must be cut approx. 10-20 cm from the edge beginning. The PVB sheet with width around 2-3 meters has very high material shrinkage in this place. The edges can be replaced back to the extrusion process for re-extruding [10].

3.2. Trim

The first step in LSG manufacturing is the layering of PVB sheet between two glasses. It this part, probable defects on laminate edges must be reduced. It is performed by layering of PVB sheet between glasses with larger sheet surface than the glass surface is. Prepared “sandwich” is fixed by nipp-roll pre-lamination process and consequently it is possible to trim off oversized PVB sheet. While the sheet oversize would not be used, the laminate would be produced with visible defects (it does not meet the quality specifications) [4, 10].

The quantity of trim generation depends on geometry of produced windshield and geometry of used PVB sheet surface. Width of trim obtained from pre-laminating process is around 1–20 cm, bades on glass geometry. Therefore, the trim quantity is between 5-10% from total amount of processed PVB sheet and the worldwide PVB trim capacity obtained from windshield laminating process is approx. 4-6 million kg [4, 10]. Sure, automotive trim is fully recyclable. One of several companies, deals with its re-processing by extrusion is company Retrim *(Czech Republic)*.

The trim is created also at manufacturing of architectural LSG. Nevertheless, the ratio of collected architectural trim is lower than amount of automotive trim. It is influenced by higher glass powder contamination of this trim (different trimming technology) [10].

3.3. PVB sheet from windshield

Some specialized companies are deals with the application possibility of PVB sheet obtained from recycled windshield. All present recycling processes produce a good quality of glass scrap which is fully re-used in glass batch. However, separated PVB waste is not recyclable due to high amount of glass, water content in the sheet, parts of color PVB sheets, mixed of various PVBs (after blending a haze is produced) and foreign plastic matters [10, 30, 31]. Nevertheless, if somebody would develop the recycling technology ensures high-grade of glass separation, obtained PVB sheet may be re-processable to new PVB sheet without optical defects.

4. DILLEMA OF WINDSHIELD RECYCLING

As mentioned, the main rationale application of LSG is the absorbing of kinetic energy from impacted objects concurrently with keeping of glass fragments on the PVB sheet surface. Admittedly, the PVB must have sufficient adhesion grade. Hence, just adhesion is the obstruction for effective windshield recycling and obtaining of uncontaminated PVB sheet.

With regard to increasing worldwide production of PVB sheet and following PVB waste generating *(see chapter 1)*, it is necessary to focus on effective glass separation in order to obtain uncontaminated PVB sheet. Contrarily, PVB sheets from windhield will burned or land-filled [6, 8]. This is in the reason of separated PVB sheet is not possible to re-process to a new PVB sheet suitable for glass lamination, especially due to high amount of glass scraps and water content in the sheet [6]. If separated PVB sheet is supposed to be used in production of new laminated glass, the PVB sheet has to contain no more then 100 ppm of glass fragments and other contaminations – higher amount negatively influences a PVB optical properties. In addition, the higher residual glass content also negatively affects PVB sheet processing [10]. Therefore, it was necessary to focus on a finding of an effective windshield recycling.

Moreover, it is necessary to remaind that the laminated (interglassed) PVB is not essentially exposured by UV radiation (up to 320 nm), mechanical stress, elevated temperature, oxygen and any various substances. Hence, the interglassed PVB sheets should keep very similar physical properties as extruded material before the lamination process.

5. DEGRADATION OF PLASTICIZED PVB

The polymers show higher resistance to corrosion and oxidative degradation in comparison with other chemical substances. Due to it, the polymers have found application as lacquers, coatings, protection agents, building materials and others. Nevertheless, some undesirable changes of chemical compounding are observed. These occur not only during their application. Changes already run through the polymer production or its processing. Chemical reactions are mostly caused by influence of temperature, oxygen or ozone exposure or by mechanical stress [32]. Mentioned polymer reactions are generally described as polymer degradation. Therefore, the study of corrosion a degradation of polymers provides knowledge which extinguishes or minimizes mentioned negative changes [33].

5.1. PVB resistance to mechanical stress

When the polymer substances are processed at temperature lower than material melt point, the high viscosity degree must be overcame. It is responsed in high energy consumption of forming machine and also by high production of energy dissipation. Mentioned effect is multiplied with the material molecular weight (high Mw = high resistance to material flow). Processing at described conditions causes shortening of macromolecular chain and polymer degradation proceed during the mechanical stress; for example at rolling, kneading and milling process. The degradation can be advanced by oxygen environment.

Mechanical degradation can runs according to radical or ion mechanism. Ion mechanism runs only when the macromolecule has lower ionic bond strength than common covalent bond (ionic bond strength can be reduced by polarity of solvent). The degradation speed is influenced by temperature, frequency of movement, presence of environment oxygen, character and size of added substances and also on the polymer compounding and the structure [9, 33, 34].

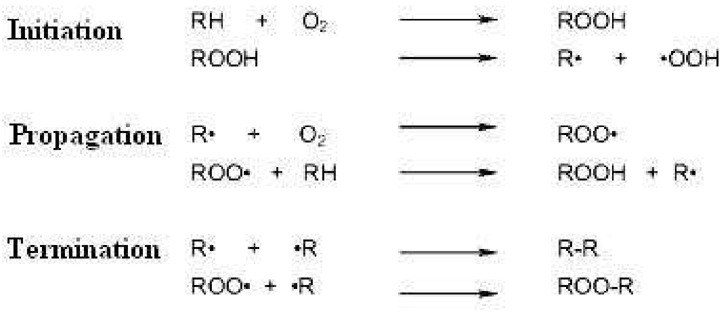
5.2. PVB resistance to elevated temperature

The effect of elevated temperature and following material melting causes growing polymer reactivity and its destruction. Some macromolecular substances can be depolymerized. Especially, the PVB polymer chain contains removable functional group which can be evaporated at critical temperature in form of low-molecular substances. These are water, organic acid, alcohol or aldehyde (in case of PVB) [6, 35]. The finish part of degradation process is either mostly proved by olefinic bond creation and following polymer carbonization or the intermolecular bonding creation which provides polymer cross-linking [9, 33, 34].

5.3. PVB resistance to oxygen

Generaly, environment oxygen reacts with the major part of all chemical substances. The oxidative rate is directly proportional to temperature; accordingly to Arrhenius equation. Polymers are sensible to oxidative degradation at conformable conditions as similarly as low-molecular chemicals. Unfortunately, in the case of high-molecular substances, changes of physical properties are multiple larger. Therento, important role to oxidative degradation plays the gas diffusion and oxygen solubility into the polymer matrix polymer [9, 32, 34].

As mentioned, the oxidative degradation mostly runs at elevated temperature (above 150°C). This thermaloxidative polymer degradation is autocatalytic process. Genered hydroperoxides and following degradation products initiate a chain radical mechanism and the reaction is accelerated by the same products. The autooxidative polymer behavior can be described by following sheme:



To sum up, it is possible to elevate plasticized PVB as very sensitive material to disposing to degradation. Hence, re-processing conditions should be choosing with carefulness and knowledge of PVB degradation mechanisms.

AIMS OF WORK

The aim of the Doctoral thesis is a study of PVB waste application obtained from recycled windshield. The windshield recycling process should produce PVB sheet at glass content which is re-processable by extrusion and produce PVB sheet at required optical properties (glass achives a haze). Simultaneously, the plasticized PVB should be re-processed with minimal degree of PVB degradation.

Partial aims are:

- Evaluation of obtained PVB waste, chemical compounding and physical properties and suggestion of applicable windshield recycling technology in high efficiency degree
- Study of PVB adhesion adjustment and influence of water and applied agents to optical and adhesive PVB property changes (mentioned PVB properties are fundamental for the application to safety glass)
- Based on experiences designe more effective windshield recycling technology which produce PVB sheet without glass slivers and other contamination
- Recycled PVB sheet should be fully re-processable to new PVB sheet, either single or in mixture with origin PVB sheet, in this reason the sheet can not be degraded by separation (delamination) environment
- Observe various PVB sheet re-processing condition and suggest optimal range of re-processing conditions in minimal degradation degree

SUMMARIES OF PAPERS

The problem of windshield recycling is possible to determine in two phases. The results of first phase are reported in Papers I-III and describe experiences with adjustment of optical and adhesive properties and effective technology for recycling of windshield. Paper IV deals with PVB sheet re-processing. Short summaries and main objectives of appended the papers are mentioned below:

Paper I deals with finding of causation of the haze increasing and light transmittance change in various PVB sheets. Tested samples from various manufacturers were different in –OH group content and content of adhesion modifiers. It was found that increased water content in PVB sheet scatter the day-light and also reduce the light transmittance of windshield. Moreover, the study found out that added magnesium cations (adhesion modifiers) have positive influence on optical properties with growing water content. On the other hand, the higher –OH group composition in PVB chain has a reverse influence than addition of alkali ions (K^+, Mg^{2+}).

Paper II – it was confirmed that in case of safety glass the adhesion between PVB and the glass is based on Van der Waals bond between the –OH groups of PVB chain and the –OH groups of glass. The study found that activity or passivity (inhibition) of –OH groups depends on pH of polymeric system and on the water content in PVB matrix. Alkali modification decreases the adhesion of PVB to glass and acidic modification the adhesion increase. Nevertheless, the adhesion was decreased with increased water content in the sheet in every case. However, this effect was detected only on “tin side” of the laminated glass. The adhesion on “air side” was no stable in dependence with water content in PVB and the adhesion fluctuation was observed. Mentioned phenomenon and shape of the fluctuation curve was typical for each type of PVB sheet. The adhesion fluctuation plays important role when the water content is in range 0.3-0.6% that is just the range set by PVB manufacturers. The study also found that the acidic modification sharply reduces adhesion fluctuation in function of water content.

Paper III is based on foregoing results. These were used for developing of effective 3-stage recycling process of windshield in keeping of origin physical properties of the PVB sheet. The 1st stage, based on glass cracking, was used as pre-operation for ideal contact of polymer matrix with delamination environment. The 2nd stage is based on the reduction of the adhesion strength between PVB and air side and tin side of the glasses. It was achieved by water, elevated temperature and alkali environment. Optimal delamination process conditions used for all worldwide manufactured PVB sheets were determined. These are process time 1 hour, temperature at 100°C, atmospheric pressure, 1.0 % NaOH. This alkali concentration achieved not only faster chemical glass separation but also peeling simplicity of residual glass in 3rd stage. The process produces recycled PVB sheet with glass content up to 100 ppm. Mentioned residual glass amount is acceptable for industrial PVB sheet re-processing. Following analysis of recycled PVB sheet assessed that the application of alkali strength up to 1.0 % did not cause emphatic reduction of plasticizer content (saponification incluence). Although the delamination process produces alkali water, this effluent should be also fully recyclable. Described technology process points out to ecological recycling of windshield without secondary environment pollution which reduces the worldwide problem with windshield waste disposal.

Paper IV is focused on a finding of conditions for optimal plasticized PVB sheet re-processing. The degradation influence on temperature, air oxygen and mechanical stress was studied. In order to find the possibility for the reduction of energy consumption during re-processing, effect of moisture content in PVB sheets on processing parameters and degradation was examined. The obtained results show that based on the evaluation of MFI and mechanical properties the optimal conditions for PVB re-processing by kneading occur at the temperature of about 150°C and rotation speed of kneader lower than 60 rpm. These conclusions are in the good agreement with the measurement of PVB yellowness. Below 150 °C yellowness remained almost unchanged and increased significantly above this temperature. GPC measurements corroborate the above conclusions showing minimal changes of PVB molecular weight for this temperature. Increased amount of water in PVB sheet can act as and additional plasticizer improving workability of polymer melt and decreasing thus energy consumption. However the “wet” samples are more susceptible to hydrolytic degradation and compromise decision has to be taken to find the balance between these two effects.

CONCLUSION

With regard to the increasing worldwide production of PVB sheet and creating giant amount of the PVB waste in a form of laminated safety glasses, it is necessary to deal with finding of effective glass separation process and obtaining re-processable PVB sheet. Therefore, the aims of my Doctoral thesis were focused on possibility of PVB sheet and windshield recycling with keeping of required optical and adhesive PVB sheets properties. In connection with mentioned some partial aims were studied.

The first part was focused on PVB sheet adhesion adjustment. It was found that the adhesion is based in acid-base environment ant the water content in the sheet. The acidic pH activates hydroxyl groups on PVB chain and the result is hydrogen bond between the PVB and the glass. Main gain is the describing of PVB adhesion to glass in dependence on different water content and used adhesion modifiers. Testing was carried out with various worldwide manufacturers and in their various adhesive grades.

Obtained knowledge provides the way for effective chemical separation (delamination) of glass from waste windshield. In this case, alkali environment and elevated temperature were used. The result was a self-falling of glass fragment out of the windshield. Because the PVB sheet spectrum is wide (different adhesion system, different, etc.), optimal delamination conditions for all manufactured PVB sheets had to be investigated. This delamination process produces re-processable PVB sheet with required remain glass content.

Second part of Doctoral thesis was centered on PVB sheet re-processing. It was modeled on kneading and rolling with the present of air. Due to high level of tested process conditions optimal conditions for PVB re-processing with minimal PVB degradation were founded. The manner for operating cost reduction was also tested. For this aim was taken PVB hygroscopicity on the ground of application the water as next PVB plasticizer. It carried out a decreasing of PVB sheet strength, in particular at temperatures bellow 150°C. However, at temperatures over 180°C was PVB hydrolyzed.

Complete results of Doctoral thesis should be helpful in a technical practice. Results should investigate the manner for effective glass separation from PVB sheet, adjust the PVB adhesion to a required value and assess the PVB adhesion and optical properties sensibility in the dependence on the water content in PVB sheet. Simultaneously, results should be subservient to finding the optimal process conditions in industry practice. Overall, the PVB recyclate should be fully or partly re-applicable for new glass lamination process.

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REFERENCES

[1] IVANOV I.V., Analysis, modeling, and optimalization of laminated glasses as plane beam, *International Journal of Solids and Structures*, Vol. 43, 2006, p. 6887-6907

[2] IWASAKI R, SATO C., The influence of strain rate on the interfacial fracture toughness between PVB and laminated glass, *Journal de Physique IV*, Vol.134, 2006, p. 1153-1158

[3] KELLER U., MORTELMANS H., Adhesion in laminated safety glass–what makes it work, *Glass Processing Days*, Vol. 8, Jun 13–16, 1999, p. 353-56

[4] SVOBODA J., BALAZS M., SEDLAR J., Industry glass. *Glass union concern*: Research and developing institute of industrial glass in Teplice 1988, C(1)

[5] WADE B.E., D'ERRICO J.J., THOMPSON H.M., YU M.K., Polymer sheets and methods of controlling adhesion of polymer sheets to glass, *United States Patent Application US 20050208315*, 2004 Mar 16

[6] DHALIWAL A.K., HAY J.N., The characterization of poly(vinyl butyral) by thermal analysis. *Journal Thermochemica acta*, Vol. 391, 2002, p. 245-255

[7] OCIA, The International Organization of Motor Vehicle Manufacturers, 2007, [cit.: june 21, 2011] – Available on World Wide Web: <*http://www.oica.net/category/production-statistics/*>

[8] GOROKHOVSKI A.V., ESCAPANTE-GARCIA J.I., GASHNIKOVA G.Y., NIKULINA L.P., ARTEMENKO S.E.. Composite materials

based on wastes of flat glass processing, *Waste Management,* Vol. 25, 2005, p. 733-736

[9] PIŠTĚK D., Assessment of chemical PVB properties change at various types of degradation, *Diploma thesis, UTB in Zlin, Faculty of technology,* 2008

[10] ZVONÍČEK J., Collection of findings close to PVB extrusion process, *Non-publish message, Retrim-CZ,* Zlín, 1999

[11] D'ERRICO J.J., JEMMOTT B.A., KRACH M.S., MORAN J.R., Plasticized polyvinyl butyral and sheet, *European Patent EP 0,877,665,* 1996, Dec 24

[12] NGHUEN F.N., BERG J.C,. The effect of vinyl alcohol content on adhesion performance in poly(vinyl butyral)/glass systems, *Journal of Adhesion Science and Technology,* Vol. 18(9), 2004, p. 1011-1026

[13] SVOBODA J., et al., Research message No.895, New ways for PVB processing, *VÚGPT Gottwaldov*, 1970

[14] Saflex laminated guide – physical properties and laboratory methods, *Monsanto,* 1973

[15] MRKVIČKOVÁ L., DAŇHELKA J., POKORNÝ S., Characterization of commercial PVB by gel permeation chromatography, *Journal of Applied Polymer Science,* Vol. 29, 1984, p. 803-808

[16] Physical Properties of PVB sheet SEKI-SUI, The Sekisui Chemical Co., Copyright 2008, [cit.: june 21, 2011] – Available on World Wide Web: <*http://www.sekisui.co.jp/cs/eng/products/type/slecbk/tech/1183758_5127.html*>

[17] PHILLIPS T.R., Process for the aqueous plasticization of polyvinyl acetal resins, *United States Patent 7,285,594*, 2005, Apr 5

[18] AOSHIMA Y., SHOHI H., Intermediate film for laminated glass and laminated glass, *European Patent EN1227070A1*, 2000, Jun 6

[19] MISTER R.E., BIANCHI E., WADE B., HURLBUT J., *31st International Cocoa Beach Conference of the American Ceramic Society*, Daytona Brach, Jan 21-26, 2007.

[20] SMITH R.L., RYMER D.L., HARPER L.R., McKIERMAN D.J., Polyvinylbutyral interlayer sheet with improved adhesion to glass and a process for preparing same, *United States Patent Application US 20080277045*. 2008, Nov 13

[21] D'ERRIC J.J., JEMMOTT B.A., KRACH M.S., MORAN J.R., Plasticized polyvinyl butyral and sheet, *United States Patent 6,559,212*, 1995, Dec 29

[22] D'ERRICO J.J., Control of adhesion of polyvinyl butyral sheet to glass, *European Patent EP 0,938,519B1*, 1997 Nov 12

[23] FOWKES F.M., Role of acid-base interfacial bonding in adhesion, *Journal of Adhesion Science and Technology*, Vol. 1, 1987, p. 7-27

[24] HERMANN H.D., Fabian K, EbigtJ. Polyvinylbutyral films which contain plasticizer and have a reduced adhesive power to glass, *United States Patent 4,533,601*, 1984, Jan 31

[25] SHICHIRI T., MIYAI J., BANDO A., TOYAMA K., AOSHIMA Y., Sannomiya I, Nakajima M. Interlayer for laminated glass and laminated glass, *United States Patent 7,074,487*, 2002, Mar 28

[26] NAGAI K., Laminated glass, *United States Patent 6,686,032*, 2001, Jul 6

[27] NEHER H.T., Laminated glass process preparing, *United States Patent 2,032,663*, 1936, Mar 30

[28] SVOBODA J., Candidate thesis, *VUT in Brno, Faculty of technology - placed in Gottwaldov*, 1987

[29] MATYS V., Study of adhesive properties of PVB to glass, Diploma thesis, *VUT in Brno, Faculty of technology - placed in Gottwaldov,* 1973

[30] PLAČEK T., Study of impurities separation and PVB trim waste re-processing, *Sindat engineering,* 2006

[31] Recycling of windshields glasses in fired bricks industry, *Key engineering materials,* Vols.132-136, Switzerland, 1997

[32] LAPČÍK L., RAAB. M, Material Science II, *UTB in Zlin, Faculty of technology,* 2004, p. 35-67

[33] MOLLINKOVÁ E., Degradation of polymer materials, *prelection ZS 03/04 KOPL – př.III*

[34] KRÁLOVÁ A., KLIMÁNEK L., Polymers processing, *SNTL – Technical literature publisching,* 1986

[35] GRACHEV V.I., KLIMENKO I.B., SMIRNOV L.V., GLADKIKH A.F., A spectroscopic study of the kinetics of thermal-oxidative degradation of PVB, *Vysokomol Soysed.,* Vol. 16, No. 2, 1974, p.367-373

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Influence of water and magnesium ion to the optical in various plasticized poly(vinyl butyral) sheets

Tupý M. (70%), Meřinská D., Svoboda P., Zvoníček J.

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PAPER II

Effect of water and acid-base reactants on adhesive properties of various plasticized poly(vinyl butyral) sheets

Tupý M. (65%), Meřinská D., Klásek A., Zvoníček J., Svoboda P.

Submitted for publication in *Journal of Applied Polymer Science*

PAPER III

Windshield recycling focused on effective separation of PVB sheet

Tupý M. (65%), Měřínská D., Mokrejš P., Zvoníček J.

Submitted for publication in *Resources, Conservation and Recycling*

PAPER IV

Degradation of plasticized PVB during re-processing by kneading

Měřínská D., Tupý M. (40%), Kašpárková V., Popelková J., Zvoníček J., Pištěk, D., Svoboda P.

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Paper I

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 acoutooptical properties which allow using them for acoutooptical modulators.[1] Acoutooptical 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 laminated 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-lec, 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 mentioned 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.

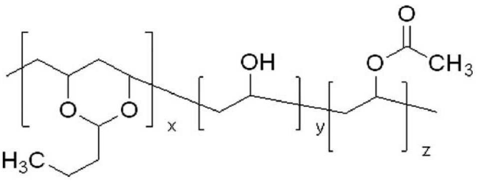

Figure 1 Poly(vinyl butyral) chain structure.

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 among 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 (manufacturerDuPont, 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 (manufacturerSolutia, USA) and in PVB sheet S-lec (manufacturerSeki-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 mm^2. 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% SiO_2, 13.4% Na_2O, 9.2% CaO, 4.15% MgO, 0.7% of Al_2O_3, 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

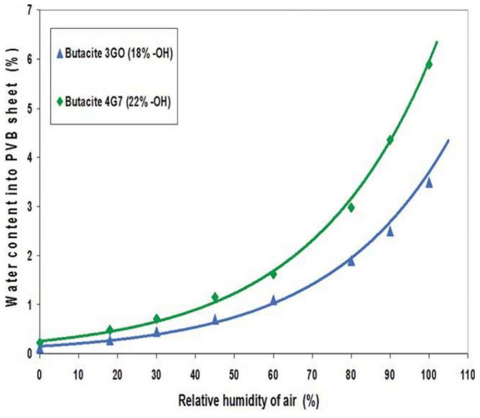

Figure 2 Influence of —OH group content on water absorbability. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

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

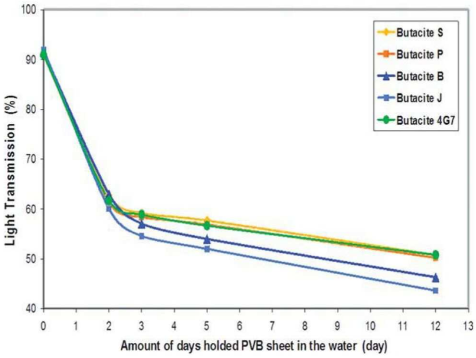

Figure 3 Dependence of light transmission on water content in Butacite sheets. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

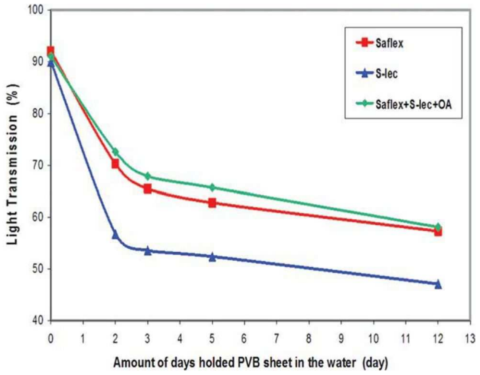

Figure 4 Dependence of light transmission on water content in Saflex, S-lec, and blended sheets. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

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

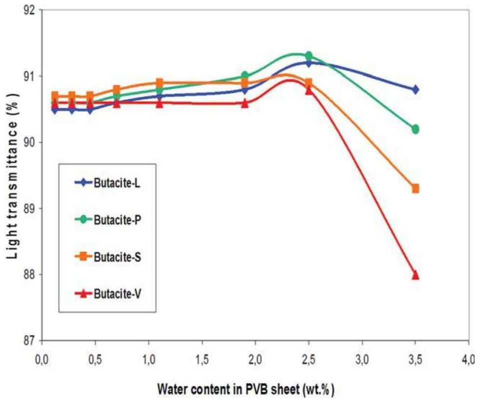

Figure 5 Light transitions on Butacite 3GO sheets—measured through glass laminate. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

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 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

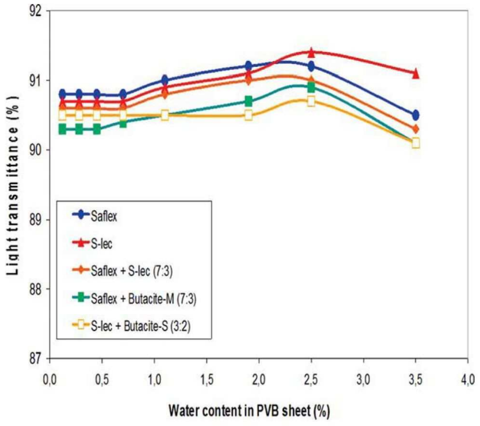

Figure 6 Light transmissions on Saflex, S-lec and its blended sheets—measured through glass laminate. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

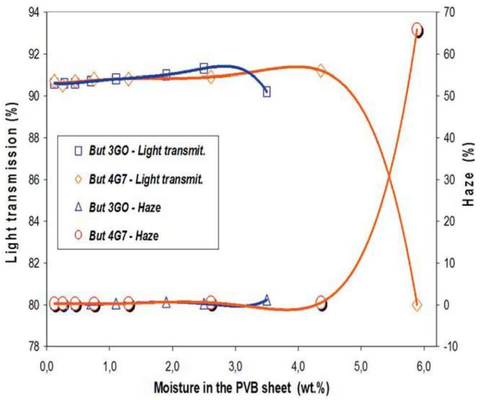

Figure 7 LT dependence on haze detected in Butacite 3GO (type P) and Butacite 4G7—measured through glass laminate. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

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

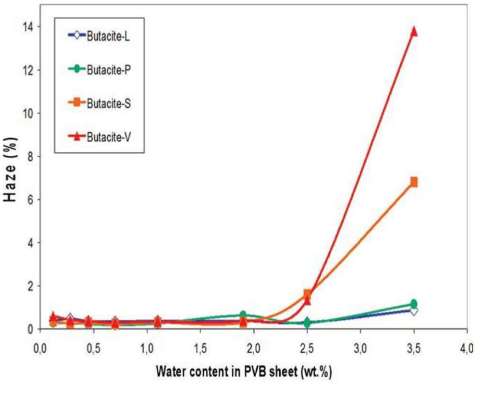

Figure 8 Haze intensity in Butacite sheets—measured through glass laminate. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

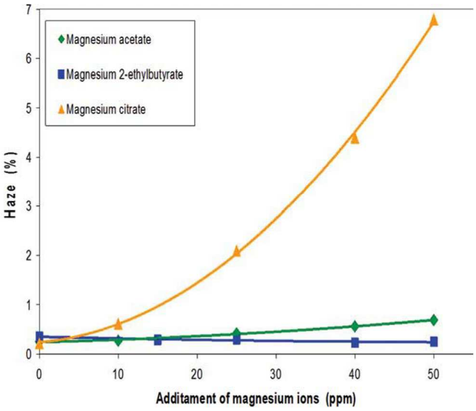

Figure 9 Dependence of haze increasing to modification of Butacite-V material by organic magnesium salts. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

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%. It 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,

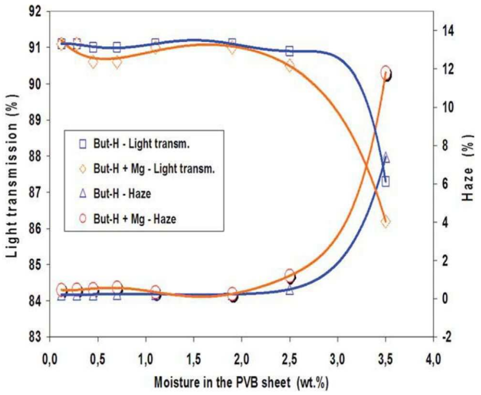

Figure 10 Change of optical properties as a function of increasing water content in Butacite-H material with/without a Mg^{2+} additive. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Type H and its modified material with 50 ppm of Mg^{2+}. Both types of sheet were conditioned to predetermine 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 a eq. (1):

$$I = Io \times \exp(-L \times \tau) \tag{1}$$

Absolute scattered light is influenced by PVB thickness L and turbidity coefficient τ. It depends on magnesium fragments amount ${}^{1}N$ 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]

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

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.

References

1. Kityk, I. V.; Kasperczyk, J.; Sahraoui, B.; Yasinskii, M. F.; Holan, B. Polymers 1997, 38, 4803.
2. Dhaliwal, A. K.; Hay, J. N. Thermochem Acta 2002, 391, 245.
3. Seo, J. J.; Kuk, S. T.; Kim, K. J Power Sources 1997, 69, 61.
4. Gorokhovsky, A. V.; Escapante-Garcia, J. I.; Gashnikova, G. Yu.; Nikulina, L. P.; Artemenko, S. E. Waste Manage 2005, 25, 733.
5. Iwasaki, R.; Sato, C. J Phys IV 2006, 134, 1153.
6. Ivanov, I. V. Int J Solids Struct 2006, 43, 6887.
7. Nghuen, F. N.; Berg, J. C. J Adhes Sci Technol 2004, 18, 1011.
8. Demalder, P. Saflex laminated guide, Solutia, St. Louis, Missouri, USA, 1991.
9. Kondo, T. (to Central Glass Co.) U.S. Pat. 6,315,848 (2001).
10. Joeng, S. Y.; Han, O. H. Bull Korean Chem Soc 2007, 28 (4).
11. Aoshima, Y.; Shohi, H. (to Sekisui Chemical Co.) Eur. Pat. EP 1,227,070 (2000).
12. Phillips, T. R. (to E. I. du Pont de Nemours and Co.) U.S. Pat. 7,285,594 (2005).
13. Tupý, M.; Měřínská, D.; Kašpárková, V.; Popelková, J.; Svoboda, P.; Zvoníèek, J.; Pištìk, D. Macromol Symp 2009, submitted.
14. Mister, R. E.; Bianchi, E.; Wade, B.; Hurlbut, J. Presented at 31st International Cocoa Beach Conference of the American Ceramic Society; Daytona Brach, January 21–26, 2007;
15. Sita, C.; Burns, M.; Hassler, R.; Focke, W. W. J Appl Polym Sci 2006, 101, 1751.
16. Papenfuhs, B.; Steuer, M. (to Kurray Specialties Europe GmbH) U.S. Pat. 6,984,679 (2001).
17. Tupý, M.; Měřínská, D.; Zvoníček, J. Plastics and Rubber; Tomas Bata University: 2008; Vol. 45: 208–211.
18. D'Errico, J. J.; Jemmott, B. A.; Krach, M. S.; Moran, J. R. (Solutia Inc.) Eur. Pat. EP 0,877,665 (1996).
19. Wade, B. E.; D'Errico, J. J.; Thompson, H. M.; Yu, M. K. (to Solutia Inc.) U.S. Pat. 7,125,607 (2004).
20. Smith, R. L.; Hayes, R. A. (to E. I. du Pont de Nemours and Co.) U.S. Pat. 11,647,735 (2006).
21. D'Errico, J. J.; Jemmott, B. A.; Krach, M. S.; Moran, J. R. U.S. Pat. 6,559,212 (1995).
22. D'errico, J. J. (to Solutia Inc.) Eur. Pat. EP 0,938,519B1 (1997).
23. Fish, B.; Lee, C. (to E. I. du Pont de Nemours and Co.) U.S. Pat. 7,138,454 (2003).
24. Takeshi, I.; Kenro, S.; Kohei, M.; Hideyo, T.; Yusuke, I.; Isao, S.; Morihide, M.; Toshio, W. E.; Genki, H. (to Staas & Hasley LLP) AB32B302 (2009).
25. Trainor, N. H. (to Rohm & Haas) U.S. Pat. 2,032,663 (1936).
26. Nagai, K. U.S. Pat. 6,686,032 (2001).
27. Shichiri, T.; Miyai, J.; Bando, A.; Toyama, K.; Aoshima, Y.; Sannomiya, I.; Nakajima, M. (to Sekisui Chemical Co., Ltd.) U.S. Pat. 7,074,487 (2002).
28. Aoshima, Y.; Shohi, H. (to Sekisui Chemical Co., Ltd.) Eur. Pat. EN1,227,070A1 (2000).
29. Hermann, H. D.; Fabian, K.; Ebigt, J. (to Hoechst Aktiengesellschaft) U.S. Pat. 4,533,601(1984).
30. Shichiri, T.; Miyai, J.; Bando, A.; Toyama, K.; Aoshima, Y.; Sannomiya, I.; Nakajima, M. (to Sekisui Chemical Co., Ltd.) U.S. Pat. 6,387,516 (1999).
31. Brdička, R.; Dvořák, J. Foundamentals of Physical Chemistry; Academia: Praha, 1977; Vol. 2, Chapter 7C, p 640.

Paper II

Effect of water and acid-base reactants on adhesive properties of various plasticized poly(vinyl butyral) sheets

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ABSTRACT

The study is focused on influences of adhesive properties change 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 and thermo-mechanical mixer processes etc. Some samples were modified either by magnesium acetate or by oligo-functional organic acid in order to either reduce the adhesion to glass or to increase it. The study discovered the method for both ways. 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 to glass in particular conditions.

The analysis evaluates the best and the worst blend combinations and their modification on the adhesion change. It was focused on adhesion sensitivity to increasing water content and the amount of added adhesion modifier. However, the most important discovery of this work is evaluation of 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 PVB sheets industry and for industry dealing with lamination of laminated glasses.

Keywords: Laminated glass, Poly(vinyl butyral), Adhesion, Acid-base agent

1 INTRODUCTION

The plasticized polyvinyl butyral sheet is extensively used for laminated safety glasses for an automotive and a building industry. At present time, worldwide PVB manufacturers are Solutia, DuPont, Sekisui and Kuraray. Generally, polyvinyl materials possess excellent acoutooptical properties which allow using them for acoutooptical modulators [1]. Acoutooptical 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 [2,3,4,5,6,7,8]. 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 adhesion level around 50% of maximal adhesion [2,10,11]. High adhesion degree causes PVB breakage during the car-crash. On the other hand, low adhesion degree does not keep the glass on PVB surface after the crash. The laminated glass used in building industry (safety glass of glazed skyscraper) has the adhesion requirement to be near to the maximal adhesion level [2,9].

The adhesive bonding grows during two independent steps. The first of them is a transport of PVB macromolecule towards the interface. This is generally described by 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 bridging is provided by hydrogen bonding (H-bond) between –OH group of PVB chain and the oxygen in the glass [2,7,8,13,14]. This theory supports that PVB adhesion depends on water content in PVB matrix [2]. The water adsorbed into PVB matrix is bonded to –OH groups of PVB macromolecule [17]. Hence, the measurement has revealed that water content around 2 wt.% in PVB caused the saturation of binding sites [16,17]. Adhesive forces decrease and residual adhesion originates only from weak dispersion forces.

The observation has also revealed some cases of unstable H-bond and possibilities of H-bond breakage. E.g., addition of alcohol, salts dissolution, pH deviation or increase of temperature above the critical value denatures double-helix in proteins irreversibly. Another case is elevated boiling point of water, alcohols or organic acids caused by H-bond aggregation of molecules. However, this H-bond disappearance is reversible. The conclusion is that the H-bonding stability depends on temperature, molecule solubility and amount of dissolved salts, conforming polarity and pH of the system [2,14]. In the case of PVB it was observed that the adhesion is reversible. As mentioned above, the PVB adhesion is generated by H-bond [2,14].

Nowadays, the PVB material must be re-processed due to the increasing amount of the PVB waste [3,5,12,16,17]. The recyclable PVB is created as waste during PVB sheet manufacturing (does not meet quality specifications). The next source of a recyclable PVB material is a trim of the PVB sheet lamination between glasses. 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 in order to obtain the required adhesion grade. Moreover, PVB re-processing degrades polymer and it changes the adhesion to the glass [16]. The PVB sheet with an adhesion degree which 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 type to water content in PVB sheet. Therefore, this study describes all these above mentioned problems.

The paper is also focused on the field of the primary adhesion adjustment during a production of PVB polymer. The polymer made by an acetalysation of polyvinyl alcohol has the "virgin adhesion" excessively high for direct use. Above mentioned high adhesion degree is caused by high activity of unacetalyzed hydroxyl groups in PVB chain (15-23 wt% of –OH groups) [3,8,18,19]. 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 used substances modifying the adhesion are salts of Na^+, K^+ and Mg^{2+} ions in strictly specified ion ratio and its total amount [11,20,21,22,23,24]. Moreover, the keeping of water content in PVB at a range 0.3-0.5% is necessary for maintaining the required adhesion grade [2,19,20,24]. This mentioned 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 PVB chain and the interaction between the glass and the PVB is not disturbed. On the other hand, higher water content in PVB causes sharp adhesion reduction on "tin side" of the laminated glass. In addition, it is possible to clearly see the non-linear adhesion development on the "air side" of the laminate as a function of the water content in PVB. In spite of the effort to find the description of this phenomenon similar observation has not been published yet.

In summary, with respect to higher mentioned PVB adhesion requirements it is possible to summarize all to the main aim of the work. This is the study of possibility of PVB adhesion adjustment at different water levels in the PVB matrix and by various reagents. Nowadays, there exists only one acceptable way for the float glass preparation. The float glass is made by the casting of the glass melt on the surface of the melt tin. Due to this fact, prepared float glass has the 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, which is determinable by UV-rays reflections, causes totally different adhesion response between PVB and glass with increasing moisture in a polymer [9]. Therefore, the laminated glass contains layers “air side–PVB–tin side”.

Manufacturing of PVB sheet is generally based on following principles. Melt plasticized PVB is extruded through sheet extrusion die at temperature 160-210℃ to water. The PVB melt retains its shape, thickness and specific sheet surface, which is necessary for de-aeration at pre-lamination process [12]. Consequently, the PVB sheet must be placed between two (or more) clear shaped glasses with PVB oversize around 5 mm. This sandwich is pre-laminated between two rolls or by vacuum in temperature range 90-140℃ and pressure 0.2-1.0 MPa [9,12]. The pre-laminated product is still not transparent on all laminate surfaces, it contains residual air. Following steps are PVB trim cutting near the glass edge and autoclaving at temperature 130-150℃ and pressure 0.9-1.5 MPa for several tens of minutes [9,12,25,26]. After the autoclaving the generated adhesive bond keeps glass fragments on PVB sheet after potential accident. This is most important property of PVB sheet.

2 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 [8,19,20]. 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 [2,8,13,14,16]. While 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 ter-polymer of vinyl butyral, vinyl alcohol and vinyl acetate (see Figure 1). This atactic copolymer structure contains 18-22% of hydroxyl groups (depends on PVB type), less than 2% of acetate and about 76-80% of butyric acid [8,9,20]. 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 used [3,9,12,16,18,27,28,29,30]. The different hydroxyl group content in PVB chain requires also different modification way and its adhesion stabilization of PVB to glass.

Samples

Virgin plasticized PVB sheets were commercial ones from DuPont, Solutia and Sekisui. Some of them are suitable either for automotive industry or for building industry laminate glasses. PVB sheets with trade name Butacite B3 *(manufacturer DuPont, USA)* made before year 2003 were plasticized by tetraethylene glycol bis(heptanoate) (labeled 4G7); the polymer contains 22% of non-acetalyzed hydroxyl groups in the polymer chain [35,36]. Butacite B5 made since year 2003 contains plasticizer triethylene glycol bis(2-ethylhexanoate) (labeled 3GO); the polymer contains 18-18,5% of hydroxyl groups in polymer chain [19,31,35]. The same plasticizer 3GO and amount of hydroxyl groups in polymer chain contains tested Saflex PVB sheet *(manufacturer Solutia, USA)* and PVB sheet S-lec *(manufacturer Sekisui, Japan)* [19,27,28]. Samples mixed with modifications and blended materials were obtained by extrusion process which is described in chapter “Samples preparation”. All tested samples are described in Table 1.

Strictly assigned amount of unacetalyzed hydroxyl group in polymer chain along with applied plasticizers is necessary for determination of stability of polymer system [2]. The different hydroxyl group content would cause the plasticizer migration out of PVB matrix; in particular at higher temperatures [16]. The content of added adhesive adjusting agents (adhesive modifiers) is not available for all PVB sheets. Amount of cations addition and hydroxyl group content are described in literature [11,19,23,24]. These values are used for comparison and evaluation described in the paper.

Sample preparation

A material blending and the modification mixing were carried out in the single-screw extruder, screen system with an apertures size up to 60 µm and sheet extrusion die [12]. PVB sheets are conditioned in air-conditioning cabinet *(Weiss, Deutschland)* in order to achieve the required water content in the sheet at 40℃. Conditioned sheets were put between two glasses previously washed with demineralized water. Both glasses are 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 a temperature 130℃. Fixed PVB layered samples were laminated in the autoclave with pressure 1.2 MPa and temperature 140℃ for 20 minutes. After that it was slowly cooled to room temperature [12]. Finally, samples of laminated glass were cut out to the size 150x100mm^2. Humidity and adhesion by Pummel test were measured.

The float glass used for samples preparation had common chemical composition 71.5% SiO_2, 13.4% Na_2O, 9.2% CaO, 4.15% MgO, 0.7% of Al_2O_3 and also other minor compounds. Float glasses were delivered from company AGC Teplice *(Czech rep.)*. 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 lightly 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 (down side of the laminate).

Methods

The purpose of adhesion Pummel test is to measure the relative bond strength between PVB and glass. The method is described by US Patent [2,33]. Deep-frozen samples at -18 ℃ has undergone 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 1.92µm by water (*PIER Electronic GmbH*). The lab equipment was calibrated to the standard type Butacite B5 at water content 0.16 and 0.75%. Measured glass was placed towards the equipment in angle 60° of detected infrared ray. The measured background was a common mirror.

Water quantifying assessment in PVB sheets before lamination was performed by Karl Fischer method. The method is based on conduktimetric assessment of evaporated water from sample to a special solution of iodine and sulphur dioxide in methanol (*Metrohm*).

Alkali titer (total alkalinity of the product) of PVB sheet solution was determined by titration of 0.01 M - HCl with solution of 7.0 g of PVB sheet dissolved in 250 cm^3 of ethanol (ethanol is neutralized by 0.01 M - HCl with bromphenyl blue indicator).

The FTIR spectroscopy was employed to study the specific PVB adhesion bonds with glass in particular conditions. The measurement equipment Avatar 320 *(NICOLET, CZ*) with Attenuated Total Reflection (ATR) technique with 64 scans was used. Spectra were collected over the range 4000–550 cm^{-1}.

3 RESULTS AND DISCUSSION

Mechanism of PVB adhesion to glass and the possibility of the adhesion modification

The adhesion bond causing PVB adhesion to the glass was tested in order to find the adhesion fluctuation in case of such PVB sheet and confirm the adhesion mechanism. Simultaneously, the adhesion change was estimated as alteration of various physical conditions together with chemical reactants. The PVB adhesion to glass is based on specific bond creation and it sharply depends on polar group number in PVB chain [2,13,14]. The result from observation suggests that in the case of safety glass, the adhesion is based on linkage between hydroxyl group in a structure of the glass and the hydroxyl group of the PVB chain [2]. This bonding structure is shown in Figure 1.
Each of –OH groups on the glass and PVB influence on specific adhesion bridging which causes following PVB adhesion to glass as Figure 2 shows [2,8,14]. Admittedly, the hydrogen bonding is not created sooner than the autoclaving process reaches higher temperature and pressure. Moreover, the generation of inferior physical bonds was observed. However, this linkage provided only very weak coupling between glued materials. Thereto, both types of adhesion bond were supported by vacuum used during the pre-lamination process. It was achieved by venting of the air interlayer that separates the glass and the PVB. Mentioned effect was clearly observable with low adhesion level.

The finding of adhesion basis in influence on water content into PVB sheet brings two important observations for an industry. The first one is an acceptable manner of glass delamination (separation) from PVB sheet of the safety glass and obtaining of recyclable PVB [3,12]. The second one is possibility to adjust the PVB adhesion to glass to required value. This is achieved either by inhibition or activation of adhesive hydrogen bonding. The adjusting of the PVB adhesion is indispensably requested during PVB sheet re-processing due to un-homogeneous or un-requested adhesion grade of entering material.

PVB hydrophility, the influence of water and acid-base reactants on the adhesion to the glass

As mentioned, for the comprehension of adhesion mechanism it was necessary to know the adhesion sensitivity of every PVB and its affectability by suitable agent. Moreover, one of the most important points is the knowledge of interaction of this modifier (agent) with water adsorbed in the PVB matrix. The activity or passivity of added adhesion modifiers is mainly influenced just by water present in the PVB matrix. Moreover, even low water content (sometimes only 0.1%) primarily influences the activity of hydroxyl groups in PVB chain. Due to this fact, the water content is very important for final adhesion degree on the air side and on the tin side of the laminate; even without addition of modifiers [2].

The influence of the humidity of environment on the water absorbability rate in PVB sheets with various plasticizers and with different hydroxyl group content in PVB chain was observed. PVB sheets Saflex, S-lec and Butacite (type 3GO) have similar –OH group content and water absorbability. The ability of water absorption of these PVB sheets is described 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, PVB chain (higher chain polarity) which has higher hydroxyl group has also higher water absorbability.
Obtained results indicate that water plasticize the PVB matrix. This is observed on physical properties of PVB sheets; with increasing water content its strength reduces [16]. Accompanying effect was significant whitening of PVB sheets, sharp haze increase and extreme light transmittance decline when the water content is in the range 3.0-5.0% (based on manufacturer and PVB type) [17].

Next tests were focused on the influence of water on PVB adhesion change. PVB 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%, see 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 adhesion of „air side" of the glass provided totally different behavior. Therefore, acceptable reactants and its quantity for required adhesion degree were assessed. Results shown in Figure 4 and Figure 5 confirm suggestion of mentioned public [14]. These are explained the influence of acid-base agents on the change of the adhesion forces and explain 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 organic acid solution (pH = 1.5-2.0). The adhesion grade was assessed at laminated glasses prepared from modified PVB sheet conditioned to water content

0.5%. This water content was chosen because industry manufactured PVB sheets have just 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 adjustable in manufacturing.

Inhibition of hydroxyl groups in PVB chain

As demonstrated by preliminary tests shown in Figure 4 and Figure 5, magnesium ions interact with –OH groups in polymer chain and due to this fact they were inhibited [2,14]. Following adhesion reduction was directly proportional to alkali reacting ion content, respectively to the active –OH group content in PVB chain (see Figure 2). According to results in following proved tests (see Figures 14-16) the higher –OH group content in PVB chain needed the higher amount of adhesion modifier for the same adhesion change.

The adhesion modifiers define the dependence of adhesion on the water presence. 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 based 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 [25].

In addition to the previous observation, reagents with various alkalinities were tested in order to compare the adhesion reduction ability. It was found that the influence of reactants on adhesion is in the following order: NaOH > KAc > MgAc > H_3BO_3 > 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. In spite of 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 PVB –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 –OH groups and their silanol counterparts. Resulting is weakening of the adhesive bond. Therefore, alkali reacting ions can interact directly with PVB –OH groups and rendering them unavailable for bonding. This process promotes “alkali deactivation” of polar groups which cannot generate intermolecular bonding in mentioned conditions [2]. However, the active acidic center can be generated. This adhesion way 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 (done by different alkali ions content) were tested. The ratio of ions were each time K:Mg = 3:1. Based on various alkali ion contents 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 (added by manufacturer); at this sample the lowest adhesion degree is detected (approx. 20% of maximum – measured at 0.5% of water content). On the other hand, Butacite labeled as But-3GO-V belongs to the lowest content of alkali modifier (added by manufacturer); and the adhesion degree reaches the maximum (100%). It was found But-L sheet contains approx. three times more of alkali ions than But-3GO-V. Results are shown in Figure 6 and Figure 7.

Based on 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 that is independent on alkali ions content as it is shown on Figure 7. The reason for absence of adhesion fluctuation in the “tin side” could be explained by the generation of hydrolysis of tin nano-layer. The hydrolysis product forms interlayering between the PVB and the glass. This product should be complex compound of $[Sn(OH)_6]^{2-}$ with alkali ion which does not react with free –OH groups of PVB and the glass and inhibiting the adhesion bridging.

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 zero. 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 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 grown at water content in the range 0.8-2.5%. This trend was clearly observed for all of tested PVB sheets (including acidic modified materials). Above mentioned abnormality caused by sharp adhesion increase was caused by alkali reacting hydrolysis modifiers. Products of the hydrolysis re-activate free –OH groups of polymer chain and free –OH groups of the glass. Probable structure of generated chemical compound is shown in Figure 8. Generated strong intermolecular adhesive bonding can be a combination of the Van der Waals and the ionic bond. This structure was analyzed by FTIR spectroscopy and the result is shown in Figure 9.

These FTIR spectra evaluated PVB with water content < 0.3 % and the PVB 0.8-2.5 % treated with alkali ions. Specific bands were detected at 3499, 3398 cm^{-1} due to intramolecular and intermolecular -OH bonds, 2633 cm^{-1} -OH bonds overtones of stretching vibrations, 1379, 683 cm^{-1} coming from -OH deformation vibrations, 2954, 2870, 2735, 1434, 1342, 997, 810, 743 cm^{-1} due to $-CH_3$ asymmetric and symmetric stretching, overtones and rocking vibrations, 2936, 2855, 2735, 1434, 969, 731 cm^{-1} from CH_2 asymmetric, symmetric stretching, overtones, rocking vibrations, 1732 cm^{-1} due to C=O, 1458 cm^{-1} characterizing CH_3-O deformation vibration, 1240 cm^{-1} from tertiary butyl group, 1164 cm^{-1} shoulder due to C–O–C–O–C stretching vibrations and 1130, 1105, 912 cm^{-1} coming from C-O-C stretching were observed in PVB.

As could be seen in Figure 9, changes in -OH vibration area are occurred by sample with water content 0.8-2.5%. The intensity of intermolecular -OH bonds at 3398 cm^{-1} is growing and this fact is also confirmed by peak area evaluation. For PVB material (But-3GO-P) in water content < 0.3 % is the peak area 4.97 in region 3769-3002 cm^{-1}. On the other hand, for this PVB material in water content 0.8-2.5 % treated with alkali ions it is 11.58. Also new peaks at 3680, 1688 and 1639 cm^{-1} were observed. These vibrations are connected with predicted bond in Fig. 8 and the results indicated that the new adhesion bond between PVB and glass is arising at present of specific water content.

Nevertheless, mentioned adhesion bonding (on air side) disappeared when the water content exceeds 2.5%. In this case, present water generated interlayer that separates the two surfaces [11,17]. However, precise value of such adhesion loss for various types of PVB depends on the amount and the type of added alkali metal ion and its anion of adhesion modifier. Comparison of influence of water content to adhesion of such PVB sheets is described in last capture “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 (see Figure 10b) (0.3-0.6%) the glass fragments had very small dimensions (0.1x0.1mm) and these small fragments could be broken into the dust. On the other hand, in case of higher water content (see Figure 10a) (0.8-2.5%) the fragmented pieces had much higher size of glass fragments (0.5x0.5mm). In both cases the adhesion had high level but the structure of broken glass was quite different.

Following tests were focused on adhesion fluctuation confirmation and comparison modified and original sheets. PVB sheet But-3GO-P (low adhesion) and the same PVB material modified by 4 ppm Mg^{2+} were tested. Similarly, PVB sheet But-3GO-S (intermediate adhesion) and the same PVB material modified by 14 ppm Mg^{2+} (both added as magnesium acetate), were tested. Obtained adhesion stability in relation to water content in the sheets is presented in Figure 11 and Figure 12. Addition of magnesium ions to both Butacite sheets caused only slight adhesion change on tin side. This confirms obtained results from adhesion testing of commercial sheets (see Figure 7). Moreover, the addition of 4 ppm of Mg^{2+} to material But-3GO-P was extremely low for generation of any significant change in adhesion. However, higher addition (14 ppm Mg^{2+}) to material But-3GO-S was sufficient for visible adhesion change when the water content was about 0.5%. Important result is that addition of magnesium ions to both Butacite materials evokes more pronounced “adhesion fluctuation” on the air side of the laminate. It reconfirms results from the testing of commercial PVB sheets (see Figure 6).

Activation of hydroxyl groups in PVB chain

The successful testing of alkaline PVB modification indicates that acidic reacting agent can cause an adhesion growth. The modification by oligo-functional 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 added organic acid as shown on Figures 14-22. The addition of acid agent neutralized alkali ions present in PVB matrix and thus activates –OH groups of 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 results, higher cation content in PVB matrix or higher hydroxyl group content in polymer chain required higher amount of acid adjusting agents in order to attain the same adhesion degree. It is perceivable from the results illustrated in Figures 14-16. Generally, the adhesion increase is achieved by protonating of hydroxyl groups and by creation of active centers on polymer chain. The chemism of hydroxyl group activation is explained by Figure 11. Acidic modified PVB sheets assigned many times higher adhesion stability on the air side and on the tin side of the laminate with changing water content, the adhesion curves had no fluctuation. Thus, this shape of the adhesive curve has distinctively different behavior than the curve in case of alkali modified PVB. It is the best visible in case of sample But-3GO-S + 7 ppm OA (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 marginally drops again to zero. Generally, the shapes of the curves of acidic modified PVB sheets are similar; the adhesion fluctuations are suppressed.

Following text describe a comparison of such PVB types before and after acidic modification. Samples contained original addition of alkali ions (modifier) from manufacturer; But-3GO-P contains approx. twice more of the alkali ions than But-3GO-S. Due to above mentioned different amount of alkali ions we have decided to apply several times more of organic acid in order to observe a significant change. Therefore, 5 times more organic acid was added to material But-3GO-P in order to achieve the same adhesion degree as for But-3GO-S. Certainly, required adhesion degree was expected when the water content was around 0.4-0.5%. According to expectation, adhesion level increased proportionally to the amount of added organic acid as it is shown in Figures 14-15. Final adhesion curves of both compared materials are very similar and these do not assigned the adhesion fluctuation. Thereunto, while the acidity of PVB matrix increased sensitivity of adhesion to water content change decreased.

In the case of alkali modified PVB sheets Butacite-3GO, the water content in range 0.6-0.8% evoked sharp adhesion increase on the air side. Moreover, these sheets assigned much higher adhesion fluctuation and with water content above 2-3 % (based on modification degree) the adhesion goes to zero value. On the other hand, acidic modified sheets assigned much stable dependence of adhesion to water content and the adhesion was kept with higher water content in the sheet (compare Figures 14-22).

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 dissimilar hydroxyl group content (22 versus 18%). Moreover, these materials have not only dissimilar –OH group content but also they have different adhesion adjusting system. While 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 [11,19,33]. Moreover, PVB type But-4G7-Z with higher content of –OH groups in polymer chain has to contain approx. 5 times more of alkali ions to reach the same adhesion degree [11]. It is obvious that the amount of added organic acid is 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 in order to achieve the same change of adhesion degree. The dissimilar hydroxyl group content and the adhesion adjusting system caused higher hydroscopic behavior of polymer system But-4G7-Z which multiplies the influence of the adhesive centers. Influence of it, 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 change of adhesion as a function of a change in the water content.

Since 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 most differences between materials were either in –OH group content or in adhesion adjusting system. From these differences comes various adhesion degree and therefore these blends must be modified. Consequently, virgin materials and their modified blends of common materials from various worldwide manufacturers were tested to find adhesive behavior as a function of water content in PVB. Tests on But-3GO-M sheet and Saflex sheet and its extruded blend in wt. ratio 1:1 and the blend modified by 7 ppm of organic acid were carried out. Moreover, tests on Saflex and S-lec sheet and its extruded blend in wt. ratio 7:3 and 3:2 and the same blends modified by 45 ppm of organic acid were performed. This higher content of organic acid was experimentally found in order to aim the adhesion of blended sheets to be in the same range. 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 17-22. Obtained adhesion properties as a function of water content of blended material Saflex and S-lec were similar to the case of modified Butacite sheets. Comparison of such PVB sheets is described in following capture.

The evaluation of acceptable behavior of adhesion curve (air and tin side)

Firstly, the evaluation is focused on comparing of adhesive properties on tin side of laminates of all tested materials. The obtained adhesion properties were similar, mostly without “adhesion fluctuation”. The abnormality was observable in Saflex and S-lec sheets and their blends. in the range of water content 0.3-0.8%. 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.

Generally, very important property of adhesion behavior part is a width of wave of adhesion fluctuation of such PVB sheet (large drop followed by sharp increase). Just 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 PVB sheet manufacturers). On the other hand, narrow adhesion fluctuation changed the PVB adhesion abruptly with a low difference of water content. Because all industrially PVB sheets have to be manufactured at water content 0.3-0.6% mentioned region significantly influences the PVB adhesion just with the change of 0.1% many times.

Comparison of adhesion behavior on air side of laminates of Butacite 3GO, Saflex and S-lec sheets provides 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 implicated to narrowing of the fluctuation until it disappeared. Similar trend was observed for But-4G7-Z but with different localization of adhesion fluctuation (different PVB hydroscopic behavior).

Consequently, the text is focused on comparison of obtained results for individual materials. First blended PVB sheet Butacite+Saflex did not bring any significant change in adhesive behavior. It was caused only by small addition of organic acid. The decline of adhesion fluctuation on air side of the laminate was in the water content range 0.3-1.3%.

Next blended PVB sheet Saflex+S-lec has adhesion fluctuation in region 0.3-0.7% for both tested wt. material ratios (7:3 and 3:2). It is necessary to mention that blended PVB 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 range of water content in the sheet. Including above mentioned facts, the acidity promotes a stability of adhesive humidity curve, predominantly in observed region 0.3-0.8% of water content. Nevertheless, the comparison of blended PVB sheets Saflex+S-lec with the same acidic addition in different material ratios still points out on the high adhesion degree of these materials. The material ratio of Saflex 60% (blending 3:2, see Figures 19-20) provides higher adhesion variation than the material with 70% of Saflex (see Figures 21-22). However, in case of blends with Saflex sheet results point out to the necessity of use 5 times more of acidic modifier in order to achieve the same adhesion degree. Furthermore, the difference of Saflex material was observable particularly above water content 3.0%. Very high adhesion degree was kept in very high water content level approached to 7-8%. However, the Butacite and S-lec materials did not shown any adhesion value at mentioned water content in PVB; the adhesion falls down to zero value in water content around 3-4% (according to the type of used PVB).

All obtained results are very significant for the use of PVB sheets in industry. For example, PVB sheet stored at relative humidity 80% contains approx. 2% of absorbed water in polymer matrix. The lamination of this PVB sheet renders the “safety glass” with absolutely inadequate safety properties. Moreover water can cause haze and reduces the light transmission [17]. Admittedly, such type of PVB sheet has various sensitivities 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 zero value is accessible either by higher water content in the sheet or by present of alkali reacting ions. This can be applied at windshield recycling process. However, the obtaining of pure PVB without glass contamination is not still solved. High alkali solution can reduce the PVB adhesion to value that could provide separable and re-processable PVB sheet. The research of mentioned technology is subject of our present work.

Summary of this study can be described by the best and the worst type of the PVB sheet including sheet modifications. The blend of acidic modified PVB 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 air side. Together with that, the tin side was also highly stable; the adhesion did not vary till water content 1.3%. The similar adhesion behavior was not found in any other case of tested PVB sheets. On the other hand, absolutely unsuitable PVB sheet was the type But-4G7-Z. Although, this material was modified by 140 ppm of organic acid; the adhesion increased only slightly. Moreover, But-4G7-Z was highly hydroscopic and the adhesion gradually falls down to zero value. This material had water content 3% at relative humidity 80%. The other tested PVB sheets had adhesion grade between 4-7°P on air side at the same relative humidity; adhesion of But-4G7-Z dropped down to almost zero value.

CONCLUSIONS

This study confirmed that in case of safety glass the adhesion between PVB and the glass is based on Van der Waals bond between the –OH groups of PVB chain and the –OH groups in glass. However, these –OH groups shouldn't be chemically or physically inhibited or in these cases the adhesive bridging does not create (–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 to adhesion was compared at various PVB sheets. Certain PVB sheets were modified by either alkali or acid modifiers. It was confirmed that alkali modification decreases the adhesion of PVB to glass. On the other hand it was discovered that acidic modification increases the adhesion of PVB to glass. Moreover the acidic modification renders much smaller adhesion fluctuation and thus higher stability of adhesion in regards to water content in PVB sheet.

Obtained test 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 from "air side" had unstable dependence with increasing water content in PVB, an adhesion fluctuation was observed. Shape of the fluctuation curve was typical for each type of PVB sheet and each type of modification (pH influence). Thus this adhesion fluctuation plays important role when the water content is in range 0.3-0.6% that is just the range set by PVB manufacturers. The most stable adhesion with regard to water content in PVB matrix was observed for blends of Saflex and S-lec sheets modified by an acid. The least suitable type of the sheet was But-4G7-Z (22 wt% of –OH groups). This sheet contained large amounts of potassium ions and –OH groups that affect the sheet to be hydrophilic, which causes much faster decrease in adhesion caused by increasing relative humidity. Moreover, in order to increase the adhesion of this sheet it was necessary to add approximately 5 times higher amount of adhesion modifier compared to Butacite 3GO sheets (18 wt% of –OH groups) to get the same adhesion level.

Obtained 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.

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REFERENCES

1. Kityk I.V., Kasperczyk J., Sahraoui B., Yasinskii M.F. & Holan B.; Polymers, 1997, Vol. 38, No. 19, pp.4803-4806
2. Keller U., Mortelmans H., Glass Processing Days, 13–16 June 1999, Session 8, pp.353-536
3. Dhaliwal A.K., Hay J.N.; Thermochem. acta, Vol.391, 2002, pp.245-255
4. Seo J.J., Kuk S.T., Kim K.; J Power Sources, Vol.69 1997, pp.61-68
5. Gorokhovsky A.V., Escapante-Garcia J.I., Gashnikova G.Yu., Nikulina L.P., Artemenko S.E.; Waste Management, Vol.25, 2005, pp.733-736
6. Iwasaki R., Sato C.; J de Physique IV, Vol.134, 2006, pp.1153-1158
7. Ivanov I.V.; Inter J Solids and Struct, Vol.43, 2006, pp.6887-6907
8. Nghuen F.N., Berg J.C.; J Adhes Sci Technol, Vol.18, No.9, 2004, pp.1011-1026
9. Svoboda J., Balázš M., Sedlář J.; Glass union concern: Research and developing institute of industrial glass in Teplice, series C, No.1, Teplice, 1988
10. Wade, B.E., D'Errico J.J., Thompson H.M., Yu M.K. (Solutia Inc.); U.S. Patent 7,125,607, March 16, 2004

11. Smith R.L., Hayes R.A. (E. I. du Pont de Nemours and Co.); U.S. Patent 11647735, December 29, 2006
12. Tupý M., Měřínská D., Zvoníček J.; Tomas Bata University: Plastics and Rubber, Vol.45, 2008, pp.208-211
13. Nguyen F.N.; Berg J.C., Journ Adhes Sci Techn, Vol.18, No.9, 2004 , pp.1011-1026
14. Fowkes, Frederick M., Journ Adhes Sci Techn, Vol.1, No.1, 1987, pp. 7-27
15. Joeng S. Y., Han O. H.; Bull Korean Chem Soc, Vol. 28, 2007, No. 4
16. Měřínská D., Tupý M., Kašpárková V., Popelková J., Zvoníček J., Pištěk D., Svoboda P.; Macromol Symp, 2009, Vol. 286, pp.107-115
17. Tupý M., Měřínská D., Svoboda P., Zvoníček J.; J Appl Polym Sci, 2010, Vol.118, pp.2100-2108
18. D'Errico J.J, Jemmott B.A., Krach M.S., Moran J.R. (Solutia Inc.); European Patent EP 0,877,665, December 24, 1996
19. Wade B.E. (West Springfield, MA, US), D'errico J.J. (Glastonbury, CT, US), Thompson H.M. (Somers, CT, US), Yu M.K. (Ludlow, MA, US), U.S. Patent Appl 20050208315, March 16, 2004
20. D'Errico J.J., Jemmott B.A., Krach M.S., Moran J.R.; U.S. Patent 6,559,212, December 29, 1995
21. D'Errico J.J. (Solutia Inc.); European Patent EP 0,938,519B1, November 12, 1997
22. Shichiri, T., Miyai, J., Bando A., Toyama K., Aoshima Y., Sannomiya I., Nakajima M. (Sekisui Chemical Co., Ltd.); U.S. Patent 7,074,487, March 28, 2002
23. Aoshima Y., Shohi H (Sekisui Chemical Co., Ltd.); European Patent EN1227070A1, June 6, 2000
24. Hermann H.D., Fabian K., EbigtJ. (Hoechst Aktiengesellschaft); U.S. Patent 4,533,601, January 31, 1984
25. Trainor, Neher Harry (Rohm & Haas); U.S. Patent 2,032,663, March 30, 1936
26. Nagai K.; U.S. Patent 6,686,032, Jul 6, 2001
27. Phillips, T. R. (E. I. du Pont de Nemours and Co.); U.S. Patent 7,285,594, April 5, 2005
28. Mister R.E., Bianchi E., Wade B., Hurlbut J.; 31st International Cocoa Beach Conference of the American Ceramic Society, Daytona Brach, January 21-26, 2007.
29. Sita C., Burns M., Hassler R., Focke W. W.; J Appl Polym Sci, Vol.101, Issue 3, pp.1751-1755, 2006
30. Papenfuhs B., Steuer M. (Kurray Specialties Europe GmbH); U.S. Patent 6,984,679, December 22, 2001

31. Fish, Robert B., Lee, Win-Chung, (E. I. du Pont de Nemours and Co.); U.S. Patent 7,138,454, September 4, 2003

32. Takeshi I**.,** Kenro S**.,** Kohei M**.,** Hideyo T**.,** Yusuke I**.,** Isao S**.,** Morihide M**.,** Toshio W**.**E**.,** Genki H**.** (Staas & Hasley LLP); AB32B302**,** 2009

33. Smith R.L., Rymer D.L., Harper L.R., McKierman D.J., (E. I. du Pont de Nemours and Co.); U.S. Patent Appl 20080277045, November 13, 2008

Table 1: Sources and description of virgin, mixed and blended PVB sheets

Labeling and Polymer description	Type of PVB material	Adhesion grade	Modification	Plasticizer	-OH group content in PVB chain (wt.%)
But-3GO-L, M	Virgin	low	no added agents *)	type 3GO	18,0-19,0
Butacite-3GO-P	Virgin	intermediate	no added agents *)	type 3GO	18,0-19,0
Butacite-3GO-S, V	Virgin	high	no added agents *)	type 3GO	18,0-19,0
Butacite-4G7-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
But-3GO-P +Mg	Alkali Modified	low	single material + 4 ppm Mg^{2+}	type 3GO	18,0-19,0
But-3GO-S +Mg	Alkali Modified	intermediate	single material + 14 ppm Mg^{2+}	type 3GO	18,0-19,0
But-3GO-S +OA	Acidic Modified	high	single material + 7 ppm of organic acid	type 3GO	18,0-19,0
But-3GO-P +OA	Acidic Modified	high	single material + 35 ppm of organic acid	type 3GO	18,0-19,0
But-4G7-Z +OA	Acidic Modified	high	single material + 140 ppm of organic acid	type 3GO	22,0
Saflex + But-3GO-M +OA	Blended	intermediate	blended material (1:1) + 7 ppm of organic acid	type 3GO	18,0-19,0
Saflex + S-lec +OA	Blended	intermediate	blended material (7:3 ; 3:2) + 45 ppm of org. acid	type 3GO	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.

The Caption of Figures:

Figure 1:	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%
Figure 2:	Influence of active –OH groups to adhesion of PVB to glass [9]
Figure 3:	Influence of –OH group amount to absorbability of water
Figure 4:	Dependence of alkali titer and adhesion (air side) to organic acid additament to But-3GO-P sheet, modified PVB sheet always conditioned to water content 0.5%
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Figures 6-7:	Adhesion behavior of Butacite sheets on water content increasing
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Figure 9:	FTIR spectra 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%, b) 0.3-0.6%
Figure 11:	Activation of –OH groups by organic acid; generation of intermolecular adhesion bonding is achieved by protonization of –OH group (in this case –OH group in glass structure)
Figures 12-13:	Adhesion behavior of But-P and But-S sheets and these sheets modified by Mg^{2+} ions on water content increasing
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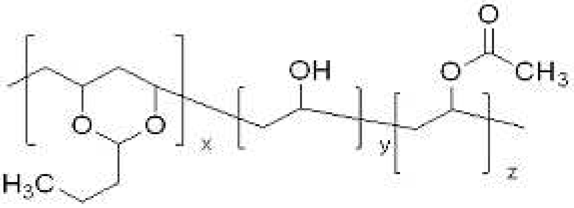
Figure 16:	Adhesion behavior of But-4G7-Z and its modifying by organic acid on water content increasing
Figures 17-18:	Adhesion behavior of Saflex and But-3GO-M sheets and blended material and blend modified by organic acid on water content increasing
Figures 19-20:	Adhesion behavior of Saflex and S-lec sheets and blended material in ratio 3:2 and the blend modified by organic acid on water content increasing
Figures 21-22:	Adhesion behavior of Saflex and S-lec sheets and blended material in ratio 7:3 and the blend modified by organic acid on water content increasing



Poly(vinyl butyral) chain structure, (PVB)

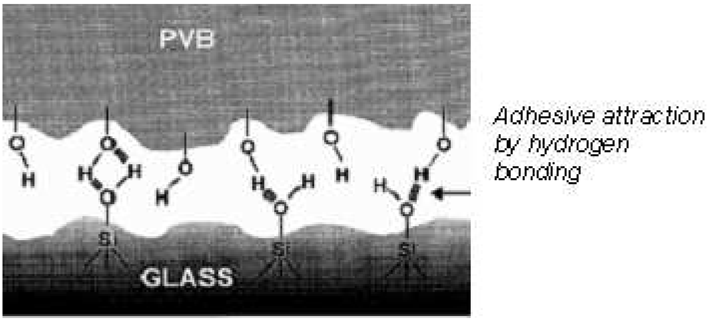


Figure 1: Adhesive hydrogen bonding between the hydroxyl group in a structure of the glass and the hydroxyl group of the PVB chain [2]. The bonding is present in the case of PVB without modifiers or at water content in PVB matrix up to 0.1%

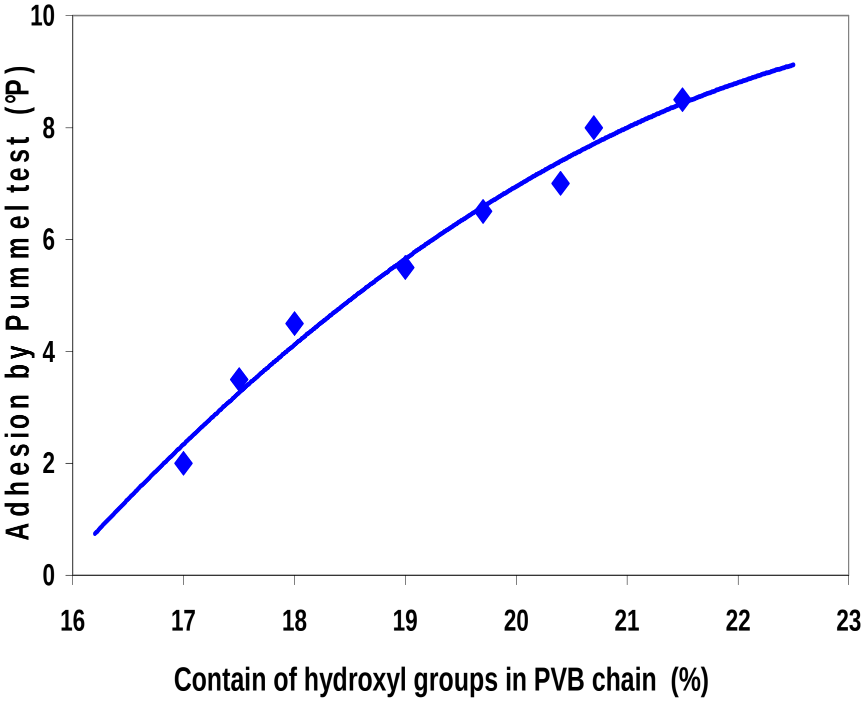


Figure 2: Influence of active –OH groups to adhesion of PVB to glass [9]

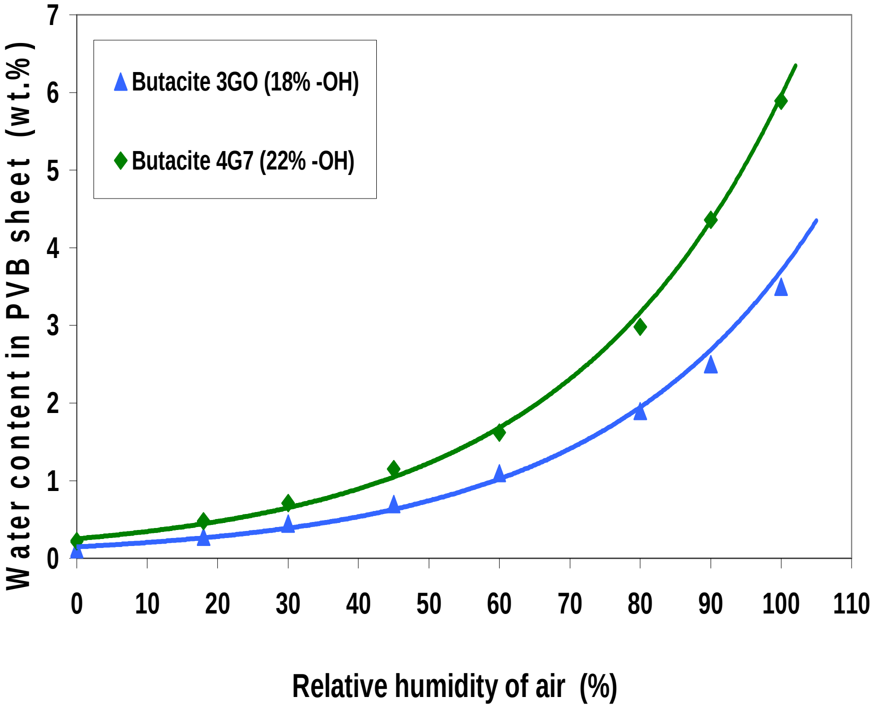


Figure 3: Influence of –OH group amount to absorbability of water

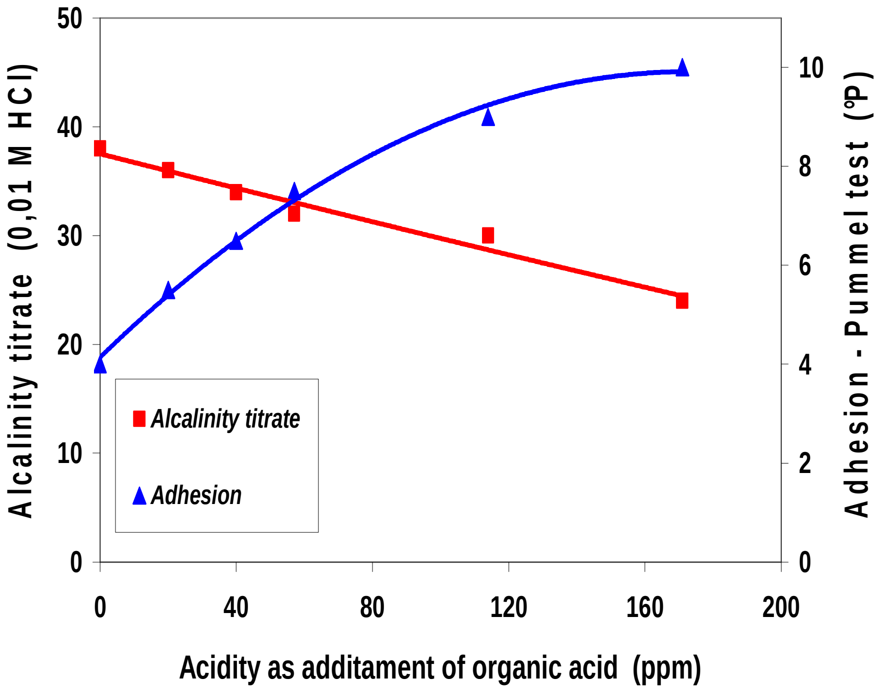


Figure 4: Dependence of alkali titer and adhesion (air side) to organic acid additament to But-3GO-P sheet, modified PVB sheet always conditioned to water content 0.5%

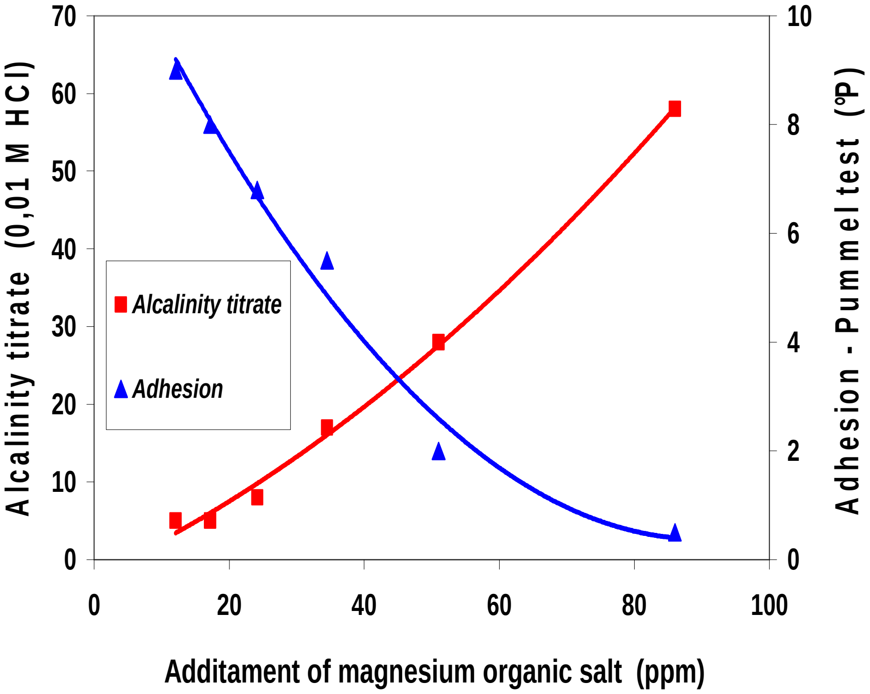
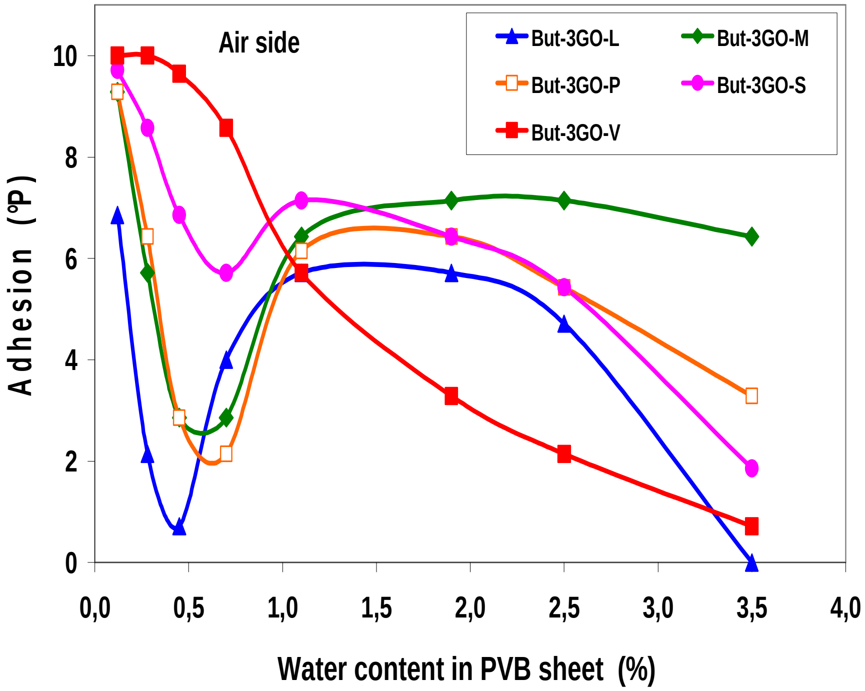
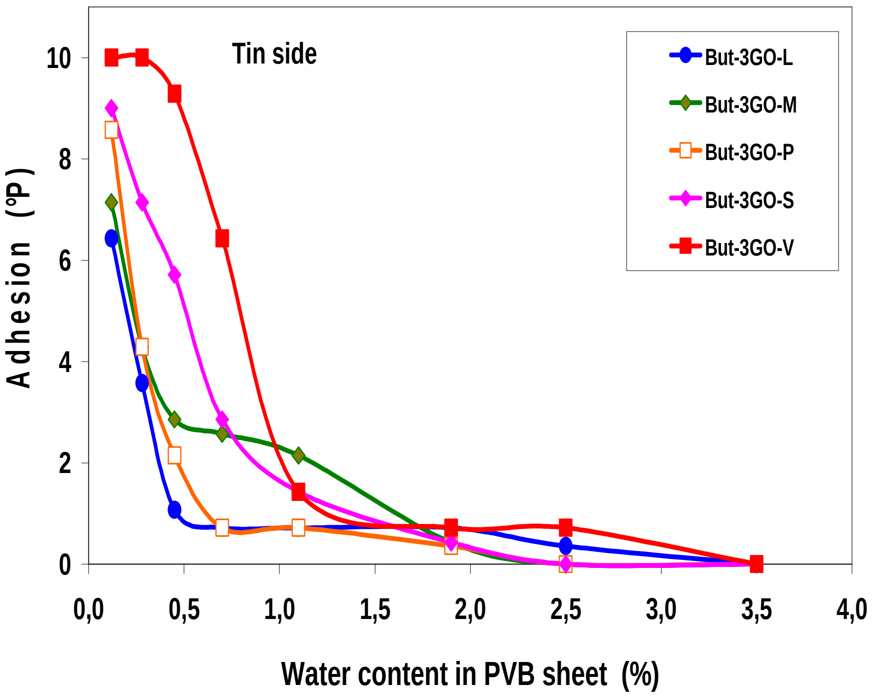


Figure 5: Dependence of alkali titer and adhesion (air side) to magnesium acetate additament to But-3GO-V sheet, modified PVB sheet always conditioned to water content 0.5%



Figures 6: Adhesion dependence of Butacite sheets with various adhesion degrees on water content increasing, air side of the laminate



Figures 7: Adhesion dependence of Butacite sheets with various adhesion degrees on water content increasing, tin side of the laminate

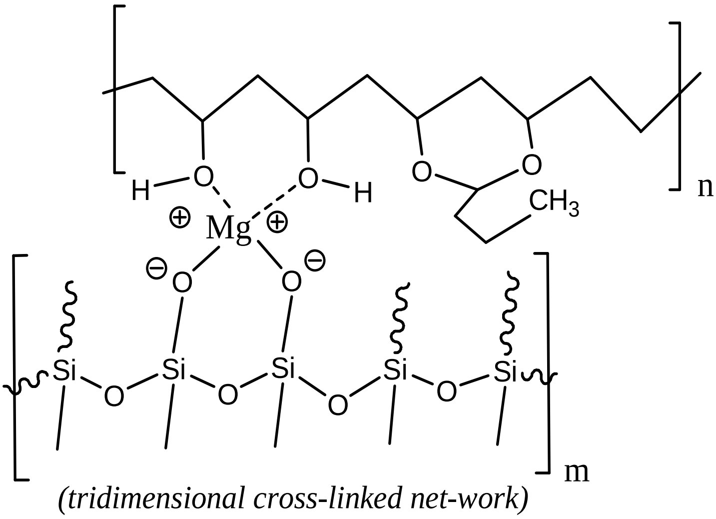


Figure 8: Generation of new adhesion bonding between PVB and glass at present of water content in range 0.8-2.5%

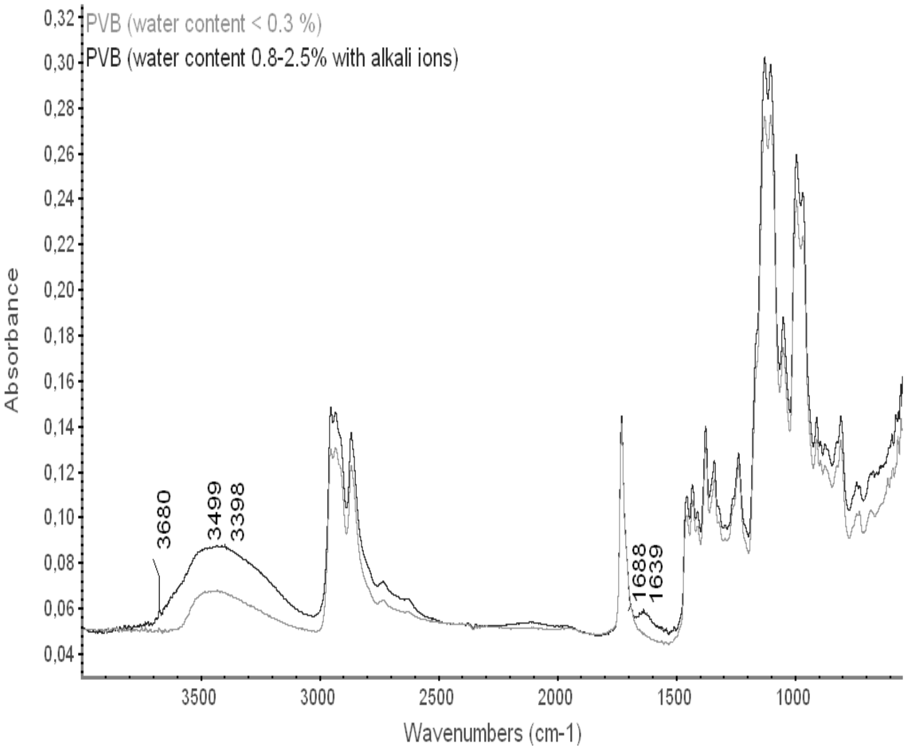


Figure 9: FTIR spectra of PVB treated by alkali ions with different water content

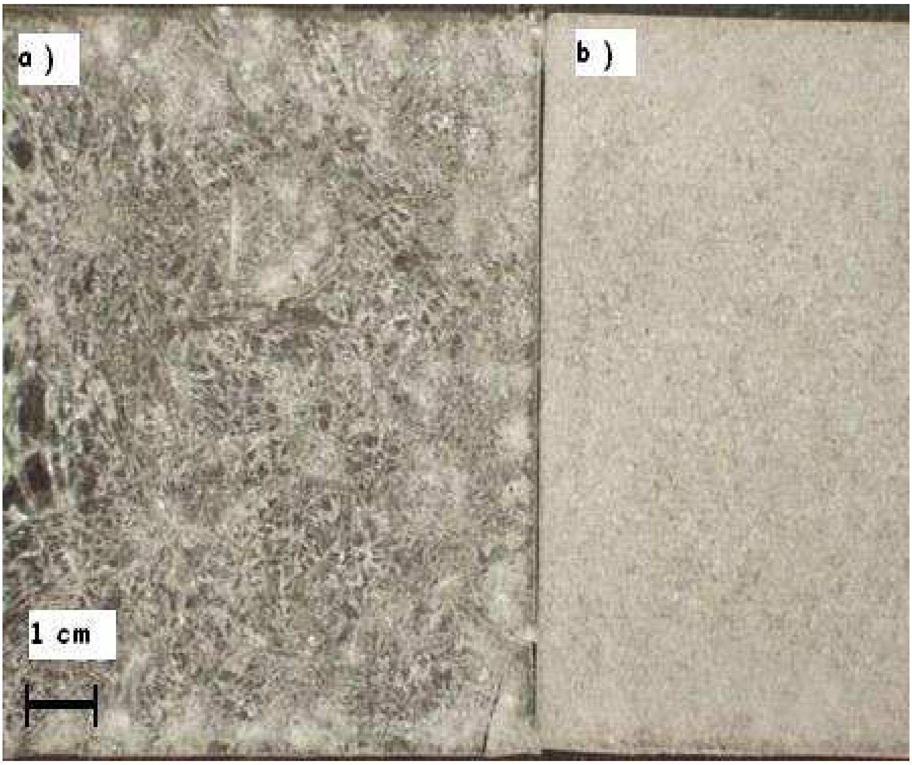
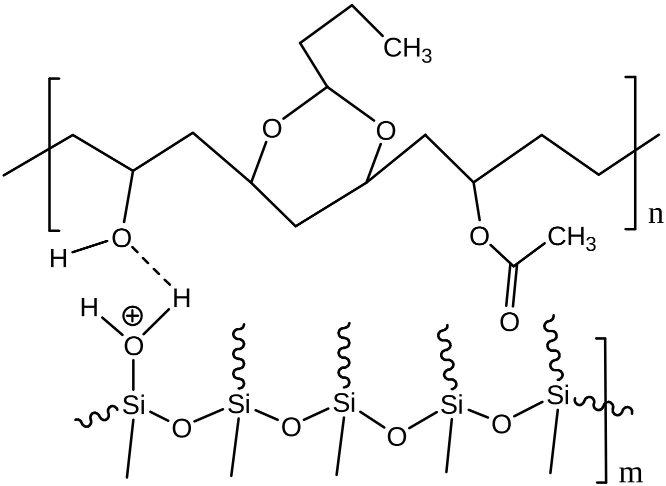
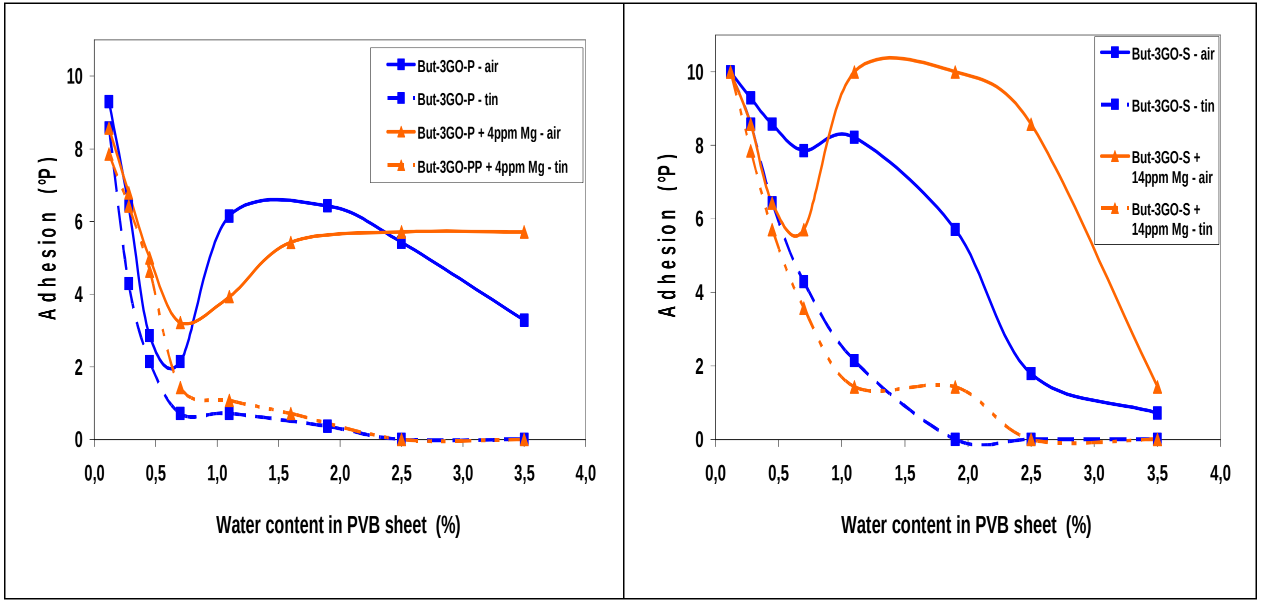


Figure 10: Air side of cracked alkali modified laminates with water content a) 0.8-2.5% b) 0.3-0.6%,

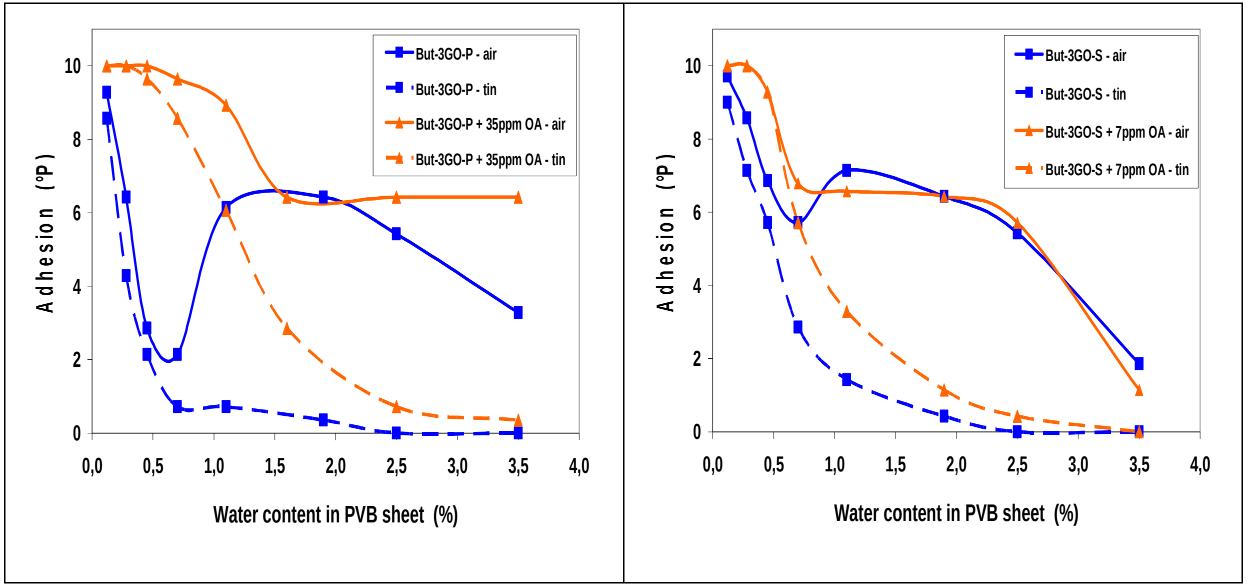


(tridimensional cross-linked net-work)

Figure 11: Activation of –OH groups by organic acid; generation of intermolecular adhesion bonding is achieved by protonization of –OH group (in this case –OH group in glass structure)



Figures 12-13: Adhesion behavior of But-P and But-S sheets and these sheets modified by Mg^{2+} ions on water content increasing



Figures 14-15: Adhesion behavior of Butacite 3GO, type P // type S and its modifying by organic acid on water content increasing

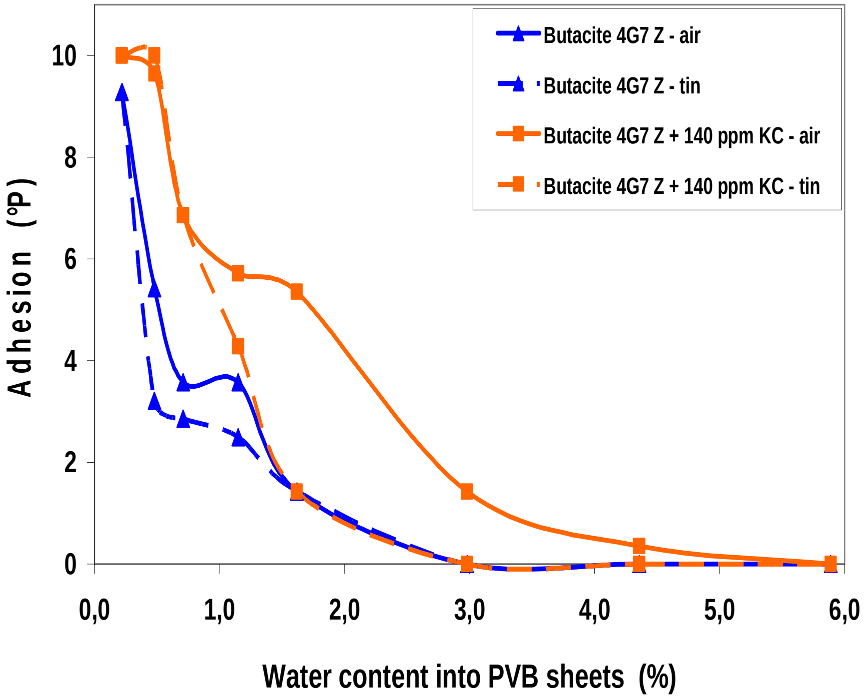
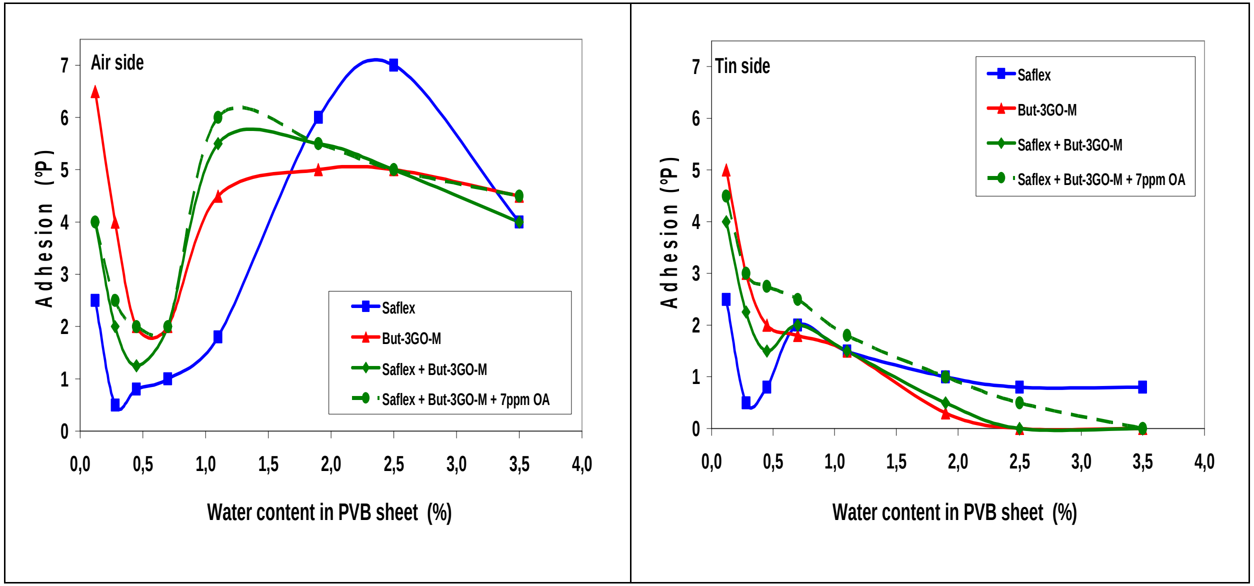
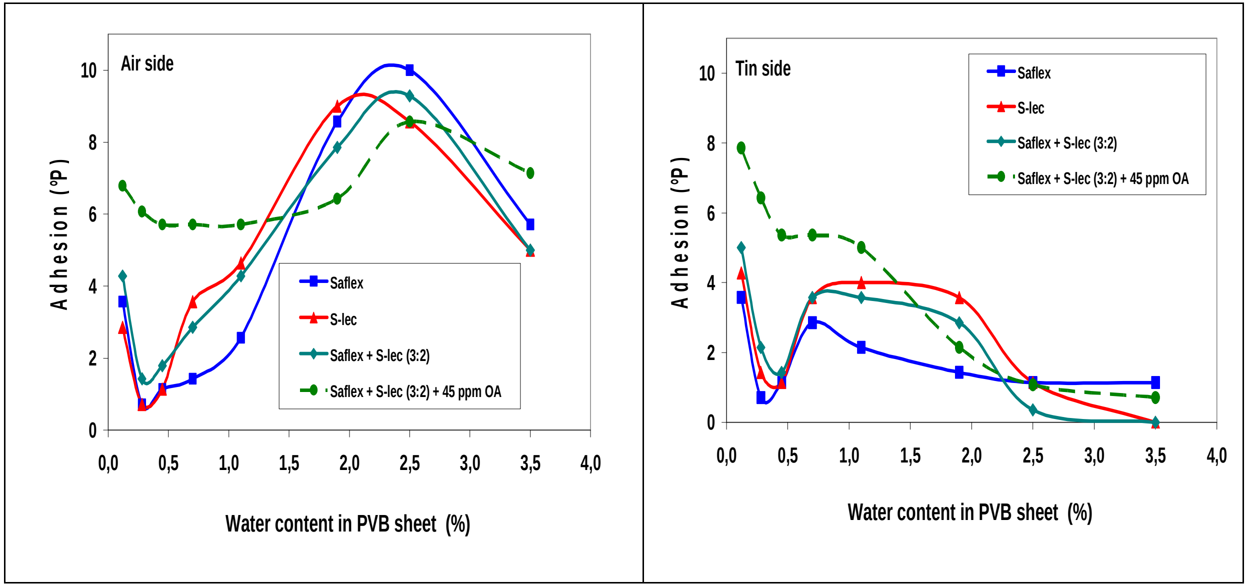


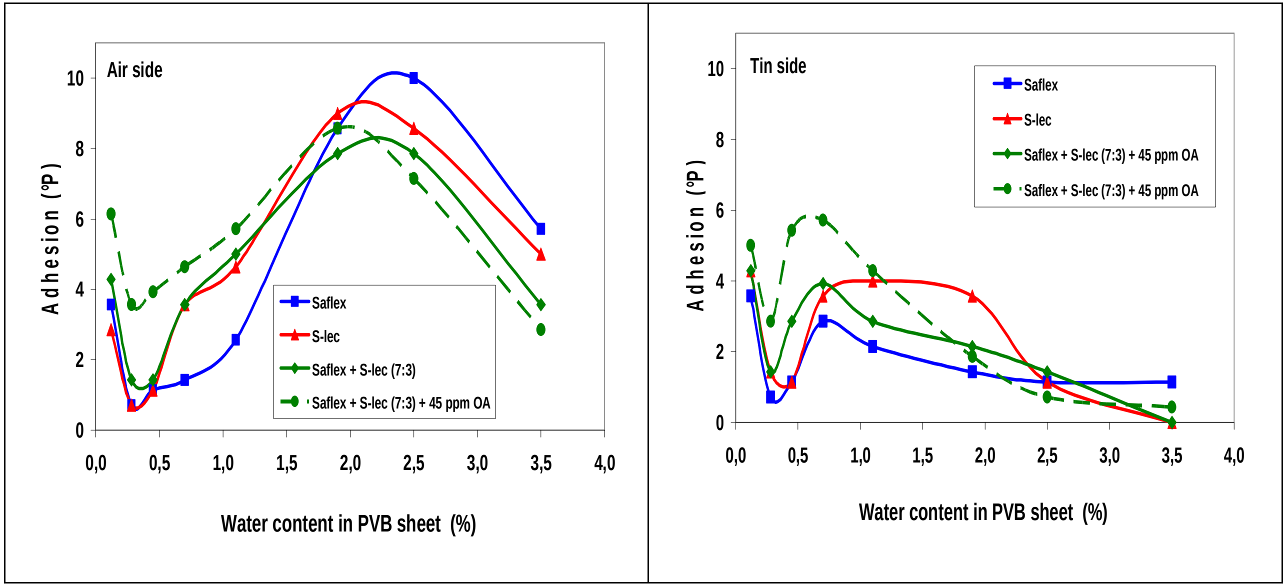
Figure 16: Adhesion behavior of But-4G7-Z and its modifying by organic acid on water content increasing



Figures 17-18: Adhesion behavior of Saflex and But-3GO-M sheets and blended material and blend modified by organic acid on water content increasing



Figures 19-20: 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



Figures 21-22: Adhesion behavior of Saflex and S-lec sheets and blended material in ratio 7:3 and the blend modified by organic acid on water content increasing

Paper III

Windshield recycling focused on effective separation of PVB sheet

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ABSTRACT

The study is focused on windshield recycling process resulting in poly(vinyl butyral) (PVB) sheets without residual glass particles. PVB sheets were obtained from various worldwide manufacturers or by blending extrusion process and these were laminated by standard autoclaving process. Some samples of PVB sheet were modified by oligo-functional organic acid in order to compare various levels of adhesion. Three-stage technology was proposed for recycling PVB sheets. In the first-stage laminated safety glass was mechanically cracked. In the second-stage the adhesion reduction to minimal degree was followed by chemical separation. It causes self-falling of the glass out of the PVB sheet. The third-stage mechanically peeled remaining glass on PVB sheet and it finished the recycling process. The adhesion between glasses and PVB was in second-stage reduced by three agents - water, alkali environment and elevated temperature - to minimal value. The optimal process conditions for the most effective delamination process available for all manufactured PVB sheets were found. Delamination technology produces PVB sheet with minimal residual glass content (approx. 50 ppm) and minimal changes in PVB sheet properties. Whole recycling technology is ecologically friendly (the effluent is fully recyclable as well) and reduces the worldwide problem with windshield waste disposal.

<u>Keywords:</u> *Windshield, Laminated glass, Poly(vinyl butyral), Recycling, Separation, Adhesion*

1. INTRODUCTION

1.1 PVB sheet compounding

Poly(vinyl butyral) (PVB) is a polyacetal produced by the condensation of polyvinyl alcohol with n-butyraldehyde in the presence of an acid catalyst (Nghuen and Berg, 2004; Wade et al., 2004). The condensation reaction produces 1,3-dioxane rings but the reaction does not run to 100% conversion. Residual un-precipitated hydroxyl groups promote indispensable adhesion to the glass substrate through the lamination (Fowkes, 1987; Keller and Mortelmans, 1999; Merinska et al., 2009; Tupy et al., 2010-a). Similarly to the polyvinyl alcohol production (hydrolysis) also in case of PVB some amount of residual –OH group stays in the PVB chain. The final structure can be considered to be a random atactic ter-polymer of vinyl butyral, vinyl alcohol and vinyl acetate in composition 18-22% (w/w) of hydroxyl groups (according to PVB type), less than 2% (w/w) of acetate and the rest is created by butyric groups (around 76-80%, w/w) (Nghuen and Berg, 2004; D'Errico et al., 1995). Moreover, all PVB films must be quite highly plasticized, mostly branched ethylene glycol esters (Dhaliwal and Hay, 2002; Phillips, 2005; Sita et al., 2006; Papenfuhs and Steuer, 2001).

PVB sheet are mostly utilized for lamination of safety glasses. At present time, Solutia, DuPont, Seki sui and Kuraray are worldwide PVB manufacturers. The PVB is the material which can stick together float glasses with holding excellent optical and mechanical properties of the laminate (Ivanov, 2006; Iwasaki and Sato, 2006; Keller and Mortelmans, 1999; Merinska et al., 2009; Tupy et al., 2010-b). Most significant PVB properties are elasticity, strength, toughness, high light transmission and adhesion to glass and metals. Significant toughness of PVB sheet is based on high molecular weight of PVB chain. However, it has to be plasticized for achieving high material strength and elasticity [Iwasaki and Sato, 2006; Keller and Mortelmans, 1999; Svoboda et al., 1988). Admittedly, the plasticizer must not reduce light transmittance through the sheet, PVB adhesion to glass, generate haze and yellowness, and migrate out of the polymer matrix (Tupy et al., 2010-b; Wade et al., 2004). In addition, plasticizer must have perfect compatibility with the polymer and low evaporability during processing conditions.

1.2 PVB sheet manufacturing, PVB adhesion, lamination of windshield

Based on the several authors (Keller and Mortelmans, 1999; Nagai, 2001; Neher, 1936; Svoboda et al., 1988; Tupy et al., 2008), manufacturing of PVB sheet is generally based on similar principles. Melt plasticized PVB is extruded through sheet extrusion head at temperature 160-210°C to water. The PVB melt retains its shape, thickness and specific sheet surface, which is necessary for de-aeration at pre-lamination process. Consequently, the PVB sheet must be layered between two (or more) clear shaped glasses with PVB oversize around 5 mm. This multiple-layer sandwich is pre-laminated between two rolls or by vacuum at temperature 90-140°C and pressure 0.2-1.0 MPa. The pre-laminated product still is not transparency at all laminate surface, it also contains a residual air. Oversized PVB is cut near the glass edge and autoclaved at temperature 130-150°C and pressure 0.9-1.5 MPa for several tens of minutes. The adhesive bonding grows during two independent steps.

The first of them is a transport of PVB macromolecule moving toward to phase interface. This is generally described by diffusion effect (Dhaliwal and Hay, 2002; Tupy et al., 2008). Second part is generation of Van der Waals interaction between materials. The intermolecular distance and similarity of material polarities determinates strength of the adhesion. Therethrough, polar –OH group of PVB provides adhesive hydrogen bridging with free oxygen bond of the glass (Keller and Mortelmans, 1999; Nghuen and Berg, 2001; Tupy et al.; 2010-a).

The most important characteristics of PVB laminated glass are high strength and absorbability of mechanical energy at car-crash or another accident (Keller and Mortelmans, 1999; Svoboda et al., 1988). Moreover, PVB interlayer must keep glass particles on its surface in status quo of adsorbing of kinetic energy by polymer toughness (Iwasaki and Sato, 2006; Keller and Mortelmans, 1999; Tupy et al., 2008]. All these described properties provide exactly adjusted adhesion grade of PVB to glass. However, commercially produced plasticized PVB has exceedingly high adhesion degree and it cannot be used for automotive glass lamination. According to (D'Errico et al., 1996; Keller and Mortelmans, 1999; Smith et al., 2008; Wade et al., 2004), high adhesion degree is necessary to reduce to ½ of the original adhesion value. The adhesion would be able to reduce by addition of salts of alkali metals or salts of alkaline-earth metals as it is described in these patents (Aoshima and Shohi, 2000; D'Errico et al., 1995; D'Errico, 1997; Hermann et al., 1984; Schichiri et al., 2002). Due to influence of it, the PVB chain contains lower number of free hydroxyl groups, some of them are inhibited.

1.3 Worldwide problem of windshield recycling

The main use of PVB is in safety glass laminates, particularly in automotive, and architectural. Worldwide, 65% of all PVB is used in automotive applications (Dhaliwal and Hay, 2002). According to data from IOCA (2010), the worldwide car's production estimated around 60-70 millions cars per a year. Considering the consumption of 1 kg of PVB per windshield it gives approx. 70 million kg of PVB sheets. In addition to this amount, by-products from PVB sheets manufacturing (5%) and trimmings (10%) arising from windshield production must be added (Gorokhovsky et al., 2005) so it represents total amount of approx 80 million kg of PVB waste annually. Total amount of PVB sheet produced by automotive and architectural industry is estimated around 120 million kg per year. With regard to increasing worldwide production of PVB sheet thus generating PVB waste, it is necessary to focus on glass separation in order to obtain clear PVB sheet; otherwise, it is incinerated or land-filled (Dhaliwal and Hay, 2002; Gorokhovsky et al., 2005). PVB sheet obtained from windshield recycling is not possible to be reprocessed to a new PVB sheet suitable for glass lamination especially due to high amount of glass scraps and water content in the sheet (Dhaliwal and Hay, 2002). If recycled PVB sheet is supposed to be used in production of new laminated glass, recycled PVB sheet has to contain no more then 100 ppm of glass fragments and other contaminations – higher amount negatively influences a PVB optical properties. In addition, the higher residual glass content also negatively affects PVB processing (Tupy et al., 2010-a).

At present time, the windshield recycling process is mostly based on dry process of mechanical peeling. Unfortunately, obtained PVB contains high degree of glass dust (1-5%, w/w) and other contaminants (sludge, paper, and other plastics) (Dhaliwal and Hay, 2002; Gorokhovsky et al., 2005; Tupy et al.; 2008; Tupy et al., 2010-b). Contrary to the dry recycling process, wet process seems to be better for the delamination and glass separation from PVB sheet. Aqueous medium can more effectively wash out the glass and break the hydrogen bonds between the –OH group and the glass (Sita et al., 2006). Hydrogen bonding stability depends on temperature, molecule dissolvent and amount of dissolved salts, conforming polarity and pH of the system (Fowkes, 1987; Keller and Mortelmans, 1999; Tupy et al., 2010-a). It was observed that the adhesion is reversible and the PVB adhesion is in majority generated by H-bonds. Hence, the utilization of the wet separation process requires to study the influence of water and chemical agents on the change of PVB adhesion to glass (Tupy et al., 2010-a). PVB adhesion to glass depends on water content in PVB matrix (Keller and Mortelmans, 1999; Tupy et al., 2010-a). Measurement found that water content around 2% (w/w) in PVB causes the saturation of binding sites (Merinska et al., 2010; Tupy et al., 2010-a). Adhesive forces fall down and residual adhesion has corresponded only on weak dispersion forces (Tupy et al., 2010-a). Nevertheless, this method produces recycled PVB sheet with less glass dust content (0.5-3%, w/w) than the dry separation process (Tupy et al., 2008). However, the recycling process must be efficient enough and simultaneously the recycled PVB must not be degraded by delamination agent [Merinska et al., 2009; Rong et al., 2009; Tupy et al., 2010-a). Therefore, the solution of this problem still was not found.

The paper focuses on separation of PVB sheet from windshield by 3-stage recycling process combining mechanical cracking of laminated glass, followed by wet process and finished with mechanical peeling. Several agents in the wet process were tested in order to clarify the adhesion interference of polymer to glass. The aim of the study was focused on founding of optimal process conditions for effective glass separation of laminate glass.

2 MATERIAL AND METHODS

2.1 PVB sheet and glass samples

In all, six PVB sheet samples were used. Four original plasticized PVB sheets were delivered by DuPont, Solutia and Sekisui as commercial PVB sheets. All tested PVB sheets with trade name But-M and But-S *(DuPont, USA),* Saflex *(Solutia, USA)* and S-lec *(Seki-sui, Japan)* contain approx. 28% (w/w) of plasticizer triethylene glycol, bis(2-ethylhexanoate) (labeled 3GO) [Wade et al., 2004; Fish and Lee, 2003). Some of them are suitable for automotive industry (sheets contain higher amount of alkali ions) and some for utilization in building industry. Two PVB sheets were blended and mixed with 5% (w/w) water solution of oligo-functional organic acid (pH = 1.5-2.0) during the extrusion process. These were labeled Saflex+S-lec+OA and But+OA. Used PVB sheets were different in the content of adhesive agents (e.g. K^+, Na^+, Mg^{2+}) (Tupy et al., 2010-a). Hence, amount of organic acid for adjusting adhesion was also different. The Butacite sheet with labeling But-M contains 120 ppm (w/w) of all added alkali ions; But-S contains only 40 ppm (w/w). Addition of 45 ppm organic acid in modified PVB sheets But+OA and Saflex+S-lec+OA was tested in order to confirmation of increasing PVB sheet adhesion and its influence on laminated glass recycling process.

The float glass used for the glass lamination process is generally made by the casting of glass meltage on the surface of melt tin. Due to prepared glass has the uniform thickness and absolutely smooth surface. This is necessary for the perfect PVB contact with glass during the laminating process. However, microscopic tin layer remains on the bottom side. This surface is named “tin side”. The tin film causes totally different adhesion response between PVB and silicate with increasing moisture in a polymer (Svoboda et al., 1988; Tupy et al., 2010-a). The float glasses *(AGC Teplice, Czech rep.)* used for sample preparation had thickness of lime-soda glass 2.1mm and chemical composition 71.5% SiO_2, 13.4% Na_2O, 9.2% CaO, 4.15% MgO, 0.7% of Al_2O_3 and other compounds.

According to (Svoboda et al., 1988), 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 lightly visible white reflexive layer. 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 (down side of the laminate).

2.2 Equipment and methods for analytical assessment

The measurement of PVB adhesion to glass was carried out by Pummel test. The purpose of Pummel test is to measure the relative strength bond between PVB and glass. This method is described by (Keller and Mortelmans, 1999) and it is also according to the U.S. Patent (Smith et al., 2008). Deep-frozen samples at -18°C are undergone to repeating impact of hammer at frequency 130 impacts per minute (weight of hammer 450 grams) under controlled conditions. The test samples were held at about 5 degrees angle to plane of the Pummel plate, in order to impact the edge of the unbroken glass which is in contact with the plate. The strength of the adhesion was subjectively evaluated by visual comparison with standards. Standard for the lowest adhesion was totally naked plastic PVB sheet and it was marked as degree 0.0; standard for the highest adhesion was the plastic covered in the entire surface by stuck glass splinters and it was marked as degree 10.0.

The rate of delamination was evaluated by weight loss of glass from PVB sheet during 3-stage delamination process.

Residual glass content was assessed by turbidimetric analysis of scattered day-light. The light scattering was determined by measurement through the laminated glass contains of glass/recycled PVB/glass in thicknesses 2.1/0.8/2.1 mm. Measurement was evaluated by VIS spectrometer *(BYK-Gardner)* in a wavelength range 320-900 nm. All measurements were done at room temperature. The evaluation of glass content was proved from calibration curve obtained for every particle size fraction of the glass in dependence on scattered light. The particle size fraction was determined by common laboratory microscope with magnificence approx.100x.

The plasticizer content was measured according to ISO norm (DIN EN ISO 6427). Approx. 2 grams of PVB sheet was cut in size 2x2 mm and these were immersed into the extraction cartridge. The cartridge was filled in the Soxhlet extraction equipment. The extraction process with hexane was carried out in water bath for 6 hours. The most part of thinner was distilled off when the extraction process finished. The plasticizer with residual hexane was dried at 100 °C in water bath to constant weight. The plasticizer content was assessed by gravimetric method.

Thermo-gravimetric analysis (TGA) was determined by thermogravimetric analyzer TGA Q500 (TA Instruments, New Castle, USA) in open platinum crucibles and weighed-in. Amount of PVB sample for thermal analysis was approx. 8 mg and measurements were taken in temperature interval 20-500 °C, dT/dt = 10 °C min^{-1} in protective nitrogen atmosphere (150 mL min^{-1}).

Rheological properties of re-processed samples were tested according to ISO norm (EN ISO 1133, 2005) in terms of MFI measurements using the extruding plastometer M201 *(Haake)*. This norm corresponds with (ASTM D1238-10, 2010). Samples were conditioned at 25% relative humidity and then extruded at 150 °C through the 2 mm capillary using the load of 100 N. The MFI correlates to the polymer mass passing through a standard capillary in an interval of 10 minutes, at a given load.

Other equipment used: drier WTB Binder E/28 *(Germany)*, laboratory heater single-plate unit Eta Domo DO 309 KP with power input 1500 W *(The Czech Republic).*

Chemicals: NaOH, p.a. grade (CAS No.: 95077-05-7) was supplied by LACH-NER *(The Czech Rep.),* Hexane, p.a. grade (CAS No.: 110-54-3) was supplied by PETR LUKES *(The Czech Rep.).*
Delamination mediums: water, 0.125, 0.25, 0.5, 1 and 2% (w/w) of NaOH in demineralized water. Prepared solutions were stored at room temperature.

2.3 Preparation of laminated glass

Blending of different PVBs and the modified mixtures were carried out in the single-screw extruder, screen system with an apertures size up to 60 µm and sheet extrusion die (Tupy et al., 2008). PVB sheets are conditioned in air-conditioning cabinet *(Weiss, Deutschland)* in order to achieve the required water content in the sheet at 40°C. Conditioned sheets were put between two glasses previously washed with demineralized water. Both glasses are 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 a 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 it was slowly cooled to room temperature

(Keller and Mortelmans, 1999; Svoboda et al, 1988; Tupy et al., 2008). Finally, samples of laminated glass were cut out to the size 150x100mm^2. Adhesion by Pummel test was measured.

2.4 Windshield 3-stage recycling process

Laminated safety glasses were prepared by usual autoclaving process. Samples were stored for one week in order to laminate relaxation. Consequently, laminated glass samples were tested by 3-stages technological recycling process. The first technological step was cracking of the laminate.

1st stage:

Samples of laminated glass were undergone to repeating impact of hammer at frequency 130 impacts per minute (weight of hammer 450 grams) under controlled conditions. The test specimens were held at about 5 degrees angle to plane of the specimen plate. The hammering was carried out to achieve a particle size of cracked glass in ration 0.5-5 mm; samples were flexible in radius approx. 1cm. Hammered laminates were weighted before the chemical delamination. The laminate lost distinct amount of glass and this amount depends on PVB adhesion to glass. The higher adhesion the lower lose. Obtained glass powder was directly utilizable for next re-melting process. The dependence of adhesion on glass mechanical peeling is shown in Table 1. Mentioned part of technological process was named ”1st stage” and including whole process it is described in Fig.1.

2nd stage:

Cracked laminated glass samples were placed in boiled water and water solutions of sodium hydroxide with concentration 0.25 – 2.0% NaOH (w/w), per constant time 60 minutes. The system was occasionally stirred. The self-falling of glass from PVB surface was observed and measured by gravimetric method during the delamination process. Behavior of the delamination process was depended on amount of glass reminds after 1st stage of recycling process (effect of PVB adhesion to glass). Results of delamination behavior on various PVB samples are described in Table 1. The kinetics of delamination behavior of single PVB laminate is shown in Fig.2-8.

The attention was also focused on effluent generated by 2nd stage of separation process. Used alkali water solution can be re-used for next delamination process. However, alkali concentration and temperature of NaOH solution must be controlled.

3rd stage:

Chemical separation of glass is based on the reduction of PVB adhesion; however, this process is not efficient enough. Hence, it is necessary to fulfill completed operation by mechanical peeling of residual glass. The PVB adhesion is reasonably reduced by the delamination process and the process is carried out at 3rd stage needs only minimal strength for peeling of the glass. It is convenient to do this by means of wire brush which does not contaminate separated PVB sheet. Delaminated PVB sheet can be washed with water or slightly acid solution, before and after the 3rd stage to wash-away remind glass particles and neutralize the sheet. Washing-away of remind glass particles is achieved by this process and it neutralize high pH value. Washed PVB sheets are dried at 100 °C. Recycled PVB sheet is prepared for re-extrusion process and for manufacturing of new PVB sheet assigned for lamination of new windshield or laminated architectonical glass. The efficiency of completing operation for single PVB type is shown in Table 1.

3. RESULTS AND DISCUSSION

3.1 Evaluation of recycling process efficiency

1st stage:

The efficiency of 1st stage was sharply influenced by PVB adhesion to glass. It was mostly sensible in the case of S-lec sheet which has low degree of PVB adhesion to glass. Therefore, hammering of S-lec laminate caused glass loss around 70% (w/w). Impact of S-lec was also observed at modified sheet Saflex+S-lec+OA which lost 54% (w/w) of glass. The other laminates produced with Butacite sheet (including But+OA) and Saflex sheet lost between 42-48% (w/w) of glass, in dependence on PVB adhesion to glass. Results are shown in Table 1. It is necessary to remind all laminates was hammered by the same hammering intensity to similar size of glass slivers (0.5-5 mm).

2nd stage:

First of all, the influence of organic dissolvent on PVB adhesion reduction (hydrogen bond breakage) was tested. Based on observations, ethanol and other polar organic dissolvent show its possibility to use in delamination process, already at room temperature (Tupy et al., 2010-a). Unfortunately, insufficient manipulation, flammability, dissolvent evaporability and price complicate the application of this medium in practice. Hence, due to deficiency usage of organic dissolvent less problematic liquid was chosen. Everything points out to water application in the reason of cheap, nontoxic, renewable and nonflammable delamination environment. However, opposite to “common wet process” intensification of the delamination process had to be used. It was achieved by acid-base agents. Experimental work discovered that alkali pH was very effective for the auto-self glass delamination out of the PVB sheet. Moreover, alkali pH helps to obtain PVB sheet with extremely low content of the glass and it obviously accelerates the delamination process. Measurement found that delamination strength significantly rose with increased water content into PVB sheet and pH value of environment system. The water content (with pH = 7) when adhesion fade out was assessed in range 2.5-.3.5 % (w/w), based on various PVB sheet (Tupy et al., 2010-b). The dropping of adhesion was caused by inhibition of –OH groups in PVB chain (Tupy et al., 2010-a). Adsorbed water behaved as a plasticizer and along with alkali pH it was reduced van der Waals adhesive forces. Thereunto, alkali pH stabilizes PVB degradation at elevated temperature (Rong et al., 2008).

Due to large dissimilarities of tested PVBs; the study was focused on finding of optimum delamination process conditions based on influence to temperature, delamination exposition time and mostly on the concentration of alkali delamination agent. These were tested in order to find the capability of recycling process for all manufactured PVBs. Cracked laminated glass was immersed into delamination medium at various temperatures (25°C; 50°C; 80°C; 100°C) and the delamination speed was tested in different boiling times (see Figures 2-8). Observation found that elevated temperature intensifies a diffusion of delamination agent to PVB and speed up the delamination process. Hence, process longevity in one hour and the highest possible temperature (100°C) at atmospheric pressure was found to be sufficient. The same conditions were used for study of 2nd stage of recycling process mentioned below. These are temperature at 100°C, atmospheric pressure, delamination agent concentration in a range 0.0-2.0 % and the process time 1 hour.

The delamination kinetics of every PVB sheet type was studied separately. First of all, evaluation of self-falling of glass was focused on Butacite sheets with various adhesion grades. The most effective delamination of laminates with Butacite sheets was observed in the case type But-M with low adhesion value. In this case, chemical separation with 2.0 % NaOH achieved a glass loss 56% (w/w). The sheet But-S with higher adhesion value was also chemically separable. However, the delamination speed was reduced with lower concentration of NaOH, as Figs.2-3 show. Moreover, different delamination behavior was observed in the case of But+OA which is acidic modified sheet But-M. The acidic modified But+OA is shown in Fig.4. The dissimilarity cased by modification was detected in the time lag before the delamination start. Results confirmed that delamination power ratio depends on adhesion grade. Acidic modifier had to be neutralized as first and following delamination behavior can be as similar as in the case of un-modified PVB sheet (see Fig.2 and Fig.4). Final efficiency of chemical separation of sheet But+OA with 2% NaOH was lower about 14% than in the case of But-M sheet. Results are written in Table 1.

The sheet But-M was chemically separable with usage of boil water environment. However, increased acidity of the sheet But-M caused high resistance to glass peeling with NaOH concentration up to 0.5%. Nevertheless, chemical glass separation above mentioned concentration of NaOH achieved high efficiency of delamination process and simplicity at peeling of residual glass in 3rd stage. The glass separation efficiency and following process completion was depended on used NaOH concentration as shown in Table 1.

Overall, the easiest separable was S-lec sheet. The sheet lost adhesion already at delamination with water. Moreover, the delamination with 2.0% NaOH achieved complete glass loss since 15 minutes in the process, see Fig.5. When it is calculated that hammering achieved 67% (w/w) of glass loss, chemical separation approx. 30-33% (w/w), for final treatment lost only up to 1.0% of residual glass. The sheet easily lost the glass at every stage of recycling technology process. Results are written in v Table 1.

All tested PVB sheets have shown the same behavior of loss of adhesion on air side and on tin side of laminate in the course of delamination process. However, largely different behavior of delamination process on air and tin sides was observed in the case of laminate with Saflex sheet. The abnormality was occurred by differently adjusted adhesion system from the manufacturer (Aoshima and Shohi, 2000). Compare of chemical separation kinetic of Saflex sheet, described in Figs.6-7, points out that the delamination on tin side was as similar as the delamination of But-M. However, delamination behavior on air side of the laminate was too arduous. Regarding to different adhesion system, the Saflex laminate had to be delaminated for longer boiling time 90 minutes in every case. While the glass on tin side of the laminate was separable by hot water after 60 minutes, the glass on air side was not removable. On the other hand, the glass separation with 2.0% NaOH was success on tin side after 30 minutes, full separation on air side was accessed after 90 minutes. Total delamination power ratio carried out by hot water was only 25% (w/w) of removed glass content and the delamination carried out by 2.0% NaOH was in efficiency 51% (w/w). Hence, balance of glass for mechanical peeling in 3.stage was 24% (w/w) of the glass, in dependence on used concentration of NaOH. Generally, delamination speed and efficiency of self-falling of glass graduated with basicity increased, especially on air side of Saflex laminate. To sum up, Saflex sheet was recyclable only with NaOH concentration above 1.0% (w/w). Glass fragments were with a dilute medium un-removable. The evaluation is the best to see in graphic chart, Figs.6-7. Comparing and recommendations are described in chapter “Optimal process conditions”. Moreover, Table 1 shows differences between PVB sheets in the course of 3-steps recycling process. The evaluation is described as glass loss achieved by every separation process stage.

Next diagram, see Fig.8, describes the dependence of the alkali strength to delamination of blended sheet Saflex+S-lec+OA in ratio 7:3 with added 45 ppm of organic acid. This sheet lost 27-45% (w/w) of glass during chemical separation. The glass loss was based on NaOH concentration (0-2 % NaOH). Similarly as in case of Saflex sheet delamination behavior largely depends on NaOH concentration. The process time at least 60 minutes should be used in order to achieve high glass separation efficiency. Nevertheless, content of S-lec was sensible. It caused the same behavior of self-falling of glass on air side and on tin side of the laminate. When the delamination with alkali strength up to 0.5% NaOH was not absolutely perfect, the completion mechanical peeling was very smooth than in case of Saflex sheet. Recycling with alkali strength above 0.5% obtained PVB sheet with minimal glass content. Thereunto, similar time lag in delamination with water was observed as in case of But-OA. This is caused by present of organic acid.

3^rd^ stage:

Obtained PVB sheets were washed out by water to neutralize pH. Although, the chemical separation has high process efficiency, the glass still kept on the polymer surface and following completion stage had to be used in many times. All of this glass must be removed (can be till 25%, w/w). For all that, residual glass particles were easily separable in every PVB sheets expect to Saflex and acidic modified sheets. Hence, it was necessary to remove the glass manually, simultaneously PVB sheets recycled by dilute NaOH solutions. Principally, stage 3 had not problem with the glass scraping by a wire brush. It was carried out with trust between 2-10 N for 30 seconds by the reason of minimal adhesive strength. Nevertheless, un-cracked glass-pairs were arduously removable from the sheet.

Moreover, problem complicates the glass separation is a vacuum between glass-pairs. The influence of vacuum has to be eliminated by cracking of glass to lower fragments. Authors have experiences that tin side should be peeled off as a first.

As mentioned, the process was considerably different for every type of PVB sheet. The lowest amount of remind glass was peeled from S-lec sheet which contains up to 1% (w/w) of the glass; and it was observed already at delamination with water. Every type of Butacite sheets needed to remove between 0.4-22% (w/w) of glass at 3rd stage, based on PVB adhesion degree and predominantly on concentration of used NaOH solution (see Table 1). Nevertheless, the efficiency of finishing process was fully success in every case; the recycling process obtained PVB with glass content no more than 50 ppm. This value was measured by light scattering analysis, according sufficient calibration). This residual glass content should be acceptable for industry PVB sheet re-processing.

The distinction is only Saflex sheet which needed for delamination with 2% NaOH longer process time (90 minutes). Moreover, the completion stage has never been fully success. In case of delamination up to 0.5% NaOH small particles of remain glass still had high adhesion degree on air side and these were not removable by wire brush. The delamination with hot water produced recycled Saflex with 20% (w/w) of residual glass content; this glass was not removable in 3rd stage. Blended sheet "Saxlex+S-lex+OA" was fully recyclable according of present of S-lec sheet. It was observed in particular at delamination with NaOH concentration above 0.5%. All results and observations are summarized in Table 1 and Figs.2-8.

3.2 Optimal process conditions

Manly it is necessary to remind the worldwide collection of windshields and architectural laminates is the mixture of various adhesion grades and PVB from various manufacturers. Based on previous experiences, optimal process conditions for all PVB sheets were determined at temperature 100°C (with atmospheric pressure), the process time 1 hour and NaOH concentration in 1.0%. This alkali strength was sufficient for glass separation process in every case of windshield. The delamination process achieved very effective self-falling of glass and amount of residual glass particles was in reasonable range. Moreover, in this case residual glass was removable very easily. On the other hand, concentration of NaOH up to 0.5% caused higher amount of residual glass particles on PVB sheet surface. Hence, residual particles must be mechanically removed.

However, the process is not sufficient for recycling of PVB sheet with thickness under 0.38mm because thin film can be easily broken and present particles of un-separated laminate contaminate clear recycled PVB and clear separated glass. Thus, authors (Tupy et al., 2008) point out that obtaining of pure uncontaminated PVB sheet is possible only if collected undamaged windshields are free from putty, foreign plastics and color PVBs. Usage of uncontaminated PVB sheets provide necessary requirement for achieve sufficient optical properties of new (re-processed) PVB sheet. Optical properties are important in industry use and these were described in this paper (Tupy et al., 2010-b).

3.3 Separated PVB sheet

Over the success of mentioned recycling process and the thermal stabilization of bases, the polymer system can be saponified by used alkali pH (Rong et al., 2008). During the delamination process saponification of plasticizer was occurred. It was proved by migrating of triethylene glycol and sodium 2-ethylhexanoate (saponification products of plasticizer 3GO). The leach out of plasticizer caused following changes of PVB sheet property. These are rising of transition glass temperature (sheet hardening) and decreasing of melt flow index (sheet toughness). Mentioned property change was directly proportional to the ion concentration of used alkali environment. It was verified by several subsidiary following tests, mentioned below. Nevertheless, the range of the study cannot successfully focuses on the analysis of saponified PVBs. The upcoming future work deals with this exigent appendix because we know that it is necessary in more details.

In order to determine exact results, mass loss of the PVB sheet was tested separately by cooking of weighted PVB sheet without glass (not a laminate). The mass loss of plasticizer was weighted after sheet boiling ran for 60 minutes and sheet drying at 80°C to constant weight. This property rose with an alkali concentration. This change was assigned to plasticizer saponification, not to change of PVB chain structure or molecular weight. The most mass loss was assessed in the case of Saflex sheet. It lost from 1.6% till 1.8% of mass weight after 60 minutes of exposure in NaOH solution (0.0-1.0% NaOH). On the other hand, positive result was observed with S-lec sheet which lost only between 0.2-0.5% (w/w) of its mass, depending on alkali strength. Similar loss of PVB sheet mass was assessed at all tested Butacite sheets. They lost 0.1-0.2% by exposure in hot water and exposure in 1.0% NaOH caused mass loss of PVB sheet between 1.0-1.2%.

The statement that alkali environment reduces content of plasticizer in PVB sheet was also found by extraction assessment. Origin Butacite PVB sheet contains 27.2% (w/w) of plasticizer 3GO. The same PVB sheet exposed in hot water for 60 minutes had plasticizer content only 26.8% (w/w). Following loss of plasticizer was observed in dependence with increased alkali concentration. Butacite sheet exposed in 0.5% (w/w) NaOH contained 26.5% (w/w) of plasticizer 3GO and the sheet exposed in 2% (w/w) NaOH had plasticizer content 25.3% (w/w).

The confirmation that water alkali environment has influence on plasticizer content in PVB sheet was determined by TGA analysis. The Fig.9 point out to slowed-down of plasticizer evaporability in case of exposed PVB sheet. It means higher plasticizer content caused faster mass loss of the sheet (original Butacite PVB sheet). Samples exposed by delamination medium have the mass loss a little bit slow (lower plasticizer content). For comparison, TGA measurement with 3GO plasticizer was carried out. It was found that plasticizer was evaporated at 300°C (see Fig.9). Tested PVB sheets were stable till 175°C and during raised temperature the plasticizer evaporation begin. Measurement found that mass loss of original Butacite sheet at 325°C is 27.3%. This temperature corresponds with the plasticizer content in the sheet assessed by extraction measurement (see above). Exposed Butacite sheets in water or NaOH solutions have mass loss at 325°C only 19-20% which refer about lower plasticizer content.

Flow property (rheological characterization) of recycled PVB sheet was analyzed by melt flow index (MFI) assessment. Generally, the MFI value is very important for re-processing by extrusion. The analysis determined that alkali environment saponified used plasticizer. Hence, measurement point out that plasticizer is more sensible to alkali pH than the polymer. It confirms mentioned sheet hardening and tensile strength increasing. The highest flow property change was observed at all Butacite sheets. The MFI value 5.2 g/10min dropped by delamination in 1.0% NaOH to MFI = 4.5 g/10min (decreases about 14%). The others PVB sheets reduced MFI by delamination in 1.0% solution only about 3–5 % of its origin value. Saflex sheet reduced MFI by delamination in 1.0% NaOH from 3.1 to 3.0 g/10min, S-lec sheet reduced MFI from value 4.2 to 4.0 g/10min and MFI value of blended sheet Saflex+S-lec+OA decreased from 3.9 to 3.7 g/10min. To sum up, worldwide manufacturers of PVB sheets adjust melt flow index of these sheets in wide range (1.5–6.0 g/10min.), flow properties of recycled PVBs are fully in required specification.

It was found that water and every alkali concentration during the delamination process caused changes in properties of PVB sheet. Therefore, limiting concentration of NaOH providing suitable efficiency of 3-stages recycling process was found. Simultaneously the process produced the PVB sheet utilizable for PVB sheet re-processing. Moreover, the PVB sheet still has required safety properties. The study found that the limiting value for obtaining un-degraded plasticized PVB sheet is approx. 1.0% NaOH. This ideal concentration also allows obtaining PVB sheet devoid of glass particles. As mentioned, the saponification can have an influence on windshield safety properties. Thus, it is necessary to obtain next analysis of recycled PVB sheets in order to evaluation, if this study of “Effective windshield recycling” can be used to in industry windshield recycling. Next study must clarify right “optimal process conditions” and assign these condition for every type of PVB sheet.

CONCLUSIONS

This study describes the process of effective glass separation from various PVB sheets; in all probability without polymer degradation. Common worldwide separation methods based on mechanical peeling have very low efficiency and high energy consumption. Authors proposed 3-stage recycling process which uses a combination of physical a chemical delamination of the glass.

The 1st stage, based on glass cracking, was used as pre-operation for ideal contact of polymer matrix with delamination environment. This stage must crack glass particles in size 0.5-5 mm which allows diffusion of delamination agent onto PVB surface. The diffusion phase runs during following stage.

The 2nd stage is based on reduction of adhesion strength between PVB and air side and tin side of the glasses. It was achieved by water, raised temperature and alkali environment. Delamination power content in the sheet assessed by extraction measurement (see above). Exposed Butacite sheets in water or NaOH solutions have mass loss at 325°C only 19-20% which refer about lower plasticizer content.

Flow property (rheological characterization) of recycled PVB sheet was analyzed by melt flow index (MFI) assessment. Generally, the MFI value is very important for re-processing by extrusion. The analysis determined that alkali environment saponified used plasticizer. Hence, measurement point out that plasticizer is more sensible to alkali pH than the polymer. It confirms mentioned sheet hardening and tensile strength increasing. The highest flow property change was observed at all Butacite sheets. The MFI value 5.2 g/10min dropped by delamination in 1.0% NaOH to MFI = 4.5 g/10min (decreases about 14%). The others PVB sheets reduced MFI by delamination in 1.0% solution only about 3–5 % of its origin value. Saflex sheet reduced MFI by delamination in 1.0% NaOH from 3.1 to 3.0 g/10min, S-lec sheet reduced MFI from value 4.2 to 4.0 g/10min and MFI value of blended sheet Saflex+S-lec+OA decreased from 3.9 to 3.7 g/10min. To sum up, worldwide manufacturers of PVB sheets adjust melt flow index of these sheets in wide range (1.5–6.0 g/10min.), flow properties of recycled PVBs are fully in required specification.

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The 2nd stage is based on reduction of adhesion strength between PVB and air side and tin side of the glasses. It was achieved by water, raised temperature and alkali environment. Delamination power ratio graduated with increased alkali ion concentration and also with influence on residual glass content which comes from 1st stage of mentioned recycling process. Regarding to high efficiency of chemical separation to some PVB laminates, we can use only hot water or dilute NaOH solution in order to obtain PVB devoid of the glass. On the other hand, glass fragments from Saflex sheet and acidic modified PVB sheets were un-removable by dilute medium. Regarding the results, optimal delamination process conditions used for all PVB sheets were determined. These are process time 1 hour, temperature at 100°C, atmospheric pressure, 1.0 % NaOH. This alkali environment was strong enough for effective glass separation from every type of windshield. Hence, collected mixture of windshield with various PVB sheets was fully recyclable.

Over the success of mentioned recycling process, the polymer system can be saponified by used alkali pH. The extraction analysis found that the application of alkali strength up to 1.0 % did not cause sharp reduction of plasticizer content. The reduction had low influence on decreasing of flow properties of PVB sheets. Reduction of plasticizer content was conformed by TGA measurement. However, the range of the study cannot successfully focuses on analysis of saponified PVBs. The upcoming future work deals with this exigent appendix because we know that it is necessary in more details.

Higher alkali strength used in 2nd stage achieved not only faster chemical glass separation but also peeling simplicity of residual glass in 3rd stage. Out of anomaly with Saflex sheet, it was possible to obtain recycled PVB sheet with glass content not exceeding 50 ppm. This residual glass amount should be acceptable for industrial PVB sheet re-processing. Moreover, separated slivers of glass are fully recyclable by addition in new glass meltage. Although the delamination process produces not negligible amount of alkali water, this effluent is fully recyclable. Described technology process points out to ecological recycling of windshield without secondary environment pollution which reduces the worldwide problem with windshield waste disposal.

REFERENCES

Aoshima Y, Shohi H. Intermediate film for laminated glass and laminated glass. European Patent EN1227070A1. 2000 Jun 6

ASTM D1238-10: Standard Test Method for Melt Flow Rates of Thermoplastics by Extrusion Plastometer; 2010

D'Errico JJ Jemmott BA, Krach MS, Moran JR. Plasticized polyvinyl butyral and sheet. European Patent EP 0,877,665. 1996 Dec 24

D'Errico JJ. Control of adhesion of polyvinyl butyral sheet to glass, European Patent EP 0,938,519B1. 1997 Nov 12

D'Errico JJ, Jemmott BA, Krach MS, Moran JR. Plasticized polyvinyl butyral and sheet, United States Patent 6,559,212. 1995 Dec 29

DIN EN ISO 6427: Plastics - Determination of matter extractable by organic solvents, 1998

Dhaliwal AK, Hay JN. The characterization of poly(vinyl butyral) by thermal analysis. Journal Thermochemica acta 2002;391:245-55

Fish RB, Lee WCh. Toughened, glass filled polyamide compositions and blends having improved stiffness, and articles made therefrom, United States Patent 7,138,454. 2003 Sep 4

EN ISO norm 1133:2005: Plastics - Determination of the melt mass-flow rate (MFR) and the melt volume-flow rate (MVR) of thermoplastics, 2005

Fowkes FM, Role of acid-base interfacial bonding in adhesion Journal of Adhesion Science and Technology, 1987;1(1):7-27

Gorokhovsky AV, Escapante-Garcia JI, Gashnikova GY, Nikulina LP, Artemenko SE. Composite materials based on wastes of flat glass processing, Waste Management 2005;25:733-36

Hermann HD, Fabian K, EbigtJ. Polyvinylbutyral films which contain plasticizer and have a reduced adhesive power to glass, United States Patent 4,533,601. 1984 Jan 31

Ivanov IV. Analysis, modeling, and optimalization of laminated glasses as plane beam, International Journal of Solids and Structures 2006;43:6887-907

Iwasaki R, Sato C. The influence of strain rate on the interfacial fracture toughness between PVB and laminated glass, Journal de Physique IV 2006;134:1153-58

Keller U, Mortelmans H. Adhesion in laminated safety glass–what makes it work, Glass Processing Days, 1999 Jun 13–16;8:353-56

Merinska D, Tupy M, Kasparkova V, Popelkova J, Zvonicek J, Pistek D, Svoboda P. Degradation of plasticized PVB during reprocessing by kneading. Macromolecular Symposia 2009;286:107-15

Nagai K. Laminated glass, United States Patent 6,686,032. 2001Jul 6

Neher HT. Laminated glass process preparing, United States Patent 2,032,663. 1936 Mar 30

Nghuen FN, Berg JC. The effect of vinyl alcohol content on adhesion performance in poly(vinyl butyral)/glass systems, Journal of Adhesion Science and Technology 2004;18(9):1011-26

OCIA, The International Organization of Motor Vehicle Manufacturers. Displayed in: http://www.oica.net/category/production-statistics/; 2010 [available: 20.12.10]

Papenfuhs B, Steuer M. Plasticizer-containing polyvinylbutyrals, method for producing the same and the use thereof, especially for producing films for use in laminated safety glasses, United States Patent 6,984,679. 2001Dec 22

Phillips TR. Process for the aqueous plasticization of polyvinyl acetal resins, United States Patent 7,285,594. 2005 Apr 5

Rong L, Bobing H, Xian Ch. Degradation of poly(vinyl butyral) and its stabilization by bases. Polymer Degradation and Stability 2008;93:846-53

Shichiri, T, Miyai, J, Bando A, Toyama K, Aoshima Y, Sannomiya I, Nakajima M. Interlayer for laminated glass and laminated glass, United States Patent 7,074,487. 2002 Mar 28

Sita C, Burns M, Hassler R, Focke WW. Tensile properties of thermoplastic starch-PVB blends. Journal of Applied Polymer Science 2006;101(3):1751-55,

Smith RL, Rymer DL, Harper LR, McKierman DJ. Polyvinylbutyral interlayer sheet with improved adhesion to glass and a process for preparing same, United States Patent Application US 20080277045. 2008 Nov 13

Svoboda J, Balazs M, Sedlar J. Industry glass. Glass union concern: Research and developing institute of industrial glass in Teplice 1988;C(1)

Tupy M, Merinska D, Svoboda P, Zvonicek J. Influence of water and magnesium ion on the optical properties in various plasticized poly(vinyl butyral) sheets. Journal of Applied Polymer Science 2010-a;118:2100-08

Tupy M, Merinska D, Svoboda P, Zvonicek J. Effect of water and acid-base reactants on adhesive properties of various plasticized poly(vinyl butyral) sheets. Journal of Applied Polymer Science; Submitted for publication in Jul 27, 2010-b

Tupy M, Merinska D, Zvonicek J. Problems of recycling PVB sheet used for production laminated safety glass. Tomas Bata University, Plastics and Rubber 2008;45:208-11

Wade BE, D'errico JJ, Thompson HM, Yu MK. Polymer sheets and methods of controlling adhesion of polymer sheets to glass, United States Patent Application US 20050208315. 2004 Mar 16

The list of table:

Tab.1: Summarized results of 3-stages glass separation process efficiency

Type of the PVB sheet	**PVB adhesion grade** [*]	Glass separation efficiency (%) [c]			**Total glass separation efficiency (%)** [b,c]
		1st stage	**2nd stage**	**3rd stage**	
		Windshield cracking	**Chemical glass separation** [2]	**Mechanical peeling** [2]	
But-M	3.0	48.0 ± 4.6	27.3 – 56.5	0.4 – 22.1	99.0 - 100
But-S	8.0	41.9 ± 2.8	47.5 – 55.4	3.4 – 9.1	93.3 - 100
But+OA	10.0	47.8 ± 4.4	27.3 – 42.8	9.7 – 19.5	99.6 - 100
Saflex	7.0	44.0 ± 4.6	24.6 – 51.0 [d]	4.5 – 24.0 [d]	80.5 – 99.9 [d]
S-lec	2.0	66.9 ± 2.0	30.5 – 33.4	0.1 – 0.9	99.3 - 100
Saflex+S-lec+OA	6.5	54.3 ± 4.0	27.1 – 45.3	3.3 – 15.5	99.6 - 100

[a]) according to Pummel test (0 = no adhesion, 10 = high adhesion)
[b]) depends on concentration of NaOH solution in 2nd stage (0 – 2 % NaOH, w/w)
[c]) based on initial glass content in PVB sheet solution
[d]) delamination process time 90 minutes

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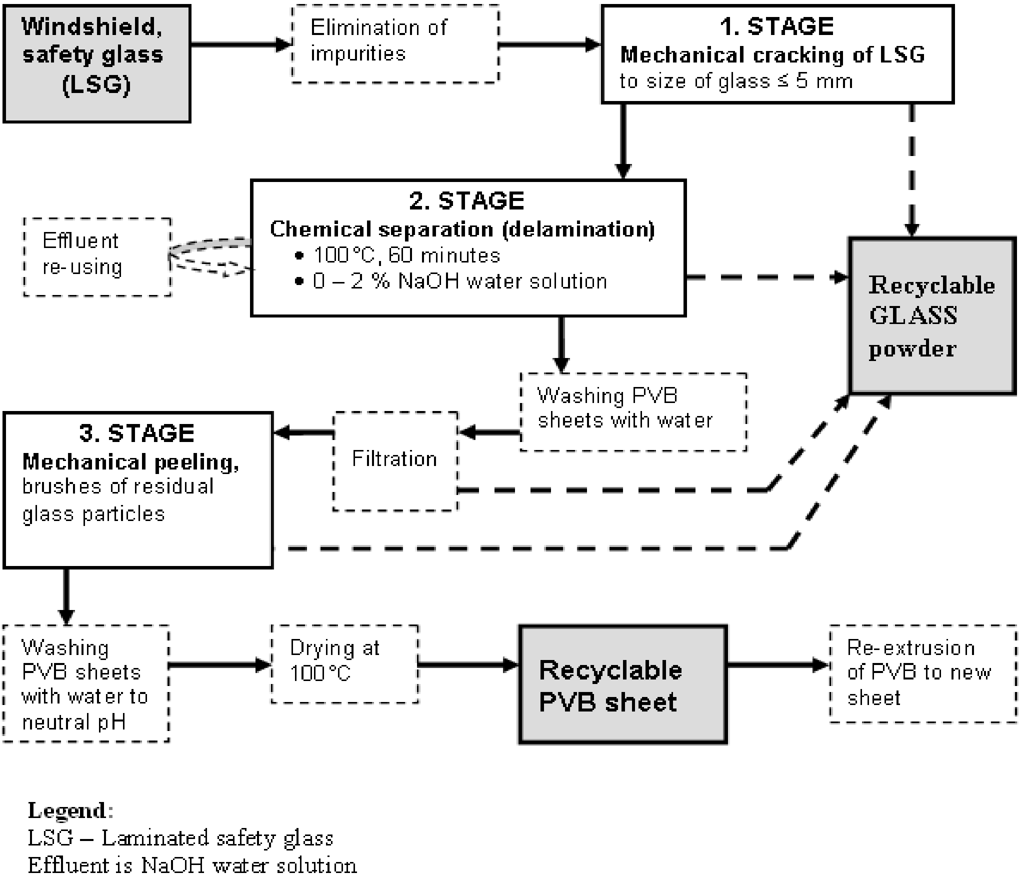

Fig.1: Scheme of 3-stage recycling process

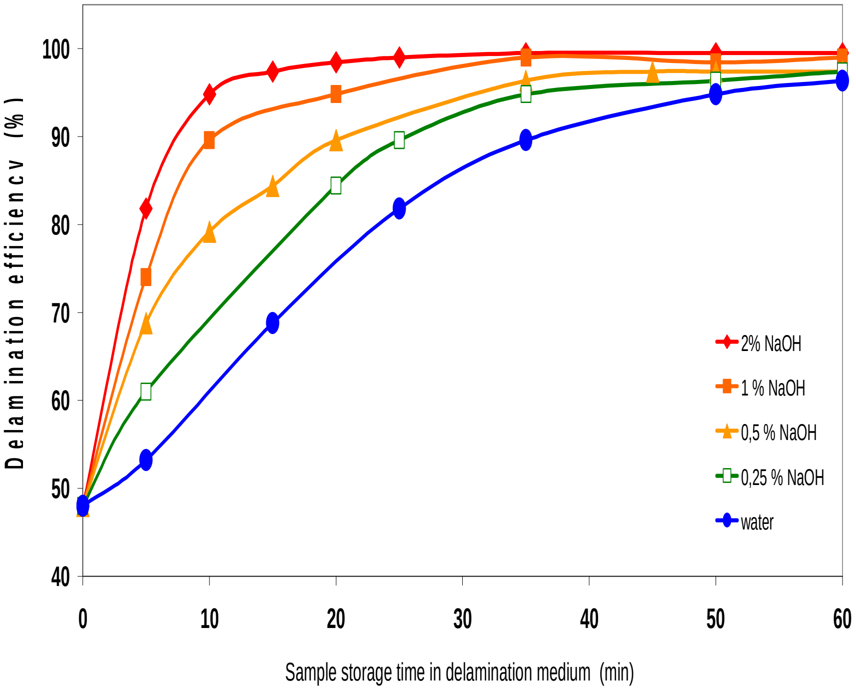

Fig.2: Glass delamination efficiency of PVB type But-M in 2nd stage of recycling process in different NaOH solutions

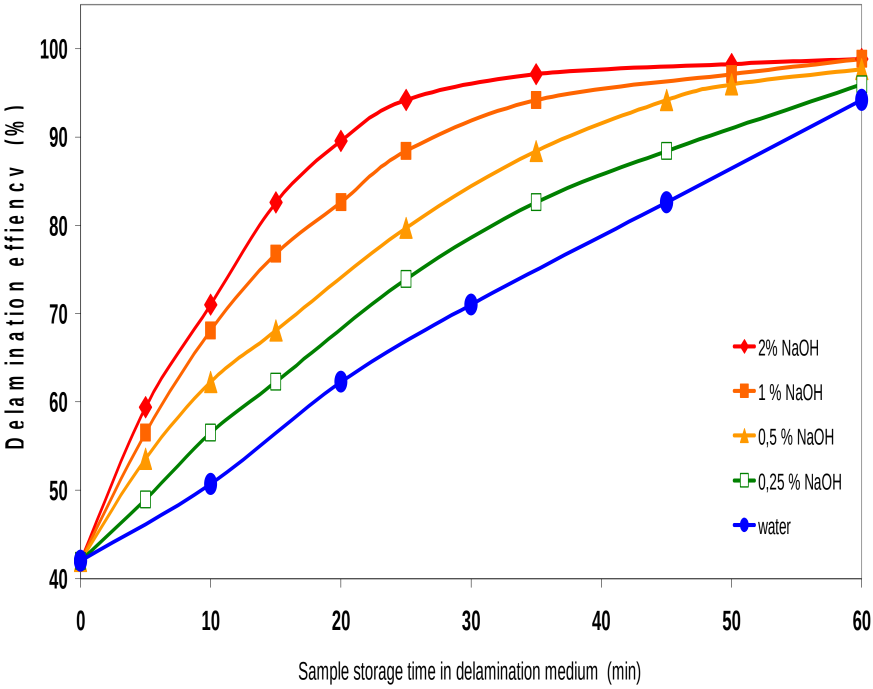

Fig.3: Glass delamination efficiency of PVB type But-S in 2nd stage of recycling process in different NaOH solutions

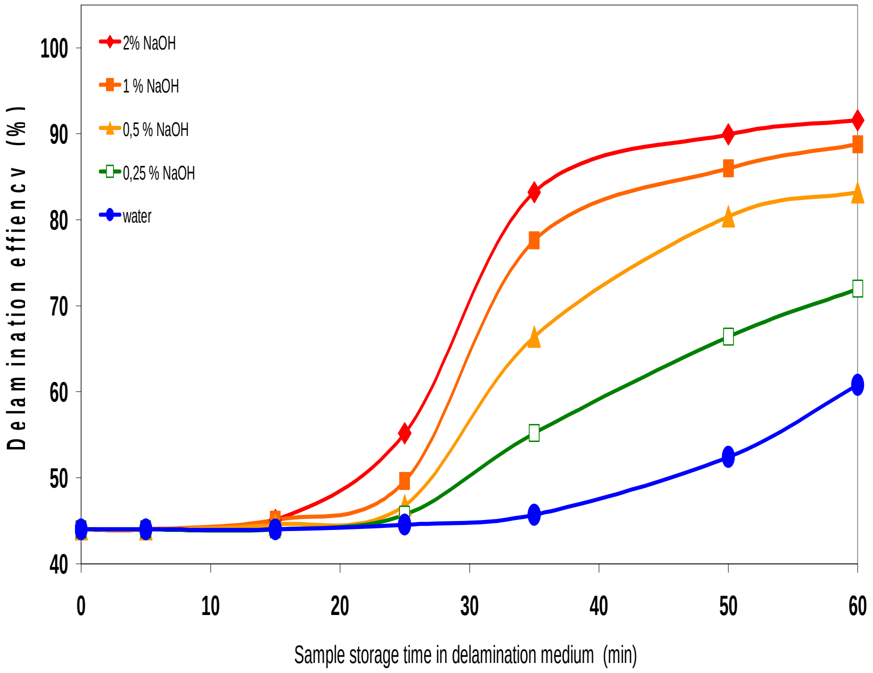

Fig.4: Glass delamination efficiency of PVB type But+OA in 2nd stage of recycling process in different NaOH solutions

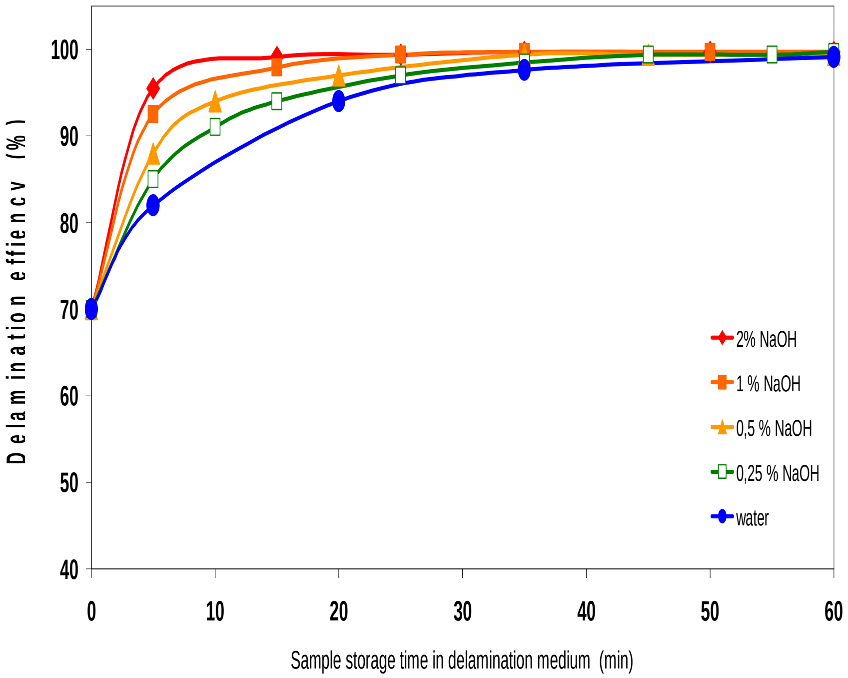

Fig.5: Glass delamination efficiency of PVB type S-lec in 2nd stage of recycling process in different NaOH solutions

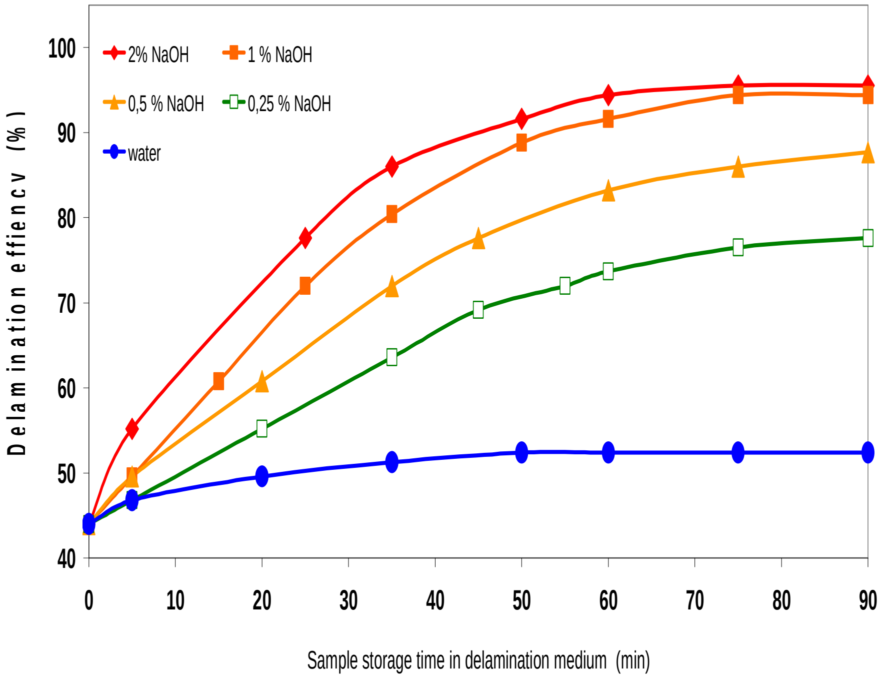

Fig.6: Glass delamination efficiency of PVB type "Saflex-air" in 2nd stage of recycling process in different NaOH solutions

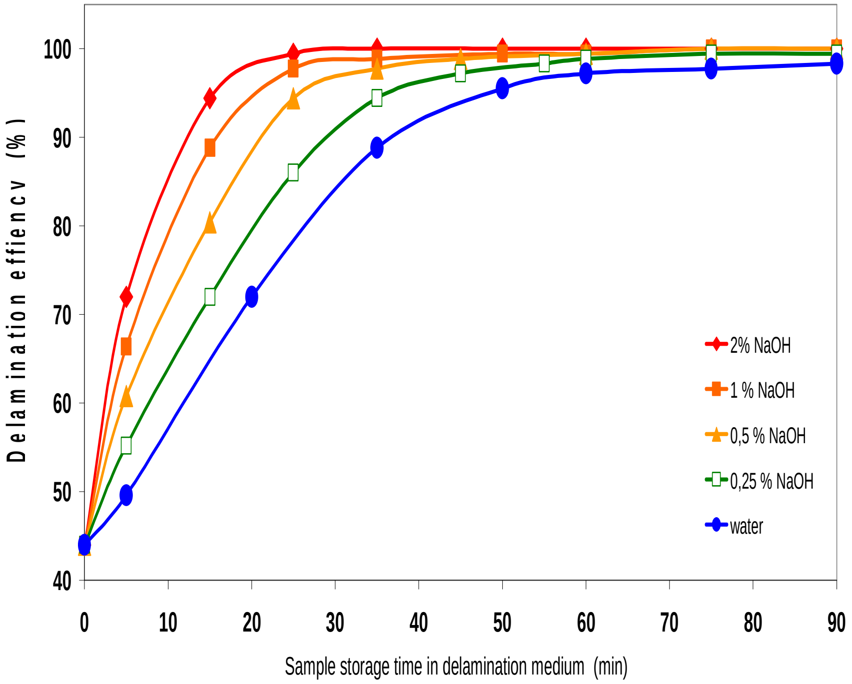

Fig.7: Glass delamination efficiency of PVB type “Saflex-tin” in 2^{nd} stage of recycling process in different NaOH solutions

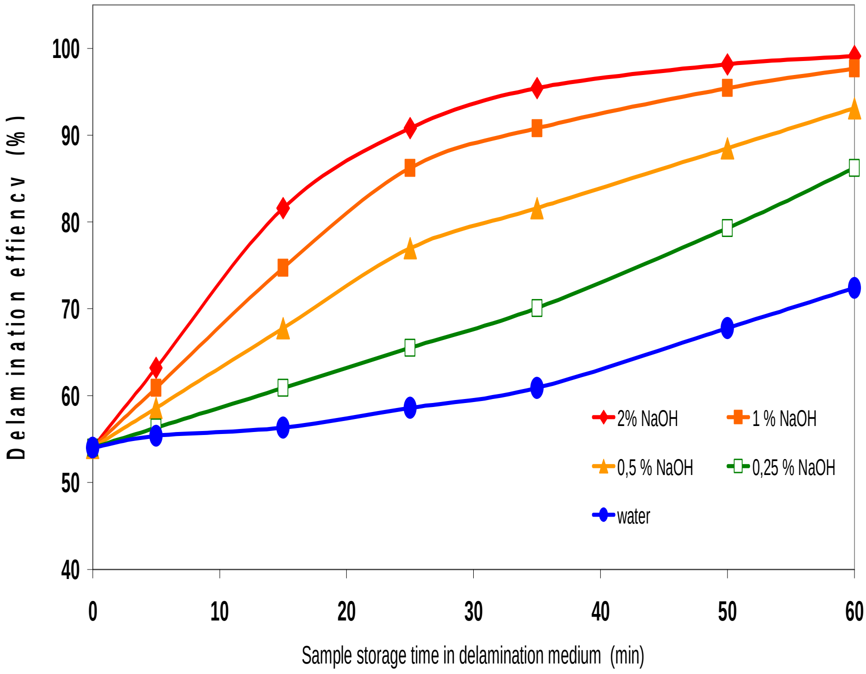

Fig.8: Glass delamination efficiency of PVB type Saflex+S-lec+OA in 2nd stage of recycling process in different NaOH solutions

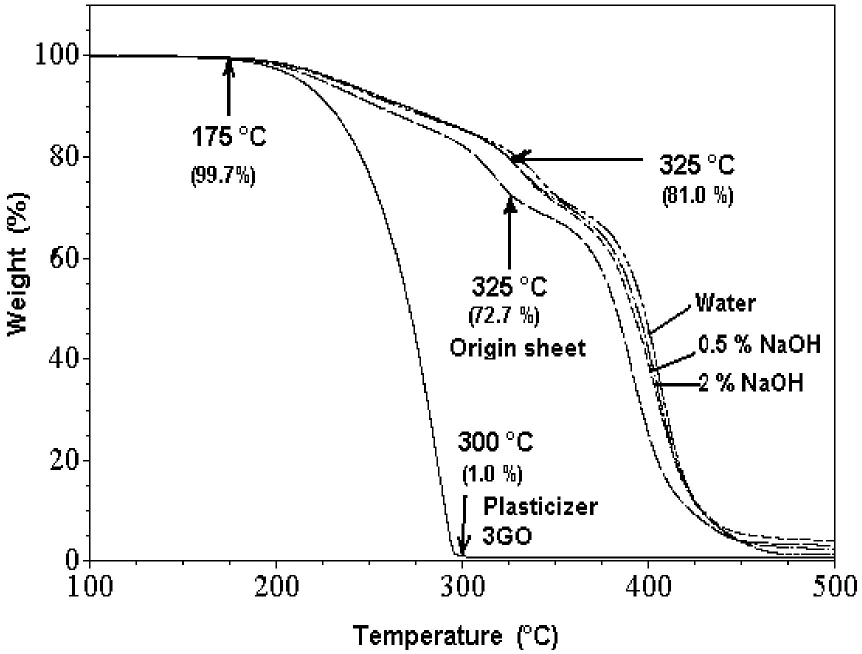

Fig.9: Thermogravimetric evaluation of origin PVB sheets and sheets exposed in various delamination environments

Paper IV

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Degradation of Plasticized PVB During Reprocessing by Kneading

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Summary: Possibility and conditions for optimal re-processing of plasticized polyvinylbutyral (PVB) were tested. The aim of this work was to investigate degradation of PVB sheet at various kneading conditions and to estimate the influence of temperature, air oxygen and mechanical stress on the progress of degradation process. In order to confirm the influence of humidity on the PVB properties during reprocessing, the sheets with the humidity content of 0.5 and 8.0% were tested. The PVB degradation was determined from the changes of melt flow index, mechanical properties in terms of stress and elongation at break, yellowness and molecular weight distribution. The optimal recycling conditions for PVB were estimated from the evaluation of all measured properties and their changes.

Keywords: degradation; kneading; polyvinyl butyral; recycling; thermo-oxidation process

Introduction

Increasing growth of raw material prices, environmental aspects and still growing landfill fees bring about the increasing interest encountered with the plastics waste recycling. Globally, the problem has been solved for the common plastics such as polyolefins, polyethylene-terephtalat and polystyrene. Though extensively used for the glass lamination, polyvinyl butyral (PVB) does not belong to this group. It is generally known that during the glass lamination process, large volume of trim is formed. The formation of the trim is the consequence of the production technology, where the PVB sheet is used larger than the glass so that the edge is perfect. This extra material after pre-pressing is cut. The trim is usually recycled together with the waste sheets originating from the PVB manufacturing.[1] However, to find an ideal PVB recycling conditions is not easy. Due to its composition, PVB is very sensitive to degradation and migration of plasticizer. It was found, that at the atmospheric pressure, plasticizer migrates at the temperature of 260 °C.[2] During repeated processing of plasticized PVB, both water and plasticizer were reported to be extracted from polymer by vacuum. However, the loss of plasticizer at the common processing temperatures (up to 200 °C) is minimal.[3]

More serious problem observed during reprocessing represents shear and thermo oxidative degradation of the polymer. Both degradation types induce the breakdown of polymer chains, even though the degradation mechanism is not the same. Generally, the shortening of polymer chains negatively influences mechanical properties of PVB, resulting in undesirable lowering of safety characteristics of the produced sheet. Deterioration of mechanical properties of PVB consequently decreases its ability to absorb the mechanical energy (when it is used for the safety glass in the car) in the case of an accident.[1,4] On the other hand, decreasing of molecular weight and decreasing of viscosity caused by degradation can favorably influence rheological properties of PVB melt during extrusion in the flat die.

In order to decrease power consumption during re-processing, it is possible to take

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advantage of PVB hygroscopicity. As water contained in PVB matrix can act as an additional plasticizer and lower rigidity of the material, processing of ''wet'' PVB can be advantageous.[4] However, during reprocessing of material containing high moisture content (8%), water can react with butyric groups, which induces the change of the polymer structure. As the consequence, hydrolysis occurs significantly changing the final properties of the reworked PVB.[2,5]

The aim of this work was to determine degradation of PVB sheet at different kneading conditions and to estimate an influence of temperature, air oxygen and mechanical stress on the progress of degradation process. The work is also focused on the possibility to find the optimal re-working conditions of PVB when the mechanical and thermal degradation as well as yellowness of the reprocessed polymer are minimal.

Experimental Part

Samples

Plasticized polyvinylbutyral sheet (moisture content of 0.5 wt%) from RETRIM (part of DuPont *Czech Republic)* was used in the study. The sheet was of the Butacite B5 type, containing butyric (80%), hydroxyl (18–19%) and acetate (less than 2%) units.[1,2,4] Tested PVB film was highly plasticized with 28 wt% of triethyleneglycol bis (2-ethylhexanoate) (3GO).[6].

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Sample Preparation

PVB was reprocessed by kneading, callendering and pressing. Both dry (0.5 wt% water) and wet (8 wt% water) sheets were tested. Increasing moisture content was reached by the soaking of ''dry'' PVB sheet in distilled water for 14 days.

Samples processed by kneading were prepared in the Brabender kneader with two rotors W50, and the friction of 2:3. Volume of the heated chamber was of 55 cm^3. Always the same amount of 40 g PVB was placed in the chamber and processed for 10 minutes at various temperatures (100, 130, 160, 190, 220 °C) and at various rotation speeds (40, 60, 80 rpm). The chamber of internal mixer was filled only to the ¾ of the volume so that there is sufficient amount of oxygen for thermo-oxidative degradation study. During kneading, both thermo-oxidative and shear degradation are supposed to take place.

In order to simulate solely shear degradation with absence of thermal stress, PVB sheets were re-processed by calendering at the temperature of 78 °C in the presence of air. Laboratory callender was used. Rollers were preheated to 60–70 °C. After the initial preheating, the roller temperature was kept only by the energy dissipation. After 10 minutes the temperature reached 78 °C and this value remained almost unchanged.

Pure thermal degradation with low shear stress was simulated by pressing. PVB was placed between two PET sheets preventing the contact with air and thus oxidative degradation. Then, the material was pressed at 1 MPa at various temperatures 160, 190 a 220 °C for 10 minutes.

Dry PVB was tested at all the above presented conditions; wet one was tested at all temperatures but only at 60 rpm.

Methods

Mechanical properties were measured using a T 2000 Tensile tester (Alpha Technologies) with the displacement rate of 500 mm/min at room temperature. For testing, material was pressed into a sheet 1.0 mm thick at the temperature of 130 °C and the standard testing specimens were prepared. Tensile strength and elongation at break were evaluated.

Rheological properties of re-processed samples were tested in terms of MFI measurements using the extruding plastometer M201 (Haake) according to EN ISO 1133.[7] Samples were conditioned at 25% relative humidity and then extruded at 150 °C through the 2 mm capillary using the load of 100 N. The MFI correlates to the polymer mass passing through a standard

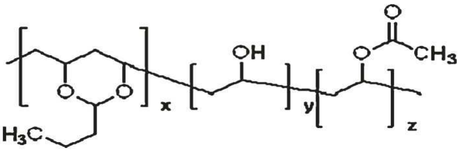

Figure 1.
Polyvinyl butyral chain structure.

capillary in an interval of 10 minutes, at a given load.

Quantification of water content was carried out by the Karl Fischer method *(Metrohm AG)*. The method is based on the conductometric determination of water evaporated from the sheet into the iodine solution and sulphur dioxide in methanol.

Yellowness was evaluated using the CIE Lab. colour scale. Handy Color *(BYK Gardner)* instrument was applied and calibrated with the white and black standards. Measurement was carried out against the white background at the angle of 10°. Illumination type of D65 corresponding to daylight was applied. Yellowness $\underline{Y_{ID}}$, was calculated from the measurements of spectroscopic values $\underline{L}$, $\underline{a}$ and $\underline{b}$. Obtained value was converted to the value corresponding to the PVB sheet with the standard thickness of 0.76 mm, which is typical for applications in automotive industry and in architecture.

GPC analyses were performed using a PLGPC-50 (Polymer Laboratories,) equipped with a PL differential refractometer (DRI) and on-line viscometer detectors (VIS). Analyses were performed with a PL gel Mixed-C column *(7.8 × 300 mm; Polymer Laboratories)* at 30 °C with the mobile phase flow rate of 1 mL/min. Tetrahydrofurane was used as a mobile phase. The column was calibrated using narrow molecular weight polystyrene standards (Polymer Laboratories Ltd, Church Stretton, United Kingdom) with molecular weights ranging from 580 to 451 000 $g \cdot mol^{-1}$ (given by supplier). A 100 μL injection loop was used for all measurements. Universal calibration was applied for the determination of molecular weight from the DRI and the VIS signals. Data processing was performed with Cirrus GPC, Multi Detector Software. The concentration was of about 0.2 g/100 ml and samples were dissolved at room temperature for 20 hours under stirring. The combination of both types of detectors enabled exact determination of molecular weight as well as detect the PVB aggregation.

Results and Discussion

The Influence of the Kneading Conditions on the Change of Mechanical and Rheological PVB Properties

From the theory and practice it is confirmed that the PVB re-processing brings about the shortening of macromolecular chains, which induces the change of its mechanical properties. The results show that increasing of the re-processing temperature causes lowering of melt viscosity (measured as MFI), lowering of tensile strength and also lowering elongation at break. These changes are presented in Figure 2–3.

The MFI values are shown in Figure 2. To sum up, the MFI increases with increasing re-working temperature and increasing rotation speed systematically up to 60 rpm. It is consequence of thermo-oxidative degradation, which causes reduction of polymer molecular weight. However, at the rotation speed of 80 rpm, the MFI values behave differently. Degradation of PVB macromolecular chains (expressed as increasing of MFI) is reduced at the temperatures above 190 °C, which is indicated by no increase or even slight drop of MFI (see Figure 2). The lower degradation at the higher rotation speed (above 80 rpm) is possible to explain by polymer chain slipping in the stressed melt that results in the lower kneading effect.

The results obtained from the measurement of tensile strength of the "dry" PVB samples (0.5% moisture content) in dependence on speed of rotors are shown in Figure 3. At lower temperatures, degradation of "dry" PVB is proportional to increase of the rotation speed. For example, during processing at 100 °C degradation increased, which can be concluded from the

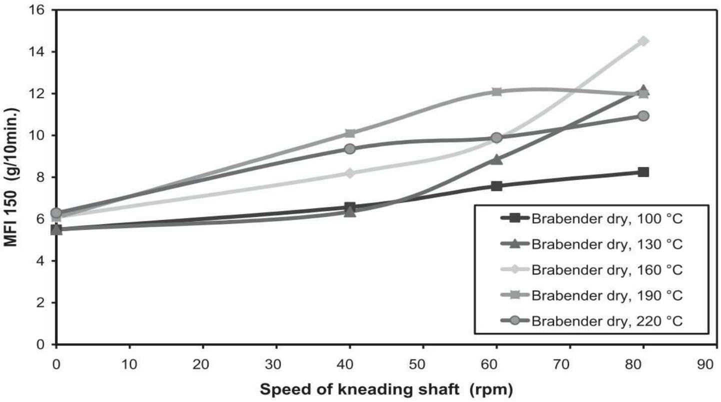

Figure 2.
The change of MFI at the various conditions of the kneading.

lowering of stress at break values (shape of the curve in concave). On the other hand, increasing of temperature caused straightening of this dependence and for the samples processed above 160 °C the curves exhibit the convex curve. Minima in the curves observed at rotation speed of 60 rpm and temperatures 190 and 220 °C indicate, hence, the highest degradation of PVB. Samples re-worked by pressing were used as a background for the kneaded samples at the same temperatures. Slight increase of tensile strength, elongation at break, MFI and yellowness were observed for the samples pressed for 10 minutes at all tested temperatures.

Transformation of the Process Energy into Heat

During the PVB re-processing on the Brabender internal mixer the temperature of the kneading chamber was measured. The chamber was kept at required temperature, but with on-going process of kneading, the temperature slightly increased. The progress of temperature changes is

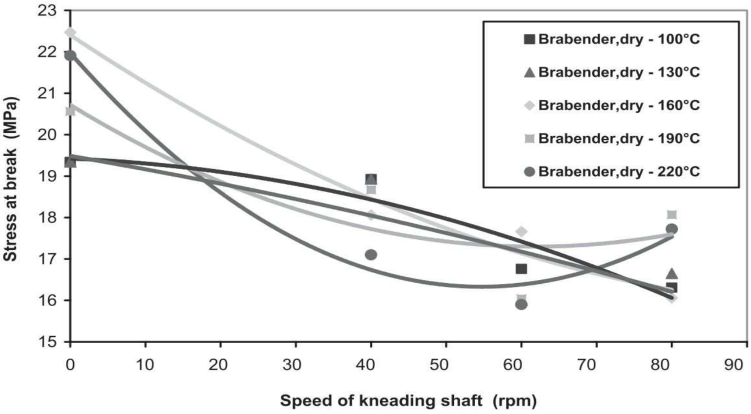

Figure 3.
Tensile strength of the re-processed PVB sheet at the various conditions of the kneading.

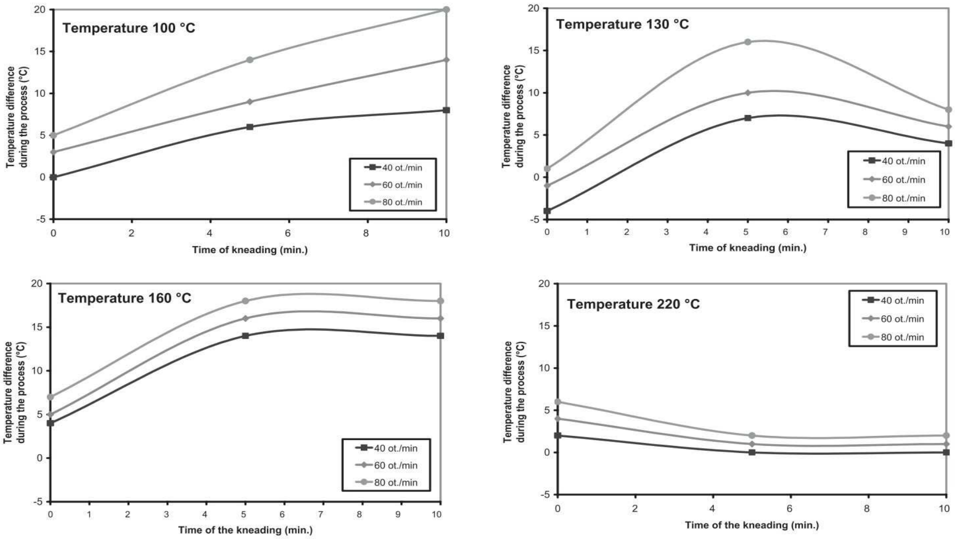

Figure 4.
The temperature procedure during the kneading process.

summarized in Figure 4. More remarkable energy transformation was observed at lower processing temperatures (100 and 130 °C). This effect is clearly correlated to higher viscosity of processed material. It is also demonstrated that evolution of dissipation heat depends on the rotation speed and kneading time. With the higher rotation speed, the amount of dissipated heat increases significantly. Above 130 °C the heat was formed only at the beginning of the kneading, when the material was still with high viscosity. At 220 °C, due to the low material viscosity, the development of the transformation heat is minimal.

The Influence of Water on the Mechanical Property Change

In order to lower the energy consumption during the PVB re-processing, its hydroscopicity was employed. As water contained in the PVB matrix can act as an additional plasticizer, it can decrease PVB viscosity.[3] It is supposed that lower material viscosity can decrease the energetic intensity of the reprocessing. Comparison of MFI values measured for dry (0.5% water) a wet sample (8% water) shows that MFI increased proportionally to the water content (see Figure 5). On the contrary, the tensile strength decreased. The change of the mechanical properties of ‘‘wet’’ PVB was caused by higher polymer plasticity and reduction of intermolecular forces.

During the re-processing of wet PVB material at the increased temperature, hydrolysis and elimination of butyric groups can occur. This process results is the formation of hydroxyl groups and consequently conjugated double bonds, which brings the change of PVB chain structure.[2,5] Thus, the hydrolysis causes considerable changes of the final properties of re-processed PVB. Due to this information, effort was made to find the optimal conditions for PVB re-processing with the lowest possible hydrolysis. Hydrolysis was qualitatively estimated from the changes of molecular weight and from the increase of the sheet yellowness.

Although water that was present in PVB evaporated very quickly at the beginning of the process, it influenced the results of all the tests. The values of MFI for re-processed ‘‘wet’’ PVB show in the

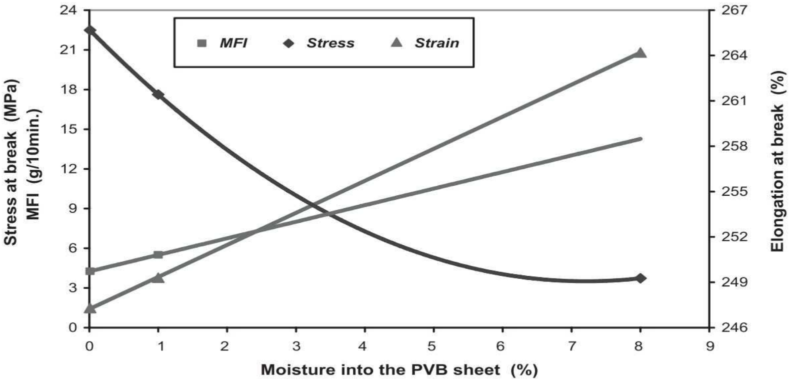

Figure 5.
The influence of water content on the change of mechanical properties of no re-processed PVB sheet.

comparison with the "dry" PVB a significant increasing in the dependence on temperature (see Figure 6) Notable increasing of MFI values observed for wet PVB is caused by degradation, which is induced by the thermo oxidative reactions and better diffusion of gases into the PVB melt.

The comparison of mechanical properties of "dry" and "wet" PVB is presented in Figure 7. The figure shows tensile strength and elongation at break of both PVB types kneaded at various temperatures at constant rotation speed of 60 rpm. Arrows denote the values measured for the original "dry" PVB. Optimal processing temperature for "dry" PVB, where the degradation was the lowest, is determined at the temperature of 150 °C as the maximum of the curve. This maximum, with the highest values of tensile strength, corresponds to minimum degradation of PVB. Below and above 150 °C tensile strength is decreasing, which can be caused by the lowering of the molecular weight induced by degradation. Regarding the degradation mechanism, the scission of the "dry" PVB chains at temperature lower than 150 °C is prevailingly caused by shear

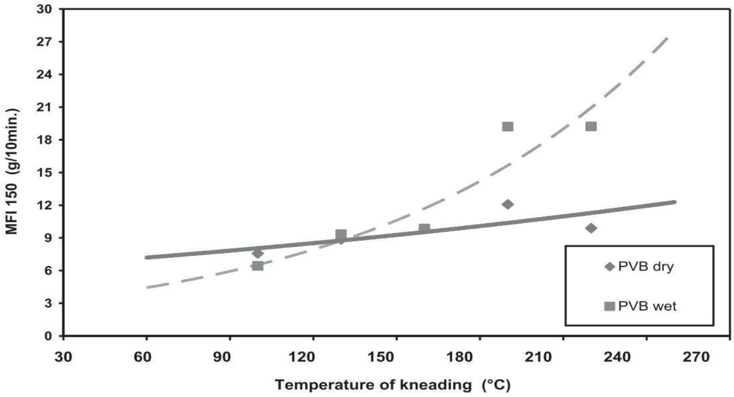

Figure 6.
MFI of kneaded PVB samples ("dry" and "wet") at 60 rpm after ten minutes.

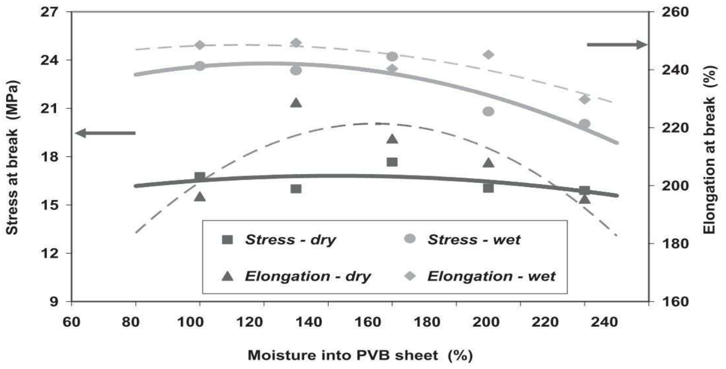

Figure 7.
Tensile strength of kneaded PVB samples (“dry” and “wet”) at 60 rpm.

stress, while at higher temperatures thermo-oxidative degradation takes place.

For wet PVB, the values of stress and elongation at break and strain are systematically higher compared to those measured for dry sample. Moreover, dependence of stress and strain *vs*. temperature is monotonously decreasing there is no maximum or minimum. The increase can be explained by the intramolecular crosslinking formed by the hydrogen bonding.

The comparison of “dry” and “wet” PVB indicates that water acted as a plasticizer and “wet” material was less stressed during reprocessing. Hence, the more plasticized “wet” PVB was not significantly stressed by shear and was mostly degraded by thermo-oxidative degradation.

The Influence of Water on the Yellowness

The PVB degradation was the most remarkably reflected through the changes of PVB yellowness. Visually and also instrumentally, the yellowness (sometimes even brownness) of re–worked PVB samples was noticeable. Yellowness increased significantly with increase of re-processing temperature. In the case of “dry” PVB, significant color change was observed above 130 °C. Color of “wet” PVB was significantly changed above 160 °C (Figure 8). Measurements demonstrated that during kneading at

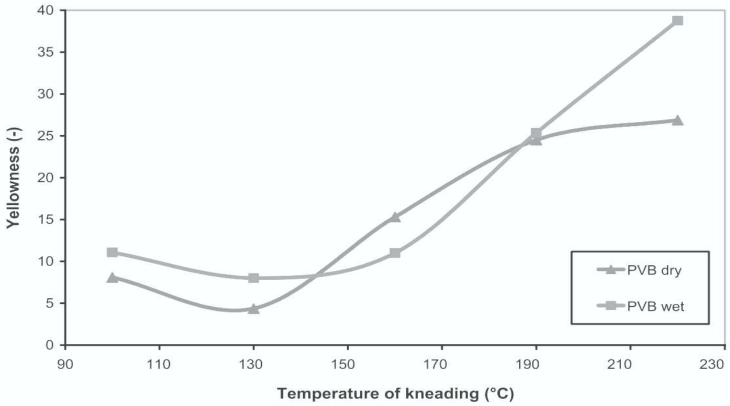

Figure 8.
Yellowness of kneaded PVB samples (“dry” and “wet”) at 60 rpm after ten minutes.

the temperatures below 160 °C yellowness was almost unchanged. This can be explained by the stabilizing function of higher moisture content and consequently higher degree of PVB plasticization. At temperatures lower than 130 °C, the change of the yellowness is insignificant irrespective of water content. With the increasing temperature, the yellowness grows remarkably. This can be explained by thermo-oxidative reactions between oxygen and PVB accompanied by better gas diffusion as well as by water induced hydrolysis. It was reported that during hydrolysis, conjugated double bonds are formed.[5] These are more reactive and bring more intensive decrease of molecular weight. The results from the yellowness measurements relate to the results from determination of MFI (see Figure 6).

The Change of Solution Properties Influenced by the Degradation

Changes in molecular weight and molecular weight distribution of virgin and processed material were measured by gel permeation chromatography.

Differential distribution curves of virgin and processed samples (kneading, 100 °C, dry) are compared in Figure 9. From figure it is clear that the entire distribution of the processed sample compared to the virgin one is shifted to lower molecular weight region, which indicates degradation. Moreover the processed sample contains small but distinct peak with molecular weights higher that $2 \times 10^6\,g \cdot mol^{-1}$ (indicated by arrow). This peak was observed for all of the processed samples irrespective to temperature and type of processing and its presence indicates that diluted solutions of processed samples contain structures with high molecular weight – aggregates. The aggregation of PVB solution and difficulties with polymer dissolution, even in thermodynamically good solvents, has been reported by several authors.[9,10]

Changes of molecular weigh in terms of M_w as a function of increasing kneading temperature are for wet and dry samples depicted in Figure 10. For dry sample, the lowest M_w values were measured on samples processed below 150 °C. Under these conditions, predominantly shear degradation takes place resulting in chain scission caused by mechanical stress. Temperature region between 150 °C and 180 °C seems to be favorable for reprocessing of dry PVB. Here, only minor changes in the sample are observed and molecular weight stays almost unchanged. For wet PVB which exhibits at lower temperatures low stiffness, molecular weight tends to decrease with increasing processing temperature. At temperatures above 190 °C, molecular weight of dry PVB is comparable to that measured for wet sample. Therefore, it can be assumed

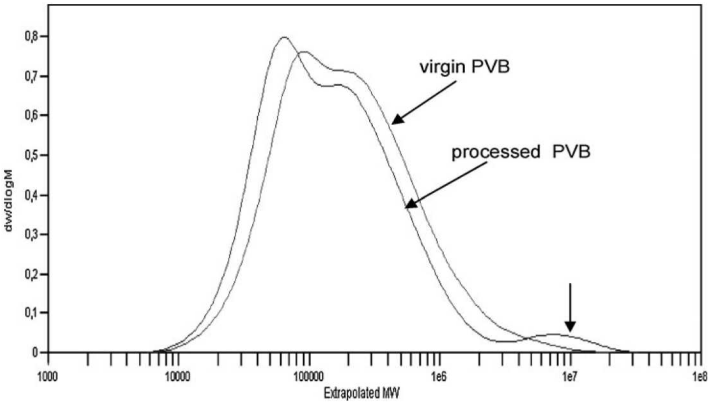

Figure 9.
Comparison of differential distribution curves of virgin and processed PVB (100 °C, dry).

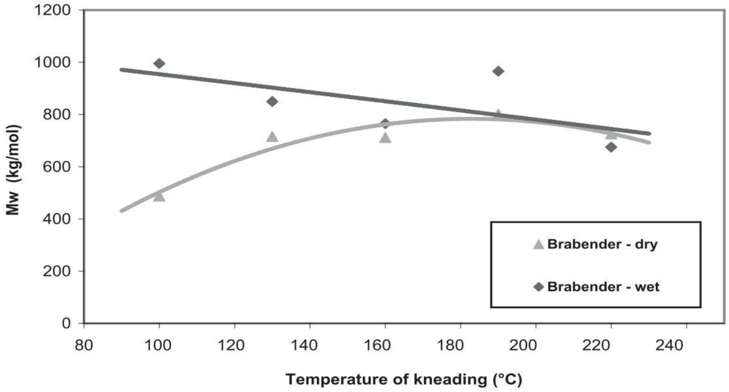

Figure 10.
Influence of kneading temperature on molecular weight changes (M_w) recorded for dry and wet PVB.

that degradation mechanism in this temperature range is similar. From Figure 10 it is also clear that molecular weight of the wet PVB samples, with the exception of the sample processed at 220 °C, was systematically higher compared to the dry ones.

Conclusion

In the presented work, conditions for reprocessing of plasticized PVB sheets were investigated and influence of temperature, air oxygen content and mechanical stress on the progress of degradation was studied. In order to find the possibility for reduction of energy consumption during re-processing, effect of moisture content in PVB sheets on processing parameters and degradation was examined. The obtained results show that, based on the evaluation of MFI and mechanical properties, the optimal conditions for PVB re-working by kneading occur at the temperature about 150 °C and rotation speed of rotors lower than 60 rpm. These conclusions are in the good agreement with the measurement of PVB yellowness. Below 150 °C yellowness remained almost unchanged and increased significantly above this temperature. GPC measurements support above mentioned conclusions showing minimal changes of PVB molecular weigh for this temperature. Increased amount of water in PVB sheet can act as additional plasticizer that improves processability of the polymer melt and decreases thus energy consumption. However the ''wet'' samples are more susceptible to hydrolytic degradation and compromise decision has to be done having in mind these two effects.

[1] M. Tupý, D. Měřínská, J. Zvoníček, *Plastic and rubbers*, **2008**, 208–211.
[2] A. K. Dhaliwal, J. N. Hay, *Thermochemica acta*, **2002**, *391*, 245–255.
[3] Industrial glass, Glass union concern, Research and developing institute of industrial glass in Teplice, series C, No.1, Teplice, **1988**.
[4] M. Tupý, D. Měřínská, J. Zvoníček, Publication at preparing, it will be submitted to *Macromolecular Research*.
[5] V. I. Grachev, I. B. Klimenko, L. V. Smirnov, A. F. Gladkikh, *Polymer science U.S.S.R.*, **1974**, *16*(2), 367–373.
[6] Material Safety Data Sheet of Butacite PVB sheet, DuPont, **2006**.
[7] Euronorm ČSN EN ISO 1133, Melt flow index assessment, **2005**.
[8] L. A. Salam, R. D. Metthews, H. Robertson, *Journal of European ceramic society*, **2000**, *20*, 1375–1383.
[9] L. Mrkvičková, J. Daňhelka, S. Pokorný, *Journal of Applied Polymer Science*, **1984**, *29*, 803–808.
[10] E. E. Remsen, *Journal of applied polymer science*, **1991**, *42*, 503–510.

LIST OF USED SYMBOLS AND ABBREVIATURES

PVB	Poly(vinyl butyral)
PVAc	Poly(vinyl acetate)
PVAl	Poly(vinyl alcohol)
OA	Organic Acid
MgAc	Magnesium Acetate
LSG	Laminated Safety Glass
THF	Tetrahyrdofurane
MFI	Melt Flow Index
TGA	Thermalgravimetric Analysis
GPC	Gel permeation Chromatography
EN	European Norm
ISO	Internacional Organisation for Standardization
DIN	Deutsches Institut für Normung
ASTM	American Society for Testing and Materials

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2006 – 2011	Doctoral study of the Technology of polymer materials in Tomas Bata University in Zlin

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2005 – 2008	RETRIM-CZ: laboratory technician focused on quality control, controlling of polyvinyl butyral sheet, research about industry utilization of recycled PVB obtained from windshields, analysis and evaluation of claims, coordination of external premix manufacturing
2006 – 2010	member in two commitments of Council of Zlín for: Environment; Town Health and Agenda 21
2009 – to date	D Plast Eftec: R&D work focused on developing of new coating, sealant and cavity materials based on PVC plastisols, acrylic, SBR and PUR dispersions or water waxes; usage in automotive, bus and truck industry

Books (chapter):

- TUPÝ M., MĚŘÍNSKÁ D., KAŠPÁRKOVÁ V..: *Recycling / Book 1*, PVB Recycling and Degradation, 1st ed. Rieka: Intech, 2011, ISBN 979-953-307-329-2

Presentations at international conferences:

- MĚŘÍNSKÁ D., TUPÝ M., KAŠPÁRKOVÁ V., et al.: Description of degradation influence on the plasticized PVB during its re-working by kneading, *4th International Conference on Times of Polymers and Composites, SEP 21-24, 2008 Ischia, ITALY; Book Series: AIP Conference Proceedings,* Vol.1042, pp.327-329

List of publications:

- PŠEJA J., HRNČIŘÍK J., KUPEC J., CHARVÁTOVÁ H., HRUZÍK P., TUPÝ M.; Effect of cross-linking waste protein with diepoxides on its biodegradation under anaerobic conditions, *Journals of Polymers and the Environment*, Vol. 14, Issue 3, p. 231-237, 2006

- HRNČIŘÍK J., PŠEJA J., KUPEC J., TUPÝ M.; Contribution to assessing cross-linking of protein hydrolyzate with diepoxides, *Journal of the American Leather Chemists Association*, Vol. 102, Issue 12, p. 393-403, 2007

- TUPÝ M., ZVONÍČEK J., MĚŘÍNSKÁ D., Problems of recycling PVB sheet used for production laminated safety glass, Tomas Bata University, Faculty of Technology: *Plastics and Rubbers*, Vol.45, p. 208-211, 2008

- MĚŘÍNSKÁ D., TUPÝ M., KAŠPÁRKOVÁ V., POPELKOVÁ J.; ZVONÍČEK J., PIŠTĚK D., SVOBODA P.; Degradation of plasticized PVB during re-processing by kneading, *Accepted for publication in Macromolecular symposia*, Vol. 286, p. 107-115, 2009

- TUPÝ M., MĚŘÍNSKÁ D., SVOBODA P., ZVONÍČEK J.; Influence of water and magnesium ion on the optical properties in various plasticized PVB sheets, *Accepted for publication in Journal of Applied Polymer Science*, Vol. 118, p. 2100-2108, 2010

- TUPÝ M., MĚŘÍNSKÁ D., KLÁSEK A., ZVONÍČEK J., SVOBODA P.; Water and acid-base reactants impact to adhesives properties of various plasticized PVB sheets, *The Paper submitted to Journal of Applied Polymer Science*, 2010

- TUPÝ M., MĚŘÍNSKÁ D., MOKREJŠ P., ZVONÍČEK J.; Windshield recycling focused on effective separation of PVB sheet, *The Paper submitted to Resources, Conservation and Recycling*, 2011

Ing. Michael Tupý

The study of PVB waste application obtained from recycled windshields

Studium možností použití odpadního PVB z recyklovaných automobilových skel

English Doctoral Thesis

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