

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 with very low amount of remain glass particles. PVB sheets were obtained from worldwide manufacturer DuPont and then they were laminated by standard autoclaving process. One sample of PVB sheet was modified by multi-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-physical assisted separation. It causes self-release of the glass out of the PVB sheet. The third-stage was mechanical peeling of the remaining glass from the PVB sheet which completed the recycling process. The optimal process conditions for the most effective delamination process were found. Delamination technology produces PVB sheet with minimal residual glass content (up to 300 ppm) and minimal change in PVB sheet properties. Described recycling technology is ecologically friendly (the effluent is fully recyclable as well) and could reduce the worldwide problem with windshield waste disposal. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 39879.

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INTRODUCTION

PVB Sheet Properties

PVB sheets are mainly used for lamination of safety glass. Solutia, DuPont, and Seku-Sui are major PVB worldwide manufacturers now. The PVB is the material which can connect together two sheets of float glass resulting in the laminate with excellent optical and mechanical properties.^{1–6} Most significant PVB properties are elasticity, strength, toughness, high light transmission and adhesion to glass and metals. Toughness of PVB sheet depends mainly on the molecular weight of PVB. However, it has to be plasticized to become softer (decrease modulus).^{1,4,5} However, the plasticizer should not reduce light transmittance through the sheet, PVB adhesion to glass, generate haze and yellowness, and migrate out of the polymer matrix.^{6,7} In addition, plasticizer must have perfect compatibility with the polymer and should not be volatile during the processing conditions.

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.⁸ According to data from,⁹ the worldwide car's production estimated around 60–70 million cars per a year. Considering the consumption of 1 kg of PVB per windshield it gives ~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 added¹⁰ so it represents total amount of ~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.^{8,10} At present PVB sheet obtained from windshield recycling cannot be reprocessed to a new PVB sheet suitable for glass lamination especially due to high amount of glass scraps and due to high water content in the sheet.⁸ If we wanted to use recycled PVB sheet in production of new laminated glass, recycled PVB sheet has to contain no more than 300 ppm of glass fragments or other contaminants, because higher amount negatively influences PVB's optical properties. In addition, the

higher residual glass content also negatively affects PVB processing.¹¹

At present time, the windshield recycling process is mainly based on dry of mechanical peeling. Unfortunately, PVB obtained in this way contains high degree of glass dust (1–5%, w/w) and other contaminants (sludge, paper, and other plastics).^{6,8,10,12} In contrast to the dry recycling process, wet (water based) process seems to be better for the delamination and glass separation from PVB sheet. Aqueous medium more effectively wash out the glass and other contaminations; moreover water also break the hydrogen bonds between the glass and the –OH groups of PVB.^{6,13} It was found that water content around 2% (w/w) in PVB saturated adhesion bridges.^{2,6,11} Residual adhesion is caused only by weak dispersion forces as well.^{6,11} Nevertheless recycled PVB obtained by water based method contain only smaller glass dust in content (0.5–3%, w/w). Glass ratio is lower than the dry separation process but the glass quantity used for PVB relamination to be new safety glass as still very wild.¹²

According the observation of authors,^{1,2,11,14} the PVB adhesion to glass is in mainly generated by H-bonds. The stability of hydrogen bonding between PVB and glass depends on temperature, amount of dissolved salts, polarity system, and pH of the matrix. Hence, the utilization of the wet separation process requires a study of the influence of water and chemical agents on the change of PVB adhesion to glass.⁶ However, the recycling process must be efficient enough and simultaneously the recycled PVB must not be degraded by delamination agent.^{2,11,15} Lower described solution of this problem has not yet been found. Hence, this article focuses on separation of PVB sheet from windshield by a three 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 this study was focused on founding the optimal process conditions for effective glass separation from laminated glass.

MATERIALS AND METHODS

PVB Sheets and Glass Samples

Poly(vinyl butyral) (PVB) is a polyacetal produced by the condensation of polyvinyl alcohol with *n*-butyraldehyde in the presence of an acid catalyst.^{7,16} The condensation reaction produces 1,3-dioxane rings but the reaction does not run to 100% conversion. Residual unreacted hydroxyl groups promote indispensable adhesion to the glass substrate during the lamination.^{1,2,11,14} 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 vinyl alcohol groups (according to PVB type), less than 2% (w/w) of vinyl acetate and the rest is created by vinyl butyric groups (around 76–80%, w/w).^{16,17} Moreover, all PVB films must be plasticized, mostly by branched ethylene glycol esters in amount 25–30%.^{8–18}

Tested original commercially available PVB sheets were supplied by DuPont Company (USA). Tested PVB sheets had trade names Butacite and in the manuscript are labeled But-M and

But-S. Tested PVB sheets contained ~28% (w/w) of plasticizer triethylene glycol, bis(2-ethylhexanoate) (labeled 3GO).^{7,19} Butacite sheet with labeling But-M is suitable for automotive industry and contains 120 ppm (w/w) of all added alkali ions; But-S contains only 40 ppm (w/w) and the use is better for civil engineering. Some part of sheet But-M was re-extruded and simultaneously mixed with 5% (w/w) water solution of multifunctional organic acid (pH = 1.5–2.0). Total addition of organic acid in sheets But-M was 45 ppm. This step was done in order to confirm increasing PVB sheet adhesion and investigate the acid-base characteristics of tested PVBs with different content of adhesive agents (e.g., K⁺, Na⁺, Mg²⁺ salts).^{6,11}

All recycled types of Butacite PVB sheets used for sample preparation of following optical measurement or used for optical and tensile strength measurement were homogenized by kneading. The roll mill used was a Collin W100T. The composites were prepared at 130°C for 10 min at 10 rpm. The gap between the rolls was 0.35 mm. The samples were then pressed to a thickness of 125 × 125 × 1 mm³ by heating in a table press them for 5 min to 130°C, sample mass was 19 g, and then cooled in a cold press. Samples used for optical measurements were laminated according chapter 2.2.

The float glass used for the glass lamination process was made by the casting of glass melt on the surface of molten tin (AGC Fenestra Teplice, Czech Republic). Glass prepared in this way has uniform thickness and extremely smooth surface. This is necessary for the perfect PVB contact with glass during the lamination process. However, very thin layer of tin remains on the bottom side of the glass. This surface is called a “tin side”. The tin film causes quite different adhesion properties between PVB and silicate with increasing moisture in a polymer.^{5,6,11} The float glass used for sample preparation was lime-soda glass with thickness of 2.1 mm and chemical composition being: 71.5% SiO₂, 13.4% Na₂O, 9.2% CaO, 4.15% MgO, 0.7% of Al₂O₃ and other compounds.

According to,⁵ the tin side of float glass was detected by UV radiation and all tested glass panes were oriented with tin side facing up. There is a UV scattering on tin side of the glass which appears as slightly visible white reflexive layer. Hence the PVB sheet was in contact with air side of the glass (upper side of the laminate) and with tin side of the glass (bottom side of the laminate).

Preparation of Laminated Glass

Acidic modified mixture of But+OA sheet was carried out in the single-screw extruder, screen system with an apertures size up to 60 μm and sheet extrusion die.¹² Before lamination, all PVB sheets were conditioned in air-conditioning cabinet (Weiss, Deutschland) in order to achieve required water content in the sheet at 40°C. Conditioned sheets were put between two glass panes previously washed with demineralized water. Both glass panes were oriented with “tin side” facing up. The glass sandwich was pre-laminated in the oven by nip-roll using calender rolls with pressure 0.4 MPa and temperature 130°C. Intermediate PVB layered samples were laminated in the autoclave at pressure 1.2 MPa and temperature 140°C for 20 min. After that they were slowly cooled down to room temperature.^{1,5,12} Finally,

samples of laminated glass were cut out to the size $150 \times 100 \text{ mm}^2$. Then the adhesion was measured by Pummel test.

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 relative strength of the bond between PVB and glass. This method is described by¹ and it is also according to the U.S. Patent.²⁰ Deep-frozen samples at -18°C have undergone repeating impact by a hammer at frequency 130 impacts per minute (weight of the hammer was 450 g) under controlled conditions. The test samples were held at about 5° angle to plane of the Pummel plate, in order to suffer impact of 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 delamination degree was evaluated by gravimetric measurement of the glass loss from PVB sheet during 3-stage delamination process.

Residual glass content was assessed by turbidimetric analysis of the visible light scattering. In general, all optical properties like light transmittance and the light scattering were determined by measurement through the laminated glass containing glass/recycled PVB/glass in thicknesses 2.1/1.0/2.1 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 remain glass content was proved from calibration curve obtained for every particle size fraction of the glass as a function of scattered light. The particle size fraction was determined by common laboratory microscope with magnification 100x.

The plasticizer content was measured according to ISO norm.²¹ Approximately 2 g of PVB sheet was cut into pieces $2 \times 2 \text{ mm}^2$ and these were immersed into the extraction cartridge. The cartridge was immersed into the Soxhlet extraction equipment. The extraction process with hexane was carried out in water bath for 6 h. The majority of solvent evaporated 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 performed by thermogravimetric analyzer TGA Q500 (TA Instruments, New Castle, USA) in open platinum crucibles. Amount of PVB sample for thermal analysis was $\sim 8 \text{ mg}$ and measurements were performed in temperature range $20\text{--}500^\circ\text{C}$, with heating rate being $10^\circ\text{C min}^{-1}$ in protective nitrogen atmosphere (150 mL min^{-1}).

Rheological properties of reprocessed samples were tested according to ISO norm²² in terms of MFI measurements using the extruding plastometer M201 (Haake). This norm corresponds with.^{23,24} 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 min, at a given load.

The tensile test was carried out at room temperature tensile testing machine Tensometr 2000. The crosshead speed was 500 mm/min and the initial gauge length was 20 mm. This method was provided under the test standard EN ISO 527-1, 3 (DIN 53 453) and DIN EN ISO 527-3 (DIN 527-3).

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 Media. Pure water or 0.125, 0.25, 0.5, 1, and 2% (w/w) of NaOH in demineralized water. Prepared solutions were stored at room temperature.

Windshield 3-Stage Recycling Process

Laminated safety glass panels were prepared by usual autoclaving process. Samples were stored for one week in order to allow the relaxation of the laminate. 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 have undergone repeating impact by a hammer at frequency 130 impacts per minute (weight of the hammer was 450 g) under controlled conditions. The test specimens were held at about 5° angle to plane of the specimen plate. The hammering was carried out to achieve a particle size of cracked glass in range 0.5–5 mm. Some changing of mentioned process were not major influences on following separation process but described conditions were used as the standard for the test. Hammered laminates were weighted before the chemical delamination. The laminate lost distinct amount of glass and this amount depended on PVB adhesion to glass. The higher adhesion the lower was the glass loss. Obtained glass powder was directly utilizable for next remelting process in glass manufacturing. The dependence of adhesion on glass mechanical peeling is shown in Tables (I–III) (compare glass loss in 1st stage and adhesion of PVB). Mentioned part of technological process was named “1st stage”. The illustration of the whole process it is described in Figure 1.

2nd Stage

Cracked laminated glass samples were placed in boiling water and water solutions of sodium hydroxide with concentrations 0.25–2.0% NaOH (w/w), for a constant time 60 min. The system was occasionally stirred. The self-releasing glass from PVB surface was observed and measured by gravimetric method during the delamination process. Behavior of the delamination process depended on amount of glass remaining after 1st stage of recycling process (effect of PVB adhesion to glass). Results of delamination behavior on various PVB samples are described in Tables (I–III). The kinetics of delamination behavior of single PVB laminate is shown in Figures 2–4. The attention was paid

Table I. Summarized Results of Three-Stages Separation Process Efficiency with PVB Sheet But-M

Type of the PVB sheet/ PVB adhesion grade ^a	Glass separation efficiency (%)				
	1st Stage	2nd Stage		3rd Stage	
	Windshield cracking ^b	Used concentration of NaOH	Chemical separation of glass ^{b,c}	Mechanical peeling ^{b,c}	Remaining glass (%) ^d
But-M / 3.0	48.0 ± 4.6	0.00 %	48.4	3.6	0.1–0.2
		0.25 %	49.4	2.6	0.05–0.1
		0.50 %	50.2	1.8	0.02–0.07
		1.00 %	51.0	1.0	≤0.03
		2.00 %	51.5	0.5	≤0.03

^aAdhesion according to Pummel test (0 = no adhesion, 10 = excellent adhesion).

^bPercentage glass loss in each recycling stage - evaluated as separated part of total amount of glass.

^cError of measurement is approx. ± 1% (important was remaining glass in the end of the process).

^d0.1 % = 1000 ppm of the remaining glass; assessed by measurement of scattered day-light.

also to effluent generated by 2nd stage of separation process. Used alkali water solution can be reused 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 complete the previous operation by mechanical peeling of residual glass. The PVB adhesion was reasonably reduced by the delamination process and the process which is carried out at 3rd stage requires only minimal effort to peel of the glass. It is convenient to do this with the help of steal brush which does not contaminate separated PVB sheet. Delaminated PVB sheet can be washed with water or slightly acidic solution, before and after the 3rd stage to wash-away reminding glass particles and neutralize the sheet. Washing-away of reminding glass particles is achieved by this process and it lowers high pH value. Washed PVB sheets were 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 architectural glass. The efficiencies of the whole processes for the individual PVB types are shown in Tables (I–III).

RESULTS AND DISCUSSION

Evaluation of Recycling Process Efficiency

1st Stage. The efficiency of 1st stage was significantly influenced by the adhesion of PVB to glass. The most sensitive it was in case of But-M sheet which has low degree of PVB adhesion to glass. Therefore, hammering of But-M (including But+OA) laminates caused glass loss ~48% (w/w). The laminate But-S lost ~42% (w/w) of glass. Results are shown in Tables (I–III). It is necessary to remind that all laminates were hammered by the same hammering intensity to similar size of glass slivers (0.5–5 mm). According observations it can suggest that glass slivers in size up to 3 mm fallen down without help, glass slivers in size

Table II. Summarized Results of Three-Stages Separation Process Efficiency with PVB Sheet But-S

Type of the PVB sheet/ PVB adhesion grade ^a	Glass separation efficiency (%)				
	1st Stage	2nd Stage		3rd Stage	
	Windshield cracking ^b	Used concentration of NaOH	Chemical separation of glass ^{b,c}	Mechanical peeling ^{b,c}	Remaining glass (%) ^d
But-S / 8.0	41.9 ± 2.8	0.00 %	52.2	5.8	3.5 – 5.0
		0.25 %	53.9	3.4	0.6 – 1.6
		0.50 %	55.7	2.3	0.03 – 0.3
		1.00 %	56.8	1.3	≤0.03
		2.00 %	56.8	1.3	≤0.03

^aAdhesion according to Pummel test (0 = no adhesion, 10 = excellent adhesion).

^bPercentage glass loss in each recycling stage - evaluated as separated part of total amount of glass.

^cError of measurement is approx. ± 1% (important was remaining glass in the end of the process).

^d0.1 % = 1000 ppm of the remaining glass; assessed by measurement of scattered day-light.

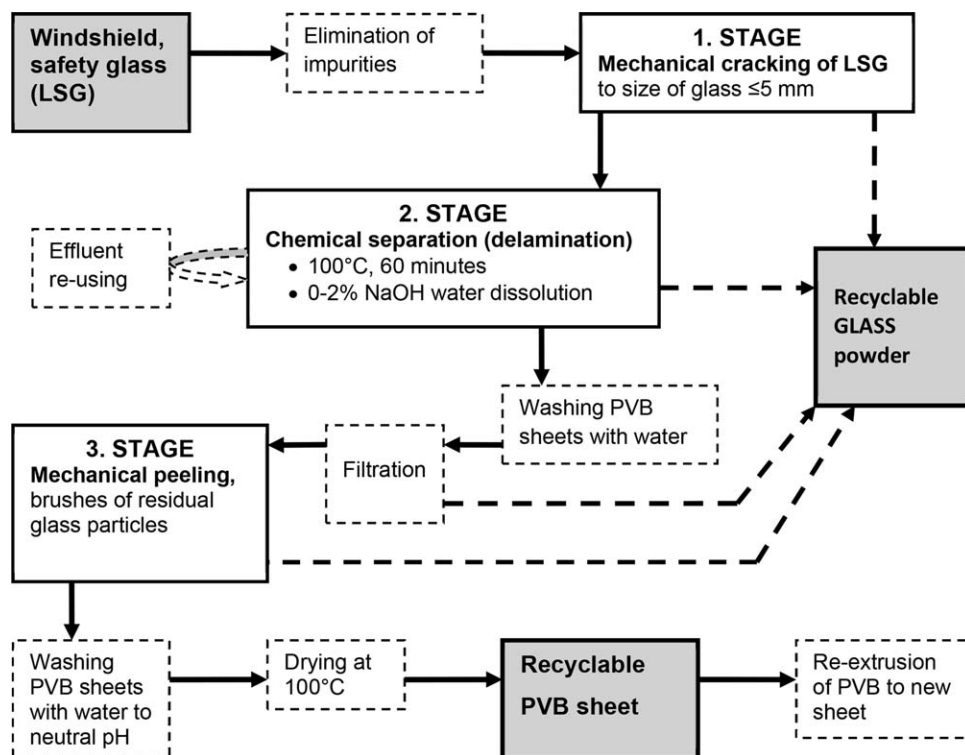


Figure 1. Scheme of 3-stage recycling process; LSG, laminated safety glass, effluent is NaOH water dissolution.

3–7 mm was possible to remove easily and glass slivers in size more than 7 mm were irremovable.

2nd Stage. First of all, the influence of organic solvent on PVB adhesion reduction (hydrogen bond breakage) was tested. On the basis of observations, ethanol and other polar organic solvents show their possibility to use them in delamination process, even at room temperature.^{6,11} Unfortunately, problematic manipulation, flammability, solvent volatility and price complicate the application of these solvents in practice. Hence, due to deficiency of organic solvent usage less problematic liquid was chosen. Everything points out to water application because it is

cheap, nontoxic, renewable, and nonflammable delamination environment.

Thus, “common wet process” intensification of the delamination process had to be used. It was achieved by acid–base reagents. Experimental work discovered that alkali reagents were very effective for the auto-self glass delamination from the PVB sheet. Moreover, alkali reagents help to obtain PVB sheet with extremely low content of the glass and it clearly accelerates the delamination process. Measurement leads to conclusion that delamination strength significantly rose with increasing water content in PVB sheets and with increasing pH value of the surrounding environment. The adhesion drop was discovered when the water content (with pH = 7) was in range when 2.5–3.5%

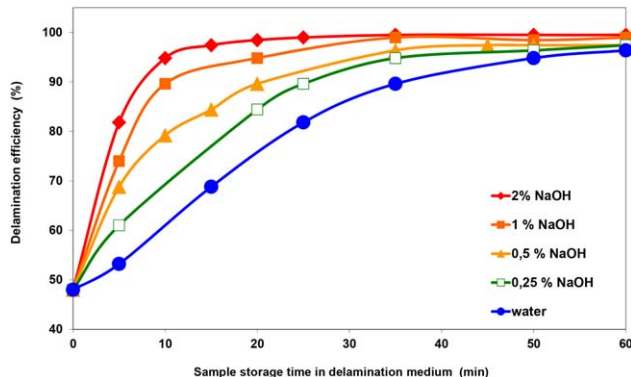


Figure 2. Glass delamination efficiency of PVB type But-M in 2nd stage of recycling process in different NaOH solutions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

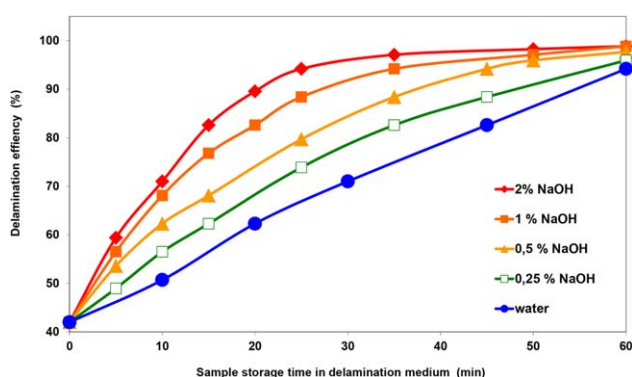


Figure 3. Glass delamination efficiency of PVB type But-S in 2nd stage of recycling process in different NaOH solutions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

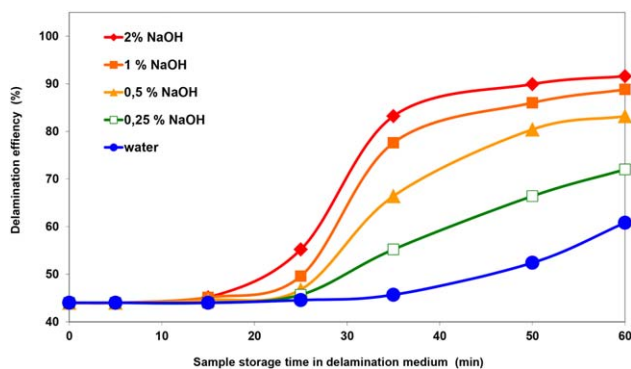


Figure 4. Glass delamination efficiency of PVB type But+OA in 2nd stage of recycling process in different NaOH solutions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(w/w) for various PVB sheet.¹² The decrease in adhesion was caused by inhibition of $-OH$ groups in PVB chain.^{6,11} Adsorbed water behaved as a plasticizer and along with alkali pH it reduced van der Waals adhesive forces. In addition, alkali pH prevents PVB degradation at elevated temperatures.¹⁵

Because of large dissimilarities of tested PVBs; this study was focused on finding of optimum delamination process conditions based on influence of temperature, delamination exposition time, and most importantly of the concentration of alkali delamination agent. These were tested in order to find the capability of recycling process for one of the major worldwide manufacturer of PVBs. Cracked laminated glass was immersed into delamination medium at various temperatures ($20^{\circ}C$; $50^{\circ}C$; $80^{\circ}C$; $100^{\circ}C$) and the delamination speed was tested after different exposure times (see Figures 2–4). Observation led to conclusion that elevated temperature intensifies diffusion of delamination agent to PVB and speeds up the delamination process. Hence, process duration one hour and the highest possible temperature ($100^{\circ}C$) at atmospheric pressure were found to be sufficient. The same conditions were used for study of 2nd stage of recycling process mentioned below. These were:

temperature at $100^{\circ}C$, atmospheric pressure, delamination agent concentration in a range 0.0–2.0% and the process time 1 h.

The delamination kinetics of every PVB sheet type was studied separately, such as described Butacite sheets with various adhesion grades. The most effective delamination 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 51.5% (w/w). The sheet But-M was chemically separable in boiling 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 at above mentioned concentration of NaOH achieved high efficiency of delamination process and simplicity in peeling of residual glass in the 3rd stage. The glass separation efficiency and following process completion was depended on used NaOH concentration as shown in Table I and Figure 2.

The sheet But-S with higher adhesion value was also chemically separable. However, the delamination speed was reduced with lower concentration of NaOH, as shown in Figure 3 and the glass separation efficiency is shown in Table II. 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 Figure 4. The dissimilarity caused by modification was detected in the time lag before the delamination started. Results confirmed that delamination power ratio depends on adhesion grade. Initially acidic modifier had to be neutralized and following delamination behavior could be similar to the case of unmodified PVB sheet (see Figures 2 and 4). Final efficiency of chemical separation of sheet But+OA with 2% NaOH was about 14% lower than in the case of But-M sheet. Results are listed in Table III.

To sum up, all laminates with Butacite sheets were recyclable only with NaOH concentration above 0.5% (w/w). Glass fragments were with a dilute medium unremovable. Comparison and recommendations are described in chapter “Optimal process conditions”.

Table III. Summarized Results of Three-Stages Separation Process Efficiency with PVB Sheet But+OA

Type of the PVB sheet/ PVB adhesion grade ^a	Glass separation efficiency (%)				
	1st Stage	2nd Stage		3rd Stage	
	Windshield cracking ^b	Used concentration of NaOH	Chemical separation of glass ^{b,c}	Mechanical peeling ^{b,c}	Remaining glass (%) ^d
		0.00%	13.0	35.7	2.6–4.4
		0.25%	24.2	28.0	0.8–2.1
But+OA / 10.0	47.8 ± 4.4	0.50%	34.4	17.8	0.03–0.4
		1.00%	41.0	11.2	≤0.03
		2.00%	43.8	8.4	≤0.03

^a Adhesion according to Pummel test (0 = no adhesion, 10 = excellent adhesion).

^b Percentage glass loss in each recycling stage - evaluated as separated part of total amount of glass.

^c Error of measurement is approx. ± 1 % (important was remaining glass in the end of the process).

^d 0.1% = 1000 ppm of the remaining glass; assessed by measurement of scattered day-light.

3rd Stage. Extracted PVB sheets were washed by the water to adjust pH. Although, the chemical separation has high process efficiency, the glass still remained on the polymer surface and following completion stage had to be used many times. All of this glass must be removed (can be still up to 25%, w/w). Because of that, residual glass particles were easily separable from every PVB sheets. Nevertheless, in case of But+OA, some residual glass particles were necessary to remove the glass manually, mainly PVB sheets recycled by water. Principally, Stage 3 did not have problem with the glass scraping by a steel brush. It was carried out by force in range 2–10 N for 30 s because glass-PVB adhesive strength was already very low. On the other hand, it was difficult to remove uncracked large glass fragments which were still laminated on the sheet. Therefore it was necessary to break the glass to pieces smaller than 5–7 mm as it was described in the 1st stage.

The final peeling process was considerably different for used NaOH solution. The highest amount of remaining glass was peeled from Butacite sheet, it has been already observed during delamination by water. Butacite sheets But-M and But-S needed to remove between 0.5 and 5.8% (w/w) of glass at 3rd stage, But-+OA needed to remove between 8 and 36% (w/w) of glass. It depended on PVB adhesion degree and predominantly on concentration of used NaOH solution (see Tables (I–III)). Thus, the efficiency of the 3rd stage was always very high; PVB obtained by the recycling process had the glass content up to 300 ppm. This value was measured by light scattering analysis, after initial calibration. Residual glass content 300 ppm is acceptable for following extrusion process which produce new PVB sheet used in automotive safety glass industry. All results and observations are summarized in Tables (I–III) and Figures 2–4.

Optimal Process Conditions

Most of all it is necessary to remind that there is a broad worldwide collection of windshields and architectural laminates which contain various adhesion grades of the PVBs. On the basis of previous experiences, optimal process conditions for all PVB adhesion grades were determined at temperature 100°C (with atmospheric pressure), the process time 1 h and NaOH concentration being 0.5%. This alkali strength was sufficient for glass separation process for all of the examined windshields. These process conditions accomplished very effective self-releasing of glass and reasonable amount of residual glass particles. Moreover, in this case residual glass was removable very easily. On the other hand, chemical separation without NaOH caused higher amount of residual glass particles on PVB sheet surface. Hence, residual particles had to be removed mechanically.

It is necessary to mention that the process is not suitable for recycling of PVB sheet with thickness smaller than 0.4 mm because thin film can easily break and present particles of unseparated laminate contaminate recycled PVB and also recycled glass. Thus, authors¹² point out that obtaining of pure uncontaminated PVB sheet is possible only if collected undamaged windshields are free from paper, sand, foreign plastics, and colored PVBs. Usage of uncontaminated PVB sheets provide necessary requirement for achieving of sufficient optical properties of

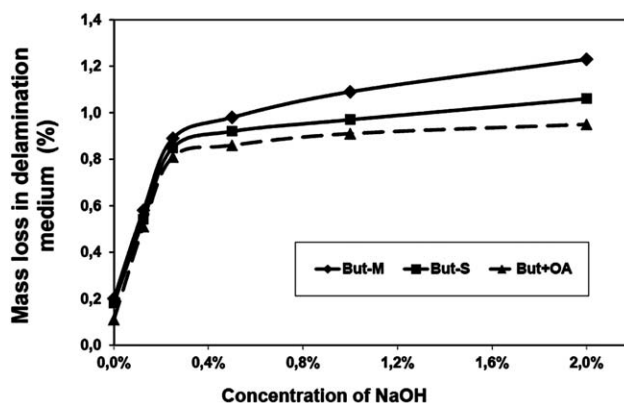


Figure 5. Loss of plasticizer in dependence of used the concentration of delamination medium (NaOH).

new (reprocessed) PVB sheet. Optical properties are very important in automotive industry and they were described in detail in this article.⁶

Separated PVB Sheet

Although the 3-stage recycling process was successful and alkali environment stabilizes the PVB polymer,¹⁵ the polymer plasticizer can be saponified by using alkali reagents. The saponification can leach plasticizer and causes following changes of PVB sheet property. Changes were observed as increase of glass transition temperature and decrease of melt flow index (sheet hardening). Mentioned property changes were directly proportional to the ion concentration of used alkali environment. It was verified by several subsidiary following tests, mentioned below. Nevertheless, the scope of this study does not focus on the analysis of saponified PVBs. The upcoming future work should deal with this significant appendix because it would be useful to know about it in more detail.

The loss of the plasticizer was determined by gravimetric analysis of PVB sheet (not a laminate). The mass loss was detected after exposing of the sheet to various delamination environments for 60 min and it's drying of the sheet at 80°C to constant weight. The loss of the weight rose with increasing alkali concentration. This weight change was assigned to plasticizer saponification followed by leaching, not to change of PVB chain structure or molecular weight. Plasticizer losing of all Butacite sheets exposed in hot water loss was discovered in 0.1–0.2%; and exposure in 0.5% NaOH caused weight loss in range 0.85–1.0%. All results are summarized in Figure 5. Besides, the figure also imagine lower level of leaching in case of sheet But+OA (which is But-M with additional of 45 ppm of organic acid). This effect may be described as a saponification reduction by present acid neutralization.

The statement that alkali environment reduces content of plasticizer in PVB sheet was verified by extraction assessment. Original But-M sheet contained 27.2% (w/w) of plasticizer 3GO. The same PVB sheet exposed in hot water for 60 min had plasticizer content only 26.8% (w/w). Following loss of plasticizer was observed in dependence on increasing alkali concentration. But-M sheet exposed in 0.5% (w/w) NaOH contained 26.5% (w/w)

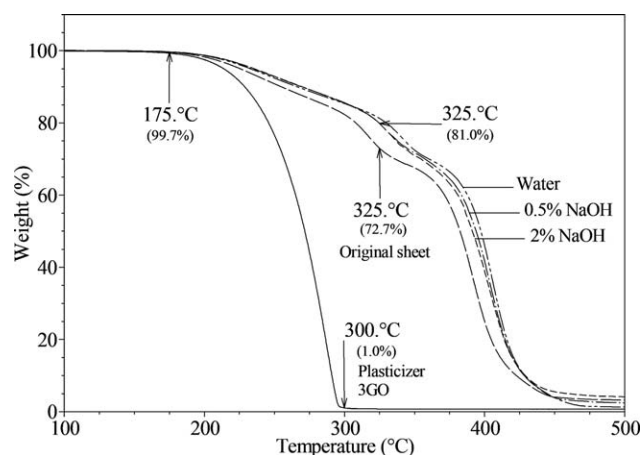


Figure 6. Thermogravimetric evaluation of original But-M sheet and But-M sheets exposed in various delamination environments.

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 losing of plasticizer content in PVB sheet was determined by TGA analysis. The Figure 6 points out to increased thermal stability of exposed PVB sheet. It means higher plasticizer content caused faster mass loss of the sheet (see original But-M sheet). Samples exposed to delamination medium have the mass loss shifted to higher temperature. For comparison, TGA measurement only with 3GO plasticizer was carried out. It was found that plasticizer was evaporated at 300°C (see Figure 6). Tested PVB sheets were stable till 175°C and during elevated temperature the plasticizer evaporation begins. By this measurement it was found that mass loss of original Butacite sheet at 325°C was 27.3%. This temperature corresponds with the plasticizer content in the sheet assessed by extraction measurement (see above). Exposed But-M sheets in water or NaOH solutions have mass loss at 325°C only 19–20% which means much lower plasticizer content compared with original Butacite sheet.

In general, the rheological characterization of melt flow index (MFI) is very important for extrusion re-processing and the analysis can also determine changes of amount of present plasticizer in the sheet. By the reason, MFI value of original and recycled PVB sheet was analyzed. Measurement confirmed slight sheet hardening and tensile strength increase. The changes of all Butacite sheets observed that MFI value 5.2 ± 0.2 g/10 min dropped by delamination in 0.5% NaOH to $MFI = 5.0 \pm 0.1$ g/10 min (decreases about 2%) and by delamination in 1.0% NaOH the value dropped to $MFI = 4.9 \pm 0.1$ g/10 min (decreases about 4%). Nevertheless, worldwide manufacturers of PVB sheets need to use MFI of extruded material in wide range 1.5–6.0 g/10 min, it means flow properties of recycled PVBs are fully in required specification.

In the last but not least, the optical properties of recycled and commercial PVBs were tested. It was carried out with PVB sheet type But-M. Results of the light transmittance of recycled PVB But-M were slightly lower but similar with comparison of commercial PVB sheet Butacite. The lowest light transmittance was

Table IV. Mechanical Properties of Original and Recycled PVB Sheet But-M

But-M	Used concentration of NaOH	Tensile at break (MPa)	Elongation at break (%)
	Original sheet	26.1 ± 1.4	367 ± 31
	0.50%	27.8 ± 1.2	417 ± 20
	1.00%	28.5 ± 1.6	428 ± 28
	2.00%	28.5 ± 0.8	418 ± 19

achieved in the case of PVB elated in 2% NaOH and the optical properties were elevated in case of reduced NaOH concentration. Total light transmittance reduction was maximally about 0.5–1.2%. Although the light transmittance was reduced, its value seems to be still acceptable for secondary relamination use of separated PVB.

The last analysis of mechanical properties of original and recycled PVB was added. The mechanical properties of plasticized PVB samples were measured at room temperature on standard dumbbell-shaped specimens cut directly from the films. All the samples were amorphous and above their glass transition at room temperature ($T_g \sim 15^\circ\text{C}$). Results written in Table IV show the tensile stress and the maximal elongation at break. The values of tensile stress point out that the strength was very similar for all recycled and original PVB. Actually, tensile stress of recycled PVBs is a little bit higher than the original sheet (5–9%). However, the difference is imponderable. Opposite trend was observed in case of the elongation of the break, the value increased about 11–14%. The change of mechanical properties was most likely caused by slight plasticizer leaching which generates sheet hardening.

CONCLUSIONS

The study describes the process of effective glass separation from various PVB sheets; most likely 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 and chemical delamination of the glass.

The 1st stage, based on glass cracking, was used as preoperation for ideal contact of polymer matrix with delamination environment. In this stage glass must be cracked into particles with size in range 0.5–5 mm which allows diffusion of delamination agent onto PVB surface. The diffusion occurs during following stage.

The 2nd stage is based on reduction of adhesion strength between PVB and air side and tin side of the glass panes. It was achieved by water, elevated temperature and alkali environment. Delamination power grows with increasing alkali ion concentration. Nevertheless, the process was also influenced by the residual glass content which comes from 1st stage of mentioned recycling process. Regarding to high efficiency of chemical separation, dilute NaOH solution can be used in order to obtain

PVB with very low amount of the glass. Optimal delamination process conditions used for all PVB sheets were determined. These conditions are: process time 1 hour, temperature 100°C, atmospheric pressure, 0.5% (w/w) NaOH. This alkali environment was strong enough for effective glass separation from every type of windshield.

Higher alkali strength used in 2nd stage achieved not only faster chemical glass separation but also easier peeling of residual glass in 3rd stage. To sum up, it was possible to obtain recycled PVB sheet with glass content not exceeding 300 ppm. This amount of residual glass should be acceptable for industrial PVB sheet reprocessing. Moreover, separated slivers of glass are fully recyclable by addition during new glass melting. 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.

Regarding the success of mentioned recycling process, the polymer plasticizer can be saponified by used alkali reagent. It was found by the extraction analysis that the application of alkali strength up to 0.5% did not cause significant reduction of plasticizer content. The reduction had low influence on decrease of flow, optical and mechanical properties of PVB sheets. Reduction of plasticizer content was confirmed by TGA measurement. The summarize view to recycled PVB material point out that its properties are not mostly changed and the polymer can be used for safety glass production again. Nevertheless, the scope of this study does not focus on the analysis of saponified PVBs. The upcoming future work should deal with this significant appendix because it would be useful to know about it in more detail.

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