

Use of Recycled PVB as a Protection against Carbonation

Michael Tupý, Vít Petránek

Abstract—The paper is focused on testing of the poly(vinyl butyral) (PVB) layer which had the function of a CO₂ insulating protection against concrete and mortar carbonation. The barrier efficiency of PVB was verified by the measurement of diffusion characteristics. Two different types of PVB were tested; original extruded PVB sheet and PVB sheet made from PVB dispersion which was obtained from recycled windshields. The work deals with the testing CO₂ diffusion when polymer sheets were exposed to a CO₂ atmosphere (10% v/v CO₂) with 0% RH. The excellent barrier capability against CO₂ permeability of original and also recycled types of PVB layers was observed. This application of PVB waste can bring advantageous use in civil engineering and significant environmental contribution.

Keywords—Windshield, Poly(vinyl butyral), Mortar, Diffusion, Carbonation, Polymer waste.

I. INTRODUCTION

THE Poly(Vinyl Butyral) (PVB) polymer is mostly used in the form of plasticized PVB sheet for production of laminated safety glass used as windshield and safety glass in civil engineering. The PVB can create a connection of two float glasses in order to make a laminate with excellent optical and mechanical properties [1]-[6]. The most significant properties of plasticized PVB are elasticity, strength, toughness, high light transmission and adhesion to siliceous substances. Toughness and excellent tensile properties of PVB sheet are achieved due to high molecular weight of PVB. Nevertheless, this polymer has to be plasticized to become softer in order to increase elasticity [1], [2].

Worldwide, total amount of PVB sheet produced by automotive industry and civil engineering is estimated around 120 million kg per year [7]. The current windshield recycling process is based on mechanical peeling. This type of recycling technology provides the PVB which contains high degree of residual glass dust (1-5%, w/w) and other contaminants: water, parts of color PVB sheets, mixed of various PVBs, sludge, paper and foreign plastic matters [8], [11]. This PVB by-product cannot be reprocessed to be new PVB sheet suitable for glass lamination. Furthermore, this PVB scrap is incinerated or land-filled [9], [12]. Thus, present used

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recycling processes produce a good quality of glass scrap which could be partly re-used in the glass batch or in other technologies. As mentioned, the separated PVB waste is not recyclable [10]. In case of possible application for recycled PVB it would solve a major environmental problem. The indisputable advantage of such PVB is that the laminated (interglassed) PVB is not degraded. The PVB is not essentially exposed to UV radiation (up to 320nm), mechanical stress, elevated temperature, oxygen and any corrosive damaging substances [8], [10]. Therefore, the interglassed PVB sheets should keep very similar physical properties as extruded material before the lamination process. Due to this knowledge, the PVB has still excellent mechanical properties. This is also one of the assumptions for use of recycled PVB as the protection of concrete structures against environmental influences which cause the degradation.

II. EXPERIMENTAL

A. Materials

Poly(vinyl butyral) (PVB) is a polyacetal produced by the condensation of polyvinyl alcohol with n-butyraldehyde in the presence of an acid catalyst [5]. The condensation reaction produces 1,3-dioxane rings but the reaction does not run to 100% conversion. Residual un-reacted hydroxyl groups promote indispensable adhesion to the glass substrate during the lamination [2], [3], [13]. The final structure can be considered to be a random atacticter-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) [14]. Moreover, all PVB films must be plasticized, mostly by branched ethylene glycol esters in amount 25-30% [15].

Tested original extruded commercially available PVB sheets were supplied by DuPont Company (USA). Tested PVB sheets had trade name Butacite and in the manuscript are labeled Butacite S. Tested PVB sheets contained approx. 28 % (w/w) of plasticizer triethylene glycol, bis(2-ethylhexanoate) (labeled 3GO) [16], [17].

Tested water based dispersion of PVB was obtained from Company (Shark Solutions, Belgium). Tested PVB dispersion with trade name Shark Dispersion MW™ was made of 100% post-consumer recycled windshields and laminated architectural/building glass PVB in (d₅₀) particle size of PVB less than 0.15µm, with a milky color and dry content approx. 55% (w/w). The value of pH was 9-10, density 1.03 g/mL and the Brookfield viscosity < 600 mPas (LVF NO 3 spindle, 20

rpm (@ 20°C). Due to high mechanical properties of used PVB, the dispersions can be used as a concrete surface protection / binder or as a performance enhancing additive in water-based coatings. The dispersion is film forming and dries at temperature.

Acronal S 400 (BASF, Germany), which is an aqueous anionic dispersion of a copolymer of an acrylic ester and styrene (AC-S). The product is mainly used to modify hydraulic binders and to manufacture flexible coatings. Dry content approx. 57% (w/w). The value of pH was 7.0-8.5, density 1.04g/mL.

Specimens of recycled PVB sheet (prisms: Ø110mm x 0.8 mm) were prepared. The PVB dispersion obtained from recycled windshields was left in the Petri dish at 30-40°C for 24 hours and then air-cured with ventilation at 80±2°C for 3 hours in order to remove adsorbed water.

B. Tests

The determination of carbon dioxide permeability was measured according to the norm EN 1062-6 [18]. The method covers a procedure for determination of the steady-state rate of transmission of carbon dioxide gas through plastics in the form of film, sheeting, laminates, plastic-coated papers or fabrics. It provides determination of carbon dioxide gas transmission rate, the permeance of the film to carbon dioxide gas and carbon dioxide permeability coefficient in the case of homogeneous materials. The diffusivity of CO₂ through PVB layers was tested in the chamber with CO₂ atmosphere (10% v/v CO₂) with 0% RH at temperature 23°C. The chamber with sample is showed in Fig. 1.

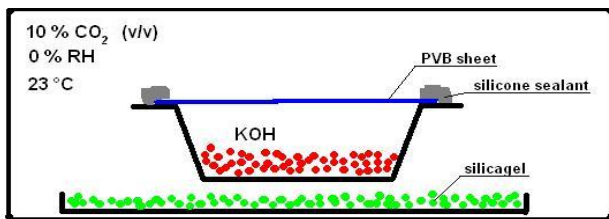


Fig. 1 Schematic diagram of the diffusion measurement test set-up

The CO₂ concentration was controlled by infrared detection in the chamber and the humidity was reduced in zero value by silica gel. The diffusivity was evaluated by mass increase due to CO₂ diffusion through the PVB layer and reaction with potassium hydroxide to create K₂CO₃. Samples were weighed every day for 35 days and the CO₂ permeability was determined according to (1):

$$i = \frac{d_M \times K_1 \times K_2 \times p}{t \times A \times c \times p_{atm}} \quad (1)$$

where i is the carbon dioxide permeability in unit [g/m².d]; d_M is mass difference between two following weighting [g]; K_1 is the re-calculation from hours to days [-], K_2 is the concentration coefficient in 10% (v/v) [-], t is the time between such measurements [hours], A is the polymer surface

where is the diffusion running [m²], c is the concentration of carbon dioxide [% (v/v)], p_{atm} is the atmospheric pressure [kPa], and p is the reference pressure (= 100) [kPa].

Diffusion-equivalent thickness of air layer S_D [m] was determined according to (2):

$$S_D = \frac{D_{CO_2} \times |\Delta c|}{i} = \frac{248}{i} \quad (2)$$

where D_{CO_2} is the diffusion coefficient of carbon dioxide [$D_{CO_2} = 1.38\text{m}^2/\text{day}$ at temperature 23°C]; $|\Delta c|$ is difference between concentration of CO₂ in the air with/without added CO₂ [$\Delta c = 180\text{g}/\text{m}^3$ for 10% (v/v) at 23°C]. The value 248 was calculated in case of concentration difference of CO₂ between 0% (v/v) and 10% (v/v) and the reference pressure 100 kPa.

III. RESULTS AND DISCUSSION

A. Viscosity

It is generally known that the various types of polymer dispersions are used for surface treatment of concrete structures. However, PVB dispersions are not used. Authors decides to test this new product and various partial benefits were observed. The first benefit is low viscosity of the product. It makes easy polymer penetration into the structure of the mortar or the concrete. Moreover, tested PVB dispersion was in high matter content which supported to be diluted with water in order to obtain better penetration effect. Another advantage of PVB dispersion is high pH value which helps to its stabilization and causes a positive effect on the corrosion properties of coating (pH < 7 causes acidic attacked of concrete).

B. Drying Speed

The coating of PVB (*Shark Dispersion MWTM*) and AC-S (*Acronal S 400*) dispersions were tested by the application on mortar specimen surface when the thickness of the coating was about 0.50mm. The comparison of drying speed was carried out. It was found that the drying speed of PVB undiluted dispersion was about 2-3 times higher than typical acrylate-styrene dispersion Acronal S 400 was. Certainly, the drying speed depended on polymer thickness environment conditions like air humidity, ventilation, temperature, etc. It was simultaneously observed that the PVB polymer had very high tensile strength in comparison with AC-S polymer.

C. PVB Barrier Capability

Thus, the CO₂ diffusivity and the barrier efficiency of PVB sheet were controlled. The measurement was carried out with two different types of PVB sheets in mentioned standardized conditions. The reference sample was an original extruded PVB sheet Butacite which has stable sheet thickness and the sheet composition. Obtained results were compared (in the same time) with the PVB sheet made drying of the layer of PVB dispersion (product of recycled windshields). The mass behavior of tested samples was recorded in Figs. 2, 3. These figures describe the mas which slightly increased. The weight

increasing was due to the reaction of absorber with CO₂ (potassium hydroxide, see Fig. 1). The CO₂ diffused inside the test body, whereby it reacted in potassium carbonate. Thus, the addition of the mass means absorbed amount of CO₂. The thickness of original PVB sheet and the PVB sheet made by dispersion drying was approx. 0.8mm. Certainly, the exact thickness was measured and the clear diffusion coefficient was calculated according it. As measurement discovered, the mass increasing was very small (see Figs. 2, 3).

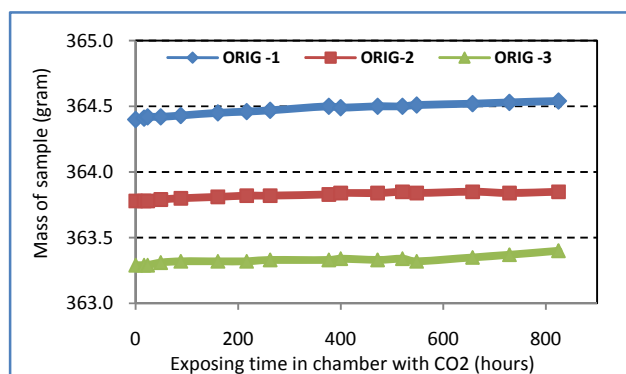


Fig. 2 Mass increasing of original PVB sheet

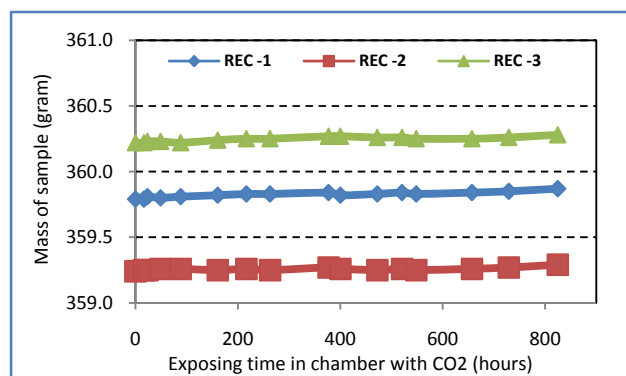


Fig. 3 Mass increasing of recycled PVB sheet

The results of diffusion-equivalent thickness (S_D) point out those original and recycled PVBS have excellent barrier properties. Although the diffusion-equivalent thickness of recycled PVB was only 318m, which was lower about 45% than the barrier property of original PVB, this number still provides a very good resistance as protective coatings for concrete structures, the required (S_D) value is 50m and the best barrier materials have value in range 200-500m. Moreover, the efficiency of PVB-based coating material could be further enhanced by the addition of montmorillonite or other clay fillers.

IV. CONCLUSIONS

The PVB dispersion with small particle size (d_{50}) of recycled polymer less than 0.15 μ m was tested. This newly developed product points out to some partial successes. The first benefit is a low viscosity of the product which makes easy polymer penetration into the porous structure of the mortar.

Tested PVB dispersion has high dry matter content which provides better penetration effect when the dispersion is diluted. Another advantage was fast drying speed of PVB dispersion. In case of undiluted PVB dispersion was the drying speed about 2-3 times higher than typical acrylate-styrene dispersion was.

The standardized measurement of CO₂ diffusivity and the barrier efficiency of PVB sheet were performed. It was found that average diffusion-equivalent thickness (S_D) of recycled PVB was 318m which is the value lower of about 45% than the barrier property of original (reference) PVB sheet. However, the required (S_D) value of the best barrier materials is starting in value 200m. Thus, determined values still provide excellent capability against CO₂ permeability. This new application of PVB waste can bring significant environmental contribution including new material use in the civil engineering.

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REFERENCES

- [1] I.V. Ivanov, "Analysis, modeling, and optimization of laminated lasses as plane beam", *Inter Jour Solid and Structures*, vol. 43, pp. 6887-6907, 2006.
- [2] U. Keller, H. Mortelmans, "Adhesion in laminated safety glass—what makes it work", *Glass Processing Days 8*, pp. 353-356, June 1999
- [3] D. Merinska, M. Tupy, V. Kasparkova, "Degradation of plasticized PVB during reprocessing by kneading", *Macrom Symposia*, vol 286, pp. 107-115, 2009.
- [4] R. Iwasaki, C. Sato, "The influence of strain rate on the interfacial fracture toughness between PVB and laminated glass", *JourPhys IV*, vol 134, pp. 1153-1158, 2006
- [5] M. Tupy, D. Merinska, P. Svoboda, "Effect of Water and Acid-Base Reactants on Adhesive Properties of Various Plasticized Poly(vinyl butyral) Sheets", *JourApplPolymSci*, vol. 127, issue 5, pp. 3474-3484, 2013
- [6] J. Svoboda, M. Balazs, J. Sedlar, "Industry glass, Glass union concern: Research and developing institute of industrial glass in Teplice, vol. C, issue 1, 1988
- [7] IOCA, The International Organization of Motor Vehicle Manufacturers, Displayed in: <http://www.ioica.net/category/production-statistics/>, 2010
- [8] M. Tupy, P. Mokrejs, D. Merinska, P. Svoboda, J. Zvonecek, "Windshield recycling focused on effective separation of PVB sheet", *JourApplPolymSci*, vol. 131, issue 4, article in press
- [9] A.K. Dhaliwal, J.N. Hay, "The characterization of poly(vinyl butyral) by thermal analysis", *JourThermochemacta*, vol. 391, pp. 245-255, 2002
- [10] M. Tupy, D. Merinska, P. Svoboda, J. Zvonecek, "Influence of water and magnesium ion on the optical properties in various plasticized poly(vinyl butyral) sheets", *JourApplPolymSci*, vol. 118, pp. 2100-2008, 2010
- [11] M. Tupy, D. Merinska, V. Kasparkova, *PVB sheet Recycling and Degradation*, Recycling / Book 1, 1st ed. Rieka: Intech, 2012, ch. 5.
- [12] A.V. Gorokhovskiy, J.I. Escapante-Garcia G.Y. Gashnikova, L.P. Nikulina, S.E. Artemenko, "Composite materials based on wastes of flat glass processing", *Waste Manag*, vol. 25, pp. 733-736, 2005

- [13] F.M. Fowkes, "Role of acid-base interfacial bonding in adhesion", *JournAdhesSciTechnol*, vol. 1, issue 1, pp. 7-27, 1987
- [14] J.J. D'Errico, B.A. Jemmott, M.S. Krach, J.R. Moran, "Plasticized polyvinyl butyral and sheet", US Patent 6,559,212, Dec 29, 1995
- [15] B. Papenfuhs, M. Steuer, "Plasticizer-containing polyvinylbutyrals, method for producing the same and the use thereof, especially for producing films for use in laminated safety glasses", US Patent 6,984,679, Dec 22, 2001
- [16] B.E. Wade, J.J. D'errico, H.M. Thompson, M.K. Yu, "Polymer sheets and methods of controlling adhesion of polymer sheets to glass", US Patent Application US 20050208315, Mar 16, 2004
- [17] L. Rong, H. Bobing, Ch. Xian, "Degradation of poly(vinyl butyral) and its stabilization by bases", *PolymDegradStabil*, vol. 98, pp. 846-853, 2008
- [18] EN 1062-6, "Paints and Varnishes - Coating materials and coating systems for exterior masonry and concrete - Part 6: Determination of Carbon Dioxide Permeability", 2004.