

# Secondary Polyvinyl Butyral Modified with Potassium Polytitanate for Coatings with Improved Mechanical Properties

Igor Burmistrov<sup>1,2,a)</sup>, Lydia Panova<sup>2,b)</sup>, Khabib Yusupov<sup>1,c)</sup>  
Anna Ermolenko<sup>2,d)</sup>, Egor Yakovlev<sup>2,e)</sup>, Anna Godymchuk<sup>2,3,4,f)</sup>  
and Tamara Yudintseva<sup>1,g)</sup>

<sup>1</sup> National University of Science and Technology "MISIS", Moscow, 119049 Russian Federation

<sup>2</sup> Yuri Gagarin State Technical University of Saratov, 77 Polytechnicheskaya Street, Saratov 410054 Russian Federation

<sup>3</sup> Tomsk Polytechnic University, 30 Lenina Avenue, Tomsk 634050 Russian Federation

<sup>4</sup> Derzhavina Tambov State University, 33 Internatsionalnaya Street, Tambov 392000 Russian Federation

<sup>a)</sup> corresponding author: [glas100@yandex.ru](mailto:glas100@yandex.ru)

<sup>b)</sup> [xt.techn@sstu.ru](mailto:xt.techn@sstu.ru)

<sup>c)</sup> [xabib.yusupov@yandex.ru](mailto:xabib.yusupov@yandex.ru)

<sup>d)</sup> [molish01@rambler.ru](mailto:molish01@rambler.ru)

<sup>e)</sup> [reddeade@gmail.com](mailto:reddeade@gmail.com)

<sup>f)</sup> [godymchuk@mail.ru](mailto:godymchuk@mail.ru)

<sup>g)</sup> [yudintsevatoma@gmail.com](mailto:yudintsevatoma@gmail.com)

**Abstract.** The technology of laminated glass is accompanied with a large amount of polyvinyl butyral wastes, which are used for recycling due to mechanical properties of recycled PVB as these properties are lower than those of the original polymer. The properties of composite coatings based on secondary polyvinyl butyral modified with potassium polytitanate were investigated. The composite coating was obtained by polyvinyl butyral dissolved in ethyl alcohol and then dispersed potassium polytitanate into a solution. The resulting suspension was poured onto the surface of a solid substrate and then dried. The research shows that the surface modification of potassium polytitanate with different coupling agents significantly improves the polymer composite mechanical properties. The investigation of various homogenization techniques established a possibility for a significant improvement in the properties of a polyvinyl butyral composite by treatment in a ball mill. The mechanism interactions among the coupling agents, binders, and surface fillers were determined. The research also highlights the possibility of secondary polyvinyl butyral recycling and the production of films with high mechanical properties.

## INTRODUCTION

Polyvinyl butyral (PVB) is widely used in various fields of technology. Plasticized PVB is applied in manufacturing windscreens and safety glass; solutions of PVB in alcohol form the basis for the production of certain synthetic glues varnishes, primers, enamels, and mastics. The flame spraying of PVB solutions onto metal surfaces allows producing some anticorrosive and decorative coatings [1]. Composite materials based on a PVB matrix filled with montmorillonite, silica, glass-ceramic powders, and barium titanate are common in the production of different functional materials [2-4].

It is well known that technological processes of laminated glass manufacturing are accompanied with a large amount of PVB wastes, which can not always be collected and used for recycling. Several attempts to develop new composite materials based on secondary PVB (sPVB) were performed [5]. However, mechanical properties of recycled sPVB are much lower as compared to the original polymer, and any modification of PVB is required for its efficient application [6,7]. To increase mechanical properties, chemical resistance, and other exploitation

properties, the sPVB can be modified with thermoset and thermoplastic polymers, silicones, and other additives [8-11]. On the other hand, an increase of wear resistance could be obtained by the introduction of fillers, characterized by a layered structure, in a polymer matrix [2]. Nevertheless, the application of well-known layered minerals, i.e., natural clays, is related to such problems as an unstable chemical and phase composition and the presence of abrasive contaminations (quartz) [12]. Synthetic fillers in the form of micro- and nano-scaled powders are a promising alternative due to their carefully controlled chemical composition, particle size distribution, shape, morphology, and some other properties [13-15].

Different synthetic potassium titanates ( $K_2Ti_nO_{2n+1}$ ) (PT) can be used as prospective platy fillers for different polymer-matrix composites due to high mechanical properties [16-18], a low friction coefficient, and wear resistance of these fillers [19-21].

Several methods have been developed to synthesize different potassium titanate nanostructures [22-24]. A Molten salt synthesis and an ion-exchange technique are the main methods to produce layered potassium titanates [23,24]. Potassium titanates produced by a molten salt method at temperatures lower than 500 °C and characterized with a molar ratio of  $n = TiO_2: K_2O$  less than 4 shows a layered morphology with a high intercalation and a catalytic activity, low energy of an interlaminar shear, which, therefore, can be applied as catalysts, ion exchange materials, and antifriction fillers [23-25]. The crystalline forms of potassium titanate with  $n > 4$  produced at temperatures higher than 900 °C show a whisker-like morphology and therefore can be used as strengthening fillers in manufacturing of polymer-matrix composite materials [23-25].

PT's are promising materials to be applied as antifriction and strengthening fillers for composite materials, catalysts, and ion exchange materials due to their relatively low cost and an easy chemical modification useful to regulate adhesion and functional properties of these powders.

The aim of this work was to develop new polymer-matrix composites based on modified sPVB, which can be used as wear resistant coatings, and also to investigate the influence of PT powder admixtures on structural and exploitation properties of the composites obtained.

## EXPERIMENTAL PART

### Materials

Wastes (offcut) of the PVB film (WINLITE®, Taiwan) used in windscreen glass manufacturing were applied to produce polymer matrix composites for coatings. Trimming of the PVB offcut was made with an industrial cutting device for strand (QLJ-250, China) to produce pieces in the form of noodles of 0.5-2.0 cm in length and 1-3 mm in width. Further, the PVB noodles were dissolved in the 96% ethyl alcohol (technical grade, Russia) at 50 °C under continuous stirring with a magnetic stirrer during 150 min (optimal concentration of 10 wt%). The obtained solution was used to obtain films of secondary PVB (sPVB) by pouring onto the surface of a solid substrate (glass plate or aluminum foil) and then the films were dried at room temperature to constant weight.

The PT powder was produced in accordance with [10,24] by the treatment of a  $TiO_2$  powder (average size of particles 7  $\mu m$ ) in the molten mixture of KOH (purity of 99%, Aldrich) and  $KNO_3$  (purity of 99%, Aldrich) (the weight ratio of components 3:2:5, respectively) at 525 °C for 1h. After the cooling, the product was washed with distilled water until neutral pH, treated with 1% aqueous solution of a surfactant (by stirring for 1h), decanted, and dried at 50° C for 4 hours.

The surface treatment of PT powders with surfactants was performed in order to improve the interfacial interaction between the fillers and the polymeric matrix. The PT powder was treated with commercially available nonionic surfactants that can react with hydroxyl groups on the surface of the titanate.

The following substances were used as surfactants:  $\gamma$ -aminopropyltriethoxysilane (AGM-9,  $(H_2N(CH_2)_3Si(OC_2H_5)_3)$ , trademark AGM-9, «Penta», Russia),  $\gamma$ -glycidoxypropyltrimethoxysilane (A-187,  $(C_9H_{20}O_5Si)$ , trademark Silquest A-187, MPM Inc.). For comparison, the surface of the PT powders was treated with oxyethylated alkylphenoles ( $R-C_6H_4O(CH_2CH_2O)_nH$ , where R is  $C_8-C_{10}$  alkyl radical,  $n=7...10$ , trademark OP-10, «VitaChim», Russia). Selected surfactants have active functional groups that can interact with both PT and a binder.

Chemically pure led phosphoric acid (PhA, purity of 98%, Aldrich), and tetraethoxysilan (ETS-40, trademark «ETS-40» «Penta», Russia) were used as additives to improve strength characteristics of the PVB-based films. In addition, the films were filled with various modifications of PT's to achieve some functional properties of a composite polymer matrix material. The compounds containing ETS-40 and PhA were prepared as follows. The alcoholic PhA solution was introduced into a PVB solution and carefully mixed; further, the ETS admixture was poured into the obtained solution and thoroughly homogenized by stirring for 50 minutes. 75-80% of the total amount of ethanol was taken to dissolve PVB wastes, and remaining 20-25% was used to dissolve PhA.

A quantity of the applied additives was defined taking into account the results of the previous work [26]. The

content of PhA was determined in the study of a swelling process. PhA contents less than 6.7 wt. % showed an increased degree of swelling and a slight dissolution of the PVB films. The PhA contents higher than 8.5 wt. % led to sweating on the film surface. The introduction of ETS in the PVB film led to an increased chemical resistance in water and aqueous solutions of some electrolytes. However, when the ETS content increased by more than 10 wt % a crispness of the PVB films increased.

The PT powders were introduced into the PVB solution by two methods: a simple mixing process and a dispersing mixing process. The simple mixing process was performed by adding a proper amount of a PT powder to the alcoholic solution of PVB and vigorous stirring of the mixture obtained at room temperature for 1 h. The dispersing mixing process was performed by milling of PT in a planetary mill (MP05, Russia) together with an alcoholic solution of sPVB at 50 rpm and the weight ratio of the grinding balls to a ground material equal to 8:1. The composite films were produced by pouring of the PVB solution onto the surface of a solid substrate (glass plate or Al foil) with subsequent drying at room temperature to constant weight.

## Research Methods

The structure, morphology, and chemical composition of the PT particles and PT-filled composites were studied using a transmission electron microscope JEOL JEM 1400 (accelerating voltage of 120 kV) and by a scanning electron microscope Hitachi TM-1000 (accelerating voltage of 20 kV) equipped with the EDS analyzer.

The particle size distribution was determined by a laser diffraction analyzer Fritsch Analysette-22 Nanotech in the range of 0.01-1000  $\mu\text{m}$  using water as a dispersive environment.

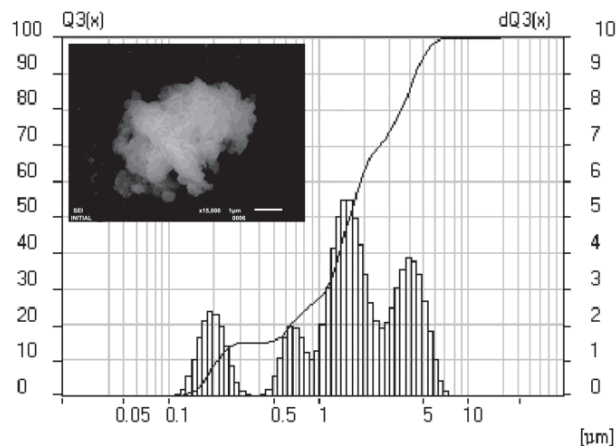
The viscosity of the PVB solutions was measured with a glass capillary viscometer with a diameter of 4.66 mm.

The adhesion properties and the mechanical strength of the produced films were carried out with a test machine IR 5046-5 (Russia), according to the ISO 4624-2002 (Paints and varnishes – Pull-off test for adhesion) and ASTM D638 (Standard Test Method for Tensile Properties of Plastics) standards.

All the properties of the investigated composite materials were compared with the data obtained for the commercial analogue (paint P-VL-213E), which is the most common type of commercially available paints based on PVB and used to form coatings for the protection of metal articles from water and aqueous solutions of electrolytes. The P-VL paint is a homogeneous mixture of the poly(vinyl)butyral solution, pigments, fillers, and plasticizers.

## RESULTS AND DISCUSSION

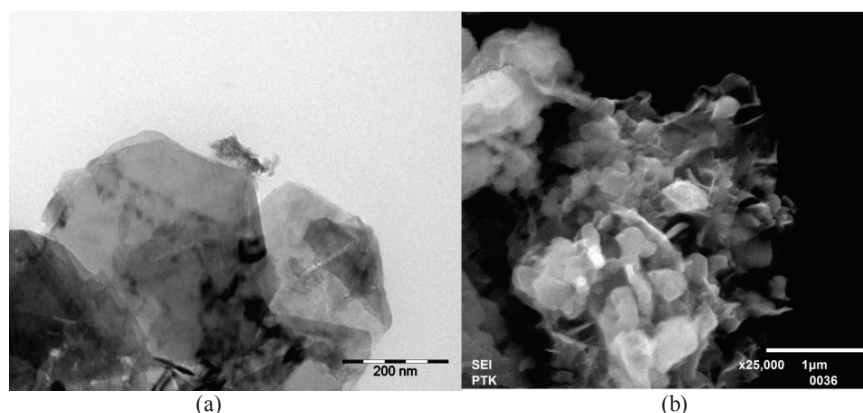
The size distribution of the powdered filler as well as the morphology of its particles significantly affect on the mechanical properties of polymer composites. Therefore, particle size distribution of the basic PPT powder is shown in Fig. 1.



**FIGURE 1.** Particle size distribution and SEM of the PPT powder.

The basic PT powder is characterized by a multimodal particle size distribution, which is apparently due to the formation of various aggregates of parent particles of 0.1-0.3  $\mu\text{m}$  in diameter. The morphology of the individual particles of the PT can be recognized by a transmission electron microscopy (TEM). Our research has

shown (Fig.2) that platy PT particles have a layered structure, an irregular shape and a large variation in size. At the same time, the particles of 100-500 nm in diameter and 5-10 nm in thickness dominate (Fig.2).



**FIGURE 2.** The shape and size of the particles of the PPT, investigated by transmission (a) and scanning (b) electron microscopy.

In accordance with the preliminary experimental data based on the investigation of 5, 10, and 15 wt.% sPVB alcohol solutions, the 15 % solution is characterized by high viscosity (7.9 mPa·s), which does not allow obtaining the homogeneous polymer films by pouring, while the 5 % solutions is impractical due to a high solvent consumption. That is why, the 10 wt.% solutions were used in the main experimental series.

The most important characteristic of polymer coatings is their adhesion strength to the protected surface. Therefore, the influence of various modifying agents and potassium polytitanate admixtures on the adhesion of sPVB to aluminum foil has been determined (Table 1).

**TABLE 1.** Adhesive property of the modified sPVB films to aluminum foil.

PVB	Composition (wt. parts)		PPT	Adhesion N/m
	PhA	ETS		
100	-	-	-	614±5
100	6.7	-	-	787±6
100	8.5	100	-	1330±8
100	8.5	100	77	800±5
Commercially produced analogue (paint P-VL-213E)				450±50

The investigated source sPVB has a higher adhesion than the commercial paint (P-HV-213E) as paints contain different particulate fillers and pigments that degrade adhesive interaction.

The effect of a reducing adhesion to a lesser extent was also observed in case of adding a modified PVB particulate filler (adhesion is decreased from 1330 to 800 N / m).

The introduction of PhA into the sPVB solution only slightly increased this characteristic. However, the adhesion doubles for PVB coatings containing both PhA and ETS. The introduction of the filler (PT) decreases the adhesion the parameter is higher than in the films based on unmodified secondary PVB and industrial analogues (primary PVB film obtained with the paint P-VL-213E, Table 1). Thus, the modification of the sPVB with the admixtures of PhA and ETS significantly improves the adhesion of the film, based on the sPVB, to metal substrates.

The mechanical properties of the investigated polymer films based on the modified sPVB (Table 2) correlated well with their adhesive properties (Table 1).

The introduction of pure PhA into the PVB solution considerably increases the tensile strength of the produced films and decreases the relative and residual elongation of the samples at break (Table 2). This effect can be related to the formation of a cross-linked structure of the PVB macromolecules in the presence of acids (proton additions due to the presence of hydroxyl groups in PVB chains contributes to the emergence of a larger number of hydrogen bonds, and even the chemical cross-linking). The films obtained with the addition of PhA together with ETS admixture show the best mechanical strength properties. The ETS improves the elasticity of the PVB film (coating), increases the elongation of the samples at break by more than 10 times, while the tensile strength increases more than twice.

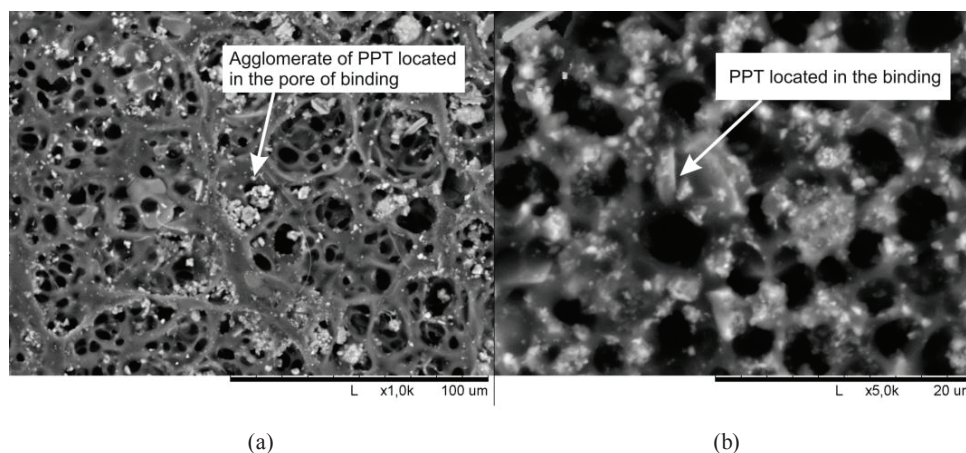
**TABLE 2.** Mechanical properties of the modified films based on sPVB.

Contents of the components (wt. parts)				Tensile Strength (MPa)	Strain at Break (%)	Permanent Strain at Break (%)
PVB	PhA	ETS	PPT			
100	-	-	-	78 ± 1	90 ± 10	30 ± 5
100	6.7	-	-	13 ± 1	63 ± 10	20 ± 5
100	-	-	100	12 ± 1	36 ± 10	30 ± 5
100	8.5	-	100	12 ± 1	10 ± 5	10 ± 5
100	8.5	-	-	7 ± 1	100 ± 10	20 ± 5
100	8.5	100	-	15 ± 1	770 ± 30	15 ± 5
100	8.5	100	15	16 ± 1	150 ± 10	10 ± 5
100	8.5	100	-	9 ± 1	80 ± 10	10 ± 5
Commercially produced analogue (paint P-VL-213E)				26 ± 2	6 ± 1	-

When the basic PPT is introduced into the investigated composition, there is an insignificant increase of the tensile strength (an increase in the strength is in the range of the experimental error). At the same time, there is a significant reduction in the relative elongation at break.

The reason for the reduction of the composite properties was the uneven distribution of the filler in the composite structure and the PPT's agglomerates formation.

The samples of the compositions based on different PPT's modifications were treated with a planetary mill to improve the distribution homogeneity and the PPT's agglomerates disintegration.



**FIGURE 3.** The SEM of several PVB films (A - prepared by simple mixing the components, B – prepared by joint milling).

The scanning electron microscopy (SEM) micrographs of the tested composite samples are shown in Fig. 3. The investigation of the samples structure by SEM revealed the unequal distribution of particles in the volume and a large number of agglomerates with a size of about 10 μm. The agglomerates are located in the pores of the polymer matrix and hardly interact with the binder. This result can be associated with a better interaction at the interface, during the joint milling. In the process of milling the surface mechanical activation of the filler is carried out which can cause the improvement of filler wetting with binder solution.

In this regard, a series of samples was produced by mixing of the components in collaboration with dispersion in the planetary mill. At the same strength values increase significantly, and the elongation at break decreases (Table 3).

**TABLE 3.** Mechanical properties of the modified PVB films (PVB solution was treated by a planetary mill).

Contents of the components (wt. parts)							Tensile Strength (MPa)	Strain at Break (%)
PVB	PhA	ETS	TiO <sub>2</sub>	PPT treated with OP-10	PPT treated with AGM-9	PPT treated with A-187		
37	51	6	6	-	-	-	19 ± 1	2 ± 1
37	51	6	-	6	-	-	42 ± 1	4 ± 1
37	51	6	-	-	6	-	29 ± 1	3 ± 1
37	51	6	-	-	-	6	29 ± 1	3 ± 1
Commercially produced analogue (paint P-VL-213E)							26 ± 2	6 ± 1

To compare the mechanical properties of the composites filled with modified potassium polytitanates and traditional oxide filler, the TiO<sub>2</sub> powder (average particle size of 3-5 μm) was applied in the same proportion. The data on the mechanical properties of the obtained composites (Table 3) have shown that the tensile strength and elongation at break for the composite filled with TiO<sub>2</sub> are significantly less.

The investigation of morphology and the structure of the composites obtained by mixing the components in a planetary mill, using scanning electron microscopy, revealed a uniform distribution of the PPT particles in terms of binder and a small amount of agglomerates (Fig. 3b). It should be noted that this method allows obtaining a system where practically all filler particles are embedded in the matrix. The planetary mill treatment parameters also influence the structure of the polymer matrix; for the samples obtained by joint milling and simple mixing, the average pore size is of 2-4 and 4-20 μm respectively (Fig. 3). This effect could possibly be related to both surface activation, processing with a planetary mill, and the reduced size of the PT particles.

The introduction of the PT by simple mixing of the components significantly reduces the strength and increases the deformation ability of the composite (Table 2), due to a larger size of micropores formed in the matrix, and the uneven distribution of the filler (Fig. 3a).

A reduced value of the mechanical strength for the samples based on the titanates that were introduced in the system by simple mixing could be explained by the replacement of a significant part of the filler in the pores of the binder. This part of the filler does not interact with the binder. At the same time, the major part of the PT aggregates is destroyed after the joint milling of the PT powders in the planetary mill together with sPVB alcohol solution; and this fact promotes a significant increase of the mechanical properties with regard to a homogeneous distribution of the filler in the polymer matrix.

The experimental results obtained with the samples based on the platy particles of the PT filler activated by milling of the filler in presence of the secondary PVB solution in alcohol are similar to the data obtained for the composites based on high-strength but dangerous fiber-shaped fillers. For example, the introduction of carbon nanotubes in the amount of 1-8 wt.% allowed obtaining the composites characterized by a tensile strength of 40-100 MPa.

## CONCLUSIONS

In this paper, the particle size distribution, the size and shape of the fillers based on PPT were investigated. In the research we discovered that the PPT formed quite stable agglomerates (Fig. 1 and Fig. 3a).

The influence of different modifiers was investigated and the increase of adhesion at the introduction of organosilicon was showed; the introduction of dispersed fillers reduced adhesion, which was shown as well.

The strength of PVB compounds was increasing significantly with a phosphoric acid and the ETS introduction (Table 2), whereas with the PPT's introduction, the elasticity decreased and the tensile strength was almost constant.

Combining the components in the planetary mill led to improvement of strength properties of the composites.

Various coupling agents that influence on the strengthening effect of the introduction of the PPT to the secondary PVB were investigated. It was found that positive reinforcement is possible by using treated OP-10 PPT, which functional groups are closest to PVB.

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