

The Structure and Adhesive Properties of Poly(vinyl acetate) Dispersion Modified with Organosilicon Compounds

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Among many polymeric adhesives used in wood processing industry polyvinyl acetate has a rather wide application. It is used to glue tenon joints, doors, windows and other wooden articles. Bond strength is much higher than that of the wood itself. However, polyvinyl acetate is nonresistant to moisture polymer and if such adhesive joints are exploited in moist environment its strength substantially decreases. Sufficiently moisture resistant adhesive joints are obtained by modifying PVA dispersion with special compounds characterized by high reactivity. Such monomers have chemically active groups with the aid of which spatial structures of molecules are formed. Halogensilans are known as having high reactivity with hydroxylic groups, including polyvinyl acetate, acting as netting agents. Unplasticized poly(vinyl acetate) dispersions were modified with organosilicon compounds. The adhesive properties of the modified dispersions were evaluated after preparation of adhesive joints with birch strips according to requirements of EN205. Moisture resistance was evaluated by the experiment sequence according of EN 204. Strength of the adhesive joints were up to 2.5 time higher than EN204 requirements. IR spectra show formation of the new chemical bonds with some of the organosilicon compounds in the modified poly(vinyl acetate) dispersion.

Keywords: timber, polyvinyl acetate dispersion, bond strength, splitting stresses, silica derivatives.

INTRODUCTION

Among many polymeric adhesives used in wood processing industry poly(vinyl acetate) has a rather wide application. It is used to glue tenon joints, doors, windows and other wooden articles. Bond strength is much higher than that of the wood itself. However, poly(vinyl acetate) is nonresistant to moisture polymer and if such adhesive joints are exploited in moist environment its strength substantially decreases. This is caused by the hydrolysis of polyvinyl acetate present in adhesive joints when hydrophilic vinyl alcohol chains are formed in the macromolecule. Therefore, it is rather important to produce such a poly(vinyl acetate) (PVA) dispersion which would make an adhesive joint sufficiently strong under moist conditions [1]. Increment in moisture resistance of joints made by PVA dispersion is one of the most urgent objectives today.

Many ways to modify PVA dispersions have been described. They are applied seeking to reduce the solubility of poly(vinyl alcohol), to change OH groups by hydrophobic ones, to make induce the netting of molecules. For example, as modifying the dispersion additive is suggested monoaldehyde – formaldehyde [2]. However, the drawback of this method lies in free formaldehyde, i.e. in isolation of a poisonous substance from adhesive joints. There was suggested a method how to modify PVA dispersion by dialdehyde – glyoxal. However, this is an expensive product. Other substances to modify PVA dispersion are known as well, such as isoprophylene alcohol, iron trichloride, potassium bichromate, butyl acrylate, methyl methacrylate [3], alkoxy silane [4], polyisocyanate [5].

Good results were obtained modifying PVA dispersion with the resin of carbamide, melamine, furool, formaldehyde [6], with the resin of epoxy “YII-160” [7, 8]. Sufficiently moisture resistant adhesive joints are obtained by modifying PVA dispersion with special compounds characterized by high reactivity. Such monomers have chemically active groups with the aid of which spatial structures of molecules are formed. Halogensilans are known as having high reactivity with hydroxylic groups, including polyvinyl acetate, acting as netting agents.

EXPERIMENTAL

During the studies unplasticized polyvinyl acetate dispersion (NPVA) produced in JV “Achema” was used as the study object. Its trademark is “D 51”. This dispersion was modified with silica derivatives. Acronyms presented in the paper correspond to compositions listed in Table 1.

The amount of modifying additive is given as the percentage of the mass of unplasticized dispersion. Bond strength and its water resistance were assessed in accordance with the European standards EN 204 and EN 205. Tests with birch timber were carried out according to the third series of EN 204 standard: samples after bonding were kept for seven days under normal air conditions, then they were soaked in water for four days and tested by splitting at the place of bond line. The bond strength was assessed by universal tensile testing machine “P-0.5”.

Films from unplasticized poly(vinyl acetate) dispersion (NPVA) and those of modified with halogensilane (SFTC) were casted for the molecular absorption spectrum analysis in the range of infrared spectrum. For this purpose a spectrometer “Specord 75 IR” was used.

The same film was used for differential-thermal analysis. This analysis was performed by “Derivatograph Q-1500D” device.

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RESULTS AND DISCUSSIONS

Having tested a series of silica derivatives (Fig. 1) it can be seen, that the strength of adhesive joints bonded with dispersion modified by the last five (Table 1) considerably exceeds the strength required by the standard. Further studies are based on PVA dispersion modified by silica derivative *SFTC*, as far as the strength of its bonding after soaking was the highest (4.82 N/mm²).

Table 1. Compositions of PVA dispersions

Marking of composition	PVA dispersion modifying substances
NPVA	unplasticized poly(vinyl acetate) dispersion
SCE	NPVA + 8 % tetrahydrofurane + 0.5 % polymethylphenylsilane
SCDE	NPVA + 50 % dioxane + 0.5 % polymethylphenylsilane
SLO	NPVA + 0.5 % UMS-182 (dimethylsiloxane)
SA	NPVA + 10 % UMS-182 (dimethylsiloxane)
SFTC	NPVA + 5 % halogensilane
SDCMV	NPVA + 5 % halogenmethylsilane
SMTC	NPVA + 5 % halogenmethylsilane with high halogen content
SETC	NPVA + 5 % halogenethylsilane
SDCMF	NPVA + 5 % halogenmethylphenylsilane

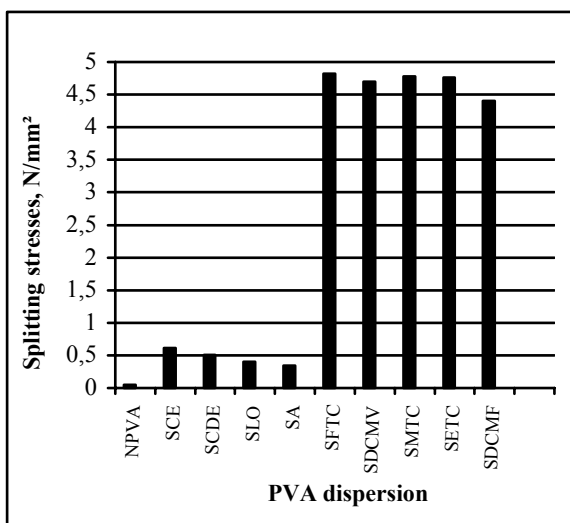


Fig. 1. Humidity resistance of adhesive joints bonded with PVA dispersion modified by silica derivatives

The influence of amount of modifying *SFTC* additive on the strength (Fig. 2) of unplasticized PVA dispersion has been ascertained. The latter was mixed with various amounts of *SFTC* additive and samples bonded with this dispersion after soaking, as required in EN 204 standard, were tested by splitting in the place of a bond line.

It has been ascertained, that a sufficient amount of modifying *SFTC* additive needed for adhesive joints to exceed splitting stresses required by EN 204 standard comprises 1 % from the dispersion mass.

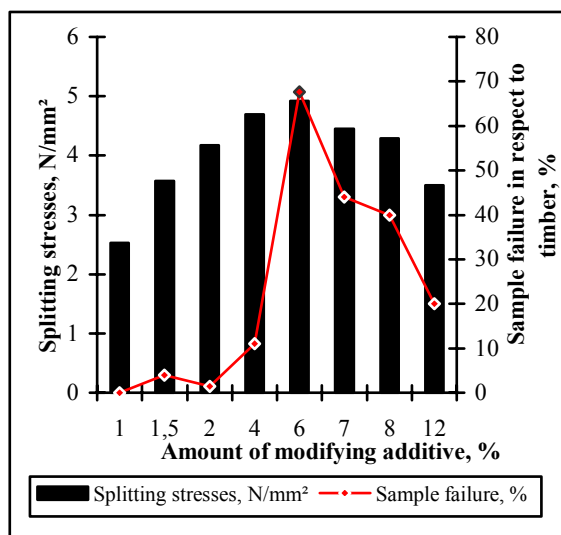


Fig. 2. Dependence of the strength of adhesive joints bonded with modified dispersion on the amount of modifying *SFTC* additive

Mixing into the dispersion more than 6 % of the additive causes coagulation and the strength of adhesive joints decreases. Sample failure in respect of wood shows, that adhesive joints bonded with 1 % modified dispersion failed completely in the place of the bond line, while bonded with 1.5 % modified dispersion failed also in the wood, therefore, for further studies was chosen dispersion containing 1.5 % *SFTC* additive (further as *MPVA*). A molecular absorption spectrum analysis of the infrared spectrum of *MPVA* film was measured (Fig. 3).

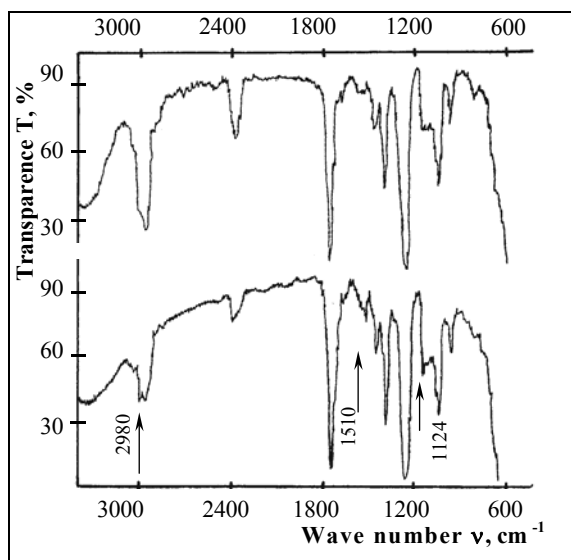


Fig. 3. Infrared absorption spectrum of films obtained from NPVA and MPVA dispersions

The obtained infrared spectrum of *MPVA* dispersion was compared with *NPVA* dispersion spectrum, where the main absorption bands correspond to acetate groups. In this spectrum the area where the wave number is equal 1740 cm⁻¹, is characteristic of all esters, however, absorption bands of C–O relations at 1240 cm⁻¹ are characteristic only for acetates and carbonates [9]. Comparing *MPVA* spectrum with the discussed, changes in absorption bands

were observed. Tapering at wave number 2980 cm^{-1} shows valency vibrations of C–H relation [10]. Tapering of absorption bands at 1510 cm^{-1} is characteristic of C–C relations within phenylgroup, while tapering at 1124 cm^{-1} belongs to Si–O relations. The results show, that chemical structure of the polymer has not changed, while the modifier reacted with groups possessing a liable proton. This is confirmed by differential-thermal analysis (Fig. 4), i.e. an expression of melting and changes in thermal phases of the study object by differential heating curves.

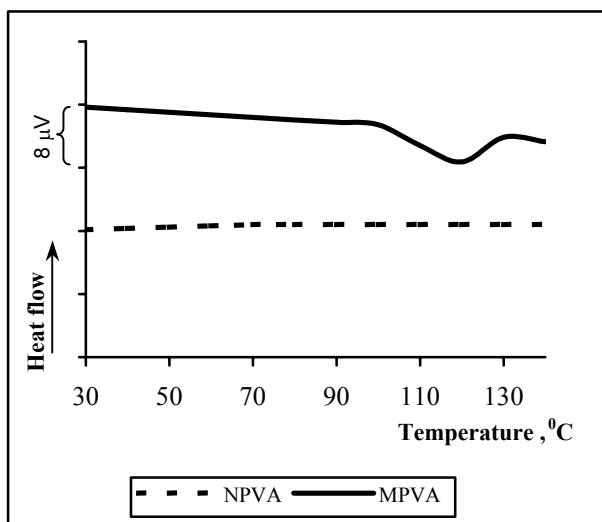


Fig. 4. DTA curves of NPVA and MPVA samples

NPVA dispersion film is a polymer of amorphous structure and its differential-thermal curve is straight and even. This shows that, increasing the temperature of NPVA dispersion, thermal reaction or conversion of phases followed by heat isolation or absorption fail to occur [11]. However, analyzing the curve of samples obtained from MPVA dispersion within $115\text{--}140\text{ }^{\circ}\text{C}$ temperature range, heat absorption may be observed - this is an endothermal process. This effect confirms the fact, that mixing MPVA with SFTC additive causes changes in polyvinyl acetate structure.

CONCLUSIONS

A new PVA dispersion has been obtained meeting D3 class requirements of EN 204 standard. During the studies its advantages have been revealed: preparation of a modified composition is not complicated; the additive SFTC used as a modifier is an industrial product, therefore, it does not need to be synthesized or cleaned; changing the amount of modifying additive, it is possible to attain a 2.5 times higher bonding strength than it is required in EN 204 standard.

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