

THE MECHANISMS OF MODIFYING AGENTS INTERACTION WITH COMPONENTS OF ADHESIVE COMPOSITIONS OF PVA DISPERSIONS

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Abstract:

To modify polyvinylacetate dispersions, it was proposed to use the redox complex – Fenton reagent as a source of free radicals and oxidant for individual constituents, also it was proposed to use the acid-salt complex of nitric acid and aluminium nitrate as the mixture oxidant and the structure-forming agent (due to the formation of coordination bonds with functional groups of polymeric chains). The article presents the results of theoretical studies on possible mechanisms of chemical interaction between PVA dispersion-based adhesive composition (PVAD-51P trade mark) and modifying agents; also given here are the results of experimental investigation by infrared spectroscopy in transmittance of polymeric films formed both by modified and non-modified polyvinylacetate adhesive compositions.

Key words: adhesive compositions; Fenton reagent; aluminium nitrate; nitric acid; polyvinylacetate; polyvinyl alcohol; infrared spectroscopy.

INTRODUCTION

Amongst the rich variety of polymeric adhesive compositions that are used in woodworking industry, polyvinylacetate dispersions (PVAD) occupy a prominent place. The polyvinylacetate-based adhesives are easy to apply, they are non-toxic and have found a wide use in furniture making, manufacture of millwork (windows, doors, molded products, multilayer boards, etc.), packing and others, while the glue line provides high strength and elasticity of bonded joints (Villenave 2007, Mishra and Yagci 2008).

However, in the present state of woodworking and chemical industries, there is no adhesive composition that would meet in full measure requirements for adhesive (operating, technological, economic and ecological) (Rowell and all 2005, Villenave 2007, Ebnesajjad and all 2011). Polyvinylacetate dispersions are not an exception although due to a large variety of their properties depending on the brands and modification methods, the disadvantages of these adhesives will vary. In order to systematize thermoplastic adhesives, in particular PVA dispersion (PVAD), the European standard EN 204:2001 «Classification of thermoplastic wood adhesives for non-structural applications» is used, which subdivides all compositions into four classes of durability according to their operating performance starting with D1 (to form adhesive joints that will be operated in dry internal rooms and moisture content of the wood does not exceed 15%) to D4 (for use in internal areas where adhesive joints may be exposed to long-term exposure to running or condensed water, and in providing appropriate protective and decorative coating can be used outdoors). As Ukraine's chemical industry produces mostly adhesive compositions of durability classes D1 and D2, the joints based on such compositions have low resistance to water and moisture, elevated temperatures; they are also characterized by the creep of glue line at static loads, which seriously limits the area of their application. That is why such PVAD-based joints are primarily used in dry places or under conditions of short-term exposure to water or high air humidity at temperatures no higher than +40...+50 degrees Celsius, also they are not suitable for outdoor service.

The top-priority task in modifying PVAD is ensuring durability of glued wood joints as to the influence of water and moisture. There are several ways of obtaining such characteristics; however the most popular method today is application of modifying agents in the form of reaction initiators and curing agents, as well as accompanying additives that perform functions of stabilizers for the systems obtained (Gražulevičius *et al* 2003, Zanetta and Chiozza 2013).

The objective of the studies is modification of adhesive compositions on the basis of PVA dispersions as well as predicting chemical and structural processes which will take place between the modifying agents and the polymer basis during formation of polymeric films. The study is also aimed at validating the given processes by investigation of the adhesive films transmittance in the infrared spectrum.

MATERIAL AND METHODS

The PVAD-51P dispersion was chosen as the base composition for modification. It is plasticized by a 15% dibutyl phthalate produced by Omega Ltd., Ukraine, in accordance with TU U 24.3-25101682-010-2004 standard. The mass fraction of dry residue amounts to 51±2%, while pH-value is 4,5...5,5. The protective colloid of the study dispersion is polyvinyl alcohol. Fenton reagent was used to modify PVA dispersion

(Knunians et al 1990); the reagent consists of 35% hydrogen peroxide (H₂O₂) in accordance with TU U 24.1-25548331.002-2001, and a 20% aqueous solution of ferrous sulphate (II) (FeSO₄, GOST 6981-94); as well as a 30% mixture of aqueous solutions of nitric acid (HNO₃) and aluminium nitrate (Al(NO₃)₃).

The films to carry out the spectral investigation were obtained by moulding films of 0.1–0.2 mm in thickness. The infrared spectra of the films of PVAD-based compositions were taken by means of a Specord-M80 spectrophotometer (produced by Karl Zeiss, Jena, Germany) within the range of wave numbers of 4000–400cm⁻¹.

DISCUSSION AND RESULTS

Modification of any adhesives depends on the properties of the composition components, the type of solvents and fillers, as well as the physical state. The main film-forming component of PVAD is polyvinylacetate, chemical properties of which are mainly determined by the presence of ester (–O–COCH₃) groups (Rosenberg 1983, Rowell and all 2005). In other words, polymer-base is mostly able to enter into the reaction of oxidation, saponification and hydrolysis (acid and alkaline). In addition to polyvinylacetate, polyvinyl alcohol plays an important role when forming adhesive films, it is present in the adhesive composition and acts as a protective colloid (Michailivska and Panov 2003). Its chemical properties are mainly determined by the presence of hydroxyl groups (–OH) (Rosenberg 1983, Lewin and all 2006), which indicates the ability to interact with active metals and entering the reaction of oxidation, esterification and substitution of hydrogen atoms and (–OH) groups.

The selection of modifiers was made with consideration for the analyzed chemical properties of polyvinylacetate and polyvinyl alcohol. An important factor in choosing modifiers was the use of domestic resources for the purpose of obtaining adhesive compositions exclusively from the products of Ukraine's own chemical industry. For this purpose, the mixture of 30% aqueous solution of nitric acid and aluminium nitrate as well as Fenton reagent were chosen to be introduced into PVAD-51P. The use of nitric acid for modification of PVAD is not new, it has been used repeatedly during the last few decades (Freidin 1985). In this case, it is the use of nitric acid/aluminium nitrate complex that is new, nitric acid here provides formation of waterproof products in the adhesive mixture, while aluminium nitrate ensures formation of coordination bonds with the polymer-base.

Fenton reagent application in chemical industry is rather diverse. It is used not only for oxidation reaction, but also for the reaction of hydrolysis and cross-linking. Since this reagent is subtitle to participate in cross-linking reaction, it was first proposed to modify exactly PVAD of Ukrainian production. However, based on the chemical properties of the film-forming components, it may be concluded that there will not take place any direct interaction between polymer macromolecules and modifying agents in the form of chemical reaction yielding three-dimensional structures. A more suitable reagent for chemical reactions is polyvinyl alcohol. In order to enhance the modifying effect by reduction oxidation complex (Fenton reagent), the polyvinyl alcohol concentration in the adhesive composition was increased by introducing aqueous solution of the alcohol.

Thus, the addition of «Fenton reagent» to the PVAD-51P adhesive composition results in reaction product of a sparse-net branched structure with partially substituted hydrogen groups –OH and formation of ether bonds –O–Fe–O– (Solonyuka 2012) (Fig. 1):

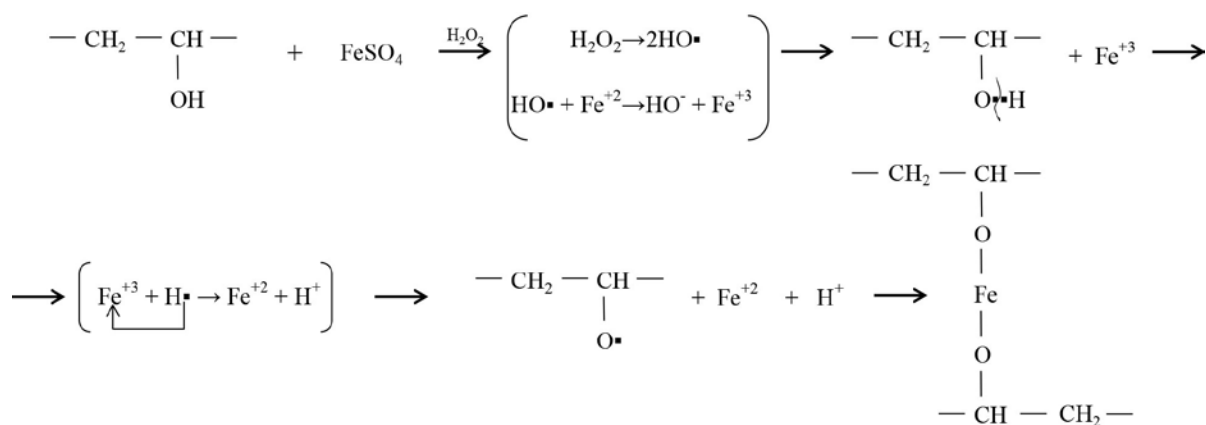


Fig. 1.
Schematic representation of polyvinyl alcohol reaction with the Fenton reagent.

However, when adding nitric acid to the mixture, the greatest possible attention should be centred on the amount and concentration of its aqueous solutions as disruption of necessary proportions will cause complete decomposition of polyvinyl alcohol into monomeric compounds.

Besides, as the organic acid esters may be hydrolyzed under acid environment, introduction into the composition 30% of nitric acid solution leads to the fact that part of dibutyl phthalate reacts with the formation of organic acids and product which increases the proportion of hydroxyl groups in the mixture (Fig. 5):

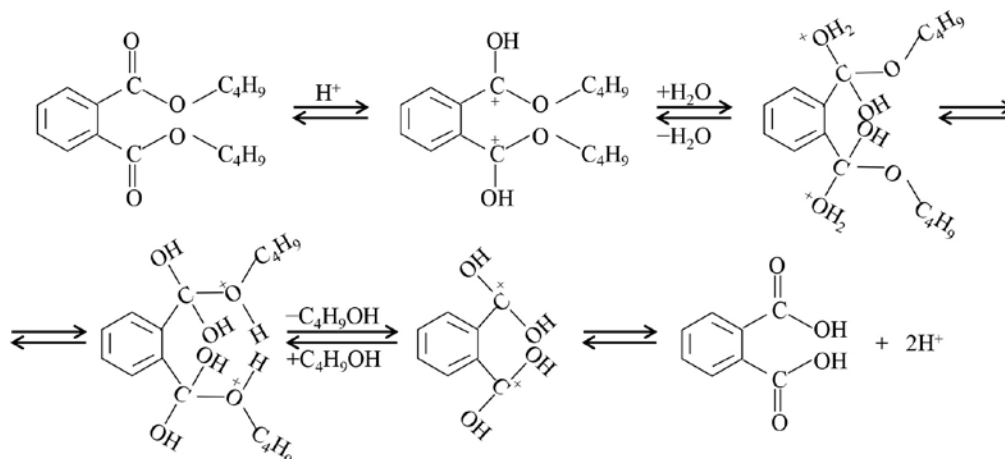


Fig. 5.
Schematic representation of dibutyl phthalate hydrolysis under the action 30% solution of nitric acid.

At the same time, chemical interaction between the 30% solution of aluminium nitrate and PVA proceeds by way of forming donor-acceptor bonds. As a result of such interactions, a system structuration is observed (see Fig.6), while the energy of these bonds, low as it is, ensures enhanced water resistance as well as increased viscosity of the adhesive mix.

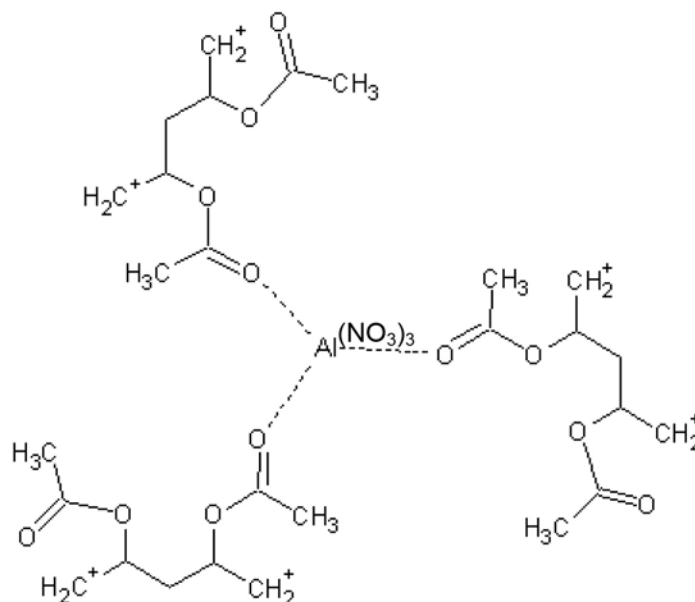


Fig. 6.
Schematic representation of structuration of polyvinylacetate molecules, in the adhesive composition due to forming donor-acceptor bonds.

On the whole, the enhanced water resistance on introducing 30% aqueous solution of nitric acid and aluminium nitrate into the adhesive composition PVAD-51P can be accounted for by formation of hydrophobic groups in the main chain of polyvinyl alcohol, as well the formation of high-energy hydrogen bonds between $\sim\text{C}=\text{O}\cdots\text{H}-\text{O}-$ groups. In addition, at the expense of formation of double bonds in the

carbon chain, there is a decline in the number of free carboxyl groups that are capable of forming hydrogen bonds with water molecules. The structurization of the mix leads to increased density of macromolecules packing and, as a consequence, to increased number of intermolecular and intramolecular interactions (between PVA macromolecules and macromolecules of PVA and polyvinyl alcohol).

In order to support the theoretical assumptions, a study was conducted to examine transmittance of the polymeric films by means of infrared spectroscopy. For this purpose, films 0.1 mm and 0.2 mm thick were formed from the non-modified adhesive composition PVAD-51P as well as from the adhesive composition containing modifying agents. The results of the infrared spectra study are presented in the form of curves in Fig. 7.

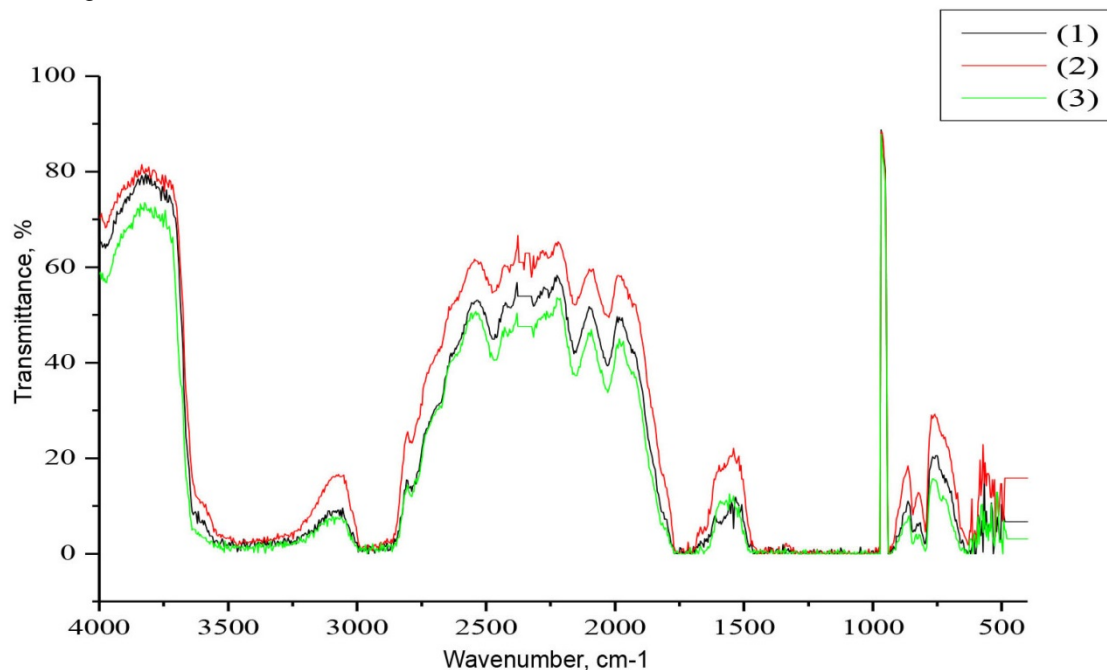


Fig. 7.

Infrared spectra of adhesive films.

(1) – PVAD-51P adhesive films; (2) – adhesive films formed by PVAD-51P composition modified by Fenton reagent; (3) – adhesive films formed by PVAD-51P composition and modified by 30% aqueous solutions of nitric acid and aluminium nitrate.

In the study, infrared spectrum of the starting PVAD-51P composition (curve 1, Fig. 7), an intensive broad absorption band is observed in the region of $3700\text{--}3300\text{ cm}^{-1}$ which can be assigned to valence vibration of (--OH) group in polyvinyl alcohol which is partially associated as a result of the formation of hydrogen bonds with oxygen atoms of ester acetate functional groups of polyvinylacetate and residual H_2O molecules.

The initial portion of the absorption band of medium intensity ($3100\text{--}2800\text{ cm}^{-1}$) can be interpreted as a result of overlapping absorption bands of bonded hydroxyl group and the band of valence vibration of methyl and methylene groups that is part of polyvinylacetate and polyvinyl alcohol macromolecules.

The spectra of all types of carbonyl compounds are characterized by intense absorption ($\epsilon=300\text{--}2000$) in the region of $1900\text{--}1580\text{ cm}^{-1}$.

The intense broad absorption band that is present in this IR-spectrum of $1900\text{--}1580\text{ cm}^{-1}$ is most likely due to characteristic oscillations involving ($\sim\text{C=O}$) groups which are part of carbonyl macromolecular compounds of PVAD-51P composition, and whose absorption bands position depends on intramolecular effects and intermolecular interactions (this may be ester groups of polyvinylacetate with absorption peaks at $1730\text{--}1740\text{ cm}^{-1}$). Valence vibrations of ($\sim\text{C--O--}$) groups are characteristic of alcohol and esters of carboxylic acids, they appear in the wavenumber from 1290 to 1100 cm^{-1} . Very intense absorption bands in the region of wavenumbers of $1300\text{--}1050\text{ cm}^{-1}$ (Fig. 5) also confirms indirectly the presence of etheric functional groups in the macromolecular structure as it is in this range of the wavenumbers that one or several intense bands appear in the ether spectra, which is caused by vibrations involving the etheric bond ($\sim\text{C--O--C--}$), this is the so-called "etheric band" that is stronger and broader than carbonyl one and which sometimes splits into several bands depending on the atomic environment in the macromolecular structures and intermolecular interaction.

When studying the transmittance of the PVAD-51P composition (curve 2, Fig. 7) modified by aqueous solution of ferrous sulphate (II) and hydrogen peroxide (35%), we notice that a decrease in the intensity of the absorption bands arm is taking place at wavelength of $3700\text{--}3600\text{cm}^{-1}$, which corresponds to a decrease in the total number of non-associated alcohol ($\sim\text{C}\text{--}\text{OH}$) groups in polyvinyl alcohol. This is, evidently, attributed to participation of hydrogen atoms of these groups in reactions with free radical particles and possibility to form Fe^{3+} ion – involved structures. Also, the study of infrared spectra at $3700\text{--}2500\text{cm}^{-1}$ shows narrowing half-width of the total absorption band, which may correspond to a decrease in the portion of associated (--OH) groups. This points to the fact that, in addition to reactions with ferrous sulphate (II), polyvinyl alcohol enters into oxidation reactions, which reduces the total content of hydroxyl groups in the adhesive composition.

On analyzing the characteristic curve 3 (Fig. 7) it can be concluded that the introduction of 30% aqueous solutions of nitric acid and aluminium nitrate the PVAD-51P composition leads to increased halfwidth of the absorption band for the associated (--OH) groups in the region of wavenumbers of $3700\text{--}3000\text{cm}^{-1}$, which is the result of the increased number of intermolecular hydrogen bonds. This effect can be obviously explained by a decrease in molecular weight of polyvinyl alcohol in the modified composition as well as by structurization of the whole system, which results in increased packing density of molecules as well as increased number of centers of intermolecular interaction, which leads to the absorption band expansion of ether group in the region of wavenumbers of $1900\text{--}1580\text{cm}^{-1}$ compared to other specimens. Besides, one can mark increasing intensity of absorption bands in the range of wavenumbers of $1290\text{--}1050\text{cm}^{-1}$, which is, evidently, due to appearance of additional number of oxidized alcohol (--HC=O) and (--COOH) groups in the composition.

CONCLUSIONS

The infrared spectroscopy conducted at the values of wave number ranging from 4000cm^{-1} to 400cm^{-1} have confirmed the theoretically assumed mechanisms of interaction between PVA and other components of the adhesive on the one hand, and modifying agents, on the other hand. In particular, the analysis of adhesive films transmittance conducted by infrared radiation in the range of wave numbers from 3700cm^{-1} to 2500cm^{-1} made it possible to clarify the quantitative change in associated and non-associated (--OH) groups on introducing corresponding target additives into PVA composition.

The theoretical assumptions and the results of the studies show that, on introducing hydrogen peroxide (35%) and a 20% aqueous solution of ferrous sulphate (II) into the PVAD-51P composition, an interaction takes place not between PVA and modifying agents but between polyvinyl alcohol and modifying agents. The result of such reaction is formation of dimensional sparse-net polymeric structure and reduced number of associated and non-associated hydroxyl groups. It should be noted that reaction progress resulting in formation of three-dimensional bonds through intermediate radicals will show increasing intensity as the moisture content in the composition is reduced, that is directly during the glueing process, by this is meant that the shelf-life of the prepared adhesive before its immediate application will not be essentially reduced compared to non-modified specimens, thus no deterioration of technological characteristics both at the stage of the adhesive composition preparation and during its application is observed.

At the same time, chemical transformations of polyvinylacetate macromolecules are observed during modification of the PVAD-51P by way of introducing 30% aqueous solutions of nitric acid and aluminium nitrate. Besides, this leads to increased number of associated hydroxyl groups as well as increased portion of carboxylic and carbonyl groups, which is the result of more intensive oxidation of polyvinyl alcohol under the action of nitric acid; also this leads to a change in rheological properties and, as a consequence, to increased adhesive composition viscosity due to formation of coordination bonds with the aluminium nitrate.

Thus, the above-examined types of interaction allow for more detailed understanding of the processes taking place at both the modification stage and during formation of adhesive films. This enabled us to make assumptions about the applicability of modified adhesive compositions for formation of joints of wood and wood-based materials with high resistance to the ambient moisture and direct effects of water. Moreover, as a result of further experimental studies on test specimens formed by means of such adhesives, we were able to empirically demonstrate increasing performance characteristics of joints, among which water resistance occupying a prominent place.

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