

Визначення еквівалентного діаметра та питомої поверхні солом'яних частинок

Визначенні значення еквівалентного діаметра й питомої поверхні солом'яних частинок за їх розмірами, формою та середньоарифметичним діаметром отворів сит після ситового аналізу частинок. Графічно описано залежності питомої поверхні солом'яних частинок від частки їх поздовжнього поділу, співвідношення довжини до діаметра солом'яних частинок та коефіцієнта кратності цього співвідношення.

Ключові слова: еквівалентний діаметр, питома поверхня, солом'яна частинка, коефіцієнт сферичності.

WATER EFFECT ON THE STRUCTURE OF ADHESIVE FILMS FORMED BY PVA DISPERSION-BASED COMPOSITION

The results of studies of water effect on the structure of polymeric films formed by modified and non-modified polyvinylacetate dispersion-based adhesives (PVAD-51P trade mark) are given. Also, conclusions have been drawn concerning applicability of PVA adhesives, modified with Fenton reagent or acid-salt complex, for glueing wood parts depending on the usage environment for the produced articles.

Key words: modifying agent, polyvinylacetate (PVA) dispersion, polyvinyl alcohol, spectrophotometer, infrared (IR) spectroscopy, absorption rate, transmission capacity.

Problem formulation. The manufacture of products in joinery, furniture making and other branches of woodworking industry involves application of glueing operations, proper choice of adhesive compositions being of great importance. The choice is primarily influenced, along with economic factors, by the product's intended use and service conditions. However, it is not unfrequent practice in furniture industry to brush aside demands for ensuring appropriate water- and heat resistance of adhesive joints when making articles for indoor area service. It should be noted that such an approach is unacceptable for kitchen furniture, bathrooms as well as wares to be used in unheated housekeeping areas.

For the purpose of ensuring appropriate service characteristics of glued articles, a great variety of PVA dispersion-based composition have been developed in woodworking industry, while a large number of researchers all over the world are engaged in finding ways of enhancing operational performance of adhesive joints [3,4,6,7]. However, despite the fixed interest in this direction of investigations, the majority of the research works give little attention to the study of aggressive environment effects on polymeric films. That is why the objective of this work is to investigate the direct water effect on polymeric films which are formed by modified and non-modified PVA dispersions. This is to be done by studying chemical transformations of their composition by means of infrared spectral characterization of adhesive films transmission capacity.

Methods and materials. The dibutyl phthalate-plasticized PVAD-51P dispersion was chosen as the basis composition to conduct the experiments. Fenton reagent was used as a modifying agent (an oxidation-reduction complex composed of ferrous sulphate (II)(FeSO₄) and hydrogen peroxide (H₂O₂, 35%), alternatively was used the mixture of a 30% aqueous solution of nitric acid (HNO₃) and Aluminium nitrate (Al(NO₃)₃) as modifying agent. The infrared spectra within the range of wavenumbers of 4000–400

cm⁻¹ were measured by means of a Specord – M80 spectrophotometer (produced by Karl Zeiss, Jena, Germany), which made it possible to record changes in the transmission capacity of polymeric films 0.1...0.2 mm thick formed by adhesive compositions under study.

In order to reveal changes in chemical composition of the polymeric films and, as a consequence, changes in their transmission capacity, part of the test specimens had been kept in a water-filled reservoir for 24 hours at a temperature of 20±2°C prior to measuring IR-spectra. The rest of the specimens, designed to taking check measurements, were used to determine transmission capacity of the films without preliminary water-soaking.

Results and discussion. In order to make effective use of modified adhesive compositions, it is essential to know the mechanism of joints formation at the glueing stage, similarly important is a knowledge of glued joint failure mechanism while in operation. A certain information on this area can be obtained not only by way of destructive or non-destructive joint testing [2], but also by investigating adhesive films in conditions similar to the environment in which these adhesive films are to be operated.

When analyzing the mechanism of wood joint formation by PVA dispersion-based compositions, of primary importance are both the number of contact points and the number of groups available for forming hydrogen bonds [1, 4, 5]. This is precisely why compositions containing polyvinyl alcohol which acts as protective colloid (emulsifying agent) have found widespread application in woodworking industry. Polyvinyl alcohol is a substance that contains a large number of easy-to-interact hydroxyl groups (–OH). However, the presence of a certain quantity of such emulsifying agent also leads to negative effects the most important of which is low resistance to direct water contact and high ambient humidity.

To obtain initial data, testing at the first stage was performed on polymeric films formed by PVA-51P dispersion of domestic production. The results of determining transmission capacity of the films prior and after water-soaking for 24 hours are presented in Fig.1.

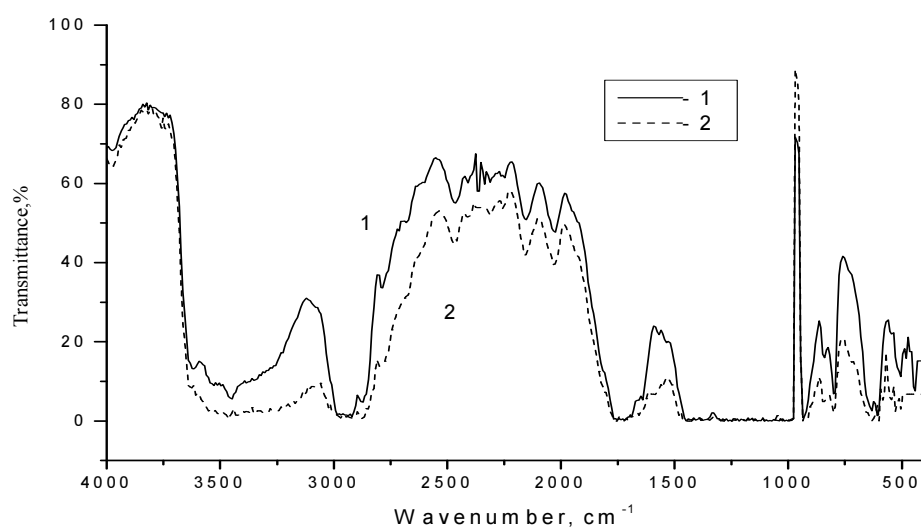


Fig. 1. IR-spectra of films transmission capacity:

1 – PVAD-51P-formed films soaked in water environment at a temperature of 20±2°C for 24 hours; 2 – adhesive films of a check specimens formed by PVAD-51P

From characteristic curves 1 and 2 one can observe a decrease in absorption capacity of films at the wavenumber of 3700–3600 cm^{-1} . Such processes are attributed to the reduction in the number of non-associated alcohol groups ($-\text{C}-\text{OH}$) which belong to a great extent to polyvinyl alcohol macromolecules. When comparing the wider portion of IR-spectrum within the wavenumber of 3700–3600 cm^{-1} , one can observe an increase in transmission capacity of the films after water-soaking. This corresponds to a decrease in the share of associated alcohol groups ($-\text{OH}$), which is also confirmed by narrowing half width of the aggregate absorption band at the wavenumber of 3700–2500 cm^{-1} .

Besides, when examining spectral dependences at the wavelength of 3100–3000 cm^{-1} , one can observe an increase in transmission capacity of water-soaked films. Since this zone of the absorption band is conditioned by the presence of ($=\text{C}-\text{H}$) groups of dibutylphthalate aromatic rings in the solution, it may be concluded that the quantity of plasticizer in the films after testing also diminishes. Moreover, a spectral analysis at the wavenumber value of 1900–1600 cm^{-1} has shown that the obtained absorption band is decreasing. Such phenomenon can be attributed to a slight decrease in the share of carbonyl groups that enter into the composition of PVAD-51P. Furthermore, since butyl phthalate groups of the plasticizer belong to carbonyl compounds, the increase in transmission capability at the wavenumber of 1900–1600 cm^{-1} is also a confirmation of decrease in its share in the water-soaked films.

Consequently, it may be concluded that the direct contact with water of polymeric films formed by PVAD-51P results in washing-out of hydrophilous emulsifying agent – polyvinyl alcohol (mostly these are macromolecules in the surface layers of the film and are accessible for interaction, as well as macromolecules from the boundary layer), this occurring due to interaction of alcohol groups ($-\text{OH}$) with H_2O molecules. The process of washing-out of polyvinyl alcohol macromolecules favours the removal of plasticizer not only from the surface, but from inner layers as well.

The analysis of the results of spectral studies of adhesive films formed by PVAD-51P and modified with Fenton reagent (Fig.2) show that the pattern of change in absorption capacity prior and after specimens water-soaking is somewhat different for the specimens of non-modified dispersion.

The examination of characteristic curves 1 and 2 (Fig.2) shows no evidence of substantial decrease in films absorption capacity at the wavenumber value of 3700–3600 cm^{-1} (except for the end part of the band absorption arm at wavenumber up to 3600 cm^{-1}), yet the spectral region of the 3700–3300 cm^{-1} wavenumber still shows an increase in the film transmission capacity, while the region of 3700–2500 cm^{-1} shows narrowing halfwidth of the aggregate absorption band for the water-soaked specimens. Such change in spectra pattern points to a decrease in the number of associated groups ($-\text{OH}$) as well as slight decrease in the number of non-associated alcohol groups.

On examination of IR-spectra within the wavenumber of 3100–3000 cm^{-1} (absorption band zone is conditioned by the presence of ($=\text{C}-\text{H}$) groups of dibutyl phthalate aromatic ring in the mixture), no decrease is observed in the absorption capacity of the water-soaked films (with the exception of the initial part of the absorption band arm at wavenumber up to 3100 cm^{-1}). Similarly, no substantial increase in transmission capacity is observed for the region within 1900–1600 cm^{-1} . This is attributable to the retention in the mixture of the most part of macromolecules with ($-\text{C}=\text{O}$) groups which enter into the composition of PVA and dibutyl phthalate, this being true even un-

der the action of water. Therefore, the introduction of Fenton reagent into adhesive composition can produce adhesive films that have better strength characteristics for glued joints with short-term contact with water. This is due to the fact that the rate of film transmission capacity increase in the regions associated with valent oscillation of hydroxyl or other oxygen-containing compounds capable of formation hydrogen bonds is far lower than similar characteristics of films formed by non-modified PVA dispersion.

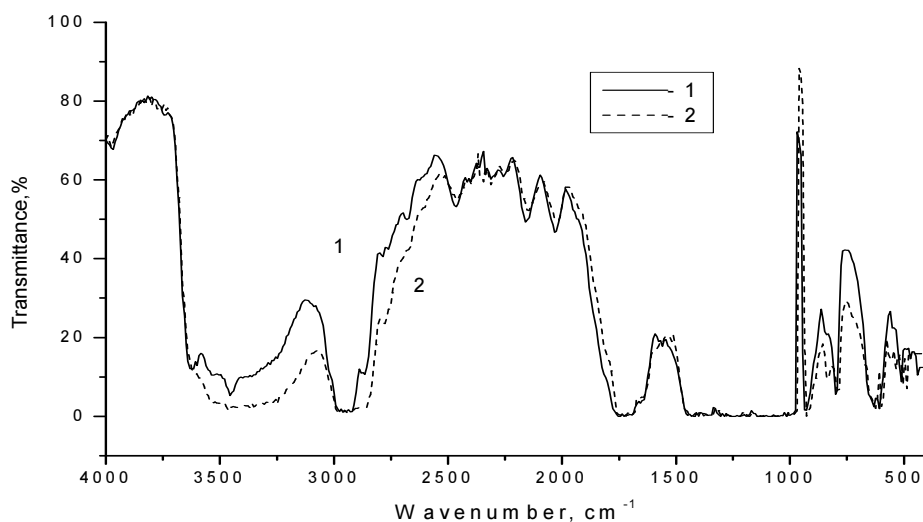


Fig.2. IR-spectra of film transmission capacity:

1 – adhesive film formed by PVAD-51P modified with Fenton reagent and water-soaked at a $20\pm 2^{\circ}\text{C}$ temperature for 24 hours; 2 – adhesive film of check specimens formed by PVAD-51P and modified by Fenton reagent

That is, even after the direct contact of polymeric films with water, there remain a large number of groups that are capable of chemical interaction (first of all to form hydrogen bonds) with wood components. Practical application of such compositions favors strength retention of glued joints in service. Besides, the direct contact of polymeric films with water does not cause the plasticizer washing-out, which ensures high elasticity of the films. Technologically, plasticizer retention in the film has a positive effect since this prevents from accumulating strains in adhesive joints at alternating loads thus enhancing their durability and operating strength.

The best results, from the standpoint of ensuring high strength characteristics of adhesive wood and wood-based joints glued with PVA dispersions, are obtained by films formed by PVAD-51P compositions modified with a 30% aqueous solution of nitric acid (HNO_3) and Aluminium nitrate ($\text{Al}(\text{NO}_3)_3$) (see Fig.3).

The examination of characteristic curves 1 and 2 (Fig. 3) as well as comparison with the results of similar investigation of other adhesive formulations presented in Figs.1-2 point out that the decrease in the absorption rate of films formed by dispersion modified with acid-salt complex at the wavenumbers of $3700\text{--}3300\text{ cm}^{-1}$ is lower than that for the two previous formulations. The narrowing halfwidth of the aggregate absorption band in the region with the wavenumbers of $3700\text{--}2500\text{ cm}^{-1}$ is also less due to water action as compared with all other adhesive formulations. Initial characteristic figures when determining absorption capacity of PVAD-51P modified with nitric acid (HNO_3) and Aluminium nitrate ($\text{Al}(\text{NO}_3)_3$) are the highest of all the three study compositions, while the rate of increase in the films transmission capacity due to water action is the least. Hence, it can be assumed that there is a small portion of oxygen-containing

compounds that are capable of forming hydrogen bonds both at the stage of wood adhesive joint formation and during these joints service. Besides, both the films formed by PVAD-51P and modified with Fenton reagent, and those formed by the same dispersion but modified with HNO_3 and $\text{Al}(\text{NO}_3)_3$ at the wavenumbers values of $3100\text{--}3000\text{ cm}^{-1}$ and $1900\text{--}1600\text{ cm}^{-1}$ show no decrease in the film absorption capacity. This points to the absence or a slight washing-out of plasticizer from the mixture, which has a positive influence on the strength and performance of adhesive wood joints.

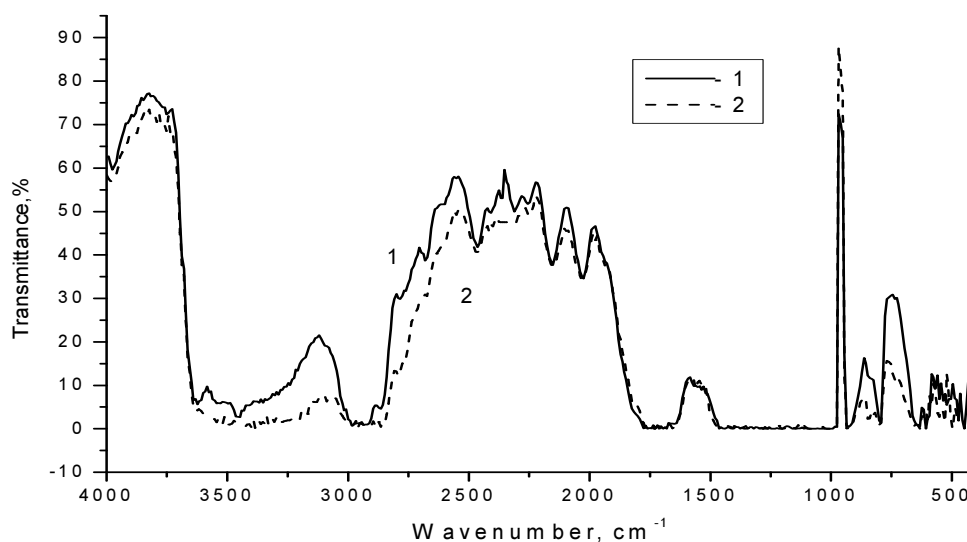


Fig. 3. IR-spectra of film transmission capacity:

1 – adhesive films formed by PVAD-51P composition modified with nitric acid (HNO_3) and Aluminium nitrate ($\text{Al}(\text{NO}_3)_3$), water-soaked at a $20\pm 2^\circ\text{C}$ temperature for 24 hours;
2 – adhesive films of check specimens formed by PVAD-51P composition and modified with nitric acid (HNO_3) and Aluminium nitrate ($\text{Al}(\text{NO}_3)_3$)

Conclusions. Based on the examination of the IR-spectroscopy of specimens formed by PVAD-51P prior and after water-soaking at a $20\pm 2^\circ\text{C}$ temperature for 24 hours, it was established that there occurs washing-out of hydrophilous emulsifying agent (polyvinyl alcohol) during its interaction with water molecules, the process taking place both in the surface layers and in the inner layers of the films. This is favored by partial soaking of polyvinylacetate macromolecules. In addition, along with the removal of the emulsifying agent macromolecules, there occurs washing-out of the plasticizer. This results in increasing rigidity and decreased elasticity of the films due to reduced mobility of polymeric basis chains (PVA). The above- described processes, which take place when glueing wood with non-modified PVA dispersion is characterized by a drastic reduction of joints strength resulted from direct contact with water, increased rigidity and brittleness, which is also due to accumulated stress set in the glue line.

On analyzing IR-spectroscopy curves for films formed by PVA dispersions and modified with Fenton reagent or with the mixture of nitric acid and Aluminium nitrate, it was found that although the specimens water-soaking for 24 hours results in polyvinyl alcohol washing-out, this rate of washing-out is lower than that for non-modified specimens, while the plasticizer removal from the mixture, except for the surface layers, does not take place. That is why modified PVA dispersions are useful in formation of wood and wood-based joints for those articles which are to be used in the environment with possible short-term water influence or ambient long-term high relative humidity.

Also, the comparison study of different adhesive composition formulations, whether the study films were exposed to water or not, has shown that the best indexes of absorption capacity within the range from 3700 cm⁻¹ to 2500 cm⁻¹ in the regions with the presence of associated and non-associated (–OH) hydroxyl groups in the layers are referred to those specimens that are formed by PVAD-51P dispersion modified with 30% aqueous solutions of nitric acid (HNO₃) and Aluminium nitrate (Al(NO₃)₃). In practical terms this means it is precisely this kind of composition that is able of forming the most durable and water-resistant adhesive joints.

References

1. **Freidin, A.** (1985) *Vodnye polimernye klei* [Polymer aqueous adhesives]. Moscow: Khimiya (in Russian).
2. **Muchailivska, G., Panov, V.** (2003) *Kley dlya skleivaniya drevesiny* [Adhesive for bonding wood]. Lviv: Poster (in Ukrainian).
3. **Barkauskas, A.E., Buika, G., Juodeikiene, I., Minelg, D.** (2003) The Structure and Adhesive Properties of Poly(vinylacetate) Dispersion Modified with Organosilicon Compounds. *Materials Science*, 9.1, 80-82.
4. **Rosenberg, M.** (1983) *Polimery na osnove vinilatsetata* [Polymers based on vinyl acetate]. Leningrad: Khimiya (in Russian).
5. **Zigelboym, S.** (1978) *Termoplastichnye klei v proizvodstve mebeli* [Thermoplastic adhesives in the production of furniture]. Moscow: Lesnaya promyshlennost (in Russian).
6. **Zanetta, T., Chiozz, F.** (2013) Wood adhesive compositions. Patent WO 2013057214 A1.
7. **Solonyinka, V.** (2008) The research of the stability of adhesive joints of hard-wooded species (oak wood), formed by modified polyvinyl-acetate composition, towards the influence of water and high temperatures. *Forestry, Forest, Paper and Woodworking Industry*, 38, 91-95.

УДК 674.028.9

*Асист. В.Р. Солонинка; проф. Б.Я. Кшивецький,
д-р техн. наук – НЛТУ України*

Вплив води на структуру клейових плівок сформованих за допомогою композицій на основі ПВА дисперсій

Наведені результати досліджень впливу води на структуру полімерних плівок отриманих з модифікованих і немодифікованих клеїв на основі полівінілацетатної дисперсії марки ПВАД-51П. Зроблені висновки щодо можливостей використання ПВА клеїв модифікованих реактивом Фентона або кислотно-соляним комплексом в залежності від можливих умов експлуатації сформованих ними виробів.

Ключові слова: модифікуючі добавки, полівінілацетат, дисперсія, полівініловий спирт, спектрофотометр, ІЧ-спектроскопія, інтенсивність поглинання, пропускну здатність.

UDC 674.028.9.004.15:519.216.3

Assoc. prof. B.Ya. Kshyvetskyi – UNFU

OPTIMIZATION OF MOISTURE AND TEMPERATURE EFFECTS ON STRENGTH AND DURABILITY OF THERMOPLASTIC ADHESIVE WOOD JOINTS

Presented is optimization methodology, also a gradient method is proposed to estimate optimum values of atmospheric moisture and ambient temperature effects on strength and durability of thermoplastic adhesive wood joints. By means of the proposed gradient method and methodology as well as mathematical modeling stress-strain state of bonded wood joints, the optimization of atmospheric moisture and ambient temperature influence on strength and durability of thermoplastic adhesive wood joints under operating conditions has been carried out. Optimum values for atmospheric