Combined physical modification of polymer adhesives used in woodworking

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Abstract. There is a shortage of valuable wood species in the world. One of the easiest and affordable ways to replace is to create glued products from scarce wood species by gluing oversized blanks. Products made of glued blanks are not inferior to the products made of solid wood in quality and properties. These products have the properties of rare wood species. However, growing demand on the quality of glued products constantly challenge technologists to increase the strength of adhesive joints. This problem can be solved in several ways: development of new bonding technologies, creation of special adhesives for a specific task and modification of known adhesives. The aim of the research is to increase the adhesive strength of wood due to decrease of adhesive viscosity and decrease in wetting angle. It is achieved due to directional effects of combined physical field to resin. Urea-formaldehyde resin and oak wood specimens have been considered as the object of the research. As a result of the resin modification, strength of the adhesive joint along the fibers increased by 2 times (196%), while the values of the viscosity and wetting edge angle were reduced by 62% and 82%, respectively.

1. Introduction

Reduction of forests in the world and difficulty of restoring them in the near future has inevitably led to a shortage of valuable wood species. One of the solutions of this problem is the possibility of using waste of valuable hardwood production and non-standard raw materials for the manufacture of glued products. Such products can replace most of the valuable raw materials. They can increase the degree of rational forest management.

Polymer adhesives are widely used in modern enterprises related to wood processing [1, 2]. They are used for the manufacture of plywood, furniture, and panel parquet [3]. The main criterion of quality is the strength of the adhesive joint. The ability to modify applied adhesives mainly depends on their properties, brand and glue quality [4]. The entire range of adhesives used in wood processing industry is classified by chemical composition, physical properties, and field of application (construction, furniture manufacturing, and woodworking).

According to the chemical classification, urea-formaldehyde (UF) adhesives belong to the most significant and frequently used group [5]. Urea-formaldehyde resin (UFR) belongs to the group of formaldehyde resins of increased viability. It is widely used in wood processing industry for the production of furniture parts, wood-based panels and glued wood constructions.

Production of such products consumes more than 90% of UF adhesives produced in the world [6].
Hence, it is necessary to study UF adhesives in order to develop a method for modifying urea-formaldehyde glues. It reduces the wetting angle of the adhesive contact edge, which indirectly indicates viscosity decrease of the used adhesive and, consequently, an increase in the strength of the adhesive joint. Technologies have been developed in the world practice to improve the reliability of such products operating under high mechanical loads and new bonding [7-10]. Modification of polymer adhesives can be carried out by chemical and physical methods. The method of chemical modification is widely used. Various additives are introduced into the composition of the adhesive. It helps to change chemical composition, adhesion, and cohesion of the material.

In [11] heat treatment of sulfite liquor subjected to heat treatment is proposed. This method enables to increase water resistance of the adhesive joint by reducing the strength of the adhesive joint. In the [12] a modification of phenol-formaldehyde resin at the stage of oligomer synthesis is proposed. The authors used caprol as a modifier. This method increases bonding strength but reduces pot life. Phenol-formaldehyde resin is used as a shunting modifier in [13]. It enables to increase strength of adhesive joint, while reducing viability of the adhesive. The described methods were developed for special problems, and do not allow improving the quality of adhesives in general.

During operation, adhesive joints in such structures experience increased mechanical loads [14]. Previously developed technologies for gluing wood are used to improve the reliability of products (glued wooden structures in particular). They are based on the influence of temperature and time factors, the accuracy of surface treatment of substrates (wood), size of adhesive joints, adhesion and cohesion, and other less significant factors. However, as it is evidenced by the practice of using products made of glued wood, the proposed technologies do not fully solve the problem of performance reliability. For this reason, more expensive and scarce adhesives are used instead of cheap and common ones in many cases. This approach naturally leads to an increase in the cost of finished products. In this paper we propose a method for modifying UF resin using the example of urea formaldehyde liquid (UFL) resin, when it is processed by electric field and ultrasound.

2. Materials and methods

The object of the study was UFL resin, which was purchased from the Infrahim Co. (Yaroslavl, Russia). In appearance the UFL resin was a homogeneous suspension from white to light yellow color free of foreign matter. Mass fraction of free formaldehyde was not more than 0.9%. Conditional viscosity was 15-35 seconds for plywood and 35-50 seconds for furniture at 20±0.5°C with a nozzle diameter of 6 mm. Viscometer was a tank shaped one. Mass fraction of non-volatile substances was 65-69 %. The value of pH was equal to 7.5-8.7. According to the manufacturer’s (Infrahim Co., Yaroslavl, Russia), UFL resin gelatinized at 100°C for 40-65 s. Gel time was at least 10 h at 20± 1°C. 5-10% solution of oxalic orthophosphoric acid (Infrahim Co., Yaroslavl, Russia) was used to gelatinize the resin at 20±1°C. The amount of hardener (from 5 g to 10 g) per 100 g of resin was established experimentally, in the required pot life of the glue of 0.5-4.0 h. A number of special studies were conducted to study the combined effect of the electric and ultrasound fields on the physical properties of glue or its polymer base. Viscosity of the glue was measured during the studies. VM-246 viscometer (Group of companies “Chimmed”, Moscow, Russia) was used to measure the viscosity of urea-formaldehyde resin of the UFL brand, treated and untreated in a combined physical field (electric field and ultrasound).

The procedure for measuring the viscosity of treated and untreated resin was as follows. The nozzle of the viscometer was closed. Then we took the viscosity of the VM-246 viscometer as the time of the resin flow in the form of a continuous jet (in seconds). The result was taken as the arithmetic average of three measurements.

Wetting the substrate with glue is one of the most important technological parameters. This, along with the pressure between the specimens during bonding, temperature and glue viscosity, has a significant impact on the strength of the adhesive joint. Therefore, the study of the influence of the electric and ultrasound field on this parameter of glue was very interesting from the point of view of bonding process technology. The contact angle meter consisted of a projector with a sample holder where wood veneer specimen was placed. A drop of resin was placed on the surface of wood specimen.
The procedure for conducting the experiment was as follows: first, a drop of resin (0.1 mg) was applied to the wood surface. Then the specimen installation was set up. The duration of the experiment was 30-40 minutes approximately. The equilibrium edge angle was set after applying a drop to an oak wood substrate with a maximum roughness of 16 microns (µm) after 6 minutes without treatment and 2.5 minutes after treatment with an electric field and ultrasound.

Data analysis consisted in finding the wetting angle \( \theta \) and comparing it for the treated resin in the electric and ultrasound field and untreated glue resin. The glue was liquid urea-formaldehyde one. Wettability and ability of the liquid to flow freely over the glued surfaces was determined by the free energy of liquid-gas-solid system, adhesive and cohesive forces. The scheme of surface tension forces on a liquid drop on the surface of a solid body is shown in figure 1.

From the diagram shown in figure 1, it can be seen that there were three forces acting tangentially to the surface of the liquid drop at O point. They were expressed by the Young equation

\[
\gamma_{SV} - \gamma_{SL} = \gamma_{LV}\cos \theta
\]  

(1)

where \( \gamma_{SV} \) is interfacial surface tension between solid and vapor; \( \gamma_{SL} \) - interracial surface tension between solid and liquid; \( \gamma_{LV} \) – interfacial surface tension between liquid and vapor; \( \Theta \) – contact angle. Later, Dupre developed an equation for the thermodynamic energy of interaction. It was widely known as the work of adhesion, \( W_A \):

\[
W_A = \gamma_{SV} + \gamma_{LV} - \gamma_{SL}
\]  

(2)

Hence, combining 1 and 2 equations we got the following:

\[
W_A = \gamma_{LV}(1 + \cos \theta)
\]  

(3)

where, \( \gamma_{LV} \)– surface tension of the liquid; \( \Theta \) – contact angle formed between liquid and substrate.

In the case of a constant value of \( \gamma_{LV} \), wetting of a solid was described by \( \Theta \). Based on the foregoing, it follows that the smaller the value of \( \Theta \), the better the spreading of the liquid on the surface and the greater the adhesion force. For the values \( \Theta = 0 \), \( \cos \Theta = 1 \), then \( W_{SL} = 2\gamma_{SL} \), then adhesion to a solid is equal to the liquid cohesion. This condition ensures complete wetting of the surface. When \( \Theta = 90^\circ \), \( \cos \Theta = 0 \), the work of the liquid to the solid is equal to \( \gamma_{LV} \). It is assumed that a solid substance does not wet at all at \( \Theta > 90^\circ \) and at \( 180^\circ \).
The adhesive strength of the adhesive joint, which is the basis of the overall strength, was formed mainly due to the adhesion forces that occur at the adhesive-substrate interface. This process was influenced by glue viscosity and contact angle as the main factors. Special studies were conducted to determine the advantages of the combined effect of electric field and ultrasound on the resin, and therefore the strength of the adhesive wood joint. To modify the glue, an installation was created (figure 2) for the joint effect of electric field and ultrasound on the glue. The basis of the installation was a working cell that simulates the capacitor plates. Ultrasonic generator with magnetostrictive effect was used to create an ultrasonic field with a frequency of vibrations up to 22 kHz. The main element of the installation was a working cell, which was the lining of a flat capacitor and ultrasonic generator with magnetostrictive effect. The electric field was measured by the distance between the capacitor plates and variation in the voltage of the supplied current. A high-voltage transformer was used as a current source, supplying a current of 10 kV. A constant electric field was created when using a battery of capacitors that served to accumulate electric charge and a cascade of rectifiers. Voltmeter was included in the installation circuit to monitor the voltage in the circuit and the field strength.

Figure 2. Schematic diagram of the installation for exposure to electric and ultrasonic field: 1 – high voltage transformer; 2 – switch; 3 – flat capacitor with a specimen; 4 – voltmeter; 5 – galvanometer; 6 – resistance; 7 – capacitor; 8 – spark gap switch; 9 – ultrasonic generator; 10 – transducer with magnetostrictive effect.

To change the voltage, an autotransformer was used that supplied current to a high-voltage transformer (Soyuz-Elektropribor, USSR). The electrical part of the unit enabled to create a constant electric field with a voltage ranging from 0 to 2000 V/cm. During the work, the electric field strength did not exceed 1500 V/cm, because such a phenomenon as “electric breakdown” occurred at a higher voltage of the current supplied to the working cell.

The electric field was considered equal to the energy of a fully charged capacitor, where

\[ C = \frac{e \varepsilon_0 S}{d} \]

flat capacitance, F

Substituting equation (2) in the formula (1) we obtained:

\[ E = \frac{e \varepsilon_0 S U^2}{2d} \]

where, S – capacitor area, m²; U – charged capacitor voltage, V; \( \varepsilon \) – relative permittivity (air \( \varepsilon=1.0006 \)); \( \varepsilon_0 \) – permittivity of free space or vacuum, \( \varepsilon_0=8.85\cdot10^{-12} \); d – distance between plates.

The tests included the selection of specimens, testing, and processing of the results. Oak wood (Voronezh, Russia) was selected as a sample material for determining the strength of the adhesive seam. The influence of species on the bonding strength was mainly manifested through two factors – wood density and its adhesive properties. That is, the ability to stick together. The general pattern was that when gluing solid wood with an increase in density, the strength of the glue joints increased. For
example, the ultimate strength when chipping along the glue seam increased. Preparing specimens for chipping was as follows. The blanks were glued together in the form of a bar. The length of the workpiece was set according to the available standards (SO 12578:2016(en) Timber structures - Glued laminated timber - Component performance requirements) depending on the required number of specimens for testing (figure 3).

![Figure 3. Specimen for determining the strength limit of the adhesive joint of wood for chipping (a); unit cell with the placed specimen (b).](a) (b)

It was not allowed to cut the adhesive layer when forming ledges in the specimen. Wood fibers from the surface of the adhesive layer on the ledges should be carefully removed. Prior to testing, the specimens were kept in a room at a temperature of 20±2°C and a relative humidity of 65±5% for at least 3 days after gluing without heating. The width and length of the splitting zone of the specimen were measured with a caliper with an accuracy of ±0.1 mm. The specimens were placed in a standard device for testing. The surfaces of the specimen ledges must fit snugly to the corresponding surfaces of the fixture. Fixture with installed specimen was placed on a support platform of testing tensile machine IR-50-3 (Kiev, Ukraine) so that the axis of the punch fixture coincided with the axis of the loading device the testing machine. The tests continued until the specimen was destroyed.

### 3. Results

The combined effect of electric field and ultrasound has a significant effect on the ultimate strength of adhesive joint, which, in its turn, depends on adhesion and cohesion forces of the adhesive seam. It is known that adhesive forces occur at the interface between glue and wood, and cohesive forces occur in the adhesive layer. The electric field generated by the electrode (when constant voltage is applied to it) leaves an imprint on the resin drop. Ordered flows of aeroions occur near the electrode. Dipole moment increases when the electric field and ultrasound act together. Lorentz force acts on moving aeroions, and such a phenomenon as the drift of charged particles occurs. It affects the process of wetting and film formation.

Special studies on the effect of electric field on the viscosity of UFL glue in the initial state and during processing of polymer components in an electric field and ultrasound at different electric field strength and ultrasound frequency were conducted. The data obtained during the tests (in the form of dependence of the adhesive viscosity on the field strength) are shown in table 1. Based on these data, it is clear that conditional viscosity of modified adhesives is significantly lower than that of the original ones. This effect is observed in all the cases. This phenomenon can be explained with a high probability by decrease in internal friction between the links of polymer macromolecules and a higher degree of their orientation along the influence lines of force fields.
Table 1. Dependence of UFL resin viscosity on the combined effect of electric field and ultrasound.

| Electric field strength, $E$, V/cm | Frequency of ultrasonic vibrations, $f$, Hz | Conditional viscosity, $n$, sec |
|-----------------------------------|-------------------------------------------|--------------------------------|
| 0                                 | 0                                          | 98                             |
| 190                               | 5                                          | 91                             |
| 650                                | 14                                         | 84                             |
| 770                                | 14                                         | 75                             |
| 960                                | 17                                         | 65                             |
| 1 210                              | 20                                         | 61                             |

The processes of wetting and liquid spreading on the surface of a solid body are determined by adhesive and cohesive forces, as well as free energy of the surface of solid – liquid – gas system. The effect of surface tension forces on a liquid drop on the solid surface can be traced from the data in table 2.

Table 2. Dependence of the edge angle value on time for UFL resin in the state of a control specimen and specimens processed in electric and combined field.

| Time of measurement, min | Contact angle $\theta$ of the control specimen | Contact angle $\theta$ for a specimen processed in electric field | Contact angle $\theta$ for a specimen processed in combined field |
|-------------------------|-----------------------------------------------|---------------------------------------------------------------|---------------------------------------------------------------|
| 1                       | 91°                                           | 75°                                                           | 64°                                                           |
| 2                       | 78°                                           | 67°                                                           | 63°                                                           |
| 3                       | 68°                                           | 63°                                                           | 56°                                                           |
| 5                       | 62°                                           | 60°                                                           | 54°                                                           |
| 7                       | 59°                                           | 54°                                                           | 52°                                                           |
| 10                      | 58°                                           | 53°                                                           | 51°                                                           |
| 12                      | 57°                                           | 52°                                                           | 50°                                                           |

As it can be seen from table 2, contact angle of the resin processed in the combined field is significantly less than that of the untreated one with the same fixing time. Thus, it can be concluded that combined effect of electric and ultrasound field increases wetting ability of glue on the wood surface. This effect can be explained by the fact that combined field implements the process of building molecular chains of the polymer glue along the lines of field strength more intensively. Ultrasound exposure intensifies this process. An increase in the adhesive strength of wood glue joints during processing in electric and ultrasound field can be associated with an increase in molecular, electrical, diffusion and other adhesive bonds. Tests of strength limit when splitting glue joint along the fibers were performed. To obtain comprehensive information about the proposed method for the effect of increasing the adhesive strength of wood glue joints during processing in an electric field and ultrasound (table 3). The data of the conducted research enable to conclude that the proposed technological method will improve the quality of glued wood products. The information is useful for woodworking enterprises.
Table 3. Dependence of the strength of oak wood adhesive joints on UFL brand on the influence of electric and ultrasound field.

| Electric field strength, \( E, \text{ V/cm} \) | Frequency of ultrasonic vibrations, \( h, \text{ Hz} \) | The ultimate strength of the shear, \( \tau, \text{ MPa} \) |
|----------------------------------------------|------------------|------------------|
| 0                                           | 0                | 5.3              |
| 600                                         | 5                | 6.1              |
| 1200                                        | 5                | 6.6              |
| 1200                                        | 10               | 8.9              |
| 1440                                        | 22               | 10.4             |

4. Conclusion
The edge angle of wetting \( \theta \) changes from 91° to 57° on the oak wood substrate for UFL resin without processing and from 61° to 50° - with combined processing. The difference between the edge angle readings \( \Delta \theta \) confirms the effect of electric and ultrasound field treatment on the wetting process of the substrate. It provides better wetting of the substrate surface with UFL resin, which is confirmed by a decrease in the edge angle. Reducing the edge angle, improving wetting and increasing the adhesion of UFL resin to the substrate is provided by creating additional energy on the surface from the electric field and ultrasound. The obtained data enable to assert an electrical theory of the formation of adhesive bonds that occur between contacting surfaces. The resulting intermolecular bonds cause redistribution of electrons at the interface between the two media and the appearance of double electric layer in UFL resin studied on the substrate. The boundary layers of the contacting media receive different-named charges, the interaction of which explains the increase in adhesion.

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