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M. M. Revyako, D. Sc. (Engineering), professor (BSTU);
A. F. Petrushenya, PhD student (BSTU);
V. V. Yatsenko, PhD (Chemistry) assistant professor (BSTU)

METHOD FOR INCREASING ADHESIVE PROPERTIES IN COMPOSITE MATERIALS BASED ON VENEER AND THERMOPLASTICS.

The article discusses the creation of laminated composite materials based on wood veneer using polyolefin films as a binder. The problems of combining components that differ in nature are presented. Goals for creating composite materials are achieved by modifying the polymer binder. The adhesion properties of measuring the contact angle and adhesive strength, were assessed and defined by their dependence on the concentration of modifying agents.

Introduction. Nowadays creation of polymer composite materials is an urgent task of industry. In this class of materials a special place is taken by reinforced materials based on laminated wood fillers. These materials are of good appearance, environmental security, unlimited in domestic raw materials. From a technical standpoint a wide use of such materials is problematic due to the fact that wood is a polar material with a high surface energy which values may vary depending on the composition and structure [1], and polyethylene has a low surface energy.

Urgent task of modern technology is the modification of large thermoplastics in particular polyethylene, substances that have the ability to increase the surface energy of a weak boundary layer in the composite material.

Targeted modification of polymeric binders that increase the adhesion strength is an effective method of controlling the properties of composites based on polyolefins.

Main part. In this paper the adhesive properties of the laminated composite material based on polyethylene and wood veneers were studied. Polyethylene was introduced as a film modified on the step of obtaining using additives based on a modified rosin. Substances increasing the tacking of the material represent a unique class of materials having low molecular weight and which are resinous materials with specific glass transition temperatures and softening, often higher than room temperature. This combination of properties makes these materials suitable for use in hot melt adhesives formulation. Resins increasing tackiness are usually obtained from natural products or petroleum fractions. These materials are classified according to the materials that are involved in their synthesis [2]. Known substances which increase the tackiness are rosin derivatives of abietic acid. Rosin acid is obtained as a byproduct of the processing of timber such as gum resin, wood rosin and tall oil. Abietic acid may itself be used as a substance that increases the tackiness, but in most cases this material is chemically modified in various ways. Unsaturation of abietic acid leads to oxidation and discoloration. This problem can be eliminated by hydrogenation of the double bonds. Rosin acid is also used in esterified form. Typically, abietic acid is esterified with glycerol or pentaerythritol to obtain a material with a higher softening point.

The modifying additive must be compatible with the base polymer, as otherwise undesirable phase separation might occur during storage or application of the adhesive. Modifying additives compatible with the base polymer can be assessed by changes in physical and mechanical characteristics of the composition such as tensile strength and tensile elongation. Another important criterion when choosing a supplement is its volatility at the melting temperature. Undesirable loss of product may occur if you don't comply with this criterion**.** Therefore modifying additives were selected based on the fact that their melting or softening points are in the range of melting temperature of polyethylene (about 105°C). Among the known methods for producing polymer compositions having improved adhesion properties, the most frequent is the method of preparing modified polyolefins by grafting of maleic anhydride (MA) [3–6]. Known methods include the step of graft of MA on polypropylene or polyethylene using organic peroxide or containing a diazo group initiators, dispersible into polyolefin in the melt, together with MA.

In our work as modifying additives that enhance the stickiness were used based derivatives of disproportionated rosin and rosin modified by maleic anhydride:

– CD – the reaction product of diethylenetriamine with rosin (softening point 79–83°C, acid value 66);

– GGKMA – the reaction product of rosin and hexylamine hexanol (viscous product, acid number 129);

– OKMA – modified adduct of rosin and maleic anhydride (softening point 90°C);

– GKKMA – the reaction product of rosin with maleic anhydride and hexylamine (viscous product).

In our opinion, the additives derived from wood chemical raw material are capable of provid-

ing the desired level of interaction with the wood components, including lignin, by the presence within their structure of an acidic group and terpenoid moiety. In turn, the presence of an aliphatic radical of different length in the structures of modifying additives allows to provide compatibility of additives with polyethylene macromolecules. The most simple method to determine the surface energy of the solid is based on measurement of contact angle. The same method evaluates wettability of the substrate surface by adhesive melt. When measuring the contact angle a drop of liquid is deposited on a solid surface. In the case of hot-melts the method is complicated because even in the molten state the polymer has higher viscosity. In this paper the authors attempted to solve this problem by replacing the high molecular weight polyethylene with its analogue, that is nonpolar polyethylene wax of grade PW-200, which in comparison with the polymer has a lower molecular weight and in a molten state may be applied as a droplet on the substrate surface. Method of determining the contact angle comprises the following steps. Hitch of polyethylene wax PW-200 is mixed with modifying additives (OKMA, CD, GGKMA, GKKMA) in an amount of up to 7% and the melt is obtained by heating the sample with constant stirring on a sand bath until complete melting of components (Fig. 1, *a*). With the help of a glass rod drops are applied to the surface of the veneer with a height of 10 mm (Fig. 1, *b*).

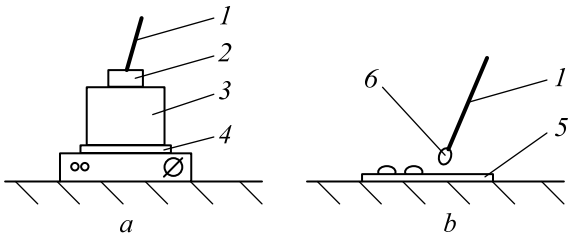


Fig. 1. Scheme of applying a droplet determining the contact angle:
1 – glass rod; *2* – heat-resistant glass; *3* – sand bath; *4* – hotplate; *5* – veneer; *6* – drop

The test samples were photographed with a focal length of 500 mm, using the effect of macro – aligned interfacial substrate – gas in a horizontal line of the frame of the camera. To determine the contact angle the package MatLab was used which processed the received pictures. Equation of the boundary of drops was determined. It is enough reliably described by an elliptic curve of the second order and has the form

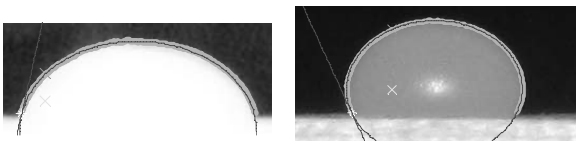
$$a_{22}y^2 + 2a_{12}xy + 2a_{13}x + 2a_{23}y + a_{33} = 0.$$

a_{ij} coefficients in the equation of an ellipse were found with the help of function presented in [7].

The contact angle is determined from the slope of the tangent at the point of three phase section (x_1, y_1) by the equation

$$\mathrm{tg}\varphi = -\frac{a_{11}x_1 + a_{12}y_1 + a_{13}}{a_{12}x_1 + a_{22}y_2 + a_{23}}.$$

The output for the cases where the adhesive wets (*a*) and does not wet (*b*) the substrate surface can be evaluated according to Fig. 2.



angle: 77.3° angle: 114.5°
a *b*

Fig. 2. Examples of definitions of contact angle by the modified (*a*) and unmodified (*b*) wax PW-200

All additives used in this study alter the surface energy of polymeric binder, increasing the wettability of wood veneer. The best effect is achieved with the introduction of wetting modifiers GGKMA, GKKMA and OKMA of 7%, the contact angle is reduced by 1.5 times. At a much lower (1–3%) introduction of additive CD the effect of reducing the contact angle can be achieved by 1.4 times (Fig. 3).

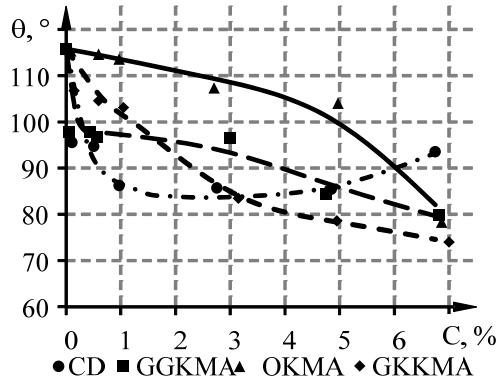
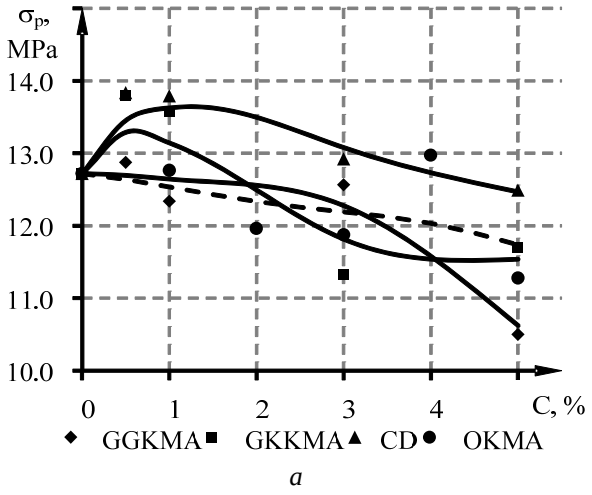


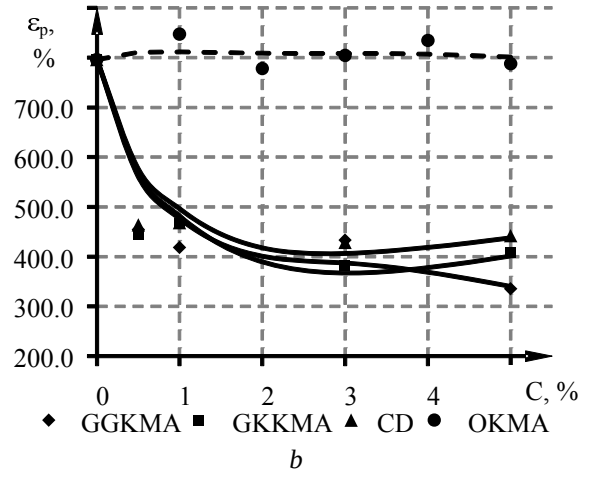
Fig. 3. Dependence of a contact angle (θ) from the concentration (C) of the modifying additive in the PW-200

Strength of adhesive joints is determined not only by wetting properties and viscosity of the adhesive, but by the deformation properties of adhesives and substrates (different in volume and in the surface layers of phases) and appearing in them stresses at the adhesive contact. On the strength parameters it can also be judged on the compatibility with the polymer modifiers, as noted above. The work was carried out to study the influence of modifying additives on the basis of rosin on the strength properties of the polyethylene polymer compositions of brand 15803-020

(Fig. 4).Polymer compositions were obtained by rolling at 150°C followed by compression in film samples at 170°C.



a



b

Fig. 4. Strength (*a*) and tensile elongation (*b*) of modified films

All the additives have complex effects on the tensile strength of the modified polyethylene films, however there is tendency to decrease in strength properties. For additives CD and GKKMA strength dependences pass through a local maximum at concentrations of 0.5–1.0%.

Input enhancing tackiness and adhesive properties may inherently be related to the plasticizers in view of their low molecular weight. The introduction of plasticizers into the polymer accelerates the ordering because of the change of free volume of cristallizing system and the increase of kinetic flexibility of the macromolecules, which leads to some increase in tensile strength [8]. Lacking thermodynamic compatibility with the polymer modifiers are localized in the interstructural field of polymers, thereby increasing the packing density of supramolecular structures, reducing mobility of macromolecules tie chains in disordered zones. Such distribution of modifier in the polymer may reduce the tensile elongation, which is consistent with the work results [9, 10].

Good compatibility with the polymer is observed in OKMA modifier, the remaining additives have sufficient interoperability as tensile elongation is at 400%, and the tensile strength is retained above the value of 11.3 MPa.

For quantity characterizing the adhesion, taking into account the complexity of methods for its determination and difficult dependence on many factors, such parameter as the adhesive strength was taken, which can be determined fairly by simple destructive methods, including GOST 14759. Determination results of the adhesive strength by the method of determining the shear strength of the samples glued overlap, are presented in Fig. 5.

The graph shows that for all modifiers maximum adhesive strength is achieved at a concentration of modifier equal to 3%. Moreover the additive GGKMA does not increase substantially adhesive bonding strength. The best effect was observed in the additive CD, but GKKMA OKMA additives can also be used. They have the effect of increasing the adhesive properties at 29 and 17% respectively.

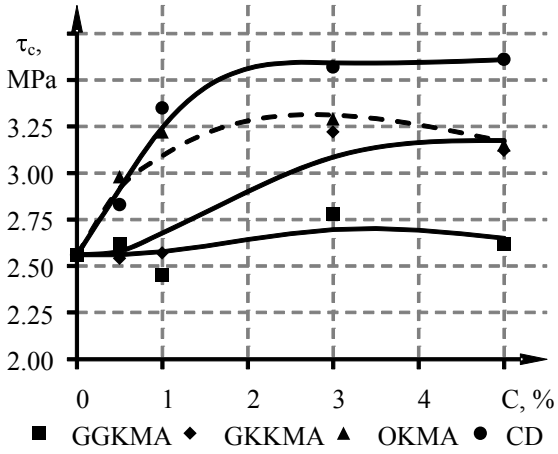


Fig. 5. Dependence of the shear strength(τ_c) on the concentration (C) of modifier

Conclusion. Taking into account that OKMA additive in an amount of 3% leads to an increase in adhesion strength and in minor degree but impairs the physical and mechanical properties of polymer composition, it may be recommended for the adhesive basis for modifying a polyethylene film in the production of laminated composites based on thermoplastics and veneer.

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