CHEMISTRY AND TECHNOLOGY OF WOOD PROCESSING

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APPLICATION OF MODIFIED FILMS IN THE PRODUCTION OF WOOD-PLASTIC LAYERED MATERIALS

We propose the possibility of obtaining layered composite materials on the basis of based on wood-veneer with the use of thermoplastic polyolefin film binders and a copolymer of ethylene with vinyl acetate. A method for increasing the adhesion of polymer compositions to wood filler was specified. The effect of modification on the strength of the composition of the material was studied. The test results of physical and mechanical properties of composite materials obtained by using the modified films were shown.

Introduction. Today, composite materials based on polymer binders acquire more and more importance. This is due to the presence a special set of properties in these materials that meet the requirements of the end user, which is achieved by the summation of the qualities of individual components of the composition, and sometimes by synergies.

The production of composite materials based on thermoplastics, where glass, carbon and aramid fibers are used as the reinforcements or fillers increased significantly. In this case, obtaining of composite materials with the use of natural fibers, such as wood fibers or fibers of annual plants as well as layered wood materials is of great interest. Such composite materials have long been used in the car industry, including manufacture of instrument and door panels, seat backs and other elements of the car interior [1].

The ability of thermoplastics to soften when heated expands the technological capabilities of formation of products compared with to thermosets. And the fact that the transition temperature of thermoplastic resins in a plastic condition is relatively low, makes them a suitable binder for natural fibers in composite materials. Thus, a mixture of thermoplastic and wood particles or fibers can be recycled by the methods used in polymer technology: extrusion, injection, compression [2].

The process of modernization of the existing techniques of composite materials with the purpose of replacing outdated polymers by more modern, environmentally friendly and safe in the production of the final product is becoming very important.

However, widely used industrial and manufactured thermoplastic of polyolefin series (polyethylene, polypropylene) are non-polar polymers, and to increase adhesion between the components in a layered composite the authors of the article proposed to introduce functional groups to adhesive molecules, which increase the surface energy and the flexibility of the molecules of contacting phases. This approach is the basis of the development recipes of adhesives and processes for preparing substrates for gluing or coating.

Main part. To study the properties of the composite material on the basis of functionalized polyolefins and wood veneers films, the following polymers were selected: high-density polyethylene (LDPE) grade 15803-020 State Standard (GOST) 16337, polyethylene (HDPE) grade PE 4FE 69 TU 6-11-00206368-25, polypropylene (PP) grade PP1500J TU 2211-136-05766801, as well as compositions with high adhesion characteristics, modified by grafting a dicarboxylic acid grade PF-7 TU RB 03535279.015-97. Adhesive compositions based on functionalized polyethylene (KKFPEVD1, KKFPEVD2) adhesive composition based on a copolymer of ethylene and vinyl acetate (KKSEVA), the adhesive composition based on a functionalized ethylene-vinyl acetate (KKFSEVA) were applied as modified compositions.

The strength of the finished product is determined primarily by the phenomenon of adhesion of contacting the connected components.

These components form the basis for the resulting molecular (i.e. across the whole interphase area) contact of adhesive joint and are called substrates, and substances that provide a connection of substrates – adhesives [3]. In our case, the substrate is a birch wood veneer 1.5 mm thick, prepared according to Standard 99, and the adhesive - thermoplastic film material.

Considering the complexity of the methods of determining the adhesion and its dependence on many factors, a parameter such as adhesive strength, which can be determined by rather simple

destructive methods, in particular by determining the shear strength for adhesive layer was adopted in the work as a connection strength indicator.

In order to determine optimal conditions for obtaining a composite material of this kind, an active multifactorial experiment was planned and carried out.

The pressing process of a composite material in which press temperature (°C), compression pressure (MPa) and binder layer thickness (μm) have been chosen as the variable input parameters were the subject of this study.

Compacting pressure of samples varied in the range 1.0–1.8 MPa, temperature range of compression was selected depending on the type of polymer and its melting temperature (glass transition temperature for amorphous polymers or the melting point of the crystalline phase for crystallizing polymers). It should be noted, however, that the upper limit of intervals (200°C) was chosen based on the fact that at temperatures higher than that of the mentioned above chemical reactions that lead to the degradation of wood components actively proceed in wood. Table 1 shows the ranges of variation of independent control variables.

Table 1

Change intervals of experimental parameters

Polymer	Parameter		
	Temperature t, °C	Pressure p, MPa	Film thickness δ, μm
LDPE	110–150	1.0–1.8	50–250
HDPE	180–200		90–360
PP	170–200		85–255
KKFPEVD1	180–200		150–250
KKFPEVD2	180–200		150–250
KKSEVA	170–190		150–250
KKFSEVA	180–200		150–250

Adhesive bond strength was monitored by the method of determining the shear strength according to State Standard (GOST) 14759. The essence of the method is to establish the value of the tensile breaking strength of standard form, spliced by the efforts tending to move one half of the sample relative to the other.

The results of the experiments on determination of shear strength showed that the increase in temperature and pressure leads to an increase in adhesive strength, and the dependence is an increasing curve with a saturation point, after which a further increase in temperature and pressure does not lead to significant changes in adhesive strength.

This is explained by the fact that the formation of interphase adhesive contact is to a large extent determined by the actual contact area S_n and maximum (molecular) S_m. Contact formation is accelerated by the increase of pressure and contact time, as well as the decrease of adhesive viscosity, for example by increasing the temperature or decreasing the molecular weight of the polymer macromolecules. The maturity of the micro-relief of the substrate surface, and the resistance of bordering layers of adhesive, especially significant in the case of polymer melts due to the nature of their non-Newtonian rheological behavior impedes the achievement of S_m. The rate of establishment of interphase contact determined by the value of an adhesive drop formed on a substrate of the contact angle θ. The duration of achieving S_m in real substrates compounds obtained with polymeric adhesives, reaches 10^{-2}–10^{-3} hours. It may be reduced by the intensification of adhesive leaking into micro-trenches on the substrate surface and the expulsion of air from the trenches with the deformation of the microscopic valleys, as well as the increasing the mobility of adhesive molecules [4].

Saturation point on the dependences of the adhesive strength of the pressing parameters corresponds to the equilibrium value of S_m. When equilibrium is reached, a compound is being formed, which is destroyed under the action of mechanical load on the weakest element (usually the adhesive). A cohesive fracture pattern is observed in this case.

The destruction is less likely in the interphase. It is realized in the presence of contaminants on the interacting surfaces formed as a result of insufficient cleaning of adhesive and substrate or destruction of phases in the process of contacting.

In practice, the criterion of optimality conditions for the formation of adhesive joints was to ensure their high durability and cohesive character of the failure [5].

Table 2

Optimization results

Material	Temperature, °C	Film thickness, μm	Pressure, MPa	Shear strength, MPa
LDPE	150	250	1.8	1.9
HDPE	200	360	1.8	2.8
PP	190	170	1.8	4.0
KKFPEVD1	170	250	1.8	3.2
KKFPEVD2	180	250	1.8	4.1
KKSEVA	190	200	1.8	4.8
KKFSEVA	180	250	1.8	3.6

According to the results of experimental studies the optimal values of the technological parameters of obtaining laminated composite material resented in Table 2 were found.

The interaction between the contact surfaces of non-polar adhesives and polar substrate realize primarily Van der Waltz interactions or hydrogen bonds. However, when functionalized or adhesive compositions are used as adhesives, containing in its structure functional groups capable of interacting with the functional groups of the components of cellulose, preconditions are created for the reactions of exchange or merger of the chemical bond at the at the phase boundary, which explains the significant increase in the adhesion strength of the compound. The samples obtained with the modified film possess cohesive nature of their destruction.

In a series of LDPE, HDPE, PP, an increase in shear strength is observed. This is because the strength of adhesive joints is determined not only by interphase interaction, but also by deformation properties of the adhesive and the substrate, and stresses that appear in them during adhesive contact.

Chemical, physical and performance properties of polyethylene depend on the density and molecular weight of the polymer, and therefore different for different types of polyethylene. Comparative analysis of the characteristics of HDPE and LDPE shows that HDPE, due to the higher density, has higher strength properties. Tensile strength for LDPE is 11.3 MPa. For HDPE this index is 2 times higher. The strength of PP is 3 times higher than that of LDPE, and is 34 MPa.

Copolymer of ethylene and vinyl acetate is a macromolecular compound relating to polyolefins. It is produced by the method analogous to the method of production of high pressure polyethylene. EVA surpasses polyethylene in transparency and elasticity at low temperatures. EVA properties depend mainly on the content of vinyl acetate (5–30 wt.%). With increasing content of vinyl acetate hardness, heat resistance, crystallinity (breaking stress at yield) are reduced, while density, flexibility, transparency and adhesion are increased. In order to maintain the strength of the polymer and obtain a composition with high adhesion, we decided to use a copolymer of vinyl acetate content of 5–7% by exposing further polymer grafting modification by dicarboxylic acid.

It should be noted that the expected result of increasing the strength of adhesive bond with the introduction of of modifying additives is leveled by low rheological properties of the polymer composition presented in Table 3.

It was found that the adhesive composition of functionalized copolymer of ethylene and vinyl acetate shows the results 25% lower compared to the adhesive composition of the copolymer of ethylene and vinyl acetate A similar result can be observed in the case of significant differences in the parameters of the melt flow of the adhesive compositions based on LDPE. Increasing the viscosity creates large flow resistance to the melt and prevents it from flowing into the porous structure of the wood, thus reducing the actual contact area, and hence the adhesive bond strength.

Table 3

Melt Flow Rate

Material	Conditions (kgf/°C)	MFR, g/10 min
LDPE	2.16/190	2.0
HDPE	21.6/190	10.0
PP	2.16/230	3.1
KKFPEVD1	5/190	0.09
KKFPEVD2	2.16/190	2.0
KKSEVA	2.16/190	4.8
KKFSEVA	5/190	0.5

Based on the results from Table 2 material of adhesive composition of copolymer of ethylene and vinyl acetate was selected for studying the properties of the composite laminate, such as tensile strength at shearing, bending strength, and tensile strength.

The results of mechanical tests of samples of composite material based on wood veneer and film adhesive copolymer of ethylene with vinyl acetate, obtained by pressure, are shown in Table. 4.

Table 4

The strength characteristics of the composite material

Property	Value
Tensile strength, MPa	36.4
Flexural strength, MPa	76.5
Shearing strength on adhesive layer after soaking 24 hours	1.3

The standard value of tensile strength along the fibers for plywood grade FK, WBP thickness from 3.0 to 6.5 mm is not less than 30 MPa. The standard value of flexural strength along the fibers of the outer layers of veneer grade FC, PSF thickness from 7 to 30 mm, is not less than 25 MPa. The standard value of tensile strength by shearing adhesive layer for plywood FC after soaking for 24 hours for birch veneer is not less than 1.5 MPa [6].

Conclusion. Producing quality layered composite materials based on thermoplastic is possible if to apply extrusion grades (MFR 2 to 6) of

polymer composites based on functionalized polyolefins or copolymer of ethylene with vinyl acetate as adhesives containing in their structure functional groups capable of reacting with the functional groups comprised in timber, forming strong bonds of polymer – wood. Adhesive composition based on a copolymer of ethylene with vinyl acetate can serve as such adhesive. Developed on its basis eco-friendly wood-polymer composite material by its properties corresponds to a general-purpose plywood for interior use and can be recommended for obtaining general-purpose eco products and used in the furniture industry.

References

1. Древотермопласт [Электронный ресурс] / Инжиниринг оборудования. – М., 2010. – Режим доступа: http://recyclers.narod.ru/10_1.htm. – Дата доступа 24.03.2010.

2. Расплавы полимеров как адгезивы конструкционных материалов: обзор. инф. / Бережная Г. В., Каган Д. Ф. НИИТЭХИМ, НПО «Пластик» – М.: НИИТЭХИМ, 1977. – 35 с.

3. Басин, В. Е. Адгезионная прочность / В. Е. Басин. – М.: Химия, 1981. – 208с.

4. Дерегин, Б. В. Адгезия твердых тел / Б. В. Дерегин, Н. А. Короткова, В. П. Смилга. – М.: Наука, 1973. – 327 с.

5. Вакула, В. Л. Физическая химия адгезии полимеров / В. Л. Вакула, Л. М. Притыкин. – М.: Наука, 1984. – 286 с.

6. Фанера общего назначения с наружными слоями из шпона лиственных пород: ГОСТ 3916.1-96. – Введ. 14.08.1996. – М.: ЦНИИФ: СТАНДАРТИНФОРМ, 2008. – 26 с.

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