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Bonding Strength Investigation of Shoe Materials with Dispersion Adhesives

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Abstract. The article is devoted to a promising direction in the production of footwear - the use of polyurethane dispersion adhesives for gluing soles in shoes with natural leather uppers, instead of traditionally used polyurethane adhesives-solutions, one of the disadvantages of which is the content of volatile organic solvents from sole materials (leather-like rubber, thermoplastic elastomer) and natural leathers with various topcoats. To optimize the bonding modes, the method of mathematical planning of the experiment was used. During the investigation the optimal modes of the process of gluing natural leather for the upper of shoes and synthetic sole materials with polyurethane adhesives-dispersions were established. The developed modes make it possible to obtain a consistently high strength when gluing thermoplastic elastomer soles to the upper of natural leather shoes using environmentally friendly dispersion adhesives.

INTRODUCTION

The glue method of fastening the bottom parts is a promising direction in the manufacture of footwear. The method has become widespread due to a number of its advantages: high strength and durability of joints, low dependence of bonding strength on the thickness of the parts being fastened, high elasticity of glue seams, no violation of the integrity of the materials being joined, high labor productivity and the ability to quickly change the assortment.

The further development of the method is facilitated by the use of new compositions of shoe adhesives. At the same time, the introduction of new adhesives requires a detailed development of the technology for gluing shoe materials, optimization of the technological modes of gluing and soles-fastening operations, and the development of recommendations for improving the quality of finished shoes.

Despite the listed advantages, a significant disadvantage of the adhesive fastening method is the widespread use of adhesive solutions based on organic solvents. The last ones harm the environment and worsen the sanitary and hygienic working conditions of workers performing gluing and spreading operations. When applying glue-solutions, the laborious manual method of applying glue with a brush is most often used. The use of specialized equipment is limited due to the complexity of cleaning the glue feeders.

That is why, dispersion adhesives are of main interest. Dispersion adhesives are colloidal systems in which the dispersed phase is polymer particles, and the dispersed medium is water, therefore such adhesives are more environmentally friendly, they are well applied by spraying, which makes it possible to automate the process of their application.

Nowadays, dispersion adhesives have proven themselves well for secondary and auxiliary joining operations, such as gluing backs and toes, insoles.

In this regard, a promising direction in bonding technology is the expansion of the area of application of dispersion adhesives in the manufacture of footwear, including for essential joints when attaching soles.

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For gluing soles, polyurethane adhesives are traditionally used, since the film-forming agents used in their composition - urethane rubbers provide versatility, good adhesion to almost all shoe materials, allow you to obtain high-strength, elastic, heat-resistant, adhesive compounds resistant to the action of fats, oils and gasoline.

Recently, various authors have studied the adhesive ability of polyurethane adhesive solutions used in the manufacture of shoes, and the influence of various factors on it. Close attention was paid to the methods of preparing the unused surface of the soles and the tightening edge of the shoe samples made of various materials for gluing, the establishment of technological regimes when performing the sole support operations [1–6], the modification of adhesives, taking into account the requirements for them [7,8].

Currently, leading manufacturers of shoe adhesives offer a wide range of polyurethane adhesives, both solutions and dispersions.

The works aimed at the study of dispersion adhesives are devoted to assessing the effect of the components on the rheological characteristics of aqueous polyurethane dispersions and their relationship with technical and operational characteristics [9–10].

The use of dispersion adhesives for sole supporting operations is currently a fairly new direction for domestic shoe enterprises. So, attempts to use polyurethane dispersion glue at one of the shoe enterprises of the republic showed instability of the strength of the adhesive bond when gluing the soles to the shoe upper sample made of various materials.

The issues of the fastening strength of the shoe bottom parts to the upper sample with dispersion adhesives were studied in [11], but were limited to artificial leather for the upper materials. However, at Belarusian enterprises, they mainly use genuine leather for the samples of the upper part of the footwear.

Based on the above stated, the purpose of this work is to study the possibility of widespread use at enterprises of the Republic of Belarus of polyurethane dispersion adhesives for fixing soles in shoes and to establish optimal technological modes of the gluing process that provide standard strength for materials most often used in shoe production.

MATERIALS AND METHODS

During the study, genuine leathers (GL) with various top coatings were selected as the material for the upper part of the shoe.

Elastic genuine leather, produced according to TUBY 600208238.007-2010:

- GL "Comfort", with a natural, unpolished front surface, with a wax finish.
- GL "Lazur", with a ground and embossed front surface.
- Genuine leathers of the chrome tanning method, produced in accordance with GOST (All union state standard) 939-94.
- GL "Lola", with a polished front surface, emulsion coating.
- GL "Natural", with a natural front surface, semi-aniline finish.

The thickness of the studied materials of the upper part of the shoe is 1.2 mm.

The most common synthetic materials for shoe bottoms were chosen as the bottom material:

- leather-like rubber (L-LR) of the "Kozhegum" brand.
- "Solen" brand thermoplastic elastomer (TPE).

The thickness of the studied materials of the bottom of the shoe is 4.0 mm.

For gluing the samples, polyurethane adhesives of various phase states were used:

- water-dispersive adhesive "Ecostic".
- glue-solution based on organic solvents "Luch PU".

Glue "Ecostic 1820S 1K" is intended for the first spreading of the tightening edge and soles, has a low concentration (apparent viscosity according to Brookfield 350 - 50 mPa, which allows it to be applied to the glued surfaces by spraying using a spray gun.

Glue "Ecostic1820 1K" is intended for the second spreading in combination with glue "Ecostic 1820S 1K", or for a single spreading of the tightening edge and soles. The glue has a higher concentration (apparent Brookfield viscosity 2400 м200 mPa)·, can be applied with the brush.

Glue "Luch PU 3110" has a concentration of 12.0-13.0% and is intended for the first spreading of the tightening edge and soles. Luch PU 3072 glue has a concentration of 16.5-17.5% and is intended for the second spreading of the tightening edge and soles. For application, a manual method is used with a brush.

All of the above mentioned adhesives are recommended for essential joints of various materials of the top and bottom of shoes.

The durability of the adhesive joints was determined according to GOST 28966.1-91 "Polymer adhesives. Method for determining peeling strength" [12]. The method consists in determining the load that destroys the adhesive joint by measuring the forces causing peeling of the materials glued together and reduced to the linear dimensions of the adhesive seam.

With the working area of 170×25 mm, the samples of 120×25mm were cut out. Preparation of the surfaces for gluing was carried out according to the technology used in shoe factories. Before applying the glue, genuine leather was ruffled and dust-free, leather-like rubber was polished, athermoelastoplast was halogenated. The samples were glued in accordance with the normative and technical documentation for the glue.

When gluing samples with glue-solutions, the drying of the adhesive films after the first spread was carried out during 15 minutes, after the second - 30 minutes under normal environmental conditions.

When gluing the samples with dispersion adhesives, the adhesive films were dried after the first spread during 20 minutes, after the second –30 minutes under normal environmental conditions.

The activation of adhesive films on all samples was carried out by the radiation method at a temperature of 130 ° C for 30 s. The samples were glued and pressed on a laboratory press with a pressure of 0.3 MPa for 60 s. The glued sample was kept under normal conditions for 24 h for complete crystallization of the glued joint. For each variant of the front surface treatment, five samples were prepared.

The peeling test was carried out on a Frank tensile testing machine at a moving grip speed of 100 mm / min.

Breaking force P (N) was determined by the formula

$$P = \frac{\sum_{i=1}^{n} P_i}{n}, \tag{1}$$

where P_i - destructive force of the i-th dimension, N; n is the number of measurements (n = 5).

The arithmetic mean of five parallel determinations was taken as the test result, which meets the requirements established in the normative and technical documentation for polymer glue [12].

The strength of the adhesive bond during peeling g_{peel} (N / cm) was calculated by the formula

$$g_{pac} = \frac{P}{b}, \tag{2}$$

where P is the breaking force, N; b - the width of the glue line, cm.

RESULTS AND DISCUSSION

During the test, fracture diagrams were recorded, according to which durability bonds were calculated (Table 1).

TABLE 1. Indicators of durability of adhesive bonds

Upper material	Bottom material	Group of samples			
		glued with adhesive solution	Δ,%	glued with dispersion adhesive	Δ,%
GL Comfort	L-LR "Kozhegum"	44,8	4,1	50,3	3,6
	TPE "Solen"	43,1	3,8	48,0	4,2
GL Lasur	L-LR "Kozhegum"	48,5	4,2	53,9	3,0
	TPE "Solen"	45,2	5,1	50,6	4,6
GL Lola	L-LR "Kozhegum"	46,8	2,9	51,4	4,3
	TPE "Solen"	44,9	3,5	49,2	3,9
GL Natural	L-LR "Kozhegum"	43,7	4,8	46,1	4,1
	TPE "Solen"	42,0	4,6	42,5	4,7

Analysis of the obtained data shows that the strength of adhesive joints when gluing genuine leather with leather-like rubber glue-solution is in the range from 43.7 to 48.5 N / cm, and when gluing with adhesive dispersion from 46.1 to 53.9 N / cm; when gluing genuine leather with thermoplastic elastomer with glue-solution - in the range from 42.0 to 45.2 N / cm, and when gluing with glue-dispersion from 42.5 to 50.6 N / cm.

It should be noted that, regardless of the type of topcoat and the type of surface treatment of genuine leather, when glued to leather-like rubber using glue-solutions, the durability indicators exceeded the standard values by 4 to 16% (standard - 42 N / cm for men and women shoes [13]). When gluing genuine leathers with thermoplastic elastomers with adhesive solutions showed lower strength, the maximum excess of the strength standard was only 8%.

The bonding (gluing place) obtained with the use of dispersion glue showed a better result in comparison with solution adhesives: the strength when gluing with leather-like rubber exceeded the standard values by 10 to 28%, and when gluing natural leather with thermoplastic elastomer, the excess of the strength standard was from 1 up to 20%.

In addition, during the tests, the nature of the destruction of the adhesive bond (adhesion, cohesion, autohesion) was recorded. When using a glue-solution, the adhesive nature of destruction was mainly observed, which indicates the possibility of increasing the strength of the adhesive bond by increasing the adhesion forces. When using a dispersion adhesive, the cohesive nature of destruction in the material of the top and bottom prevailed, which indicates higher adhesion forces of the dispersion adhesive. An increase in adhesion durability in this case is possible by increasing the adhesion forces, which depend on the modes of the gluing process, as well as by increasing the cohesive strength by choosing stronger materials for the upper and sole samples.

Thus, the studies carried out have shown that the use of dispersion glue can significantly increase the adhesion strength of soles made of various materials to the samples of upper part of shoes made of genuine leather in comparison with the traditionally used glue-solution, but requires optimization of technological modes in order to obtain a consistently high durability for all types of materials.

Among the materials studied, the lowest durability was shown by gluing GL "Natural" with thermoplastic elastomer, the strength index reaches the standard value, but without a safety margin.

In order to increase the durability of the glued bonds of GL "Natural" with thermoplastic elastomer the method of planning the experiment was used. When choosing the factors to be investigated, the experience of introducing dispersion adhesives at a shoe factory was taken into account, which showed that technological factors have a significant effect on the durability of adhesive joints: drying time and activation temperature of adhesive films.

The problem was solved using the second-order D-optimal plan, which assumes the variation of factors at three levels: the drying time after the second application of the glue film (tc) and the activation temperature of the glue films (Ta) are chosen as variables; the factors are constant: time drying after the first application of the adhesive film (20 min) and the activation time of the adhesive films (30 s) (table 2).

TABLE 2. Factor variation levels

Levels of variation	Variable factors	
	Drying time (tc), min; (X1)	Activation temp (AT), °C; (X2)
Max (-)	20	110
0	30	130
Min (+)	40	150

Plan of the experiment is in the table as follows 3:

TABLE 3. Experiment Plan

№ Experiment	X1	X2	g_{peel}	№ Experiment	X1	X2	g_{peel}
1	-	-	36,6	6	0	+	49,3
2	-	0	38,5	7	+	-	38,4
3	-	+	40,4	8	+	0	46,2
4	0	-	40,6	9	+	+	49,8
5	0	0	42,5				

Using the STATISTICA 6 program, a mathematical model was obtained in coded values of the variables, which shows the dependence of the adhesive bond strength during peeling, during the drying time after the second application of the adhesive film (tc) and the activation temperature of the adhesive films (Ta).

The resulting equation has the following form:

$$g_{peel} = 42,5+3,2X1+4,0\ X2+1,9\ X1\ X2 \quad (3)$$

It can be seen from the equation that with an increase in the activation temperature and the drying time of the adhesive film, the durability of the adhesive bonds increases. The activation temperature has the greatest influence on the durability index.

In accordance with the resulting model, a graph is built that allows determining the rational parameters of gluing genuine leather "Natural" with thermoplastic elastomer (Figure 1).

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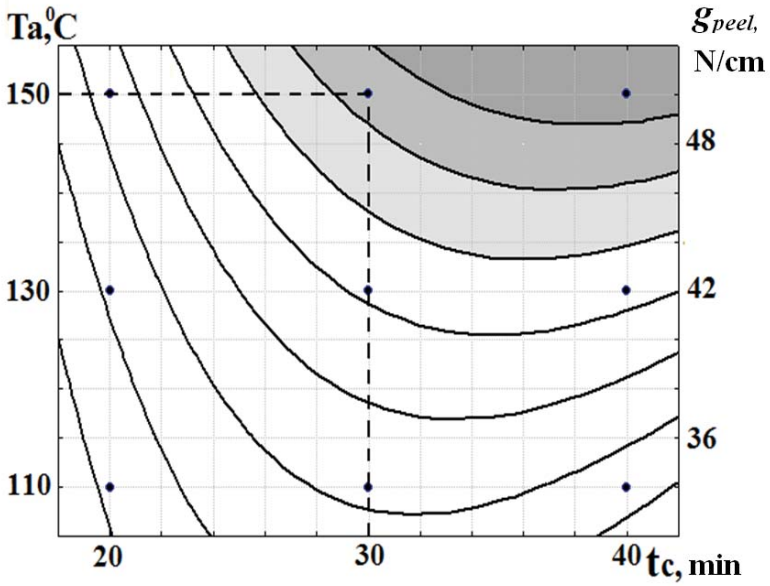

FIGURE 1. Cross-sections of the surfaces of the adhesive strength indicator

The resulting graph shows that the maximum strength of the adhesive bond (more than 49 N / cm) in the studied intervals is achieved when the duration of drying the adhesive film after the second spread is 30 and 40 minutes and the activation temperature of the adhesive film is 150C. Taking into account the need to reduce the time of the production cycle of making shoes, we recommend the drying time after the second application of the glue film to be 30 minutes and the activation temperature of the glue films - 150°C as the optimal gluing modes.

CONCLUSION

Thus, the studies carried out have shown that gluing genuine leathers with synthetic materials of the bottom of shoes and polyurethane glue-solution, and polyurethane glue-dispersion allows achieving standard durability.

At the same time, the use of polyurethane dispersion glue for performing sole supporting operations in shoes with upper parts made of genuine leather made it possible to obtain higher durability values compared to the traditionally used glue-solution. Of the sole materials under consideration, leather-like rubber compared to thermoplastic elastomer showed better adhesion properties, regardless of the type of glue used.

For samples with the maximum permissible adhesion strength (GL art. "Natural" and TPE "Solen"), using the mathematical method of planning the experiment, the optimal modes of the process of adhesion were obtained with polyurethane adhesives-dispersions.

Thus, the expediency of using polyurethane adhesives-dispersions for gluing soles made of synthetic materials with the tops of shoes made of genuine leather has been experimentally proven, since they are not only more environmentally friendly, but also allow achieving high values of the durability of the soles.

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