Analysis of the quality of modern polymer materials of sole.

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Abstract. Modern polymer sole materials used in the molding of the sole in the production of shoes are considered. A qualitative analysis of the composition of the compositions used was carried out. The positive and negative characteristics of the resulting products are revealed. In the course of the analysis, a table was created comparing the characteristics of the materials considered for the optimal and effective choice of production material in the shoe industry.

1 Introduction

Today, the shoe industry is an important branch of the national economy, producing consumer goods.

A special feature of the injection molding method of fastening is that the process of fastening the bottom of the shoe is combined with its molding. Such shoes do not have any mechanical fasteners of the sole to the upper of the shoe (nails or threads), and there is also no use of chemical connectors, such as glue. [1]

Sole polymer materials are divided into the following groups (Figure 1):

Fig. 1. Groups of sole polymer materials.

Rubbers based on various rubbers

Compositions based on ethylene polymers with vinyl acetate (EVA)

Injection molded polyurethane compositions

Compositions based on thermoplastic elastomers

Compositions based on plasticized PVC

Thermoplastic polyurethane compositions
The widespread use of polymer materials as a basis for the manufacture of shoe soles is primarily due to the low price of polymers used in the shoe industry, which significantly reduces the price of the finished product in comparison with shoes with soles made of natural materials. Another significant factor in the prevalence of shoes with polymer soles today is the specific physical and mechanical properties of polymer sole materials, which are superior in many respects to natural leather, wood, etc., also used for the production of shoe soles.

These sole compositions have different properties. However, even within each group, materials of different structures and with different physical and mechanical characteristics are produced. The groups of sole polymer materials are considered below.

2 Rubber sole

According to statistics, about 30% of all shoe soles in the world's shoe production are made of rubber. This material is most often used in the production of special footwear soles, it is slip-resistant, durable, frost-resistant.

Rubber for soles is made from the main component-rubber and other auxiliary ingredients such as: fillers, vulcanizing substances, vulcanization accelerators and their activators, softeners, antioxidants, pore-forming agents, dyes and pigments, regenerates.

All these components form a rubber compound and are included in it in certain quantities. Various powdery materials are used as fillers, such as soot, kaolin, chalk, lignin, diatomites, magnesia carbonic acid, talc, etc. Fillers increase the yield of rubber and reduce its cost.

3 Soles made of thermoplastic rubber (TPR, TPR)

Thermoplastic rubber is a shoe rubber that consists of synthetic rubber, which is more durable than natural, but at the same time retains the properties of elasticity.

Thermoplastic rubber has fairly average density properties and specific gravity, and this is an advantage. Soles made of it are not slippery, have good cushioning properties, are quite light in the standard version of manufacture, and in the new generation of the material, the weight is reduced significantly. [3]

4 The soles on the basis of plasticized PVC

For direct casting of the bottom on shoes, the most effective materials are injection-molded polyurethanes and PVC-plasticates.

Polyvinyl chloride (PVC) is obtained by polymerization of vinyl chloride at temperatures from 20 to 100 degrees with peroxide initiators.

To improve the elastic properties of soles, plasticizers such as acid esters (phthalic, sebacic and adipic) are introduced into the polymers. To increase the resistance to external influences, stabilizers (barium, cadmium and other fatty acid salts) are introduced into the composition, as well as converters, dyes and other ingredients change the properties of the polymer.

PVC soles are produced by injection molding. According to the structure of the material, they can be monolithic and porous-monolithic (microporous) and are mainly used for walking shoes and sports style shoes.

The advantages of PVC soles include the following:
- high strength and wear resistance (due to the high density of the material);
- high frost resistance (which causes the use of soles for the manufacture of winter shoes);
- high flexibility and elasticity;
ease of manufacture (the material allows you to add almost any plasticizers to the composition, which allows you to seriously expand the range of its application—from special shoes to children's shoes).

Among the disadvantages, we can note a fairly large weight (due to the high density of the material). Also, over time, plasticizers can begin to evaporate from the material, which can lead to a loss of elasticity, the appearance of cracks, and a decrease in frost resistance.

5 Soles made of polyurethane (PU)

Polyurethane is a promising material for use in the production of shoes.

The different ratio of the components of the polyurethane composition allows you to obtain different properties of molded polyurethane soles: semi-rigid, of different thickness, quite light, heat-proof; rigid and solid microcellular, imitating hard wood, used for the production of summer shoes such as clogs. [4]

Products made of injection molded polyurethanes are made by liquid molding, which combines in one process the production of a high-molecular polymer and the molding of products from it.

Polyurethane soles are characterized by reliability, exceptional wear resistance, good mechanical memory, low coefficient of friction, abrasive resistance, elasticity, resistance to deformation and aggressive environments, and resistance to sticking. Suitable for operation at temperatures in a wide range. Due to its acid resistance, wear resistance, oil-and-gas resistance, and high dielectric properties, injection-molded polyurethane perfectly replaces rubber.

However, due to the porous structure, the polyurethane sole has a poor grip on snow and ice, so winter shoes with a PU sole are very slippery. Also a disadvantage is the high density of the material and the loss of elasticity at low (-20 degrees) temperatures. As a result, there are cracks in the places where the sole bends, the rate of occurrence of which depends on the characteristics of the operation of the shoe, in particular, on the gait of a person, the degree of his mobility and other factors.

Due to its high adhesive properties, injection-molded polyurethanes are the most effective material for direct casting of the bottom on shoes. This method produces shoes for outdoor activities, walking, and many types of casual sports shoes.

6 PU/PU-outsole – outer sole on a dual-layer polyurethane

To give additional strength, many manufacturers produce two-layer PU soles with a second running layer, more monolithic, thereby increasing the weight of the sole and the sliding of the running surface.

The running layer is denser in composition than the second, and the intermediate layer is foamed, cushioning, and lighter. [5] PU/The PU sole is very slippery, so it is recommended to use shoes with such a sole indoors. The sole provides flexibility of the shoe, increased wear resistance, shock-absorbing properties (reduction of shock loads when walking). The temperature range of use is similar to the PU sole—from -35°C to +80°C.

7 Thermoplastic polyurethanes (TPU)

TPU is a modern material of the group of polymers (polyurethanes), made on the basis of polyesters.
In the manufacture of composite materials, special-purpose ingredients, as well as stabilizers, fillers, plasticizers, etc., are either introduced into the original components or added to the thermoplastic polyurethane before processing into products.

Modification of the properties of urethane thermoplastic elastomers can be carried out by combining them with other polymer materials: chloroprene rubber, copolymers of acrylonitrile with vinylidene chloride, vinyl chloride with vinylidene chloride, butadiene with acrylonitrile, phenol formaldehyde, coumaronoinidene resins and other polymers. [6]

Sole compositions based on TPU are divided into non-porous and porous, standard and with increased mechanical properties, elastic and rigid. Depending on the purpose of the shoe and the application of the compositions in the details of the bottom, materials based on TPU are produced for the outer layers of the soles, forming the soles entirely.

The advantages of the TPU soles are the soles with a deep tread, which provide excellent grip on the surface. Also, the advantages of TPU are high wear resistance and resistance to deformation, including cuts and punctures.

Disadvantages of TPU soles - due to the high density of thermal polyurethane, the weight of the sole is quite large, and the elasticity and thermal insulation leave much to be desired.

8 Thermoplastic elastomers (TPE) or thermoplastic elastomers

Thermoplastics can also be called thermoplastic rubber, which is a mixture of polymers or certain compounds that exhibit their thermoplastic properties at high temperatures during the melting process.

This type of sole is made of thermoplastic rubber, elastomer. Currently, TEP is the most popular sole. It combines the elastic properties of rubber (the ability to highly elastic deformations and high frost resistance) and the thermoplastic properties of thermoplastics (high fluidity in the molten state and the ability to be processed by injection molding) For casting the bottom on the basis of TEP, injection molding machines "Industrial service mini 2E" and "Crom 16"are used.

By changing the formulations of thermoplastic elastomers, you can adjust their basic physical, mechanical and consumer properties: hardness, elasticity, oil and gas resistance, frost resistance, fire resistance, color. Products made of thermoplastic elastomers have a homogeneous structure.

The formulation of the sole compositions is usually a trade secret of the manufacturers. However, the main ingredients of the compositions that determine the physical, mechanical and technological properties of soles based on thermoplastic elastomers are known.

Approximate composition of sole compositions based on thermoplastic elastomers:
- Thermoelastoplast (types DST-30, DST-45RM, DMSTR-50, etc.);
- Thermoplastic polymer (emulsion polystyrene, copolymers of butadiene with styrene, ethylene with vinyl acetate, PVC, chlorinated polyethylene, etc.);
- Fillers (chalk, kaolin, carbon black, mineral fillers);
- Plasticizers (petroleum jelly, naphthenic, transformer, industrial oils);
- Stabilizers (Agidol, the product is NG-2264, inaly, tinuvin, TBTM etc.);
- Blowing agents (CHS-21, microspheres "Expencel", etc.);
- Dyes (titanium oxide, zinc whitewash, pigment concentrates).

The main advantages of the sole based on TEP: it retains elasticity even at the highest temperature, the material is resistant to moderate frosts, retains heat well. The sole made of TEP is not corroded by acids, alkalis and natural organic matter. Shoes with a sole made of thermoplastic elastomer are quite light. Thanks to the porous structure, the sole has a cushioning effect [10].

The main disadvantage of compositions based on thermoplastic elastomers is their low heat resistance.
9 Combined (PU+TPU) polymers

TPU (TPU) is often combined with polyurethane (PU), where the outer layer is TPU, and the intermediate damping — polyurethane low density. From TPU, it is possible to manufacture shoes with a deep tread, largegrunt hooks. Special shoes with TPU soles/PU also resists sliding as well as TPU and is better than products made of single-layer polyurethane and, moreover, double-layer; it has less weight than single-layer TPU, but is heavier than shoes with PU soles, but, at the same time, strength characteristics at a height. This sole will not break and will not burst in the cold. The polyurethane layer insulates the safety shoes well and is well bonded to the top of the safety shoes billet.

Realizing the disadvantages of polyurethane and thermo-polyurethane soles, the manufacturers decided to combine the positive aspects of each type. The bottom surface is in contact with the surfaces made of TPU, and the top, which is attached to shoes made of polyurethane. These soles can be identified by its kind of a layered look, the visible structure of different materials.

All the best qualities of these two materials are present – excellent thermal insulation properties due to porosity, as well as excellent adhesion to any type of surface and increased wear resistance. Soles of this type are quite light, which reduces the load on the spine and joints of the legs. Shoes with such soles are suitable for both winter and demi-season.

Due to the fact that the sole is integrated from two parts, for the production of each of which you need your own equipment and technology, the production of such soles is quite an expensive process. As a result, the price of such soles is already more expensive. [7-9, 11]

The combination of strong and frost-resistant TEP and light and soft PU makes the material especially valuable. The sole of TEP/PU combines all the advantages of both materials, in addition, it is available in a variety of colors. This is especially important in the production of bright and beautiful children's shoes.

10 Soles made of ethylene vinyl acetate (EVA, EVA)

Ethylene Vinyl acetate (EVA) — this substance belongs to polyolefins, it is obtained as a result of copolymerization of ethylene and vinyl acetate monomer. The vinyl acetate content determines the mechanical properties of the copolymer, as well as its type (elastomer or thermoplastic). EVA with 10-50% vinyl acetate content is most often used. At 100 % vinyl acetate, polyvinyl acetate (PVAC) is obtained. Due to the high content of vinyl ethylene vinyl acetate, it is highly resistant to oils, solvents, ozone and high temperature. Low-acetate copolymers have properties similar to those of low-density polyethylene. In addition, the properties of ethylene vinyl acetate copolymers depend on the formation of side chains and molecular weight.

This composite polymer material is characterized by lightness, excellent shock-absorbing properties and a high level of environmental safety. It is used mainly in children's, home, summer and beach shoes, and in sports shoes - in the form of inserts, because it is able to absorb and distribute shock loads. [8, 12-14]

Over time, EVA soles lose their cushioning properties. This is due to the fact that the pore walls are destroyed, and the entire mass of EVA becomes flatter and less elastic. Also EVA is a slippery material. To remove this drawback, manufacturers make a deep tread in the sole.

11 SPU/PU-double-layer soles

The modern chemical industry has developed a material called "special polyurethane", which has a high density and viscosity, like TPU, well resists slipping, frost-resistant, strong and
durable, resistant to abrasion, the sole with a running layer of it can be with large and deep ground hooks.[15-16] This material is sometimes called "rubber-like polyurethane", HD PU, or Velcro. Special footwear equipped with SPU/PU soles easily bypass TPU/PU by numerous qualities. Great for all-season safety shoes. Not thermoplastic [17-19]. The running surface in combination with the intermediate polyurethane combines the best characteristics of these materials. SPU, as a material, is more expensive than PU, but cheaper than TPU. The sole made of "pure" special polyurethane is not used because of its large weight and high price, but in combination with an intermediate layer of foamed polyurethane, it is an excellent sole for special shoes for all seasons.

12 Conclusion

Based on the individual analysis of modern polymer materials, a comparative table of different types of soles for shoes was created, taking into account all the current characteristics of the finished product (Table 1):

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Rubber</th>
<th>PVC</th>
<th>PU</th>
<th>PU/PU</th>
<th>TPU</th>
<th>TPE</th>
<th>TPU/PU</th>
<th>EVA</th>
<th>SPU/PU</th>
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<td>2</td>
<td>2</td>
<td>1</td>
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<td>1</td>
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<td>2</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>2</td>
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<tr>
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<td>2</td>
<td>0</td>
<td>2</td>
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<td>2</td>
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<td>2</td>
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<td>Resistance to repeated bending</td>
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<td>1</td>
<td>2</td>
<td>0</td>
<td>2</td>
</tr>
</tbody>
</table>

The table uses special symbols: "2" - high values,"1" - average values,"0" - small and low values of indicators.

With the help of this table, it is possible to select the actual material for the manufacture of the sole, taking into account the requirements of the buyer and the influence of the environment.

Sole polymer materials have a complex of physical and mechanical, technological and operational properties, which determines the possibility of their use for the manufacture of parts of the bottom of shoes for various purposes.
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