

Main Aspects of Processing Secondary Polymer Raw Material for Creating Technology for Manufacturing Shoe Sole

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ABSTRACT

In the article the main aspects of processing secondary polymer raw materials are analyzed. The essence of the chemical modification of the polymer base is revealed, which is one of the cardinal ways to solve the problem of creating polymer composite materials with a controlled set of properties. Particular attention is paid to composite materials.

The development of modern science and technology is unthinkable without the use of polymeric materials. At present, there is not a single branch of the national economy where plastic masses are not used. The bulk of plastics produced in the world falls on thermoplastic materials: polyolefins, polyvinyl chloride and polystyrene plastics.

Polyvinyl chloride is one of the largest and most widely used synthetic polymers, which is largely due to its high mechanical strength, chemical resistance in various environments, high elasticity, incombustibility (which is due to the content of up to 56.8% combined chlorine), good electrical and thermal insulation properties, relatively low cost of raw materials, the possibility of varying properties over a wide range [1–9].

PVC-based materials are used for the manufacture of technical and medical products, electrical insulating coatings, packaging, artificial leather, shoes, linoleum, and others.

The tightening of conditions for storage and disposal of waste containing polymeric materials complicates the activities of enterprises in the leather and footwear industry. For the production of competitive products, it is necessary to use artificial materials, which, in turn, creates difficulties for enterprises due to the multicomponent composition of these materials and the presence of elements in them that are not biodegradable for a long time during traditional burial in the soil at municipal solid waste (MSW) landfills. To solve this problem, it is advisable not only to reduce the amount of waste generated, but also to develop and implement processes for their recycling. One of the promising areas for expanding the range and reducing the cost of footwear is the use of materials based on production waste. This ensures that economic benefits are obtained by increasing the scale of production with an unchanged size of the raw material base and a partial solution to the environmental problem.

Products made of plasticized PVC from these compositions, as a rule, are homogeneous in structure, which determines the uniformity of properties over their cross section. Meanwhile, during operation, their surface layers are mainly exposed to external influences. This is especially evident in the example of products subjected to intense surface wear: linoleums, shoe soles, etc. The low wear resistance of PVC compounds does not provide the possibility of their use in the production of soft, elastic products used in friction-rolling and friction-sliding units, for example, tires for children's bicycles [10–15].

One of the cardinal ways to solve the problem of creating polymer composite materials with a controlled set of properties is the chemical modification of the polymer base (grafting of monomers onto PVC, grafting of vinyl chloride onto other polymers). However, under conditions of work for a specific consumer and often the release of relatively small batches of material, this way is not always economically justified (requires special reactor equipment, environmental issues, etc.). In this regard, the development of methods for increasing the wear resistance of PVC-based materials during their processing is of great importance. An effective way to partially solve the problem of increasing the wear resistance of products made of polymeric materials is to control the composition and structure of their surface layer. Works are known on the surface treatment of finished products from polymers by chlorination, impregnation with reactive oligomers, metallization, etc. However, the objects of impregnation were mainly products made of unplasticized PVC. It should be noted that these methods of surface hardening of plastic products are very laborious, cumbersome and inefficient.

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However, at present, the use of PVC is gradually limited, which is primarily due to environmental problems that arise during the operation of products, their disposal and recycling. During the aging of PVC-based polymers, along with the loss of physical and mechanical properties, there is a negative impact on the environment and humans, due to PVC dehydrochlorination processes, which increase at a temperature of 50–80 °C (highly toxic chlorine-containing polyaromatic compounds are formed).

This determines the relevance of the problem of developing safe technologies for the disposal and processing of waste products containing PVC. The main methods of waste disposal of polymeric materials include: thermal decomposition in an inert atmosphere (pyrolysis); burning; decomposition to obtain the original low molecular weight compounds (depolymerization); recycling (injection molding, extrusion, pressing, etc.) [23-28] .

The most difficult issues are the disposal of a mixture of polymer waste containing, along with PVC, polyolefins (polyethylene, polypropylene), polystyrene, polyurethanes, polyamides, etc.

An analysis of the existing technologies for the neutralization of a mixture of polymeric wastes allows us to conclude that it is expedient to use thermal processing based on degradation processes in an inert atmosphere.

During the pyrolysis of polymers, gases are formed, some of which are capable of condensing to form high-calorie liquid fuels, non-condensable gases containing methane and hydrogen, which have

a high calorific value, and carbonizate , which can be used in technological processes. The high energy potential of pyrolysis gases allows the recycling process to be carried out in an autothermal mode.

Among all shoe materials, natural leather occupies a special *place* . Natural leather is obtained from various leather raw materials. *Raw hides* are animal skins suitable for leather production. *The skin* is called the outer cover, removed from the carcass of an animal (steam skin) and preserved from decay (preserved skin). The main raw materials for the production of leather are the skins of mammals, mainly domestic animals (cattle, horses, pigs, sheep, goats, etc.) and less often wild animals (moose, deer, wild boars, etc.). Skins of reptiles (snakes, lizards, crocodiles), marine animals (walruses, seals, dolphins, whales, etc.), fish (cod, catfish, sharks, eels, etc.) and birds (ostrich, etc.) are processed in small quantities .) [29-31] .

Depending on the type of animal, the mass of the skin in a paired state, its area, raw hides are divided into small , large and pork. *Small leather raw materials* include the skins of calves of cattle (sklizok, calf, outgrowth), foals (sklizok, foal, markup), sheep, goats (domestic and wild), camels and deer calves. *Large leather raw materials* include the skins of adult animals: cattle (half-skin , bull, bull, bull, yalovka), horses, buffaloes, donkeys, mules, camels, deer, elks. *Pig skins* of domestic and wild animals are divided by area into small ($30-70 \text{ dm}^2$), medium ($71-120 \text{ dm}^2$) and large (over 120 dm^2).

Skins that are in a paired state *are preserved* by drying, salting, freezing and other methods to preserve their original properties, which can be lost under the action of microorganisms before entering the leather industry. The essence of canning is to create conditions unfavorable for microbial and enzymatic processes to occur in the skin. This is achieved by removing moisture from the skin, lowering the ambient temperature, modifying skin proteins with various chemicals [32].

The properties of the finished leather depend primarily on the structure and properties of the dermis, which is isolated as a result of the technological processes of leather production. The hairline, epidermis and subcutaneous fat layer are removed.

The dermis makes up the main layer of the skin (84-86% of its thickness). It distinguishes networks of fibers from collagen and elastin proteins and transitional formations (formations) of these fibrous proteins. Collagen formations predominate over all the protein components of the dermis. Intertwined with each other in different directions, bundles of collagen fibers form a complex tissue of the dermis.

There are significant differences in the structure of the dermis in thickness , which is the basis for dividing it into two layers - papillary and reticular. *The papillary layer* occupies the upper part of the dermis and is formed from connective tissue components (fibers, cells), among which are hair follicles, sweat and sebaceous glands, vessels of the circulatory system and ducts of the lymphatic network. The bundles of collagen fibers in the papillary layer are thin and randomly arranged. The lower *mesh layer* of the dermis is formed from thicker bundles of collagen fibers, forming a dense and strong weave - ligature. There are few cellular elements and elastic fibers in the reticular layer. Such a fibrous structure of the mesh layer provides it with a decisive role in the formation of the strength and elastic-plastic properties of the skin. The thickness of this layer is not the same in different parts of the skin and varies depending on the species and age of the animal. Thus, the share of the mesh layer of the skins of young cattle accounts for 50-60% of the total thickness of the dermis, and in adult animals - 65-80%.

After removing the hairline and epidermis, the dressed leather has a certain natural pattern of the front surface, characteristic of this type of raw material, which is called *mereya*. Mereya serves as a sign in recognizing the raw materials from which the skin is made.

The structure and properties of the skin cover depend not only on the species, sex and age characteristics of the animal, the conditions of its development, but are also different in the topographic areas of the same skin. *Topographic* parts of the skin are called, corresponding to certain

parts of the animal's body and differing in structure, chemical composition and physical and mechanical properties. These differences significantly affect the commercial properties and quality of the leather, determine the production purpose of the skin, the nature of the technological processes of its processing, and are also taken into account when cutting leather into certain parts of footwear.

Depending on the location of the skin section, its thickness, density, mechanical strength, extensibility, and arrangement of structural elements change.

The range of *synthetic leathers* for shoe uppers is extremely wide, which is explained by a very good set of properties. The disadvantages of this material are the low ability to mold to the foot when wearing shoes, insufficient hygroscopicity and moisture transfer. In order to eliminate the noted shortcomings, it is promising to use specially treated waste from leather production for the fibrous base of synthetic leather. Leather waste is converted into fibers with a length of 20 to 40 mm by chemical or physical-mechanical methods. Fibers, consisting mainly of the protein substance collagen, have high rates of hygroscopicity, strength, extensibility. To make the base, collagen fibers are mixed with polyamide, polyester or polypropylene fibers. Synthetic leathers with such a basis have satisfactory indicators of hygienic and physical and mechanical properties.

Three-layer synthetic leathers include corfam (USA), patora and hitellac (Japan) and many others, which differ from each other in the nature of the fibers and the type of base, the feedstock of polyurethane compositions, and the features of the production technology. Two-layer synthetic leathers - xyle (Germany), clarino, eikas (Japan), gentra (USA), etc. - also differ mainly in the fibrous base materials. Two-layer synthetic leathers are more ductile compared to three-layer ones, have a slightly lower density and stiffness. A representative of single-layer synthetic leathers for uppers is porvair (Great Britain). It is a film (without a base) consisting of a porous inner and a monolithic outer layer of polyurethane compositions, and therefore has an extremely high extensibility [33].

Some of the best synthetic leather brands today are: SKNI — new generation synthetic leather (Russia), sofrina (Japan); Synthetic skins on a fibrous collagen basis are widely used. The structure of the SKNP base consists of bundles of ultrathin fibers 0.14–4 μm thick with a high packing density, linked into split knots, but retaining the mobility of the structural elements relative to each other. The ratio of the mass fractions of the fibrous base (impregnated with a polymer binder) and the polymer coating is 95 : 5, the thickness of the coating based on polyurethanes is 60–70 μm . The properties of SKNP are close in value to the properties of natural leather. Synthetic leather sofrina has a similar structure - the base, consisting of bundles of ultra-thin synthetic fibers, with a very thin polyurethane coating. The deformation-strength and hygienic properties of this material and natural leather are close, and in terms of operational durability, sofri does not surpass natural leather.

Synthetic leather on a fibrous collagen basis (“pressed leather”) is obtained from leather waste - (leather scraps) mixed with polyamide, polyester or polypropylene fibers. By chemical or physical-mechanical methods, leather waste is converted into ultra-thin fibers, after which a canvas is formed, subjected to needle punching and heat shrinkage. Coating is possible by direct and transfer methods. Trim synthetic leather with an airbrush or mesh roller, can be embossed. Pressed leathers are resistant to abrasion, repeated bending, elastic at low (up to -50 °C) temperatures, resistant to solvents and oils. They are used for both uppers and linings.

Artificial and synthetic lining leathers must have high vapor permeability, hygroscopicity, perspiration resistance, as well as high abrasion resistance and low stiffness. The range of these materials is quite diverse both in terms of the type of base and the type of coating. As a lining, vinyl artificial leather -T, elasto-leather -T, amidoelasto-leather -T, novellet (Finland), Zeef (Germany), duport (USA) and others are used.

Artificial midsole materials include materials used for rigid heels and toe caps. They must have rigidity and elasticity, the ability to take the shape of the heel or toe part of the shoe, resistance to moisture and abrasion.

Along with shoe cardboards, for the manufacture of hard backs and toes, artificial materials with a fibrous base or without a base are used: shoe nitro-leather -T, thermoplastic materials (thermoflex , sTallinn-400, etc.), elastic materials. *Thermoplastic materials* are produced , as a rule, multilayer , on a non-woven or woven basis, impregnated with a mixture of latexes and coated with a polymer film. The materials are easy to shape, water -resistant , soften during the production process and firmly glue ! vayutsya with leather and fabric; moreover, no adhesives or solvents are required. Thermoplastic backs and toes best meet the requirements of shoe technology with progressive methods of molding the top using thermal influences .

Elastic materials are used for toe caps in textile, unlined , and women's chrome shoes with tapered toe. They have a small thickness and differ from toe socks made of other materials in flexibility and elasticity. A promising direction is the introduction into the production of shoes of the method of molding under socks made of *hot melt adhesive*, which softens under the influence of high frequency currents.

To artificial and synthetic materials for bottom "shoes include rubber, plastics, thermoplastic elastomers (TEP); as well as shoe cartons.

Rubber is a fairly common material used for the manufacture of shoe bottom parts. Shoe production uses: molded rubber parts (soles, heels, heels, etc.); rubber plates, from which shoe parts are cut down and called stamped ;

Rubbers of various types are formed during the vulcanization of raw rubber compounds consisting of natural or synthetic rubber, a vulcanizing agent and various additives (ingredients). The composition of mixtures includes up to 20 components, the number and ratio of which are selected depending on the technological and operational properties and structure that rubber should have in accordance with its purpose. The vulcanizing agent is most often sulfur, which reacts chemically with rubber and turns it into rubber. Of the additives, regenerate is important (used, as well as defective crushed rubber products); fillers (soot, kaolin, chalk, fiber processing waste, synthetic resins); softeners (mineral oils, stearin, rosin, etc.); antioxidants (paraffin, ceresin, amines, etc.); pore-forming agents (to obtain porous rubbers - ammonium carbonate, sulfoazides and sulfohydrazides , porophores , etc.); pigments and dyes (soot is used to obtain black rubbers; oxides of zinc, titanium, iron, etc. are used for colored rubbers).

The most important classification features are the structure and composition, which determine the properties and purpose of rubber of each type.

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