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Study of the Resistance of Shoe Sole Compositions to various Aggressive Environments

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ABSTRACT
In this paper, the stability of shoe sole compositions to various aggressive media was studied: in water, in gasoline, in diesel fuel, in antifreeze, in industrial oil, in acetone and ethyl acetate. The kinetics of swelling of polymer compositions in various aggressive media for 3 days was determined. It has been determined that the type of filler in the composition has a significant impact on the oil and petrol resistance of the material, therefore, a correctly selected filler will make it possible to significantly improve the ability of sole materials to resist aggressive media. Samples of sole materials were subjected to natural, thermal and light aging. It has been proved that the obtained compositions for casting parts of the bottom of the shoe well withstand tests for natural and artificial aging and can be recommended for use in working conditions with increased thermal and light exposure.

Key words : copolymer of ethylene with vinyl acetate, suspension polyvinyl chloride, filled composition, chemical resistance, aggressive environment, resistance to natural.

1. INTRODUCTION

When developing prescription and technological parameters for the production of the bottom of special shoes for hot operating conditions from compositions based on domestic suspension polyvinyl chloride and ethylene-vinyl acetate copolymer, it is necessary to take into account the influence of various aggressive media on the quality of finished products.

It should be noted that the sole materials being developed should meet the requirements of consumers to the maximum extent while ensuring the high quality of the products. For products operating in harsh climatic conditions, it is necessary to introduce an additional check for climatic resistance.

From a practical point of view, the most important task is to determine and predict the climatic stability of polymeric materials, which is assessed in most cases by changes in the performance properties of the materials under study.

1. MATERIALS AND METHODS

Aging is a factor that determines the durability and reliability of products. Two methods of testing for aging according to GOST 9.708-83 were used in the work:

- natural aging method;
- method of artificial aging.

Natural aging is understood as a change in the values of the physical and mechanical properties of materials over time. Artificial aging is understood as a change in the physical and mechanical properties of materials as a result of exposure to factors that accelerate this process. The artificial aging of the polymer composition was determined using a solar collector D-50354 Huerth (Germani) on xenon emitters providing a luminous flux with a surface energy density of the integral radiation of 1000 W/m^2. The essence of the method lies in the fact that the samples are exposed to artificially created climatic factors in an artificial weather apparatus for a given duration of testing and the resistance to the specified effect is determined by changing the physical and mechanical properties and appearance. A description of the methodology for testing for artificial aging is given in the source [1]-[5].

Swelling in liquids is one of the characteristic properties of macromolecular compounds. The change in the properties of thermoplastic materials during swelling is associated with the penetration of liquid molecules into the intermolecular space of the polymer and the weakening of its intermolecular bonds. The resistance of materials to swelling in liquids depends on the nature of the initial polymer and its content in the composition, on the properties and dosage of ingredients, the conditions for obtaining and processing the mixture, etc. In this case, the properties of the liquid in which swelling occurs, the duration and temperature of the process are of great importance.

The degree of swelling of a thermoplastic polymer composition based on suspension polyvinyl chloride and an ethylene-vinyl acetate copolymer in various aggressive media was determined by the formula:

$$\alpha = [(m - m_0)/m_0] \times 100$$

where a - is the degree of swelling, %

m - is the mass of the polymer after swelling, g;

m_0 - is the mass of the polymer before swelling, g.

Swelling for 3 days was subjected to 3-5 samples of various shapes weighing 0.1 g for a polymer composition based on suspension polyvinyl chloride and an ethylene-vinyl acetate copolymer (PVC-S/SEVA) in water, oil, diesel fuel, gasoline and antifreeze.

The procedure for testing thermoplastic polymer compositions for swelling in liquids and corrosive media is described in [2], [3].

The processes of interaction of polymers with low molecular weight liquids, leading to swelling and dissolution of polymers, are of great practical importance, both in the processing of polymers and in the operation of polymer products.

In practice, spontaneous dissolution of polymers is often observed, but this process has a characteristic feature: before dissolving, the polymer swells, i.e. absorbs low-molecular liquid, increasing in mass and volume.

From a practical point of view, it is important to know the ability of "thermomechanically" mixed polymers to swell in various aggressive media. This ability is evaluated by the degree of swelling, which is expressed as the amount of liquid absorbed by the polymer, per unit mass of the polymer.

Taking into account the possible cases of contact of the developed polymeric sole materials with aggressive media during the operation of shoes, the chemical resistance of the samples during long-term (2-72 hours) immersion in water, gasoline, diesel fuel, antifreeze, industrial oil, acetone and ethyl acetate

The studied compositions were assigned indices

Composition index	The composition of the plantar composition
1	Unfilled composition based on PVC-S:SEVA-18
2	Filled composition based on PVC-S:SEVA-18:M:K:T:PEV:PM:ED
3	Filled composition based on PVC-S:SEVA-18:T:PEV:DBF:ED
4	Filled composition based on PVC-S:SEVA-18:M:K:T:PEV:DBF

Table 1 shows the kinetics of swelling of polymer compositions in various aggressive environments for 3 days. Based on the data in Table 1, the curves of the swelling kinetics of the base composition were plotted (Figure. 1). Figure 1 shows the resistance of the base sole composition to swelling in various aggressive environments. The type of solvent was chosen based on considerations of checking the sole composition for oil-benzo resistance [2,3]. Analyzing the curves (Fig. 1), it can be noted that the most aggressive medium out of the seven used for the base composition is acetone, followed by: ethyl acetate, gasoline, diesel fuel and industrial oil. All dependences are typical for swelling curves, i.e. first, the solvent is absorbed, and then saturation occurs and the mass does not change.

Table 1: The degree of swelling of polymer compositions over time in various aggressive environments

Aggressive environment	Time, hour / composition index	Degree of swelling. Q,%					
		2	4	8	24	48	72
1	2	3	4	5	6	7	8
Water	1	Samples from 2 hours to 3 days of exposure at a temperature 23 ± 2^0 C in water absolutely do not swell					
	2						
	3						
	4						
Petrol	1	1,8	2,7	3,4	3,8	4,0	4,0
	2	1,6	2,5	3,3	3,6	3,7	3,7
	3	1,5	2,6	3,2	3,4	3,6	3,6
	4	1,7	2,4	3,0	3,3	3,4	3,4
Diesel fuel	1	1,1	1,8	2,3	2,9	2,9	2,9
	2	1,0	1,5	2,0	2,5	2,5	2,5
	3	0,8	1,3	1,9	2,3	2,3	2,3
	4	0,7	1,1	1,7	2,1	2,1	2,1
Antifreeze	1	Samples from 2 hours to 3 days of exposure at a temperature 23 ± 2^0 C in antifreeze absolutely do not swell					
	2						
	3						
	4						
Industrial oils	1	0,8	1,3	1,7	2,0	2,0	2,0
	2	0,7	1,1	1,5	1,9	1,9	1,9
	3	0,6	0,9	1,2	1,5	1,5	1,5
	4	0,5	0,8	1,1	1,3	1,3	1,3
Ethyl acetate	1	18	41	52	58	58	58
	2	17	37	48	52	55	55
	3	16	35	45	48	53	52
	4	15	36	49	51	56	55
Acetone	1	25	50	58	65	65	65
	2	23	45	56	63	64	64
	3	21	38	43	51	62	62
	4	23	39	46	60	60	60

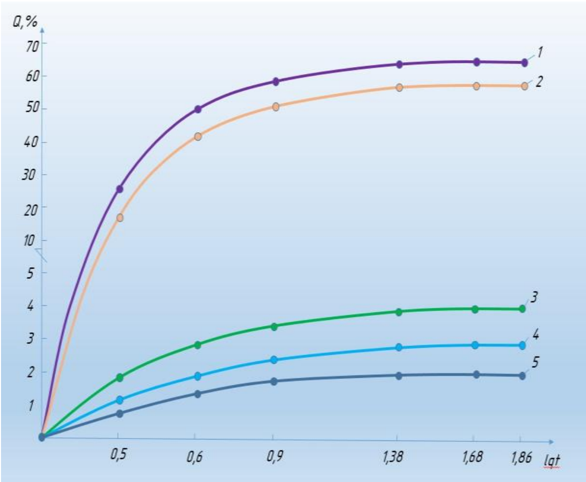

Figure 1. Swelling kinetics of the base composition based on PVC-S:SEVA-18=85:15 in various aggressive media:
1-acetone; 2-ethyl acetate; 3-gasoline;
4-diesel fuel; 5-industrial oil.

Analyzing the obtained results, we can draw the following conclusions:
- the type of filler in the composition has a significant impact on the oil and petrol resistance of the material, therefore, a correctly selected filler will make it possible to significantly improve the ability of sole materials to resist aggressive media;
- acetone and ethyl acetate can be used as solvents for adhesives used to attach soles from the developed compositions;
- the resulting sole materials are actually oil-resistant, which makes it possible to use them for special footwear operated in aggressive environments.

2. RESULTS AND ITS DISCUSSION

The degree of aging of sole materials over time is usually estimated by changes in their main physical and mechanical parameters. Depending on the operating conditions, the impacts experienced on the material, one or more parameters are selected, which evaluate the aging rate of polymeric materials and their performance.
In the work samples of sole materials were investigated for natural, thermal and light aging.
The natural aging resistance of the sole materials was evaluated after 720 hours (1 month), 1440 hours (2 months) and 2160 hours (3 months). The samples were kept under natural atmospheric conditions at temperatures from +20^0 C to +50^0 C. After 1.2 and 3 months, the samples were tested for rupture and their deformation-strength characteristics were evaluated. The main disadvantage of natural aging methods is duration. However, natural aging provides an accurate assessment of the resistance of sole materials to aging under specific climatic conditions.

Changes in the deformation-strength characteristics during natural aging are presented in Table 2**.**

Table 2: Influence of the natural aging process on the deformation-strength properties

Index compositions	**Aging, hour**	**Indicators of deformation and strength properties**		
		G, МПа	**ε rel,%**	**ε res,%**
1	2	3	4	5
1	720	11.9	249	22
	1440	11.7	247	24
	2160	11.3	248	27
2	720	11.3	342	28
	1440	11.2	346	33
	2160	10.9	343	37
3	720	11.4	345	27
	1440	11.4	342	32
	2160	11.3	343	35
4	720	11.5	343	28
	1440	11.3	340	36
	2160	11,2	346	40

An analysis of the results shows that the obtained thermoplastic materials are little subject to natural aging, as evidenced by a slight change in the deformation-strength characteristics. According to the results of tables 2, it is possible to compare the dependences of the base composition (No. 1) based on PVC-S and SEVA with filled polymer compositions (No. 2,3,4) based on them.
It can be seen from the results that the properties of the filled sole material do not change significantly in contrast to the base compound. Consequently, these materials are more suitable for the manufacture of shoe bottom parts used in hot climates.
Methods of artificial aging (thermal, light) make it possible to induce changes in the sole material in a short period of time, which appear in it during natural aging after several years. Table 3 shows the results of the deformation-strength properties of compositions based on PVC-S:SEVA and filled materials based on them from the duration of thermal aging at a temperature of T = 100 ° C for 3 days, which is identical to the change in properties during atmospheric aging in within 5 years.

Table 3: Influence of the process of thermal aging on the deformation-strength properties

Composition index	**Aging, hour**	**Indicators of deformation and strength properties**		
		G, MPa	**ε отн, %**	**ε ост, %**
1	**2**	**3**	**4**	**5**
1	24 48 72	12.0 11.9 11.8	250 248 248	18 19 19
2	24 48 72	11.5 11.4 11.3	350 347 345	25 **26** **27**
3	24 48 72	11.4 11.3 11.2	355 345 340	28 28 29
4	24 48 72	11.3 11.1 11.0	342 340 338	28 29 29

An analysis of the results shows that under conditions of thermal aging, samples of sole compositions exhibit relative stability of properties, which indicates the presence of a certain margin resistance to thermal aging at given temperatures. The non-change in the value of the nominal tensile strength during the first day of thermal aging with a simultaneous slight decrease in the relative elongation and an increase in the residual elongation can be explained, possibly by the formation of double bonds, due to the effect of temperature. In general, the ε_{rel} and ε_{res} are more sensitive to the effects of thermal aging, but the decrease in these indices is within acceptable limits.

In general, the studies of finished samples for thermal aging at a temperature of 100 ° C for 3 days (72 hours) showed that the sole compositions are sufficiently resistant to thermal aging and can be recommended for operation at elevated temperatures.

The results obtained are in good agreement with the results of DSC, DTA, and TGA [6]-[12].

During operation, the details of the bottom of the shoe are subjected, in addition to thermal aging, to light aging, i.e. exposure to ultraviolet radiation.

According to [3]-[5], the destruction of polymeric materials proceeds most intensively when they are irradiated with light of 260-310 nm, which approximately coincides in intensity with solar irradiation.

Table 4 shows the results of changes in the deformation-strength properties of sole compositions from the duration of exposure to UV rays.

Table 4: Influence of light aging process on deformation-strength properties

Composition index	**Aging, hour**	**Indicators of deformation and strength properties**		
		G, МПа	**ε rel, %**	**εres ,%**
1	**2**	**3**	**4**	**5**
1	12 24 48 72	12.0 12.0 11.9 11.8	250 250 250 245	18 15 20 19
2	12 24 48 72	11.5 11.5 11.3 11.3	350 351 355 345	25 25 27 27
3	12 24 48 72	11.4 11.3 11.5 11.3	355 360 358 359	29 25 26 28
4	12 24 48 72	11.3 11.3 11.2 11.1	350 355 347 332	28 28 30 34

3. CONCLUSION

A comparative analysis of the results shows that the aging process is more intense than with thermal aging. And all samples are relatively lightfast systems. The indicator of deformation-strength properties of sole materials for 72 hours of irradiation change within acceptable limits. This is due to the good compatibility of SEVA in the PVC matrix, as well as the presence of light stabilizers in the system, which provide the composition with high resistance to photooxidative degradation.

Thus, the study of sole materials for aging resistance allows us to conclude that the resulting compositions for casting parts of the bottom of the shoe well withstand tests for natural and artificial aging and can be recommended for use in working conditions with increased thermal and light exposure.

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