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IMPACT OF MICROWAVE ENERGY AND LEUCONATE HARDENER ON THE ADHESIVE JOINT STRENGTH

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Abstract. The aim of the study is to increase the bond strength of polychloroprene adhesives for footwear production. The main components of the polychloroprene adhesive composition is nairit NT, petrol BR1 or BR2, ethyl acetate grade A, leuconate. It has been found that leuconate in an amount of 5 % and microwave irradiation will increase a bond strength by 59 %. Modified adhesive composition may be recommended for production of special shoes that can withstand high mechanical loads.

Keywords: polychloroprene, adhesive composition, leuconate, microwave energy, the strength of adhesion.

1. Introduction

One of the conditions for the development of light industry is the creation of high-performance and cost-effective manufacturing processes of competitive products.

Expanding the range of special shoes and improving their functional and performance requirements lead to a search for new technological solutions, optimization of existing shoe adhesives and creation of new processes of gluing shoe parts.

Analysis of Ukrainian and foreign scientists works in the footwear production [1-6] showed the possibility of effective optimization of adhesive compositions and control of physical and mechanical properties of the adhesive joint. A promising area of research is the issue of increasing the bond strength of existing adhesive compositions, through the introduction of additional components of the adhesive system or additional processing of the adhesive joint.

The application of microwave radio wave energy in industry has been considered in many papers [7-9]. The advantages of microwave-heating include the high intensity of the process and three-dimensional uniformity. The possibility of implementation and practical application of new and unusual kinds of heating, such as selective, uniform, ultra-pure and self-regulating opens new prospects for microwave-energy use.

Basing on theoretical information about the microwave-energy and its effect on linking of polymer macromolecules, it is advisable to conduct a study to determine the influence of microwave-energy on the strength of the glue line, that determines the urgency of the study.

2. Experimental

Adhesive line in the shoes of special purpose should maintain a baseline of strength throughout the life of the shoe, not to give off volatile products while hardening and have high physical and mechanical characteristics.

Taking into account physical and mechanical characteristics of modern natural and synthetic materials, their hygienic properties [10] and economic effect of the use of these materials, leather for shoe uppers and rubber for the bottom of the shoe still remain the most suitable in all respects for the manufacture of footwear. Polychloroprene adhesives are usually used for adhesion of rubber soles to leather uppers. That is why adhesive compositions based on polychloroprene were chosen for the research in this paper.

To improve physical and mechanical properties of the existing adhesive compositions and creation of new cost-effective technology solutions of the bonding process of shoes upper and sole, the following researches have been conducted:

– the impact of the adhesive composition changes on the bond strength has been determined;

– the optimization of composition has been carried out; change of the bonding strength of soles in service after three months of wearing has been established;

– the effect of microwave-energy on the strength of the adhesive joint has been studied.

Composition based on polychloroprene rubber (nairit NT) was chosen as the basic adhesive composition, the receipt of which is proposed in [11] and is presented in Table 1.

Table 1

Formulation of basic polychloroprene adhesive composition

Constituent elements	The percentage of the component, %
Nairit NT	14.2
Zinc oxide	1.4
Magnesium oxide	1.1
Modified kaolin	0.4
Diphenylguanidine (DPG)	0.3
Pine soot (DW-100)	0.3
Resin 101 K – phenol formaldehyde	4.2
Ethyl acetate grade A	39.05
Gasoline BR1 or BR2	39.05
Total	100

Adhesive was produced with the help of laboratory mixer. The viscosity of the adhesive is 1.3 s by Hetchinson, bonding ability – 35.9 N/cm at the rate of 26 N/cm.

Application of hardener improves the adhesive and cohesive properties of the glue. To improve the adhesive strength leuconate (20 % solution of 4,4',4''-triphenylmethanetriisocyanate in dichloroethane, which is used as a hardener (curing agent) for cold curing adhesive [12]) was added to the adhesive composition. It was added to the adhesive prior to use, the viability of such glue is 7–8 h. Chemical formula of leuconate is $C_{22}H_{13}N_3O_3$, chemical formula of 4,4',4''- triphenylmethanetriisocyanate is shown in Fig.1.

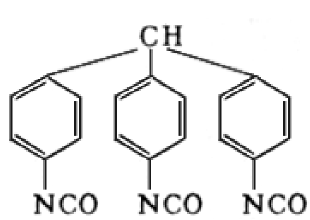

Fig. 1. Chemical formula of 4,4',4'' – triphenylmethanetriisocyanate

The studies were conducted in accordance with standards [12]. Leather samples were prepared from cattle hide of chrome tanning method and rubber of 140 mm length, width 25 mm, length 100 mm, four samples for each study. Working area of the sample was divided into 8 parts. 10 g of glue for the first and second spreading were applied to the prepared samples. Bonding strength was checked in the tensile testing machine RT 250-2M after 24 h exposure at 293 ± 2 K and after three months. Adhesion strength was determined by the formula (1):

$$g = \frac{\sum_{i=1}^{n} P}{b} \quad (1)$$

where g – the bond strength, N/cm; P_1–P_n – layer separation force of the sample on sections, N; n – number of portions equal to 8; b – width of glued sample, cm.

Household microwave-oven was used as the microwave-set, which is a metal chamber that concentrates the high-frequency radiation, frequency of 2450 MHz. It consists of a microwave emitter-magnetron, waveguide, transformer, fan and control circuits.

3. Results and Discussion

When connecting polymers of similar chemical structure the adhesive bond can occur as a result of diffusion processes at the limit of distribution. Eventually interdiffusion of molecular chains of polymers which contact may cause the disappearance of the distribution limit and the strength of the glued polymers will be determined by the cohesion strength. Therefore, the high bonding strength can be achieved with an adhesive based on the polymer chemically homogeneous with materials which are glued together.

It is known that the polychloroprene adhesives have high adhesion to many substrates. Adhesive bond strength depends on the interaction strength of connected materials macromolecules with the adhesive. The strength of intermolecular interaction is determined by the diffusion of chain molecules or their segments, that provides the maximum possible interpenetration of macromolecules for each system, which increases the molecular contact.

The degree of crosslinking of the adhesive film increases and its strength can be determined while stretching as the content of the hardener increases in the adhesive. The optimum amount of the hardener in the adhesive composition was set experimentally adding 3, 5, 7 and 9 % of leuconate and determining the speed of adhesion. When less than 5 % of leuconate was added to the adhesive system, the rate of adhesion reduced by 28–30 %. This lengthens the drying process of the adhesive film and substantially reduces productivity. When you add more than 5 % of leuconate, the rate of adhesion increases by 45–50 %, which is impractical in the production of shoes.

Therefore, the optimum value of the amount of the hardener in leuconate adhesive compositions based on polychloroprene is 5 wt % of the finished adhesive.

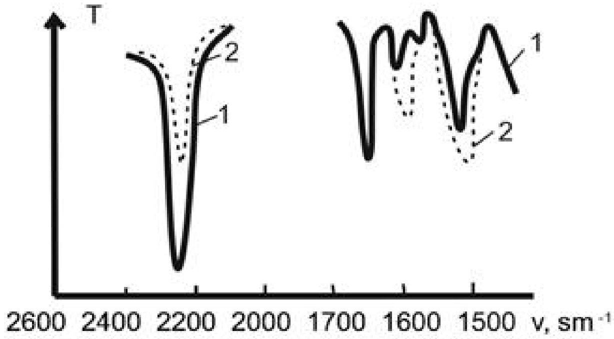

Fig. 2. IR-spectrum of the polychloroprene adhesive compositions: without (1) and with leuconate (2)

Introduction of 5 % of leuconate into the adhesive composition increases the bonding strength up to 49.67 N/cm after 24 h exposure, which is 38.3 % higher than the bonding strength without leuconate. After 3 months the bond strength decreases by ~ 3 % and makes up 48.24 N/cm.

With the introduction of the hardener into the adhesive solution, in our opinion, the chemical interaction between polychloroprene and NCO-groups of leuconate occurs and IR-spectroscopy confirms that fact. Fig. 2 shows that in IR-spectrum of the adhesive film with leuconate the relative intensity of 2277 cm^{-1} band is reduced, corresponding to the vibrations of NCO-group of leuconate, and polychloroprene bands at 1525 and 1510 cm^{-1} become more intense, extend and shifted.

Furthermore, NCO-groups which did not react with the polychloroprene can directly participate in the formation of the adhesive bond with the surfaces of leather or rubber, which are glued together. There are enough known theories of adhesion, including diffusive, explaining film adhesion with the substrate surface [4]. However, none of these theories explain the effect of the microwave-energy on the adhesive joint that connects the sole and the shoe upper.

Even when the adhesion is due purely to the adsorption interactions, the adhesive strength almost never reaches its limit because the active groups of the adhesive molecules never exactly fit the active site of the substrate. However, it can be assumed that with increasing time or contact temperature the laying of molecules will become more sophisticated due to the surface diffusion of macromolecules individual segments. An increase in the density of the molecules packing is possible by improving their mobility. Consequently, the strength of adhesive bonding will increase.

According to the diffusion theory, the strength of the adhesive bonding is caused by conventional molecular forces acting between the mutually interwoven macro-molecules. Microwave-irradiation of polymeric materials leads to the structuring of their composition. The energy of the particles of the primary radiation of industrial accelerators by tens of thousands times is greater than the energy required for the ionization process, *i.e.* stimulation of one chemical bond. Passing in the substance the primary particles transfer energy to numerous molecules, causing initiation and ionization. The initiated molecule, *i.e.* those that have excess of energy (electronic, vibrational or rotational), can transmit it to other molecules.

The secondary radiation and chemical processes in which redistribution of primary absorbing energy occurs, define the structure of the end products of radiation transitions. These are monomolecular processes of fragmentation.

New active particles which arise in this case-free radicals and secondary ions react, thereby changing the molecular structure of the material and the material with new properties is formed. On the basis of these factors the increase of adhesion of the adhesive film with the substrate surface under the influence of microwave-energy has been hypothesized.

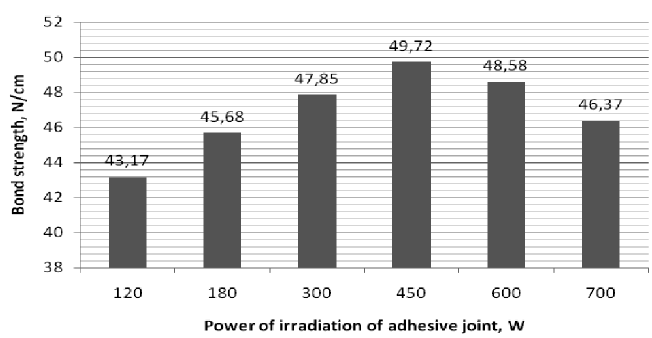

Fig. 3. The effect of microwave irradiation on the adhesive ability

The bond strength increases to a certain level of microwave treatment and then begins to decline (Fig. 3). Influence of microwave irradiation on the adhesive ability of a glue line was determined by different capacities: 120, 180, 300, 450, 600 and 700 W. The optimal power of microwave energy radiation of the adhesive joint is 450 W. It can be seen from Fig. 3, the process of cross-linking of the adhesive film with the substrate occurs to a certain extent, there is an active interaction between the molecules of the material on the surface and within the material (a kind of "acceleration" of the diffusion process).

The bond strength of adhesive joint increased to 49.79 N/cm after irradiation with a microwave-energy 450 W after exposure for 24 h and 47.88 N/cm after storage for three months. The materials are structured and turn into a single system with common molecular lattices. Such interaction conditions the increase of the adhesive joint strength by 39 % after exposure for 24 h and 38 % after storage for three months due to the structuring of leather, changing the adhesive and the substrate into a single whole.

After adding of leuconate to the adhesive composition in the amount of 5 wt % of the final adhesive and microwave radiation of the glue line adhesion increased by 59 % (57.1 N/cm after exposure for 24 h) and 62 % (57.26 N/cm after exposure for 3 months).

Comparative characteristics of leuconate (5 %) influence in the polychloroprene adhesive composition and microwave radiation (450 W) of the adhesive joint on the bond strength is presented in Fig. 4.

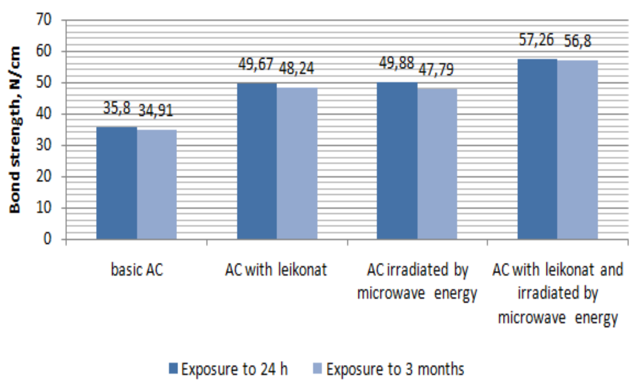

Fig. 4. The effect of introduction of leuconate (5 %) into the polychloroprene adhesive composition and microwave radiation (450 W) of adhesive joint on the bond strength

The results showed that the bond strength exceeds the strength of the material – rubber for the bottom of the shoe. The nature of the destruction is cohesive. This is due to the formation of additional linking and crosslinking of the adhesive layer with the substrate. Polychloroprene adhesive, rubber and leather materials are related. The molecules of the adhesive composition react with the substrate molecules (most with molecules of rubber) and form a single spatial grid between the adhesive layer and rubber. Thanks to such a conversion the strength of the adhesive joint has increased.

4. Conclusions

Thus, in this paper, to improve the performance strength of adhesives for the manufacture of footwear:

– the necessity of modifying domestic polychloroprene adhesive compositions has been shown;

– hardener leuconate and microwave radiation were used as modifiers;

– it has been found that adding of 5 % leuconate to the adhesive composition increases the bonding strength to 49.67 N/cm after exposure for 24 h, 38.3 % higher than the bonding strength without leuconate. After three months the bond strength decreases ~ 3 % (48.24 N/cm).

– the adhesion after irradiation with the microwave-energy increased to 49.79 N/cm after exposure for 24 h and 47.88 N/cm after storage for three months.

– after the introduction of leuconate into the adhesive composition in the amount of 5 % by weight of the finished adhesive and after microwave irradiation strength of the adhesive seam has increased by 59 % (to 57.26 N/cm after exposure for 24 h) and has increased by 62 % (to 56.8 N/cm after exposure for 3 months).

– created adhesive composition can be recommended for the production of special shoes that will withstand high mechanical loads.

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ВПЛИВ НВЧ-ЕНЕРГІЇ ТА ЗАТВЕРДЖУВАЧА ЛЕЙКОНАТУ НА МІЦНІСТЬ КЛЕЙОВОГО ШВА

Анотація. *Мета дослідження полягає у підвищенні міцності склеювання поліхлоропренових клеїв для виробництва взуття. За базову клейову композицію обрано композицію на основі поліхлоропренового каучуку (найриту НТ). Основними компонентами поліхлоропренової клейової композиції є найрит НТ, бензин БР1 або БР2, етилацетат марки А, лейконат. Виявлено, що додовання лейконату в кількості 5 % та опромінення НВЧ-енергією дає можливість підвищити міцність склеювання на 59 %. Модифікована клейова композиція може бути рекомендована для виготовлення спеціального взуття, яке може витримувати високі механічні навантаження.*

Ключові слова: *поліхлоропрен, клейова композиція, лейконат, НВЧ-енергія, міцність склеювання.*