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IMPACT OF ZEOLITE ON OPERATING PERFORMANCE OF POLYURETHANE ADHESIVE COMPOSITIONS

В роботі досліджені експлуатаційні показники теплостійких поліуретанових клейових композицій, модифікованих природнім мінералом цеолітом.

Ключові слова: теплостійкість, клейова композиція, взуття.

The thesis investigates the operational performance heat-resistant polyurethane adhesive compositions modified natural zeolite mineral.

Keywords: heat resistance, adhesive composition, shoes

Introduction

For the manufacturing of shoes that will withstand the high temperature load it is necessary to create a variety of heat-resistant adhesives with a wide range of properties. Polyurethane adhesives best meet requirements of the adhesive joints of shoe made of ceramic materials, which provide not only high strength of glue line in the initial state, but also preservation of strength parameters during operation at elevated temperatures.

Heat resistance is the upper limit temperature at which in certain conditions and for a given exposure time there is no significant change of physical and mechanical properties [1,2].

Currently there are about a hundred brands of domestic synthetic adhesives that are based on the ability to withstand more or less heat load. They can be divided into three groups: adhesives that can withstand prolonged exposure to temperatures around 60°C; heat-resistant adhesives that can withstand long or short-term effect of temperature of 100°C; highly heat-resistant adhesives that can withstand short-term effect of temperature to 300°C.

Two-component adhesive based on Desmokol400 and isocyanates containing vulcanizing agent Desmodur (R-types) (producer – company «Bayer» (Germany) has long been proven in the domestic footwear industry. Component Desmodur promotes adhesion and acts as a component-stapler, so that you can significantly improve the heat resistance of adhesive joints. However, it is scarce, expensive and toxic component and does not provide a high strength adhesive connection [2].

The purpose of the given work

Therefore, the search for materials that improve the heat resistance of adhesive connection together with the other performance indicators is rather urgent and became the purpose of this study.

Based on the results of previous studies [3] the use of the mineral zeolite in the adhesive compositionfor this purpose has been proposed by the authors.

The frame structure of zeolite (Fig.1), general formula $\mathbf{MeO\times[(Al_2O_3)\times (SiO_2)_y]\times zH_2O}$, its physical and chemical characteristics (Table1), especially high thermal stability, suggest that as the modifier it will increase the heat resistance performance of adhesive joints [4].

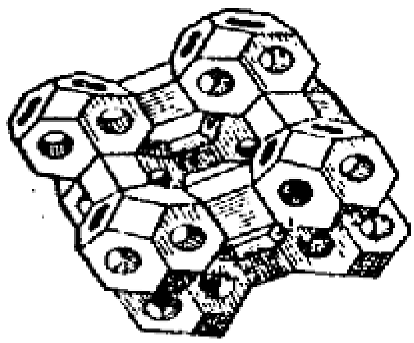

Figure 1. Frame-crystal lattice structure of zeolite

Table 1

The separate physical and chemical characteristics of the zeolite

Porosity	34 %
Density	2,3g/cm^3
Specific surface	413 m^2/g
Content of the sorbent	70 %
Ion exchange capacity	1,5mg×eq/g
Humidity	4 – 6 %
Thermal stability	to 700^{0}C
Size micropores	0,3-2 nm
Powder dispersion	0,08mm
Cost	50 € /t

This paper investigates four most used polyurethane adhesive compositions (AC) in the domestic shoe industry: AC1 (PU-503), AC2 (VU-252), AC3 (KYSPO-1) and AC4 (D-274), in which natural mineral – zeolite of

Sokyrnytsky deposits (Khust, Transcarpathian region, Ukraine) at a rate of 0-2,5 % of the total was added as a filler-modifier.

For all compositions recipe of the first part consists of polyurethane adhesive rubber type Desmokol530, solvent – ethyl acetate and diluent – acetone. Recipe of the second part of polyurethane adhesives is:

- to AC2 Desmodur, polyvinyl chlorideacetate, silicon dioxide powder – aerosil was added;
- to AC3 – Desmodur;
- to AC4 – Desmodur, chlorinated natural rubber.

Establishing the optimal ratio of components in the adhesive composition was carried out by means of mathematical modeling experiment [5], the results are presented in Table 2.

20 recipes of adhesives (depending on the % content of zeolite – 5 for each composition) have been developed. For each recipe strength of adhesive (glue ability), heat resistance, water resistance and frost resistance have been determined.

Table 2

Optimal compounds of the investigated adhesive compositions

Name of composition	Name of components	Amount of component, (mass fr.)
Adhesive composition № 1 (PU-503)	Polyurethane rubber type "Desmokol-530" Acetone Ethyl acetate	17 20 63
Adhesive composition № 2 (VU-252)	Polyurethane rubber type "Desmokol-530" Copolymers of vinyl acetate and vinyl chloride Silica powder Acetone Ethyl acetate Vulcanizing agent containing isocyanate Desmodur (R-type)	16 2 1 20 61 5 (%)
Adhesive composition № 3 (KYSPO 1)	Polyurethane rubber type "Desmokol-530" Acetone Ethyl acetate Vulcanizing agent containing isocyanate Desmodur (R-type)	17 20 63 10 (%)
Adhesive composition № 4 (D-274)	Urethane rubber type "Desmokol-530" Chlorinated Natural Rubber Acetone Ethyl acetate Vulcanizing agent containing isocyanate Desmodur (R-type)	10 10 20 60 20 (%)

The research results

Analysis of adhesive ability tests showed that the strength of the studied modified bonding adhesive compositions is much higher than normal (24N/cm). As it is shown in Figure 2, the strength of all compositions with the addition of 1-1,5 % of zeolite slightly decreases, and by adding 2-2,5 % – of it significantly reduces. AC3 (88,3 N/cm) and AC1 (81,4 N/cm) have the greatest strength, but at 2,5 % content of zeolite in AC1 strength is 56,5N/cm, more than twice the normative requirements.

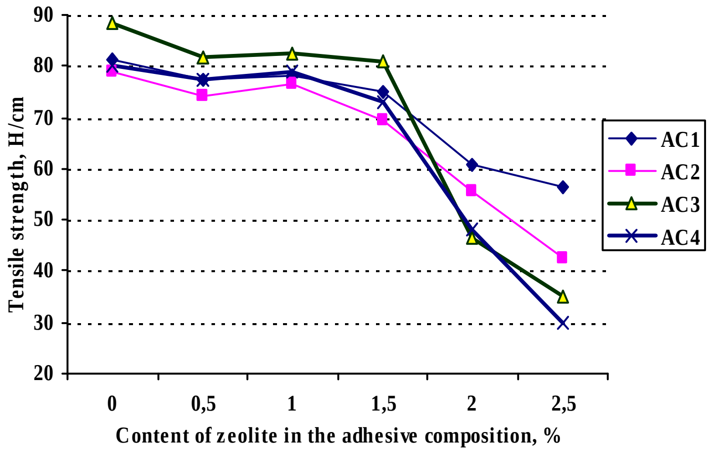

Figure 2. The dependence of the adhesive ability of investigated adhesive compositions on the content of the zeolite

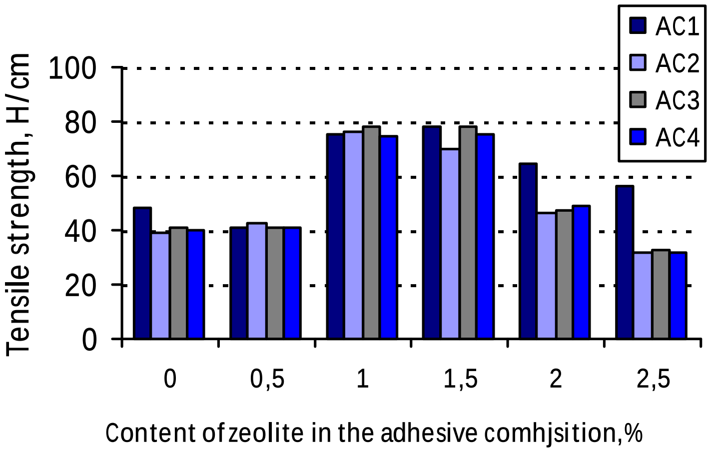

Figure 3. Dependence of strength on the zeolite content at 50^{0}C for the investigated adhesive compositions

Adhesive ability for each of the compositions individually for 24h, 7 days, 30 days and 3 months have been determined. Indicators of strength after 3 months decreased by 10 %.

Heat resistance has been determined by the degree of reduction of the strength of adhesive joints due to thermal processing – exposure in a thermostat for 1h at 50±2°C, 100±2°C, 150±2°C, 200±2°C, 250±2°C.

Test results show that the investigated adhesive compositions with zeolite have higher heat-resistant characteristics. At 50±2°C, with the introduction of 1 % of zeolite to adhesive compositions, tensile strength increased by an average of 55 %, reflecting the influence of zeolite frame structure on heat-resistant adhesive properties (Fig.3).

According to the research the adhesive compositions modified with zeolite in the amount of 1-1.5 %, heat load at 150°C does not reduce the strength ratios, they conform to the standards (Fig.4).

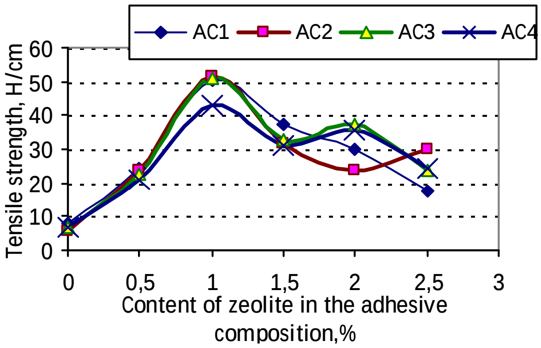

Figure 4. Dependence of the ultimate strength on the zeolite content for the investigate adhesive compositions at 150^{0}C

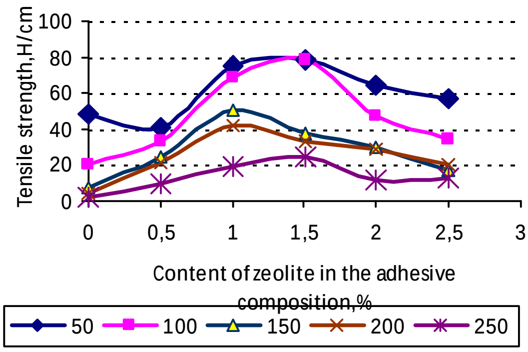

Figure 5. Dependence of strength on the zeolite content by changing the temperature from 50^{0}C to 250^{0}C for AC1

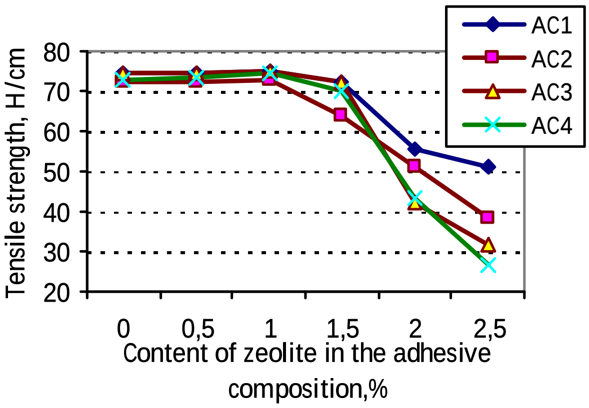

Figure 6. Dependence of waterproof performance on % of zeolite content in the studied AC

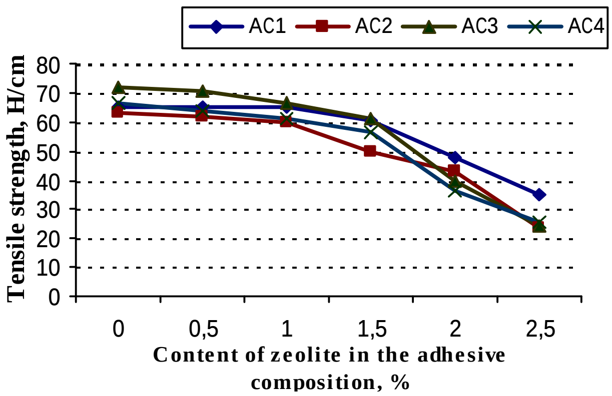

Figure 7. Dependence of frost resistance on % of zeolite content in the studied AC

For AC1 (PU-503) containing Desmokol530, zeolite, ethylacetate and acetone, changed in the amount of 1-1,5 % will increase the heat resistance up to 200°C (Fig.5) and tensile strength is 32,8 N/cm, i.e. within normal limits.

Indicators of water resistance, which were investigated by testing adhesive joints for strength after immersion of samples into water for 30 min, correspond to the standard requirements and constitute 95-90 % of initial strength of adhesion (Figure 6).

Frost resistance of modified adhesive joints established by exposure of samples for 24 h at a temperature -250^{0}C (Figure 7). Indicators of resistance are high enough, conform to the standards and make up 95-85 %.

Conclusion

Thus, the aim of this study is to improve the heat resistance performance of adhesives for the manufacture of shoes:

- the necessity of modifying domestic adhesive compositions has been substantiated and as a modifier natural mineral – zeolite was used, which increases the heat resistance, it is environmentally friendly and inexpensive;
- it has been found that the modification of all the studied compositions with zeolites in the amount of 1-1.5 % will allow to increase the heat resistance to 150^{0}C, and the adhesive composition number 1 (PU-503) – to 200^{0}C;
- adhesive connection is quite stable over time (up to 3 months);
- the adhesive composition number 1 (PU-503) with 1 % of zeolite content has best operating performance;
- indicators of water and frost resistance of the adhesive joint if the content of modifier is 1-1.5 % corresponds to standards and constitute 95-85 % strength bonding;
- physical and mechanical properties of investigated adhesive compositions can be recommended for making shoes that resist high temperature load.

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СТРУКТУРА ОСНОВОВ'ЯЗАНОГО ТРИКОТАЖУ З ВИСОКОРОЗТЯЖНИМ ПОВЗДОВЖНІМ УТОКОМ

В статті представлено результати дослідження структури та розмірів чарунок основов'язаного трикотажу утоково-філейного переплетення, який утворено чергуванням рядів трико та ланцюжка в рапорті і в якому високорозтяжна утокова нитка розташовується за рапортом то на лицьовій, то на виворотній стороні полотна. Встановлено залежності досліджуваних параметрів від рапорту філейного переплетення та варіанту розташування утокової нитки. Визначено варіанти структур, які матимуть кращі ауксетик-властивості

Ключові слова: основов'язаний трикотаж, утокова нитка, філейне переплетення, варіант введення утоку, розміри чарунки, кут нахилу, коефіцієнт Пуассона.

The research's results of a structure and the cells' sizes of warp knitted fabric of inlay-fillet interlacing which has been made by alternation of tricot and chain courses at repeat and in which the high elastic filling yarn is positioned at front and at back side according to repeat are presented in an article. Analytical dependences of parameters of the knitted fabric on the interlacing repeat and on the inlay model are fixed. The variants of structures, which have better auxetic property, were found.

Keywords: WARP knitting, weft thread, fillet weave, weft input option, mesh size, angle, Poisson's ratio.

В структурі основов'язаного трикотажу утокові нитки можуть виконувати роль: каркасних, зв'язуючих, підкладкових, бахромних, візерункових. Останніми роками найчастіше їх використовують для зміни властивостей трикотажу: розтяжності, розпускальності, формостійкості тощо. Так використання еластомерної нитки в якості утокової призводить до значного зростання пружності та розтяжності трикотажу в напрямку її прокладання [1]. Властивості трикотажу утокових переплетень залежать як від властивостей ґрунтового переплетення, так і від ступеня релаксації еластомерної нитки.

Так при введенні в структуру філейного трикотажу, який має чарунки гексагональної форми,