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Preface

This special issue of Key Engineering Materials contains selected papers of the XII international conference Baltic Polymer Symposium 2012, which was held in Liepaja, Latvia, from 19[th] of September until 22[nd] of September.

Since 2001 the event is annually organized by the technical universities of the three Baltic States. Twelve year experience permits to make out obvious value and productivity of the meetings. The Symposium has become a recognized forum for polymer researchers of the Baltic States which work in the field of polymer chemistry, physics and technology. The major advantage of the conference is good opportunity to exchange ideas between scientists as well to start collaboration and partnership. Symposium is an excellent chance for young researchers to master their ability to present the achievements of their research.

Baltic Polymer Symposium 2012 in Liepaja was visited by participants not only from the three Baltic States, but also by participants from Taiwan, Germany, Finland, United Kingdom, Poland, Ukraine and Russia. In parallel with the conference a demonstration session was held by manufacturers of the specific research and analysis equipment, representing Netzsch Group, Postnova Analytics/Norlab Oy and Bose Corporation/Electro Force Systems Group.

The scope of the Conference comprised all aspects of modern polymers science:

- synthesis,
- processing,
- recycling,
- composites,
- nanotechnologies.

Table of Contents

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Improvement of thermal polyurethane adhesive compositions parameters by modification with zeolite

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Keywords: shoes, adhesive composition, thermal stability

Abstract. The aim of this study is to improve the heat resistance performance of polyurethane based adhesives for the manufacture of shoes. Four polyurethane adhesive compositions must used in the domestic shoe industry have been investigated: PL-503, VU-252, KYSPO-1 and D-274. The main components of polyurethane compositions are urethane rubber, zeolite, ethyl acetate and acetone. It has been found that modification of VU-252, KYSPO-1 and D-274 with zeolite in the amount of 0.5-1% allow to increase the heat resistance to 150 °C while that of PL-503 - to 200 °C. Besides it has been found that adhesive compositions can be recommended for the manufacture of special fire-resistant shoes that could withstand high thermal loads.

Introduction

Polyurethane adhesives best meet the requirements of adhesive attaching of shoe artificial and synthetic materials. These adhesives provide not only high strength of the adhesive joint in the initial state, but maintain strength parameters for prolonged exposure times at the temperatures of 60-150°C, have the ability to harden at low temperatures and pressures, do not produce volatile products during hardening and have high physical and mechanical properties.

Currently, there are about one hundred brands of domestic synthetic adhesives, which, depending on the ability to withstand heat loads can be divided into three groups: adhesives that can withstand prolonged exposure to temperatures of around 60 °C, heat-resistant adhesives that can withstand long or short-term effects of temperature about 100 °C, highly heat-resistant adhesives that can withstand the impact of short-term temperatures up to 300 °C [1, 2].

It is necessary to create a variety of heat-resistant adhesives with a wide range of properties for making shoes that can withstand prolonged or short-term temperature load around 60-150 °C. This fact indicates the urgency of this study.

"Heat endurance" is the softening temperature range of adhesive tapes and characteristic of the upper limit temperature at which, under certain conditions and for a given time of exposure there are no significant changes in physical and mechanical properties. Time and exposure conditions are established to meet the requirements of these specific applications.

Heat and thermal stability relate to chemical structure and are defined by physical and chemical factors. For the short-term thermal effect properties of materials are often defined solely by influence of physical factors. In case of prolonged thermal effect chemical factors are crucial. Hence, the thermal stability is dependent on time [3, 4].

The purpose of the given work

The firm «Bayer» (Germany) makes adhesives used in the domestic market. They are a mixture of polyurethane rubber type Desmokol and isocyanates containing vulcanizing mixture type Desmodur. Two-component adhesive based on Desmokol-400 and Desmodur R (20 weight percent of Desmokol 400 , 80 weight percent of ethyl acetate) has long been proven in the footwear industry. Desmodur R promotes adhesion and also acts as a component-stapler, so it can improve the thermal stability of adhesive joints. However, this footwear cement contains scarce, expensive and toxic components in its composition and does not provide high strength of glued connection.

In terms of health, these components are toxic. German research center set maximum concentration in the air of the room in 0.02 ppm for the most technically important diisocyanate. This regulatory requirement should be followed when using isocyanate components.

To increase the initial strength and heat resistance of one-component shoe adhesives the company "Bayer" has developed special brand of urethane rubber – Desmokol-530 and Desmokol-540 [1], which have stronger crystallization and bond strength, better adhesion to many materials and enhanced hydrolytic stability than urethane rubber type Desmokol-400 widely used in the shoe industry.

The purpose of this study is to improve the heat resistance performance of polyurethane adhesive compositions that could be used for making shoes, operated at elevated temperatures. At the same time non-toxic and inexpensive products are introduced as modifier of adhesive compositions.

Materials and methods

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

The frame structure of zeolite (Fig 1), its physical and chemical characteristics (Table1), especially high thermal stability (up to 700°C), suggest that as the modifier it will increase the heat resistance performance of adhesive joints [4].

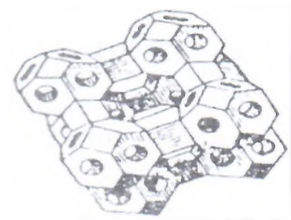

Fig. 1. Frame-crystal lattice structure of zeolite

Table 1. Some physical and chemical characteristics of the zeolite

Porosity	34(%)
Density	2,3(g/cm³)
Specific surface	413 (m²/g)
Content of sorbent (active component in the mineral – clinoptilolite)	70 (%)
Ion exchange capacity	1,5(mg · eq/g)
Humidity	4 – 6 (%)
Thermal stability	to 700(°C)
Size of micropores	0.3-2 (nm)
Powder dispersion	0,08(mm)
Cost	50 (€/t)

Zeolite is a natural hydrated silicate of alumina of alkali and alkaline earth metals of crystal structure, the general formula $MeO\cdot[(Al_2O_3)_x\cdot(SiO_2)_y]\cdot zH_2O$, which has adsorption, ion exchange, catalytic, non-toxic, bactericidal and other valuable and unique properties. Each particle of zeolite flour has many pores with a diameter 0.3-2nm. Only molecules whose dimensions do not exceed the size of the input windows can penetrate into the inner molecular space of zeolites. Therefore, zeolites are also called molecular sieves.

The chemical nature of the zeolite surface can adsorb water molecules, CO_2, H_2S, NH_3, other inorganic substances; organic compounds: C_2H_2, CH_3OH, CH_3Cl, CH_3COOH, other organic alcohols, aldehydes, acids and fats. It is a good sorbent, of both liquid and gaseous phases. General description of the separate physical and chemical characteristics of zeolite of Sokyrnytsky deposits is shown in Table 1.

Four polyurethane adhesive compositions most used in the domestic shoe industry have been investigated: one-part system PU-503 (AC1), and three different two-part systems - VU-252 (AC2), KYSPO-1 (AC3) and D-274 (AC4). As hardener, vulcanizing agent containing isocyanate Desmodur (R-type) is used in AC2, AC3 and AC4 in the concentrations of 5, 10 and 20%.

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

Table 2 Optimal compounds of the investigated adhesive compositions

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

20 recipes of adhesives (depending on the weight percentage of zeolite - 5 for each composition) have been developed.

Polyurethane adhesive composition is prepared as follows. Certain amount of urethane rubber is dissolved in a solvent in the usual glue mixer. 1/3 of the total amount of solvent is added into mixer together with urethane rubber, and after the formation of a viscous smooth consistency zeolite is added and heated with careful stirring for 30 minutes, then the rest of the solvent is added. Dissolution takes 7-8 hours at room temperature. In order to accelerate the dissolution of rubber heating is used (heating temperature of water is 35-40 °C). One-component polyurethane composition is obtained after complete dissolution. The solvents are carefully checked for moisture content, because water dramatically reduces the strength of the connection, according to [6,7].

The viscosity of the adhesive according to viscosimeter of Hetchinson is 2.5 - 2.6 seconds at 19° C. Viability of the finished adhesive after the introduction of a hardener at 10-20 °C is 4-6 hours.

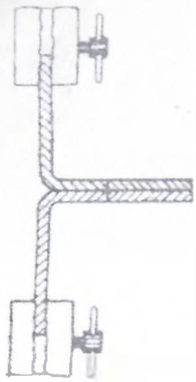

Fig. 2. Device for tensile testing machine to determine the ultimate strength of the bond

Bonded samples were used for testing: two-layer tarpaulin (code 812), cut along the base 25 × 140 mm, heat-resistant leather, heat-resistant polyurethane and heat resistant yuft (Russian leather) of the same size.

Samples after bonding were kept at standard conditions (t = 20 ± 2°C, φ = 65 ± 5%) for 24 hours. Then were kept in a thermostat for an hour at temperatures of 50 ± 2°C, 100 ± 2°C, 150± 2°C, 200± 2°C, 250± 2°C.

Adhesion strength has been determined on the tensile machine Fig. 2 Device for tensile testing machine to determine the ultimate strength of the bond.

Heat resistance was determined by the degree of reduction of strength of adhesive joints as a result of heat treatment - exposure in a thermostat for 1h at 50±2°C, 100±2°C, 150±2°C, 200±2°C, 250±2°C.

Results

Analysis of test results shows that the studied adhesive compositions, when zeolite was added in their composition as a modifier, have elevated-temperature characteristics.

Already at 50±2°C after adding 1% of zeolite to all the adhesive compositions tensile strength increased by an average of 55%, which shows the influence of the framework structure of zeolite on physical and mechanical properties of the composition. The effect of the zeolite content on the tensile strength of the adhesive compositions at temperature of 50±2°C is shown in Figure 3.

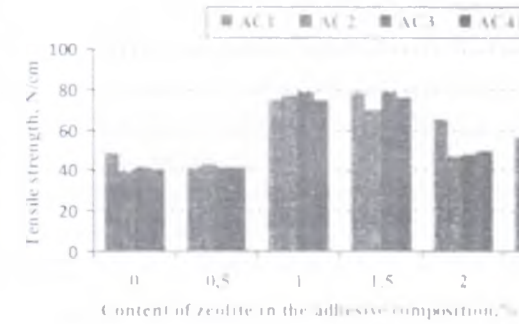

Fig. 3. The dependence of the ultimate strength on the content of the zeolite at 50°C for tested adhesive compositions

As it is shown in Figure 4, at 150°C with the increase of zeolite content up to 1% heat resistance increases, but in the range of zeolite content 2-2,5% - heat resistance decreases sharply.

According to GOST 9292-82 [8] value of heat resistance of adhesive joints (tensile strength) should be 60% of the value of strength after holding the samples at 50°C for 60 minutes.

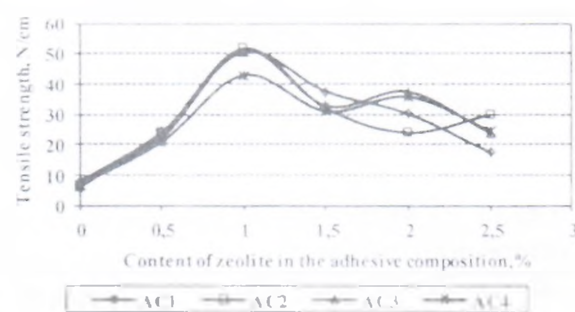

Fig.4. The dependence of the ultimate strength on the content of the zeolite for the experimental adhesive compositions at 150°C

According to the research of the adhesive compositions modified with 1% of zeolite, heat treatment up to 150°C does not considerably reduce the strength ratios, i.e., they meet the regulatory requirements stated in [8].

For №1 (PU-507) containing Desmokol-530, zeolite, ethyl acetate and acetone, modification with 1.5 % of zeolite increase heat resistance to 200 °C. Tensile strength of AC1 at this temperature is 32.8 N/cm, that is higher than critical value of GOST 9292-82 (24 N/cm).

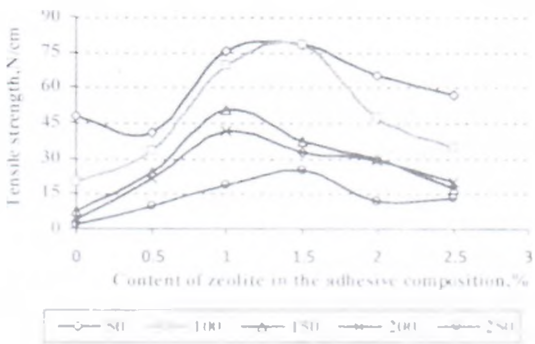

Fig.5. Dependence of strength on the zeolite content by changing the temperature from 50 °C to 250 °C for AC1

Conclusions

According to the aim of the study – to improve the heat resistance performance of adhesives for the manufacture of shoes – it has been found that:

- modification of AC2, AC3 and AC4 with zeolite in the amount of 0.5-1 weight % allow to increase heat resistance to 150 °C, while modification of AC1 with the same amount of zeolite- to 200 °C.

- investigated adhesive compositions can be recommended for the manufacture of special fire resistant shoes that can withstand high thermal loads.

- development of the process of manufacturing shoes using new modified adhesive compositions require additional research.

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