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Qualitative Evaluation of the Possible Application of Collagen Fibres: Composite Materials with Mineral Fillers as Insoles for Healthy Footwear

DOI: 10.5604/01.3001.0012.2536

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Abstract
The research presented in this paper focuses on determination of the physical and mechanical properties of composites made on the basis of natural polymer, i.e., crushed collagen fibres which are waste from the leather industry. Mineral supplements such as dolomite, bentonite and kaolin were the filling of the composite produced. Their application was dictated by increasing the application range, and we strove to optimise the composition of the composite in terms of physical and mechanical properties determined in static tensile tests. An analysis of the water absorption capacity was also carried out in order to select optimal compositions which have the best properties. The test results indicate extensive application possibilities of the composites produced, one of which is in footwear insoles, whose quality is an important element determining the hygienic qualities of shoes due to the high density of sweat glands in the plantar part of the foot. This research indicates the possibility of individual development of the composite properties of collagen fibres and mineral supplements in terms of their application, taking into account the medical aspect.

Key words: *composites, collagen fibres, mineral fillers, insoles, healthy footwear.*

Introduction

In the last few decades, there has been an intensive search for materials which could replace currently used and well-defined structures, such as metals, ceramics and polymeric materials [1] in order to obtain better properties of the materials and reduce the costs of their production at the same time. For example, such criteria are met by composite materials which are produced by combining materials with properties other than the final product. In cases where at least one of the components of the composite is biodegradable or bio-derived, we are dealing with biocomposites [2-4]. Their most important advantage is the fact that they are obtained with the use of renewable raw materials [5]. At the same time, there also appear materials of a composite nature produced based on raw materials which are industrial waste, e.g., hydrolysates of keratin, which is a leather tannery waste [6]. Actions taken to combine optimal constituents are aimed at achieving appropriate properties imposed by the use of the final product.

One of the known methods of modification of materials combined in a composite is the use of so-called fillers. Literature on the subject provides numerous examples of the use of mineral additives as well as studies of composites filled with various types of powders, indicating differences in the physical and mechanical properties of the materials obtained [7-11]. This is influenced by the type of filler used, the source of its origin, the degree of fragmentation, and the forming process.

The authors of work [12] showed a change in the structure and selected physical and mechanical as well as hygienic and microbiological parameters of shoe leathers with fillers based on zeolite and montmorillonite. It is worth noting that montmorillonite was used as a filler in combination with nylon for the first time in work [13], and as a result, a significant improvement in mechanical and thermal properties was observed. After this success, research was intensified on the possibility of using other mineral fillers, e.g., aluminosilicates, currently used in the aviation, automotive and space industries for the production of elements with specific properties [14, 15].

The present study investigated the physical and mechanical properties of newly developed composites based on collagen fibres contained in waste generated by the leather industry. As fillers, readily available natural minerals were used: bentonite, dolomite and kaolin, while Winacet DP50 homopolymer was used as a compatibiliser. The purpose of the preliminary tests was to determine the basic properties of the composite material obtained, thanks to which it will be possible to achieve such a composition of the composite which in effect gives the

Table 1. Strength tests for composites with 0, 5 and 10% bentonite addition.

Bentonite content, %	Tensile stress, MPa	Sample strain for Fmax, mm	Fmax, N	Young's modulus, GPa
0	7.78	2.8	699	0.0916
5	5.43	2.4	465	0.0923
10	3.36	2.6	339	0.0621

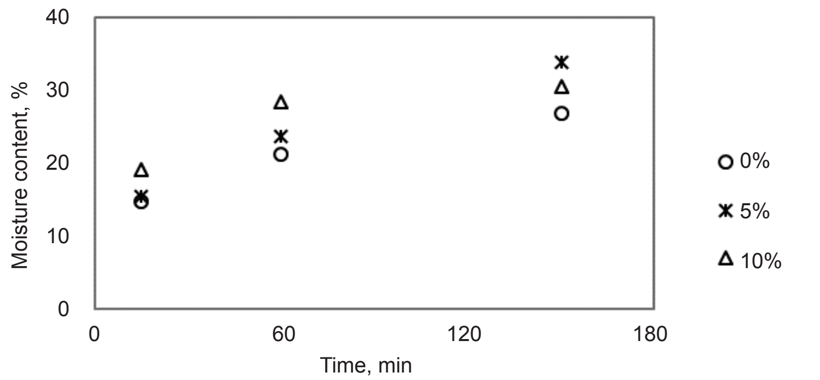

Figure 1. Water absorption capacity for composites with 0, 5 and 10% bentonite addition.

Table 2. Velocity of moisture content change between time points for composites with 0, 5 and 10% bentonite addition.

Bentonite content, %	Time intervals		
	0-15 min	15-60 min	60-150 min
0	0.9803	0.1444	0.0628
5	1.0308	0.2255	0.1128
10	1.2727	0.2062	0.0234

greatest utility of its applications. These measures are in line with current issues concerning the sustained development of the global economy, including the renewability and biodegradability of composite materials [16].

Materials and methodology

Composition of the composite

As part of the research, new composites were made on the basis of crushed collagen fibres contained in waste leather shavings, which are resistant to biological degradation and are a result of the processing of wet-blue leather semi-finished products [17, 18]. Shavings with 50% humidity and fractions below 8 mm were used. In the process of forming composites, moisture-free, natural mineral fillers in the form of powder were used in the amount of 5% and 10% in relation to the mass of the shavings, i.e.:

- kaolin (kaolinite content 81%, grain size 0.002 mm);
- dolomite (natural calcium-magnesium carbonate, grain size < 0.045 mm);
- bentonite (colloidal clay, montmorillonite content minimum 75%, grain size ≤ 0.056 mm).

Winacet DP 50 homopolymer, a water dispersion of vinyl polyacetate, was used to combine the components. The percentage of mass shavings in relation to the matrix (binder) in the composites tested was 60:40.

Process of forming the composite

The process of forming the composite consisted in adding a mineral supplement in the role of filler and matrix (binder) to shavings obtained from the national tannery in order to combine the constituents. The gaining of formable cohesion and homogeneity of the material has a direct impact on its physical and mechanical properties. The mixture of all components was pressed in a hydraulic press at a constant pressure of 20 MPa with the possibility of heating. Moulded composites of 280 x 280 mm and 3.9 mm thickness were dried in a laboratory drier at 25 °C for 24 hours. After the next 72 hours of air conditioning, tests of the physical and mechanical properties of the composites obtained were carried out.

Composite tests

Physical and mechanical properties of the composites obtained were tested using a Zwick/Roell Z010 strength machine. Performing a static test of axial stretching (at a test speed of 50 mm/min) of the composites, the force value and accompanying strain were determined until the sample was broken.

The ability to absorb water (absorbability) by the composites was also tested and expressed using the moisture content coefficient. For this purpose, samples of 3 x 3 cm composites after acclimatisation (72 h) were placed in beakers with 20 ± 2 °C distilled water in such a way that they did not touch each other and the height of the water column above them was 30 mm. The samples were then left in a vessel with water for 15 min, 60 min and 150 min. After this time, the samples were removed, and in order to remove droplets of water from their surface they were dried between two layers of tissue paper. After drying for one minute, the samples were weighed. The arithmetic mean of the results of two parallel samples was adopted as the final result.

Results and discussion

With reference to the axial tension tests, the results of the stress dependence on the strain of the sample made it possible to determine the module of linear deformation ***Equation (1)***. Knowledge of these values allowed to place the composite produced in a given spectrum of materials.

$$E = \frac{\sigma}{\varepsilon} = \frac{\frac{F}{S}}{\frac{l - l_0}{l_0}} \tag{1}$$

where:

σ – tension illustrated by the quotient of the tensile force F [N] to the cross-sectional area of the sample S [m^2],

ε – strain as the quotient of the difference in the length of the measurement section before the test l_0 [m] and after the test l [m] to the length of the measuring section before the test.

The moisture content coefficient m_c ***Equation (2)*** was determined to assess the water absorption capacity of the samples tested, defining the water content m_w in relation to the mass of the composite after its immersion (taking into account its own mass m_m and that of absorbed water m_w):

$$m_c = \frac{m_w}{m_m + m_w}. \tag{2}$$

In the qualitative analysis, the change in water content in particular time intervals was described by means of the tangent of the slope angle of the curve connecting the neighboring measuring points to the positive half-axis representing the time.

The test results obtained for composites with individual mineral additives are presented in the following: ***Tables 1, 2** and **Figure 1*** – for bentonite addition; ***Tables 3, 4** and **Figure 2*** for dolomite addition and ***Tables 5, 6*** and ***Figure 3*** for kaolin addition.

Test results indicate that the obtained values of individual properties of the composites with mineral additives tested depend on the specifics of the filler used. The analysis of selected strength parameters revealed a common trend for kaolin and bentonite, manifested by a decrease in the strength of newly formed materials along with an increase in the percentage of mineral additives. In the case of bentonite, the weakening of the material manifested itself almost linearly for such parameters as maximum stress (decrease from the strongest material without addition, to the weakest with 10% additive confirmed by the determination coefficient $R^2 = 0.99$), maximum force at break ($R^2 = 0.97$). In the case of kaolin, linear decreases in properties took place in the area of maximum stress values ($R^2 = 0.91$) and maximum forces ($R^2 = 0.91$). In the case of Young's modulus, no clear trend was observed. The reason for this is poor variation (coefficient of variation at the level of 21%) of the values obtained.

In the case of material with dolomite addition there was no clear trend in the analysis of strength parameters. Analysing values of Young's modulus for the composites produced, they can be classified as polymer foams and certain materials from the group of elastomers, i.e., materials capable of reversible deformations under the influence of mechanical forces without the risk of losing the integrity of their structure, which considerably extends the field of their application [17].

A very important aspect from the point of view of the potential applicability of the material produced is the effect of the additive used on the ability to absorb water from the environment. This process is intensified with an increase in the additive content – kaolin and bentonite, in particular during the first 15 minutes of im-

***Table 3.** Strength tests of composites with 0, 5 and 10% dolomite addition.*

Dolomite content, %	Tensile stress, MPa	Sample strain for Fmax, mm	Fmax, N	Young's modulus, GPa
0	2.35	2.9	328	0.0390
5	0.75	3.3	184	0.0144
10	2.22	2.1	341	0.0543

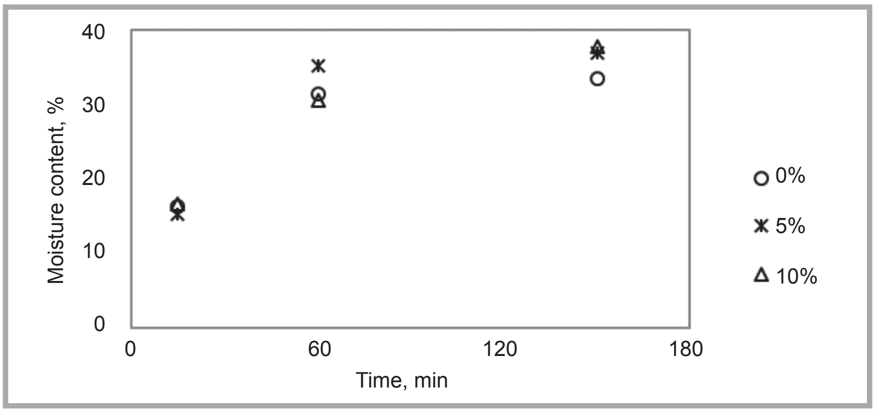

***Figure 2.** Ability to absorb water for composites with 0, 5 and 10% dolomite addition.*

***Table 4.** Velocity of moisture content change between time points for composites with 0, 5 and 10% dolomite addition.*

Dolomite content, %	Time intervals		
	0-15 min	15-60 min	60-150 min
0	1.0871	0.3355	0.0228
5	1.0200	0.4412	0.0205
10	1.1089	0.3076	0.0812

***Table 5.** Strength tests for composites with 0, 5 and 10% kaolin addition.*

Kaolin content, %	Tensile stress, MPa	Sample strain for Fmax, mm	Fmax, N	Young's modulus, GPa
0	2.96	5.40	407	0.0235
5	2.13	3.50	330	0.0362
10	1.87	4.00	308	0.0242

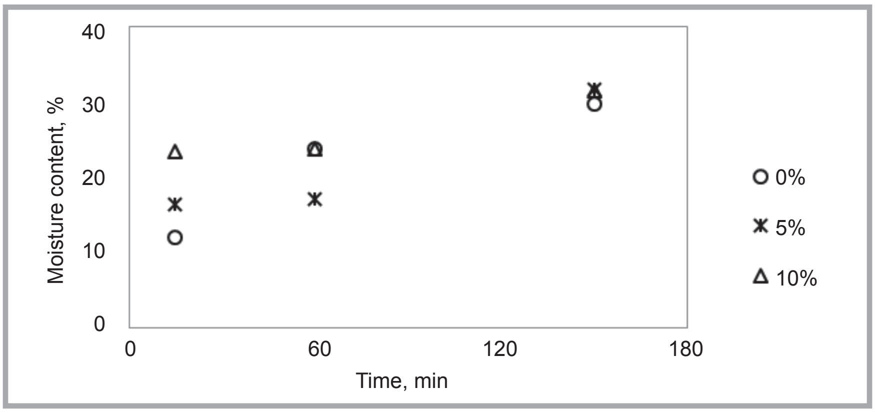

***Figure 3.** Ability to absorb water for composites with 0, 5 and 10% kaolin addition.*

***Table 6.** Velocity of moisture content change between time points for composites with 0, 5 and 10% kaolin addition.*

Kaolin content, %	Time intervals		
	0-15 min	15-60 min	60-150 min
0	0.8004	0.2615	0.0650
5	1.0903	0.0151	0.1611
10	1.5592	0.0064	0.0868

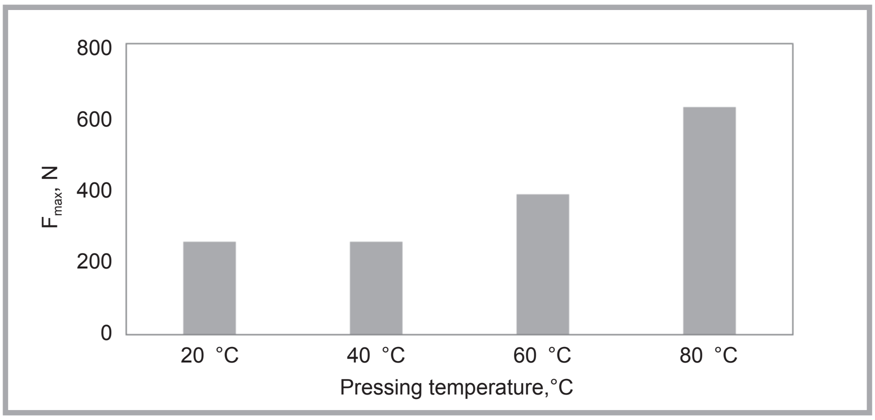

Figure 4. *Breaking force value (F_{max}) for composites formed at different pressing temperatures.*

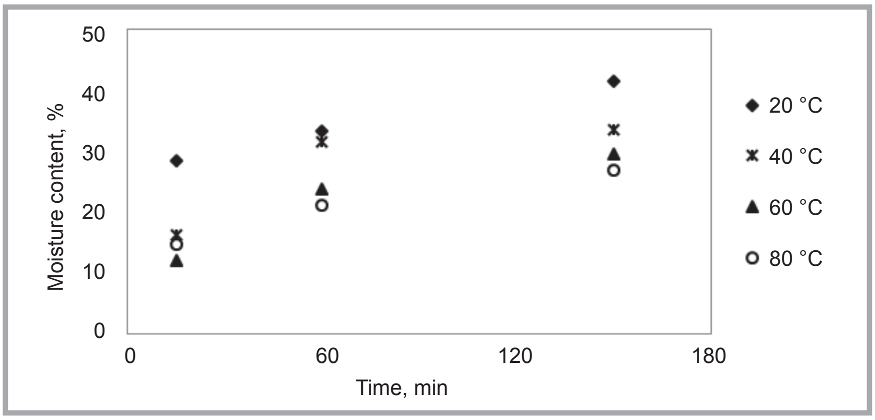

Figure 5. *Moisture content for composites formed at different pressing temperatures.*

mersion. When bentonite is used, there is almost a linear increase ($R^2 = 0.86$) in the soaking rate of materials. An almost linear increase ($R^2 = 0.98$) was also observed for kaolin. In the case of dolomite, these properties were revealed after exceeding 60 minutes of immersion. The linearity obtained is described by the coefficient of determination $R^2 = 0.72$.

The specific properties of the fillers used underlie the increasing intensity of soaking along with the increase in the percentage of mineral additive. For example, in the case of bentonite and kaolin, these materials are characterised by their high absorbability and swelling capacity [20, 21]. In the case of dolomite there were fluctuations in the level of water absorption, confirmed by its chemical nature, i.e., the presence of MgO and CaO oxides, which increases the affinity for hydration. Stabilisation of the system took place after a soaking time of 60 minutes [22, 23]. It is worth noting that the largest amounts of absorbed water appear in the first fifteen minutes of immersion. However, the materials have the ability to absorb water all the time, which was most evident for the material with dolomite addition, where after 60 minutes the material absorbed almost as much water as in the first fifteen minutes. In the next interval, absorption subsided. Materials with kaolin and bentonite addition behaved similarly, namely the greatest intensification of water absorption took place during the first 15 minutes of immersion, after which absorption subsided. This was demonstrated by kaolin, which after 60 minutes absorbed water in an amount not exceeding 25% of that of water absorbed in the 0-15 min interval.

Based on the test results, one can conclude that the influence of the mineral additive is important in the context of creating a suitable system in terms of its resistance to water. Under certain conditions, it is possible to reduce the absorbability of materials; a feature which is used, for example, in building construction, while in other conditions it is desirable that the material can absorb water well. Such materials are used for insoles, for instance, which have a large impact on the durability of footwear and prevent deformation under the influence of forces acting on the footwear during its use [24]. In addition, they play a significant part in creating the micro-climate around the foot [25] as they have to react quickly to a change in humidity parameters inside the footwear, i.e., to absorb and drain sweat secreted by the skin of the foot. Since the concentration of sweat glands occurs mainly in the plantar part of the foot, it is reasonable to take measures to establish an appropriate composition of materials which can be used for footwear insoles. In this study, the best conditions in line with values determining the high usability of such materials for insoles were obtained for a bentonite-modified composite (33-35% in the first 15 minutes and 19% in the 60-150 minute interval, respectively). In the case of a mixture enriched with dolomite, reasonable values were obtained for the 10% additive.

The analysis shows that it is possible to apply these materials for footwear insoles for feet with specific health requirements, neutralizing the negative effects of excessive sweating of the feet. These aspects are closely related, for example, to the age of the user [26], type 1 diabetes [27], or for specific work environments (e.g., hot environments) [28, 29].

The literature on the subject gives examples of the improvement of sorption properties with a simultaneous decrease in mechanical parameters for composites with the addition of water-insoluble fibrillar protein [30-32]. There are several possibilities to prevent the lowering of strength parameters using a set of materials, proposed in this study, for forming a new composite, for example in the field of elastic properties. One of them is the use of plasticisers (e.g., resins) which can interact with collagen structures and the polymer structure of the matrix (binder), providing a structure with specific properties, e.g., enhancing its deformability and elasticity. This stage is the next one to be carried out as part of work implemented under the project.

The tests carried out as part of this work indicate that the strength and hygienic properties of composites based on collagen fibres can be individually shaped according to demand. ***Figure 4*** and ***5*** show the effect of the pressing temperature on the properties of the composites tested. In most cases, an increase in the pressing temperature results in a rise in the breaking force (F_{max}). The highest values of the maximum force at which the first break occurred were obtained for the highest pressing temperature (80 °C). On the other hand, composites formed at lower pressing temperatures (20 °C, 40 °C) have better sorption properties.

Conclusions

- The addition of bentonite, dolomite and kaolin to composites based on crushed collagen fibres in a system with a homopolymer, which is a water dispersion of vinyl polyacetate, reduces their strength parameters.
- The use of mineral additives in the same system improves the sorption properties of the composites obtained.
- The research indicates the possibility of using the composite produced for footwear insoles.
- Properties of the composites obtained can be individually shaped according to the demand and application, through the selection of process parameters, for example the pressing temperature.

Acknowledgements

The study presented in this paper was carried out as a part of research project No. DEC-2017/01/X/ST8/01045 titled "Specification of an optimum composition of a composite of collagen fibres originating from leather industry waste and mineral additives", financially supported by the National Science Centre.

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Received 27.04.2018 Reviewed 03.07.2018