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Chapter 3
Utilisation of Production Residue from the Footwear and Clothing Industry

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3.1. Characteristics of the Footwear and Clothing Industry in terms of Waste Management

The leather industry covers a wide range of sectors ranging from the leather markets that provide the tanning industry with raw materials from meat abattoirs to the leather goods manufacturers. Some of those sectors are highly industrialised, others are based mainly on arts and crafts, and still others focus on trade and ancillary services.[1] Leather manufacture is one of the world's oldest handicrafts. Thanks to appropriate processing, we achieve an extremely durable raw material that is used for manufacturing common goods. The leather tanning process consists of a series of mechanical processes and chemical reactions. As a result, unstable raw leather is

1 All-European Industry Federation, (2012), Social and Environmental Report of the European Leather Industry, COTANCE.

transformed into a finished product with enhanced resistance to external factors, while maintaining the natural features resulting from the specific structure of the leather tissue. Leather tanning is the basic process, that, together with a series of mechanical leather processing operations, leads to obtaining a finished product with specific properties such as appearance, durability, flexibility, resistance to water and temperature, air and sweat permeability. After tanning, tanning hides may be used for manufacturing footwear, clothing, leather goods, furniture upholstery, cars, boats, and planes.[2]

The analysis of the leather industry production output in Poland in terms of animal typology indicates that the major raw material processed by this industry mainly includes large bovine hides (71% of the total) followed by sheepskin (14%), goat skin (8%) and veal (6%). Other processed animal skin (particularly reptile, pig, deer) accounts for a small part of the leather industry (less than 1%). This raw material segmentation is closely related to the meat industry [1]. According to estimates, 50% of the leather manufactured in the European Union is used in the footwear industry. The garment industry processes 20% of Europe's tanners' output, while the leather for upholstery accounts for 17% of the production output. Therefore, the Polish tanning industry is characteristic of a strong dependence on the economic situation in the footwear industry,[3] which is evidenced by the related figures presented in Table 3.1.1.

Table 3.1.1. Leather manufacturing processes in Europe

Use of Leather	Share [%]
Footwear industry	50
Clothing industry	20
Upholstery	17
Other industries	13

Source: Reference Document for the Best Available Technology: Leather tanning, Joint Research Center Institute for Prospective Technological Studies, Sustainable Production and Consumption Unit European IPPC Bureau 2013. [Available at: https://docplayer.pl/8261017-Garbowanie-skor-dokument-referencyjny-dotyczacy-najlepszych-dostepnych-technik-bat-dla.html (accessed: 07.08.2023)] (in Polish).

2 W. Domański, J. Surgiewicz, (2001), *Chemical hazards in the tanning industry*, "WORK SAFETY science and practice", vol. 4, pp. 6–9.

3 Reference Document for the Best Available Technology: Leather tanning, Joint Research Center Institute for Prospective Technological Studies, Sustainable Production and Consumption Unit European IPPC Bureau 2013. [Available at: https://docplayer.pl/8261017-Garbowanie-skor-dokument-referencyjny-dotyczacy-najlepszych-dostepnych-technik-bat-dla.html (accessed: 07.08.2023)] (in Polish).

According to the data published by the Central Statistical Office, in 2018 the sales revenue in the leather industry in Poland amounted to PLN 2.57 billion. 5,350 of companies operated in Poland in 2019 in the leather industry, which was 3.78% lower than the number of companies operating in that industry in 2018. According to the latest "Statistics of the Footwear Industry" developed by the Polish Chamber of Leather Industry, in Poland in 2019 there were 3,265 footwear manufacturers; 1,717 manufacturers of luggage bags, handbags and similar leather goods as well as saddlery; and 368 companies dealing with leather tanning, and fur tanning. The leather industry production output in the years 2017–2019 is presented in Table 3.2. The production output figures include the total volume of finished products manufactured from own or entrusted raw materials in a calendar year, intended for sale, as well as for further processing within the enterprise (i.e. used for manufacturing purposes). The footwear production output in Poland in 2019 decreased by 15% as compared to 2018. The production output of tanned bovine hides or tanned equine skin without hair on substantially decreased (38%). In 2019 the production output of hand-made leather bags increased by 8.77%.[4]

Table 3.1.2. Leather industry production output for 2017–2019

Sector	Unit	2017	2018	2019	Change % 2019/2018
Footwear production output, including:	million pairs	46.61	43.43	36.88	–15.08
Waterproof footwear		3.74	4.05	3.96	–2.22
Outdoor shoes		13.97	13.89	11.36	–18.21
Slippers or other indoor footwear		2.54	2.70	1.91	–29.26
Leather footwear		14.85	11.46	9.84	–14.14
Textile footwear		8.79	8.07	7.21	–10.66
Production output – bovine hide/horse skin, without hair on	t	22 589	20 310	12 578	–38.07
Including soft cowhide with full grain for footwear		13 496	11 999	4 429	–63.09
Production output – luggage bags, handbags and the like made of any raw material	million	4.04	4.66	3.92	–15.88
Including leather handbags		0.35	0.52	0.57	8.77

Source: Polish chamber of shoe and leather industry. Statistics of the footwear industry for 2019, source: annual collection of the Department of the Analytical Center of the Tax Administration Chamber in Warsaw approved by the Central Statistical Office, Poland, 2019, pp. 1–13.

4 Polish chamber of shoe and leather industry. Statistics of the footwear industry for 2019, source: annual collection of the Department of the Analytical Center of the Tax Administration Chamber in Warsaw approved by the Central Statistical Office, Poland, 2019, pp. 1–13.

Recently, the Polish footwear market has been growing at a high rate, as shown by the sales revenue of over EUR 4.5 billion in 2019. Poland ranks among the top fifteen exporters and importers of footwear in Central Europe. In 2015–2019 exports of the footwear industry from Poland increased by 131.3% from EUR 943 million to EUR 2.2 billion, and imports by 100.9% from EUR 1.4 billion to EUR 2.7 billion. Polish shoes are mainly exported to the EU Member States. For many years the largest importer has been Germany, accounting for 39% of the Polish exports (the figures from 2019), followed by the Czech Republic, Romania and Italy. The footwear is mainly imported from China that dominates the global market as a manufacturer of cheap footwear. In 2019 as many as 133.17 million pairs of shoes were imported from this country to Poland, which accounts for an increase of 8.79% as compared to 2018.[5] A huge amount of solid waste, a significant amount of which consists of organic matter, i.e. hair, wool, scraps, fleshing waste, planing, fats and tallow, is inherent in the processing and tanning of hides. Table 3.1.3. shows the types and amounts of solid waste output arising from processing 1 tonne of raw bovine hide.[6]

Table 3.1.3. Type, amounts of solid waste when processing 1 tonne of raw bovine hide

Type of solid waste	Treatment	Amount [kg]
Salt	Untanned	300
Hair		100
Untanned scraps		40
Lime slime		60
Fleshing waste		120
Tanned leather shavings	Tanned	95
Tanned peels		65
Dust		65
Tanned leather scraps		35
Sediments		125

Source: C.P. Framis, (2018), *Assessment of tannery solid waste management, A case of Sheba Leather Industry in Wukro (Ethiopia) – report*, Wydawnictwo ETESEIB, pp. 2–92.

5 Reference Document for the Best Available Technology: Leather tanning, JOINT RESEARCH CENTER Institute for Prospective Technological Studies, Sustainable Production and Consumption Unit European IPPC Bureau 2013. [Available at: https://docplayer.pl/8261017-Garbowanie-skor-dokument-referencyjny-dotyczacy-najlepszych-dostepnych-technik-bat-dla.html (accessed: 07.08.2023)] (in Polish).

6 C.P. Framis, (2018), *Assessment of tannery solid waste management, A case of Sheba Leather Industry in Wukro (Ethiopia) – report*, Wydawnictwo ETESEIB, pp. 2–92.

According to the Central Statistical Office, the volume of solid waste generated in this section in 2019 equaled 55.1 thousand tonnes, out of which as much as 53.6 thousand tonnes was handed to be reused. However, it should be remembered that animal skin itself is a by-product of the meat industry. Within this context, leather manufacturing itself is an example of effective management of production residue, which is in line with the principles of the circular economy. According to the figures published by the Central Statistical Office and the reference document (BREF) for tanning,[7] in 2019 the domestic leather industry generated approx. tonnes of solid waste. For every 4 tonnes of raw leather subjected to tanning processes, 1 tonne of solid waste is estimated to be produced. Furthermore, residue typically makes up 2 to 20% of the weight of tanned leather – that's more than 2 kg of solid waste for every square meter of a finished leather product. The amounts of solid waste output in the leather industry in 2018 are listed in Table 3.1.4.

Table 3.1.4. Solid waste output in the leather industry in 2018

	Annual Solid Waste Volume		Solid Waste Stored so far in 2018
	In general	Provided to be reused	
Manufacture of textile products [thousand of tonnes]	6.6	6.6	–
Manufacture of leather and leather goods [thousand of tonnes]	55.1	53.6	31.4

Source: Reference Document for the Best Available Technology: Leather tanning, Joint Research Center Institute for Prospective Technological Studies, Sustainable Production and Consumption Unit European IPPC Bureau 2013. [Available at: https://docplayer.pl/8261017-Garbowanie-skor-dokument-referencyjny-dotyczacy-najlepszych-dostepnych-technik-bat-dla.html (accessed: 07.08.2023)] (in Polish).

The physical and chemical characteristics of solid tannery waste depend on the composition of the hides and the agents applied the hides. Raw hides contain over 50% of carbon, 25% of oxygen, 17.8% of nitrogen and 7% of hydrogen, as well as small amounts of mineral salts and sulphur. In the case of goat skin, the average fat content is 5–10%, in sheepskin it is 5–30%, in pig skins it can even reach 40%. Leather with a significant fat content will actually consist of proportionally less

7 Reference Document for the Best Available Technology: Leather tanning, Joint Research Center Institute for Prospective Technological Studies, Sustainable Production and Consumption Unit European IPPC Bureau 2013. [Available at: https://docplayer.pl/8261017-Garbowanie-skor-dokument-referencyjny-dotyczacy-najlepszych-dostepnych-technik-bat-dla.html (accessed: 07.08.2023)] (in Polish).

water. In turn, bovine hides contain about 60–65% of water, 30–33% of protein, 0.5% of minerals, 2% of fats and other ingredients.[8] The composition of leather waste depends on the stage from which it is obtained. For example, waste obtained after the fleshing process will be characterised by a higher amount of fat, while after the chrome plating process it will contain chromium (III). Sewage sludge, in turn, contains less organic matter (65%) than waste obtained from the tanning process (87.5%). By-products in the leather industry are primarily an important source of good quality collagen and collagen hydrolysates, which may have many applications in various industries. Collagen hydrolysates contain, depending on the method of obtaining them, from 8% to 35% of solid matter, from 0.5% to 35.5% of ash, from 14% to 16% of nitrogen, 83% to 87% of organic matter, 0–2% of nitrogen amide.[9]

Utilisation of untanned waste does not pose major problems, as it is processed into gelatine, adhesives, cosmetic preparations, artificial intestines, foil, feed or fertiliser ingredients.[10] [11] Technical gelatine may be used in cosmetics, photography or adhesives. A much bigger problem is tanned waste that may be used as secondary raw material. Therefore, effective methods of disposal management in respect of those types of solid waste have been sought for many years, e.g. for the purpose of producing biodiesel, biogas, biopolymers, adsorbents and for use in agriculture.[12] Research on the possibility of producing biodiesel and biogas from those types of solid waste seems necessary due to the ecological benefit of such a solution. Tannery waste is also an alternative to synthetic additives in the production of such materials as polymers, foil, and elastomers. Leather waste may also be used in the fertiliser industry and the production of fodder, that are crucial for the development of agriculture in Poland. The growing number of scientific reports on new methods of tanning waste management will contribute to the systematic reduction of environmental pollution. Thanks to the effective

8 S. Famielec, (2014), Doctoral dissertation *Tanning waste burning process In the tunnel furnace as their method Disposal*, Politechnika Krakowska, , Kraków.

9 D. Gendaszewska, M. Lasoń-Rydel, K. Ławińska, E. Grzesiak, P. Pipiak, (2021), *Characteristics of collagen preparations from leather wastes by the high pressure liquid chromatography method*, "Fibres & Textiles in Eastern Europe", vol. 29, pp. 75–79.

10 M. Parisi, A. Nanni, M. Colonna, (2021), *Recycling of Chrome-Tanned Leather and Its Utilization as Polymeric Materials and in Polymer-Based Composites: A Review*, "Polymers (Basel)", vol. 13, pp. 2–23.

11 K. Ławińska, M. Lasoń-Rydel, D. Gendaszewska, E. Grzesiak, K. Sieczyńska, C. Gaidau, D.G. Epure, A. Obraniak, (2019), *Coating of seeds with collagen hydrolysates from leather waste*, "Fibres & Textiles in Eastern Europe", vol. 27, pp. 59–64.

12 C.V.T. Rigueto, M.T. Nazari, C.F. De Souza, J.S. Cadore, V.B. Brião, J.S. Piccin, (2020), *Alternative techniques for caffeine removal from wastewater: an overview of opportunities and challenges*, "Journal of Water Process Engineering", vol. 35, pp. 1–12.

management of waste, benefits such as reducing CO_2 emissions to the atmosphere or obtaining new composite materials are also achieved.[13]

In the leather industry, as in many other technological industries, there is a process of automation and robotisation of the most burdensome work for human health. This process also makes it possible to increase the efficiency of the use of materials and raw materials thanks to optimisation based on more objective criteria including the reduction of the human factor as the evaluation criterion. According to Marek Górecki, President of the Management Board of the Polish Chamber of Leather: *The most important thing for the footwear and leather industry is the protection of the internal market by limiting the import of low-quality footwear and leather products from third countries, which carry the risk of substances banned in the EU and may pose a threat to consumer health. We also strive for the introduction of mandatory marking of the country of origin of all goods introduced to the intra-Community market, the so-called MADE IN. We also want to change the consumer's awareness towards perceiving leather products as fully ecological and natural products. The mission of the leather and footwear industry is the rational use of goods of natural origin, in accordance with the principles of sustainable management and widely understood recycling.*[14]

3.1.1. Implementation of the Principles of Sustainable Development

The principle of sustainable development is at the heart of all current and applicable environmental law systems. In accordance with this conceptual framework, individual legal systems seek a compromise between the needs of environmental protection and the need to influence the environment. Therefore, the principle of sustainable development focuses on finding solutions that will allow to reconcile the values protected by law and will take into account the needs of future generations.[15]

The conceptual framework of sustainable development has been the subject of interest in legal, economic and social sciences for many years. In the international arena, this conceptual framework began to take shape from 1968, during the proceedings of the UNESCO International Conference of Scientific Experts, as a result of which the "Man and the Biosphere" Programme was created. In 1972, the "Stockholm Declaration" was issued, which contained the principles of rational

13 D. Gendaszewska, D., Wieczorek, (2022), *Solid tanning waste as secondary raw materials*, "Environmental protection – new solutions and perspectives for the future", TYGIEL Scientific Publishing House, Lublin, pp. 18–36.

14 https://www.pracujwlogistyce.pl/raporty/21-raporty/7372-polskie-firmy-produkuja-46-5-mln-par-butow-rocznie-a-wartosc-tego-rynku-wynosi-3-3-mld-euro (accessed: 07.08.2023).

15 B. Rakoczy, (2015), *The procedural dimension of the principle of sustainable development*, Białostockie Studia Prawnicze, vol. 18, pp. 35–44,

resource management and planning, which is a tool for combining the needs of development with the needs of environmental protection. In 1983, on behalf of the UN, the World Commission for Environment and Development was established, which four years later presented a definition of sustainable development that is still valid in Poland. According to the Report of the World Commission on Environment and Development of the United Nations entitled "Our Common Future" (the so-called Brundtland Report) sustainable development was defined as "development that meets the needs of the present without compromising the ability of future generations to meet their own needs". The next step in the development of the conceptual framework of sustainable development was the organisation of the First Earth Summit in 1992, at which two documents were drawn up, i.e. the Declaration on Environment and Development (Earth Charter) and the Global Action Program (Agenda 21). The Earth Charter states that people are the focus of sustainable development and have the right to a healthy and creative life in harmony with nature. Agenda 21, on the other hand, is a set of recommendations and guidelines for activities in the field of protection and shaping of the human living environment in order to ensure sustainable development. In turn, in 2000, at the Millennium Summit, the United Nations Millennium Declaration was signed, according to which natural resources should be protected in a prudent manner and in accordance with the assumptions of sustainable development, and production and consumption patterns should be changed in the name of a better future for the next generations. Another declaration "The future we want" from 2012 was adopted at the World Summit in Rio de Janeiro. It defines sustainable development as "development that meets the needs of the present generations without compromising the ability to meet the needs of the next generations".[16] In 2015, during the Sustainable Development Summit, the 2030 Agenda was adopted, which includes 17 global goals and 169 related tasks. This document is historically significant as it establishes an action plan for people, planet and prosperity. The Sustainable Development Goals are interdependent and indivisible and ensure a balance between the three aspects of sustainable development – economic, social and environmental. The 2030 Agenda, which is to be fully implemented by 2030, strongly emphasises human rights and dignity, the rule of law, justice and non-discrimination. Economic growth based on sustainable consumption and production patterns is essential, and the use of natural resources – from air to soil, from rivers, lakes and aquifers to seas and oceans – is sustainable.[17]

The conceptual framework of sustainable development can also be found in publications by foreign authors and has been proposed by institutions dealing directly

16 *The Future We Want*, RIO+20, United Nations Conference on Sustainable Development, Rio de Janeiro, Brazil, June 20–22, 2011.

17 https://izrs.eu/aktualnosci/prawnik-przyszlosci---lider-zrownowazonego-rozwoju (accessed: 07.08.2023).

or indirectly with monitoring the degree of achieving sustainable development. Table 3.1.5. presents exemplary definitions of this term. The analysis of those definitions indicates that the conceptual framework of sustainable development is defined in various ways and, depending on the approach, it may refer to various aspects of the social life. The common element is paying special attention to the environment of a given society and the role and place of man in taking care of natural resources and the quality of life. As mentioned earlier, the conceptual framework of sustainable development can be analysed in economic and environmental terms.[18]

Table 3.1.5. The conceptual framework of sustainable development in international terms

Definition source	What should be balanced	What should be developed
Wellbeing Index	A state in which an ecosystem maintains its diversity and quality, and therefore its ability to support humans and other living things, and the potential to adapt to change and provide a wide range of choices and opportunities in the future.	A state in which all members of the society are able to identify and meet their needs and have a wide range of options to realise their potential.
Environmental Sustainability Index	Maintaining key environmental systems at a „healthy" level and improving them instead of worsening, with low anthropogenic stress that does not threaten those systems.	Immune to environmental disturbances. Humans and social systems are not sensitive to health or food, and become less sensitive to environmental disturbances; it is a sign that society is on the way to greater ‚sustainability'; Social institutions and patterns, skills, attitudes and networks effectively support action on environmental challenges and cooperation between countries in managing common environmental problems.
Global Reporting Initiative	Reduced consumption of raw materials and reduced emissions and environmental pollution from the production or use of the product.	Profitability, employment, workforce diversity, workforce dignity, employee health/safety in professional and private life.

Source: A. Rudnicka, M. Kostrzewska, (2020), *Sewn with class. The clothing industry in the face of social and environmental challenges*, University of Lodz Publishing House, Lodz [Available at: https://wydawnictwo.uni.lodz.pl/wp-content/uploads/2020/07/Rudnicka_UszyteZklasa_ONLINE-.pdf (accessed: 07.08.2023)]; R.W. Kates et al., (2005), *What is sustainable development? Goals, indicators, values, and practice*, "Environment: Science and Policy for Sustainable Development", vol. 47, no. 3, pp. 8–21.

18 A. Rudnicka, M. Kostrzewska, (2020), Sewn with class. The clothing industry in the face of social and environmental challenges, University of Lodz Publishing House, Lodz [Available at: https://wydawnictwo.uni.lodz.pl/wp-content/uploads/2020/07/Rudnicka_UszyteZklasa_ONLINE-.pdf (accessed: 07.08.2023)].

Globalisation and technological progress have a significant impact on the operations of most industries, including the footwear industry. In order to maintain a strong position in the market, enterprises in the textile, clothing and leather industry need to set out the effective strategies and constantly solve problems that directly affect them. The well-known consumerism, in which social, individual and ecological costs do not count, begins to take on enormous proportions. This may have an impact on the natural environment through its excessive pollution. Observing current trends, contemporary consumers are increasingly aware of the negative effects on the environment that the products purchased and used by them may have. For this reason, modern product design increasingly focuses on natural materials or refers to ecology.[19] Unfortunately, the leather industry itself is associated with harmful processes that have an adverse impact on the environment and the health of workers. The most damaging processes include: tanning, processing of animal skin into finished leather products and the leather goods manufacturing stage. The use of chemicals and improper disposal of waste, including the discharge of untreated wastewater, is also a huge health and safety concern for the industry. Unfortunately, there are many threats, from chemicals used in the leather manufacturing, toxins contained in adhesives and plastics, through cheap labour, to environmental costs of production – contamination of water, soil and air resources by waste, sewage.[20] It is therefore necessary to increase efforts in the leather industry in the field of systematic business risk self-assessment and ensure respect for labour and human rights throughout the global supply chain, in particular in the aspects of ensuring a living wage, health and safety and transparency. Such activities for sustainable development and environmental protection are carried out by the nationwide Buy Responsible Foundation established in 2002. It places great emphasis on the cooperation with other NGOs, both at the national and international level. This organisation is also active in the field of responsible consumption and production as well as respecting human rights and environmental protection principles in business.[21] The Foundation focuses on five key areas:

- Improving working conditions in all parts of the production supply chain (from tanneries to factories), including decent wages, permanent employment contracts, protection of vulnerable groups of workers, acceptable working hours;

19 P.K. Olszewski, J. Kwiecień, (2017), *Slow fashion in the footwear industry – consumer and entrepreneur perception in the light of sustainable development policy*, "Product Technology and Quality", vol. 62, pp. 39–52.

20 P. Portich, Footwear Industry, ILO [MOP], 29 March 2011, http://iloencyclopaedia.org/part-xiv-42166/leather-fur-and-footwear/143-88-leather-fur-and-footwear/footwear-industry (accessed: 07.08.2023).

21 https://ekonsument.pl/s56_co_robimy.html (accessed: 07.08.2023).

- Occupational health and safety (OSH) for workers in all parts of the manufacturing supply chain, including safety measures and audits for hazardous substances and materials used in the production process;
- The right to freedom of association, including ensuring good labour relations, effective resolution of labour disputes and active support for labour and trade union rights;
- Counteracting environmental problems in the production of leather and footwear, including striving to eliminate toxic and hazardous substances, increasing the use of environmentally friendly materials and processes, sustainable waste management, transport;
- Transparency and traceability of the supply chain, including the publication of audit results, supplier lists, information on grievance mechanisms, disclosure of wages.[22]

The Foundation emphasises that a permanent solution to the problems common in the production of footwear and leather tanning can only be solved by key stakeholders in this industry, i.e. brands, suppliers, trade unions, employers' federations, NGOs, and government representatives. Currently, the term responsible fashion, i.e. one that is created in a way that respects the natural ecosystem and man, in the social and ecological aspect, is gaining importance.[23] It is important to realise that sustainability is not a matter of choice. It is a key element in ensuring a secure future for each company and creating value for all consumers and stakeholders. Due to the increased awareness of the conceptual framework of sustainable development, a number of activities are implemented to implement it. Such actions include selective collection of solid waste, application of the best available techniques (BAT) and product life cycle planning.

The conceptual framework of sustainable development results in the implementation of the principles of selective solid waste collection. Thanks to it, you can reduce the space for solid waste and landfills. One of the most important aspects is that the solid waste becomes a raw material, so there is a saving of real raw materials. Thanks to that, the raw materials will suffice for a longer period of time. The next step will be to plan the consumption of energy and raw materials through an in-depth analysis of the production process. In this way, it will be possible to implement modifications, thanks to which it will be possible to minimise the amount of raw materials and energy used, as well as solid waste output. The Polish law has already set forth the obligation to use the best available techniques (BAT). The idea of implementing this standard is to introduce the most material- and

22 D. Muller, A. Paluszekiw, (2017), *Towards better solutions. Good practices in the footwear industry* – Report prepared as part of the international campaign Buy Responsibly Shoes. Publisher: Buy Responsibly Foundation, Krakow/Warsaw 2017, https://www.ekonsument.pl/materialy/publ_660_strone_lepszych_praktyk_strony.pdf (accessed: 07.08.2023).

23 https://ekonsument.pl/s56_co_robimy.html (accessed: 07.08.2023).

energy-intensive and economical techniques. In 2013–2016, the Life+ ShoeBAT Project was implemented in Poland, Spain and Italy. That Project analysed the BAT knowledge of companies in the leather and footwear industries. The aim of the Project was to increase the knowledge and use of the most environmentally friendly technologies in the tanning and footwear industries. In the initial phase of the Project, more than 80 best available techniques (BAT) were identified and companies' knowledge in this area was assessed. The results of the survey showed that 65% of the surveyed footwear companies had never heard of the BAT. Interestingly, the BAT awareness was higher (61%) for tanneries, which is probably the result of the development of the BAT reference document for tanning technologies.[24] The footwear industry does not have any of the BAT reference documents, therefore, as part of the ShoeBAT Project, a list of technologies meeting the criteria for this industry was developed.[25] In order to expand the knowledge in the area under consideration, an internet platform was created to contain information on the best available techniques (BAT) for the leather and footwear industries. The platform is available in four languages, i.e. Polish, English, Italian and Spanish.[26] It includes an intuitive graphical interface, showing the various stages of the footwear and leather goods manufacturing process. A data sheet has been developed for each technique, containing, among others, technical descriptions of equipment necessary to implement production processes, obtained environmental benefits, economic factors related to their introduction, applicable laws and regulations. The result of the Project is the implementation of the following best available technologies (BAT) in 17 European companies producing footwear and leather products: replacement of halogen organic compounds used for degreasing leather, computer-aided design of footwear and cutting elements, use of water-based adhesives (100% solid adhesives or hot-melts), replacement of pigments and dyes containing metal complexes and replacement of nitrogenous compounds used in the post-tanning phase, prevention of hexavalent chromium formation in the post-tanning phase, use of biocides approved by the European Union and efficient use of rainwater. The effect of those activities is to reduce the impact of enterprises on the natural environment and human health. Enterprises, that have implemented the BAT, have reduced the number of hazards at work (thanks to the reduction of solvent emissions), reduced the number of stages in the gluing process, which saves time and energy consumption in the footwear production process, and saves time

24 Reference Document for the Best Available Technology: Leather tanning, JOINT RESEARCH CENTER Institute for Prospective Technological Studies, Sustainable Production and Consumption Unit European IPPC Bureau 2013. [Available at: https://docplayer.pl/8261017-Garbowanie-skor-dokument-referencyjny-dotyczacy-najlepszych-dostepnych-technik-bat-dla.html (accessed: 07.08.2023)].

25 http://www.life-shoebat.eu/pl/ (accessed: 07.02.2023).

26 https://www.parp.gov.pl/storage/publications/pdf/sektor-moda_raport_24-06-2020.pdf (accessed: 07.08.2023).

and materials in the punching process. In addition, it has caused the reduction in the amount of nitrogen in the tannery effluent, the reduction in the toxicity of the effluent due to the presence of biocides, and the reduction in hexavalent chromium and metal content in the finished leather. In effect it has also mitigated problems related to allergic reactions caused by contact with leather products. Moreover, the absence of chlorides in the degreasing phase of the tanning process has been noted. Finally, a 20% reduction in water consumption in the tanning process, a 20% reduction in pollutants in the tanning wastewater, an 80% reduction in the sulphide content in the wastewater, a 60% reduction in the chromium salt content in the wastewater and a reduction in the amount of water used in the leather production process have been accomplished. The analysis of the life cycle of products from the moment of their production through operation and use to withdrawal from use is also important in the perspective of implementing the principles of sustainable development. The point is that each item is designed in such a way that it is as durable as possible and can be used for as long as possible. Care is taken to ensure that no waste is generated during its operation, so that there is no emission of pollutants. Such an object, after its use, is to be easily disassembled into parts consisting of one type of raw material, and those raw materials are to be reused.[27]

Summing up, it should be emphasised that although the principle of sustainable development is not a procedural principle, it plays an important role in the application of law, especially as far as the environmental protection law is concerned. Hence, we can talk about its procedural dimension. Sustainable development-oriented fashion requires joint actions and consistency from the entire business sector. Only in this way is it possible to achieve an optimal state. Managing environmental and social aspects in the footwear and clothing industry in a conscious and comprehensive manner requires rethinking such basic business constructs as the main purpose of operation, the method of creating value or building relationships in the supply chain.

3.1.2. Utilisation of Production Residue

3.1.2.1. Plant Biostimulators

Modern agriculture is associated with intensive production, which is aimed at improving the quantity and quality of the crop, as well as increasing the profitability of farms. Therefore, proper nutrition of cultivated plants has become of great importance for agriculture. In the agriculture of the 20th century, mineral fertilisers were the main source of nutrients for crops. At present, efforts are being made to precisely adjust appropriate fertilisation to soil conditions as well as

27 https://histmag.org/Ekologia-spoleczenstwo-gospodarka-koncepcja-zrownowazonego-rozwoju.-952 (accessed: 07.08.2023).

to the requirements of specific varieties of crops. Their role is to provide plants with easily assimilable nutrients in the form of single elements or simple organic compounds.[28] Increasing the value of food products should go hand in hand with maximising production per unit area while minimising the environmental impact. Achieving this goal will be possible thanks to the use of economically viable, ecologically sustainable and socially acceptable means in agricultural crops. Those features are characteristic of plant biostimulants that are becoming more and more popular among breeders, as evidenced by the constant increase in their economic importance.[29] Pursuant to the Act of 10 July 2007 on fertilisers and fertilisation,[30] a growth stimulant is an organic or mineral compound, or a mixture thereof, which has a positive effect on plant development or other plant life processes, with the exception of a growth regulator being a plant protection product within the meaning of the provisions on plant protection. The latter is understood as agents that affect the life processes of plants, for example through substances that regulate the plant, other than nutrients.[31] The association of producers of biostimulants, the European Biostimulants Industry Council (EBIC), has proposed a definition of a biostimulant as a fertilising product that, regardless of the content of nutrients, contains an active substance(s) or microorganisms. When applied to a plant, this material stimulates natural processes that lead to an improvement in one or more of the following characteristics of the plant: nutrient utilisation efficiency, tolerance to abiotic stress, or crop quality characteristics. During the First World Scientific Congress devoted to the use of biostimulants in agriculture, which took place in November 2012 in Strasbourg, their classification was presented, taking into account the following groups: humic substances, complex organic materials, components of mineral origin, inorganic salts (containing phosphite), seaweed extracts sea salts, chitin and chitosan derivatives, antitranspirants (substances used as foliar that limits transpiration) and free amino acids and other nitrogenous compounds. The latter are particularly noteworthy because they can be obtained from the waste biomass of the tanning industry. It is one of the methods of solid waste management in line with the principles of circular economy. Plant stimulants also include microbial inoculants. The operational efficiency of the most common groups of stimulants in the Polish market, including biostimulants obtained from tannery waste, is discussed below.[32]

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28 P. Pipiak, M. Skwarek, (2020), *The use of amino acid fertilizers in agriculture*, "Technology and Quality of Products", vol. 65, pp. 144–157.

29 P. Hara, (2019), *The importance of biostimulators in potato cultivation*, "Polish potato", vol. 2, pp. 18–24.

30 Dz.U. Nr 147, poz. 1033, 2007: Act of 10 July 2007 on fertilizers and fertilization.

31 Dz.Urz. WE, 24.11.2009: Regulation (EC) No. 1107/2009 of the European Parliament and of the Council of 21 October 2009 concerning the placing of plant protection products on the market and repealing Council Directives 79/117/EEC and 91/414 EEC.

32 A. Rutkowska, (2016), *Biostimulators in modern plant cultivation*, "ISSUE", vol. 48, pp. 65–80.

Microbial inoculants, or in other words, microbial stimulators, contain microorganisms that, when applied to grain, plant surface or soil, support plant growth through various mechanisms, including: increasing the uptake of nutrients, root mass growth or accumulation of plant biomass. Microbial preparations contain free-living bacteria and fungi, including mycorrhizal fungi, which are isolated from soil, plants, water and composted manure. Microbial stimulators include, among others: plant-growth promoting rhizobacteria (PGPR) (Figure 3.1.1.). Currently, several dozen PGPR strains are known. Bacteria that promote plant growth and development belong to different phylogenetic groups. The most abundant group includes bacteria of the genus Pseudomonas, as well as Bacillus, Enterobacter and Erwinia.[33] PGPR bacteria colonise the soil thanks to their ability to adapt to various environmental conditions, the ability to grow quickly and metabolise many compounds. PGPR stimulate plant growth in a direct and indirect way. The first one consists in the production of growth-stimulating phytohormones, reducing the level of ethylene and facilitating the uptake of mineral compounds. On the other hand, indirect stimulation is based on protection against phytopathogens.[34] The improvement of the nutritional status of plants under the influence of the use of microbial inoculants also occurs by increasing the pool of soil nitrogen, derived from the binding of atmospheric nitrogen by the so-called diazotrophic bacteria.[35] Biopreparations containing beneficial soil microorganisms isolated from climatic and soil conditions other than Poland are already available in the European market, but their use in combating diseases and pests in Polish conditions is often associated with low effectiveness. The number of offered natural fertilisers enriched with useful microorganisms, suitable for organic cultivation of horticultural and agricultural plants, is still small. On the other hand, the interest of the market in microbiological bioproducts is dynamically growing, which creates the need to implement new microbiological bioproducts into agricultural practice.

Humic acids constitute another important group among biostimulators. Those are preparations containing humic substances (HS) including humic and fulvic acids. HS improve the structure and fertility of the soil and influence the uptake of nutrients by plants. Those substances, affecting the physical, chemical and microbiological properties of the soil, facilitate the absorption of nutrients by plants and thus affect their growth and development of the root system. Changes in plant physiology result mainly from increased enzymatic activity and water

33 Ibidem, pp. 65–80.

34 G. Dąbrowska, E. Zdziechowska, (2015), *The role of rhizobacteria in the stimulation of the growth and development processes and protection of plants against environmental factors*, “Progress in Plant Protection”, vol. 55, no. 4, pp. 498–506.

35 A. Rutkowska, (2016), *Biostimulators in modern…*

retention in the leaves.[36] Anjum et al.[37] showed that the treatment of maize with fulvic acid caused an increase in the intensity of photosynthesis, transpiration rate and intercellular CO2 concentration, which was associated with the stimulation of plant growth. In turn, Ezzat et al. (2009) showed that the use of 4% of the solution of humic substances in the form of foliar application significantly improved the physiological parameters of potato plants, expressed in height, number of stems, leaf area and dry weight of plants. The authors attributed those changes to increased water retention, nutrient uptake, and improved photosynthesis. An important problem in agricultural crops is the progressive shortage of water in the soil. The key to solve this problem is the optimal management of organic matter and the more widespread use of biotechnological solutions based on natural biohumus and humic acids obtained from domestic raw materials such as peat, compost or lignite. Actions to increase the content of humus in Polish soil constitute the strategy that will allow to increase the water capacity of agricultural land in the long term.[38]

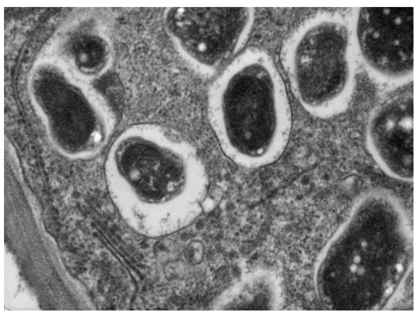

Figure 3.1.1. The rhizobacteria colonises the soybean roots
Source: https://en.wikipedia.org/wiki/Rhizobacteria (accessed: 07.08.2023).

Seaweed extracts are also products that are increasingly used in agriculture around the world. Particular interest in those products is associated primarily with the pro-ecological trend in plant cultivation and greater care for the natural environment and food safety. Literature reports emphasise the beneficial effect of algae on increasing the yield of plants, their condition, increasing resistance to pests or pathogens. Many researchers also emphasise the importance of marine algae in counteracting the effects of stress factors for crop plants, such as: excessive salinity, high temperature, cold, etc., and attribute an antioxidant effect in the

36 P. Hara, (2019), *The importance of …*
37 S.A. Anjum, L. Wang, M. Farooq, L. Xue, S. Ali, (2011), Fulvic acid application improves the maize performance under well- watered and drought conditions, "Journal of Agronomy and Crop Science", vol. 197, pp. 409–417.
38 D. Gawroński, (2021), *Reducing the effects of drought in crops by using humic acids and biohumus*, "Agricultural advisory issues", vol. 2, no. 104, pp. 48–59.

plant to them.[39] Sea algae-based biostimulants are mainly obtained by extracting red or green seaweed. However, a lot of attention is also paid to the production of natural preparations from brown algae (Phaeophyceae), from such species as: Ascophyllum nodosum, Ecklonia maxima, Durvillaea potatorum, Durvillaea antarctica, Fucus serratus, Himanthalia elongata, Laminaria digitata. Sea algae vary in chemical composition and, to some extent, also in their properties.[40] The greatest biostimulating properties are attributed to brown algae (Figure 3.1.2.). The physiological activity of algae extracts is due to the alginic acids, numerous polysaccharides and amino acids contained in them, but in particular the plant hormones found in all plants: auxins and cytokinins.

Figure 3.1.2. Brown seaweeds
Source: http://www.wildsingapore.com/wildfacts/plants/seaweed/phaeophyta/phaeophyta.html (accessed: 07.08.2023).

Prajapati et al. (2016), evaluating the possibility of using Kappaphycus alvarezii and Gracilaria edulis extracts in potato cultivation, found that their foliar application resulted in taller plants and more stems as compared to the control group, where only water was used. According to the authors, this effect was possible due to the content of growth regulators in biostimulators: auxins, cytokines and gibberellins.[41] In turn, Matysiak et al. (2012) conducted a field study to evaluate the effect of Ecklonia maxima (kelp) algae extract used as Kelpak SL on winter wheat plants. In the course of the research, the beneficial effect of sea algae extract on the weight of 1000 grains, yield, grain density, protein, starch and gluten content in the period of drought or semi-drought was confirmed. An increase in plant yield was noted on all objects where algae were applied.[42] It can therefore be concluded

39 K. Matysiak, S. Kaczmarek, R. Kierzek, (2012), *Effect of Ecklonia maxima (Kelpak SL) marine algae extract on winter oilseed rape plants*, "OILSEED CROPS", vol. 33, pp. 43–49.
40 P. Hara, (2019), *The importance of …*
41 P. Hara, (2019), *The importance of …*
42 K. Matysiak, S. Kaczmarek, D. Leszczyska, (2012), *Influence Of Liquid Seaweed Extract of Ecklonia Maxima On Winter Wheat Cv Tonacja*, "Journal of Research and Applications in Agricultural Engineering", vol. 57, no. 4, pp. 44–47.

that marine algae, especially from the brown algae class, are a valuable source of bioactive substances that stimulate plant life processes, have a beneficial effect on the soil and soil microorganisms. Their stimulating effect has been scientifically proven many times but some of the mechanisms of action remain unexplained, which poses a number of challenges to scientists.

Biopreparations based on free amino acids constitute still another group of biostimulants called protein hydrolysates. Those preparations are defined as "mixtures of polypeptides, oligopeptides and amino acids that are produced from protein sources by partial hydrolysis".[43] Fertiliser products based on protein can be divided into protein hydrolysates consisting of a mixture of peptides and amino acids or preparations containing single amino acids.[44] It is extremely important that protein hydrolysates can be produced from animal waste, e.g. animal and fish skin or plant biomass, e.g. from legume seeds.[45] Obtaining those hydrolysates is possible thanks to chemical, thermal or enzymatic hydrolysis.[46] The use of animal waste for the production of biostimulants is consistent with the circular economy and is the opportunity to reduce environmental pollution associated with the storage of this type of solid waste. It is estimated that the market of biostimulants in 2018 reached USD 2.241 billion. In Europe, the economic value of those preparations is estimated to amount to EUR 200–400 million.[47] On a global scale, most amino acid fertilisers for agriculture are produced in Italy, Spain, the United States, China and India. Amino acid fertilisers are available in the form of liquid extracts, soluble powder or granules and can be applied to the soil or foliar. Commercially available preparations vary in composition and content of amino acids.[48]

Amino acids are well-known biostimulants that directly and indirectly affect the growth and yield of plants. This is due to the fact that they are known precursors of proteins that perform building, metabolic and transport functions in plants. Those compounds, thanks to their structure, act as buffers that help maintain a favourable pH in the plant cell. They can also mitigate the effects of environmental stress on plants. In addition, amino acids have a positive effect on the photosynthesis process and mitochondrial respiration of plants. The advantage of their use as biostimulants is their mobility and easy transport in plants.[49] Examples of selected amino acid functions in plants are shown in Table 3.1.6.

43 P. Hara, (2019), *The importance of …*

44 P. Pipiak, M. Skwarek, (2020), *The use of amino acid…*

45 G. Colla, L. Hoagland, M. Ruzzi, M. Cardarelli, P. Bonini, R. Canaguier, Y. Rouphael, (2017), *Biostimulant action of protein hydrolysates: unraveling their effects on plant physiology and microbiome*, "Frontiers in Plant Science", vol. 8, p. 2202.

46 P. Pipiak, M. Skwarek, (2020), *The use of amino acid…*

47 P. Hara, (2019), *The importance of …*

48 P. Pipiak, M. Skwarek, (2020), *The use of amino acid…*

49 Ibidem.

Table 3.1.6. Selected functions of amino acids in plants, where Gly – Glycylglycine, Ala – Alanine, Pro – Proline, Hyp – Hydroxyproline, Phe – Phenylalanine, Ser – Serine, Thr – Threonine, Arg – Arginine, Asp – Aspartic acid, Glu – Glutamic acid

Code	Role in plant
Gly	Chelating agent; chlorophyll precursor that boosts the efficiency of photosynthesis.
Ala	Participates in resistance to low temperature; stimulates the synthesis of chlorophyll; participates in hormone metabolism; stimulates the mechanism of resistance to viruses.
Pro	Stress response marker; improves pollen fertility and fruit setting; regulates water management in the plant.
Hyp	Stress response marker; improves pollen fertility and fruit setting; regulates water management in the plant.
Phe	Triggers germination; precursor of lignin and lignified tissues.
Ser	Auxin precursor; participates in the regulation of water balance; necessary for the synthesis of chlorophyll.
Thr	Stimulates seed germination.
Arg	Participates in resistance to low temperature; polyamine precursor; necessary to trigger cell division.
Asp	Stimulates seed germination.
Glu	Chelating agent; growth stimulator; stimulates germination; is a reserve pool of organic nitrogen necessary for the synthesis of other amino acids and proteins.

Source: P. Pipiak, M. Skwarek, (2020), *The use of amino acid fertilizers in agriculture*, "Technology and Quality of Products", vol. 65, p. 144–157.

In the related literature one can find many studies describing the beneficial effect of amino acid agents on plant growth, especially in conditions of environmental stress. The study by Sadak et al. (2015) describes the assessment of the effect of exogenous amino acid treatment on faba bean growing under salt stress conditions. They aimed at assessing the reduction of salinity damage to faba bean by using a mixture of amino acids in order to improve morphological and biochemical parameters, and thus to increase the plant yield. The application of amino acids in the form of foliar spray significantly improved all the reduced parameters caused by sea water stress.[50] Studies conducted by Cuin et al. (2007) confirm that the use of amino acids under conditions of salt stress enables plants to maintain an optimal ratio of potassium to sodium and ultimately reduces their sensitivity to salinity.[51] In addition to salinity, water shortages also affect the deterioration of

50 M.S.H. Sadak, M.T. Abdelhamid, U. Schmidhalter, (2015), *Effect of foliar application of aminoacids on plant yield and some physiological parameters in bean plants irrigated with seawater*, "Acta Biologica Colombiana", vol. 20, pp. 141–152.

51 T.A. Cuin, S. Shabala, (2007), *Amino acids regulate salinity-induced potassium efflux in barley root epidermis*, "Planta", vol. 225, pp. 753–761.

crops. Drought is a global problem that severely limits global crop production, and recent global climate change has made this situation even worse. For this reason, Hammad and Ali (2014) conducted experiments to assess the effect of foliar spraying with amino acid biostimulants on reducing the risk of drought stress on common wheat. The obtained results showed that the use of amino acids significantly increased all the assessed parameters. It was found that the interaction between the tested water stress and biostimulants was significant for the majority of physiological characteristics as well as yield and its components.[52] The effectiveness of amino acid preparations was also demonstrated in the cultivation of alfalfa in conditions of excess water in the soil. Foliar application of amino acid preparations resulted in an increase in plant height, an increase in the amount of dry matter and an increase in protein content after the application of the tested amino acid biostimulators.[53] Temperature stress is also an important factor limiting the growth of most crop plants. The research conducted by Matysiak et al. (2020) confirmed that the exogenous application of certain amino acids had a positive effect on the growth and development of plants under stress conditions. In plants that had been obtained from seeds pretreated with L-arginine and L-glycine, the amino acids increased both root length and the number of lateral roots.[54] The growth and yield of plants are also affected by biotic stress factors, i.e. mainly microorganisms and pests. The possibility of using amino acids in plant protection against pathogens was studied, among others, at the Institute of Horticulture in Skierniewice. The amino acid preparations showed effectiveness in inhibiting the development of the fungus Sclerotinia sclerotiorum causing black bean rot. The conducted tests confirmed the effect of biostimulators on the pathogen during cultivation and storage of the tested plants. Field studies have shown high effectiveness of amino acid preparations in limiting fungal infections of beans and induction of resistance in plants.[55]

The effect of amino acid fertilisers on plant growth and crop quality is positive. Currently, in the related literature much attention is paid to the possibility of using amino acids and peptides for plant nutrition.[56] The effectiveness of the use of

52 A.R. Hammad Salwa, A.M. Ali Osama, (2014), *Physiological and biochemical studies on drought tolerance of wheat plants by application of amino acids and yeast extract*, "Annals of Agricultural Sciences", vol. 59, no. 1, pp. 133–145.

53 M. Pooryousef, K. Alizadeh, (2014), *Effect of foliar application of free amino acids on alfalfa performance under rainfed conditions*, "Research on Crops", vol. 15, pp. 254–258.

54 K. Matysiak, R. Kierzek, I. Siatkowski, J. Kowalska, R. Krawczyk, W. Miziniak, (2020), *Effect of Exogenous Application of Amino Acids L-Arginine and Glycine on Maize under Temperature Stress*, "Agronomy", vol. 10, no. 6 p. 769.

55 A.T. Wojdyła, J. Sobolewski, (2016), *The possibility of using agents containing amino acids in the protection of beans against black rot*, "Scientific Journals Institute of Horticulture", vol. 24, pp. 131–140.

56 G. Colla, L. Hoagland, M. Ruzzi, M. Cardarelli, P. Bonini, R. Canaguier, Y. Rouphael, (2017), *Biostimulant action…*

amino acid preparations in stimulating the growth of shoot and root biomass was tested during tomato cultivation in a greenhouse. Studies have shown that soil or foliar application of amino acid biostimulators increases crop yield by increasing the number of fruits and their average weight as well as the total amount of dry matter.[57] The observed increased nitrogen content in the leaves of tomatoes treated with biostimulators results from increased nitrogen assimilation, which may be based on an increase in enzyme activity or may be related to the development of the root system.[58] Another interesting solution is the use of collagen hydrolysates obtained from tannery waste in the process of coating leguminous seeds. The developed seed coats are designed to increase resistance to drought and pests during seed germination and emergence of seedlings. The encapsulation process was carried out in a disc granulator separately for three different species of legumes, including: pea, bean and soybean. For that purpose, collagen hydrolysate isolated from tannery waste was used as a binding liquid as well as a fungicide and a mineral additive. Figure 3.1.3. shows pea grains after the encapsulation process.

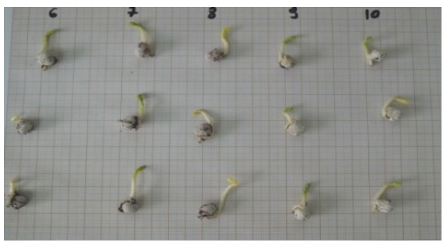

Figure 3.1.3. Pea grains after the encapsulation process
Source: own elaboration.

After the capsule had been formed, the seeds were sown in universal soil along with the control group, i.e. the seeds without the capsule. After a certain time following the sowing procedure, the average length of the seedlings was measured. The coating containing the collagen preparation provided the plant with favorable conditions in the early growth phase by creating a barrier protecting the sprouts against attack by pathogens. Good wettability of the granulated material, non-toxicity and adequate strength of the granule after drying are the features that justify the possibility of using collagen preparations in the seed coating process.[59, 60] This study

57 K. Ławińska, D. Gendaszewska, E. Grzesiak, J. Jagiełło, A. Obraniak, (2017), *Use of tanning waste in seed production*, "Chemical industry", vol. 96, pp. 2344–2347.

58 G. Colla, L. Hoagland, M. Ruzzi, M. Cardarelli, P. Bonini, R. Canaguier, Y. Rouphael, (2017), *Biostimulant action…*

59 K. Ławińska, M. Lasoń-Rydel, D. Gendaszewska, E. Grzesiak, K. Sieczyńska, C. Gaidau, D.G. Epure, A. Obraniak, (2019), *Coating of Seeds…*

60 K. Ławińska, D. Gendaszewska, E. Grzesiak, M. Lasoń-Rydel, A. Obraniak, (2017), *Coating legume seeds with collagen hydrolysates from tannery waste*, "Chemical Industry", vol. 96, no. 9, pp. 1877–1880.

confirmed that crop productivity was related to the availability of nutrients in the soil during the development of a given plant species.[61]

Biostimulators are natural preparations that are safe for human and animal health, and do not burden the natural environment. Their use in plant cultivation can bring many undeniable benefits.[62] Particularly noteworthy is the use of tannery waste for the production of amino acid biostimulators. Those activities make up the trend related to the concept of "clean production", waste management and minimisation of environmental burden, including the use of environmentally friendly technologies.[63]

3.1.2.2. IPS21 Strain

Leather industry waste is a serious problem for tanneries and the leather industry. It is estimated that for every tonne of raw material, as much as 50 kg of solid waste is produced. Approximately 6.5 million tonnes of raw hides are processed annually in the world.[64] That process generates approximately 325,000 tonnes of solid waste per annum. That waste, due to its harmfulness, should be properly treated. This is a problem as tanneries do not have the technology to dispose of or fully utilise this type of waste. Appropriate management and/or transformation of that waste is required in accordance with the idea of sustainable development and economic growth. In some countries, leather waste is used as a raw material for producing adhesives, gelatine, collagen, fodder or fertilisers.[65, 66] New waste treatment methods in tanneries are focused on biodegradation,[67] waste reuse[68, 69] or removal and recovery of heavy metals.[70] Tanned waste is a protein-based waste

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61 D. Gendaszewska, D. Wieczorek, (2022), *Solid tanning…*

62 P. Hara, (2019), *The importance of biostimulators…*

63 K. Ławińska, D. Gendaszewska, E. Grzesiak, J. Jagiełło, A. Obraniak, (2017), Use of tanning…

64 FAO (2013), *World Statistical Compendium for Raw Hides and Skins, Leather and Leather Footwear 1993–2012*.

65 D. Masilamani, B. Madhan, G. Shanmugam, S. Palanivel, B. Narayan, (2016), *Extraction of collagen from raw trimming wastes of tannery: a waste to wealth approach*, "Journal of Cleaner Production", vol. 113, pp. 338–344.

66 M. Łaczkowska, D. Gendaszewska, E. Grzesiak, M. Lasoń-Rydel, (2016), *Review of collagen extraction methods from leather waste*, "Technology and Quality of Products", vol. 61, pp. 74–79.

67 M.S. Sanjay, D. Sudarsanam, G.A. Raj, K. Baskar, (2020), *Isolation and identification of chromium reducing bacteria from tannery effluent*, "Journal of King Saud University – Science", vol. 32, no. 1, pp. 265–271.

68 M. Skwarek, M. Wala, J. Kołodziejek, K. Sieczyńska, M. Lasoń-Rydel, K. Ławińska, A. Obraniak, (2021), *Seed coating with biowaste materials and biocides—environment-friendly biostimulation or threat?*, "Agronomy", vol. 11, p. 1034.

69 K. Ławińska, S. Szufa, R. Modrzewski, A. Obraniak, T. Wężyk, A. Rostocki, T.P. Olejnik, (2020), *Obtaining granules from waste tannery shavings and mineral additives by wet pulp granulation*, "Molecules", vol 25, no. 22, 5419, pp. 1–13.

70 L. Pietrelli, S.Ferrom, A.P. Reverberi, M. Vocciante, (2020), *Removal and recovery of heavy metals from tannery sludge subjected to plasma pyro-gasification process*, "Journal of Cleaner Production", vol. 273, p. 123166.

consisting of splits, offcuts and chips (so-called shavings) from chrome-tanned leather. Tannery chrome shavings (CTS) are small, thin pieces of leather produced during the shaving operation. They are not bio-stabilised but they contain a large amount (up to 90%) of valuable collagen.[71]

It has been proven that microorganisms can degrade collagen-based matter. The mechanism of biodegradation consists in the enzymatic decomposition of protein using alkaline proteases produced by microorganisms. Those enzymes catalyse the decomposition of protein waste, e.g. keratin and collagen, derived from technological processes in tanneries. Enzymatic hydrolysis, however, requires the use of acid and alkali pretreatment methods for the solid waste management purpose. Muhammad et al. (2006)[72] and Pillai et al. (2012)[73] describe the method of hydrolysing tannery shavings and using *Bacillus subtilis* bacteria as a chromium-resistant strain. *B. subtilis* is an alkaline protease producer that can hydrolyse chromium shavings. Those bacteria have the ability to use the thermally treated collagen contained in the shavings as the only source of protein. In the described studies, the strain tolerated chromium in the amount of up to 35 ppm and 350 ppm of Cr(VI) and Cr(III) salts and showed bioaccumulation and biosorption of chromium. In turn, another paper describes the enzymatic hydrolysis of chromium shavings by means of Alcaligenes faecalis bacteria that also show proteolytic abilities and resistance to chromium. The strain was found to have degraded about 90% of the chromium shavings within 120 hours. The analysis of the composition of the collected hydrolysates showed the content of 12% ash and 80% protein, with the main component of the hydrolysate being small peptides with a molecular weight within the range of 3–30 kDa.[74] The effective degradation of protein waste often depends on the enzymatic potential of microorganisms or on the activity of enzymes used for hydrolysing leather waste.

Candida lipolytica, Aureobasidium pullulans and *Yarrowia lipolytica* are among the yeasts reported to produce various proteases.[75, 76] Hydrolysis of solid waste,

71 K. Ławińska, S. Szufa, R. Modrzewski, A. Obraniak, T. Wężyk, A. Rostocki, T.P. Olejnik, (2020), *Obtaining granules…*

72 M.N. Aftab, A. Hameed, I. Haq, C. Run, (2006), *Biodegradation of Leather Waste by Enzymatic Treatment*, "The Chinese Journal of Process Engineering", vol. 6, no. 3, pp. 462–465.

73 P. Pillai, G. Archana, (2012), *A novel process for biodegradation and effective utilization of chrome shavings, a solid waste generated in tanneries, using chromium resistant Bacillus subtilis P13*, "Process Biochemistry", vol. 47, pp. 2116–2122.

74 C. Babu Shanthi, P. Banerjee, N.K. Babu, G. Rajakumar, (2013), *Recovery and characterization of protein hydrolysate from chrome shavings by microbial degradation*, "Journal of the American Leather Chemists Association", vol. 108, pp. 231–239.

75 R. Hernández-Martínez, A. Sancho-Solano, O. Loera-Corral, A. Rojo-Domínguez, C. Regalado-González, S. Huerta-Ochoa, L.A. Prado-Barragán, (2011), *Purification and characterization of a thermostable alkaline protease produced by Yarrowia lipolytica*, "Revista mexicana de ingeniería química", vol. 10, no. 2, pp. 333–341.

76 B. Bessadok, M. Masri, T. Brück, S. Sadok, (2017), *Characterization of the Crude Alkaline Extracellular Protease of Yarrowia lipolytica YlTun15*, "Journal of FisheriesSciences.com", vol. 11, no. 4, pp. 19–24.

generated in various industrial processes, by means of efficient yeast proteases has been widely adopted as an environmentally friendly waste management strategy.[77] The use of *Yarrowia* yeast to the extent of various waste disposal management, including fat waste or hydrocarbon impurities, is known from few literature reports.[78] The research conducted by a team of scientists from the Łukasiewicz Research Network of the Lodz Institute of Technology in 2022 focused on assessing the possibility of biodegradation of chromium shavings contained in the liquid medium by means of isolating *Yarrowia lipolytica* yeast strain. That yeast was isolated from a soil sample contaminated with petroleum hydrocarbons and a high content of sulphates, chlorides, phenols, cyanides and heavy metals. The soil sample was placed in sterile bags and transported to the laboratory. Then, cultivation, isolation and purification of the isolated microorganisms were proceeded. Several microbial isolates were obtained, including the *Yarrowia lipolytica* yeast isolate (IPS21), in result of molecular biology methods that had been applied (Figure 3.1.4.).

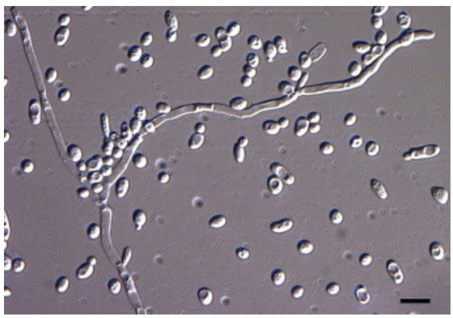

Figure 3.1.4. Single cells and filamentous cell state of *Yarrowia lipolytica*
Source: own elaboration.

The *Yarrowia lipolytica* IPS21 strain has been deposited in the patent deposit at the Institute of Biotechnology of the Agricultural and Food Industry in Warsaw under the number KKP 2089p. It is a strain of wild origin, that was selected for the research purpose out of several others belonging to the collection of the Łukasiewicz – Lodz Institute of Technology. The ability to secrete extracellular proteases had been chosen to be the selection criteria. Subsequently, studies were carried out to the extent of the utilisation of chromium protein waste arising from

77 S. Ariaeenejad, K. Kavousi, A.S.A. Mamaghani, R. Ghasemitabesh, G. Hosseini Salekdeh, (2022), *Simultaneous hydrolysis of various protein-rich industrial wastes by a naturally evolved protease from tannery wastewater microbiota*, “Science of The Total Environment”, vol. 815, 152796.

78 A. Domínguez, F. J. Deive, M. Angeles Sanromán, M. A. Longo, (2010), *Biodegradation and utilization of waste cooking oil by Yarrowia lipolytica CECT 1240*, “European Journal of Lipid Science and Technology”, 112(11), 1200–1208.

leather production with the use of an isolated strain of yeast. The studies resulted in the submission of a patent application No P.442578, entitled "Method of utilisation of protein waste obtained in leather production". The aim of the invention is to use the *Yarrowia lipolytica* IPS21 yeast strain to obtain a method that allows for easy and one-stage utilisation of protein waste arising from leather production – especially chrome shavings arising from tanning processes, often stored so far at the tannery plant or disposed of at landfill sites. The research outcome also included the publication in 2021, in which the authors proved the yeast used in the study to absorb the source of carbon and nitrogen from collagen. Increased pH values in the medium as well as an increased amount of selected amino acids in the relevant samples resulted from the intensive metabolism of microorganisms.[79] The subsequent publication in this regard is currently in process to confirm that *Yarrowia lipolytica* IPS21 is an ideal candidate for converting protein-rich waste into high-value products.

3.1.3. Activities for the Benefit of the Local Community

Corporate social responsibility is a management strategy according to which enterprises voluntarily take into account social interests, environmental aspects or relations with various stakeholder groups, in particular employees, as far as their business operations are concerned. Being socially responsible means investing in human resources, environmental protection, public relations, and publicity to the extent of those activities, which contributes to the increase of the company's competitiveness and triggers the conditions for sustainable social and economic development.[80] In accordance with this idea, on July 1, 2021, the Ministry of Education and Science announced the Programme titled "Science for Society", the purpose of which is to support the higher education and science system and other institutions working to the extent of the dissemination of science. Co-financing may be granted to projects focusing on the cooperation of scientists with non-governmental and social organisations and the economic operators. The Programme comes forward with financial support within the framework of three priority thematic areas: scientific excellence, science for innovation, humanities. The list of projects approved for funding under this Programme included three projects implemented in whole or in part by the Centre for Footwear Materials, Dyed Products and Food of the Łukasiewicz – Lodz Institute of Technology Research Network.

79 D. Wieczorek, M. Lasoń-Rydel, D. Gendaszewska, (2021), *The influence of the presence of tanning shavings on the growth of yeast from the Dipodascaceae family*, "Technology and Quality of Products", vol. 66, pp. 170–184.

80 https://www.parp.gov.pl/csr (accessed: 07.08.2023).

The first Project entitled „The impact of construction, materials and proper fitting of footwear on the health of children and adolescents" falls into two priority areas, i.e. scientific excellence and science for innovation. The strategic aim of the Project is to tighten cooperation between scientific and research units and the social-and-economic organisations. Accomplishment of this goal will increase the recognition of the Łukasiewicz – Lodz Institute of Technology Research Network and ensure the development of innovative projects in the field of foot prophylaxis for children and adolescents up to 15 years of age, the correct selection of footwear and insoles, and the dependence of the target solutions on the child's physical activity. The operational objective of this Project is to develop attitudes promoting a healthy lifestyle among children, parents, educators and teachers in terms of the selection of footwear by means of developing a scientific monograph as well as recommendations, guidelines and good practices to this end. Within the framework of that Project four tasks are intended to be delivered. The first task will be to carry out anthropometric measurements of the feet of children and adolescents. The second task will be completed through delivery of an educational offer and demonstration lessons as well as a media information campaign. The third task will be to develop a scientific monograph, taking into account social aspects and the relationship between science, innovation and the economy. The Project titled "The impact of construction, materials and proper fitting of footwear on the health of children and adolescents" perfectly fits into the target of the Science for Society Programme. The interdisciplinarity of the research and related outcome will raise the interest in the social concern to improve the comfort of physical activity through the appropriate selection of insoles and footwear.

The second project, that has been awarded with funding from the Ministry of Education and Science, is entitled "Innovative system of distribution of healthy and regional food". That Project, in turn, fits into three thematic areas, i.e. scientific excellence, science for innovation, humanities – society-identity. The Project comes forward with the creation of an economically and organisationally strong agricultural and food industry in Poland through effective cooperation between entities operating in the field of science, society, and economy. The major activities of the Project aim to support the creation of new distribution channels for regional food products to easily reach a wide group of potential customers with them while maintaining the highest quality standards. The Project will be implemented in three stages. The first stage will cover quantitative and qualitative analyses in the field of food along with the development of optimised methodologies as part of the control system and indication of competitive advantage. The second stage will be completed through development of an innovative distribution system for healthy and regional food, together with promotional and information activities. The third stage will encompass the dissemination of the Project deliverables in the form of international publications. In summary, the Project titled „Innovative system of distribution of healthy and regional food" will provide for the complementary system of protection, quality assurance and promotion of regional products, that will significantly enhance the sustainable development of rural areas. The aim is also to protect and promote the cultural heritage of the countryside, which increases the attractiveness of rural areas and the development of agritourism.

The third Project, that has been implemented by the Centre for Shoe Materials, Coloured and Food Products since 2022, is entitled "Łukasiewicz for children – educational classes and workshops". That Project fits into two thematic areas of the Science for Society Programme, i.e. scientific excellence and science for innovation. The former thematic area is intended to support projects aimed at developing and implementing conceptual framework for the development of the research and teaching staff and the target relevant shape of the public perception of the Polish science. In turn, the latter thematic area, i.e. science for innovation supports projects aimed for instance at improving the effectiveness of the cooperation between science and business and disseminating knowledge about the relationship between science, innovation, and the economy. The aforementioned Project is aimed at establishing the cooperation between the Łukasiewicz Research Network – the Institute of Leather Industry and educational and care institutions in Lodz. Successful delivery of workshops offering fun in the field of ecology and innovative Polish solutions that have been created thanks to science and research as well as the cooperation with industry will allow for efficient time management in an interesting way and help broaden horizons. In addition, soft skills training conducted by employees involved in the Project will contribute to the development of specific interpersonal skills, and above all, qualifications related to presentation and public speech delivery. Four tasks are intended to be delivered within the framework of the Project. The first task will consist in delivery of an educational offer for preschool and early school children. The second task will be completed through a media campaign. Demonstration lessons will be conducted to effectively complete the third task. The fourth task will come forward with a script publicising projects implemented at the Centre for Footwear, Coloured and Food Products as well as a scientific publication. The Project will contribute to the increased recognition of the SBL-Lodz Scientific Institute.

3.2. Unit Processes for Selected Waste Disposal Management Methods in the Tanning Industry

Natural leather is the main product of the tanning industry and an intermediate product used in the consumer goods sector (footwear, clothing, haberdashery, furniture and motor cars). The solid waste generated by the leather industry may be used as a raw material for the production of new and advantageously economical products, thus ensuring sustainable and environmentally friendly industrial practices.[81] In the leather tanning processes (chemical processes and mechanical operations that shape the leather structure) various forms of solid waste are generated[82] – those are both biologically unstable waste (untanned trimmings, peelings) and waste resulting from the tanning process (shavings, unusable splits) and dust (from dyeing and finishing processes). The related literature indicates that tannery waste is used for producing for instance biogas, biofuels, biocarbons and used as bioabsorbents, soil fertilisers, and even as adsorbents or used for treating wastewater containing dyes.[83, 84, 85, 86, 87]

According to the data of the Statistics Poland,[88] the domestic sector of leather and leather products annually generates approx. 54.5 thousand tonnes of waste, while the estimated amount of solid waste stored so far (on the premises of the plants) equals 32.9 thousand tonnes. From one tonne of rawhide, only about 225 kg accounts for the finished product, and 75% of this weight is made up of production residue. Converted to the final assortment, over 2 kg of waste falls on a square meter of finished leather. Each tannery has its own leather tanning technologies, in which individual processes depend on the selection of products for which the leather is produced.

Leather waste may be considered as a composite material that has an extensive structure due to the collagen fibre it contains.[89] The structure, density (1.30–1.34 g/cm^3) and high strength of collagen fibre (tensile strength 147.1 MPa) as well as the fact that collagen can adsorb water vapour in the amount reaching almost a half of its weight, proves the high potential of reusing that waste in circular economy.

81 A.K. Singh, A. Raj, (2020), *Emerging and eco-friendly approaches for waste management*, "Environmental Sciences Europe", vol. 32, p. 107.

82 B. Ravindran, J.W.C. Wong, A. Selvam, K. Thirunavukarasu, G. Sekaran, (2016), *Microbial biodegradation of proteinaceous tannery solid waste and production of a novel value added product – Metalloprotease*, "Bioresource Technology", vol. 217, pp. 150–156.

83 C.B. Agustini, F. Spier, M. da Costa, M. Gutterres, (2018), *Biogas production for anaerobic co-digestion of tannery solid wastes under presence and absence of the tanning agent*, "Resources, Conservation and Recycling", vol. 130, pp. 51–59.

84 S. Amdouni, A.B.H. Trabelsi, A.M. Elasmi, R. Chagtmi, K. Haddad, F. Jamaaoui, H. Khedhira, C. Chérif, (2021), *Tannery fleshing wastes conversion into high value-added biofuels and biochars using pyrolysis process*, "Fuel", vol. 294, 120423.

85 X. Huang, F.Yu, Q. Peng, Y. Huang, (2018), *Superb adsorption capacity of biochar derived from leather shavings for Congo red*, "RSC Advances", vol. 8, pp. 29781–29788.

86 N.S.C. Pinheiro, O.W. Perez-Lopez, M. Gutterres, (2020), *Solid leather wastes as adsorbents for cationic and anionic dye removal*, "Environmental Technology", vol. 43, no. 9, pp. 1285–1293.

87 J.A. Arcibar-Orozco, B.S. Barajas-Elias, F. Caballero-Briones, L. Nielsen, J.R. Rangel-Mendez, (2019), *Hybrid carbon nanochromium composites prepared from chrome-tanned leather shavings for dye adsorption*, "Water Air and Soil Pollution", vol. 230, p. 142.

88 Rocznik Statystyczny Przemysłu. Statistical Yearbook of Industry – Poland, Warsaw 2020.

89 G. Bufalo, C. Florio, G. Cinelli, F. Lopez, F. Cuomo, L. Ambrosone, (2018), *Principles of minimal wrecking and maximum separation of solid waste to innovate tanning industries and reduce their environmental impact: The case of paperboard manufacture*, "Journal of Cleaner Production", vol. 174, pp. 324–332.

The amount, structure, and composition of the generated tannery waste were the factors determining the choice of the subject matter of this research. The activities include, in particular, tannery shavings, that have irregular shapes (which causes them to bundle up), are characterised by a very low bulk density of up to 0.1 g/cm^3 (dust over long distance), high humidity of up to 70%, which makes them environmental burden.

3.2.1. Purpose of the Work

The main objective of the research is to extend the scope of recycling of tannery waste (especially its components) and to increase the application potential of the technological solutions developed on the basis of the production residue. In addition, the work is aimed at confirming the hypothesis that individual unit processes allow for the processing of hazardous industrial waste (as exemplified by tannery residue) and increase the possibility of its reuse in other technological operations, obtaining new material as a result.

The following specific objectives have been set out:

- Identification of prospective application areas for tanning residue, given the related properties.
- Optimisation of respective unit processes in the field of waste management (i.e. screening, pressureless granulation, mixing).
- Verification of new solutions based on tannery waste (i.e. composites based on shavings and mineral additives, granules and seed coats based on collagen preparations obtained from tannery waste).

There are numerous literature reports on the potential of using waste biomass of animal and plant origin,[90] including those in the form of various granulates.[91]

3.2.2. Identification of Prospective Application Areas for Tanning Residue, Given the Related Properties

Identification of prospective application areas for tanning residue, given the related properties, was conducted on the basis of the results obtained in the field of analyses of selected (significant in terms of potential use) properties of shavings obtained in domestic tanneries. To this end, the shavings were classified in terms of the grain size and shape (according to the Zingg classification) the specific surface area, chemical composition, and the content of volatile organic compounds (VOC).

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90 A. Rostocki, K. Ławińska, R. Modrzewski, G. Siegień, R. Hejft, A. Obraniak, (2022), *Methods for treatment of animal and plant-based biomass waste*, “Fibres & Textiles in Eastern Europe”, vol. 30, no. 4, pp. 32–42.

91 A. Rostocki, H. Unyay, K. Ławińska, A. Obraniak, (2023), *Granulates based on bio and industrial waste and biochar in a sustainable economy*, “Energies”, vol. 16, p. 56.

Table 3.2.1. Granulometric composition of tannery shavings

Fraction, mm	Weight Share, %
0–0.5	18.0
0.5–1.0	16.0
1.0–1.6	14.5
1.6–2.5	11.0
2.5–4.0	12.0
4.0–8.0	10.0
8.0–12.5	18.5

Source: own research data.

The granulometric composition of tannery shavings (Tab.3.2.1.) was determined based on a sieve analysis (on a laboratory shaker with a set of testing sieves). In order to characterise the shape of shavings, the analysis was carried out according to the Zingg classification (using the Kamik analyser) in relation to four basic grain shapes (Tab. 3.2.2.).

Table 3.2.2. Shape of shavings (according to Zingg classification)

Shape	Volume Share, %
Disc	4.93 ± 0.71
Sphere	70.14 ± 1.02
Wedge	1.17 ± 0.48
Cylinder	23.77 ± 1.52

Source: own research data.

As part of the work carried out, porosimetry testing was carried out using low-pressure gas adsorption of selected fractions of tannery shavings. Structural tests were performed by means of the volumetric adsorption analyzer ASAP 2020 (Micromeritics). On the basis of equilibrium sorption points of nitrogen adsorption, the parameters of maximum sorption capacity and specific surface were determined (the correlation coefficient of 0.999). The Brunauer-Emmett-Teller – BET model[92] was used for characterising pores filling in a multilayer manner.

92 L. López-Pérez, V. Zarubina, I. Melián-Cabrera, (2021), *The Brunauer-Emmett-Teller model on alumino-silicate mesoporous materials. How far is it from the true surface area?*, "Microporous and Mesoporous Materials", vol. 319, 111065.

Table 3.2.3. Structural parameters of the tested shavings

Fraction of shavings	Total sorption capacity cm^3/g STP	Specific surface area BET m^2/g	Adsorption equilibrium constant
< 0.5	0.60	2.63 ± 0.01	23.85
0.5–1	0.61	2.66 ± 0.01	23.67
1–2.5	0.65	2.84± 0.02	19.13
2.5–4	0.59	2.55± 0.02	20.72
> 4	0.81	3.51± 0.02	12.97

Source: own research data.

Using the method of optical emission spectrometry with inductively coupled plasma ICP-OES (spectrometer ICP-OES 5110 Agilent), the chemical composition of tannery shavings was determined in terms of the content of selected elements (metals) (Table 3.2.4.). The content of the tested elements in the samples of shavings was read from the standard curves prepared from the standards of respective metals.

Table 3.2.4. Chemical composition of shavings – content of elements in the sample [mg/kg], ND – below the detection limit

Element	Content [mg/kg]	Element	Content [mg/kg]
Ag	ND	Mn	3.095
Al	47.751	Mo	ND
As	ND	Ni	4.687
Ba	1.697	Pb	ND
Bi	ND	Sb	ND
Ca	2056.97	Se	ND
Cd	ND	Sn	<
Co	ND	Sr	1.193
Cr	10371.6	Ti	ND
Cu	ND	V	ND
Fe	490.561	Zn	6.173
Ge	ND	Zr	ND
Hg	ND	S	3231.75
Mg	1380.45	P	85.806

Source: own research data.

The gas chromatography method with mass spectrometry (GC/MS/HS) at 150°C was used for determining the content of volatile organic compounds (Tab. 3.2.5.). Samples were analysed by means of the Nexis GC-2030 Shimadzu's chromatograph equipped with MS model GCMS-QP2020 and AOC-20i headspace auto sampler.

Table 3.2.5. VOC content in tannery shavings

Substance name	Content [%]	Substance name	Content [%]
3,3-dichloropropene	1.37	triethylene glycol monododecyl ether	0.30
methylhydrazine	0.29	tetradecanal	0.22
formic acid	2.11	myristic acid	0.37
methylphosphine / formic acid	2.78	hexadecanal	2.41
propylene glycol	0.84	pentadecanal	0.26
benzaldehyde	1.04	palmitic acid methyl ester	0.88
carbitol	0.38	palitol acid	0.35
benzosulfonosal	8.75	pentadecanoic acid	3.09
8-methylnonanoic acid	0.32	linoleic acid methyl ester	0.41
4-chloro-m-cresol	16.11	methyl oleate	7.91
2-undecenal	0.29	9-octadecenoic acid methyl ester	2.51
o-hydroxybiphenyl	43.57	methyl stearate	0.41
tridecanal	0.39	cis-10-pentadecenoic acid	0.63
2-methylthiobenzothiazole	0.86	other substances	0.92
2-octylfuran	0.23		

Source: own research data.

Results obtained

- A large variation in the dimensions of respective shaving fractions has been observed (differences in the range of 0.5–12.5 mm).[93]
- The shape of the shavings is varied, but the dominant form is a sphere (70.14%) and a cylinder (23.77%).[94]
- The pore structure of the tested tannery shavings consists mainly of mesopores and macropores. This is evidenced by the relatively low value of the BET specific surface area (SSA), in the range of 2.55–3.51 m^2/g.

93 K. Ławińska, A. Obraniak, R. Modrzewski, (2019), *Granulation process of waste tanning shavings*, "Fibres & Textiles in Eastern Europe", vol. 27, no. 2(134), pp. 107–110.
94 K. Ławińska, (2021), *Production of agglomerates, composite materials, and seed coatings from tannery waste as new methods for its managemen*, "Materials", vol. 14, no. 21, p. 6695.

Comparing the tested samples to natural meso and macroporous matter, such as e.g. carbonate rocks and dolomites, tannery shavings have a similar surface area.[95]

- The analyses carried out indicate that tannery shavings contain significant amounts of elements. They constitute a useful waste from the point of view of elemental composition due to the high content of Ca, Mg, S and P as a valuable source of macroelements, structural elements. High Ca content, and additionally Na content in shavings are also indicated by the authors of the paper.[96] Taking into account the environmental aspect, it is important that there is no Pb or As.[97]
- The compounds obtained in the VOC analysis (e.g. organic acids, preservatives, surfactants, alkanes) are components of chemical preparations commonly used in leather tanning processes. The amount of substances classified (in accordance with Regulation (EC) No 1272/2008 of the European Parliament and of the Council of December 16 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45 /EC and amending Regulation (EC) No 1907/2006) as irritating or harmful to the environment constitutes a small percentage of the analysed waste.[98] In addition, there are solutions to reduce VOCs in tanning processes.[99]

3.2.3. Optimisation of Respective Unit Processes in the Field of Waste Management (i.e. Screening, Pressureless Granulation, Mixing)

The optimisation of the sieving process and non-pressure granulation[100] of tannery waste was carried out. Granulation processes were used for obtaining agglomerates from waste shavings and forming seed shells (of varied size and shape) based on

95 K. Ławińska, R. Modrzewski, A. Obraniak, (2020), *Comparison of granulation methods for tannery shavings*, "Fibres & Textiles in Eastern Europe", vol. 28, no. 5(143), pp. 119–123.

96 A. Pati, R. Chaudhary, S. Subramani, (2014), *A review on management of chrome-tanned leather shavings: a holistic paradigm to combat the environmental issues*, "Environmental Science and Pollution Research", vol. 21, pp. 11266–11282.

97 K. Ławińska, (2021), *Production of agglomerates…*

98 Ibidem.

99 R. Cuadros, A. Solà, I. Ollé, L. Otero, A. Bacardit, (2016), *Reducing the use of volatile organic compoundsin the leather industry*, "Journal of the Society of Leather Technologists and Chemists Journal", vol. 100, pp. 1–7.

100 A. Obraniak, K. Lawinska, (2017), *Spectrophotometric analysis of disintegration mechanisms (abrasion and crushing) of agglomerates during the disc granulation of dolomite*, "Granular Matter", vol. 20, p. 7.

collagen preparations (obtained from tannery waste) in order to increase their drought resistance.

Screening of shavings was carried out on steel mesh sieves with square openings (vibration frequency at 50 Hz and vibration amplitude of 1.0 mm). In the first stage, the input was sieved in a sieve with a mesh opening of 2.5 mm in size (during 20 min), while in the next stage, a fraction of shavings of 0–2.5 mm in size was sieved in a sieve with a mesh opening of 1.0 mm in size (during 10 min). In both series, it was fed to the sieve in such an amount that the initial thickness of the material layer in the sieve did not exceed twice the maximum size of the grains (the length of shavings) in the feed (it had a significant impact on the screening efficiency, which decreased sharply with the increase of the layer thickness in the sieve). The phenomenon of blocking the sieve openings, especially by grains with dimensions similar to the sieve openings (especially those with dimensions equalling or slightly larger than the mesh opening of the sieve), significantly hinders the sieving process. The dependencies in this regard are presented in the related publications[101, 102] that elaborate the description of the phenomenon of screen blocking upon by various model shapes of granular materials and types of laboratory and industrial screens (including vibrating, rotary, with a conical and drum screen), along with a statistical analysis of the obtained results.[103] The graph presented in Chart 3.2.1. shows that the optimal time for screening raw tannery shavings is 20 minutes. After this time, the change in screened and sifted matter is very small and amounts to approx. 1% of the input. Nevertheless, shavings should be considered difficult to sieve because the optimal sieving time of typical granular matter (e.g. mineral aggregates – sharp-edged shape, sand – irregular shape) usually do not exceed 5 minutes.[104] The process of sifting shavings in a sieve with mesh openings of 1.0 mm in size requires much shorter time.

101 K. Lawinska, R. Modrzewski, (2017), *Analysis of sieve holes blocking in a vibrating screen and a rotary and drum screen*, “Physicochemical Problems of Mineral Processing”, vol. 53, no. 2, pp. 812–828.

102 K. Lawinska, R. Modrzewski, P. Wodzinski, (2016), *Mathematical and empirical description of screen blocking*, “Granular Matter”, vol. 18, no. 13.

103 K. Lawinska, R. Modrzewski, W. Serweta, (2018), *The phenomenon of screen blocking for mixtures of varying blocking grain content*, “Gospodarka Surowcami Mineralnymi – Mineral Resources Management”, vol. 34, pp. 83–96.

104 K. Lawinska, R. Modrzewski, P. Wodzinski, (2015), *Comparison of the potential of using drum and vibrating screens for segregating mineral and municipal waste*, “Rocznik Ochrona Środowiska”, vol. 17, no. 2, pp. 1365–1388.

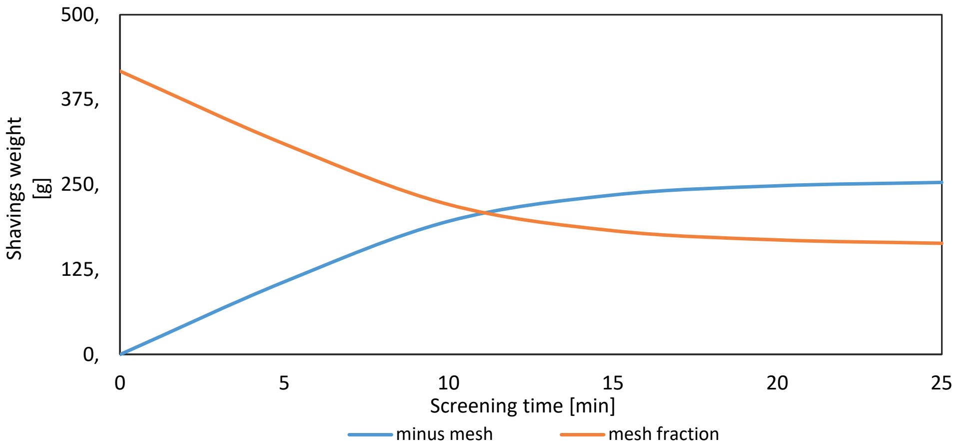

Chart 3.2.1. Determining the time of sifting shavings in a sieve with mesh openings of 2.5 mm in size
Source: own research data

Results obtained

Taking into account the large variation in the dimensions of respective fractions (differences in the range of 0.5–12.5 mm) and their tendency to agglomerate into larger agglomerates (larger fractions), it is recommended to use preliminary screening of tannery shavings for the purpose of other technological processes, especially in respect of fractions of 0–2.5 mm in size, which in total constitutes approx. 60% of total weight.[105] Thus, only approx. 40% of the input (2.5–12.5 mm fraction) requires grinding.

The process of non-pressure granulation results in agglomerates derived from tannery shavings. Three methods of shavings granulation were developed and carried out (Table 3.2.6.). The variable parameters were: the type and amount of mineral additives as well as the amount and concentration of the binding liquid (bed moisture), the method of sprinkling the bed and the sequence of adding respective components to the plate granulator. The graphs presented in Chart 3.2.2. show the granulometric composition obtained by means of the methods 1, 2 and 3 (three selected research series for each method).

105 K. Ławińska, A. Obraniak, R. Modrzewski, (2019), *Granulation process…*

Table 3.2.6. Process parameters of the tannery shavings granulation process

Conditions	Method 1	Method 2	Method 3
Apparatus	Disc granulator, disc of 1 m in diameter, disc rotation speed at 9–15 RPM, disc inclination angle of 0.15–0.3o		Vibrating disc granulator, disc of 0.55 m in diameter, inclination angle of 45o, rotational speed at 30 RPM, vibration frequency at 50 Hz, amplitude of 1 mm
Fraction of shavings, mm	0–12.5; 0–2.5	0–2.5	0–2.5; 0–1
Fine-grained additives	gypsum* (dry and wet), dolomite	gypsum* (dry and wet)	gypsum* (dry and wet), dolomite
Binding liquid	aqueous glass solution R-145 (50–75%)	aqueous glass solution R-145 (75%)	aqueous glass solution R-145 (75%)
Course of granulation processes (stages)	shavings were fed onto the granulator disc, then the mineral additive was sprinkled on the bed through a hydraulic nozzle, shavings were fed onto the granulator disc, the bed was sprinkled and then the mineral additive was applied	shavings were soaked in a binding liquid (pulp), then the granulation process of the moist pulp was carried out with the addition of selected mineral fine material (along with gradual wetting of the bed)	shavings were soaked in a binding liquid (pulp), which followed by draining the pulp, then pulp granulation was proceeded with the addition of selected mineral fine material (without addition of binding liquid/no bed sprinkling)
Other operations	–	dry shavings were mixed in a mixer with 75% glass solution until they were completely wetted (a cylindrical mixer with a low-speed anchor agitator was used)	dry shavings were mixed in a mixer with 75% glass solution until they were completely wetted (a cylindrical mixer with a low-speed anchor agitator was used), then the pulp was drained by placing it on a vibrating sieve (removal of excess moisture)

* waste gypsum, sourced from the Belchatow Power Plant, from a flue gas cleaning system
Source: own research data.

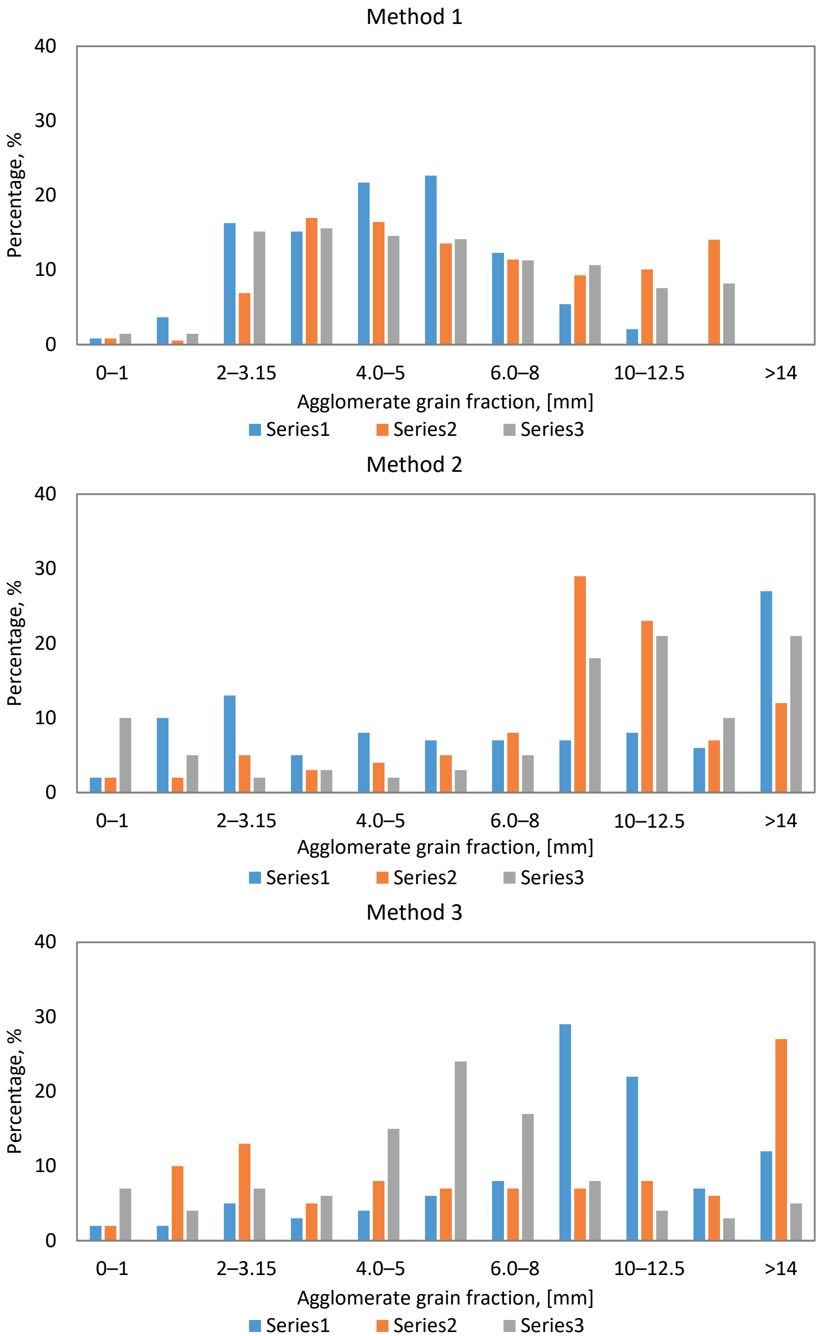

Chart 3.2.2. Granulometric compositions of the obtained agglomerates from tannery shavings (according to methods 1–3)

Source: own research data.

Results obtained

- Non-pressure granulation processes allow for granulation of the entire bed of shavings (0–12 mm fraction). It should be noted that the granules produced according to the developed methods contain a significant proportion of grains with fractions of 2–6 mm in size (especially method 1 and 3), that have the greatest application potential for their use in other processing methods (e.g., composite materials).[106]
- The developed methods of non-pressure granulation of waste allow for minimising environmental burden (related to landfilling and secondary dusting), reducing storage and transportation costs while maintaining potential reuse of processed waste.[107, 108, 109]
- Based on the research, it can be concluded that the best quality pellets are obtained from shavings previously mixed with water glass solution (pulp). Shavings that are too dry do not granulate well.[110]
- The easiest way to granulate tannery shavings is to combine them in a granulator with mineral material after the wetting stage.[111]
- The analysis of the test results indicates that granules with larger diameters were obtained for the tests carried out with higher final moisture content.[112]
- The granulation processes of waste shavings gave them regular, spherical shapes forming a loose granular bed with a bulk density on average about 5 times higher (0.4–0.6 g/cm^3) than that of loose, dry shavings (0.1 g/cm^3).[113]
- Agglomerates from tannery shavings containing both mineral and organic components can be easily stored, transported and dosed in subsequent technological operations.[114]

Non-pressure agglomeration was also used in the processes of forming capsules based on collagen preparations (obtained from tannery waste) of respective seeds. The possibility of using a disc granulator for coating seeds of leguminous plants (pea, field bean, soybean) and rape was assessed. The resulting coatings are designed to increase resistance to drought and pests during seed germination and emergence of seedlings. The characteristics of the collagen preparations used (also in terms of

106 K. Ławińska, (2021), *Production of agglomerates…*

107 K. Ławińska, S. Szufa, R. Modrzewski, A. Obraniak, T. Wężyk, A. Rostocki, T.P. Olejnik, (2020), *Obtaining granules from waste tannery shavings and mineral additives by wet pulp granulation*, “Molecules”, vol. 25, no. 22, p. 5419.

108 K. Ławińska, R. Modrzewski, A. Obraniak, (2020), *Comparison of granulation…*

109 K. Ławińska, A. Obraniak, R. Modrzewski, (2019), *Granulation process…*

110 K. Ławińska, R. Modrzewski, A. Obraniak, (2020), *Comparison of granulation…*

111 K. Ławińska, A. Obraniak, R. Modrzewski, (2019), *Granulation process…*

112 K. Ławińska, R. Modrzewski, A. Obraniak, (2020), *Comparison of granulation…*

113 K. Ławińska, A. Obraniak, R. Modrzewski, (2019), *Granulation process…*

114 K. Ławińska, S. Szufa, R. Modrzewski, A. Obraniak, T. Wężyk, A. Rostocki, T.P. Olejnik, (2020), *Obtaining granules…*

a valuable source of nitrogen) were presented in the work output,[115, 116, 117] specifying the physicochemical properties and the content of respective amino acids. The collagen preparations used are transparent liquids with an average density of 1.1125 g/mL (20°C), 67.19% water content, pH 7.5. They are characterised by high contents of glycine, alanine, proline and hydroxyproline.

Optimum conditions for the encapsulation process were determined, including: disc rotational speed at 20 RPM, disc inclination angle of 45°, binding liquid was applied directly to the bed fed with seeds by sprinkling through a hydraulic nozzle. The respective layers of the shell were formed in a specific order (Figure 3.2.1.). The centrally placed seed (1) was first covered with a protective layer, e.g. of fungicides (2). The next layer was a collagen preparation (3). The outer layer of the shell (4) was a fine-grained mineral additive conducive to seed germination (e.g. dolomite, peat, waste soot was used as a source of carbon, etc.). In order to compare the obtained results, yellow dextrin and polyvinyl acid were used as a classic reference liquid[118] for the purpose of collagen preparations. In selected tests, the addition of latex (CAS: 25085-39-6) was also used for improving the stability of the collagen preparation. Output molasses derived from the sugar industry was also used as another type of binding liquid.

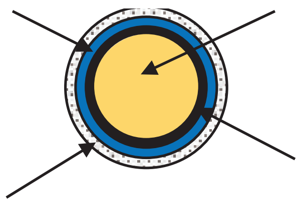

Figure 3.2.1. Layered seed coat produced on a disc granulator
Source: own research data.

As a result of seed coating on a disc granulator, complete, closed coatings were formed on single grains of legumes and rape (no agglomerates were formed) (Figure 3.2.2.). They proved good adhesion to the resulting otoliths (better for

115 K. Ławińska, M. Lasoń-Rydel, D. Gendaszewska, E. Grzesiak, K. Sieczyńska, C. Gaidau, D.G. Epure, A. Obraniak, (2019), *Coating of seeds…*

116 K. Ławińska, D. Gendaszewska, E. Grzesiak, J. Jagiełło, A. Obraniak, (2017), *Use of tanning waste in seed production*, "Przemysł Chemiczny", vol. 96/11, pp. 2344–2347.

117 D. Gendaszewska, M. Lasoń-Rydel, K. Ławińska, E. Grzesiak, P. Pipiak, (2021), *Characteristics of collagen…*

118 M. Domoradzki, W. Korpal, (2005), *Dobór materiałów do otoczkowania nasion rzodkiewki roztworem dekstryny*, "Inżynieria Rolnicza", vol. 11, no. 71, pp. 69–74.

samples in which collagen hydrolysate was the binding liquid). Granules with a homogeneous shape close to spherical were obtained.[119, 120, 121]

Figure 3.2.2. The process of pea seed coating on a disc granulator
Source: own research data.

The analysis of the differences amongst respective samples in terms of the value of the average weight of one pelleted grain and 100 grains with coating indicated the durability of the obtained casings stored with air access. The phenomenon of crushing seed coats during storage was not observed. The largest differences in the average weight of 1 grain were observed in the first days after the pelleting process. In the following days, the matter stabilised. The analysis of the decrease in the weight of the encapsulated grains indicated a greater durability of the coatings with collagen hydrolysate as compared to the durability of coatings made of substances used in studies by other authors (yellow dextrin, polyvinyl alcohol). A smaller decrease in the weight of grains coated with collagen hydrolysate resulted from the specific properties of this preparation (biopolymer, network structure, fibrous structure). The collagen hydrolysate formed a hydrophilic film on the surface of the grain, thanks to which the loss of water was limited. For most of the samples, the average weight of one grain on the day of pelleting was close to the values obtained after 15 days. The initial increase or decrease in the average weight of one grain resulted from the shell composition, including the properties of the materials used.[122, 123] In addition, in order to verify the process, a chromatographic analysis was carried out, which confirmed the presence of amino acids in a randomly selected series of pelleted seeds.

119 K. Ławińska, S. Szufa, R. Modrzewski, A. Obraniak, T. Wężyk, A. Rostocki, T.P. Olejnik, (2020), *Obtaining granules…*
120 K. Ławińska, D. Gendaszewska, E. Grzesiak, J. Jagiełło, A. Obraniak, (2017), *Use of tanning…*
121 K. Ławińska, D. Gendaszewska, E. Grzesiak, M. Lasoń-Rydel, A. Obraniak, (2017), *Coating of leguminosarum seeds with collagen hydrolyzates from tanning waste*, "Przemysł Chemiczny", vol. 96/9, pp. 1877–1880.
122 K. Ławińska, D. Gendaszewska, E. Grzesiak, J. Jagiełło, A. Obraniak, (2017), *Use of tanning…*
123 K. Ławińska, D. Gendaszewska, E. Grzesiak, M. Lasoń-Rydel, A. Obraniak, (2017), *Coating of leguminosarum…*

Results obtained

- It is possible to form durable, stable and complete seed coatings (for grains of varied sizes and shapes) on the basis of waste collagen preparations obtained from tannery waste, using a disc granulator.[124, 125]
- Compatibility of the produced capsule also allows for the use of a layer of fungicides and zoocides protecting the seeds against pathogens and pests.[126]

3.2.4. Verification of New solutions Based on Tannery Waste (i.e., Composites Based on Shavings and Mineral Additives, Granules and Seed Coatings Based on Collagen Preparations Obtained from Tannery Waste)

Verification of new solutions based on tannery waste was carried out by means of creating composite materials and analysing the parameters of the products obtained by pressure-free granulation, i.e. granules and seed coats.

As part of the conducted research, new materials of a composite nature were formed by using a combination of components in the form of tannery shavings and mineral fillers in combination with a suitable adhesive medium, bonding discontinuous, chaotically oriented fibre. The process of pursuing this goal was focused on determining the physical and mechanical properties of the newly created composites, based on a natural polymer, that were fragmented collagen fibre contained in the waste arising from the leather industry. Tannery shavings originating from chrome tanning technology (about 70% of domestic tanneries use chrome tanning technologies) constituted the essential ingredient of the new composite materials. Moisture-free, natural mineral fillers in the amount equivalent to 5% and 10% of the shavings weight were used in the composite moulding process. The mineral additives were readily available powdered mineral raw materials:

- natural calcium-magnesium carbonate (dolomite flour with an average grain size of 0.045 mm),
- kaolin (kaolinite 81%) with a grain size of 0.2–0.002 mm,
- bentonite (montmorillonite > 75%) with a fraction smaller than 0.056 mm.

Tannery shavings with a moisture content of 50% along with mineral additives were mixed using four different types of adhesive medium, that is: Homopolymer (that is an aqueous dispersion of polyvinyl acetate), a modified gelatinous adhesive of animal origin, an adhesive based on low-ammonia natural latex,

124 K. Ławińska, D. Gendaszewska, E. Grzesiak, J. Jagiełło, A. Obraniak, (2017), *Use of tanning…*

125 K. Ławińska, D. Gendaszewska, E. Grzesiak, M. Lasoń-Rydel, A. Obraniak, (2017), *Coating of leguminosarum…*

126 K. Ławińska, M. Lasoń-Rydel, D. Gendaszewska, E. Grzesiak, K. Sieczyńska, C. Gaidau, D.G. Epure, A. Obraniak, (2019), *Coating of seeds…*

and a solvent-free, clear epoxy resin with hardener (for liquid epoxy resins). The optimal weight percentage of shavings in relation to the compatibiliser was determined in the preliminary tests to equal 60:40. The process of forming the composite was proceeded by adding mineral filler and adhesive medium to the shavings in order to combine the components. The mixture of all components was pressed in a heated hydraulic press at the constant pressure of 20 MPa. The moulded composites were dried in a laboratory dryer at 25°C for 24 hours. After another 72 hours of conditioning, the physical and mechanical properties of the obtained composites were tested. The moulded composites were subjected to static tensile tests conducted by means of a Zwick/Roell Z010 type testing machine. The dependence of the increase in the length of the composite specimens on the magnitude of the tensile force applied parallel to the specimen axis was recorded. In the course of the static axial tensile test of the moulded composites, the breaking stress [MPa], breaking force F_{max} [N], sample deformation for F_{max} [mm] were inter alia determined. The strength tests of the moulded composites made it possible to determine the linear deformability modulus (Young's modulus) that assessed their elasticity (Table 3.2.7.). In addition, the water absorption capacity (absorbability, i.e., water content defined as the ratio of the water volume to the weight of the composite specimen in the dry state) and the ability to dewater during the drying process were examined in respect of each of the composites. Taking into account the environmental aspect, the total chromium content (by means of the iodometric titration method) and extracted chromium VI (by means of the spectrophotometric method using 1,5-diphenylcarbazide) in the shavings and produced composites underwent analyses.

Table 3.2.7. Average values of Young's modulus and average density of the produced composites

	Adhesive medium			
	Homopolymer	**Gelatine glue**	**Glue based on low ammonia natural latex**	**Epoxy resin with hardener**
Young's Modulus [GPa]	0.0517 ± 0.00981	0.0365 ± 0.00771	0.000594 ± 0.000136	0.000586 ± 0.0000926
Density [g/cm³]	0.901 ± 0.08	0.699 ± 0.09	0.509 ± 0.07	0.420 ± 0.08

Source: own research data.

The research on composites made from tannery shavings was carried out within the framework of the Project entitled "Determination of optimal composition of collagen fibre composite derived from leather industry waste and mineral additives" funded by the National Science Centre, Miniature 1, DEC 2017/01/X/ST8/01045.

Results obtained

- The obtained values in respect of the properties of the tested composites with mineral additives depend on the specificity of the filler (additive) used. The type of mineral additive used affects e.g. tensile strength, maximum strength and deformation of composites based on tannery shavings. Composites with the addition of bentonite are characterised by the highest tensile strength and the highest breaking strength. The amount of the added natural filler, inter alia, shapes the deformation value due to the maximum force of the formed composites. The formulated conclusions are confirmed by the resulting figures of the statistical significance arising from the conducted analyses.[127, 128]
- The physicochemical parameters are also affected by the apparatus and process conditions for producing composites from tannery shavings, including, among others, ironing temperature. In the case of the homopolymer-bonded composites, the highest values of the maximum force at which the first fracture of the sample occurred were obtained for the highest pressing temperature (80°C). On the other hand, composites formed at lower pressing temperatures (20°C, 40°C) showed better sorption properties.[129, 130, 131]
- The analysis of the values of Young's modulus obtained for the created composites is indicative of the classification of polymer foams (VLD, LD, MD) and some materials within the group of elastomers (IR, CR, EVA), i.e. materials capable of reversible deformation under the influence of mechanical forces without the risk of losing the continuity of their structure, which significantly extends the area of their application.[132, 133]
- The influence of the mineral additive is important in the context of creating an appropriate system in terms of its resistance to water. The source of the increase in the intensity of soaking together with the increase in the percentage content of the mineral additive accounts for the specific properties of the fillers used. In the case of bentonite and kaolin, the characteristic feature of is their high water absorption and swelling capacity. However, the chemical

127 K. Ławińska, R. Modrzewski, W. Serweta, (2019), *Tannery shavings and mineral additives as a basis of new composite materials*, "Fibres & Textiles in Eastern Europe", vol. 27, no. 5(137), pp. 89–93.

128 K. Ławińska, W. Serweta, R. Modrzewski, (2019), *Studies on water absorptivity and desorptivity of tannery shavings-based composites with mineral additives*, "Przemysł Chemiczny", vol. 98/1, pp. 106–109.

129 K. Ławińska, R. Modrzewski, W. Serweta, (2019), *Tannery shavings…*

130 K. Ławińska, W. Serweta, R. Modrzewski, (2019), *Studies on water…*

131 K. Ławińska, W. Serweta, R. Modrzewski, (2018), *Qualitative evaluation of the possible application of collagen fibres: Composite materials with mineral fillers as insoles for healthy footwear*, "Fibres & Textiles in Eastern Europe", vol. 26, no. 5(131), pp. 81–85.

132 K. Ławińska, R. Modrzewski, W. Serweta, (2019), *Tannery shavings…*

133 K. Ławińska, (2021), *Production of agglomerates…*

nature of dolomite (the presence of MgO and CaO oxides) that increases the affinity to hydration, reduces the sorption capacity of composites with this addition. The analysis of the water absorption capacity of the newly developed composite materials showed that the optimisation problem related to the tested property can be steered in many ways. The observed statistically significant differences, due to the differentiating factor – the binding material, allow for the formulation of recommendations as to the type of adhesive medium used.[134]

- The type of adhesive medium significantly affects the ability to absorb and release water. This means that, depending on the purpose of the material, the water absorption capacity can be reduced or increased, as well as the drying rate can be accelerated or delayed. A global comparison of the produced composites indicated the existence of differences due to the proportions of the filler in relation to the weight of shavings. The change in the properties of composite materials also manifested itself in the location of the equilibrium points defined as the intersection points of the drying curves with the soaking curves.[135]
- With regard to environmental tests, composites made of collagen fibre from leather industry waste and mineral additives are safe for the environment, which is confirmed by the lack of Cr(VI) mg/kg content (the determination was made by means of the spectrophotometric method using 1,5-diphenylcarbazide). The total Cr in the tested composites and shavings equalled 3.7%–4.2% Cr_2O_3.[136]

As far as the tannery shavings agglomerates created by non-pressure granulation processes are concerned, their strength properties were defined to prove their potential application (taking into account transport, storage and dosage to other process operations).

The value of the maximum compressive stress causing the produced granules to be destroyed was analysed. The tests were carried out by means of an Instron Tester, measuring the value of the stress in terms of a function of the displacement of the apparatus head that compressed the granules. Each time, the resistance of five granules from each size class was tested, and the arithmetic mean was calculated (Table 3.2.9.). The tests were carried out for selected granules produced by means of the Method 3 (process parameters are shown in Table 3.2.8.).

134 K. Ławińska, W. Serweta, R. Modrzewski, (2019), *Studies on water…*
135 Ibidem.
136 K. Ławińska, (2021), *Production of agglomerates…*

Table 3.2.8. Parameters of tannery shavings granulation processes

Sample	Shavings Fraction [mm]	Water glass Solution [g]	Mineral Additive	Weight of Mineral Additive [g]	Granulation Time [min]
1	0–2	1000	wet gypsum	500	10
2	0–2	1000	wet gypsum dry gypsum	500 285	10
3	0–2	800	wet gypsum	500	10
4	0–2	800	dolomite	1700	13
5	0–2	600	dolomite	1500	8
6	0–1	800	wet gypsum dolomite	400 950	15
7	0–1	800	wet gypsum dolomite	400 1250	18

Source: own research data.

Table 3.2.9. Average destructive force applied to created granules according to the parameters indicated in Table 3.2.8.

Granulate Fraction [mm]	Average Value of Destructive Stress [N]						
	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7
0–1	1.83	3.5	1.3	2.9	3.5	2.7	0.5
1–2	3.46	5.6	4.8	6.1	8.3	4.1	0.9
2–3	4.07	6.8	5.2	25.1	21.2	5	1.2
3–4	4.34	7.8	6.2	30.6	29.1	5.2	1.6
4–5	6.65	9.7	7.7	60.2	67.2	6.6	2.2
5–6.3	7.02	23.1	8.4	82.5	73.5	7.1	2.7
6.3–8	18.34	29.8	11.6	129.8	126.0	13.8	4.4
8–10	39.97	31.5	26.0	158.8	185.4	27.8	10.3
10–12.5	43.99	40.2	28.6	190.9	198.7	28.8	13.1
12.5–14	65.438	41.9	34.9	200.0	200.0	35.9	17.1
>14	149.838	95.4	96.3	200.0	200.0	48.1	26.2

Source: own research data.

For the selected fractions, the drop resistance (resistance to breakage) of the created granules was also analysed. Out of the granules obtained as the output of the trials 1–7 (Table 3.2.8.), 60 pellets were selected and then dropped onto a concrete floor from a height of 1 m, counting the number of unbroken pellets[137] (Table 3.2.10.). The resistance to breakage of the granules is crucial with regard to their transport and further processing.[138]

Table 3.2.10. Number of unbroken (drop resistant) granules

Granulate Fraction [mm]	Number of unbroken (drop resistant) granules [unit]						
	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7
5–6.3	60	60	56	59	60	55	54
6.3–8	59	60	57	60	60	59	59
8–10	59	60	59	58	60	58	59
10–12.5	59	60	58	59	59	59	58
12.5–14	60	60	57	60	59	58	54
>14	60	60	57	60	58	60	58

Source: own research data.

Results obtained

- The highest values of the average stress destroying the granules of respective fractions were obtained for samples 4 and 5 with the highest addition of dolomite. High values were also obtained for samples 1 and 2 with the highest addition of the water glass solution. In those cases, the resistance of the granules to the discharge was also the highest.[139] Those dependencies were also confirmed by granulating fly ashes from hard coal combustion.[140]
- Soluble water glass-based binders are widely used in industry due to their low cost and non-toxicity. They also allow for the production of granules with high strength parameters, high durability and water resistance.[141, 142]

137 T. Dzik, M. Hryniewicz, A. Janewicz, B. Kosturkiewicz, (2017), *Agglomeration of solid fuels in a roll press*, “Przemysł Chemiczny”, vol. 96, no. 6, pp. 1852–1855.

138 R.F. Rodrigues, S.R. Leite, D.A. Santos, M.A.S. Barrozo, (2017), *Drum granulation of single super phosphate fertilizer: Effect of process variables and optimization*, “Powder Technology”, vol. 321, pp. 251–258.

139 K. Ławińska, S. Szufa, R. Modrzewski, A. Obraniak, T. Wężyk, A. Rostocki, T.P. Olejnik, (2020), *Obtaining granules…*

140 A. Obraniak, T. Gluba, K. Ławińska, B. Derbiszewski, (2018), *Minimisation of environmental efects related with storing fly ash from combustion of hard coal*, “Environment Protection Engineering”, vol. 44, pp. 177–189.

141 K. Ławińska, S. Szufa, R. Modrzewski, A. Obraniak, T. Wężyk, A. Rostocki, T.P. Olejnik, (2020), *Obtaining granules…*

142 F. De Castro Dutra, M. Emrich, G. Magela da Costa, A. Dias, (2016), *Influence of drying temperature and atmosphere on the mechanical strength of iron-ore agglomerates and*

- The obtained agglomerates, due to the identity of the mineral additives used, are dedicated to the producers of leather-like materials and composites. On the other hand, binders used for producing secondary, ground leather (eco-leather), e.g. synthetic resins, butadiene-styrene latexes or acrylic latexes may be added in appropriately smaller amounts already at the granulation stage of shredded tannery shavings. In addition, the produced agglomerates may be used as: additives in construction, road construction and as fillers of mining voids.[143, 144, 145, 146]

In order to benchmark the developed method of granulating production residue, waste generated by the food (sugar) industry was also granulated. This waste was selected taking into account, among other things, high moisture content of about 40% (similar to tannery shavings), similar chemical composition especially in terms of high Ca and Mg content (potential use in agriculture). Saturation mud, also called defecation mud, was used, which is a by-product of sugar production (arising from the purification of beet raw juice). On average, more than 12,000 tonnes of that type of waste is obtained during the operation of one factory during the campaign. It is stored in heaps and requires the development of methods for its disposal management.

Agglomeration was carried out using a disc granulator (disc speed at 9.5 RPM). In this case, the additives were dolomite and gypsum (similarly to tannery shavings) as well as lime meal and chalk. Due to the environmental focus of the study, the aqueous glass solution was replaced with an aqueous solution of molasses, which is also a byproduct of food sugar production. 33% and 66% solutions of molasses were used (better results in terms of the granules obtained, as well as strength parameters, were obtained for the 66% solution). For selected fractions of the produced granules, the average values of destructive stress were also determined (Table 3.2.11.). On the other hand, Chart 3.2.3. shows the granulometric compositions of agglomerates produced from shavings and from saturation mud under similar process conditions (with the addition of dolomite).

sodium silicates for application in sintering processes, "The Canadian Journal of Chemical Engineering", vol. 94, pp. 75–80.

143 K. Ławińska, A. Obraniak, R. Modrzewski, (2019), *Granulation process…*

144 K. Ławińska, (2021), *Production of agglomerates…*

145 K. Ławińska, R. Modrzewski, A. Obraniak, (2020), *Comparison of granulation…*

146 K. Lawinska, R. Modrzewski, W. Serweta, (2018), *The phenomenon…*

Table 3.2.11. The average destructive stress in respect of saturation mud granules containing various mineral additives (forthe 66% solution of molasses)

Average Destructive Stress [N]				
Granulates Fraction [mm]	Additive			
	Gypsum	Dolomite	Chalk	Limestone Powder
4.0	9	13	15	11
5.0	11	16	13	18
6.3	25	21	29	20
8.0	26	24	42	28
10.0	25	46	12	27

Source: own research data.

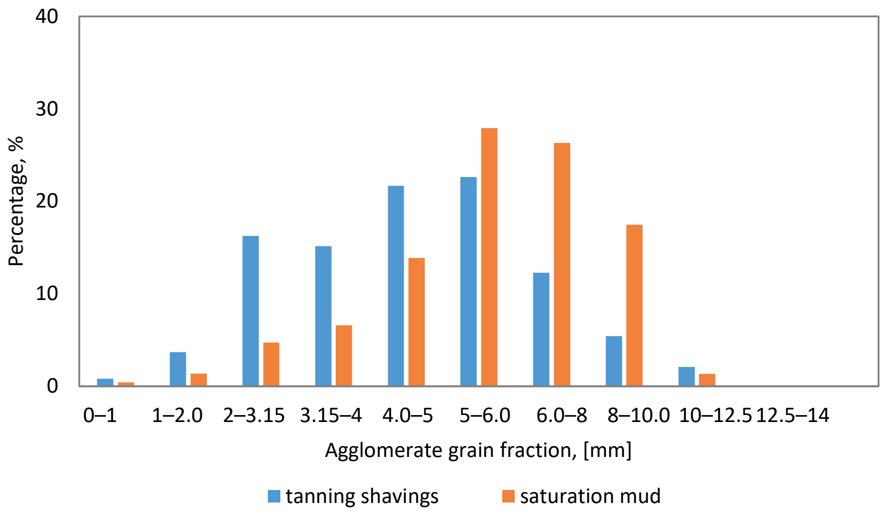

Chart 3.2.3. Granulometric composition of agglomerates made of tannery shavings and saturation mud (samples with dolomite as an additive)
Source: own research data.

Results obtained

- The granulometric compositions of tannery shavings and saturation mud agglomerates clearly indicate that the disc granulation process allows for the processing of the entire material (in both cases).[147]

147 K. Ławińska, S. Szufa, A. Obraniak, T. Olejnik, R. Siuda, J. Kwiatek, D. Ogrodowczyk, (2020), *Disc granulation process of carbonation lime mud as a method of post-production waste management*, "Energies", vol. 13, 3419.

- Non-pressure granulation facilitates the processing of various types of waste (solids, liquids) generated by various industries.[148, 149]
- In terms of application for the agritechnical purposes (as fertiliser additives, soil improvers), the optimal fraction is 2–8 mm in size and the required compressive strength should not be less than 10N (the indicated requirements have been met). In both cases, the maximum activity was obtained from the 5–6 mm fraction for the produced granules.[150, 151, 152]

In further studies, the impact of collagen preparations contained in seed coats created using a disc granulator on the growth and condition of plants was verified. For this purpose, seeds capsules were sown in universal soil, and then the lengths of the obtained seedlings were analysed at certain intervals (Figure 3.2.3.). The related exemplified analyses resulting figures are presented in Table 3.2.12.

Figure 3.2.3. Coating, sowing, seedling length analysis (rapeseed)
Source: own research data.

Table 3.2.12. Average seedling length for seeds of varied seed coatings

Coating Composition	Seed Type	Average Seedling Length, mm
collagen preparation, soot	pea	35.58 ± 1.55, 10 days after sowing
molasses solution, soot	pea	33.28 ± 1.89, 10 days after sowing
reference liquid*, soot	pea	34.46 ± 0.88, 10 days after sowing
collagen preparation	rape	12.1 ± 1.51, 10 days after sowing
reference liquid*	rape	11.56 ± 1.66, 10 days after sowing
collagen preparation, dolomite	rape	11.45 ±1.15, 10 days after sowing
reference liquid*, dolomite	rape	11.075 ± 1.25, 10 days after sowing
collagen preparation, dolomite, peat	rape	11.75 ± 0.35, 10, days after sowing
reference liquid*, dolomite, peat	rape	10.7 ± 0.54, 10, days after sowing

* yellow dextrin, polyvinyl alcohol
Source: own research data.

148 K. Lawinska, R. Modrzewski, W. Serweta, (2018), *The phenomenon…*
149 K. Ławińska, S. Szufa, A. Obraniak, T. Olejnik, R. Siuda, J. Kwiatek, D. Ogrodowczyk, (2020), *Disc granulation…*
150 K. Ławińska, (2021), *Production of agglomerates…*
151 K. Lawinska, R. Modrzewski, W. Serweta, (2018), *The phenomenon…*
152 K. Ławińska, S. Szufa, A. Obraniak, T. Olejnik, R. Siuda, J. Kwiatek, D. Ogrodowczyk, (2020), *Disc granulation…*

Results obtained

- The analysis of the length of the seedlings confirms the effective action of collagen preparations as plant biostimulators – an improvement in the growth and condition of the plants was obtained. Their advantage over the reference liquid and other selected production residue (molasses solution) is also important.[153 154 155 156]
- The developed method provide for the production of multi-component and multi-layer coatings proving a wide range of activity. The type and amount of additives used as well as the order of the layers from which they are formed, also have a significant impact.[157, 158, 159]
- The proposed solution can increase the yields of various plant species by using the by-products of the leather industry.

3.2.5. Overview of the Obtained Results in terms of Application Prospects in Industrial Practice

The results obtained within the framework of the research carried out and the conclusions arrived at on their basis in respect of the unit processes in waste disposal management methods, including tanning, are currently being verified for their potential use in order to raise the level of technological readiness of the developed solutions.

The positive verification of the developed methods in terms of the application of disc granulation for the purpose of producing seed coats (agricultural application) has been confirmed in the framework of the completed two international Projects: Eureka EUREKA/COLL-RAPE/5/2017 (New treatment for rapeseed based on collagen hydrolysates in order to increase the drought resistance of the rape seedling) and Era.Net Rus Plus Innovation 6/RUSPLUS-INNO/2016 (New treatment based on collagen hydrolysates for the purpose of increasing the drought resistance of Leguminosarum seedlings).

Furthermore, application prospects for the output of the research that has been carried out include:

153 K. Ławińska, (2021), *Production of agglomerates…*
154 K. Ławińska, M. Lasoń-Rydel, D. Gendaszewska, E. Grzesiak, K. Sieczyńska, C. Gaidau, D.G. Epure, A. Obraniak, (2019), *Coating of seeds…*
155 K. Ławińska, D. Gendaszewska, E. Grzesiak, J. Jagiełło, A. Obraniak, (2017), *Use of tanning…*
156 K. Ławińska, D. Gendaszewska, E. Grzesiak, M. Lasoń-Rydel, A. Obraniak, (2017), *Coating of leguminosarum…*
157 K. Ławińska, (2021), *Production of agglomerates…*
158 K. Ławińska, D. Gendaszewska, E. Grzesiak, J. Jagiełło, A. Obraniak, (2017), *Use of tanning…*
159 D. Gendaszewska, M. Lasoń-Rydel, K. Ławińska, E. Grzesiak, P. Pipiak, (2021), *Characteristics of…*

- road construction – it is possible to use tannery shavings and their granules in the processes of modifying asphalt binders and as an addition to mineral and asphalt mixtures.
- construction – the research output has indicated the application of shavings (in the amount equivalent to 10, 20 and 30%) in wood-like boards pressed at the temperature of 180°C due to the microbiological resistance (as compared to boards without that additive) (tests according to instruction 355/98).[160] The research was carried out as part of the Project entitled "Materials for the prefabrication of building partitions, agglomerated from secondary raw materials, including demolition wood, textile and leather industry waste" co-funded under the special-purpose subsidy awarded by the President of the Łukasiewicz Centre, Co-financing Agreement 1/Ł-ITD/CŁ/2021.
- composite materials and plastics processing – the possibility of producing biodegradable composites from waste biomass products of animal origin (including shavings and granulates) and plant origin, intended for use in the agri-food, packaging and horticultural industries, has been confirmed. The research was carried out as part of the Project titled "Establishment and launch of the BIO-MAS Research and Development Centre" under the Regional Operational Programme of the Lodzkie Voivodeship, Co-financing Agreement no RPLD.01.01.00-IP.02-10-069/20 (RPLS.01.01.00-10-0002/20-00 of May 10, 2021).
- mining industry – studies have confirmed the possibility of producing agglomerates from flotation waste and fly ashes in the process of non-pressure disc granulation as a method of effective waste disposal management (mitigation of its environmental adverse impact).

The research output indicated above confirms the wide applicability of the developed solutions. The research areas were also selected on the basis of the related literature reports on the leather waste disposal management, and related recycling to be reused, among others, as an additive for acoustic panels,[161] for cement panels (due to mechanical strength as well as insulating properties), for concrete,[162]

160 K. Ławińska, (2021), *Production of agglomerates…*

161 M. Vidaurre-Arbizu, S. Pérez-Bou, A. Zuazua-Ros, C. Martín-Gómez, (2021), *From the leather industry to building sector: Exploration of potential applications of discarded solid wastes*, "Journal of Cleaner Production", vol. 291, 125960.

162 G. Zainescu, (2018), *Polymer Compositions from Leather Fibers (Leather Shavings) for Mortar in Constructions*, In Proceedings of the 18th SGEM International Multidisciplinary Scientific GeoConference SGEM2018, Energy and Clean Technologies Stef92 Technology, Albena, Bulgaria, 2–8 July 2018, pp. 79–86.

and for the manufacture of new composite and biocomposite materials,[163, 164, 165] including packaging materials (e.g. collagen preparation with dialdehyde starch) for packaging pharmaceuticals, food and cosmetics[166] as well as an additive for paper (with improved water resistance and air permeability properties).[167]

163 G. Ramamurthy, B. Ramalingam, M.F. Katheem, T.P. Sastry, S. Inbasekaran, V. Thanveer, S. Jayaramachandran, S.K. Das, A.B. Mandal, (2015), *Total elimination of polluting chrome shavings, chrome, and dye exhaust liquors of tannery by a method using keratin hydrolysate*, “ACS Sustainable Chemistry & Engineering”, vol. 3, pp. 1348–1358.

164 J. Zhang, Z. Yan, X. Liu, Y. Zhang, H. Zou, Y. Le, J.-F. Chen, (2020), *Conductive skeleton-heterostructure composites based on chrome shavings for enhanced electromagnetic interference shielding*, “ACS Applied Materials & Interfaces”, vol. 12, pp. 53076–53087.

165 C. Ding, M. Zhang, L. Dai, Y. Qi, R. Shi, J. Yang, (2017), *Fabrication and characterization of regenerated leather using chrome shavings raw material*, “The Journal of the American Leather Chemists Association”, vol. 112, pp. 145–152.

166 F. Langmaier, P. Mokrejs, K. Kolomaznik, M. Mladek, (2008), *Plasticizing collagen hydrolysate with glycerol and low-molecular weight poly(ethylene glycols)*, “Thermochimica Acta”, vol. 469, pp. 52–58.

167 O.A. Mohamed, N.F. Kassem, (2010), *Utilization of waste leather shavings as filler in paper making*, “Journal of Applied Polymer Science”, vol. 118, pp. 1713–1719.