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Granulation Process of Waste Tanning Shavings

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Abstract

The tests presented describe a method of pressureless agglomeration of waste shavings derived from chrome tanning processes with the addition of gypsum obtained from the Bełchatów Power Plant, from the filtering of sulphur compounds from exhaust gas and widely available dolomite. The aim of the granulation process is to minimise the environmental impact of the storage and transport of tanning shavings. The method proposed of rendering this waste harmless through its granulation on a disk apparatus using a soluble glass solution to moisten the deposit is simple and its cost remains economically reasonable. As a result of the completed tests, a loose, agglomerated particulate deposit was produced containing both mineral and organic components, and which can also be easily stored, transported and dosed in other process operations. Agglomerates produced using the method devised in the invention may be used in place of the loose, wet, dusty shavings for manufacturing composite materials based on fragmented collagen fibres.

Key words: *granulation, tannery shavings, mineral fillers.*

Introduction

Shavings are a waste product of leather tanning technology, remaining after the proper tanning process, which makes them waste resistant to biological degradation. It is, therefore, a material that is hard to dispose of in any manner. It is estimated that 1 ton of waste tanning shavings is produced for each 4 tons of raw leather undergoing tanning. This gives more than 2 kg of waste for each square metre of finished leather. Annually the manufacturing of leather and leather products in Poland generates approx. 46.000 tons of industrial waste, most of which are tanning shavings. Current data of the Polish Statistics Office show that the amount of leather industry waste stored on companies' own premises equals 28.000 tons. A future increase in the amount of waste generated by the leather industry resulting from the production growth that we have been observing for several years may be predicted. The fibre and textile industry is a diverse sector that covers the entire production chain of transforming natural and chemical fibers into end-use products [1].

The total content of the organic substance in the dry mass of tanning shavings is high, reaching 85-90%, while the permanent residue after their incineration is 7.8-8%. The average moisture content of shavings reaches 50-60%. Moreover chrome shavings have a significant amount of proteins (78.6-75.2%) [2].

Shavings are characterised by multiple unfavourable physical properties, such as a very low bulk density that does not exceed 0.1 g/cm^3 for the dry material. They are, therefore, characterised by high volume, which makes their storage and transport difficult. They have irregular, flocculent shapes, which is why they tend to form larger agglomerates, which, in turn, hinders operations such as screening, dosing, pouring and loading into containers. The solution to these problems would be to give shavings regular, spherical shapes and, thus, obtain a loose particulate deposit. This can be ensured by processes using pressureless disk or drum granulation [3-5]. A deposit in the form of granulated shavings with the addition of relevant mineral substances may then be used for the production of leathery materials [6], composition leather, composite materials based on fragmented collagen fibres [7, 8], fibrous materials, and protein hydrolysates used, above all, for shaping seed-grains [9, 10]. Charging granulation processes are commonly used in the case of agglomerating post-manufacturing waste [11-13] and fly ash, e.g. derived from hard coal and brown coal combustion [14].

The aim of the paper was to determine the possibility of minimising the environmental impact of the storage and transport of tanning shavings through their disk granulation using mineral fillers.

Method and materials

Waste chrome shavings derived from a Polish tannery were used for the tests. Attempts at screening and granulating the waste material were then made one by one.

Tanning shavings were screened using a laboratory vibrator with a sieve diameter of 400 mm, sieve vibration frequency of 50 Hz and vibration amplitude of 1.0 mm [15], along with a set of woven control sieves made from a wire mesh with square holes [16-18]. The first stage of the preliminary tests was to screen the starting material (raw shavings) using a sieve with a hole size of 2.5 mm in order to screen the largest fraction containing the longest leather fibres with the most irregular shapes. The screening time for each sample was 20 minutes. The second testing series involved the screening of the previously produced fraction (0-2.5 mm) of fine shavings using a sieve with a hole size of 1.0 mm (for 10 minutes). In both series the feed was fed onto the sieve in such an amount that the starting density of the material layer on the sieve did not exceed 25 mm, i.e. double the maximum size of grains (fibres length) in the feed. This has a significant impact on the screening efficiency, which decreases rapidly with an increase in the thickness of the layer on the sieve. The course in time of raw shaving screening using a 2.5 mm sieve was also determined. For this purpose changes in the minus mesh and mesh fraction mass after specific screening times were determined.

The granulation of waste tanning shavings took place in a disk granulator [19]. A soluble glass solution, i.e. a sodium and potassium silicate solution (so-called mixed soluble glass) was used as the moistening liquid. Soluble glass is a liq-

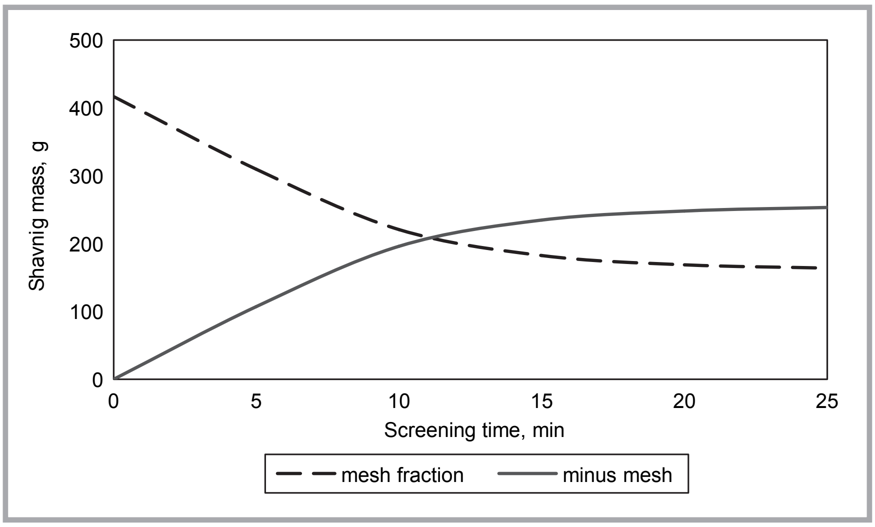

Figure 1. Determining shaving screening time using a 2.5 mm sieve.

Table 1. Process parameters of disc granulation.

Test number	Concentration of soluble glass solution, %	Deposit moisture content, %	Mineral filler
P1	50	50	wet gypsum
P2	75	40	dry dolomite
P3	75	35	dry dolomite
P4	75	30	dry dolomite
P5	50	55	dry gypsum
P6	50	107	dry gypsum
P7	50	135	wet gypsum

Table 2. Grain-size composition of shavings.

Fraction, mm	Mass fraction, –
0-1.0	0.34
1.0-2.5	0.255
2.5-12.5	0.405

uid whose viscosity increases rapidly with an increase in the concentration of silicates in water. A soluble glass solution with concentrations selected on the basis of a paper concerning limestone flour, gypsum and dolomite granulation [20] was used for the tests. The preliminary attempts at granulation revealed difficulties in granulating a deposit containing shavings only. That is why it was decided to granulate a mixture of shavings and a fine-grained mineral material. Dry dolomite of a graining below 0.3 mm and gypsum with a grain size below 0.5 mm obtained as a result of exhaust gas sulphur-recovery at the Bełchatów Power Plant were used as a mineral filler. The benefits of using this waste material include the environmental and costefficiency aspects. In the tests analysed gypsum was added in its dry and wet (moisture content of 0.11) forms. Shavings were poured onto the granulator disk in such an amount that the ratio of their volume to that of the granulator disk equalled 0.25, which in this case ensured optimal granulation conditions. A single batch contained 200 grams of dry material. Next the dry mineral component was added [20] in the form of powdered dolomite or gypsum in the amount of 800 grams, and both components were mixed at a disk rotational speed of 15 RPM for 3 minutes. In some of the tests, the mineral material was fed onto the disk following moistening. Granulation took place for 15 minutes, with simultaneous deposit drenching with a 50% or 75% soluble glass solution of a temperature of 20 °C. The moistening liquid was fed using a hydraulic nozzle in the form of drops of 0.01-0.5 mm in diameter under a pressure of 30 kPa. Following the conclusion of moistening, granulation continued for 5 minutes at constant rotations of the disk. The agglomerate obtained was dried at a temperature of 50 °C for 24 hours and then screened using laboratory screens in order to determine the mass fractions of the granulated products obtained. Seven attempts at granulating shavings were made during the tests. The tests were done with variable process parameters and two mineral fillers. The parameters of all the tests are given in ***Table 1***. The individual tests varied in terms of the mass of the fed moistening liquid and, consequently, the end moisture content of the deposit. In the case of test No. 4, shavings were moistened, and dolomite was fed onto the disk after all of the moistening liquid was added to the deposit.

The end moisture content of the granulated product was calculated using dependence ***Equation (1)***.

$$w = \frac{m_w - m_s}{m_s} \cdot 100\% \qquad (1)$$

Where, m_w is the mass of the wet granulated product and m_s the mass of the dry granulated product. The bulk density of all granulated products obtained, defined as the ratio of their mass to their volume, was determined for all granulation attempts.

Tests results

The preliminary granulation of raw leather shavings that are non-fragmented and non-classified according to grain size is a time-consuming process, and the particulate material obtained is irregular. The deposit produced contains very large grains next to completely non-granulated material, and the individual granules significantly differ from each other in terms of their mineral filler content, which is caused by excessively long leather fibres. In the course of granulation, they tend to form large agglomerates that do not properly absorb the binding liquid. The above-mentioned problems do not occur if screened or fragmented shavings with shorter fibres are subjected to granulation. The initial tests showed that the best results are produced by granulating shavings that are screened using a sieve with a 2.5 mm hole, i.e. those whose fibre length is between 0 and 2.5 mm. The total, average grain-size composition of raw tanning shavings is given in ***Table 2***.

It is worth noting that the content of the fraction intended for granulation (0-2.5 mm) equals by weight almost 60% in total, therefore only approx. 40% of the starting material (fraction 2.5-12.5 mm) requires fragmenting or managing in a different manner. The chart in ***Figure 1*** shows that the optimum screening time for raw tanning shavings equals 20 minutes. After that time the change in the minus mesh and mesh fraction is negligent, equalling approx. 1% of the feed mass. Nevertheless material in the form of shavings must be deemed hard to screen because the maximum screening time for typical particulate materials [22] (above all mineral aggregates and sand) does not usually exceed 5 minutes. It may be observed that after having screened the coarse fraction (the longest fibres) using a 2.5 mm sieve, the rest of the screening process using a 1.0 mm sieve posed no problems and required shorter time.

The results of tests concerning a comparison of the mass fractions of granulated products derived from waste tanning shavings are shown in ***Figure 2*** and ***3***. ***Figure 2*** shows a comparison of the mass fractions of agglomerates obtained as a result of tests involving the addition of dolomite (tests P2, P3 & P4). The tests were done with a constant concentration of the moistening liquid (75%), differing in terms of the mass of the liquid added and, as a result, the end moisture content of the granulated deposit. When analysing the test results, it may be observed that the tests done with a higher end moisture content produced a granulated product with larger diameters. Test P4, done with the lowest mass of the liquid fed to the deposit, seems to be the best considering economical criteria (lower costs of drying and soluble glass addition). The granulated product obtained as a result of this test, on the other hand, contains a large share of the 0-2 mm fraction that may be non-granulated material (socalled undersize material). An organoleptic inspection of the deposit obtained in test P4 showed very large granules, while undersize material was observed near its rotation axis.

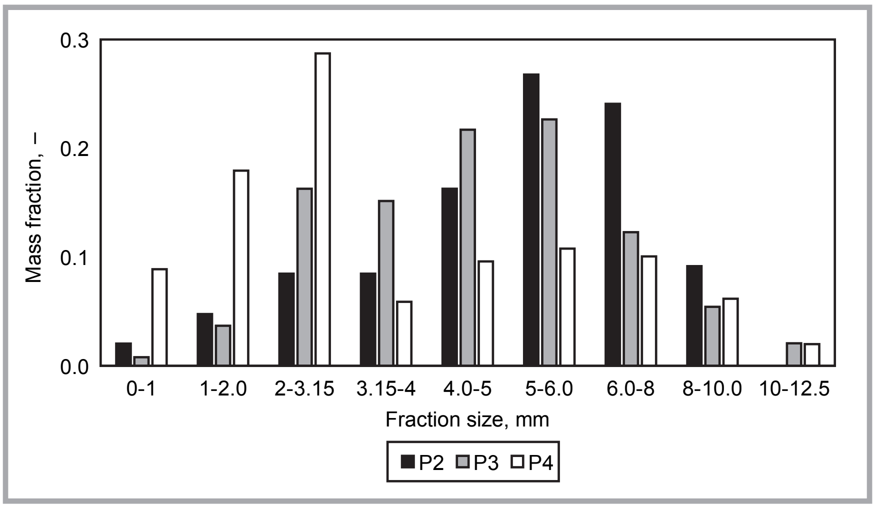

Figure 2. *Comparison of mass fractions of the granulated product obtained for tests P2, P3 and P4.*

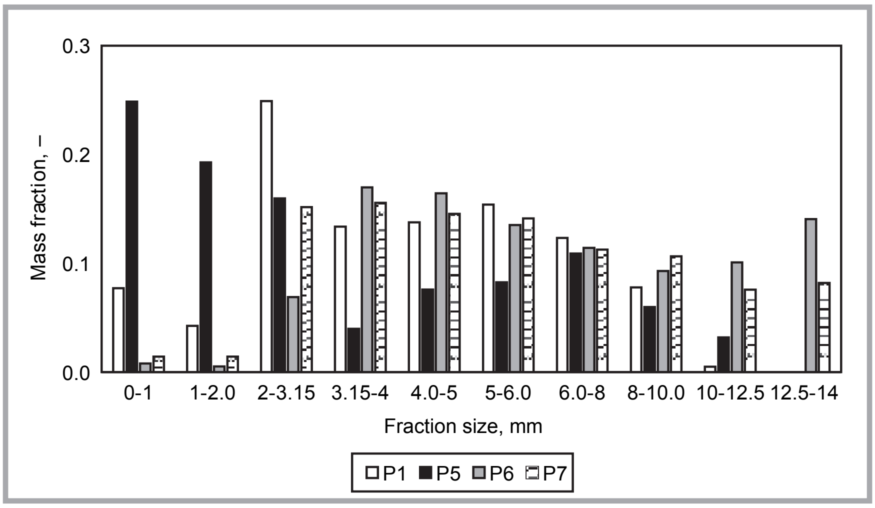

Figure 3. *Comparison of the mass fractions of granulated products for tests P1, P5, P6 and P7.*

Figure 3 shows a comparison of the mass fractions obtained for tests P1, P5, P6 & P7 with the addition of gypsum. In test No. 1 wet gypsum was added to the granulator disk before moistening. In the case of the other experiments, irrespective of the initial moisture content of gypsum, it was added after the deposit moistening stage. Observations made during test P1 showed that by moistening the mixture of wet gypsum and shavings, earlier agglomeration of gypsum grains was first initiated as a result of these materials' segregation on the disk and a difference in the starting moisture content, and consequently many of the granules obtained did not contain shavings. In order to eliminate this problem, tests P5 and P6 were done using dry gypsum (dried using a laboratory dryer), dosing it following the moistening of shavings so that it adhered to the previously formed aggregates. A comparative analysis of the mass fractions obtained shows that satisfactory results were produced in tests P6 & P7 (moisture content exceeding 100%). Practically the entire material was granulated. Those tests, however, generate high costs of drying such a wet material. It seems that the most cost-efficient solution would be to use the moisture content characteristic for test P5 and return the undersize material back to granulation. Granules obtained in this test had a spherical shape, which is important for other process operations and is beneficial in terms of the requirements of potential consumers. During test P7, wet gypsum was used once again. and this time, due to the method of its dosing, no unfavourable phenomena were observed during granulation. The feeding of wet gypsum directly following sulphur recovery reduces costs because the material does not have to be dried.

Fiure 4 shows the bulk density of granulated products obtained in each test. The granulation processes of waste tanning shavings provided them with regular, spherical shapes, forming a loose particulate deposit with a bulk density 5 times (and in the P4 test even 8 times) that of a loose, dry shaving deposit, containing both mineral and organic components that are easy to store, transport and dose in other process operations.

The tanning shaving granulation method described in this paper using dolomite and gypsum was used as the basis for relevant patent applications. Agglomerates obtained using this granulation method, due to identical mineral fillers, such as gypsum, dolomite, limestone flour and

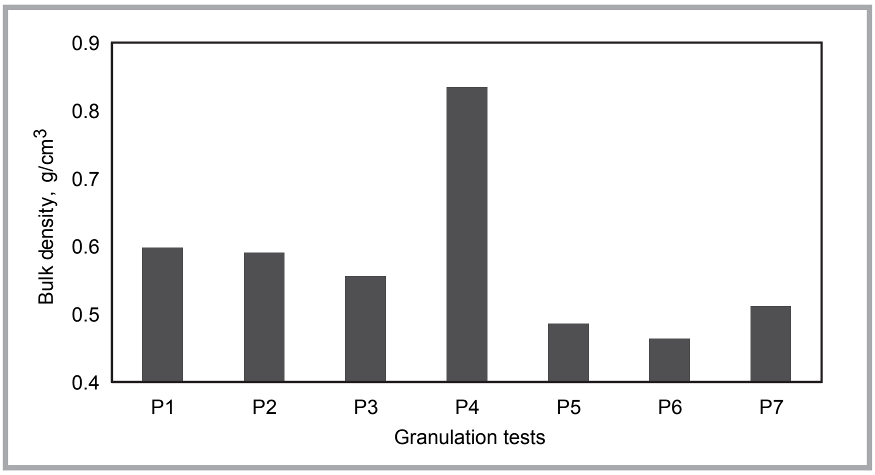

Figure 4. *Bulk density of granulated products obtained in each test, P1-P7.*

chalk flour being used, may be intended for leathery materials and leather component manufacturers. What is more, binding agents used in the production of composition leather, above all synthetic resin, styrene-butadiene latex and acrylic latex may be added in smaller doses as early as at the stage of granulating fragmented tanning shavings.

Conclusions

The tests results prove that the method of granulating chrome tanning shavings described may become a significant solution to the problem of managing and utilising waste from the leather industry. Further tests are necessary to optimise this method. On the basis of the tests completed, it may be concluded that it is easiest to granulate tanning shavings by combining them in the granulator with a mineral material after the moistening stage. The soluble glass solution concentrations applied ensured permanent particles, while the selection of an optimum moisture content of the deposit requires further tests for the range above 30%. Granulation during tests using dolomite produced satisfactory results for a lower deposit moisture content; however, it requires mineral filler purchase, adding to the overall cost. In the case of waste gypsum, a cost is often that of its transport. Another advantage of this solution is the fact that sulphur-gypsum, similar to tanning shavings, is a waste product. It may be concluded that the waste tanning shaving disk granulation process may solve the problem of their processing and make it possible to obtain a durable, mechanically stable, easy to transport and store semi-finished product.

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