Sustainable building materials based on hemp shives and geopolymer paste

L. Vitola¹,a, M Vilnitis², I Pundiene¹,³ and D Bajare¹

¹Institute of Materials and Structures, Riga Technical University, Kalku 1, LV – 1658, Riga, Latvia
²Institute of Construction Technology, Riga Technical University, Kalku 1, LV – 1658, Riga, Latvia
³Institute of Building Materials, Vilnius Gediminas Technical University, Sauletekio av. 11, Vilnius, LT-10223, Lithuania

aE-mail: laura.vitola_1@rtu.lv

Abstract. European regulations states that the construction industry must encourage the rational and prudent use of non-renewable natural resources, as well as and increase the use of reusable resources and promote the use of renewable natural resources in production. Bio-composites based on natural aggregates such as hemp shives are widely studied and used in building sector due to their extensive properties of a range that primarily is so wide, as hemp shives are increasingly combined with various binders and as their production technology is evolving rapidly. In this study three series of geopolymer paste (GP) samples were studied to obtain the most suitable binder for the production of hemp shive-based bio-composites, as well as a bio-composites were created from the most suitable binder and described their compressive strength and thermal conductivity performance.

1. Introduction
Since 1987, along with publication of report of Brundtland Commission the sustainability has become an important aspect in all areas, as well as in Building sector. In accordance to this report sustainable development is defined as development that meets the needs of the present without compromising the ability of future generations to meet their own needs [1]. To ensure the sustainability in civil engineering sector and the well-being of ecosystem different type of solutions are being sought [2]–[5], including the production of new environmentally friendly building materials using renewable natural resources and industrial by-products and waste [5]–[10].

Several researchers have emphasized the potential of geopolymers in the production of sustainable building materials [5], [11]–[13]. Assi et.al. has compiled the available literature on geopolymers as sustainable materials and a potential alternative to ordinary Portland cement [13]. Geopolymers can be made of commercially available raw materials (for example, calcinated clays and alkali solutions), as well as from lower quality materials, industrial by-products, construction demolition wastes, and other type of wastes. Geopolymers may present lower CO₂ emission (so do impact on environment) and competitive mechanical and durability properties comparing to ordinary Portland cement based materials [13].

During recent decades bio composites have became more and more popular in building industry as primary building materials because they provide an environment that is favourable to the environment and human [14], [15]. There are plenty of variations of different type of plant origin aggregates used for bio-composite production (such as hemp and flex fibres and shives, oat and wheat husk e.c.) [16], [17]. New plant origin aggregates-based bio-composites presents potentially long-term durability,
improved physical, mechanical, and thermal properties, and low impact on the environment, as well as recyclability [17]. The use of plant origin aggregates provides sustainable solution for reduction of resource depletion and CO₂ emissions [18].

In this study three series of geopolymer paste (GP) samples were studied to obtain the most suitable binder for the production of hemp shive-based bio-composites, as well as a bio-composites were created from the most suitable binder and described their compressive strength and thermal conductivity performance.

2. Materials and methods

2.1. Raw materials

In this research commercially available metakaolin ASTRA MK-40 (MK) produced by ASTRA (Poland) has been used as aluminum silicate source. The SiO₂ and Al₂O₃ make up, respectively, 57.30% and 35.73% of the MK content. MK has amorphous phase (halo at 15-30°), as well as crystalline phases of quartz (SiO₂), kaolinite (Al₂(OH)₄Si₂O₅) and mullite (Al₆Si₂O₁₃).

To ensure the geopolymerisation reaction three type of activation solutions have been used – 8M NaOH (A1) solution and two modified 8M NaOH solutions. The 8M NaOH solution was modified by substituting 10% (A2) and 20% (A3) solution mass by sodium metasilicate solution (also known as waterglass).

Two type of hemp shives have been studied; A – commercially available hemp shives grown and processed in Latvia (Zalers) as a by-product of hemp fiber production, B – commercially available hemp shives grown and processed in Lithuania (Naturalus Plostas).

2.2. Testing methods

Flowability of geopolymer pastes was characterized by flow table test in accordance to ASTM C 1437. The density was performed by dividing the sample’s mass by the respective volume.

The bulk density of obtained geopolymer pastes were calculated as mass and volume division, for 28-days old samples with dimensions 20 mm × 20 mm × 20 mm. While the bulk density of obtained bio-composites were tested in accordance to EN 1602 plate shaped samples with dimensions 350 mm × 350 mm × 50 mm.

Compressive strength of 6 parallel samples (20 mm × 20 mm × 20 mm) of each geopolymer paste composition using different mixing times were tested on Day 3 and Day 28. Samples were tested by using a Zwick Z100 universal testing system (ZwickRoell, Kennesaw, GA, USA) with a testing speed of 0.5 mm/min. Compressive strength was calculated from force applied to the sample’s specific area.

Compressive stress at 10% deformation rates was tested according to the EN 826 method by using a Zwick Z100 universal testing system. The maximum loading force was 10 kN, the loading accuracy was ± 0.5% and the loading speed accuracy was ± 0.05%. Six specimens were tested for each composition with the dimensions 100 mm × 100 mm × 70 mm. Prior to conducting the test, the specimens were conditioned for six hours at 23°C ± 5°C. The specimens were then aligned on the bottom support and subjected to an initial loading pressure of 250 ± 10 Pa. The loading speed during the tests was 0.7 mm/min.

Thermal conductivity of bio-composites has been determined using Fox 600 heat flow measuring device. Samples with dimensions 350 mm × 350 mm × 50 mm were fixed horizontally. During the test temperature of lower surface was +20°C and 0°C of upper surface (mean temperature +10°C). Heat transmission coefficient was determined considering constant heat flow between two sides of sample.

2.3. Samples’ compositions and preparation process

2.3.1. Composition and preparation of geopolymer pastes.
In this study 3 series (3 mixtures of each series) of geopolymer paste (GP) have been studied (Table 1), metakaolin (MK) was activated with three different alkaline solutions (A0, A10 and A20, respectively) using 3 different MK/activation solution ratios – 0.5, 0.6 and 0.7. Activation solutions were prepared and kept at room temperature (20 ± 2ºC) for several hours before preparation of GP. Powdered MK was dosed and mixed together with certain amount of chosen activation solution in accordance to table 1. for 1, 3, 5 and 7 minutes. Immediately after mixing moulds (20 mm × 20 mm × 20 mm) were filled with prepared paste and parallelly the flowability of paste was tested. Specimens were put into sealed bags and kept at room temperature (20 ± 2ºC) for 1 h, and then curried at 85ºC for 24 h. After demoulding samples were kept at room temperature (20 ± 2ºC) until Day 3, when part of samples was tested and the rest of samples were after-cured in air and in water media at room temperature (20 ± 2ºC) until Day 28.

The percentage of oxides in compositions was calculated using data given by producers of raw materials.

| Name of composition | Mixture design, mass part | Main oxides, % | Ratios of main oxides in pastes, % in weight |
|---------------------|--------------------------|----------------|----------------------------------------------|
| MK-0-0.5            | 1.0 A0 0.5 0.5           | SiO2 38.2 Al2O3 23.8 Na2O 13.4 | SiO2 / Al2O3 1.6 SiO2 / Na2O 2.9 Al2O3 / Na2O 1.8 |
| MK-0-0.6            | 1.0 A0 0.6 0.6           | SiO2 35.8 Al2O3 22.3 Na2O 12.5 | SiO2 / Al2O3 1.7 SiO2 / Na2O 2.9 Al2O3 / Na2O 1.7 |
| MK-0-0.7            | 1.0 A0 0.7 0.7           | SiO2 33.7 Al2O3 21.0 Na2O 11.8 | SiO2 / Al2O3 1.6 SiO2 / Na2O 2.9 Al2O3 / Na2O 1.6 |
| MK-10-0.5           | 1.0 A10 0.5 0.5          | SiO2 40.2 Al2O3 23.8 Na2O 14.0 | SiO2 / Al2O3 1.7 SiO2 / Na2O 2.9 Al2O3 / Na2O 1.7 |
| MK-10-0.6           | 1.0 A10 0.6 0.6          | SiO2 37.7 Al2O3 22.3 Na2O 13.1 | SiO2 / Al2O3 1.7 SiO2 / Na2O 2.9 Al2O3 / Na2O 1.7 |
| MK-10-0.7           | 1.0 A10 0.7 0.7          | SiO2 35.4 Al2O3 21.0 Na2O 12.4 | SiO2 / Al2O3 1.6 SiO2 / Na2O 2.9 Al2O3 / Na2O 1.6 |
| MK-20-0.5           | 1.0 A20 0.5 0.5          | SiO2 42.1 Al2O3 23.8 Na2O 14.7 | SiO2 / Al2O3 1.8 SiO2 / Na2O 2.9 Al2O3 / Na2O 1.6 |
| MK-20-0.6           | 1.0 A20 0.6 0.6          | SiO2 39.5 Al2O3 22.3 Na2O 13.8 | SiO2 / Al2O3 1.8 SiO2 / Na2O 2.9 Al2O3 / Na2O 1.6 |
| MK-20-0.7           | 1.0 A20 0.7 0.7          | SiO2 37.2 Al2O3 21.0 Na2O 13.0 | SiO2 / Al2O3 1.8 SiO2 / Na2O 2.9 Al2O3 / Na2O 1.6 |

2.3.2. Composition and preparation of bio-composites
The most appropriate GP were chosen for production of hemp-based bio-composites. First paste was mixed in accordance to the procedure mentioned above, then GP were covered with plastic bag and left for 1 h. Exact amount of GP (2.0, 3.0 or 4.0 mass parts) were added to the wet hemp shives (1.0 mass part of dry hemp shives mixed with 1.0 mass part of water) and mixed manually until the homogenous structure were obtained (for ~ 5 min). The obtained fresh material was inserted, pressed into moulds and covered with PVC film, after which the sample was compressed to the required height (50 mm) with the help of threads and spacers. The material was pressed under pressure for 30 minutes and then placed in an oven at 85ºC for 24 hours.

3. Results and discussions
3.1. Assessment of GP suitability for bio-composites production
As can see in figure 1, spread diameter of GP increases by increasing the solid/liquid ratio. Also, type of used activation solution and mixing time have some impact on fluidity of GP. As activation solutions A10 and A20 have been obtained by modifying 8M NaOH solution by sodium metasilicate solution, both A10 and A20 have higher viscosity comparing to activation solution A0. That promotes the different fluidity behaviors between pastes with the same L/S (liquid to solid) ratio, but different activation solution used. Additional metasilicate solution in activation solution decreases fluidity of fresh paste. Role of mixing time in fluidity behavior of studied GP depends on L/S ratio (table 1.), higher the ratio is, more noteworthy the impact of mixing time becomes. As presented in figure 1, studied GP presents spread diameter in a range from 9.85 to 22.10 cm, depending on the composition.
The most fluid composition is MK-0-0.7 (19.55 – 22.10 cm), but the less fluid – MK-20-0.5 (9.85 – 10.75 cm).

**Figure 1.** Spread diameter of GP depending on mixing time.

As can see in figure 2 (c). GP made with activation solution A10 (8M NaOH of which 10% replaced by sodium metasilicate solution) presents lower compressive strength comparing to GP obtained with activation solution A0. Respectively, on Day 3 compressive strength is in range from 6.0 to 12.1 MPa, while on Day 28 7.6-14.9 MPa (curried in the air) and 8.2-15.6 MPa (curried in the water).

**Figure 2.** Properties of hardened geopolymer pastes; (a) bulk density, (b) compressive strength of
studied GP obtained with activation solution A0, (c) compressive strength of studied GP obtained with activation solution A10, (d) compressive strength of studied GP obtained with activation solution A20.

Obtained GP present bulk density in range from 1303 ± 19 to 1552 ± 14 kg/m³ depending on the composition and fresh paste’s mixing time. The bulk density of GP is presented in figure 2 (a), as can see in the graph, density depends on L/S ratio (table 1) and as well as on the used activation solution. Meanwhile the effect of mixing time on bulk density does not have the same tendency for all GP.

Results of compressive strength tests are given in figure 2 (b, c, d). Each composition was tested on the Day 3 and on Day 28 (after air curing and after water curing) (table 1). GP with compressive strength in range from 3.6 to 13.5 MPa on Day 3 have been obtained.

GP containing activation solution A0 (8M NaOH solution, respectively) presents compressive strength on the Day 3 in range from 7.5 to 13.5 MPa depending of L/S ration and mixing time of fresh paste. While on the Day 28 the compressive strength increases up to 19.7 MPa for samples with water curing and up to 18.4 MPa for samples curried in the air (figure 2 (b)).

GP made with activation solution A20 (8M NaOH of which 20% replaced by sodium metasilicate solution) presents compressive strength in the range from 3.6 to 10.2 MPa on Day 3 (figure 2 (d)) depending on the L/S and mixing time of the fresh paste. Until Day 28 compressive strength increases up to 5.2 – 11.9 MPa in case of air curing and up to 5.5 - 12.8 MPa in case of water curing.

Comparing all three series it can be argued that addition of sodium metasilicate to the 8M NaOH solution decreases the compressive strength on Day 3 for up to 22.7% if 10% of 8M NaOH replaced by sodium metasilicate solution and for even up to 53.4% if 20% of 8M NaOH replaced by sodium metasilicate solution. On Day 28 similar behavior has been detected. Sodium metasilicate solution consists of Na₂O, reactive (amorphous) SiO₂ and H₂O, all these three chemical compounds are needed to provide geopolymerisation reaction. As can see in table 1 different L/S ratios do not change the main oxide ratios but impacts the total main oxide amount in the composition. Higher amount of reactive silica and sodium in the composition of geopolymer pastes might cause the formation of the reaction by-products – zeolites [19], [20]. Structure of GP can be damaged during the formation of the zeolites crystals material structure gets damaged. Also, as zeolites and geopolymer gel need the same main oxides and zeolites can format faster than geopolymer gel, less main oxides are free for geopolymerisation reaction.

In accordance to results GP needs time to gain the maximal compressive strength, in further researches development of compressive strength of geopolymer pastes in time period longer than 28 day should be studied deeper.

The relationship between the spread diameter of the fresh GP and compressive strength on Day 3 is given in figure 3. The relationship between compressive strength and fluidity obviously depends on L/S ratio and type of used activation solution.

![Figure 3](image-url)

**Figure 3.** Relationship between average flowability and average compressive strength of geopolymer pastes on Day 3.
From the point of fluidity (figure 1) and bulk density (figure 2 (a)) results fresh GP should be mixed at least for 3 min. As the highest compressive strength is presented by GP made with activation solution A0 (8M NaOH) and higher fluidity, which is important for workability during the production of bio-composites, is presented by GP with S/L ratio 0.7, the GP MK-0-0.7 is chosen for the further study of bio-composites.

3.2. Hemp shive based bio-composites bounded by geopolymer paste

The results of bulk density and compressive strength of obtained bio-composites are given in the figure 4 (a). In this study six different bio-composites have been made, using two type of hemp shives and three geopolymer paste/hemp shive ratios. Obtained bio-composites presents bulk density from 261 - 403 kg/m$^3$. As can see in figure 4 (a) bulk density depends on GP/hemp shives ratio, while type of hemp shives do not impact the bulk density noteworthy. Increasing the GP/hemp shives ratio twice (from 2.0 to 4.0) the bulk density increases for 54.4% in case of hemp shives A and for 52.3% in case of hemp shives B.

Obtained bio-composites present the compressive strength up to 0.48 MPa on Day 28. As can see in figure 4 (a) bio-composites with GP/hemp shives ratio 2.0 presents the compressive strength lower than 0.10 MPa. As expected the increase of GP/hemp shives ratio increases the compressive strength of the obtained bio-composite. The hemp shives A promotes slightly higher compressive strength comparing to hemp shives B.

The thermal conductivity of obtained bio-composites depending on the GP/hemp shives ratio is given in figure 4 (b). Obtained bio-composites bounded by GP MK-0-0.7 presents thermal conductivity in the range from 0.061 to 0.077 W/(m·K) As can see in the graph lower the geopolymer paste/hemp shive ratio, lower the difference between bio-composites with different hemp shives (hemp shive A and hemp shives B, respectively). Meanwhile using the highest GP/hemp shives ratio (4.0) the difference is 0.003 (0.074 of BC-A-4 and 0.077 of BC-B-4), that fall within the permissible error of the measuring equipment.

In accordance to results the properties of bio-composites bounded by GP depends on the amount of geopolymer paste used in the production of bio-composites, while noteworthy the impact of the type of used hemp shives (type A or type B) have not been detected.

4. Conclusions

The following conclusions have been drawn from this study:

1. the optimal SiO$_2$/Al$_2$O$_3$ ratio and liquid to solid ratio for fresh geopolymer paste to ensure flowability (spread diameter $>$180 mm) and compressive strength on Day 3 ($>$7 MPa) should be, respectively, 1.6 and 0.7;
2. the 3 min long mixing by mechanical hand mixer is the optimal time for the geopolymer paste preparation from the point of fluidity of fresh geopolymer paste and compressive strength of hardened geopolymer paste;
3. to ensure compressive strength of bio-composites bounded by geopolymer paste higher than 0.05 MPa the geopolymer paste / hemp shive ratio should be at least 3.0, but to ensure higher than 0.25 MPa – at least 4.0, respectively;
4. type of used hemp shives does not impact the properties of obtained bio-composites bounded by geopolymer paste noteworthy;
5. using hemp shives and a metakaolin-based geopolymer binder, it is possible to obtain a self-supporting building material with bulk density 260-400 kg/m3, compressive strength up to 0.26 MPa and thermal conductivity 0.061-0.077 W/(m·K).

References
[1] UNICEF-ONU-UNESCO, “Our Common Future - Brudtland Report,” Brudtland Report, p. 383, 1987.
[2] R. Cardoso, A. Paiva, J. Pinto, and J. C. Lanzinha, “Structural and Material Characterization of a Haussmann Building Complex at La Madeleine, Paris. The First Step Before Sustainable Rehabilitation and Strengthening”.
[3] M. H. Roushdy, “Recycling of Cullet, Waste Clay Bricks and Wastes Resulted from Wheat and Sugarcane Cultivations in the Manufacture of Fired Clay Bricks”, doi: 10.37394/232015.2021.17.19 M.
[4] K. W. Chau, “Incorporation of sustainability concepts into a civil engineering curriculum,” Journal of Professional Issues in Engineering Education and Practice, vol. 133, no. 3, pp. 188–191, 2007, doi: 10.1061/(ASCE)1052-3928(2007)133:3(188).
[5] K. A. Komnitsas, “Potential of geopolymer technology towards green buildings and sustainable cities,” Procedia Engineering, vol. 21, pp. 1023–1032, Jan. 2011, doi: 10.1016/J.PROENG.2011.11.2108.
[6] K. Ruģele, G. Būmanis, L. Mežule, T. Juhna, and D. Bajare, “Application of industrial wastes in renewable energy production,” undefined, 2015.
[7] D. Vaičiukynienė, D. Nizevičienė, A. Kielė, E. Janavičius, and D. Pupeikis, “Effect of phosphogypsum on the stability upon firing treatment of alkali-activated slag,” Construction and Building Materials, vol. 184, pp. 485–491, Sep. 2018, doi: 10.1016/J.CONBUILDMAT.2018.06.213.
[8] D. Vaičiukynienė, A. Kantautas, V. Vaitkevičius, L. Jakevičius, Ž. Rudžionis, and M. Paškevičius, “Effects of ultrasonic treatment on zeolite NaA synthesized from by-product silica,” Ultrasonics Sonochemistry, vol. 27, pp. 515–521, Nov. 2015, doi: 10.1016/J.ULTSONCH.2015.06.001.
[9] R. Gailitis, A. Sprince, T. Kozlovskis, L. Radina, L. Pakrastins, and N. Vatin, “Long-Term Properties of Different Fiber Reinforcement Effect on Fly Ash-Based Geopolymer Composite,” Crystals 2021, Vol. 11, Page 760, vol. 11, no. 7, p. 760, Jun. 2021, doi: 10.3390/CRYST11070760.
[10] R. Gailitis, K. Korniejenko, A. Sprince, and L. Pakrastins, “Comparison of the long-term properties of foamed concrete and geopolymer concrete in compression,” AIP Conference Proceedings, vol. 2239, no. 1, p. 020012, May 2020, doi: 10.1063/5.0007787.
[11] B. Panda, S. C. Paul, L. J. Hui, Y. W. D. Tay, and M. J. Tan, “Additive manufacturing of geopolymer for sustainable built environment,” Journal of Cleaner Production, vol. 167, pp. 281–288, Nov. 2017, doi: 10.1016/J.JCLEPRO.2017.08.165.
[12] A. Hassan, M. Arif, and M. Sharig, “Use of geopolymer concrete for a cleaner and sustainable environment – A review of mechanical properties and microstructure,” Journal of Cleaner Production, vol. 223, pp. 704–728, Jun. 2019, doi: 10.1016/J.JCLEPRO.2019.03.051.
[13] L. N. Assi, K. Carter, E. Deaver, and P. Ziehl, “Review of availability of source materials for geopolymer/sustainable concrete,” Journal of Cleaner Production, vol. 263, p. 121477, Aug. 2020, doi: 10.1016/J.JCLEPRO.2020.121477.

[14] N. N. Shalobyta, V. V. Tur, T. P. Shalobyta, and V. I. Rakhuba, “ENERGY EFFICIENT COMPOSITES USING NATURAL ORGANIC MATERIALS,” in E3S Web of Conferences, 2019, vol. 136. doi: 10.1051/e3sconf/201913602027.

[15] F. Asdrubali, F. D’Alessandro, and S. Schiavoni, “A review of unconventional sustainable building insulation materials,” Sustainable Materials and Technologies, vol. 4, pp. 1–17, Jul. 2015, doi: 10.1016/j.susmat.2015.05.002.

[16] M. Lagouin, C. Magniont, P. Sénéchal, P. Moonen, J. E. Aubert, and A. Laborel-préneron, “Influence of types of binder and plant aggregates on hygrothermal and mechanical properties of vegetal concretes,” Construction and Building Materials, vol. 222, pp. 852–871, 2019, doi: 10.1016/j.conbuildmat.2019.06.004.

[17] G. Bumanis, L. Vitola, I. Pundiene, M. Sinka, and D. Bajare, “Gypsum, geopolymers, and starch-alternative binders for bio-based building materials: A review and life-cycle assessment,” Sustainability (Switzerland), vol. 12, no. 14, Jul. 2020, doi: 10.3390/SU12145666.

[18] A. Laborel-Préneron, C. Magniont, and J. E. Aubert, “Characterization of Barley Straw, Hemp Shiv and Corn Cob as Resources for Bioaggregate Based Building Materials,” Waste and Biomass Valorization, 2018, doi: 10.1007/s12649-017-9895-z.

[19] J. Davidovits, “PROPERTIES OF GEOPOLYMER CEMENTS”, Accessed: Aug. 04, 2021. [Online]. Available: www.geopolymer.org

[20] A. de Rossi et al., “In-situ synthesis of zeolites by geopolymerization of biomass fly ash and metakaolin,” Materials Letters, vol. 236, pp. 644–648, Feb. 2019, doi: 10.1016/J.MATLET.2018.11.016.

Acknowledgements
Publication is created with support of European Regional Development Fund project “A new concept for low-energy eco-friendly house”, Grant Agreement No 1.1.1.1/19/A/017.