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Sapropel as a Binder: Properties and Application Possibilities for Composite Materials

V Obuka[1,3], M Šinka[2], M Kļaviņš[1], K Stankeviča[1] and A Korjakins[2]
[1] Department of Environmental Science, University of Latvia, Raina Blvd. 19, LV 1586 Riga, Latvia
[2] Riga Technical University, Faculty of Civil Engineering, Institute of Materials and Structures, Kalku Str. 1, Riga, LV-1658, Latvia

E-mail: vaira_obuka@outlook.com

Abstract. Recent development trends largely look for possibilities of a wider use of natural materials and local resources. In this perspective, the use of organic rich lake sediment – sapropel – as a binding material in line with other environmentally friendly filling materials can be considered as a challenge. Sapropel itself is a valuable resource with multiple areas of application, for example, medicine, veterinary, agriculture, livestock farming, balneology, cosmetic applications, construction, and its application options have been widely studied in the 20th century in the Baltic countries, Ukraine and Russia. Birch wood fibre and sanding dust, hemp shives, 'Aerosil' are used as a filler and three types of sapropel are used as a binder in making composites. After material preparation and curing, physical and mechanical properties - density, thermal conductivity, compressive and flexural strength, were determined and compared to the data in the literature, and the opportunities to use them in the ecological construction were considered. The obtained results give insight into possibilities to use sapropel as a raw material, which can be considered as prospective material for construction materials and design products.

1. Introduction

Sapropel is a partially renewable geological resource [1], it is a fine-grained organic-rich sediment or sedimentary rock, it refers to lacustrine environment inland waters [2]. Organic rich lake sediment – sapropel – is a valuable resource of natural origin. In Latvia, its estimated reserves amount to 700-800 million m^3, 1.5 billion m^3 underlie the peat layer, 2 billion m^3 in total [1]. Sapropel, like, for example, peat has extensive opportunities and can be used in many fields, which vary depending on the composition of sapropel and its properties, and the availability of resources. Sapropel can be used in

[3] To whom any correspondence should be addressed.

various economic fields such as agriculture, medicine, veterinary medicine, construction, livestock farming, balneology, cosmetic applications. Sapropel has adhesive properties with high abilities to glue as well as shape holding ability; it can be used as a binder for manufacturing of environmentally friendly, natural nanostructured materials. Development of composites made from sapropel as a binder and birch wood sanding dust and fibre, hemp shives as a filler contributes to the rational use of natural resources, recultivation of the lakes and production of renewable energy, obtaining materials with the possibilities to manufacture ecological construction products.

Sapropel is the bottom deposits of fresh water bodies containing organic matter up to more than 15% [3]. Sapropel is formed from residues of the plankton and benthos rests – phytoplankton and zooplankton [4]. These elements multiply in large quantities, especially in standing or poorly through running shallow overgrown lakes [5].

One of the most important properties of moist sapropel is a colloidal suspended phase structure, which determines the ability of sapropel organic colloidal particles to absorb large quantities of water, so it has a high moisture capacity, which amounts to 70-97% [6] and low filtration rate [7]. Relative humidity of sapropel is associated with organic matter and its value increases with the content of organic matter [8].

In this research, significant characteristics of organic rich lake sediments are adhesive properties and water repellence [9], [10], [11]. Adhesive capacity of sapropel is determined by the presence of animal and vegetable residues. Green algae shells consist mostly of cellulose, which has weak decomposing properties. Organic sapropel proportion of matter is formed by green algae and is rich with cellulose but is poor in minerals, it consists of ash content, low humic substance level content, formed mainly by peat meristem [12]. It should be noted that the adhesive properties give higher organic nitrogen amounts of sapropel, also including free amino acids [4].

Composition of sapropel can be affected by molecular structure of humic substances and their quantity, respectively, if the content of humic substances increases then ramification of peripheral parts of molecules also increases. This contributes to the emergence of strong links between the molecules of the material at the time of creation. Molecules of humic substances remain flexible, malleable composite material comprises particles capable of providing material durability and high strength [4]. Therefore, it is rational to use sapropel with the above-mentioned properties as an adhesive for various ecological construction materials – plaster/finishing materials and thermal insulation materials, which could replace the traditionally used materials – stone wool and expanded polystyrene. Adhesive properties of sapropel are important in the production of building materials, i. e., if cold techniques compaction and techniques with hot glue presses at elevated temperature and pressure are applied [13].

The aim of this study is to explore different options to produce sapropel-wood fibre, sapropel-hemp shives, and sapropel-wood sanding dust composites and to determine the optimal composition ratio of certain raw material components and to characterize the resulting material properties.

2. Materials and methods

2.1. Sapropel sampling
In this research, organic rich freshwater sediments (further – sapropel) were used. Sapropel sediments were sampled from three lakes in Latvia – Padelis, Pilcenes and Pilvelu, located in Rezekne District, Latgale Region.

Table 1. Characteristics of the sapropel samples.

Lake	Sample Nr.	Moisture,%	Organic matter,%	Carbonates,%
Padelis	Sample 1	85.97	15.27	35.57
Pilvelu	Sample 2	94.99	84.51	1.26
Veveru	Sample 3	97.66	86.25	1.18

Sapropel samples differ from one another in terms of moisture (%), organic matter (%) and carbonates (%). Characteristics of the sapropel samples are shown in table 1. For example, Lake Padelis sapropel sample contains 35.57% carbonates, moisture is 85.97%, but colour – pale gray-pink and its density is 1.24 g/cm^3. Lake Pilvelis sapropel sample is dark greenish brown with homogeneous and jelly-like structure and density of 1.10 g/cm^3. Lake Veveru sapropel sample moisture level is high – 97.66%, it has low density – 1.08 g/cm^3 and organic matter reaches 86.25%.

2.2. Loss on ignition
Loss on ignition (LOI) method was applied in order to estimate moisture content, content of carbonate matter and organic matter of sediments [14]. Moisture content of sapropel was determined after drying at 105°C, following organic matter estimation at 550°C for 4 h. The content of mineral substances was determined after heating at 900°C for 2 h.

2.3. Fillers for composite materials
Birch wood sanding dust (also known as wood dust) and fibre (also known as wood fibers), and hemp shives were selected as fillers for production of composite materials. Birch wood sanding dust and fibre is industrial by-product from JSC "Latvijas finieris" – a plywood manufacturing company. Birch wood fibre is up to 15 mm long and up to 0.1 mm thick in diameter. In addition, hemp shives ("Bialobrezeskie") were taken from "Zalers" Ltd. Hemp shive slices were maximal 5.5 cm long and up to 0.6 cm thick in diameter. In producing of composites, an additional thickening additive filler was used – colloidal silica product "Aerosil". It is a filler that creates a smooth mixture, often in combination with other fillers.

2.4. Sample preparation and curing
For the developed composite materials raw sapropel was used as a binder (adhesive). Mixing of sapropel-filler mass was done manually until homogeneous and smooth mixture was reached at the stage where filler was fully covered with sapropel. Sapropel was mechanically treated by mixing together with electrical hand mixer until smooth and homogeneous material was formed. Metal mould with dimension of 30×30 cm and with adjustable height was used for composite material production. The mixture of raw materials was laid in by layers in mold for more dense composite material structure, higher mechanical strength and for minimizing final product shrinkage. Sapropel-filler samples were cured at the temperature of 80 – 105°C for 36 – 72 hours.

2.5. Thermal conductivity test
Before the thermal conductivity test, the density of the samples was calculated by weighting the samples and measuring the dimensions. Thermal conductivity was measured using LaserComp FOX 600 heat-flow measurer. Test settings were 0°C upper and 20°C lower plate. Automatic determination of sample thickness was chosen for this study.

2.6. Compressive and flexural strength tests
For testing compressive and flexural strength, the samples were specially prepared (sawed in necessary dimensions). The dimensions were 27-60×27-55×27-55 mm cubic forms for compressive tests (parallel and crosswise to the tamping direction) and 27-60×27-55×120 mm pieces for flexural strength tests. Mechanical tests were performed on ZWICK Z100 universal testing machine. For compressive strength, a stress at 10% deformation was recorded, for compressive crosswise and flexural strength – until failure. For sapropel-hemp shives, a layer of gypsum was spread over the interfaces to ensure even pressure application.

3. Results and discussion

3.1. Thermal conductivity test results
Paying particular attention to shrinkage cracks, thermal properties of the composite materials (wood sanding dust and 'Aerosil' with sample 2) were tested by heating the material in the oven. Shrinkage cracks impacted the quality of material for further tests, but in this case gypsum was used to fill the cracks and to do a thermal conductivity test. The measurement results also indicate a higher thermal conductivity of the material, that is, 0.080 W/m*K. This value can be explained by the fact that all the cracks were not sufficiently filled, gypsum also influenced the result, as thermal conductivity of gypsum is around 0.18 W/m*K. Thermal conductivity test of sapropel – filler composite was carried out by changing the types of sapropel and fillers. The results obtained are shown in table 2.

Table 2. Thermal conductivity of the studied materials.

Material: binder-filler	Density, kg/m^3	Thermal conductivity, W/m*K
Sample 1 and sample 3 - hemp shives	191	0.063
Sample 1 and sample 2 - hemp shives	200	0.059
Sample 3 - wood fibre	153	0.055
Sample 3 - wood fibre	202	0.060
Sample 3 - wood sanding dust	214	0.061
Sample 3 – wood sanding dust - 'Aerosil'	376	0.080

According to the results obtained, the composite made from sapropel sample 3-wood fibre (density 153 kg/m^3) has the best results of thermal conductivity. From visual aspect, it is a material different from another sample 3 sapropel-wood fibre (figure 2) with density 202 kg/m^3, because it has a denser structure and it has comparatively better resistance with respect to deformation. Results indicate that these composites have similar characteristics, thereby they have similar possibilities of use and potential. Thermal conductivity of air-dried composites is relatively low because of the organic origin of raw materials, detailed cellural mixed structure and homogeneous fibres with interconnected and open pores.

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Figure 1. Sample 1 and sample 3 – hemp shives.

Figure 2. Sample 3 – wood fibre.

While sapropel-hemp shives composites (figure 1 and 4) are characterized by a heterogeneous structure due to different size of particles, having cavities and uneven composition with weaker inclusions, deforming more quickly. However, composite (density 376 kg/m^3) made from wood sanding dust and 'Aerosil' with sample 3 sapropel binder, and composite made from sample 3 sapropel and wood sanding dust (figure 3) with density 214 kg/m^3, formed shrinkage cracks during drying indicating the inferiority of the technology. Composite structure is made of densely grouped wood sanding dust particles with a sapropel binder.

In the study of sapropel-sawdust and peat-sawdust composite materials [15], the results obtained in thermal conductivity measurements were 0.067 W/m*K and 0.060 W/m*K. The study considered the freezing cycles and moisture of the tested materials. It shows that sapropel-sawdust thermal conductivity coefficient becomes lower after freezing cycles. If the composite material is resistant to freezing cycles, this material is applicable for Latvian conditions [15]. When compared with the results obtained, where composite's humidity is from air - dry state and a moisture saturated material (12%), thermal conductivity coefficient for sapropel-sawdust composite material is 0.050 – 0.060 W/m*K and for peat-sawdust composite material is 0.055 – 0.064 W/m*K, respectively, which is very similar to the results of this research. In the study of sapropel-straw panels where composition is similar to the composites created in this research and the samples from the study of sapropel and peat sawdust composite material [15], the result obtained is 0.055 W/m*K and it is stressed that with varying fillers and sapropel ratio, it is possible to produce a more effective thermal conductivity material [16].

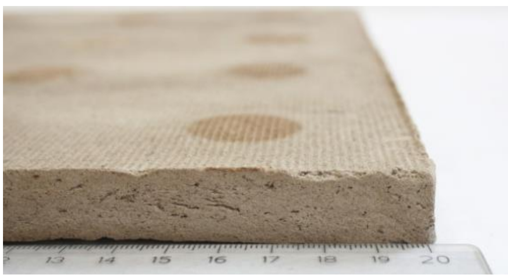

Figure 3. Sample 3 – wood sanding dust.

Figure 4. Sample 1 and sample 2 – hemp shives.

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In the study by Binici and colleagues on the insulation materials made from the sunflower stems, textiles and agricultural by-products as a filler, epoxy resin was used as the binder for better fiber strength and binding efficiency. An average thermal conductivity coefficient of 0.1642 W/m * K was obtained. However, the thermal conductivity coefficient of the sample with less epoxy resin added and made only from sunflower stems and sunflower stem fibers reached 0.0728 W/m*K [17]. In research of bamboo fiber and polyester composite Mounika et al. conclude that thermal conductivity coefficient decreases with the increase in the proportion of fiber. Thermal conductivity coefficient ranged from 0.185 to 0.196 W/m*K [18]. Literature on materials based on natural fibres from renewable raw material resources (flax, hemp, wood, bamboo, sheep's wool) shows that they possess very good sound and thermal insulation properties. This is due to material's low density and natural character of input fibres ("airy", lightweight material) [19], [20].

In the study about lime-hemp concrete, a variety of binders were compared, including metakaolin, obtained by burning kaolin clay (40% by mass) at 800°C and dolomitic lime (60% by mass), produced by "Saulkalne" Ltd. 8 different types of hemp shives were used as filler. The obtained results shows lime-hemp concrete material has a density of 312-337 kg/m^3, thermal conductivity of the material is more diverse than its density – from 0.0718 to 0.0778 W/m*K [21].

In the research about the use of agricultural waste in sustainable construction materials, Madurwar et al. compared the measurements of insulation materials of different origin. The results ranged from 0.046 to 0.056 W/m*K for rice husks to 0.118 to 0.240 W/m*K for oil palm leaves. The authors concluded that there are significant similarities between the corn's cob and the extruded polystyrene (XPS) material in terms of microstructure and chemical composition. Materials made from rice husk and coconut coir demonstrated the best results [22]. Previously discussed results of thermal conductivity showed similar values comparing with the results obtained in the current study.

3.2. Mechanical resistance and stability test results

The results obtained from the compressive deformation test (figure 5) show that composites where sample 3 sapropel was used as a binder with a filler of birchwood sanding dust and 'Aerosil' have the best result among the analysed samples. Compressive deformation results vary from 0.724 MPa sample 3 sapropel-wood sanding dust composite to 0.674 MPa for sample 3 sapropel-wood sanding dust and 'Aerosil' as a filler, while compressive strength crosswise shows respectively 0.669 MPa and 0.760 MPa.

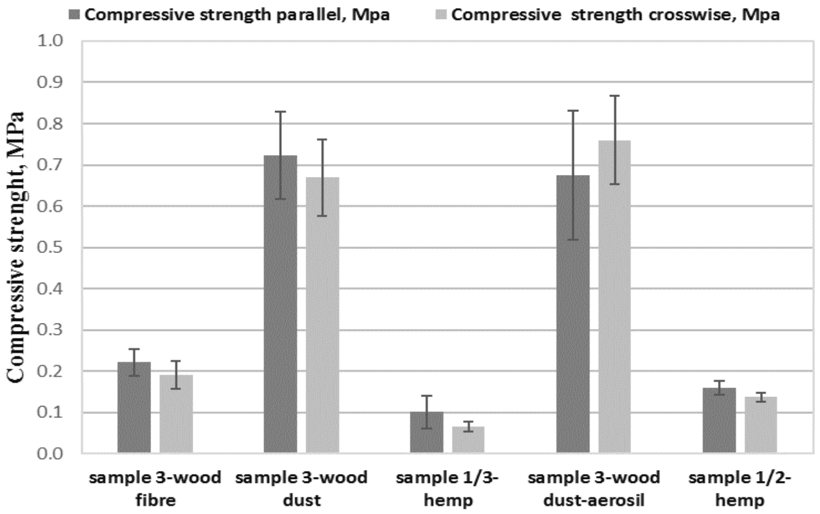

Figure 5. Compressive strength parallel and crosswise of different composites.

Composites made from hemp shives and wood fibre as a filler in compressive deformation obtain the rate of 0.221MPa for sample 3 sapropel-wood fibre and hemp shives materials 0.101 (Sample 1 and 3 – hemp shives) and 0.159 MPa (Sample 1 and sample 2 – hemp shives), while compressive strength crosswise shows respectively 0.191 MPa, 0.066 MPa and 0.138 MPa. The aforementioned materials have relatively lower rates due to lower intensity of filler and binder bonding. The mixing of the binder with the filler is more complex, because for the binder it is more difficult to enter the filler structure as its particles are larger. This was observed with wood fibre composite and sample 3 as a binder. However, filler (birch wood sanding dust and 'Aerosil'), which contains a mass of dust particles, mixes with the binder evenly, entering filler's structure. The structure of the material is smoother and will increase the mechanical resistance of the composite. Compressive strength results are influenced by the mode of sample preparation as they are sawn before, disrupting the structure of the material. The use of various fillers and binders affects physical and mechanical properties of composite materials, so changing the type of fillers and binders can induce change in physical and mechanical properties.

Comparing to the compressive strength results, the flexural strength results (figure 6) show that the material strength is relatively lower. It can be seen considering the results that the samples which have been made from hemp shives show lower values, the reason could be granulometric composition, as there are many large shives that create voids and uneven composition with weaker inclusions resulting in faster deformation of the samples [21]. In the process of making wood fibre-sapropel composite, the mixing of the binder with the filler is more complex, because for the binder it is more difficult to enter the filler structure, forming tangles and air gaps. Therefore, there are voids which can reduce mechanical strength of the obtained material.

Composites made from hemp shives and wood sanding dust as a filler in flexural deformation strength obtain a value of 0.069 MPa for sample 3 sapropel – wood fibre and 0.164 MPa (sample 3 sapropel – wood sanding dust) and 0.203 MPa (sample 3 sapropel – wood sanding dust – 'Aerosil'), while compressive strength crosswise shows 0.066 MPa for sample 3 – wood fibre 0.182 MPa for sample 3 sapropel – wood sanding dust – 'Aerosil', respectively. These results are relatively lower due to the lower intensity of the filler and binder bonding. The mixing of the binder with the filler is more complex, because for the binder it is more difficult to enter the filler structure as its particles are larger, longer (with each of different size). For all measurements, the values are higher using mix of sample 1 and sample 2 sapropel, as the reason could be higher sapropel adhesive capacity and lower amount of moisture.

In the study of sapropel and peat sawdust composite material [15], similar composites were created and results show that the type of filler and binder, as well as the preparation technology, change composite compressive and flexural strength. Accordingly to the indicated results, average compressive resistance is 0.03 MPa, but compressive resistance of peat-sawdust composite (activated peat binder) is 0.3 MPa.

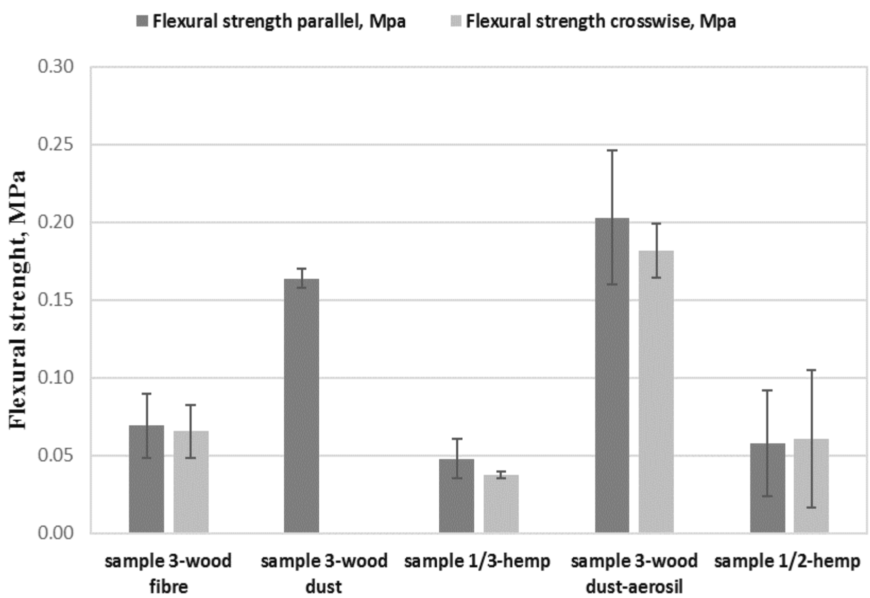

Figure 6. Flexural strengths parallel and crosswise of different composites.

Comparing the results of this work with the research into sapropel–concrete, the results of the current study show lower rates of wood fibre and hemp shives materials. During preparation 1 % NaOH solution was added. The obtained results of the studies showed that compressive strength of absolutely dry composite materials is 0.55 MPa, while that of air-dried – 0.56 MPa [11]. In the study about lime-hemp concrete, a variety of binders including metakaolin and dolomitic lime were compared. The obtained results show that compressive strength of different lime-hemp concrete materials ranges from 0.140 to 0.337 MPa, flexural strenght – from 0.021 to 0.059 MPa [21]. In the study on the composite material, which was created from agricultural by-products, it was concluded that the highest strength indicators were shown by durian peel and coconut-fiber composites, which range from 2.9 to 36 MPa [22]. In turn, the results of the study on the composite of sunflower stems and epoxy resin show compressive strength tests scores of 0.283 to 0.312 MPa. Flexural deformation strength results are from 0.06 to 0.09 MPa. High porosity is the reason of low mechanical strenght of the derived materials.

4. Conclusions

Using natural materials and local resources, such as sapropel, as well as industrial by-products such as birch wood sanding dust and fibre, and hemp shives it is possible to develop environmentally friendly composite materials for the construction industry, adjusting for the need for utilization. Granulometric composition of the particles, surface area and other characteristics of the material used as a filler have an effect on the binding with sapropel. Composite materials, which are made of birch wood sanding dust, 'Aerosil' and sample 2 and sample 3 sapropel, are characterized by relatively high mechanical strength, shape holding ability and easily amenable texture imprint. The composites sample 3 – wood sanding dust, sample 3 – wood sanding dust and 'Aerosil' during heating formed shrinkage cracks, thereby showing technological inferiority, as well as the need for evenly temperature raise and reduction of moisture in sapropel samples.

5. References

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