

Article

Gypsum, Geopolymers, and Starch—Alternative Binders for Bio-Based Building Materials: A Review and Life-Cycle Assessment

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Abstract: To decrease the environmental impact of the construction industry, energy-efficient insulation materials with low embodied production energy are needed. Lime-hemp concrete is traditionally recognized as such a material; however, the drawbacks of this type of material are associated with low strength gain, high initial moisture content, and limited application. Therefore, this review article discusses alternatives to lime-hemp concrete that would achieve similar thermal properties with an equivalent or lower environmental impact. Binders such as gypsum, geopolymers, and starch are proposed as alternatives, due to their performance and low environmental impact, and available research is summarized and discussed in this paper. The summarized results show that low-density thermal insulation bio-composites with a density of 200–400 kg/m³ and thermal conductivity (λ) of 0.06–0.09 W/(m × K) can be obtained with gypsum and geopolymer binders. However, by using a starch binder it is possible to produce ecological building materials with a density of approximately 100 kg/m³ and thermal conductivity (λ) as low as 0.04 W/(m × K). In addition, a preliminary life cycle assessment was carried out to evaluate the environmental impact of reviewed bio-composites. The results indicate that such bio-composites have a low environmental impact, similar to lime-hemp concrete.

Keywords: bio-composites; hemp; lime-hemp concrete; gypsum; starch; geopolymer; life cycle assessment

1. Introduction

Energy consumption in the building maintenance and construction sector constitutes 40% of the total energy consumption in the European Union (EU). To decrease this impact, the EU's "Energy Performance of Buildings Directive" was created. It states that by 31 December 2020, all new buildings should be built as nearly zero-energy buildings [1]. Many EU member states, including Latvia, aim to achieve this target. The Latvian national development plan, the "National plan for increasing the number of nearly zero-energy buildings in Latvia," was developed [2]. Construction processes and operations play significant roles in achieving sustainable development goals. For example, it is calculated that by creating sustainable building operation and construction processes in EU countries, the total energy consumption could be decreased by 40%, total CO₂ greenhouse gas emissions could be decreased by 35%, and construction material consumption could be decreased by 50% [3]. Recently, Nordic countries have shown that the eco-friendly building industry is one of the most successful businesses concerning high-technology and knowledge-based bio-economics. Building products made

of renewable resources significantly decrease CO₂ emissions in the building sector. According to Bosman and Rotmans [4], Finland's transition to bio-economics at the governmental level is based on the development of the ecological construction industry, where the role of renewable resources, including agricultural waste, in the production of building materials has increased.

One of the aims of eco-friendly material design is to increase plant origin fiber content in insulation products, which can decrease thermal conductivity, increase sound absorption, and decrease environmental impact. Previous testing has shown that many qualities of insulation materials made of recycled agricultural waste are comparable with contemporary insulation requirements, although these can vary with structure and environment [5]. Testing measurements often yield better results than theoretical calculations and simulations, and it is necessary to take this into consideration [6]. However, the non-homogeneous structure of natural fibers can make it difficult to predict their behavior, and they can pose challenges and problems related to fire resistance, stability, durability, and acoustic properties [7].

Insulation materials made of the fiber of plant origin represent a significant potential to eliminate the environmental burden in relation to the use of building materials. They have properties that can meet the criteria for low-energy, eco-friendly buildings. In recent years, bio-composites have been increasingly used as primary building materials, not only because of their environmental quality, but due to their association with nature and because they ensure a healthy living environment [8,9]. Bio-composites can be made of fillers of various origins, such as straw, hemp and flax shives, wheat husk (Figure 1), maize, and sunflower [10]. Environmental impacts are usually evaluated through the life-cycle assessment (LCA), which encompasses the different life stages of the material.



Figure 1. Bio-based fillers used in bio-composites—hemp shives (a,b), oat husk (c) and flax shives (d).

LCA results of bio-composites made of such bio-based fillers show that they have a lower environmental impact than other conventional products [11,12]. However, adding flame retardants or other additives to bio-composites to improve their performance may render them less environmentally friendly [11]. Bio-based fillers have different physical properties and chemical compositions, and they influence various properties of bio-composites [13–15]. As fillers have been widely researched, this paper focuses on the binder aspect of bio-composites.

One of the most common bio-composites used in construction is lime hemp concrete, which consists of the by-products of industrial hemp production, namely hemp shives and lime-based binders. During growth, hemp absorbs CO₂ through photosynthesis, and carbon is trapped in lime by carbonation, resulting in a carbon-neutral or even negative product, accumulating up to 130 kg of

CO₂ eq/m³ [16]. The material has good thermal insulation properties, with λ ranging from 0.05 to 0.12 W/(m × K) [17], excellent moisture buffering, and acoustic properties. It has a lower environmental impact than traditional building materials. However, the material is mainly used as a self-supporting thermal and barrier material in conjunction with a constructive wooden structure.

One material that can be used to replace lime-based binders in lime hemp concrete and increase its mechanical properties is the magnesium-based binder, known as magnesium oxychloride cement. This binder is commonly used in combination with various fillers of biological origin [18], such as wood chips, rapeseed straws, and other agricultural by-products. Studies at Riga Technical University (Latvia) have shown that magnesium oxychloride cement and hemp shives can be used to produce high-density load-bearing and low-density thermal insulation composites with a density from 200 to 520 kg/m³, compressive strength from 0.15 to 1.5 MPa, and thermal conductivity (λ) from 0.062 to 0.13 W/(m × K) [12,19]. The advantage of magnesium binders, as opposed to lime-based binders, is their significantly better compatibility with organic fillers [20] and increased mechanical strength. In contrast to lime binders, magnesium oxychloride cement does not carbonate after setting. Thus, no CO₂ is sequestered in this way. However, as lower amounts of binder can be used to achieve the same compressive strength compared with lime hemp concrete, bio-composites with magnesium binders show a similarly low environmental impact [12].

Although lime and magnesium binders have shown their applicability with bio-based fillers, these binders have several disadvantages, such as low mechanical strength and compatibility issues for lime binders [20,21], local unavailability, and long-term durability for magnesium binders. Thus, this study considers three alternative binders that can be used in conjunction with a bio-based filler to form bio-composites for thermal insulation and envelope structures. These binders are gypsum, geopolymers, and starch. Although all these binders have, to varying degrees, been used with bio-based fillers, there are still gaps in our knowledge of bio-composite materials made from these binders. Hence, this study will review the available scientific research and summarize the used mixture compositions, manufacture technologies, and achieved properties. This study will justify the applicability of bio-based fillers and recommend more research on bio-based materials using these alternative binders to close our knowledge gap. Additionally, a preliminary LCA will be carried out to compare these alternative binders with the existing bio-based material binders, as information available on this subject is somewhat limited.

2. Raw Materials and Preparation Methods

The manufacturing process and final properties of bio-composites are highly affected by the type of binder and bio-based fillers used. The specific nature of the binder's preparation, set, and consistency must be considered when using gypsum, geopolymer, or starch binders. There have been published several attempts to obtain bio-composites with different types of bio-based fillers, and often advanced approaches were integrated, such as the modification of the binder, treatment of bio-based fillers to remove hazardous constituents, or the adjustment of the pH of the mixture.

2.1. Alternative Binder Materials Proposed for Bio-Composites

The gypsum binder is widely used in construction due to its low price and availability [22]. Despite these benefits, the disadvantages of the gypsum binder are its brittleness, poor resistance to cracking, and unsuitability for damp conditions. Traditional gypsum binder use has been defined in EN 12859, where the main gypsum application is associated with the production of plasters, blocks, tiles, and boards [23]. The density of traditional gypsum ranges from 600 to 1500 kg/m³, as given in Clause 4.8.1. of EN 12859. This well-known standard covers the gypsum application range, and beyond this range, research is being conducted to make gypsum material more sustainable. Attempts to produce lightweight gypsum with foaming admixtures have yielded a material with a density ranging from 300 to 600 kg/m³ [24]. Such material has low density, superior sound, and thermal insulation and can be considered a sustainable high-performance material. Another way

to achieve lightweight gypsum materials is associated with the incorporation of lightweight aggregates. This group is typically represented as lightweight granular-based materials, which include expanded polystyrene [22], cork [25,26], lightweight clay aggregates (mica) [27], vermiculite [28], and pumice [29]. The new trend is to combine gypsum with bio-based materials as a filler to produce lightweight materials (Figure 2, top). Some companies have released new building materials that compound gypsum with wood shavings and have developed several kinds of manufacturing methods for such materials [30]. However, this such composite has a density from 1000 to 1200 kg/m³, with good thermal and sound insulation properties, and a high strength/density ratio as declared by the manufacturer. The wide range of raw material sources used for wood-shaving blocks keeps their production costs comparatively low, and thanks to simple manufacturing technology, large-scale production is applicable. Further challenges are associated with the production of lighter materials and the use of a wide range of agricultural waste, bio-based fillers, or organic materials coming from construction and demolition waste (CDW).



Figure 2. Bio-composites with alternative binders: gypsum (**top**), geopolymer (**middle**) and starch (**bottom**).

The geopolymer binder is regarded as a feasible alternative to Portland cement binders [31]. The geopolymer binder typically comprises of two components: an aluminosilicate source and a chemical activator. The aluminosilicates are split into two categories: industrial by-products and rock-based raw materials [32]. Most studies have considered the use of industrial by-products, such as fly ash or blast furnace slag, as potential raw materials [33–35], while other precursor sources are raw rock-based materials, with a high kaolinite content [32]. The second component required to form a geopolymer binder is a chemical activator commonly used in the form of a mild alkaline reagent. This reagent is an aqueous solution of silicate containing silica and alkali metal, with a $\text{SiO}_2:\text{M}_2\text{O}$ molar ratio greater than 1.65, where M is an alkali metal, either sodium (Na) or potassium (K) [32]. Dense geopolymers are durable (with compressive strength up to 80 MPa), while thermal conductivity

(λ) is as high as 0.75 W/(m $\times$ K) [36–38]. An alternative way is to use porous geopolymers with a density of <500 kg/m³. For such a material, thermal conductivity (λ) can be in the range of 0.05–0.2 W/(m $\times$ K), while significant strength reduction is expected to 0.1–3 MPa [39,40].

Several efforts have been made to produce geopolymer-based bio-composites. Geopolymer composites with natural plant origin components (aggregates and/or fibers) are innovative materials that have not been studied as extensively as other composites with natural plant origin aggregates (Figure 2, middle). Because geopolymers present good mechanical properties as a constructive building material [41,42], in most studies on geopolymer composites with natural plant origin components, natural plant origin fibers have been used [43–46]. Ye et al. [47] reported in their study of cellulose, hemicellulose, and lignin impacts on the morphology and mechanical properties of geopolymers. It has been shown that low lignin, cellulose, and hemicellulose contents (up to 5% by weight) can improve the flexural and compressive strength of a pure geopolymer. First, the increased hemicellulose content lowers the degree of geopolymerization due to the alkaline decomposition of hemicellulose to form carboxylic acids, which weakens the alkaline environment for geopolymerization. Second, elevated lignin and hemicellulose content results in a porous morphology, lower density, and the fracture of fragile geopolymer-based composites, thus reducing its flexural and compressive strength. Third, the increase in cellulose content results in a denser structure, fewer pores, constant density, and noticeable damage to the geopolymer-based composite duct (due to the fiber bonding mechanism that limits crack propagation) [47]. Even if the fibers were exposed to the highly alkaline geopolymer surrounding conditions, no remarkable degradation of cellulose fibers was observed. The noteworthy aspect is that preheating treatment can decrease the density and mechanical strength of the geopolymer-based natural aggregate composites.

Starch is a natural polymer directly extracted from renewable plant resources and is widely used for bio-composite production [48]. Starch is a white powder with grains of 2 to 150 μ m in size, the morphology of which depends on its plant origin and growth conditions [49]. Compared to many traditional synthetic polymers, starch has notable advantages such as renewability, low cost, wide availability, and complete biodegradability without toxic residues. Drawbacks associated with the starch-based materials are that they usually possess low mechanical properties compared with most traditional synthetic polymers, which greatly limit their application. Starch with a plasticizer (water, glycerin, sorbitol) melts at high temperatures (90–180 $^{\circ}$ C); thus, it can be used in extrusion or other types of bio-composite production (Figure 2, bottom) [50]. Starch-based bioplastics can be made from wheat, potatoes, and rice starch. However, due to its low price, corn starch is used extensively. In addition, corn starch has better adhesive properties compared with other types of starch. However, low resistance to water and changes in mechanical properties arising from changes in the environmental conditions limit the wider use of starch in bio-composite production [51,52].

As research [53,54] shows, corn starch is an excellent alternative to traditional binding materials. However, products containing corn starch need to be improved to meet the more rigorous requirements for mechanically stronger building materials. Compared to bio-composites made from binders based on lime, cement, or sapropel, such starch-based bio-composites have lower mechanical properties; compressive strength from 0.57 to 0.63 MPa at 25% deformation and a tensile strength from 0.080 to 0.11 MPa [55]. Such low mechanical properties were obtained after the application of a starch and water paste to dry and untreated hemp shives, which quickly absorbed most of the water from the paste. Compared to bio-composites produced using lime and cement binders, starch bio-composites have better thermal insulation properties due to their low density and high porosity (approximately 89%) as well as their thermal conductivity (λ) of 0.0634 and 0.0738 W/(m $\times$ K).

2.2. Bio-Composite Treatment Methods

Some researchers have made an effort to identify the best way to treat bio-fillers before their use for bio-composite production. Obtaining an excellent thermal conductivity/strength ratio of the bio-composite is an important issue. Several pretreatment methods have been identified that can

yield high-performance bio-composites for building applications. The pretreatment of hemp shives is desirable for the production of high-performance bio-composites. The main structural part of hemp shiv is cellulose, which contains free hydroxyl groups responsible for characteristic hydrophilicity of the material [56]. Untreated hemp shives and other bio-fillers have poor interfacial adhesion with the binder matrix being extremely sensitive to moisture, which could cause microbial growth, promote intensive degradation of the hemp wall, and decrease the durability of the bio-composites. It has been reported that wood extracts can slow the hydration process of the inorganic binders. Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) characterizations show that the main components of the sawdust water extracts are hemicellulose, lignin, tannins, and acetic acid [57].

Extracts from sawdust have been identified to have adverse effects on the exothermic hydration (or setting) of gypsum [58]. The addition of sawdust undermines the mechanical performance of gypsum bio-composites significantly; for example, 20% of sawdust bio-filler from the gypsum mass decreases both flexural strength and compressive strength by up to 64% [57].

The pretreatment of plant origin aggregates is also an important step in geopolymer-based bio-composite production. The pretreatment of the plant origin aggregates has been identified to be able to improve the durability of geopolymer-based bio-composites. Pretreatment with the polyvinyl alcohol (PVA) solution, as well as pretreatment with NaOH solution, improves geopolymer-based bio-composite durability, such as sulfuric acid resistance [59]. Due to their porous nature, hemp shives and other bio-fillers have a higher water absorption rate and absorb high amounts of water in the first few minutes compared with inorganic fillers. Therefore, additional preparation and pretreatment of bio-based particles and fiber surfaces are necessary for their use in bio-composites with a starch binder. A few studies [60] have described the impact of hot water-treated aggregates on the final properties of bio-composites. In these studies, the hemp shives were treated with hot water (100 °C) instead of the chemical modification of aggregates' surfaces by NaOH, titanites, and silanes, which were used for improving interfacial adhesion between hemp shives and starch. All fractions were treated with 100 °C water and left for 2 h, after which they were drained for 10 min to eliminate any excess of water. Treatment with hot water softens hemp shives, allows easier adherence, and more evenly distributes starch between binder particles. Additionally, hot water treatment decreased hemp shiv hydrophilicity through the partial removal of hemicellulose.

Several researchers have identified the positive effects of the bio-filler pretreatment (mineralization) procedure:

1. Mineralization of straw bio-fillers (mineralized by 5% of CaCl_2 and $\text{Ca}(\text{OH})_2$ solutions) considerably improves the properties of gypsum bio-composites, increasing their strength from 2.5 to 3.1 MPa (by 5–20%) and reducing thermal conductivity (λ) from 0.49 to 0.52 W/ (m × K) [61]. Gypsum bio-composite samples were prepared from a mixture containing straw fillers.
2. Mineralization of cotton stalk fibers with styrene-acrylic emulsion improves the combined interface condition and mechanical properties of the cotton stalk fiber/gypsum bio-composite material [30]. Improved flexibility eases the shaping of the materials and improves strength and water-resistant properties of the composites remarkably, increasing bending strength from 5.6 to 10 MPa, reducing absorbed water content from 20.2% to 14.3%, and decreasing strength after water saturation reaching 91.4% compared with 66% for untreated bio-composite.
3. Bio-based filler can be treated with various substances (sodium hydroxide (NaOH), ethylenediaminetetraacetic acid (EDTA), calcium hydroxide ($\text{Ca}(\text{OH})_2$), polyethyleneimine (PEI), and calcium chloride (CaCl_2)) to increase the effectiveness of the contact zones between bio-fillers and binders in the bio-composites [53]. Alkaline treatment with 1% of NaOH removes amorphous compounds from the surface of hemp shives and improves the ability to activate hemp shives' surface by degrading extracts.
4. Several studies have shown that, prior to compounding, hemp shives can be subjected to reflux in a cyclohexane/ethanol mixture for 24 h [62]. This pre-treatment removes pectin, wax, and other

components present on the surface of the hemp shives without affecting the morphological characteristics of the bio-based filler.

2.3. Specimen Manufacture

Some studies have explained the manufacturing methods for each type of binder, along with suggestions of adjustments. As such, a high-performance bio-composite with low density, low thermal conductivity, comparatively high mechanical properties, and a low impact on the environment could be obtained. The most effective production methods are described below.

Several methods have been used to produce lightweight gypsum-based bio-composites. In the first method, straw fibers are used in their original length, just like in straw bales. The straw fibers are then pre-moistened in a mixer for 60 s, using one-third of the water from the W/B ratio. The gypsum powder with the remaining water is then added and mixed for 60 s. The length of the fibers causes significant mixing problems and the results of the composite blocks are poor. Another method can be employed whereby straw fibers are crushed and then mixed with the gypsum powder in the same way as described above [63]. The brittle blocks with poor mechanical properties and several problems, such as the absence of binder between the fibers and the segregation of the plaster at the bottom of the mold, are obtained using this procedure. Another method involves changing the volume of water to prepare a mixture of water and binder outside the mixer. This method involves mixing the straw fibers with 15% water for 60 s, adding the binder and water mixture, and then mixing for five minutes. Before adding to the mixer, the binder is mixed with 85% water. The finished mixture is inserted in a 300 × 300 × 100 mm mold without vibration or compaction. The resulting blocks are removed from the molds one hour after molding and are dried in a ventilated oven at 45 °C until a constant weight is obtained.

Cherki et al. [25] have described more simple mixing techniques for the production of bio-composites using natural fillers with smaller sizes (granular cork). The apparent volume of the mold is filled with the granular cork, and for each size fraction the mold is filled accordingly. Thus, the apparent volume fraction of the granulated cork is constant in all samples. Gypsum paste is then added to fill the intergranular space. As the volume of the mold is filled with a granular cork, this is the maximum content of cork that the mixture can contain [25].

To produce geopolymer bio-composites, the specifics of the material production must be taken into account. Lui et al. present the foamed geopolymer bio-composite preparation scheme (Figure 3) [64]. It is very important to start with binder mixing, which involves the proper mixing of the chemical activator (alkaline solution) with the amorphous aluminum silicate source (metakaolin, fly ash, etc.) The geopolymer paste can be used to decrease the density of the bio-composite material foaming agent (H_2O_2 or Al paste). If the foamed geopolymer paste is used, the plant origin aggregate should be added to the geopolymer paste immediately after the foaming agent is mixed with the paste [54]. For wood chips or other small-sized bio-fillers, spraying with a geopolymer paste during bio-filler mixing is preferred to decrease adhesive substance consumption and ensure a smooth particle deposition [65].

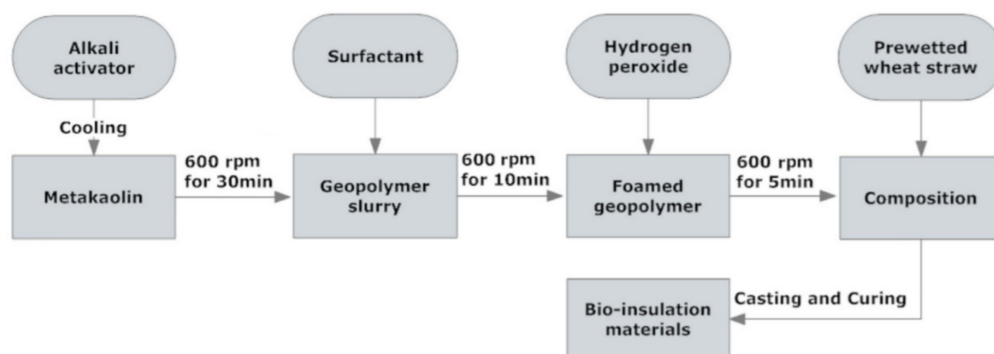


Figure 3. The experimental preparation procedure for geopolymer bio-composites by Lui et al. [64]

The most common methods employed for starch-based bio-composite manufacturing are extrusion [66,67], injection molding, hot pressing [54,68], hot-pressing [67], compaction at load [55,69,70], and further curing at temperatures from 120 °C to 180 °C [48,53,69,71,72]. Compression molding is generally used for thermoplastic matrices [72]. The degradation of the fibers can occur when the curing temperature is too high. In contrast, there is a limit on the minimal temperature necessary to reach the melting point of the thermoplastic matrices used. This means that the heat treatment temperature must be above the melting temperature of the starch binder and below the temperature where the degradation of bio-fillers starts. High-quality bio-composites should be produced using precise control of the mix viscosity, pressure, holding time, and temperature, considering the fiber type and matrix. Some researchers [50,55] have used compression molding with a load of 0.25 MPa without further curing at high temperature but using drying at a temperature of $20\text{ °C} \pm 2\text{ °C}$ and a relative humidity of $50\% \pm 5\%$. A disadvantage of such a process includes prolonged curing time, which takes 40–50 days. The duration of curing at high temperatures varies greatly from several minutes to several hours (6–8 h) [48,68,69], and it mostly depends on hemp shives/starch ratio and water/starch ratio. With an increase in the curing temperature, the gelatinization process advances and results in a rapid increase in the compressive strength of the material [73]. To gain better interconnection between the bio-filler and the binder, compression molding of the mixture is necessary.

3. Properties of the Bio-Based Materials with Alternative Binders

The properties of the bio-based materials are affected by the selected materials, their treatment methods, and mixture proportions. Results that have been published typically pay particular attention to such technological properties as thermal conductivity, density, and the mechanical properties of bio-composites. Limited research has been dedicated to the evaluation of the durability regarding the interaction with moisture and fungus, fire resistance, and the environmental impact of bio-composites.

3.1. Mixture Compositions and Physical and Mechanical Properties

Two main parameters are normally considered for designing the mixture composition of bio-composites, namely the water/binder (W/B) ratio and the bio-filler/binder ratio. Most often, these values are expressed as weight ratios. The W/B ratio of mineral binder–straw composites with gypsum binder typically varies between 0.8 and 1.6 [61,74]. This is affected by the binder properties and the amount of bio-based filler used to produce the composites, mainly because bio-fillers have high water absorption, which is counted in the W/B ratio. Traditionally, the strength of the gypsum products decreases when the W/B ratio increases. As reported by Vegas et al., an increase in the W/B ratio from 0.3 to 0.8 decreases the compressive strength from 30 to 6.4 MPa [75]. The other most important parameter is the bio-filler/binder ratio. The straw/binder ratio can be selected in a wide range (0.2–0.4) and depends on the intended properties. The lowest ratio is often defined by structural integrity and strength. Bio-composites with a density from 184 to 456 kg/m³ have a compressive strength of 4–71 kPa and a thermal conductivity (λ) of 0.058–0.086 W/(m × K), obtained from straw–gypsum binder ratios between 0.2 and 0.4 [74]. The use of bio-fillers, such as cork (density: 150 kg/m³ and thermal conductivity: 0.049–0.05 W/(m × K)) yields gypsum bio-based composites with a density up to 800 kg/m³ with thermal conductivity remaining comparatively high (i.e., 0.3 W/(m × K)) [25]. The results show that an increase in the amount of wood waste in the composition decreases the density, Shore C hardness, and thermal conductivity of the bio-composites [76]. The percentage rise of the wood waste fillers in the composition slightly lowers the thermal conductivity of wood–gypsum composites. Morales-Conde et al. have developed gypsum bio-composites with recycled wood shaving or sawdust filler coming from CDW, yielding a lightweight material with a bulk density from 600–800 kg/m³ with λ up to 0.20 W/(m × K) [76]. Other researchers have reported that 2–6% of wheat straws from the gypsum mass can be used in the bio-composite composition; however, there are recommendations not to use more than 3% [61]. The apparent density ranges from 800 to 980 kg/m³, compressive strength from 2 to 2.5 MPa, and λ from 0.49 to 0.66 W/(m × K) for the obtained bio-based composites.

Several studies have been published on geopolymer-based bio-composites, as well as their compositions and properties. The mixture composition of geopolymer-based bio-composites can vary from the type of solid raw materials used, namely amorphous aluminum silicate sources and liquid chemical activators [41]. To avoid material cracking during the hardening process and ensure more stable mechanical strength, inert mineral fillers can be added [77]. Furtos et al. have revealed that substituting the geopolymer binder weight with up to 10% of wood fibers increases the compressive strength of the geopolymer-based composites, and up to 35% of weight replacement is acceptable to develop low thermal conductivity materials. [43].

Geopolymer bio-composites with hemp fibers outperform flax fiber geopolymers in their flexural and compressive strength characteristics. The best results are achieved when using fine fibers such as microfibers. Even though the fiber addition does not significantly improve bio-composite ultimate strength, the mechanical strength parameters are positively influenced. The fiber addition changes the nature of the failure mechanism from brittle to ductile. The bamboo-reinforced geopolymer bio-composites have been recognized as a potential sustainable green material for construction [45].

Geopolymers have proven their significant role as a thermal-isolation building material [78]. Porous geopolymers have been studied extensively, and one of the latest innovations in the studies of geopolymers as isolation materials is presented by Liu et al. [64]. Scientists from China have developed and characterized the eco-friendly composites made of foam geopolymers and wheat straw. Obtained materials have a compressive strength from 0.5 to 5.5 MPa and thermal conductivity (λ) from 0.095 to 0.19 W/(m × K).

Starch-based bio-composites can be produced with low density and excellent thermal conductivity. The density of these bio-composites can be between 130 and 420 kg/m³ [50,55,79]. The porous structure determines low thermal conductivity, which varies from 0.048 to 0.11 W/(m × K), but it is strongly affected by the forming parameters and methods used [55,79]. The hemp shives fractions used for bio-composites vary from 0.5 to 20 mm [55,68]. The prepared composite mixtures are usually compressed with a compressing load of around 0.25 MPa and then dried at a temperature of 20 °C ± 2 °C and relative humidity of 50% ± 5%. For composites with shorter fractions of hemp shives, density is from 163.6 to 169.1 kg/m³. Compressive strength at 5% of relative deformation varies from 0.03 to 0.08 MPa, while longer hemp shives of 0–20 mm slightly increase the density from 168.1 to 174.3 kg/m³, with compressive stress at 5% of relative deformation varying from 0.014 to 0.045 MPa [50].

The water/starch ratio in bio-composites mostly varies in a range from 4 to 6 [55,69]. The properties of hemp–starch bio-composites are mostly affected by variations in the hemp shives/starch ratio, which can vary in a wide range from 2 to 14 [50,55,69,79]. Compressive strength is the most important parameter for the building application of the hemp–starch bio-composite, and it could be in a range from 0.03 to 4.0 MPa. However, it still strongly depends on the hemp shives/starch ratio [79]. An increase in hemp shives/starch ratio in bio-composites increases water absorption up to 12% with 56% humidity [50,55,69,79].

It can be concluded that by increasing the hemp shives/starch ratio, the composition density and compressive strength of bio-composite decrease, but thermal insulation properties increase. As always, it is necessary to obtain bio-composites with high-performance properties suitable for energy-efficient and ecological buildings.

The physical and mechanical properties of bio-composites made from different binders are summarized in Table 1. It can be concluded that all selected binders (gypsum, geopolymers, starch) can be used to produce bio-composites with high-performance properties. Generally, low density and thermal conductivity can be obtained from starch as a binding material, hence the limited production of high-density and high-strength materials. A wide range of materials can be produced using gypsum as the binding material. This possibility allows us to produce both lightweight and dense materials, with a wide variety of mixture compositions being possible. Geopolymer binder has been investigated on a small scale, as this field of material has gained popularity only in the last decade, with a dramatic increase in the number of scientific publications.

Table 1. Summary of physical and mechanical properties of bio-composites with alternative binders.

Binder	Binder Type	Aggregate	Liquid/Binder ¹ , by Weight	Straw/Binder	Density, (kg/m ³)	Thermal Cond., (W/ (m × K)	Compressive Strength, (MPa)	Bending Strength, (MPa)	Water Absorption, %	Ref.
Gypsum	Gypsum	Straw	1.1–1.6	0.2–0.4	184–456	0.058–0.086	0.004–0.071	-	-	[74]
	Gypsum	EPS	0.5	0.2–0.8	527–1088	0.055–0.260	0.82–3.29	-	31–44	[22]
	Gypsum	Cork	0.7	-	472–801	0.124–0.299	-	-	-	[25]
	Gypsum	Straw	0.8–1.0	0.02–0.06	774–984	0.36–0.66	2.1–3.9	0.5–1.8	35–49	[61]
	Gypsum	Sawdust/wood shavings	0.55–1.25	0.1–0.4	602–1260	0.199–0.25	1.7–13.3	1.09–9.02	-	[76]
	Gypsum	Wood sawdust	0.65	0.1–0.2	870–1080	-	3.80–8.68	1.59–3.33	-	[57]
Geopolymer	Metakaolin	Wheat straw	1.0–5.0	0.064–0.558	290–320	0.099–0.120	0.7–1.7	-	65–105	[64]
	Fly ash	Cotton stalk	0.67	0.3–0.9	1479–1517	-	16–24	-	6.7–8.6	[59]
	Clay based	Wood sawdust	7–10	0.27	570–660	0.088–0.110	1.8–2.8	-	-	[65]
Starch	Wheat starch	Hemp shives 1–7 mm	4	6–14	159–171	-	0.03–0.08	-	-	[69]
	Wheat starch	Hemp shives 0–20 mm	5.6	8–10	134–143	0.048–0.071	0.57–0.63	-	8–10	[55]
	Corn starch	Hemp shives 2.5–20 mm	4	2–10	319–374	0.061–0.063	-	-	4.8–6.1	[69]
	Corn starch	Hemp shives 2–8 mm	4	9	175–240	0.052–0.057	1.05	-	11–12	[54]

¹ For geopolymers, the liquid is alkali activation solution; for gypsum and starch, it is water.

3.2. Moisture and Water Resistance

Accelerated aging methods are used to assess the potential long-term issues of building materials faced with different environmental conditions. Fluctuations in temperature and humidity can significantly degrade materials and adversely affect safety and comfort. Therefore, in order to meet the technical and safety criteria for their use in buildings, the long-term behavior and durability of the materials must be taken into account [74].

Gypsum-based bio-composites are not normally directly exposed to long-term water exposure. To characterize water resistance the drying–wetting cycles are used instead. It is reported that gypsum-based bio-composites can resist up to 40 of such cycles. In fact, a decrease in strength has been observed in many cases due to the leaching of the binder on the surface of bio-fillers because of the immersion of the specimens. Some reports indicate that dynamic wet and dry cycling has greatly accelerated fiber degradation. This is suggested to be due to the accelerating effects on both the alkaline hydrolysis of the amorphous components of the fiber and the cell wall mineralization of the fibers, as indicated by the higher crystallinity and minimum cellulose content [80]. It is possible to increase gypsum bio-composite water resistance by using a gypsum-cement-pozzolan binder [81].

The effect of freezing–thawing on gypsum-based bio-composites can be affected by the type of bio-fillers used to prepare composites. The barley straw composite shows less resistance than the wheat straw composite because of its high moisture absorption and a high percentage of micro-porosity [63,74]. It has been proven that the thermal conductivity of gypsum-based wheat or barley straw bio-composites can increase 2–3 times if the materials are exposed to moisture and drying–wetting processes can happen. The moisture resistance of gypsum bio-based composites can be improved by adding lime and silica fume (1.7–11% of lime and 2–5.3% of silica fume) to gypsum binder where lime acts as an alkaline activator of the pozzolan reaction [82].

Geopolymers are prone to efflorescence formation in a water environment. The alkalis of pore solution can diffuse toward the surface of geopolymers, particularly when geopolymers are exposed to cycles of wetting–drying or moisture transfer. The reduction in pH is the result of three simultaneous mechanisms: the continuous dissolution of the precursor, alkali leaching, and carbonation of NaOH in the pore solution [83,84]. Alkali leaching has been identified to be the main cause of the neutralization of geopolymers. The alkalinity of geopolymer mortar is much easier to decrease regardless of the environments above compared with Portland cement mortar [85]. Such a phenomenon can occur in bio-based composites, which can lead to alkali leaching from the geopolymer matrix and interaction with bio-fillers. This can degrade hemicellulose under an alkaline environment and have a negative effect on bio-filler treatment with alkalis before mixing, as the hemp shives' surface will be damaged by degrading extracts. However, such a process can be bypassed during the activation process of geopolymers under alkaline conditions.

Corn-starch-based composites, similar to gypsum-based bio-composites, are not water-resistant, and the degradation of the material can happen even within one day [73]. The significant decrease in the mechanical properties of starch-based bio-composites is explained by the degradation of all main polymeric components, such as cellulose, hemicelluloses, and lignin leading to the formation of a sufficient number of carboxyl and vinyl groups with the concomitant decrease in the molecular weight [72]. Bio-composites' resistance to moisture can be increased by alkali and silica treatment of the natural fibers, including hemp shives [53,54,86]. Alkali treatment enables an increase in the compressive strength of the bio-composites up to two times and a decrease in water absorption up to 1.6 times. The hydrophobization of bio-fillers can decrease water absorption by up to 5.75 times. Bio-composites' resistance to accelerated aging strongly correlates with the density of the material: bio-composites with a higher density are more resistant to environmental impacts. The pretreatment and hydrophobization of the bio-fillers can improve the durability and service life of the starch-based bio-composites.

3.3. Resistance to Microorganisms

Resistance to microorganisms strongly depends on the environmental conditions to which bio-composites are exposed. Even increased moisture in the air can initiate the biological degradation of bio-composites if they are not treated. The commonly occurring mold on the surfaces of bio-composites is *Cladosporium cladosporioides*, *Asperigillus versicolor*, *Stachybotrys chartum*, *Penicillium purpurogenum* [87], and *Alternaria alternata* [88]. Krejsová and Doleželová have researched the possibility of improving gypsum-based material resistance to mold by adding lime and silica fume to the gypsum binder [87]. They concluded that tested mortars do not have enough essential nutrients for mold growth, but this can change if the bio-fillers are used. Molds grow on the gypsum mortar, and the mortar with the composite binder is initiated if nutrients are added to the mixture composition. Results indicate that molds grow quicker on samples with a lower pH (around 6) or on samples without lime additives [87].

Several microbiological tests of gypsum-based bio-composites were conducted due to a potential hazard of biological corrosion of bio-composites [61]. After merging the gypsum binder with a wheat straw filler (mineralized with calcium hydroxide), the pH of material increased to 7.3 [61]. Under such neutral pH conditions, bacterial flora may grow. The amount of fungi placed in the gypsum composite mixture together with organic fillers decreased rapidly. In terms of mesophilic bacteria, more were found in the gypsum composite than on the bio-filler surface alone.

Bacterial respiration on geopolymers is reported to be up to four times lower than on Portland cement when the biofilm formations during field exposure to real municipal wastewaters on geopolymer mortar are compared [89]. The intensity of fungal development on the surface of the perlite-based geopolymer during the germination of spores and conidia under the microscope was not detected. This is related to the total effect of the biocidal component and the composite matrix, which forms a protective film that prolongs the fungal resistance. In contrast, a fly ash-based geopolymer binder is much more vulnerable to microscopic fungal activity. *Paecilomyces* and *Penicillium cyclopium* were observed on the geopolymers during the tests [90]. These studies provided controversial results. Therefore, geopolymers' resistance to microbiological attack should be considered for each composition, especially with the bio-based filler in the material.

Filamentous fungi are one of the main degraders of plant biomass, as they are able to produce enzymes that can break down complex polysaccharides in plant cell walls, including cellulose, hemicellulose, pectin, and starch [91]. Thus, starch and bio-filler are vulnerable to fungal attack. A promising technique to counter this is to use modified starch. Chemically modified starch, formed either by binding or by the addition of chemical derivatives, changes the starch structure and partially limits the enzymatic hydrolysis of the starch molecule, resulting in starch that is more resistant to fungal attack [92].

3.4. Resistance to Fire

Resistance to fire is one of the most essential properties of materials used for buildings that are subjected to fire conditions described by the standard ISO 834 curve [93]. Some of the binders used for bio-composites are resistant to fire. For example, gypsum plasterboards are widely used in buildings due to their availability, low price, ease of production, and quality as a fire barrier. When gypsum is exposed to fire, the endothermic dehydration process consumes some of the energy of the fire [94]. Research results of gypsum lightweight bio-composites' fire tests show that the bio-composite panel can be used as a passive fire protection material for 2 h. The gypsum-based bio-composite panel has been tested under ISO 834 fire conditions [27].

There are no reports about positive fire resistance test results when starch alone is used as a binder for bio-composites. For example, bio-composites produced with rice husks as bio-filler have low resistance to fire [95]. Since rice husk is a crop by-product with low heat release, the addition of a starch binder undermines bio-composites' fire resistance. However, compared with other organic foamy insulation materials commonly used in buildings such as polystyrene and polyurethane, the tested

bio-composites' fire properties are very favorable. To solve the problem and increase the fire resistance of bio-composites, biodegradable flame-retardants are developed [96]. As a result, bio-composites with satisfactory fire resistance have been developed from corn starch, flax fabric, and ammonium polyphosphate. The flame-retardant properties of ammonium polyphosphate are related to the presence of flame-retardant components, such as phosphorus and nitrogen, in its structure.

The treatment of fibers before their use in composite materials has been analyzed, taking into account possible changes in their thermal decomposition properties. The addition of flame retardants to lignocellulosic materials has been extensively studied, and phosphorus-based ones, such as diammonium phosphate (DAP) and sulfamic acid salts (such as ammonium sulfamate), have been used as retarders [93]. Fire reaction tests indicate that the use of alginate (linear unbranched polysaccharides) as a binder improves the properties of the crop by-product alone, especially in the case of corn pitch, where both the total heat release and the peak of heat release rates are decreased by 30% [93].

4. Preliminary LCA

LCA was used in this research to preliminarily assess the environmental impact of the alternative binders for bio-composite production reviewed in this research. The environmental impact of the chosen binders has rarely been studied. Only starch and geopolymers as pure binders have been studied somewhat more deeply. The environmental impact of geopolymers cannot be described unambiguously and narrowly as geopolymers can be made of solid and liquid raw materials of different origin. The choice of raw materials is one of the most important factors in assessing the environmental impact of geopolymers [41].

4.1. Definitions of Goal and Scope and Inventory Analysis

In this research, all alternative binders were assessed and compared with the most commonly used binders for bio-based materials, namely lime and magnesium, as well as cement, using "cradle-to-gate" system boundaries. This allowed us to include all processes and emissions associated with the production of the material. Although there are many different impact categories, in this research, the GWP100a impact assessment method was used, focusing on the global warming potential (GWP) measured in CO₂ equivalents (CO₂ eq.). This is the most typical environmental impact, and the construction industry contributes significantly to global CO₂ emissions. LCA calculation software SimaPro 8 was used.

The functional unit is defined as 1 m³ of bio-composites with a bulk density of 400 kg/m³. To achieve such density, various amounts of dry binders are needed; 122 kg of bio-based filler was assumed, as the same amount is required for all binders, hence its exclusion from the calculation. To achieve such a density, 230 kg of gypsum binder is required. In the case of starch, 200 kg of starch is required, as these materials use more pressing during the manufacturing process. In the case of geopolymers, raw materials consisting of 239 kg of fly ash, 100.4 kg of the 8 molar NaOH solution, and 5.75 kg of hydrogen peroxide are required for around 270 kg of a hardened binder. Additional heating needed for geopolymer production is not considered. As alternative binders, 270 kg of cement, 270 kg of hydraulic lime binder, and 210 kg of magnesium oxychloride cement is used. Data and LCA processes were taken from previous studies [12].

The Ecoinvent database was used for most of the processes. Additional data were supplied from studies on LCA of lime-hemp concrete and hemp-magnesium panels [12,97]. Fly ash is not currently included in the Ecoinvent database. Thus, new processes were created as per other studies [98]. According to Chen [99], fly ash should be regarded as an industrial by-product. Therefore, an economic allocation is necessary. Fly ash constitutes 1% of the economic allocation of 1 kWh of coal-fired electricity production, considering that only 0.052 kg of fly ash is created while producing 1 kWh.

4.2. Impact Assessment and Interpretation

LCA calculation results for alternative and traditionally used binders can be seen in Figure 4. Preliminary LCA results indicate that geopolymer and starch binders have a similar environmental impact as traditionally used. If the environmental impact of geopolymer raw materials is examined separately, fly ash and alkali activation solutions have the same effect in most categories, including GWP, although their mass differs four times. This leads to the conclusion that by choosing an alternative activation solution, it is possible to decrease the environmental impact of geopolymers. The gypsum binder shows the lowest impact across all categories, which is associated with low firing temperature and the straightforward production technology process.

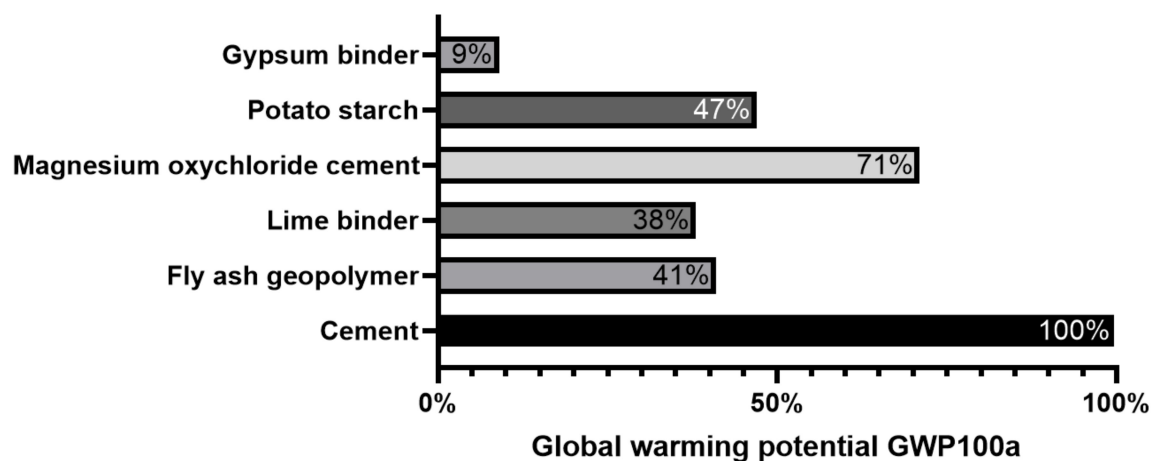


Figure 4. GWP100a impact of various bio-composite binders.

It should be noted that further bio-composite properties, such as strength, are not considered in this calculation. However, the materials are compared only in terms of their density and binder content. Therefore, it is not possible to draw precise conclusions from these results as to which binder percentage has the lowest effect; only the overall trend should be observed. The trend is as follows: in general, the chosen alternative binders, namely gypsum, geopolymers, and starch, have a similar or lower environmental impact than the traditional binders already used for bio-composites (i.e., lime and magnesium binders). Thus, these alternative binders are also promising from an environmental point of view. It must be noted that some alternative binders may be waste or by-products (e.g., phosphogypsum in the case of natural gypsum) with similar properties, and this could improve the LCA of the developed bio-composite [100].

In previous research, bio-composites with magnesium oxychloride cement binder were compared with traditionally used materials with similar U-values, such as aerated concrete or ceramic block walls with insulation or wooden frame walls with mineral wool [97,101]. The impact of the magnesium oxychloride cement bio-composite is lower than that of the traditionally used materials by 5–6 times. This allows us to conclude that bio-composites with alternative binders reviewed in this research have an even lower environmental impact compared with traditionally used materials if similar properties to the magnesium oxychloride cement binder can be achieved.

5. Conclusions

- A review of alternative binders shows that gypsum, geopolymer, and starch can be good alternatives to lime and magnesium-based binders for building materials made of bio-composites.
- Starch is the most widely used and researched binder for bio-composites. It can provide low density and low thermal conductivity with a relatively high-compressive strength if the hot-pressing

manufacturing method is used; additives for enhancing resistance to fire and biodegradation are necessary.

- Gypsum is a moderately common binder for bio-composites, it can provide average mechanical strength and thermal conductivity, as well as good resistance to fire and biodegradation.
- Geopolymer is the least used binder from this group, it can provide low thermal conductivity if a foamed geopolymer is used.
- All the described alternative binders can be vulnerable to aging in the changing surrounding environment, as wetting and drying cycles can change their physical and mechanical performance. Microbiological and fire tests must be carried out for each mixture, as very few articles have addressed these topics in the scientific literature.
- Preliminary LCA results indicate that geopolymer and starch binders have a similar environmental impact as traditionally used binders, with gypsum having a significantly lower impact. According to previous research, bio-composites with such binders would have lower CO₂ emissions than standard building materials, such as aerated concrete.

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