Evolutionary Approach Based on Thermoplastic Bio-Based Building Material for 3D Printing Applications: An Insight into a Mix of Clay and Wax

Yohan Jacquet(✉) and Arnaud Perrot

University of South Britany, UMR CNRS 6027, IRDL, 56100 Lorient, France
yohan.jacquet@univ-ubs.fr

Abstract. Digital manufacturing technique is becoming one of the most promising ways to automate construction. While applications of 3D printed concrete daily increase, those of bio-based or earth-based materials remain rather confidential at this time. The reduction of environmental footprint is one of the major 21^{th} century issues for the construction industry. For this purpose, a now common strategy has progressively been adopted to design material mixes by reducing the amount of cement and sometime substitute this one by less impacting earth-based materials. Another strategy would consist in designing material with only bio-based and earth-based materials. Whereas the capability of earth-based material to sustain compressive load has been proven, two major challenges are remaining: the first is related to its water sensibility, while the second one deals with material drying kinetic. Common ways to build with earth-based material refer to vernacular techniques that leads to handling, insurability, and variability of materials issues. This study proposes to focus on a bio-earth-based material, mainly dedicated to 3D printing applications, that presents a thermo-dependant behaviour able to comply with industrial building rate, and to display a high potential to increase water-resistance whatever the raw resources variability, using a mix of clay and a low amount of vegetal wax. This paper aims to build the path towards thermoplastic material solutions for 3D printing in construction, targeting thus to automate, industrialize and insure 3D printed structures.

Keywords: 3D printing · thermoplastic · clay · wax · water-resistance

1 Introduction

Gradually forgotten and recently regaining interest, earth material represents today one of the most promising ways to reduce carbon footprint in the construction sector. Earth-based materials are often associated to mechanical poor properties and durability issues mainly because of raw material variable properties, the different vernacular existing techniques, and the high-water sensitivity. Stabilization of earth-based material is essential to enhance mechanical strength and water-resistance: a small addition of hydraulic blinder, such as cement, is a common way to stabilize this kind of material, increasing

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at the same time its mechanical strength by up to four times compared to the non-treated material. However, using hydraulic binder in earthen material cannot be considered as an effective solution because of its huge impact on recycling possibilities and the associated carbon footprint [1]. Different kinds of natural additives can be extracted from plants, minerals or even animal and can be used to improve mechanical strength or water resistance of material [2–4]. Among the multiplicity of theses natural admixture, some of these can be encountered in traditional construction material recipes. It can be noted that these natural admixtures have an effectiveness highly dependent on the chemical composition of the media. The stabilization mechanisms can be correlated for instance to polymerization, ionic or hydrogen bonding. Making a focus on 3D printing applications, earth-based material differs by their flow behavior; while 3D printing of cement-based materials usually requires increasing the viscosity of the mixed material, earth-based one is usually too viscous to be pumped or extruded and need some mix adjustment to fulfil the requirement of this process. While cementitious materials often exhibit a frictional granular like behavior [5], the use of clay induces on the contrary a too sticky, and too viscous, behavior leading to high extrusion and pumping pressure. Clay can sometimes be advantageously added to mix design of 3D printed concrete mix design to ease extrusion process. One strategy to reduce viscosity of this clay-based mixture consists in an addition of non-clayey material to the mix design: in the same way than for concrete, the paste (exhibiting a clayey behavior) can be distinguished to the granular filler (lime, silt, sand, …). The amount of paste is thus related to its capability to create and mobilize viscosity. Another way is to control viscosity by controlling temperature of material during extrusion process. The viscosity of liquid always decreases when temperature increases: influence of this phenomenon can be balanced because the liquid phase in construction material is rather limited, reducing de facto the sensitivity of material to temperature change.

This study proposes to focus on phase-change thermoplastic material based on mix of clay, solid particles, and wax. Several kinds of vegetal wax are experimented in this study, but a same effect can be underlined: a very low content of wax allows to drastically decrease the stickiness induced by clay. This phase change behavior requires to fully reconsider the rheological test to evaluate the setting, or hardening, of cooling material. This paper proposes successively an overview on mix design possibilities, on rheological characterization, on mechanical assessment, and on the water-repellent aspect.

2 Materials

The phase-change thermoplastic material investigated in this study is based on mix of clay, sand, and wax. The choice of clay and sand is not the main purpose of this study, that’s why only three kinds of mixes are considered. Three kinds of binders are used: the first one is mainly composed of kaolinite with a Methylene Blue Value (MBV) of 1.54, while the second one consists of a mix of clay and sea sediments, both from Brittany. The first one is envisioned to establish the proof of concept, while the second one aims to assess representativeness of the use of a given local resource and how a highly water-sensitive material can be upgraded in the construction field and thus become water-resistant by using very low amount of wax.

To go a step further, a last part of this paper investigates the influence of manufactured sand addition into the mix design regarding a particle size distribution between 0 and 1 mm, following various ratio between 0% and 70% in 10% increment. The goal is to maximize the amount of sand (or the amount of material unsensitive to water) to decrease the amount of sensitive material that must be protected (e.g. mud, sludge, clay, …), even without compromising the mechanical performances.

The origin of this wax can be mineral, animal or vegetal, but considering the amount of wax required and the potential negative impact on environment, special emphasis is given to the vegetal based ones (e.g. soy, rapeseed, sunflower, hemp, palm, or coconut), and more precisely to three of these: soy, rapeseed and coconut (see Table 1). Depending on its nature, the wax can exhibit different melting point usually from 30 °C to 90 °C.

Table 1. Description of melting points of three different common waxes

Wax	Coconut	Soy	Rapeseed
Melting point	30 to 35 °C	55 to 60 °C	80 to 85 °C

Vegetal waxes are obtained from hydrogenation reaction of a vegetal oil: the more oil is hydrogenated; the more stable the wax will be. Supposing that the provenance and the quality of raw material presents a low environmental impact, this process of hydrogenation can be responsible for the major carbon footprint of this mix design strategy. Amount of wax added into a mix design must be well-thought considering the context of use and the proportion of material in this mix effectively sensitive to water. In this way, it is important to recall that the addition of sand decreases de facto the amount of clay, highly sensitive to water, and allows thus to decrease the quantity of clay required to guarantee the wholeness of printed material. Different mass ratio of wax compared to the mass of clay are discussed in this study, but it is interesting at this point to note that a wax to clay ratio higher than 1% can improve the water-resistance of material effectively. For the sack of clarity, only the results obtained using soy wax will be presented in this study.

3 A Proof of Concept for Sustainable 3D Printing Applications

3.1 A Thermoplastic Behavior as a Way of Control Material Setting

Materials designed for building usually rely on setting mechanism such as for cement-based materials. The material printed in this study is based on a mix of clay and wax for which clay plays the rule of binder, and the wax is responsible of the thermoplastic behavior. Some aggregates can be mixed with this earth and bio-based paste to increase the building ability, to avoid shrinkage and to increase its compressive strength.

Considering the typical amount of wax used in this material (i.e. 2% ± 1%), the consequences on hardened material properties can be neglected. However, concerning the rheological behavior, influence of wax content must be assessed because of the huge changes that occurs. The melting point of wax being reached, this kind of material indeed presents an important slipping at the wall of the characterization device: a Couette geometry for example in this study.

Rheological methods have been adapted and deals with 22 mm in diameter and 40 mm in height vane geometry, combined with a customized 40 mm diameter cup within which 1 cm length fins are spread out the cup wall to avoid slippage after heating (see Fig. 1). The main concern is related to the difference between the heat capacity and thermal conductivity of clay and wax respectively, as well as their specific dependency upon water content. Material is heated 10° higher than the melting point of wax and mixed several times during temperature increase to ensure homogeneity inside the material. A thermocouple sensor is then introduced into material during the rise of temperature and until the beginning of shear test to control and manage thermal control of Peltier system. When the setpoint temperature is reached, shear test is started according to a shear rate of 0.1 s^{-1}.

Fig. 1. Cup with ribbed wall surface, vane tool geometry, and temperature sensor

Assessment of cement-based materials are usually made in time to evaluate hydration rate influence of cement. In the same way, evolution in time of the thermal setting of the mix of clay and wax must be assessed. The cooling of this mix is mainly governed by its heat capacity and the thermal exchanges with the ambient environment, so from a temperature of 70 °C to and ambient one near to 25 °C.

The rheological method to characterize this thermal setting consists in a measurement of shear strength of material after different resting time. The correlation between this resting time and the temperature of the mix is represented in the background of the Fig. 2. Each measuring point plotted in this graph is obtained thanks to independent tests, or about ten points to analyze the influence of one hour of thermal setting. This test is performed on two different materials: the first with a water to clay mass ratio of 35%, while the second one is performed regarding a ratio 10% higher. The difference between thermal dissipation of these two mixes is negligible (lower than 1% in this case), that's why only one curve of the evolution of temperature in time is proposed.

After the first five minutes of cooling, the material shear strength is multiplied by three for the material with the lower solid volume fraction (i.e. water to clay ratio of 45%), while for the other one, the shear strength is multiplied by four to reach a value near to 2.6 kPa at 40 °C. All other things remaining equal, only the amount of water changes the thermal dependency of the material's behavior.

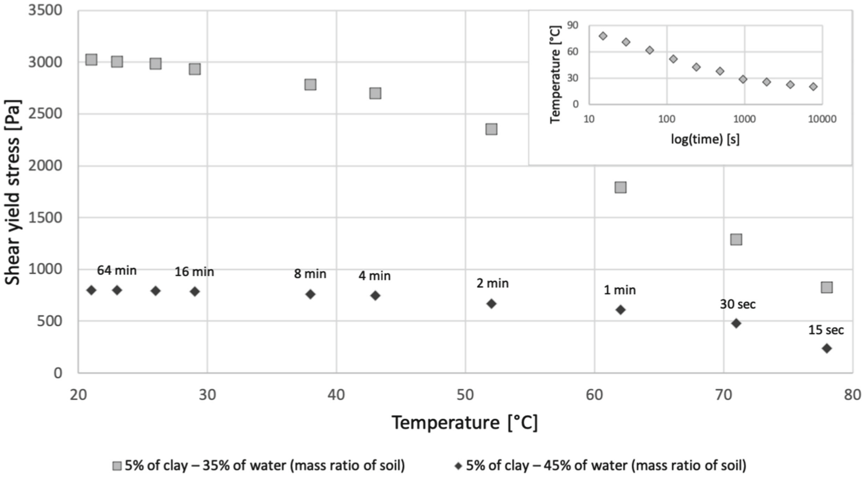

Fig. 2. Evolution of shear yield stress with the temperature of mix design

Over 5 min of cooling, the material that presents the highest solid volume fraction exhibits shear strength which is not progressing any longer. However, for the lowest one, the shear strength increases by 15% for about one hour of cooling. For 3D printing process, a short time of setting is preferred to enhance buildability. This setting time is not sufficient to ensure mechanical performances and only allows to increase the printing rate compared to common raw earth-based materials: drying of material still being a necessary condition to provide the intended final mechanical properties to the printed structure.

Finally, it has been shown the localization of wax on the walls when heating material makes difficult to perform rheological measurement without wall slipping, but, in return, allows to drastically decrease stickiness usually induced by clay. This sticky behavior is one of the major challenges for printing and/or pumping earth-based materials. By the same way, when this heated mix of clay and wax is extruded, shear stress decreases significantly, especially at the extruder die, improving thus the surface quality (see Fig. 3).

Fig. 3. Printed sample of clay and soy wax with 10 × 30 cm cross section extruder die

3.2 Assessment of Water-Resistance from Mechanical Performances

In addition to the thermo-dependent behavior, the major interest of this material is based on its ability to resist when exposed to water. We can distinguish two typical behaviors of materials: the water repellency and the water-resistance. For the first one, material can be exposed to water while rendering it impervious to water incursion for a limited period according to the natural water repellency power of raw earth material: in the field of earthen construction, this kind of behavior can be often encountered in vernacular technics. The second one consists in adding some bio-sourced or earth-based materials to enhance the water-resistance potential. Both technics are fully adapted to the earthen construction, but the respect of the standards of professional practices is crucial to limit direct exposure to water and ensure structure durability, while the other one can be favorably envisioned for different and more complex shapes when a physical protection against water cannot be totally guaranteed.

In this study, the material can be considered as highly water-resistant, especially for an earth-based one. A low dosage of wax leads indeed to a huge increase of water-resistance potential when samples are entirely immersed in water. For this purpose, a choice has been made to assess the material ability to resist water by measuring the degradation rate of different immersed samples.

This test is intended to be the simplest as possible and consists in immerging printed samples into tap water at 20° to estimate their performances when submitted to accidental water exposure. The compressive strength of these sample is measured depending on this time of direct exposure to water: in this study, tests are performed at 30 min and 12 h after the first contact of dried sample with water for each mix design respectively. Compressive tests are made on sample regarding a cross section near to 1600 mm^2 with a of 2:1 aspect ratio: depending on the water content, shrinkage can occur, and the cross section can be thus updated to increase computation accuracy of compressive strengths. Figure 4 shows the ratio between the compressive strength of a control sample printed and stored in controlled conditions (25 °C and between 5 and 10 h%), and the compressive strength of a sample immersed in water for 30 min and 12 h respectively. Half an hour after immersion, compressive strength is reduced by more than 90% without any wax in the mix and is destroyed 12 h after. Only 2% of soy wax into this mix design are sufficient to obtain a compressive strength decreased by 30%. Once wax is added into a mix design, the increase of immersion time always leads to an adverse effect on mechanical properties. The concept of accidental exposure to water ingress must be defined to push for a suitable dosage for human safety.

3.3 Mix Design Optimization and Outcomes

Two different strategies are envisioned in this study to reduce environmental impact of this material intended to be used for additive manufacturing purpose. The first one consists in optimizing mix design by adding manufactured sand (granular size distribution between 0 and 1 mm), while the second one aims to use and recover only local raw resources, regardless of their physical or chemical properties (water resistance, MBV, stickiness, viscosity, and so on).

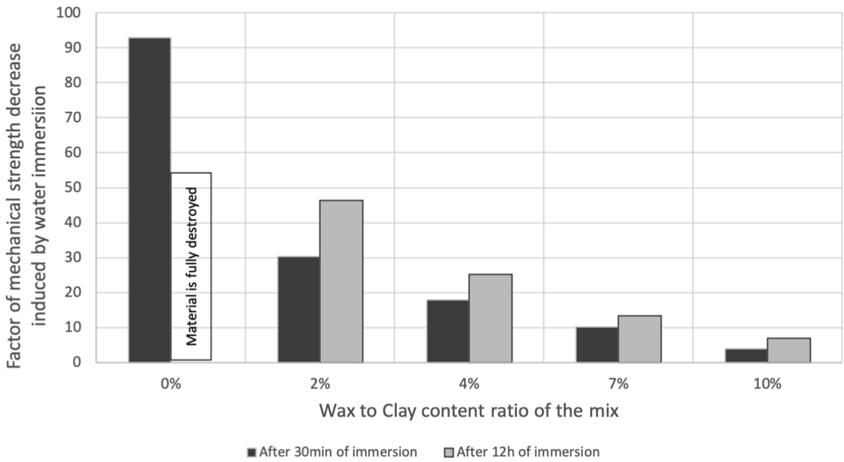

Fig. 4. Influence of immersion of samples on compressive strengths measurements

Based on the same mix design than the proof of concept exposed earlier in this study, a sand volume fraction is adjusted in 10% between 0% and 70% compared to the volume of binder (kaolinite, soy wax, and water). This protocol aims to investigate effect of addition of water-unsensitive solid particles on compressive strength. The material only composed of kaolinite following a water content of 45% exhibits a compressive strength near to 800 kPa. Figure 5 shows the evolution of this strength with addition of sand until a maximum value of 1.2 MPa for a sand ratio ranging between 50 and 60%. This means that only 50 to 40% of this mix design presents a poor water resistance and must be protected from water ingresses.

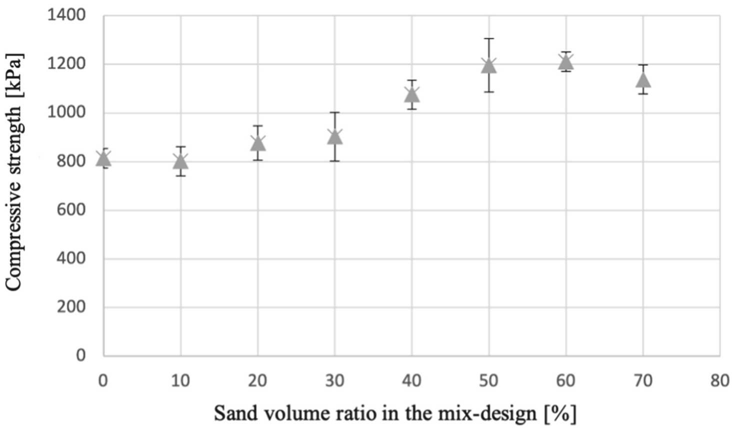

Fig. 5. Effect on compressive strength of the increase of sand volume fraction in a thermoplastic binder composed of clay, wax, and water.

The second strategy consists in a material based on a mix of local clay and sea sediments from Brittany. Both being sensitive to water ingresses, soy wax ratio of 1% is defined compared to the amount of clay and sediments. The first sample is only composed of clay (C) and presents a compressive strength of 2.35 MPa. With the addition of sediments comes an increase in mechanical strength until an optimal addition ratio of 20%, which could be explained by the optimization of granular packing. Over 70% of sediment, these mechanical properties decrease because of the poor particles bond properties of sediments compared to those of clay (see Fig. 6).

In any case, considering the water sensitivity of these both raw and by-products materials respectively, the wax content must be maintained at the same mass ratio value of at least 1%. Using by-product such as sediments sludge, can be a means to reduce environmental footprint of mix design and preserve resources.

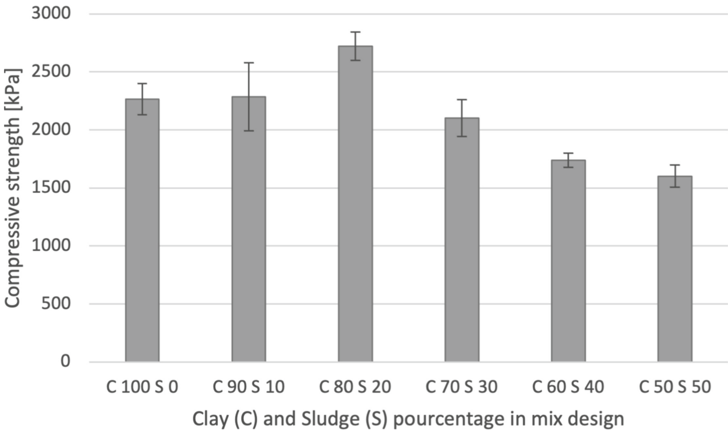

Fig. 6. Mixes of local resources regarding varying proportions (clay, sediments and soy wax)

4 Conclusion

This paper aims to propose a proof of concept of a new kind of earth-based material intended to be used for 3D printing applications in the field of construction industry. Insurability and buildability represent the two major challenges in the field of additive manufacturing of earth-based materials, especially because of their difficulties to reach an industrial building rate and their water sensitivity.

Firstly, the addition of a low amount of wax into a mix design of bio-reinforced earth materials allows to increase the acceptability of earth-based materials because of the high water-resistance properties of the dried material products. Secondly, thanks to various thermo-dependent properties of wax, thermal setting can be envisioned to pave the way toward industrial building rate during printing. The thermal setting provided by wax cannot be a substitute to drying and only aims to increase printability and buildability of printed earth-based structures.

In addition to these both main points, this thermo-dependent behavior results in two benefits; the first is related to the ability of heated wax to eliminate stickiness of clay regardless their initial viscosity, while the second provides a thermo-dependent behavior of a printed wall depending on the environmental conditions.

This last point allows to envision some outcomes dealing with thermos-hydric exchanges through materials porosity: depending on the ambient temperature and melting point of vegetal wax, pore size distribution can vary locally. High temperature can be responsible of a decrease pore surface tension, that therefor favors water vapor exchanges trough the walls and vice-versa. This thermo-dependent capillary network can be interesting both for housing and for solving urban heat island issues for instance.

Bibliography

1. Van Damme, H., Houben, H.: Earth concrete. Stabilization revisited. Cem. Concr. Res. **114**, 90–102 (2018). https://doi.org/10.1016/j.cemconres.2017.02.035
2. Guihéneuf, S., Rangeard, D., Perrot, A., Cusin, T., Collet, F., Prétot, S.: Effect of bio-stabilizers on capillary absorption and water vapour transfer into raw earth. Mater. Struct. **53**(6), 1–18 (2020). https://doi.org/10.1617/s11527-020-01571-z
3. Losini, A.E., Grillet, A.C., Bellotto, M., Woloszyn, M., Dotelli, G.: Natural additives and biopolymers for raw earth construction stabilization – a review. Constr. Build. Mater. **304**, 124507 (2021). https://doi.org/10.1016/j.conbuildmat.2021.124507
4. Achenza, M., Fenu, L.: On earth stabilization with natural polymers for earth masonry construction. Mater. Struct. **39**(1), 21–27 (2007). https://doi.org/10.1617/s11527-005-9000-0
5. Jacquet, Y., Perrot, A., Picandet, V.: Assessment of asymmetrical rheological behavior of cementitious material for 3D printing application. Cem. Concr. Res. **140**, 106305 (2021). https://doi.org/10.1016/j.cemconres.2020.106305