RHEOLOGICAL AND MECHANICAL BEHAVIOR OF EARTH MATERIALS / STARCH MIXES

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Abstract

This research work highlights a new approach in the sector of building materials based on bio resources. An experimental investigation was conducted in order to study the rheological and mechanical behavior of earth/starch mixes. In this study, two types of earth materials have been studied: quarry fines and a model material which was kaolinite. For starches, two categories have been used: native and derivative. Starch with a chemical modification has also been studied. The earth/starch composite material specimens were manufactured with a constant ratio of 1%. The water content has been fixed by the flow table test. The rheological and mechanical tests have shown a significant effect of starch on the earth material properties. In the rheological part of the study, two starches have shown an increase of the thixotropic index for quarry fines. From a mechanical point of view, all starches increase mechanical strengths.

Keywords:
Earth materials, Starch, Rheological properties, Mechanical behavior

1 INTRODUCTION

For millenaries, earth has been used in the construction of buildings and approximately one third of the world population still lives in earthen structures [Coffman 1990]. Earth as a building material is economical, environmentally friendly and abundantly available. It has been used extensively for wall constructions around the world. Moreover, Romans usually used raw earth as building material in-situ [Adam 1984]. They knew very well that it was hardly possible to use only earth to produce large bearing bricks because of their excessive shrinkage and consequently cracking, and because of the limited workability of the mixture. Then they found that sand or coarse sand added to the mixture was a solution [Adam 1984] to "degrease" clay and to turn it into a mixture.

The world heritage for earth building can be seen in a lot of countries; i.e. the city of Shibam in south Yemen, or the walls of Marrakech in Morocco, to name but a few. The use of local materials in the construction of dwellings is one of the ways to support sustainable development on the entire planet, because it meets the needs of the present without compromising the ability of future generations to meet their own needs [Morel

2001]. However, the construction of dwellings using local materials, in developed countries, has become marginal. These techniques were abandoned because it is not possible to standardize the composition of materials with variable properties according to their localization. Raw earth construction is no exception.

In the present environmental context, civil engineering companies aim to use materials with low environmental impact (local resources, low energy consumption and low gas emission during manufacturing…). The unfired earth materials (UEMs) may fulfill this criterion and provide a sustainable and healthy alternative to conventional construction materials. Moreover, raw earth materials require very little energy to produce and outgas little CO_2 [Morton 2006].

The main drawback of raw earth is the high water supply necessary to achieve adequate workability for placement operations. Contrary to concrete which hardens through a chemical process UEMs solidify when losing water during drying which can take a long time for elements of considerable sizes. Furthermore, UEMs have low mechanical performances and require large units to build bearing walls.

To be competitive in comparison with concrete or plaster, UEMs need to widen their use domains thanks

to, for example, an easier use at fresh state and an improvement of mechanical performances while keeping their environmental advantages. A combination of UEMs with environmentally-friendly admixtures could be a solution.

In this research work, the combination of UEMs with starch is studied in order to design mixes for use in prefabricated products. Starch is chosen for its capacity to modify the rheological behavior of materials and for its "glue effect", very much like wallpaper glue. For prefabrication, mixes must fit into molds easily in order to be handled after manufacturing, have a short drying time and satisfying long-term mechanical performances.

2 MATERIALS

2.1 Quarry fines (QF)

The unfired earth materials for the experiments are quarry fines (QF) from the storage site of "Carrières du Boulonnais", a company located in the north of France. These fines include clay and limestone. QF properties were measured by Carrières du Boulonnais. Fig. 1 gives the average mineralogical compositions. Despite a relatively small proportion of clay in these materials, they present similar physical clay behavior. The clay portion is composed of two types of clay (kaolinite (12%) and illite (7%)) which have low sensitivity to swelling phenomena.
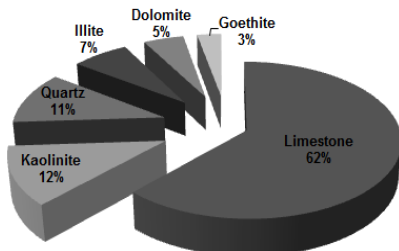

Fig.1: Mineralogical composition of QF.

The grain size distribution is shown on Fig. 2. The graph was drawn by the company "Carrières du Boulonnais" via a laser granulometer measurement. The granular distribution allows us to observe the fineness of these materials with grain sizes inferior to 100 μm (Fig.2).
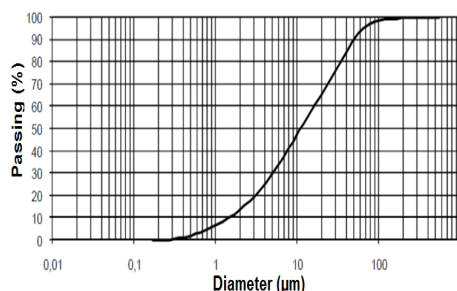

Fig.2: Granulometric curve.

2.2 Kaolinite

Kaolinite ($Al_2Si_2O_5$ $(OH)_4$), an aluminosilicate mineral, is the most common constituent mineral in clay used for manufacturing traditional ceramics such as whitewares.

Kaolinite is white powder clay made up of two layers. The first is an octahedral layer (O), the other is tetrahedral (T), and therefore its structure is TO (Fig. 3). It only has negative charges on the outside of its sheets. Each sheet is linked to the other by hydrogen

bonding; the interlayer distance is 7 Å. This link has properties giving cohesion to the crystal, while leaving the possibility of cleavage of the various sheets. Fig. 3 presents a diagram of the structure of kaolinite [Cabane 2004].
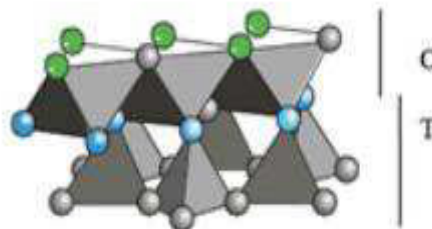

Fig.3: Kaolinite structure [Cabane 2004].

2.3 Starch

Starch is a homopolymer of D-glucose present in the form of a white powder of micron grains of 1 to 100 microns; which vary in size and shape according to their botanical origin. Starches, used for this work, were furnished by Roquette; a company specialized in the manufacturing of starches.

Eleven types of starch were chosen for the experimental campaign with several botanic sources: maize, potato, wheat, waxy maize and peas. These studied starches include five types of native starches called A, B, C, D, E and the others being derivate (pregelatinized or esterified) called F, G, H, I, J, K.

To compare the effect of each type of starch on the properties of QF or kaolinite, the percentage of starch in the mixture was fixed at 1% of the amount of QF or kaolinite.

3 METHODOLOGY

3.1 Mixing steps

The Perrier mixer was chosen in this study to mix these materials. Two mixing protocols have been designed from the norm EN 196-1 [AFNOR 2006], one for cold mixtures (including pregelatinized starches) and the other for warm mixtures (including the other starches).

Cold:
- Mixing starch + UEM (30s - 100 rpm)
- Adding water (30s - 100 rpm)
- Mixing assembly (30s - 100 rpm)
- High speed mixing (60s - 200 rpm)
- Scraping the bowl (15 to 20 s - stop)
- Mixing at high speed (30s - 200 rpm)

Warm:
- Divide the amount of water in two parts (hot and cold)
- Mixing cold water to the starch until homogeneity
- Mixing the starch milk with hot water
- Adding starch milk to UEM (30s - 100 rpm)
- Mixing assembly (30s - 100 rpm)
- High speed mixing (60s - 200 rpm)
- Scraping the bowl (15 to 20 s - stop)
- Mixing at high speed (30s - 200 rpm)

For the warm method, quarry fines have been left at ambient temperature (20°C) or heated to 120°C, before mixing. The heating to 120°C of part of the

UEMs aims to maintain a higher temperature of mixtures than that of mixes with UEMs at 20°C, thus promoting the gelatinization of native starches.

3.2 Flow tests

The flow table test is a method to determine the consistency of fresh mortars. This method is used to select the suitable water content necessary to obtain a spreading of each mixture according to the French standard NF EN 1015-3 [AFNOR 1999].

For each mix, three measurements are made and an average is used to define the spreading diameter. The reference spreading is taken following the spreading of masonry mortar (155 ± 5 mm).

3.3 Rheology and thixotropy measurement

Rheology is the study of the flow and deformation of materials. The movement of a fluid due to the application of force induces deformation according to speed or strain rate. The purpose of rheology is to describe the relationship between stress, strain and speed or deformation rate of a volume.

In this work, the rheological study aims to compare the influence of different starches on the UEM properties, determine the plastic viscosity and yield stress, and explore the thixotropic of each mixture. The amount of mixture used has been chosen to avoid edge effects and obtain real values. Tests were performed with five different strain rates for each formulation: 1, 10, 50, 100, and 150 s^{-1}. The temperature was maintained at 55°C for the warm mixtures and at ambient temperature for the cold ones. The maximum shear stress and the equilibrium shear stress (corresponding to the stabilization at the end of the test) were inferred thanks to the rheological device HAAKE Viscotester 550.

The thixotropy makes it possible to obtain a "gel-state" material which will facilitate the handling of the product after manufacture. Several models exist in the literature to describe the behavior of materials [Banfill 2003], [Ferraris 1999], and [Yahia 2001].

3.4 Mechanical tests

After determination of the water amount in each paste, the obtained material composite was used to make standard prismatic specimens of 4x4x16 cm^3 necessary to evaluate the performances of the mixes in flexure and compression. All UEM/starch specimens were cast on a vibrating table to ensure optimum compaction. The drying of the specimens took place in a climatic chamber stabilized at a temperature of 20 °C and with a relative humidity of 40%. The water contents of the specimens decreased rapidly during the drying process. The volume shrinkage is important and seems directly related to the initial amount of water. The duration of the drying time is 21 days. During the drying time, the evolution of the water content and the state of the specimens were monitored until the day of mechanical tests. There was a continuous decrease in the weight and in the dimensions of all specimens with curing age of various degrees during the first week of exposure.

The unmolding was done for most of the specimens after two days. After a drying period of 21 days, both flexure and compressive strength tests were applied to each type of specimens. The flexural and compressive strengths of the earth mixes were determined with an electromechanical testing machine (50 kN). The tests were carried out according to the French standard NF EN 1015-11 [AFNOR 2000].

Specimens were tested under force-controlled loading. Flexural tests have been done with a velocity of 4 N/s on 4x4x16 cm^3. Compressive tests have been done with a velocity of 48 N/s on each half specimen obtained after failure with flexural test.

4 RESULTS

4.1 Flow tests

The water quantity necessary to obtain a paste according to the standard according to the standard is shown on Tab. 1, considering that B is the quantity of QF and W is the amount of water. This W/B ratio varies according to the botanic source of each starch. On the other hand, the variation of the QF temperature has no effect.

In the same way, the Tab. 2 shows the results with kaolinite. Kaolinite needs twice the quantity of water as the QF to become homogeneous.

4.2 Rheological results

The graph of shear stress curves (at maximum and equilibrium) according to shear rate (Fig. 4) shows that QF + starch mixtures generally have a shear thinning behavior corresponding to the modified Bingham model:

$$\tau = \tau_0 + \mu_P \times \dot{\gamma} + c \times \dot{\gamma}^2$$

Where:

τ: shear stress (Pa),

μ_P: the plastic viscosity (Pa.s),

τ_0: yield stress (Pa),

c: insignificant coefficient expressed in (Pa.s^2),

$\dot{\gamma}$: shear rate (s^{-1}).

Fig. 5 shows an example of typical stress-strain curves for the QF/starch H mix and for the QF alone.

The curves $\tau_{max} = f(\dot{\gamma})$ and $\tau_{eq} = f(\dot{\gamma})$ are placed on the same graph to determine τ_0, μ_P and the thixotropic index.

The initial shear strength is determined graphically as the intersection point of the regression line between the shear stress values (at the corresponding pre-compression loads) and the vertical axis of the shear stress.

Tab. 3 shows the values of the modified Bingham equation for the QF/starch mixes and Tab. 4 for the kaolinite/starch mixes.

The results of this study with the QF and eleven starches have shown, for some formulations, a significant increase in the thixotropy of QF/starch mix in comparison with the QF alone.

Tab.1: Water/Binder (W/B) ratio for each mixture with QF.

	References	Spreading diameter (mm)	QF at (T°C)	W/B
	QF	155	20	0.44
Native starches	QF + Starch A	150	20	0.62
	QF+ Starch A	150	120	0.64
	QF+ Starch B	156	20	0.76
	QF+ Starch B	150	120	0.76
	QF+ Starch C	150	20	0.57
	QF+ Starch C	150	120	0.60
	QF+ Starch D	155	20	0.72
	QF+ Starch D	152	120	0.72
	QF+ Starch E	160	20	0.65
	QF+ Starch E	155	120	0.65
Derivate starches	QF+ Starch F	151	20	0.43
	QF+ Starch G	158	20	0.60
	QF+ Starch H	151	20	0.75
	QF+ Starch I	156	20	0.60
	QF+ Starch J	155	20	0.46
	QF+ Starch K	155	20	0.51
	QF + Starch G and H	150	20	0.67

Tab.2: Water/Binder (W/B) ratio for each mixture with kaolinite.

References	Kaolinite (K)	K+ Starch A	K+ Starch B	K+ Starch C	K+ Starch D	K + Starch E	K+ Starch H
W/B	0.85	1.04	1.18	0.99	1.15	1.12	1.19

Tab.3: Values of the modified Bingham equation and thixotropic index for QF / starch mixes.

References	Modified Bingham				Thixotropic index ($J.m^{-3}.s^{-1}$)
	c	μ_P (Pa.s)	τ_0 (Pa)	R^2	
QF at 20°C	-0.0137	4.5	313	1	33043
QF at 20°C + Starch A	-0.003	1.7	199	0.97	47782
QF at 120°C + Starch A	0	0.4	316	1	59480
QF at 20°C + Starch B	-0.0019	0.5	90	0.89	64389
QF at 20°C + Starch C	-0.0127	3.4	117	0.92	56148
QF at 120°C + Starch C	-0.0225	5	120	0.99	66019
QF at 20°C + Starch D	-0.0108	2.3	73	0.99	50769
QF at 120°C + Starch D	-0.0054	1.8	77	0.97	57789
QF at 20°C + Starch E	-0.008	2.5	146	0.97	50212
QF at 20°C + Starch F	-0.02	5.3	305	0.96	40854
QF at 20°C + Starch G	-0.0025	1.1	55	0.92	62391
QF at 20°C + Starch H	-0.004	1.5	91	0.99	143237
QF at 20°C + Starch I	-0.0084	2.5	242	1	57851
QF at 20°C + Starch J	-0.0251	5.6	371	1	23594
QF at 20°C + Starch K	-0.0132	4.3	422	1	24951
QF at 20°C + Starch G+H	-0.0103	4.8	366	1	69430

Tab.4: Values of the modified Bingham equation and thixotropic index for kaolinite / starch mixes.

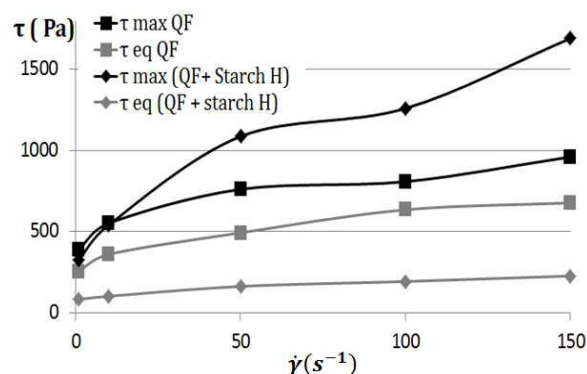| References	Modified Bingham				Thixotropic index (J.m^{-3}.s^{-1})
	c	μ_P (Pa.s)	τ_0 (Pa)	R^2	
Kaolinite	-0.0141	4.9	276	0.95	57609
Kaolinite + Starch A	-0.0103	3.3	251	1	42860
Kaolinite + Starch B	0.00004	1.4	203	0.97	38790
Kaolinite + Starch C	0.0037	1.5	322	0.99	45437
Kaolinite + Starch D	-0.0109	2.6	198	0.94	30931
Kaolinite + Starch E	-0.0154	3.5	173	1	23263
Kaolinite + Starch H	-0.0121	4	166	0.98	32280

Fig.4: Example of stress-strain curves.

Based on the results presented in Tab. 3 which shows the values of the modified Bingham equation and thixotropic index for the QF/starch mix, the results are as follows:

1) For some formulations, there is a significant increase in the thixotropic index of QF/starch mix in comparison with the QF alone.
2) QF+ Starch H mix gives the greatest thixotropic index in comparison with the other types of starch.
3) QF at 20°C + starch B mix corresponds to the best thixotropy for native starches.
4) A large difference can be observed between two starches with the same botanic source. Thus, the botanic source is not the only influent parameter. The treatment of starch (pregelatinization, esterification…) is another influent parameter.
5) Starches J and K decreased the QF thixotropy.
6) In mixing two types of derivate starches G and H (0.5% for each type) with the QF at 20°C, the values of water content and thixotropy were closer to the QF/starch G mix values. This result highlights that a starch can be more influent than another.

After replacing the QF with kaolinite, the results were different. Tab. 4 shows the high thixotropy of the kaolinite mix and the decrease of this parameter when adding the starch, which contrasts with the results obtained with quarry fines.

4.3 Mechanical results

Mechanical tests have been done when the specimen mass was stabilized close to a water content of 0% (dry state). Specimens containing starches J and K have undergone degradation and cracking (Fig. 5). No mechanical tests have been done with these mixes.

Fig.5: Specimens of earth/starch mixes (with starch J on the left and starch K on the right).

The results for flexural strength (R_f) and compressive strength (R_c) of the earth material / starch mixes are listed in Tab. 5 and 6.

The results of this study with the eleven starches and QF have shown, for some formulations, a significant increase in the mechanical resistance of QF/starch mixes in comparison with earth alone. The raise of the initial temperature of QF from 20°C to 120°C has had little effect on the mechanical resistance of mixes.

For kaolinite/starch mixed prismatic specimens, the drying of the specimens has also taken place in the climatic chamber stabilized at a temperature of 20 °C and with a relative humidity of 40%. Tab. 6 shows the results of compression strength of kaolinite/starch mixes. The specimens have a very high shrinkage, so the flexure strength tests could not be done.

Starch D gives the best mechanical strength value when mixed with the QF and the Kaolinite.

The treatment given to the derivate starch induces variable types of performances. Thus the classifying of performances according to the botanic source is not similar between native and derivative starches.

The mechanical properties of earthen materials depend on their suitable water content and on their storage conditions. In order to quantify the magnitude of this variation, flexure and compressive strength tests were performed on specimens of the QF/starch mixes exposed to different temperatures and relative humidity.

Therefore, according to the first results, two types of starch were chosen for the second step: starch D and starch H. Starch D has been chosen for its high mechanical performances. Starch H has been chosen for the high increase of thixotropic index given to QF.

Tab.5: Flexure and compressive strengths of earth material / starch mixes.

References	Quantity of specimen	R_f (MPa)	Standard Deviation (MPa)	Quantity of specimen	R_c (MPa)	Standard Deviation (MPa)
QF	8	1.62	0.19	14	3.29	0.20
QF at 20°C + Starch A	3	2.73	0.17	5	4.01	0.40
QF at 120°C + Starch A	2	3.46	0.25	6	5.18	0.30
QF at 20°C + Starch B	3	2.7	0.13	6	3.94	0.46
QF at 120°C + Starch B	2	2.99	0.42	3	4.82	0.43
QF at 20°C + Starch C	3	2.50	0.10	4	4.04	0.58
QF at 120°C + Starch C	3	4.09	0.13	5	6.37	0.04
QF at 20°C + Starch D	3	4.29	0.13	6	6.44	0.27
QF at 120°C + Starch D	3	3.37	0.14	6	6.46	0.35
QF at 20°C + Starch E	2	2.64	0.24	6	3.78	0.23
QF at 120°C + Starch E	3	2.30	0.15	4	3.62	0.14
QF at 20°C + Starch F	2	2.25	0.21	4	4.74	0.35
QF at 20°C + Starch G	3	3.33	0.37	5	5.60	0.22
QF at 20°C + Starch H	5	2.68	0.33	10	4.76	0.51
QF at 20°C + Starch I	8	3.45	0.35	16	5.67	0.48
QF at 20°C + Starch G+H	3	3.62	0.08	6	6.02	0.64

Tab.6: Compressive strengths of kaolinite / starch mixes.

References	Quantity ofspecimen	R_c(MPa)	Standard Deviation (MPa)
Kaolinite	6	1.04	0.11
Kaolinite + Starch A	6	1.86	0.33
Kaolinite + Starch B	6	1.39	0.12
Kaolinite + Starch C	6	1.39	0.14
Kaolinite + Starch D	4	2.26	0.67
Kaolinite + Starch E	6	1.44	0.22
Kaolinite + Starch H	6	1.29	0.24

This step aims to study the effect of storage conditions on the physical and mechanical stability of performances for the two previously mentioned starches. For that purpose several conditions had been applied such as:

A. Conditions in the climatic chamber for 21 days:
   1) Three specimens at 20°C and a 70% RH until mass stabilization, then at 20°C and 40% RH to 21 days;
   2) Three specimens at 40°C until mass stabilization, then at 20°C and 40% RH to 21 days;
   3) Three specimens at 60°C until mass stabilization, then at 20° C and 40% RH to 21 days;
   4) Three specimens at 100°C until mass stabilization, then at 20°C and a 40% RH to 21 days;
   5) Three other specimens at 20°C. 40% RH for 14 days. Then these specimens were placed in the climatic chamber at 100% RH for 7 days.
B. Conditions in the climatic chamber for 28 days:
   1) Three specimens at 20°C and a 40% RH for 28 days;
   2) Three specimens were stored at 20 °C and a 40% RH for 21 days. These specimens were then subjected to temperature and moisture variation cycles. Each cycle starts at 20°C and a 40% RH and consists of:
   - Decreasing to 5°C and 100% RH for 2 hours;
   - Holding at 5°C and 100% RH for 1 hour;
   - Raising to 20°C and 40% RH for 2 hours;
   - Holding at 20°C and 40% RH for 1 hour.
   These steps were repeated 28 times in 7days.
   3) Three specimens at 20°C and 40% RH for 21 days. Then these specimens were placed in the climatic chamber at 100% RH for 7 days.
The results are shown on Tab. 7 and 8.

The mass was stable after 7 days for specimens, which were stored at 20°C with 40% RH and 12, 4, 3 and 2 days respectively for the conditions 20°C with 70% RH, 40°C, 60°C and 100°C. The specimens starch H at 100°C, starch D at 40°C, 60°C and 100°C were subjected to cracking so were not tested mechanically.

Tab. 7 and 8 show that a strong correlation was observed between mechanicals strengths and the various conditions. However, within the 20°C and 40-70% RH range, strength values are relatively constant but with a very important relative humidity, the mechanical strength decreased considerably. The increase to temperature 40°C or more has a negative effect on the specimen forms.

Tab.7: Flexure and compressive strengths of QF / starch D and H mixes according to the curing.

References	Quantity of specimen	R_f (MPa)	Standard Deviation (MPa)	Quantity of specimen	R_c (MPa)	Standard Deviation (MPa)
QF + Starch D (20°C.40%HR)/(21d)	3	4.29	0.13	6	6.44	0.27
QF + Starch D (20°C. 70%HR)/(12d) +(20°C.40%HR)/(9d)	3	3.99	0.23	6	6.46	0.25
QF + Starch D (40°c) /(7d) +(20°C.40%HR)/(14d)	-	-	-	6	5.78	0.51
QF + Starch D (60°c) /(7d) +(20°C.40%HR)/(14d)	-	-	-	4	4.56	0.31
QF + Starch D (20°C.40%HR)/(14d) +(100% HR)/(7d)	3	0.78	0.13	5	1.90	0.29
QF + Starch H (20°C.40%HR)/(21d)	5	2.68	0.33	10	4.76	0.51
QF + Starch H (20°C.70%HR)/(12d) +(20°C.40%HR)/(9d)	3	2.81	0.15	6	5	0.58
QF + Starch H (40°c)/(7d) + (20°C.40%HR)/(14d)	3	3.28	0.25	6	5.63	0.61
QF + Starch H (60°c)/(7d) + (20°C.40%HR)/(14d)	3	2.70	0.23	6	4.06	0.15
QF + Starch H (20°C.40%HR)/(14d) + (100% HR)/(7d)	3	0.67	0.18	6	1.95	0.13

Tab.8: Flexure and compressive strengths of QF / starch D and H mixes according to exposure conditions (7 days) after curing.

References	Quantity of specimen	R_f (MPa)	Standard Deviation (MPa)	Quantity of specimen	R_c (MPa)	Standard Deviation (MPa)
QF + Starch D (20°C,40%HR)/(28d)	3	5.17	0.16	6	7.91	0.86
QF + Starch D (20°C,40%HR)/(21d) + (cycle)/(7d)	3	3.32	0.09	5	5.64	0.67
QF + Starch D (20°C,40%HR)/(21d) + (100% HR)/(7d)	2	0.87	0.07	4	1.65	0.51
QF + Starch H (20°C,40%HR)/(28d)	3	3.42	0.06	6	5.75	0.40
QF + Starch H (20°C,40%HR)/(21d) +(cycle)/(7d)	3	2.20	0.19	6	5.08	0.19
QF + Starch H (20°C,40%HR)/(21d) + (100% HR)/(7d)	3	0.78	0.05	6	1.85	0.18

4.4 Chemical modification

In addition, chemical modifications of starches have been done in order to improve their physical properties. In particular, reduction of water added to the crude material would be of great interest in order to get shorter drying times and small volumetric shrinkage for the final product. In this context, and based on previous work [Crépy 2013], modifications of starch with sulfobutyl groups have been selected.

After the first set of experiments employing the different starches as additives, two of them presenting singular results were selected as good candidates to be modified. They were starches D and H. Indeed, these starches respectively yield to materials with high thixotropic character and high mechanical resistance.

The synthesis of each starch was done as follows:

A sodium hydroxide solution (30%. 2 eq. NaOH) was added dropwise, under vigorous stirring, to a suspension of starch (17.1 g; 1 eq. based on glucose unit) in isopropanol (8 ml/g starch) and water (0.9 ml/g starch). The reaction mixture was stirred at 45 °C for 1 h. and 1.4-butanesultone (1 eq.) dissolved in acetone (1 ml/g sultone) was then added. The suspension was stirred for 6 h at 45 °C and allowed to stand at room temperature. After 12 h of stirring, the reaction mixture was poured into methanol (15 ml/g starch), and neutralized with acetic acid. The product was filtered, washed with methanol and dried at room temperature (isolated yield 97%).

The substitution degree of starch H' (modified H) was equal to 0.31 and was determined by ^{1}H NMR spectroscopy. However, the substitution degree of starch D' (modified D) could not be done by this technique as the crude material was partially soluble

in conventional NMR solvents. However, organic elemental analysis could be a great alternative to overcome this issue.

Flow and mechanical tests have been done with these two chemically modified starches and the quarry fines. Flow tests show that the suitable water content decreases by 40% with the two starches. Conversely, some of the manufactured prisms had not strengthened during drying and had a large shrinkage. So, this chemical modification has a negative effect on the mix mechanical strength.

5   CONCLUSION

This paper aims to prove that starch has an influence on the unfired earth materials' properties. The results of this study could be concluded as follows:

- At fresh state, the addition of starch increases the thixotropic index of quarry fines whereas the thixotropy is decreased for kaolinite.
- The QF/ starch H mix has the best thixotropic material in comparison with the other QF/starch mixes.
- The specimens with starch J and K showed degradation and cracking in the drying period. Associated to QF, these starches were the only products which had decreased the thixotropic index.
- Starches improve the mechanical strengths of the two studied clayey materials.
- The best mechanical strengths with the warm protocol were obtained with QF/starch D mixture.
- A strong correlation between mechanical strengths and the various conditions was observed. However, within the 20°C and (40-70%) RH range, strength values are relatively constant but with a very important relative humidity the mechanical strength decreased considerably. The increase at temperature (40°C or plus) of storage has a negative effect on the specimen forms.
- Chemical modification with sulfobutyl groups has had a negative effect on the specimen forms and also on the mechanical strengths but has decreased the water demand of materials.

6   ACKNOWLEDGMENTS

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