Journal of applied research and technology
ISSN: 1665-6423

UNAM, Centro de Ciencias Aplicadas y Desarrollo Tecnológico

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Journal of applied research and technology, vol. 16, no. 4, 2018, July-August, pp. 287-298
UNAM, Centro de Ciencias Aplicadas y Desarrollo Tecnológico

DOI: https://doi.org/10.14482/INDES.30.1.303.661

Journal of Applied Research and Technology

www.jart.ccadet.unam.mx
Journal of Applied Research and Technology 16 (2018) 287-298

Original

Physicochemical and mechanical study of Mayan Archeological stony constructive materials

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Received dd mm aaaa; accepted dd mm aaaa
Available online dd mm aaaa

Abstract: Mayan civilization monumental architecture has been a vital source of information to gain acknowledgement about its way of life, science and political hierarchy; consequently, examination of constructive materials of Mayan structures by using materials science characterization techniques are noteworthy. This work focuses on the study and characterization of archeological stony materials taken from the main structure on Witzinah archeological site located south of Yucatan, Mexico, in order to determine its constituted elements and chemical components. Such materials were observed under scanning electron microscopy (SEM) to establish, in accord to its micro-structural patterns, the porosity and morphology, and energy-dispersive X-ray spectroscopy (EDX) to determine the chemical compounds. Calorimetric analysis through TGA was carried out in order to identify the presence of organic elements as well as Infrared analysis (FTIR) and nuclear magnetic resonance (1H NMR) to detect polymeric components. Preliminary results indicated that mortars contain saturated fats (esters) that were possibly originated by degradation of natural polymer (elastomeric rubber) known as polyisoprene as well as nano-clay material named Palygorskita (typified in Maya as Sak lu'um), and that both had a direct influence on the properties of the evaluated mortars used for the construction of the site Principal Building.

Keywords: Mayan Civilization; Mayan constructive techniques, materials characterization; stony materials; environmental raw materials

1. INTRODUCTION

Mayan civilization prevailed along Yucatan peninsula where 1,850 registered archeological sites were reported in 1980 just in Yucatan State (Garza Tarazona & Kurjack, 1980). Prehispanic constructive materials have been in the interest of archeology scientists since many years ago specially to understand its process of manufacture, properties and overall, its primary constituents. Previous works have been carried out in several Mayan archeological sites and important comparisons have been stated intending to find out about the ingredients and

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manufacture processes (Fletcher, 2002). It is also noticeable that chemical constituents of the materials depend greatly upon the geographical situation where an archeological structure is found (Fletcher, 2002; Goodall et al., 2007; Hueda-Tanabe et al., 2004; Villaseñor & Price, 2008) due to different access to raw materials and different building traditions at each site; although some researchers (Villaseñor & Price, 2008) suggest the use of raw materials other than local stones outside Mayan area. Owing to Mayan area in Yucatan State is formed of carbonate platform, raw ceramic materials such as calcareous limestone for architecture applications were widely available. Stony building materials mainly used by Prehispanic Mayans have been calcareous stone, argamassa (mortar and stucco) and organic elements such as straw and wood. From these, the mortars with binder have been applied in Mayan buildings in order to confer mechanical and adherence properties while stuccos are applied for good surface finishing. The calcareous rocks of the Yucatan Peninsula have a very heterogeneous distribution due to the various diagenetic environments involved in their formation therefore they present high variation in the physical, mechanical and chemical characteristics (Espinosa, Ceron & Sulub, 1998). It has been also reported that some minerals known as sak lu'um are composed of Palygorskite clay (Bautista, Palacio Aponte, Quintana, & Zinck, 2011; Isphording & Wilson, 1974). Mayan constructors selected the most resistant and durable rocks for the monumental buildings that have lasted through the time without important subsidence and deformation. Previous investigations have established that the building constructive materials main constituents were taken from natural resources nearby the Mayan settlements such as calcareous rock powder, underground powder obtained from quarry (known as *Sahcab* in *Maya*), lime powder and gravel as solid aggregates, and as binder natural terpenoids based resins obtained from local trees such as Chakah (*Bursera Simaruba*), Chucúm (*Pithecellombium albicans*), Holol (*Trichospermum mexicanun*), Pixoy (*Guazuma olmifolia*) and K'iik-ché (*Castilla elastica*) (Littmann, 1960; Vázquez de Agredos Pascual, Domenech Carbo, & Doménech Carbó, 2008; Wernecke, 2008). Fray Diego de Landa described in his chronicles the abundance of limestone in the Yucatan Peninsula, and its suitability for producing materials for architecture applications such as stuccos and mortars by mixing lime with a juice obtained from the bark of certain trees (Tozzer, 1941). Magaloni, Pancella, Fruh, Cañetas, and Castaño (2011) identified high levels of organic additives in Mayan mortars. They stated that such organic compounds came from orchid bulbs and holol bark extracts. Some others works are related to the identification of organic additives in Maya archaeological mortars and stuccos; all of them relate their findings to natural resin obtained from local trees and plants such as nopal, chacah, jabin and holol (Cárdenas, Arguelles, & Goycoolea, 1998; Hansen, Hansen, & Derrick, 1994; Pérez, Charua, & Fernández, 2015; Ruiz Martín, 2010). However, it is important to emphasize that characterization of natural organic materials (rubber, dyes, additives, etc.) as constituents of ancient archeological stony structures is somehow complex since such compounds could have experienced physicochemical alterations through time. It is important to remark that during restoration for preservation of an archeological building, different methodologies are needed including tests to determine the suitable filling for each application since in diverse situations the lack of detailed studios has led to wrong decisions generating a negative effect that worsen the state of the edification even after the intervention. Villaseñor-Alonso and Barba-Pingarrón (2011) expose that a generalized disinterest exists in studying stony building materials since these seem to contribute with few diagnostic information at bare sight at least for the non-specialized researcher. Nonetheless, they propose that building materials hold a special potential for archaeological research and need to be incorporated as part of archaeological projects. Consequently, the purpose of this work is to contribute with analytical evidence regarding a combination of characterization techniques undertaken on Mayan archeological stony materials providing complementary data about the chemical and mineralogical compositions of the stuccos/mortars, as well as their micromorphological characteristics. Additionally, it establishes the importance of standard materials characterization techniques such as EDX, SEM, FTIR, etc on archeological materials from Prehispanic Mayas that are intimately related with the technology and constructing system of the monumental buildings and, in particular for this case, to materials that corresponds to UO-1 structure, room 3 from the archeological site of Witzinah, located in Yucatan state, Mexico. Archeology needs to be supported by Materials Science in order to analyze and characterize diverse kinds of archeological materials such as ceramics, organic compounds, stones, paints, etc. to be fully understood. In this work, such methods and analysis techniques were used for interpretation and comprehension of data in order to strengthen and define the importance about conservation and restoration of archeological-architectonic patrimony of the Prehispanic Mayan Civilization in south Yucatán zone evidencing its constitutive components.

2. MATERIALS AND METHODS

2.1 ARCHEOLOGICAL STONY MATERIALS

2.1.1. Archeological site

Witzinah, dated 800 A.C., is located in Peto county in south Yucatan State in Mexico also known as "South Cone" (*Cono Sur*) approximately 164 Km from Merida Capital City. Witzinah presents a total of 50 Prehispanic structures distributed in a surface of 77,243 m^2 and it is formed by edifications generally oriented at 10º NE, meanwhile the rest exhibit small variations (349º NW). Main structure (UO-1) is a pyramidal basement in a 14 m high slope, its architectural plant is 35 m by side and above there is a "C" shape structure that was constituted by five rooms with overhang covers, three in the main part of the building and one in each lateral side. Figure 1 exhibits Witzinah archeological site and location of evaluated stuccos.

Stony archeological samples to be studied were classified in two materials, first corresponding to mortars and second referring to stuccos. Mortars: Sample 1 (noted as M-1) corresponds to the mortar from the constructive filler found in the overhang cover, sample 2 (M-2) was obtained from the mortar on the posterior loading wall, sample 3 (M-3) was taken from the mortar on the frontal loading wall and finally sample 4 (M-4) refers to the mortar that joined the stones in the overhang cover. Stuccos: Sample 1 (S-1), corresponds to screed stucco from de posterior loading wall, sample 2 (S-2) was obtained from the coating of the north wall. Natural resin extracted from *Hevea brasiliensis* was also obtained for chemical characterization in order to be compared with extracted residues obtained from stony archeological samples. This latex, although it is believed that was not available in Mesoamerica in Prehispanic time, was chosen for comparison purposes since a plus intention of this research is to assist in producing a durable yet accurate modern mortar that could be used in present archeological building reconstruction and preservation. Despite the various possible sources of naturally occurring rubbers, latex from *Hevea brasiliensis* remains the most widely used (Bhowmick & Stephens, 2001), therefore its availability and affordableness make it an excellent option to be used as preserving and conserving material in building restoration.

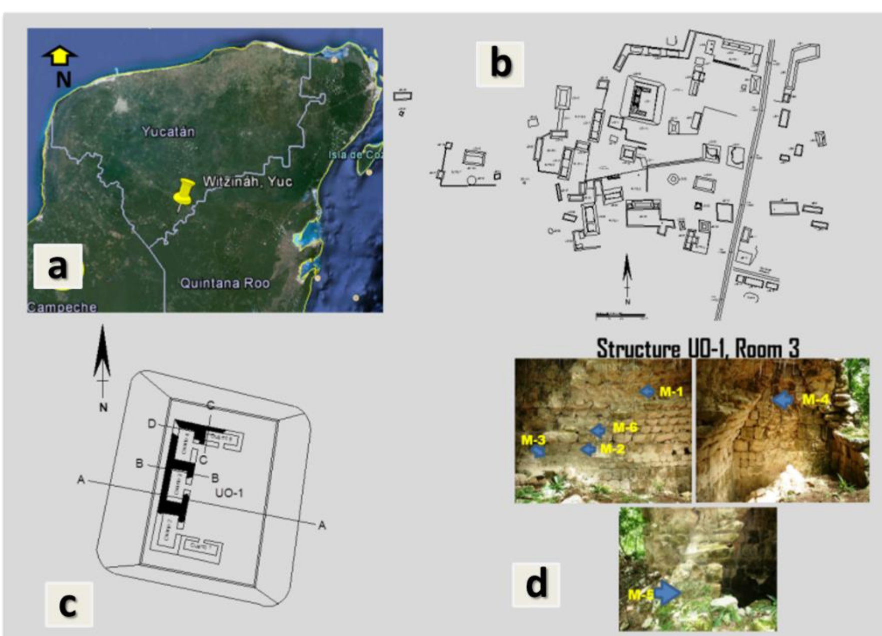

Fig. 1. a) Witzinah location, Yucatán peninsula, b) Archeological site scheme, c) UO-1 building structure. d) Stuccos and mortars sample position.

2.1.2. Soxhlet Extraction

Four samples of each archeological mortar and stucco were chosen to undertake Soxhlet extraction as selective removal. 30 g of the material (granules and powder) were placed in a filter cone to be introduced into the main chamber in the Soxhlet system. Toluene was used as organic solvent and the system was heat at 55°C in order to initiate the filtration cycles during 6 hr. When cycling time was finished, the solvent remained inside the flask was carried to gradual evaporation until the obtaining of wax-like solid residues. Such deposits were taken to be analyzed by FTIR and ^{1}H NMR.

2.1.3. Scanning Electron Microscope (SEM) with EDX spectroscopy

Stuccos and mortars image analysis were carried out in a SEM model JEOL JSM-6360LV in order to study granular surface and distribution at different magnifications at high resolution. Mortar and stucco samples were taken in powder and granules to obtain additional granulometric and particle dimensions information. Each sample was analyzed and several images were captured with a power and resolution of 15 kV to X15, 15 kV to X50, 10kV to X20,000 and X30,000; 10kV to 5,000; 10kV to 1,000 and 1,500; 10 kV to 10,000; 10 kV to 500. Such images were used to identify representative patterns in the materials samples. Energy-dispersive X-ray spectroscopy (EDX) analysis was also performed in SEM equipment to obtain quantitative and qualitative identification of the main constituent elements in the studied materials.

2.1.4. Thermogravimetric Analysis (TGA)

This technique senses weight changes in a material in function of the temperature (or time) under a controlled atmosphere and allows the evaluation of mass loss in order to evaluate thermal stability and materials composition. A thermogravimetric analyzer model TGA 8000 from Perkin Elmer was used. An amount of 5 to 10 mg approximately of the petrous material were placed on the TGA to be analyzed under a Nitrogen atmosphere with an interval of temperature between 50 to 650°C on a heat speed of 10°C/min.

2.1.5. Fourier Transform Infrared Analysis

FTIR spectrogram was carried out in Nicolet 460 equipment placing the wax-like residue, obtained by Soxhlet extraction, in KBr to prepare a solid sample that was examined at 100 scans in a specter interval of 4000 a 400 cm^{-1} with a resolution of 4 cm^{-1}.

2.1.6. Nuclear magnetic resonance (^{1}H NMR)

^{1}H NMR spectra was obtained in a Varian 600 MHz equipment using deuterated chloroform as diluent. Wax-like extracts were also analyzed by ^{1}H NMR.

2.2. EXPERIMENTAL MORTARS

2.2.1. Elaboration of experimental mortars

Experimental mortars were manufactured using the fundamental elements found in the archeological petrous samples analyzed such as *sahcab* (calcareous stone powder), lime, water and natural polymer (latex), in order to represent the viability of reproduce such materials and compare them in applicability. *Sahcab* was obtained from a quarry nearby to *Chan Chen* archaeological site belonging to Cholul area in Yucatan. The lime used was commercially available as "*Lime American finish*" while piped drinking water and latex obtained from local tree (*Hevea brasiliensis*) were also used as components in the experimental mortar. Samples preparation included sieving, hydration of lime, mixing and finally mechanical compression tests. *Sahcab* was dried at room temperature (35°C - 37°C) exposed under natural sunlight for 10 h during three consecutive days previous to separation. Subsequently, standardized mesh sizes of 40, 50, 60 and 70 having an aperture 0.420, 0.297, 0.250, and 0.210 mm respectively were used in order to obtain a granulometric separation. Powder passing through the sieve was collected and used in the mortar manufacture, retained material was discarded. Lime (CaO) was hydrated by mixing in a water/lime ratio of 2:1 and the samples were left on the lab bench for 6 months to obtain slaked/hydrated lime ($Ca(OH)_2$). Latex was obtained by bleeding tree conventional process and treated with ammonia (NH_3) as a stabilizing agent, with a ratio of 3 to 4 g/l of latex (polyisoprene). All materials were mixed in a mechanical blender adding 275 g of hydrated lime, 525 g of calcareous powder (*Sahcab*), 100 g of latex and 100 g of water in cycles of 3 to 5 min per aggregate to obtain the ideal mixture, that is, with good plasticity and malleability. The experimental mortars system was poured in 2" cube molds elaborated according to ASTM (C 349-14) previously surface cleaned and covered with a polymer film based on alcohol in order to avoid mortar adhering to the surface of the molds. Cube molds were placed in a vibrating table for a period of 10 min. to allow the mortar system to cover all the mold area. Finally, the mold is left for curing during 14 days until it hardens and solidifies for further testing. Cubic mortar samples obtained were mounted into the mechanic test machine by ensuring that the upper and lower faces of the cubes, that are being loaded, are parallel in order to homogenize the compression stress through the sample.

2.2.2. Mechanical testing of experimental mortars

Compression test was carried out in five experimental mortars samples per formulation using a universal testing machine Shimadzu AG-I, with a load cell of 5 KN at room temperature with humidity of 80 to 90% and a crosshead speed 0.4 mm/min until fracture. Acoustic emission equipment, model MICRO 11PCl-2 was used in order to monitor the mechanical tests in real time to identify the failure mechanisms. Piezoelectric peak sensors were fixed on one side of the cube leaving 20 mm between them using silicone grease as coupling agent. Threshold was set at 20 dB, with a gain of 40 dB to determine the onset of failure (Figure 2).

3. RESULTS AND DISCUSSION

3.1. ARCHEOLOGICAL MORTARS AND STUCCOS

3.1.1. Scanning Electron Microscope with EDX spectroscopy

EDX is a method of spectroscopy that is useful in identifying the composing elements of materials; however, it does not reveal chemical bonding information. Hence EDX is more suited for the analysis of inorganic materials, rather than organic materials, which contain for the most part all the same elements bonded differently. For this reason, EDX analysis results carried out to mortar and stuccos revealed high values of C,O and Ca mainly forming part of the stony material namely calcium carbonate, 3($CaCO_3$) (*Sahkab*). Although organic materials cannot be reliably identified using EDX, it can bestow a broad idea about the possibility of encountering organic molecules that can be useful to localize characteristic structures and allow a comparison and potential identification of them supported by additional characterization techniques such as FTIR. Previous studies carried out by Ruiz Martín (2010) on endemic trees in Yucatan peninsula such as Pixoy, Chucúm, Chacá and Jolol indicated that resin extracts from those trees were used by Mayan builders as adhesive in their building constructive materials. Therefore, is highly possible that organic substances are also being sensed by EDX as fragments of the analyzed samples. Figures 3a and 3b show SEM images examination in mortars and stuccos, which determined the presence of nanometric clayey material such as Palygorskite displaying

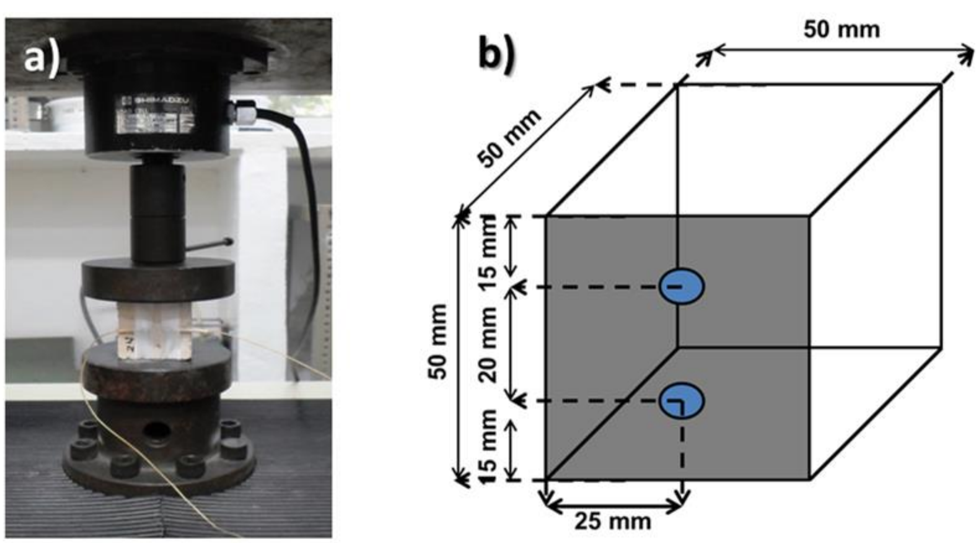

Fig. 2. a) Compression test for experimental mortars, b) Sample dimensions with AE sensors attached.

a long and tubular morphology. These nanoclays are reported to be found in the south west of Yucatan State and are associated to tertiary calcareous material that are exposed as fine Palygorskite lentils. They use to be found along Sepiolite in larger amounts. Those mineral formations are due directly to precipitation of marine waters (Martín, 2002).

SEM/EDX analysis allowed identifying Palygorskite $4H_2O((Mg_2Al_2)Si_8O_{20}(OH)_2 \cdot 4H_2O))$ that exhibited, as chemical elementary constitution, C, O, Mg, Al and Si, and has been reported locally as *Sak lu'um* clay (Soberanis Monforte, Gordillo Rubio, & González Chi, 2015). Morphologically, too many particles are mostly ovoid although it is also possible to find shapeless solids (Figures 3c and 3d). All samples showed clay particles in fiber-like shape in a nanometric scale of about 0.1 μm a 35.09 μm in length and 0.02 μm a 0.99 μm in diameter.

3.1.2. Thermogravimetric Analysis

Figure 4 presents TGA analysis results performed to mortar and stuccos. This study allows estimating the possible presence of organic material in the analyzed constructive materials. Results exhibited in Figure 4 identified a mass loss between 3 and 5% in samples indicating elimination of humidity around 70°C, then and apparent stabilization is seen until 250°C where initiates a stage in which a notorious declination in the curve appears indicating organic mass loss until 600°C. Mineral solid residue remains after the test (96%).

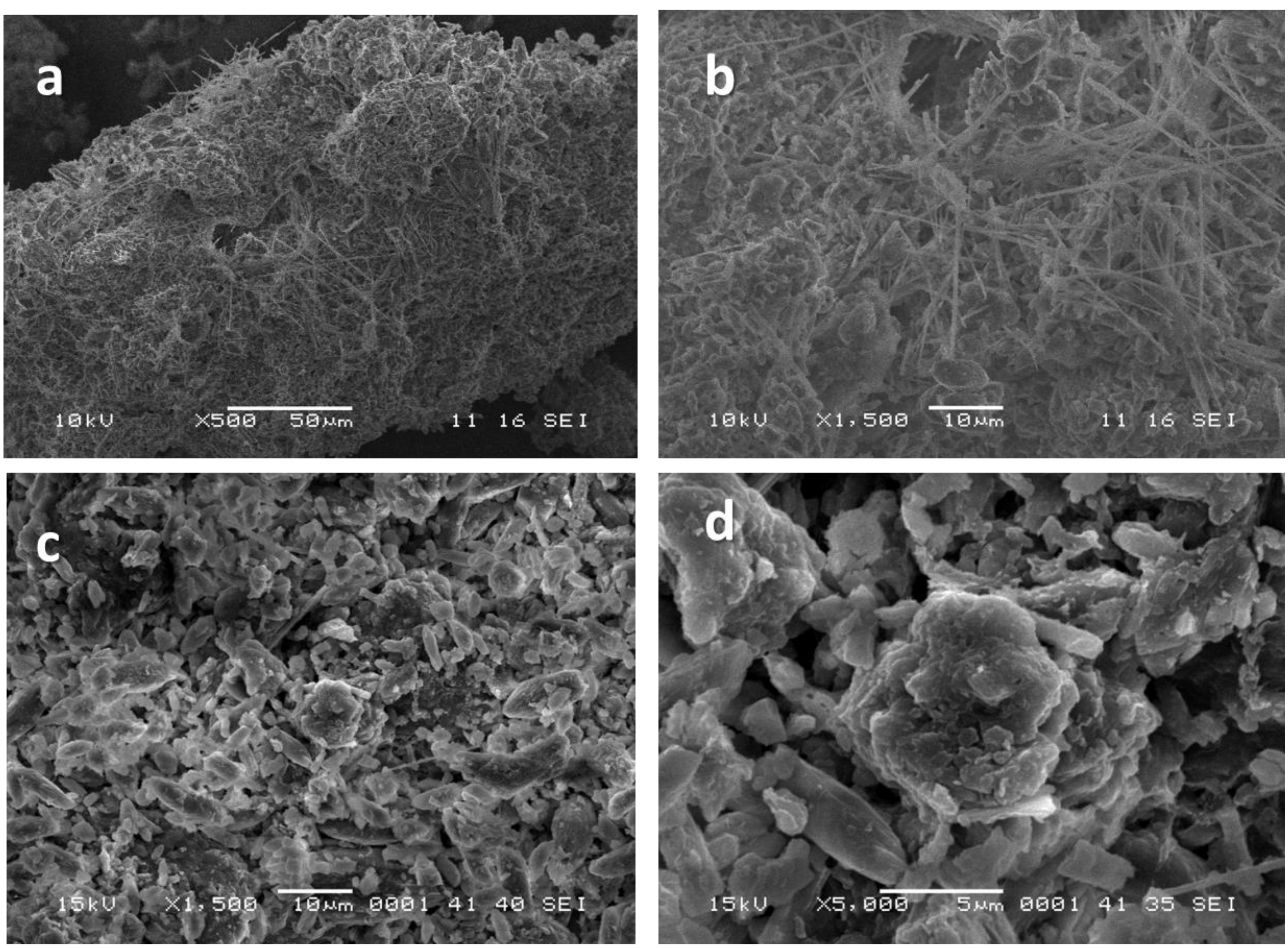

Fig. 3. SEM micrographics of archeological stony particles, a) and b) Palygorskite nanoclay, c) and d) nanoscale clay structures agglomerates.

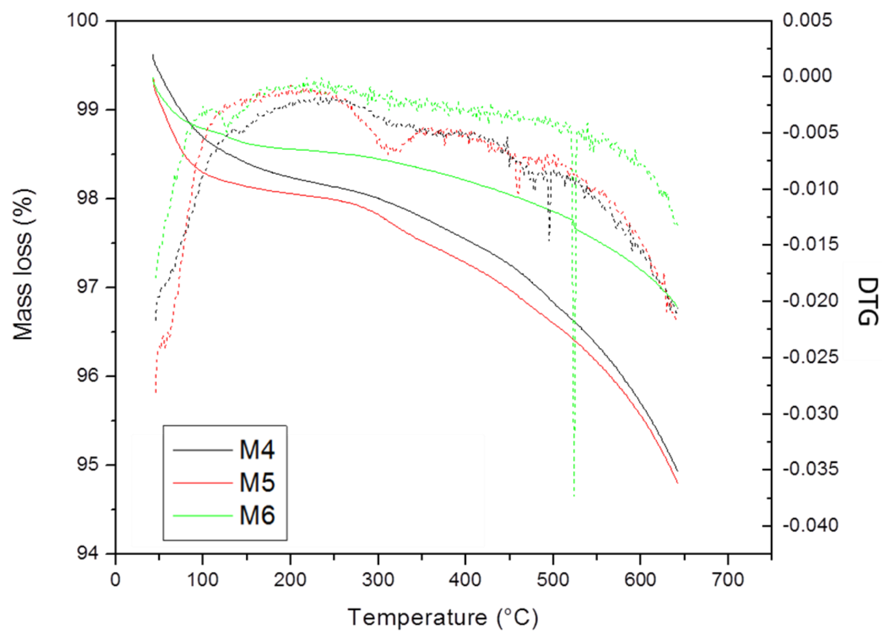

Fig. 4. Thermogravimetric analysis (TGA) thermogram for petrous materials samples.

3.1.3. Fourier Transform Infrared Analysis

Archeological mortar samples underwent Soxhlet extraction in order to separate and obtain possible organic component present on them. A yellowish waxy residue was acquired to be analyzed qualitatively by FTIR and ^{1}H NMR techniques. As shown in Figure 5a the FTIR spectrum exhibits bands at 2950, 2920 y 2850 cm^{-1}, which are typically associated to C-H stretching of methyl and methylene groups. Bands at 1460 y 1380 cm^{-1} related to bending vibration confirm the existence of these groups. A signal in carbonyl zone at 1730 cm^{-1} suggests the presence of ester groups which is also supported by C-O stretching bands at 1280 cm^{-1}. Natural latex used to elaborate the experimental mortars was also analyzed by FTIR in order to identify functional organic groups and correlate them to original stuccos characterization (Figure 5b). C-H bands, typically associated to methyl and methylene stretch vibrations were observed at 2932 cm-1. At 1460 cm-1 additional bands, related to bending vibrations, confirm the presence of such groups. Esters groups were also observed at 1730-1750 cm-1and 1280-1300 cm-1 linked to C-O stretching vibrations. Additionally, the presence de of bands associated to C=C a 832 cm-1and 3036 cm-1, suggest the occurrence of isoprenoids, characteristics of natural rubber cis 1-4 isoprene.

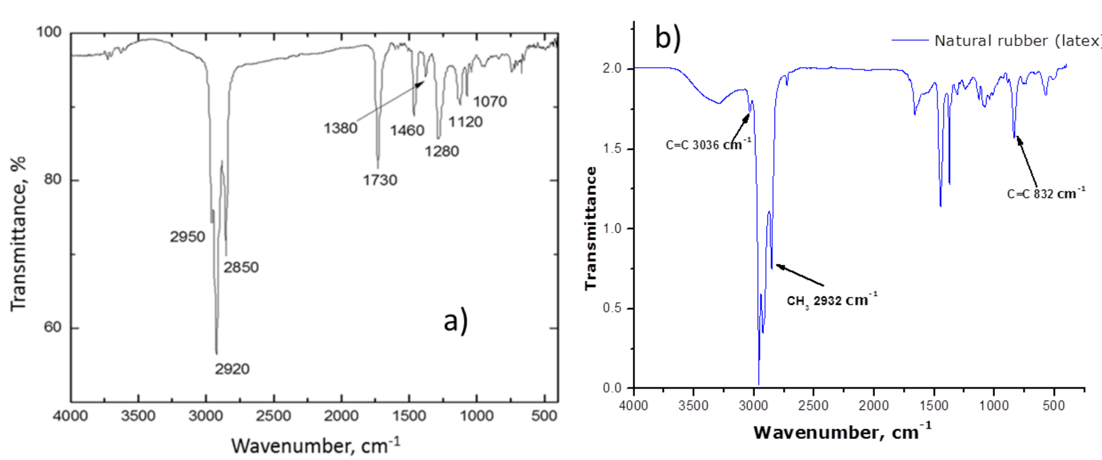

Fig. 5. FTIR spectra a) waxy residue obtained after Soxhlet extraction, b) natural rubber extracted from *Hevea brasiliensis* tree.

3.1.4. Nuclear magnetic resonance

^{1}H NMR spectrum displayed in Figure 6 exhibits intense signals at 1.5, 1.18 y 0.8 ppm along with a weak signal at about 3.57 ppm. Signal at 0.8 ppm is generally associated to methyl group terminal protons in hydrocarbonated chains. On the other hand, signals at 1.18 and 1.5 ppm can be related also to methyl group protons affected by different environments. Band at 3.57 ppm could also be due to methylene protons but bonded to an oxygen atom (as in an ester group as shown in FTIR) which promotes the signal location to be lower due to the electronegativity of O.

Considering the information obtained by FTIR and ^{1}H NMR, it is possible to state that mortar and stucco systems are constituted by a mixture of fatty acids esters since the presence of sutured hydrocarbonated chains and carbonyl compounds were identify. However, it was not found any clear evidence to link the wax-like extractions to the incidence of natural rubber (polyisoprene) due to the lacking of signals related to double bonds (C=C) characteristics of terpenoids such as stretching bands absorbed around 1664 cm-1, or through unsaturated methyl protons (HC=C) of cis-1,4-isoprene localized around 5.1 ppm (Chaikumpollert et al., 2011). Those signals were not evinced by the applied techniques. While it is true that there are literature reports (Rose & Steinbüchel, 2005) that indicate it is possible the identification of carbonyl groups such as ketones, carboxylic acids and esters during natural rubber degradation, in all mechanisms reported, invariably double bonds of isoprenoids remain. Therefore, it is highly probable that the analyzed samples are formed by a mixture of fatty acids esters proceeding from natural rubber degradation which is reduced to elemental chains (oligomers) that make difficult the C=C bond identification. It has been demonstrated that biotic degradation originates a significant decrement in double bonds in the polymeric chain and that its final chemical groups are rich in carboxylic fatty acids (Linos et al., 2000; Sakdapipanich & Rojruthai, 2012). In contrast, Fletcher, (2002) carried out FTIR and ^{1}H NMR analysis in stuccos taken from Maquixco Bajo archaeological site at Teotihuacan in order to search for the presence of organic gum binders. However, such results did not produce any definitive evidence for the presence of organic binders. So they proposed that calcite was used as binder in those stony materials.

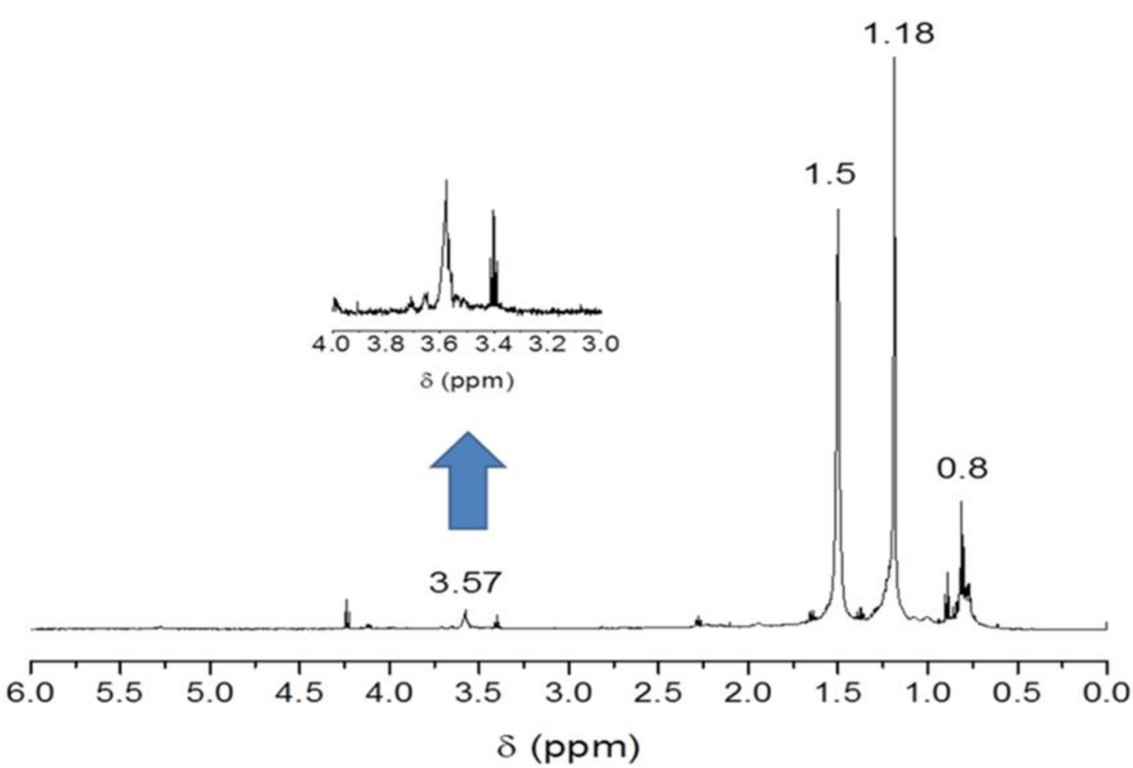

Fig. 6. Proton nuclear magnetic resonance (1H NMR) spectra for waxy residue obtained after Soxhlet extraction.

3.2. EXPERIMENTAL MORTARS

3.2.1. Particle Size distribution

Experimental mortars were elaborated following the sieving of calcareous stone powder (*Sahkab*). Figure 7 exhibits the particle size distribution where is notorious the diminishing of powder dimensions when the mesh size augments. For this analysis a Coulter counter equipment was used by placing the particles in question into distillated water presenting a hydrophilic character that generates a rapid absorption by the sample and continues changes in the particles affecting the determination of its average size. Despite such variations, results displayed in Figure 7 gives a comprehensive impression of the majority distribution and the differences between the sieved particles. Sieve number 70 presented the lower particle size meaning a higher contact surface.

3.2.2. Mechanical Testing

Mechanical compression tests were carried out on 10 samples of each formulation (mesh size). Results showed that experimental mortars exhibit fracture mode II, which basically are shear strength, since the load was uniformly distributed over the sample generating first cracks in the cube corner sections that act as stress concentrators within the mortar causing it to crack. Porosity and internal imperfections affect the cracking progression along the sample which in some cases led and directed the cracking development both internally and externally.

Based on the mechanical tests results shown in Table 1 it is clear the effect induced by the particle size in the experimental mortars. As the calcareous stone powder (sahcab) particle size is smaller, such grains exhibit higher surface area that interacts favorably providing higher modulus.

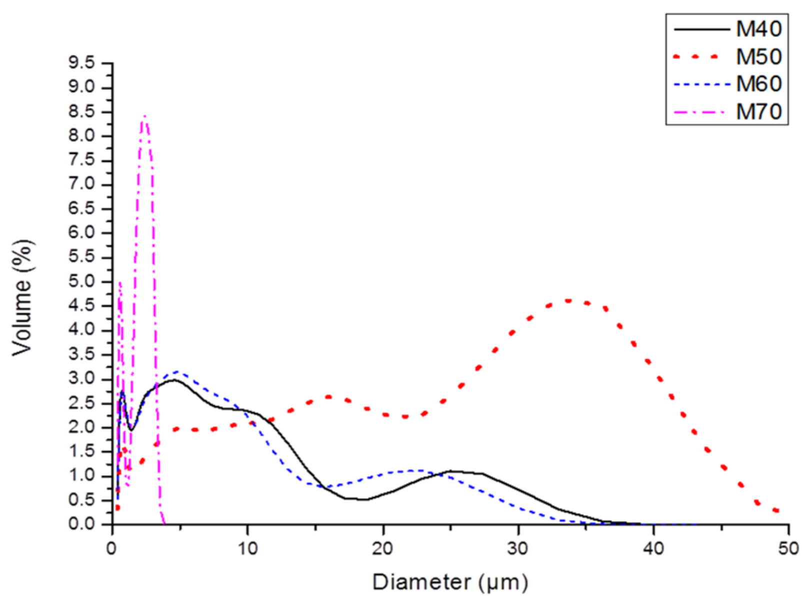

Fig. 7. Calcareous stone powder (*sahcab*) particle size distribution to manufacture experimental mortars.

Table 1. Mechanical parameters exhibited by the particle size in the experimental mortars.

Mesh	Max. Load	Max. Stress	Max. Strain	Elastic Module
	(N)	(MPa)	(%)	(MPa)
40	1085.47	0.43	5.46	13.26
50	1571.25	0.63	5.23	20.65
60	2017.19	0.81	4.05	24.31
70	2367.19	0.95	3.02	28.96

Acoustic emission signals displayed in a representative stress-strain-AE amplitude curves in Figure 8 exhibit those events involved in experimental mortars compression tests. Mechanical damage events are intimately related to signal characteristics such as amplitude, energy, etc. The amount and type of events also depends on failure mechanisms from crack initiation and propagation until fracture. Results determine that amount of events are low in all cases since the mortars are porous materials they are fractured rapidly with the first internal cracks. Mortars made of 60 and 70 sieve particle size showed lesser events with lower energy.

4. CONCLUSIONS

Archeological stony materials analysis by diverse characterization techniques allowed determining the elemental chemical constituents used in its manufacture in order to be able to reproduce the process used anciently by Mayan constructors. Physicochemical analysis identified fatty acids esters as main agglutinant component; such organic fragments are highly believed they proceed from natural rubber degradation which is reduced to elemental chains by age weathering. Essential studies have demonstrated that Prehispanic Mayan builders used organic substances in the stucco and mortar preparation such as blood, eggs and natural rubber obtained from local trees, being the latest the most used. Ruiz Martín (2010) specified that due to high volume of binder used, it was clear that natural rubber was the main adhesive component in Maya stony materials. However, it is important to note that organic substances degrade through time, which results in changes of the characterization analysis spectra (FTIR, Chromatography, etc).

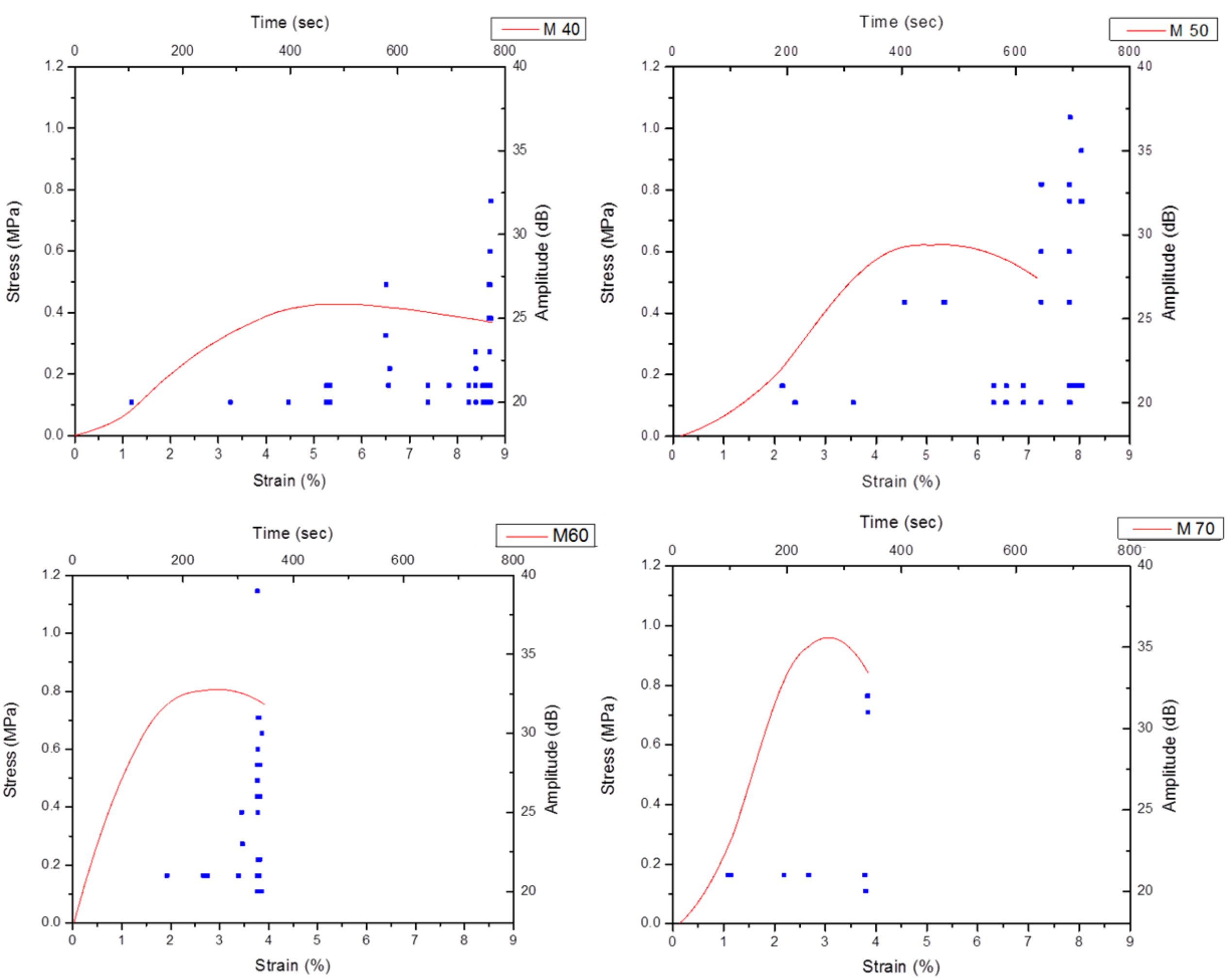

Fig. 8. Acoustic emission signals displayed in stress-strain-amplitude curves for experimental mortars according the particle size.

The difficulties in characterizing organic additives in Maya archaeological plasters have also been noted by Hansen et al. (1994). Additional noteworthy findings was the identification of chemical elements and compounds such as Magnesium sulfate (Mg, S and O2), plaster (Ca, S and O2) and the inclusion of Palygorskite clay that, in the right deification, time of mixture and knead were used to consolidate the Mayan structures during one of the most developed constructive era of the Mayan culture in Yucatan Peninsula (Late Classic/terminal 800 A.C.). Experimental mortars were manufactured employing same materials used by Mayan constructors in order to evaluate mechanical behavior in compression stress. It was found that granular size is an important factor to improve mechanical properties by reducing interstitial space and augmenting the surface area. Acoustic emission technique determined the mechanical events presented during compression mechanical test indicating that progression of damage is slightly higher when particle size is sieved between 40 and 50 (0.420, 0.297 mm) and have a reduction into AE damage signals in 60 and 70 sieves due to a higher compaction reducing stress concentration sites such as voids and pores. Finally, experimental mortar under compression highlighted the best conditions to obtain resistant and manageable materials to be applied in archeological/architectonic restoration. This information is significantly essential since this material can be used in applications were structural restoration is evident.

ACKNOWLEDGEMENT

The authors are grateful to the Mexican Council for Science and Technology (CONACYT) for the provision of grant 60204/ CM0042 and the scholarship for PhD student V. Ley-Paredes. Also gratitude to National Institute of Anthropology and History (INAH) for providing the archeological materials from Witzinah archeological Mayan site.

CONFLICT OF INTEREST

The authors have no conflicts of interest to declare.

REFERENCES

Bautista, F., Palacio-Aponte, G., Quintana, P., Zinck, J.A. (2011). Spatial distribution and development of soils in tropical karst areas from the Peninsula of Yucatan, Mexico. Geomorphology, 135, 308–321.

Bhowmick, A.K. & Stephens, H., (2001). Handbook of Elastomers, Second Edition, Revised and Expanded. *Marcel Dekker Publishers*. USA.

Cárdenas, A., Arguelles, W., & Goycoolea, F., (1998). On the possible role of Opuntia ficus-indica mucilage in lime mortar performance in the protection of historical buildings. *Journal of the professional Association for Cactus Development*,3, 64-71.

Chaikumpollert, O., Sae-Heng, K., Wakisaka, O., Mase, A., Yamamoto, & Y., Kawahara, S. (2011). Low temperature degradation and characterization of natural rubber. *Polymer Degradation and Stability*, 96(*11*), 1989-1995.

Espinosa, L., Ceron, M., & Sulub, Y. (1998). Limestone rocks of the Yucatan peninsula. Description of the lithology and physical properties based on the results of exploration, investigation and laboratory tests. *International Journal of Rock Mechanics and Mining Sciences*, 35(*4-5*), 410-411.

Fletcher, J.M., (2002). Stuccoed Tripod Vesselsfrom Teotihuacan: An Examination of Materials and Manufacture. *Journal of the American Institute for Conservation,* 41(*2*), 139-154.

Garza-Tarazona, S.; Kurjack, E.B., (1980). Atlas arqueológico del Estado de Yucatán. *Mexico City.*Instituto Nacional de Antropologia e Historia.

Goodall, R.A., Hall, J., Edwards, H.G.M., Sharer, R.J., Viel, R., & Fredericks, P.M. (2007). Raman microprobe analysis of stucco samples from the buildings of Maya Classic Copan. *Journal of Archaeological Science,* 34(*4*), 666-673.

Hansen, E.F., Hansen, R.D., & Derrick, M.R. (1994). Los análisis de los estucos y pinturas arquitectónicas de Nakbe: resultados preliminares de los estudios de los métodos y materiales de producción. *VIII Simposio de Investigaciones Arqueológicas en Guatemala*, pp. 456-470.

Hueda-Tanabe, Y., Soler-Arechalde, A.M., Urrutia-Fucugauchi, J., Barba, L., Manzanilla, L., Rebolledo-Vieyra, M., & Goguitchaichvili, A. (2004). Archaeomagnetic studies in central Mexico—dating of Mesoamerican lime-plasters. *Physics of the Earth and Planetary Interiors,* 147(*2-3*), 269-283.

Isphording, W.C., Wilson, E.M., (1974). The Relationship of" Volcanic Ash," sak lu'um, and Palygorskite in Northern Yucatan Maya Ceramics. American Antiquity, 39 (*3*), 483-488.

Linos, A., Berekaa, M.M., Reichelt, R., Keller, U., Schmitt, J., Flemming, H.-C., Kroppenstedt, R.M., & Steinbüchel, A. (2000). Biodegradation of cis-1, 4-polyisoprene rubbers by distinct actinomycetes: microbial strategies and detailed surface analysis. *Applied and environmental microbiology,* 66(*4*), 1639-1645.

Littmann, E.R., (1960). Ancient Mesoamerican mortars, plasters, and stuccos: The use of bark extracts in lime plasters. *American Antiquity*, 25(*4*), 593-597.

Magaloni, D., Pancella, R., Fruh, Y., Cañetas, J., & Castaño, V. (2011). Studies on The Mayan Mortars Technique. *MRS Online Proceeding Library Archive,* 352.

Martín, J.M.B., (2002). Inventario nacional de arcillas especiales: (palygorskita/attapulgita, sepiolita y bentonita). *Intituto Tecnologico Geominero de España*, 3.

Pérez, N.A., Charua, D., & Fernández, S. (2015). Extracción y purificación del mucílago y goma de nopal para su uso en conservación. Estudios sobre conservación, restauración y museología. Estudios sobre conservación, restauración y museología. Vol. II. 156-166.

Rose, K., & Steinbüchel, A.(2005). Biodegradation of natural rubber and related compounds: recent insights into a hardly understood catabolic capability of microorganisms. *Applied and Environmental Microbiology,* 71(*6*), 2803-2812.

Ruiz-Martín, M.C. (2010). El pixoy como material de conservación de pintura mural y relieves policromos en el área maya. *Estudios de cultura maya,* 35, 63-90.

Sakdapipanich, J.T.,& Rojruthai, P. (2012). *Biotechnology - Molecular Studies and Novel Applications for Improved Quality of Human Life*. Chapter 3: Molecular structure of natural rubber and its characteristics based on recent evidence. InTech publishers.

Soberanis-Monforte, G.A., Gordillo-Rubio J.L., González-Chi P.I. (2015). Influence of Chemically Treated Palygorskite Over the Rheological Behavior of Polypropylene Nanocomposites. Ingeniería Investigación y Tecnología, vol XVI, 4, 491-501.

Tozzer, A.M., (1941). Landa's Relacion de las Cosas de Yucatan. Papers of the Peabody Museum of Archaeology and Ethnology, vol. 18. *Cambridge*, MA: Harvard University.

Vázquez de Agredos Pascual, M.L., Domenech Carbo, M., & Doménech Carbó, A., (2008). Resins and drying oils of precolumbian painting: a study from historical writings. Equivalences to those of european painting, Arché. Instituto Universitario de Restauración del Patrimonio de la UPV, 3, 185-190.

Villaseñor, I., & Price, C.A. (2008). Technology and decay of magnesian lime plasters: the sculptures of the funerary crypt of Palenque, Mexico. *Journal of Archaeological Science*, 35(*4*), 1030-1039.

Villaseñor-Alonso, I. & Barba-Pingarrón, L.A. (2011). El estudio de materiales constructivos en la arqueología mesoamericana. *Anales de Antropología.*, 45, 79-98.

Wernecke, D.C., (2008). A Burning Question: Maya Lime Technology And The Maya Forest. *Journal of Ethnobiology,* 28(*2*), 200-210.