Optimal PVA/Starch Complex by Cryogel Synthesis Intended for Artifact Cleaning

LIBERTY UNIVERSITY

Mallory Warfield and Michael Korn, PhD

Background

The art conservators traditional use of cotton swabs in the cleaning of artifacts had shown to result in the unwanted removal of material and mechanical stress to the piece. [1] In an effort to minimize these issues, new conservation techniques have been developed including gels, micellar solutions and microemulsions. However, gels have the current limitation of leaving behind polymeric residue that must be mechanically removed. Further research has been done into "green" alternate biopolymers composed of gellan gum and agar. However, these do not show the water retention needed to reduce over-wetting and for the ability to load solvents into the gels for tailored cleaning. [2]

Bonelli et al. in 2019, investigated the methodology for cast-drying (CD) and freeze-thawing (FT) routes for the preparation of gels using poly (vinyl alcohol) (PVA) and poly (vinyl pyrrolidone) (PVP). The characteristics of the gels was determined by rheology (measured by a parallel plate rheometer), porosity (measured by CLSM and FE-SEM), water retention (measured by gravimetrically determined water release), and crystallinity (measured by specific melting enthalpies). A mock painting sample was used to determine the effectiveness of the gel and the polymeric residue, analyzed by 2D microFTIR. It was determined that FT was more effective as CD did not give adequate PVP pore formation as determined by SEM. [1]

Rosicardi et al. in 2022, further investigated a "green" alternative to the past study by substituting rice starch (RS) for PVP. Using two FT cycles and the same methodology, they determined the role of starch constituents in gelation in that it is reliant on PVA-amylose interactions, while amylopectin acts as a porogen. Furthermore, Rosciardi et al. tested the retention of the cryogels using surfactants. [3]

Research Question

(1) Can banana and tapioca, the proposed alternate starches, successfully complex with PVA as seen in the PVA/RS cryogel by Rosciardi et al.?
(2) If they can successfully complex, are the proposed gels retentive enough to "load" with the surfactants, TAC and MPD, for tailored conservation?

Methods*

Synthesis:

1. 9g/100 mL of reagent (in 1:0, 2:1, 1:1. 1:2 ratios of w:w PVA to starch) was added to water in a r.b.f. and heated at 98°C for 3 hrs. under vigorous stirring
2. Two FT cycles were completed at -20°C and 25°C
3. The gels were stored in water for 2 weeks to allow the non-complexed polymeric fraction to leave

Structural Analysis:

1. The gel fraction was calculated (G%: $\frac{W_d}{W_0}x100$, W_d=weight of xerogel (dried gel), W_0= weight of the initial polymer)
2. The water content was calculated (WC: $\frac{W_w - W_d}{W_w}x100$, W_w= weight of wet gel, W_d=weight of dry gel)
3. The gels were analyzed by FE-SEM (5 kV, 2.7-4.4 nm) for morphology of pores and polymer alignment
4. The gels were analyzed by FTIR-ATR (650 cm^{-1} to 4000 cm^{-1}, resolution of 2 cm^{-1}, 128 scans/spectrum) to look for OH_v shift to show successful H-bond formation

Cleaning Assessment:

1. Mockup paintings were created using alkyd paint and kaolin (grime)
2. 4x4 cm^2 gels were loaded with either water for the tailored cleaning of particulate soil or triammonium citrate (TAC 97%) and methoxy-pentadeca(oxyethylene)dodecanoate (MPD) surfactant at 7% and 3% w/w, respectively, for the tailored cleaning of sebum soil
3. The loaded PVA/starch (2:1) gels were compared to the industry standards: Gellan sheet (3% w/w), a pHEMA/PVA hydrogel (Nanorestore Gel®) and a PVA hydrogel (Nanorestore Gel® Peggy 6)
4. The gels were left on the painting for 5 min with no mechanical cleaning
5. The cleaning effectiveness was analyzed by FTIR for the peaks 1517 cm^{-1} (CH_2 bending of alkyd resin) and 3670 cm^{-1} (OH bending of kaolin in grime)
6. Polymeric residue was analyzed by FTIR for the peaks 1094 cm^{-1} (C-O stretch of PVA), 3237 cm^{-1} (OH bending), and 1082 cm^{-1} (C-O-C stretching vibrations) for banana starch/PVA. [13] 3477 cm^{-1} (OH stretching vibrations) and 2150 cm^{-1} (combination OH stretching) were used for tapioca starch/PVA.

*Methodology was primarily adapted from Rosciardi et al. (2022) [3]

Figure 1. The importance of correct conservation practices highlighted by the infamous "botched Jesus" restoration from Borja, Spain in 2012. [14]

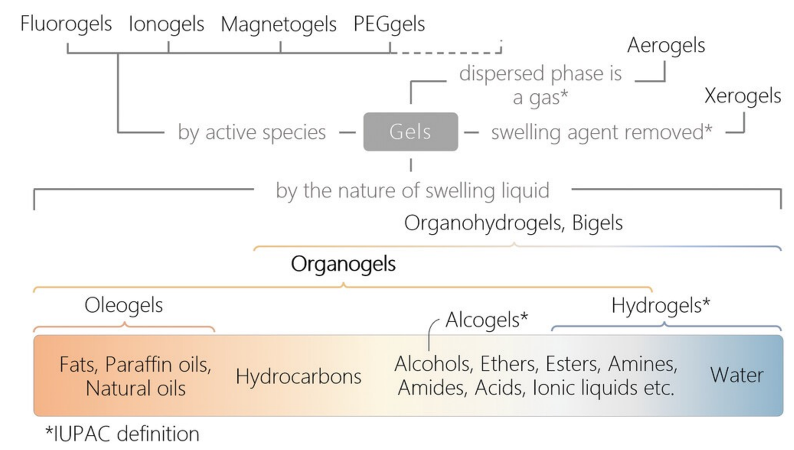


Figure 2. Flowchart of gel type determination. [6]

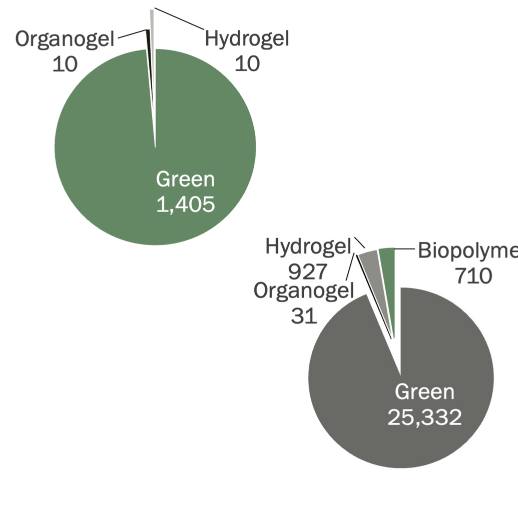


Figure 3. Results for the queries of "art conservation" and keywords for SciFinder (top left) and ScienceDirect (bottom right). (English results only).

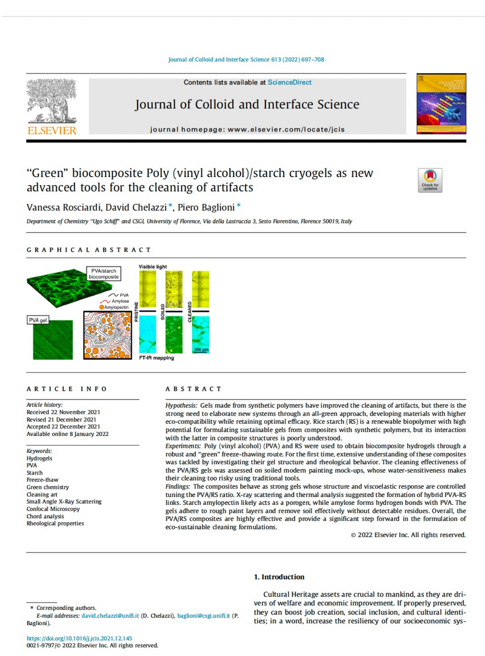


Figure 4. Main article with research from the University of Florence and the USGI. Currently Italy is 81.3% Christian, but only 1.46% evangelical. [3], [17]

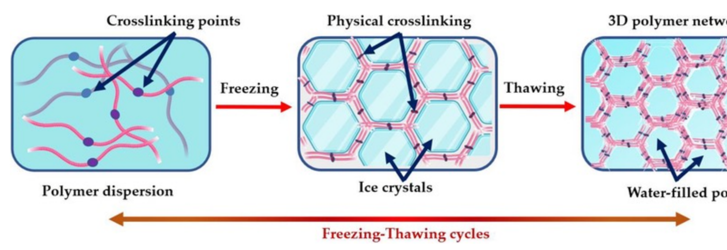


Figure 5. Formation of cryogels by the freeze-thaw (FT) method. [16]

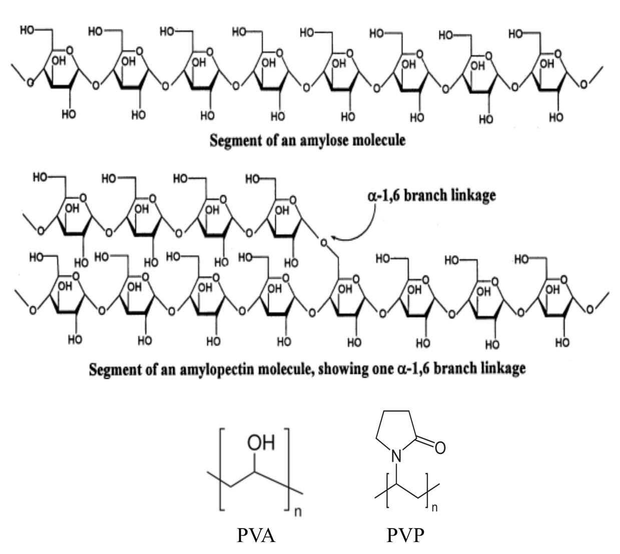


Figure 6. Structure of amylose and amylopectin, the main components of starch (top), the structure of PVA (bottom left), and the structure of PVP (bottom right). [4], [7], [8]

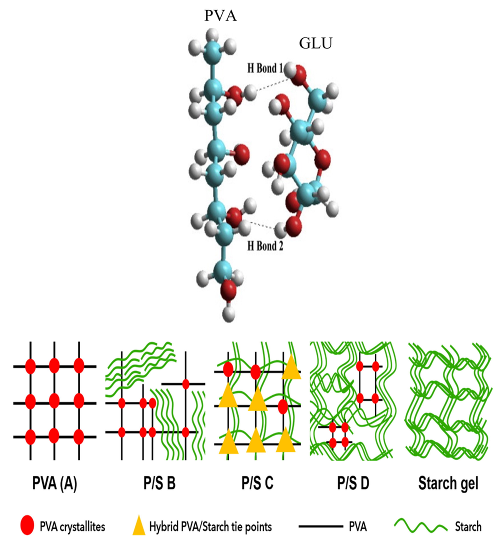
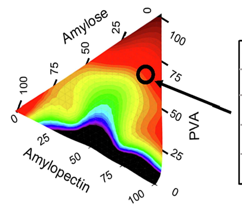


Figure 7. The proposed polymer complex formation between PVA and starch constituents (top) and the schematic of DSC and SAXS data for the nanoscale evolution of hydrogels for **(B)** PVA/RS (2:1), **(C)** PVA/RS (1:1), **(D)** PVA/RS (1:2) (bottom). [3]



PVA	66,66%
Amylose	5,67%
Amylopectin	27,66%
G% (predicted)	≈72%
G% (calculated)	72,36±0,25%

Starch	Amylose^a(%)	Amylopectin^a(%)
Maize	25	75
Waxy maize	0	100
Amylomaize-5	53	47
Amylomaize-7	70	30
Potato	22	78
Wheat	23	77
Rice	19	81
Tapioca	17	83
Banana	20	80
Shoti	30	70

Figure 8. Determination of starch alternatives using the experimentally calculated G% value for PVA/RS cryogels (top) and the percent constituents for various starches (bottom). [4], [5]

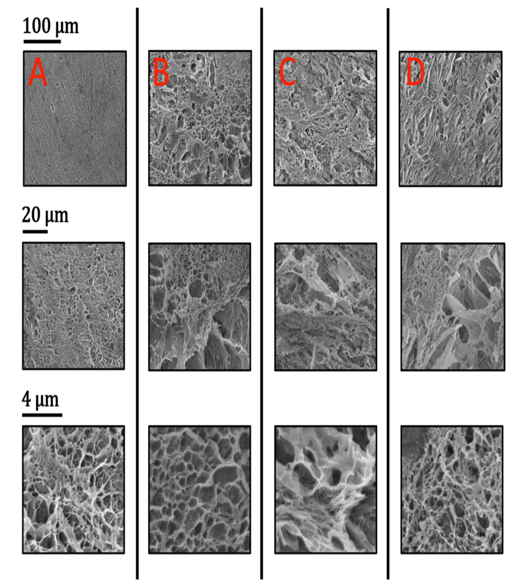


Figure 9. FE-SEM imaging of xerogel samples **(A)** PVA, **(B)** PVA/RS (2:1), **(C)** PVA/RS (1:1), **(D)** PVA/RS (1:2) (bottom). [3]

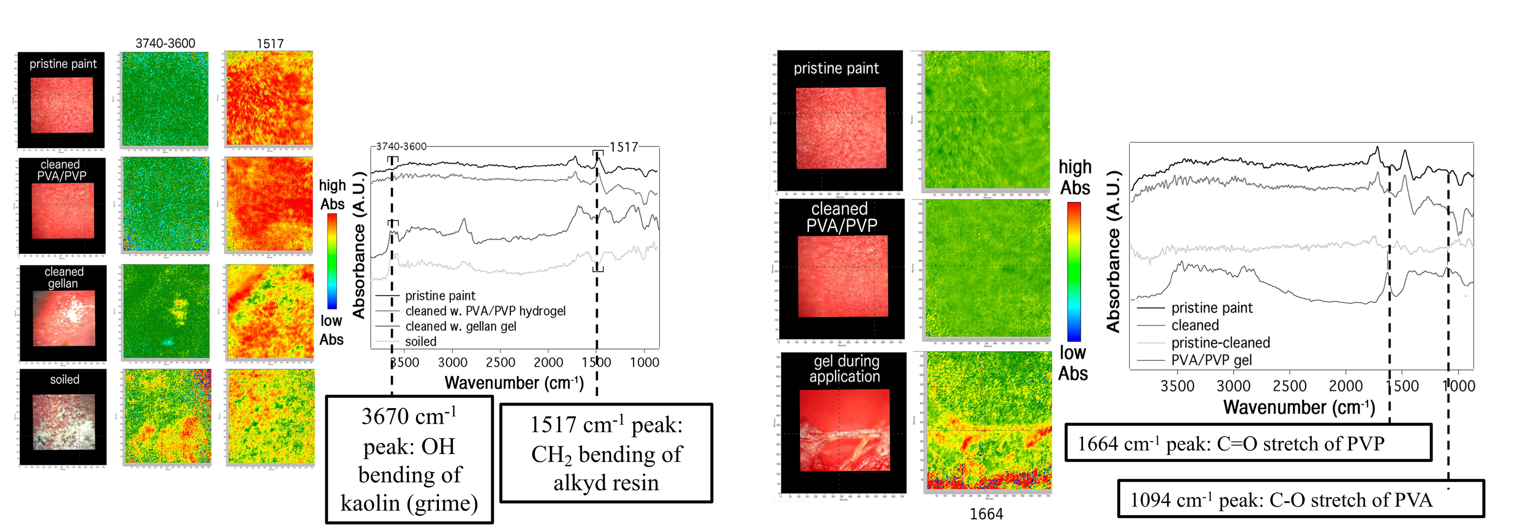
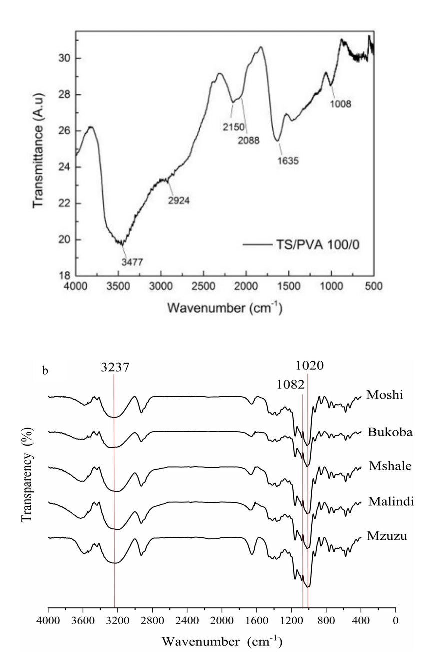


Figure 10. Micro FTIR 2D with FPA (128x128) image of gel effectiveness (left) and gel residue (right) on non-mechanically cleaned mockup painting of alkyd paint and kaolin (grime) (700x700 μm^2 maps with 50 μm axis marks). [1]



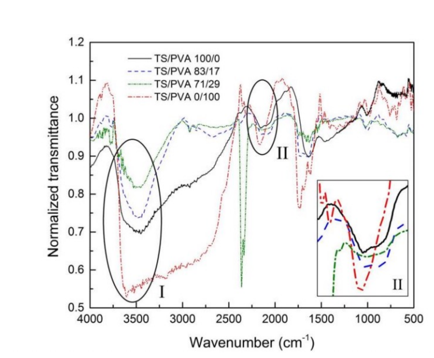


Figure 12. FTIR of tapioca starch (top left), banana starch (bottom left), and an example of what a PVA/RS (PVA/tapioca starch) FTIR may look like (bottom right). [12], [13]

Sample	Decomposition times
Bioplastic cassava starch filler nanoclay 5.0% (b/b)	6 days
Bioplastic cassava starch	12 days
Bioplastic cassava starch filler chitosan	8 days
Bioplastic potato starch	5 days
Bioplastic corn starch	7 days
Bioplastic Gluten	50 days
Synthetic plastic	> 50 years

Genesis 1:28, "And God blessed them. And God said to them, "Be fruitful and multiply and fill the earth and subdue it and have dominion over the fish of the sea and over the birds of the heavens and over every living thing that moves on the earth.'" (ESV)

Figure 13. Decomposition of different bioplastics made from starches and the biblical importance of green chemistry. [15]

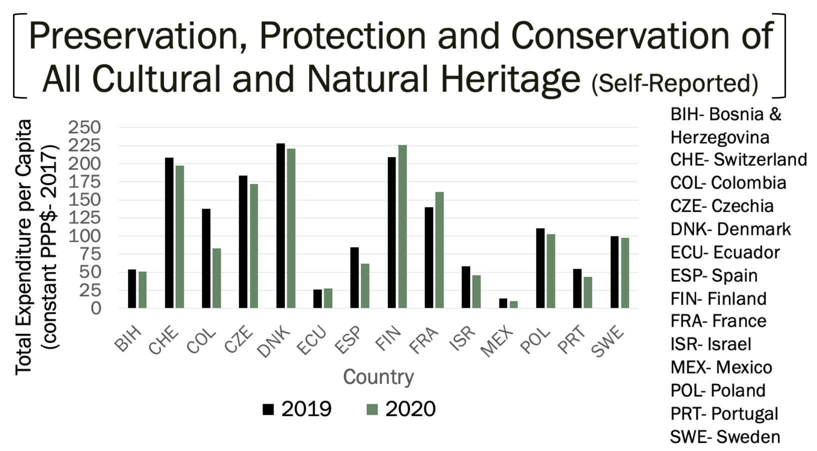


Figure 14. Determination of marketability of innovations in art conservation based on self-reported data from UNESCO (United Nations Education, Scientific and Cultural Organization). [9]

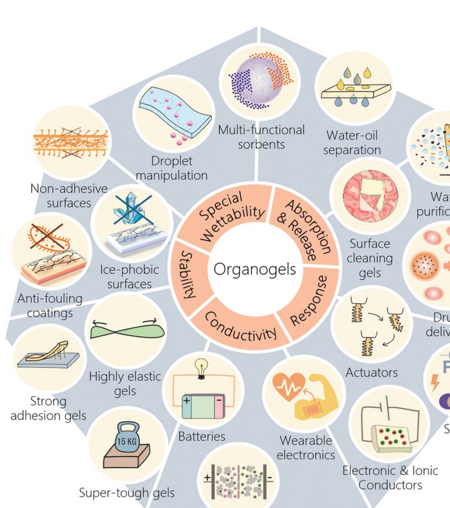


Figure 15. Different applications of organogels for marketability. [6]

Results and Conclusions

Literature Search

The keywords "green", "hydrogel", "organogel" and "biopolymer" (only used for ScienceDirect) were chosen for the search queries in SciFinder and ScienceDirect for the general research topic of "green" gels used in art conservation. The main research articles chosen, on PVA/PVP and PVA/RS were from the University of Florence and the Center for Colloid and Surface Science (CSGI). Based on these articles the research topic was then narrowed down to alternative starches for PVA/starch complexes for the tailored cleaning of artifacts.

Biblical Integration

•bārā' (בָּרָא, "he-created"):

Bara is used 54 times in the Old Testament, including 11 times in Genesis. The first example is in Genesis 1:1: "In the beginning, God created the heavens and the Earth" (ESV). God is the only one capable of creating from nothing. However, Genesis 1:27 "So God created man in his image, in the image of God he created him…" (ESV) shows that we who are made in his image can create art that uses and reflects God's creation.

•Stewardship:

Genesis 1:28 says, "And God blessed them. And God said to them, "Be fruitful and multiply and fill the earth and subdue it and have dominion over the fish of the sea and over the birds of the heavens and over every living thing that moves on the earth.'" (ESV). We are called to be good stewards of the earth, so it should be a goal to develop "greener" alternatives in industry.

Future Work

Future research can be done on other applications of organogels. One such application is the use of the PVA/RS complex as a polystyrene substitute in packaging. Rigidity can be changed by manipulating the G% by use of different amylose and amylopectin ratios, as seen in **Figure 8.** Rigidity can also be changed by using the cast-drying method (CD) or by changing the number of freeze-thaw (FT) cycles. [4]

Another application is in the field of medicals gels. Rosciardi et al. (2024) showed initial research into a PVA-hydantoin/starch hybrid gel used to reduce the activity of *Bacillus subtilis*. [18]

References

[1] Bonelli, N., Poggi, G., Chelazzi, D., Giorgi, R., & Baglioni, P. (2019). Poly(vinyl alcohol)/poly(vinyl pyrrolidone) hydrogels for the cleaning of art. *Journal of Colloid and Interface Science, 536*, 339-348. 10.1016/j.jcis.2018.10.025

[2] Baglioni, P., Berti, D., Bonini, M., Carretti, E., Dei, L., Fratini, E., & Giorgi, R. (2014). Micelle, microemulsions, and gels for the conservation of cultural heritage. *Advances in Colloid and Interface Science, 205*, 361-371. 10.1016/j.cis.2013.09.008

[3] Rosciardi, V., Chelazzi, D., & Baglioni, P. (2022). "Green" biocomposite Poly (vinyl alcohol)/starch cryogels as new advanced tools for the cleaning of artifacts. *Journal of Colloid and Interface Science, 613*, 697-708. 10.1016/j.jcis.2021.12.145

[4] Robyt, J. (2008). Starch: Structure, Properties Chemistry, and Enzymology. In: Fraser-Reid, B.O., Tatsuta, K., Theim, J. (eds) *Glycoscience*, 1437-1472. 10.1007/978-3-540-30429-6_35

[5] Rosciardi, V., & Baglioni, P. (2023). Role of amylose and amylopectin in PVA-starch hybrid cryo-gels networks formation from liquid-liquid phase separation. *Journal of Colloid and Interface Science, 630*, 415-425. 10.1016/j.jcis.2022.10.092

[6] Kuzina, M. A., Kartsev, D. D., Stratonovich, A. V., & Levkin, P. A. (2023). *Organogels versus Hydrogels: Advantages, Challenges, and Applications*. Wiley. 10.1002/adfm.202301421

[7] https://www.sigmaaldrich.com/US/en/product/aldrich/341584

[8] By NEUROtiker - Own work, Public Domain, https://commons.wikimedia.org/w/index.php?curid=3784899

[9] https://uis.unesco.org/en/news/unesco-institute-statistics-releases-data-and-key-findings-cultural-and-natural-heritage

[10] By Elías García Martínez - http://epdlp.com/cuadro.php?id=4316, Public Domain, https://commons.wikimedia.org/w/index.php?curid=37611657

[11] By Cecilia Giménez - https://www.nytimes.com/2012/08/24/world/europe/botched-restoration-of-ecce-homo-fresco-shocks-spain.html, Fair use, https://en.wikipedia.org/w/index.php?curid=54153025

[12] Judawisastra, H., Sitohang, R. D. R., Marta, L., & Mardiyati. (2017). *Water absorption and its effect on the tensile properties of tapioca starch/polyvinyl alcohol bioplastics*. IOP Publishing. 10.1088/1757-899x/223/1/012066

[13] Yang, M., Chang, L., Jiang, F., Zhao, N., Zheng, P., Simbo, J., Yu, X., & Du, S. (2022). Structural, physicochemical and rheological properties of starches isolated from banana varieties (Musa spp.). *Food Chemistry: X, 16*, 100473. 10.1016/j.fochx.2022.100473

[14] https://nypost.com/2016/03/12/infamous-botched-jesus-painting-now-a-major-tourist-attraction/

[15] Wahyuningtiyas, N. E., & Suryanto, H. (2018). *Properties of Cassava Starch based Bioplastic Reinforced by Nanoclay*. State University of Malang (UM). 10.17977/um016v2i12018p020

[16] Bernal-Chávez, S. A.,et al. (2023). *Enhancing chemical and physical stability of pharmaceuticals using freeze-thaw method: challenges and opportunities for process optimization through quality by design approach*. Springer Science and Business Media LLC. 10.1186/s13036-023-00353-9

[17] https://joshuaproject.net/countries/IT#Religions

[18] Rosciardi, V., Bandelli, D., Bassu, G., Casu, I., & Baglioni, P. (2024). Highly biocidal poly(vinyl alcohol)-hydantoin/starch hybrid gels: A "Trojan Horse" for Bacillus subtilis. *Journal of Colloid and Interface Science, 657*, 788-798.10.1016/j.jcis.2023.11.142