Optimising Resin and Fumed Silica Infills for Porcelain Conservation

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Abstract:
This project investigates the impact of fumed silica on the long-term properties of two-part epoxy resins, with specific focus on colour stability, chemical structure, and adhesive strength. The research was carried out in two phases. The first phase artificially aged blocks of resin to view long-term colour change. The second phase artificially aged porcelain tiles repaired with the resin before strength testing was completed. I intend to publish the results in a conservation subject journal and cannot disclose results, however visual trends did emerge. Through the project I developed my time management skills and will use these during my final year of studies to improve my project execution. I enjoyed my experience with the Undergraduate Research Opportunities Scheme (UROS) and hope to complete more research projects in the future.

Keywords: ceramics conservation, artificial ageing, epoxy resin, UV stability, heritage science

Introduction

This project was funded by the Undergraduate Research Opportunities Scheme (UROS) at the University of Lincoln and investigates optimising the use of fumed silica for stabilising the colour of epoxy resin during ageing. Epoxy resins are used by ceramics conservators to repair breaks and can also be used as a fill material for areas of loss, however they often discolour with age and there is limited successful research in ways to stabilise the material. I proposed the project to my supervisor and applied for the UROS funding to allow me to complete my research during the summer of 2023. The project was supervised by Lynda Skipper, with technical support provided by the conservation lab technicians.

The article explores the methodology used as well as discussing and reflecting on the lessons I learned during the project. It also offers recommendations for other students completing similar research projects.

Project Background

My research has been informed by two modules I took during my second year studying Conservation of Cultural Heritage. The first was *Applied Practical Skills* where I worked on a porcelain cup that had been broken into 37 pieces with large areas of loss. It had previously been repaired, but the adhesive had deteriorated over time. I repaired the cup and created translucent supporting fills using a two-part epoxy resin with fumed silica as a bulking agent.

The second module that informed my UROS project was *Analytical Techniques* where I carried out an independent research project using techniques I had learned in the module. As I was interested in the ageing properties of the fill material that I had chosen for my porcelain cup, I sought to artificially age surrogate samples to investigate the long-term colour stability of my selected materials. Resource limitations and methodological challenges showed me that there was plenty of scope to continue the project further.

As such, my research aim for my UROS project was to investigate the optimal amount of fumed silica to add to a two-part epoxy resin, taking into account various properties. Firstly, the resin should be colourless and not discolour over time. Secondly, the resin should be strong enough to hold porcelain fragments together without breaking, while not being too strong as this could damage the ceramic further. Thirdly, the adhesive must be able to be drawn along the break edge via capillary action to ensure good adhesion.

My personal goals for the research included: gaining experience with scientific techniques and research, developing project execution skills including time management and planning, and sharing technical information in accessible ways.

Literature Review

Ceramics have different properties depending on the temperature at which they were fired. Therefore, when choosing adhesives for ceramics conservation, properties such as shrinkage, viscosity, reversibility, cure time, strength, and colour stability must be considered (Buys & Oakley, 1993). The adhesive should also be weaker than the material it is bonding to, so that the adhesive fails first in the event of a future breakage, reducing the risk of new breaks in the original material.

High-fired ceramics such as porcelain are non-porous, so during conservation a low-viscosity adhesive is applied in small beads between break edges and then gets drawn into the break via capillary action to ensure complete contact between pieces (Ashley-Smith & Newey, 1992).

A recent international survey of 139 ceramics conservators resulted in 116 responses saying that they use epoxy resins when bonding ceramics (Conceição, 2022). Epoxy resins are clear, low-viscosity adhesives that cure at an appropriate rate for capillary action and do not shrink (Oakley & Jain, 2002), (Acton & McAuley, 1996).

Conservation materials with a lifetime lower than 20 years are considered “unstable or fugitive” (figure 1) (Feller, 1994). Unfortunately, epoxy resins are prone to yellowing with age, with some resins becoming visibly yellow after the equivalent of 7 years in a museum (Coutinho, et al., 2008).

Class	Classification	Intended useful lifetime	Approximate equivalent standard of photochemical stability
T	Materials in temporary contact	Less than 6 months?	–
C	Unstable or fugitive	Less than 20 years	BS1006 class 3 or less
B	Intermediate	(20–100 years)	(3 to 6)
A	Excellent	(A2?) greater than 100 years	Greater than BS1006
		(A1?) greater than 500 years	?

Figure 1 Feller’s 1975 Standards of Intended Use and Photochemical Stability for Materials in Conservation (Feller, 1994)

There is limited research about improving the colour stability of epoxy resins, although a 2001 review summarised that while some stabilising additives may reduce yellowing, the impact varied between resin types and would need further research before application to conservation (Down, 2001). However, research in adjacent fields suggests that fumed silica could act as an ultra-violet light (UV) barrier and had a positive impact on the ageing of bitumen samples (Cheraghian & Wistuba, 2021). Fumed silica is currently used as a bulking agent in epoxy resins for ceramic fills (Oakley & Jain, 2002). Additionally, my previous research suggested that the addition of fumed silica to epoxy resins could have applications to ceramic conservation for use of resins as an adhesive. However, further research had to be completed before any conclusions could be formed.

Methodology

A two-part epoxy resin was mixed with six different amounts of fumed silica to investigate the optimal concentration for long-term colour stability, chemical structure, and strength of resin samples.

The resin was prepared according to manufacturer instructions and fumed silica was weighed to the nearest 0.01g using electronic scales.

Phase One: Colour Stability and Chemical Structure

Identical resin samples were created by pipetting resin into hexagonal silicone moulds (figure 2). Two batches were created at different times to allow for sample repeats to identify potential outliers.

Figure 2 Two labelled silicone moulds with hexagonal resin blocks.

After curing, the samples were artificially aged for up to the equivalent of 120 years in the ClimaCell 111 chamber under UV light at standard museum conditions. One resin sample from each of the six test groups was removed at each age being investigated.

The colour of each sample was then measured using a Konica Minolta Spectrophotometer CM-2600d. Five measurements were taken for each sample before calculating an average. All data was recorded and imported to SPSS where it was analysed and converted to a 3D scatterplot graph.

To investigate the chemical structure of the samples, Fourier-transform infrared spectroscopy (FTIR) was carried out using the Agilent 4300 FTIR using the MicroLab PC software to collect the data and Spectragryph 1.2 to analyse the data.

Phase Two: Adhesive Strength
Identical porcelain samples were created and broken in half using a hammer and chisel to simulate a natural break edge. Each sample had a small hole along the top edge in the centre to allow for strength testing.

After breakage, the samples were prepared for the addition of resin using thin sheets of dental wax to create a channel between the two halves (figure 2). The six resin groups were added to the channels using a pipette then left to cure. Some resin leaked and had to be topped up while the samples were being prepared.

Figure 3 The researcher preparing porcelain samples.

Once they had cured, the dental wax and excess resin was removed from the porcelain samples before being artificially aged following the same procedure as phase one. The strength testing was then completed by clamping the sample at one end and attaching an s-shaped hook through the pre-made hole. Weights were then added in 20g increments until the sample broke, allowing a few seconds between each new weight to allow the sample to settle (figure 4).

Figure 4 The researcher adding a weight to a clamped porcelain tile.

Results

As my research has applications to ceramics conservation, I intend to publish my full results in a conservation-specific journal.

Interim results indicate that after artificial ageing of my resin samples, some clear visual trends have emerged, although I will be carrying out statistical analysis to understand if my results are significant. Additionally, the trends I found appear consistent across both batches of samples which is promising in terms of reliability and repeatability.

The results from artificially ageing the porcelain samples were less consistent. While the samples all broke in similar ways, the weight they supported before breaking was highly inconsistent. The differences in the sample characteristics may explain some of these variations, so I will be collecting additional data to compare similar samples.

Discussion

Lessons learned

Completing my UROS project gave me a valuable insight into scientific research and materials science. Before beginning my project, I had identified time management and project execution as areas I wanted to develop. While I have improved these skills through my experience with UROS, I still have room for improvement.

One of the key lessons I have learned is that, while having a clear plan is useful, it is important to not get stuck in the details as this can delay the project unnecessarily. I knew that the artificial ageing would take a long time and I wanted to make sure that I avoided making mistakes. However, this ultimately meant that I took a long time deciding on the specific details meaning I was eventually forced to make a decision or risk not completing my project. Understanding that research exists to inform the next step allowed me to give myself permission to make choices about the samples I would need and move on to the next phase. Learning this early on in the project helped me keep momentum through the remaining stages and ultimately complete my research to a standard I am proud of.

Completing my research also helped me learn how to adapt plans to changing circumstances. I had originally hoped to use both visible light and UV light when artificially ageing the samples, however due to limitations of the ageing chamber I had to choose between the two light types. I therefore reviewed my research aims and decided on UV light. Although I worked independently, being able to confirm my plans with my research supervisor and the conservation lab technicians was invaluable. Having support from experienced staff gave me more confidence in my choices and allowed me to learn a number of new skills, including using FTIR and carrying out longer academic research projects with long-term deadlines.

Challenges

Throughout the project, I also faced a number of methodological challenges. As I was weighing fumed silica to the nearest 0.01g, the weighing scales did not always register the weight accurately, so I mitigated this impact by creating two batches of resin. Additionally, when breaking the porcelain samples in half, a number of them broke incorrectly, meaning I had fewer samples than I had originally planned, despite creating plenty of spare tiles.

My biggest challenge was in planning how long each project phase would take. I had to adjust my plans for artificial ageing a number of times to ensure I was using the chamber as efficiently as possible. I had originally planned to use the ageing chamber for six weeks with visible light. However, I eventually reduced this to one week using UV light by optimising my use of the chamber and leaving some samples in overnight instead of taking them out each day.

Phase 2 took a lot longer than I had anticipated as I had to remove more excess resin than planned, and the samples held significantly more weight than I had expected which meant that the strength testing also took more time. However, in both instances, once I had established how long one sample group took, I was able to accurately adjust my plans and ensure that I still had time to finish my project.

Next steps

There are a number of options for future research, including different resin types, different artificial ageing methods, different ceramic types and thicknesses, and different additives and stabilisers.

Completing the UROS project has helped me realise that research is a career I could pursue further as I enjoyed the work I have done and there is plenty of scope to continue my research. In the immediate future, I could continue similar research in my undergraduate dissertation or potentially expand it into a Masters project. More long-term options could involve a career in conservation science or academic research, however I am not fully decided on this at present.

Conclusion

Overall, I have thoroughly enjoyed my experience with UROS and I would highly recommend it to students who are interested in research. I believe it would especially benefit students approaching their final year of study as it has helped me develop my project management skills and better understand what my strengths and current limitations are. This means I know what support to ask for as I go into my final year which will help me achieve the results I want.

For students considering a research project like UROS, I would recommend allowing plenty of time to finish everything. Giving myself several weeks of buffer time meant that when things did not go to plan, I was still able to finish everything on time. Additionally, keeping track of what you do and how long things take will help you better manage your time in the future. I knew before I started that I need time to process new stages which meant I gave myself enough leeway when planning. This summer, I learned that I need to limit the amount of time I spend planning, especially once I have collected the sources and outlined the project.

Finally, UROS should be something you enjoy and learn from. Ambition is not a bad thing, but perfect research does not exist, and your mental and physical health is more important. It is okay to step back and give yourself permission to move on to the next thing, even if the next thing is to take some time off and start again later.

References

References

Acton, L. & McAuley, P., 1996. *Repairing Pottery and Porcelain.* London: Herbert Press.

Ashley-Smith, J. & Newey, C., 1992. *Science for Conservators Volume 3: Adhesives and Coatings.* 2 ed. London: Routledge.

Buys, S. & Oakley, V., 1993. *Conservation and Restoration of Ceramics.* Oxford: Elsevier Butterworth-Heinemann.

Cheraghian, G. & Wistuba, M., 2021. Effect of Fumed Silica Nanoparticles on Ultraviolet Aging Resistance of Bitumen. *Nanomaterials,* 11(2), p. 454.

Conceição, L. C., 2022. *Filling in the Gaps: the conservation and restoration of a Ming dynasty porcelain dish from the Monastery of Santa Clara-a-Velha,* Lisbon: Nova University Lisbon.

Coutinho, I, Lima, A, Braz Fernandes, FM & Ramos, AMM 2009, Studies on the Degradation of Epoxy Resins Used for the Conservation of Glass. in J Ambers, C Higgitt, L Harrison & D Saunders (eds), Holding it All Together, Ancient and Modern Approaches to Joining Repair and Consolidation. Archetype Publications, London, pp. 127-133.

Down, J., 2001. Review of CCI research on epoxy resin adhesives for glass conservation. *Studies in Conservation,* 46(sup1), pp. 39-46.

Feller, R., 1994. *Accelerated Aging: Photochemical and Thermal Aspects.* Michigan: Getty Conservation Institute.

Oakley, V. & Jain, K., 2002. *Essentials in the Care and Conservation of Historical Ceramic Objects.* London: Archetype Publications Ltd..