Thermally and photochemically re-workable epoxy adhesives for use in artifact repair

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Introduction: Epoxies are commonly used to repair ceramic and glass cultural materials. Current epoxies have superior strength but are non-reversible after they have cured. We have tailored two epoxies: one that is reversible by applying heat and another by ultra violet light, transforming the cured epoxy from a solid to a liquid state. This quality of reversibility utilizes the desirable mechanical properties of epoxies and adapts them to benefit the conservation community.

Project objectives: Epoxies used for conservation must be optically clear, have low viscosity before cure, maintain mechanical strengths similar to non-reversible commercial epoxies, and refrain from yellowing over time. Our current major objectives are to produce an optically clear and low viscosity thermally-reversible epoxy through compound purification and addition of flexible chemical linkages.

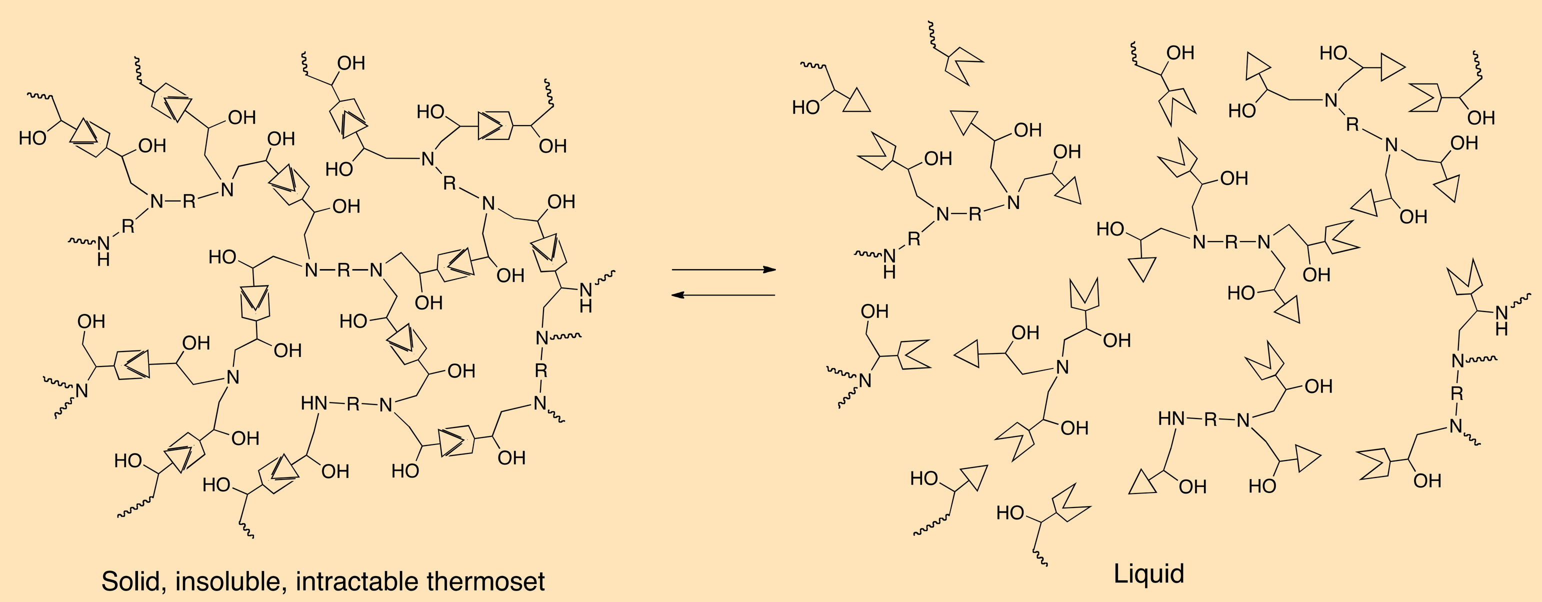

Figure 1: Schematic of solid epoxy structure with weak links intact and liquid epoxy structure with weak links detached

Background: Epoxy reversibility is achieved by incorporating weak links into the epoxy chemical structure which break apart upon exposure to a stimulus (Figure 1). Thermal weak links are governed by Diels-Alder reactions and ultraviolet weak links are governed by coumarin dimer reactions. At temperatures below 90 °C the Diels-Alder weak link will remain intact and the epoxy will be solid. At temperatures above 90 °C the Diels-Alder weak link will dissociate to produce a liquid epoxy (Figure 2). Similarly, exposure to light wavelengths below 300 nm will cause the coumarin dimer weak link to break apart and the epoxy to liquefy (Figure 3).

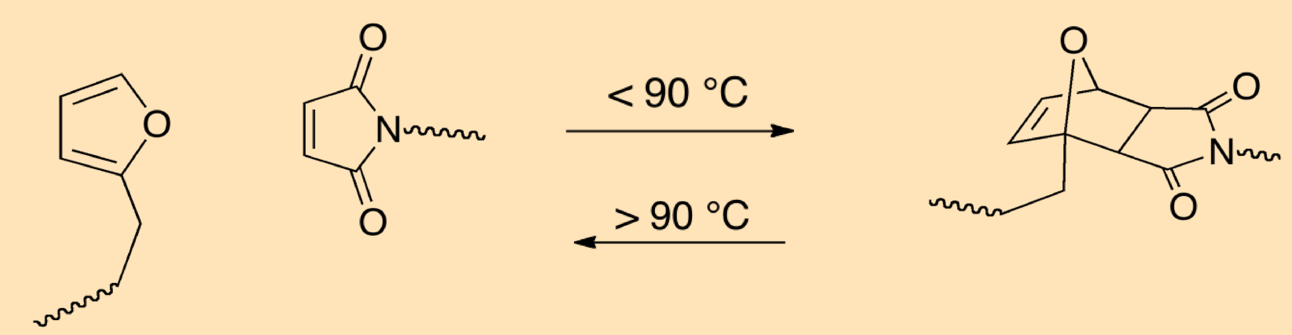

Figure 2: Diels-Alder reaction incorporated into epoxy. Epoxy is solid at temperatures below 90 °C and liquid above 90 °C

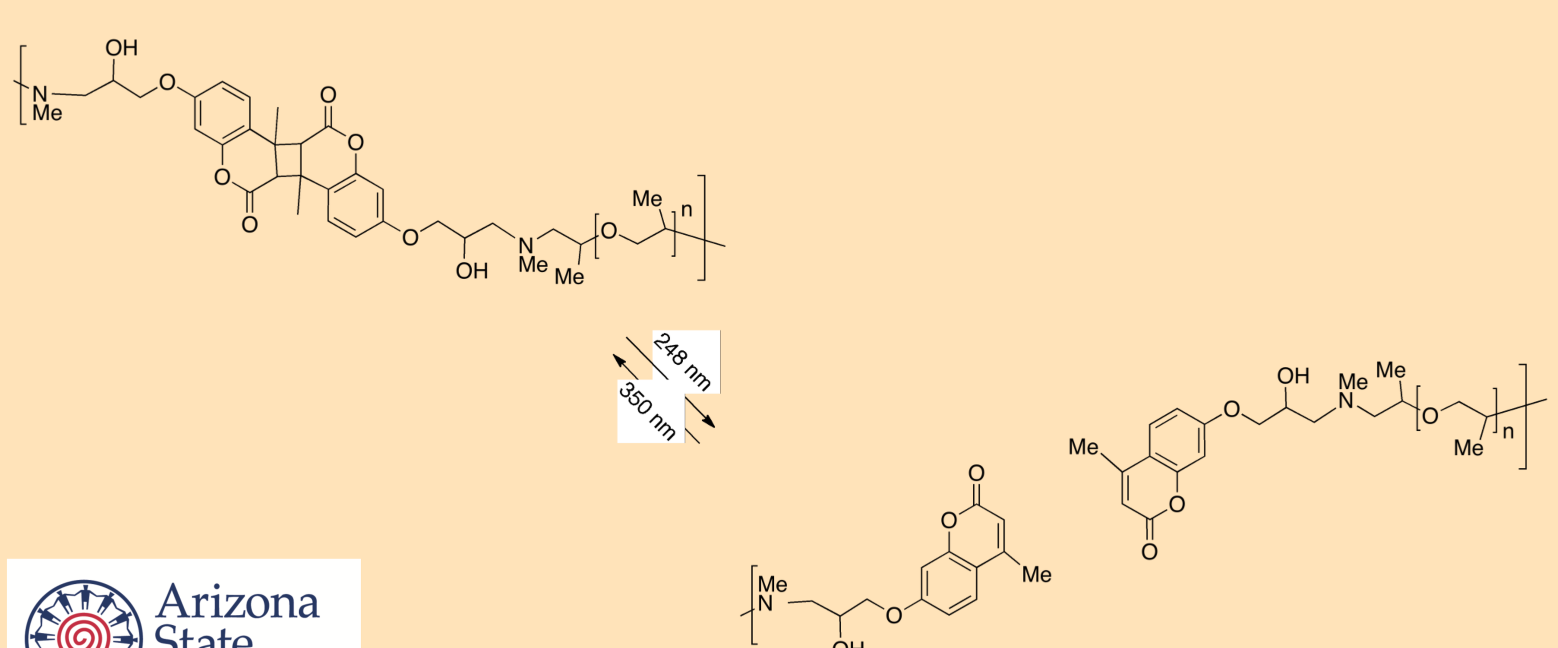

Figure 3: Coumarin dimer reaction incorporated into epoxy. Epoxy is solid at wavelengths above 300 nm and liquid at wavelengths below 300 nm

Methodology for synthesizing a clear, low viscosity thermally-reversible epoxy:

(1) Original epoxy resin: synthesized using 1,1'-(Methylenedi-4,1-phenylene) bismaleimide and furfuryl glycidyl ether. The resulting product (before cure) was a brown, glassy solid (Figure 4).

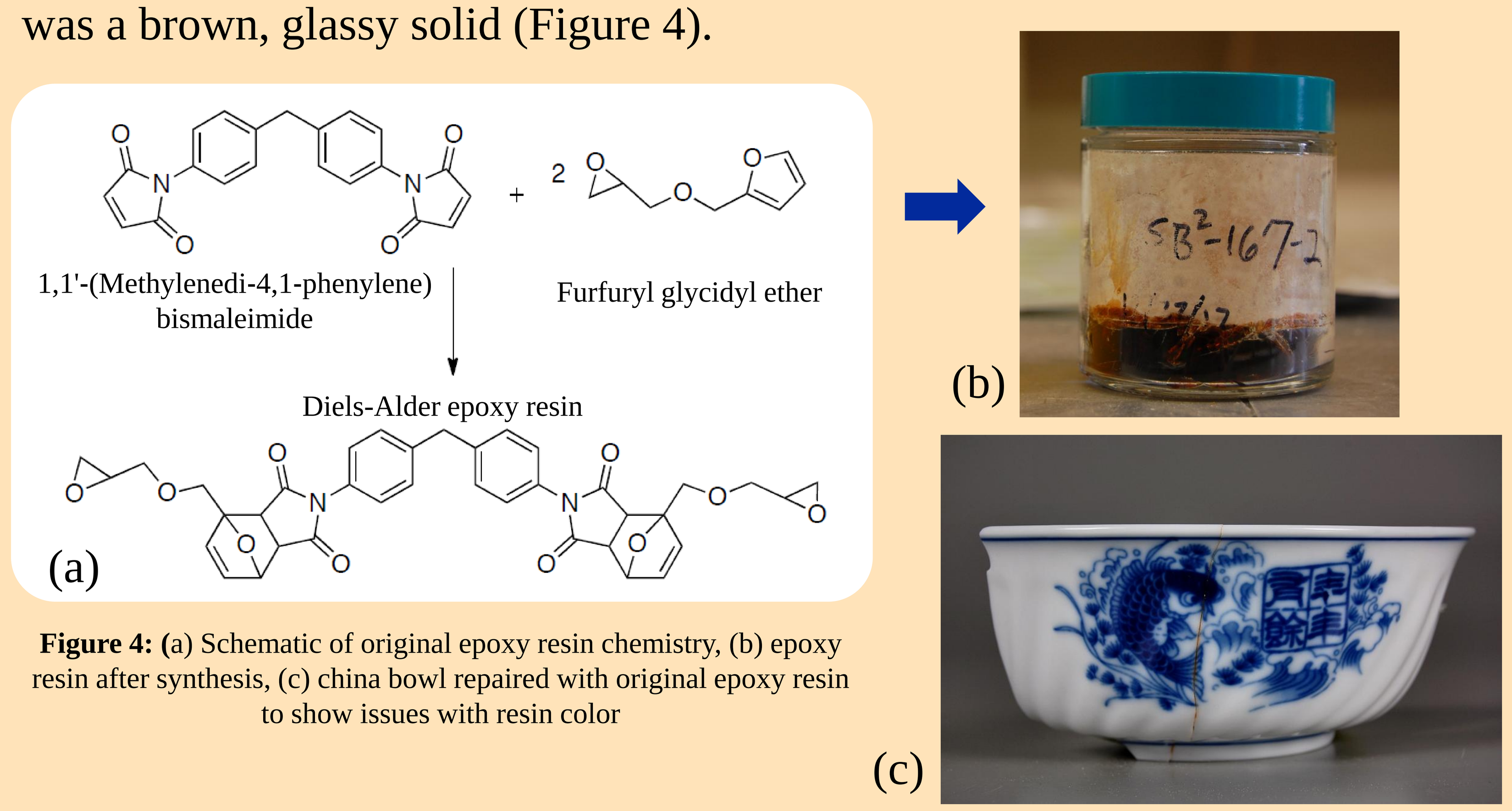

Figure 4: (a) Schematic of original epoxy resin chemistry, (b) epoxy resin after synthesis, (c) china bowl repaired with original epoxy resin to show issues with resin color

Figure 5: Original and purified furfuryl glycidyl ether

(2) The furfuryl glycidyl ether was purified by vacuum distillation to remove color (Fiigure 5). Original furfuryl on left, purified furfuryl on right.

(3) The 1,1'-(Methylenedi-4,1-phenylene) bismaleimide was purified by filtration and recrystallization to remove color. (Figure 5, center)

(4) Alternatively, the 1,1'-(Methylenedi-4,1-phenylene) bismaleimide was substituted with purified 1,6-hexylenebismaleimide (Figure 6) to remove color and reduce the epoxy resin viscosity (Figure 5, right)

Figure 5: Color comparison between original phenylene bismaleimide (left), purified phenylene bismaleimide (center), and hexylene bismaleimide (right)

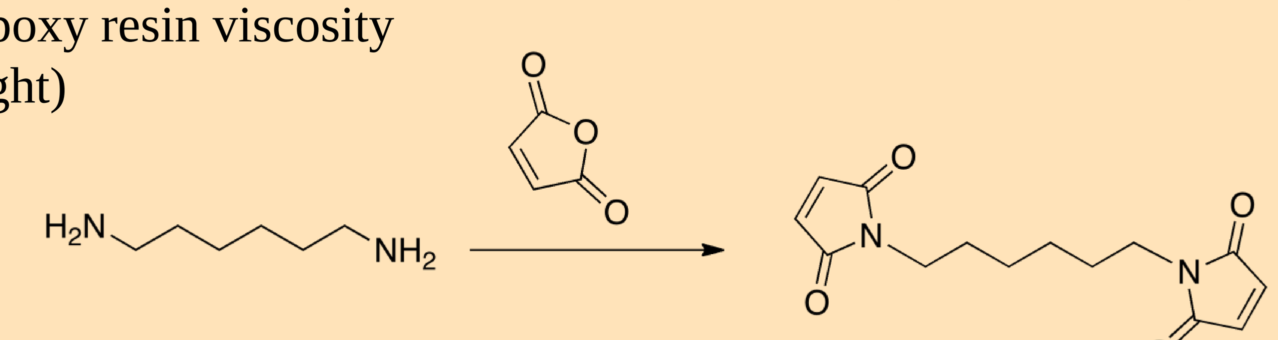

Figure 6: Schematic of 1,6-hexylenebismaelimide chemical structure

(5) Two new epoxy resins were synthesized, shown in comparison with the original epoxy resin : (a) Purified 1,6-hexylenebismaleimide combined with purified furfuryl glycidyl ether which produced a waxy, light yellow epoxy resin; (b) Original brown and glassy epoxy resin with unpurified components; (c) Purified 1,1'-(Methylenedi-4,1-phenylene) bismaleimide combined with purified furfuryl glycidyl ether which produced a yellow glassy solid (Figure 7).

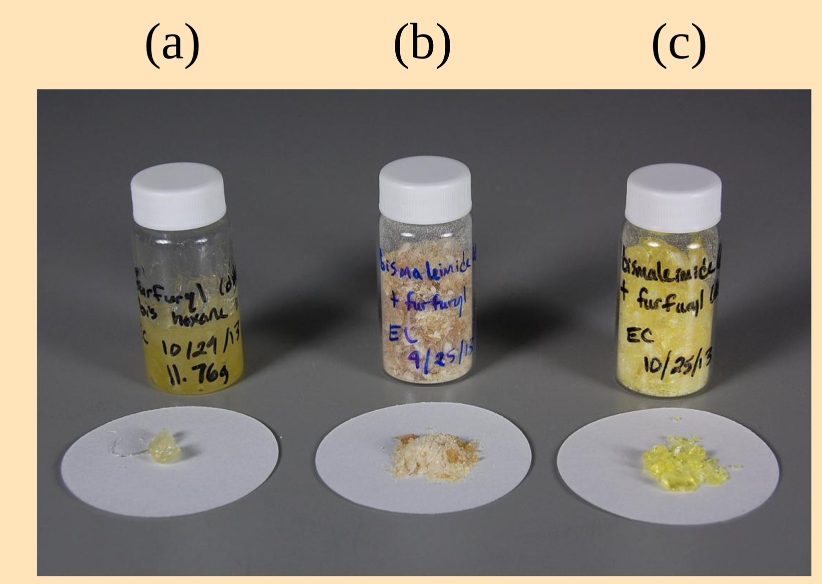

Figure 7: Epoxies synthesized from purified and unpurified components.

Results and Conclusions: We were able to synthesize an epoxy resin which thermally reversed from a solid state to a liquid at 90 °C, and improved the original color and viscosity through purification and substitution of the resin components. Synthesis and purification of the UV reversible epoxy is currently in progress.

Future Work: It is necessary to lower the viscosity of the epoxy resin even more and to completely remove color. This will be done by incorporating flexible siloxane bonds into the bismaleimide component and synthesizing an epoxy resin with this precursor.(Figure 7).

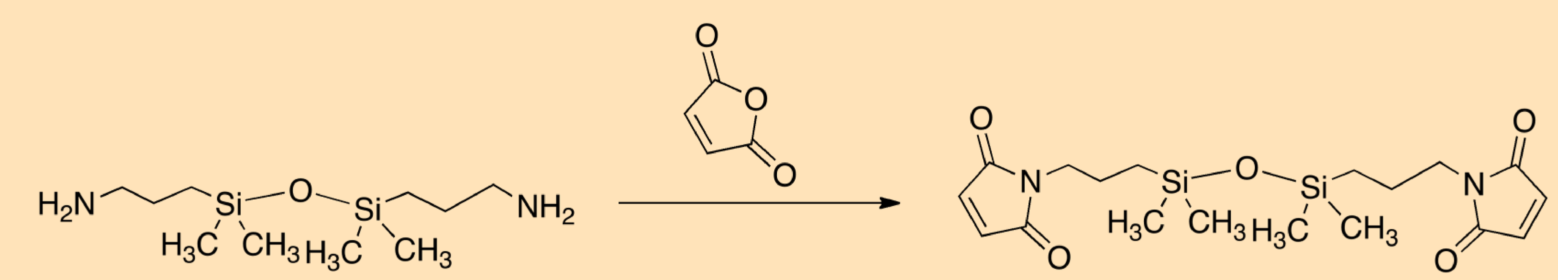

Figure 8: Schematic for siloxane bridged bismaleimide

It is also necessary to cure our epoxy, test its mechanical strength, and compare it with commercial epoxies commonly used in conservation. Such tests are currently being performed using lap shear samples on aluminum coupons and an MTS tensile mechanical tester (Figure 8).

Figure 9: MTS Criterion mechanical testers available in the materials science and engineering department at the University of Arizona

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