

A Tough Hydrogel Adhesive for the Repair of Archeological Pottery

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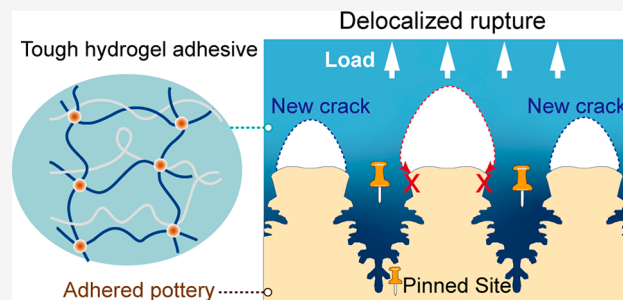
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ABSTRACT: Pottery is the oldest art and plays a landmark role in human civilization. The repair of ceramic relics often uses acrylic resins and cyanoacrylate adhesives. However, existing adhesives often take hours to get cured, and wet adhesion is not possible. We herein propose a redox initiator-triggered hydrogel adhesive, of which robust ($\sim 700 \text{ J m}^{-2}$) and wet adhesion with potsherds can be achieved within a few seconds. The high toughness lies in the self-limited delocalized rupture of the porous interface, and the wet adhesion is due to the hydrophilic precursor and its free radical polymerization. The hydrogel adhesive also exhibits high aging resistance for stable preservation of ~ 400 annuals. We have applied the adhesive to the restoration of artifacts excavated from Yinxu, Anyang ($\sim 1300 \text{ BC}$) and the Xia Jiao Shan site ($\sim 4000 \text{ BC}$, Neolithic), and the adhesive is expected to be extended to applications beyond archeology.

KEYWORDS: Hydrogel, redox initiator, heritage restoration, wet adhesion, self-limited rupture



Archeological ceramics provide valuable information to understand the early settlements, diet, economic level, and artistic development of human beings.^{1–3} About 20,000 years ago, early humans started to fire clay to form vessels and other tools to free them from the dependence on natural tools.⁴ Most ancient ceramics, including earthenware, terracotta, and unfired clay, have been broken into shreds and lost their original shapes, and repairing the ceramic fragments to reproduce complete ware is the most widely used way to conserve and bond ceramic objects of historical value.^{5,6}

The bonding of potsherds often uses polymer adhesives.⁷ The early adhesive for pottery repair is cellulose nitrate,⁸ but this material is readily deteriorated and has been replaced by the durable Paraloid B72 and other adhesives with stronger chemical bonds.⁹ These adhesives, however, can still not well meet the requirements for the conservation and restoration of ceramic relics. First, such adhesives take a long time to get cured because time-consuming processes are involved, such as slow solvent evaporation, anionic polymerization with a few active centers, and cross-linking reaction with high activation energy.¹⁰ Second, tough and strong adhesion is required to sustain gigantic wares such as the Terra Cotta Warriors, whereas traditional adhesives (e.g., Paraloid B72 and ethyl cyanoacrylate, ECA) are too brittle to achieve robust interfaces because of their linear or single-networked chain structure.¹¹ Third, existing adhesives are water-insoluble, and thus they cannot be used to repair hydrated sherds unless the sherds are transferred for drying. However, this additional process will disturb the shape and relative positions of the pottery pieces. Therefore, the archeology world requires an adhesive with rapid, robust, and wet adhesion.

Bioadhesive hydrogels have been a class of emerging materials in tissue engineering and bioelectronics because they can form robust interfaces with wet biotissues within a few seconds.^{12–15} The exciting properties of bioadhesive hydrogels inspire us to use hydrogels in archeological applications. Hydrogels have been used for the cleaning of contemporary paintings and exhibited high efficiency, safety, and selectivity.¹⁶

Herein, we report a tough hydrogel adhesive (THA) to bond potsherds and other archeological relics with porous surfaces. Due to the low activation energy of the decisive step in the redox polymerization, the THA can cure within 5 s. The THA is an interpenetrating polymer network (IPN) of hydroxyl-rich poly(vinyl alcohol) (PVA) and amide-rich cross-linked polyacrylamide (PAAm), for which the precursor solution can penetrate in the micropores, forming dense hydrogen bonds with the sherds surface, either dry or wet. In addition, the interaction of the soft THA and the hard microporous ceramic material significantly toughens the interface, preventing catastrophic interfacial failure. Furthermore, the THA is predicted to have a long service time of at least 400 annuals (a.) at standard conservation conditions. We have applied our THA to repair earthenware excavated in Yinxu, Anyang ($\sim 1300 \text{ BC}$, the Capital of the Shang Dynasty

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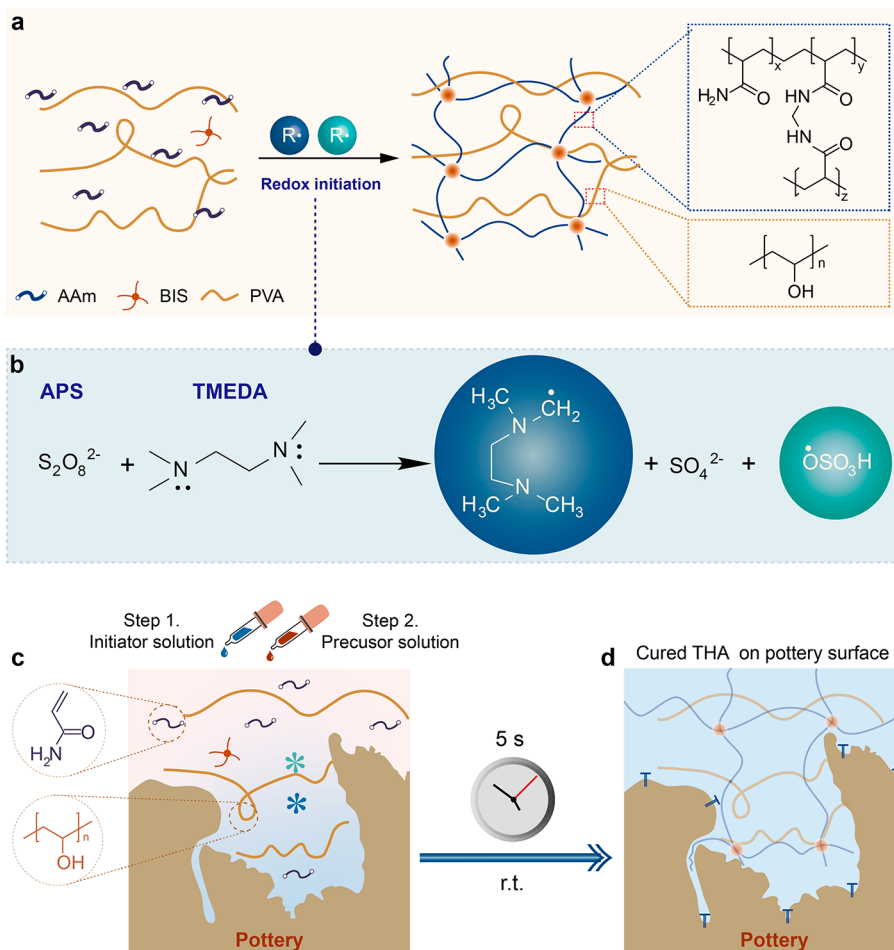


Figure 1. Fabrication and structure of the THA. (a) Mechanism of the curing of the THA and its molecular structure. (b) Redox initiating system that is used to trigger the curing of the THA. (c) Procedure of using the THA in repairing pottery and the molecular structures of the main components. (d) Interface between the cured THA and the pottery surface.

located in Anyang) and the Xia Jiao Shan site (~4000 BC, Neolithic), which have a long history of thousands of years. We expect that our adhesive will find much broader applications beyond archeology.

The THA is a two-part adhesive: part A is an ammonium persulfate (APS) aqueous solution, and part B consists of a precursor solution composed of monomer acrylamide (AAm), mechanical enhancer PVA, cross-linker methylene-bis-acrylamide (BIS), accelerator *N,N,N',N'*-tetramethylethylenediamine (TMEDA), and solvent water. When the part A and part B solutions are successively applied on the ruptured surface of pottery sherds, polymerization of AAm is triggered, and the cross-linked PAAm and PVA form an interpenetrating polymer network (IPN). The IPN consists of single-networked PAAm and linear-structured PVA, of which the molecular structures are shown in Figure 1a. In the system, the APS in part A and the TMEDA in part B form a redox initiating system to trigger the *in situ* polymerization of AAm (Figure 1b), which is the decisive step for the reaction, and its role will be discussed hereinafter. Practically, the part A solution with a low viscosity is first coated on the fractured sherd surface to allow the solution to penetrate the micropores, and the part B solution with a higher viscosity is then applied to the initiator for polymerization (Figure 1c). It takes a few seconds (~5 s) for the solution to cure and form self-limited structures with the pottery surface (Figure 1d). The adhesive property is

determined by both the chemical and mechanical properties of the IPN, as well as the unique topological morphology of the potsherd surface.

It takes only a few seconds to join two sherds together using the THA. High initial viscosity and fast chain initiation rate are necessary conditions for self-accelerated radical polymerization and rapid gelation.¹⁷ We introduced 10 wt % PVA aqueous solution as a thickener in the precursor solution to give the system a high viscosity of 0.114 Pa s (298 K) at the beginning, endowing the precursor solution a high self-accelerating tendency and curing rate (Supplementary Figure 1).

The decomposition of the initiator is the decisive step in free radical polymerization, while traditional systems are limited by high initiation activation energy (~105–150 kJ mol⁻¹) and cannot polymerize rapidly at room temperature (Supplementary Table 1).¹⁸ Here, we use the APS-TMEDA redox initiation system to construct a fast-curing adhesive. With the application of the redox initiator, the gel transition of the THA occurs in 1.7 s, and adequate adhesive strength can be achieved within 5 s (Supplementary Figure 2). Furthermore, the curing time can be tuned on demand by controlling the concentration of the TMEDA in part B (Supplementary Figure 3). Such rapid curing can be achieved over a wide range of repair temperatures. We operated the THA at different temperatures, in a refrigerator at 7.5 °C or in an oven at 42 °C, to bond the

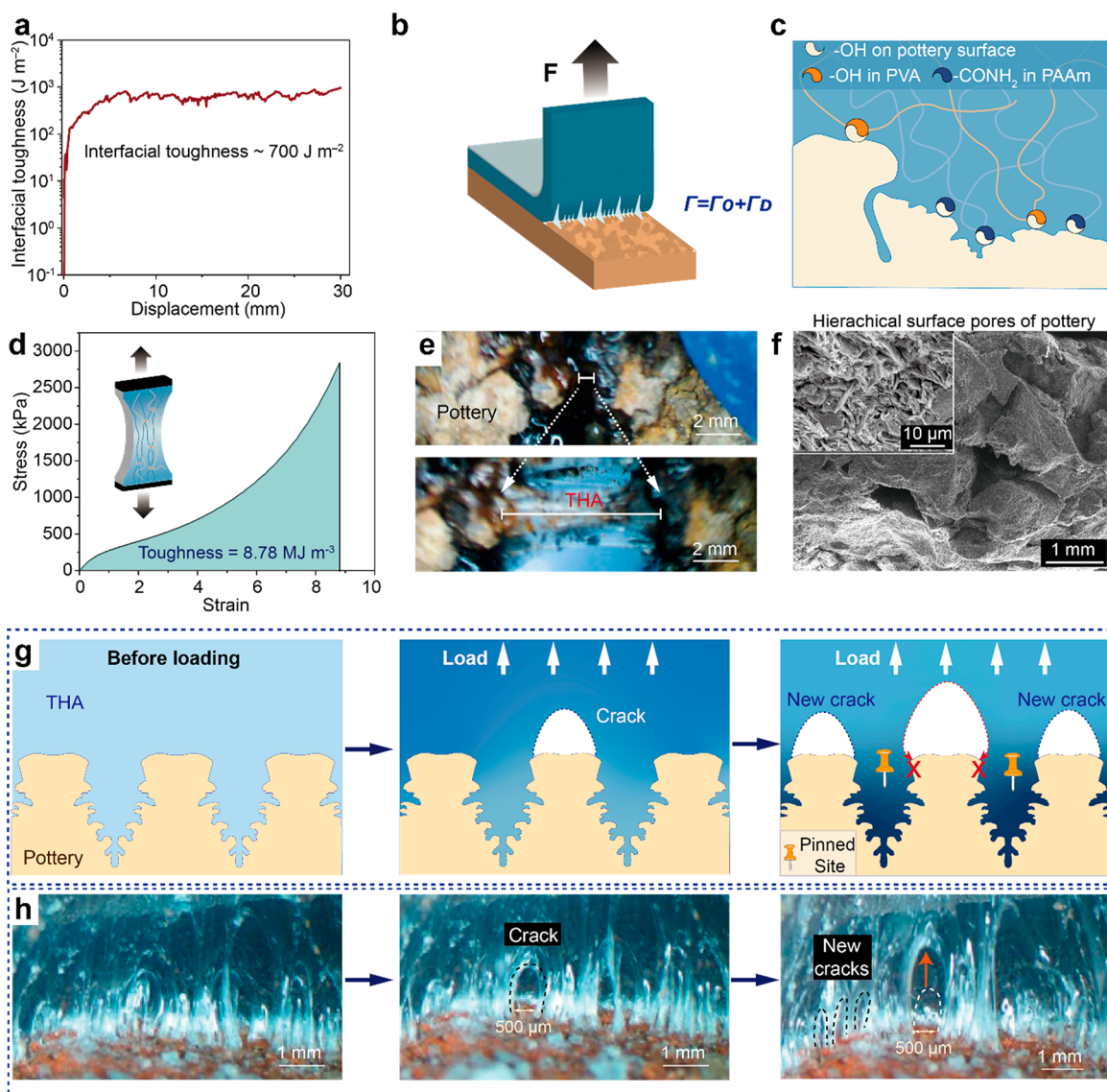


Figure 2. Adhesive properties of the THA and the bonding mechanism. (a) Peeling curve of the THA on the pottery surface, of which the interfacial toughness is as high as $\sim 700 \text{ J m}^{-2}$. (b) Schematic diagram of the peeling test. (c) The THA forms hydrogen bonds with the hydroxyl groups on the pottery surface via the hydroxyl and the amide groups of the chains. (d) Fracture toughness (8.78 MJ m^{-3}) of the THA contributed by the interpenetrating network structure. (e) Photographs of the large elongation of the THA before rupture. (f) SEM image of the hierarchical pores in the pottery surfaces. (g) Schematic diagram of the self-limited rupture, which shows that cracks are pinned and cannot propagate across the pores. (h) Photographs of the self-limited rupture in the experiment.

pottery sherds, and the results showed that rapid polymerization occurs at both extremes (Supplementary Figure 4).

In comparison with our THA, traditional adhesives have a long and fixed curing time. For example, the ECA glue solidifies through the anionic polymerization of ethyl α -cyanoacrylate, of which the concentration of the active centers determines the overall curing rate. The active centers can easily transfer to protonic terminators (such as CO_2 , O_2 , and H_2O molecules), decreasing the concentration of the active centers and thereby the curing rate.¹⁹ The curing process of another important adhesive, Paraloid B72, relies on the evaporation of the solvent, a time-consuming step that often requires a long curing time (more than 3 h).²⁰ Such a problem is also prevalent in other niche glues (such as polyvinyl acetate adhesives and epoxy resins) and often accompanied by other issues, as elaborately discussed in Supplementary Table 2.

The bonded interface is robust: the interfacial toughness is as high as 700 J m^{-2} (Figure 2a). The formation of such a robust adhesive–ceramic interface requires both strong interfacial interactions and effective mechanical dissipation at the interface. The total interfacial toughness between the adhesive and the substrate can be expressed as $\Gamma = \Gamma_0 + \Gamma_D$, where Γ_0 represents the intrinsic work per unit area of adhesion relying on chemical interactions at the interface and Γ_D is the mechanical energy per unit area dissipated via the deformation of adhesive,^{21,22} as indicated in Figure 2b.

Both large Γ_0 and Γ_D are preferred for the THA to form a tough interface. First, dense hydrogen bonds are formed at the adhesive–ceramic interface, offering a large Γ_0 . This is because the potsherds have oxygen-rich components, while the hydrogel has dense hydroxyls and amide groups to the backbones (Figure 2c). Furthermore, the dynamic breaking and formation of hydrogen bonds in this system, as well as the

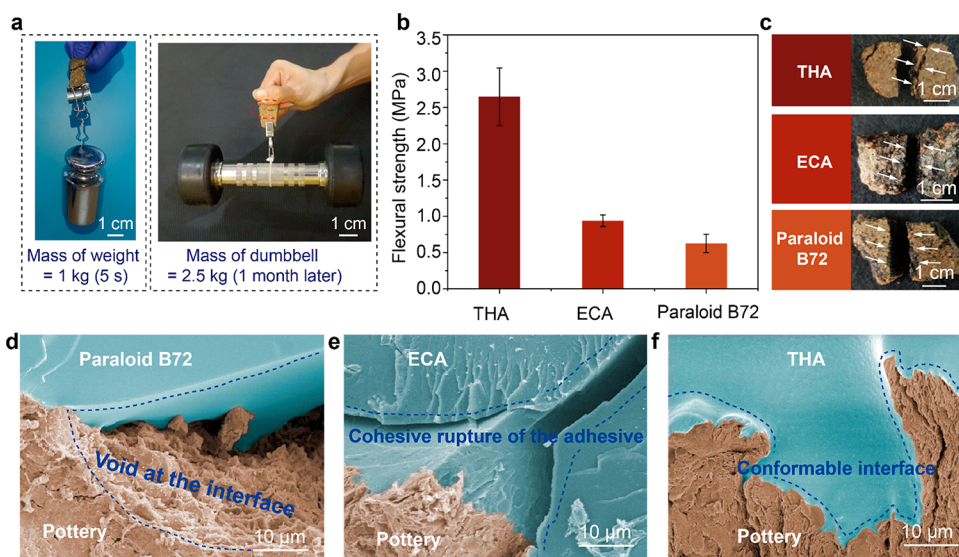


Figure 3. Adhesive strength of THA. (a) The interface is adequately strong to lift a weight of 1 kg within 5 s of curing or a dumbbell of 2.5 kg after one month. (b) Flexural strengths of potsherds repaired using the THA and using conventional adhesives. (c) Fracture mode of potsherds repaired with different adhesives. (d) SEM image of the voids at the interface of Paraloid B72 and pottery. (e) SEM image of the crack of ECA at the interface. (f) SEM image of the stable interface between the THA and pottery.

large specific interface area, could contribute to the enhancement of Γ_0 .^{23,24}

Second, the IPN structure of the THA and the self-limited rupture mode of the interface contribute to the large Γ_D , and this part (Γ_D) is believed to contribute more to the interfacial toughness than the hydrogen bonds do. On one hand, the THA is an interpenetrating polymer network with a high toughness of $\sim 8.78 \text{ MJ m}^{-3}$, allowing the material to significantly dissipate energy through its deformation (Figure 2d).^{25,26} We can see from Figure 2e that the adhesive at the interface can be greatly elongated, forming large-area fibrillar bridges.

On the other hand, the pinning effect enabled by the hierarchical pores and rough surface contributes to increased Γ_D . The surface structures such as micropores and ducts (Figure 2f) play a critical role to stabilize the cracks. Upon loading, cracks are initiated from the ridges of the ceramic surface, but they are pinned by the pores and ducts of the sherds and do not propagate across the fibrillar bridges that are grown from the pores (Figure 2g). This is because the pores and ducts can effectively pin the cracks to prevent their coalescing along the interface, while causing the cracks to grow vertically. The hydrogel in between the cracks presents a fibrillar morphology to be significantly elongated to dissipate energy. As a result, dense microvoids or cracks are formed here and there with a small crack size that is self-limited by inter-pore distance, as evidenced by our optical microscopic observation and scanning electron microscopy (SEM) inspection shown in Figure 2h and Supplementary Figure 5, respectively. The pinning effect of the pores is also observed in other porous systems such as a nickel foam (Supplementary Figure 6). Overall, the cracks at the interface can be pinned and stabilized by the pores to prevent their catastrophic propagation, and the fibrillar bridges can greatly dissipate energy through their elongation.

The effect of the self-limited rupture of the porous adhesive–ceramic interface recalls the delocalized rupture that stabilizes two-dimensional structures such as metal films or gold nanomeshes supported on an elastomeric sub-

strate,^{27,28} as well as the pinning effect of dispersed second-phase particles in a metal matrix that hinder dislocation motion and thereby strengthen the material.^{29,30} Without the porous structures of the sherds, cracks will easily propagate along the flat interface and lead to brittle and catastrophic failure. Therefore, the interfacial toughness is much smaller (Supplementary Figure 7).

Because of the robust interfaces, the bonded potsherds can lift a weight of 1 kg ($\sim 10 \text{ kPa}$) right after being reassembled for only 5 s (Supplementary Movie 1). The interface will be further strengthened with the evaporation of water in the hydrogel. After a long curing time, the potsherds reassembled by the THA can lift a dumbbell of 2.5 kg that generates a 20 kPa pressure (Figure 3a).

The interface is so robust that cohesive rupture of the ceramic substrate occurs in a flexural strength test. The strong interface ($\sim 2600 \text{ kPa}$) results from the fact that the THA precursor can fully wet the sherds and penetrate in the pores and ducts of the ceramic to form a “composite” and thus strengthens the substrate near the interface. In comparison, the Paraloid B72 and ECA adhesives are more brittle and both rupture across the adhesive or along the bonded interface; thus, they exhibit much lower flexural strengths ($\sim 750 \text{ kPa}$ for the Paraloid B72 and $\sim 1000 \text{ kPa}$ for the ECA) (Figure 3b,c; Supplementary Figure 8). The differences in the fracture modes have also been verified in our SEM observation (Figure 3d–f): large voids or long cohesive rupture along the Paraloid B72/ECA–ceramic interfaces are clearly seen, while there is no damage observed along the THA–ceramic interface.

Note that a low interfacial strength is required for the conservation purpose of certain cultural heritage objects, and the cohesive strength of the THA can be tuned by changing either the concentration of AAm or PVA to meet this need (Supplementary Figure 9).

Rapid adhesion of hydrated pottery sherds is highly desired. The buried sherds in humid regions are often wet, and they need to be bonded together at the excavation site to avoid the confusion in positions and the damage of such sherds. Wet adhesion can significantly improve the efficiency of excavation.

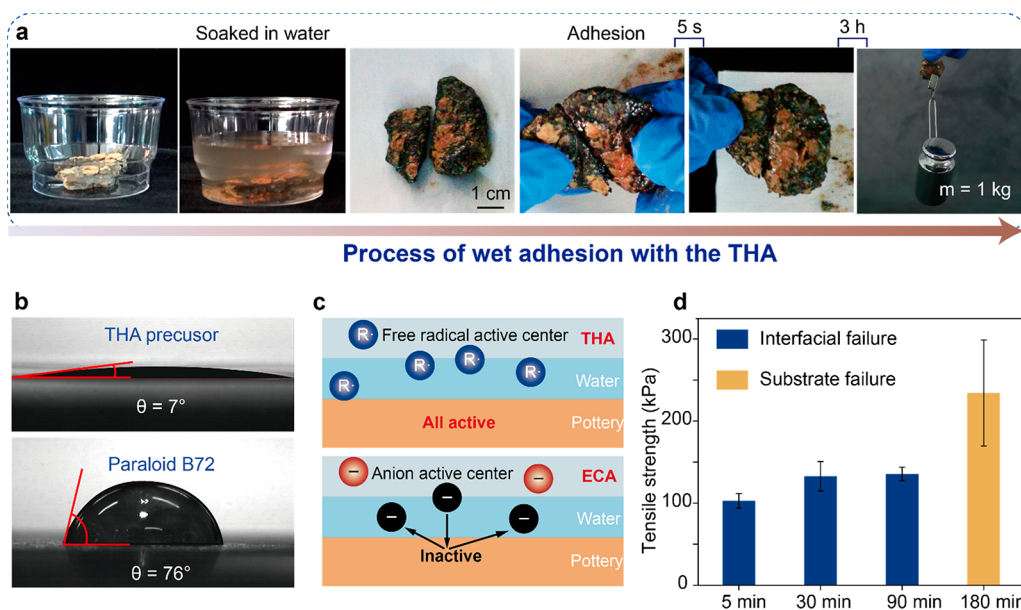


Figure 4. Wet adhesion of the THA. (a) Process of wet adhesion. Two pieces of sherds were soaked in and taken out of water and reassembled using the THA. After the THA is cured for 5 s, the assembly was able to sustain itself. The joined sherds could further lift a weight of 1 kg after drying for 3 h. (b) Contact angles of the precursor of the THA and that of the Paraloid B72 on the wet frosted glass surface, which are 7° and 76° , respectively. (c) Schematic diagram of the activity of the active centers on the wet surface, where the free radicals are all active and the anions lose their activity. (d) Tensile strengths of the wet-adhered interface at different curing times.

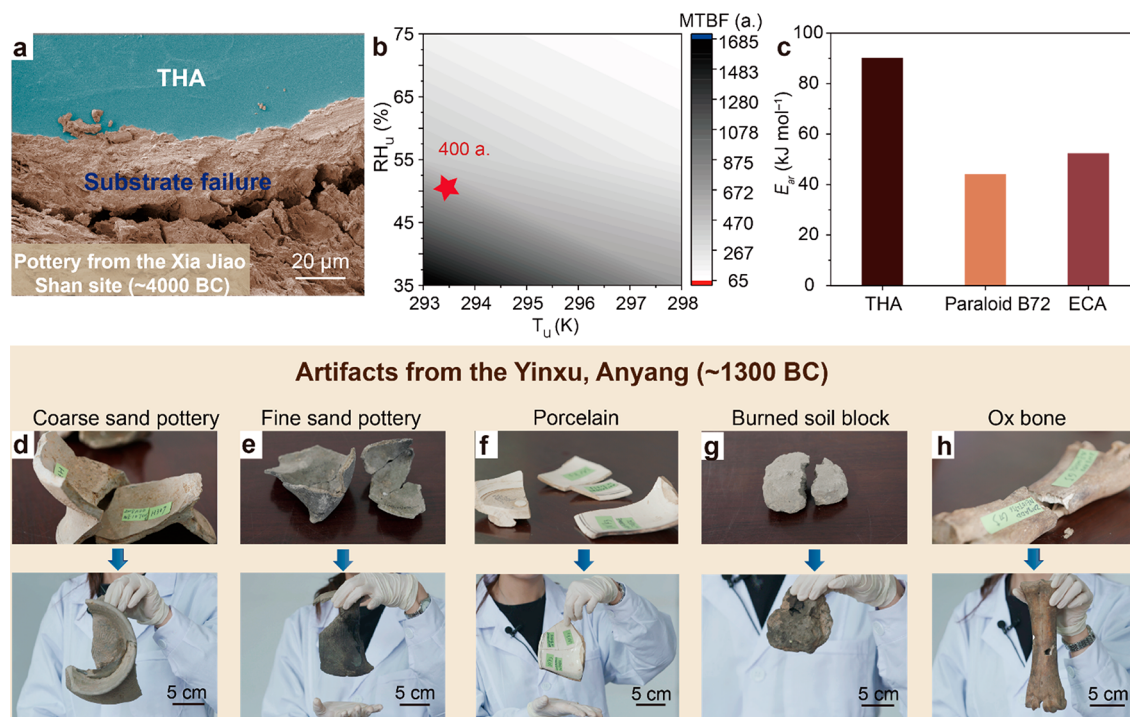


Figure 5. Stability and applications of the THA. (a) SEM image of the stable interface and cohesive failure of the ceramic substrate after hydrothermal aging treatment. (b) MTBF of the THA at different preserving conditions. The star shows the standard preserving condition, at which the MTBF is over 400 a. (c) Activation energy of relaxation (E_a) of the THA, the Paraloid B72, and the ECA adhesives. (d) Photograph of the original shape of two pieces of coarse sand sherds from Yinxu, Anyang, and the sherds are bonded together using the THA. Each piece weighs about ~ 2 kg. (e) Original shape and bonding of two fine sand potsherds, for which surface pores are smaller and shallower than that of the coarse sand pottery, and the cross sections of the fracture are irregular. (f) Bonding of porcelain pieces. (g) Bonding of two pieces of burned soil block. (h) Ox bone bonded using the THA.

For example, the Xia Jiao Shan site, a representative excavation in the South China, is located near the coast and presents abundant hydrated potsherds (Supplementary Figure 10), and its excavation is long-lasting because sherds need to be

carefully labeled, dried, and restored before the next task can be started. Whereas the Paraloid B72 and ECA adhesives are incapable of wet adhesion, our THA can well bond wet potsherds in a short time. Figure 4a and Supplementary Movie

2 show that two pieces of pottery sherds presoaked in water can be bonded together using the THA within 5 s, and the bonded wet interface is adequately strong to lift a 1 kg weight after 3 h. In addition, the adhesive strength of wet adhesion after drying is close to that of dry adhesion (Supplementary Figure 11).

The wet adhesion is enabled by the unique chemistry of the THA. On one hand, our THA is a water-based adhesive of which the precursor solution fully wets hydrated ceramic surfaces, whereas those organic-based adhesives are hydrophobic. We tested the contact angles of the THA and the Paraloid B72 precursors on wet frosted glass surfaces that mimic the sherds, and it shows that the THA precursor has a low contact angle of 7° on the sherd surface, indicating high wettability. In contrast, the Paraloid B72 precursor has a much larger contact angle of 76° on the glass surface, at which complete wetting is difficult (Figure 4b). On the other hand, the THA can gelate in water because it is a free radical polymerization-based adhesive using water as the solvent. In contrast, water is an effective inhibitor of anionic polymerization that prevents polymerization of the ECA on hydrated surfaces (Supplementary Figure 12; Figure 4c).

The interface formed by wet adhesion is adequately strong to maintain the pottery shape. We tested the tensile strengths of four samples by wet adhesion with 5, 30, 90, and 180 min of curing. The tensile strength of the interface is ~ 100 kPa with 5 min of curing and increases as curing time increases. After 180 min, the tensile strength increases to >240 kPa (Figure 4d), and cohesive rupture rather than interfacial rupture of the ceramic substrate is observed. With such a high tensile strength, the interface can withstand heavy ceramic items as thick as ~ 8 m (assuming a density of 3 g cm^{-3}), indicating that the THA is sufficient to bond most gigantic pottery artifacts.

The aging resistance of the adhesive is critical to the long-time conservation of bonded earthenware. The chemical stability of adhesives is often affected by temperature and humidity. We carried our accelerated aging test at a hygrothermal aging condition (95% RH and 328 K) and found that the fracture mode of the potsherds reassembled with the THA maintains substrate failure (Supplementary Figure 13). SEM images also demonstrate no cracking or debonding at the interface after accelerated aging (Figure 5a).

The activation energy for the degradation (E_{ad}) of the THA was tested using thermogravimetric analysis.^{31–33} We heated the THA from 273 to 873 K at constant heating rates of 5, 10, 15, and 20 K min^{-1} , and the derivative curves of mass loss are shown in Supplementary Figure 14. We figured out that E_{ad} is $133.2 \text{ kJ mol}^{-1}$, corresponding to a long mean time between failure (MTBF) of at least 68 a. (Supplementary Method 1) for the THA via the Hallberg-Peck mode.³⁴ The lifetime of the bonding agent can further be extended by decreasing the environmental temperature or relative humidity (Figure 5b). At the standard condition (50% RH and 293 K temperature) for relic preservation, the MTBF is determined to be over 400 a. (Supplementary Table 3).

The creep resistance of the adhesive is another parameter that affects the stability of the adhesive. The deformation of polymers under long-term stress conditions is dominated by plastic deformation, which can be observed in the short-term by increasing the temperature, based on the time–temperature superposition principle.^{35–37} Therefore, we tested the creep performance of the THA and compared it with that of conventional adhesives. The THA exhibits a creep compliance

value of 0.0008 MPa^{-1} at 340 K and a relaxation activation energy of 90.2 kJ mol^{-1} (Figure 5c and Supplementary Figure 15), which indicate that the THA is not prone to failure due to deformation. In contrast, conventional adhesives exhibit much higher creep compliance ($\sim 0.017 \text{ MPa}^{-1}$ at 340 K for ECA and 14.79 MPa^{-1} at 340 K for the Paraloid B72) and lower relaxation activation energy values (44.1 kJ mol^{-1} for the Paraloid B72 and 52.4 kJ mol^{-1} for the ECA) (Figure 5c; Supplementary Figure 16 and Supplementary Method 2), such that the occurrence of cold flow lowers the long-term stability of the assemblies.³⁸

We have used the THA for the restoration of various types of pottery artifacts. Repairing huge artifacts is one of the challenges because of the high stresses at the interfaces and the long curing time required to secure the artifact (Supplementary Figure 17). In contrast, the use of the THA eliminates such a setup because a tough and strong interface can be formed within a few seconds. Figure 5d shows that our adhesive works well in bonding two pieces of coarse sand earthenware fragments (~ 2 kg each) excavated from YinXu, Anyang (~ 1300 BC, the Shang Dynasty). After the adhesive is applied to the potsherds and cured for 10 s, the bonded joint can withstand the gravity of each sherd.

Another challenge for heritage restoration is that the adhesives need to be applicable to various types of artifacts. This is because raw materials, processing conditions, and firing temperatures will affect the surface and mechanical properties of artifacts. In addition to the aforementioned coarse sand potsherds, we further revealed that the THA can be applied to the repair of fine sand pottery, porcelain, and fired soil blocks with different topologies (Figure 5e–g). Furthermore, THA can also be applied to the repair of nonporcelain artifacts. For instance, ox bones, artifacts with numerous micropores, indicating the use of tools by humans, can also form a stable interface with THA for repair (Figure 5h).

The THA can be used as a general adhesive in many more applications other than repairing archeological artifacts. Other materials of woods and rocks can also be well assembled using the THA if they have oxygen-rich components to introduce hydrogen bonding, together with rough surfaces for structure-induced mechanical dissipation. Wood is a material that has dense, natural, and microscale vascular bundles, which can be glued together using the THA (Supplementary Figure 18a). Wood is widely used in furniture, decoration, crafts, and other fields, and a nontoxic, strong, and tough bonding agent is beneficial for more imaginative processing of wood. In addition, we have also used the THA to bond granite pieces, which also show highly stable interfaces (Supplementary Figure 18b). It is expected that the THA can be used in many other applications to achieve robust adhesion between objects with rough surfaces.

The THA also shows superior advantages over the currently used ECA and acrylic resins (such as Paraloid B72) in terms of safety. The solvent of the Paraloid B72 (acetone) and the ECA monomers are toxic and volatile organic chemicals with a pungent smell that have potential risks to our health.^{39,40} In contrast, the THA is an aqueous solution without any volatile components, being a safer and environmentally friendly selection for users.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.nanolett.2c04642>.

Fast and robust bonding of potsherds with THA in dry conditions (Movie S1) (MP4)

Fast and robust bonding of potsherds with THA in wet conditions (Movie S2) (MP4)

Details of experimental methods for the THA and conventional adhesives, calculation of the accelerating factor in chemical aging and corresponding TGA curves, calculation of the relaxation activation energy in physical aging and DMA results, comparison of THA and other systems, MTBF of THA at different service conditions, viscosity and gel transition of precursor solution with a rheometer, interfacial toughness measurement via 90° peeling test, adhesive strength characterization via three-point bending test, stress–strain curve of adhesives, photographs of wet excavation and of a conventional adhesive fixture, SEM image of a permeable brick surface, morphology of the nickel foam surface and that of the fibrillar bridges at the interface observed through optical microscopy, and photographs of applying THA and the restored artifacts (PDF)

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Author Contributions

[†]M.G. and G.L. contributed equally to this work. C.F.G. conceived the idea and designed the research. C.F.G. and J.T. directed the whole study. M.G. performed the majority of the experiments. G.L. designed the adhesives. M.G., G.L., M.C., X.H., K.H., and C.F.G. analyzed the experimental data. M.G. and G.L. performed the mechanical tests, and M.G. and M.C.

analyzed the microstructure of the assemblies. M.G. and K.H. calculated the aging resistance, and M.G., G.L., and C.F.G. discussed the adhesion mechanism. C.F.G., M.G., and G.L. drafted the manuscript, and all authors contributed to the writing of the manuscript.

Notes

The authors declare no competing financial interest.

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