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Application of epoxy resin in cultural relics protection

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ABSTRACT

Cultural relics have their unique artistic, cultural and historical value, and the protection of important cultural relics is conducive to the inheritance of historical culture. As a kind of cementing agent and binder commonly seen in cultural relics protection, epoxy resin is widely used in the bonding and consolidation of various materials in cultural relics, which has important practical application value. In this review, a systematic classification of commonly used epoxy resins, including their molecular structures, synthesis reactions and properties are provided, the problems and solutions of epoxy resin in cultural relics protection are summarized. The solutions are classified into three aspects: functional epoxy resin, blending modification, and other modification. Representative application examples of epoxy resin are listed in the field of cultural relics protection, and the development direction of epoxy resin in cultural relics protection in the future is proposed, which provides useful guidance for the modification of epoxy resin and its application in cultural relics protection in the future.

1. Introduction

Artworks are creations with artistic value, cultural relics are a kind of precious artworks with historical and cultural value, which reflect the vitality and creativity of human beings. For example, in our country China, the long history of over 5000 years brought us a large number of cultural relics. Currently, there are about 767,000 immovable cultural relics in China, including over 50 World Heritage Sites and around 5000 key cultural relics under national protection [1]. However, due to various natural and human-made factors, many cultural relics still suffer deterioration after being exposed to the air for a long time, which inevitably resulted in the destruction of cultural relics. Without necessary protection, these cultural relics will gradually disappear, resulting irreparable loss to historical research and cultural relics. Therefore, protecting cultural relics is necessary and urgent, and developing effective cultural relics protection materials is essential [2]. Only materials with excellent performances can effectively protect cultural relics. Scholars have developed a variety of cultural relics protection materials, which can be classified into inorganic and organic materials. Inorganic materials mainly include calcium barium system [3] (such as calcium hydroxide and calcium carbonate [4]) and sodium silicate system [3] (such as high modulus potassium silicate solution [5], oil and wax [6]). These materials could strengthen stone, bone, soil, and paper relics. Furthermore, these materials could seal the surface of stone relics and enhance their hydrophobic [7], as well as lift the deacidification of paper relics [4]. When inorganic materials act as protection material, the reinforcement mechanism is that some salts in the inorganic solution could condense in the internal void of stone relics or react with stone to block the pores, thus enhance the internal structure of stone and block water [3]. Inorganic materials have advantages such as good compatibility, anti-aging performance, long service life, and relatively low cost. However, these inorganic materials suffer from weak bonding, poor permeability, limited reinforcement strength, and the easy precipitation of soluble salt in aqueous environment [5,8,9]. Compared with inorganic materials, organic materials have good adhesion, water resistance, acid and alkali resistance, permeability and other desirable properties, which overcome shortcomings of inorganic materials [3,6,10-14]. Nevertheless, organic materials possess drawbacks that cannot be disregarded. Specifically, they are prone to degradation, lack stability in protecting cultural relics, and exhibit poor compatibility with inorganic cultural relics [15,16]. Common organic materials used in cultural relics protection mainly include epoxy resin, acrylic resin, ethyl silicate, wax and polyethylene glycol, in addition, organic polymers such as PEI and PVDF also have great application potential in cultural relics protection [14]. Among the commonly used organic materials for cultural relics protection,

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epoxy resin is a cultural relics protection material that possesses strong adhesion and strength. However, it exhibits poor weather resistance, is prone to yellowing, and has limited impact resistance. Wax, as a traditional natural protection material, has the advantage of easy access, but it is easy to absorb dust particles in the air. Acrylic resin offers good stability, transparency, and weather resistance, but it lacks proper air permeability and water resistance. Silicone resins exhibit excellent hydrophobicity and weather resistance, nevertheless, they have poor mechanical properties and are not resistant to acid and alkali. Clearly, epoxy resin serves a specific purpose and function in cultural relics protection, primarily as a binder [16–19].

Epoxy resin has been utilized for cultural relics restoration since the early 1960s and is one of the most important materials for cultural relics protection [20]. In the 1990s, colorless and transparent epoxy resin was developed, mainly used for consolidation and adhesive in cultural relics protection [21–25]. The structure of epoxy resin includes an "epoxy" function group and often contains aliphatic, aromatic, heterocyclic structures, making epoxy resin exhibits different physical properties [26,27]. Among them, bisphenol A epoxy resin is the most widely used epoxy resin in cultural relics protection. However, epoxy resin used for cultural relics protection cannot be used directly, which always requires a reaction with a curing agent, undergoing a transformation from a linear thermoplastic polymer to a thermosetting polymer with a three-dimensional chemical bond network structure. During the curing process, the epoxy resin exhibits excellent mechanical properties, low shrinkage, low residual stress [28], good heat and chemical resistance [29,30]. Moreover, due to by-products-free and ability to penetrate and form a network structure within porous materials, epoxy resin has good durability, viscosity, mechanical ability. After the curing process, epoxy resin is a high strength thermosetting resin with a flexible, viscous, and chemical corrosion-resistant long chain network structure, cross-linking degree could be lifted [31,32] and cannot be melted or reshaped [33]. However, some shortcomings of epoxy resin still exist, such as poor UV radiation resistance, easy degradation [34–36], low impact toughness (three-dimensional network), and brittleness [37,38]. Generally, modifications are always required for its application in cultural relics protection to achieve better performance.

Herein, this review provided a systematic classification of commonly used epoxy resins, including their molecular structures, synthesis reactions and properties. Moreover, this review also summarized the problems that arise when using epoxy resins in the protection of various cultural relics and provide solutions for addressing these issues. Main solutions were categorized according to the different methods of modifying epoxy resins, such as functionalization, blending and other approaches. The blending modification is further divided into organic and inorganic blends. Finally, this review provided representative examples of using epoxy resins in cultural relics protection, including the bonding of bronzes and the strengthening of cultural relics in various grottoes. This review is intended to serve as a valuable guide for the modification and application of epoxy resins in cultural relics protection in the future.

2. Introduction to epoxy resin

Epoxy resins, which are low molecular weight prepolymers with multiple epoxy groups, exhibit varying properties influenced by the specific type of epoxy and combination of curing agents [39]. Epoxy monomers commonly result from the condensation reaction of epichlorohydrin with various substances such as aromatic amines, diphenylmethane, polyhydroxyphenol with polyhydric alcohols, olefin or polyolefin compounds. Another method involves epoxidation of olefin by peroxy acid [40].

Epoxy resin possesses outstanding characteristics such as strong adhesion, resistance to wear and chemical corrosion, excellent mechanical properties, effective electrical insulation, low shrinkage rate, ease of processing and forming, affordability, and no by-products during curing. It is widely used in adhesives, sealants, electronics, and coatings [39]. There are many types of epoxy resin, which can be roughly divided into aliphatic epoxy resins, biobased epoxy resins, fluorine-containing silicone epoxy resins, double-functional epoxy resins, trifunctional epoxy resins, four-functional epoxy resins, multifunctional epoxy resins, *etc.* [41,42]. The details are shown in Table S1 and Fig. S1 (Supporting information).

One commonly used epoxy resin for protecting cultural relics is bisphenol A epoxy resin in bifunctional epoxy resin. This resin is formed by condensing bisphenol A and epichlorohydrin with the help of sodium hydroxide. Generally, bisphenol A epoxy resin with terminal epoxy groups can be prepared at 110 °C for 16 h under excessive epichlorohydrin. When the mole ratio of bisphenol A to epichlorohydrin is 1:10 to 1:20, low molecular weight bisphenol A epoxy resin can be prepared. Low molecular weight bisphenol A resin molecules are typically liquid, while those with high molecular weight are generally more viscous, either in liquid or solid form [40]. Because epoxy resin has a thermoplastic linear structure and cannot be directly applied directly, it is necessary to use the curing agent in combination with bisphenol A epoxy resin in cultural relics protection, such as diethylenetriamine (DETA), triethylenetetramine (TETA), amine curing agent HY965, Jeffamine-230.

3. Main problems and solutions faced by the application of epoxy resin in cultural relics protection

The protection of cultural relics presents challenges due to the shortcomings of common epoxy resin which include brittleness, poor impact resistance, cracking resistance, fatigue resistance, and weak UV resistance. Specifically, the poor compatibility of epoxy resin, poor UV radiation resistance, and low impact toughness caused by the three-dimensional network are the primary issues. Therefore, to address these issues, researchers have extensively investigated and found several coping strategies and solutions for the protection of cultural relics using modified epoxy resins.

3.1. Functionalized epoxy resin

Some functional groups are often introduced into common epoxy resins to make them more suitable for the field of cultural relics conservation. By introducing silica-related groups and fluorine-related groups to improve compatibility and hydrophobic properties. Cardiano *et al.* [43] prepared Silicon-epoxy complexes that are covalently linked with organic polymer chains and inorganic domains, when applied to rocks, porosity, water absorption, and dynamic contact angle measurements demonstrated that the material was effective in preventing water penetration into the inner layer of rocks with low porosity. Xu *et al.* [44] prepared (3-glycidyloxypropyl)methyldiethoxysilane and (3-aminopropyl)triethoxysilane in the presence of poly(dimethylsiloxane) hydroxyl terminated (PDMS-OH) as additives to obtain epoxy-SiO_2-PDMS-OH polymer, When the addition of PDMS-OH was 30% (by weight), the microcracks of the polymer were significantly reduced, the material should be used as a cementing agent and a hydrophobic product for high porosity carbonate rocks without any volatile organic components. Brifa *et al.* [45] applied a water-based epoxy-silica consolidation agent to Globigerina Limestone (GL) through brush coating and full soaking technology, and its water absorption rate decreased. The drilling resistance curves showed that the mechanical properties of the system improved significantly, but the color also changed significantly, and the problem of long-term environmental stability

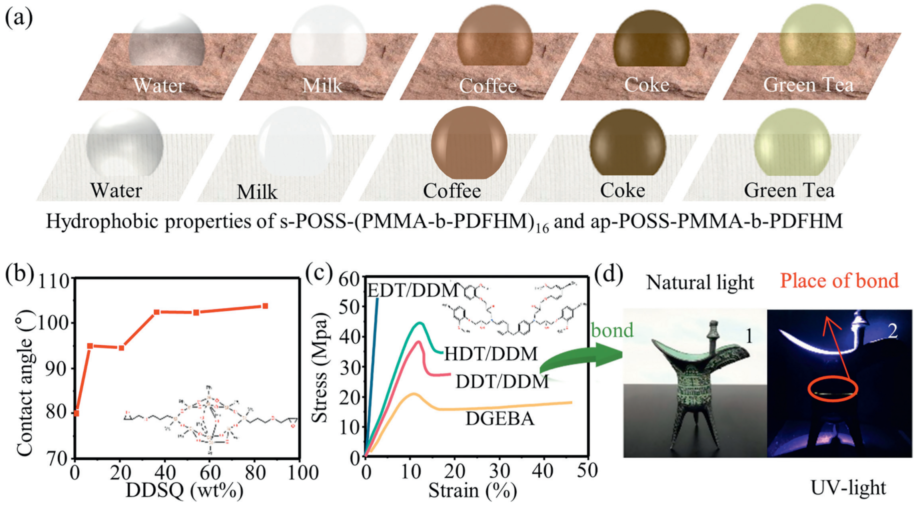

Fig. 1. (a) Hydrophobic effect of protected sandstone and fiber and SEM images, and their resistance to coffee, milk, cola and tea. (b) Surface water contact angle as a function of the POSS content in organic-inorganic copolymer. Reproduced with permission [47]. Copyright 2011, the Royal Society of Chemistry. (c) Tensile test curve (Different dithiols were used.). Reproduced with permission [48]. Copyright 2022, the Springer Nature. (d) Photos of restored bronzes under natural light 1 and ultraviolet light 2. Copied with permission [48]. Copyright 2022, the Springer Nature.

still existed. Some researchers [46] have synthesized two types of POSS-based fluoropolymers with star structure and tadpole structure, respectively. When applied to protect sandstone and fiber, it has an obvious hydrophobic effect and has outstanding resistance to the invasion of coffee, milk, cola and tea, showing an excellent protective effect, as shown in Fig. 1a. Wang *et al.* [47] prepared an organic-inorganic poly(hydroxyether of bisphenol A) (pH) copolymer with polyhedral oligomeric silsesquioxane (POSS) as the main chain using diepoxy POSS macromer as raw material and based on the epoxy-phenol reaction. When change the mass ratio of diglycidyl ether of bisphenol A to double-decker silsesquioxane (DDSQ), a series of pH copolymers containing POSS were obtained. When 50% DDSQ was added, the contact angle between the epoxy coating and water increased from the unmodified 80° to 102°, as shown in Fig. 1b, it can be applied to waterproof repair of cultural relics, especially stone cultural relics. Lu *et al.* [48] successfully synthesized a multifunctional eugenol-based epoxy resin (EBER) using photochromic fluorescent dye with good mechanical properties using eugenol, epichlorohydrin, dithiol and 4,4-diaminodiphenyl-methane as raw materials, and it is applied to repair the cracks of bronze ware. The results of the tensile test and the cyclic tensile test show that EBER has better mechanical properties (45 MPa, 20%), even better than the commercial diglycidyl ether of bisphenol A (DGEBA) epoxy resin (55 MPa, 5%), and its mechanical properties can be adjusted by changing the chain length, as shown in Fig. 1c. In addition, EBER is photochromic after curing, so the curing condition can be observed by color without the use of fluorescent agents. The observed fluorescence enables us to know whether the adhesive is firm, uniform, cracked, and aging, which facilitates the protection personnel to know the condition of cultural relics, as shown in Fig. 1d. Some researchers [49] selected the optimal graft modification ratio as a 6:1 mass ratio of epoxy resin to hexafluorobutyl methacrylate through the experiments of different mass ratios of epoxy resin and hexafluorobutyl methacrylate, as well as the characterization of the UV resistance of the product, the graft rate and the experimental appearance, the optimal graft reaction temperature was 110 °C. The amination time and temperature were determined by the amine value. The optimal amination temperature was 100 °C and the amination time was 2 h. The degree of neutralization is determined by the stability of the modified resin, and the degree of neutralization is selected as 90%. Through research on the properties of the modified resin (weather resistance, acid resistance, alkaline resistance, water resistance, adhesion, contact angle and water absorption), it is concluded that the modified epoxy resin has the excellent properties of the fluorine-containing resin, especially good weather resistance, and also maintains the excellent adhesion and hardness of the epoxy resin, as shown in Table S2 (Supporting information). A summary of the functionalized epoxy resins is given in Table S3 (Supporting information).

3.2. *Blending modified epoxy resin*

3.2.1. *Organic blending modification*

Epoxy resin modified with rubber elastomer is a mature toughening method. To achieve the toughening effect, the rubber particles must dissolve and disperse evenly with the epoxy resin before curing, and they must also form a strong chemical crosslinking point with the epoxy matrix. Commonly used rubber for modifying epoxy resins includes carboxyl-terminated butadiene acrylonitrile copolymer (CTBN), hydroxyl–terminated polybutadiene (HTPB) [50,51]. Ramos *et al.* [50] found that CTBN is more strongly bound to the rubber matrix than HTPB is to the rubber matrix, both of which play a role in improving the impact strength of pure epoxy resin. Among them, the fracture morphologies of pure epoxy resin, epoxy resin modified with 10 phr HTPB and epoxy resin modified with 15 phr CTBN were shown by SEM in Fig. 2a. The specific concentration dependence on impact strength is shown in Fig. 2b. Chen *et al.* [51] used 2-ethyl-4-methylimidazole as a curing agent on the basis of CTBN-modified epoxy resin, and the bending strength and bending modulus of the resin decreased, the tensile shear strength increased, and the heat resistance improved significantly. Yang *et al.* [38] used epoxidized hydroxyl–terminated polybutadiene (EHTPB) as a modified raw material to prepare a high performance environmentally friendly solid epoxy resin by the one-step melting blending method, and its modified morphology and performance were tested, the SEM of the fracture morphology of epoxy resin containing 10 wt% EHTPB is shown in Fig. 2c. The study found that the modified epoxy resin has excellent toughness, compared to the pure epoxy resin, its break elongation increased by 100%. When 10% EHTPB is added, the modified epoxy resin with EHTPB shows higher strength, the flexural strength and impact strength were increased by 22% and 101%, re-

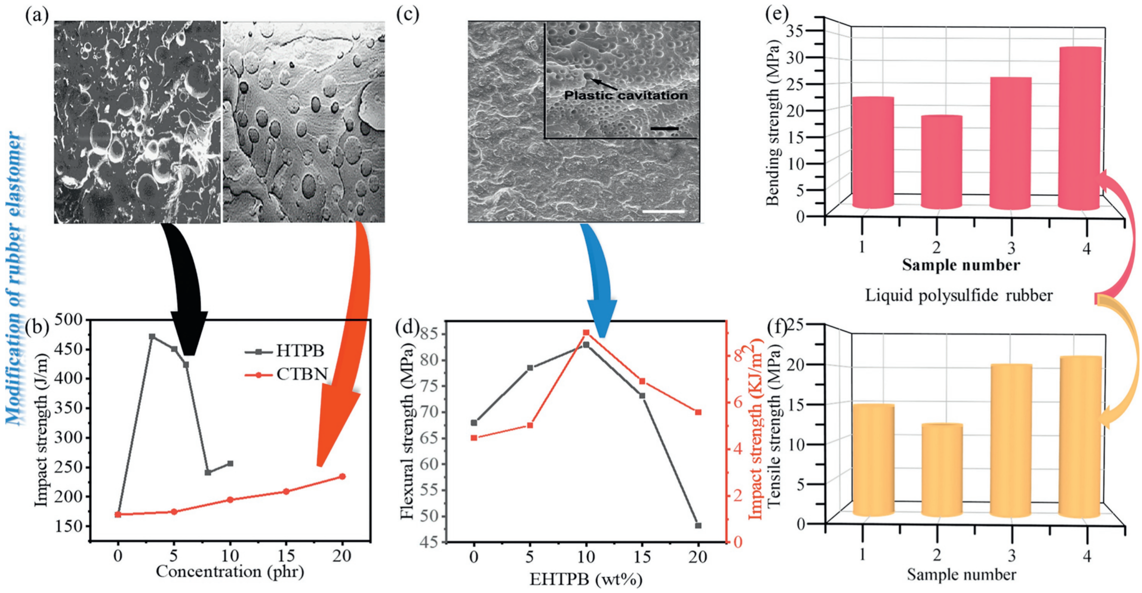

Fig. 2. (a) SEM of fracture morphology: 10 phr HTPB (left) and 15 phr CTBN modified (right). Copied with permission [50]. Copyright 2005, the Elsevier. (b) Impact strength of epoxy resin with different concentrations of elastomers. Reproduced with permission [50]. Copyright 2005, the Elsevier. (c) SEM of fracture morphology with EHTPB added in a mass fraction of 10%. Copied with permission [38]. Copyright 2019, the John Wiley and Sons. (d) Flexural strength and impact strength of neat epoxy and EHTPB-modified epoxy resins. Reproduced with permission [38]. Copyright 2019, the John Wiley and Sons. (e) Schematic diagram of bending strength of 25% liquid polysulfide rubber modified epoxy resin. (f) Schematic diagram of tensile strength of 25% liquid polysulfide rubber modified epoxy resin.

spectively, as shown in Fig. 2d. In addition to good thermal stability, the initial decomposition temperature increases from 249 °C to 313 °C. Ma *et al.* [52] changed the types and amounts of epoxy resins, curing agents, fillers, additives, and tested their mechanical properties, shrinkage and expansion properties, viscosity changes, simulated field, and other aspects, it is found that the adhesive prepared with epoxy resin as matrix, adding 20% DETA, 20% acetone, 20% phenolic resin, 25% liquid polysulfide rubber, 2% rock powder and Al_2O_3, 1% coupling agent (KH-560) can be used as an adhesive for stone cultural relics with excellent comprehensive properties, the gel time is suitable, the operation performance is good, easy to prepare, and has excellent resistance to water, acid and alkali, aging and other properties, and the expansion rate is close to the rock. Specific bending strength and tensile strength are shown in Figs. 2e and f. In addition to stone artifacts, holes in wooden artifacts have also been documented to be filled with epoxy resins containing polysulfide rubber [53]. This modification method mainly aims to improve the toughness of cultural relics protection materials.

Thermoplastic epoxy resin has good toughness, modulus, heat resistance, and glass transition temperature. In the 1980s, scientists used thermoplastic resins to toughen epoxy resins. Commonly used thermoplastic resin modifiers include polyether sulfone (PES), polysulfone (PSF), polyether imide (PEI), polyether ketone (PEK), polyphenyl ether (PPE), polystyrene (PS), *etc.* [54,55]. Sun *et al.* [54] prepared a series of soluble polyether ether ketone (s-PEEK) modified epoxy resin (EP) by the hot melt method. Compared to the ordinary polyether ether ketone (PEEK) modified epoxy system, it is concluded that both can improve the impact strength, bending strength, bending modulus and other mechanical properties of the system, the three-dimensional structure of PEEK is shown in Fig. S2a (Supporting information), and the influence of the dosage of PEEK and s-PEEK on the impact strength and bending modulus of the epoxy resin system is shown in Figs. S2b and c (Supporting information). Brooker *et al.* [56] studied the toughening effect of PES copolymers with active end groups in different proportions on epoxy resins, as measured by the uniaxial tensile test, it was found that the addition of thermoplastic resin increased the ultimate tensile strength and the strain to break of epoxy polymers, besides, the addition of thermoplastic toughening agent improved the fracture toughness and fracture energy of epoxy resin, the addition of 35% thermoplastic toughening agent increased the fracture toughness of the epoxy resin from 0.68 MPa/m^2 to 1.11 MPa/m^2, and the fracture energy from 215 J/m^2 to 530 J/m^2. Jin *et al.* [55] investigated the impact of PSF-modified epoxy resin on thermal stability, fracture toughness, bending strength, and fracture surface. They found that the modified epoxy resin exhibited a decrease in both bending strength and initial decomposition temperature, compared to the pure epoxy resin. However, a significant improvement in fracture toughness was observed for the modified epoxy resin. The SEM observation revealed that the PSF-modified epoxy resin had a rough surface with shear deformation and tortuous cracks, effectively preventing deformation and crack propagation. Feng *et al.* [57] introduced thermoplastic polyurethane (TPU) into epoxy resin containing thermoreversible Diels-Alder bonds (EP-DA). The specific structure is shown in Fig. S2d (Supporting information), with the increase of TPU introduced into EP-DA-TPU, the bending load gradually decreases, while the bending displacement gradually increases; in addition, the impact strength of EP-DA-TPU also increases with increasing TPU. When the TPU content reaches 10 phr, the maximum value is 6.2 kJ/m^2, as shown in Figs. S2e and f (Supporting information). Moreover, the addition of TPU significantly accelerated the self-healing speed of EP-DA.

Thermoplastic resin enhances the fracture toughness of brittle epoxy resin, thereby improving its toughness while maintaining the original glass transition temperature and modulus. When thermoplastic resin is used, epoxy resin can be toughened by effective regulation of the induced phase separation process, so that it can meet the mechanical properties and aging resistance required for cultural relics application, which has potential development prospects.

Core-shell polymers (CSP) have many excellent properties due to their unique properties [58]. Specifically, core-shell polymer particles added to epoxy resin can play a toughening role. The particle size of the core-shell polymer particles and the interaction with

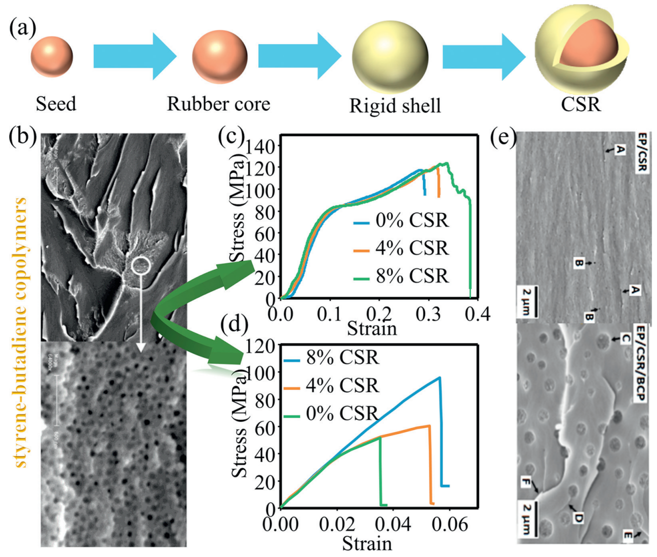

Fig. 3. (a) Schematic diagram of the core-shell polymer. (b) SEMs of OC/DDM/CSR fracture surfaces at 8% CSR. Copied with permission [59]. Copyright 2004, the American Chemical Society. Room temperature mechanical properties tests: (c) compression; (d) tension. Reproduced with permission [59]. Copyright 2004, the American Chemical Society. (e) Fracture surfaces of CSR and CSR/BCP(block copolymers)-toughened EP, showing various features (A: bridges, B: voids or cavities, C: transparticle fracture, D: crack pinning, E: crack deflection, F: ribbon formation). Copied with permission [62]. Copyright 2021, the Springer Nature.

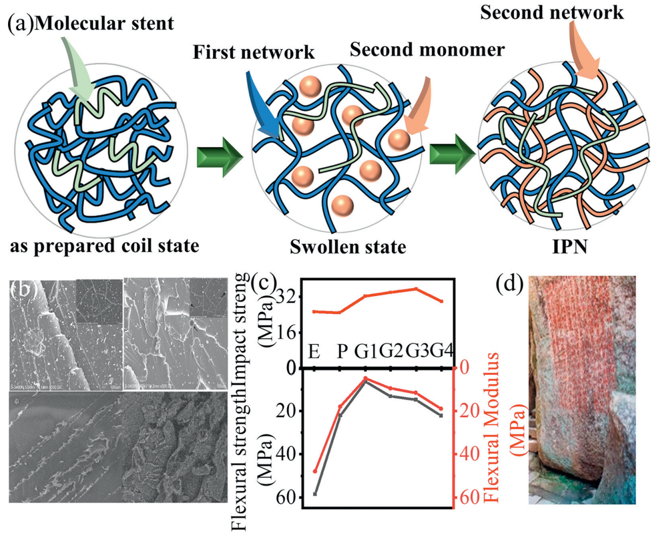

Fig. 4. (a) Schematic diagram of the interpenetrating structure. (b) SEM images of different interpenetrating compounds, namely G1-PU/EP, G2-PU/EP, and EP/PU in different preparation sequences. Copied with permission [63]. Copyright 2013, the Elsevier. Copied with permission [64]. Copyright 2020, the John Wiley and Sons. (c) Impact strength and flexural strength. Reproduced with permission [63]. Copyright 2013, the Elsevier. (d) Potential application in stone carvings.

the epoxy resin matrix are key factors to regulate the toughening effect and also affect the curing and thermal-mechanical properties of epoxy resin. Commonly used core-shell polymers are generally butadiene rubber (BR), polybutyl acrylate (PBA), styrene butadiene rubber (SBR) or polysiloxane (PSi) as the core, polymethyl methacrylate (PMMA) as the shell, the specific structure diagram is shown in Fig. 3a. In addition to butyl acrylate (BA) as the core, glycidyl methacrylate (GMA) and methyl acrylate (MMA) copolymer as the shell, the urea-formaldehyde prepolymers were coated on the surface of epoxy natural rubber by polycondensation reaction to form nanometer-scale and micrometer-scale core-shell rubber particles (E-CSPs). Choi *et al.* [59] used a rubber granule styrene-butadiene copolymer to make a core-shell copolymer and added siloxane to form a three-component system. The SEM image of the fracture surface of the three-component system with 8% core-shell copolymer is shown in Fig. 3b. It was found that its impact resistance and tensile resistance improved (Figs. 3c and d). Tang *et al.* [60] synthesized epoxy core-shell particles using epoxy natural rubber (ENR) latex, which contained 30% natural rubber, and urea-formaldehyde prepolymers (UF) for the UF shells. The resulting ENR-based core-shell particles exhibited a core-shell structure. These ENR-based core-shell particles were then utilized as a toughening agent in epoxy resin, leading to a significant improvement in its impact strength. It is worth noting that the addition of the ENR-based core-shell particles caused a reduction in the Young modulus and tensile strength of the epoxy resin, while leaving the glass transition temperature unaffected. Zhang *et al.* [61] functionalized core-shell nanoparticles (CSNPs) with BA as the core and MMA copolymerization with GMA as the shell by emulsion polymerization were synthesized. CSNPs were used as the toughening agent for epoxy resin, it was found that the obtained CSNPs were near-spherical particles with a particle size of 50–100 nm, the compatibility between the CSNPs and the epoxy resin matrix increases with increasing GMA concentration. The epoxy resin toughened with 10 wt% CSNP (containing 10 wt% GMA) shows the best mechanical properties, while heat resistance is not affected. Mousavi *et al.* [62] strengthened epoxy resins by adding different amounts of methyl methacrylate-butadiene styrene core-shell rubber particles (MBS CSR), fracture and physical and mechanical properties of epoxy resin were studied, the results showed that the addition of CSR in epoxy resin increased K_{IC} (Fracture toughness) and G_{IC} (Fracture energy) by 121% and 420%, respectively, and the roughness of the modified EP fracture surface increases with the increase of MBS content. In addition, various characteristics of toughening are summarized by the fracture surface, as shown in Fig. 3e.

The Core-shell particles have a distinct double-layer or multilayer structure, with different components inside and outside. Each layer has separate functions, and this core-shell structure offers unique advantages. Compared to other epoxy resin toughening methods, the biggest advantage of core-shell modification is its strong controllability, which can be modified by controlling the particle size and changing the composition of core-shell polymer, thus making it more suitable for cultural relics protection.

The interpenetrating network polymer (IPN) can play a role in improving the toughness of epoxy resin. IPN is formed by two or more types of cross-networking polymer that interpenetrate or entangle each other, which most main preparation method is shown in Fig. 4a. It is characterized by the irregular penetration of one material into another material, so that the synergistic effect between the two components of the system will produce a better performance than ordinary blends. Common interpenetrating network polymer modified epoxy resin systems include epoxy resin/acrylate system, epoxy resin/polyurethane system, epoxy resin/phenolic resin system, and epoxy resin/polyphenylene sulfide system. Manjula Dhevi *et al.* [63] synthesized four types of hyperbranched polyesters (HBPs) with increasing generations using dipentaerythritol and dimethylol propionic acid as raw materials by *pseudo* one-step melt polycondensation, 1–4 generations, denoted as HBP-G1 ~ HBP-G4. SEM images of the first two generations are shown in Fig. 4b. It is used to prepare HBP polyurethane/epoxy interpenetrating polymer network composites. Compared to pure epoxy resin and linear polyol-based epoxy resin, modified HBP epoxy resin has higher toughness, and its impact strength is shown in Fig. 4c. However, due to the existence of flexible polyurethane bonds and the reduction in the crosslinking density of the epoxy matrix, the bending properties, thermal stability, and glass transition temperature of the modified sample are lower than those of the pure epoxy sample, as shown in Fig. 4c. Cheng *et al.* [64] prepared epoxy resin with Epon828 and TETA as raw materials and modified epoxy resin with polytetramethylene ether glycol (PTMG), isophorone diisocyanate (IPDI), and dibutyltin dilaurate (DBTDL) as raw materials. The analysis and comparison found that if EP/TETA/PTMG/IPDI/DBTDL is mixed at the same time, or EP resin and PU resin are prepared respectively before mixing, the resulting structure of the EP/PU composite material has a phase separation phenomenon, the best blending method was EP mixed with PTMG, IPDI and DBTDL, and TETA was added 10 min later. The SEM images of the EP/PU compounds prepared by different methods are shown in Fig. 4b. Li *et al.* [65] mixed the self-made isocyanate-based end-sealed prepolymer with epoxy resin E-51, then synthesized a series of amino polysiloxane (AG) with different relative molecular weights, and made a series of AG/polyurethane/epoxy interpenetrating network polymers using polyamines as curing agent. The results show that the AG/polyurethane/epoxy interpenetrating network polymer is a new type of low surface energy material with good hydrophobic properties, and its mechanical properties are closely related to the content of AG. The mechanical properties decreased with the increase in AG content. Wang *et al.* [66] synthesized an interpenetrating polymer network adhesive using epoxy resin and polyacrylate, applied it to Dazu stone, and found that the synthetic adhesive could enhance the strength of the rock while maintaining its breathability. Fig. 4d shows the potential of interpenetrating network polymers to be applied to stone carvings. Epoxy resin modified by interpenetrating network polymer can be successfully toughened by controlling the IPN phase composition and crosslinking degree. This modification has various polymer properties.

The natural rubber-modified epoxy resin is the most traditional toughening method, which is renewable and environmentally friendly. The actual picture is shown in Fig. S3a (Supporting information). Natural rubber is composed of a monomer chain structure diagram as shown in Fig. S3b (Supporting information). Because the dispersion of solid natural rubber in epoxy resin is not good, so natural rubber modification epoxy resin usually uses natural rubber degradation liquefied natural rubber made after liquefaction. The epoxy resin was modified by Mathew *et al.* [67] using natural epoxy rubber that was prepared in advance. The analysis of this modification indicates that the energy storage modulus and glass transition slightly decrease when rubber is added. However, the impact strength and fracture toughness of the modified epoxy resin are greater than those of the unmodified epoxy resin. The thermal stability, on the other hand, remains largely unchanged. Figs. S3c-e (Supporting information) presents the SEM images of the epoxy resin that has been modified with varying quantities of rubber. Seng *et al.* [68] prepared an epoxy resin modified with natural rubber and studied its morphology and mechanical properties. Natural rubber is shown to be used as an energy dissipation center, which can cause ductile fracture of the rubber modified epoxy resin. Natural rubber increased the fracture toughness of epoxy resin, which reached the maximum value when the amount of addition was 3 phr, and then gradually decreased. The impact diagram is shown in Fig. S3f (Supporting information), and the tensile strength showed a similar trend to the impact strength and Young's modulus. Aiza Jaafar *et al.* [69] combined silica, liquid rubber, and epoxy resins for toughening epoxy/kenaf composites, 30% polymethyl methacrylate liquid rubber composites (LMG30) with different contents of 1–7 phr were prepared by the hand lay-up method. Subsequently, impact and bending mechanical tests were performed according to ASTM standards. Impact strength and bending strength of epoxy/silicone/kenaf composites with three parts of LMG30 per 100 parts of resin are the highest, which are 13.83 kJ/m^2 and 62.2 MPa, respectively. As shown in Figs. S3g and h (Supporting information). However, in the current process of modification of epoxy resin by natural rubber, potassium permanganate is used, which is harmful to the environment.

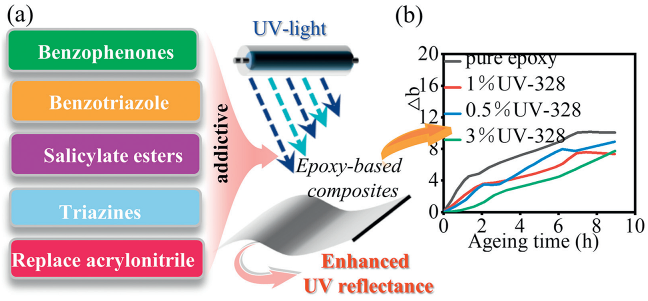

Fig. 5. (a) Mechanism diagram of UV absorbers. (b) Variation of b values with time during photoaging of epoxy resins and various modified epoxy resins.

The UV absorbent-modified epoxy resin enhanced the UV-radiation resistance of epoxy resin. Common UV absorbers can be divided into five categories: (1) benzophenones, such as UV-9, UV-214, UV-531, UV-1200; (2) benzotriazole, such as UV-P, UV-327, UV-326, UV-328; (3) salicylate esters, such as BAD, TBS, OPS; (4) triazines, such as ultraviolet absorbent triazine-5; (5) replace acrylonitrile, such as UV-317. UV absorbers can effectively absorb UV rays, converting them into harmless forms of light energy to be released. The specific mechanism is shown in Fig. 5a, Yang *et al.* [70] used UV-328 to modify epoxy resins. The UV reflecting ability, coating hardness and chroma of the unmodified epoxy resin were compared with those modified by 0.5% UV-328, 1% UV-328 and 3% UV-328, respectively. 3% of the modified epoxy resin UV-328 was found to have the strongest resistance to UV radiation, and the growth of color changes with aging time is minimal, as shown in Fig. 5b. Therefore, adding UV absorbers can improve the service life of protective coatings for outdoor cultural relics.

Thermotropic liquid crystal polymer (TLCP) contains a large number of rigid mesocrystal units and a certain number of flexible spacers. That makes the TLCP modified epoxy resin has higher physical and mechanical properties, heat resistance than the general polymer, with high strength, high modulus, and other excellent properties. In addition, it also integrates the advantages of liquid crystal order and network crosslinking. The addition of TLCP to epoxy resin enhances its mechanical properties. The introduction procedure is shown in Fig. S4a (Supporting information). Commonly used materials are homemade polyester epoxy resin with liquid crystal group, hydroquinone, and chloroethanol synthesis of a new type of liquid crystal epoxy prepolymer. Zhang *et al.* [71] studied the modification of the toughening of the epoxy resin E-51 using a self-made polyester epoxy resin with liquid crystal group. The results showed that the optimized formulation of the toughened epoxy resin potting material had good potting performance, while maintaining high compressive strength, the impact strength increased by 4.1 times. Gui *et al.* [72] synthesized liquid crystalline polyurethane-imide (PUI) through polymerization. They then characterized this polymer and utilized it as a modification in epoxy resin. The objective was to enhance the thermal and mechanical properties of composites. The SEM images of pure epoxy resin, 15% PUI and 35% PUI modified epoxy resin are shown in Fig. S4b (Supporting information). It is found that the PUI/ER material has not only good thermal stability but also excellent mechanical properties. When the PUI content is 15 wt%, the mechanical properties of the PUI/ER compounds reach the maximum, the bending strength reaches 178 MPa, and the bending strain at break reaches 10.65%, which are increased by approximately 32% and 33%, respectively. As shown in Figs. S4c and d (Supporting information). At present, because of the high price of thermotropic liquid crystal

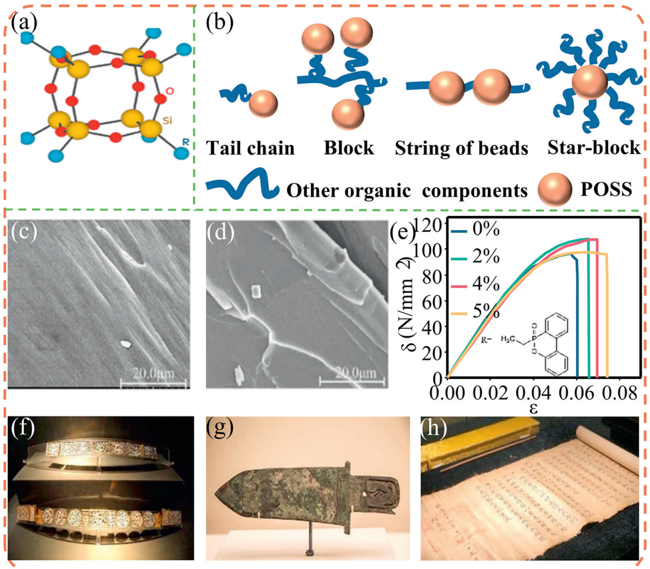

Fig. 6. (a) Schematic diagram of the three-dimensional structure of POSS. (b) Modification method of POSS. (c) SEM images of VE-1 (2%), and (d) VE-3 (5%). Copied with permission [74]. Copyright 2021, the Multidisciplinary Digital Publishing Institute. (e) σ-ε curves of the VE composites. Reproduced with permission [74]. Copyright 2021, the Multidisciplinary Digital Publishing Institute. (f-h) Potential application in metal cultural relics consolidation and paper cultural relics surface sealing.

polymers, synthesis is difficult, and because of the high thermal deformation temperature of the liquid crystal polymer, it is difficult to match with the universal matrix polymer, resulting in the processing and forming difficulties.

Polyhedral oligomeric silsesquioxanes (POSS) modified epoxy resin has been attracting much attention, and its structure is shown in Fig. 6a. The composite obtained by this method has the advantages of good heat resistance, good dielectric property, reduced degree of crosslinking of the epoxy resin, and improved toughness. The common modification modes of POSS are shown in Fig. 6b. Jerman *et al.* [73] studied whether the coating prepared by the silane-functionalized U_2IO_6 POSS precursor system has a corrosion inhibition effect on the alloy AA 2024-T3. The U_2IO_6 POSS coating is found to have a good blocking effect, which was reflected in the considerable drop (10^2 times) in the anodic current densities. Han *et al.* [74] synthesized cage and ladder phosphorus-containing polyhedral oligomeric silsesquioxanes (DOPO-POSS) by hydrolyzing and condensation reaction of 9,10-dihydro-9-oxa-10-phosphenanthrene-10 oxide (DOPO)-vinyltriethoxysilane (VTES), and add DOPO-POSS to the vinyl epoxy resin (VE). The SEM images are shown in Figs. 6c and d. The experimental results showed that the ultimate oxygen index (LOI) of the pure epoxy resin increased from 19.5 to 24.2 with only 4 wt% of DOPO-POSS and 0.5 wt% of tetrabutyltitanate added. In addition, the thermal stability and mechanical properties of epoxy resin composites are better than those of pure epoxy resin. The σ-ε curves of the VE composites are shown in Fig. 6e. Li *et al.* [75] prepared epoxy/polysiloxane (EP/PSI) hybrid membrane material by crosslinking epoxy resin with epoxy-containing agglutinated PSI. The effect of UV curing on the structure and properties of hybrid membrane materials was also studied. The results show that in the UV curing process of PSI and epoxy resin, rapid *in situ* hybridization to form epoxy/PSI hybrid film material, no phase separation, the obtained hybrid film material has high permeability, high temperature resistance, UV resistance, good adhesion, and so on. This modification has potential application in the consolidation of metal cultural relics and the surface sealing of paper cultural relics, as shown in Figs. 6f-h.

The block copolymer is composed of several different molecular chain segments connected by covalent bonds; usually, the central block and adjacent blocks are incompatible, in the structure microphase separation will occur, but because of the chemical bond between different chain segments, the phase separation is restricted. The assembly diagram of the front-end polymer is shown in Fig. 7a, which includes gyroid structure, mixed structure, and irregular bicontinuous structure. The epoxy resin modified by block copolymer can be mainly used to improve toughness. Commonly used materials are block copolymers with *n*–butyl acrylate (nBA), methyl methacrylate (MMA), and glycidyl methacrylate (GMA) as monomer block copolymers, molecular self-assembly of two parent block copolymers, *etc.* Liu *et al.* [76] toughened bisphenol A epoxy resin by using poly(ethylene-*alt*-propylene)-*b*-poly(ethylene oxide) (PEP-PEO) diblock copolymer loaded at 5%. A spherical micellar polystyrene-polybutadiene block copolymer (BCP) of about 15 nm was self-assembled and well dispersed in the matrix, as shown in Fig. 7b. The mechanical properties showed that the PEP-PEO diblock copolymer could significantly improve the fracture toughness of the epoxy resin without affecting the modulus of the epoxy resin. Furthermore, it was found that its modulus did not decrease at room temperature and that the glass transition temperature only decreased slightly, as shown in Fig. 7c. Pang *et al.* [77] studied the effects of additives on the tensile mechanical properties of cured epoxy resin. They modified DGEBA solidified by a linear diamine curing agent using nano SiO_2 particles and PEP-PEO diblock copolymer. The uncured resin and cross-linked epoxy resin both contained uniformly dispersed spherical micelles formed by the diblock copolymer, with a diameter of 20~30 nm. The combination of both modifiers led to a slight aggregation of SiO_2 particles in the epoxy resin. The SEM image of the epoxy resin fracture surface modified with 10% SiO_2 is shown in Fig. 7d. As the nano-SiO_2 concentration increased to 45%, the toughness of the material K_{IC} increased by 50%. When 4% diblock copolymer was added to pure epoxy resin, K_{IC} increased by 100%. At low concentration of diblock copolymers (4 wt%), K_{IC} increased linearly with nano SiO_2 concentration. Wang *et al.* [78] used octadecylamine and ethylene glycol diglycidyl ether as raw materials to synthesize admixtures with epoxy groups at both ends and long hydrophobic side chains attached to intermediate nitrogen atoms. A latent epoxy curing agent with long hydrophobic side chains (LCA) was then prepared by sealing the admixture with the remaining secondary amine on the self-made imines. The epoxy grouting material suitable for the wet base surface was prepared with the curing agent. The effects of curing agent, diluent, and accelerator on mechanical properties of epoxy grouting materials under different surface conditions were studied. The results show that the epoxy grouting material has the advantages of long operating time, high shear strength, and bonding strength on dry and wet bases. Fig. 7e shows its potential application. The specific data are shown in Figs. 7f and g. Zhou *et al.* [79] synthesized a room-temperature curing flexible water-based epoxy curing agent using the two-step chain extension method, prepared it with liquid epoxy resin into a two-component water-based epoxy coating, and found that the shortcoming of brittle performance of epoxy resin after curing was improved.

3.2.2. Inorganic blending modification

Adding inorganic nanoparticles to epoxy resin can toughen epoxy resin. Commonly used inorganic nanoparticles are TiO_2, Al_2O_3, ZnO, $CaCO_3$, silicate, clay, carbon black, *etc.* The crystal structures of TiO_2 and $CaCO_3$ are shown in Figs. 8a and b. Liu *et al.* [80] prepared the epoxy resin matrix modified with nano-Al_2O_3 particles by the mechanical blending method, effectively improving the anti-crack propagation ability of the resin matrix, and the modulus of the resin matrix first increased and then decreased with the increase of the content of nanoparticles. Bray

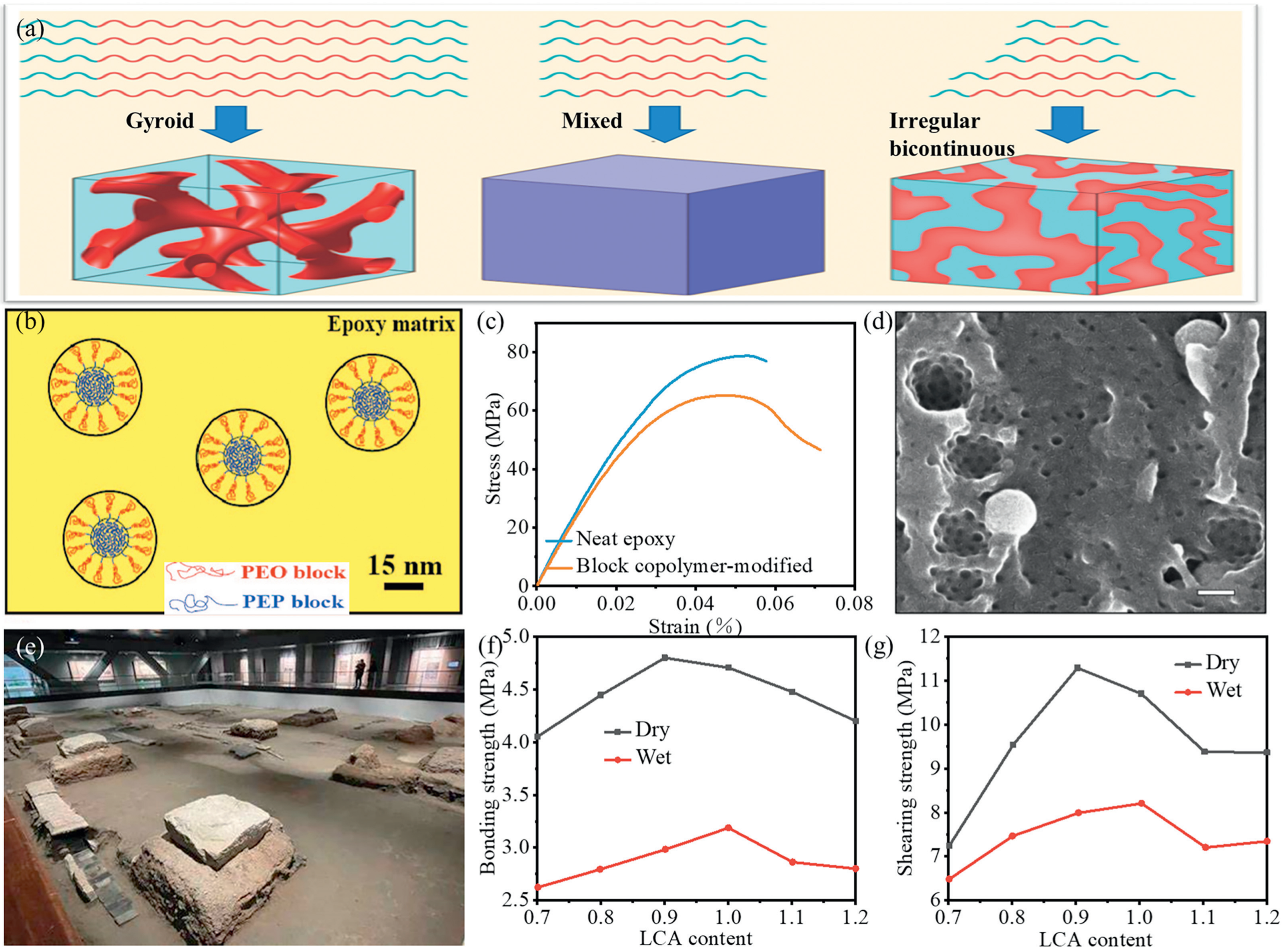

Fig. 7. (a) Schematic diagram of block copolymer assembly. (b) Schematic diagram of the BCP nanostructure. Copied with permission [76]. Copyright 2008, the American Chemical Society. (c) Engineering stress-strain curves of pure epoxy and BCP-toughened epoxy. Reproduced with permission [76]. Copyright 2008, the American Chemical Society. (d) SEM image of the 10% nano SiO_2 fracture surface. Copied with permission [77]. Copyright 2021, the American Chemical Society. (e) Potential application in earthen site. (f, g) Effect of curing agent on bond strength and shear strength of epoxy grouting materials.

et al. [81] compared the piperidine cured epoxy polymer modified by SiO_2 nanoparticles with three diameters-23 nm, 74 nm, and 170 nm. The results show that the toughness value increases steadily with increasing concentration of SiO_2 nanoparticles. Jia *et al.* [82] prepared titanium dioxide superfine powders with microsphere structure (S-TiO_2) by hydrothermal method and prepared S-TiO_2/EP composite material by blending S-TiO_2 as modifier with EP matrix. It is found that a reasonable addition of S-TiO_2 can improve the thermal conductivity of S-TiO_2/EP. When the S-TiO_2 content was 4.0 wt%, the thermal conductivity of the S-TiO_2/EP compound reached the maximum value of 0.1976 W m^{-1} K^{-1}, which was 16.2% higher than that of pure EP resin. However, the addition of too much S-TiO_2 is not conducive to the thermal conductivity of S-TiO_2/EP compound, as shown in Fig. 8c, which is caused by the cavity in the material caused by the agglomeration of S-TiO_2. Compared to pure EP resin (74.32 MPa), the maximum bending strength of the S-TiO_2/EP composite resin added with 4.0 wt% S-TiO_2 reached 96.18 MPa, an increase of 29.4% (Fig. 8d). Khoee *et al.* [83] modified bisphenol A epoxy resin using elastomeric nanoparticles (ENP) and nanostructured epoxy adhesive. The experimental study investigated the adhesion strength of a single-lap joint on various metal surfaces, including aluminum, copper, and steel. According to the findings, the adhesion of the modified epoxy resin was considerably stronger compared to the unmodified epoxy resin. Interestingly, the highest adhesion was observed when the nanomaterial content reached 20% (Fig. 8e). Yoon *et al.* [84] found that with the addition of nanomaterials, the viscosity of the color stable hydrogenated bisphenol A (HBA) epoxy resin adhesive using poly(propylene glycol)bis(2-aminopropyl ether) (D230) as a curing agent slightly increased. Through the analysis of the relationship between the shear and compressive strength of the adhesive and the viscosity, it is found that the optimization of the viscosity is the key to develop a new type of tablet protective adhesive. In addition, adjusting the coefficient of thermal expansion by adding nanomaterials is also important for adhesives applied to open stone tablets. Later, Xu *et al.* [85] prepared an HBA epoxy polymer containing TiO_2 nanoparticles using D230 as curing agent. Used to remove methyl orange (MeO) deposited on the limestone surface, the effect of TiO_2 particles with different particle sizes on the color stability of HBA epoxy resin was studied by dyeing degradation test. When TiO_2 was P200–400 and MeO concentration was 0.001 mol/L, degradation efficiency was the highest. The limestone surface was treated with HBA/D230/TiO_2 and the results show that the limestone surface has good resistance to sulfuric acid corrosion, as shown in Figs. 8f and g. Bai *et al.* [86] modified epoxy organosilicone resin with KH560-modified nano SiO_2 blending to improve the heat resistance of the resin, while showing toughening characteristics and nano effects. Luan *et al.* [87] developed a protective agent for cultural stone relics by mixing a water-based epoxy emulsion with silicate and adding an appropriate amount of matting agent and other additives. The sample was evenly coated with a brush and dried for 48 h. Stability, soluble salt corrosion,

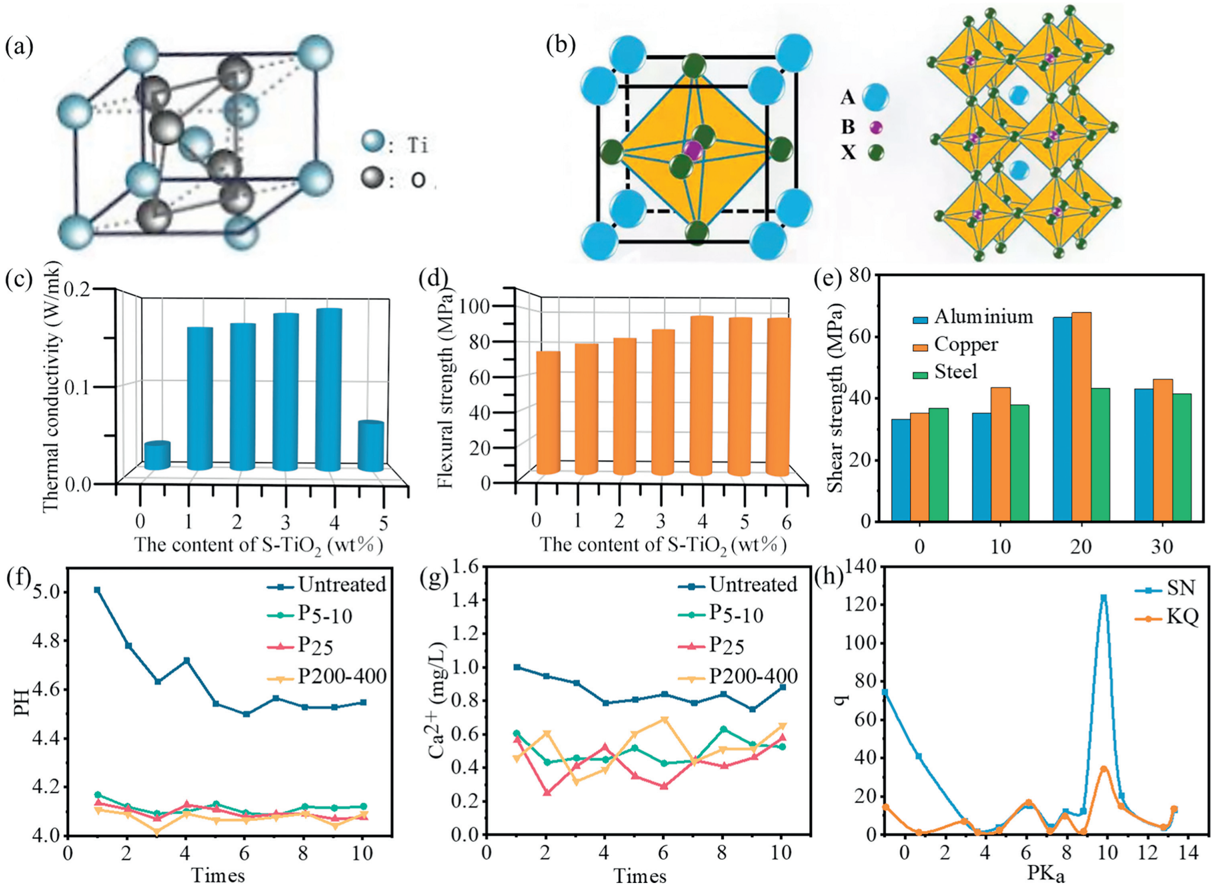

Fig. 8. (a) Schematic diagram of the TiO_2 crystal structure. (b) Schematic diagram of the $CaCO_3$ ABO_3 crystal structure. (c) Thermal conductivity of S-TiO_2/EP with different S-TiO_2 content. Reproduced with permission [82]. Copyright 2021, the Springer Nature. (d) Flexural strength of S-TiO_2/EP with different S-TiO_2 contents. Reproduced with permission [82]. Copyright 2021, the Springer Nature. (e) The relationship between shear strength and ENP content. Reproduced with permission [83]. Copyright 2010, the Elsevier. (f, g) Changes in pH and Ca^{2+} of periodic spraying in simulated acid rain with a pH value of 4.0. Reproduced with permission [85]. Copyright 2016, the Springer Nature. (h) pK_a spectra of acid-base active centers on the surface: q: A specific number of active centers on the surface, pK_a: negative logarithm of surface-active central acid hydrolysis constant.

and ultraviolet irradiation tests in stone samples show that the sealant material of the modified silicate water-based epoxy resin emulsion has an obvious protective effect on stone cultural relics, and the waterproof and respiratory properties are the best when the epoxy emulsion: silicate is 1:0.4 (Table S4 in Supporting information). Danchenko *et al.* [88] selected the polymer composition of ED-20 brand epoxy resin and DETA curing agent as the research material. Fillers are air-dried dispersed materials of different properties: oxides, clays, and quartz. Studies have shown that to obtain a material with improved protective properties, it is necessary to use an oxide or clay filler with basic (alkaline) surface function, as shown in Fig. 8h. Blending modified epoxy resins are summarized in Table S5 (Supporting information).

3.2.3. Other modification methods

In order to better adapt to the complex actual situation of art protection, a variety of modification methods are often used. Chen *et al.* [89] added nano-SiO_2 coated with $Al(OH)_4$ to the epoxy silicone resin modified with 4-fluorophenyl isocyanate to improve the densification of the resin and make it difficult for corrosive media to invade. Tulliani *et al.* [90] studied composites based on epoxy silicone resin and ethyl silicate as potential gypsum consolidation materials, and ytterbium as acid catalyst for thermal curing. The hardness of the mixed system increases significantly and the water absorption rate of the gypsum treated with this material decreases, while the hydrophobic capacity remains unchanged, as shown in Fig. 9a. In addition, even with artificial aging, the color change and yellowing are minimal (Fig. 9a, inset). Wan *et al.* [91] prepared organic-inorganic composite materials, namely epoxy-silica-acrylate (ESA) hybrid materials, which were used

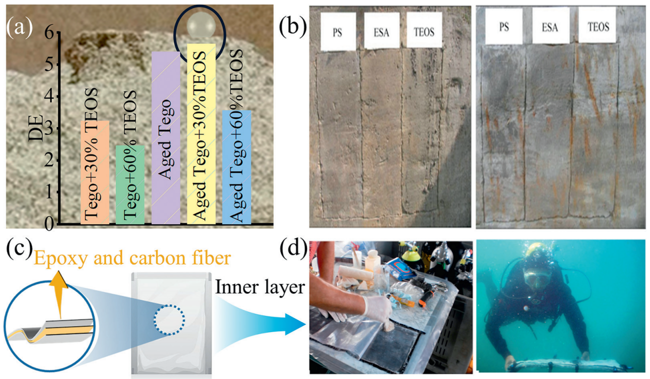

Fig. 9. (a) A drop of water deposited on the surface of gypsum treated with TEGO + 3% Yb + 60% TEOS, inset: color changes of the treated plaster before and after artificial aging. (b) Consolidation comparison of different consolidation materials of the Jinsha archeological earth wall (left: wet earth wall, right: dry earth wall). Copied with permission [91]. Copyright 2014, the Springer Nature. (c) Schematic of the multilayer structure. (d) Preparation stage: epoxy resin is applied to multiple layers in the bag and then the bag is closed and Fragile artifacts recovered from carbon fiber sheets vacuumed in plastic bags were brought to the surface by restorers. Copied with permission [92]. Copyright 2014, the Springer Nature.

to consolidation the Jinsha archeological site in Chengdu, China (Fig. 9b). The results show that the consolidated soil is relatively flat with some fine pores and the consolidation properties are ESA $>$ K_2SiO_4(PS) $>$ ethyl orthosilicate (TEOS). For the protection and transfer of underwater cultural relics, a multi-layered structure was made to transfer the relics (Fig. 9c). Petriaggi *et al.* [92] made a vacuum bag in the National Museum of Denmark (Fig. 9d, left). Inside the vacuum bag there is a sandwich-structure composite, consisting of: an aerating felt that absorbs excess resin and, depending on its thickness, serves as a soft contact layer; a peel ply (A release fabric to allow the venting of excess resin. It is easily removable and leaves a roughened surface suitable for further bonding.); an impregnated carbon fiber laid up as required, and peel ply again. Tests have shown that the carbon fiber fabric, impregnated with epoxy, is a true protective shell that protects the cultural relics through rapid drying and prevents possible trauma caused by poor material preservation. This system can be used for small and large artifacts (light and heavy) as well as an effective container for temporary storage of waterlogged organic artifacts (Fig. 9d, right). But this method requires moving objects, and it is important that bamboo slips remain pristine, therefore, Wang *et al.* [93] used 3,4-dimethoxy-benzaldehyde as primary reinforcement, epoxy resin adsorbed polyurethane sponge as secondary reinforcement, and adhesive tape as tertiary reinforcement for in-situ reinforcement and salvage of underwater bamboo slips. The porous polyurethane sponge replaces the traditional carbon fiber cloth because the sponge has a certain thickness (0.5 cm), which can effectively cushion the impact of the collision of the internal material. Polyurethane sponges, meanwhile, are loose, porous materials that can quickly absorb large amounts of epoxy, eliminating the time needed for underwater reactions, and this method can ensure that the bamboo slips are still in the original position when they are salvaged. Later, Wang *et al.* [94] made an improvement for the fixed collection of underwater lacquerware. They used a super hydrophobic/super oil-philic multi-walled carbon nanotube polyurethane sponge as secondary reinforcement. The flexural strength after reinforcement can reach 3.56 MPa, which can resist external force. Other modified epoxy resin summary as shown in Table S6 (Supporting information).

4. Application of representative examples of large-scale cultural relics protection

Currently, epoxy resin is the most widely used reinforcement material in our country. Domestic brands used for cultural relics repair include 6101, 618 and AAA super glue, all of which are low molecular weight bisphenol A type epoxy resin. The main amine curing agent has shortcomings such as brittle bonding surface, yellowing and curing for 24 h. Foreign brands include Hxtal NYL-1, Araldite 2020, and their advantages are colorless and transparent products, a refractive rate close to glass, not easy to age yellow, the disadvantages include slow curing speed (1 week for complete curing) and limited bond strength [95].

Epoxy resin is widely used in strengthening cultural relics. For metals [96], the cracks of iron and bronze can be reinforced by epoxy resin or by measures of epoxy resin and silica point reinforcement [97]. For example, the ancient small-mouthed wine vessel at the Shanghai Museum in the late Shang Dynasty is unique in shape and beautifully decorated. But the defect is greater, nearly half of the total area of the original utensil. In order to present a complete look of the utensil, we improve it on the basis of the traditional method of turning molds and replicating original mover patterns. By cutting resin repair pieces and borrowing correction, the common problem of micro differences between overturning mold repair pieces and parts of original decoration and shapes has been solved, and good results have been achieved in an ancient restoration of small-mouthed wine vessels (Fig. 10a) [98]. The residual round bronze tripod of the Western Han Dynasty was formed and supplemented with the casting cover button after the preparation of 815 epoxy resin (Fig. 10b) [99]. Our famous grottoes, such as Longmen Grottoes, Yungang Grottoes, Maijishan Grottoes, Dazu Grottoes, are reinforced with epoxy resin. Internationally, Switzerland, Japan, the United States, Italy have used this material as a reinforcement. Japan used it to restore the Guili palace and Horyuji Temple; several churches in California and Louisville have also been reinforced with epoxy resins; Andrea in Italy experimented with an epoxy resin that also worked well. Figs. 10c-f show some of the images before and after the epoxy resin was used [100,101]. It can be seen that it was severely weathered before restoration, such as corrosion, collapse, and other phenomena. After restoration, its morphology was basically completely restored.

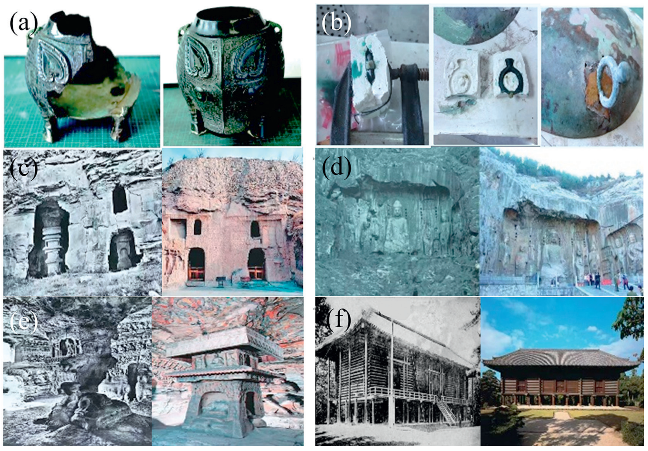

Fig. 10. (a) Condition of primeval an ancient small-mouthed wine vessel before and after restoration. (b) Repair the cover button with 815 epoxy resin. (c) Comparison before (left) and after (right) restoration of Grottoes 1 and 2 in Yungang Grottoes. (d) Comparison before (left) and after (right) restoration of "Epoxy resin grouting technology for surrounding rock reinforcement" at the Great Shrine of Fengxian Temple. (e) Comparison before (left) and after (right) restoration of the central tower column in Cave 1 of Yungang Grottoes. (f) Comparison before (left) and after (right) restoration of Horyuji.

5. Conclusion

This work summarized epoxy resin and its classification. In a word, epoxy resin can be classified according to their functional groups. Significantly, this work concluded the key issues of using epoxy resin for protecting cultural relics and corresponding solutions, as well as their specific applications. The main challenges of epoxy resin used for cultural relics protection are the weak anti-ultraviolet ability and poor impact toughness, leading to the blackening, yellowing, or damage of cultural relics over long time. Focused on these problems, adding UV absorbents could improve UV resistance of epoxy resin, introducing inorganic nanoparticles and block copolymerization could enhance their impact toughness. Moreover, adding copolymers into epoxy resin could utilize the enhancement of the waterproof properties of cultural relics.

Despite that epoxy resin has achieved much successes in cultural relics protection, some problems still exist in several aspects. Firstly, the bonding and reinforcement of epoxy resin is primarily chemical reaction, which depend on the formation of chemical bonds at interfacial areas between the epoxy groups and the relics. Usually, these chemical reactions are irreversible. Furthermore, since the epoxy resins are organic materials, their durability is inevitable lower compared with inorganic materials. Importantly, most achievements in this field are short-term experimental success, which have not been applied to cultural relics for an extended period. Therefore, it is still difficult to evaluate the long-term efficiency of modified epoxy resin in the application of cultural relics protection. Focused on these issues, several suggestions are proposed for the future development of epoxy resin in cultural relics protection. First of all, it is necessary to select an appropriate modification method, which could achieve a balance between the combining capacity of epoxy resin and their removability in specific solvents, thereby preserving its binding ability and reversibility. Secondly, inorganic materials are recommended to be selected to modify epoxy resin, which expected to ensure the aging synchronism of protective materials and the relics as much as possible. Finally, it is critical to evaluate the practical application value of the new-type modified epoxy resin, they should be applied to the imitation cultural relics and long-duration tests are also required.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2023.109194.

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