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A Review on The Properties of Repairing and Complementing Materials for Ancient Porcelain

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Abstract

In the process of ancient ceramic restoration, filling is an important link. In order to improve the repair effect, scholars have made some important research results on the properties of repair materials in recent years. Repair materials can make the display effect of broken porcelain better and the information expression more complete. The above research results are summarized in this paper. It gives readers a more comprehensive view of the latest advances in the study of complementary materials for ancient ceramics.

Keywords

Repair materials; Complementary properties; Hardness.

1. INTRODUCTION

China has a long history of porcelain making with many varieties. In the long history of thousands of years, the ancient ceramics have been broken and incomplete in different degrees due to the influence of natural and human factors, which seriously damaged the original value of the ancient ceramics. For the restoration of damaged ancient ceramics, mature restoration techniques and rich restoration materials have been gradually formed since ancient times. Complementation is an important link in the restoration process of ancient ceramics, which can restore complete information of cultural relics for archaeological typology reference and audience viewing.

At present, there is no standardized standard for the use of supplementary materials in ceramic restoration, and the supplementary methods show a variety. Generally, the damaged and incomplete parts of the ware are filled with plastic materials that have no impact on the body on the basis of following the repair principle, so as to restore the integrity of the original shape of the ware. In recent years, Restoration workers have explored the properties of the supplementary materials such as bending strength, hardness, light transmittance and aging resistance based on the conservation concept of cultural relics, the exhibition effect after restoration and the display and preservation, but most of them are scattered in various journals. In view of this, this paper summarizes the application status and performance research of the supplementary materials, so as to show readers the latest progress in the current research on the properties of the supplementary materials. The readers have a more comprehensive understanding of the research and development of the properties of complementary materials.

2. COMPLEMENTING METHOD AND APPLICATION OF COMPLEMENTING MATERIALS

In the Neolithic Age, many holes were drilled and repaired along the body and mouth of the pottery POTS and deep-vented pottery POTS unearthed from the site, as shown in Figure 1[1], indicating that at that time, there was a sense of natural repair with the main purpose of

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restoring and practical artifacts. The repair method was only to connect the broken parts and tie the broken parts with vines after drilling. The repair material comes from nature.

Figure 1. Pottery POTS unearthed from the Neolithic site of Gaotai Mountain, Xinmin City, Shenyang, Liaoning Province

In ancient times, it can be known from the literature records that the ancient ceramic complementing process includes re-burning (FIG. 2), glazing, repairing of the fixed body (FIG. 3), curium nail bonding (FIG. 4) and other ancient ceramic complementing methods with commercial value, recovery and appreciation as the main purposes. The binder uses glutinous rice porridge, egg white, bletilla striata, white wax, lacquer, shellac, gum, yellow fish gum and other natural adhesives. In the filler are additives such as lime, gluten and fixed powder [2].

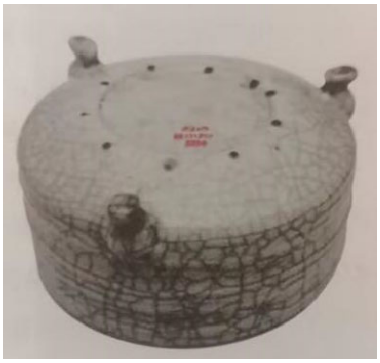

Figure 2. The three-legged furnace of the Imperial Kiln, a relic of the Qing Dynasty in the Palace Museum (with new fire at the back of the furnace foot)

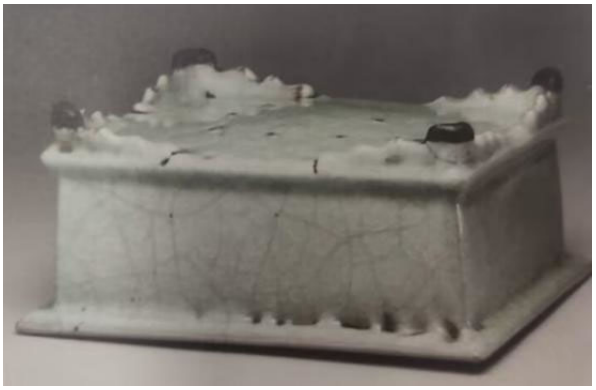

Figure 3. Taipei National Palace Museum Collection (black and brown supplementary materials)

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Figure 4. Yongzheng Malachite Green glazed plate Collection in the Palace Museum (metal complement)

During the period of the Republic of China, it can be seen from the earlier Restoration and Preservation of Antiquities that the restoration materials were mainly animal glue casein adhesives, pyrocotton adhesives, burned gypsum, etc. [3], and no new supplementary materials were seen. In the 1950s, the Jia family became the concentrated representatives of the restoration of cultural relics in this period, and they made great contributions to the rescue restoration of museums and archaeological institutes. In this period, the restoration trend for the purpose of display was formed, and cultural relic restoration workers used the materials and tools used in the repair of bronzes in the restoration of porcelain. At this time, Ancient porcelain restoration materials were still mainly composed of natural adhesives such as shellac, gum, yellow fish gum, and Rumi gum mixed with gypsum and putty [4]. Until the 1990s, colorless and transparent epoxy resin binder appeared, basically replacing the traditional curium pinning technology and the use of shellac and gum adhesives, and the porcelain patching in the modern sense began to emerge. According to Yu Hui et al., the adhesives used to repair porcelain include epoxy resin, acrylic resin, cellulose nitrate, polyurethane resin, etc. The fillers include quartz powder, kaolin, aluminum oxide powder, talc powder, gypsum, calcium carbonate, titanium dioxide, white cement, white-black carbon, barium sulfate, etc. [5]

With the development of science and technology, the repair methods and materials are constantly changing. It can be seen from Jia's restoration of old cultural relics that gypsum repair has a long history (FIG. 5) [6]. Recently, some scholars have proposed the compatibility of gypsum and ancient ceramics and the application of cemented gypsum on the basis of ordinary gypsum repair of ancient ceramics. In 1997, Jiang Daoyin proposed the means of complementing ceramic with ceramic and porcelain with porcelain (FIG. 6) [7]. However, ceramic with ceramic and porcelain with porcelain are difficult and have high firing cost, which often presents a waste phenomenon and is not easy to be widely used. With the development of digitalization, in 2014, Liu Yahui proposed to apply 3D printing to the restoration of ancient ceramics (FIG. 7) [8]. The complementary method can improve the restoration efficiency of restorers on the basis of not wearing the broken sections of the repaired porcelain, and has made good progress in the current work. In the use of 3D technology, different printing materials can also be applied, such as polymer materials, metal materials, acrylic glass, light sensitive materials, light curing materials, nylon materials, etc. In 2020, Wu Yanfang proposed that ML algorithm has significant application value in AM precision manufacturing of high-performance ancient ceramic restoration parts. It also provides a new design idea for the accurate development direction of AM manufacturing technology [9]. At the same time, new materials are constantly used. In 2020, Li Qijiang proposed that alkali-excited gel polymeric materials have good bonding properties, and their comprehensive properties are superior to the current ceramic complement materials, and should be applied to the complement of ancient ceramics [10]. In 2022, Li Qi proposed that the materials should be applied to the handed down cultural relics with large quantity of existence and low cultural relic value. It can return to the tradition before the appearance of chemical materials, and use fiber, metal, wood carving and

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other complementary materials suitable for the artistic characteristics of porcelain to repair the missing parts (Figure 8); In 2023, Song Zixian discovered 3MTM solid ceramic microspheres, which can be used as a new complement material for porcelain restoration [11].

Figure 5. Jia's restoration of the old photo

Figure 6. Effect of repairing porcelain with porcelain

Figure 7. 3D printing effect

Figure 8. Fiber-braided porcelain pot cover

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However, in the restoration of ancient ceramics at this stage, porcelain restorers still mostly use epoxy resin adhesives mixed with inorganic fillers to supplement porcelain. The specific replenishment process is to mix inorganic fillers into epoxy resin adhesives, and fill the defective parts of porcelain after curing, so that the porcelain shape can be restored to its original appearance, and its performance is the interaction between binder and filler. After the repair of damaged porcelain is completed, the integrity of the ware can be maintained without falling off, which requires the bonding strength, plasticity and surface hardness of the repair material. Secondly, the repaired parts will generally undergo varying degrees of color change over a period of time, which affects the late preservation and aging effect of ancient ceramics, so it is particularly important to select materials with good color resistance before restoration.

Among these indicators, there is no standard document to regulate its performance strength. For this, Wang Huizhen proposed that in the application of cultural relic restoration materials, the materials used should be coordinated with the strength and color of cultural relics. In the process of restoration of Han Dynasty pottery in Qingzhou, Shandong Province, Rand Province also put forward the restoration concept that "the mechanical properties of the supplementary materials should be similar to the mechanical properties tested on the Han Dynasty pottery in Qingzhou, Shandong". However, the restoration workers mostly evaluated the excellent properties of the supplementary materials, ignoring the matching degree with the porcelain itself. At present, Wen Jianhua only evaluated the mechanical properties of ancient ceramics, complementary materials and the repaired ancient ceramics respectively in the destructive research of hardness of complementary materials on ceramics in 2020, and proposed that after the complementary materials bonded with porcelain and pulled apart, the complementary materials with stronger mechanical properties than ancient ceramics would cause certain damage to the ancient ceramic matrix.

3. RESEARCH STATUS OF PROPERTIES OF REPAIR MATERIALS

3.1. Bonding strength of the supplementary material

For the bonding strength of supplementary materials, from the ancient literature "uncooked gluten into the sieve net lime less, pestle hundreds of times, suddenly open like water, to stick, bind the dry and never come off [12]" we can know that at that time, people have the awareness that adding fillers can increase the bonding strength. Until 2009, Yang Zhizhen used Instron1121 static material testing machine to test the shear strength and tensile strength of talc filler mixed with adhesive, and clarified the change curve of mechanical properties of the supplemented part with the increase of filler in a scientific way, and proposed that both tensile strength and shear strength were not reduced much when talc particles were mixed with adhesive. That is, the bonding strength of the binder does not decrease much, and the degree of decline does not affect the bonding fastness or stability of the porcelain after repair [13]. In 2012, it was further clarified the specific proportion of filler that the addition of filler reduced the shear strength of the binder. Yang Zhizhen proposed that the shear strength gradually increased with the addition of filler, but the shear strength decreased significantly after the addition of more than 75%. Therefore, when the amount of resin filler per 100 parts was 75%, the adhesive operability and bond strength were better. This is also the best ratio of micron particle size filler mixed in binder. As for the use of nano-sized inorganic fillers, Wang Shujuan proposed that the toughening and modifying effect of nano-sized materials on epoxy resins is more obvious [14] .The application of nano-sized materials is also one of the new development directions of ancient ceramic complementary materials. It is completely different from ordinary micron crystal particles, and nanoparticles have the characteristics of extremely small particle size and extremely high specific surface area. When it is added to epoxy resin, it can bond with the long chain of epoxy resin, thereby improving the intermolecular bond force and forming a good

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interfacial force between the matrix to toughen the epoxy resin glue, so that the complementary material is not easy to break. However, nanomaterials are small in particle size, easy to agglomerate, not easy to operate, and are currently used in a small range.

3.2. Hardness of the supplementary material

In the study of hardness of supplementary materials, some scholars proposed to modify epoxy resins by adding hardener or crystal particles, such as polyurethane, silica, silicon carbide powder, etc., but the above problems still exist. Fillers with small particle size are prone to agglomeration phenomenon, and while increasing the hardness of supplementary materials, other properties of epoxy resins are prone to decline. Therefore, in the actual operation at this stage, the modification of nanoparticles and reactive solvents is still not the mainstream way to improve hardness, and more is to replace the filler or control the proportion of its incorporation to achieve the purpose of improving hardness.

For the research on the proportion of filler mixture, Mao Xiaohao proposed that "the proportion of gypsum in the formula should be appropriately increased. The amount of gypsum used is inversely proportional to the hardness and strength of the curing product of the supplementary material. The more gypsum used, the lower the hardness and strength of the curing product [15]".However, according to the study of Tang Jin et al. [16], there is a certain extreme value of the admixture, and the hardness increases first and then decreases with the increase of the filler. This is because the filler mixed with the binder can significantly improve the modulus of the composite material and increase its strength. However, when the filler is too much to a certain extent, more particles filled with the binder gather on the surface of the composite material, and the binder can no longer wrap all the particles. When the supplementary material is subjected to force, the particles are easy to fall off from the epoxy resin base;In order to replace different filler particles, most researchers use relevant hardness testing instruments to directly evaluate and study the complementary materials, but different experiments show different screening and evaluation ranges, hardness characterization methods, and experimental conditions. Although Vickers hardness and inner hardness can be converted into each other through formulas, the adhesive matrix is different. The influence on its hardness is unknown, and it is often impossible to compare its experimental results horizontally, so that the research results of a subject can only be used in this subject, and can not be referred to by another subject, resulting in a waste of experimental results.

3.3. Anti-aging properties of supplementary materials

The anti-aging property of the complement material is crucial to the restoration of ancient porcelain and is related to the maintenance time of the repair effect, so the anti-aging property is also the concern of researchers for a long time, and there are many research results in this aspect.

Yang Zhizhen et al. first studied the optimal applicable environment of epoxy resin adhesive, and proposed that when the adhesive is cured at room temperature 30℃, it shows good bonding strength and good operability, and the relative humidity is less than 90%, and the shear strength of epoxy resin adhesive decreases with the increase of humidity [17]. Then Zhang Hui et al. tested the external factors affecting the aging of the complementary materials and came to the conclusion that both high temperature and ultraviolet light would affect the yellow of organic materials. However, the dominant factor of high temperature and ultraviolet light could not be verified [18]. In terms of the influence of the colloid itself on the aging properties of the supplement material, Yang Zhizhen analyzed it with infrared spectrometer and proposed that the yellow problem of AAA super adhesive was mainly caused by the poor stability of Group B fatty amines and amides curing agents [19]. In 2010, Yang Zhizhen improved the yellow aging properties and proposed that titanium dioxide has good ultraviolet absorption ability. FD-2, the

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main component of titanium dioxide, is added to the acrylic paint and sprayed on top of the supplementary material as a base, which can effectively delay the yellowing of epoxy resin [20].

In addition, in the screening and evaluation test of commonly used binders, Liu Chao and Wu Qichang et al., among the commonly used binders, confirmed that AAA adhesive has the worst color change resistance to various aging factors, and proposed that it should not be used in ancient ceramic restoration. Hxtal(NYL-1) imported from the United States is the best resistance to ultraviolet light and alternating high and low temperature color change among commonly used binders. It can be used in outdoor and northern environments with large temperature difference between day and night [21].

3.4. Light transmission intensity of the supplementary material

In the study of the permeability of supplementary materials, there is currently relatively little research on the permeability of porcelain, leaving a lot of research space. The earliest reference we found in this regard is in 1993, when Mao Xiao-Hou mentioned "[22],visible light composite resin, photo-sensitive adhesive, and special pigments. These three materials are capable of repairing deformed, semi-deformed, and fine porcelain varieties. The visible light composite resin repair material represents an advanced and comprehensive solution that was first developed in foreign countries in the mid-1970s. China began importing this material in 1985 and conducted clinical trials for dental repair of diseased teeth before applying it to porcelain restoration. Subsequent research has suggested incorporating white and black carbon into the supplementary material to enhance the transparency of the repaired area. For instance, Yu Hui proposed in the Foundation of Ancient Ceramic Restoration that 'fumed white carbon black can effectively restore thin and highly transparent porcelain,' although there is currently a lack of corresponding theoretical research and specific operational data to provide a thorough explanation.

There are two primary reasons for this. Firstly, it is challenging to investigate the light transmission properties of ancient ceramics. According to Feng Bing et al.'s study [23], the intensity of light transmission in porcelain is influenced by various factors leading to light loss, such as impurities, glass phase, grain boundary structure, porosity, and surface finish. However, the formation of these factors can be attributed to multiple variables including raw materials themselves, processing methods of raw materials, and firing temperature of porcelain. This complexity makes it difficult to establish a consistent law governing transmittance intensity. Secondly, existing instruments for testing light transmission intensity do not adequately meet the requirements for assessing semi-transparent white porcelain without altering the original state of ancient ceramics. For instance, optical transmittance irradiation instruments are unsuitable for testing foggy or non-transparent materials; meanwhile fog transmittance instruments impose strict sample thickness requirements. Although Wang Zhen's research has addressed thickness issues [24], she suggests that using a curve method for measuring transmittance does not necessitate precise control over sample thickness and can yield superior experimental results. However, this approach requires cutting and polishing samples which significantly contradicts the principle of preserving ancient ceramics in their original state and fails to fulfill non-destructive testing requirements for assessing light transmission intensity.

4. CONCLUSION

From the perspective of the development process of supplementary materials, the application of new materials and new technologies is an inevitable trend. We must evaluate, practice and update previous materials on the basis of inheritance, so as to better serve the protection of cultural heritage. In addition, by combing and summing up the properties of the current complementary materials, it can also be found that with the development of restoration technology and concept, the requirements of ancient porcelain complementary materials are

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more refined, and restoration workers are more and more in-depth research on their adhesive strength, hardness, aging and other application properties. Restoration workers have gradually changed from the previous empirical judgment to the scientific analysis and measurement of the application of restoration materials.

However, there are still many problems in the study of the properties of complementary materials at this stage. For example, in the evaluation experiment of complementary materials, the experimental conditions of each study are different, which is difficult to compare with each other, and the application range of conclusions is small. In addition, the performance standard of the supplementary material is not clear, too large strength has an impact on the restoration operation, too small strength will affect the exhibition and preservation of porcelain, so it should continue to strengthen the scientific research on the performance of the supplementary material, quantify its standard, in order to better scientific application.

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