Investigation of the renewable diseases in the Maiji Grottoes: some reflection for PVAc

Chenglei Meng

Zhejiang Provincial Institute of Cultural Relics and Archaeology

Fang Shiqiang

Zhejiang University

Ma Qian

Maijishan Grottoes Art Research Institute

Hu Wenjing

Zhejiang University

Liu Xiaobin

Zhejiang University

Zheng Ye

Zhejiang University

Dong Guangqiang

Maijishan Grottoes Art Research Institute

Yue Yongqiang

Maijishan Grottoes Art Research Institute

Zhang Bingjian (✉ chrismeng@vip.qq.com)

<https://orcid.org/0000-0003-0316-6332>

Research article

Keywords: Maiji Grottoes, murals, PVAc, renewed disease

Posted Date: July 8th, 2020

DOI: <https://doi.org/10.21203/rs.3.rs-40594/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License. [Read Full License](#)

Abstract

The Maiji Grottoes a famous grotto group located on the ancient "Silk Road". It occupies a significant place in the history of grottoes and has also contributed to the communication of Buddhist art. Since the 1970s, the Chinese government and restoration professionals have made many efforts to restore the Maiji Grottoes for purposes of both scientific research and cultural protection. However, some severe diseases have repeatedly broken out in several grottoes, which require urgent treatment. In this paper, 21 grottoes and about 137.72 m² of murals from 21 grottoes reinforced by PVAc emulsion were investigated. The results indicated the most common diseases are cracking, hollowing, discoloration, mildew, saline-alkaline and flaking. These diseases have a close relationship with the microenvironment of each grotto. Moreover, the LC analysis showed the PVAc look like remained practically the same reinforce effect, regardless of changes in time and climate. Thus, the PVAc could be used in the protection of murals for which a controlled environment should be provided to prevent these renewed diseases.

1. Introduction

The Maiji Grottoes (34°21'09"N, 106°00'10"S), located on the ancient "Silk Road", are one famous grotto group in China. It occupies a significant place in the history of grottoes and has also contributed to the communication of Buddhist art. According to the ancient literatures and inscriptions remained in some caves, researchers inferred the grottoes had been initially excavated in Later Qin Dynasty (384–417 AD). Due to several serious earthquakes, part of the grottoes had been destroyed. Today, the remaining 3938 sculptures and 979.54 m² of murals scattered in 221 grottoes were built from the Northern Dynasties (386–581 AD) to Qing Dynasty (1636–1912 AD)

However, various sculptures and murals had been destroyed due to vast geological disasters (the area have suffered from several earthquakes of magnitude 7 or over) [1], man-made destruction, environmental pollution and protection deficiency. Since the 1970s, the Chinese government and restoration professionals have made many efforts to restore the Maiji Grottoes. The work included reinforcing the cliff of Maiji Mountain and protecting the sculptures and murals in the caves. The record indicated the PVAc emulsion was kept using to protect and repair murals in the Maiji Grottoes. After a series of tests and study on craftsmanship, a formula using earth, sand, oakum or cotton and put in 10 to 15 percent of PVAc emulsion was concluded [2]. The above materials could be used for reattaching, reinforcing and restoring the deciduous murals. Moreover, 1 to 5 percent of PVAc emulsion was applied to reinforce the surface of the murals. These jobs received many experts' affirm at that time.

PVAc emulsion is widely used around the world as a fresco's protective material due to its good performances [3–4]. Unfortunately, this material also has drawbacks such as vulnerability to acid and light aging, and susceptibility to bacterial decomposition [4–7]. These disadvantages force the researchers to develop better material for mural protection. On the contrary, some studies indicate PVAc used for mural reinforce in the harsh condition had little changes [8–9]. Moreover, some experienced craftsmen told the repair technology is more important than the material to control the renewed diseases' occurring. In the field of historic preservation, more and more scholars approved the importance of the craftsmen's experience and knowledge to conservation work [10]. Unfortunately, there was little work aimed at the on-site tracking survey of PVAc emulsion applied in one place for a long time due to various difficulties. And much work was done in lab.

In August of 2013, the Maiji Grottoes Art Research Institute offered us an opportunity to investigate the renewed diseases after reinforcement by PVAc emulsion. PVAc emulsion is applied to reinforce the murals in Maiji Grottoes since the 1970s and it is still in use today. And the reinforced areas of murals exceed 10 percent of the total area of murals. Thus, investigating the service condition of this material is very important and the available information is reliable. We hope this investigation could provide some useful information to protect the Maiji Grottoes and other similar cultural heritage much better.

2. Investigation And Methodology

The Maiji Mountain locates in the rain forest area. According to the meteorological statistics since 1970s, the annual sunlight is about 1200 to 1600 hours, the mean annual precipitation and evaporation capacity is about 840 ml and 1000 ml, the relative humidity is 74% and the extreme maximum and minimum temperature are 32.5 °C and - 16.8 °C (on July 20, 1997 and January 15, 1992, respectively). Under this environment, the grottoes which locate at the bottom and top of the mountain are much different in the micro-climate. Thus in this investigation the grottoes located at the top and middle of the mountain were chosen to study the renewed diseases over time (the surveyed areas were about 137.72 m², covering above 14% mural areas in the Maiji Grottoes). And the grottoes located at the bottom of mountain as control groups to study on the influence of humidity on renewed diseases after reinforcement by PVAc emulsion (Fig. 2).

The area of diseases was measured by ruler and laser range finder. The areas of discoloration, mildew and glare were estimated based on the change of surface directly. The area of hollowing was checked by the finger tapping method [11]. And the area of cracking was calculated using extend 1 to 2 cm around each side of the crack as width then multiply the length of the crack.

The ageing and degradation of mimical PVAc samples and practical samples were detected by means of liquid chromatogram (WATERS 2690). The mimical samples were pure PVAc and PVAc mix with soil. After curing 28 d, these samples were soaked in tetrahydrofuran respectively and sonic oscillation for 24 h. The turbid liquid was separated by centrifuge (4000r/min), and then the supernate was taken for LC analysis. The analysis of practical samples was operated as above.

3. Results And Discussion

3.1 Influence of time

The investigation result was listed in Table 1. Overall, the renewed diseases occupied 6.43%, 5.76%, 5.77% and 0.43% of the recovered areas in each decade (the 1970s, the 1980s, the 1990s and the 2000s, respectively). The area proportions of renewed diseases in the first 3 decades (from the 1970s to the 1990s) were similar. This means the protective effect of PVAc almost had no change during this long period. And the renewed diseases occurred seemed to have had little relation with time. On the contrary, there were little renewed diseases in the murals repaired after 2000. This unusual difference might be caused by different repair crafts. The traditional edge strengthening, recovering or imitating the base layer of murals no longer appeared in the murals repaired after 2000 (Fig. 3).

Table 1
Areal statistics of renewed diseases

Time		1970s	1980s	1990s	2000s
Area of renewed diseases (%)	Cracking	2.5	0.67	0.94	0.2
	Hollowing	2	0.13	3.45	< 0.1
	Discoloration	1.7	2.5	0.58	< 0.1
	Mildew	0.16	2.47	0.79	/
	Glare	/	/	/	0.15
	Total	6.43	5.76	5.77	0.43

It could also be seen from the statistics that there wasn't a clear pattern as to which diseases were the most common and severe ones. The heaviest disease in the murals repaired during the 1970s was hollowing (2.0%) followed by cracking and discoloration (both 1.7%). In the murals repaired during the 1980s, the heaviest renewed diseases were discoloration and mildew (2.5% and 2.47%, respectively). Moreover, hollowing was the biggest renewed disease in murals which were repaired during the 1990s (3.45%).

3.2 Influence of environment

In order to find out the factors causing the renewed diseases, sunlight, humidity, ventilation and other environmental conditions were discussed at this part.

3.2.1 Sunlight

The biggest affect of sunlight on repaired murals is cracking. In this investigation the grottoes 43rd and 44th are sister grottoes. Factors such as repair time, location and circumstance are almost the same except for sunlight. The sunlight shines directly on grotto 44th (the sunshine duration may reach above 7 hours per day in summer) while grotto 43rd is barely shined. The statistical results are as follows (Fig. 4).

The results showed the area of renewed diseases accounted for 1.12% of the repaired area in grotto 43rd, while this figure reached 17.74% in grotto 44th and it was much higher than the average (6.43%). The types of renewed diseases in the two grottos were the same (cracking, discoloration and hollowing) (Fig. 5) and the ratios of these diseases were also similar. According to the above analysis, sunlight had much relation with the renewed diseases after the murals had been recovered by PVAc. This might due to the decomposition of PVAc under direct sunlight to which PVAc has low resistance [12–13]. Different restoring techniques might also cause the difference in the severity of cracking between the grottoes, since record showed that these two grottoes were repaired by different craftsmen in the same period.

3.2.2 Humidity

In order to show the effect of humidity on the restoration works, grottoes at different height (grotto 191st and 59th (recovered in the 1980s and the 1990s, respectively)) were selected for comparison. The results were listed in Table 2.

Table 2
Renewed diseases caused by humidity

Number	Time	Repaired area	Renewed diseases and their areas (%)				
			Cracking	Hollowing	Discoloration	Saline-alkaline	Flaking
191	1980s	10.95	0.10	/	10.43	/	16.34
Average	1980s		0.67	0.13	2.5	/	/
59	1990s	5.10	1.49	11.25	/	3.29	/
Average	1990s		0.94	3.45	0.58	/	/

The areas of renewed diseases in grottoes 191 and 59 accounted for 26.89% and 16.04% of recovered areas, respectively. Among them a new disease (Fig. 6) which caused by humidity was very universal. The areas of saline-alkaline and flaking accounted for 16.34% and 3.29% of recovered areas in grotto 191st and 59th. Previous research [4] found that PVAc had low water resistance due to its carboxyl and hydroxyl groups. Rain washing and water penetration of cliff body also lead to the burst of the new disease in these two grottoes. Thus, the PVAc was not an ideal repairing material under a humid circumstance according to this investigation.

(left is the 191st grotto and right is the 59th grotto)

3.2.3 Enclosed environment

Enclosed environment is another factor which would probably result in diseases. In the investigation we found that much repaired area mildewed in the 123rd grotto and the 135th grottoes (Fig. 7), which was hardly found in other grottoes from the same height. The only difference might be that the 123rd and the 135th grottoes were always closed. Therefore, the microenvironment (humidity and temperature) of these two grottoes remained steady and created a good condition for microbial growth. However, no mould was found on the surface of the original fresco and the render layer (Fig. 7C and D). This indicated that the necessary nutrient offered by PVAc might favor the microbial growth.

Compared with other polymer (like acrylic resins) used in heritage conservation, PVAc is easily attacked by biological agents [14–15]. Francesca et al. [14] noted the PVAc is more resistant to attacks in a dry environment, while under favourable conditions of temperature and relative humidity, it is likely to be susceptible. This might explain why the mildew concentrated in the 123rd grotto and 135th grottoes. Moreover, some researches [14–16] reported that impurities and additives in commercial PVAc such would also make it more vulnerable to fungi. Given the long years (several decades) of repairing work in the Maiji Grottoes, the PVAc used in restoration might have been purchased from different companies, but this conjecture couldn't be confirmed for now. But on the whole, the specific conditions in these two grottoes likely played an important role in causing this renewed disease.

(A and B: the 123rd grotto; C and D: the 135th grotto)

3.3 Material analysis

The above field investigation demonstrated PVAc applied in restoration work arise some new diseases associated with conservation environment. However, the nature caused these problems was still not sure. Nowadays, some elements of the scientific community have repeatedly recommended use traditional materials to restore the heritages. And some authors completely exclude the use of organic protective and reinforcement agents due to their incompatibility with heritage sites and weak ageing resistance. Nevertheless, other authors state the execution conditions and technical skills and knowledge of the artisans might play a crucial role in determining the effect of restoration work.

In this part, LC analysis of mimical PVAc samples and practical samples were applied to explain the results of above investigation. The analytical results were shown in Fig. 8. First, comparing the curves of modeling samples (Fig. 8A, B and C), it was found that the peak of PVAc appeared after 12 to 18 minutes. The retention times corresponding to this peak in sample B and C were 14.270 and 14.205, respectively. Similarly, the values of MP were 28845 and 29797, respectively. The gap between these two groups of data fell entirely within the range of allowable error of instrumental analysis (10%). This means the existence of soil in the sample had no effect on the detection of PVAc by this method.

Second, the curves of practical samples (Fig. 8D, E and F) displayed there was a peak appeared between 12 to 14 minutes in these samples. The values of MP were 47446, 51867 and 58679, respectively. In addition to this, no other obvious peaks were found during the first 19 minutes in these samples (the peak appeared at a later time might be caused by the soil and solvent). We know that PVAc could occur ageing and degradation which result in PVAc's molecular weight increase and reduction, respectively. These behaviors could lead to the peaks of PVAc in LC analysis broaden or rise new peaks. However, these situations seemingly didn't appear according to the experimental data. This means the ageing and degradation of PVAc might be relatively infrequency.

Moreover, investigation data (annexed table) showed sample F (105th grotto) was attacked by renewable diseases lightly, while sample D (147th grotto) and E (123rd grotto) were attacked very heavy. However, there was no obvious difference in the LC analysis besides the value of MP. This suggested the intrinsic characteristic of PVAc is relatively stable and could be used for restoration under a reasonable environment. In addition, it also inspired us don't scare modern organic materials due to their durability.

4. Conclusion

According to the on-site investigation of the Maiji Grottoes, 6 kinds of renewable diseases were categorized. Among them the more common ones are crack, hollowing, discoloration and mildew. Saline-alkaline and flaking only appear where rain washing and water penetration of cliff body is heavy. Moreover, the environmental factors have strong influences on the renewable diseases.

The LC analysis of the modeling samples and practical samples selected from grottoes found that the PVAc had one broad peak on the LC curve and this peak was not affected by soil content in the sample. The results indicated the PVAc in practical samples had little change in 20–40 years. Thus, the renewable diseases were mostly caused by environmental factors rather than the ageing and degradation of PVAc.

Declarations

5. Funding

This work was supported by the grants from the National Key Basic Research Program of China (973 Program) (No.2012CB720902) and the National Technology Support Program of China (No. 2012BAK14B05).

6. Statement

To the best of our knowledge, the named authors have no conflict of competing interest, funding or otherwise.

References

1. Chen YM, Shi YC, Wang XD. An evaluation of seismic tectonic environment of Tianshui maiji grottoes. *Dunhuang Res.* 2005;05:78–82. (in Chinese).
2. Ma Q: The primary problem presented in the protection of maiji grottos and its relative solution. *The yngang international academic symposium in 2005 (protection volume), The yngang international academic symposium in 2005 in Datong, China*, 2005: 421–429. (in Chinese).
3. Kim S, Kim HJ. Thermal stability and viscoelastic properties of MF/PVAc hybrid resins on he adhesion for engineered flooring in under heating system; *ONDOL. Thermochim Acta.* 2006;444:134–40.
4. Kaboorani A, Riedl B, Blanchet P, Fellin M, Hosseinaei O, Wang SQ. Nanocrystalline cellulose (NCC): A renewable nano-material for polyvinyl acetate (PVA) adhesive. *Eur Polym J.* 2012;48:1829–37.
5. Kim S, Kim HJ. Effect of addition of polyvinyl acetate to melamineformaldehyde resin on the adhesion and formaldehyde mission in engineered flooring. *Int J Adhes Adhes.* 2005;25:456–61.
6. Kaboorani A, Riedl B. Improving performance of polyvinyl acetate (PVA) as a wood adhesive by combination with melamine based adhesives. *Int J Adhes Adhes.* 2011;31:605–11.
7. Kaboorani A, Riedl B. Effects of addition of nano-clay on performance of polyvinyl acetate (PVA) as a wood adhesive. *Compos Part A.* 2011;42:1031–9.
8. Liu TJ. An overview of historical restoration of maiji grottoes. *The silk road studies.* 2004;S2:34–7. (in Chinese).
9. Zhang HB, Su BM, Duan XY, Zhang WY. characterization of the properties of PVAc, PVA used in mural protection. *Dunhuang Res.* 2011;6:29–35. (in Chinese).
10. Pacheco-Torgal F, Faria J, Jalali S. Some considerations about the use of lime–cement mortars for building conservation purposes in Portugal: A reprehensible option or a lesser evil? *Constr Build Mater.* 2012;30:488–94.
11. Bodnar JL, Candore JC, Nicolas JL, Szatanik G, Detalle V, Vallet JM. Stimulated infrared thermography applied to help restoring mural paintings,*NDT. E* *Int.* 2012;49:40–6.
12. Kaczmarek H. Photodegradation of Polystyrene and Poly (Vinyl Acetate) Blends.1. Irradiation of PS/PVAc Blends by Polychromatic Light. *Eur Polym J.* 1995;31:1037–42.
13. Wei SY, Pintus V, Schreiner M. Photochemical degradation study of polyvinyl acetate paints used in artworks by Py–GC/MS. *J Anal Appl Pyrol.* 2012;97:158–63.
14. Cappitelli F, Zanardini E, Sorlini C. The Biodeterioration of Synthetic Resins Used in Conservation. *Macromol Biosci.* 2004;4:399–406.
15. Cappitelli F, Vicini S, Piaggio P, Abbruscato P, Princi E, Casadevall A, Nosanchuk JD, Zanardini E. Investigation of Fungal Deterioration of Synthetic Paint Binders Using Vibrational Spectroscopic Techniques. *Macromol Biosci.* 2005;5:49–57.
16. Domenech-Carbo MT, Bitossi G, Cruz-Canizares J, Bolivar-Galiano F, Lopez-Miras MD, Romero-Noguera J, Martin-Sanchez I. Microbial deterioration of Mowilith DMC 2, Mowilith DM5 and Conrayt poly(vinyl acetate) emulsions used as binding media of paintings by pyrolysis-silylation-gas chromatography–mass spectrometry. *J Anal Appl Pyrol.* 2009;85:480–6.

Annexed Table

Annexed table: the original information of the 21 grottoes

Number	Repair time	Total area (m ²)	The name and area of renewable diseases (cm ²)															
			Cracking			Hollowing			Discoloration			Mildew		Glare			Saline-a	
			h	m	s	h	m	s	h	m	s	h	m	s	h	m	s	h
39	1970s	12.444	480	220	460			25	900	900	500	600						
40	1970s	1.1025		330	10	100	30	15										
43	1970s	16.53	78	550	249	355	154	190	78	150	49							
44	1970s	11.368	7687.5	240	220	4900	625	2000	4200	300								
59	1990s	5.1		760		5740												1680
70	2000s	0.8277		160	15			2										
71	2000s	0.6028		150	40			5		5	90							
74	2000s	16.5																
91	2000s	1.4445		200				10										
92	2000s	0.4009		20														
93	2000s	2.125			60													
105	1990s	7.845	50	110	55			30										
122	1990s	2.4866		140	60			15										
123	1990s	17.1825			580	8600	225	400				2275						
126	1990s	1.1375	120	1225	360	400		225		1225	450							
132	1980s	1.024	50	200	130		40	70		14	75							
135	1980s	10.84		40	520				4500	400			10000					
146	2000s	5.235															400	
147	1980s	0.3225		220	15		225	205	31	28	46							
165	1980s	28.3	40	1140	350					975	4100							
191	1980s	10.95			120				25	7200	4200							

Remark: h represent heavy, m represent middle and s represent serious.

Figures

Figure 1
The Maiji Grottoes and their sculptures and murals

Figure 2

the whole picture of maiji mountain grottoes and the surveyed caves in this work (marked with black box)

Figure 3

Different repair crafts between the works made in the 1980s and the 2000s (A. repaired in the 1980s and B. repaired in the 2000s)

Figure 4

the renewed diseases caused by sunshine in grotto 43rd (left) and 44th (right)

Figure 5

the picture of renewed diseases at the repaired area in the 44th grotto

Figure 6

rainfall and humidity caused the repaired materials flaking (left is the 191st grotto and right is the 59th grotto)

Figure 7

the white and black moulds grow on the surface of repaired areas (A and B: the 123rd grotto; C and D: the 135th grotto)

Figure 8

the LC analytical results of modeling (A. pure soil; B. pure PVAc; C. soil mixed with PVAc) and practical samples (D. 147th grotto; E. 123rd grotto; F. 105th grotto)