Aging mechanism and surface properties of Silica fluoropolymer coating and its application

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Abstract
The hydrothermal aging cycles experiment was carried out on synthetic Silica fluoropolymer coating (SiO2-FP). The hydrothermal aging mechanism, surface properties and protective efficacy on sandstones was studied. For comparison, the same study was conducted for commercial protective material acrylic resin Paraloid B72 (PB72). The hydrothermal aging mechanism was studied by Fourier infrared spectroscopy attenuated total reflection technique (ATR-FTIR) and x-ray photoelectron spectroscopy (XPS) technology. The surface properties were characterized by field emission scanning electron microscope (SEM), the CR-400 color difference meter, static contact angle and GMT6503 Electronic universal Tensile machine. The capillary water absorption, water absorption by complete immersion (CI) and water vapor permeability were measured to evaluate the protective efficacy on sandstones after treatment. The results of ATR-FTIR and XPS indicated that part of the ester groups in PB72 was hydrolysed and the chemical structure of SiO2-FP was not changed but only microphase separation occurred after 360 h of aging. After 360 h of aging, the PB72 film had obvious change and the SiO2-FP film only shown a minor change; the color change of PB72 film was very obvious and the color change of SiO2-FP film was within the acceptable range; the PB72 film changed from hydrophobic to hydrophilic and the SiO2-FP film still retained high hydrophobicity (119.3°); the SiO2-FP had a higher adhesive strength than PB72 at the end of aging. Compared with PB72, the SiO2-FP can obviously reduce the capillary water absorption and had a higher protective efficiency (97.25%), much lower soakage capacity (0.60%), higher water vapor permeability (267.0 ± 2) and less influence on the water vapor permeability. All the results demonstrated that the SiO2-FP has much better anti-aging ability and longer durability under hydrothermal condition. The SiO2-FP can provide adequate protection for sandstones. The SiO2-FP can be used as a suitable protective coating on sandstones.

1. Introduction
The Silica fluorinated polymers have low surface energy, excellent hydrophobicity, thermal stability and chemical stability [1–4]. The Silica fluorinated polymers have been found to have wide applications as coating materials with some interesting properties [5–7]. They have been widely used in anti-fouling coating [8], anti-corrosion coating [9], hydrophobic coating [4], anti-UV coating [6] and low refractive index coating [10], among others. In the past few years, Silica fluorinated polymers play a role in the protection and consolidation of ancient cultural relics [11]. The use of polymer protective coating materials to protect the surface of the cultural relics can reduce the adverse effects of various factors in the natural environment on the cultural relics and improve the surface and internal properties of the cultural relics [12]. The conditions such as light [13, 14],
temperature [15], humidity [14, 16], oxygen [17] and microorganisms [18] can cause changes in the properties of protective coating materials resulting in degrade performance, even lose the function. Under the influence of various these factors, the surface properties, physical properties and mechanical properties of materials will change. Therefore, it is necessary to study the anti-aging properties of protective coating materials.

The anti-aging ability of coating materials can be characterized by surface properties [19–21]. The changes of surface properties include change in color [21, 22], change in hydrophobic [23], change in surface morphology [24] and change in adhesion strength [25]. If polymer materials are applied to cultural relics, they may change the surface color of cultural relics, thus changing the important information carried by cultural relics. The changes of color can be determined by diffuse reflectance spectroscopy to obtain the chromatic variations ($\Delta E$) of the materials and the larger the $\Delta E$, the more obvious the color change. The hydrophobic property of the materials can be characterized by the contact angle to evaluate the water resistance of the materials. The protective coating material should not change the surface morphology of the cultural relics as much as possible. The small change of surface morphology indicates that the protective coating materials have less influence on cultural relics and they are suitable for use as protective materials. On the other hand, adhesion strength refers to the binding strength between the coating materials and the matrix. An adequate adhesive property can prevent the separation and falling off between the protective material and the cultural relic substrate. At present, the research on silica fluorinated polymers protective coating materials mainly focuses on the synthesis, preparation and characterization of the materials, while the aging properties of silica fluorinated polymers are seldom studied.

The water penetration through the sandstones surface easily causes deterioration [26]. Water can indirectly affect the cohesion properties of the stone structure under wet conditions. Hence, preventing water penetration is an important requirement for protective coating materials to be applied on the sandstone surfaces of cultural relics. It is desirable to reduce the water absorption in most cases, but it should not reduce the water vapor transmission rate, thus allowing the water vapor to evaporate from the sandstones [27]. The capillary water absorption, water absorption by complete immersion (CI) and water vapor permeability could be measured to evaluate the resistance to water of protective coating materials [21]. The sandstone cultural relics are vulnerable to damage by water, so it is necessary to find an effective protective coating for protection. Before the coating is applied, we should evaluate its aging resistance and application protection efficacy.

In this paper, we carried out the hydrothermal cycles aging experiment on synthetic Silica fluoropolymer protective coating (silica-g-poly (methyl methacrylate)-b-poly (dodecafluorheptyl methacrylate, SiO$_2$-FP) and studied its hydrothermal aging mechanism and surface properties during aging process and protective efficacy on sandstines. For comparison, we also conducted the same experiment and study on commercial protective material acrylic resin Paraloid B72 (PB72), which is widely used in the protection of cultural relics [28]. The hydrothermal aging mechanism of the PB72 and SiO$_2$-FP was based on measuring the changes of chemical structural by Fourier infrared spectroscopy attenuated total reflection technique (ATR-FTIR) and x-ray photoelectron spectroscopy (XPS). The surface morphology, chromatic variations, water contact Angle and adhesion strength were measured to evaluate the surface properties of PB72 and SiO$_2$-FP during aging process. After the sandstone samples were treated with PB72 and SiO$_2$-FP, the capillary water absorption, water absorption by complete immersion (CI) and water vapor permeability were measured to evaluate the protection efficacy of protective materials to be applied on the sandstone.

![Scheme 1. The process of one cycle of hydrothermal aging cycle.](image-url)
2. Materials and methods

2.1. Materials

The materials were shown as follows. Silica fluoropolymer coating (silica-g-poly-methylmethacrylate-b-poly-dodecafluoroheptyl methacrylate, SiO2-FP) was synthesized in our previous work [29]. Acrylic resin Paraloid B72 (Sigma Aldrich Shanghai, China). Their chemical structures and molecular weights were shown in Table 1.

2.2. Methods for evaluation of the protective coating

2.2.1. Hydrothermal aging cycles

The PB72 and SiO2-FP films were prepared by dropping the 5 wt% THF solution on aluminum foil (30 mm × 30 mm × 0.2 mm) and dried at ambient (50%–55% RH) for 48 h and then in vacuum oven (50 °C) for 24 h with a thickness of about 800 μm. Then, the prepared films were put into a programmable constant temperature and humidity box (Hongzhan Instrument Co. LTD, Dongguan, China) for the hydrothermal aging cycles experiment with 15 cycles (one cycle for 24 h) according to the GB/T 12000-2003, China. The procedure of hydrothermal aging cycle was shown in Scheme 1. The first step is to heat the samples from 25 °C to 65 °C with 2.5 h and the samples was maintained at 65 °C for 3 h. Then, the samples were cooled from 65 °C to 25 °C with 2.5 h. The second step is to repeat the above process once, and then keep the samples at 25 °C for 1.5 h. The third step is to cool the samples from 25 °C to −20 °C with 0.5 h and keep the samples at −20 °C for 3 h. Then, the samples were heated from −20 °C to 25 °C with 1.5 h and keep the samples at 25 °C for 1.5 h. The changes of chemical structure of PB72 film was determined by Fourier infrared spectroscopy attenuated total reflection technique (ATR-FTIR, Bruker, Karlsruhe, Germany). The changes of chemical structure of SiO2-FP film was evaluated by ATR-FTIR and x-ray photoelectron spectroscopy (XPS, AXIS ULTRA, KRATOSANALYTICAL Ltd, Manchester, England) with an Al-Ka monochromatic x-ray source (1486.6 eV) operated at 150 W.

2.2.2. Surface morphology, chromatic variations and static contact angle of films

The preparation of samples is the same as hydrothermal aging cycles. Samples were measured at 0 h and 360 h of aging to evaluate the anti-aging performance of the coating films. The surface morphology of protective coating films was observed by field emission scanning electron microscope (SEM, JSM-7800F, Tokyo, Japan) at 3.0 kV accelerating potential. The chromatic variations (ΔE) were obtained by the CR-400 color difference meter (Konica Minolta, Tokyo, Japan). The contact angle of water of the protective coating films was determined by static contact angle (SCA) at 25 °C and ±0.5° instrument error.

2.2.3. Adhesive strength

The two pieces of glass (100 mm × 20 mm × 2 mm) are glued together by adding 25 μl solution with the square contact area of 15 × 20 mm² to prepare Samples for adhesive strength. The prepared samples were dried at room temperature for 48 h and then vacuum dried for 24 h. The experiment was carried out at room temperature (50% RH). The adhesive strength was measured by GMT6503 Electronic universal Tensile machine (MTS, Minnesota, USA) and the continuously increased forces is 2 mm min⁻¹. The force (in N) to pull open the two pieces of iron was recorded, and the adhesive strength (in MPa) was calculated through the force divided by the contact area.

Table 1. Chemical structure and molecular weight of PB72 and SiO2-FP.

| Samples  | Chemical structure | Mw g⁻¹ mol⁻¹ |
|----------|--------------------|--------------|
| PB72     | ![Chemical structure of PB72](image1) | 105 000      |
| SiO2-FP  | ![Chemical structure of SiO2-FP](image2) | 18 800       |
2.3. Evaluation of protection on sandstone

The sandstones are composed of 30% quartz, 25% feldspar and 30% rock with 35% porosity and 2.29 g cm$^{-3}$ average density (collected from ancient Dafo Temple Grotto, one of the famous heritage sites, Binxian County, Shaanxi Province, China). The sandstones were cut into about 5.0 × 5.0 × 2.0 cm$^3$ samples for capillary water absorption, water absorption by complete immersion tests and the Φ4.0 × 1.0 cm$^3$ cylindrical samples for water vapor permeability test, which was shown in figure 1. The sandstone samples were rinsed with deionized water and dried in vacuum until constant weight before using. The sandstone samples were immersed in 3%wt PB72 and SiO$_2$-FP THF solution and followed by drying at ambient (50%–55% RH) for 72 h to constant weight. The untreated and treated sandstone samples were put into the programmable constant temperature and humidity box for hydrothermal aging cycle tests. Then, the capillary water absorption, water absorption by complete immersion and water vapor permeability of the untreated and treated sandstone samples were measured to evaluate the protective efficacy of protective coating materials.

2.3.1. The capillary water absorption

The gravimetric sorption technique accorded to the Normal protocol [30] was used to determine the capillary water absorption. The treated sandstone samples were placed on a 1 cm thick filter paper pad and partially immersed in deionized water. The weight of the samples ($M_i \pm 0.0001$ g) was recorded to determine the amount of water absorbed by capillarity forces after 10, 20, and 30 min and 1, 2, 4, 8, 24, 48, 72, 96, 120, 144, 168, 192, 216, 240, 264, 288, 312, 336 and 360 h. The water absorption ($Q_i$) per unit area at the time $t_i$ is defined as follows:

$$Q_i = \frac{M_i - M_0}{S}$$

Where $M_i$ is the mass of sample (in grams) at time $t_i$ (in seconds), $M_0$ is the mass of dry sample (in grams) and $S$ is the contact surface (in cm$^2$). The capillary absorption curve is drawn with $Q_i$ (in g cm$^{-2}$) as the ordinate and the square root of time ($t^{1/2}$) as the abscissa.

The capillary water absorption coefficient (CA) could be calculated by the angular coefficient of the first part of the curve. The protective efficiency (EP) against capillary water absorption can be defined as follow:

$$EP = \frac{Q_0 - Q_t}{Q_0} \times 100$$

Where $Q_0$ is the average value of untreated sandstone after 1 h and $Q_t$ is the average value of treated sandstone after 1 h.

2.3.2. The Water absorption by complete immersion

The gravimetric method accorded to the Normal protocol [31] was used to measure the water absorption by complete immersion. The sandstone sample was completely immersed in deionized water for 48 h at room temperature.
temperature and pressure. Then, the excess water on the sample surface was sucked by dry with filter paper and the mass of the sandstone sample was weighed and recorded as $M_{\text{max}}$ (in grams). The dry sample mass is recorded as $M_0$ (in grams). The capacity of imbibition (CI) is defined as follows:

$$CI = \frac{M_{\text{max}} - M_0}{M_0} \times 100\% \quad (3)$$

### 2.3.3. The water vapor permeability

The determination of the vapor permeability was carried out according to the corresponding Normal protocol [32]. A cylindrical poly (vinyl chloride) (PVC) container with an open top was used as the measurement cell and the cell is injected with 1/2 amount of deionized water. The stone sample was employed as the lid of the PVC container and then the container is sealed by an O-ring rubber seal ring and the silicone. The cell was placed in a desiccator with a certain vacuum (~0.09 Mpa) and constant temperature $20 \pm 0.5 \degree C$, which was shown in figure 2. Therefore, the amount of water vapor diffusing through the stone sample could be determined by gravimetric method. The weight ($M \pm 0.0001$, in grams) of the cell was measured every 24 h. When the daily weight variation of cell from two consecutive measurements is less than 5%, the diffusion of water vapor is considered to reach stationary flow. The water vapor permeability ($P$) is defined by determining the weight decrease per surface unit (in m$^2$) in unit time (24 h):

$$P = \frac{M_i - M_{i-1}}{S} \quad (4)$$

The reduction of the water vapor permeability (RP) was also evaluated and the RP is defined as follows:

$$RP = \frac{P_0 - P_t}{P_0} \times 100\% \quad (5)$$

where $P_0$ is the water vapor permeability of the untreated sandstone and $P_t$ is the water vapor permeability of the treated sandstones.

### 3. Results and discussion

#### 3.1. The hydrothermal aging mechanism

In the process of hydrothermal aging, the protective coating materials will be affected by temperature and wet, and the chemical structure will change accordingly, which will cause the change of coating materials performance. The ATR-FTIR spectrogram of PB72 film at different aging time is shown in figure 3, which was measured at 0 h and 360 h, respectively. After aging for 360 h, the ATR-FTIR spectrum of PB72 changed significantly. After aging for 360 h, the absorption peak of the associated hydroxyl group appears at 3436 cm$^{-1}$ in the figure and the absorption peak of C–H bond appeared at 2,980 cm$^{-1}$ and its absorption peak strength increased. At the same time, the intensity of absorption peak for C=O bond at 1728 cm$^{-1}$ and –CH$_3$ at 1447 cm$^{-1}$ in ester group decreases after 360 h of aging. These results show that part of ester bonds in PB72 were hydrolyzed under hydrothermal aging condition, thus leading to the appearance of hydroxyl groups, the reduction of absorption peak intensity for C=O and C–O–C bond and the increase of C–H bond absorption.
peak intensity. The results of ATR-FTIR spectra shown that the chemical structure of the side chain in 72 was changed and part of the ester groups in the side chain were hydrolyzed after 360 h of aging.

The ATR-FTIR spectrogram of SiO2-FP film at different aging time is shown in figure 4, which also was measured at 0 h and 360 h, respectively. After 360 h of aging, the main structural characteristic peaks of SiO2-FP (C=O, C–O–C) has little change, but it also shows some new changes. As can be seen from the figure, the absorption peak intensity of Si–O–Si at 1120 cm$^{-1}$ and –Si–CH$_2$– at 620 cm$^{-1}$ is significantly enhanced after 360 h of aging. At the same time, the intensity of absorption peak for C–H bond at 1456 cm$^{-1}$ obviously increased after 360 h of aging. This result shows that the main structure of SiO2-FP is not destroyed, but the microphase separation occurred in materials after 360 h of aging. In our previous work, during the film-forming process of SiO2-FP, the fluorine side chain would migrate to the surface to form a hydrophobic surface. But under the influence of wet and temperature, the structure of fluorine-containing chain segments on the surface changes and microphase separation occurs. silica particles and the grafted polymers gradually migrate to the film surface while fluorine-containing chain segments relatively migrate to the lower layer, resulting in changes in the surface structure. This is coherent with a significant increase in the intensity of the absorption peaks of Si–O–Si, Si–CH$_2$ and C–H bonds. Therefore, it leads the content of C, O and Si to increase and the content of fluorine to decrease on the film surface after 360 h of aging.

In order to further confirm the results of ATR-FTIR, the XPS measurement was used to test the content of C, O, F and Si element on the film surface during the aging process. The results of XPS for SiO2-FP at 0 h and 360 h are shown in figure 5. It can clearly see the characteristic signal peaks of C, O, F and Si elements in the figure. Moreover, the content of F element decreases, while the content of C, O and Si element increases after 360 h of aging.

### Table 2. Element contents for SiO2-FP film at different aging time.

| Aging time / h | F (%) | C (%) | O (%) |
|---------------|-------|-------|-------|
| 0             | 26.60 | 53.88 | 18.22 |
| 360           | 18.10 | 58.99 | 21.05 |

![Figure 4. ATR-FTIR spectra of SiO2-FP at different aging time.](image4.png)

![Figure 5. XPS results of SiO2-FP film at different aging time.](image5.png)
aging. Their element contents are listed in table 2. The content of fluorine was reduced from 26.60% to 18.10% and the content of C, O, Si was increased from 53.88%, 18.22% and 1.30% to 58.99%, 21.05% and 1.86%, respectively. This result indicates that during the aging process, the silica migrates to the surface and some fluorine elements migrate to the lower layer, which just coincides with the result of ATR-FTIR spectrum. The results of ATR-FTIR spectrum and XPS show that the chemical structure of SiO2-FP was not changed but microphase separation occurred after 360 h of aging. These results show that SiO2-FP has much better resistance to hydrothermal aging than PB72.

3.2. Analysis of anti-aging performance

3.2.1. Changes of the surface morphology
In the process of hydrothermal aging, the surface morphology of protective coating materials will change due to the influence of wet and temperature. We measured the changes of surface morphology for the protective coating materials by SEM to evaluate their anti-aging ability. The SEM images of PB72 and SiO2-FP are shown in figure 6 at different aging time. The SEM images of PB72 at 0 h and 360 h are shown in figures 6(a), (b). The surface of PB72 film is smooth and flat before aging (figure 6(a)). After 360 h of aging, many tiny holes appeared on the surface of the film (figure 6(b)). Due to the hydrolysis of some ester groups in the side chain, the destruction of the structure of the film was destroyed and many holes appeared. The SEM results show that the structure of PB72 film was destroyed after 360 h of aging and it does not have adequate resistance to hydrothermal aging. The SEM images of SiO2-FP at 0 h and 360 h are shown in figures 6(c), (d). The film surface of SiO2-FP formed is relatively smooth before aging (figure 6(c)). The SiO2-FP film does not change significantly after 360 h of aging (figure 6(d)). The film surface only shows a few micropores and some white dots. It is believed that this is related to the aging mechanism discussed above. After 360 h of aging, the chemical structure of SiO2-FP did not change and only microphase separation occurred. This result indicates that the SiO2-FP has excellent anti-aging ability. The SEM results show that SiO2-FP has much better resistance to hydrothermal aging than PB72.

3.2.2. Changes of the chromatic variations
In order to quantitatively describe the color changes of the protective coating materials during the hydrothermal aging cycles, the chromatic variations (namely the color difference value, ΔE) were obtained by diffuse reflectance spectroscopy using the CR-400 color difference meter. The chromatic variations of protective coatings range in acceptable range when parameter ΔE is <5. The ΔE of PB72 and SiO2-FP is listed in table 3 at different aging time. As the aging time increases, their ΔE gradually becomes larger. After 360 h of aging, the ΔE of PB72 reached 10.021 and the color change on the film surface was very obvious. This result shown that PB72 was no longer suitable as a protective coating material to continue to play its role after 360 h of aging. However, the ΔE of SiO2-FP was only 4.0 after 360 hours of aging and the color change on the film surface was within the acceptable range as a protective coating [33], which was indicated that SiO2-FP can maintain sufficient durability for a long time even in moist heat environment and can be used as a protective coating material. The results of the chromatic variations are consistent with the SEM results discussed above and also show that SiO2-FP has better resistance to hydrothermal aging.
3.2.3. Changes of the contact angle and adhesion strength

The changes of water contact angle with time for PB72 and SiO2-FP is shown in Figure 7. As the aging time increases, the contact angles of PB72 and SiO2-FP decrease, but their magnitude of decrease is different. The contact angle of PB72 was 94.0° at 0 h, and decreased to 83.3° at 360 h. The contact angle reduced 11.4% for PB72 and it shows that the surface of PB72 changes from hydrophobic to hydrophilic after 360 h of aging. This is due to the hydrolysis of part of the ester groups in PB72 that led to the appearance of hydrophilic groups on the film surface, which is related to the ATR-FTIR result discussed above. The SiO2-FP has excellent hydrophobicity (124.0°) at 0 h. After 360 h of aging, it still retains good hydrophobicity (119.3°). This is because that only microphase separation occurred in SiO2-FP and its chemical structure was not destroyed during the hydrothermal aging. At the same time, there is still a lot of fluorine on the surface to help keep an adequate hydrophobicity. This result shows that the SiO2-FP can maintain sufficient hydrophobicity for a long time even in moist heat environment and has better resistance to hydrothermal aging.

**Figure 7.** The contact angle of PB72 and SiO2-FP at different aging time.

| Aging time/h | ΔE     |
|--------------|--------|
| PB72         | SiO2-FP|
| 72           | 0.283  | 0.159 |
| 144          | 0.408  | 0.559 |
| 216          | 0.440  | 2.832 |
| 288          | 0.422  | 3.079 |
| 360          | 10.021 | 4.025 |

**Table 3.** Chromatic variations (ΔE) of protective coating at different aging time.

**Figure 8.** The adhesive strength of PB72 and SiO2-FP at different aging time.

3.2.3. Changes of the contact angle and adhesion strength

The changes of water contact angle with time for PB72 and SiO2-FP is shown in figure 7. As the aging time increases, the contact angles of PB72 and SiO2-FP decrease, but their magnitude of decrease is different. The contact angle of PB72 was 94.0° at 0 h, and decreased to 83.3° at 360 h. The contact angle reduced 11.4% for PB72 and it shows that the surface of PB72 changes from hydrophobic to hydrophilic after 360 h of aging. This is due to the hydrolysis of part of the ester groups in PB72 that led to the appearance of hydrophilic groups on the film surface, which is related to the ATR-FTIR result discussed above. The SiO2-FP has excellent hydrophobicity (124.0°) at 0 h. After 360 h of aging, it still retains good hydrophobicity (119.3°). This is because that only microphase separation occurred in SiO2-FP and its chemical structure was not destroyed during the hydrothermal aging. At the same time, there is still a lot of fluorine on the surface to help keep an adequate hydrophobicity. This result shows that the SiO2-FP can maintain sufficient hydrophobicity for a long time even in moist heat environment and has better resistance to hydrothermal aging.
The changes of adhesive strength with time for PB72 and SiO2-FP is given in figure 8. It is observed that the adhesive strength of PB72 (1.49 MPa) is higher than SiO2-FP (1.32 MPa) at the 0 h. As the increase of aging time, their adhesive strength has been obviously reduced. The adhesive strength of PB72 decreased from 1.49 MPa to 0.31 MPa with about 79.2% decrease. However, the adhesive strength of SiO2-FP had a lower reduction with about 56.8% and decreased from 1.32 MPa to 0.57 MPa. These results are believed to be related to the mechanism of hydrothermal aging discussed above. Part of the ester groups in PB72 was hydrolysed and SiO2-FP only undergoes microphase separation without chemical structure change after 360 h of aging. The results of adhesive strength show that SiO2-FP has a higher adhesive strength than PB72 after aging for 360 h and has better resistance to hydrothermal aging.

3.3. Evaluation of protective efficacy on sandstone

3.3.1. Analysis of the capillary water absorption and the water absorption by complete immersion

The capillary water absorption reflects the long-term water resistance for untreated and treated sandstone surface. The capillary water absorption with time for untreated and treated sandstone is shown in figure 9. It could be observed that the untreated sandstone absorbed rapidly a large amount of water. and the amount of water absorbed by sandstone treated with PB72 and SiO2-FP was reduced immediately. The values of the capillary absorption coefficient (CA) and protective efficiency (EP), which is calculated from the curves of figure 9, are listed in table 4. The capillary water absorption coefficient of sandstones treated with PB72 and SiO2-FP was obviously reduced. However, the sandstone treated with SiO2-FP has a lower capillarity water absorption coefficient than the sandstone treated with PB72. The value of protective efficiency for SiO2-FP is very high (99.1%) and it is higher than that of PB72(70.9%). These results are coherent with better resistance to hydrothermal aging of SiO2-FP and the sandstones treated by SiO2-FP is more resistant to water penetration than the PB72.

At the same time, we conducted the water absorption by the total immersion test. The percentage of the absorbed water at the end of the test was expressed by soakage capacity (CI). The values of CI are listed in table 3.
The untreated sandstone sample absorbs a lot of water. After treatment with PB72 and SiO$_2$-FP, the CI of sandstones was reduced. However, the CI of sandstone treated with SiO$_2$-FP (0.60%) is much lower than those treated with PB72 (4.72%). The results show that the sandstone treated by SiO$_2$-FP has excellent water resistance and the SiO$_2$-FP is more resistant to water penetration than the PB72.

3.3.2. Analysis of the water vapor permeability

The water vapor permeability (P) and reduction of permeability (RP) of treated and untreated sandstones are shown in Table 5. It could be observed that the water vapor permeability of sandstones treated with PB72 and SiO$_2$-FP is reduced. The reduction of permeability for PB72 and SiO$_2$-FP is approximately 14.8% and 28.5%, respectively. The reduction of permeability of stone treated with PB72 is higher than that treated with SiO$_2$-FP. This result indicates that SiO$_2$-FP has less effect on the permeability of stone and is more suitable for use as a protective coating.

4. Conclusions

We have carried out hydrothermal aging cycles experiment on synthetic protective coating material SiO$_2$-FP and commercial protective coating material PB72. The hydrothermal aging mechanism was studied by ATR-FI-IR and XPS technology. The changes in surface morphology, chromatic variations, contact angle and adhesion strength during the hydrothermal aging cycles were studied to evaluate the anti-aging performance of protective coating materials. At the same time, we also evaluated the protective efficiency of the protective coating materials after being applied to the sandstone samples. The evaluations were made in terms of capillary water absorption, water absorption by complete immersion, and water vapor permeability of the protective coating materials. The results of the comparative assessment studies can be summarized as follows:

- Part of the ester groups on the side chain in PB72 had been hydrolyzed and the chemical structure of SiO$_2$-FP was not changed but only microphase separation occurred after 360 h of aging.
- After 360 h of aging, the PB72 membrane had many tiny holes on the surface, while the SiO$_2$-FP had little change with only a few micropores and some white dots; the color change on the surface of PB72 was very obvious with 10.021 value of $\Delta$E and the color change on the surface of SiO$_2$-FP was within the acceptable range with 4.025 value of $\Delta$E; the surface of PB72 changed from hydrophobic (94.0°) to hydrophilic (83.3°) and the SiO$_2$-FP still retained high hydrophobicity (119.3°); the reduction of adhesion strength for PB72 (79.2%) was larger than that of SiO$_2$-FP (56.8%) and the SiO$_2$-FP had a higher adhesive strength than PB72 at the end of aging.
- The capillary water absorption coefficient of sandstones treated with PB72 and SiO$_2$-FP was obviously reduced. The sandstone treated with SiO$_2$-FP had a lower capillary water absorption coefficient than the sandstone treated with PB72. The SiO$_2$-FP had a higher protective efficiency (97.25%) than that of PB72 (45.60%). The soaking capacity of sandstones treated with PB72 and SiO$_2$-FP was reduced. The SiO$_2$-FP had much lower soaking capacity (0.60%) than that of PB72 (4.72%).
- The water vapor permeability of sandstones treated with PB72 and SiO$_2$-FP was reduced. The water vapor permeability of stones treated with PB72 (224.1 ± 2) was lower than those treated with SiO$_2$-FP (267.0 ± 2). The reduction of permeability of stone treated with SiO$_2$-FP (14.8%) was lower than the sandstone treated with PB72 (28.5%).

This research demonstrated that the SiO$_2$-FP has much better anti-aging capability and longer durability under hydrothermal condition. The SiO$_2$-FP can obviously reduce the capillary water absorption of sandstone, but has less effect on its water vapor permeability. The SiO$_2$-FP can provide adequate protection for sandstones with adequate water resistance and water vapor permeability. The SiO$_2$-FP can be used as a protective coating material and is suitable for the protection on sandstones.

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