Preparation of Healable Shellac Microcapsules and Color-Changing Microcapsules and Their Effect on Properties of Surface Coatings on Hard Broad-Leaved Wood Substrates

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Abstract: In order to protect the wood surface and improve the properties of coatings, microcapsules with healable and discoloration functions are produced, and their healable function is obtained using shellac, which can be cured at room temperature, as the repairing agent. In this paper, self-made shellac microcapsules and color-changing microcapsules were added to varnish in different proportions to form the composite coating on a wood board, and the color difference of the coating was measured at different temperatures to study the influence of microcapsules on the degree of surface color on the substrate. The effect of microcapsules on the healable performance of coatings on a wood board was studied by scratching the surface of the coating with a utility knife and observing the process of repair. The optimal sample was selected from the orthogonal experiment for the independent experiment. The surface roughness, hardness, infrared spectrum, and scanning electron microscopy of the optimal sample were tested, and the content in the optimal sample was further investigated. The results show that color-changing microcapsules have a color-changing effect on surface coatings based on wood boards, and shellac microcapsules inhibit the color-changing effect of color-changing microcapsules. Composite microcapsules can repair the cracks on the surface coatings of wood boards. In cases where shellac microcapsules can self-repair the coating, the color-changing effect is best when the content of color-changing powder is 15.0%.

Keywords: microcapsule; hard broad-leaved wood; discoloration; self-repair

1. Introduction

As a natural polymer composite material, wood has a unique texture and color. It is the main material of furniture [1,2]. However, since it contains lignin, cellulose, and hemicellulose, wood is easily degraded to glucose, water, and carbon dioxide, leading to wood deterioration, and shortening the service life of wood products [3]. However, the use of water-based wood coatings can close wood tube holes, protect the quality of the wood surface, and improve the wood utilization rate [4,5]. The coating on the surface of furniture can effectively improve the drying, shrinkage, and swelling of wood and play the roles of decoration and protection [6–9]. Compared with traditional organic coatings, waterborne coatings on wood surfaces offer the advantages of safety, nontoxicity, abrasion resistance, chemical resistance [10–13], etc. However, water-based wood coatings are inevitably affected by the external environment during use, and microcracks are very likely to occur due to factors such as wet expansion and dry shrinkage of the wood substrate [14,15].

Recent studies have broadened research prospects in adjusting the properties of wood surface coatings and suppressing their defects by adding microcapsules [16–18]. In view of this, numerous researchers in recent years have provided a novel and effective way to repair microcracks by mimicking the healable function of living organisms and using healable technology. Healable microcapsules technology has been introduced into the
field of wood coatings [19–21] to achieve the purpose of repairing cracks in coatings and improving the usability and safety of wood coatings [22]. Healable microcapsules are a kind of external aid repair material. Microcapsules coated with repair agent are implanted into the matrix material. When cracks occur in the material, the microcapsules rupture. The repair agent is released from the microcapsules and infiltrate the microcracks in order to repair the cracks and restore the material’s properties.

The surface of thermochromic wood is coated with a thermochromic coating, which makes the color of the wood change with temperature, meeting people’s interest in intelligent and diversified wood products. Thermochromic microcapsules are intelligently responsive materials that can change their color with changes in ambient temperature [23]. That is to say, when microcapsules are heated to a specific temperature, they can change from one color to another, and when the temperature drops to a specific temperature [24], they can change back to the original color [25].

In this experiment, the reactive repair mechanism was used to repair the cracks on the surface of the substrate and to prepare the self-repairing, discoloration microcapsules of shellac that can be applied to water-based coatings. The microcapsules were added into water-based coatings to study the restoration and color-change effect of the paint film, in order to lay the theoretical foundation for the industrial application of healable and color change coatings.

2. Materials and Methods

2.1. Experimental Materials

Formaldehyde solution with a mass fraction of 37.0% and citric acid monohydrate were purchased from Xilong Science Co., Ltd., Shantou, China. Urea was purchased from Shandong Vousuo Chemical Technology Co., Ltd., Linyi, China. Triethanolamine was purchased from Nanjing Chemical Reagent Co., Ltd., Nanjing, China. Sodium dodecylbenzene sulfonate was purchased from the Tianjin Beichen Fangzheng reagent factory, Tianjin, China. Anhydrous ethanol was purchased from Wuxi Yasheng Chemical Co., Ltd., Wuxi, China. Dulux waterborne paint (waterborne acrylic copolymer dispersion, dimming agent, additive, and water; solid content of about 30.0%) was purchased from Dulux Paint Co., LTD (Slough, UK). Zingana (Microberlinia sp.) plates (100 mm × 100 mm × 10mm) were obtained from Beijing Jinyu Tiantan Furniture Co., Ltd., Beijing, China. Purple shellac tablets, Yunnan special grade 2 were purchased from Jinan Dahui Chemical Technology Co., LTD., Jinan, China.

2.2. Preparation Methods

2.2.1. Preparation of Shellac Microcapsules

(1) Preparation of wall material: 20.0 g of urea and 27.0 g of formaldehyde were added in a sealed beaker and stirred until completely dissolved. Triethanolamine was dripped into the mixed solution under stirring, the pH value was adjusted to 8.5–9.0, and the solution was stirred for 60 min to obtain the wall solution.

(2) Preparation of core material: 22.5 g of shellac tablets and 112.5 g of anhydrous ethanol were dissolved and placed into a centrifuge to obtain clear liquid. Then, 1.76 g of sodium dodecyl benzene sulfonate white powder was added into 174 g of distilled water and stirred until in a transparent and granular state. The emulsifier and dissolved shellac were added into the rotor stirrer to emulsify for 30 min, and the core material solution was obtained.

(3) Microencapsulation: The wall material of the urea–formaldehyde prepolymer was dropped into the core material solution. Next, 1.0 g of hydrated citric acid was added to water and dropped into the mixed solution of wall material and core material, and the pH was adjusted to 2.5–3.0. Then, the temperature of the water bath was raised to 70 °C and stirred for a reaction for 3 h. Afterward, the water bath was placed at room temperature for 48 h.
2.2.2. Preparation of Discoloration Microcapsules

1. Preparation of wall material: 3.00 g of urea and 4.05 g of formaldehyde were added in a sealed beaker and stirred until completely dissolved. Triethanolamine was dripped into the mixed solution under stirring, the pH value was adjusted to 8.5–9.0, and the solution was stirred for 60 min to obtain the wall solution.

2. Preparation of core material: 1.35 g of emulsifier (gum arabic powder) and 43.65 g of distilled water were mixed and stirred until completely dissolved to obtain the 3% solution. Then, 2.57 g of the color-changing compound made of crystal violet lactone, bisphenol A, and tetradecanol was added at the mass rate of 1: 3: 60 to the above solution. Then, it was placed in a magnetic stirrer, heated to 65 °C, and stirred for 60 min to obtain the core material solution.

3. Microencapsulation: The wall material solution was added to the core material solution, citric acid was added, and the pH was adjusted to 2.5–3.0. The mixture was stirred for 1 h, the temperature of the mixture was raised to 70 °C, and the mixture was stirred for 30 min. After stirring, the mixture was left to precipitate at room temperature for 48 h.

4. Suction filtration: After standing, the liquid part was filtered and washed with distilled water and absolute ethanol. The final granular powder was put into a 40 °C oven to dry for 48 h, and then it was allowed to dry at room temperature. Finally, the microcapsule powder was obtained.

In order to further confirm that color-changing microcapsules have a color-changing effect, the microcapsules were put into the oven and heated at 60 °C for 2 h. It can be seen in Figure 1 that the color-changing microcapsules have a color-changing effect and were easy to agglomerate after being heated at a high temperature.

![Figure 1](image_url). The discoloration effect of microcapsules (A) after heating and (B) at room temperature.

2.2.3. Preparation of Coating

The coating preparation process was carried out by controlling factors such as the content of discolored microcapsules, content of shellac microcapsules, and the microcapsule addition method in order to obtain a variety of coatings with different structures and morphologies. An orthogonal test with three factors and two levels was used to analyze and determine the effect of process parameters on the performance of the coatings. The test factors and levels are shown in Table 1.
Table 1. Orthogonal experiment table.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Content of Color-Changing Microcapsules (%)</th>
<th>Shellac Microcapsule Content (%)</th>
<th>Adding Situation of Microcapsule</th>
</tr>
</thead>
<tbody>
<tr>
<td>1#</td>
<td>10.0</td>
<td>5.0</td>
<td>primer with color-changing microcapsules and topcoat with shellac microcapsules</td>
</tr>
<tr>
<td>2#</td>
<td>10.0</td>
<td>15.0</td>
<td>topcoat with color-changing microcapsules and primer with shellac microcapsules</td>
</tr>
<tr>
<td>3#</td>
<td>20.0</td>
<td>5.0</td>
<td>topcoat with color-changing microcapsules and primer with shellac microcapsules</td>
</tr>
<tr>
<td>4#</td>
<td>20.0</td>
<td>15.0</td>
<td>primer with color-changing microcapsules and topcoat with shellac microcapsules</td>
</tr>
</tbody>
</table>

Firstly, sandpaper was used to polish the surface of the wood, and then the sawdust on the surface of the plate was removed. Taking sample 1# as an example, the 1.8 g of primer and 0.2 g of color-changing microcapsules were weighed in a beaker. The paint was stirred well and applied to the board in three coats. Each time it was coated, it needed to be placed in the oven and baked until the surface was dry. Next, it was followed by a second and third coat. After the third coat, it was placed in the oven to dry. Then, 1.9 g of topcoat and 0.1 g of shellac microcapsule were weighed and stirred in evenly. The above steps were repeated. Finally, they were put into a 40 °C oven to dry for 2 h, and then the boards were placed at room temperature for 24 h.

Table 2 shows the samples with and without microcapsules. Sample 5# was an optimized sample after the orthogonal test: it contained 1.8 g primer, 0.2 g color-changing microcapsules, 1.7 g topcoat, and 0.3 g shellac microcapsules. Samples 6# to 8# were control samples. Sample 6# contained blank pairs without microcapsules: it contained 2.0 g primer and 2.0 g topcoat. For sample 7#, only color-changing microcapsules were added: it contained 1.8 g primer, 0.2 g color-changing microcapsules, and 2.0 g of topcoat. For sample 8#, only shellac microcapsules were added: it contained 2.0 g primer, 1.7 g topcoat, and 0.3 g shellac microcapsules. The coating preparation method was the same as the orthogonal test.

Table 2. Comparison of the coating with and without microcapsules.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Content of Color-Changing Microcapsules (%)</th>
<th>Shellac Microcapsule Content (%)</th>
<th>Adding Situation of Microcapsule</th>
</tr>
</thead>
<tbody>
<tr>
<td>5#</td>
<td>10.0</td>
<td>15.0</td>
<td>primer with color-changing microcapsules and topcoat with shellac microcapsules</td>
</tr>
<tr>
<td>6#</td>
<td>0</td>
<td>0</td>
<td>no microcapsules</td>
</tr>
<tr>
<td>7#</td>
<td>10.0</td>
<td>0</td>
<td>primer with color-changing microcapsules</td>
</tr>
<tr>
<td>8#</td>
<td>0</td>
<td>15.0</td>
<td>topcoat with shellac microcapsules</td>
</tr>
</tbody>
</table>

2.3. Testing and Characterization

An SEGT-J portable chromatic aberration instrument (Zhuhai Tianchuang Instrument Co., Ltd., Zhuhai, China) was used to measure the color difference of the surface coating. By heating to 26 °C, four points of each paint film were taken. The average value was calculated as the color value of the paint film and recorded as L, a, b respectively. By heating
to 40 °C, four points of each paint film were taken. The average value was calculated as the color value of the paint film and recorded as \( L', a', b' \), respectively. \( \Delta L^* \) represents the difference in brightness, \( \Delta a^* \) represents the difference in red and green, and \( \Delta b^* \) represents the difference in yellow and blue. According to CIELAB color difference Formula (1), the color difference value of the water-based film was calculated:

\[
\Delta E^* = \left[ (\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2 \right]^{1/2}
\] (1)

Cracks were made on some of the prepared healable film samples using a blade 2 cm in length and with a depth of approximately 100 µm. Using a Zeiss Axio Scope A1 optical microscope (OM, Carl Zeiss AG, Oberkochen, Germany) and a Quanta-200 scanning electron microscope (SEM, FEI Company, Hillsboro, OR, USA), the changes in the coating scratches before and after repair were observed for 5 d. The self-repair effect was analyzed according to the results. The roughness tester J8-4C (Shanghai Taiming Optical Instrument Co., Ltd., Shanghai, China) was used to place the experimental material on the detection table, and the probe was moved to the contact board. The position of the probe was adjusted, and the roughness value was observed and recorded after the probe stabilized at 0 coordinate. According to the standard GB/T 6739-2006 [26], the pencil hardness tester was used to test the pencil hardness of 6 B–6 H: 6 B was the softest, 6 H was the hardest, and HB was the middle value. The appearance of microcapsules was observed using an SEM. The chemical composition of microcapsules was analyzed using a VERTEX 80V Fourier-transform infrared spectrometer (FTIR, Shanghai Smio Analytical Instrument Co., Ltd., Shanghai, China).

All tests were repeated 4 times with an error of less than 5%.

3. Results and Discussion

3.1. Color Difference Analysis

The color difference meter was used to measure the color difference value of the film at a room temperature of 26 °C and high temperature of 40 °C, and Table 3 was calculated. The obtained color difference values were calculated to obtain Table 4.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( L )</th>
<th>( a )</th>
<th>( b )</th>
<th>( c )</th>
<th>( h )</th>
<th>( L' )</th>
<th>( a' )</th>
<th>( b' )</th>
<th>( c' )</th>
<th>( h' )</th>
<th>( \Delta L^* )</th>
<th>( \Delta a^* )</th>
<th>( \Delta b^* )</th>
<th>( \Delta E^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1#</td>
<td>55.3</td>
<td>16.2</td>
<td>18.4</td>
<td>24.5</td>
<td>48.6</td>
<td>52.7</td>
<td>16.8</td>
<td>16.0</td>
<td>23.2</td>
<td>43.5</td>
<td>-2.6</td>
<td>0.6</td>
<td>-2.4</td>
<td>3.6</td>
</tr>
<tr>
<td>2#</td>
<td>58.8</td>
<td>13.1</td>
<td>16.6</td>
<td>21.2</td>
<td>51.7</td>
<td>59.9</td>
<td>12.8</td>
<td>14.7</td>
<td>19.5</td>
<td>48.8</td>
<td>-1.1</td>
<td>-0.3</td>
<td>-2.9</td>
<td>2.2</td>
</tr>
<tr>
<td>3#</td>
<td>56.9</td>
<td>15.7</td>
<td>17.7</td>
<td>23.7</td>
<td>48.4</td>
<td>57.2</td>
<td>14.5</td>
<td>16.3</td>
<td>21.8</td>
<td>48.4</td>
<td>0.3</td>
<td>-1.2</td>
<td>-1.4</td>
<td>1.9</td>
</tr>
<tr>
<td>4#</td>
<td>60.1</td>
<td>10.9</td>
<td>11.3</td>
<td>15.7</td>
<td>46</td>
<td>57.7</td>
<td>13.4</td>
<td>11.0</td>
<td>17.4</td>
<td>39.5</td>
<td>-2.4</td>
<td>2.5</td>
<td>-0.3</td>
<td>3.5</td>
</tr>
</tbody>
</table>

As seen in Table 4, the range value for the discoloration microcapsules was 0.2, for the shellac microcapsules was 0.1, and for the adding situation was 1.5. From the data, it is clear that the adding situation has the greatest influence on the color-change effect. The color differences between the 1# and 4# primers with color-changing microcapsules and topcoats with shellac microcapsules are 3.6 and 3.5, while 2# and 3# topcoats with color-changing microcapsules and primer with shellac microcapsules are 2.2 and 1.9. The analysis shows that the color-changing effect of “primer with color-changing microcapsules and the topcoat with shellac microcapsules” is better.

In order to detect the effect of the microcapsule addition method and content on the healable and color-changing properties of the coating, the color difference values of the control plates at a normal temperature of 26 °C and a high temperature of 40 °C were measured with the color difference instrument, and Table 5 was calculated.
Table 4. Analysis results of orthogonal experiment.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Content of Color-Changing Microcapsules (%)</th>
<th>Shellac Microcapsule Content (%)</th>
<th>Adding Situation of Microcapsule</th>
<th>Chromatic Aberration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1#</td>
<td>10.0</td>
<td>5.0</td>
<td>primer with color-changing microcapsules and topcoat with shellac microcapsules</td>
<td>3.6</td>
</tr>
<tr>
<td>2#</td>
<td>10.0</td>
<td>15.0</td>
<td>topcoat with color-changing microcapsules and primer with shellac microcapsules</td>
<td>2.2</td>
</tr>
<tr>
<td>3#</td>
<td>20.0</td>
<td>5.0</td>
<td>topcoat with color-changing microcapsules and primer with shellac microcapsules</td>
<td>1.9</td>
</tr>
<tr>
<td>4#</td>
<td>20.0</td>
<td>15.0</td>
<td>primer with color-changing microcapsules and topcoat with shellac microcapsules</td>
<td>3.5</td>
</tr>
<tr>
<td>Mean 1</td>
<td>2.900</td>
<td>2.750</td>
<td>3.550</td>
<td>-</td>
</tr>
<tr>
<td>Mean 2</td>
<td>2.700</td>
<td>2.850</td>
<td>2.050</td>
<td>-</td>
</tr>
<tr>
<td>Range</td>
<td>0.200</td>
<td>0.100</td>
<td>1.500</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 5. Color difference value (room temperature 26 °C: L, a, b, c, h, and high temperature 40 °C: L’, a’, b’, c’, h’).

| Sample | L   | a    | b    | c    | h   | L’  | a'   | b'   | c'   | h’  | △L  | △a  | △b  | △E  |
|--------|-----|------|------|------|-----|-----|------|------|------|-----|-----|-----|-----|
| 5#     | 63.2| 10.5 | 11.7 | 15.8 | 48.1| 58.9| 10.0 | 10.4 | 14.5 | 46.2| -4.3| -0.5| -1.3| 4.5 |
| 6#     | 51.4| 16.6 | 29.4 | 33.8 | 60.5| 50.5| 15.5 | 29.1 | 35.1 | 56  | -0.9| -1.1| -0.3| 1.5 |
| 7#     | 58.3| 15.2 | 22.9 | 27.4 | 56.3| 54.7| 16.4 | 19.8 | 25.8 | 50.3| -3.6| 1.2 | -3.1| 4.9 |
| 8#     | 59.1| 13.3 | 13.3 | 18.8 | 45.0| 58.0| 12.0 | 14.1 | 18.6 | 49.6| -1.1| -1.3| 0.8 | 1.9 |

According to Table 5, the color difference value of sample 5# is 4.5, sample 6# is 1.5, sample 7# is 4.9, and sample 8# is 1.9. The color difference value of 5# with both color-changing and shellac microcapsules was smaller than that of 7# with only color-changing microcapsules but larger than that of 8# with only shellac microcapsules. The analysis shows that color-changing microcapsules have a great color-changing effect on the board, and that shellac acts as a disincentive to the color-changing microcapsules. Therefore, the proportion of color-changing microcapsules and shellac microcapsules should be carefully controlled in the preparation of microcapsules to ensure the color-changing effect and the healable effect of the coating.

3.2. Healable Analysis

A box cutter was used to cut a thin sheet of the board to make sure it was not too large to make sure that the light could penetrate through the wood boards under the microscope, and the microcapsules in the sheet could be observed. Then, a cross was gently made on the sheet, without too much pressure; otherwise, it would easily damage the sheet. Cut sheets were stuck on the glass sheet in turn, and then, the scratches were observed using a microscope.

Figure 2A,C,E,G contains the images of the films at the beginning of the scratch. Five days later, the same scratch was observed under a microscope, and the scratch on the film was obtained as shown in Figure 2B,D,E,H.
The data obtained before and after repairing are shown in Table 6. According to the data in Table 6, after five days, the scratch widths of films 5# and 8# were correspondingly smaller than that of films 6# and 7#. According to the composition of the film in the previous independent experiment, films 6# and 7# did not contain shellac, and the scratch widths were almost unchanged, indicating that the healable function of the film is related to the content of shellac.

**Table 6.** The difference in width data before and after repairing.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Before Repairing (µm)</th>
<th>After Repairing (µm)</th>
<th>Difference (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5#</td>
<td>14.21</td>
<td>8.81</td>
<td>5.40</td>
</tr>
<tr>
<td>6#</td>
<td>15.39</td>
<td>15.27</td>
<td>0.12</td>
</tr>
<tr>
<td>7#</td>
<td>14.81</td>
<td>14.81</td>
<td>0</td>
</tr>
<tr>
<td>8#</td>
<td>10.88</td>
<td>7.99</td>
<td>2.89</td>
</tr>
</tbody>
</table>
3.3. Roughness Analysis

Films 5#–8# were placed in the roughness-measuring instrument to detect their surface roughness, as shown in Figure 3, and the data are shown in Table 7. According to the analysis in Table 7, the surface roughness of film 8#, which contains only shellac, is the largest at 3.858 µm, and the roughness of 6#, which does not add any microcapsules added to both the primer and topcoat, is the smallest at 0.294 µm. The roughness of both 5# and 7# is smaller than that of 8# and larger than that of 2#; therefore, it can be seen that the content of shellac microcapsules in the topcoat has a greater effect on the roughness. The roughness is larger when the content is higher than 15.0%, which affected the flatness of the waterborne film.

![Figure 3. Surface roughness of films (A) 5#, (B) 6#, (C) 7#, (D) 8#](image)

Table 7. Roughness data of the coating.

<table>
<thead>
<tr>
<th>Sample</th>
<th>5#</th>
<th>6#</th>
<th>7#</th>
<th>8#</th>
</tr>
</thead>
<tbody>
<tr>
<td>Roughness (µm)</td>
<td>2.808</td>
<td>0.294</td>
<td>2.075</td>
<td>3.858</td>
</tr>
</tbody>
</table>

The higher the shellac content in the capsule, the greater the surface roughness of the paint film, and adding microcapsules in the topcoat has a greater impact on the surface roughness of the paint film than adding microcapsules in the primer.

3.4. Hardness Analysis

The films were placed in a pencil hardness tester to test their hardness, as shown in Table 8. According to the data in Table 8, the hardness of sample 5# with microcapsules is 6 H, the hardness of sample 6# without microcapsules is 5 H, the hardness of sample 7# with only discoloration microcapsules is 4 H, and the hardness of sample 8# with only shellac microcapsules is 5 H. It can be seen from Table 8 that the composite microcapsules have little influence on the hardness of the paint film, and that the paint film can maintain a high hardness.

![Table 7. Roughness data of the coating.](image)
Table 8. Hardness data of the samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>5#</th>
<th>6#</th>
<th>7#</th>
<th>8#</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness</td>
<td>6 H</td>
<td>5 H</td>
<td>4 H</td>
<td>5 H</td>
</tr>
</tbody>
</table>

3.5. Microstructure Analysis

SEM diagrams of shellac microcapsules and discoloration microcapsules are shown in Figure 4A-B. The shellac microcapsules, with a diameter of around 9 μm, are evenly distributed. Discoloration microcapsules are easy to agglomerate, although their distribution is not very uniform. The discoloration microcapsules have a similar diameter to the shellac microcapsules at around 9 μm. The average size of the composite microcapsules does not affect the thickness of the film.

![SEM images](image_url)

Figure 4. SEM (scanning electron microscope) images of (A) shellac microcapsules and (B) discoloration microcapsules. SEM of films: (C) 5#, (D) 6#, (E) 7#, and (F) 8#.

The SEM of paint film 5#–8# is shown in Figure 4C–F. The color-changing microcapsules and shellac microcapsules were added in 5#, no microcapsules were added in 6#, the color-changing microcapsules were added in 7#, and the shellac microcapsules were added in 8#. Therefore, the more shellac microcapsules that were added, the rougher the paint film surface became.
3.6. Infrared spectroscopy

The core material of color-changing microcapsules is a complex of crystal violet lactone, bisphenol A, and tetradecanol, and the wall material is urea–formaldehyde resin. From Figure 5, it can be seen that the peaks at 1130 cm\(^{-1}\), and 1074 cm\(^{-1}\) correspond to the symmetrical telescopic vibration peak of lactone C=O=C. The peak at 1627 cm\(^{-1}\) corresponds to the asymmetrical telescopic vibration of the carbonyl group in the carboxylate, and the peak at 1368 cm\(^{-1}\) corresponds to the symmetrical telescopic absorption peak of the carboxylate, which proves that the lactone in the molecule is ring-opened and forms a conjugated color structure. The peaks at 2955 cm\(^{-1}\) and 2917 cm\(^{-1}\) belong to the asymmetrical telescopic vibration and symmetrical telescopic vibration of C–H in tetradecanol and methyl in CVL. The peak at 3352 cm\(^{-1}\) belongs to the N–H absorption peak in the urea–formaldehyde resin, and the peaks at 1238 cm\(^{-1}\)–1350 cm\(^{-1}\) are the characteristic absorption peaks of CH\(_3\)O, which proves the success of the preparation of color-changing microcapsules.

![Figure 5. The infrared spectrum of microcapsules.](image)

In the infrared spectrum of the coating film (Figure 6) with the shellac microcapsule, the peak at 3360 cm\(^{-1}\) is the N–H absorption peak. The peaks at 2929 cm\(^{-1}\) and 2865 cm\(^{-1}\) are the stretching vibration peaks of C–H. The peak at 1639 cm\(^{-1}\) is the stretching vibration of C=O in the urea–formaldehyde resin in wall material. The peaks at 1465 cm\(^{-1}\), 1423 cm\(^{-1}\), and 1255 cm\(^{-1}\) are the characteristic peaks of the shellac resin microcapsule. At 1465 cm\(^{-1}\) and 1423 cm\(^{-1}\), the carbonyl anion COO of carboxylic acid is antisymmetric and symmetric stretching vibration, respectively. At 1255 cm\(^{-1}\), it is the C=O–C stretching vibration in the ester molecule. In the infrared spectrum of pure water-based coating, the peaks at 2929 cm\(^{-1}\), 2865 cm\(^{-1}\), and 1447 cm\(^{-1}\) were the stretching vibration peak of –CH\(_2\), and the peak at 1730 cm\(^{-1}\) was the vibration absorption peak of C=O. There was no disappearance or appearance of multiple peaks between the coating samples. There was no chemical reaction between the microcapsules and the coating.
4. Conclusions

The orthogonal experiment showed that the method of adding microcapsules had a great influence on the color difference of the healable, composite, color-changing coating. When the content of color-changing microcapsules was 10.0%, the shellac microcapsules content was 15.0%, and the color-changing microcapsules were added to the primer and shellac microcapsules to the finish, the color change was the most obvious, and the color difference was 4.5. After 5 days of repair, the crack width reduced by 5.4 µm, which showed a good repair effect. After the shellac microcapsules were added into the finish coating, the roughness of the coating was greatly affected, and the roughness was 2.808 µm. When the shellac and color-changing microcapsules were added to the coating at the same time, the hardness of the coating was higher than 6 H. There was no chemical reaction between the coating and the microcapsules. By adding 10.0% color-changing microcapsules in the primer and 15.0% shellac microcapsules in the topcoat, the coating has the best comprehensive performance and ensured a healable performance, which lays the technical foundation for the application of dual-function, color-changing, composite coatings.

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