Preparation and performance characterization of asphalt sustained-release capsules

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Abstract

In order to improve the self-repairing performance of asphalt pavement, emulsified-solvent evaporation method was used to prepare sustained-release capsules which wrap asphalt rejuvenator. The effects of stirring rate, core to shell mass ratios, stirring time and the amount of surfactant on the final morphology, particle size and yield of sustained-release capsules were studied by orthogonal experiment of four factors and three levels. The optical microscope and scanning electron microscope were used to characterize the sustained-release capsules. The experimental results show that the stirring rate has a great influence on the preparation of sustained-release capsules. The optimum conditions for preparing the sustained-release capsules are determined as the core to shell mass ratio of 0.6:1, the surfactant of 1 g sodium dodecyl sulfate and 2 g gelatin, the stirring rate of 700 r/min, the stirring time of 30 min. The sustained-release capsules prepared under these conditions have a compact structure and good surface morphology. The sustained-release capsules are distributed uniformly in particle size, mainly in the range of 20–50 μm. The sustained-release capsules produced in this way have a high yield of 89.3%. Thermogravimetric analysis shows that the sustained-release capsules have good thermal stability.

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Keywords: Sustained-release capsules; Performance characterization of preparation; Orthogonal experimental design; Bitumen self-healing

1. Introduction

Under the long-term effect of the driving load and natural environment such as sunniness, road materials will gradually age and the performance will decline. As a result, tiny cracks and damage in pavement will occur inevitably. How to repair the cracks and damages timely and effectively has become an important issue for road workers. At present, the remedial measures are taken only obvious cracks appear in the pavement, which usually affect traffics and consume more manpower and material resources. Therefore, there is an urgent need for a new technology to independently block the expansion of the emerging cracks and repair the existing damage [1]. In order to ameliorate this problem, the concept of self-healing is introduced into road rehabilitation. The mechanism of self-healing is to imitate the ability of living organisms to sense and repair their injuries in time.

In early 1980s, the United States put forward the concept of self-healing polymer materials. Afterward, a lot of research has been done by many scholars from the United States and Europe [2,3]. At present, the self-healing polymer materials mainly use capsule technology. White et al. [4] first studied the application of self-healing polymer materials. They successfully dispersed the urea-formaldehyde microcapsules and Grubbs catalysts encapsulating cyclopentadiene dimer in epoxy resin, and made the self-healing of matrix materials come true. Keller et al. [5] used dicyclopentadiene as the core material and
urea formaldehyde resin as the shell material. The microcapsules are synthesized by in-situ polymerization and added to the epoxy resin to form a thermosetting resin-based composite material. The mechanical properties of the microcapsules were also studied. Leyang Lv et al. [6] made a self-healing cement by adding polyphenol-formaldehyde microcapsules containing healing rejuvenator to the cement concrete to improve its durability. Gircia et al. [7–9] used epoxy resin and cement as the capsule shell to make microcapsules containing rejuvenator. When applied in asphalt mixture, this material will successfully revert the aging of the asphalt concrete. However, the splitting strength and fatigue life of asphalt concrete will be reduced SU Jun-feng et al. [10–13] synthesized microcapsules using methanol-melamine-formaldehyde resin as shell material and asphalt regenerating agent as core material, and incorporated them into aged asphalt to realize the self-healing of aged asphalt.

At the moment, the mechanism of the most microcapsules is the core rejuvenator will be released when the material cracks due to stress concentration. However, this release is uncontrollable [14]. In order to solve this problem, emulsion - solvent evaporation method is used in this paper to prepare sustained-release capsules, from which the core rejuvenator can be released slowly. Polymethylmethacrylate (PMMA) is selected as the shell material and asphalt rejuvenator is selected as the core material. The effects of stirring rate, mass ratio of the core to shell, stirring time and the amount of surfactant on the final morphology, particle size and yield of sustained-release capsules are studied. The thermal stability of the prepared sustained-release capsules is also analyzed.

2. Materials and experimental methods

2.1. Material selection

2.1.1. Selection of core and shell materials of Sustained-release capsule

In the preparation of sustained-release capsules, it should be made sure to filter the appropriate raw materials so that the capsules could get good coverage. Two problems must be considered when selecting shell materials [15]. First, the shell material needs good compatibility with the repaired substrate. If the rejuvenator does not match the properties of the matrix material, it will affect the performance of the matrix material. Second, shell materials need to have the right intensity. Poor shell intensity can lead the capsule to break without cracking and the rejuvenator will be released in advance. Therefore, after comparison, PMMA is selected as the shell material of the sustained-release capsule.

The selection of sustained-release capsule core material should follow the following four principles [16]. First, good chemical stability. Self-polymerization does not occur during long-term storage or at elevated temperatures. Second, stable physical performance, such as lower freezing point and vapor pressure, so that the core material will not easily penetrate and volatilize from the capsule. Third, high reactivity. At the corresponding ambient temperature, polymerization can occur rapidly and repair the crack surface. Fourth, low viscosity. After the core material is released, it can smoothly flow into the micro-cracks. By contrast, a certain brand asphalt rejuvenator (90 °C viscosity is about 3500–4500 cP, flash point is greater than 220 °C) is chosen as the core material of sustained-release capsules. Compared with the traditional rejuvenator, this rejuvenator synthesizes the polymer material through the chain scission link technique to disperse and crack the asphaltene in aged asphalt. Hence, the high temperature stability, the low temperature crack resistance and the fatigue performance of the recycled asphalt mixture will improve remarkably.

2.1.2. Raw materials

The main raw materials required for the experiment are shown in Table 1

2.2. Preparation of sustained-release capsules

2.2.1. Preparation of sustained-release capsules principle

The dispersed oil-in-water emulsion droplets contain a polymer that has not been encapsulated in a mixed solvent. Among them, the mixed solvent is composed of a good solvent with low boiling point and a core material (poor solvent with high boiling point). During evaporation process, the low-boiling good solvent is gradually removed from the emulsion droplets, while the previously dissolved polymer phase-separates and migrates to the oil core and polymer interface. After the low-boiling solvent is completely evaporated, the polymer is sheathed at the oil-phase droplet and aqueous phase interface [17].

2.2.2. Sustained-release capsules preparation process

1. Preparation of surfactant solution

A certain amount of gelatin and SDS was weighed accurately, and then were added into a 500 ml beaker. Next, 200 ml of deionized water was added, and the mixture was heated and stirred on a magnetic stirrer (HJ-4A, China) at the temperature of 40 °C. Until all the gelatin particles in the solution disappeared. The uniformly mixed surfactant solution is put in cold water and cooled to room temperature.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Specifications</th>
<th>Producer</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA</td>
<td>M.W. 35,000</td>
<td>SCRC, China</td>
</tr>
<tr>
<td>Sodium Dodecyl Sulfate (SDS)</td>
<td>CP</td>
<td></td>
</tr>
<tr>
<td>Gelatin</td>
<td>CP</td>
<td></td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>AR, ≥99.5%</td>
<td></td>
</tr>
</tbody>
</table>
2. Preparation of mixed solution of core and shell material

Weigh a certain amount of rejuvenator in a 50 ml beaker, and then pour into the beaker a certain amount of dissolved in methylene chloride solution of PMMA. After the beaker was sealed with plastic wrap, then placed on a magnetic stirrer (HJ-4A, China) and stirred at room temperature until the solution is homogeneous.

3. Sustained-release Capsule Suspension Formation

The surfactant solution cooled to room temperature was placed on the base of an electric mixer (AM90L-H, China). The rotor of the electric mixer was turned down to a depth of 2/3 of the solution, then the electric mixer was turned on slowly, the electric mixer was adjusted to the desired speed. When the desired stirring rate was reached, the mixed solution of the prepared core material and shell material was slowly and dropwise added to the surfactant solution by using a plastic dropping pipette. The stirring speed was maintained for a certain period of time.

4. Solvent removal and sustained-release capsules drying

At the temperature of 40 °C, the sustained-release capsule suspension was placed on a magnetic stirrer (HJ-4A, China) to volatilize the solvent for a period of time. After the volatilization was complete, the solution was filtered through a vacuum pump (SHZ-D, China) to obtain sustained-release capsules. Finally, the product was placed in an oven at 50 °C for 4 hours to obtain the sustained-release capsules.

2.3. Sustained-release capsules performance characterization method

2.3.1. Sustained-release capsules morphology characterization

The surface morphology of sustained-release capsules is observed by a scanning electron microscopy (JSM6390A, Japan) and morphology of the capsules is characterized. The magnification of the test is 500–2000 times.

2.3.2. Sustained-release capsules particle size determination

A three-dimensional stereoscopic microscope (VHX-900F, Japan) is used to observe the particle size of the sustained-release capsules. The test method is to drop the droplets containing the sustained-release capsules on a glass slide and observe the images under a microscope. Then the microscope image processing software was used for statistical determination.

2.3.3. Determination of sustained-release capsules yield

After the sustained-release capsules being fully dried, its quality is weigh accurately. According to the quality of the core and shell material, get the total mass of raw materials. Yield(Y) of sustained-release capsules was calculated by Eq. (1).

\[ Y = \frac{W_1}{W_2} \times 100\% \]  

where \( W_1 \) is the weight of dried sustained-release capsules and \( W_2 \) is the weight of the raw materials.

3. Results and discussion

3.1. Orthogonal experiment analysis

In the preparation process of sustained-release capsules, the mass ratio of the core shell, the stirring rate, the stirring time and the amount of the surfactant have an impact on the performance of the sustained-release capsules. Taking these factors into account, orthogonal experimental design is used in this study to explore. According to the orthogonal experimental design table, L9 (3^4) orthogonal experimental design table is selected to analyze the impact of various factors on the reaction. The following is the specific orthogonal experimental design process.

1. Factors and levels table (see Table 2)

2. Results of the orthogonal experiment

This experiment is a multi-index orthogonal experiment. Results and evaluation indicators are shown in Table 3.

3. Analysis of the range of orthogonal experiment results (see Tables 4, 5)

4. Determination of the best plan

From Table 4, it can be seen that for the sustained-release capsules yield, the best factor combination is A_2B_1C_2D_3. That is, core: shell is 0.6: 1, the surfactant is 2 g SDS and 1 g Gelatin, stirring rate is 700 r/min, stirring time is 30 min. Table 5 shows that A_2B_1C_2D_3 is the best combination for morphological properties of sustained-release capsules. That is, core: shell is 0.6: 1, the surfactant is 1 g

Table 2
Orthogonal experiment factors and levels table.

<table>
<thead>
<tr>
<th>Levels</th>
<th>Core: shell (A)</th>
<th>Surfactant (B)</th>
<th>Stirring rate (r/min) (C)</th>
<th>Stirring time (min) (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.4:1</td>
<td>1 g SDS + 2 g gelatin</td>
<td>500</td>
<td>40</td>
</tr>
<tr>
<td>2</td>
<td>0.6:1</td>
<td>2 g SDS + 1 g gelatin</td>
<td>700</td>
<td>20</td>
</tr>
<tr>
<td>3</td>
<td>0.8:1</td>
<td>1.5 g SDS + 1.5 g gelatin</td>
<td>900</td>
<td>30</td>
</tr>
</tbody>
</table>
The core to shell mass ratio is 0.6:1, surfactant is 1 g SDS and 2 g gelatin, stirring rate is 700 r/min and the stirring time is 30 min.

3.2. The impact of various factors analysis

Orthogonal experiments are helpful to analyze various factors and their interactions. Only conducting part of the tests Therefore, it is necessary to perform sustained-release capsule performance verification at each level of the four factors on the basis of the optimum level obtained from the orthogonal experiment [18]. The range analysis shows that the stirring rate has the greatest impact on the morphology of sustained-release capsules.

3.2.1. Effect of stirring rate on the properties of sustained-release capsules

In general, as the stirring rate increases, the particle size of the dispersed droplets becomes smaller and smaller. When the stirring rate is low, the oil phase is difficult to disperse evenly, which leads to poor encapsulation of the sustained-release capsules. When the stirring rate is too high, liquid phase loss easily occurs and the yield of the sustained-release capsules is affected. As shown in Fig. 1, when the stirring rate is 500 r/min, some of the sustained-release capsules are not completely encapsulated. When the stirring rate is 900 r/min, the yield of the sustained-release capsules decreases significantly. Therefore, 700 r/min is selected as the stirring rate of the preparation of sustained-release capsules.

3.2.2. Effect of core to shell mass ratio on the properties of sustained-release capsules

Core to shell mass ratio affects the shell thickness, stability and densification of the sustained-release capsules. When the core to shell mass ratio is relatively large, the probability of generating holes on the shell will be greater. Sustained-release capsules are incompletely encapsulated, causing sustained-release capsules to break without cracking [19]. The rejuvenator is released in advance and cannot repair the crack when it actually cracks. As shown in Fig. 2,

### Table 3
Orthogonal experiment results.

<table>
<thead>
<tr>
<th>Expt.</th>
<th>Core: shell (A)</th>
<th>Surfactant (B)</th>
<th>Stirring rate (C)</th>
<th>Stirring time (D)</th>
<th>Yield</th>
<th>Score</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0.811</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>0.868</td>
<td>2</td>
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<tr>
<td>3</td>
<td>1</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>0.814</td>
<td>1</td>
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<tr>
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<td>2</td>
<td>3</td>
<td>0.893</td>
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<td>2</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td>0.843</td>
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</tr>
<tr>
<td>6</td>
<td>2</td>
<td>3</td>
<td>1</td>
<td>2</td>
<td>0.863</td>
<td>2</td>
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<tr>
<td>7</td>
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<td>2</td>
<td>0.827</td>
<td>1</td>
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<td>8</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>3</td>
<td>0.858</td>
<td>2</td>
</tr>
<tr>
<td>9</td>
<td>3</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>0.861</td>
<td>3</td>
</tr>
</tbody>
</table>

Note: The score is based on the observation of scanning electron microscopy, including sustained-release capsules surface morphology, particle size, distribution, the degree of agglomeration and other factors. If the surface of the sustained-release capsule is densely packed, the particle size distribution is relatively average, less or no reunion occurs, and the corresponding score will be higher. The results of the experiment are divided into four grades according to the observation: bad = 1, medium = 2, good = 3, excellent = 4.

### Table 4
Range analysis of yield.

<table>
<thead>
<tr>
<th>Factors order</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>C &gt; A &gt; D &gt; B</td>
<td>2.493</td>
<td>2.531</td>
<td>2.532</td>
<td>2.515</td>
<td></td>
</tr>
<tr>
<td>A_{2}B_{2}C_{2}D_{3}</td>
<td>2.599</td>
<td>2.569</td>
<td>2.622</td>
<td>2.558</td>
<td></td>
</tr>
<tr>
<td>2.546</td>
<td>2.538</td>
<td>2.484</td>
<td>2.565</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.106</td>
<td>0.038</td>
<td>0.138</td>
<td>0.050</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 5
Range analysis of score.

<table>
<thead>
<tr>
<th>Factors order</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>C &gt; B &gt; D &gt; A</td>
<td>6</td>
<td>8</td>
<td>7</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>A_{2}B_{1}C_{2}D_{3}</td>
<td>7</td>
<td>5</td>
<td>9</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>3</td>
<td>3</td>
<td>7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>6</td>
<td>2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In conclusion, the optimal level of sustained-release capsules determined by orthogonal experiment design is: the core to shell mass ratio is 0.6:1, surfactant is 1 g SDS and 2 g gelatin, stirring rate is 700 r/min and the stirring time is 30 min.
the sustained-release capsules are poorly encapsulated when the core to shell ratio is 0.8:1, whereas the sustained-release capsules form better when the core to shell ratio is 0.6:1 and 0.4:1. However, when the core shell is relatively small, the shell is thick and not conducive to release core material. Therefore, the core to shell ratio of 0.6:1 is chosen as the core to shell ratio for preparation of sustained-release capsules.
3.2.3. Effect of stirring time on the properties of sustained-release capsules

The length of the stirring time has an impact on the yield and the surface morphology of the sustained-release capsules. When stirring time is short, the emulsification reaction does not proceed completely. At this time, the shell material is not completely adhered to the core material, which will lead to great loss in filtration of the suspension. When the stirring time is too long, the sustained-release capsules have been already fully molded. Too much stirring easily leads to capsules reunion, and it is also a waste of the energy. As shown in Fig. 3, when the stirring time is 20 min, some of the sustained-release capsules are not wrapped yet; and when the stirring time is 40 min, agglomeration occurs. Hence, 30 min is selected as the stirring time during the preparation of sustained-release capsules.

3.2.4. Effect of the amount of surfactant on the properties of sustained-release capsules

Sustained-release capsules are prepared in an oil-in-water emulsion environment. Due to the great difference in surface energy between the core material and the shell material, the core material is difficult to be uniformly dispersed in the water phase without help of the surfactant. And the shell material is difficult to aggregate on the surface of the core material to form a stable shell. The addition of surfactant in water-oil system can reduce the oil-water interfacial tension and ensure the stability of the water-oil system. As shown in Fig. 4, the sustained-release capsule has a good morphology when surfactant is 1 g SDS and 2 g gelatin.

From all above, it can be determined that the optimal conditions for preparation of sustained-release capsules are as follows: core to shell ratio of 0.6:1, surfactant of 1 g SDS and 2 g gelatin, stirring rate of 700 r/min, stirring time of 30 min.

3.3. Sustained-release microcapsules morphology

The shape of the sustained-release capsules was photographed by a three-dimensional stereomicroscope. The micrographs are shown in Fig. 5.

As can be seen from Fig. 5, sustained-release capsules have a uniform particle size distribution. After computer statistical analysis, it can be known that the particle size distribution is mainly between 20 μm and 50 μm.

As shown in Fig. 6, the morphology of sustained-release capsules prepared under the optimal conditions was observed with a scanning electron microscope. As shown in Fig. 6, the sustained-release capsules prepared according to the optimal preparing conditions have a good spherical shape with a dense and slight rough surface. The rough surface of sustained-release capsules can increase its contact area with asphalt. When it is incorporated into asphalt system, it is in favor of the stable existence of sustained-release capsules in asphalt system and ensure the stability of the water-oil system.
makes good contact with the surrounding asphalt [20]. When cracks occur, the sustained-release capsules can smoothly burst and flow out of the rejuvenator, thus contributing to the repair of the crack.

3.4. Thermogravimetric analysis of sustained release microcapsules

In this study, the thermal stability of sustained-release capsules was analyzed by a thermogravimetric analyzer (TG209 F3, Germany). Fig. 7 is the test results of the thermal stability of the sustained-release capsules.

The continuous curve in Fig. 7 shows the mass change curve of sustained-release capsule, while the discontinuous point line shows the temperature change. It can be seen that when the temperature range is 20–200 °C, the change of the quality of sustained-release capsules is small, that is, the thermal stability of sustained-release capsules in the range of 20–200 °C is good.
4. Conclusions

1. Polymethylmethacrylate is selected as the shell material of sustained-release capsules, and a certain brand of asphalt rejuvenator is used as the core material of sustained-release capsules. Through the range analysis of orthogonal experiment, it can be concluded that the stirring rate has a great impact on sustained-release capsules morphology, particle size and yield.

2. After orthogonal experimental design and experimental verification, the optimal conditions for preparing the sustained-release capsules are determined, the core to shell mass ratio is 0.6:1, the surfactant is 1 g sodium dodecyl sulfate and 2 g gelatin, the stirring rate is 700 r/min, and the stirring time is 30 min.

3. The morphology and structure of the sustained-release capsules prepared according to the optimal conditions were characterized. The results show that sustained-release capsules prepared by this method are compact in structure and have a good surface morphology. The distribution of the particle size is uniform, mainly concentrating in 20–50 μm. Moreover, the sustained-release capsules have a high yield of 89.3% and good thermal stability.

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Conflict of interest

The authors declare that there is no conflict of interest regarding the publication of this article.

References


Fig. 7. 20–200 °C sustained-release capsules thermogravimetric curve.


