Preparation of Polypropylene Microcapsules and Study on Self-healing Properties of Cement Mortar

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Abstract. Cement concrete has the advantages of abundant sources of raw materials, low cost, convenient molding, etc., and is extremely widely used in the field of building construction. Whereas, due to the high brittleness and low tensile strength of concrete, cracks are easy to occur during use, resulting in a great reduction in its mechanical properties and impermeability, which seriously affects the durability of concrete. In order to prolong the service life of concrete, a new self-healing microcapsule was prepared by melting, dispersion, and condensation by using polypropylene as the wall material and isophorone diisocyanate (IPDI) as the core material. The particle size distribution, mechanical properties, morphology, and structure of microcapsules were characterized by a laser particle size analyzer, a nanoindentation tester, a scanning electron microscope, and infrared spectroscopy, and the self-healing effect of cracks in cement mortar mixed with microcapsules was evaluated. The results showed that when the temperature was 155 °C, the stirring speed was 600 rpm, and the polypropylene/IPDI mass ratio was 1:2, the prepared microcapsules were coarse spheroids with a mass leakage rate of 7.8%. The presence of an asymmetric stretching vibration peak (2270 cm^{-1}) of IPDI in the infrared spectrum of the microencapsulation demonstrates that IPDI has been successfully coated into polypropylene wallcovering. When the microcapsule content is 3.0% of the cement mass, the cement mortar crack with a width of 0.33 mm can be self-repaired.

Keywords: Concrete, Self-healing, Microcapsules, IPDI, Polypropylene.

1 Introduction

Due to its low energy consumption, low cost, and high durability, nowadays, concrete is the most commonly used building material worldwide. [1]. However, in the general natural environment, concrete is susceptible to environmental erosion, coupled with the aging of the concrete itself, which may cause micro-cracks in the concrete, causing local damage or fracture. Due to some limitations of current detection techniques, microcracks in concrete structures are difficult to detect, and conventional

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means are difficult to effectively repair them, which in turn affects the normal performance and service life of the structure, further causes macroscopic cracks, causes brittle fractures of the structure, and even causes catastrophic accidents. Therefore, a new type of repair technology is needed that can sense the damage inside the concrete, and then automatically repair the damage to restore the mechanical properties and durability of the concrete material. Many researchers are interested in so-called self-healing or self-healing concrete because it can potentially meet this requirement. [2-5]. As an emerging new self-healing technology, microencapsulation technology has been widely studied because of its self-healing properties, which offers a workable solution to increase concrete's durability. [6-9]. Microencapsulation technology is a technology that forms tiny containers with a core-shell structure by coating dispersed solids, liquids, or gases with film-forming materials, and nanocapsules can be synthesized [10], and microencapsulation technology is widely used in industrial fields such as medicine, food, and printing, and has made significant progress [11]. Microcapsules are coated with self-healing materials that can self-heal some hard-to-find microcracks [12]. Nishiwaki et al. [13] reported that microencapsulation is a very effective method to completely seal the crack with a chemical reaction, preventing corrosive materials from penetrating and, in certain situations, obtaining a partial recovery of mechanical properties. This last goal is crucial for maintaining performance over the course of the concrete's service life (continuity of crack formation) and offers a workable solution to increase the material's durability.

At present, most of the concrete self-healing microcapsules use thermosetting resins with high molecular weight and high strength as wall materials, such as urea-formaldehyde resin and melamine formaldehyde resin. These microcapsules have high strength and are not easy to break during the concrete mixing process. However, when microcracks occur in concrete, the stress at the tip of the crack also makes it difficult to rupture the microcapsules, resulting in the inability of the internal repair agent to flow out and repair the cracks [14]. Most of the existing microcapsule repair agents use reactive resins, such as epoxy resins. These remedial agents are viscous and need to react with the curing agent to repair the crack [15].

In order to achieve the above purpose, a new type of self-healing microcapsules were prepared by melting, dispersion and condensation using polypropylene as the wall material and isophorone diisocyanate (IPDI) as the core material. The effects of preparation process parameters, wall material types and core-to-wall material ratio on the particle size, morphology and core content of microcapsules were studied.

2 Materials And Methods

2.1 Materials

Polyphenylene powder: softening point 145~155 °C, density 0.88~0.91 g/cm^3, average molecular weight 5000±500, Maclean's Chemical Reagent Co., Ltd.; Isophorone Diisocyanate (IPDI): MW: 174.16, Shanghai Aladdin Biochemical Science & Technology Co., Ltd., Perfluorotributylamine: density 1.87 g/cm^3, relative

molecular weight 671.10, content 99%, analytical pure AR, Beijing Jintong Loctite Chemical Products Co., Ltd.; Ordinary Portland cement (PO 42.5): Hubei Huaxin Cement Co., Ltd.; Sand: fineness modulus 2.35, Wuhan Shengli Sand Plant; Gravel: particle size 5~31.5 mm, Yangxin Fuchao Gravel Co., Ltd.;

2.2 Microcapsules Preparation

The microcapsule core material prepared in this paper is IPDI, which has high chemical activity and can quickly react with a variety of substances containing active hydrogen. To guarantee that there is not a chemical reaction while preparing IPDI, polypropylene-coated isophorone diisocyanate microcapsules are prepared by melting, dispersion, and condensation method, by uniformly dispersing the IPDI core material into the molten liquid wallmaterial, adding perfluorotributylamine (a solvent that does not contain reactive hydrogen and does not react with IPDI), so that the temperature of the mixture drops rapidly below the melting point of the wallmaterial, and the wallmaterial solidifies and coats IPDI to obtain microcapsules. The method is simple and has high preparation efficiency. The preparation process is shown in Fig.1and the specific process steps are as follows:

(1) Put the three-mouth flask into the induction heating constant temperature oil bath, weigh a certain amount of polypropylene powder and put it into the three-mouth flask, heat and stir to melt the polypropylene evenly to obtain liquid polypropylene.

(2) Keep the temperature and stirring rate constant, add an appropriate amount of IPDI to the three-mouth flask, and then continue to stir at a constant speed for 1 h.

(3) Turn off the heating device, and increase the stirring rate, and quickly add a certain amount of perfluorotributylamine to the three-mouth flask, so that the temperature of the polypropylene/IPDI mixture is rapidly reduced, and the suspension of microcapsules is obtained.

(4) The microcapsule suspension was poured into a beaker, dispersed by ultrasonic, filtered and washed, and dried for 24 h to obtain polypropylene-coated IPDI microcapsules.

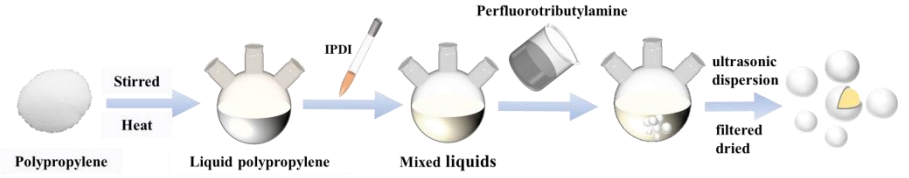

Fig. 1. Preparation process of microcapsules

2.3 Preparation of microcapsule cement mortar

At the dosage of microcapsules of 3% of the mass of cement, the ratio of water and lime and sand is 0.5:1:3 mixing, the concrete doped with polypropylene coated IPDI microcapsules was prepared. In accordance with the specimen production and curing method of the "Standard for Test Methods for Long-term Performance and Durability of Ordinary Concrete" (GB/T 50082-2009), self-healing concrete mixed with microcapsules was prepared. The specific process is as follows: the weighed crushed stone, cement and sand are added to the mixer and stirred for 30 seconds. Then add

water, polycarboxylate superplasticizer and microcapsules, the total feeding time does not exceed 2 minutes, followed by continuous stirring for 3 minutes. After mixing, the concrete is poured into molds with dimensions of 70 mm× 70 mm×70 mm. Immediately after molding, cover with a waterproof membrane and move into a standard curing chamber (20±2 °C, 95% relative humidity). After 24 hours, the mold is removed, and the curing is at the specified age, and then removed for testing.

2.4 Morphology testing of microcapsules

With the use of scanning electron microscopy (S-4800, Hitachi, Japan), the microcapsules' morphology was observed. In order to avoid damage to the microcapsules and affect the observation results, the observation time should be shortened as much as possible.

2.5 Particle size distribution test

Mastersizer 2000 laser particle size analyzer (Mastersizer 2000, Malvern Instruments Ltd., England) to determine the particle size distribution of microcapsules.

2.6 Fourier transform infrared spectroscopy

Characteristic peaks of polypropylene, IPDI, and microcapsules were analyzed by Nexus-type FTIR spectroscopy (Thermo Nicolet Corporation, America). In order to avoid the reaction between the IPDI flowing out of the ruptured microcapsules and the moisture in the air and affecting the test results, infrared spectroscopy was carried out immediately after sample preparation.

2.7 Thermal stability test

The thermal stability of the microcapsules was tested using the German NETZSCH-TG209F3 thermogravimetric analyzer. The temperature range is 30 °C~500 °C, the heating rate is 10 K/min, and the test atmosphere is high-purity nitrogen.

2.8 Determination of sealing performance of microcapsules

After the microcapsules are ready, they are weighed and kept in a chamber with a controlled temperature and humidity of 25% and 50%, respectively. In order to study the compacting performance of microcapsules, the quality change of microcapsules was monitored in time, and the microcapsules in the constant temperature and humidity chamber were taken out after 3 d, 7 d, 14 d and 28 d, respectively, and weighed to obtain the quality difference. The mass leakage rate (P) of the microcapsules can be calculated using equation (1):

$$P = \frac{M0 - Mi}{M0} \times 100\% \quad (1)$$

where M0 is the initial mass of the microcapsule, and Mi is the mass of the microcapsule after storage for different times.

2.9 Concrete self-healing performance test

Use the splitting test device to pre-crack the prepared mortar, and then use the compression testing machine, first put a thin steel bar on the compression device, and

then put the sample on it, and test at a constant rate of 0.1 kN/s, after a certain time, end the loading, remove the sample, observe the cracks, and then put the sample into the standard curing box for seven days to observe the crack repair.

3 Results & Discussion

3.1 Morphology analysis of microcapsules

Fig.2 shows the morphology of the microcapsules under a scanning electron microscope (SEM) and the microcapsules were prepared at 155 °C, 1:2 polypropylene/IPDI ratio, 600 rpm, and 1 hour of agitation. It can be found that the shape of the microcapsule particles is irregular and coarse spherical, which may be due to the poor dispersion caused by the large viscosity of polypropylene, when perfluorotributylamine is added to quenching, the liquid polypropylene is bonded together, and it is difficult to form a spherical shape with regular shape， which ultimately makes the surface rougher, and the rough surface increases the friction between the microcapsule and the cement matrix, thereby enhancing the adhesion between the microcapsule and the cement matrix, which facilitates interfacial bonding.

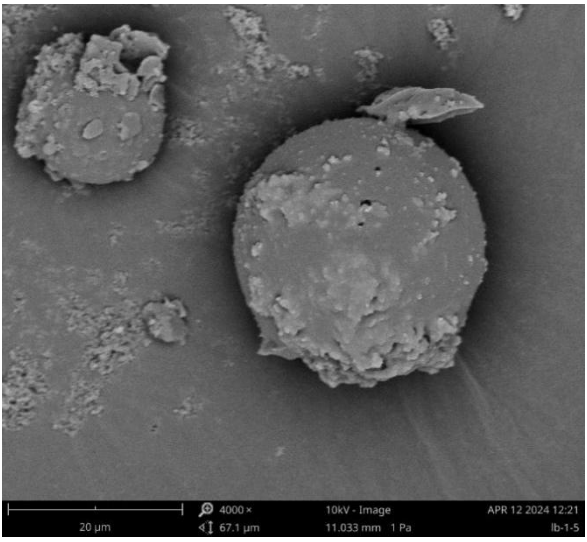

Fig. 2. Microencapsule morphology under scanning electron microscopy

3.2 Analysis of the stirring speed's impact on microcapsule particle size

Fig.3 shows that the distribution of microcapsule particle size becomes more and more uniform with the increase of rotational speed. When the stirring speed is relatively slow (400 rpm), the particle size of microcapsule is mainly distributed in a relatively broad area, but tends to be larger. The microcapsules' particle size distribution became more uniform when the stirring speed was increased to 800 rpm,

and more inclined to a smaller particle size range, at this stage, the average particle size of the microcapsules reached the minimum value. When stirring, the dispersion effect of particles will be affected by different rotational speeds. When the rotational speed is low, the particles may not disperse completely, which may cause the volume fraction to remain in a relatively low range, but this effect improves as the mixing speed increases, and the mixing of the polypropylene /IPDI mixture through the mixing rod can produce greater shear forces, which leads to better dispersion of the particles. At the same time, IPDI is dispersed in smaller droplets in the polypropylene. After the addition of perfluorobutylamine, it is easier to generate micro-capsules with relatively small particle size during the curing process. As the stirring speed decreases, the shear force decreases, and after the coolant is added, the droplet size of the IPDI increases, resulting in an increase in the size of the microcapsules. With the extension of stirring time, the shear effect was enhanced and the microcapsules' particle size decreased. However, when the mixing speed is consistent, a large number of small vortices will form on the paddle shaft, and the shear force generated by these vortices will exceed the shear force on the edge of the paddle shaft. As the propeller speed increases, the number of bubbles also increases, but the centrifugal force prevents these bubbles from aggregating into larger diameter microcapsules. Therefore, in the central area of the impeller shaft, tiny granular microsacs are still formed.

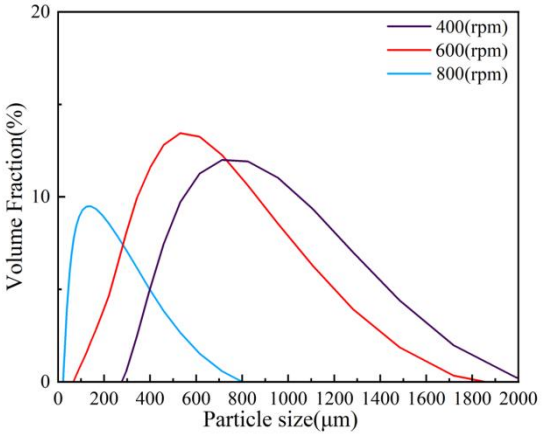

Fig. 3. Particle size distribution curves of microcapsules made with varying speeds of stirring

3.3 Infrared spectroscopy of microcapsules

Fig.4 shows the infrared spectrum of the microcapsules, where a is the infrared spectrum of the IPDI and b is the polypropylene microcapsules' infrared spectrum. The isocyanate group has several characteristic peaks in the infrared spectrum. As can be seen from the figures, the most significant of these are the strong absorption peaks located around 2270 cm^{-1}, which correspond to the wavenumber caused by the asymmetric stretching vibration of N=C=O in the isocyanate group, the methylene C-H stretching vibration at 2956 cm^{-1}, and the inclusion of benzene ring in the IPDI, so characteristic peaks associated with the benzene ring may be observed, such as multiple weak or moderately strong peaks located between 1400 cm^{-1} and 1600 cm^{-1},

which correspond to the skeleton vibration of the benzene ring, This indicates that the microcapsules contain IPDI that does not react.

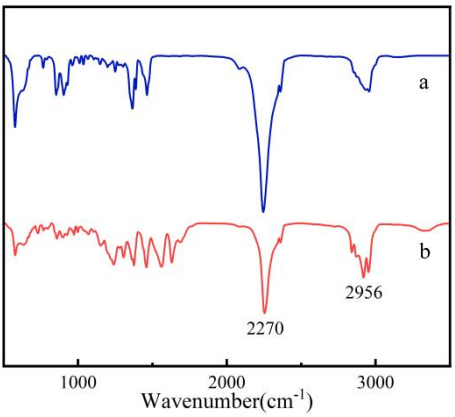

Fig. 4. Infrared spectroscopy of polypropylene-coated IPDI microcapsules

3.4 Thermal stability analysis of microcapsules

Fig.5 shows the thermogravimetric analysis (TG) curve of microcapsules. As the temperature gradually rises, the mass percentage of microcapsules gradually decreases. This means that in this temperature range, there is a loss of quality in the microcapsules. When the temperature is lower than 145℃, the mass decline rate of microcapsules is relatively slow. At this stage, the main mass loss factors of microcapsules are evaporation of water and decomposition of small molecules, rather than polymerization. As the temperature continues to rise, the polymer shell begins to break down and separate from the water. In the temperature range of 145-250 ° C, IPDI begins to gradually differentiate at this stage. As the temperature continues to rise, some new substances appear inside the microcapsules and polymerization occurs. In the temperature range of 250 ° C to 500 ° C stage, the shell of polypropylene began to gradually decompose, and the quality loss rate was relatively high. When the temperature finally rises to 500°C, the thermal decomposition process of the microcapsules is basically complete.

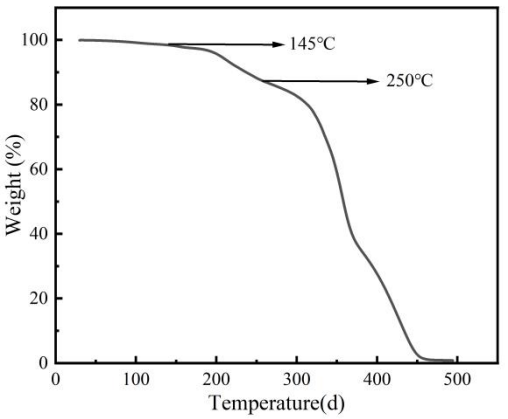

Fig. 5. Thermogravimetric analysis curves of microcapsules

3.5 Analysis of the sealing properties of microcapsules

As illustrated in Fig.6, it can be seen that when the prepared microcapsules are placed in a constant temperature and humidity chamber, the mass leakage rate of microcapsules increases rapidly from 1 d to 7 d with the extension of time, and gradually slows down after 15 d, and the leakage rate was 7.8% on the 28th day, indicating that the microcapsules with polypropylene as wall material had good sealing. This is because the molecular weight and density of polypropylene is relatively large, the intermolecular force is stronger, the gap between the molecular chain segments is smaller, and the crystallinity is higher, so the sealing of the microcapsule is better.

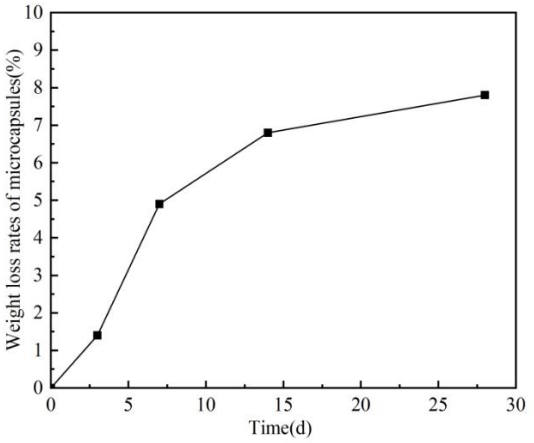

Fig. 6. Mass leakage rate of polypropylene-coated IPDI microcapsules

3.6 Analysis of self-healing performance of mortar cracks

In order to explore the actual repair effect of polypropylene-coated IPDI microcapsules on concrete cracks, the initial crack and final crack width of concrete with 3% microcapsule content were tested before and after 7 days of standard curing, and Fig.7 displays the test results. As can be seen from Figures 6a and b, a crack with a width of 0.33 mm can be self-repaired. As illustrated in Fig.7b, the white substance in Fig.7b that fills the crack is the polyurea formed by the polymerization of isophorone diisocyanate (IPDI) with water. As can be seen from the picture, the generated polyurea bonds the cracks well. Therefore, it can be concluded that the prepared isophorone diisocyanate microcapsules are incorporated into the cement mortar at 3.0% of the cement mass, which has a good crack repair effect on the concrete.

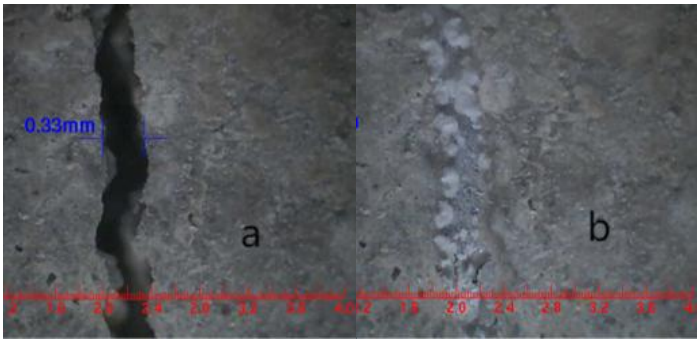

Fig. 7. a and b are the initial crack width and crack self-repair of 3% microcapsulated concrete, respectively

4 Conclusion

In this paper, polypropylene coated IPDI microcapsules were successfully prepared, microcapsule morphology and chemical composition were characterized, and the impact of stirring speed on the particle size distribution of microcapsules was investigated, and the actual repair effect of microcapsules on concrete cracks was explored. The following are the study's primary conclusions:

(1) Scanning electron microscopy can clearly show that the prepared polypropylene-coated IPDI microcapsules have a core-shell structure, and their appearance and morphology are spherical with rough surface. At the same time, infrared spectroscopy confirmed that IPDI was successfully coated in polypropylene wall covering.

(2) The comprehensive performance of the microcapsules prepared under the process conditions of stirring temperature of 155 °C, mass ratio of polypropylene and IPDI of 1:2, stirring time of 1 hour and rotation speed of 600rpm was the most ideal, the particle size distribution of microcapsules was between 550 μm~650 μm, and the leakage rate of the obtained product was 7.8% at 28 d and its thermal stability was good.

(3) When the content of polypropylene-coated isophorone diisocyanate microcapsules in cement mortar is 3%, the cracks of 0.33 mm can be self-repaired, have good self-healing ability for concrete cracks, and can effectively improve the service life of concrete.

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