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Optimization of CNTs and SiO_2 for thermostability and mechanical properties of PF microcapsules: used for self-healing of closed wall cracks in goaf

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Abstract: Air leakage of closed wall in coal mine goaf would cause spontaneous combustion of remained coal. Most of measures to repair cracks are carried out after cracks are penetrated, which is not conducive to early prevention of spontaneous combustion. Repairing damage at the initial stage of cracking makes prevention effect to the best. Phenol-formaldehyde resin (PF) microcapsules embedded in closed wall to achieve self-healing of initial cracks, but the actual repair effect is often less than expected. PF microcapsules (PFM) of carbon nanotubes (CNTs) and silicon dioxide (SiO_2) decorated shell for self-healing of closed wall cracks were prepared by in-situ polymerization. The effects of nanomaterials on morphology, chemical constitution, thermal performance and mechanical properties of PF microcapsules were characterized by scanning electron microscopy (SEM), fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and nanoindentation test. The test results indicated that nanomaterials were successfully introduced into the shell of PF microcapsules. The CNTs-SiO_2@PF microcapsules were uniformly dispersed, the thermal decomposition was delayed, and the residual carbon was significantly increased, and the brittleness of PF microcapsules was significantly enhanced. The 0.2CNTs-SiO_2@PF microcapsules (0.2CNTs-SiO_2@PFM) had a uniform and full particle size, the initial decomposition temperature was 267.6 ℃, the residual mass was 41.3%, the maximum load on the capsule wall reached 94.79 mN, and the load dropped sharply after the capsule wall rupture. Finally, the self-healing mechanism of closed wall doped with microcapsules was discussed. The exploration of modified phenolic microcapsules provides a new idea for the repair of closed wall in goaf.

Keywords: PF microcapsule, crack repair, closed wall, nanomaterials, heat resistance, brittleness

1. Introduction

Air leakage in goaf may cause underground fire in coal mine. The construction of the closed wall plays a role in isolating coal from outside oxygen, but it tends to form cracks under the action of mining stress (Pan et al., 2018). If the repair is not timely, the internal cracks of closed wall are connected to form air leakage channels. Residual coal is oxidized gradually in high concentration oxygen environment, and its surface heat accumulation induces spontaneous combustion (Zhang et al., 2023; Wang et al., 2015; Zhuo et al., 2021; Li et al., 2020). The introduction of microcapsules could achieve self-healing of initial cracks (Kayondo et al., 2019; Dong et al., 2013). The healing agent flows out under the stress of crack tip, and solidifies with the catalyst during the flow process, ultimately achieving self-repair of the crack (Hia et al., 2018).

Scholars have conducted a lot of research on the modification of microcapsules and achieved certain research results in the field of microcapsule self-healing. Mohammed et al. (2022) embedded PMMA microcapsules filled with bisphenol a epoxy resin in epoxy coatings. The performance of coating was analyzed by scratch test and microhardness test. The results showed that the coatings containing

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microcapsules obtained excellent self-healing properties. Ji et al. (2021) successfully synthesized microcapsules for asphalt pavement by high-speed shear interfacial polymerization, and characterized their microstructure and thermal properties. It was found that the microcapsules showed excellent chemical stability and quality stability in high temperature environment. Tang et al. (2022) prepared microcapsules with sodium silicate and bentonite as core materials and ethyl cellulose as wall materials by physical method. The microcapsules and graphene oxide were added to the cement-based materials. The effects of graphene and microcapsule content, and curing time on the self-healing properties of specimens were investigated. The optimum ratio of microcapsules and graphene oxide was determined to be 2% and 0.1%. Jiang et al. (2021) reported SA/MPF-E44 microcapsules with sodium alginate/melamine phenolic resin as shell and epoxy resin as core. It was found that the coverage of the composite microcapsule was greatly improved, and the concrete containing SA/MPF-E44 microcapsules had good self-healing ability. The wall and core materials of microcapsule, the ratio combination and so on would affect the healing of cracks, and the ability of microcapsules to repair cracks is limited by working environment. In order to improve the air leakage prevention ability of the closed wall in goaf, it is necessary to optimize the performance of PF microcapsules.

Carbon nanotubes (CNTs) has become a widely concerned carbon material in recent years due to its excellent electrical conductivity, mechanical properties and high aspect ratio (Nurazzi et al., 2020). Niu et al. (2022) embedded 9,10-dihydro-9-oxa-10 phosphaphenanthrene-10-oxide (DOPO) modified flame retardant carbon nanotubes (d-CNT) in MPCM (d-c-MPCM). d-CNT improves the thermal stability of d-c-MPCM. After adding d-c-MPCM to rigid polyurethane foam, the heat release of RPUF/d-c-MPCM during combustion is reduced and the foam residue is increased. Wang et al. (2022) introduced 0.5–2wt% CNTs into biobased poly (1,3-propylene 2,5-furandicarboxylate) (PPF) to prepare nanocomposites. CNTs were well dispersed in PPF matrix, and did not change the crystallization mechanism of PPF. Carbon nanotubes improved the heat resistance and storage modulus of PPF-CNTs nanocomposites. Kosarli et al. (2021) added multi-walled carbon nanotubes to urea-formaldehyde resin microcapsules, and studied the effect of multi-walled carbon nanotubes on the healing rate of microcapsules. The study found that the introduction of 0.5% w/v CNTs did not change the healing rate of microcapsules, but it increased the mechanical properties of epoxy resin. Dong et al. (2020) synthesized microcapsule phase change materials (MEPCMs) with nanoaluminum optimized n-dodecane (C_{12}) as core materials and modified carbon nanotubes (CNTs) optimized melamine-formaldehyde (MF) resin as shell materials. The results showed that carbon nanotubes and nanoalumina did not change the spherical structure of MEPCMs. The optimized MEPCMs had excellent thermal stability, and the decomposition temperature is increased by about 10 °C.

The comprehensive performance of SiO_2 is outstanding, mainly manifested in excellent thermal stability, large specific surface area and environmental friendliness. Studies have shown that the addition of silica nanoparticles can significantly improve the properties of resin-based materials (Xiong et al., 2020; Zhuang et al., 2019). Li et al. (2020) added dispersed polyethylene glycol nano-SiO_2 solution to melamine formaldehyde (MF) resin, and the addition of nano-SiO_2 improved the toughness of MF resin. Du et al. (2020) reported the self-healing microcapsule of toluene-diisocyanate (TDI) coated with nano-SiO_2/paraffin /PE wax as composite shell. The experimental results show that the elastic modulus and hardness of the microcapsule are enhanced after the introduction of nano-SiO_2 into the capsule wall, and the microcapsules have good self-healing ability for cementitious materials. Sun et al. (2022) embedded calcium alginate containing tung oil self-healing microcapsules (TO@CA) in silicone rubber (SR) coating (TO@CA/SR). The TO@CA/SR coating performed best when the average particle size of TO@CA was 63.84 μm with a content of 10%. The mechanical properties of the TO@CA/SR composite coating were not affected by nano-SiO_2. The results showed that when 2% nano-SiO_2 modified TO@CA, T/SiO_2-2% had the best self-healing, corrosion resistance, and mechanical properties.

The initial cracks of the closed wall can be repaired by microcapsule embedding technology. Nanomaterials have excellent mechanical and thermal properties, and their introduction into phenolic resin (PF) microcapsules tends to improve the self-healing ability of closed wall. In this paper, the performance of PFM was optimized, and CNTs-SiO_2@PF microcapsules (CNTs-SiO_2@PFM) were prepared by compounding SiO_2 and CNTs into the microcapsule wall. Scanning electron microscopy (SEM), Fourier infrared spectroscopy (FTIR), thermogravimetric analyzer (TGA) and nanoindentation

test were utilized to characterize the surface morphology, functional group, thermogravimetric process, and rupture load of the capsule wall. Finally, the repair mechanism of microcapsules was discussed. By analyzing the effects of SiO_2 and CNTs on the performance of PF microcapsules, modified PF microcapsules with excellent performance for application in underground coal mine closed wall were obtained.

2. Experimental

2.1. Materials and instruments

Materials: Silicon dioxide (AR) was produced by Beijing Deke Daojin Science And Technology Co., Ltd. Formaldehyde solution (AR) was purchased through Shanghai Aladdin Bio-Chem Technology Co., Ltd. Phenol (AR) was produced by Hebei Runde Yongbang renewable resources utilization Co., Ltd. Melamine (AR) was produced by Zaozhuang Luheng Fine Chemical Co., Ltd. Carbon nanotubes (CNTs,15 μm) was produced by Jiangsu Xianfeng Nanomaterials Technology Co., Ltd. Sodium dodecyl benzene sulfonate (SDBS, AR) was produced by Shanghai Aladdin Biochemical Technology Co., Ltd. Sulfuric acid (AR) was produced by Chongqing Junheng Chemical Co., Ltd. Deionized water were produced by Shanghai Jingchun Water Technologies Co., Ltd. Epoxy resin (E-51) was produced by Jinan Qingtian Chemical Technology Co., Ltd. Acetone (AR) was produced by Leping Zhongsheng Chemical Co., Ltd. Triethanolamine (AR) was produced by Tianjin Hengxing Chemical Reagent Manufacturing Co., Ltd.

Instruments: Digital display electric blender, (MYP2011–100, Shanhai Meiyingpu Manufacturing Co., Ltd); Electric-heated thermostatic waterbath, (DZKW-4, Beijing Zhongxing Weiye Instrument Co., Ltd); Electronic balance, (FA2204B, Shanghai Youke Instrument Co., Ltd); Vacuum drying oven, (DZX-6090B, Shanghai Fuma Experimental Equipment Co., Ltd); Scanning electron microscope, (S–4700, Hitachi, Japan); Thermal gravity analyzer, (Discovery TGA55, TA, USA); Fourier infrared spectrometer, (IR Prestige–21, Shimadzu Corporation, Japan). Nanoindentation micromechanics comprehensive tester, (keysightG200, NYSE: A).

2.2 Preparation of modified PF microcapsule

The synthesis of modified PF microcapsule is shown in Fig. 1. The preparation of microcapsules is broadly divided into the following four stages: preparation of prepolymer, preparation of emulsion, acidification and curing, cleaning and drying.

Preparation of prepolymer: Phenol (6 g) and formaldehyde solution with a concentration of 30% (8.5 g) were placed in a beaker and mixed evenly, then dropped triethanolamine dropwise to the solution with a rubber-tipped dropper and let the pH of the solution stabilize in the range of 8~9. SiO_2 (3 g) and melamine (2.7 g) were added to the pH adjusted solution, and transferred the solution to a three-necked flask, put it into a constant temperature water bath at 80 °C and stirred at reflux for 1.5 h. Finally, 0.1 g and 0.2 g CNTs were added to the mixture, and the mixture was moved to the sonicator and dispersed for 40min. After ultrasonic treatment, the modified phenolic resin prepolymer solution was obtained.

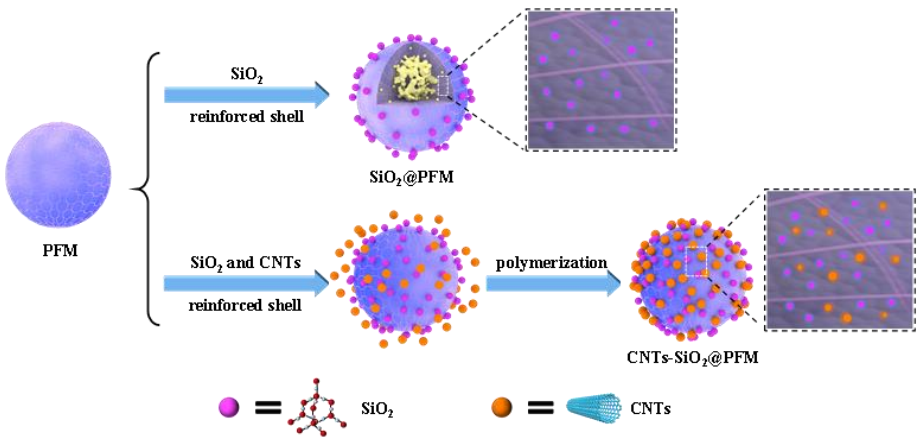

Fig. 1. The preparation process of modified PF microcapsule

Preparation of emulsion: Epoxy resin (6.25 g) and acetone (5 g) were mixed and ultrasonically dispersed. SDBS solution with concentration of 0.6% was prepared with deionized water, and the pH of sodium dodecylbenzene sulfonate solution was adjusted to neutral with dilute sulfuric acid solution, and SDBS solution was added into the above mixture.

Acidification and solidification: The modified phenolic resin prepolymer solution and the emulsion were transferred to a three-neck flask and stirred in a constant temperature water bath at 60 ℃ for 40 min. The pH of the solution was adjusted to 3 with dilute sulfuric acid. Distilled water was added dropwise to the solution and stirred at 50 ℃ for 2 h.

Cleaning and drying: Washed the microcapsules several times with deionized water and acetone alternately, and then put the washed powder into a vacuum drying oven to dry.

PF microcapsules, SiO_2@PF microcapsules and CNTs-SiO_2@PF microcapsules were prepared in a similar way, and the samples obtained were noted as PFM, SiO_2@PFM, 0.1CNTs-SiO_2@PFM and 0.2CNTs-SiO_2@PFM, respectively.

3. Results and discussion

In order to ensure the accuracy of the experiments, each experiment was conducted three times, and then the average of the three experiments was taken for the following analysis.

3.1. Microscopic morphology analysis

The microscopic morphology of microcapsules under scanning electron microscope is shown in Fig. 2. Fig. 2a exhibits the SEM image of pure PF microcapsules. PFM present irregular shape, and the surface of capsule wall is rough. The dispersion of PFM is extremely uneven. The microcapsule shells bond with each other to form a large agglomerate, and only a few number of PFM are scattered around the mass, which might be caused by the high concentration of formaldehyde solution. The surface morphology of SiO_2@PF microcapsule (SiO_2@PFM) is shown in Fig. 2b. The surface of PF microcapsules with the addition of SiO_2 particles presents a clear difference compared to PF microcapsules, with uniformly dispersed SiO_2 particles distributed on the shell surface, and the agglomeration phenomenon

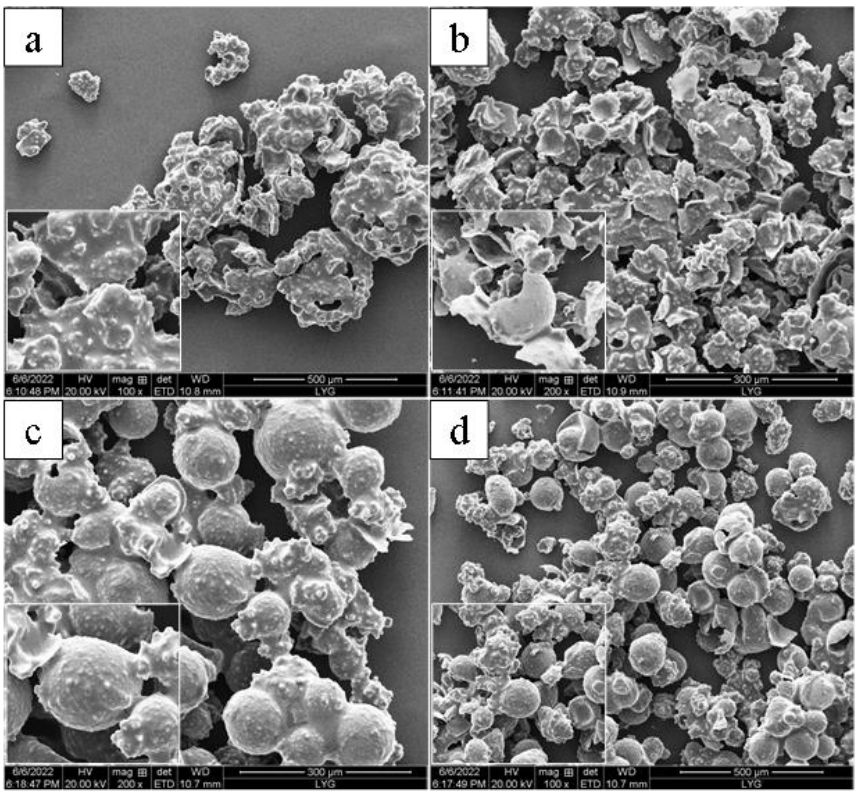

Fig. 2. SEM images of pure PF and modified PF microcapsules: (a) PFM; (b) SiO_2@PFM; (c) 0.1CNTs-SiO_2@PFM; (d) 0.2CNTs-SiO_2@PFM

is significantly improved. However, there are more empty shells of microcapsules distribute around the intact microcapsules, which may be due to the high coagulation rate during reflux mixing, resulting in a large number of damaged capsule walls of SiO_2@PFM. The enlarged image of Fig. 2b shows SiO_2@PFM with broken capsule walls. SiO_2@PFM is a shell-core structure consisting of an external modified phenolic resin and an internal epoxy resin. The microstructure of 0.1CNTs-SiO_2@PF microcapsule (0.1CNTs-SiO_2@PFM) as shown in Fig. 2c. The microcapsules present a full and uniform sphere, and the surface of capsule wall is attached to spherical particles and coated with fibrous tubular CNTs. The dispersion of 0.1CNTs-SiO_2@PFM is slightly improved compared with SiO_2 modified microcapsules. The overall morphology of the microcapsules has been greatly improved, but there are still a small number of microcapsules with irregular shapes and broken walls. In Fig. 2d, the 0.2CNTs-SiO_2@PF microcapsules (0.2CNTs-SiO_2@PFM) have full shape, and the dispersibility is greatly enhanced.

3.2. Infrared spectroscopy analysis

Fig. 3 shows the Fourier infrared spectroscopy (FTIR) curves of CNTs, PF microcapsules and PF microcapsules modified by SiO_2 and CNTs. In the spectra of PF microcapsules, the absorption peak at 2879 cm^{-1} are attributed to antisymmetric stretching vibration of methylene, the infrared peaks at 1606 cm^{-1} and 1510 cm^{-1} are related to the stretching vibration of benzene ring skeleton, and the broad peak at 1296 cm^{-1} corresponds to stretching vibration characteristic peak of C-O bond in phenolic hydroxyl group, which proved the existence of phenolic resin. In addition, the symmetric stretching vibration peak of epoxy group and the asymmetric stretching vibration peak of epoxy group appeared at 1245 cm^{-1} and 910 cm^{-1}, respectively. These fully demonstrate that PFM are composed of phenolic resin coated epoxy resin. It can be found that the curve absorption peak frequencies of PFM and SiO_2@PFM are roughly same. However, the infrared peaks of SiO_2@PFM at 1032 cm^{-1} and 572 cm^{-1} are attributed to the stretching vibration of Si−O and Si−O−Si bond, which indicates that SiO_2 nanoparticles are successfully introduced into the shell of phenolic resin microcapsule. The absorption at 3450 cm^{-1} and 1630 cm^{-1} are related to the stretching vibrations of -OH and C-C, which can be detected in carbon nanotubes. We can note that the absorption peaks of SiO_2@PFM at 2958 cm^{-1} and 1503 cm^{-1} are significantly enhanced, indicating that carbon nanotubes have been doped into microcapsule shell. The above results indicate that CNTs and SiO_2 are successfully introduced into PF microcapsule.

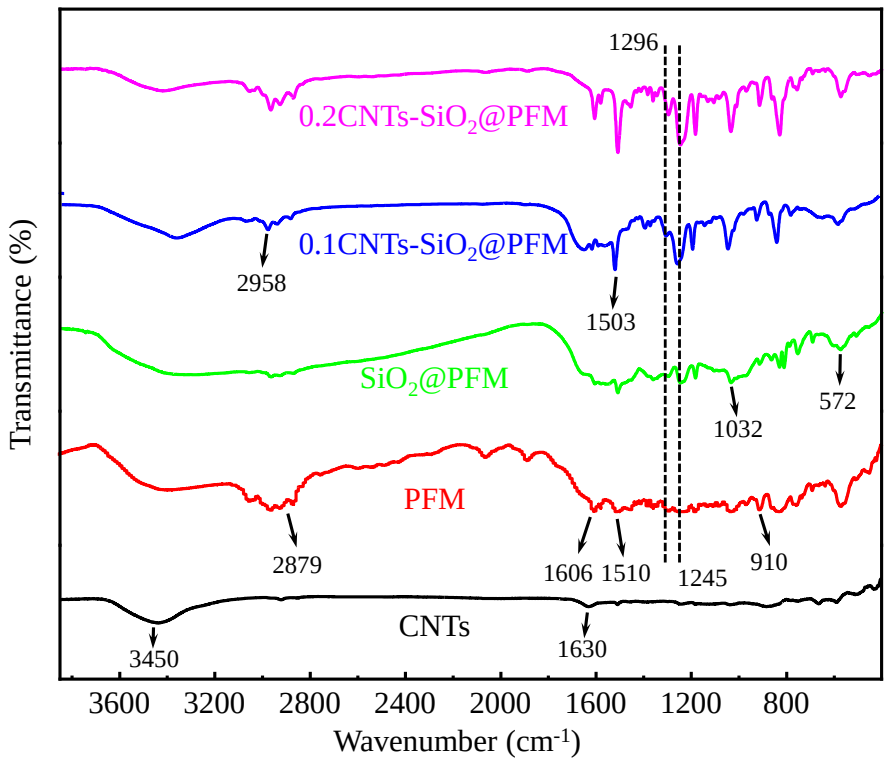

Fig. 3. FTIR spectra of CNTs, neat PF microcapsules and modified PF microcapsules

3.3. Thermal stability analysis

The effect of CNTs and SiO_2 content on the thermal degradation behavior of PF and modified PF microcapsules is shown in Fig. 4. As can be seen from the Fig., the initial degradation temperature of PFM reaches 144.9 ℃, and most of the heat is dissipated in a wide range. After 544.2 ℃, the weight of the microcapsules no longer changes, and their final residual carbon rate reaches 21.7%. This is because the stability of PF resin deteriorates after heat, and the mass change of PFM is not obvious at the beginning of thermal decomposition, but the TGA curve decreases sharply with the increase of temperature (Behzad and Meysam, 2021)). The mass of SiO_2@PFM starts to show a decreasing trend around 171.7 ℃, and remains basically stable at 581.3 ℃. The residual mass at 600 ℃ is 27.1%. The thermal decomposition behaviors of SiO_2@PFM and PFM show similarities, but the initial thermal decomposition temperature and residual carbon content of SiO_2@PFM are increased. 0.1CNTs-SiO_2@PFM begin to lose weight at 209.2 ℃, and the thermal decomposition is basically completed at 563.5 ℃. 0.2CNTs-SiO_2@PFM begin to decompose at 267.6 ℃, and the mass remains basically unchanged at 592.2 ℃. The initial decomposition temperature of CNTs-SiO_2@PFM is higher than that of SiO_2@PFM. CNTs enhance the thermal conductivity of microcapsule wall, thus accelerating the heat transfer inside the microcapsule and therefore leading to delayed thermal decomposition of the microcapsule embedded with CNTs (Huang et al., 2017). The thermal stability of 0.2CNTs-SiO_2@PFM is significantly improved compared to that of PFM. Its initial thermal degradation temperature is delayed 122.7 ℃, and the residual mass is increased to 41.3%.

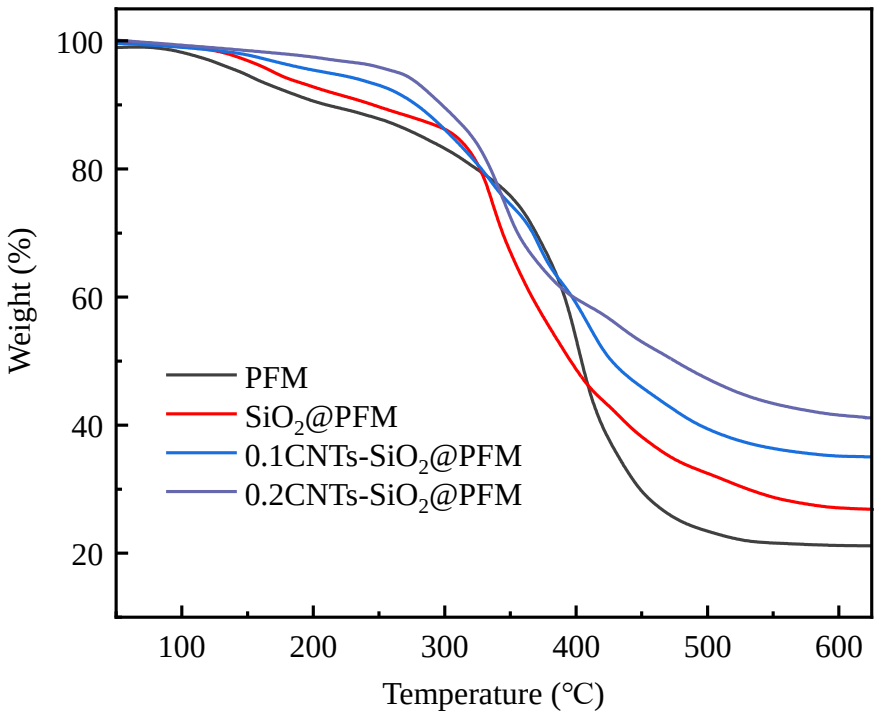

Fig. 4. TGA curves of PF and modified PF microcapsules

3.4. Rupture load of the capsule wall

The rupture load of the microcapsules was tested using a nanoindenter, and the displacement-load curves of PF and modified PF microcapsules are displayed in Fig. 5. The load of PFM in Fig. a increases linearly with the indentation depth, then remains relatively stable near the maximum indentation depth. The curve decreases slowly after the indentation depth continues to increase, which is due to the adhesion after the capsule wall is broken. The pure PF microcapsule shell belong to ductile materials, which inhibits the release of internal healing agents. Fig. b shows the load trend of SiO_2 modified PF microcapsules. The nonlinear load variation appears in the first stage of the load curve, which possibly due to the fact that SiO_2 increases the strength of capsule wall, resulting in the increase of tolerable load

at the same indentation depth. The maximum load is increased to 94.76 mN, but the capsule wall brittleness is not significantly improved. As shown in Fig. c, the addition of 0.1 gram CNTs makes the linear load growth of microcapsules not obvious in the first stage. The maximum load increases slightly compared with PF microcapsules, and loading curve decreases faster after the microcapsules are broken. The microcapsule load of 0.2 g CNTs and 3 g SiO_2 introduced in Fig. d appears an inflection point at indentation depth of approximately 1100 nm, and the load rises sharply after the turning point. The load drops sharply after microcapsule rupture, and the brittle capsule wall facilitates the outflow of the internal healing agent. The results indicate that the capsule wall rupture load of 0.2CNTs-SiO_2@PFM is enhanced to 94.79 mN, and its capsule wall brittleness is increased. Compared with the previously reported phenolic resin microcapsules with CNTs, the rupture load of PF microcapsules modified with SiO_2 and CNTs is reduced by 1.3%, and the load decreases sharply to zero after the rupture of the capsule wall (Fu et al., 2022).

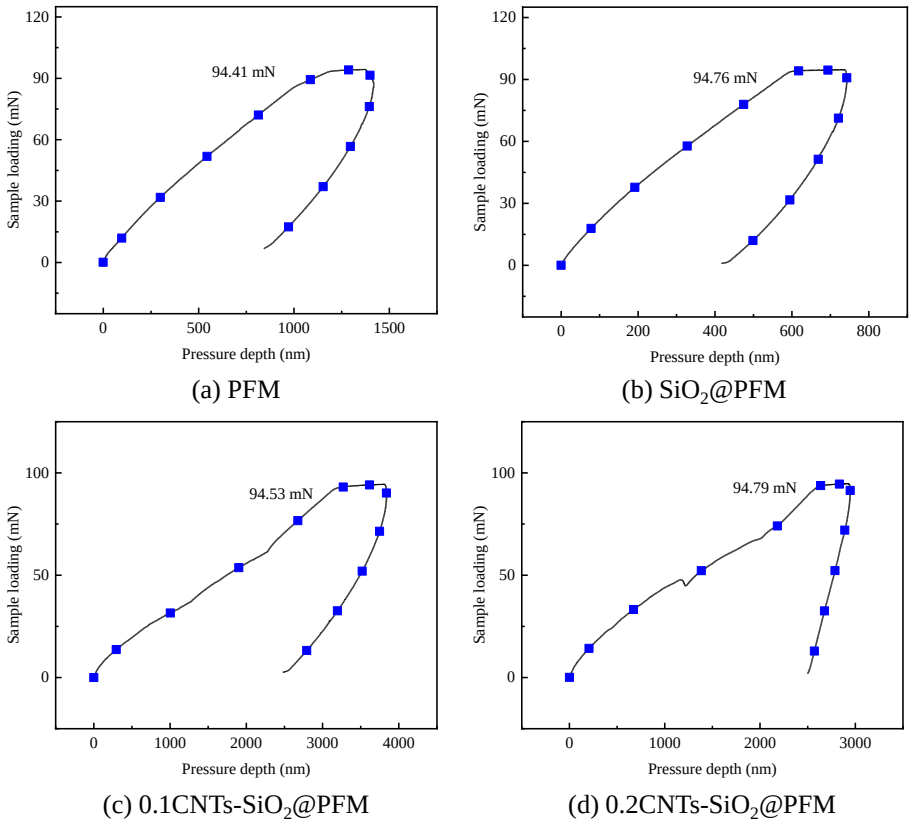

Fig. 5. Displacement-load curves of neat PF microcapsule and enhanced PF microcapsule

3.5. Analysis of self-healing mechanism

The self-healing mechanism of microcapsule repairing closed wall is shown in Fig. 6. It can be seen from Fig. a that concrete closed wall structure mixed with microcapsules and catalysts. Embedding appropriate microcapsules could realize self-healing of the initial cracks, which greatly prolongs the service life of the closed wall (Mostavi et al., 2015). The concrete closed wall in Fig. b generates microcracks under the action of mining load and other factors. The cracks formed at this stage are relatively subtle and not easy to detect at the macro level, but if they are not prevented and controlled, the closed wall will crack and leak, and the increase of oxygen concentration in the goaf will cause spontaneous combustion of residual coal. Fig. c shows the crack propagation stage. With the further growth and development of the crack, the microcapsule wall is punctured under the action of the crack tip stress (Fu et al., 2021). The concrete after crack repair is shown in Fig. d. The healing agent wrapped inside the microcapsule shell is fluid. After the capsule wall is broken, the healing agent flows out until the entire crack is filled. The healing agent undergoes a curing reaction with the catalyst embedded in the concrete during the flow process, and finally gradually solidifies and fills the crack.

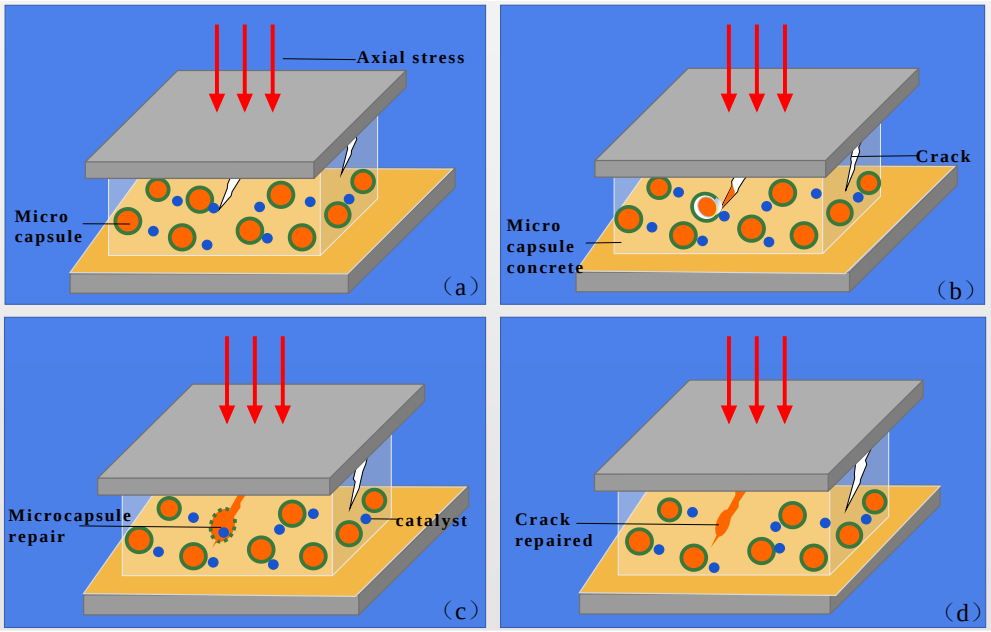

Fig. 6. Repair mechanism of microcapsules

4. Conclusions

A novel phenolic resin microcapsule CNTs-SiO_2@PFM with CNTs and SiO_2 modified capsule wall was synthesized to optimize the self-healing ability of microcracks in the closed wall of coal mining area. The optimal carbon nanotube and silica contents for the preparation of modified PF microcapsules are 0.2 g and 3 g, respectively. It has excellent microscopic morphology and thermal stability. More importantly, its capsule wall mechanical properties are significantly improved. The morphology of PF microcapsules introduced with CNTs and SiO_2 exhibits a uniform and full sphere with SiO_2 particles and fibrous tubular CNTs attached to the surface of capsule wall. The initial decomposition temperature of 0.2CNTs-SiO_2@PF microcapsules was raised to 267.6 ℃ and the residual mass reached 41.3%. The rupture load of the microcapsules reached 94.79 mN, which is much smaller than the fracture tip stress. In addition, the brittleness of the microcapsule walls is enhanced and the load dropped sharply after microcapsule rupture. The unique capsule wall properties of microcapsules ensure the implementation of self-healing of damaged closed wall.

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