Effect of Space Stabilizer on In-Situ Deposition of Polyaniline on Carbonyl Iron Powder

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Abstract. Carbonyl iron powder/polyaniline (CIP/PANI) composites were prepared by in-situ polymerization. High molecular weight PVP-K90, low molecular weight PVP-K30 and small molecular surfactant Twain-20 were used as space stabilizers for dispersion polymerization. The effects of different kinds of space stabilizers and the concentration of PVP-K90 on the in-situ deposition of PANI on the surface of carbonyl iron powder were investigated. The effect of film formation is briefly discussed and its stability mechanism is discussed. The results showed that CIP/PANI core-shell structure composites with good morphology could be prepared by dispersion polymerization with high molecular weight PVP-K90 as space stabilizer, and polyaniline film formation could not be well stabilized by low molecular weight PVP and small molecular surfactant. The conductivity of the CIP/PANI composites changed little with the concentration and type of space stabilizers, about 10⁻² S·cm⁻¹.

1. Introduction

Carbonyl iron powder/polyaniline magnetic composites with core-shell structure have broad application prospects in electromagnetic shielding, microwave absorption, electromagnetic induction and other fields. However, it is difficult to obtain uniform CIP/PANI core shell structure by traditional methods such as emulsion polymerization and solution polymerization. This is due to the larger size of the iron powder and the failure of the emulsion droplet to completely coat the iron powder. [4-5], polyaniline film can be deposited on the surface of iron powder by dispersion polymerization, forming core-shell composite with iron powder as core and polyaniline as shell. Dispersion polymerization is a special type of precipitation polymerization [6-9]. Its main characteristic is that the addition of space stabilizer in the reaction system can prevent the polymerization and sedimentation of the polymerization products and form a stable dispersion. At the same time, the results show that the polyaniline film with fairly uniform structure can be formed on the surface of glass, polymer film and carbonyl iron powder by dispersion polymerization [10-20].

Selection of space stabilizers is very important in dispersion polymerization. Several kinds of organic space stabilizers [21-29], including high molecular weight polyvinylpyrrolidone PVP-K90,
low molecular weight polyvinylpyrrolidone PVP-K30 and small molecular surfactant Tween-20, were selected in this work. The effects of kinds and dosage of stabilizers on the surface of PANI on carbonyl iron powder were investigated. The influence of in-situ deposition on film formation is briefly discussed.

2. Experimental part

2.1. Raw materials and instruments
Aniline (An, by secondary vacuum distillation), chemical purity, Tianjin Bodi Chemical Co., Ltd.; carbonyl iron powder, Beijing University of Science and Technology; ammonium persulfate (APS), analytical purity, Shanghai Epee Chemical Reagent Co., Ltd; polyvinylpyrrolidone (PVP, K90, Mn = 1-1.5 * 10^6), Shanghai Shengpu New Materials Co., Ltd; polyethylene Pyrrolidone (PVP, K30, Mn=0.05-7.0 *105), Chemical Reagent Co., Ltd. of China Pharmaceutical Group; Polyoxyethylene (20) Dehydrated Sorbitol Monolate (Tween-20), Analytical Purity, Qingdao Tianliyuan Biotechnology Co., Ltd; Concentrated Hydrochloric Acid (HCl), Analytical Purity, Yantai Sanhe Chemical Reagent Co., Ltd; Anhydrous Ethanol, Absolute Ethanol, Sorbitol Monolate (Twee Analytically pure, Yantai three and Chemical Reagent Co., Ltd.

Digital four-probe conductivity tester, SZT2000-4, Shanghai Hongqiao Detector Material Factory; Scanning Electron Microscope, JSM-6700F, JEOL Japan Electronics Instrument Company; Ultrasonic Cleaner, KQ-50B, Kunshan Ultrasonic Instrument Co., Ltd.

2.2. Preparation of CIP/PANI Composites
A proper amount of carbonyl iron powder was added into a beaker containing an appropriate amount of space stabilizer aqueous solution. The beaker was shaken by ultrasonic wave for 0.5 h and then stirred mechanically in an ice bath for 0.5 H. Then hydrochloric acid and aniline monomer (the mass ratio of aniline to carbonyl iron powder is 1:1) of 0.15 mol. L^-1 were added into the mixed solution and Pre-stirred for a period of time. Then a certain concentration of APS aqueous solution (the ratio of APS to Anmonomer is 1.25:1), ice to 0 C, its one-time addition to the above mixed solution to initiate the reaction, the initial reaction temperature is controlled at 0 ~ 2. After the reaction started, the reaction temperature was tracked and the experiment was continued after stirring for 2 h. Carbonyl iron powder/polyaniline composite p articles were obtained by magnetic separation after the reaction. The polyaniline particles deposited on the surface were washed off with ethanol and distilled water until the washing solution became colourless. After washing, the samples were taken for electron microscopic characterization. The remaining samples were placed in oven and dried and dried at 35 degrees Celsius for other characterization tests.

3. Results and discussion

3.1. The stability mechanism of dispersion polymerization.
At present, there are mainly 2 mechanisms for the stability of dispersion polymerization. One is adsorption mechanism, that is, dispersant molecules are adsorbed to the surface of polymer particles, forming a surface hydration layer, so that particles are not easy to aggregate and stable dispersion in the medium; the other is graft stabilization mechanism, that is, dispersant molecules are grafted onto the macromolecular chains of particles by chemical action, dispersant branched chains extend to the aqueous phase, forming 'wool.' 'Particle', relying on space obstacles to stabilize the system [6].Generally speaking, small molecular inorganic space stabilizers such as nano-silica conform to the adsorption stabilization mechanism, while the stabilization and dispersion of polymer space stabilizers are explained by the graft stabilization mechanism.

However, the graft stabilization mechanism was challenged in the previous experiments in our laboratory [8-9]. Infrared and ultraviolet absorption spectroscopy analysis showed that the presence of stabilizer PVP was not detected either in the spherical PANI particles obtained by dispersion
polymerization or in the PANI films prepared by in-situ deposition polymerization on different substrate surfaces, indicating that the PVP molecules did not exist. Grafting with PANI molecules. The results also show that the stabilization effect of PVP is related to the molecular weight of PVP, which indicates that the stabilization effect of PVP may be more due to its unique amphiphilic molecular structure, hydrophilic-hydrophobic interaction, surface energy driving force and larger steric hindrance effect as macromolecular surfactant.

3.2. Effect of PVP-K90 on dispersion polymerization and in-situ deposition of PANI film

3.2.1. Effect of PVP-K90 dosage on polymerization temperature time curve. The oxidative polymerization of aniline and persulfate in hydrochloric acid medium belongs to exothermic reaction. The change of temperature with time can reflect the process of polymerization. The reaction temperature-time curves of PVP-K90 in total solution with mass percentages of 0%, 0.25%, 0.50% and 1.00% are given in Fig. 1. As can be seen from Fig. 1, there are two exothermic peaks in each curve, corresponding to the oxidation reaction of iron powder and the oxidation polymerization of aniline. When PVP was not added, the exothermic peak of oxidation of iron powder (the first peak) appeared immediately after the addition of APS, and rose to the peak instantaneously, indicating that the oxidation of iron powder by APS was very intense. Due to the depletion of APS, the subsequent exothermic peak of aniline oxidation weakened. With the addition of PVP-K90, the oxidation of iron powders decreased significantly with the increase of stabilizer dosage, while the reaction of oxidative polymerization of aniline was gradually strengthened, the reaction temperature and reaction heating rate increased significantly, and the reaction induction period became longer, avoiding the polymerization of aniline. This shows that the addition of PVP-K90 not only protects iron powder and avoids early oxidation, but also has a good stabilization effect on aniline polymerization, which is conducive to stabilizing the polymerization of aniline in solution and on the surface of iron powder to form polyaniline particles with good morphology. Temperature-time curves of in-situ polymerization with different concentration of PVP-K90, as is shown in Figure 1.

![Fig. 1 Temperature-time curves of in-situ polymerization with different concentration of PVP-K90. Our laboratory system, as is shown in Figure 2.](image-url)
3.2.2. Effect of polymerization methods on the apparent morphology of composites. Fig. 3 gives SEM pictures of carbonyl iron powder and CIP/PANI complex obtained by emulsion polymerization and dispersion polymerization respectively. It can be seen from Fig. 3 (a) that the carbonyl iron powder coated before is spherical, smooth and glossy. The CIP/PANI composite particles prepared by emulsion polymerization, the surface coated polyaniline is fragmented, the binding force is not strong, and the shell is falling off (Fig. 3 (b)). The CIP/PANI composites prepared by dispersion polymerization with PVP-K90 as stabilizer are coated with a granular polyaniline shell with a multi-layer structure. Small polyaniline particles of 10-20 nm form a dense bottom layer and macroaniline particles of about 100 nm are deposited on the surface. These large particles are also composed of small particles of 10-20 nm (Fig. 3 (c)).

In the reaction system of CIP / PANI composite particles prepared by in situ polymerization, there are actually two reactions, i. e. aniline polymerization in solution and aniline in situ deposition on the surface of iron powder.

Schematic diagram of growth of PANI film on PANI and iron powder in solution, as is shown in Figure 4.
Because they are in the same reaction system, they compete and interact with each other. One is that in solution, aniline is oxidized and polymerized under the action of space stabilizer to form small PANI particles with a diameter of about 10-20 nm, and then the small particles are merged into large particles with a diameter of about 100-200 nm; the other is that aniline cations are adsorbed on the surface of iron powder to form nuclei, and then oxidized and polymerized at the growth point of the nuclei, forming 10-20 under the action of stabilizers. Under the action of hydrophilic/hydrophobic and surface energy decreasing, high quality PANI films were obtained by spreading and merging the small particles of nanometer on the surface of iron powder.

3.2.3. Effect of conductivity on the conductivity of composites. When the content of PVP-K90 in the system changes, in Figure 5, the average conductivity of the CIP/PANI complex prepared is shown in Table 1. As can be seen from Table 1, when the content of PVP-K90 changes, the conductivity of CIP/PANI composites prepared by in-situ polymerization does not change much, all at the level of $10^{-2}$ S.cm$^{-1}$. 

![Fig. 4 Schematic diagram of growth of PANI film on PANI and iron powder in solution](image)

![Fig. 5 Schematic diagram of growth of PANI film on PANI and iron powder](image)
**Table. 1** Conductivity of CIP/PANI composites prepared with different mass ratio of PVP-K90

| w(PVP-K90)/% | Average conductivity/(S·cm⁻¹) |
|--------------|-------------------------------|
| 0            | 5.00×10⁻²                     |
| 0.25         | 5.60×10⁻²                     |
| 0.50         | 3.03×10⁻²                     |
| 1.00         | 9.52×10⁻²                     |

4. Comparison of stabilizing effects of several space stabilizers

PVP-K90 is a kind of high molecular weight emulsifier. If PVP-K90 can stabilize PANI to form a good film on the surface of iron powder only because of amphiphilic interaction and surface energy tending to reduce the double effect, then the small molecular surfactant and low molecular weight PVP which have the same effect in theory should also have the above stable action. Use to make PANI good film forming. Therefore, low molecular weight PVP-K30 and nonionic surfactant polyoxyethylene (20) desorbed sorbitol monolaurate (Tween-20) were selected as space stabilizers to investigate their stability.

4.1. Influence of morphology on CIP/PANI complex

Fig. 6 SEM photographs of CIP/PANI complexes prepared under different space stabilizers. As can be seen from Fig. 6 (a), when PVP-K30 is used as a space stabilizer, the polyaniline obtained by dispersion polymerization in solution is about 300 nm long. The surface of carbonyl iron powder was not coated with polyaniline shell, but the polyaniline fibers with about 300 nm were deposited randomly on the surface. When Tween-20 was used as a space stabilizer, the polyaniline particles formed in the solution were bonded together, and the shape was distorted irregularly. Polyaniline particles on the surface of iron powder are also adhered to form sheets, and the appearance is very rough (Fig. 6 (b)). It can be seen that when low molecular weight PVP and small molecular surfactant are used as space stabilizers, polyaniline cannot be well stabilized in-situ formed film on the surface of carbonyl iron powder, and the polyaniline particles formed in the system have irregular morphology and rough surface. In addition, when low molecular weight PVP and small molecular surfactant were used as stabilizers, the reaction solution was stratified after stationary, the upper layer was clear night, and the bottom layer was dark green precipitation, which also showed that the stability was poor.

When high molecular weight PVP-K90 is used as space stabilizer, the polyaniline film coated on the surface of carbonyl iron powder is of excellent quality (Fig. 6 (c)). However, when low molecular weight PVP and small molecular surfactant are used, the polyaniline film formation cannot be well stabilized (Fig. 6 (a) and (b)). It is suggested that the good stabilization of high molecular weight PVP-K90 is not only related to the decrease of hydrophilic/hydrophobic interaction and surface energy, but
also to the long chain molecular structure and special hydrophilic group distribution of high molecular weight PVP-K90. The specific stability mechanism needs further research.

4.2. Effect of conductivity on the conductivity of CIP/PANI composite particles

The conductivity of the composites prepared with high molecular weight PVP-K90, low molecular weight PVP-K30 and Tween-20 as space stabilizers are shown in Table 2. As can be seen from Table 2, the conductivity of CIP/PANI composites prepared with different space stabilizers varies little, and all of them are in the order of $10^{-2}$ S cm$^{-1}$.

Table 2 Conductivity of CIP/PANI composites prepared with different stabilizers

| Stabilizer  | Average conductivity (S·cm$^{-1}$) |
|------------|-----------------------------------|
| PVP-K90    | $9.52 \times 10^{-2}$            |
| PVP-K30    | $6.41 \times 10^{-2}$            |
| Tween-20   | $4.10 \times 10^{-2}$            |

Note: the mass fraction of space stabilizer is 1%.

5. Summary

The core-shell structure of CIP/PANI composites with good morphology can be prepared by using high molecular weight PVP-K90 as space stabilizer. However, low molecular weight PVP and small molecular surfactant cannot stabilize the formation of polyaniline films. It is concluded that the good stabilization of high molecular weight PVP-K90 is not only related to the decrease of hydrophilic/hydrophobic interaction and surface energy, but also to its long chain molecular structure and special hydrophilic group distribution. The specific stability mechanism needs further study. The conductivity of CIP/PANI composites prepared with high molecular weight PVP, low molecular weight PVP and small molecular surfactant as space stabilizers has little change, and all of them are about $10^{-2}$ S cm$^{-1}$.

Acknowledgements

The authors thank the financial supports from National Natural Science Foundation of China(Grant no. 51165024), National key basic research development project (973 project) (2009CB724405) and New century talent support program of Ministry of Education (NCET-04-0935).

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