Preparation and Analysis of the Disperse Dyes of Polyamide Microcapsule

Rong Lu[1,*], Jing Wang[1], Xinmei Zhang[2], Xin Gao[1], Chaoxu Zhang[1], Yinghui Ren[1]

[1] College of Chemical Engineering, Northwest University, Xian 710069, P.R. China

[2] Chemistry and Chemical Engineer Department, Baoji College of Arts and Science, Baoji 721007, P.R. China

Abstract: The dyeing wastewater in textile industry would cause serious damages to water quality and environment. Microcapsule technology is a technology which encapsulates solid or liquid into small particles within micron or millimeter range using film forming material. The disperse dyes microcapsules can enhance the dye up-take rate and reduce the discharge load of wastewater. The polyamide microcapsules which will not pollute the environment in the spinning and weaving were prepared. The disperse dyes 2BLN was prepared by interfacial polymerization method, using p-benzoyl chloride and 1, 2-diaminoethane as monomer. The infrared spectra and nuclear magnetic resonance were used to characterize the structure of microcapsules, and scanning electron microscope was used to measure grain size of microcapsules gained in different condition. The structure analysis shows that the substance is the target product. The effects of preparation conditions on the grain size and spread of the microcapsule were studied. The optimum preparation conditions are: pH value, 12; temperature, 25℃; emulsifier OP-10, 1.5%; dropping time of uniformity 1, 2-diaminoethane, 5 minutes. The adding method of water phase monomer has great influence to the forming of microcapsules, only proper speed can obtain regular microcapsules.

Key words: microcapsule; disperse dyes; polyamide

1 Introduction

It is the dyeing and printing production that pollutes the environment mostly in textile industry. A lot of dyeing wastewater will cause serious damages to water quality and environment. The disperse dyes microcapsules can enhance the dye up-take rate and reduce the discharge load of wastewater. Therefore, the microcapsule technology is attractive for environmental protection.

Microcapsule technology is a technology which encapsulates solid or liquid into small particles within micron or millimeter range using film forming material. Micro-encapsulation azo dye, in which polyethylene was as film forming material, whose release characteristics in disperse medium methanol was studied by Chih Pong Chang et al [1]. Organic pigment copper phthalocyanine microcapsule taking polystyrene as wall-material was studied by Zhang Tianyong, and its dispersion and wettability were improved [2].

There are great structure differences in different dyes and pigments, therefore, the choice of material and the method of preparation play an important role for preparing microcapsule dye. The wall-materials of microcapsules are made from high porosity parts with permeability and low porosity parts without permeability. The different polymeric walls and chemical conditions of preparing microcapsules have direct effect on particle size of microcapsules and porosity of the polymeric walls [3].

In this paper, the microcapsules were prepared by interfacial polymerization. The appropriate

* Corresponding author. Phone: +86-(0)29-88302632. E-mail: lu78441@yahoo.com.cn

conditions of microcapsulating were obtained by studying the size and morphology of microcapsules with SEM and biological microscopes. The structure of the microcapsules were also analyzed and characterized by IR and NMR [4, 5].

2 Experimental

2.1 Apparatus and Materials

Photographic biological microscope，XSZ2H (Germany Laika Co.); FT-IR, EQU INOX55 (Germany Bruker Co.); NMR，Bruker2DRX2300MHz(Germany Bruker Co.)；SEM，S2570(Japan Rili Co.); High Shearing Mixing Emulsifying Machine (Shanghai Weiyu machine electron Co.)

Disperse dye 2BLN, (Zhejiang dye chemical plant, China). p-benzoyl chloride, 1,2-diaminoethane, emulsifier OP-10, Polyvinyl alcohol (PVA), acetone, trichloromethane and sodium hydroxide were all analytical reagents and used without any further purification.

2.2 Preparation of Microcapsules

Preparation of the aqueous phase: A certain amount of PVA and OP-10 were added into the distilled water，keeping stirring until it become smooth. Then a certain amount of sodium hydroxide solution was added to the emulsion. Preparation of the organic phase: A certain amount of disperse dye (core-material) and *p*-benzoyl chloride (wall-material) were dissolved in organic solvent. Then, the mixture was mechanically agitated. Emulsification: The well-proportioned organic phase was dispersed in aqueous phase under the high speed stirring. Microcapsulating: The 1,2-diaminoethane solution was added into the emulsion under a certain agitated speed and temperature. The reaction was finished when the pH value kept a constant. Discharging: The microcapsules were separated by centrifugation, and the solvent was recycled. Then, washed and modulated.

The condition of the reaction: Polyvinyl alcohol (PVA), 1%(w/w); OP-10,1.5%(w/w); stirring speed, 800 rpm; time of the emulsification, 20 min; phase ratio(v/v), 10:90; amount of substance ratio of the *p*-benzoyl chloride to 1,2-diaminoethane, 1:2; the 1,2-diaminoethane solution was added by the homogeneous speed, the reaction time is 15 min.

2.3 Analysis and Measurement

2.3.1 Infrared Spectroscopy (FT-IR)

Sampling was conducted by using KBr pellet method, and detected by using EQU INOX55 fourier transform infrared spectrometer（Germany Bruker Co.）

2.3.2 Sample Preparation to Observe the Surface Structure

A flat of double glue was sticked on the SEM sample stage, and microcapsules were scattered on the double glue, then blew away superfluous microcapsules. After the samples were metallized by spraying on surface, scanning electron microscope (SEM) was employed to characterize the microcapsules with accelerating voltage of 15 kV.

2.3.3 Measurement of Microcapsules Diameter[6,7]

The surface morphological structure and particle size were examined by SEM. Some representative areas were chosen to analyze statistically, and the statistical particle number should be less than 500. The particle size (equal-area-circle diameter) should be measured accurately.

3 Results and discussion

3.1 The Interface Polymerization Principle of Polyamide Microcapsule

The monomer diacyl chloride and the disperse dyes were dissolved in organic phase, and the O/W liquid droplet were formed as water phase added. Then, the diamine was added to make the interface polymerization. The interface polymerization reaction equation of diacyl chloride and diamine as follow:

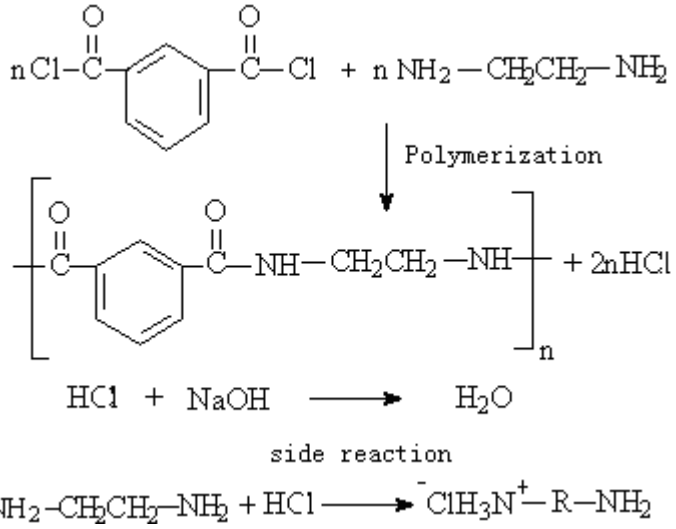

Fig.1 The interface polymerization reaction of diacyl chloride and diamine

The HCl generated from acylation which combined with the free amine, so the reaction rate of N-acylation was decreased. Therefore, the acid binding agent NaOH was needed to react with generated HCl to keep the strong base of media and reduce side reactions.

The result of diacyl chloride and diamine interface polymerization was to form continues and uniform film in organic phase emulsion surface, forming the good microcapsule at last.

3.2 Analysis of IR Spectra of the Disperses Blue 2BLN and Their Microcapsules

Fig.2 shows IR spectras of the disperses blue 2BLN (A) and the disperses blue 2BLN (B) microcapsules. In Fig.1, the spectra of 2BLN (A) show peak at 3437cm^{-1}, which is attributed to absorption peak due to the superposition of the N-H stretching of the amidocyanogen and O-H stretching of the hydroxyl of disperses dye. The IR spectra of 2BLN (B) microcapsules indicated that the absorption peak removes to low waves. Because the N-H bond of the copolymer of the membrane of microcapsule is not in benzene ring, it can form hydrogen bond. The wave of the N-H vibration removed from 3437cm^{-1} to 3302cm^{-1}, and appears the red shift phenomena. There are absorption peaks in the A and B spectrums at 1499cm^{-1}, which attributed to the N-H in-plane benting absorption peak. The intensity of absorption peak of B spectra increases obviously, which further indicated N-H bond exist in both dye and membrane copolymer. Therefore, the layer after layer of N-H absorption peak in the core-material dye of microcapsules and copolymer in wall-material increase the absorption of B spectra.

From Fig. 2, it is easily find the weak peak at 2923 cm^{-1} is assigned to the C-H stretching mode in the benzene ring, and the intensity of absorption peak of B spectra is stronger than A spectra, which indicated that the number of benzene ring in the microcapsules increase, that is to say the benzene ring is also exist in the membrane copolymer. The weak peaks at 1604 cm^{-1} and 1572cm^{-1} in A spectra are the vibration of

the benzene ring skeleton in the disperse dye structure. The peak at 1600 cm^{-1} is split into two absorption peaks due to the interaction of π-π conjugation between carbonyl and benzene ring. The intensity of the two peaks in B spectra increase obviously, which show that the membrane copolymer also contain the carbonyl that connected with benzene ring, and overlapping peaks appear at the two frequency both in microcapsule dye and membrane copolymer. Therefore, according to the monomer structure used to prepare the microcapsules, it can be concluded that the structure of theca material is (poly(*p*-phthaloyl ethylenediamine)).

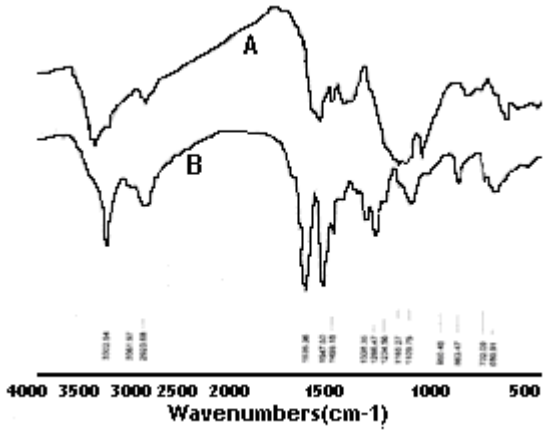

Fig. 2 IR of the disperses blue 2BLN (A) and the disperses blue 2BLN (B)

3.3 The Effect of pH Value to the Grain Size

1, 2-diaminoethane solution is added into the reaction system in 5 minutes at 5℃. Fig.3 shows the effect of the different pH value of reaction medium to the diameter size and distribution of microcapsule.

From Fig.3, we can know that the size of the prepared microcapsule are even regularly (the average diameter is about 5μm), and the distribution range of the particles becomes narrow when the pH value of the medium is 12(the proper control condition). Fig.3 also indicated that the diameter size is bigger and diameter distribution is broader when pH lower or higher than 12. This is because the wall-material polyamide was prepared by *p*-benzoyl chloride and 1, 2-diaminoethane monomer at a certain pH value with polycondensation reaction. This polycondensation reaction belongs to a reversible reaction, so moving the product hydrogen chloride will benefit to it. In our experiment, the reaction is controlled by pH value via adding sodium hydroxide into water phase medium. However, too high pH value will make the acid chloride hydrolyze, and increase the consumption. The proper pH value is vital to the forming of microcapsule.

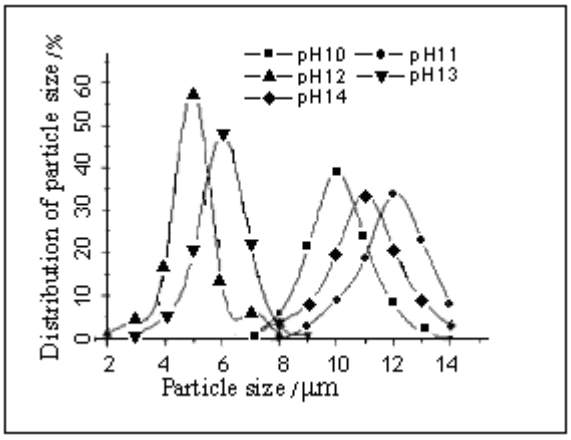

Fig. 3 The distribution of the grain size at different pH

3.4 The Effect of Temperature to the Grain Size

Under the condition of water phase medium pH at 12 and adding the 1,2-diaminoethane at homogeneous speed in 5 minutes. The effect of the diameter size and distribution of microcapsule to the different reaction temperature can be shown in Fig.4. It is easily known the prepared microcapsule is even regular, the average diameter of microcapsule focus on about 6μm and the distribution of the particles becomes narrow at 25℃, which is the optimal temperature. It indicated that the diameter size is bigger and diameter distribution is broader when the temperature above or below 25℃. It is the reason that too high temperature can lead to too fast speed of polycondensation and too heavy viscosity, so the bigger diameter microcapsule and broader diameter distribution will be formed. While a low reaction temperature can cause the long reaction time and low relative molecular mass, so it will obtain the irregular microcapsules.

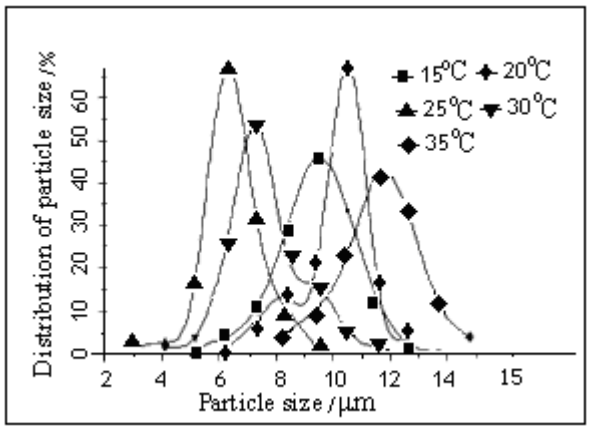

Fig. 4 The influence of the distribution of the grain size on the reaction temperature

3.5 The Effect of The Emulsifier Dosage to the Grain Size

The non-ionic surfactants and anion surfactants were often used to prepare microcapsules with interfacial polymerization method according to the reference [8, 9]. The biodegradability of non-ionic surfactants is preferable. The HLB value of the surfactants which adapt to O/W emulsion is between 8 and 18, and OP-10 satisfies this condition. The results of the average diameter of microcapsules with

different emulsifier dosage and the standard variance are listed in Table 1.

Tab.1 The influence of the grain size and distribution of the microcapsule on the quality of the emulsifier

w(OP-10)（%）	Average particle size（$\bar{d}$/μm）	Standard deviation（σ/μm）
0.5	10.5	10.89
1.0	8.2	8.64
1.5	6.1	6.14
2.0	5.9	6.01
2.5	5.6	5.62

From Table 1, it is known that the average diameter becomes small and the distribution becomes narrow as the increase of the amount of emulsifier. But the change levels off when the amount of emulsifier is over 1.5% (mass fraction).

This is because the emulsifier molecule is concentrated in the surface of droplet which formed in water dispersed phase in the process of microcapsule preparation. Furthermore, the polymerization occurs at this position, which will require that monomer molecule in organic phase can be dispersed on the surface of small droplet by the emulsifier. As the amount of emulsifier increase, the diameter becomes smaller. However, the influencing factor will weak as the using amount of emulsifier overabundance. Taking the average diameter and distribution into account, the optimum amount of emulsifier is 1.5% (mass fraction).

3.6 The Effect of the Adding Method of 1,2-Diaminoethane Solution to the Microcapsules

The SEM micrographs of microcapsules by different adding methods of water phase monomer (1, 2-diaminoethane) is shown in Fig.5. It is seen that the microcapsules are spherical when 1, 2-diaminoethane is added homogeneously in 5 minutes; the lumpish or flocculent microcapsule is formed in 2 minutes; accepting for a minority of micrographs is irregular, most of them are spherical in 10 minute. Too violent reaction between p-benzoyl chloride and 1,2-diaminoethane leads to the increase sharply of the molecular weight of microcapsules and the degree of cross linking, therefore the lumpish or flocculent microcapsules are formed easily when adding 1,2-diaminoethane quickly. However, too slow adding of 1, 2-diaminoethaneythe will cause uneven molecular weight distribution and irregular particle of the microcapsules. Thereby, the optimum adding method is even adding in 5 minutes.

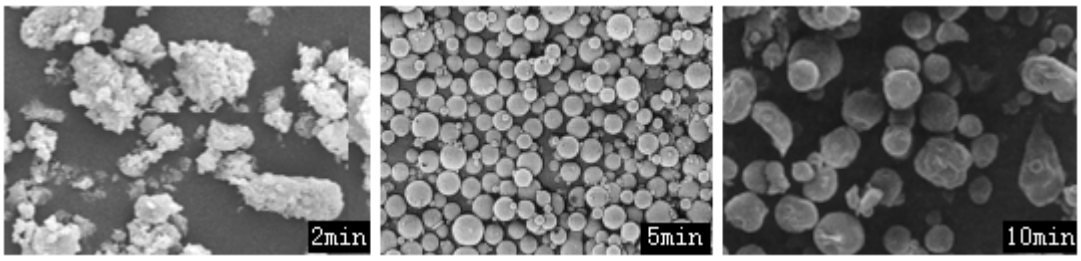

Fig. 5 The SEM pictures of microcapsule at different of dropwise speed

4 Conclusions

The FT-IR and NMR spectrum results indicate that the production is disperse dye 2BLN microcapsule with the polyamide as wall-material.

The pH value of the reaction media、reaction temperature and the using amount of emulsifier etc

have the certain influence on particle size and distribution of dye microcapsules during the preparation of disperse dye 2BLN microcapsules using p-benzoyl chloride and 1,2-diaminoethane with the interfacial polymerization method. The microcapsules are of uniform shape with a narrow diameter distribution at the pH12 and reaction temperature 25℃. Once above or below this value, irregular shape with a broad diameter distribution will be occurred. The average diameter becomes small and diameter distribution becomes narrow when the amount of emulsifier increases. However, the change leveled off when the using amount of emulsifier is over 1.5% (mass fraction). In addition, the adding method of water monomer (1, 2-diaminoethane) has great influence to the forming of microcapsule, and only proper speed can produce regular microcapsule. It's conformed that the optimum adding speed is 5 minutes.

Acknowledgments

The authors are grateful to the financial support of the Natural Science Foundation of Shaanxi Provincial Department of Education (No. 2008JK440).

References

[1] C. P. Chang; T. Yamamoto; M. Kimura; et al. Journal of Controlled Release, 2003, 86(2-3): 207-211.

[2] T. Y. Zhang; X. N. Fei; J. Song; et al. Dyes and Pigments, 2004, 44 (1): 1-7.

[3] D. Y. Chao. J Appl Polymer Sci, 1993, 47(1): 645-651.

[4] Y. C. Yuan; M. Z. Rong; M. Q. Zhang. Polymer, 2008, 49, 2531-2541.

[5] J. F. Su; L. X. Wang; L. Ren. Synthesis of polyurethane microPCMs containing n-octadecane by interfacial polycondensation: Influence of styrene-maleic anhydride as a surfactant, Colloids and Surfaces A: Physicochem. Eng, 2007, (299): 268-275.

[6] K. Nakagawa; S. Iwamoto; I. M. Nakaj. Journal of Colloid and Science, 2004, 278 (1): 198-205.

[7] L. Yuan; A. J. Gu; G. Z. Liang. Materials Chemistry and Physics, 2008,110, 417-425.

[8] H. B. Scher. Multiple types of microcapsules and their production: US, 4643764 [P]. 1987-02-17.

[9] H. H. Walter. Process for the preparation of microcapsules: US, 5837290 [P]. 1998-11-17.