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Dyes and Pigments 65 (2005) 45–49
DYES and PIGMENTS
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Preparation of photosensitive color-producing microcapsules utilizing in situ polymerization method

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Received 17 February 2004; received in revised form 14 May 2004; accepted 20 June 2004
Available online 11 September 2004

Abstract

The photosensitive color-producing microcapsules have been prepared with melamine/formalin resin by in situ polymerization method. The leucocompound and the photoacid generator dissolved in diisopropylnaphthalene were successfully loaded in the interior of microcapsules. Preparation of microcapsules that have uniform particle size could also be attained. Irreversible development of microcapsules was examined by an irradiation of UV light. The leucocompound in the microcapsule was sensitively reacted with the acid produced from the photoacid generator without destruction of capsule walls. It has also been found that the development in the microcapsule progresses quickly compared to the bulk condition.

Keywords: Microcapsule; Leucocompound; Photoacid generator; UV irradiation

1. Introduction

In recent years, applications of microcapsules have been investigated in various kinds of application fields such as recording material [1–3], medical supplies [4,5], foods [6–8], industrial material [9,10], etc. In many cases, the following two factors are mentioned as the characteristics required of microcapsules. In the first place, the contents must be held in microcapsules stably until it is required. Therefore, the interaction between the microcapsule wall and the contents and the dynamic strength of microcapsules must be taken into consideration. In the second place, it is also important to release the contents to the exterior of the microcapsule at a stretch or gradually as the occasion demands. In this case, the characteristic of a microcapsule wall must respond to an external stimulus of a certain kind alternatively, and must change to it.

At present, the example of the microcapsule which fulfills these characteristics and is generally most applied in practical use would be the non-carbon paper as a recording material. In this case, microcapsules containing a development or a color-producing material are adhered on the fibrous cells of the paper. When a certain stress is added microcapsules are destructed and the developments are attained. However, the color fastness of the developed substances is not necessarily sufficient for long time preservation because the produced substances are developed at the exterior of microcapsules and are directly exposed with various kinds of external stimulations such as gases, friction, lights, etc. If the development in the interior of the microcapsule could be achieved without destruction of capsule walls, the fastness of the developed substances would be improved. Further, introductions of the three primary colors into the interior of separate microcapsules would provide the development of various kinds of colors. Unfortunately, the development of the microcapsule with non-destructive method is restricted in industrial material like Nematic Curvilinear Aligned

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doi:10.1016/j.dyepig.2004.06.021

Phase (NCAP) for a liquid crystal display [11,12] but the application for recording materials seems to be under exploitation.

The purpose of the present study is the preparation of color-producing microcapsules with non-destructive method. In order to achieve this, we examined the irreversible development of microcapsules by UV irradiation. In the first half of this paper, we described the method for the preparation of photosensitive microcapsules. In the second half of this paper, the influence of the UV irradiation time and average particle size on the development of microcapsules was also discussed.

2. Experimental

2.1. Chemicals

Melamine and 36% formaldehyde solution were obtained from Kanto Kagaku Co., Inc. and were used as received. Methyl vinyl ether/maleic anhydride copolymer was used as a dispersing agent and was obtained from Acros Organics. Average molecular weight of methyl vinyl ether/maleic anhydride was 1 700 000. The leucocompounds used were 6-diethylamino-benzfluoran and 6-dimethylamino-3,3-bis(4-dimethylaminophenyl) phthalide and were obtained from Hodogaya Chemical Co., Inc. α,α,α-Tribromomethyl phenyl sulfone was used as a photoacid generator and was obtained from Wako Pure Chemical Industries, Ltd. Diisopropylnaphthalene was used for the solvent of a leucocompound and a photoacid generator and was obtained from Rütgers Kureha Solvents GmbH. All other chemicals used were reagent grade and were obtained from Kanto Kagaku Co., Inc.

2.2. Sample preparation

The leucocompound-loaded microcapsules were prepared with melamine/formalin resin by in situ polymerization method. The procedure for sample preparation is as follows.

2.3. o/w Microemulsion

Prescribed amounts of the leucocompound and the photoacid generator were previously dissolved in 7.5 g of diisopropylnaphthalene. The diisopropylnaphthalene solution that becomes an oil component in the system was poured into 25 g of aqueous methyl vinyl ether/maleic anhydride solutions. The mixture was then vigorously agitated with homogenizer (Tokushu Kika, Momomixer Mark II) until desired o/w microemulsion was obtained. Unless otherwise noted, concentration and pH of aqueous methyl vinyl ether/maleic anhydride solutions were previously adjusted to 50 g/l and 4, respectively.

2.4. Methylolmelamine

A total of 7 g of melamine, 14 g of 36% formaldehyde solution and 30 g of water were mixed in a separate flask and were stirred with magnetic stirrer at 353 K. After the mixture became transparent, the solution was gradually cooled to room temperature and methylolmelamine was obtained.

2.5. Microencapsulation

The methylolmelamine solution was then slowly injected into the o/w emulsion as mentioned above. The injection was carried out at room temperature with agitation at 1000 rpm using DC Stirrer Z-2100 (Tokyo Rikakikai Co., Ltd.). After an injection of the methylolmelamine solution was completed, the temperature was raised to 353 K. Polymerization of melamine/formalin and microencapsulation were attained with continuous agitation at 1000 rpm for 2 h. The prepared microcapsule slurry was washed three times with hot water. Average particle size of microcapsules was evaluated at 298 K using Horiba Laser Scattering Particle Size Distributuion Analyzer LA-300. Before recording the particle size, the microcapsule solution was equilibrated for 1 min under ultrasonic waves in order to prevent the cohesion between microcapsules.

2.6. Color-producing procedure

A total of 0.5 g of microcapsule suspension colloid was spread over a glass plate in a 0.5 mm thick layer and was dried. UV irradiation to microcapsules was carried out using low-pressure mercury lamp (Sen Lights Corporation, 40 W) at room temperature. The distance between microcapsules and the mercury lamp was adjusted at 4.5 cm. The color yield of color-produced microcapsules was evaluated as a light reflectance measured with Minolta CM-100 spectrophotometer. For comparison, the development in the bulk solution was also examined and was evaluated using Shimadzu UV–Visible Spectrophotometer UV-1650PC.

3. Results and discussion

Fig. 1 compares the relationship between average particle size of microcapsules and concentration of the dispersing agent. In Fig. 1, effects of the speed of agitation with homogenizer were also compared. In this case, agitation with homogenizer was carried out for 3 min. As shown in Fig. 1, the average particle size of microcapsules became small with increasing speed of

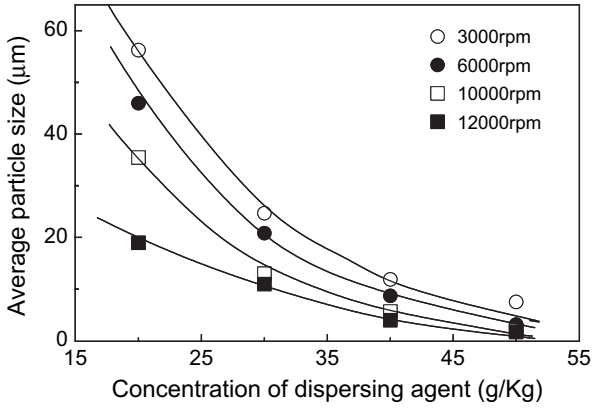

Fig. 1. Variation of average particle size of microcapsules as a function of the concentration of the dispersing agent.

agitation and was scarcely varied over 10 000 rpm. In this experimental condition, sheering stress may be equivalent at more than 10 000 rpm. On the other hand, the average particle size of microcapsules was decreased monotonously with increasing concentration of the dispersing agent. Improvements in the dispersing ability of the solution would prevent the growth of oil droplets by the incorporation with each other. We confirmed that agitation with homogenizer at more than 3 min had no effects on the average particle size of the microcapsule. Fig. 2 shows the effect of concentration of the dispersing agent on the distribution of particle size. The distribution of particle size was shown as a fluctuation coefficient. In this case, a low fluctuation coefficient implies that distribution of the particle size of prepared microcapsules is narrow. As shown in Fig. 2, the fluctuation coefficient decreased with increasing concentration of the dispersing agent. These results would relate the variation of the viscosity in the system. An increase in the viscosity of the system due to an increase in the concentration of the dispersing agent may hold the efficiency of the agitation in the system. In addition,

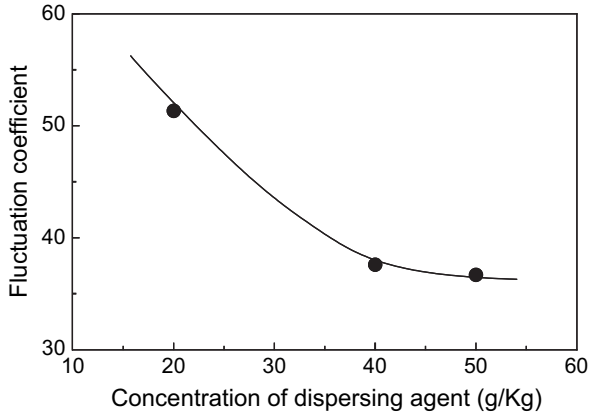

Fig. 2. Effects of concentration of the dispersing agent on the fluctuation coefficient of prepared microcapsules.

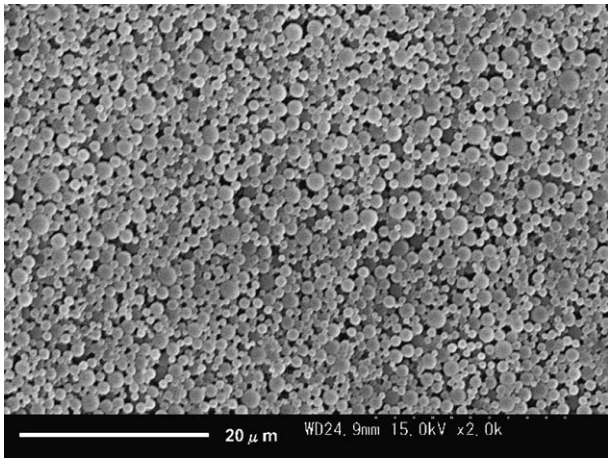

Fig. 3. Scanning electron microscope of the microcapsule.

the growth of small oil droplets by incorporation may also be prevented. Fig. 3 shows an example of the scanning electron micrograph of microcapsules. The microcapsules prepared with the above-mentioned method have uniform particle size. Destruction of the capsule walls by the mechanical agitation was not observed. We confirmed that a release of the contents to the exterior of capsules did not occur because the contact of the capsules with the developer did not result in the development.

Fig. 4 shows the variation of the light reflectance from microcapsules before and after UV irradiation. We confirmed that both 6-diethylamino-benzfluoran and 6-dimethylamino-3,3-bis(4-dimethylaminophenyl) phthalide showed similar results in the developments. Therefore, the results of the development from 6-dimethylamino-3,3-bis(4-dimethylaminophenyl) phthalide were omitted. As shown in Fig. 4, the light reflectance of UV irradiated microcapsules markedly

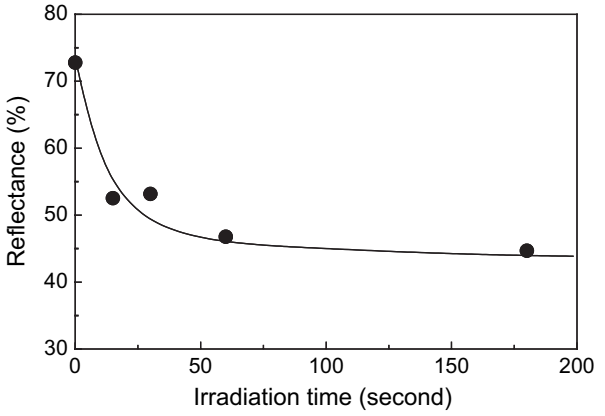

Fig. 4. Variation of the light reflectance of microcapsules as a function of UV irradiation time. Concentration of the leucocompound (6-diethylamino-benzfluoran), 2 wt%; concentration of the photoacid generator, 5 wt%; concentration of the dispersing agent, 50 g/kg.

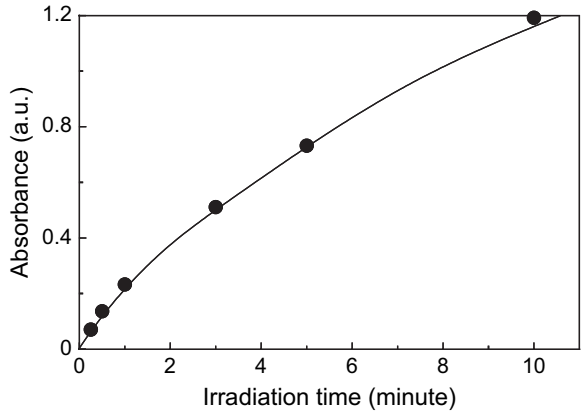

Fig. 5. Variation of absorbance from the leucocompound in a solution. Concentration of the leucocompound (6-diethylamino-benzfluoran), 2 wt%; concentration of the photoacid generator, 5 wt%; concentration of the dispersing agent, 50 g/kg.

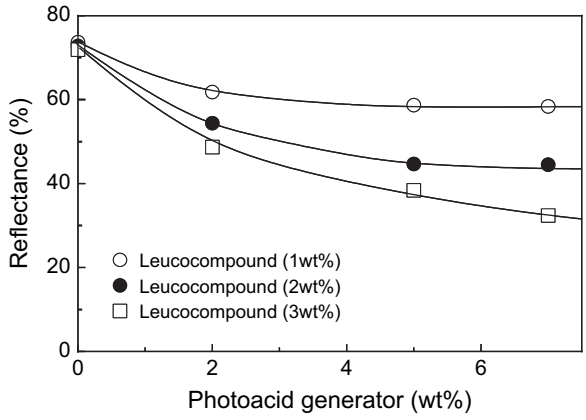

Fig. 6. Effects of concentration of the photoacid generator on the development of microcapsules. UV irradiation time, 30 s; concentration of the dispersing agent, 50 g/kg.

decreased with increasing irradiation time. The leucocompound in the microcapsule is sensitively reacted with the produced acid from the photoacid generator, indicating that UV light is effectively accessed to the interior of the microcapsule. In addition, the wall of microcapsules prepared in this study seems to have high degree of transparency because the development in the interior of the microcapsule can be accurately detected through the capsule wall. Fig. 4 also shows that photoacid generation and subsequent development processes seem to be accomplished within several seconds. In order to evaluate the velocity in the development of the prepared microcapsules, similar investigations were carried out in bulk condition, i.e., leucocompound/photoacid generator/solvent system. The results were shown in Fig. 5. The leucocompound in a solution was developed by UV irradiation in a similar manner as that of microcapsules. However, the time required to accomplish the development in a solution was quite different from that in the microcapsule. The development in a solution was continued for more than 10 min, although the development in the microcapsule was completed within 1 min. Since concentration of the leucocompound and the photoacid generator was equivalent in each system, the process in the acid production by UV irradiation would be different. In the development of microcapsules, total photo energy transmitted to the leucocompound may be higher than that in a solution system. Since amino resin has an ability to absorb ultraviolet rays, the surface of the spherical microcapsule may play the role of the light-harvesting antenna. As a result, acid generation in the microcapsule was rapidly achieved even if the light source was the same.

Fig. 6 shows the effect of concentration of the photoacid generator on the development of microcapsules. As shown in the open square plots in Fig. 6, the light reflectance of microcapsules decreased with increasing concentration of the photoacid generator when 3 wt% of the leucocompound was contained. On the other hand, the variation of the light reflectance of microcapsules that contain lower amounts of the leucocompound was different. The light reflectance of them was nearly constant at more than 5 wt% of the photoacid generator. In the former case, the number of effective leucocompounds molecule would be excessively present compared to that of the produced acid. Therefore, a part of the leucocompound was reacted with all of the produced acid and the left was present as unreacted free molecules. In the latter case, stoichiometric relationship between them may be opposite. In the range of high concentration of the photoacid generator, the produced acid would be excessively present in the system. Since all the leucocompound were reacted with the produced acid, surplus acid in the

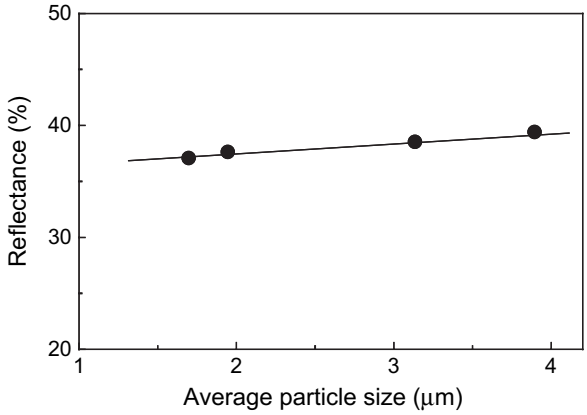

Fig. 7. Effects of average particle size of microcapsules on their light reflectance. Concentration of the leucocompound (6-diethylamino-benzfluoran), 2 wt%; concentration of the photoacid generator, 5 wt%; concentration of the dispersing agent, 50 g/kg; UV irradiation time, 30 s.

system did not provide the bathochromic effect of microcapsules.

Fig. 7 shows the effect of average particle size of microcapsules on their development. The light reflectance of microcapsules was slightly decreased by a miniaturization of the capsule. Since the weight fraction of the melamine/formalin resin is constant, miniaturization of microcapsules would result in an increase in the total surface area of the capsule. As a result, microcapsules that have smaller particle size may have an ability to take in the higher photo energy. These results also suggest the role of the microcapsule wall as a light-harvesting antenna.

References

[1] Kubota Y, Suzuki M, Shinbo K. Pressure and heat-sensitive recording material. JPN Patent 2001-174458.
[2] Seki S, Hata T. Heat-sensitive recording material. US Patent 2003036478.
[3] Halbrook WB, Wehr MA. Thermosensitive recording material with preprinted indicia and thermal paper. Eur Patent EP 1321307.
[4] Stern T, Lamas MC, Benita S. Design and characterization of protein-based microcapsules as a novel catamenial absorbent system. International Journal of Pharmaceutics 2002;242(1–2): 185–90.
[5] Bohlmann JT, Schneider C, Andresen H, Buchholz R. Optimized production of sodium cellulose sulfate (NaCS) for microencapsulation of cell cultures. Chemical Engineering Technology 2002; 2(12):384–8.
[6] Thies C. In: Vilstrup Per, editor. Microencapsulation of food ingredients. Leatherhead, U.K.: Leatherhead Publishing; 2001.
[7] Lysionek AE, Zubillaga MB, Salgueiro MJ, Pineiro A, Caro RA, Weill R, et al. Bioavailability of microencapsulated ferrous sulfate in powdered milk produced from fortified fluid milk: a prophylactic study in rats. Nutrition 2002;18(3):279–81.
[8] Zlotkin S, Arthur P, Antwi KY, Yeung G. Treatment of anemia with microencapsulated ferrous fumarate plus ascorbic acid supplied as sprinkles to complementary (weaning) foods. American Journal of Clinical Nutrition 2001;74(6):791–5.
[9] Teshima K, Aoyagi M, Hikosaka S. Charge stabilization of trimellitic anhydride microcapsule toner. Nippon Kagaku Kaishi 2002;2:169–73.
[10] Yoshida M, Mardriyati E, Hinokuchi D, Uemura Y, Kawano Y, Hatanaka C, et al. Development of core/shell type functional microcapsule for highly efficient fixation of microorganism. Kemikaru Enjiniyaringu 2001;46(11):858–65.
[11] Ju HK, Kim JW, Han SH, Chang IS, Kim HK, Kang HH, et al. Thermotropic liquid-crystal/polymer microcapsules prepared by in situ suspension polymerization. Colloid and Polymer Science 2002;280(10):879–85.
[12] Yoshida M, Mori T, Matsui T, Uemura Y, Hatate Y. Electrosensitive microcapsule immobilized ferroelectric liquid crystal. Journal of Chemical Engineering of Japan 2002;35(4):398–400.