

SHORT COMMUNICATIONS

A New Method to Synthesize Microcapsule and Its Application in Controllable Photodegradation of Polymers

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Microcapsules have been widely used in controlled release system, in separation of active component, in reduction of substance volatility, in coloring or printing materials and so on.¹⁻⁶ It is a recently developed concept that microencapsulated photodegradant was used in the controllable photodegradation of polymers⁷ although microencapsulated antioxidants were adopted in polymers.⁸ Usually the addition of photodegradant is accompanied with photostabilizers or antioxidants to overcome the problem of property decay of polymers during application.⁹ But this takes limited effect and often retards the degradation after applications. In fact, the shell of microcapsule separates the photodegradant from the polymer matrix. Before the shell is destroyed, the polymer materials keep stable properties. Once the shell is destroyed, the released photodegradant induces immediate degradation. Besides, microencapsulated photodegradant is advantageous in the following aspects: 1) degradation induction period might be adjusted by varying the shell thickness, and 2) the coloring of the composite products and the toxicity of the additives could be alleviated by the coating process. So the concept of microencapsulation is very important and meaningful in the controllable photodegradation of polymers.

Microencapsulated photodegradant should meet the following requirements: 1) the size should be small enough not to reduce the transparency, not to influence the mechanical properties of polymers, such as plastic films due to the stress concentration around the microcapsule; 2) the size distribution should be narrow; and 3) the coated fraction should be as high as possible in order to avoid the photodegradation during the application period.

Many methods can be chosen to produce microcapsules:⁶ chemical methods such as *in situ* polymerization, interfacial polymerization etc.; mechanical methods such as spray drying, vacuum vapor deposit etc.; physicochemical methods such as water phase separation, oil phase separation etc. All these methods are difficult to meet the requirements of ideal microencapsulation of photodegradant.

Herein, a new method to synthesize microcapsules was proposed and microencapsulated iron(III) tris(*N,N*-diethyldithiocarbamate), Fe(DEC)₃, was produced. Preliminary study on controlled photodegradation of low density polyethylene (LDPE) films has shown the advantages of microencapsulated photodegradant.

EXPERIMENTAL

Typically, 5 g of gelatin in 150 mL water containing NaDEC was mixed with 5 g of gum arabic in 150 mL water containing FeCl₃ at 40°C and stirred. The amount of FeCl₃ and NaDEC is stoichiometrical. After cooling to 5°C, the system was cured for 30 min by addition of formaldehyde. By raising pH to 9 with sodium hydroxide solution, the above slurry was stirred for 30 min, then heated to 50°C for 30 min. The resulting slurry was used to observe the microcapsule morphology, size and size distribution by TEM with a JEM-100CXII type electron microscope at an accelerating voltage of 100 kV in a copper grid coated with a thin carbon film. Spray drying of the slurry gave powders. The powders were hydrolyzed in 1 M HCl for different time to get different shell thickness. After the powders were dispersed in acetone, a solvent of Fe(DEC)₃ but

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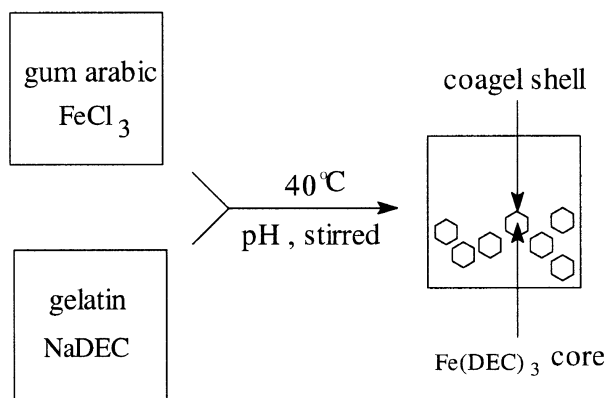


Figure 1. Diagram for reaction-coacervation to synthesize microcapsule.

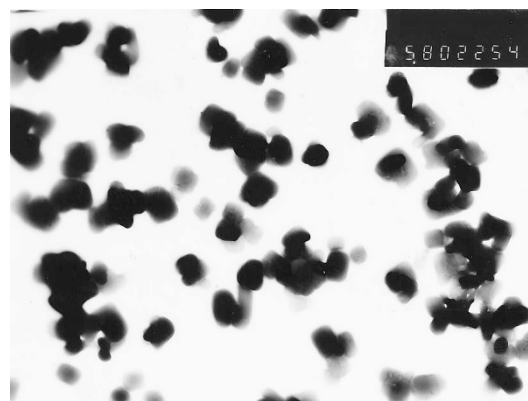
not of coagel, the absorptivity tracked by spectrophotometer was used to decide the core content and coated fraction.

RESULTS AND DISCUSSION

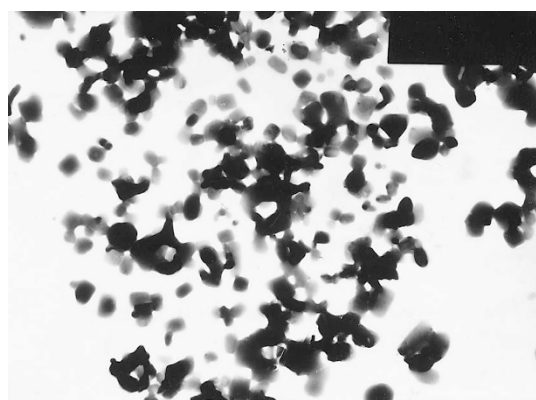
Gelatin is a protein which contains $-\text{COO}^-$ and $-\text{NH}_3^+$ groups and carries more positive charge from $-\text{NH}_3^+$ below its isoelectric point. Gum arabic is a negative charged macromolecule containing lots of $-\text{COO}^-$. So gelatin and gum arabic solution, under suitable pH, can be coacervated to form coagel. Tris(*N,N*-diethyldithiocarbamate) iron(III) ($\text{Fe}(\text{DEC})_3$) is a superior photodegradant, first proposed by Scott⁹ and was investigated in detail as photodegradant in polymers.^{10–13} $\text{Fe}(\text{DEC})_3$ can be simply synthesized by the reaction of FeCl_3 and sodium *N,N*-diethyldithiocarbamate (NaDEC) in aqueous solution. Interestingly, we arranged the reaction and the coacervation reaction of gelatin and gum arabic in the same reaction system. As soon as FeCl_3 reacted with NaDEC to produce $\text{Fe}(\text{DEC})_3$, gelatin coacervated with gum arabic to form coagel. The coagel covered the surface of $\text{Fe}(\text{DEC})_3$ crystal granule and hindered its growing. A structure of core-shell was formed. We call this technique reaction-coacervation. The main procedure is schematized in Figure 1.

The factors influencing synthesis results are complicated. An orthogonal-designing experiment ($L_8(2^7)$) was adopted to investigate such factors as concentration of FeCl_3 , time period of mixing, stirring rate, order of adjusting pH, rate of cooling, mixing order etc. The results show that pH is the most important factor on the size of microcapsule.

Figure 2 shows that the resulting particle shape is unusual, not globular but rectangular. Nearly all the size is less than $1\ \mu\text{m}$ under the experiment conditions with $0.06\ \text{mol L}^{-1}$ of NaDEC and $0.02\ \text{mol L}^{-1}$ of



(A) $\times 58000$



(B) $\times 58000$

Figure 2. TEM of microcapsules ($\text{Fe}(\text{DEC})_3$ coated with coagel from gelatin-gum arabic reaction-coacervation) NaDEC and FeCl_3 concentrations before mixing: $0.06\ \text{mol L}^{-1}$ and $0.02\ \text{mol L}^{-1}$, respectively.

FeCl_3 concentrations before mixing. The particle size is much smaller compared with the usual methods¹⁴ and is about 1% of the thickness of the usual agriculture plastic films when used as photodegradant. This would not harm mechanical properties of films.

The core-shell structure was verified by spectrophotometry. The results show that the inner material releases in acetone according to a linear relationship of absorptivity against the square root of the material release time ($t^{1/2}$). The coated fraction of particles can be calculated from this relationship since the absorptivity at $t = 0$ is related to the uncoated or partially coated particles. In this way, we found that the coated fraction of microcapsules is about 91.6% and that the value decreases to 80.4% after hydrolyzed in 1 M HCl solution at 40°C for 3 h. Compared with the degree of coating (60%) in literature,⁷ the coated fraction in our experiments is much higher.

Further identification of the existence of core-shell structure is dependent on choosing AgCl as the model core substance by substituting $0.2\ \text{mol L}^{-1}$ NaCl for NaDEC and $0.2\ \text{mol L}^{-1}$ AgNO_3 for FeCl_3 . The particle size is in the range of 100–200 nm by TEM (see

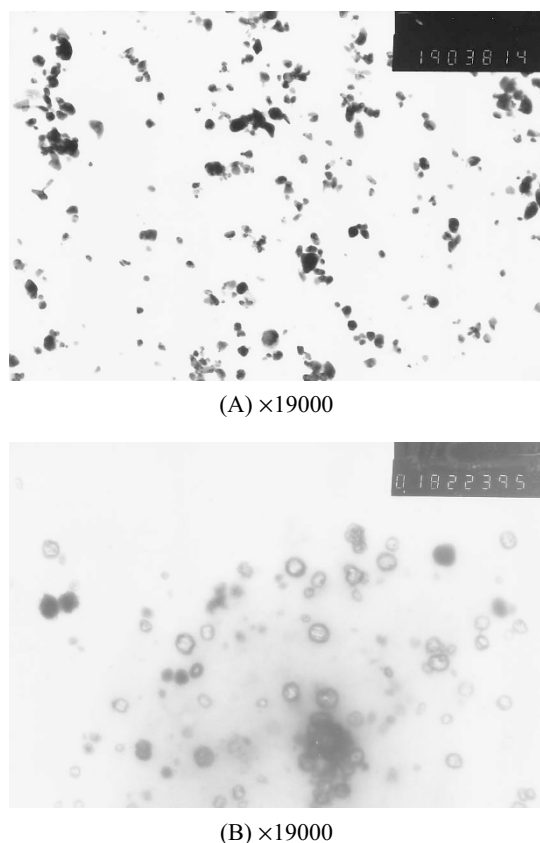


Figure 3. TEM of capsule structure with AgCl as model core substance coated with coagel from gelatin-gum arabic from reaction-coacervation NaCl and AgNO₃ concentrations before mixing: (A): 0.2 mol L⁻¹, (B): 0.2 mol L⁻¹ with AgCl core extracted by aqueous ammonia.

Figure 3A). The resulting slurry containing AgCl particle was treated by adding aqueous ammonia to extract AgCl through formation of Ag(NH₃)⁺. The remaining was observed under TEM, shown in Figure 3B. The photograph demonstrates obvious shell structure, which is the direct proof of the existence of core-shell structure.

The core weight percentage was decided also by means of the measured linear relationship of absorptivity against known amount of Fe(DEC)₃. The results show that the core weight percentage is 51.1% for unhydrolyzed and 55.4% for hydrolyzed in 1 M HCl for 3 h, which are quite high.

High core weight percentage and complete coating must correspond to thin shell of microcapsules. As a result, the pattern of microcapsule reflects approximately the shape of core crystal, shown in TEM, which also answers the problem that the resulting microcapsule is not the usually globular, but nearly rectangular shape.

Based on the difference between the core weight percentages of unhydrolyzed and partly hydrolyzed microcapsule, the hydrolyzed degree of shell can be calculated (12.4%), nearly equal to the measured value difference (11.2%) of coated fractions between unhy-

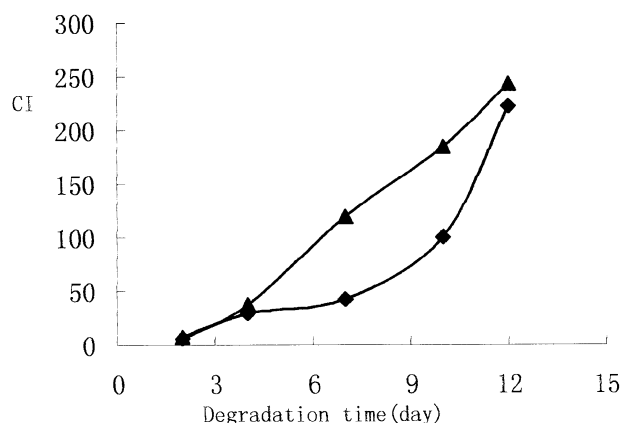


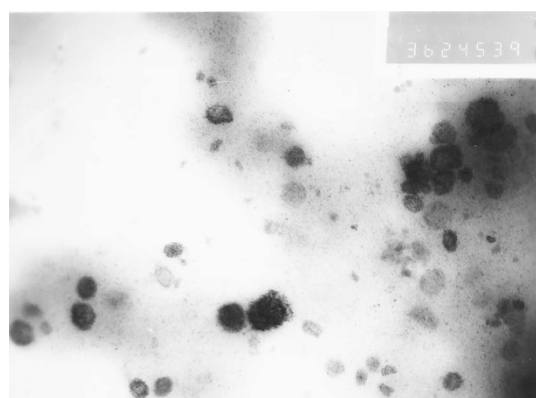
Figure 4. The influence of Fe(DEC)₃ microcapsule on LDPE films photodegradation. ▲: partly hydrolyzed, ◆: unhydrolyzed.

drolyzed and hydrolyzed. This proved the reliability of these data.

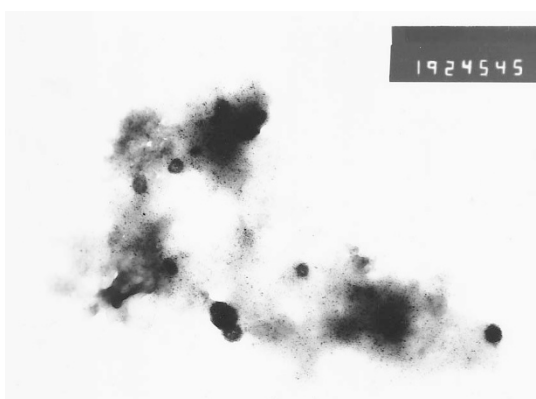
LDPE films containing 0.3 wt% microencapsulated Fe(DEC)₃ were irradiated in UV chamber. FT-IR recorded the evolution of carbonyl and hydroxyl groups of the films with irradiation time. Carbonyl index (CI) is a convenient indication of degradation degree.^{7,15} Figure 4 demonstrates the increasing of CI with photodegradation time. There is not significant difference between the films containing unhydrolyzed and partly hydrolyzed microcapsules of photodegradant at the first 4 days. CI continues to increase steadily for the films containing partly hydrolyzed microcapsules of photodegradant. Reversely, CI keeps almost unchanged from 4 to 8 days and sharply increases after 8 days for the films containing unhydrolyzed microcapsules. The results show the photodegradation controllable to some extent. We speculated that the sharp increment of CI after 8 days for LDPE films containing unhydrolyzed microcapsule should be ascribed to the shell destruction and the accelerated photodegradation by the released photodegradant.

In order to testify the speculation, an experiment was designed specially. Microencapsulated AgCl by the gelatin-arabic gum coagel was irradiated under UV light at 70°C for different time, then dispersed in water through ultrasonic wave, and observed by TEM (Figure 5). TEM photograph shows different morphology according to different irradiation time. The longer the irradiation time, the worse the microcapsule is destroyed, which means deeper degradation degree of shell. Seven days UV irradiation led to almost complete shell destruction (see Figure 5C). These observations directly testify that the coagel shell can be deteriorated and destroyed under oxygen and UV irradiation, and that the destruction can not mainly ascribed to the action from core substance, Fe(DEC)₃.

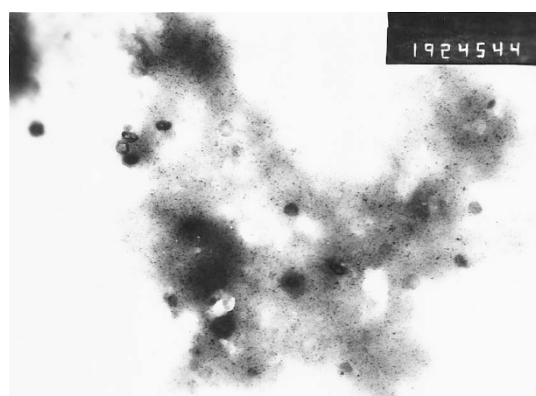
As for LDPE films containing microencapsulated



(A) ×36000



(B) ×19000



(C) ×19000

Figure 5. TEM of capsule irradiated under UV light for different time, with AgCl as model core substance coated with coagel from gelatin-gum arabic from reaction-coacervation. (A): 3 days, (B): 5 days, (C): 7 days.

$\text{Fe}(\text{DEC})_3$, UV light and produced polyethylene hydroperoxide and peroxide radical etc. after several days UV irradiation (for example, 7 days) have the similar above effect on the shell coagel of microencapsulated $\text{Fe}(\text{DEC})_3$. These reactions finally resulted in the shell structure destruction and the release of $\text{Fe}(\text{DEC})_3$. Con-

sidering that the photodegradation has begun and the induction period has passed, the released photodegradant can induce immediate degradation, showing the sharp increment of CI.

In summary, without using emulsifier, dispersant and strong stirring etc., a new and convenient method of reaction-coacervation to synthesize microcapsule was put forward. The method can produce ideal microcapsules with small size (less than $1\ \mu\text{m}$), high core weight percentage (51.1%), and nearly perfect coating percentage (91.6%). Using the microencapsulated photodegradant, LDPE films were proved to be true degradation controllable.

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REFERENCES

1. M. A. Wheatley, M. Chang, E. Park, and R. Langer, *J. Appl. Polym. Sci.*, **43**, 2123 (1991).
2. R. Bodmeier and J. Wang, *J. Pharm. Sci.*, **82**, 191 (1993).
3. C. C. Dowler, O. D. Dailey, Jr., and B. G. Mullinix Jr., *J. Agric. Food Chem.*, **47**, 2908 (1999).
4. H. Watanabe, S. Okuno, K. Tsukuda, and T. Hirokawa, Japanese Patent, P2000-143407A (May 23, 2000).
5. D. Dupuis and C. Jourdat, Patent Cooperation Treaty (PCT) International Application, WO-A1-0025908 (May 11, 2000).
6. A. Kondo, "Microcapsule Processing and Technology, Ed., J. W. Van Valkenburg, Marcel Dekker, Inc., New York, N.Y., 1979.
7. B. S. Yoon, M. H. Suh, S. H. Cheong, J. E. Yie, S. H. Yoon, and S. H. Lee, *J. Appl. Polym. Sci.*, **60**, 1677 (1996).
8. F. E. Keen, R. S. Lehrle, E. Jakab, and T. Szekely, *Polym. Degrad. Stab.*, **38**, 219 (1992).
9. G. Scott, U. S. Patent 4 121 025 (Oct. 17, 1978).
10. G. Scott, "Developments in Polymer Stabilization-1", Applied Science Publishers Ltd., London, 1979, p 167.
11. D. Gilead and G. Scott, "Developments in Polymer Stabilization-5", Applied Science Publishers Ltd., London, 1982, p 71.
12. S. Al-Malaika and G. Scott, "Degradation and Stabilization of Polyolefins", Applied Science Publishers Ltd., 1983, p 283.
13. S. Al-Malaika, A. Marogi, and G. Scott, *J. Appl. Polym. Sci.*, **33**, 1455 (1987).
14. K. Ijichi, H. Yoshizawa, Y. Uemura, Y. Hatate, and Y. Kawano, *J. Chem. Eng. Jpn.*, **30**, 793 (1997).
15. M. L. Berlanga-Duarte, J. L. Angulo-Sanchez, and M. C. Gonzalez-Cantu, *J. Appl. Polym. Sci.*, **60**, 413 (1996).