Microencapsulation of Water-Soluble Flame Retardant Containing Organophosphorus and its Application on Fabric

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ABSTRACT: Microencapsulation is based on multiple emulsion interfacial reaction technique that combines the characteristics of the interfacial reaction and conventional multiple-emulsion processes. In this study, the microcapsules were synthesized with the water-soluble dimethyl methyl phosphorate (DMMP) as the core material and the acetal product of polyvinyl alcohol (PVA) and glutaraldehyde (GA) as the shell material. The microcapsules were characterized by using DSC, IR spectrum and phosphorus qualitative analysis, and the factors affecting microencapsulation were identified and discussed. The data presented herein suggested that the size distribution of microcapsules was affected by the concentration of PVA and SPAN80 and by the phase volume ratio, while the crosslinking agent GA content has little effect. The data also showed that the microcapsules with the core of flame retardant containing organophosphorus would have promising applications in inflaming retarding of cotton fabric. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 4915–4920, 2006

Key words: organophosphorus compounds; synthesis; microencapsulation; application; cotton fabric

INTRODUCTION

For many years, halogenated hydrocarbons, such as CF_3Br were used as flame retardants. However, because of their high ozone depletion potential, the production of halogenated hydrocarbons has been banned under the Montreal Protocol and its amendments.[1,2] The search for effective replacement has led to a family of organophosphorus compounds (OPCs), which have shown considerable promise as flame retardants.[3–6] One of the promising OPCs is dimethyl methyl phosphorate (DMMP). On the basis of its extinction measurements on nonpremixed, atmospheric-pressure flame, DMMP has been demonstrated as a highly effective suppressant (two to four times more effective than CF_3Br).[7–9] In addition, DMMP has many attractive properties, such as high phosphor content (25%), low carbon, and no toxic gas formed during burning. It has been widely used in flame retarding treatment of polyurethane foam plastic, unsaturated polyester, and epoxy resin.[10,11] However, because of its water-soluble property and its toxicity to skin, the application of DMMP on fabric has been restricted. The purpose of this article is to apply the microencapsulation technique to enable the application of DMMP on textile.

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Microencapsulation is a technique, with which solid or liquid could be encapsulated by a film-forming material to form tiny particles. The encapsulated solid or liquid core is isolated from the environment, thus the property of the core is reserved completely. Under appropriate condition, the core material can be released for action, when the shell is being destroyed. In the early 60s, to solve the waterproof problem of some inorganic flame retardants (e.g., ammonium sulfate), the scientists in the US developed the microcapsules of flame retardants which could resist rainwater, while providing fire prevention for forest. Since then, the application of microencapsulation technique in flame retardants has further evolved; however, most of the use has been limited to flame retarding of polymers (e.g., plastic), and there has been little focus on the application on fabric.

Microencapsulation was archived by the complex interfacial coagulation and crosslinking between polyvinyl alcohol (PVA) and glutaraldehyde (GA). During the process, the curing of the polymer led to the formation of the capsule shell. The resulted microencapsulated flame retardant was applied to the fabric, together with suitable binder, and the flame retarding efficiency was measured.

EXPERIMENTAL

Reagents

GA (25% content in water, pure grade), PVA (1788), cyclohexane (AR), and surfactant SPAN 80 were

obtained from Guodou Chemical Reagent (Shanghai, China). Hydrochloric acid (CP) was purchased from Jindou Chemical Reagent (Shanghai). DMMP (technical grade) was obtained from Qingdao pesticide factory (Qingdao, China). Low-temperature adhesive (self-made).

Instruments

The instruments used were XSP BM digital image analysis system, DSC 2910 thermoanalysis instrument (TA Instruments), and Nicolet 760 infrared spectrum instrument (Nicolet).

Synthesis

The microencapsulation process consists of the following three main steps:

- The preparation of water/oil (w/o) emulsion by emulsifying a mixture containing crosslinking agent GA, catalyst HCl, and a water-soluble core material DMMP into cyclohexane under stirring, with SPAN 80 as the emulsifier;
- The formation of microcapsules by dispersing the w/o emulsion into the hydrophilic polymer PVA solution;
- The washing and drying of the formed microcapsules.

In w/o emulsion, the aqueous phase was composed of DMMP, GA, HCl and water while the organic phase was cyclohexane with a small amount of the emulsifier SPAN 80. The aqueous phase was dispersed into the organic phase with the aid of the emulsifier under high-speed agitation. Then the emulsion was put into PVA solution at room temperature under low-speed agitation for a period of time. An insoluble polymer film was formed by the fast crosslinking reaction between PVA and GA on the surface of the w/o/w multiple emulsion. Small stable microcapsules were formed and were collected by filtration, then washed several times with water and dried by vacuum dryer.

Formula of synthesizing microcapsule

Inner phase (aqueous phase):	DMMP, saturated solution; GA 15%(volume ratio); HCl a little
Organic phase (intermediate phase):	SPAN80 5.0% (volume ratio)
Outer phase:	PVA 3.0% (mass percentage)
inner phase/organic phase (V/V):	1 : 1–4 : 5
Outer phase/system (V%):	60%

Burning test

The burning test with cigarette was conducted according to the US Federal Government Safety Regulation of Daily Consumer Goods and the corresponding testing standard of flame retarding performance. In this article, the pin was used to fix the ignited cigarette and laid by 45°angle on the finished cotton fabric. For each test, three ignited cigarettes were used to the same fabric in different areas. The degree of damaging of cotton fabric was observed, after the fabric was contacted with ignited cigarette for a given time.

Formula of finishing bath

DMMP microcapsule:	20–40%
dispersing agent NNO:	2%
urea:	8%
low-temperature adhesive	20%
water:	appreciable proportion

RESULTS AND DISCUSSION

The size of microcapsule was dependent on various conditions of the synthesis process, such as the concentration of PVA in the aqueous solution, the content of emulsifier in the emulsion, and the content of crosslinking agent GA. For the interfacial coagulation, the capsule wall was known to grow by the diffusion of molecules between inner phase and outer phase through the intermediate phase. The speed of diffusion was one of the most crucial factors in the microencapsulation process. If the speed of diffusion was too quick, only a gel of poly(vinyl acetal), but no microcapsule, would be obtained. Therefore, we adjusted the content of multiple-emulsion to control the speed of diffusion.

The effect of different factors on the size of microcapsules

Concentration of PVA

To determine the effect of PVA concentration on microencapsulation, the mass percentage of PVA was prepared as 0.5%, 3.0%, 6.0%, 9.0%, respectively, and the other components were fixed as shown in *Synthesis*. The results were shown in Table I and Figures 1–3.

The data in Figure 1–3 indicated that the size of microcapsule became larger with an increasing PVA

TABLE I
Effect of PVA Concentration on the Size of Microcapsule

Mass percentage of PVA (%)	Average diameter (um)
0.5	No microcapsule was formed
3	5.351
6	7.869
9	12.526

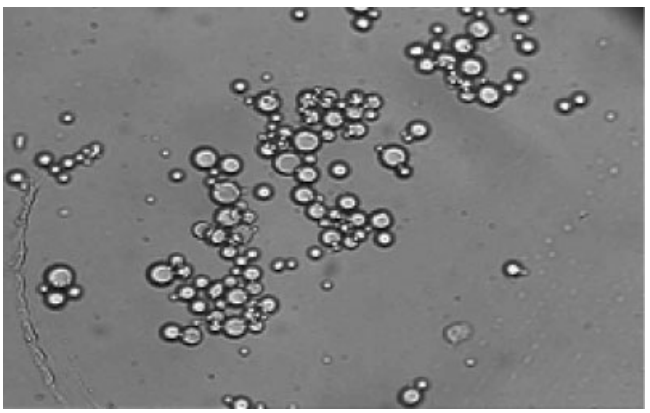

Figure 1 Aspect figure at 3.0% PVA concentration.

concentration: the higher the PVA concentration, the larger the size of microcapsules. In general, it was difficult to disperse w/o emulsion well into higher viscosity PVA solution. In addition, the stability of w/o emulsion would become low, because the micelles formed by the superfluous PVA of outer phase would have the solubilization to the emulsifier SPAN80.[12] As a result, the distribution and diameters of microcapsules became larger due to the higher PVA concentration. When PVA concentration was 1.0% or below, the microcapsules could hardly be obtained, due to the fact that the tender capsule wall was too thin, which resulted in aggregated debris. We concluded that 3.0% PVA was a suitable concentration for microencapsulation.

Concentration of emulsifier SPAN80

The formula of inner phase was fixed as shown in *Synthesis*, and the amount of emulsifier SPAN80 was changed from 1.0 to 8.0% (volume ratio). The effect of emulsifier concentration on average diameter of microcapsule was shown in Figure 4.

The data in Figure 4 indicated that up to 5% concentration, higher emulsifier content would produce

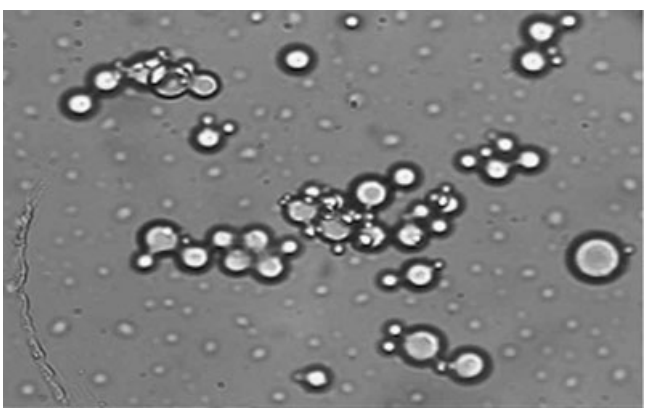

Figure 2 Aspect figure at 6.0% PVA concentration.

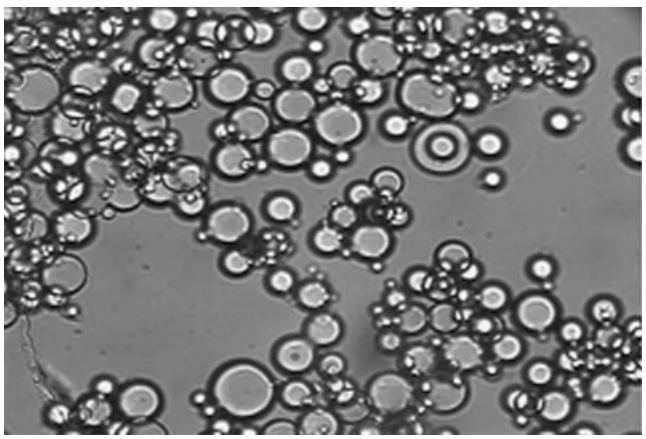

Figure 3 Aspect figure at 9.0% PVA concentration.

smaller capsules. As the concentration of emulsifier increased, the interfacial tension of the disperse phase decreased accordingly to reach a limitative value. The change in interfacial tension of the inner phase has an impact on the stability of w/o emulsion and on the size of microcapsule.[13] Therefore, the inner phase with less interfacial tension tends to break into smaller droplets and form smaller microcapsule. We also observed that as the emulsifier concentration was 6.0% or over, the average diameter of the microcapsules increased. When the emulsifier content was too high in the w/o emulsion, excess emulsifier increased the viscosity of disperse phase rather than decreasing the droplet size.[14] We concluded that 5.0% emulsifier was a preferred concentration for emulsifier.

Volume ratio between two phases

When the amount of all components in multiple-emulsion system is fixed, the effect of volume ratio between inner and organic phase on the size of microcapsules was shown in Table II.

The data indicated that the volume ratio of inner and organic phase was an important factor in microencapsulation. As the volume ratio of inner phase decreased, the average diameter of the microcapsules

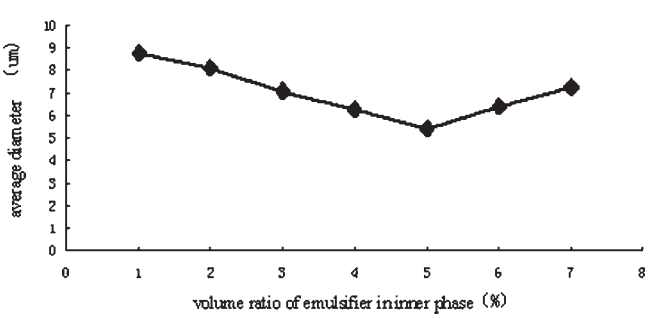

Figure 4 Effect of emulsifier concentration on the size of microcapsule.

TABLE II
Effect of the Phase Volume Ratio Between Inner Phase and Organic Phase on the Size of Microcapsule

Inner phase/organic phase (V/V)	Average diameter (um)
3:01	no capsule was formed
2:01	4.867
3:02	6.77
1:01	8.022
4:05	8.472
2:03	9.545
1:02	12.24

shifted to a larger size. When the volume ratio between the inner and organic phase was greater than 2, we only obtained poly(vinyl acetal) debris and no microcapsule was formed (the microscope picture of poly(vinyl acetal) debris was shown in Fig. 5).

The forming of debris was resulted from the increase of inner phase that would bring the thickness of organic phase down, and make the emulsion break easily. The diffusion speed of acetalation molecules was dependent on the thickness of intermediate phase (organic phase). Therefore, an appropriate ratio of the phases was very important for the stability of multiple-emulsion and microencapsulation. We concluded that the volume ratio (inner phase/organic phase) = 1:1–4:5 was appropriate.

Furthermore, we noticed that the different volume ratio between outer phase (PVA solution) and total system would also affect the size of microcapsules, as shown in Figure 6. The data indicated that the higher content of the outer phase resulted in smaller size of microcapsules. If the content of PVA solution was too high in the multiple-emulsion, e.g., in excess of 60%, the system of pure w/o/w emulsion would change into a mixture of o/w and w/o/w emulsions, thus making the yield of microcapsules drop significantly. Therefore, we concluded that 60% volume ratio (outer phase/system) was viable for microencapsulation.

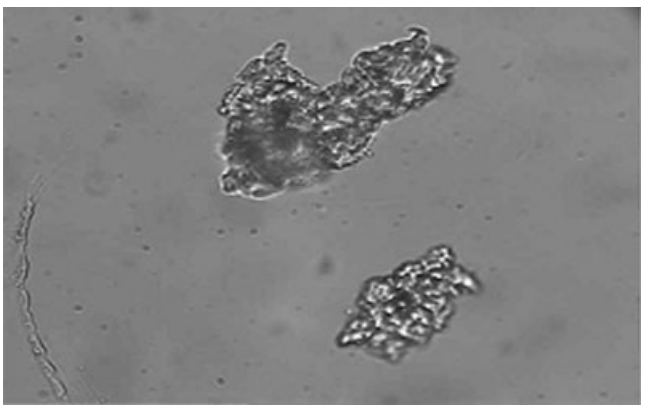

Figure 5 The microscope picture of poly(vinyl acetal) debris.

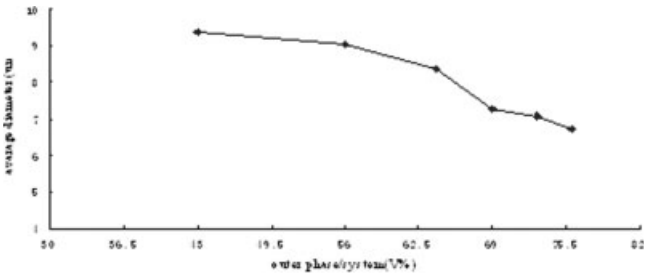

Figure 6 Effect of the phase volume ratio between outer phase and the system on the size of microcapsule.

Concentration of crosslinking agent GA

The effect of crosslinking agent GA content was investigated and the result was presented in Table III.

As discussed previously, the ultimate capsule size was determined by the size of the dispersed droplet of w/o emulsion and the thickness of organic phase. In Table III, we demonstrated that the content of crosslinking agent had little effect on the particle size of microcapsule. At below 5.0%, the capsule wall could not be formed, simply because insufficient crosslinking agent GA resulted in insufficient strength of the wall.[8] Therefore, the wall of microcapsule prepared at lower crosslinking agent concentration was too weak to maintain its shape mechanically, and would eventually be broken by shear force during the encapsulation process. We determined that 15% GA concentration would be sufficient to form stable microcapsules.

TABLE III
Effect of the GA Concentration on the Size of Microcapsule

GA/inner phase (V%)	Average diameter (um)
5	No capsule was formed
15	5.764
25	6.507
30	5.536
35	6.028

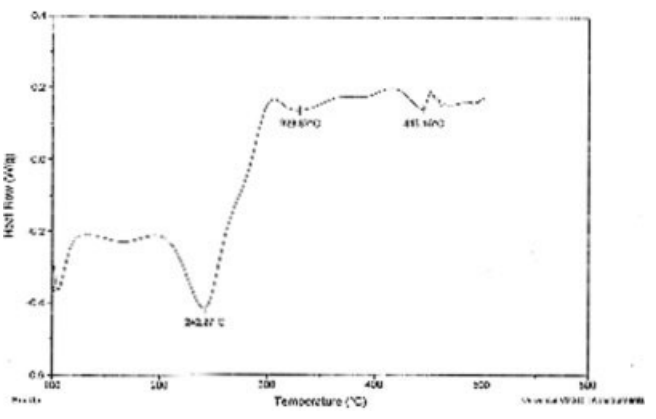

Figure 7 The DSC picture of microcapsules.

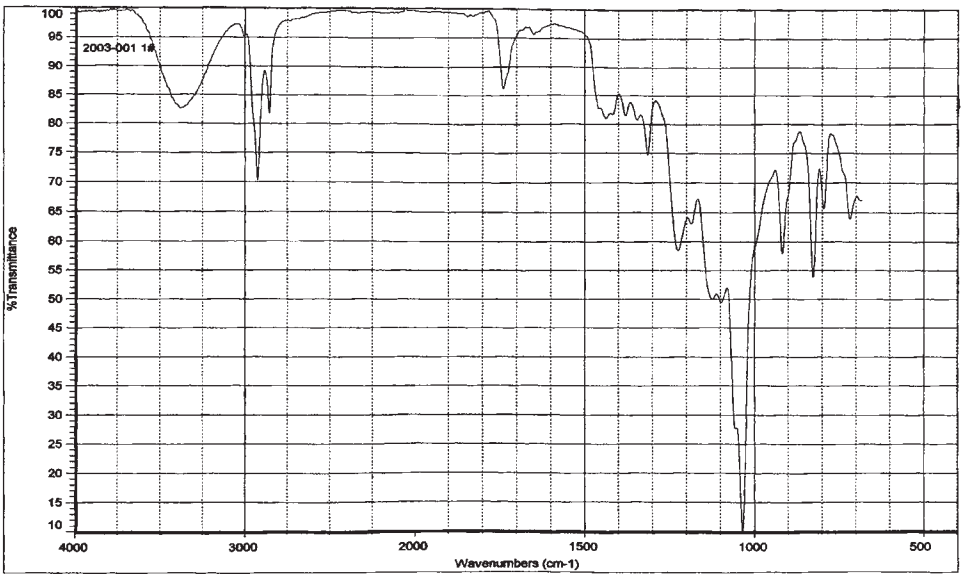

Figure 8 The IR picture of shell of microcapsules.

Identification

Differential scanning calorimetry

The result of DSC thermoanalysis of microcapsules was shown in Figure 7. We observed that the strong absorbing peak occurred at the temperature of 242.27°C, before the ignition point of cellulosic fiber (about 260°C). Therefore, the microcapsules containing DMMP could be applied as flame retardant.

IR

It was apparent in Figure 8 that the strong absorbing peak at 1030–1150 cm^{-1} was the correspondence of the bond C—O—C, which was formed during the process of PVA and GA curing reaction. The weak absorbing peak at 1740 cm^{-1} was the correspondence of the little bond —CHO on the surface of the shell, where most of the carbonyl group had already taken part in the curing reaction.

Qualitative analysis of phosphorus

After the microcapsules were burnt sufficiently in the crucible, the product of combustion was added into the solution of ammonium molybdate in the acidic condition and then heated. The yellow precipitation of ammonium phosphomolybdate was observed. In contrast, the yellow precipitation was not formed when the same test was repeated in which the DMMP core in microcapsule was replaced with a water core. We concluded that the flame retardant of DMMP was indeed encapsuled in the product.

Burning test

The cotton fabric was finished according to the formula of finishing bath and tested by ignited cigarettes according to the burning test procedure described previously. The result was shown in Table IV.

The data from Table IV indicated that microcapsuled DMMP had a good flame retarding efficiency to the fire caused by unextinguished stump. Because the ignited cigarette extinguished by itself after 2 min as the cotton sample was finished by 40% DMMP microcapsules in finishing bath, and thus, microcapsuled DMMP would have promising applications in inflaming retarding of housing decoration, such as curtain, slipcover, bedding, carpet, etc.

TABLE IV
The Result of Burning Test

Finished samples	Observations
Untreated blank cotton fabric	Overburning within 1 min
Finished cotton fabric absent of DMMP microcapsules	Overburning within 1 min
Finished cotton fabric containing 20% DMMP microcapsules in finishing bath	Leaving some combustion imprint after 3 min burning
Finished cotton fabric containing 40% DMMP microcapsules in finishing bath	Ignited cigarette extinguished by itself after 2 min

CONCLUSIONS

- The microcapsules could be prepared by interfacial coagulation and crosslinking technique in the multiple-emulsion. The size distribution of microcapsules was affected by the PVA concentration and SPAN80 and by phase volume ratio, while the crosslinking agent GA content had little effect.
- The microcapsules, with flame retardant DMMP as the core material, had a good flame retarding efficiency to the fire caused by unextinguished stump. They would have promising applications in inflaming retarding of housing decoration, such as curtain, slipcover, bedding, carpet, etc.

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