Microencapsulation of Water-Soluble Materials Using a Copolymer of Poly(vinyl Chloride)

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Synopsis

Microencapsulation of aqueous materials by the technique of organic phase separation using co-poly(vinyl chloride:vinyl alcohol:vinyl acetate) (91:3:6% by weight) resulted in microcapsules which were isolable as a free-flowing powder and were storable after drying. Using a dye marker in the core, the dried microcapsules were found to release the core contents through the spherical wall membrane in the presence of an exogenous aqueous medium. A technique was found for conveniently coating the dried microcapsules onto filter paper, and the partial constituents of an indicator system were encapsulated and coated onto filter paper pretreated with the complementary color-forming constituents. The rate of color development in the wetted paper–microcapsule system was used to assess the relative rate of release of the microcapsule core contents. Crosslinking of the poly(vinyl chloride) copolymer prior to encapsulation resulted in an attenuation of release of the microcapsule core contents.

INTRODUCTION

A number of synthetic preformed polymers have been utilized to encapsulate aqueous systems.[1,2] Some of these methods have employed the convenient technique of phase separation. Although the use of copoly(vinyl chloride:vinyl alcohol:vinyl acetate) (91:6:3% by weight) has been reported for encapsulation of aqueous materials,[3] the isolation and release properties of microcapsules prepared from this polymer have not been described. This paper addresses the isolation of these microcapsules as a free-flowing powder, prepared by the technique of organic phase separation, and describes some of the release characteristics of these capsules containing various core materials. In addition, a technique of coating these microcapsules onto filter paper is described. Using this technique, an indicating system can be formed by coating microcapsules containing some of the indicator system constituents onto filter paper pretreated with the complementary color-forming agents.

EXPERIMENTAL

Encapsulation of a Water-Soluble Dye Material

In a tall-form Erlenmeyer flask, 2.0 g of poly(vinyl chloride:vinyl acetate:vinyl alcohol) (91:3:6% by weight) (Polysciences Corp.) was added to 15 mL of hexane. The mixture was stirred at low speed using a Laboratory Dispersator (Model 2000, Premier Mill Corp.). After 5 min dichloromethane (150 mL) was added, and stirring continued for an additional 5 min, at which time a clear solution resulted. 20 g of a solution containing 1 g of Evans blue dye and 30 g of sodium

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chloride in 100 mL of water was then added. Stirring was increased to 4600 rpm, and after 5 min hexane (75 mL) was added to the stirred mixture at the rate of 3 mL/min. Phase separation of the microcapsules was completed after 25 min. The mixture was then added slowly to hexane (800 mL), which was stirred at low speed. After 15 min, the capsule walls had hardened sufficiently and the mixture was filtered under vacuum and washed with 100 mL of hexane. The resulting blue powder was dried under vacuum overnight, and the dried material was passed through a 210-μ sieve to eliminate the larger particles. The resulting crenated microcapsules containing the Evans blue dye were stored for later use.

Microcapsule–Paper Indicator System

The poly(vinyl chloride) copolymer described above (2.5 g) was used to encapsulate 10 g of a solution containing 1.25 g of *d*-glucose and 1.25 g of 3-methyl-2-benzothiazolinone hydrazone hydrochloride (MBTH) in 100 mL of water in the manner described above. The resulting colorless microcapsules were then coated onto filter paper which had been previously impregnated with an aqueous solution containing 1% chromotropic acid, 0.1% horseradish peroxidase, and 7% glucose oxidase and then dried. 1 g of dried microcapsules was dispersed into 5 mL of a 30% solution of poly(vinyl pyrrolidone) in isopropanol. This slurry was then coated onto the dried pretreated filter paper at a thickness of 8 mils using a doctor blade, and the coated paper was dried at 40°C for 5 min.

Crosslinking of Polymer

The poly(vinyl chloride) copolymer described above was crosslinked as follows: The copolymer (10 g) was suspended in 50 mL of toluene–petroleum ether (1:1) and treated with 1.0 mL of toluene-2,4-diisocyanate and the mixture was refluxed 2 h. The cooled mixture was treated slowly with 200 mL of petroleum ether, and the crosslinked polymer was filtered and washed with 100 mL of petroleum ether and dried under vacuum.

Measurement of Release Characteristics of Dye-Containing Microcapsules

Into each of four test tubes was placed 20 mg of dried microcapsules containing the Evans blue dye. To the first tube was added 5 mL of distilled water. The tube was covered with a piece of Parafilm and inverted gently every 10 s. At 25 s, the mixture was filtered by suction and the absorbance of the filtrate was immediately read at 585 nm against distilled water using a Spectronic 400 Spectrophotometer. This procedure was repeated for each successive tube using filtering times of 55, 115, and 175 s, respectively.

Measurement of Color Formation in Microcapsule–Paper Indicator System

Onto a 0.2 in. × 0.2 in. square of the microcapsule-coated paper was pipetted 15 μL of distilled water. The wetted paper was immediately placed in a scanning

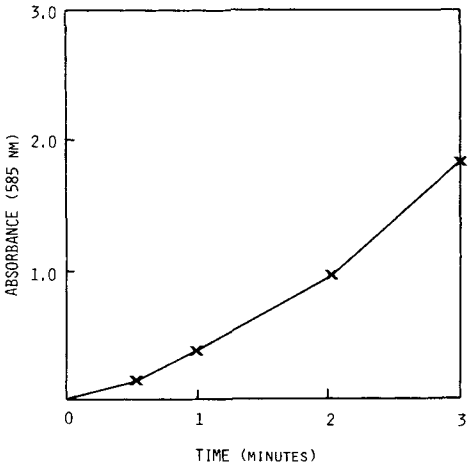

Fig. 1. Absorbance at 585 nm as a function of time for microcapsules containing Evans blue dye in distilled water.

reflectance spectrophotometer,[4] and reflectance was monitored at a wavelength of 560 nm.

RESULTS AND DISCUSSION

Release of Evans Blue Dye from Microcapsules

The rate of release of Evans blue dye from an aqueous suspension of the dried microcapsules is illustrated in Figure 1. The release rate of the dye appears to increase somewhat with respect to time as evidenced by the small increases in slope between successive measurement intervals. This corroborates the microscopic observation in which the dried, crenated microcapsules were observed to gradually swell and release the dye contents gradually into the surrounding aqueous medium. Rupturing or loss of integrity of the wall material subsequent to swelling was not observed, in spite of the presence of a high concentration of sodium chloride present in the core material, which provided a high osmotic gradient between the exogenous water and the capsule core. The core contents are likely released from within the capsule by the process of diffusion through the poly(vinyl chloride) copolymer capsule–wall matrix. Based on this observation, it appeared likely that the release rate of compounds from these microcapsules would be inversely proportional to the molecular size of the hydrated materials, and that a core material of sufficient size would be prevented from diffusion due to the pore size of the capsule–wall matrix.

Microcapsule–Paper Indicator System

The reaction involving oxidized 3-methyl-2-benzothiazolinone hydrazone (MBTH) with chromotropic acid to form a highly blue-colored complex[5] was utilized in this study. Visual observation showed that the blue color began to develop within several seconds after the colorless microcapsule-coated paper was wetted with water. Figure 2 shows the percent reflectance measured at 560 nm, the absorption maximum of the blue-colored complex over a 3-min period

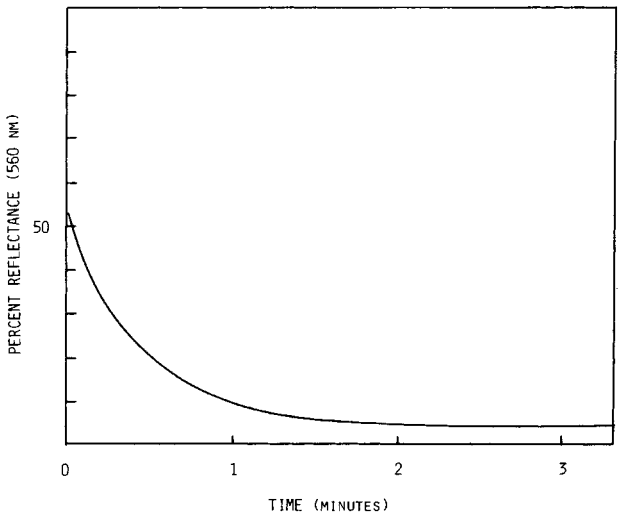

Fig. 2. Formation of color as a function of percent reflectance at 560 nm vs. time for microcapsule–paper indicator system.

subsequent to wetting of the coated paper. The bulk of the oxidized MBTH is released during the first minute after wetting of the microcapsule-coated paper. Although this study was done under different conditions than the study using the Evans blue dye, the MBTH appears to diffuse through the microcapsule wall at a rate faster than that of the Evans blue dye. This is not surprising, since the Evans blue dye molecule is of somewhat larger size than the MBTH molecule. The same study was repeated using the polymer which had been previously crosslinked using 2,4-toluene-diisocyanate. The result is illustrated in Figure 3, showing a somewhat slower release of the oxidized MBTH from the microcapsule core onto the pretreated paper. The crosslinking of the poly(vinyl

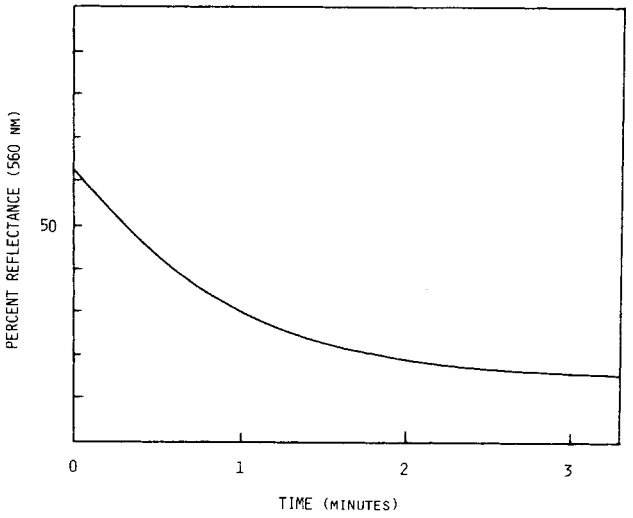

Fig. 3. Formation of color as a function of percent reflectance at 560 nm vs. time for microcapsule–paper indicator system using crosslinked microcapsules.

chloride) copolymer apparently results in a smaller pore size in the swollen matrix of the microcapsule wall, thereby slowing the rate of diffusion.

SUMMARY

Aqueous materials can be conveniently microencapsulated by the technique of organic phase separation using the poly(vinyl chloride) copolymer described above. The microencapsulated material can be isolated, dried, and stored for future use. The dried microcapsules can be coated onto filter paper to form an indicating system. The rate of release can be controlled to an extent by crosslinking of the polymeric material using a suitable crosslinking agent.

References

1. J. R. Nixon, *Microencapsulation*, Marcel Dekker, New York, 1976, p. 198.
2. J. Vandegaer, *Microencapsulation—Processes and Applications*, Plenum, New York, 1974, p. 4.
3. T. C. Powell, M. E. Steinle, and R. A. Yoncoskie, U.S. Pat. 3,415,758 (1968).
4. M. A. Genshaw and R. W. Rogers, *Anal. Chem.*, **53,** 1949 (1981).
5. R. H. White-Stevens and L. Stover, *Clin. Chem.*, **27,** 1101 (1981).

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