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LbL-Coated Microcapsules as Systems for Encapsulation of Optical Brightening Agent

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ABSTRACT: We report the encapsulation of optical brightening agent (OBA) into hollow microcapsules prepared by the controlled Layer- by-Layer (LbL) self-assembly process, achieved by the sequential adsorption of oppositely charged polyelectrolytes using negatively charged silica template. Loading takes place by spontaneous deposition method which was proved by confocal laser scanning microscopy (CLSM) using rhodamine 6G (Rd6G) as a fluorescent probe. The loading of the OBA into the microcapsules was found to be dependent on the feeding concentration, pH of the medium, and loading temperature. The encapsulation efficiency of OBA decreased on increasing feeding concentration. Maximum loading was observed at pH 4 and amount of OBA loaded decreased with increase in pH. The loaded OBA was released in a sustained manner for 8 h. No degradation of the OBA was observed during the process of encapsulation and release. Polyelectrolyte capsules potentially offer an innovative way of encapsulating large amounts of active materials for a variety of applications. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

KEYWORDS: polyelectrolyte microcapsules; encapsulation; optical brightening agents; layer-by-layer; silica microparticles

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INTRODUCTION

Optical brightening agents (OBAs) are dyes that absorb light in the ultraviolet and violet region (usually 340–370 nm) and re-emit light in the blue region (typically 420–470 nm). These additives are often used in the laundry formulations to enhance the appearance of color of textile,[1] causing a perceived whitening effect, making materials look less yellow by increasing the overall amount of blue light reflected. However, the performance activity of these actives (OBA) may be limited due to detergent matrix environment. Addition of various surfactants reduces the performance activity of this optical brightening agent. These changes are attributed to the interaction of surfactant micelle with dye molecules, resulting in change of the colored quinoid form to the colorless lactone form and vice versa. These OBA'S may also get degraded due to process conditions such as mechanical shear or may get degraded due to prolonged storage. Therefore, to solve the problems of instability of OBA's into formulations and during storage, it is essential to protect it from the environment. Microencapsulation of the actives is one of the most versatile and robust approaches to solve the problem of instability.

Layer-by-layer (LBL) assembly on sacrificial cores is a feasible technique to produce microcapsules having multicomponents.[2] Polyelectrolyte microcapsules draw tremendous interest because of their special structures, unique properties, and potential applications.[3,4] LbL approach is a facile method for the preparation of well-defined and highly uniform capsules. LbL method allows for precise control of the capsule structure and to freely choose the wall components for different possible applications. Besides the normal polyelectrolytes, various substances such as nanoparticles, proteins, lipids, etc. can also be incorporated into the system either on the capsule shells or within the capsules.[5]

The use of stimuli-responsive polyelectrolytes as constituents of multilayer shells results in the production of hollow responsive microcapsules that may be utilized for controlled loading and release. This method has proven especially useful for the encapsulation of large molecules such as enzymes, antibodies, and other proteins. Even small nanoparticles, such as magnetic or superparamagnetic nanospheres, have been successfully embedded in capsule walls. Factors such as pH,[6] salt,[7] temperature,[8] ionic strength, and solvent quality[9] can largely tune the electrostatic interaction, especially for weak polyelectrolytes, and thus can be utilized to modulate the permeability. The variation of the capsule properties is of great importance for the loading and release of desired functional materials, which is an indispensable step toward their applications.

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Prompted by fascinating properties of polyelectrolyte microcapsules, we encapsulated optical brightening agent into microcapsules based on sodium poly(styrene sulfonate) (PSS) and poly (allylamine hydrochloride) (PAH) as the counter charge polyelectrolytes and silica as the template. These capsules were characterized using confocal microscopy (CLSM) and scanning electron microscopy (SEM). Encapsulation of OBA in the (PAH/PSS)$_4$ PAH capsules was carried out as a function of pH, feeding concentration, temperature. Release of OBA from the capsules was performed as a function of pH.

EXPERIMENTAL

Materials

Poly(allyl amine) hydrochloride (PAH (M_w = 70 kDa), poly (styrene sulfonate (PSS (M_w = 70 kDa), rhodamine 6G (R6G), and hydrofluoric acid were all procured from Sigma-Aldrich, India and used without any further purification. Silica microparticles were purchased from "Microparticles GmbH," Germany. Commercially available optical brightening agent, a stilbene derivative with trade name Leucophore was received as a gift from Clariant Chemicals, Mumbai, India. Purified water (resistivity > 18 MΩ cm) from Milli-Q system was used in all experiments. A total of 0.1*M* HCl or 0.1*M* NaOH was used for the pH adjustments.

Preparation of Polyelectrolyte Microcapsules

A total of 2 mg/mL PAH and PSS solutions were prepared in 0.5*M* NaCl at pH 5. The silica particles were coated with the first polyelectrolyte layer by adding 1 mL of the above prepared PAH solution into a microcentrifuge tube which was mixed occasionally and incubated for 15 min, followed by centrifugation at 5000 rpm for 5 min. The supernatant containing the excess polyelectrolyte was removed by three washings and redispersion cycles with pH-adjusted water. The resulting cationic polyelectrolyte-coated silica particles were then coated with the second layer of opposite charged polyelectrolyte PSS by addition of 1 mL of anionic polyelectrolyte solution and incubated for 15 min. After the adsorption process, excess polyelectrolyte was removed by similar centrifugation and redispersion cycles as described above. Alternative deposition of cationic and anionic polyelectrolyte onto the silica particles was performed until the desired number, i.e., nine layers were achieved. The silica core was then dissolved using a HF/NH_4F buffer solution.[10] The capsules were washed at least six times with water at the same pH 5 to remove the excess HF, SiF_6^{2-}, and NH_4F solutions from the resulting hollow polymeric capsules.

Characterization Techniques

The extent of core dissolution and morphology of capsules was studied by SEM (FEI-SIRION, Eindhoven, Netherlands). A droplet of the aqueous capsule suspension was dried overnight on a silicon wafer in a desiccator at room temperature. Samples were analyzed after sputtering a thin gold layer of 10 nm. CLSM studies were carried out to determine the integrity and degree of filling of individual capsules on a Zeiss LSM 510 META confocal scanning system (Zeiss, Germany) using a aristoplan 100× oil immersion objective with numerical aperture of 1.4. To observe the spontaneous loading, a drop of capsule suspension was put on a thin glass slide, mixed with tiny amount of Rd6G and observed immediately at an absorption wavelength of 553 nm. ζ-potential of empty capsules after core dissolution was measured in triplicate at room temperature using the Zetasizer (Malvern Instruments, UK).

Loading of OBA into Polyelectrolyte Microcapsules

Microcapsule suspension containing 3 ± 0.2 × 10^8capsules/mL of water was centrifuged at 5000 rpm for 5 min and the supernatant removed. Then, 100 μL of the microcapsules were redispersed in 900 μL of OBA with different loading conditions such as pH and feeding concentration and incubated in a shaker at 25°C. After incubation for 2 h, the mixture was centrifuged at 3000 rpm for 8 min. The loading to volume ratio of microcapsules to OBA was maintained at 1 : 9 throughout the experiment. For temperature-dependent experiments, the same number of capsules were mixed with 0.9 mL OBA and incubated at required temperature for 2 h. The supernatant collected after the centrifugation was diluted over hundreds of times and analyzed using a spectrophotometer (ND1000, Nanodrop, USA) at a wavelength of 348 nm. The amount of the encapsulated OBA was then using the initial and final concentration of OBA. All the data are averaged from three parallel experiments.

Encapsulation Efficiency

Loading efficiency (E) was calculated using the following formula:

$$\text{Loading efficiency } (E) = \frac{[C_e]}{[C_f]} \times 100,$$

where C_e is the concentration of OBA encapsulated in mg/mL and C_f is the concentration of feeding solution in mg/mL.

Release Studies

Release studies were performed by incubating 1 mL of the OBA-loaded capsules in water at pH 7.5 and 9.5 in a shaker at 130 rpm and 37°C. A total of 0.6 mL of the supernatant was taken out at required time intervals, whilst supplementing the same volume of water to keep the total volume constant at 1 mL. The supernatant was diluted over hundreds of times and absorbance at 348 nm was recorded. The cumulative amount released and total OBA released was integrated from each measurement.

RESULTS AND DISCUSSION

Capsule Preparation and Characterization

Hollow polyelectrolyte multilayer capsules were fabricated by the electrostatic LbL assembly of polycation (PAH) and polyanion (PSS) onto colloidal silica templates (template removed after the desired self-assembly of layers). SEM studies were carried out with the hollow capsules after drying to study the extent of core dissolution and morphology of the dried capsules. Drying removes the water and causes the capsule wall to collapse. On comparison of SEM images of coated silica microparticle (Figure 1) and the hollow microcapsule (Figure 2), it can be concluded that the silica cores have been completely removed. Hollow capsules exhibited folds and creases that were typical for the capsules with ultrathin shells. Complete removal of core was

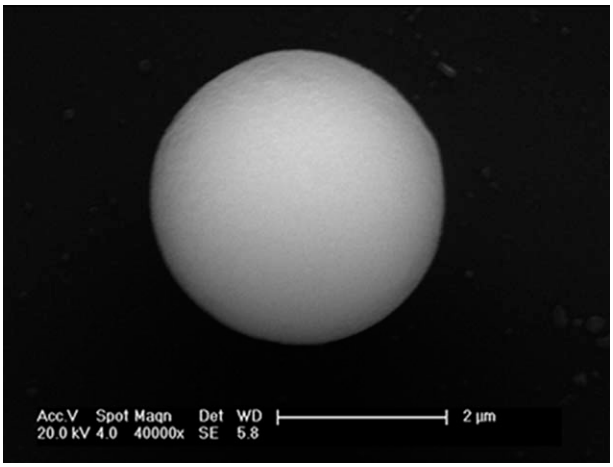

Figure 1. SEM micrograph of $(PAH/PSS)_4$ PAH-coated silica microparticle.

further confirmed by CLSM picture showing loaded R6G (Figure 3).

Encapsulation of OBA

The loading of water soluble substances into microcapsules is spontaneous process which was proved by loading R6G, which was loaded spontaneously and was homogeneously distributed inside the capsules as confirmed by the fluorescence cross section profiles shown in Figure 4.

To identify the encapsulation of OBA, the morphology of the microcapsules before and after OBA loading was compared by SEM. The loaded capsule (Figure 5) appeared thicker when compared with the empty one (Figure 2) due to the presence of OBA inside the capsule and within the capsule wall. The effect of charge on the outermost layer on loading was also examined. The loading was considerably higher when the capsule wall was positively charged, opposite to the charge of OBA (data not shown). Thus, the outermost layer determines the net charge distribution in the wall and hence the loading concentration.

The pH-controlled permeability was used to effectively encapsulate OBA. The capsules exhibited an open and closed state at

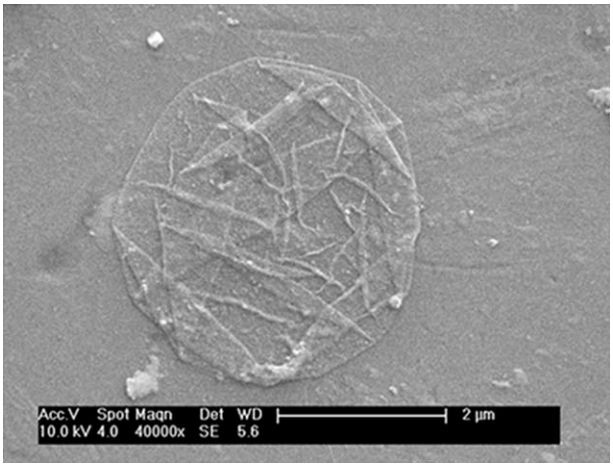

Figure 2. SEM micrograph of hollow microcapsule.

Figure 3. CLSM image of microcapsules loaded with R6G. Scale bar = 5 μm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

low and high pH, respectively, and capsules were intact from pH 3 to pH 10 as reported earlier by Sukhorukov et al.[11] Open and closed state refers to permeability of capsules. In an open state, pores are created on the wall of capsules as a result

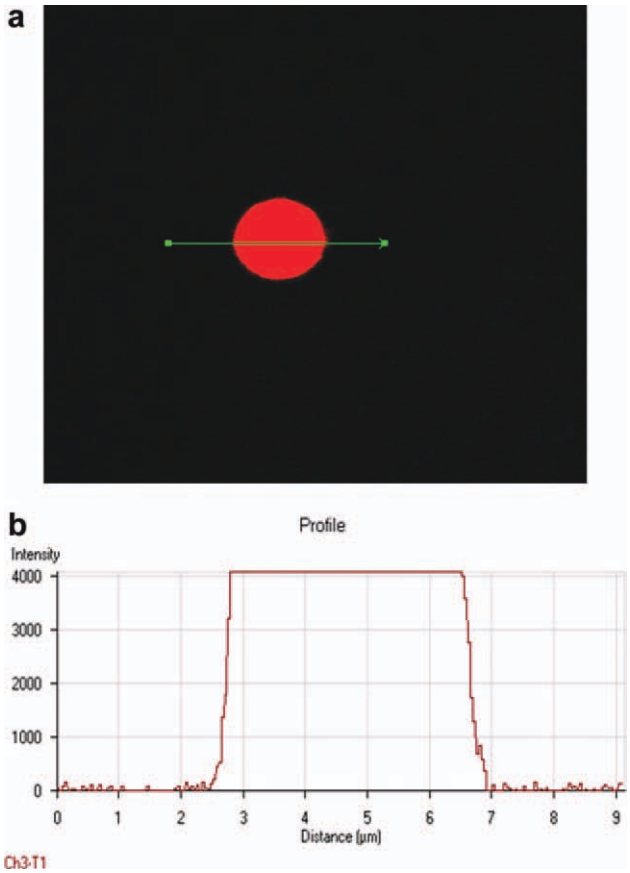

Figure 4. (a) CLSM image and (b) fluorescence profile of microcapsule at pH 4. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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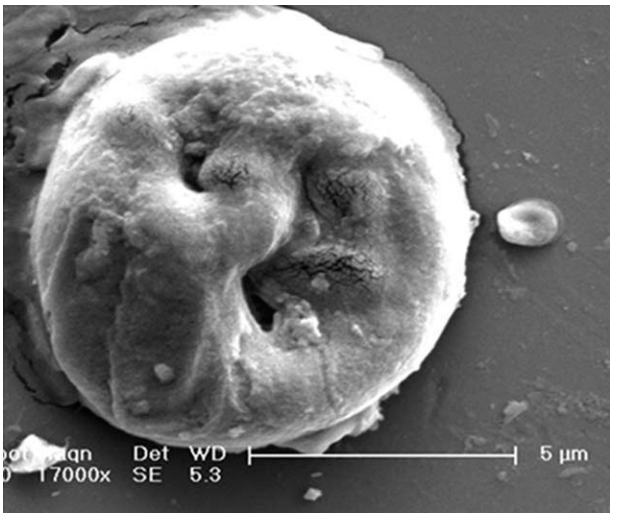

Figure 5. SEM micrograph of OBA-loaded microcapsule.

capsules become permeable, whereas in closed state pores are closed and capsules are impermeable. At acidic pH, the amino groups of PAH become protonated and result in local excess of positive charge thus inducing electrostatic repulsion. This in turn may destabilize the multilayers and cause the formation of defects or pores.[12] Whereas in basic pH, the charge of the capsule wall is reversed with change in pH, caused by the deprotonation of excess amino groups of PAH, this reduces the degree of electrostatic repulsion thus leading to compaction of the layers and closing of the pores. This is further supported by the fact that on increasing pH, zeta potential for $(PAH/PSS)_4$ PAH microcapsules decreased and became negative above pH 8.2, as shown in Figure 6. The permeability can be changed repeatedly leading the creation of pH responsive microcontainers. Hence, loading has been done at acidic pH.

The effect of pH on OBA loading concentration has been studied by varying the pH from 4 to 7 with 8 mg/mL feeding concentration and the result is shown in Figure 7. At pH 4, 17% of the OBA was encapsulated; however, OBA loading decreased with increase in pH. Only 7% was encapsulated at pH 6. This

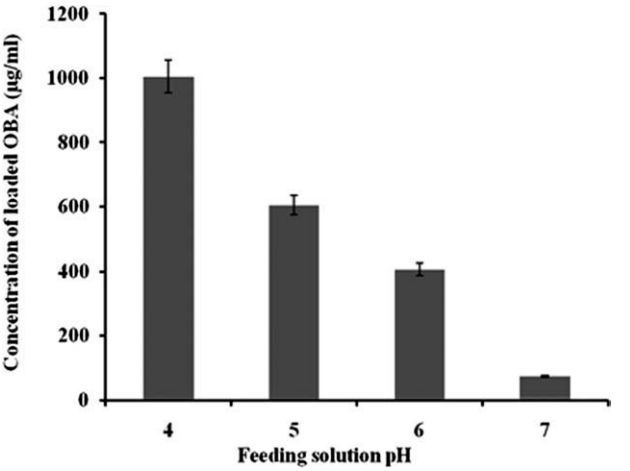

Figure 7. Effect of feeding solution pH on OBA loading into capsules.

behavior might be attributed due to pH-induced permeability. When the pH was increased, the electrostatic repulsion between polymer chains decreased which in turn decreased the pore size thus resulted in lower OBA concentration inside capsules.

When OBA concentration in the bulk solution was increased from 2 to 8 mg/mL, (Figure 8) the loading efficiency decreased from 34% to 17% and attained equilibrium loading (data not shown). This result confirmed that the loading of OBA was controlled by spontaneous deposition at lower feeding concentration, which is primarily an electrostatic phenomenon.[13] At higher feeding concentration, when the bulk OBA concentration was increased, loading concentration inside capsule increased. As a result, the ratio of interior to bulk concentration decreased and since diffusion of OBA is driven primarily by the concentration difference, loading efficiency decreased.

The temperature effect on the loading capacity is depicted in Figure 9. The loading percent increased gradually from 17 to 65%, when the loading temperature was increased from 25 to 50°C. Increasing temperature can have two effects on the OBA loading: enhancing the penetrating movement of OBA through

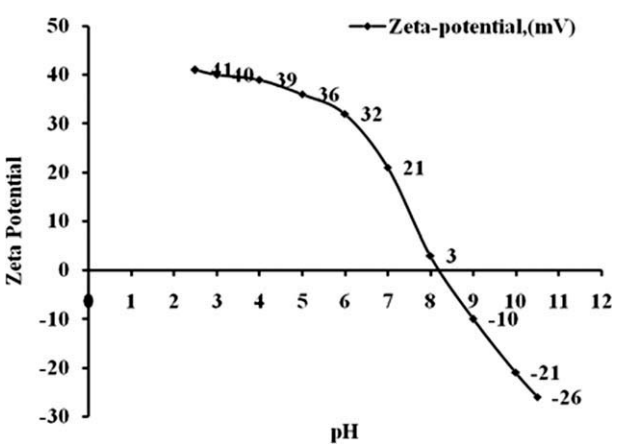

Figure 6. Zeta potential of $(PAH/PSS)_4$ PAH microcapsules as a function of pH.

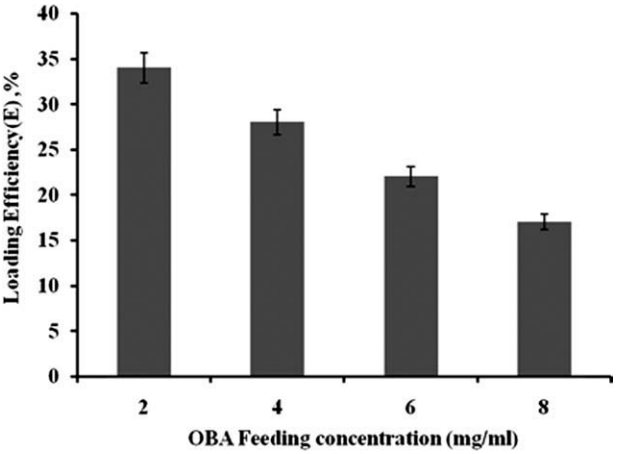

Figure 8. Effect of OBA feeding concentration on loading efficiency into capsules.

the PAH/PSS multilayer wall or rearrangement of the polymer chains in the shell to form more compact structure[14]; however, for the microcapsules loading for 2 h, the structure change of shell in relatively short time has little effect on OBA loading. The increasing temperature contributed to the movement of OBA through the multilayer wall of PAH/PSS microcapsules, so the drug loading increased.

Release of OBA

Once the deposition of OBA was successfully demonstrated and quantified, next objective was to release the encapsulated OBA, which is crucial for practical applications. To investigate the release behavior, experiments were carried out at pH 7.5 and 9.5 at 37°C and the cumulative percentage OBA released is shown in Figure 10.

The release profile has two separate regions, initial burst release in the first 1 h followed by a sustained release up to 8 h. Initial burst release can be attributed to two reasons (a) Initially, there is an imbalance between the capsule interior and the bulk which can lead to burst release[15] and (b) release of OBA present on the surface of microcapsules.[4] After the initial release, the concentration of OBA inside the capsule decreased which in turn reduced the concentration difference and hence the release rate.

A cumulative release of 58% at pH 7.5 and 65% at pH 9.5 was obtained at the end of 8 h in water. The OBA release was carried out in pH-dependent release pattern. With the increase of pH, the charge density of the PAH decreases due to deprotonation of amine groups. As a result, many charges in PSS/PAH systems are not compensated anymore hence an excess of negative charges are present due to PSS.[16] Furthermore, increase in pH results in swelling of multilayer followed by disintegration above pH 11 due to polymer chains repulsion.[17] Since, the OBA charge is negative, it preferentially moved into the solution from microcapsules due to electrostatic repulsion until the equilibrium was attained. The OBA release profile can also be demonstrated as a diffusion process due to difference in the dynamic balance between capsule interior and bulk concentration.[18] The encapsulated small molecules diffused out when the bulk concentration was decreased. Hence, pH change, which causes swelling of the layers, and dynamic concentration equilibrium acted simultaneously on the OBA-loaded microcapsule system which influenced the release of OBA from the capsules. The nature of released OBA was also examined spectrophotometrically and there appeared to be no difference in the structure of the OBA before and after encapsulation process (results not shown).

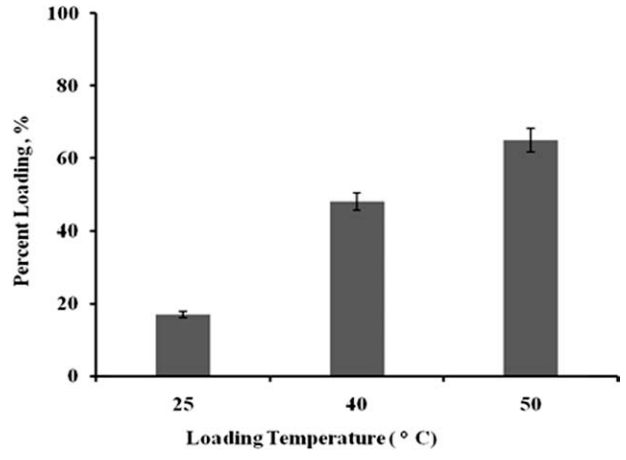

Figure 9. Effect of temperature on OBA loading into capsules.

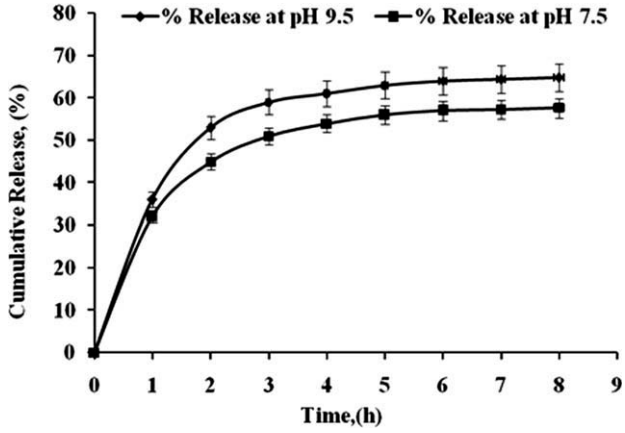

Figure 10. Cumulative release of OBA at different pH.

CONCLUSIONS

We have demonstrated the successful encapsulation of optical brightening agent into preformed $(PAH/PSS)_4$ PAH microcapsules prepared using silica microparticles as template. The encapsulation of OBA by LbL method was performed with an encapsulation efficiency of 34% at pH 4 and 2 mg/mL OBA concentration. A total of 65% of the encapsulated OBA was released in water in about 8 h. Initial release was rapid during the first hour followed by a sustained release upto 8 h. It was found that the chemical structure of the OBA was not altered during the encapsulation process. Thus, a novel method of encapsulation and release of OBA using polyelectrolyte multilayer capsules has been demonstrated.

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