Functional Materials Letters
Vol. 11, No. 4 (2018) 1850041 (4 pages)

DOI: 10.1142/S1793604718500418

World Scientific
www.worldscientific.com

Smart microcapsules for precise delivery systems

Anna Trojanowska
Departament d'Enginyeria, Química
Universitat Rovira i Virgili
Av. Països Catalans 26, Tarragona 43007, Spain

Centre Tecnològic de la Química de Catalunya
Carrer Marcelli Domingo s/n, Tarragona, 43007

Valentina Marturano
Institute for Polymers
Composites and Biomaterials (IPCB-CNR)
Via Campi Flegrei 34, Pozzuoli 80078, NA, Italy

Nuno A. G. Bandeira
Centre for Chemistry and Biochemistry, Faculty of Science
University of Lisbon, Campo Grande, Ed. C8, Lisbon, 1749-016, Portugal

Centro de Química Estrutural, Instituto Superior Técnico
Universidade de Lisboa, Av. Rovisco Pais
Lisboa 1049-001, Portugal

Institute of Chemical Research of Catalonia (ICIQ) - Avda. Països Catalans 16
Tarragona 43007, Spain

Marta Giamberini
Departament d'Enginyeria, Química
Universitat Rovira i Virgili
Av. Països Catalans 26, Tarragona 43007, Spain

Bartosz Tylkowski*
Centre Tecnològic de la Química de Catalunya
Carrer de Marcel·lí Domingo, Tarragona 43007, Spain

Departament d'Enginyeria, Química
Universitat Rovira i Virgili
Av. Països Catalans 26, Tarragona 43007, Spain
bartosz.tylkowski@ctqc.org

Received 19 February 2018; Accepted 21 March 2018; Published

Photosensitive microcapsules are important targets for medical, pharmaceutical, agriculture, consumer goods and chemical companies. In this study, we report the development of UV-sensitive capsules containing vanillin as a model encapsulated active material. Polyamide microcapsule shells containing azobenzene moieties in the main chain of the polymer were fabricated by oil-in-water interfacial polymerization method. Triggered perfume release and morphological variations of the microcapsule shell during UV light irradiation were observed by means of high-performance liquid chromatography (HPLC) and optical microscopy.

Keywords: Azobenzene; encapsulation; interfacial polymerization.

*Corresponding author.

Microcapsules are circular cross-section-shaped particles containing core material encompassed by a membrane wall.[1] According to Zhang and co-workers,[2] microencapsulation is a leading interdisciplinary research technology. The microcapsules' applicability for storage, transport and controlled release has been demonstrated in a number of publications and patents over a broad range of industries.[1,3,4] The goal and challenge of developing an effective delivery system is the controlled release of encapsulated materials. During the last decade several triggers such as: light, temperature, pH change, etc. have been applied by scientists to initiate microcapsule wall morphological changes. This includes changes in compactness and integrity to influence the shell permeability required for the release of encapsulated actives.[4] Microcapsules based on photo-responsive materials create new horizons spanning both industry and academic research, as they are capable of changing their micro-/nano-structures.[1,3] Furthermore, light-release provides numerous benefits over other external stimuli: (i) photons do not contaminate the reaction environment, (ii) the wavelength of excitation could be controlled by appropriate molecular design, (iii) the ease of scope and duration of excitation.[5] Surface science and environmental applications benefit particularly from the development of photo-triggered capsules, considering that light sometimes could be the only available trigger to drive the systems. Generation of photo-sensitive behavior in microcapsule shells by integration of photo-sensitive polymers, gold/silver nanoparticles or azobenzene-based dyes has been reported in literature.[1] For the first time, azobenzene was described by Prof. Mitscherlich in 1834,[6] but pioneer studies concerning a functional optical behavior of azobenzene, based on reversible *trans-cis* isomerization of the N=N bond upon photo-irradiation where reported by Prof. Hartley in 1937.[7] Since then this photochromic moiety has been extensively applied in the design of light-sensitive materials. In this paper, we report the preparation and characterization of photo-triggered microcapsules whose shells contain 4,4′-bis (chlorocarbonyl) azobenzene moieties in lightly-cross-linked structures. Vanillin, a well-known antioxidant compound which has been widely applied in the food industry as a conserving agent or a flavoring additive,[4] was selected as an encapsulated active. Its photo-triggered release can be simply detecting by a high-performance liquid chromatography (HPLC).[9] The photo-sensitive microcapsules were prepared by using a modified protocol of oil-in-water interfacial polymerization method developed and reported in our previous studies.[10] According to this protocol, first 22 ml of toluene (oil) phase containing 0.500 g of 4,4-bis (chlorocarbonyl) azobenzene, 0.007 g of 1,3,5-benzenetricarbonyl trichloride (Aldrich, 98%) and 3 g of vanillin (Sigma-Aldrich, 99%) was prepared. Then, to get an oil-in-water emulsion, the oil phase was slowly added dropwise into 50 ml of aqueous solution containing 0.500 g of Mowiol emulsifier (polyvinyl alcohol 18-88, Fluka) under an overhead stirrer set up at 1200 rpm. Obtained emulsion was additionally mixed for 10 min at room temperature. Next, to form the capsules' shell, the interfacial polymerization was initiated by adding to the system 25 ml of aqueous solution containing 0.250 g of 1,8-diaminooctane (Fluka, 98%), 0.290 g of sodium hydrogen carbonate (Aldrich, 99.7%) and 0.250 g of Mowiol. The reaction was carried out in darkness at room temperature for 3 h. Finally, it was stopped by adding 50.00 g of aqueous solution containing 6.00 g of sodium sulfate and 0.35 grams of xanthan gum (XG). Formed suspension was mixed for 30 min at 300 rpm in darkness. The XG was used to avoid microcapsules' aggregation.

Figures 1(a) and 1(b) show the surface and cross-section morphologies of the prepared photo-sensitive microcapsule, respectively. The micrographs were recorded by a scanning electron microscopy ESEM (Quanta 600, FEI). The outer surface of the microcapsule appears dense and well-shaped. The cross-section imagine indicates a non-porous, homogenous membrane structure. The microcapsule main size diameters (42.8 μm) as well as their wall thicknesses (67 ± 3 nm) were measured from the ESEM micrographs using an Image-ProPlus 5® software. It is worth to note that 90% of the capsule diameters were in the range between $23 \pm 2\,\mu$m and $62 \pm 2\,\mu$m. This range is comparable with the size of the polyamide microcapsules prepared by interfacial polymerization reported in the literature.[11] In order to demonstrate the consequence of the UV light irradiation on the microcapsules morphology, the obtained capsules were exposed to UV light at 365 nm emitted from a Vl-4.LC UV Vilber Lourmat lamp (230 V, 8 W).

Figure 2 shows how the microcapsule shapes changed after their exposure to UV light for 1 h. Extreme differences between the micrographs, captured by an optical microscopy, are encountered. Irradiated microcapsules look almost empty and deflated, while those which were kept in darkness have maintained their orbicular-shape. These results suggest that

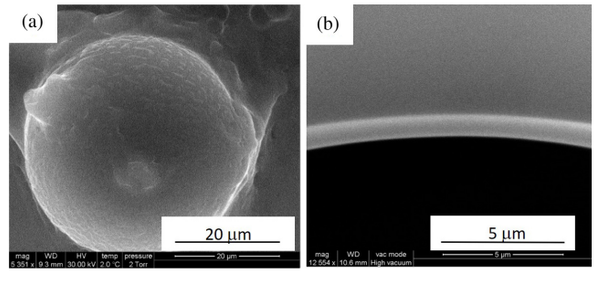

Fig. 1. ESEM micrographs of: (a) Polyamide microcapsule containing vanillin in toluene as a filler; (b) A cross-section morphology.

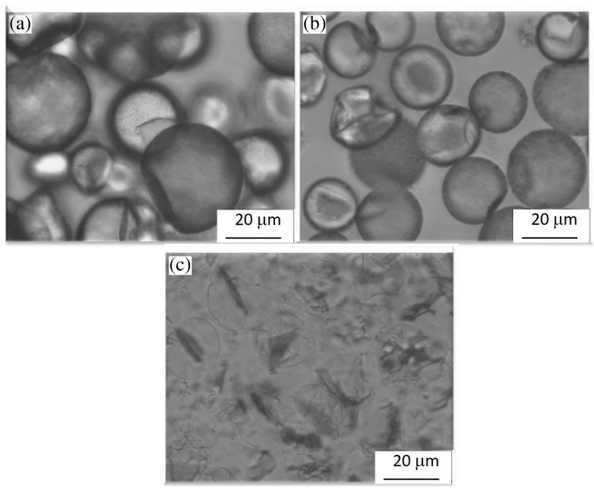

Fig. 2. Optical micrographs of: microcapsules containing vanillin as a filler, after preparation (a), after 7 days of storage in darkness (b), and after 1 h of irradiation with UV lamp at 365 nm (c).

the photo-triggered release from the microcapsules took placed due to the azobenzene *trans-cis* isomerization. In pioneer studies Higuchi and co-workers[12] demonstrated that the photo-isomerization of azobenzene molecules (MAzoM) incorporated in a main chain of polypeptide monolayer causes a decrease of the monolayer surface from 1395 Å to 1316 Å/azo-molecule. The authors have shown that the MAzoM became contracted owing to the banding shape upon the UV light irradiation. In our studies, we wish to put into evidence that the photo-simulated geometrical changes of azobenzene moiety of MAzoM can be amplified into the macroscopic structural change of microcapsule. Very recently, we published a paper in which the release mechanism is described.[13]

Upon irradiation and photo-conversion of trans-MAzoM to cis-MAzoM, the chain length of the polymer contracts by 5 Å thereby creating a squeezing effect in the backbone of the microcapsule.

Moreover, in order to unequivocally prove the triggered release of the encapsulated active materials in the presence of UV light, 1 g of the prepared capsules' suspension was mixed with 80 mL of milliQ water, stirred at 700 rpm and non-stop UV is irradiated up to 2 h. The amount of the discharged vanillin in the release medium was verified every 30 min using an Agilent 1100 HPLC equipped with a LC-8 supelcosil column and a photodiode array detector. Vanillin concentration was determined using a 80:20 water : acetonitrile mobile phase, showing a typical vanillin retention time (4.2–4.5 min) at 229 nm.

Figure 4 demonstrates the vanillin release from the photo-sensitive polyamide azobenzene-based microcapsules in milliQ water in the absence (♦) and presence (■) of UV light. The graph shows the amount of vanillin (ppm) released from 1 g of microcapsules during their continuous illumination with UV light at 365 nm. The difference between the two curves is obvious: in the absence of UV light, vanillin release practically does not occur; while after 1.5 h of non-stop irradiation, its discharge through the capsule shells is detectable. Bogdanowicz and co-workers have investigated vanillin delivery from the photo-sensitive microcapsules based on poly (α-methylstilbenesebacoate-co−α-methylstilbeneisophthalate).[4] The authors reported that during capsules irradiation with UV light, their surface morphology changed drastically, and vanillin started to be released after ca. 20 min of

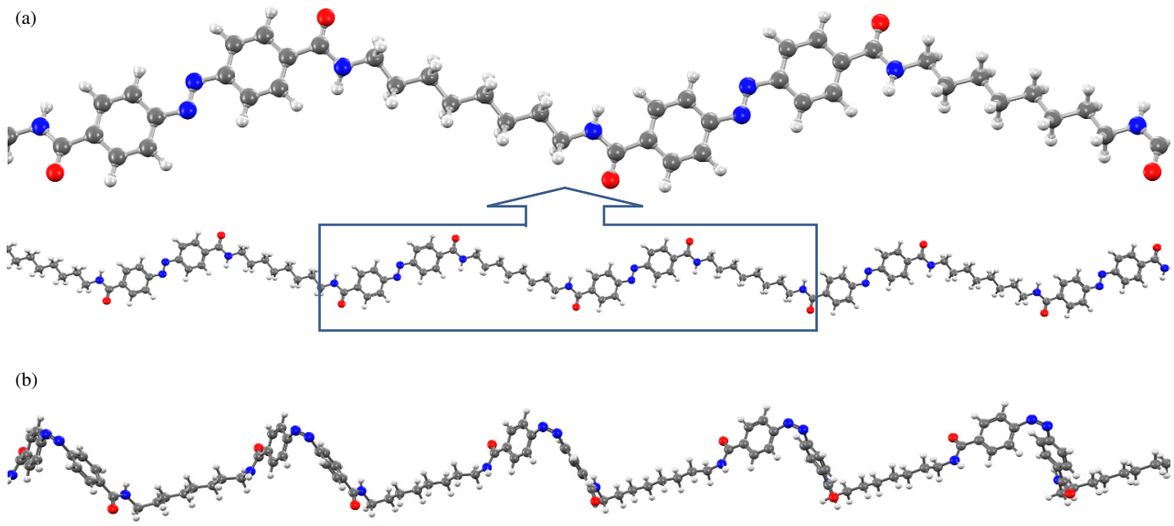

Fig. 3. Periodic models of trans (a) and cis (b) MAzoM.

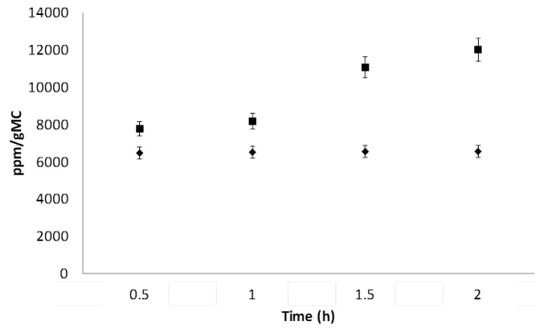

Fig. 4. Release kinetics of vanillin from photo-triggerd microcapsules in aqueous slirry at 20°C in the absence (♦) and in the presence (■) of non-stop exposure to UV light.

irradiation. In our opinion, the irradiation time required for vanillin delivery to a medium depends on: (i) type of photo-sensitive chromophore incorporated in the capsule walls, (ii) shell morphology and (iii) source of light.

In summary, this work demonstrates that the incorporation of photo-sensitive azobenzene moieties into the polyamide microcapsule walls can be used to drive a controlled release of encapsulated materials under UV light. The obtained photo-triggered capsules could find potential applications in: catalysis; electronics; textile; chemical industry, etc.

Acknowledgments

Financial support from the People Programme (Marie Curie Actions) of the Seventh Framework Programme of the European Union (FP7/2007–2013) under REA Grant Agreement No. 600388 (TECNIOspring programme), and from the Agency for Business Competitiveness of the Government of Catalonia, ACCIÓ, are gratefully acknowledged by Dr. Tylkowski.

References

1. M. Giamberini, S. F. Prieto and B. Tylkowski (eds.), *Microencapsulation Innovation Applications Computations* (DeGruyter, Berlin, 2015).
2. J. Zhang *et al.*, *Science* **335**, 690 (2012).
3. V. Marturano *et al.*, *Polymers* **9**, 1 (2017).
4. K. A. Bogdanowicz *et al.*, *Langmuir* **29**, 1601 (2013).
5. S. J. Pastine *et al.*, *J. Am. Chem. Soc.* **131**, 13586 (2009).
6. E. Mitscherlich, *Ann. Phar.* **12**, 305 (1834).
7. G. S. Hartley, *Nature* **140**, 281 (1937).
8. B. Tylkowski *et al.*, *Coord. Chem. Rev.* **351**, 205 (2017).
9. C. Panisello *et al.*, *Ind. Eng. Chem. Res.* **52**, 9995 (2013).
10. V. Marturano *et al.*, to appear in *Nano Res.*, https://doi.org/10.1007/s12274-017-1908-5.
11. Tylkowski *et al.*, *Eur. Polym. J.* **45**, 1420 (2009).
12. M. Higuchi *et al.*, *Colloid Polym. Sci.* **273**, 1022 (1995).
13. A. Trojanowska *et al.*, *App. Surf. Sci.* (2018), doi: 10.1016/j.apsusc.2018.03.061.