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Fluorescent probes based on chemically-stable core/shell microcapsules for visual microcrack detection

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ABSTRACT

Core/shell microcapsule-based fluorescent probes are presented in this work for potential use as early visual detection tool of microcracks in structural materials. A new microcapsule-based system is developed consisting of a UV-screening polyurea shell containing a fluorescent liquid core. The UV-screening functionality allows to prevent unwanted fluorescence emission from intact microcapsules upon UV-light exposure and yields excellent visibility contrast of the locally damaged region where fluorescent liquid core released from ruptured microcapsules is present. In addition, by carefully tuning the chemical composition of the shell material, microcapsules with enhanced chemical stability can be formed, as demonstrated by their superior solvent resistance over dwell time originating from the highly crosslinked shell structure that prevents core extraction from the microcapsules. A thorough chemical, thermal, morphological and optical characterization combined with a functional demonstration of the damage visualization capabilities of this new microcapsule-based system highlights its potential as a highly chemically-stable damage sensor for microcrack detection in structural materials.

1. Introduction

The lifetime of structural materials strongly depends on their mechanical integrity at the microscopic scale. For this reason, detection of microcrack-induced damages represents a key topic in a variety of engineering and industrial fields. At present, several nondestructive techniques are employed for sensing or probing the presence and propagation of microcracks in materials, including acoustic and ultrasonic methods, magnetic fields and radiographic testing [1–3]. However, all these approaches often require the use of expensive instrumentation and they cannot be easily applied *in situ*. As opposed to these damage sensing techniques, visual inspection methods represent an alternative approach that is characterized by high versatility and ease of use also by non-specialized personnel [4]. Most visual inspection methods currently rely on the use of appropriately developed mechanochromic smart materials, which are able to convert a mechanical stimulus into a definite and measurable chromatic response that can be monitored non-invasively also at a distance from the material [5–7]. Among the several examples of mechanoresponsive polymeric materials appeared in the literature in the past decades [8–11], those based on core/shell microcapsules are the nearest to commercialization as they can in principle be easily embedded into any type of coating formulation without significantly altering their functional properties [12–15].

Recently, crack detection by the use of microcapsules containing fluorescent dyes has been proposed as an effective strategy to inspect structural damages at the microscopic scale on a variety of engineering materials. In this context, one interesting approach made use of a fluorescent species (4,4'-diamino-2,2'-stilbenedisulfonic acid) microencapsulated in a melamine-urea-formaldehyde shell containing a healing agent (*endo*-dicyclopentadiene or 5-ethylidene-2-norbornene) [16]. The resulting multifunctional system was shown to be effective in both damage visualization and mending when dispersed in an epoxy resin serving as the carrier matrix. Very recently, polyurea-formaldehyde microcapsules containing a fluorescent fluid based on perylene and naphthalimide dyes have been also developed and tested as sensors for the detection of microcracks in cementitious materials [17]. While promising, these very preliminary approaches are still fundamentally limited by the transparency of the shell material to UV light, which determines that both broken and intact microcapsules (though with different emission inten-

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sities) are detected upon UV exposure. This behavior is clearly disadvantageous in terms of technological applicability of this system due to the relatively poor visibility contrast in the proximity of the localized crack. Therefore, these systems typically need to be combined with dark topcoats that prevent UV photons from penetrating the shell of intact microcapsules and exciting the encapsulated UV-sensitive fluorescent dye.

In addition to the optical properties of the shell, another key aspect for the successful incorporation of any type of core/shell microcapsule into coating materials is represented by the need of ensuring a sufficiently high chemical stability of the shell so as to prevent undesired release of the core material upon diffusion through the shell wall. Indeed, in several practical applications (e.g., solution-processing of polymer-based composites in the coating field) microcapsules are often exposed to harsh environments such as the presence of strong solvents (often combined with high processing temperatures). In particular, for damage sensing applications, the preparation and final use of microcapsules may entail their prolonged interaction with solvent media that typically act as diluting agents in several coating systems. In these circumstances, the shell wall can undergo partial chemical dissolution, and diffusion of the core material towards the dispersing medium can be significantly accelerated. This behavior causes a substantial loss of the functionality of the microcapsules prior to their actual use and results in a significant worsening of the damage visualization capabilities of the microcapsule-based composite system. Notwithstanding the importance of preserving the prolonged chemical integrity of microcapsules in such conditions, only a relatively small number of reports has tackled this fundamental technological issue [18–21]. In particular, these works have focused on the application of additional layers to the microcapsule outer shell in the form of extra-wall material [18,19] or protective coating [20,21], thus relying on the need of additional synthetic steps after microcapsule preparation to impart improved stability to the microcapsule system. On the contrary, the straightforward preparation of intrinsically robust microcapsules with superior chemical resistance to solvent attacks would be highly desirable, in view of their direct use as multifunctional damage sensing platform for coating applications.

In this work, core/shell microcapsule-based fluorescent probes are presented for potential use as early visual detection tool of damages in structural materials. Based on previous studies by our group [22], a new microcapsule system is developed here consisting of a UV-screening polyurea shell containing a fluorescent liquid core. The UV-screening functionality allows to prevent unwanted fluorescence emission from intact microcapsules upon UV-light exposure and yields excellent visibility contrast of the locally damaged region where fluorescent liquid core released from ruptured microcapsules is present. By carefully tuning the chemical composition of the shell material, significantly improved chemical stability of the newly prepared microcapsules can be achieved compared to previous systems, as demonstrated by their superior solvent resistance over dwell time. A thorough chemical, thermal, morphological and optical characterization combined with a functional demonstration of the damage visualization capabilities of this new microcapsule-based system highlights its potential as a highly chemically-stable damage sensor for smart coating applications.

2. Experimental

2.1. Materials

Gum arabic (GA), 2-amino-5-chlorobenzophenone (ACBP), 4,4′-Diaminobenzophenone (DABP), chlorobenzene (CB), dimethylformamide (DMF), petroleum ether, 1′,3′-dihydro-1′,3′,3′-trimethyl-6-nitrospiro[2H-1-benzopyran-2,2′-(2H)-indole] (SP) and all reagents and solvents for the synthesis of the fluorescent dye were all purchased from Sigma–Aldrich (Italy) and used without further purification. Sunflower oil was kindly provided by Benasedo S.p.A. (Italy), Desmodur L-75 (aromatic polyisocyanate prepolymer) by Bayer Materials Science (Germany) and Fluorolink® P56 was obtained from Solvay Specialty Polymers (Italy).

2.2. Synthesis of the UV-screening microcapsules

The synthetic procedure used in this work to produce UV-screening polyurea-based microcapsules is partly based on a previous work carried out in our group [12]. Briefly, 120 mL of deionized water and 13.5 g of GA were mixed in a flanged glass reactor equipped with a jacketed external thermal recirculation system and allowed to mechanically stir at 500 rpm for 3 h. During this time, the shell and core precursor solutions were prepared. To investigate the effect of shell composition on the chemical stability of the synthesized microcapsules, two different shell types were examined, namely ACBP-based and DABP-based microcapsules. To this end, 1.52 g of DABP (3.53 g of ACBP) was dissolved in 5 mL of DMF (15 mL of CB) under magnetic stirring. Similarly, Desmodur L-75 (9.0 g) was dissolved into 10 mL of dry CB and maintained in a nitrogen atmosphere to avoid moisture uptake. For the preparation of the core precursor solutions, the chosen chromophore was added to sunflower oil (0.35 g/40 mL) and magnetically stirred until a homogeneous mixture was achieved. The previously prepared Desmodur L-75 and core material solutions were gently poured into the stirring GA solution, and the mixture was heated up to 50 °C. Successively, the amine solution (ACBP or DABP) was slowly added to the stirring emulsion, the temperature was raised to 70 °C and the reaction was allowed to proceed for 1 h. After completion, the emulsion was cooled down to ambient temperature and the microcapsule suspension was separated from the mother liquor and left to settle overnight. Finally, the recovered microcapsules were washed repeatedly with deionized water and then with *n*-hexane before being vacuum-dried for 24 h prior to use. The average yield was ~70 wt%.

2.3. Synthesis of the fluorescent dye (VPy)

1-Vinyl-Pyrene (VPy) was synthesized by standard Wittig reaction between the commercially available 1-Pyrene-carboxaldehyde and methyltriphenylphosphonium Iodide (this salt was prepared as reported in literature [23]). In a 100 mL round bottom flask, methyltriphenylphosphonium iodide (1.23 g, 3.06 mmol) was dissolved in 15 mL of dry THF (tetrahydrofuran) then the mixture was cooled to 0 °C and potassium *t*-butyl oxide (0.43 g, 3.80 mmol) was added; the mixture was stirred for 30 min at this temperature. Then, 1-Pyrene-carboxaldehyde (0.59 g, 2.55 mmol) was added and the mixture was stirred at room temperature for 4 h. The mixture was quenched with water and then extracted with ethylacetate. The organic layer was dried on Na_2SO_4 and the solvent was removed at reduced pressure. The crude product was purified by flash chromatography on silica gel eluting with hexane/dichloromethane 4:1. A yellow solid was obtained in 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.41 (d, J = 9.3 Hz, 1H), 8.26–8.16 (m, 5H), 8.13 (d, J = 9.3 Hz, 1H), 8.034–8.00 (m, 2H), 7.82 (dd, J_1 = 10.99 Hz, J_2 = 17.31 Hz, 1H), 6.02 (d, J = 17.31 Hz, 1H), 5.64 (d, J = 10.99 Hz, 1H).

2.4. Characterization of microcapsules

Optical microscopy (Olympus BX-60 reflected-light optical microscope equipped with an Infinity 2 digital camera) was used to investigate the morphology and the surface features and to deter-