

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.

Keywords:

Fluorescence, microcapsules, chemical stability, damage sensing, polyurea, UV-screening.

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 intensities) 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) were 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 Na₂SO₄ 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. ¹H NMR (400 MHz, CDCl₃): 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 determine the average diameter of the synthesized microcapsules, the latter obtained from datasets of at least 300 measurements. To evaluate the internal and external morphology of the synthesized microcapsules and to measure the shell wall thickness, scanning electron microscopy (SEM) was employed (Carl Zeiss EVO 50 Extended Pressure, with an accelerating voltage of 15.00–17.50 kV). Fourier-transform infrared (FTIR) spectra of the microcapsules and their components were collected using a Nicolet 760-FTIR spectrophotometer at room temperature in air in the 4000–400 cm⁻¹ wavenumber range, with 64 accumulated scans and a resolution of 2 cm⁻¹. FTIR spectra were acquired in transmission mode on films cast on KBr disks (for liquid samples) or on solid pellets obtained by dispersing the sample in dry KBr powder (for solid samples). Thermogravimetric

analysis (TGA) on the microcapsules was performed by means of a Q50 TGA system (TA Instruments) by testing the samples from 0 to 600 °C at a rate of 20 °C/min in air. Differential scanning calorimetry (DSC) was carried out on a Mettler–Toledo DSC 823E instrument, indium and n-hexane calibrated. A heating scan from 0 to 400 °C was performed at a rate of 10 °C/min in a N₂ environment.

2.5. Determination of the core fraction of microcapsules

A given amount of synthesized microcapsules was thoroughly crushed with a pestle in a mortar and subsequently transferred to a glass container filled with petroleum ether. After resting for 24 h at room temperature, the mixture was carefully filtered on filter paper and the container was completely rinsed with additional petroleum ether to collect all the residual solid material. Upon complete evaporation of the solvent (petroleum ether), the final mass of the extracted core material (i.e., sunflower oil) could be measured and the microcapsule core fraction X_c could be calculated as $X_c = m_c/m_i$, with m_c and m_i being the final mass of the extracted core and the initial mass of microcapsules, respectively. It was concluded that the type of amine used in the synthesis (ACBP vs. DABP) did not affect the final core weight fraction which was found to be 70% for all microcapsule types.

2.6. Chemical resistance of microcapsules

The chemical resistance of the synthesized polyurea microcapsules was evaluated by prolonged immersion in different solvents, namely methanol (MeOH) and butyl acetate (BuOAc). 1,5 mg of microcapsules (ACBP-based and DABP-based systems, separately) were immersed in 10 mL of solvent, then the UV-vis spectra of the solvent medium were recorded at fixed time intervals up to 60 min. For ease of visualization, the model SP-chromophore was used as the encapsulated dye, because of its favorable optical properties. In particular, two distinct peaks can be observed in the UV-vis spectrum of SP at 266 nm and 345 nm (see Supporting Information). In this study, the peak at 266 nm was used for monitoring the core release rate upon solvent extraction, as this peak can be directly related to the absorbance of the spiropyran species. Following what reported in the previous Section 2.4, the core weight fraction was assumed to be 70% for all samples. This value gives an indication of the maximum amount of core material that can be released from the microcapsules upon immersion in the solvent. By knowing the amount of encapsulated core material, the maximum concentration of chromophore in the selected solvent could be evaluated, corresponding to its complete leakage from the microcapsules into the solvent. To this end, a 1 wt.% SP-dye solution in sunflower oil (the same concentration of SP-dye in oil used for microcapsules synthesis) was prepared and dissolved in the selected solvents so as to obtain a reference solution characterized by a final concentration of dye in solvent equal to the maximum concentration achievable in case of complete core release from the microcapsules under test (0.09 mg/ml, following the discussion reported above). The concentration of chromophore released from the microcapsules at a given time could be evaluated based on the absorbance value of the solvent medium at increasing microcapsule immersion times. Calibration curves (absorbance vs. concentration) were obtained with four solutions of different known concentrations of SP/oil in either MeOH or BuOAc. The correlation coefficient of such calibration curves was 0.99. UV-vis spectra were collected at

room temperature in the 250-700 nm wavelength range, using an Evolution 600 UV-vis spectrophotometer (Thermo Scientific). A liquid cell of 1 cm path length with quartz windows was used.

2.7. Preparation of the crack detection coating system containing microcapsules

For crack detection experiments, a polyurethane-based coating formulation (Fluorolink P56) was used as the carrier matrix to prepare the microcapsule-containing smart coating system. DABP (ACBP) microcapsules filled with VPy were poured into a beaker containing the polyurethane formulation and magnetically stirred until a homogenous dispersion was obtained (microcapsule concentration was 20 wt.% with respect to the dry polyurethane). The liquid formulation was cast onto a carbon fiber reinforced polymer substrate and allowed to dry in air. The thickness of the resulting coating was approximately 200 μm .

3. Results and discussion

3.1. Synthesis and characterization of microcapsules

The synthetic procedure used to prepare the new UV-screening microcapsules containing fluorescent core is schematically depicted in Figure 1. The microencapsulation process took place in an oil-in-water emulsion where the liquid core (sunflower oil containing the fluorescent molecule) was encapsulated within a polyurea-based shell resulting from the interfacial reaction between a polyisocyanate prepolymer (Desmodur L-75) based on toluene-diisocyanate (TDI) and a benzophenone-based diamine (DABP).

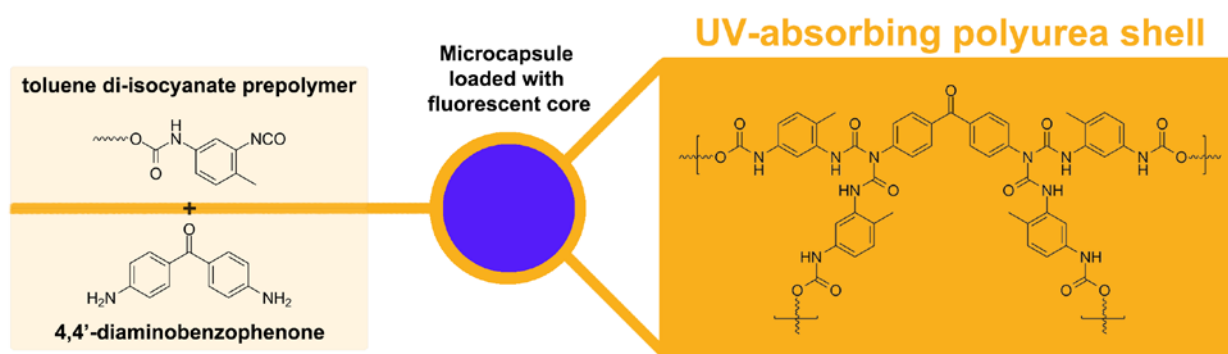


Figure 1. Schematic representation of the reaction occurring during microcapsule shell formation, in which the liquid core is encapsulated within a polyurea-based shell resulting from the reaction between a TDI-based polyisocyanate prepolymer (Desmodur L-75) and an aromatic diamine (DABP). The reaction takes place at the interface between the oil and the water phases.

A preliminary characterization of the obtained microcapsules was performed to evaluate their dimensions, size distribution and morphological properties. The determination of the mean diameter of the synthesized microcapsules was carried out making use of optical microscopy (Figure 2a) from datasets of at least 300 measurements. As reported in Figure 2b, diameters falling within the 50-400 μm range were found after the microencapsulation process, with a size distribution centered in the 50-100 μm interval. These dimensions are compatible with the use of such microcapsules in functional coatings [24]. SEM analysis was employed

to evaluate the morphological and surface features of the microcapsules. As shown in Figure 2c, the microcapsules are typically characterized by a spherical shape. In addition, the outer shell surface appears rather smooth and uniform, irrespective of the microcapsule diameter. As evident from Figure 2d, the average wall thickness was found to uniformly fall within the 3-5 μm range, while no particular correlation between the wall thickness and microcapsule diameter was observed. Both inner and outer shell surface appeared relatively rough, likely due to the presence of accumulated core material released from the microcapsules upon rupture prior to SEM analysis.

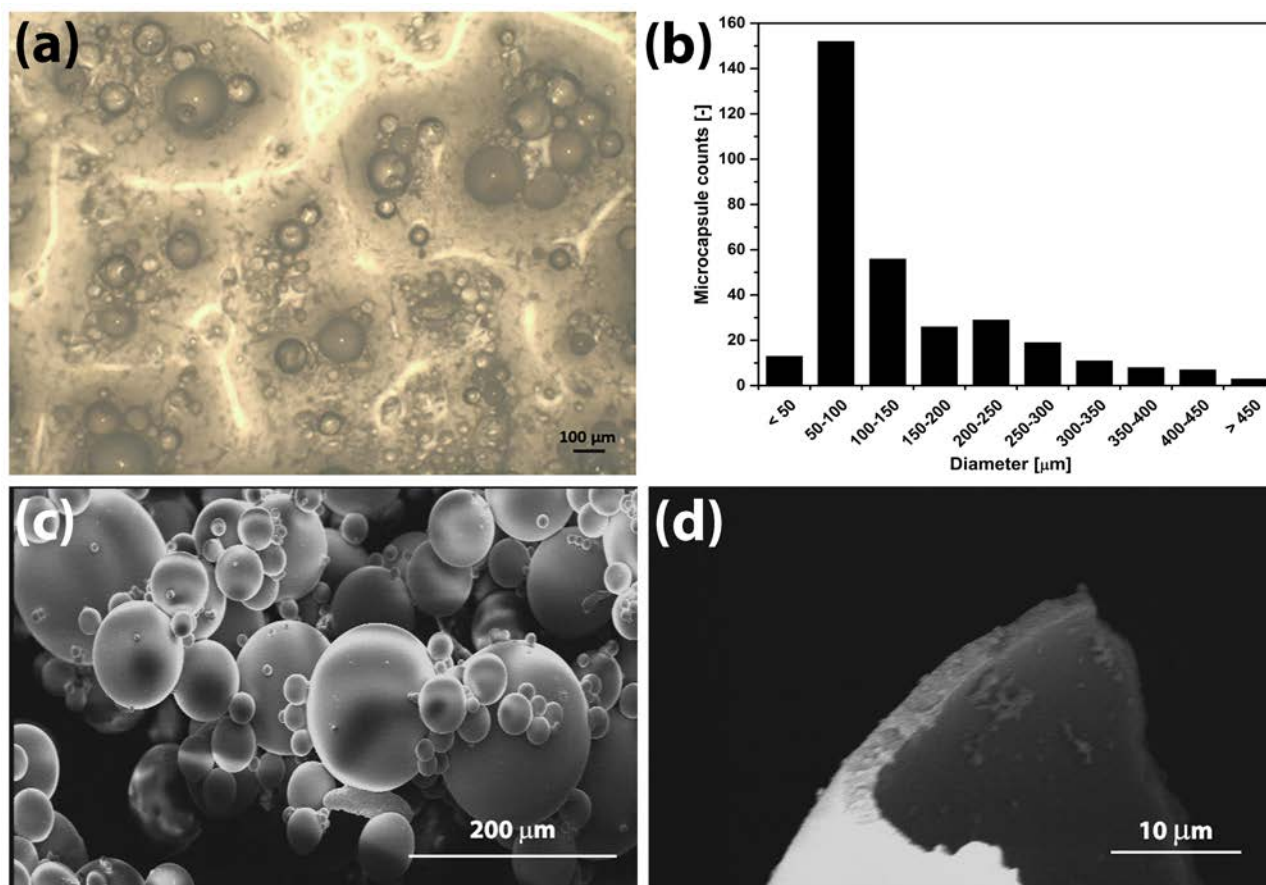


Figure 2. (a) Optical micrograph of the DABP-based microcapsules synthesized in this work, (b) their size distribution, (c) SEM image of the same microcapsules, (d) zoom on the shell wall thickness.

The microencapsulation process was chemically characterized by collecting FTIR spectra of the as-formed microcapsules and by comparing them with the FTIR spectra of the main microcapsule constituents. As shown in Figure 3, complete disappearance of the $\text{N}=\text{C}=\text{O}$ stretching signal (2270 cm^{-1}) attributable to the polyisocyanate prepolymer was observed in the microcapsule shell material, giving a first clear evidence of successful reaction between the NH_2 groups present in DABP and the NCO group in Desmodur L-75 with subsequent formation of the urea bond. In addition, the characteristic peaks of polyurea-urethane could also be easily identified in the FTIR spectrum of the microcapsule shell. In particular, the typical signals attributed to N-H stretching vibrations in the urea/urethane bond were found at 3318 cm^{-1} . In addition, a broad band centered at 1724 cm^{-1} was observed in the carbonyl region accompanied by a shoulder at 1622 cm^{-1} . These two signals are characteristic of stretching vibrations of $\text{C}=\text{O}$ bonds in urethane and urea moieties,

respectively. Finally, distinctive peaks were found at 1597 cm^{-1} , 1536 cm^{-1} , 1300 cm^{-1} and 1222 cm^{-1} that can be assigned to C-N (urethane, secondary amide), C=O (urea, secondary amide), C-N (urea, aromatic ring) and C-O-C (urethane) stretching vibrations, respectively. All these signals provide a strong evidence of the successful formation of a polyurea shell at the oil-water interface during the microencapsulation process [25]. As to the encapsulated material, excellent matching was found between the FTIR spectra of sunflower oil and the extracted liquid core. In particular, all notable peaks observed in the FTIR spectrum of sunflower oil ($3100\text{-}2700\text{ cm}^{-1}$, $1850\text{-}1650\text{ cm}^{-1}$, $1500\text{-}1000\text{ cm}^{-1}$) were also found in the FTIR spectrum of the extracted core material. These observations clearly demonstrate effective encapsulation of sunflower oil as core material in the polyurea-based shell.

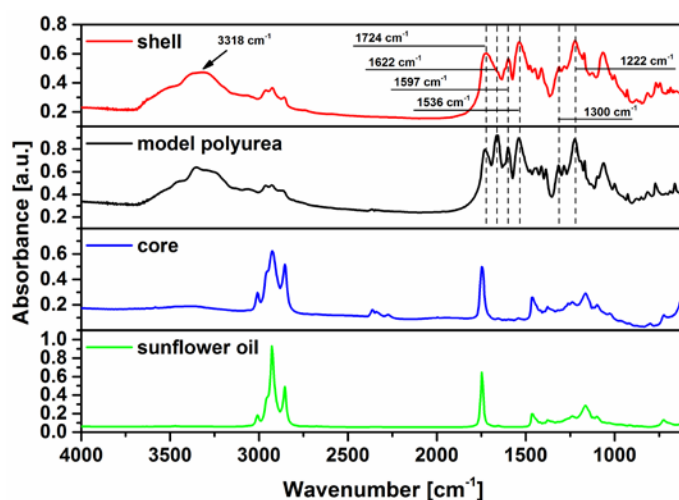


Figure 3. FTIR spectra of extracted shell material, model polyurea film obtained from reaction between Desmodur L-75 and DABP, extracted core material and sunflower oil. For these analyses, microcapsules were prepared without the addition of fluorescent species in the sunflower oil phase.

The thermal stability of the synthesized microcapsules was investigated by means of TGA. As shown in Figure 4, the microcapsules do not show significant weight losses up to $150\text{ }^{\circ}\text{C}$, thus indicating their relatively high thermal stability (a negligible $< 5\%$ mass loss contribution is observed in the $100\text{-}150\text{ }^{\circ}\text{C}$ temperature range, correlated with the evaporation of solvent (DMF) trapped in the system during microcapsule synthesis). At higher temperatures, three major mass loss events can be distinguished. In particular, a first $\sim 15\%$ mass loss is observed in the $160\text{-}250\text{ }^{\circ}\text{C}$ range, followed by another significant weight loss ($\sim 30\%$) between $250\text{ }^{\circ}\text{C}$ and $400\text{ }^{\circ}\text{C}$ and a final major thermal degradation ($\sim 45\%$ weight loss) for higher temperatures. As observed on previous works [12, 26], such three-step mass loss profile may be partly associated with thermal degradation of sunflower oil, thus providing evidence of successful encapsulation of the core material. Additionally, thermal decomposition of the shell material may also contribute to the weight loss experienced for temperatures higher than $300\text{ }^{\circ}\text{C}$. It is known that polyureas are characterized by a microphase-separated morphology that consists of hard-segment domains covalently bonded to a soft-segment matrix into a block copolymer architecture [27,28]. In particular, the hard domains are extensively hydrogen-bonded and serve as reversible physical cross-links, thus providing the material with good mechanical properties, especially toughness [29]. Based on these considerations, the second mass loss peak observed in Figure 4 may include a contribution given by the thermal degradation of the polyurea shell

hard segments, as a result of the relatively low thermal stability of the urea group [28]. Analogously, thermal degradation of the soft segments may be partly associated with the major mass loss event observed for temperatures above 400 °C. These evidences are in agreement with the thermograms of the polyurea shell, core material and sunflower oil presented in Figure 4, in which these three major weight loss events (160-250 °C, 250-300 °C and above 400 °C) can be clearly distinguished.

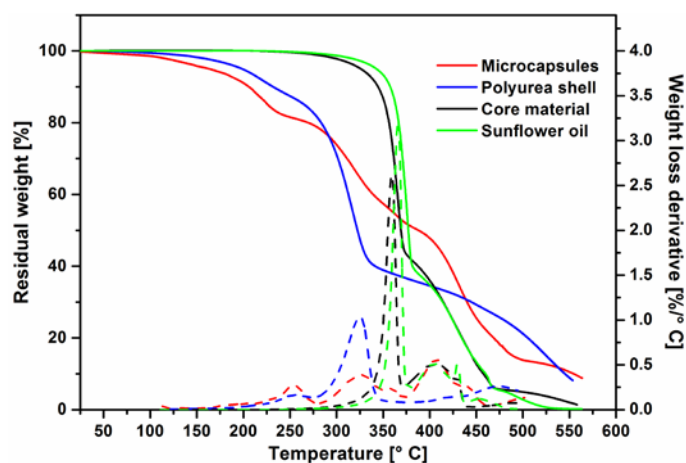


Figure 4. TGA scans in air of the UV-screening DABP-based microcapsules synthesized in this work, the polyurea shell material, the core material and sunflower oil. Residual weight traces and weight-loss derivative traces are indicated by solid and dashed lines, respectively.

3.2. Chemical stability of microcapsules

In practical applications, microcapsules have to be robust enough to survive under severe processing or application conditions, where the presence of aggressive solvents is typically encountered. Therefore their long-term chemical stability represents a key technological aspect for their successful use. Accordingly, the chemical resistance to solvent attacks of the new UV-screening microcapsules synthesized in this work was investigated by prolonged immersion in methanol (MeOH) and butyl acetate (BuOAc), separately.

These two solvents were selected because they belong to two distinct chemical classes, namely alcohols and esters. In particular, BuOAc is one of the most commonly used solvents for application in the field of industrial coatings [30]. On the other hand, MeOH was selected because of its different chemical nature, polarity and lower molecular weight that may lead to different interactions with the microcapsules. The capability of microcapsules to retain the encapsulated material and consequently their chemical resistance in solvents was evaluated using UV-vis spectroscopy. More specifically, a given amount of microcapsules loaded with a model chromophore (SP) was immersed in the solvent (MeOH or BuOAc), then UV-vis spectra of the solvent medium were systematically recorded at increasing dwell times and the release curves could be obtained. To allow swift visualization of the core release process in the extracting solvents, SP-dye dissolved in sunflower oil was the encapsulated core material used as model optical probe, due to its favorable optical properties (see Supporting Information). In addition, the absorption spectrum of SP-dye does not overlay with the optical response of the two selected solvents, thus making it easily detectable by UV-vis spectroscopy.

The release profiles of the synthesized microcapsules in BuOAc and MeOH are presented in Figure 5. For comparison, the release profiles of another microcapsule system based on UV-screening shell obtained by reaction of a polyisocyanate with a monofunctional amine (ACBP) are also reported [12]. Clearly, DABP-based microcapsules possess a significantly improved resistance in solvents compared to the previously reported ACBP-based microcapsules. Core release of the ACBP-based system in MeOH appeared to be significant (concentration of ~ 0.045 mg/ml, around 50% of the total encapsulated core) already after 10 min of immersion. For longer immersion times, the concentration of extracted core in MeOH was found to gradually increase up to a value of ~ 0.080 mg/ml after 1 day, corresponding to an extraction of about 90% of the total encapsulated core material. In BuOAc, an even faster release rate was observed for the same ACBP-based microcapsules. Approximately 60% of core material was extracted within the first minute of immersion (~ 0.060 mg/ml in BuOAc), with complete release already after 60 min. Conversely, the release rate of DABP-based microcapsules was found to be significantly reduced. In particular, the initial release observed in DABP-based microcapsules upon immersion in both tested solvents is found to maintain a constant value during the entire duration of the leakage test and may be associated with the dissolution of the non-encapsulated residual core material partially adsorbed onto the outer shell of the microcapsules during microcapsule formation (as also observed in Figure 2c). This behavior was found to be independent of the immersion solvent, clearly demonstrating the good chemical stability of the system proposed in this work, suggesting the possibility to reliably employ it in combination with commercial solvent-based coatings. To further broaden the applicability of this newly proposed system, DABP-based microcapsules were also immersed in water and a UV-vis analysis of the resulting solvent after one day of immersion was performed. As expected, no absorption signals ascribable to the encapsulated chromophore were detected, indicating the suitability of these systems also for use in waterborne coatings.

The better chemical resistance of DABP- compared to ACBP-based microcapsules may be ascribed to the higher crosslinking density of the DABP-based shell material, which results from its tetrafunctional character. In this case, more amine groups can be made available for reaction with the isocyanate groups to yield urea bonds, thus leading to a denser three-dimensional crosslinked structure that may better withstand solvent attacks compared to the bifunctional ACBP-based counterpart.

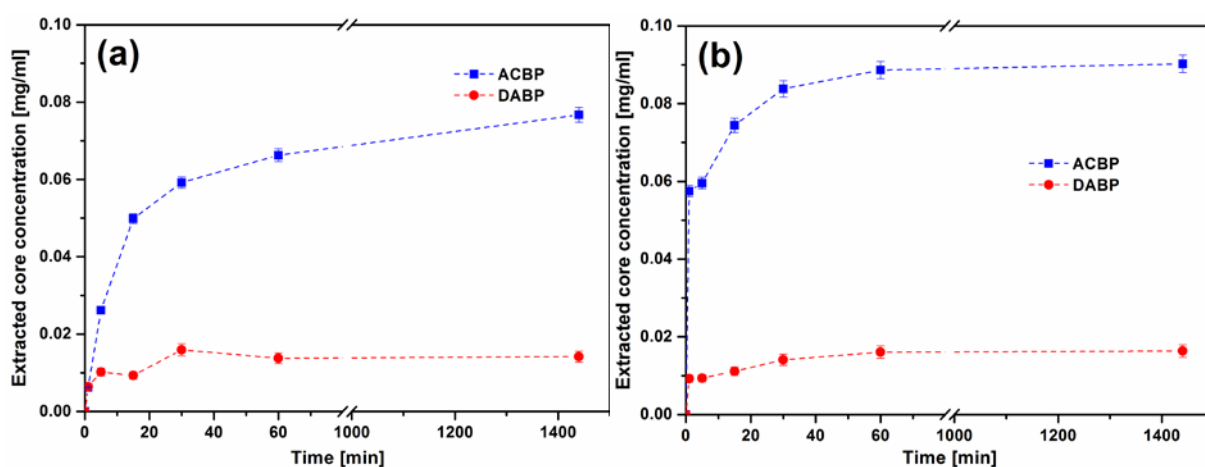


Figure 5. Core release rate profiles of DABP- and ACBP-based microcapsules in (a) MeOH and (b) BuOAc (dashed lines were drawn to guide the eye). Error bars represent deviation over three sets of measurements.

3.3. Smart coating functional demonstration

Ascertained the improved chemical stability of the UV-screening shells developed in this work, their functional response was assessed by synthesizing UV-screening microcapsules encapsulating a model pyrene-based fluorescent dye (VPy) whose optical properties well match the UV-absorption response of the new microcapsules (Figure 6a,b). In particular, the absorption spectrum of VPy fully overlaps with that reported for the synthesized microcapsules, thus prospecting effective screening of the incoming UV light that is prevented from interacting with the encapsulated fluorescent molecule. Such VPy-containing UV-screening microcapsules were placed over a microscope slide and irradiated with UV-light ($\lambda = 366$ nm). As presented in Figure 6c, no evidence of fluorescence emission was observed on intact microcapsules, clearly indicating the effective UV-screening action performed by the polyurea based shell. The same microcapsules were then crushed between two glass slides and the liquid core was allowed to be released by diffusion. As shown in Figure 6d, a strong fluorescence emission was observed after exposing the broken microcapsules to UV-light, coherently with the fluorescence emission properties of the encapsulated VPy dye.

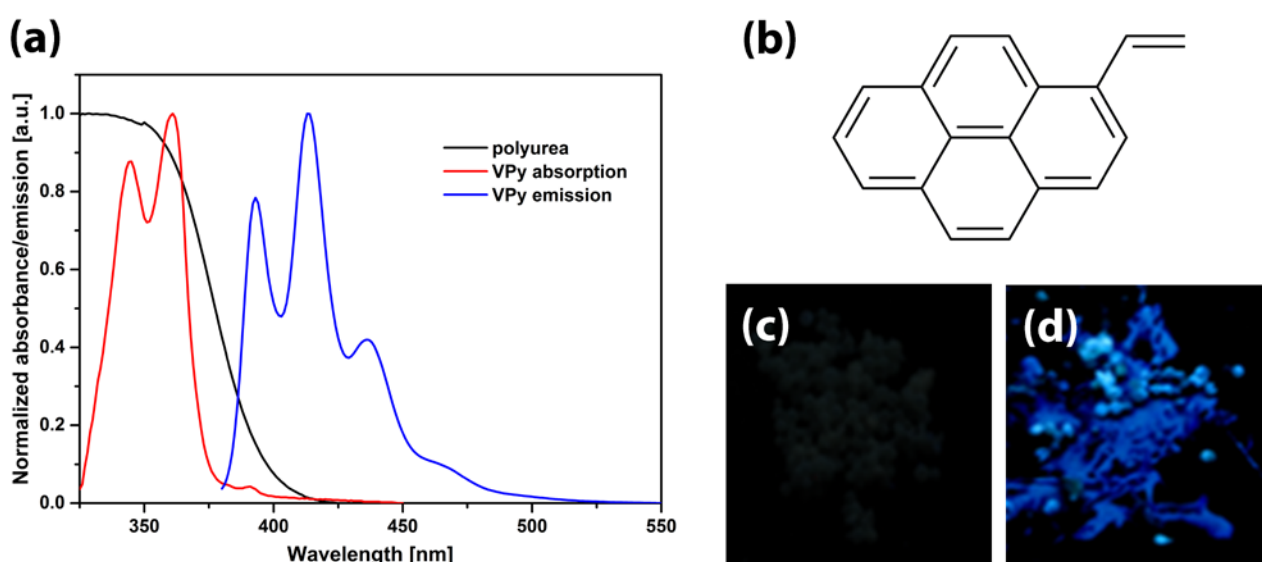


Figure 6. (a) Absorption spectrum of the polyurea-based shell material compared with the absorption/emission response of the VPy fluorophore, whose chemical structure is reported in (b). Digital photographs of the UV-screening shell/fluorescent core DABP-based microcapsules synthesized in this work: (c) as prepared intact microcapsules under UV-light, (d) broken microcapsules under UV-light.

To further highlight the potential of the proposed fluorescent core/UV-screening shell microcapsule system, a smart damage-sensing polymer coating was prepared. To this end, the as-synthesized microcapsules were dispersed into a polyurethane based matrix formulation and subsequently deposited onto a carbon-fiber reinforced polymer (CFRP) substrate and allowed to dry out in air (Figure 7a). Being CFRPs widely employed as structural materials in several engineering fields, evidence of the feasibility of the approach presented in this work on this type of substrates would give a clear demonstration of its potential as damage visualization tool in real life applications. As shown in Figure 7b, no fluorescence emission was observed on the undamaged composite coating upon UV-light exposure, which appears uniformly dark. This is a further

confirmation of the excellent UV-screening ability of the newly synthesized microcapsules, which are also found to be sufficiently stable to withstand the mechanical stresses arisen during the dispersion process. To evaluate the capability of the new microcapsule-based system to serve as fluorescent probe for damage visualization, the composite coating was mechanically damaged with a hammer shot to induce rupture of the microcapsules and release of the fluorescent core material within the polymer matrix (Figure 7c). Under visible light, no evidence of the mechanical damage could be detected. However, after exposure to UV-light, a sharp fluorescence emission was clearly observed on the cracked portion of the coating, resulting from the direct excitation of the released VPy-loaded fluorescent core from the ruptured microcapsules (Figure 7d). This behavior is a further clear demonstration of the potential of our newly proposed microcapsule system as fluorescent probe for *in situ* microcrack detection.

It is worth pointing out that a more judicious sieving and sorting process on the size of the microcapsules in addition to a thorough optimization of their dispersion process in the coating may allow for reduced agglomeration. Accordingly, these aspects will be the subject of future investigations.

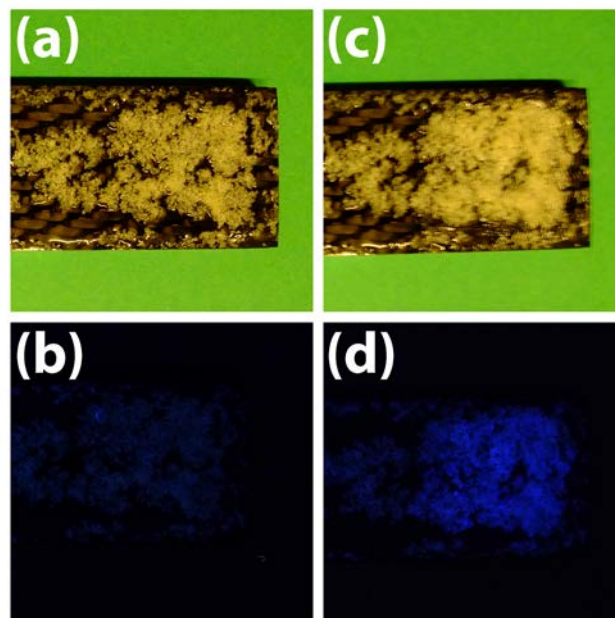


Figure 7. Digital photographs of the functional damage-sensing smart coating system developed in this work deposited onto a CFRP substrate: (a) coating before damage, (b) coating before damage under UV-light, (c) coating after a damage was applied on part of the sample, (d) damaged coating under UV-light (a clear fluorescence emission is observed on the damaged area).

4. Conclusion

In this work, new high-chemical-stability microcapsules consisting of a UV-screening shell and a fluorescent core were obtained *via* interfacial polymerization between an isocyanate prepolymer and a difunctional benzophenone amine. A thorough morphological, chemical and thermal characterization of the synthesized microcapsules evidenced successful encapsulation of the core material and excellent thermal stability of the proposed microcapsule system. In addition, the chemical resistance of these new UV-screening microcapsules was assessed by leakage tests conducted in different solvent media, which highlighted the

excellent chemical stability of this system likely originating from the highly crosslinked shell structure that prevents core extraction and subsequent diffusion outwards. This behavior was found to significantly overcome the limited chemical stability previously observed on analogous UV-screening microcapsule systems. Finally, the damage visualization ability of this new fluorescent sensor was demonstrated by embedding the newly synthesized fluorescent-core/UV-screening microcapsules into a polymer matrix to form a smart functional coating system able to visually detect (by fluorescence emission) the presence of local microcracks forming upon mechanical damage to the coating.

The excellent UV-screening ability of this new microcapsule-based sensor system combined with its exceptional resistance to common organic solvents paves the way for the development of reliable core/shell microcapsule-based smart systems for damage detection and visualization in structural materials.

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