

# Microencapsulation of a UV-Responsive Photochromic Dye by Means of Novel UV-Screening Polyurea-Based Shells for Smart Coating Applications

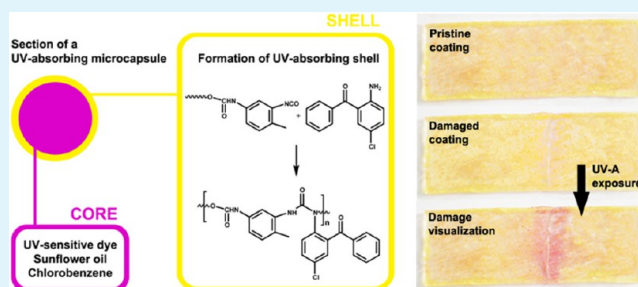
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## S Supporting Information

**ABSTRACT:** This article describes the synthesis, characterization, and application of new UV-absorbing microcapsules encapsulating a UV-responsive photochromic dye for application in the damage-sensing field. Microcapsules filled with a photochromic spiropyran, dissolved in sunflower oil as core material, were synthesized by reacting a TDI-based polyisocyanate prepolymer with a benzophenone-based amine to obtain robust UV-absorbing polyurea shells. The newly synthesized UV-screening microcapsules were embedded into a photoresist to realize a new mechanoresponsive polymer. After scratching the coating, the UV-screening microcapsules break and the UV-sensitive core material is released and diffuses into the polymer matrix. Upon exposure to UV-A light, a rapid color change in the region where the damage was made is observed, because of the photoinduced transition of spiropyran to the plane merocyanine form. The novelty of the approach presented in this work lies in the possibility to convert any type of conventional polymeric coating into a UV-light-sensitive mechanoresponsive smart coating by simple addition of our new UV-screening microcapsules.

**KEYWORDS:** smart coating, damage sensing, microencapsulation, UV curing, mechanoresponsive, photochromic



## 1. INTRODUCTION

Polymers that change color in response to a wide range of external stimuli, such as temperature, UV and visible light, and magnetic and electric field, have been extensively investigated and applied to various types of display devices and sensors.<sup>1,2</sup> Among these, a few examples of polymeric materials that exhibit a color change on the application of mechanical stresses can also be found. Such so-called mechanochromic polymers<sup>2</sup> represent a promising class of smart materials that may find interesting applications in a variety of technological fields. Indeed, self-sensing capability of changing color in polymeric coatings could be used to alert to potential component failure, thus allowing to extend the lifetime of a material through appropriate assessment, modification, and improvement of the damaged part.

Several nondestructive structural health monitoring techniques<sup>3,4</sup> are currently available, but normally they cannot be applied in situ, since they require removal of the component from the system to carry out the analysis. Therefore, it appears very interesting to develop sensitive detection methods that can be easily applied directly on the assembled system and that can be readily accessible also by nonspecialized personnel.

Despite the increasing number of examples of mechanoresponsive polymeric materials that have recently appeared in the literature,<sup>5–8</sup> until now, the mechanochromic functionality into

the polymeric matrix has been achieved by separate addition of the functional coloring agent into the coating prior to its application on a given substrate.<sup>9–12</sup> Alternatively, the mechanochromic feature has been inserted into the polymeric structure by copolymerization or by grafting the chromophoric units to the macromolecule backbone or to the side chains.<sup>13</sup> In order to do so, classical and living radical polymerization processes have been employed on both elastomers and glassy acrylics.<sup>5,10,14</sup> More recently, smart polymers capable of giving a visual indication of mechanical damage were obtained by microencapsulation of cyclooctatetraene, to give highly colored polyacetylene,<sup>15</sup> or by formulation of crystal violet lactone leuco dyes with embedded silica gel as the developer.<sup>16</sup> Finally, a multifunctional approach in the field of mechanochromics was recently presented by Urban's group, in which the damage sensing functionality of the smart coating (coloration) was combined with a self-repairing functionality.<sup>17</sup> Such a multifunctional material was obtained by copolymerization of spiropyran-based monomers with methyl methacrylate and butyl acrylate.<sup>17</sup>

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As apparent from the examples reported so far in the literature, the damage sensing functionality of the mechano-chromic material is highly dependent on the specific polymeric system used. In addition, expensive catalysts are often employed in order to achieve mechanochromic functionality in the polymeric system.

In the attempt to overcome some of these issues, this work aims at developing a general versatile approach that allows one to convert a conventional polymeric coating into a UV-light sensitive, mechanoresponsive smart coating by simple formulation with our newly prepared UV-screening microcapsules. To this end, we hereby report the synthesis of new microcapsules that have a UV-screening polyurea shell and are filled with a model UV-sensitive photochromic organic dye. To test the applicability of this new approach, these new UV-screening microcapsules were embedded into a photopolymer to form a new mechanoresponsive system. The UV-light-induced visual response of the coating could be activated by imparting a mechanical damage capable of breaking the microcapsules, thus releasing the UV-responsive photochromic dye. Upon release of the dye from the protective UV-screening shell and its diffusion through the polymer matrix, simple UV-A light irradiation allows identification of the mechanical damage by visualizing a clear color change in the damaged area. This method makes it easy to detect damaged zones without the use of color developers or expensive catalysts.

## 2. EXPERIMENTAL SECTION

**2.1. Raw Materials.** Desmodur L-75 is an aromatic polyisocyanate prepolymer based on toluene diisocyanate isomers (TDIs) in ethyl acetate with an NCO content of  $13.3 \pm 0.4$  wt %, viscosity of  $1600 \pm 400$  mPa s @ 23 °C, and equivalent weight of 315 g/equiv; it was a gift from Bayer Materials Science (Germany). Gum Arabic (GA), 1',3'-dihydro-1',3',3'-trimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-(2H)-indole] dye (SP-dye), 2-amino-5-chlorobenzophenone (ACBP), chlorobenzene (CB), *n*-hexane, tetraethylene glycol dimethacrylate (TEGDMA, MW = 258), and pentaethylene-glycole monomethacrylate (PEGMA, MW = 330) were all purchased from Sigma–Aldrich and used without further purification. Sunflower oil was kindly provided by Benasedo (Italy).

The photoinitiator used was Darocur 1173 (2-hydroxy-2-methylpropiophenone), from Ciba (Switzerland).

**2.2. Synthesis of UV-Absorbing Microcapsules Filled with SP-Dye.** At room temperature, 120 mL of deionized water and 13.5 g of GA as surfactant were mixed in a 500-mL flanged glass reactor (90 mm in diameter). The reactor walls were fitted with a jacket for an external recirculation temperature system. The solution was agitated at 500 rpm for 3 h by a mechanical stirrer, driving a six-bladed propeller (63 mm diameter) before beginning encapsulation. Desmodur L-75 prepolymer (9.0 g) was separately diluted into 8 mL of dry CB and kept under nitrogen. In another flask, the SP-dye (0.35 g) was mixed into 40 mL of sunflower oil for 1 h until a homogeneous mixture was obtained. In a third flask, ACBP (3.53 g) was dissolved in 15 mL of CB. Successively, the flasks of Desmodur L-75 and SP-dye/oil were slowly poured into the GA solution. The resulting mixture was then heated at 50 °C, and the ACBP amine solution was slowly added to the stirred emulsion. The reactor was heated at 70 °C for 1 h. Once cooled to ambient temperature, the suspension of microcapsules was separated from the mother liquor and left to settle overnight.

The microcapsules were washed with deionized water several times, separated by decantation, filtered using a Büchner funnel, washed with *n*-hexane, and dried under vacuum for 24 h. The average yield was ~60 wt %.

**2.3. Preparation of Smart Sensitive Material with UV-Absorbing Microcapsules.** A polyethylene glycol methacrylate photopolymer<sup>18</sup> was chosen as carrier to prepare the smart microencapsulated coating. The coating is composed of TEGDMA, PEGMA, and a photoinitiator (2-hydroxy-2-methylpropiophenone) in the ratio of 90.5:6:3.5 (wt %) respectively. Microcapsules filled with SP-dye (15 wt % on the methacrylate oligomers) were dispersed into the polymerization mixture by means of a glass axial flow impeller.

The liquid formulation was cast into a silicone mold and the photopolymerization was carried out under nitrogen, using a bromograph (MF 1030, Nuova Delta Elettronica, Italy) with 4 UV-A tubes ( $\lambda_{\text{emission}} = 350$  nm) with a power of 15 W.

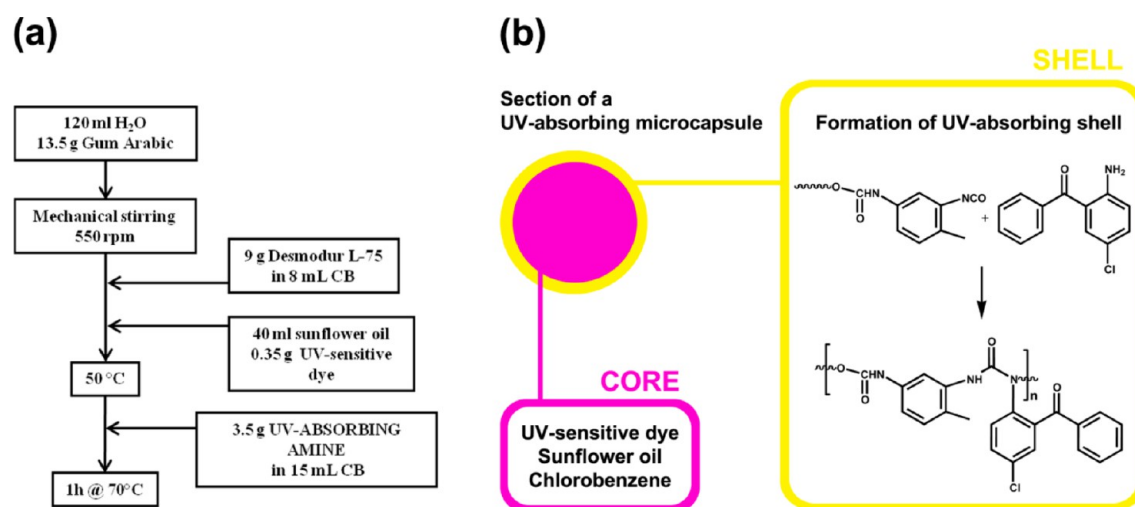
Full characterization of the cross-linked polymer film (ATR-FTIR spectroscopy, optical contact angle measurements and dynamic mechanical analysis (DMA) was reported in a previous work by the same group.<sup>19</sup>

**2.4. Morphology of Microcapsules.** Morphology and surface features of the microcapsules were observed by optical microscopy using an Olympus BX-60 reflected-light optical microscope equipped for bright-field (BF) and dark-field (DF) imaging with an Infinity 2 digital camera. Microscopy was also used to determine the average diameter of the microcapsules from datasets of at least 250 measurements. In the same way, the particle size–weight distribution was obtained by sieving the synthesized product using different mesh sizes (from 50  $\mu\text{m}$  to 500  $\mu\text{m}$ ).

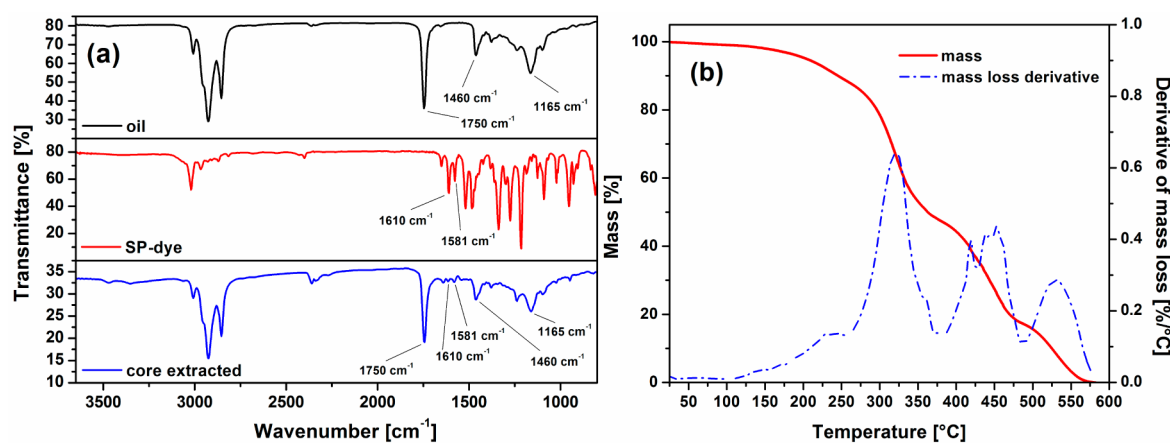
To obtain more-accurate characterization of the internal and external morphology of microcapsules and coating surfaces before and after healing, scanning electron microscopy (SEM) was employed (Carl Zeiss EVO 50 Extended Pressure, with an accelerating voltage of 15.00–17.50 kV).

**2.5. Yield of Microcapsules and Determination of Core Fraction.** The yield of microcapsule synthesis was calculated as the weight ratio between the collected microcapsules and the initial substances added (polyisocyanate prepolymer, ACBP amine, SP-dye, oil and CB). The amount of SP dye and oil into microcapsules was determined by toluene extraction of core materials. Small amounts of microcapsules were crushed and washed with toluene several times. After filtration and drying, pure microcapsule shell and core were obtained. The percentage of core and shell fraction of microcapsules was calculated as the ratio of the weight of initial SP-dye and sunflower oil and the weight of core extracted. It was concluded that ~40% SP-dye and oil, as core materials, was encapsulated within the UV-absorbing shell.

**2.6. Spectroscopic Characterization and Thermal Analysis.** Fourier Transform infrared (FTIR) spectra of microcapsules and their components were acquired in transmission mode using a Perkin–Elmer Spectrum 2000 FTIR spectrometer. Spectra were collected over a range from 4000 to 400  $\text{cm}^{-1}$ . All the output spectra are the result of the combination of 32 sequential scans for noise reduction. FTIR spectra of liquids (core, Desmodur L-75, sunflower oil) were collected on KBr or NaCl plates. FTIR spectra of solids (microcapsules, shell wall) were collected by dispersing the material in KBr powder to form a solid pellet. FTIR spectra of SP-dye was recorded in a  $\text{CHCl}_3$  solution.



**Figure 1.** (a) Procedure for the preparation of UV-absorbing microcapsules (UV-sensitive dye, 1',3'-dihydro-1',3',3'-trimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-(2H)-indole]; CB, chlorobenzene; UV-absorbing amine, 2-amino-5-chlorobenzophenone). (b) Schematic cross-section of the synthesized microcapsules with main constituents and shell formation scheme.



**Figure 2.** (a) FTIR spectra of sunflower oil, SP-dye, and extracted core material. (b) TGA curves of as-prepared UV-screening microcapsules.

UV-vis spectra were collected at room temperature in the wavelength range of 300–700 nm, using an Evolution 600 UV-vis spectrophotometer (Thermo Scientific). A liquid cell of 1 cm path length with quartz windows was used. UV-vis spectra of ACBP and Desmodur L-75 were recorded in ethanol solution, while the SP-dye was dissolved in sunflower oil in the same ratio used for the synthesis of the microcapsules.

Differential scanning calorimetry (DSC) was carried out with a Mettler-Toledo DSC 823E instrument, indium and *n*-hexane calibrated, heating from 0 to 300 °C at a rate of 10 °C/min in a N<sub>2</sub> environment.

Thermogravimetric analysis (TGA) was performed from 0 to 600 °C at a rate of 20 °C/min in air on a Q50 TGA system (TA Instruments).

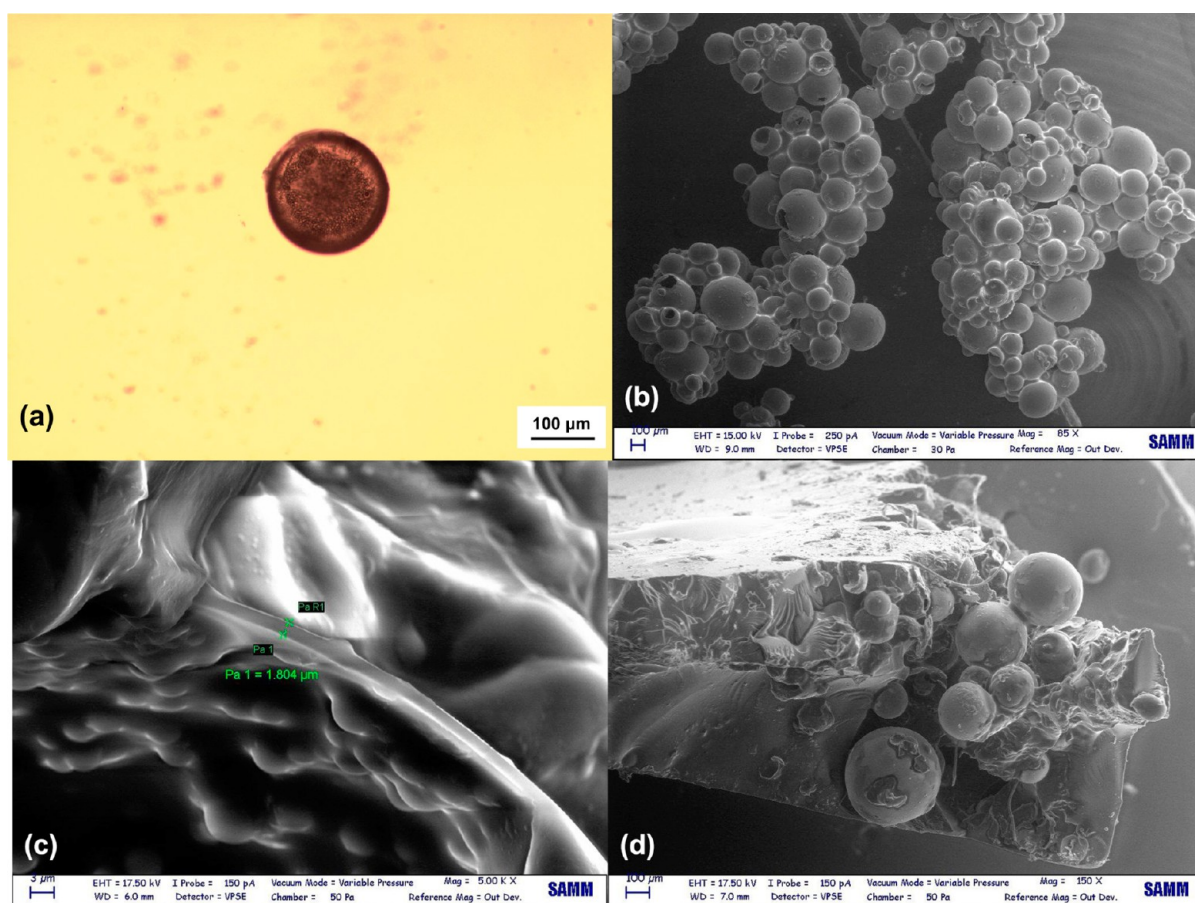
### 3. RESULTS AND DISCUSSION

The synthetic procedure used in this work to produce UV-screening polyurea-based microcapsule shells containing a UV-sensitive photochromic dye is partially based on previous work carried out by our group,<sup>20</sup> and it is schematically represented by Figure 1a. Briefly, an oil-in-water (O/W) emulsion is prepared by dispersing a polyisocyanate prepolymer and a sunflower oil solution containing the UV-sensitive dye in gum arabic-containing water under vigorous mechanical stirring. By

adding a benzophenone-based amine ACBP to the O/W emulsion, the reaction between polyisocyanate and amine can occur, leading to the formation of the polymeric microcapsule shell based on polyurea linkages (Figure 1b).

In order to chemically characterize the as-formed microcapsules, their FTIR spectra were collected. The formation of shell material—namely, the reaction of the NH<sub>2</sub> group of ACBP with the NCO group in the TDI-based polyisocyanate prepolymer—was confirmed by the disappearance of the N=C=O stretching signal (2270 cm<sup>-1</sup>) in the FTIR spectrum of the as-prepared microcapsule shell (see the Supporting Information). However, because of the presence of water in the reacting mixture, side reactions between NCO groups from the TDI prepolymer and hydroxyl groups from water cannot, in principle, be ruled out.

The FTIR spectrum of the extracted core material is shown in Figure 2a, together with that of SP-dye and sunflower oil. The FTIR spectra of oil and core material appear to be nearly overlapping. In particular, the peaks in the aliphatic C–H<sub>2</sub>/C–H stretching region (2700–3100 cm<sup>-1</sup>), the C=O stretching peak at 1750 cm<sup>-1</sup>, and the peaks at 1460 cm<sup>-1</sup> and 1165 cm<sup>-1</sup> present in the FTIR spectrum of sunflower oil are also found in the FTIR spectrum of the extracted core. This clearly indicates that sunflower oil was successfully encapsulated in the



**Figure 3.** (a) Optical microscope image of a single microcapsule; SEM images of (b) a cluster of microcapsules, (c) microcapsule shell wall profile, and (d) cluster of microcapsules embedded in a polymeric film.

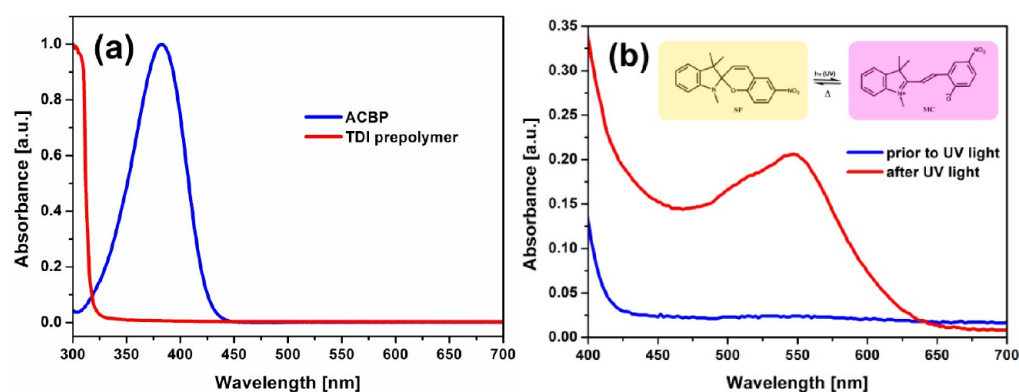
microcapsule shell. In addition, characteristic peaks of the SP-dye merocyanine form appearing at  $1610\text{ cm}^{-1}$  ( $\text{C}=\text{C}$  stretching) and  $1581\text{ cm}^{-1}$  ( $\text{C}=\text{N}^+$  stretching)<sup>21,22</sup> are also present in the FTIR spectrum of the extracted core. This also demonstrates encapsulation of the SP-dye in the microcapsule shell.

In order to further confirm microencapsulation of the UV-sensitive photochromic dye, together with sunflower oil, the extracted core material was subjected to exposure to UV-A light. As expected, after a few seconds under UV-A light, the extracted liquid core material changed from a yellow-earth color to a dark purple one, as a result of the conversion of the original spiropyran (SP) structure of the photochromic dye into its merocyanine (MC) form.<sup>6,21</sup> Such color change confirmed that the encapsulated core material contains both sunflower oil and UV-sensitive photochromic dye.

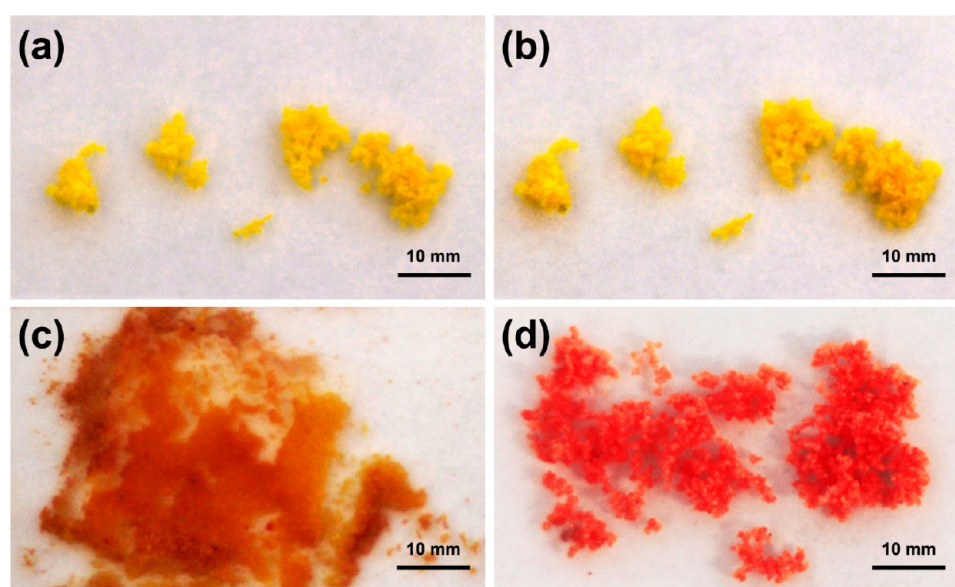
TGA was employed to examine the thermal stability of the as-prepared microcapsules. As shown in Figure 2b, no significant weight loss is observed up to a temperature of  $\sim 200\text{ }^\circ\text{C}$ , suggesting the possibility to employ this type of microcapsule also in high-temperature applications, where high-temperature curing cycles may be required. By increasing the temperature, a major weight loss ( $\sim 53\%$ ) is observed in the  $250\text{--}380\text{ }^\circ\text{C}$  temperature range, followed by a 30% mass decrease between  $380\text{ }^\circ\text{C}$  and  $480\text{ }^\circ\text{C}$ , and a further 17% decrease for temperatures up to  $600\text{ }^\circ\text{C}$ . This behavior is in agreement with that found in sunflower oil,<sup>23</sup> where a three-stage thermal decomposition is observed, resulting from decomposition of polyunsaturated ( $250\text{--}380\text{ }^\circ\text{C}$ ), monounsaturated

( $380\text{--}480\text{ }^\circ\text{C}$ ), and saturated ( $480\text{--}600\text{ }^\circ\text{C}$ ) fatty acids. This result further reveals successful encapsulation of core material within the microcapsules. Additional confirmation on the thermal behavior of the as-prepared microcapsules was given by DSC, from which no evident thermal transitions could be observed up to  $250\text{ }^\circ\text{C}$ , where decomposition starts (see the Supporting Information).

The determination of the average microcapsule diameter was carried out by means of optical microscopy (Figure 3a) from datasets of at least 250 measurements. An average microcapsule diameter of  $148.21 (\pm 42.80)\ \mu\text{m}$  was measured, having a Sauter diameter<sup>24</sup> ( $d_{32}$ ) of  $172.83\ \mu\text{m}$ . The morphological and surface characterization of the microcapsule shell was carried out by means of SEM analysis. As shown in Figure 3b, the microcapsules present an almost-spherical shape with a rather smooth outer shell surface. In addition, the presence of excess sunflower oil and photochromic dye can be observed on both shell wall sides, likely due to the liquid core released from the microcapsules purposely broken before SEM analysis. This represents a further confirmation of successful encapsulation of core material. A very uniform shell wall thickness is observed, measured to be on the order of  $2\ \mu\text{m}$  (Figure 3c). Such a shell thickness allows one to avoid the leakage of core material and diffusion of surrounding media toward the inside of the microcapsules, and can provide sufficient mechanical strength to prevent the microcapsules from breaking apart during processing or after inclusion into a polymeric carrier, as apparent from Figure 3d.



**Figure 4.** (a) UV-vis absorption spectra of ACBP and TDI-based polyisocyanate prepolymer; (b) UV-vis spectrum of the UV-sensitive photochromic dye employed in this work prior to and after UV-light exposure (the molecular mechanism responsible for the photochromic response is presented in the inset).



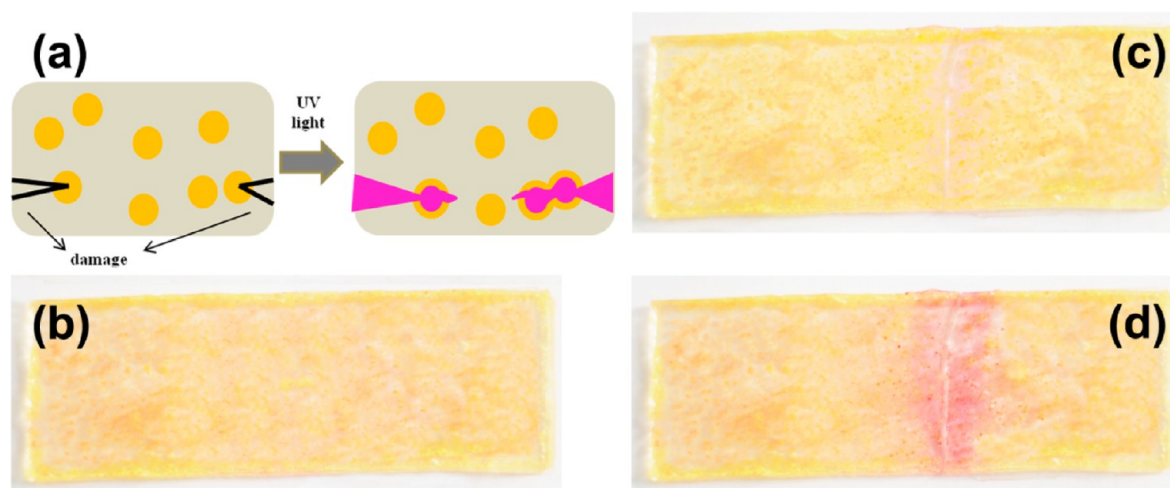
**Figure 5.** Photographs of (a) as-synthesized UV-screening microcapsules, (b) UV-screening microcapsules after exposure (10 s) to UV-A light, (c) UV-screening microcapsules after shell rupture and exposure (10 s) to UV-A light, and (d) microcapsules not containing ACBP after exposure (10 s) to UV-A light.

In addition to imparting adequate mechanical stability to the microcapsule shells, thanks to the formation of polyurea linkages by reaction with the polyisocyanate prepolymer, the benzophenone-based amine ACBP employed in this work was chosen because of its ability to impart UV-absorbing properties to the as-formed polyurea-based microcapsule shells. This is evident from its UV-vis absorption spectrum, which extends from 300 nm to  $\sim$ 450 nm, with an absorption peak centered at 383 nm (Figure 4a).

In the attempt to optimize the composition of the core material and the UV-screening properties of the synthesized microcapsule shell, different ratios between sunflower oil, photochromic dye, ACBP, and TDI-based polyisocyanate prepolymer were tested, and the resulting functional response was qualitatively examined after exposure of the microcapsules to UV-A light. In particular, the amount of photochromic dye was varied between 0.5 wt % and 2 wt %, with respect to the sunflower oil. It was found that, for dye concentrations above 1 wt %, no UV-screening effect was observed, because the microcapsules would change color rather rapidly after being UVA-irradiated for only 5 s. Conversely, for dye concentrations

of 1 wt % and lower, an efficient UV-screening effect was observed, by employing a TDI:ACBP ratio of 70:30. By varying the TDI:ACBP ratio (80:20), the UV-screening effect was found to worsen (coloration of the pristine microcapsules observed after UV-A irradiation), thus indicating the key role played by ACBP as a UV-absorbing species.

To demonstrate the potentialities of this new UV-screening approach, the newly synthesized UV-absorbing shells were used to microencapsulate a model UV-sensitive photochromic dye that undergoes a color change upon exposure to UV-A light (Figure 4b). The so-formed dye-containing UV-screening microcapsules were deposited onto a glass slide and irradiated with UV-A light ( $\lambda = 350$  nm). As shown in Figures 5a and 5b, no color change was observed after 10 s of exposure to UV-A light, indicating that the presence of the benzophenone moiety in the microcapsule shell successfully acts as a UV-absorbing filter. These microcapsules were then broken by compression between two glass slides, thus allowing the core material to be released. Upon irradiation (10 s) with UV-A light, the extracted liquid core underwent a clear color change from yellow-earth to dark red (Figure 5c), in accordance with the photochromic



**Figure 6.** (a) Schematic representation of the visual identification of the mechanical damage by exposure to UV-A light. Also shown are photographs of microcapsule-containing PEGMA-based films: (b) as-prepared, (c) after being scratched, and (d) after exposure to UV-A light ( $\lambda = 350$  nm, 10 s). Dimensions of PEGMA-based films (b, c, d) are 75 mm  $\times$  25 mm  $\times$  1 mm.

response of the UV-sensitive dye. This color change was found to last for over 60 min after exposure to UV-A light in air under ambient light (see the Supporting Information). As a control, microcapsules with shell made of diethylenetetramine (no ACBP present) were also deposited onto a glass slide and irradiated with UV-A light. As shown in Figure 5d, an immediate yellow-to-dark-red color change was observed on these microcapsules, thus confirming that ACBP is the responsible for the UV-screening properties of our newly synthesized UV-screening microcapsule shell.

Finally, our new UV-screening microcapsules were embedded in a polymeric matrix to demonstrate the possibility to produce a smart coating able to visually respond to a mechanical damage such as a scratch or a hit. In particular, PEGMA photopolymer<sup>18</sup> was chosen as the polymeric carrier to prepare such smart material. In principle, upon application of a mechanical stress such as a scratch on the coating, the UV-screening microcapsules break and the UV-sensitive core material is released and diffuses into the polymer matrix. Upon exposure to UV-A light, a rapid color change in the region where the damage was made is observed, thus serving as a visual marker (see Figure 6a).

As shown in Figure 6b, no color modifications were observed on the as-prepared PEGMA-based film containing UV-screening microcapsules upon exposure to UV-A light, indicating that, when embedded in a solid polymeric matrix, the microcapsule shells also are able to retain their UV-screening properties. In addition, no rupture of the microcapsules was observed after inclusion in the polymeric matrix, thus confirming their good mechanical stability and robustness. In order to demonstrate their potential use as visual markers, the film containing UV-microcapsules was scratched with a lancet so that the microcapsules would break and the core material would be released and would diffuse into the polymeric matrix (Figure 6c). Such a phenomenon is possible because of the ability of the carrier material—in this case, sunflower oil—to rapidly diffuse into the mechanically induced crack with a diffusion time of  $\sim 10$  s. With no UV-light shone on the coating, a uniform yellow-earth color was observed. After exposure to UV-A light, the immediate appearance of an intense dark-red/purple stain in the scratched region was observed, as a result of the photochromic response of the

released UV-sensitive dye (Figure 6d). This behavior further demonstrates the viability of our approach as a promising nondestructive in situ technique for easy visualization of mechanical damages.

#### 4. CONCLUSIONS

In this work, we have demonstrated the synthesis and potential application of a novel UV-screening microcapsule shell. By reacting a TDI-based polyisocyanate with a benzophenone-based amine, we were able to obtain mechanically robust UV-absorbing shells based on polyurea. The microencapsulation process made use of a photochromic UV-sensitive dye dissolved in sunflower oil as core material. After optimization of the UV-screening properties of the microcapsule shell by tuning the chemical composition of the core material, we were able to demonstrate the use of such UV-screening microcapsules in functional coatings for the nondestructive in situ visual detection of mechanical damages by color change.

Although, in this work, a photochromic UV-sensitive dye was employed for demonstration purposes, it is possible, in principle, to adapt our new UV-screening shell approach to any type of UV-sensitive organic dye, thanks to the versatility of our methodology.

#### ■ ASSOCIATED CONTENT

##### Supporting Information

Additional DSC analysis, FTIR, and UV-vis spectra. This information is available free of charge via the Internet at <http://pubs.acs.org/>.

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##### Notes

The authors declare no competing financial interest.

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