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Letter

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Visual Indication of Mechanical Damage Using Core–Shell Microcapsules

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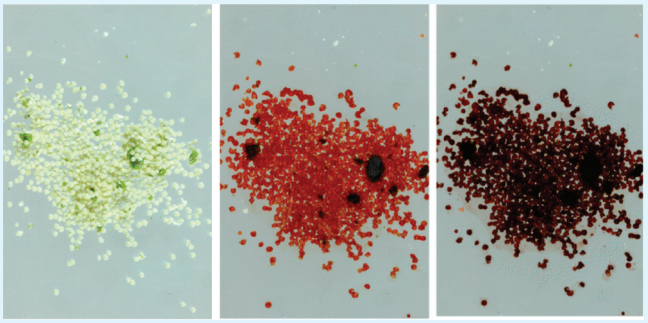
Supporting Information

ABSTRACT: We report a new core–shell microcapsule system for the visual detection of mechanical damage. The core material, 1,3,5,7-cyclooctatetraene, is a conjugated cyclic olefin and a precursor to intensely colored polyacetylene. A combination of poly(urea-formaldehyde) and polyurethane is required to effectively encapsulate the volatile core material. Increasing the outer shell wall thickness and including a core-side prepolymer improves the thermal stability and free-flowing nature of these capsules, which tend to leach and rupture with thinner shell walls. Capsules ruptured in the presence of the Grubbs–Love ruthenium catalyst show immediate color change from nearly colorless to red-orange and dark purple over time, and color change in thin films resulted from scratch damage.



KEYWORDS: *damage detection, color change, ring-opening metathesis polymerization, microcapsule, encapsulation*

1. INTRODUCTION

Indicators in polymers and composite materials can reveal mechanical damage and the need for repair before damage becomes catastrophic. Toward this goal, a variety of research groups have introduced methods of detecting mechanical damage through color change. Mechanically active small molecules incorporated into polymer backbones or as cross-links between polymer chains have shown changes in color and/or fluorescence upon fracture,[1] tension,[2,3] and shear.[4] The force-induced dissociation of dye aggregates has been used to change photoluminescent character in stretched polymers.[5−7] Changes in pH have been used to detect compression in polymer brushes,[8] and microcapsules containing a pH-sensitive dye solution have also been utilized in carbonless copy paper, in which color change occurs upon a change in pH when ruptured microcapsule cores react with acidic clay or resin coatings.[9] Fluorescent dyes have been incorporated into filled hollow fibers to enhance damage visibility in the structure of the reinforced plastic.[10] None of these systems forms a colored product in tandem − or that is necessarily compatible − with a structural healing process. Here we selected a catalyst and ROMP-based colorimetric assay to be compatible with our previously demonstrated self-healing chemistry. Such a system could enable the same embedded catalyst to detect damage and heal a structural polymer.

We previously reported the preparation of core–shell microcapsules containing the liquid monomer dicyclopentadiene (DCPD),[11] which undergoes ring-opening metathesis polymerization (ROMP) when reacted with certain Grubbs' ruthenium catalysts.[12] When both the monomer-filled capsules and catalyst are embedded in polymer composites, mechanically induced crack propagation was healed or arrested due to formation of polyDCPD at the crack interface.[13] Similarly, we sought to utilize ROMP of the cyclic monomer 1,3,5,7-cyclooctatetraene (COT) to produce polyacetylene (Figure 1a), an intensely colored conjugated polymer. This reaction has been reported with tungsten,[14−16] molybdenum,[17] and

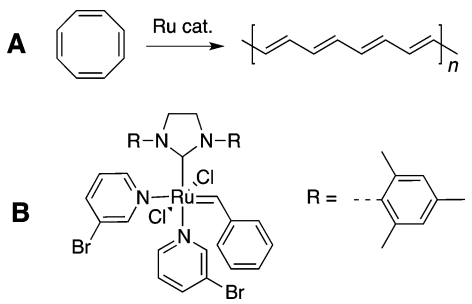


Figure 1. (A) Ring-opening metathesis polymerization of 1,3,5,7-cyclooctatetraene. (B) Grubbs–Love catalyst.

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ruthenium[17,18] catalysts. Because of its ease of synthesis, stability in ambient conditions, and fast reaction with COT, we anticipated that the Grubbs–Love catalyst (Figure 1b) would be well-suited for this work.[19] Compared to other red and purple ruthenium catalysts that polymerize COT,[18] the Grubbs-Love catalyst is a lime green color, providing a colorimetric contrast to the red/purple color of polyacetylene. This catalyst also polymerizes DCPD, enabling the possibility for damage detection and self-healing with a single catalyst. The Grubbs–Love catalyst is prepared in one step from commercially available Grubbs' second generation catalyst by reaction with 3-bromopyridine.[19]

2. RESULTS AND DISCUSSION

1,3,5,7-Cyclooctatetraene was incorporated into poly(urea-formaldehyde) core–shell microcapsules using an in situ emulsification condensation polymerization (see Figure 2 and

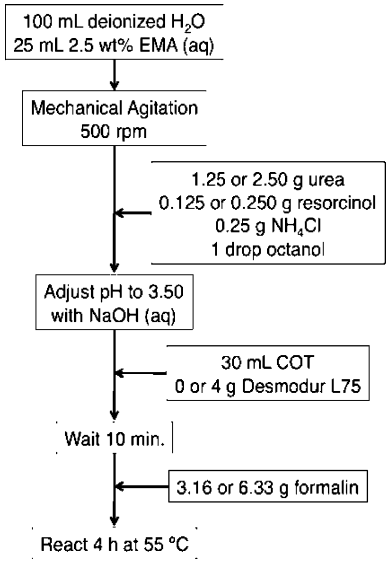

Figure 2. Procedure for the preparation of COT-filled microcapsules. Note: COT, 1,3,5,7-cyclooctatetraene; EMA, ethylene-maleic anhydride copolymer (Zemac-400) powder.

Experimental Section). In damage indication applications, it is important for the microcapsules to be thermally stable and robust to enable their survival in a variety of environmental and processing conditions. In addition, it is important to prevent capsule cores from leaching into the surrounding matrix and contacting the catalyst before a damage event, which could cause premature color change. Therefore, we tested the different encapsulation recipes to maximize the capsule thermal stability. The polymer shell wall thickness and morphology was varied by changing the amounts of urea, formaldehyde, and resorcinol incorporated into the aqueous layer and/or by adding Desmodur L75, a polyurethane prepolymer, to the COT core prior to its addition to the reaction mixture. The amounts of chemicals used in different recipes, labeled A, B, and C, are shown in Table 1. These recipes resulted in isolatable capsules, with recipe C producing the most free-flowing capsules, suggesting the that recipe C yields either the least core material leaching through the shell wall and/or the least capsule rupture during isolation and capsule manipulation.[20,21]

Table 1. Quantities of Chemicals Used in the Recipes Used to Prepare COT Microcapsules[21] [a]

component	recipe A	recipe B	recipe C
water (mL)	100	100	100
EMA, 2.5 wt % in water (mL)	25	25	25
urea (g)	2.5	1.25	2.5
resorcinol (g)	0.25	0.125	0.25
COT (mL)	30	30	30
Desmodur L75 (g)	0	4	4
Formalin (mL)	6.33	3.16	6.33

[a]Note: CO, 1,3,5,7-cyclooctatetraene; EMA, ethylene-maleic anhydride copolymer (Zemac-400) powder.

After preparation, the capsules were washed with water using Buchner filteration and were dried overnight to allow excess water to evaporate. Afterward, we sieved the capsules, collecting only those with diameters ranging from 125 to 180 μm. To determine if the COT survived encapsulation without degradation, we analyzed the capsule cores by ^{1}H NMR spectroscopy. To isolate the liquid cores from the solid polymer shell walls, we ruptured the capsules using a mortar and pestle, after which $CDCl_3$ was added to the resultant slurry. A quick filteration through a pipet containing a piece of cotton removed the polymer shell wall. ^{1}H NMR spectroscopy of this core/$CDCl_3$ solution confirmed the presence of COT with negligible degradation. Optical microscope images (see Figure S1 in the Supporting Information) and SEM images (Figure 3) show that the majority of capsules are intact and spherical in shape. SEM images of the microcapsule shell walls were consistent with expectations about thickness and morphology. For microcapsules from recipes A and C, where double the amount of urea and formaldehyde was used, a thicker outer shell wall layer was observed in comparison to the smooth morphology from recipe B. For microcapsules from recipes B and C, where Desmodur L75 prepolymer was incorporated, the dense inner shell wall was thicker at 720 and 858 nm than those from recipe A where no prepolymer was used, which resulted in inner shell walls with thickness of 220 nm.

Thermogravimetric analysis (TGA) was used to analyze and compare the thermal stability of microcapsules prepared from the three different recipes. Based on dynamic TGA (Figure 4, left), capsules lose a small amount of material below the degradation temperature of the capsules. The rate of weight loss changes depending on the particular capsule recipe employed, with recipe C having the slowest rate of weight loss. Because the boiling point of COT is 142 °C, we expected at least a portion of the weight loss results from the volatilization of COT either through diffusion through the capsule shell walls or from the capsule surface at or near that temperature. Isothermal TGA (Figure 4, right) was also performed in which the capsules were heated to 180 °C, held at that temperature for 2 h, then heated to 400 °C. Although the capsules from recipe A lost the most weight when heating to 180 °C, all three capsule types maintained the majority of sample mass once reaching that temperature, dropping 10 wt % at most over the 2 h window.

To determine the potential for the COT capsules to visually indicate mechanical damage by color change, we gently mixed capsules from recipe C – the most thermally stable capsules – with the Grubbs–Love catalyst without rupturing the capsules, and the mixture of catalyst and capsules was deposited onto a glass slide (Figure 5a). These capsules were ruptured by

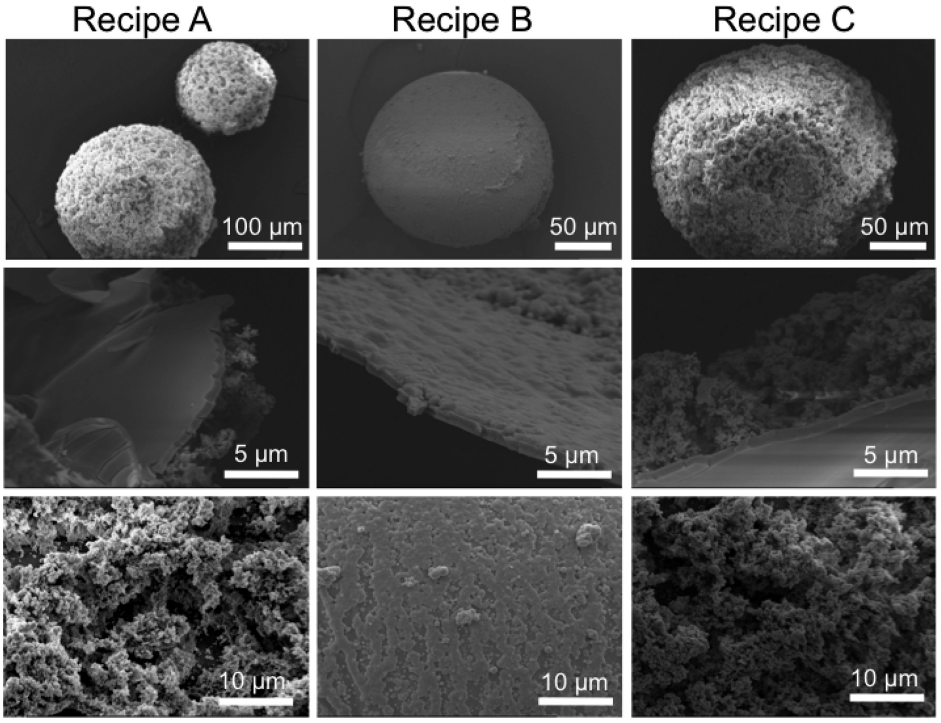

Figure 3. SEM images of COT microcapsules from recipe A (left), recipe B (middle), and recipe C (right). Top: intact capsule. Middle: cross-section of capsule shell wall. Bottom: close-up of outer side of capsule shell wall.

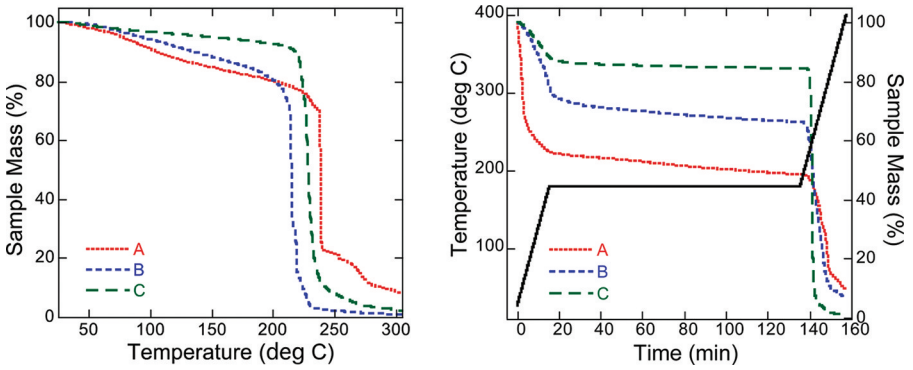

Figure 4. Left: dynamic TGA curves at 10 °C/min. Right: isothermal TGA curves for capsules plotted versus the temperature profile (25−180 at 10 °C/min), held at 180 °C for 2 h, then heated from 180 to 400 at 10 °C/min).

compression between two glass slides. Release of the core material was evident, and, immediately, a color change from pale yellow to red-orange was observed (Figure 5b). The color changed over 30 min to dark purple (see Figure S2 in the Supporting Information). This color change is consistent with an increase in the degree of polymerization (DP) of polyacetylene. As the conjugation length increases due to increasing DP, the polymer absorption should shift to the red and become more broad, eventually appearing almost black. As a control, COT capsules were deposited onto a glass slide with no catalyst (Figure 5c). Crushing these capsules between glass slides resulted in release of core contents and no change in color (Figure 5d). UV−vis absorption spectra of the capsules crushed between two glass slides in the presenence of the Grubbs−Love catalyst show new red-shifted peaks (see Figure S3 in the Supporting Information), which is consistent with the change in color and increase in conjugation length as the polymerization reaction progresses.

Lastly, we wanted to demonstrate damage indication by color change in a solid polymer film. COT microcapsules (recipe C, 15 wt %) and Grubbs-Love catalyst (1.5 wt %) were incorporated into poly(acrylic acid) (PAA) films ca. 500 μm thick. We chose aqueous PAA for processing in order to minimize catalyst degradation and leaching of the hydrophobic COT core into the polymer matrix during film deposition. Controls were prepared in which (1) only capsules were incorporated, (2) only catalyst was incorporated, and (3) neither catalyst nor capsules were incorporated. After curing overnight at room temperature (ca. 21 °C), the films were scratched with a razor blade. Within 1 min after damage, the scratched region displayed a red-orange color (Figures 6), consistent with the color change observed when crushing capsules and catalyst together. After ca. 30 min, the color at the scratched area turned a dark purple color (see Figure S4a in the Supporting Information). Color change was observed both within the trench remaining from the scratch (see Figure S4b in the Supporting Information) and underneath the film when

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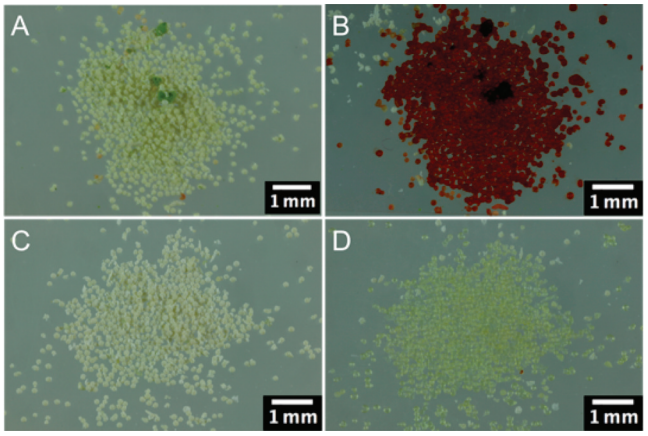

Figure 5. Photographs of COT microcapsules from Recipe C. (a) capsules mixed with 5 wt % Grubbs–Love catalyst before crushing, (b) capsules mixed with 5 wt % Grubbs-Love catalyst 1 min after crushing between glass slides, (c) capsules without catalyst before crushing, and (d) capsules without catalyst 1 min after crushing between glass slides.

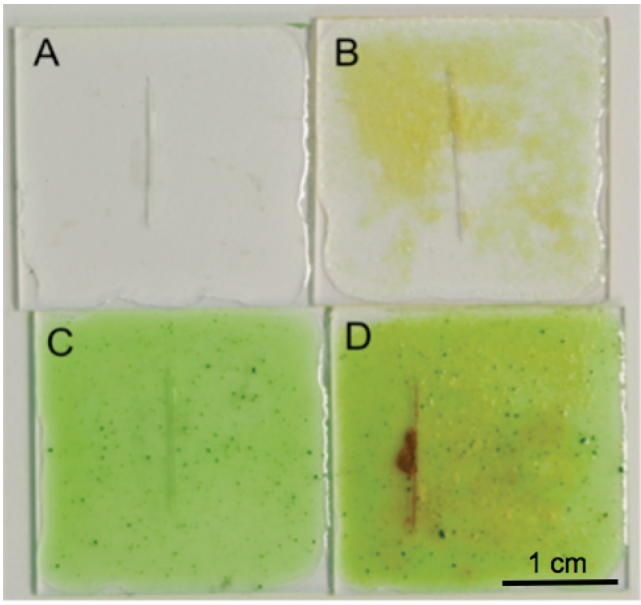

Figure 6. Photographs of PAA films containing (a) no microcapsules or catalyst, (b) 15 wt % COT microcapsules prepared by recipe C, (c) 1.5 wt % Grubbs–Love catalyst, and (d) 15 wt % COT microcapsules prepared by recipe C and 1.5 wt % Grubbs–Love catalyst. The 1 in. × 1 in. films are shown 2 min after being scratched with a razor blade.

delamination occurred (see Figure S4c in the Supporting Information). In all cases, the control samples did not show color change.

3. CONCLUSIONS

In conclusion, we demonstrated that COT released from ruptured microcapsule reacts with the Grubbs-Love catalyst, showing immediate color change. The color continues to darken from red to purple over time, consistent with the increasing degree of polymerization. Modifying the capsule preparation recipe by including more shell wall monomers and a prepolymer increases capsule stability. We were able to demonstrate color change upon mechanical damage in PAA and envision that COT or a dimer thereof may be useful in structural self-healing as well as for damage indication through the formation of a cross-linked polyacetylene, which would be both intensely colored and perhaps structurally supportive due to cross-linking. Because the Grubbs-Love catalyst also polymerizes DCPD, a structurally self-healing monomer that forms a cross-linked polymer network, it may be possible to combine these two monomers for a multifunctional approach in the autonomic damage detection and self-healing of coating materials through the formation of both polyacetylene for damage indication and poly(DCPD) for structural healing, either through a multicapsule approach or by combining DCPD and COT within one capsule.

4. EXPERIMENTAL SECTION

Urea, resorcinol, formalin, 3-bromopyridine, and the Grubbs' second-generation catalyst were purchased from Aldrich Chemical Co. Ethylene-maleic anhydride copolymer (Zemac-400) powder with an average molecular weight of 400 kDa (Vertellus) was used as a 2.5 wt % aqueous solution. Polyacrylic acid (PAA), 25 wt % in water, with an average molecular weight of 50 kDa, was purchased from Polysciences. The commercial polyurethane prepolymer, Desmodur L 75, was purchased from Bayer Material Science. 1,3,5,7-Cyclooctatetraene was purchased from Equinox Chemicals, LLC. The Grubbs-Love catalyst was synthesized as previously described.[19]

Microcapsule Preparation. One-hundred milliliters of distilled water was placed in a 600 mL beaker, along with 25 mL of 2.5% (wt/vol) ethylene co-maleic anhydride as a surfactant. The beaker was placed in a temperature-controlled water bath equipped with a mechanical stirring blade (40 mm diameter), which was brought to 500 rpm. To the aqueous solution was added the solid wall-forming materials: urea (1.25 or 2.50 g), ammonium chloride (0.125 or 0.25 g), and resorcinol (0.125 or 0.25 g). Afterward, the pH was raised from 2.7 to 3.5 by addition of NaOH (aq). Desmodur L75 (0 or 4 g) in 1,3,5,7-cyclooctatetraene (30 mL) was added to the stirring solution, creating an emulsion. After 10 min, formalin solution (3.11 or 6.33 g) was added, and the temperature was increased to 55 °C. The reaction proceeded under continuous stirring for 4 h after which the reaction mixture was allowed to cool to room temperature. The microcapsules were filtered the next day using a Buchner funnel, were washed with water, and were dried under air for 24 h before sieving to collect capsules with diameters ranging from 125 to 180 μm. A summary of the recipes used (including amounts of urea, ammonium chloride, resorcinol, and Desmodur L75) is provided in Table 1.

Microcapsule Analysis. Optical micrographs of dried, sieved capsules in mineral oil on glass slides were taken using a Leica DMR Optical Microscope. Images of dried capsules were obtained using SEM (FEI/Philips XL30 ESEM-FEG) after sputter coating with a gold–palladium source. Thermogravimetric analysis (TGA) was performed on a Mettler-Toledo TGA851^e, calibrated by indium, aluminum, and zinc standards. For dynamic TGA scans, a heating rate of 10 °C min^{-1} was used. For isothermal TGA, samples were heated from 25–180 at 10 °C min^{-1}, held at 180 °C for 2 h, then heated from 180–400 at 10 °C min^{-1}. Experiments were performed under nitrogen atmosphere. For each TGA experiment, 3–10 mg of accurately weighed sample was used.

Thin Film Preparation. To prepare PAA films, we mixed 0.037 g of COT capsules and 0.004 g of catalyst into 1 mL of a solution of PAA. The solution was placed under vacuum for 5 min to remove air bubbles and then deposited on glass slides at 0.3 mL per square inch of slide. The slide was exposed to a continuous flow of dry air for 24 h to remove water.

■ ASSOCIATED CONTENT

Supporting Information

Additional optical micrographs and photographs. This material is available free of charge via the Internet at http://pubs.acs.org/.

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