Supporting Information

Healing damaged coatings using friction-sensitive hybrid microcapsules

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Part S1. Materials and methods

Materials
All materials were used as received without further purification. Poly(ethylene-alt-maleic anhydride) (PolyEMA), formic acid, castor oil and pyrene were purchased from Sigma-Aldrich (Spain). The commercial polyurethane prepolymers Desmodur® PL340 and Bayhydur® XP2547 were supplied by Bayer (Spain). Desmodur® PL340 is a blocked aliphatic polyisocyanate based on IPDI solution in butyl acetate/solvent naphtha 100 (18:22 ratio) with a blocked isocyanate content of 7.3% (w/w). Bayhydur® XP2547 is a water-dispersible hydrophilic aliphatic polyisocyanate based on hexamethylene diisocyanate (HDI) with an isocyanate content of 22.5% (w/w). The commercial melamine-formaldehyde (MF) prepolymer Beetle® PT312 (73% solids content and 0.2% to 0.3% free formaldehyde) was purchased from BIP Limited (Oldbury). 2K Polyurethane polymer matrix (base and catalyst) was supplied by Naber S.A. (Spain).

Preparation of hybrid MF/PU microcapsules by in situ polymerization
The preparation of the MF/PU microcapsules was based on an interfacial polymerization. Melamine-formaldehyde (MF) resin and hexamethylene diisocyanate (HDI) prepolymer were used for the microcapsule shell wall, and the mixture 4:1 formed by castor oil and blocked isophoronediisocyanate (IPDI) prepolymer as core material. Experimentally, 10 g of MF resin was first dissolved (in a 250 mL beaker) in 90 g of water containing the surfactant polyEMA (3.3% wt) and sodium hydroxide (1.3% wt). Then, a mixture comprising 5 g of castor oil, 20 g of IPDI and 4 g of HDI was added slowly to the aqueous continuous phase under stirring to form the emulsion. The resulting mixture was stirred at 700 rpm for 1 hour. After this time, the pH of the reaction mixture was adjusted to 5 using formic acid, and the temperature of the reaction was raised up to 65 °C and maintained for 3 hours under stirring. After 3 hours, the synthesized MF/PU microcapsules were cooled down to room temperature, cleaned with
methanol/water and resuspended in acid water (pH =5.00). Finally, the microcapsules were
dried into a fine powder by spray-drying at 130 ºC using a Mini Spray Dryer B-290 (BÜCHI
Labortechnik AG, Flawil, Switzerland). The encapsulation efficiency (EE) was calculated
according to the equation EE(%)= [(C_{HA,total}−C_{HA,out})/C_{HA,total}] x100, where C_{HA,total} is the initial
concentration of the healing agent and C_{HA,out} is the concentration of non-encapsulated healing
agent. To measure the C_{HA,out} the final reaction mixture (2 g) in MeOH (18 g) was
centrifuged at 6000 rpm for 5 min. Supernatant aliquots were taken to quantify the
concentration C_{HA,out} by high pressure liquid chromatography coupled to UV-Vis
spectrometry (HPLC-UV; Agilent 1100 Series, Agilent Technologies, USA), where the
concentration of healing agent was linearly detected. All experiments were done in triplicate.
Fluorescent MF/PU microcapsules were also prepared using the protocol described above
with the core material formed by a mixture of castor oil, IPDI and the fluorophore pyrene
(0.12% wt).

**Preparation of pure MF microcapsules by in situ polymerization**

The preparation of the MF microcapsules was based on an interfacial polymerization.
Melamine-formaldehyde (MF) resin were used for the microcapsule shell wall, and the
mixture 4:1 formed by castor oil and blocked isophoronediisocyanate (IPDI) prepolymer as
core material. Experimentally, 10 g of MF resin was first dissolved (in a 250 mL beaker) in 90
g of water containing the surfactant polyEMA (3.3% wt) and sodium hydroxide (1.3% wt).
Then, a mixture comprising 5 g of castor oil and 20 g of IPDI was added slowly to the
aqueous continuous phase under stirring to form the emulsion. The resulting mixture was
stirred at 700 rpm for 1 hour. After this time, the pH of the reaction mixture was adjusted to 5
using formic acid, and the temperature of the reaction was raised up to 65 ºC and maintained
for 3 hours under stirring. After 3 hours, the synthesized MF microcapsules were cooled down
to room temperature, cleaned with methanol/water and resuspended in acid water (pH =5.00).
Finally, the microcapsules were dried into a fine powder by spray-drying at 130 °C using a Mini Spray Dryer B-290 (BÜCHI Labortechnik AG, Flawil, Switzerland). Fluorescent MF microcapsules were prepared using the protocol described above with the core material formed by a mixture of castor oil, IPDI and the fluorophore pyrene (0.12% wt).

**Preparation of pure PU microcapsules by in situ polymerization**

The preparation of the PU microcapsules was based on an interfacial polymerization. Hexamethylene diisocyanate (HDI) prepolymer were used for the microcapsule shell wall, and the mixture 4:1 formed by castor oil and blocked isophorondiisocyanate (IPDI) prepolymer as core material. Experimentally, 90 g of water containing the surfactant polyEMA (3.3% wt) and sodium hydroxide (1.3% wt) was added slowly to the a mixture comprising 5 g of castor oil, 20 g of IPDI and 10 g of HDI (in a 250 mL beaker) under stirring to form the emulsion. The resulting mixture was stirred at 1000 rpm for 1 hour. After this time, the temperature of the reaction was raised up to 50 °C and 10 mL of a water-based urea solution (20%) was added dropwise. The temperature of the reaction was raised up to 95 °C and maintained for 1 hour under stirring. After that, the synthesized PU microcapsules were cooled down to room temperature, cleaned with methanol/water and resuspended in acid water (pH =5.00). Finally, the microcapsules were dried into a fine powder by spray-drying at 130 °C using a Mini Spray Dryer B-290 (BÜCHI Labortechnik AG, Flawil, Switzerland). Fluorescent PU microcapsules were prepared using the protocol described above with the core material formed by a mixture of castor oil, IPDI and the fluorophore pyrene (0.12% wt).

**Microcapsule incorporation in the polyurethane-based varnish and Scratch-and-Repair experiment**

Microcapsules (from 5% to 10% wt) were homogeneously dispersed in the solvent-based 2K polyurethane varnish (base: catalyst at 2:1 ratio) under continuous stirring at 500 rpm for 15
minutes. The resulting dispersion was then sprayed on a wood substrate using a High Volume Low Pressure (HVLP) Spray Gun (Voylet H-827), and the resultant coating was cured under ambient conditions for 48 hours. To perform the Scratch-and-Repair experiment, mechanical damages (cracks) were generated in the polyurethane-based varnish with a scalpel. The damaged areas were scratched with a cloth as shown in Video S1. To obtain an optimum self-healing system, the effect of the concentration of microcapsules (5% to 10% [w/w]) on the healing behavior was studied, and a value of 10% (w/w) was found to be optimum.

**Characterization**

Microcapsule morphology was examined by Field-Emission Scanning Electron Microscopy (FE-SEM) on a FEI Quanta 650 microscope using aluminum tape as support. Microcapsule size distributions were determined by light diffraction (LD) on a Mastersizer2000 (Malvern Instruments). Microcapsule composition (shell and core) was analyzed by $^{13}$C-NMR on a Bruker DRX 400 spectrometer (400 MHz for $^{13}$C) in CDCl$_3$ at room temperature, by FTIR-ATR spectroscopy with a Bruker Tensor 27 equipped with a MVP-Pro ATR module, by MALDI-TOF–MS with a Bruker mass spectrometer UltraflleXtreme with Modus Reflection, and finally by high resolution Scanning Electron Microscopy (HR-SEM) on an Zeiss EVO microscope with the energy selective backscattered detector (EBS) and a coupled energy dispersive X-ray spectrometer (EDS Oxford INCA) at low voltage. Mechanical properties of microcapsules were tested by nanoindentation on a Nanoindenter XP (MTS Nano Instruments; see also Figure S5). Blue fluorescence optical images were taken on an Axio Observer.Z1m Carl Zeiss microscope. The *Scratch-and-Repair* experiments were followed by Confocal Laser Scanning Microscopy (CLSM) using a Leica TCS SP5. Note that the acquisition of green fluorescence corresponds to the typical pyrene excimer emission ($\lambda_{\text{em}} = 465$ nm to 500 nm) [M. J. Uddin, A. T. M. Zafrul, *Am. J. Biochem. Mol. Biol.* **2013**, 3, 174]. 3D
surface topography and roughness profiles were acquired by confocal profilometry on a Leica DCM 3D microscope combining confocal imaging and interferometry.
Figure S1. Molecular structure of the core and shell materials, and representation of the expected condensation between the MF prepolymer and HDI to form the MF/PU shell.

Shell material

[Chemical structures and reactions]

Core material

[Chemical structures and reactions]
Figure S2. Particle-size distribution for the MF/PU microcapsules, as measured by laser diffraction.
Figure S3. a) Backscattered HR-SEM image of the capsule shell acquired in a thermosetting matrix with a C, N and O profile using low-voltage EDS (2 KeV). Note that the distribution of N atoms throughout the shell is homogeneous. Scale bar: 200 nm.
Figure S4. $^{13}$C NMR spectra in CDCl$_3$ of castor oil (orange spectrum), IPDI (yellow spectrum), castor oil + IPDI (core, purple spectrum), MF (green spectrum) and HDI (red spectrum). $^{13}$C solid–state NMR spectrum of hybrid MF/PU microcapsules filled with the healing mixture (black spectrum). The latter spectrum reveals the MF/PU hybrid nature of the capsule shell, as confirmed by the disappearance of the NCO signal of HDI (*) and the appearance of two new signals: one at 183 ppm (*), which corresponds to the shift of the aromatic carbons in melamine upon urea formation; and one at 158 ppm (*), which corresponds to the carbonyl groups of the new urea groups formed upon reaction of the isocyanates of HDI with the secondary amines of the MF resin. We compared the $^{13}$C solid-state NMR spectrum to a reported spectrum of MF resin, which shows a characteristic resonance peak at 166 ppm [A. Baraka, P. J. Hall, M. J. Heslop, React. Funct. Polym. 2007, 67, 585].
Figure S5. a) Representative plot of load vs. surface displacement for compressing microcapsules to rupture. All experiments were done on a single microcapsule that was compressed to rupture using a Berkovich probe to determine their rupture force. The force resolution ranged from 3 mN to 20 mN, depending on the nature of microcapsule; the surface approach velocity was 10 nm/s and the maximum displacement was 20 μm. In a typical experiment, from point 1 to 2, the probe moves in air until it touches the superstructure. As per standard, the force increases as the microcapsule is compressed (from 1 to 2). At point 2, the microcapsule bursts, causing the force to drop. At this moment, the probe is still moving until it hits the bottom of the surface, when the force begins to increase sharply (point 3). From this study, we have determined the mechanical forces needed to rupture all synthesized microcapsules. This graphic corresponds to the hybrid MF/PU microcapsules. b) SEM image of a single nanoindented MF/PU microcapsule via Berkovich probe. Scale bar: 5 μm.
Figure S6. a-c) Representative SEM images of (a) MF, (b) hybrid MF/PU and (c) PU microcapsules after spray-drying. Note that the MF microcapsules did not survive the process. d-f) Representative fluorescence optical images of (d) MF, (e) hybrid MF/PU and (f) PU microcapsules after scratching. Note that only the PU microcapsules did not break upon scratching. Scale bars: 10 μm (a-c) and 20 μm (d-f).
Figure S7. Polyurethane coating before and after microcapsule incorporation. 3D confocal profilometry images of the surface topography and roughness profile of the polyurethane-based varnish (a) without and (b) with the microcapsules.
Figure S8. Additional examples of the Scratch-and-Repair experiment on wood surfaces. CLSM images (reflection) of fluorescent healing microcapsules dispersed in the polyurethane-based varnish after mechanical damage with a scalpel (left) and following the surface scratching (right). Scale bars: 200 µm (a), 50 µm (b) and 30 µm (c).
**Figure S9.** a) Characteristic zoomed CLSM image (reflection) of a damaged polyurethane-based varnish, showing the selective location of the microcapsules in the burrs created at the edges of the cracks. b,c) Representative FE-SEM images showing the evolution of two damaged regions before and after the *Scratch-and-Repair* experiment, highlighting the presence of microcapsules in the burrs before *Scratch-and-Repair*, and filling of the cracks after *Scratch-and-Repair*. Scale bars are 100 µm (a), 20 µm (b and c, top-left and right), and 10 µm (b and c, bottom-left).
Figure S10. 3D confocal profilometry and optical images of a polyurethane-based varnish without microcapsules after (a) mechanical damage with a scalpel and (b) subsequently, after the Scratch-and-Repair experiment. Note that we could not observe any degree of repair. Scale bars: 50 µm.
Figure S11. FTIR-ATR spectra of the castor oil and the IPDI and the healing agent mixture (IPDI/castor oil) once hardened under ambient conditions. As observed, the spectrum of the mixture does not reveal either the typical isocyanate–NCO peak (at 2265 cm⁻¹), suggesting that the isocyanate groups of IPDI had remained blocked, or the characteristic carbonyl peak (1710 cm⁻¹; C=O), indicating that no reaction had occurred between the alcohol groups of the castor oil and the isocyanate groups of the IPDI.
**Figure S12.** $^{13}$C-NMR spectra (in CDCl$_3$) of IPDI (green spectrum), castor oil (red spectrum) and the solidified core healing mixture (IPDI/castor oil) upon exposure to air and consequent solidification (blue spectrum). In this last spectrum, no new signals were observed in comparison to the pure components, meaning that no chemical reaction between the IPDI and castor oil is involved in the solidification. In addition, some peaks that are present in the $^{13}$C-NMR spectrum of IPDI disappear when the healing content solidifies; this corresponds to evaporation of the solvents butyl acetate and naphtha.
Figure S13. MALDI-TOF–MS spectra of castor oil, solid IPDI and the solidified mixture (IPDI/castor oil). Measurements were performed with a laser source operating system at 25kV. Ditrano was used as matrix. The analyzed m/z ranges were 0 to 1000 (for castor oil) and 0 to 5000 (IPDI; and IDPI/castor oil). As seen, the IDPI/castor oil spectra do not reveal new signals in comparison to the pure components (IPDI and castor oil), since all the observed peaks correspond to the pure components of the mixture. This fact further confirms that solidification of the healing mixture does not involve any chemical reaction.
Figure S14. Optical images of (a) a first polyurethane-based varnish-coated surface treated by Scratch-and-Repair and subsequently washed with (b) ethanol and (c) a commercial wood cleaner. Optical images of (d) a second polyurethane-based varnish-coated surface treated by Scratch-and-Repair and subsequently washed with (e) water and (f) acetone. Note that no changes or drag of the healing agent was observed at the repaired region or surroundings after cleaning with ethanol, the commercial wood cleaner or water. In contrast, acetone was able to drag the healing agent. Scale bars: 50 µm.
Figure S15. FTIR-ATR spectra of the healing agent mixture (IPDI/castor oil) with (at room temperature, red; at 200 °C, violet) and without (at room temperature, black; at 200 °C, blue) the catalyst DBTL. Importantly, the spectrum of the mixture IPDI/castor oil at 200 °C shows the characteristic isocyanate –NCO peak at 2265 cm\(^{-1}\) (*), which confirms the unblocking of these groups. However, these groups do not react with the hydroxyl groups of the castor oil, as indicated by the absence of the characteristic carbonyl peak at ca. 1710 cm\(^{-1}\). Contrariwise, the spectrum of the mixture DBTL/IPDI/castor oil at 200 °C lacks the isocyanate peak at 2265 cm\(^{-1}\) but shows the characteristic bands at 1636 cm\(^{-1}\) [*] and at 1562 cm\(^{-1}\) [*] associated to the CO and NH groups of the polyurethane, respectively, confirming the reaction between the alcohol groups of the castor oil and the unblocked isocyanate groups of the IPDI.
Figure S16. Scratch-and-Repair experiment on wood surfaces with the healing mixture IPDI/castor oil/DBTL encapsulated into MF/PU microcapsules. CLSM images (reflection) of (a) fluorescent catalyst based-microcapsules dispersed in a polyurethane-based varnish, (b) the surface after the mechanical damage with a scalpel, and (c) the surface following the scratching. (d) Optical image of the same repaired area after exposing it at 200 °C for 5 minutes, and then washing it with acetone. Note that in this case, no changes or drag of the healing agent were observed at the repaired region after cleaning with acetone, in sharp contrast to the case in Figure S14f. Scale bars: 100 µm (a-c) and 75 µm (d).