Electronic Supporting Information

Self-Reporting Mechanochromic Coating: Glassfiber Reinforced Polymer Composite That Predicts Impact Induced Damage

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Abbreviations

The use of abbreviations follows the conventions from the ACS Style guide.^[1] In addition, the following abbreviations were used.

Abbreviation	Meaning
ATR	Attenuated total reflection (IR)
COSY	Correlation spectroscopy
dd (NMR)	Doublet of doublets
EI	Electron ionization
FT	Fourier transform
НМВС	Heteronuclear multiple bond correlation
HSQC	Heteronuclear single quantum coherence

Analytical Equipment

NMR spectra were recorded on a Bruker Avance Neo 500 (¹H NMR: 500 MHz) FT-NMR spectrometer at 300 K. ¹H NMR and ¹³C{¹H} NMR spectra were referenced against the solvent residual proton signals (¹H) or the solvent itself (¹³C).

The exact assignment of the peaks was performed by two-dimensional NMR spectroscopy such as ¹H COSY, ¹H NOESY, ¹H/¹³C HSQC and ¹H/¹³C HMBC.

Mass spectrometric measurements were performed in the positive ion collection mode using a JEOL-Accu TOF 4GGCV EI mass spectrometer. For electron spray ionization (ESI), a Thermo Fisher Q Exactive Plus mass spectrometer with a quadrupole orbitrap was used in positive and negative ion collection mode with an ionization potential of 3.2 kV.

FTIR spectra were measured using a Perkin Elmer Paragon 1000 FT-IR spectrometer equipped with an A531-G Golden-Gate-ATR-unit.

The irradiation experiments were carried out using LED light sources with an optical power of 680 mW (360-370 nm) and 20 W (520-530 nm) at the LED.

A scanning electron microscope (SEM) from Carl Zeiss (10 kV, 10 μ A) was used to investigate the samples in the presented work.

Infrared (IR) images were obtained using a FLIR ONE camera. The images were processed and temperatures were extracted using the software FLIR Tools.

Materials

1',3',3'-Trimethyl-6-nitrospiro[chromene-2,2'-indoline]



Materials: 1,3,3-Trimethyl-2-methyleneindoline was purchased from Sigma-Aldrich Co. (Aldrich, 97%), 2-hydroxy-5-nitrobenzaldehyde was purchased from TCI Co. (>97%) and ethanol was purchased from Acros (anhydrous, \geq 99.5%, stored over molecular sieves). All reagents were used without further purification.^[2]

1,3,3-Trimethyl-2-methyleneindoline (7.80 g, 45.0 mmol) and 2-hydroxy-5-nitrobenzaldehyde (7.52 g, 45.0 mmol) were dissolved in EtOH (125 mL) and heated to 78 °C for 3 h. Then the reaction mixture was cooled to -25 °C and the crystallized product was obtained after filtration as a green powder (12.7 g, 39.4 mmol, 88 %, Lit.: 89 %).^[2]

Melting point: T = 176 °C, Lit: 178 – 179 °C^[2]

¹**H NMR** (500 MHz, CDCl₃, 300 K): δ = 8.03 – 7.99 (m, 2H, H-5, H-7), 7.21 (ddd, ³*J* = 7.7 Hz, ³*J* = 7.4 Hz, ⁴*J* = 1.0 Hz, 1H, H-6'), 7.09 (dd, ³*J* = 7.2 Hz, ⁴*J* = 1.0 Hz, 1H, H-4'), 6.93 (d, ³*J* = 10.3 Hz, 1H, H-4), 6.89 (ddd, ³*J* = 7.4 Hz, ³*J* = 7.2 Hz ⁴*J* = 1.0 Hz, 1H, H-5'), 6.77 (d, ³*J* = 8.5 Hz, 1H, H-8), 6.56 (d, ³*J* = 7.7 Hz, 1H, H-7'), 5.86 (d, ³*J* = 10.3 Hz, 1H, H-3), 2.75 (s, 3H, H-10'), 1.30 (s, 3H, H8'), 1.19 (s, 3H, H-9') ppm.

¹³C{¹H} NMR (126 MHz, CDCl₃, 300 K): δ = 160.0 (C-6), 147.8 (C-7'a), 141.1 (C-4a), 136.3 (C-3'a), 128.4 (C-4), 128.0 (C-6'), 126.0 (C-7), 122.8 (C-5), 121.8 (C-3), 121.7 (C-4'), 119.9 (C-5'), 118.8 (C-8a), 115.6 (C-8), 107.2 (C-7'), 106.5 (C-2), 52.4 (C-3'), 29.0 (C-10'), 26.0 (C-9'), 20.1 (C-8') ppm.

IR (ATR): $\tilde{\nu}$ = 3069 (w), 2966 (w), 2866 (w), 1655 (w), 1610 (m), 1575 (m), 1509 (s), 1488 (s) 1443 (m), 1364 (m), 1333 (vs), 1303 (s), 1271 (vs), 1185 (m), 1123 (s), 1089 (vs), 1022 (s), 950 (vs), 930 (s), 913 (s), 807 (vs), 752 (vs), 681 (s), 628 (m), 575 (m), 550 (m), 518 (m) cm⁻¹.

HRMS (EI-TOF): *m/z* (%): [M]⁺ calcd. for [C₁₉H₁₈N₂O₃]⁺ 322.1317; found 322.1292 (67), 159.10 (100) [M-Ph-O-NO₂-C₂H₂]⁺.

Sample Preparation

The "epoxy resin L", the "hardener S" and the woven glassfibers with an areal density of 163 gm⁻² used for the reinforcement were purchased from R&G Faserverbundwerkstoffe GmbH. The components for the PTU matrix, were bought from FPT Fluid- & Prozesstechnik GmbH. Both matrices were used and processed without further treatment, following the suppliers' instructions.

Polymer composites with and without glassfibers were produced as explained in this section. Spiropyran (SP) was used in all the samples as a stress indicator to compare the mechanochromocity and the impact resistance of the composite system. In all the samples, SP was used at a concentration of 0.5 wt% and the glassfiber concentration was at ~8 wt%. The PTU/spiropyran (PTU/SP) was coated onto the woven glassfibers as explained in the following procedure. The monomers pentaerythritol tetrakis(3-mercaptopropionate) (PETMP) and hexamethylene diisocyanate (HDI) were mixed at a weight ratio of 1:1.4 with SP. After 15 min of degassing in a decicator, 20% of the total volume of this mixture was cast into a mold so that a uniform layer was obtained. A rectangular woven glassfiber mat (70*70 mm²) was placed over the unpolymerized layer and the remaining 80% of the mixture was poured over the glassfiber mat. The sample was then placed for 20 h in a furnace at 80 °C. To compare the GFPS composite system to the commercially available epoxy polymer, epoxy/spiropyran coated glassfiber (GFES) samples were prepared similarly: PTU/SP was first hand-dispersed into the hardener and the epoxy resin (45:100 parts by volume of hardener : epoxy) was later added to the dispersion, the unpolymerized mixture was coated onto the glassfiber mat as explained earlier. PTU/SP, GFPS and GFES i.e., sheets with and without glassfiber mats (thickness, 5 mm) were then cut into smaller samples of the size 20*20 mm² for further investigations.

Stimuli Separation

When molecular switches with several stimuli are utilized in outdoor applications effects of constant UV exposure has to be taken into account. To avoid gradual material degradation under UV exposure most exterior surfaces are coating by a UV protective layer. A lab scale experiment was performed to verify if such a coating is sufficient to block UV irradiation and provide stimuli separation. For this experiment, a PTU/SP composite sample was partially coated with thin layer of a UV blocker and this sample was irradiated UV light for 30 s (see **Figure SI-3**).



Figure SI-1: On the left is the pristine spiropyran embedded PTU composite (PTU/SP) before UV treatment. On the right is the same composite partially masked with a thin layer of UV protective coating and irradiated with UV light for 30 s.

In Figure SI-1, UV protective layer appeared to be sufficient to prevent accidental switching of spiropyran and further prevention of photo bleaching.

Hammer Test

The "Hammer test" test (Figure SI-1) involved a hammer weighing 2.141 kg with a hinge at its base falling freely on the samples. The test was repeated periodically until a color change was observed. The force required to damage the system was determined by the number of hits needed to cause a color change from orange to purple.



Figure SI-2: Sketch of the "Hammer test". The hammer shaft is drawn to a defined height and released on to the sample freely.

The impact force was calculated using the following equation $F = m \cdot g \cdot sin\theta = m \cdot g \cdot \frac{n}{l}$ where **F** is Force, **m** is weight of the hammer head **g** is acceleration due to gravity. **h** is height of fall and **l** is length of the hammer. Pressure per impact was calculated using $P = \frac{F}{a}$

head, **g** is acceleration due to gravity, **h** is height of fall, and **l** is length of the hammer. Pressure per impact was calculated using $P = \frac{F}{a}$ where **a** is the area of impact or point of contact. The measured area of impact was 1.53e⁻⁴ m².

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Corresponding videos of the periodic impact test were created with ImageJ by stacking the images taken after each hit under periodic impact test of the samples PTU/SP and GFPS. An RGB hyper stack was created using ImageJ for the purpose of quantitative analysis. Videos of the impact test of the sample PTU/SP with separated red, blue and green filter served to observe which color showed the most transformation under impact and was thus most suited for the analysis. These videos are attached separately.

Infrared Imaging

To monitor the temperature changes occurring at the point of impact on a sample due to periodic impact (Hammer test) IR imaging was employed. The resulting temperatures at and around the point of impact differed by maximally ~6-8 °C (Figure SI-2).



Figure SI-3: Images of GFPS samples were taken by an infrared camera at the end of the periodic impact test. Temperatures at different spots (Sp) were measured for comparison.

Analysis of Spiropyran Degradation in the Epoxy Matrix

The molecular switch (SP) in the epoxy matrix could not be used as a stress indicator. SP is a molecule with several functional groups and the components for the synthesis of the epoxy polymer also comprise a high number of compounds with various functional groups. It is plausible that undesired reactions between these components and the SP take place and thus render the molecule inactive. In order to shed some light on this, several experiments were performed:

The supplier of epoxy system that was used, R&G Faserverbundwerkstoffe GmbH, specifies the "Epoxy Resin L" as a three-component mixture, consisting of an epoxy resin as pre-polymer, phenylglycidyl ether formaldehyde resin as reactive pre-polymer and 1,6-hexanediol diglycidyl ether as reactive monomer (shown in **Figure SI-4**). The "Hardener S" is a mixture of six components. Two styrenated phenols, 2-hydroxy benzoic acid and three primary amines are combined to ensure complete curing within 24 h above 5 °C. Since the supplier specifies only percentage ranges for each component, accurate investigation of the reaction of SP with the hardener and resin during the curing was not feasible. Instead, four model compounds representing the functional groups in both resin and hardener were chosen. Isopropyl glucidyl ether (*iPr-Epoxy*) and phenyl glucidyl ether (*Ph-Epoxy*) represent the reactive components in the "Epoxy Resin L". The "Hardener S" contains phenol groups, benzoic acid groups and amines. Here 2-hydroxybenzoic acid (HBA) and *m*-xylylenediamine (XDA) was chosen as representative components.

The four reference compounds (*i*Pr-Epoxy, 98%; Ph-Epoxy, 99%; HBA, ≥99% and XDA, 99%) were purchased from TCI Co and used without further purification.



Figure SI-4: Composition of the commercial epoxy system. Top: Composition of the purchased Epoxy Resin L and Hardener S from R&G Faserverbundwerkstoffe GmbH. Bottom: Four model compounds were selected for the investigation of the possible reaction of **SP** during the curing process. The compounds were dissolved in THF-*d*_g, before adding SP. Only the sample with **XDA** lead to decomposition of the SP as shown by NMR spectroscopy.

Each of the four compounds (20 μ mol) were mixed with SP (20 μ mol) in THF- d_8 and placed in sealable NMR tubes in a nitrogen filled glove box. To understand the interaction between SP and the components three ¹H NMR spectra were obtained: a) immediately after mixing, b) after resting for 1 h at 25 °C, and c) after resting for 20 h at 70 °C.

The ¹H spectra of the SP and the four equimolar mixtures after the complete heating cycle is displayed **Figure SI-5**. All spectra were recorded using the same settings and were not individually rescaled. The signals corresponding to the protons of the SP can be found in all spectra, however, they are notably less intense in the top spectrum, corresponding to the mixture with **XDA**. The signals of the proton *H*-3 and the methyl groups *H*-8' and *H*-9' (compare section 4) are the most distinct ones to control the SP's stability and they are highlighted in **Figure SI-5**.

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Figure SI-5: Overview of the stability test. The ¹H spectra of (bottom to top) SP, SP + *i***Pr-Epoxy**, SP + **Ph-Epoxy**, SP + **HBA**, SP + **XDA** after resting at 70 °C for 20 h are shown. All spectra were recorded with the same settings and were not rescaled. The blue box highlights the signal of the proton *H-3* and the red box highlights the signal of the methyl protons *H-8'* and *H-9'* (compare section 4) of the SP. The intensity of these signals is drastically reduced in the top spectrum, corresponding to the mixture of SP and **XDA**. The signals corresponding to the solvent THF-*d*₈ are labeled in the bottom spectrum.

In order to reveal the kind of reaction that could have occurred with **XDA**, the sample with SP and **XDA** was fully investigated using NMR methods. First, a switching to the open merocyanine form could be excluded as the characteristic signal of the ethylene bridge was absent. Whereas the coupling constant of the protons (H-3 and H-4, compare to **Chapter 3** in this SI) is approx. 10 Hz in the closed form, it increases to approx. 15 Hz in the open form.^[3] It was possible to identify 1,3,3-trimethyl-2-methyleneindoline (**Ind**) and 5-nitrosalicylaldehyde-1,3-xylylenediimine (**SXI**) as products, proving a cleavage of the ethylene bridge in the SP. ESI mass spectrometry in high resolution of the reaction mixture proved the presence of the four mentioned compounds. An additional set of signals was detected in ¹H and ¹³C{¹H} NMR. As in **SXI**, it contained signals corresponding to imine bridges. However, it might be structurally similar to **SXI** and could not be assign this set of signals to a reasonable product.



Scheme SI-1: Confirmed ring opening reaction of SP in presence of xylylenediamine (**XDA**). 1,3,3-Trimethyl-2-methyleneindolene (**Ind**) and 5-nitrosalicylaldehyde-1,3-xylylenediamine were identified as products. The broken SP bonds are indicated as red wavy lines.

The NMR shift data were obtained by measuring the reaction mixture. Assignment of the peaks was performed by using spectra of the pure compounds SP, **XDA** and **Ind** as reference. The ESI measurement was performed using an ionization potential of 3.2 kV. SP, **XDA** and **Ind** were detected in positive ion mode; **SXI** was detected in negative ion mode.

Signals assigned to SP:



¹**H NMR** (500 MHz, THF- d_8 , 300 K): δ = 8.08 (d, ⁴*J* = 2.8 Hz, 1H, H-5), 8.01 (dd, ³*J* = 9.0 Hz, ⁴*J* = 2.8 Hz, 1H, H-7), 7.12 – 7.08 (m, 2H, H-4, H-6'), 7.05 (dd, ³*J* = 7.4 Hz, ⁴*J* = 1.3 Hz, H-4'), 6.83 (d, ³*J* = 9.0 Hz, 1H, H-8), 6.79 (ddd, ³*J* = 7.4 Hz, ³*J* = 7.4 Hz, ³*J* = 1.0 Hz, 1H, H-5'), 6.54 (d, ³*J* = 7.7 Hz, 1H, H-7'), 5.95 (d, ³*J* = 10.3 Hz, 1H, H-3), 2.72 (s, 3H, H-10'), 1.28 (s, 3H, H-8'), 1.17 (s, 3H, H-9') ppm.

¹³C{¹H} NMR (126 MHz, THF-*d*₈, 300 K): δ = 160.6 (C-8a), 148.8 (C-7a'), 142.1 (C-6), 137.0 (C-3a'), 129.3 (C-4), 128.4 C-6'), 126.3 (C-7), 123.3 (C-5), 122.3 (C-3), 122.1 (C-4'), 120.4 (C-5'), 120.0 (C-4a), 116.1 (C-8), 107.7 (C-7'), 107.3 (C-2), 52.9 (C-3'), 28.9 (C-10'), 26.2 (C-8'), 20.2 (C-9'). ppm.

HRMS (ESI-Sector): *m*/*z*: [M+H]⁺ calcd. for [C₁₉H₁₉N₂O₃]⁺ 323.1390; found 323.1385.

Signals assigned to xylylenediamine (XDA):

$$H_2N$$
 1 2 3 NH_2

¹H NMR (500 MHz, THF-*d*₈, 300 K): δ = 7.30 – 7.27 (m, 1H, H-2), 7.19 – 7.11 (m, 3H, H-4, H-5, H-6), 3.76 (s, 4H, H-7), 1.39 (s, 4H, N*H*₂) ppm.

¹³C{¹H} NMR (126 MHz, THF-*d*₈, 300 K): δ = 145.3 (C-1, C-3), 128.6 (C-5), 126.4 (C-2), 125.6 (C-4, C-6), 47.4 (C-7) ppm.

HRMS (ESI-Sector): m/z: [M+H]⁺ calcd. for $[C_8H_{13}N_2]^+$ 137.1073; found 137.1072.

Signals assigned to 1,3,3-trimethyl-2-methyleneindoline (Ind):



¹**H NMR** (500 MHz, THF-*d*_{*g*}, 300 K): δ = 7.06 – 7.01 (m, 2H, H-4, H-6), 6.67 (ddd, ³*J* = 7.4 Hz, ³*J* = 7.4 Hz, ³*J* = 1.0 Hz, 1H, H-5), 6.55 (d, ³*J* = 7.8 Hz, 1H, H-7), 3.82 (d, ⁵*J* = 1.9 Hz, 2H, H-11, H-11'), 3.01 (s, 3H, H-10), 1.29 (s, 6H, H-8, H-9) ppm.

¹³C{¹H} NMR (126 MHz, THF-*d*₈, 300 K): δ = 163.4 (C-2), 147.3 (C-7a), 138.2 (C-3a), 128.2 (C-6), 122.3 (C-4), 119.1 (C-5), 105.7 (C-7), 73.5 (C-11), 44.7 (C-3), 30.2 (C-8, C-9), 28.7 (C-10) ppm.

HRMS (ESI-Sector): *m/z*: [M+H]⁺ calcd. for [C₁₂H₁₆N]⁺ 174.1277; found 174.1275

Signals assigned to 5-nitrosalicylaldehyde-1,3-xylylenediimine (SXI):



¹**H NMR** (500 MHz, THF- d_8 , 300 K):¹ δ = 8.68 (m, 2H, H-a), 8.38 (d, ⁴J = 2.9 Hz, 2H, H-6), 8.17 (dd, ³J = 9.2 Hz, ⁴J = 2.9 Hz, 2H, H-4), 7.35 (m, 1H, H-2'), 7.28 (m, H-5'), 7.18 (m, H-4', H-6'), 6.94 (d, ³J = 9.2 Hz, 2H, H-3), 4.85 (m, 4H, H-b) ppm.

¹³C{¹H} NMR (126 MHz, THF-*d*₈, 300 K): δ = 169.5 (C-2), 166.4 (C-a), 139.9 (C-5), 138.2 (C-1', C-3'), 129.1 (C-6), 128.5 (C-4), 127.5 (C-2'), 127.1 (C-5'), 126.7 (C-4', C-6'), 119.2 (C-3), 118.4 (C-1), 62.45 (C-b) ppm.

HRMS (ESI-Sector): *m*/*z*: [M-H]⁻ calcd. for [C₂₂H₁₇N₄O₆]⁻ 433.1154; found 433.1152.

¹ Due to the intensive overlap of signals with a chemical shift of 7.3 – 7.0 ppm in the ¹H NMR spectrum, it was not possible to integrate reliably.

Plotted NMR Spectra

 ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR Spectra of 1',3',3'-Trimethyl-6-nitrospiro[chromene-2,2'-indoline] in CDCl_3



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¹H NMR Spectra of SP, Phenyl Glucidyl Ether (Ph-Epoxy) and the Reaction Mixture in THF-d₈







12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 Chemical Shift (ppm)

¹H and ¹³C{¹H} NMR Spectra of SP, Xylylenediamine (XDA), 1,3,3-Trimethyl-2-methyleneindoline (Ind) and the Reaction Mixture in THF-*d*₈



L2 9.0 8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 Chemical Shift (pm)



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