Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Electronic Supporting Information (ESI) For

Real time monitoring of click chemistry self-healing in polymer composites

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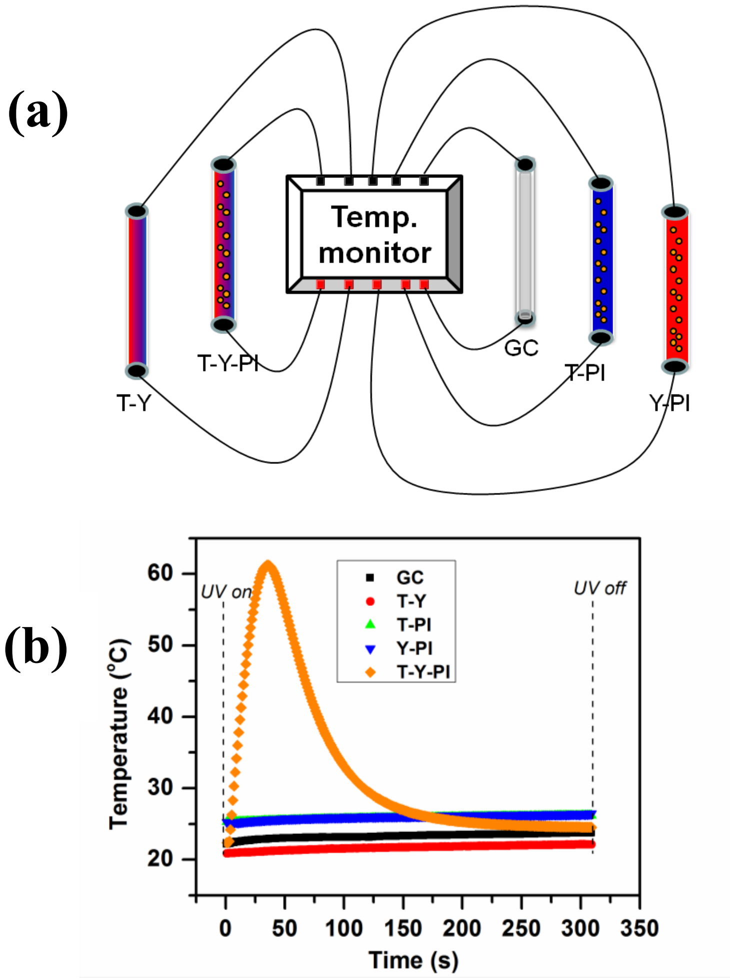

Fig. S1. Temperature monitoring of the click chemical reactions. (a) A schematic of experimental set-up; chemical components for the click reactions are thiol, T, marked in blue, alkyne, Y, labeled in red, and photoinitiator, PI, in golden. (b) Plots of temperature versus UV exposure time.

The changes in temperature were recorded at the same time when the precursor-containing glass capillaries (GCs) were exposed for 5 min to an ultraviolet (UV) light source of 365 nm wavelength and 0.4 mW/cm^2 intensity. For comparison, GCs containing the three chemical components in different arrangements (T-Y, T-PI, Y-PI and T-Y-PI) were tested under the same conditions. T refers to the thiol, Y to the alkyne and PI to the photoinitiator.

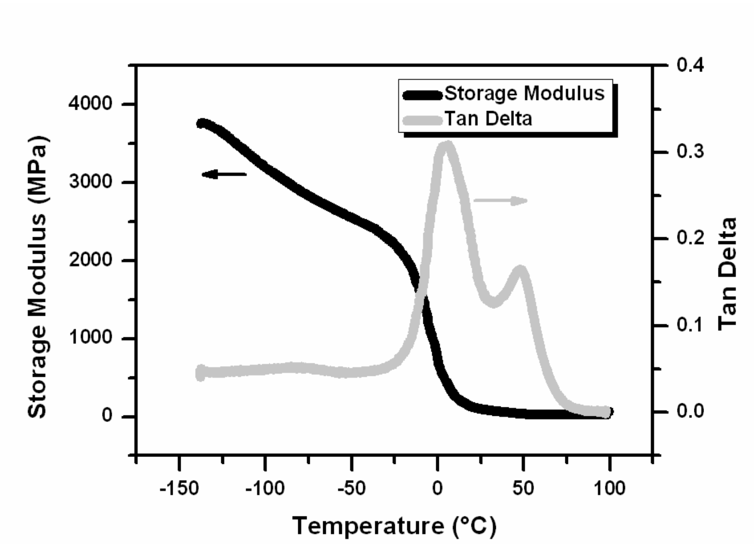

Fig. S2. Mechanical properties of the thermoset resulting from the thiol/alkyne click reaction.

The reactive components (T, Y and PI) were thoroughly mixed with a stoichiometrical ratio (2 thiols/alkyne), and cast onto a petri dish, followed by the exposure to an UV light at a wavelength of 365 nm and intensity of 0.4 mW/cm^2 (at 15 cm) for 5 min. The cured film was collected, cut, and tested in tensile mode using a DMA with liquid nitrogen cooling system.

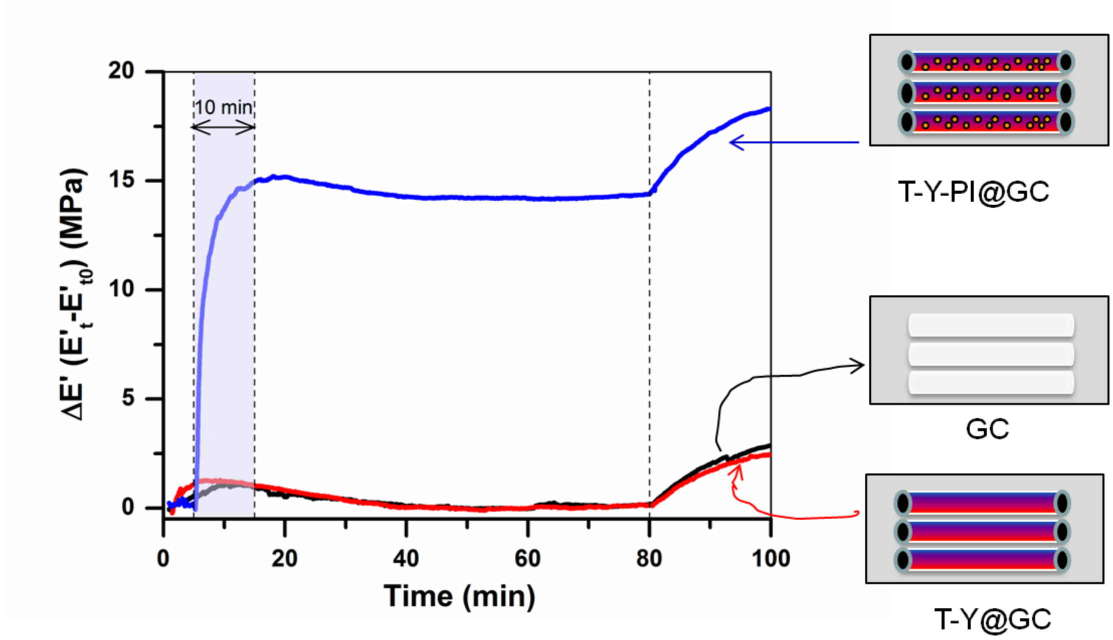

Fig. S3. Background experiments with different arrangements of self-healing reactants.

Comparison of the changes in storage modulus for three rubber composites with different arrangements of self-healing reactants is showing that the reaction only takes place when all three components are present.

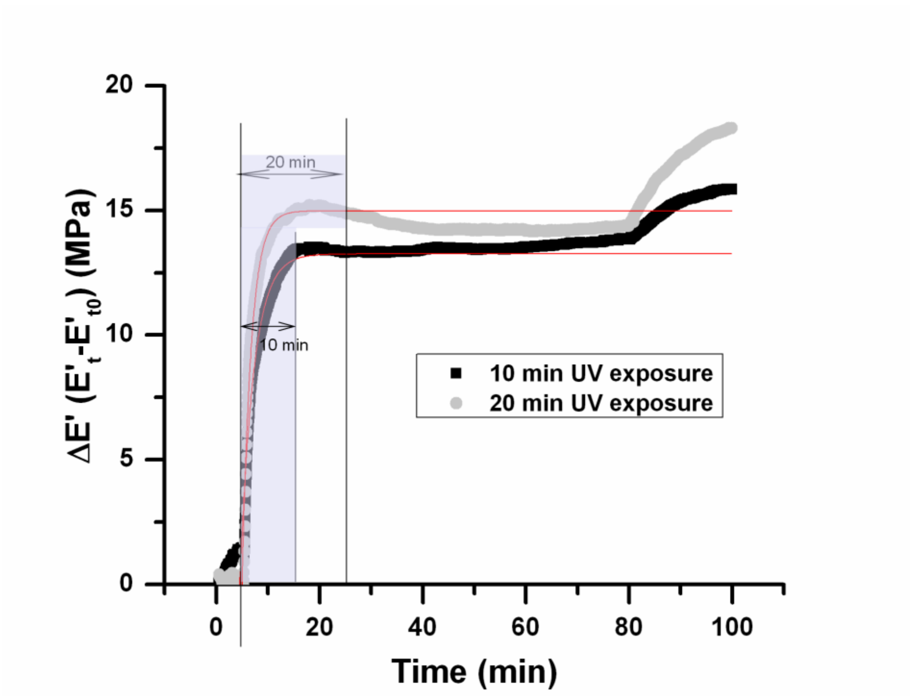

Fig. S4. The effects of UV exposure time on the storage modulus increase (self-healing efficiency) of the composite with three components stored together (T-Y-PI@GC)

The modulus increase upon UV irradiation shows an asymptotic behavior, reaching a plateau when the monomers are exhausted and the reaction terminates. Further irradiation does not have effects on the composite modulus, other than those associated with changes in the temperature of the matrix (which has a Tg close to room temperature). The longer UV exposure times used for samples with the three reaction components stored separately compensate the lower reaction rate due to independent diffusion of reactants, but still present an asymptotic behavior, again, as would be expected for this polymerisation reaction.

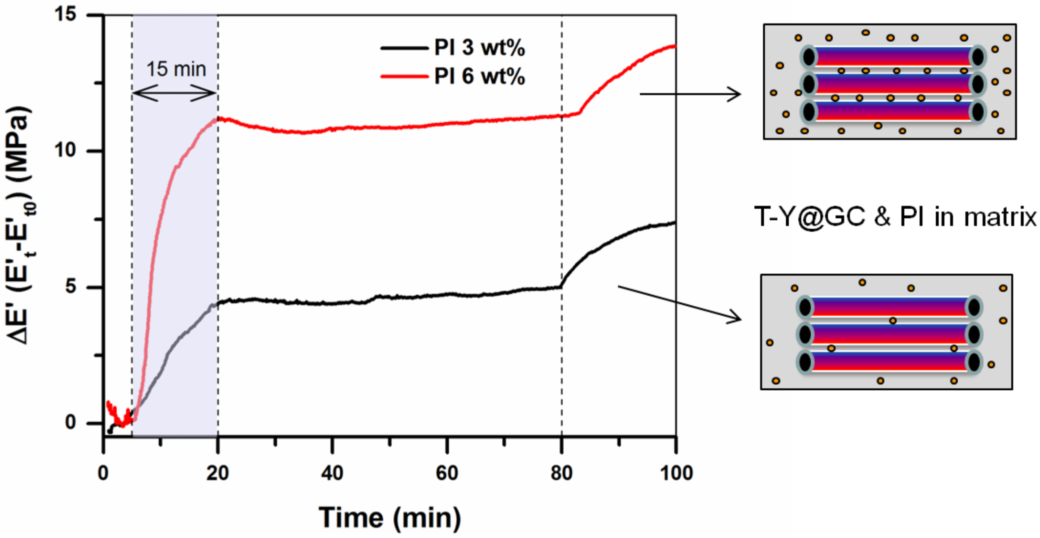

Fig. S5. Effect of photoinitiator concentration on self-healing efficiency.

The changes in storage modulus of two samples containing the same amount of monomers (T and Y) inside GCs but different photoinitiator concentrations (3 and 6 wt%) in the matrix are compared. The graph shows a higher modulus when increasing PI concentration.

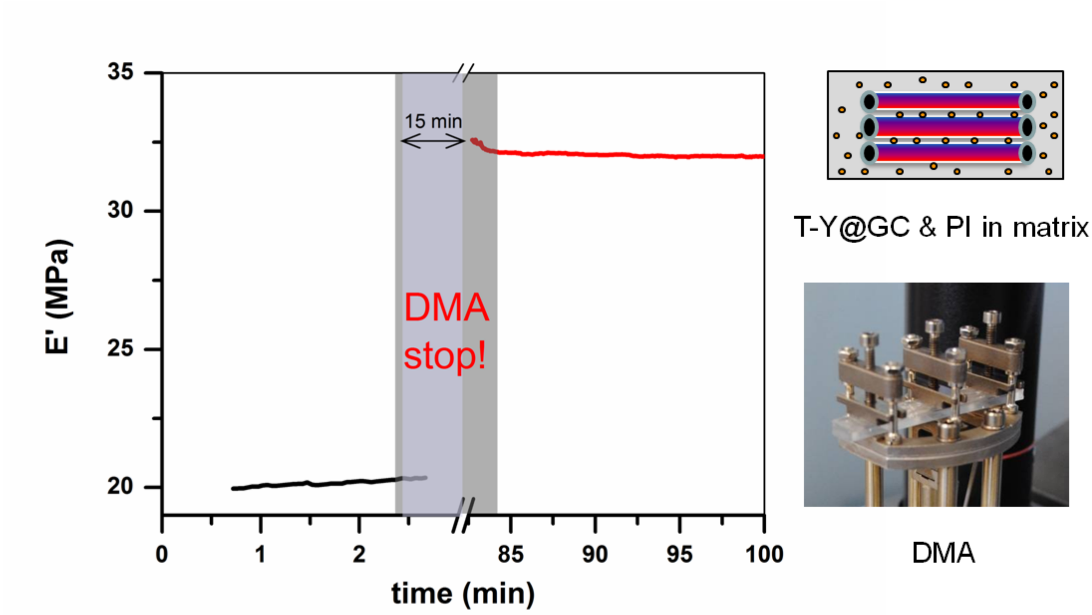

Fig. S6. Background experiments to assess the possible contribution of DMA to bleeding.

The composite contained T and Y reactants stored together in GCs and the PI dispersed in the matrix. The sample was tested in bending for only 2 min, obtaining an initial value of E'=20 MPa. Then the DMA measurement was stopped and the sample exposed to UV light for 15-min after which the DMA was restarted, showing a modulus of E'=32 MPa.

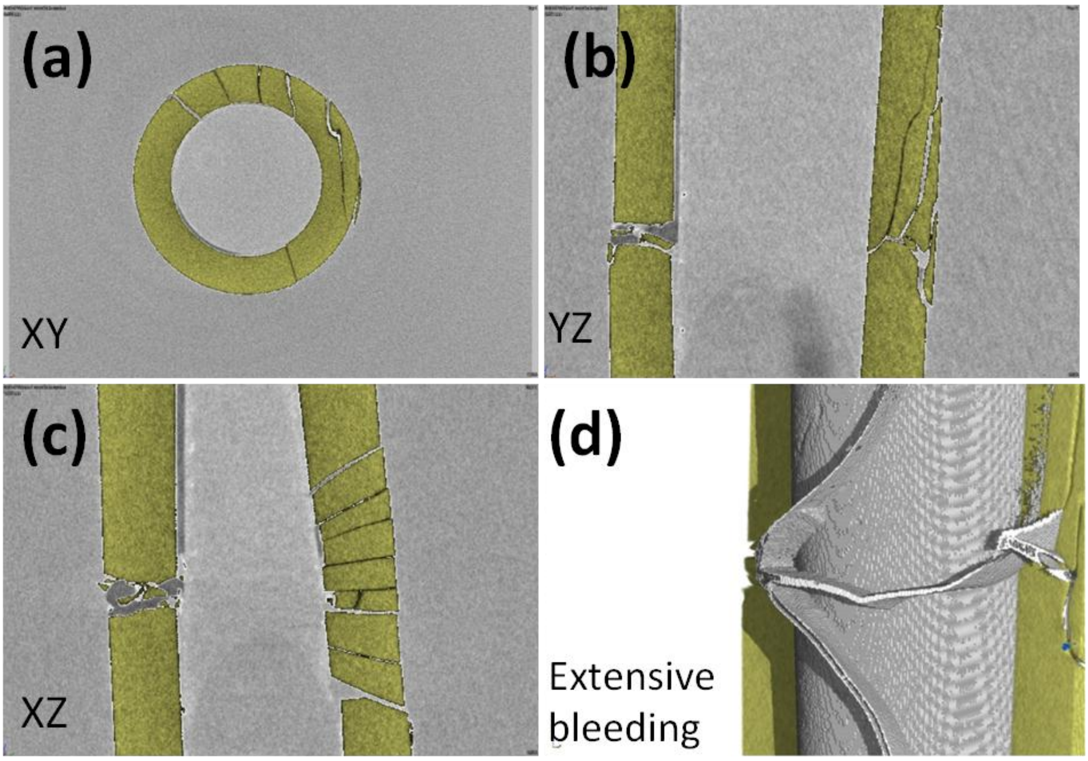

Fig. S7. Tomography images showing a close-up look of the bleeding area.

In terms of the local failure mode of the composite after the severe bending deformation applied, we note that although capillary debonding is a possible scenario, the low modulus of matrix and the brittleness of the glass capillaries would suggest that capillary fracture dominates. As a result, bleeding should be observed not throughout the whole capillary/matrix interface but mainly localised where the glass fractured, which is consistent with X-ray tomography micrographs.

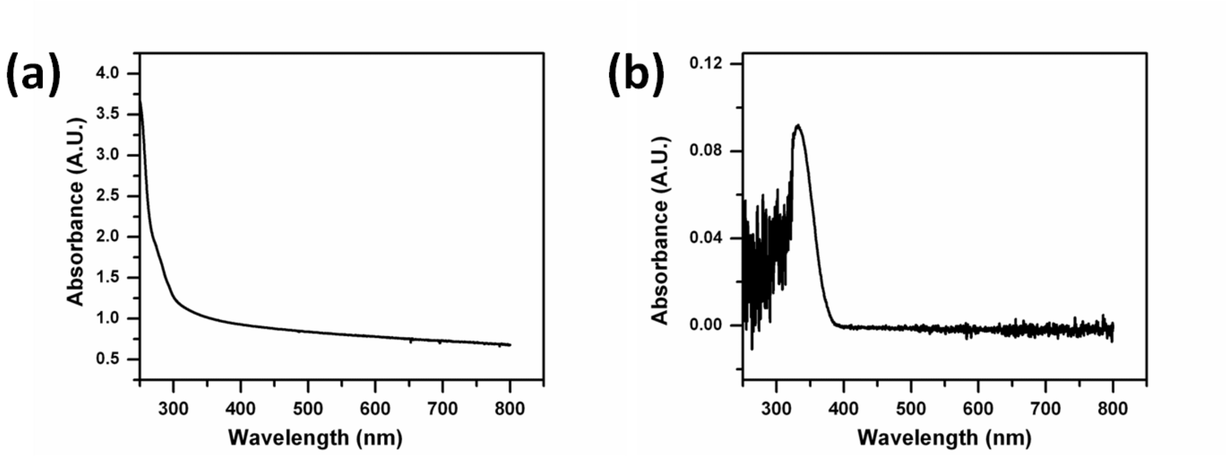

Fig. S8. UV-Vis spectra of pure silicone matrix with a 4 mm thickness (a) and the photoinitiator at 0.001M dissolved in acetone (chromatography grade) (b).

The figure clearly shows that there is little matrix absorption in the UV-A range where the photoinitiator is active.

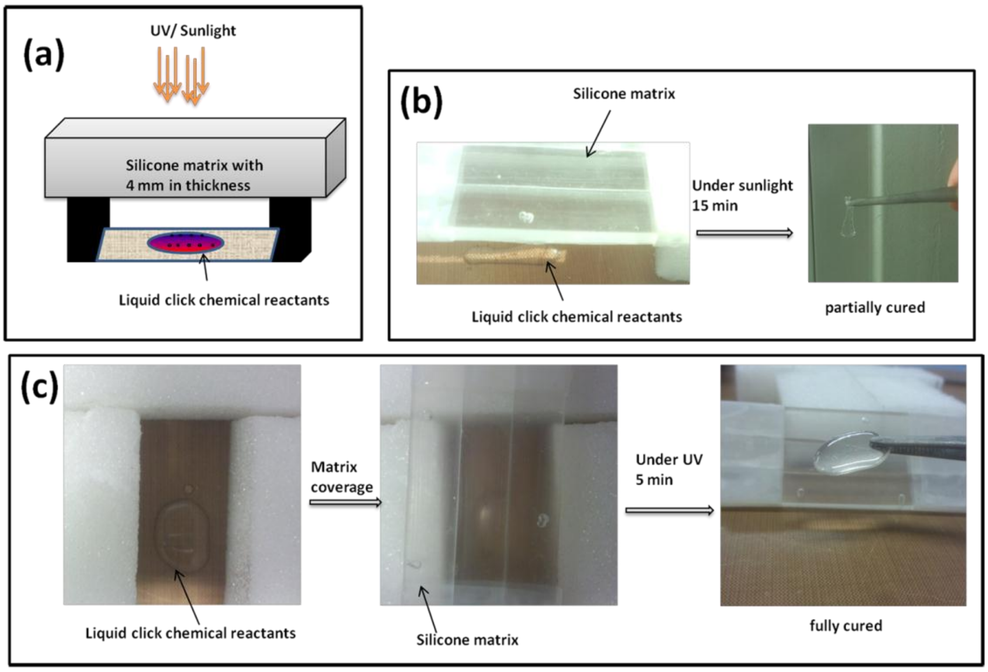

Fig. S9. Control experiments on UV transmission through silicone matrix.

We have carried out a control experiment consisting of placing a 4mm-thick silicone specimen on top of a small tray containing the click-chemistry reactants, thus, the silicone would act as a potential UV/sunlight blocking filter (if it were not transparent). The experiment shows that upon UV/sunlight irradiation the reaction take places rapidly, hence indicating that the silicone matrix does not significantly absorb light in the UV range. The fraction of UV in sunlight is sufficient to carry out the reaction, though requiring longer times.