# Mechanochemistry unveils stress transfer during sacrificial bond fracture of tough multiple network elastomers

Yinjun Chen, Gabriel Sanoja and Costantino Creton\*

<sup>*a*</sup>Laboratoire Sciences et Ingénierie de la Matière Molle, ESPCI Paris, PSL University, Sorbonne Université, CNRS, F-75005 Paris, France;

**General methods:** Uniaxial extension and fracture tests were performed on a standard tensile Instron machine, model 5565 with a 100 N load cell. All the videos recording the uniaxial extension and fracture tests were carried out with a RGB camera (SONY IMX 174, STC-MCS241U3V).

# 1. The synthesis of materials

### 1.1 Synthesis of spiropyran-diene

The spiropyran-diene was synthesized as previously described<sup>1-3</sup> (Scheme S1). Spiropyrandiol was synthesized first and its terminal groups of diol were modified by a substitution reaction of methacryloyl chloride.



Scheme S1 Synthesis of Spiropyran

### 1.2 Fabrication of labelling multiple network elastomers



Scheme S2: The synthesis of labelling multiple network elastomers

All reagents used in the article were purchased from Sigma-Aldrich and VWR. They were used as received except the ethyl acrylate (EA) and hexyl methacrylate (HMA) monomers, and 1,4butanediol diacrylate (BDA) crosslinker. EA, HMA and BDA were purified by the column of alumina to remove the inhibitor. The monomers, crosslinker and initiator were degassed by nitrogen gas and stored in a glove box before performing experiments.

As previously described<sup>4, 5</sup>, multiple network elastomers were synthesized by free radical polymerization. First, a well-crosslinked network (filler network) was prepared by photopolymerization. 0.5 mol% crosslinkers (0.05 mol% SP and 0.45 mol% BDA crosslinkers), and 1 mol% HMP UV initiator were dissolved in ethyl acrylate (EA) monomer, then poured into a metal mold and polymerized by low power irradiation of UV light in a glove box. Here, the molar percentages are relative to EA monomer. After drying in vacuum, the filler network was swollen in a monomer solution with a low concentration of BDA crosslinker (0.01 mol% relative to EA monomer) and HMP initiator (0.01 mol%) and then polymerized to prepare double network (DN) elastomers. Using the DN as a base, triple network (TN) and quadruple network (QN) elastomers were obtained by repeating the swelling and polymerization steps. Elastomers deriving from the same filler network make up a family of materials. The blank family of materials was prepared by crosslinking the filler network with BDA only. For families 3 and 4 in Table 1, the same filler networks as for the blank family were synthesized, but in the second (family 3) or the third (family 4) step of swelling SP replaced BDA (0.01mol%) as crosslinker, and was incorporated into the second or the third network, respectively (see Scheme S2). For family 5 in Table 1, the EA monomer in the filler was changed to HMA and the filler network was only crosslinked by BDA, then 0.01 mol% of SP as crosslinker was dissolved into EA monomer to make the solution for the subsequent swelling and was incorporated into the second network of family 5 of materials by the second polymerization. In the swelling and

polymerization process, the filler network is pre-stretched gradually. The pre-stretch increases with the total number of polymerization steps and can be calculated by measuring the weight of samples before and after polymerization in each step. All the information about the samples used in this manuscript are shown in Table S1.

Family	Polymers	First network	wt%	N <sub>poly</sub>	$\lambda_0$	SP location
1	EA(1)	EA(1)	100	1	1	
	EA(2)	EA(1)	23.5	2	1.62	
	EA(3)	EA(1)	7.2	3	2.4	
	EA(4)	EA(1)	3.4	4	3.1	
	EA (1)-1		100	1	1	1
2	EA (2)-1	EA (1)-1	20.2	2	1.70	1
	EA (3)-1	EA (1)-1	5.6	3	2.61	1
	EA (4)-1	EA (1)-1	2.2	4	3.55	1
	EA (1)		100	1	1	
3	EA(2)-2	EA (1)	23.5	2	1.62	2
	EA(3)-2	EA (1)	7.8	3	2.34	2
	EA (4)-2	EA (1)	3.8	4	2.98	2
	EA (1)		100	1	1	
4	EA(2)	EA (1)	26.3	2	1.56	
	EA(3)-3	EA (1)	7.8	3	2.34	3
	EA (4)-3	EA (1)	4.8	4	2.76	3
	HMA (1)		100	1	1	
5	HMA (2)-2	HMA (1)	20	2	1.71	2
	HMA (3)-2	HMA (1)	4.3	3	2.85	2
	HMA (4)-2	HMA (1)	1.8	4	3.84	2

**Table S1** List of multiple network elastomers used in the study. wt%  $N_{poly}$  and  $\lambda_0$  are the weight fraction of first network, total number of polymer networks in multiple network elastomers and degree of isotropic pre-stretch in the filler network.

# 2. Mechanical properties of multiple network elastomers 2.1 uniaxial elongation tests

All tensile tests were performed on a standard tensile Instron machine (model 5565) fitted with a 100 N load cell and custom pneumatic clamps. For uniaxial elongation tests, samples with dog-bone shape were made by using a pre-made punch as previously reported and the thickness of the samples ranged from 0.6 to 4 mm depending on the degree of swelling of the filler network. Tensile tests were performed with a stretch rate  $\dot{\lambda} = 0.05 \ s^{-1}$  and before tensile tests all the samples were exposed to white light for 5 mins to ensure that all of the mechanophores were in its inactivated colourless SP form. To precisely measure the strain during the uniaxial deformation, two black marks were made on the homogeneously deformed zone of the specimens. A RGB camera (SENTECH: STC-MCS241U3V, image sensor: SONY IMX174,

cell size: 5.86  $\mu$ m×5.86  $\mu$ m) with a frame rate of 25 fps was used to record the relative displacement of the two black markers. MATLAB scripts were used to analyze the position of the marks from the recorded videos, which allowed for accurate determination of the locally applied uniaxial stretch. The nominal extension ratio was defined as:

$$\lambda = \frac{L}{L_0}$$
 Eq. S1

where  $L_0$  and L are the distances between the centroids of the two marks before and after stretching, respectively. The engineering stress was obtained from the Instron machine. Before performing tensile tests, all specimens were exposed to white light for 5 mins to ensure that all the mechanophores were in its inactivated SP form. To study the mechanical properties of interpenetrated multiple network elastomers, tensile tests with various polymer networks were carried out.



**Figure S1** Stress-strain curves of various multiple network elastomers: (a) EA is the monomer of the filler network and SP is located in the second and third network of elastomers, respectively. Varying families of multiple network elastomers were tested in uniaxial tension. (b) HMA acts as the monomer of the filler network and SP is only incorporated into the second network of elastomers. Uniaxial tensile tests are performed for these families of materials.



*Figure S2* The stress-strain curves of EA(4)-2 samples. The strain is either calculated by the displacement of the clamps (dashed line) and by the displacement of the two marks on the samples (solid line).

### **2.2 Fracture tests**

Fracture energy of multiple network elastomers was detected by performing fracture tests on the first family of materials. **Erreur ! Source du renvoi introuvable.** shows the distinct improvement of fracture toughness ( $\Gamma$ ) as the number of networks increases. According to the Greensmith approximation for single edge notch samples<sup>6, 7</sup>, fracture toughness is calculated by using  $\Gamma = \frac{6c}{\sqrt{\lambda}} \times W(\lambda_c)$  Equation S1:

$$\Gamma = \frac{6c}{\sqrt{\lambda}} \times W(\lambda_c)$$
 Equation S1

Where  $W(\lambda_c)$  is the energy density of an unnotched sample at the critical strain of crack propagation and 'c' is the initial notch length. The results are shown in Figure S3. It is obvious that both fracture toughness and Young's modulus increase at the same time.



Figure S3 : Stress-strain curves of the single edge notched samples from family 1

Polymer	EA(1)	EA(2)	EA(3)	EA(4)
Fracture energy $(\Gamma)$	0.4	1.43	3.76	4.11
kJ · m ²	±0.02	±0.04	±0.48	±0.64
Young's modulus	0.69	1.08	1.52	3.38

**Table S2** : Fracture energy ( $\Gamma$ ) of multiple network elastomers



Figure S4 : Images of EA(4)-2 sample in fracture test

# 3. Mechano-optical response



**Figure S5 :** chromatic change  $\Delta R_{ratio}$  (red) and  $\Delta B_{ratio}$  (blue) as a function of nominal stress  $\sigma_N$  for three EA(3)-1 samples tested in uniaxial tension at three different stretch rates (0.1, 0.03, 0.01 s<sup>-1</sup>).



**Figure S6:** Uniaxial tensile tests were carried out for two different samples of HMA(4)-2 and videos were recorded. The images extracted from the videos were used for RGB analysis to determine the chromatic change in the extension. The specimen in (a) shows a second strain hardening (stress-strain curve) when the neck extends to the whole gauge length and a slight chromatic change is observed as can be seen on the images and on the curves, but the specimen

in (b) fails before the necked region extends to the whole gauge length (no second strain hardening in the stress-strain curve is observed) and no chromatic change is observed from the chromatic ratio curves.



**Figure S7** : The images of the two samples of HMA(4)-2 in Figure S6 before and after elongation tests



*Figure S8*: (a) Stress-strain curves of EA (4)-1, EA(4)-2 and EA(4)-3; (b) After the correction of areal chain density and pre-stretch of filler network, corrected stress as a function of the corrected strain in the filler network for the three samples. Correction made as in Ref 4.

#### 4. Fluorescent measurement by confocal microscope

Confocal microscopy was carried out with a Nikon AZ100 macroscope using a 561 nm laser and a Deben micro-tensile stage to detect the fluorescent signal around the crack tip in the fracture tests. The same samples as those used for the uniaxial extension test were used and the tensile velocity was set to 1 mm/min which was limited by the setup of the Deben. During the fracture test, 2D fluorescent images were made by collecting the intensity of the fluorescence between 580 nm and 650 nm. 2D fluorescent images collected over the depth of 4 mm with an interval of 20 µm were integrated to make the stacked images. Figure S9 shows the top view of the stack of 2D images of HMA(4)-2 samples at the critical strain of crack propagation and after crack propagation. Stacked images around the crack tip were scanned each 0.5 mm of displacement of the sample until the samples broke. Theses 3D images were used to detect the deformation of the second network with the fluorescence of MC (the activated state of SP).



**Figure S9 :** 3D Fluorescent stacked images of HMA(4)-2 (top view) at the critical strain of crack propagation and after the crack propagation are present on the left and right, respectively.

## References

- 1. H. Zhang, Y. J. Chen, Y. J. Lin, X. L. Fang, Y. Z. Xu, Y. H. Ruan and W. G. Weng, *Macromolecules*, 2014, **47**, 6783-6790.
- Y. Chen, H. Zhang, X. Fang, Y. Lin, Y. Xu and W. Weng, ACS Macro Letters, 2014, 3, 141-145.
- 3. G. R. Gossweiler, G. B. Hewage, G. Soriano, Q. Wang, G. W. Welshofer, X. Zhao and S. L. Craig, *ACS Macro Letters*, 2014, **3**, 216-219.
- 4. P. Millereau, E. Ducrot, J. M. Clough, M. E. Wiseman, H. R. Brown, R. P. Sijbesma and C. Creton, *Proceedings of the National Academy of Sciences*, 2018, **115**, 9110-9115.
- 5. E. Ducrot and C. Creton, *Adv Funct Mater*, 2016, **26**, 2482-2492.
- 6. H. W. Greensmith, *Journal of Applied Polymer Science*, 1963, **7**, 993-1002.
- 7. R. S. Rivlin and A. G. Thomas, *Journal of Polymer Science*, 1953, **10**, 291-318.