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Supplementary Information

Mechanics of Elastomeric Molecular Composites

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Section S1: Material and methods

Reactants: The monomer ethyl acrylate (EA) and the crosslinker butanediol bis(acrylate) (BDA) were purified over a column of activated alumina to remove the inhibitor. The UV initiator, 2-hydroxy-2-methylpropiophenone (HMP) was used as received. Ethyl acetate was used as solvent. All reagents were purchased from Sigma Aldrich.

Synthesis: The synthesis of the networks was carried out in a glove box (Mbraun Unilab) under a nitrogen atmosphere to avoid side reactions with the oxygen of the air. Before the introduction in the glove box, every reagent and solvent was bubbled with nitrogen for 45 minutes to remove the dissolved oxygen. The reaction is a free radical polymerization of a solution of monomer under UV (UV light was produced by a Vilbert Lourmat lamp, model VL-215.L, focused on 365 nm). The UV power was kept low (10 $\mu\text{W}/\text{cm}^2$) to create a slow polymerization, the goal being to decrease the number of simultaneously growing chains and the number of termination reactions. The preparation of multiple network elastomers was carried out through multiple steps of polymerization. Starting

from monomers, a filler network was synthesized, then multiple steps of swelling and polymerization were carried out to create a multiple network.

Synthesis of the filler network: The filler networks were prepared by UV free radical polymerization of a solution of monomer EA, BDA as crosslinker (1.45 mol % relative to monomer) and HMP as a UV initiator (1 mol % relative to monomer). The reactants were dissolved in ethyl acetate as solvent at 50 wt %. A solution containing all the reactants was prepared and mixed for a short time before being poured in a 1 mm thick glass mold. The reaction was initiated by UV and carried out for 2 hours. After the synthesis, the sample was removed from the mold and immersed in a bath of solvent containing 50 % of ethyl acetate and 50 % of cyclohexane. The bath was changed twice a day for three days. At the end of these three days the bath was changed to 25 % of ethyl acetate and 75 % of cyclohexane, this bath was also changed twice a day for two days. After this step the network was dried under vacuum at 80 °C. In the end a simple network was obtained and these samples will be referred to as filler network.

Preparation of multiple network elastomers with a controlled swelling of the filler network: The synthesis technique adopted during this work is inspired by the previous work of Ducrot¹ where the filler network was swollen in a bath of monomer until equilibrium and is then polymerized by UV. The synthesis was here adapted in order to obtain a larger range of swelling states of the filler network in the final material. In order to achieve that, the filler network was swollen to equilibrium in a bath composed of monomer, 0.01 mol% of BDA and 0.01 mol% of HMP and solvent. At equilibrium, the swollen piece of network was taken out of the bath and clamped between PET sheets and tightened between glass plates. Then the polymerization was conducted in a similar way as for the filler network. Finally a drying step under vacuum at 80 °C over night led to the removal of the solvent. This synthesis can be then repeated multiple times for several polymerizations allowing the creation, in several steps, of samples with different prestretching state of the filler network.

In order to evaluate the swelling of the filler network and determine the composition of the multiple network, the mass of the piece of filler network m_1 was carefully measured after each step. After drying the different multiple networks, their weight m_{MN} was measured and compared to the initial weight of the filler network as shown in Eq S1 where m_2 is the total mass fraction of matrix network added to the filler network. From the measurements of the different weights and since the swelling of the networks is considered isotropic, the stretching of the filler network over the different synthesis steps λ_0 is defined as shown in Eq. 2.

$$\phi_{SN} = \frac{m_1}{m_{MN}} = \frac{m_1}{m_1 + m_2} \quad \text{Eq. S1}$$

$$\phi_{SN} = \frac{1}{\lambda_0^3} \quad \text{Eq. S2}$$

Name	λ_0	steps	% filler network	% solvent during synthesis	% of 2nd network	% solvent during synthesis	% of 3rd network	% solvent during synthesis	% of 4th network
EA(1)	1	1	100						
EA(1.32)EA	1.32	2	42.0	50	58				
EA(1.51)EA	1.51	2	29.2	25	70.8				

EA(1.68)EA	1.68	2	20.5	0	79.5				
EA(2.18)EA	2.18	3	9.52	50	13.1	0	77.3		
EA(2.41)EA	2.41	3	7.39	25	17.9	0	74.7		
EA(2.55)EA	2.55	3	6.06	0	23.5	0	70.5		
EA(2.91)EA	2.91	4	4.19	0	16.2	0	48.7	50	31
EA(3.11)EA	3.11	4	3.53	50	4.9	0	28.7	0	62.9
EA(3.27)EA	3.27	4	3.28	25	8	0	33.2	0	55.6
EA(3.42)EA	3.42	4	2.88	0	11.2	0	33.6	0	52.4

Table S1: Composition of the multiple networks. The filler network is identical for this series and the matrix network is incorporated in one, two or three steps.

Mechanical tests: Mechanical tests were performed on a standard tensile Instron machine, model 5565, using a 100 N load. A video extensometer gave a local measurement of the stretch $\lambda = l/l_0$ where l_0 is the initial gauge length. The relative uncertainty of the measurements given by the load cell and the video extensometer are respectively 0.1 % in the range of 0 to 100 N and 0.11 % at the full scale of 120 mm. Specimens were cut into a dumbbell shape using a normalized cutter (central part: length 20 mm, cross-section 4 mm and thickness 0.6 – 2.5 mm depending on the sample). Uniaxial tensile tests from small to large strain were performed at a constant velocity of the crosshead of $500 \mu\text{m}\cdot\text{s}^{-1}$ and the typical initial strain rate on the central part of the sample was around 0.04 s^{-1} . Using the nominal stress and strain, the Young's modulus was calculated at a strain of less than 10 %.

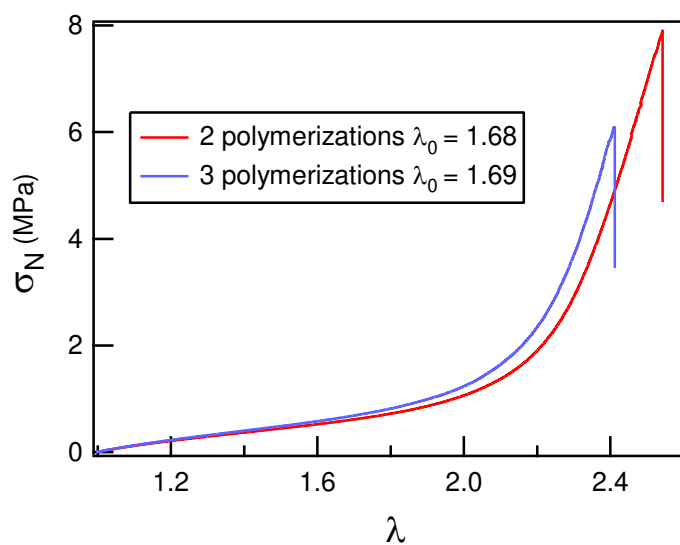


Figure S1: Stress-strain curve of two samples presenting the same prestretching of the first network but a different synthesis path. $\dot{\lambda} = 0.021 \text{ s}^{-1}$

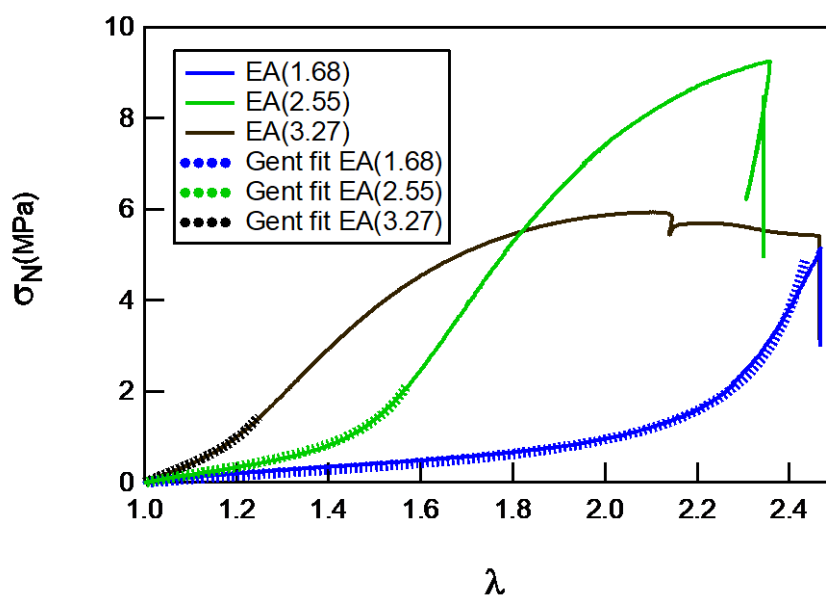


Figure S2: Stress-strain curves of different multiple networks (value of λ_0 shown in the legend) to illustrate the typical quality of the fit by Gent's model. $\dot{\lambda} = 0.021 \text{ s}^{-1}$

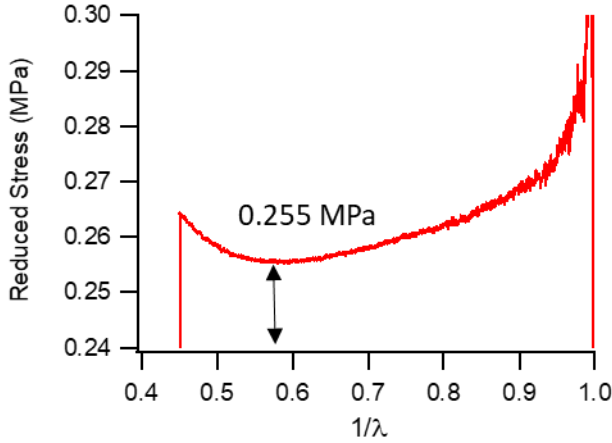


Figure S3: Reduced stress as a function of $1/\lambda$ for the filler network EA1 with 1.45 mol% of crosslinker. The minimum in reduced stress is taken as the shear modulus corresponding to the crosslink contribution only $G_x = E_x/3$.

Estimate of the limiting extensibility of EA(1) network chains

The value of average molecular weight between crosslinks can be obtained directly from the crosslink contribution of the elastic modulus using:

$$M_x = \frac{3\rho RT}{E_x}$$

For the network EA(1), ($M_x = 10.9$ kg/mol) so that the number of carbon bonds between crosslinks $N_x \approx 216$. The characteristic ratio C_∞ for a poly(ethyl acrylate) network being around 9.67^2 , the average maximum theoretical elongation of a strand between crosslinks λ_{limit} is given by:

$$\lambda_{limit} = \cos \frac{\theta}{2} \left(\frac{6\rho RT}{C_\infty M_0 E_{FN}} \right)^{1/2} \quad (3)$$

where θ is the valence angle of the C-C bond, ρ is the density of the polymer, C_∞ is its structure factor, M_0 is the molecular weight of the monomer and E_{FN} is the Young's modulus of the filler network. All of these values are known from tables and this gives $\lambda_{limit} \sim 3.9$.

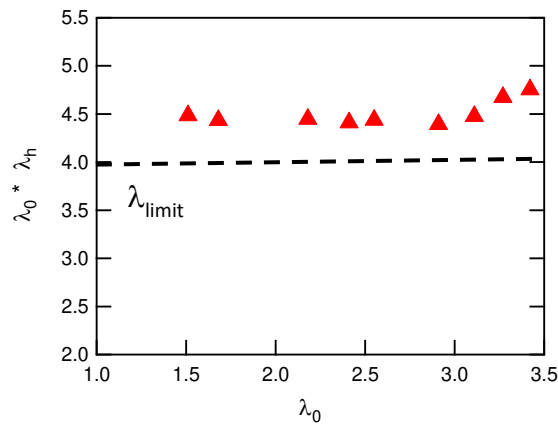


Figure S4: Limiting experimental elongation of the filler network $\lambda_0 \lambda_h$ as a function of λ_0 . The dashed black line is the theoretical value λ_{limit} obtained from chain statistics.

Example of a tensile test of a sample undergoing necking

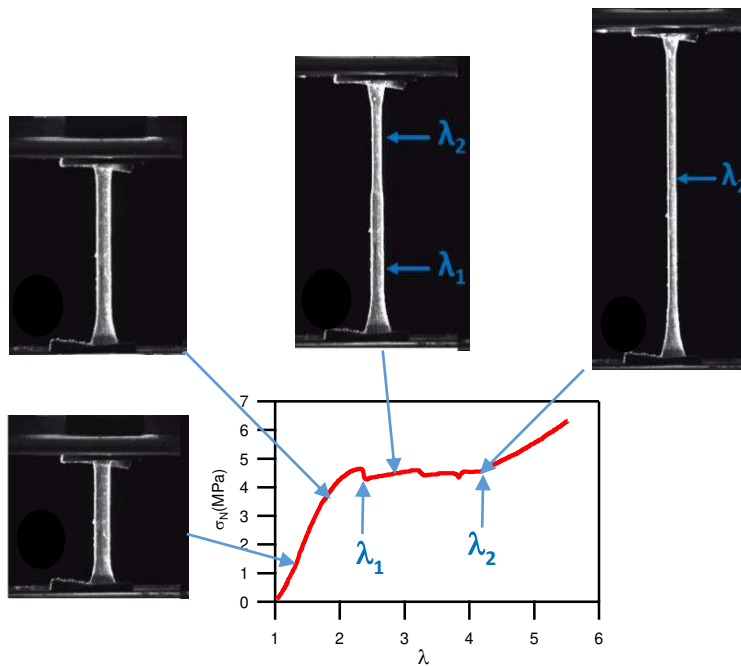


Figure S5 : Stress-strain curve of a samples with $\lambda \sim 3$ and recorded pictures describing the macroscopic state of the sample as the elongation increases. $\dot{\lambda} = 0.0039 \text{ s}^{-1}$

Figure S5 shows images and a stress-strain curve of a monotonous tensile test for EA(3.42). In the first stages of the tensile test (images 1 and 2), the nominal stress increases with elongation and the sample is homogeneously deformed. Starting at $\lambda = \lambda_1$, a necking process begins with a nucleation point that creates two fronts (image 3). Those two fronts propagate progressively through the entire sample as shown in image 3 until the complete sample is stretched to $\lambda = \lambda_2$ (image 4). During the propagation of this necked region, the sample is split into two rubber elastic domains with different non-linear elastic properties, an unnecked domain where the elongation λ_1 remains the same as that reached at the onset of necking and a highly damaged domain, where the elongation is λ_2 . Both regions coexist at the same level of nominal stress, i.e. the same force.

Determination of the necking stress

To obtain more values of the yield stress, especially for samples that soften but fail before yielding, we extrapolated the value of the yield stress based on the shape of the curves that show an actual yielding as shown in Figure S6.

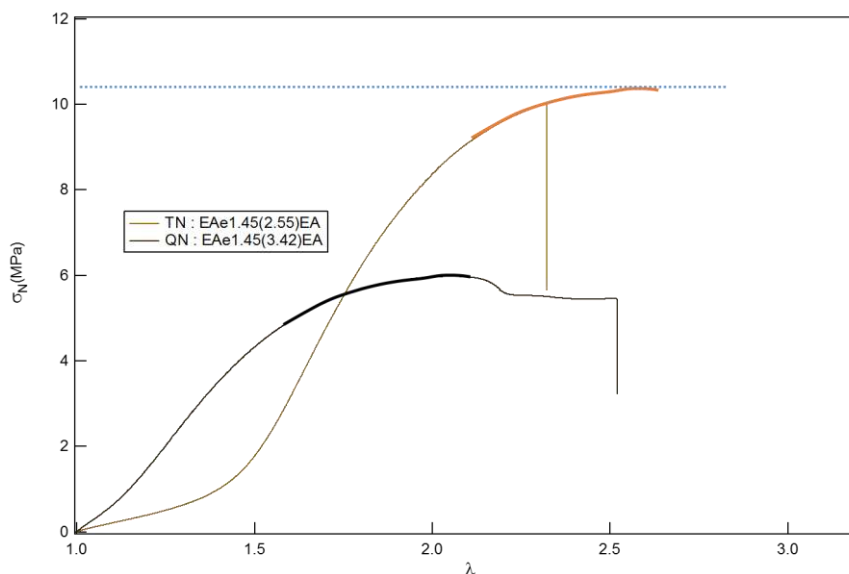


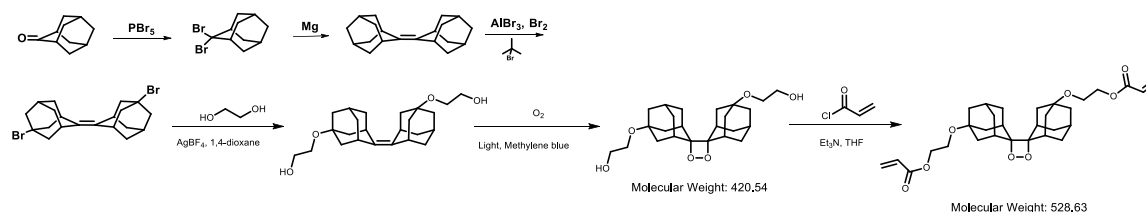
Figure S6: Stress-strain curve to show how an estimated value of the yield stress can be obtained for type 3 materials

The values of the yield stress determined in this way are plotted as a function of the filler network's surface chain density calculated based on the dilution of the filler network in Figure 7 of the main text.

Dioxetane marked samples

Following the work of Ducrot¹, we performed some experiments with samples containing mechanoluminescent crosslinkers to quantify the amount of bond scission and to correlate it with the amount of dissipated energy.

Synthesis of the Dioxetane crosslinker



2,2-Dibromoadamantane

Finely divided phosphorus pentabromide can be prepared by slowly adding 30 g phosphorus tribromide to a cold, vigorously stirred solution of 17 g bromine in 75 ml n-heptane in a 250-ml round-bottomed flask, with a dropping funnel. When addition is complete (ca. 15 min.) 15 g adamantanone is added to the suspension of phosphorus pentabromide in n-heptane and the refluxed with 1.5 h. The cooled mixture is poured to 100 ml ice water, The organic layer was separated and washed twice with 75-ml portions of dilute sodium bisulfite and with water. The organic layer is dried over anhydrous magnesium sulfate and evaporated under reduced pressure. The residue 2,2-dibromoadamantane is crystallized from ethanol to afford white needles. (22.65g, yield : 77%)

Adamantylideneadamantane

The reaction is carried out under anhydrous conditions and the reaction equipment is dried in a drying oven. In a 500-ml round bottomed flask, fitted with a reflux condenser, dropping funnel. 4 g of activated magnesium ribbons and 25 ml of anhydrous ether. To this suspension is added dropwise a solution of 10 g 2,2-dibromoadamantane in 75 ml anhydrous ether. A small crystal of iodine is added. After addition of ca.1 g of 2,2-dibromoadamantane, the reaction started, and the remainder of 2,2-dibromoadamantane is added at such a rate that gentle reflux is maintained. The reaction mixture is heated under reflux for 1 hr. Then it is cooled and poured into 100 ml water. The aqueous layer is separated and extracted twice with 50-ml portions of ether. The combined ether layers are washed with 100 ml water and dried over anhydrous magnesium sulfate. After evaporation of the ether under reduced pressure, the adamantylideneadamantane is washed with methanol and allowed to dry. (4.2 g, 91%)

Dibromoadamantylideneadamantane

To a solution of 3.8 g of adamantylideneadamantane and 1.83 ml of tert-butylbromide was added 18.13 g of AlBr₃. After good mixture 4.35 ml of bromine were added, which gave rise to the evolution of enormous amounts of HBr gas. The HBr and bromine gas evolved were trapped with an aqueous solution of sodium thiosulphate. After 2 days of standing at room temperature, the reaction mixture became solid and was very carefully quenched by adding ice-water to the reaction flask, with ice-cooling. A small amount of DCM was added during quenching to solubilize the solid reaction mixture. The product was then extracted with DCM (DCM: 1*300 ml, 1*150 ml; H₂O: 2*150 ml). The organic layer was washed with water, dried over MgSO₄, and evaporated, furnishing a brown-black solid. The solid was washed with warm ethanol (3*150 ml), followed by column chromatography (DCM, neutral Al₂O₃) yielded brown solid (4.1 g, 68%).

5,5'/7'-Di(2-hydroxyethylenoxy) adamantylideneadamantane

To a solution of 5,5'/7'-dibromoadamantylideneadamantane (1.0 g, 2.35 mmol) in 1,4-dioxane (10 ml) was added ethylene glycol (56 mL, 1 mol). The flask was brought under an Ar atmosphere. After the addition of AgBF₄ (2.0 g, 10.27 mmol), the reaction mixture was heated at 85 °C for 3 h. The solution was allowed to cool and filtered to remove silver by-products. Diethyl ether (150 mL) was added and the mixture was washed with water (2×200 mL). The organic layer was separated, dried over anhydrous Mg₂SO₄, and evaporated to dryness. The crude product was purified by silica gel chromatography eluting with CHCl₃ followed by CHCl₃/MeOH (20/1) to afford 5,5'/7'-di(2-hydroxyethylenoxy) adamantylideneadamantane as a brown solid (0.44 g, 48%).

5,5'/7'-Di(2-hydroxyethylenoxy) adamantylideneadamantane 1,2-dioxetane

To a solution of 5,5'/7'-di(2-hydroxyethylenoxy) adamantylideneadamantane (0.3 g, 0.77 mmol) in CH₂Cl₂ (60 mL) was added methylene blue (30 mg). Oxygen was bubbled through the mixture while irradiating with a 600 Watt high pressure sodium lamp. After 4 h, the reaction was complete according to ¹H NMR and the methylene blue was removed with active carbon, followed by filtration. The CH₂Cl₂ was evaporated under reduced pressure to afford 5,5'/7'-di(2-hydroxyethylenoxy) adamantylideneadamantane 1,2-dioxetane as a slight yellow solid (0.31 g, 95%).

5,5'/7'-bisacrylate-5,5'/7'-dihydroxyethylenoxy-adamantylideneadamantane 1,2-dioxetane

To a solution of 5,5'/7'-di(2-hydroxyethylenoxy) adamantylideneadamantane 1,2-dioxetane (0.4 g, 0.95 mmol) and triethylamine (1.5 mL) in dry THF (18 mL) was added dropwise a dry THF solution (20 mL) of acryloyl chloride (0.157 ml, 1.94 mmol) at 0 °C. After stirring at room temperature for 24 h, the solution was poured into water (50 mL) and extracted with diethyl ether (2×30 mL). The combined organic layer was washed with water (50 mL), dried over anhydrous Na₂SO₄ and evaporated under reduced pressure. Crude product was purified by flash chromatography on neutral alumina eluting with CH₂Cl₂ to afford the bisacrylate (0.20 g, 40 %) as a slight yellow oil.

Synthesis of the labeled network

The UV polymerization of the filler network was carried out without solvent. The starting composition of the solution was EA monomer, 0.146 mol% of dioxetane crosslinker, 0.584 mol% of BDA and 0.01 mol% of HMP. The only difference from the standard synthesis was that the polymerization was slower and the experiment was carried out overnight for approximately 16 hours. The material synthesized in the absence of solvent but with half the crosslinker amount had comparable mechanical properties than the EA(1).

After the filler network was obtained, multiple networks were synthesized at different degrees of prestretching and the properties of those networks are shown in Table S2. The uniaxial deformation of the sample EA(d20)0.73(2.94) are shown in the main text.

Sample name	λ_0	Steps	% of 1st network	% of 2nd network	% of 3rd network	% of 4th network
EA(d20)0.73(1)	1	1	100			
EA(d20)0.73(1.43)	1.43	2	26.2	75.8		
EA(d20)0.73(1.88)	1.88	3	15.1	43.7	41.2	
EA(d20)0.73(2.19)	2.19	3	7.5	21.7	70.8	
EA(d20)0.73(2.67)	2.67	4	5.2	15	48,9	30.9
EA(d20)0.73(2.94)	2.94	4	3.6	10.4	33,9	52.1

Table S2: Composition of the labelled samples.

Camera setup

Once those samples have been synthesized, uniaxial tensile tests are carried out in complete darkness and the emitted light is recorded with an EMCCD Andor ultra-sensitive camera. The Andor camera is an iXon Ultra 897 EMCCD used with a 35 mm objective with the original C mount of the camera.

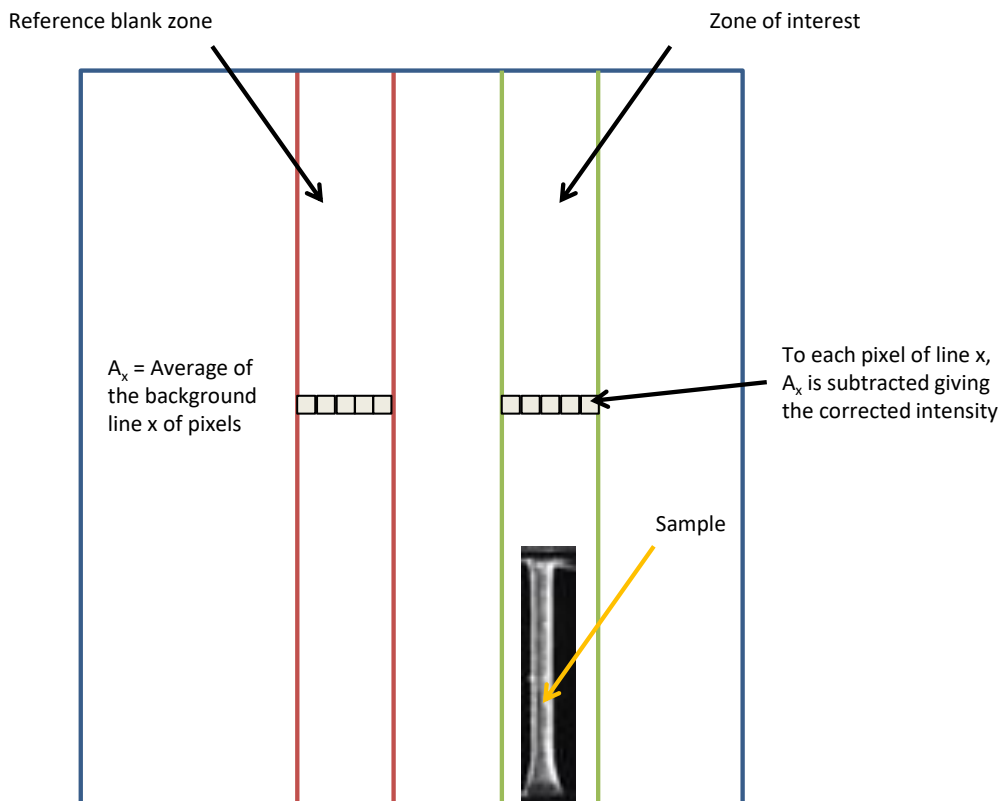
In order to collect the maximal amount of light during the experiment a long exposure time of 0.5 s was chosen meaning that 2 images were taken per second. This long time of exposure was chosen in

order to maximize the signal to noise ratio. Another argument for the long exposure time is that the camera then does not miss information between each frame which is the case at high acquisition frequency. The gain was set up at a high level of 500.

Treatment of the images obtained

Once the images were captured for several samples with the Andor camera, a suitable data treatment had to be applied to remove the amplification noise and quantify the luminescent signal. It has to be noted that on the different images of Figure 5b of the main text the clamps can be clearly seen. The presence of the clamps (due to IR emission) has to be taken into account for the integration of the intensity signal.

To remove the amplification noise, from each experiment and exclude the signal from the clamps and from background variations, a vertical column, that contains the entire sample all along the experiment, is used (green column, width of 30 pixels). To remove the effect of the clamps in each image, a neighboring column (red column) without signal is considered and the signal average is calculated for each line of pixels (A_x). Then to remove the clamps signal, this line average is subtracted to each pixel in the corresponding line in the column of interest giving the corrected signal. Then the sum of the signal of every pixel is counted for each image giving an intensity as a function of time. This intensity can be calculated as a function of deformation and presented in Figure 6a of the main text. The noise level in the signal is significant but it will still give us information.



Solvent swollen Composite networks

In DN gels, the degree of prestretching of the first network and the ratio of first to second network can be easily separated either by using a stent³ to change the stretching of the first network or a change in the pH or the ionic fraction to change the degree of swelling of certain polyelectrolytes. In elastomers, this change cannot be done in the same way. To separate the influence of λ_0 and ϕ_1 (the mass fraction of the first network), different solvents were used to swell the networks. The objective was to stretch the first network but at the same time to dilute the second network and compare their mechanical properties to the samples described in Table 1 of the main text.

To avoid the evaporation of the solvent during the mechanical tests, all solvents used have a relatively high boiling point. Three solvents have been selected: dimethylsulfoxide (DMSO), 1-methyl-2-pyrrolidone (MPD) and acetophenone (ATP). Two networks with different prestretchings were synthesised for this experiment: EAe1.45(1.68) and EAe1.45(2.53). Samples of those two materials were swollen to equilibrium into the different solvents. Once the equilibrium is reached the dimensions of the samples were measured and a uniaxial tension test was carried out. Table S3 displays the different swelling ratios that could be obtained with those three particular solvents, with λ_s being the chain stretching due to the swelling of the elastomer by the solvent only. As expected the degree of prestretching imposed by the swelling is smaller with similar solvents for the type 3 sample that is already more prestretched. It can be seen that the sample EA(2.53) swollen in ATP can reach a swelling close to that of EA(3.42).

Materials	Solvent	Stretchng due to solvent (λ_s)	Total λ_0 of first network chains	Young's modulus (MPa)
EA(1.68)	None		1.68	1.21
EA(1.68)DMSO	DMSO	1.32	2.22	1.02
EA(1.68)MPD	MPD	1.49	2.5	1.09
EA(1.68)ATP	ATP	1.6	2.69	1.36
EA(2.53)	None		2.53	1.58
EA(2.53)DMSO	DMSO	1.24	3.14	3.62
EA(2.53)MPD	MPD	1.31	3.31	4.37
EA(2.53)ATP	ATP	1.37	3.47	6.48
EA(3.42)	None		3.42	4.93

Table S3: Samples used to separate the influence of λ_0 and ϕ

The stress-strain curves of these solvent swollen samples are shown in Figure S7. Note that the first test carried out on the sample EAe1.45(2.53) swollen in DMSO slipped in the clamps. Figure S7 shows the second test on the same sample which explains the different shape of the second light blue curve.

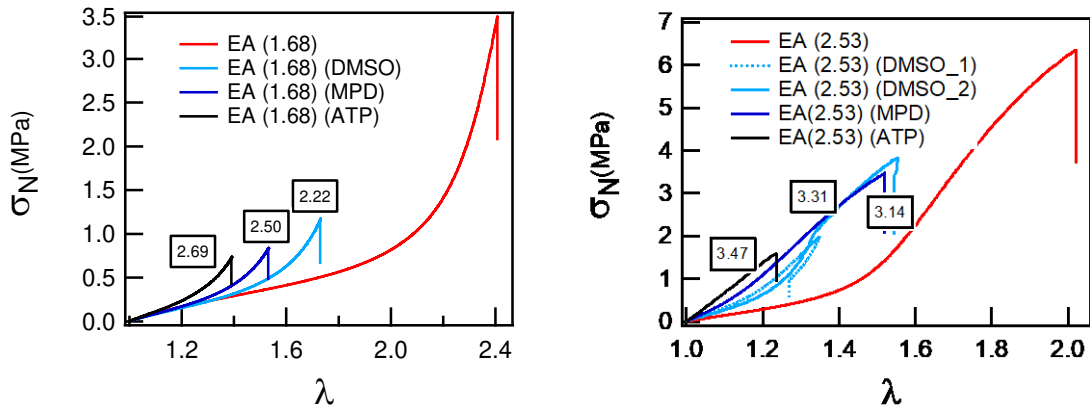


Figure S7: Stress-strain curves of multiple networks swollen in different solvents. Left starting from the sample EAe1.45(1.68) and right starting from the sample EAe1.45(2.53). $\dot{\lambda} = 0.020 \text{ s}^{-1}$

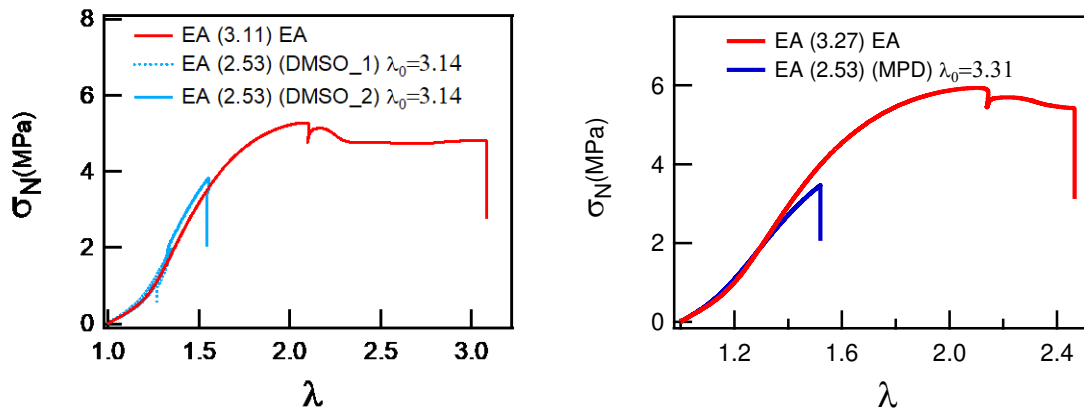


Figure S8: Additional examples of stress-strain curves of swollen solvent in comparison with samples showing a similar prestretching. $\dot{\lambda} = 0.021 \text{ s}^{-1}$

To complete the characterization of this set of samples, the strain hardening was investigated. The same methodology used for Figure 2 of the main text can be applied here: uniaxial tensile curves can be fitted to the Gent model⁴, and J_m and λ_h can be extracted. Results of the maximum extensibility of the first network chains is shown in Figure S9 alongside results for classic multiple networks. The average value of the blue triangles (swollen samples) is slightly smaller than that of the red triangles, but this might be due to the fact that the first networks used for the different sets of data are not exactly the same which could lead to small changes. Nevertheless, the tendency is very similar for both sets of data with a constant value of λ_m controlling the onset of the hardening according to Gent's model.

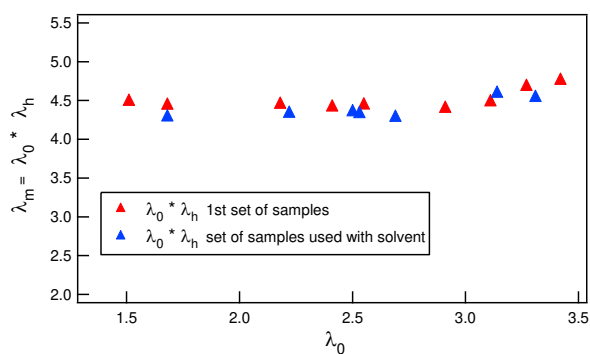


Figure S9: Maximum elongation of the filler network λ_m as function of the prestretching of the filler network λ_0 to investigate the influence of the swelling by solvent

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