Electronic Supplementary Material (ESI) for Soft Matter.
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Supporting Information

Damage Cross-effect and Anisotropy in Tough Double Network Hydrogels Revealed by Biaxial Stretching

Thanh-Tam Mai,[†] Takahiro Matsuda,[‡] Tasuku Nakajima,[§,+,#] Jian Ping Gong,[*,§,+,#] and Kenji Urayama[*,†]

[†] Department of Macromolecular Science & Engineering, Kyoto Institute of Technology, Sakyo-ku, Kyoto 606-8585, Japan

[‡] Graduate School of Life Science, [§]Faculty of Advanced Life Science, Hokkaido University, N21W11, Kita-ku, Sapporo, Hokkaido 001-0021, Japan, [+]Soft Matter GI-CoRE, Hokkaido University, [#]WPI-ICReDD, Hokkaido University

*Corresponding Authors:

E-mail: gong@sci.hokudai.ac.jp (J.P.G.).

E-mail: urayama@kit.ac.jp (K.U.)

1. The correction of elongation and cross-section area in the uniaxial stretching of subsamples

As the results in Figure S1.1a and S1.1b, the finite degrees of residual strain are observed in each direction for all type of pre-stretching. In DN gels, residual strain directly relates to the structural change due to internal fracture of the 1st network, so the effect of residual strain should be removed from stress-elongation relation in the measurement of the subsequent uniaxial stretching. In fact, the subsample has been permanently deformed by the combination of the residual strains in three directions, i.e., ε_x^r, ε_y^r, and ε_z^r, of the pre-stretched specimen in comparison with the virgin specimen. Thus, it should be reasonable to employ the initial parameters, i.e., the gauge length and cross-section area, of the virgin state for the subsequent stretching instead of using those of pre-stretched state (Figure S1.2).

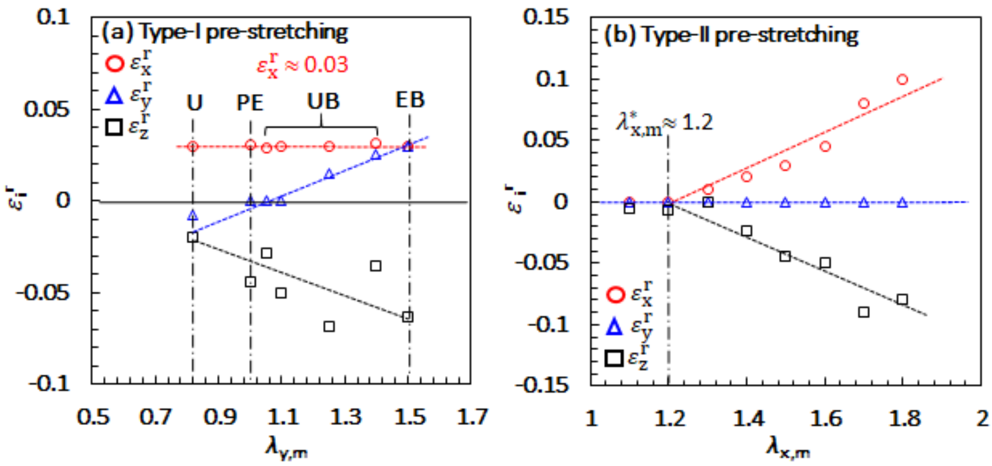

Figure S1.1. The finite residual strain in each direction, ε_i^r (i=x,y,z), for the (a) type-I and (b) -II pre-stretching. The dashed lines represent the guides for eyes.

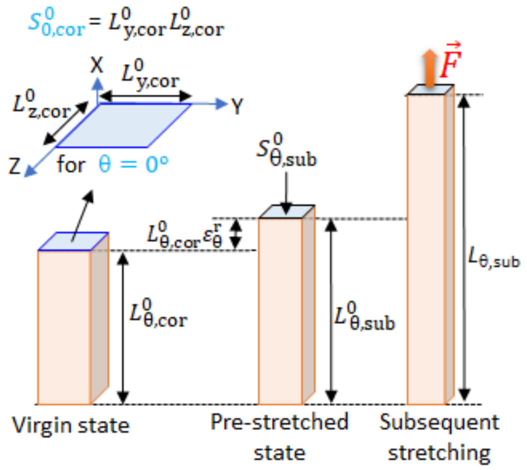

Figure S1.2. Schematic for estimation of corrected initial gauge length ($L^0_{\theta,\text{cor}}$) and cross-section area ($S^0_{\theta,\text{cor}}$) for the subsamples in the subsequent uniaxial pre-stretching in the DN gels. $L^0_{\theta,\text{sub}}$ and $L_{\theta,\text{sub}}$ are the lengths of subsample at the undeformed and deformed state. $\varepsilon^{\text{r}}_{\theta}$ denotes the residual strain in the direction of θ (θ = 0°, 45, and 90°).

Firstly, the corrected initial gauge length ($L^0_{\theta,\text{cor}}$) as well as nominal elongation ($\lambda_{\theta,\text{cor}}$) of the subsamples, which cut from pre-stretched specimen in the direction of θ (θ = 0°, 45, and 90° (Figure S1.2)), in the subsequent uniaxial stretching can be evaluated as Eq. (S1a) and (S1b).

$$L^0_{\theta,\text{cor}} = \frac{L^0_{\theta,\text{sub}}}{1 + \varepsilon^{\text{r}}_{\theta}} \tag{S1a}$$

$$\lambda_{\theta,\text{cor}} = \frac{L_{\theta,\text{sub}}}{L^0_{\theta,\text{sub}}}(1 + \varepsilon^{\text{r}}_{\theta}) = \lambda_{\theta,\text{sub}}(1 + \varepsilon^{\text{r}}_{\theta}) \tag{S1b}$$

Where $L^0_{\theta,\text{sub}}$ and $L_{\theta,\text{sub}}$ denote the initial (gauge length) and deformed lengths of the subsample in the subsequent uniaxial stretching, and $\varepsilon^{\text{r}}_{\theta}$ is a residual strain in the direction of θ (θ = 0°, 45°, or 90°) for the pre-stretched specimen correspondingly. The values of $\varepsilon^{\text{r}}_{0}$ (or $\varepsilon^{\text{r}}_{\text{x}}$) and $\varepsilon^{\text{r}}_{90}$ (or $\varepsilon^{\text{r}}_{\text{y}}$) for various types of pre-stretching with $\lambda_{\text{x,m}} = 1.5$, and for planar pre-stretching ($\lambda_{\text{y,m}} = 1$) with varying degrees of $\lambda_{\text{x,m}}$ are given in Figure S1.1a and S1.1b, respectively, while $\varepsilon^{\text{r}}_{45}$ can be measured by the relation of $\varepsilon^{\text{r}}_{45} = \sqrt{(1+\varepsilon^{\text{r}}_{0})^2 + (1+\varepsilon^{\text{r}}_{90})^2} - 1$ on the basis of Pythagorean theorem.

Secondly, the initial cross-section areas of the subsamples in the subsequent uniaxial stretching are also measured on the basis of virgin state. The corrected cross-section areas of the subsamples in the undeformed state ($S^0_{\theta,\mathrm{cor}}$) in the x- ($S^0_{0,\mathrm{cor}}$, θ = 0°), y- ($S^0_{90,\mathrm{cor}}$, θ = 90°), and bisector ($S^0_{45,\mathrm{cor}}$, θ = 45°) direction are estimated by using the initial dimension of virgin state as illustrated in Figure S1.2. The corresponding corrected stresses ($\sigma_{\theta,\mathrm{cor}}$, θ= 0°, 45° and 90°) under uniaxial stretching of the subsamples are evaluated as:

$$\sigma_{0,\mathrm{cor}} = \frac{F}{S^0_{0,\mathrm{cor}}} = \frac{F}{L^0_{90,\mathrm{sub}} L^0_{\mathrm{z,sub}}}(1+\varepsilon^{\mathrm{r}}_{90})(1+\varepsilon^{\mathrm{r}}_{z}) = \sigma_{0,\mathrm{sub}}(1+\varepsilon^{\mathrm{r}}_{90})(1+\varepsilon^{\mathrm{r}}_{z}) \tag{S1c}$$

$$\sigma_{90,\mathrm{cor}} = \frac{F}{S^0_{90,\mathrm{cor}}} = \frac{F}{L^0_{0,\mathrm{sub}} L^0_{\mathrm{z,sub}}}(1+\varepsilon^{\mathrm{r}}_{0})(1+\varepsilon^{\mathrm{r}}_{z}) = \sigma_{90,\mathrm{sub}}(1+\varepsilon^{\mathrm{r}}_{0})(1+\varepsilon^{\mathrm{r}}_{z}) \tag{S1d}$$

$$\sigma_{45,\mathrm{cor}} = \frac{F}{S^0_{45,\mathrm{cor}}} = \frac{F}{L^0_{135,\mathrm{sub}} L^0_{\mathrm{z,sub}}}(1+\varepsilon^{\mathrm{r}}_{135})(1+\varepsilon^{\mathrm{r}}_{z}) = \sigma_{45,\mathrm{sub}}(1+\varepsilon^{\mathrm{r}}_{135})(1+\varepsilon^{\mathrm{r}}_{z}) \tag{S1e}$$

where $L^0_{\mathrm{z,cor}}$ ($= L^0_{\mathrm{z,vir}}$) evaluated by Eq. (S1a), and $L^0_{\mathrm{z,sub}}$ are the initial lengths of the subsamples in z-direction (thicknesses) in virgin and pre-stretched states, respectively. $\sigma_{\theta,\mathrm{sub}}$ with θ= 0°, 45° or 90° is the uniaxial stress of the subsamples without correction.

The width of the subsample with θ = 45° in the virgin and pre-stretched states are denoted by $L^0_{135,\mathrm{cor}}$ and $L^0_{135,\mathrm{sub}}$ with θ = 135°, and corresponding residual strain in the direction of θ = 135° equals to that of θ = 45°, i.e., $\varepsilon^{\mathrm{r}}_{135} = \varepsilon^{\mathrm{r}}_{45}$, due to symmetrical strain field in each type of pre-stretching.

2. Type-I Pre-stretching with UB-1/10, UB-1/5, and UB-4/5.

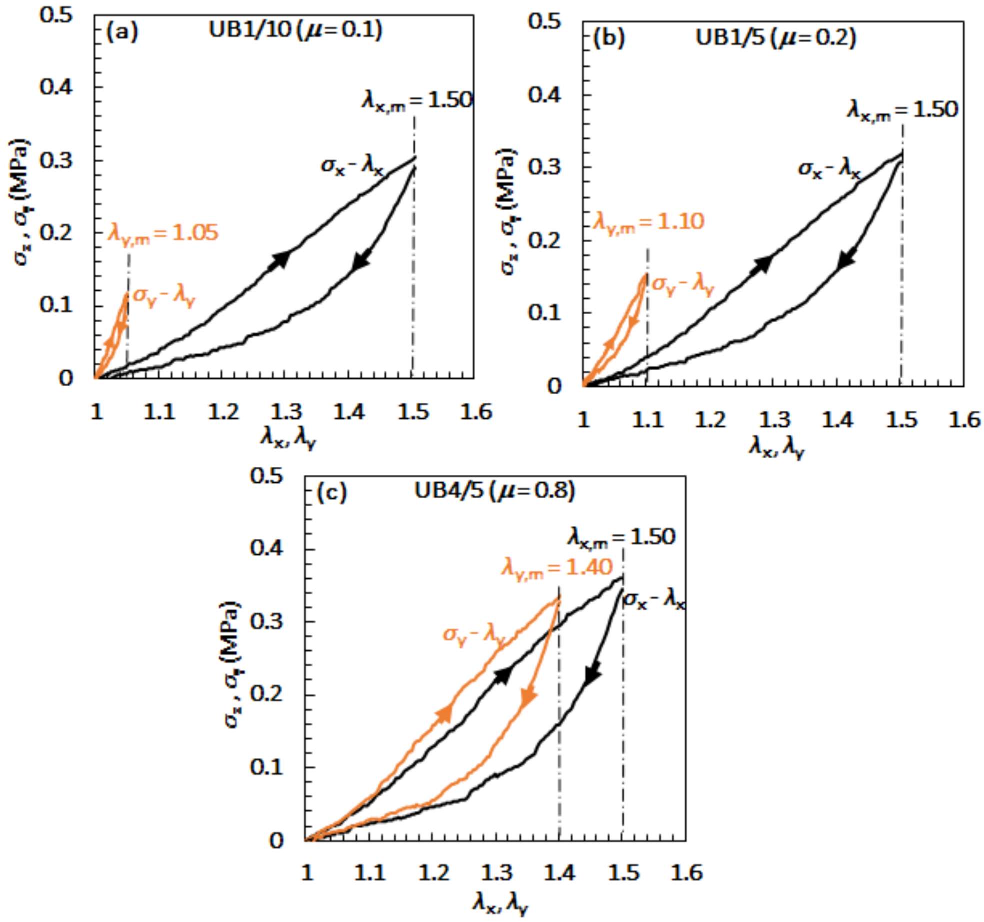

Figure S2. Nominal stress-elongation relations in x-direction (σ_x–λ_x) and y-direction (σ_y–λ_y) for the virgin specimen of the DN gels in a loading-unloading cycle of the pre-stretching process using unequal biaxial extension (UB-μ) with various values of strain ratio ($\mu = \varepsilon_y/\varepsilon_x$) using $\lambda_{x,m} = 1.5$: (a) UB-1/10 ($\mu = 0.1$), (b) UB1/5 ($\mu = 0.2$), and (c) UB4/5 ($\mu = 0.8$).

3. Uniaxial stretching of the subsamples pre-stretched by UB-1/10, UB-1/5, and UB-4/5.

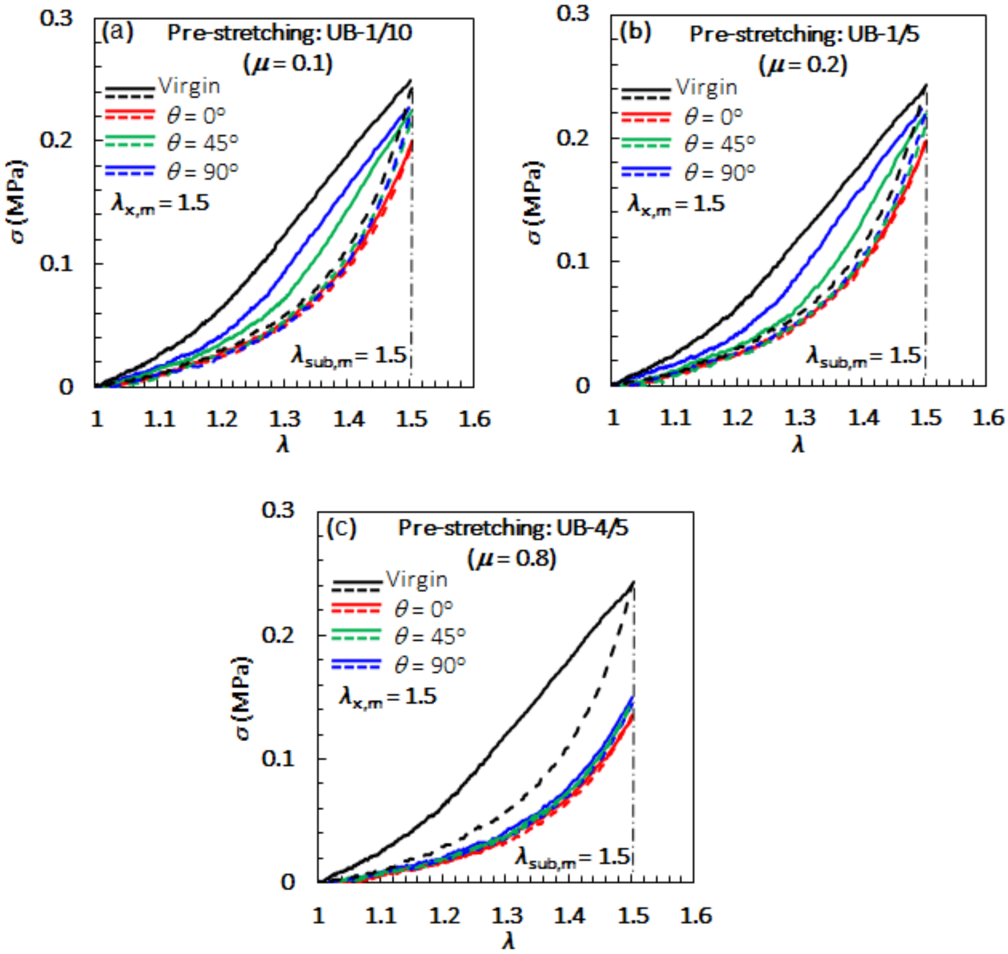

Figure S3. Nominal stress-elongation relations in a single uniaxial loading-unloading cycle for the subsamples with $\theta = 0^{\circ}$, 45° and 90°, which are cut out from the specimens after the pre-stretching of unequal biaxial extensions (UB-μ): (a) UB-1/10, (b) UB-1/5, and (c) UB-4/5. The maximum elongation ($\lambda_{sub,m}$) is identical with $\lambda_{x,m}$ (= 1.5) in each type of pre-stretching. The solid and dash lines correspond to loading and unloading curves, respectively.

4. The uniaxial nominal stress-elongation relations in a single loading-unloading cycle for the subsamples of the DN gels with $\theta = 0^{\circ}$ for the type-I (a) and -II (b) pre-stretching

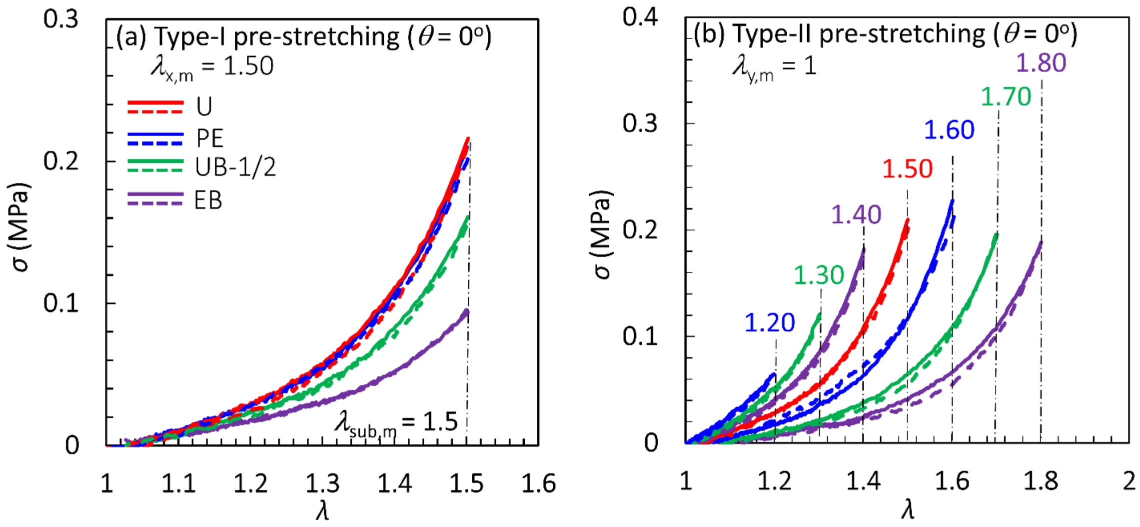

Figure S4. The uniaxial nominal stress-elongation relations in a single loading-unloading cycle for the subsamples of the DN gels with $\theta = 0^{\circ}$ for the type-I (a) and -II (b) pre-stretching. The maximum elongation ($\lambda_{sub,m}$) is identical with that in each pre-stretching ($\lambda_{x,m}$). The solid and dash lines correspond to loading and unloading curves, respectively.

5. The fitted results by Gent model for the subsamples with $\theta = 0^{o}$

Table S5: The fitted results by Gent model in type-I and type-II pre-stretching for the subsamples with θ = 0°

Pre-stretching	Mode	G (MPa)	I_m^*	λ_m^*
Type-I ($\lambda_{x,m}$ = 1.5)	PE	0.0650	3.838	1.639
	UB-1/10	0.0630	3.845	1.642
	UB-1/5	0.0629	3.870	1.653
	UB-1/2	0.0628	3.875	1.655
	UB-4/5	0.0540	3.910	1.670
	EB	0.0500	3.970	1.694
	U	0.0360	4.000	1.706
	$\lambda_{x,m}$	G (MPa)	I_m^*	λ_m^*
Type-II (PE, $\lambda_{y,m}$ = 1)	1.1	0.090	3.200	1.263
	1.2	0.087	3.300	1.337
	1.3	0.085	3.480	1.455
	1.4	0.080	3.650	1.549
	1.5	0.063	3.845	1.642
	1.6	0.050	4.100	1.744
	1.7	0.038	4.450	1.861
	1.8	0.035	4.880	1.988

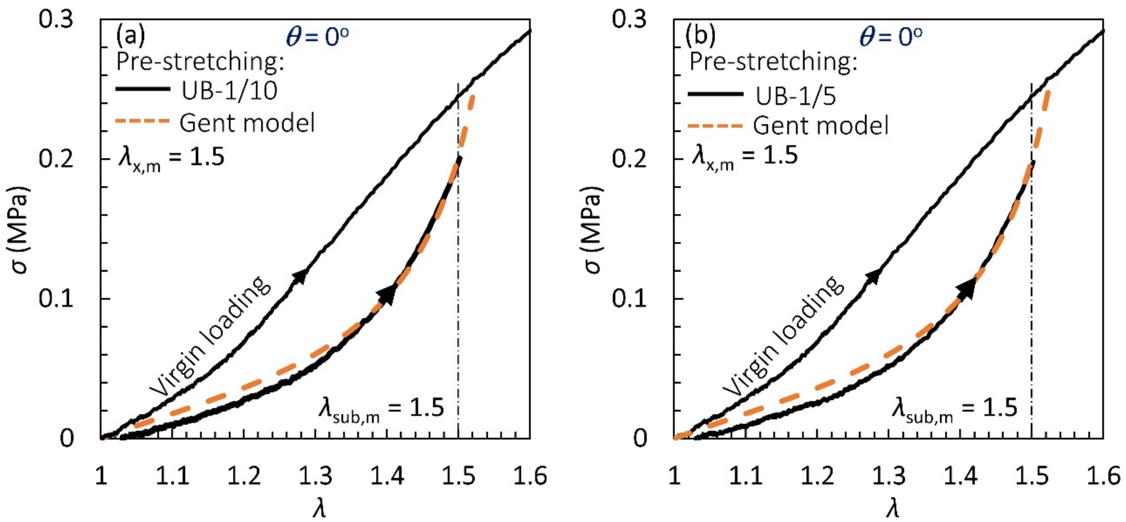

Figure S5. The fitted results for the reloading curves by the Gent model for the DN gels subsamples with $\theta = 0^{o}$ pre-stretched by UB-1/10 and UB-1/5. The dashed and solid lines depict the fitted and experimental curves, respectively.