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SUPPORT INFORMATION

Local strain-induced energy storage as driving force for autogenous scratch closure

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1. Experimental Section

Table S1. Synthesis of segmented polyurethanes: Stoichiometry and molar content.

OH (CroHeal 1000) / [OH(CroHeal) + OH (BDO)]	Nominal soft phase fraction (χ_{SF})	NCO / OH (total)
0.71	0.71	1.1
0.59	0.59	1.1
0.51	0.51	1.1
0.42	0.42	1.1
0.27	0.27	1.1

χ_{SF} = 0.71

Monomer	Mass (g)	Molar content (mmol)
CroHeal™ 1000	6.0	4.87
BuAc	0.78	6.76
BDO	0.18	1.997
TEGO270	0.028	n.a.
DBTDL	0.063	0.1
IPDI	1.678	7.550

χ_{SF} = 0.59

Monomer	Mass (g)	Molar content (mmol)
CroHeal™ 1000	6.0	4.87
BuAc	0.83	7.15
BDO	0.30	3.328
TEGO270	0.028	n.a.
DBTDL	0.063	0.1
IPDI	2.004	7.550

χ_{SF} = 0.51

Monomer	Mass (g)	Molar content (mmol)
CroHeal™ 1000	6.0	4.87
BuAc	0.87	7.53
BDO	0.420	4.660
TEGO270	0.028	n.a.
DBTDL	0.063	0.1
IPDI	2.329	10.479

χ_{SF} = 0.27

Monomer	Mass (g)	Molar content (mmol)
CroHeal™ 1000	6.0	4.87
BuAc	1.16	10.02
BDO	1.20	13.31
TEGO270	0.028	n.a.

DBTDL	0.063	0.1
IPDI	4.446	19.99

2. Characterization methods

Table S2. Stress from static force at ε_{max} ($\sigma_{SF\ at\ \varepsilon_{max}}$), maximum strain ($\varepsilon_{max}$), junction density ($\nu_j$) maximum released entropy density (ΔS_R^{max}), maximum stored entropy density (ΔS_S^{max}) for the different polyurethane formulations obtained via DMA analysis. The data reported are the average value and standard deviation calculated on a set of three DMA experiments.

χ_{SF}	$\sigma_{SF\ at\ \varepsilon_{max}}$ (MPa)	ε_{max} (%)	ν_j (mol/m^3)	$\Delta S_R^{\max}$ (kJ/m^3)	$\Delta S_S^{\max}$ (kJ/m^3)
0.71	0.243±0.018	9.4±0.30	393±30	10.16±0.90	11.75±0.94
0.59	0.202±0.014	7.9±0.45	379±11	7.23±0.66	8.20±1.02
0.51	0.190±0.013	7.5±0.22	366±24	6.23±0.62	7.35±0.64
0.42	0.159±0.007	8.3±0.19	274±16	4.45±0.45	6.80±0.19
0.27	0.0514±0.001	4.8±0.85	136±11	0.71±0.58	1.31±0.52

Table S3. Temperatures corresponding to the mid and end-point of VLT transition and corresponding ΔS_R as calculated by VLT DMA study. These points were used as healing temperatures of the PU coatings.

χ_{SF}	T_i (°C)	T_{mid} (°C)	$T_{end\text{-}point}$ (°C)	ΔS_R^{mid} (kJ/m^3)	$\Delta S_R^{end-point}$ (kJ/m^3)
0.71	3±0.2	21±0.3	35±0.3	6.68±1.44	10.62±0.89
0.59	4±0.2	23.5±0.3	38.5±0.3	4.32±1.61	7.39±0.66
0.51	9±0.2	27.5±0.3	42.5±0.5	3.46±1.05	6.62±0.62
0.42	12.5±0.3	33±0.3	48±0.5	1.39±0.41	4.51±0.57
0.27	18±0.3	55±0.5	80±1.1	0.112±0.06	0.71±0.20

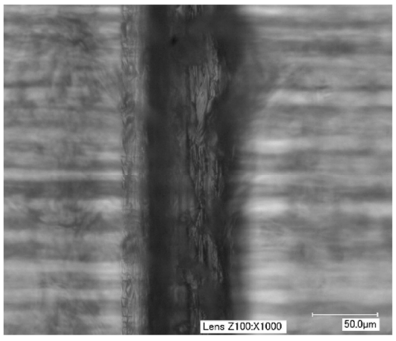
Table S4. Additional healing temperatures tested for χ_{SF} = 0.71 and χ_{SF} = 0.51 and corresponding ΔS_R as calculated by VLT DMA study.

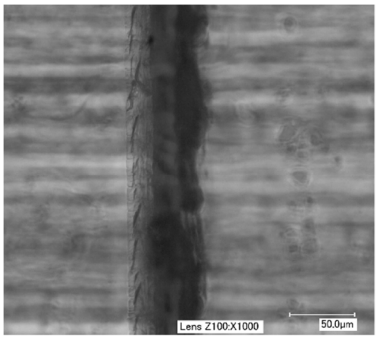
χ_{SF}	T_i (°C)	$T_{retraction}$ (°C)	ΔS_R (kJ/m^3)
0.71	3±0.2	17±0.3	0.39±0.09
		23±0.3	7.76±1.15
		30±0.3	10.55±0.92
0.51	9	24±0.3	0.69±0.18
		28±0.3	3.10±0.93
		36±0.3	6.20±0.69

3. Optical micrographs of damaged and healed coatings

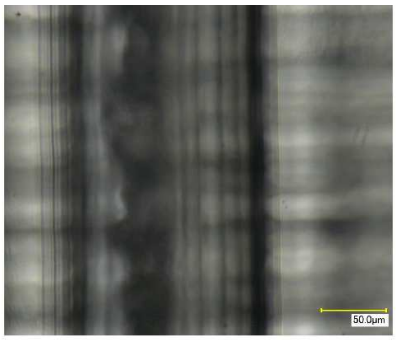
In this section we show exemplary optical micrographs of the damaged and healed coatings. Optical micrographs of the coating in the damage state are reported on the left end side, while the optical micrographs of the coating in the healed state are reported on the right end side. The scale bar measures a length of 50 µm.

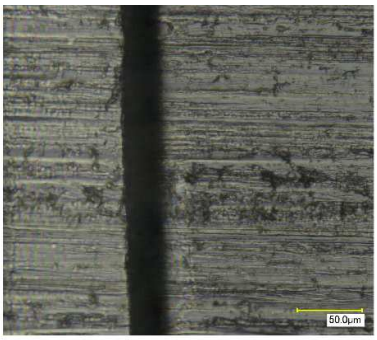
χ_{SF} **= 0.71**, T_{damage} = 3 °C, $T_{healing}$ = 17 °C



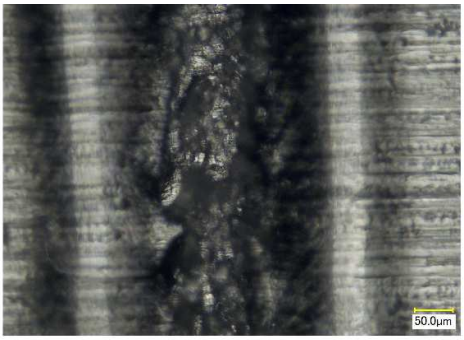


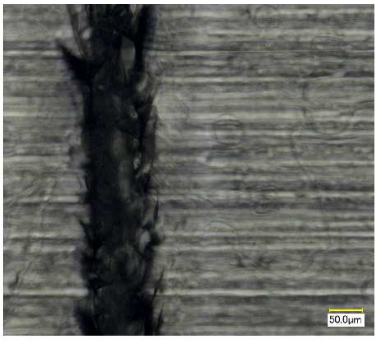
χ_{SF} = 0.71, T_{damage} = 3 °C, $T_{healing}$ = 21 °C



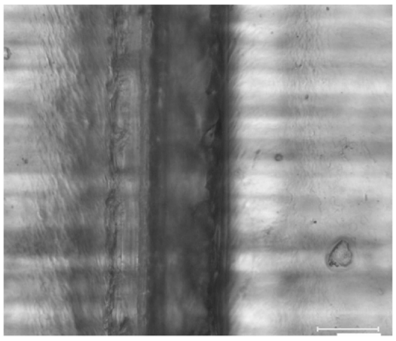
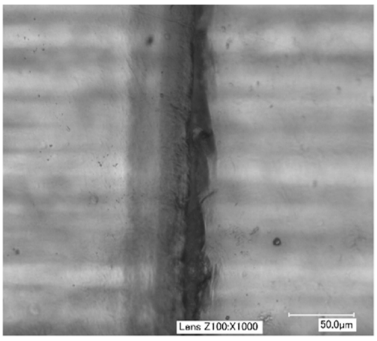


χ_{SF} = 0.71, T_{damage} = 3 °C, $T_{healing}$ = 21 °C, **Rockwell Tip**





χ_{SF} = 0.71, T_{damage} = 3 °C, $T_{healing}$ = 23 °C

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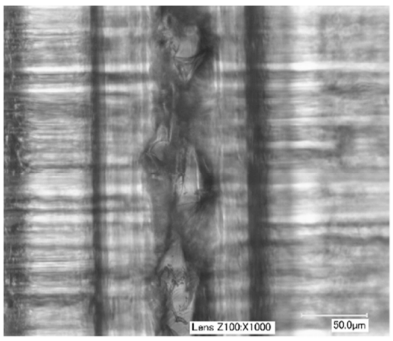
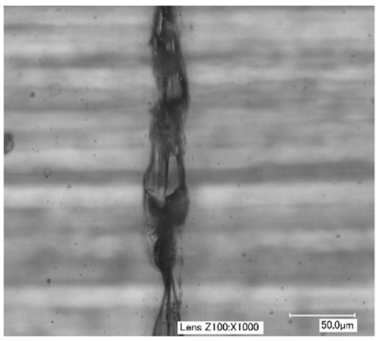
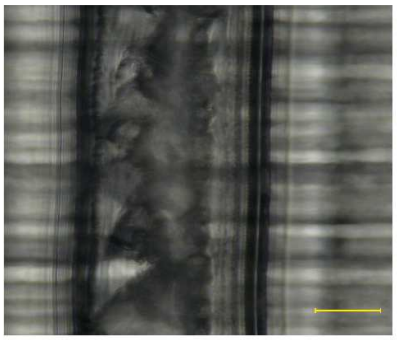
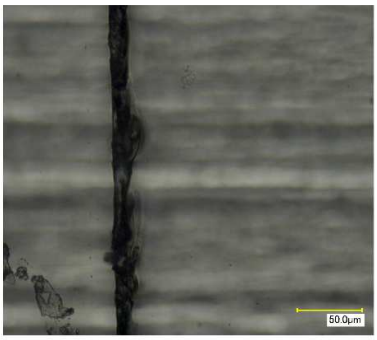


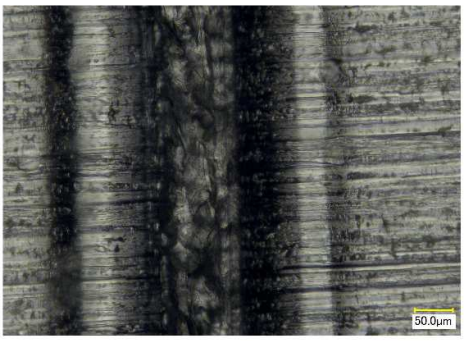


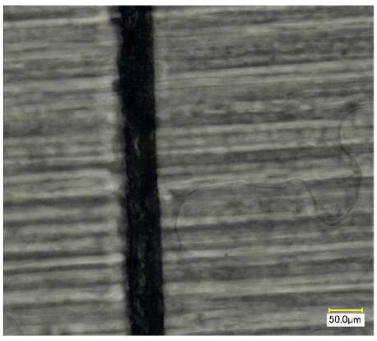
χ_{SF} = 0.71, T_{damage} = 3 °C, $T_{healing}$ = 35 °C



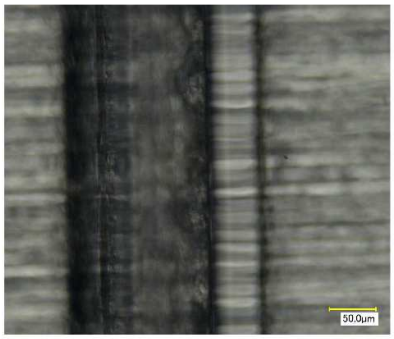


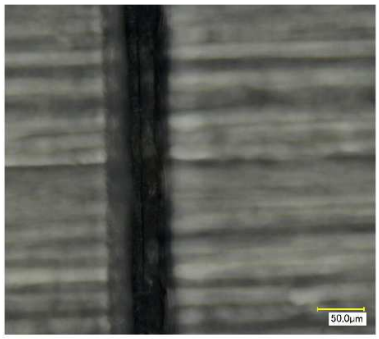
χ_{SF} = 0.71, T_{damage} = 3 °C, $T_{healing}$ = 35 °C, **Rockwell Tip**



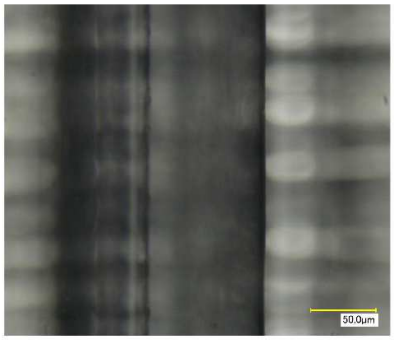


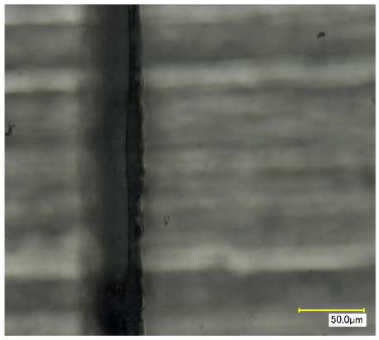
χ_{SF} **= 0.59**, T_{damage} = 4 °C, $T_{healing}$ = 23.5 °C



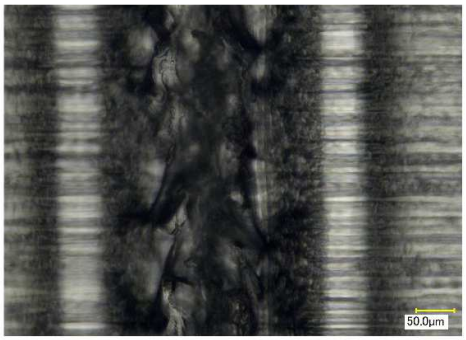


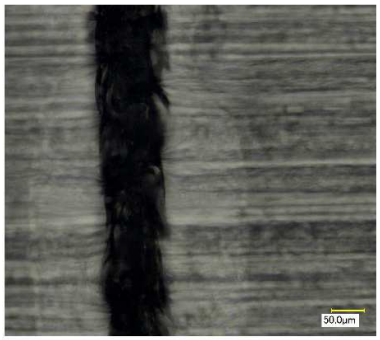
χ_{SF} = 0.59, T_{damage} = 4 °C, $T_{healing}$ = 38.5 °C



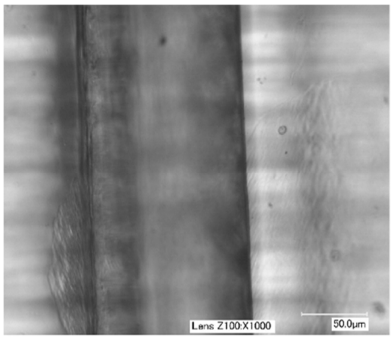


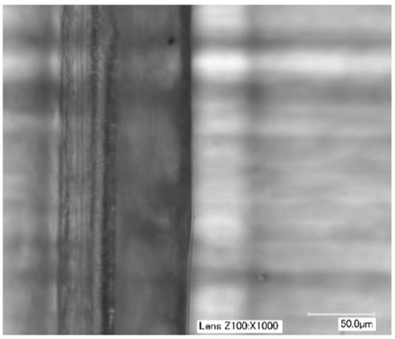
χ_{SF} = 0.59, T_{damage} = 4 °C, $T_{healing}$ = 38.5 °C, **Rockwell Tip**



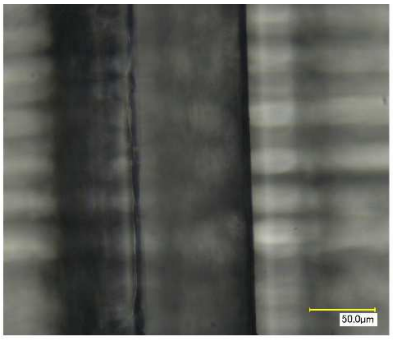


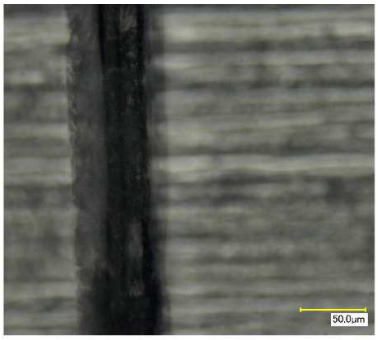
χ_{SF} **= 0.51**, T_{damage} = 9 °C, $T_{healing}$ = 24 °C



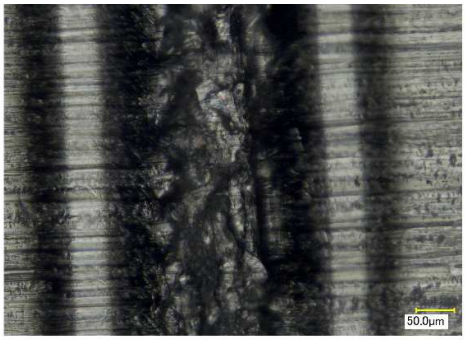


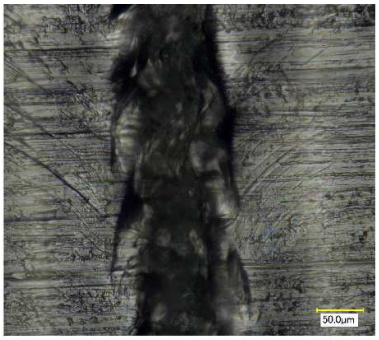
χ_{SF} = 0.51, T_{damage} = 9 °C, $T_{healing}$ = 27.5 °C



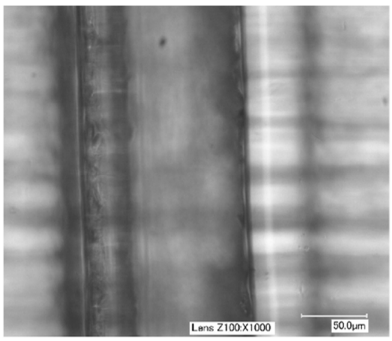


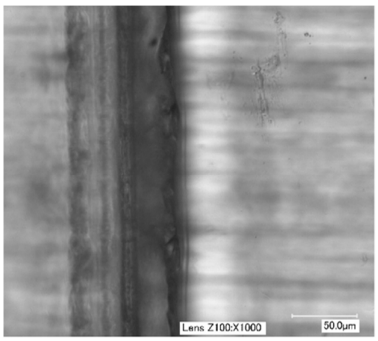
χ_{SF} = 0.51, T_{damage} = 9 °C, $T_{healing}$ = 27.5 °C, **Rockwell Tip**



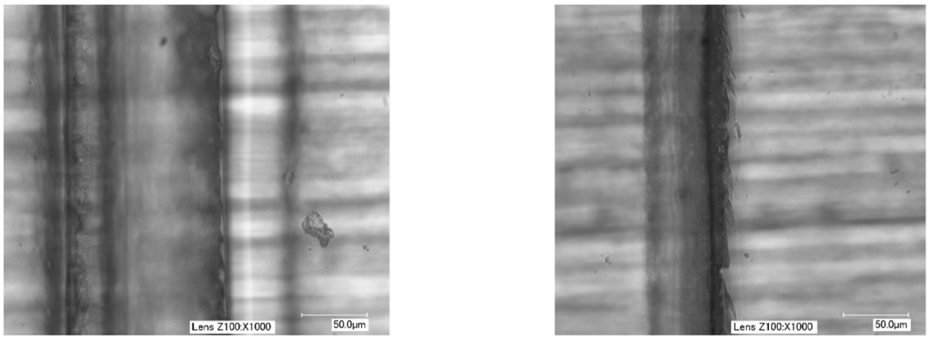


χ_{SF} = 0.51, T_{damage} = 9 °C, $T_{healing}$ = 28 °C

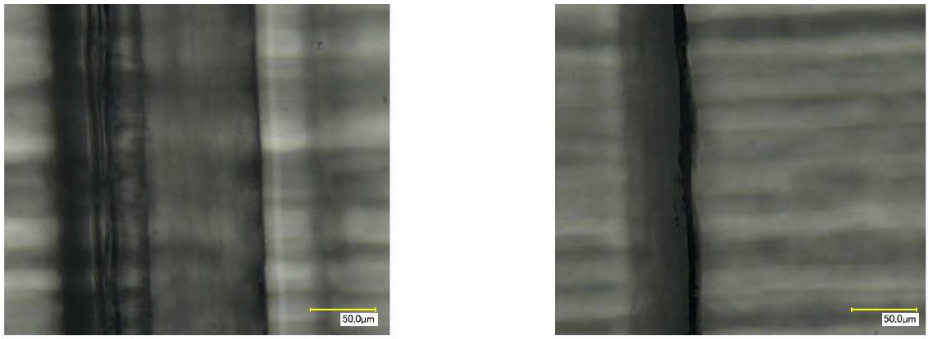




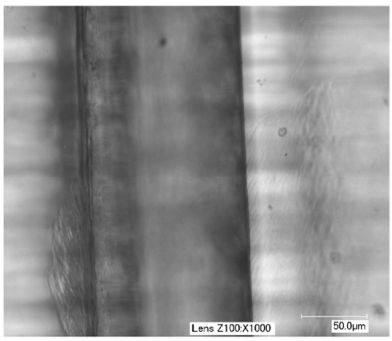
χ_{SF} = 0.51, T_{damage} = 9 °C, $T_{healing}$ = 36 °C

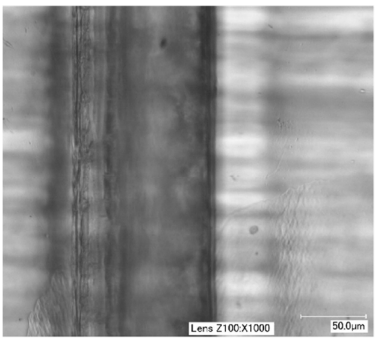


χ_{SF} = 0.51, T_{damage} = 9 °C, $T_{healing}$ = 42.5 °C

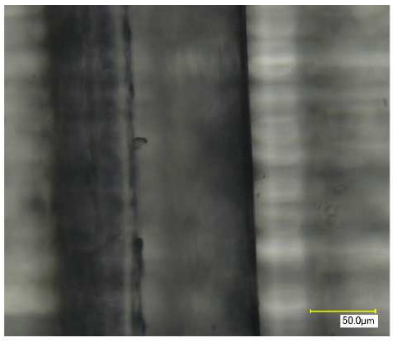


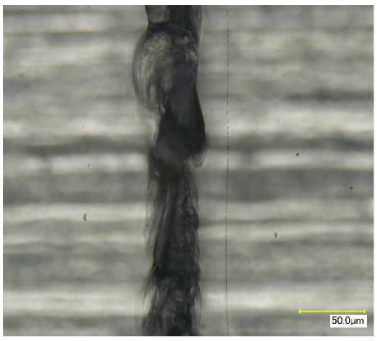
χ_{SF} **= 0.42**, T_{damage} = 12 °C, $T_{healing}$ = 33 °C



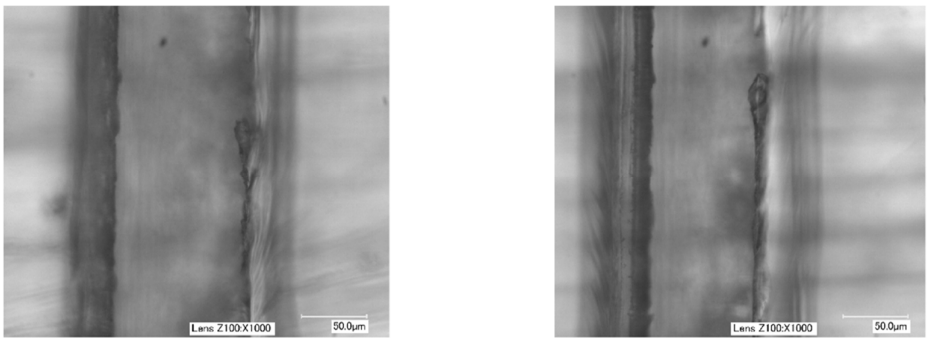


χ_{SF} = 0.42, T_{damage} = 12 °C, $T_{healing}$ = 48 °C

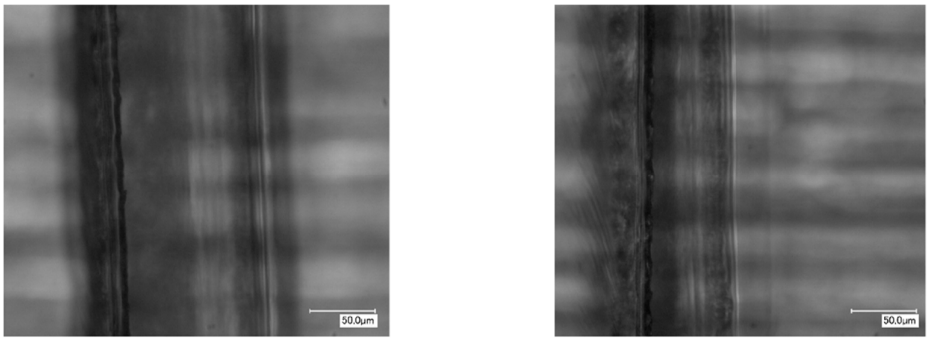




χ_{SF} **= 0.27**, T_{damage} = 18 °C, $T_{healing}$ = 55 °C



χ_{SF} = 0.27, T_{damage} = 18 °C, $T_{healing}$ = 80 °C



References

[1] C. C. Hornat, Y. Yang, M. W. Urban, *Adv. Mater.* **2017**, *29*, 1603334.