

Supplementary informations

Enhancing the robustness of thiol–thioester covalent adaptable networks through reversible thiol–Michael masking

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Model reaction

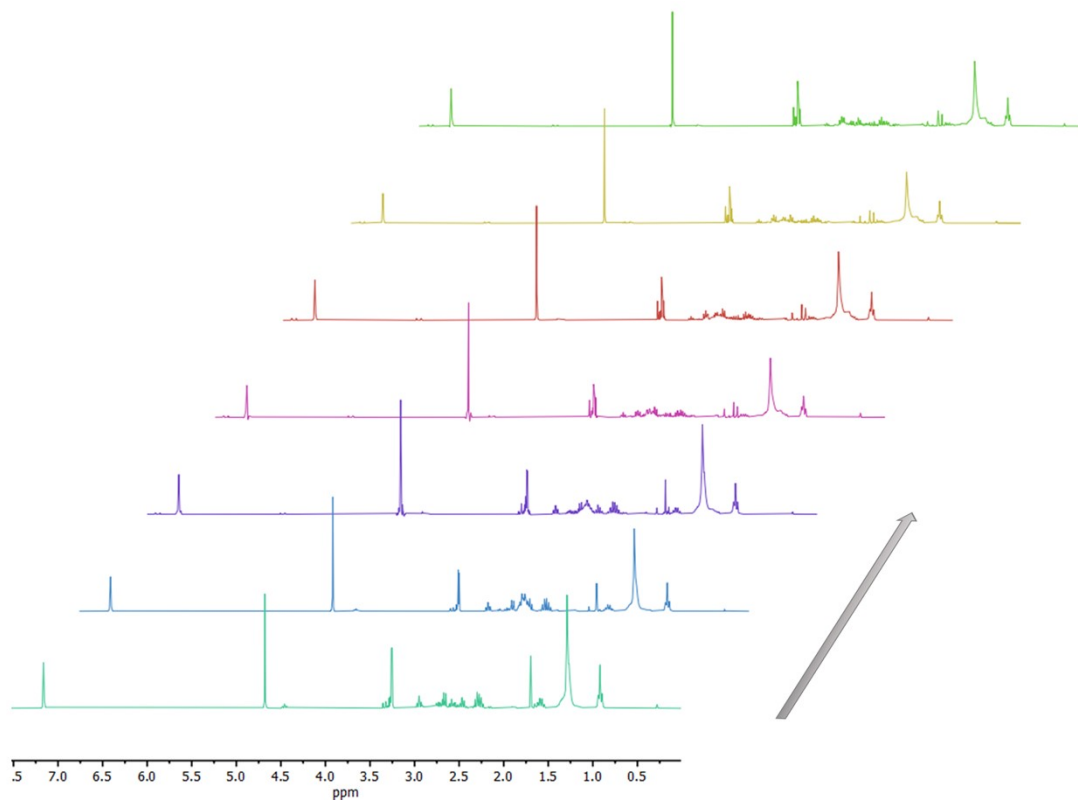


Figure S1: NMR spectra of the model reaction at 60°C with a spectrum taken after 0, 4, 10, 20, 40, 100 and 180 minutes.

NMR

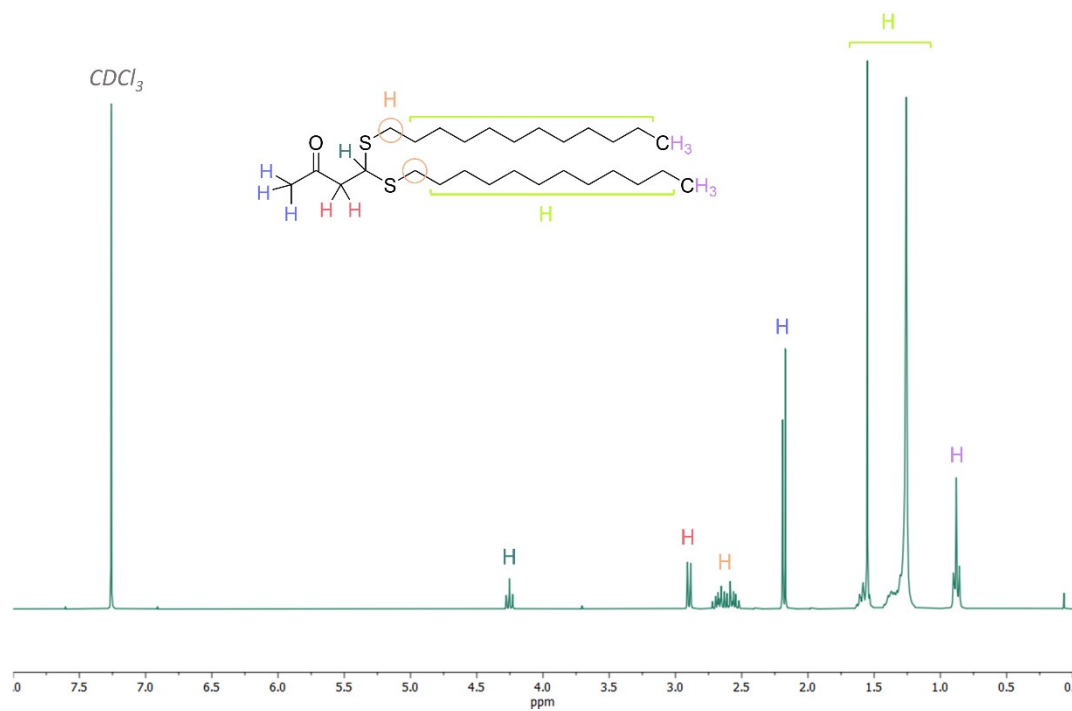


Figure S2: ^1H NMR spectrum of Model-TA in CDCl_3 at 25°C

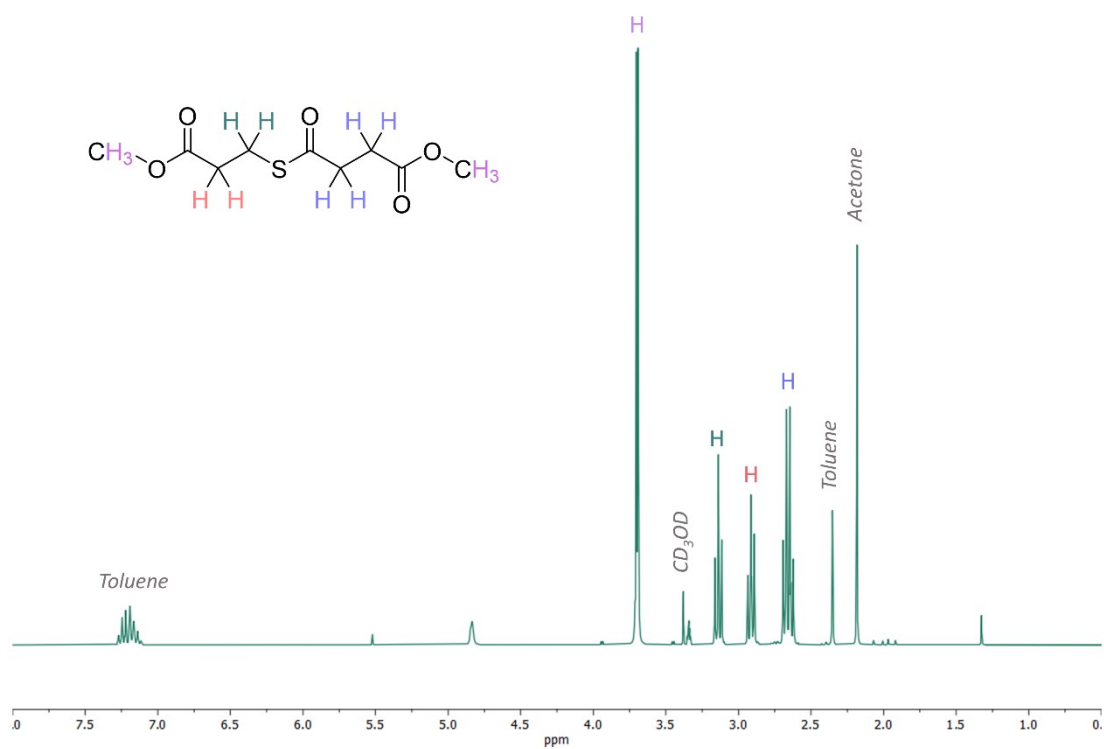


Figure S3: ^1H NMR spectrum of Model-TE in CD_3OD at 25°C

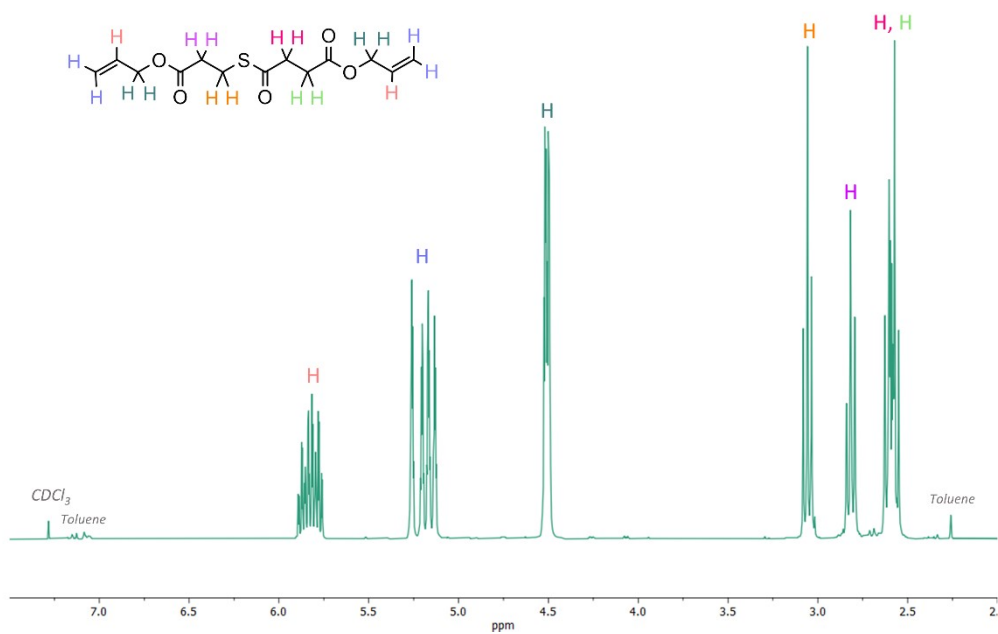


Figure S4: ^1H NMR spectrum of TE-M in CDCl_3 at 25°C

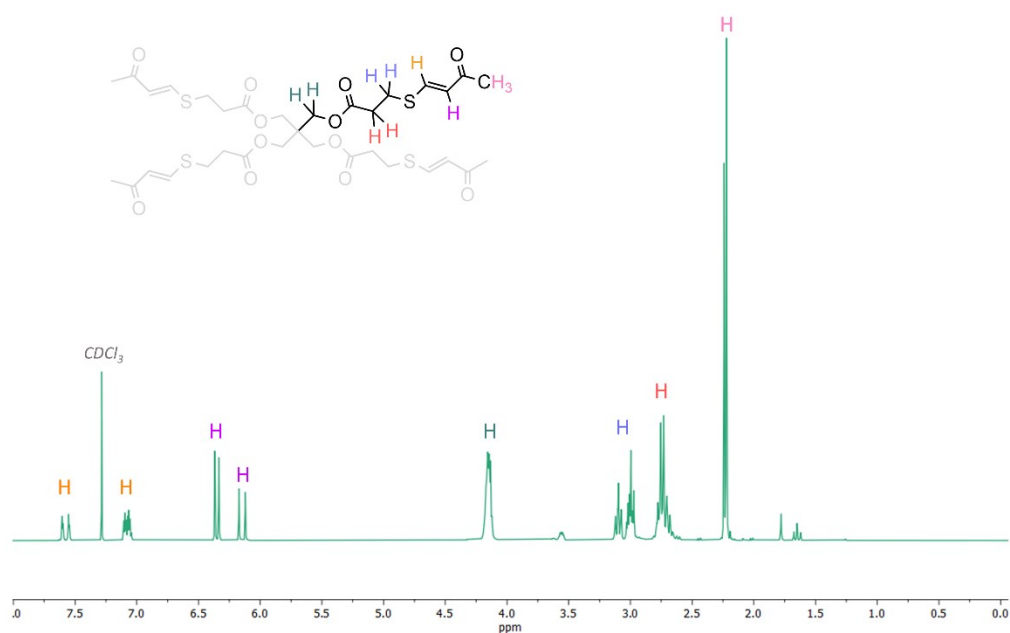


Figure S5: ^1H NMR spectrum of VTE in CDCl_3 at 25 $^\circ\text{C}$

General material properties

Sample		Free thiols (%)	Blocked thiols (%)	Catalyst amount (wt.%)	Tg ($^\circ\text{C}$)	Flow activation energy (kJ/mol)	Swelling ratio (%)		Soluble fraction (%)	
							CHCl ₃	THF	CHCl ₃	THF
C-FT / 5 %		5	-	1	-17	Too slow to obtain an accurate value	115.8	119.8	11.8	17.9
C-FT / 30 %		30	-	1	-15	194 $\pm$ 13	149.4	170.0	8.7	12.9
C-FT / 50 %		53	-	1	-26	86 $\pm$ 3	526.1	255.8	18.4	10.1
C-FT / 77 %		77	-	1	-26	82 $\pm$ 7	586.5	395.1	44.4	31.4
C-FT / 100% 1% TBD	R0	100	-	1	-29	111 $\pm$ 1	535.7	201.4	32.6	29.2
	R1	100	-	1	-30	169 $\pm$ 8	340	279	38	42
C-BT / 1% TBD		-	100	1	+1	137 $\pm$ 6	103.5	88.5	2.4	1.6
C-BT / 3% TBD		-	100	3	+3	132 $\pm$ 4	193.9	63.5	2.5	0
C-BT 5% TBD	R0	-	100	5	+4	124 $\pm$ 3	206.2	103.6	12.3	4.2
	R1	-	100	5	-18	124 $\pm$ 4	244.1	97.6	11.2	3.6

Table S1 : Material properties and composition of each C-FT and C-BT material synthesized.

Stress relaxation and reprocessing.

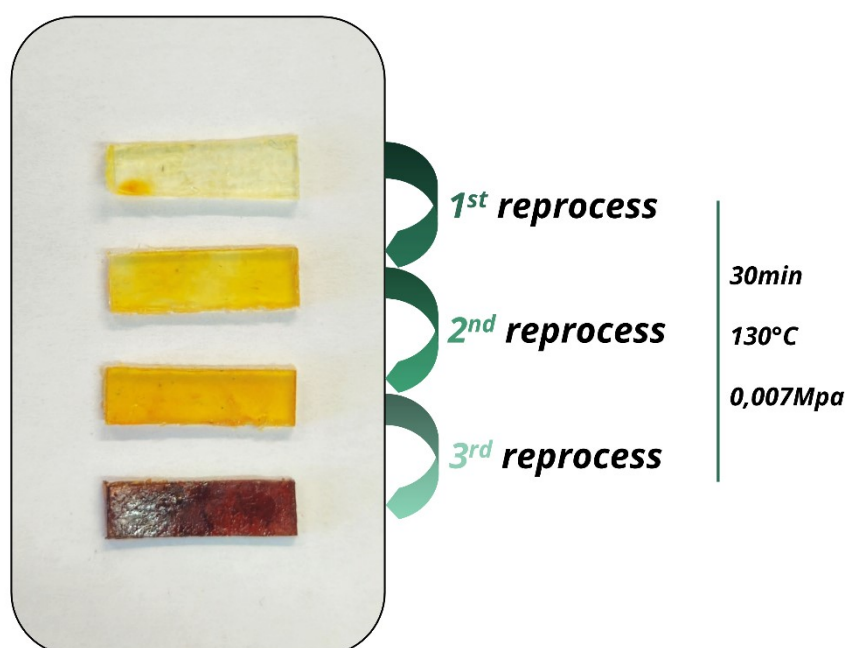


Figure S6: C-BT-5% before and after 1, 2 and 3 reprocessing cycles at 130°C under 0.007MPa for 30minutes

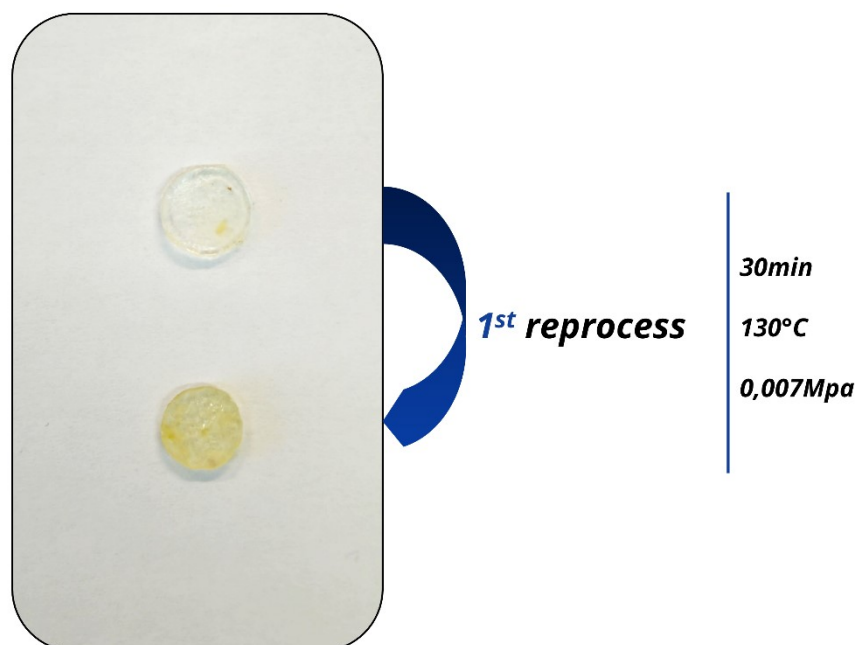


Figure S7: C-FT-1% before after 1 reprocessing cycle at 130°C under 0.007MPa for 30minutes

KWW equation / exponential decay model.

$$\frac{G}{G_0} = (1 - y_0)e^{-\frac{\tau^* \Gamma(1/\beta)}{\beta}}$$

and

$$\langle \tau \rangle = \frac{\tau^* \Gamma(1/\beta)}{\beta}$$

	C-BT 100% BT – 5wt. % TBD Before reprocessing						C-BT 100% BT – 5wt. % TBD After 1 reprocessing cycle						C-BT 100% BT – 5wt. % TBD After 2 reprocessing cycles					
T°C	τ^* (s)	$\langle \tau \rangle$ (s)	β	R^2	y_0		τ^* (s)	$\langle \tau \rangle$ (s)	β	R^2	y_0		τ^* (s)	$\langle \tau \rangle$ (s)	β	R^2	y_0	
150	31	37	0.74	0.99	0		47	67	0.62	0.99	0		60	89	0.60	0.99	0	
145	36	46	0.71	0.99	0		/						/					
140	44	58	0.67	0.99	0		72	114	0.57	0.99	0		89	135	0.60	0.99	0	
135	58	81	0.64	0.99	0		/						/					
130	80	119	0.61	0.99	0		143	248	0.54	0.99	0		181	304	0.56	0.99	0	
125	116	183	0.58	0.99	0		/						/					
120	172	295	0.55	0.99	0		386	643	0.52	0.99	0		458	887	0.51	0.99	0	
115	270	496	0.53	0.99	0		/						/					
110	443	864	0.51	0.99	0		985	1913	0.50	0.99	0		1364	2662	0.51	0.99	0	
105	742	1513	0.50	0.99	0		/						/					
100	1316	2792	0.48	0.99	0		2993	5986	0.49	0.99	0		3926	7598	0.51	0.99	0	
95	2406	5370	0.47	0.99	0		/						/					
90	4587	10632	0.46	0.99	0		9478	19667	0.49	0.99	0		12984	25112	0.51	0.99	0	
85	9593	22602	0.46	0.99	0		/						/					
80	21390	50437	0.46	0.99	0		/						/					
75	46439	103212	0.47	0.99	0		/						/					

Table S2 : Exponential decay fitting parameters C-BT / 5% TBD before and after reprocessing at several temperatures

	C-BT 100% BT – 1wt. % TBD						C-BT 100% BT – 3wt. % TBD					
T°C	τ^* (s)	$\langle \tau \rangle$ (s)	β	R^2	y_0		τ^* (s)	$\langle \tau \rangle$ (s)	β	R^2	y_0	
150	959	1289	0.66	0.99	0		385	501	0.68	0.99	0	
140	1866	2694	0.62	0.99	0		830	1249	0.6	0.99	0	
130	4647	6708	0.62	0.99	0		1837	2893	0.58	0.99	0	
120	13415	20638	0.59	0.99	0		5081	8002	0.58	0.99	0	
110	46095	74404	0.57	0.99	0		16547	26709	0.57	0.99	0	

Table S3 : Exponential decay fitting parameters for C-BT formulations with varying content of TBD at several temperatures

	C-FT 100% FT – 1wt. % TBD					C-BT 100% FT – 1wt. % TBD After reprocessing				
T°C	τ^* (s)	$\langle \tau \rangle$ (s)	θ	R^2	y_0	τ^* (s)	$\langle \tau \rangle$ (s)	θ	R^2	y_0
150	92	99	0.86	0.99	0	5671	7395	0.68	0.99	0
145	119	129	0.86	0.99	0	/				
140	179	199	0.82	0.99	0	24647	29888	0.73	0.99	0
135	254	290	0.79	0.99	0	/				
130	374	428	0.79	0.99	0	67478	81263	0.74	0.99	0
125	556	662	0.75	0.99	0	/				
120	844	1016	0.73	0.99	0	225738	311713	0.64	0.99	0
115	1293	1637	0.70	0.99	0	/				
110	1988	2671	0.66	0.99	0					
105	3131	4278	0.64	0.99	0					
100	4766	6512	0.64	0.99	0					
95	7450	10179	0.65	0.99	0					
90	12490	16517	0.67	0.99	0					

Table S4 : Exponential decay fitting parameters for C-FT-1% before and after reprocessing

	C-FT 5% FT – 1wt. % TBD					C-FT 30% FT – 1wt. % TBD					C-FT 50% FT – 1wt. % TBD					C-FT 77% FT – 1wt. % TBD				
T°C	τ^* (s)	$\langle \tau \rangle$ (s)	θ	R^2	y_0	τ^* (s)	$\langle \tau \rangle$ (s)	θ	R^2	y_0	τ^* (s)	$\langle \tau \rangle$ (s)	θ	R^2	y_0	τ^* (s)	$\langle \tau \rangle$ (s)	θ	R^2	y_0
150	/					4072	5384	0.67	0.99	0	405	451	0.82	0.99	0	/				
140	47360	74586	0.58	0.99	0	10249	16543	0.57	0.99	0	628	748	0.75	0.99	0	238	405	0.81	0.99	0
130	1654098	8318698	0.35	0.99	0	33986	59549	0.54	0.99	0	1124	1386	0.72	0.99	0	396	462	0.77	0.99	0
120	3.56E9	6.74E11	0.19	0.96	0	118425	213904	0.53	0.99	0	2147	2682	0.71	0.99	0	732	837	0.79	0.99	0
110	Too slow					771184	1911452	0.45	0.99	0	4638	5793	0.71	0.99	0	1382	1726	0.71	0.99	0

Table S5 : Exponential decay fitting parameters for C-FT formulations with varying content of free thiols at several temperatures

Stress relaxation profiles.

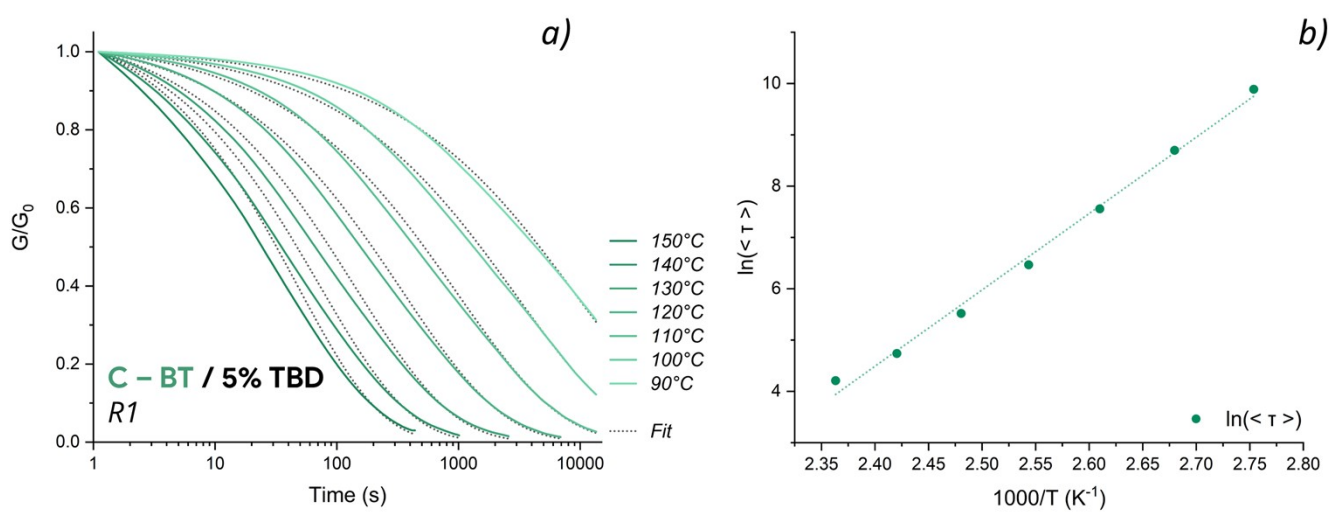


Figure S8 : Stress relaxation profiles of C-BT 5% TBD after 1 reprocessing cycle (a) and Arrhenius plot made using calculated relaxation times (b)

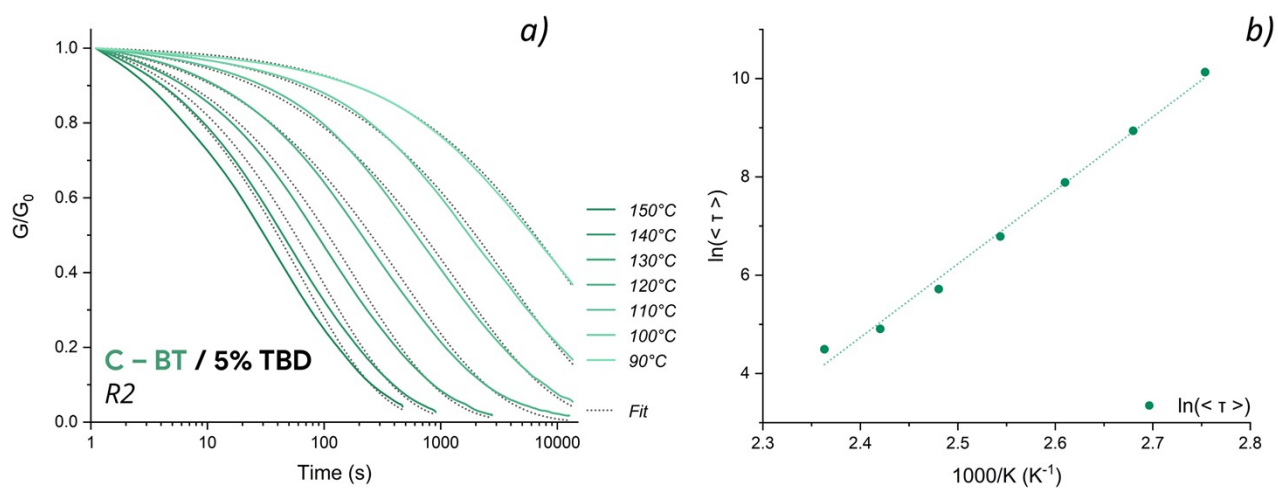


Figure S9 : Stress relaxation profiles of C-BT / 5% TBD after 2 reprocessing cycles (a) and Arrhenius plot made using calculated relaxation times (b)

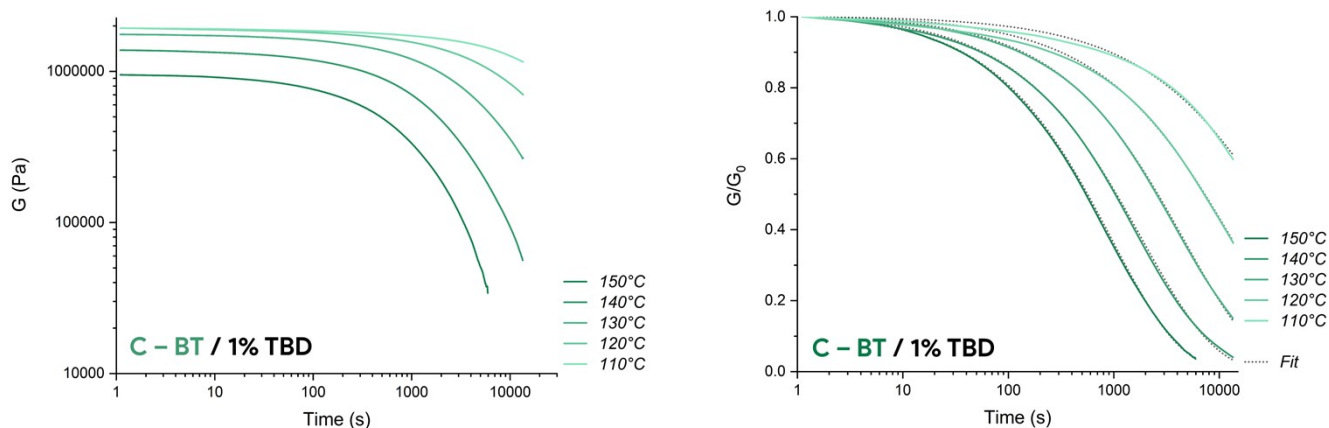


Figure S10 : Non-normalized (left) and normalized (right) stress relaxation profiles of C-BT / 1% TBD at 150°C, 140°C, 130°C, 120°C and 110°C

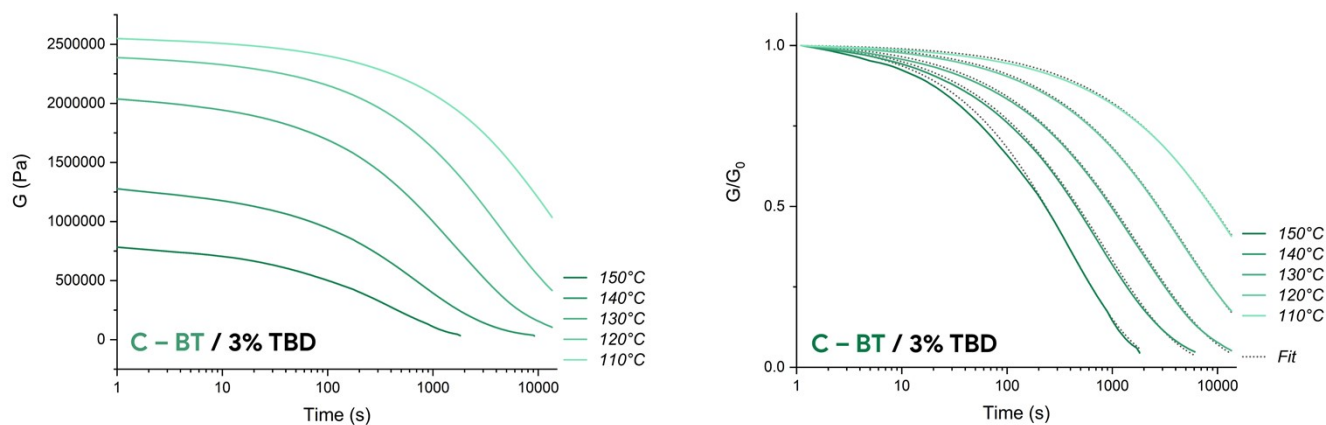


Figure S11 : Non-normalized (left) and normalized (right) stress relaxation profiles of C-BT / 3% TBD at 150°C, 140°C, 130°C, 120°C and 110°C

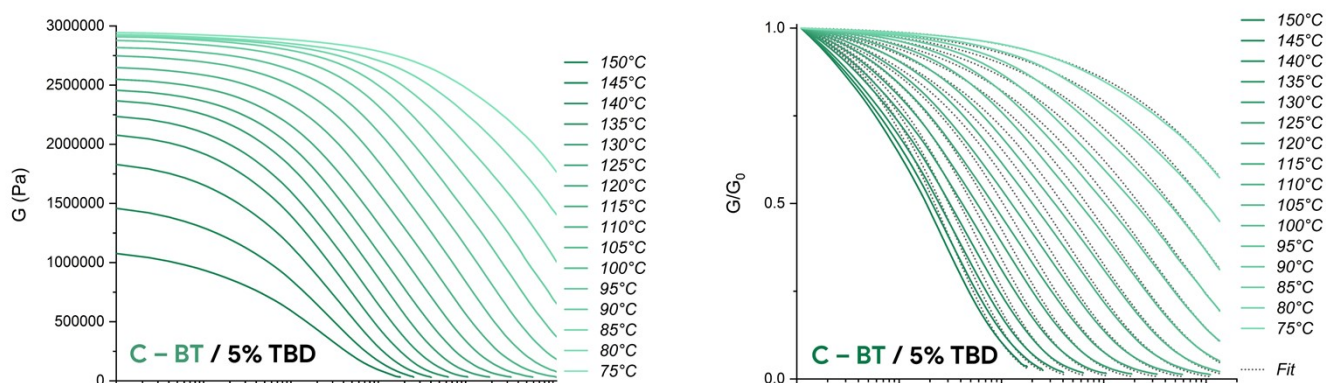


Figure S12 : Non-normalized (left) and normalized (right) stress relaxation profiles of C-BT / 5% TBD at 150°C, 140°C, 130°C, 120°C and 110°C

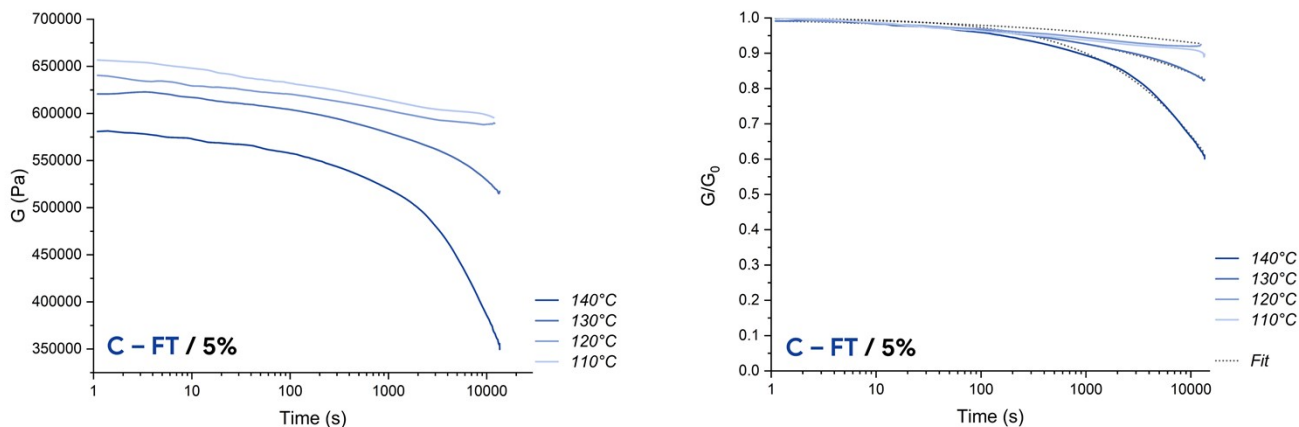


Figure S13 : Non-normalized (left) and normalized (right) stress relaxation profiles of C-FT / 1% TBD (5% Free thiols) at 150°C, 140°C, 130°C, 120°C and 110°C

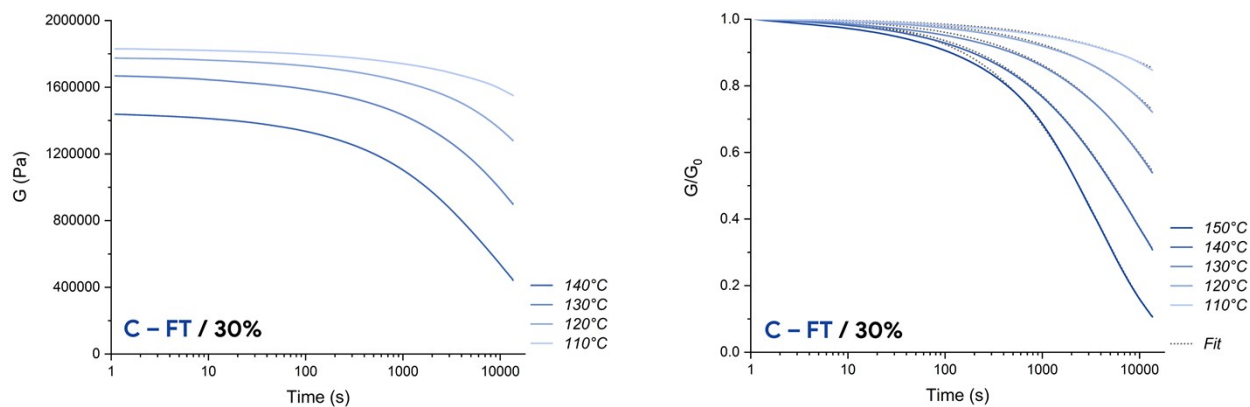


Figure S14 : Non-normalized (left) and normalized (right) stress relaxation profiles of C-FT / 1% TBD (30% Free thiols) at 150°C, 140°C, 130°C, 120°C and 110°C

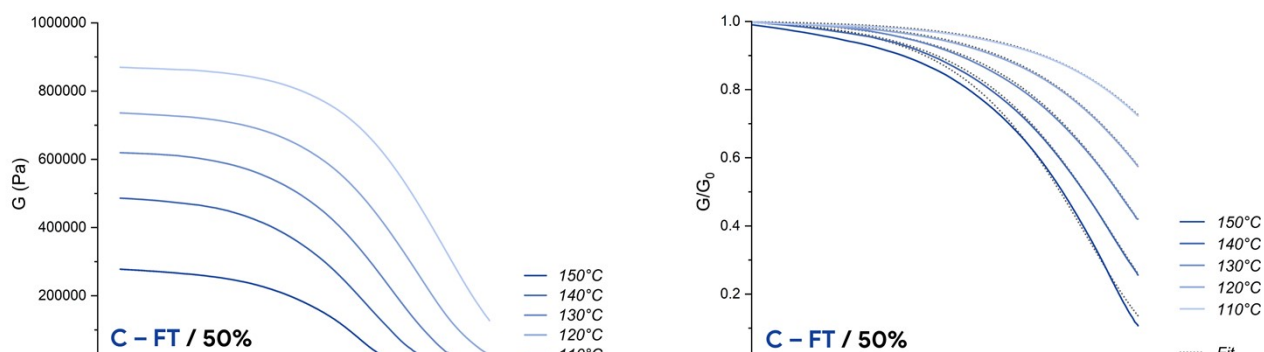


Figure S15 : Non-normalized (left) and normalized (right) stress relaxation profiles of C-FT / 1% TBD (50% Free thiols) at 150°C, 140°C, 130°C, 120°C and 110°C

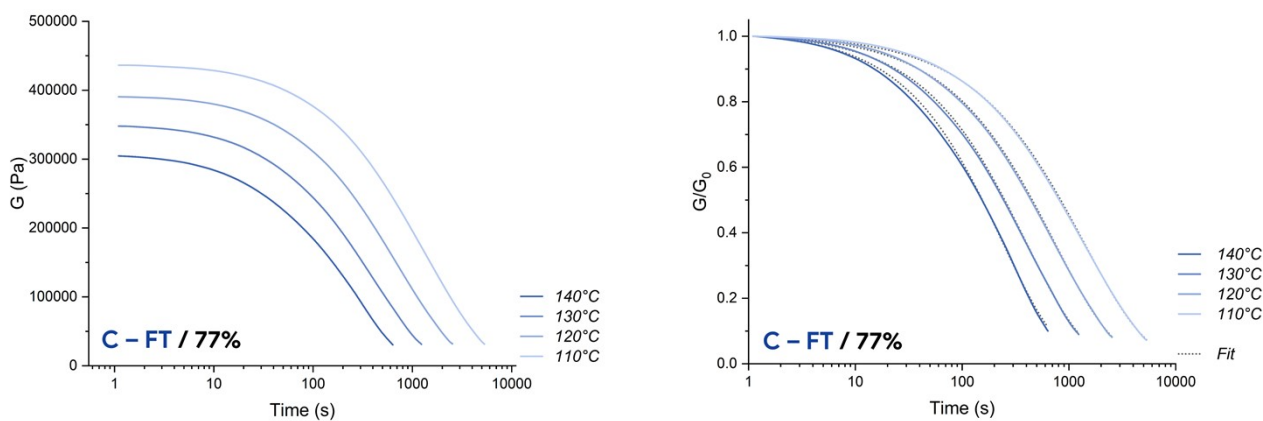


Figure S16 : Non-normalized (left) and normalized (right) stress relaxation profiles of C-FT / 1% TBD (77% Free thiols) at 150°C, 140°C, 130°C, 120°C and 110°C

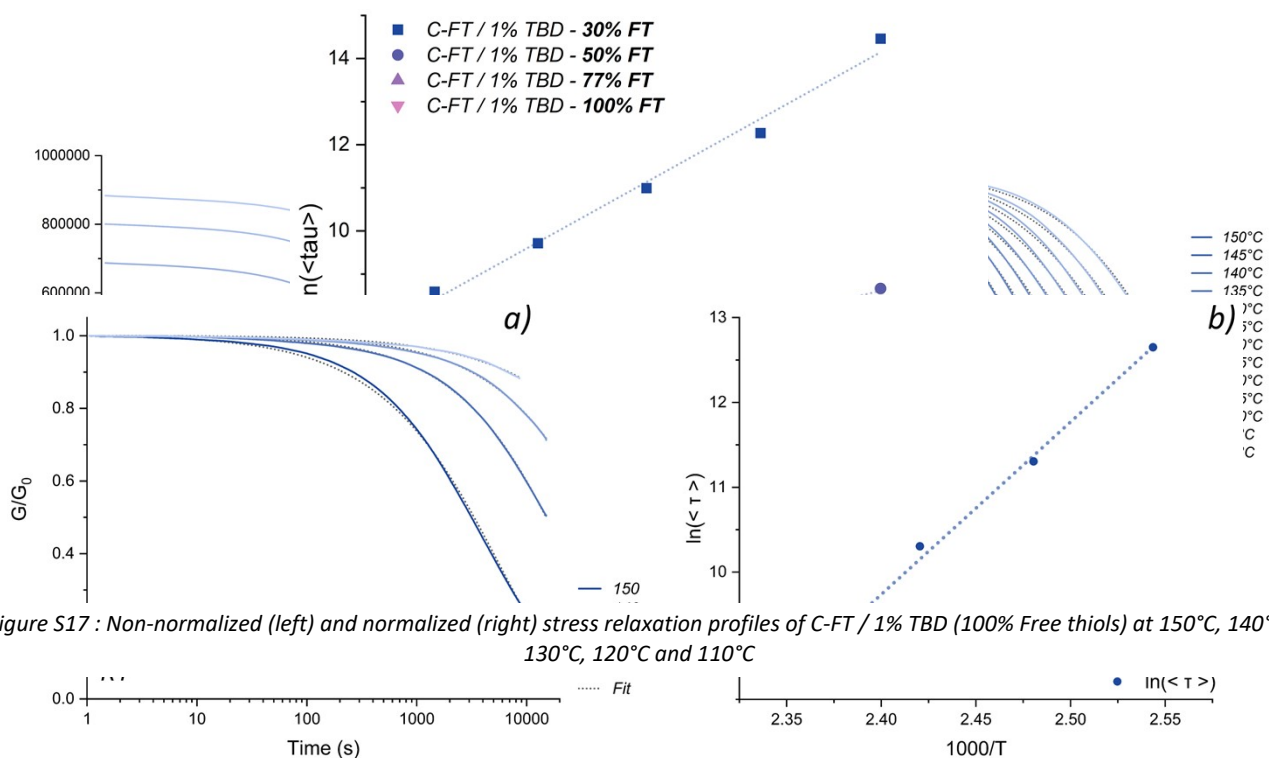


Figure S17 : Non-normalized (left) and normalized (right) stress relaxation profiles of C-FT / 1% TBD (100% Free thiols) at 150°C, 140°C, 130°C, 120°C and 110°C

Figure S18 : Stress relaxation profiles of C-FT 1% TBD after 1 reprocessing cycle (a) and Arrhenius plot made using calculated relaxation times (b)

Figure S19 : Arrhenius plot for C-FT / 1% TBD with different free thiol content calculated from stress relaxation times. With only 5% of free thiols, the material exhibited poor relaxation properties, making the calculation of a flow activation energy impossible.

DSC analysis.

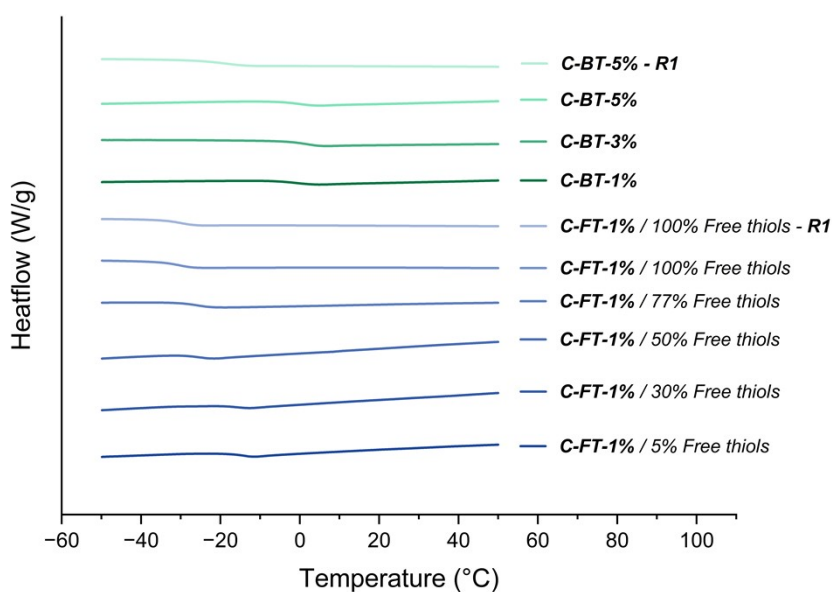


Figure S20 : Thermograms of C-BT-5% before and after reprocessing, C-BT-3% and C-BT-1% (green), C-FT-1% with 100% free thiols before and after reprocessing, as well as C-FT1% with other varying amounts of free thiols (blue)

Creep data

T	dε/dt (%/min)		ε(max) (%)		ε(res) (%)		% recovery	
	C-FT - 1%	C-BT - 5%	C-FT - 1%	C-BT - 5%	C-FT - 1%	C-BT - 5%	C-FT - 1%	C-BT - 5%
20	1,09E-18	3,84E-06	2,06	0,17	8,80E-02	0,00E+00	95,73	100,00
30	5,34E-06	7,85E-06	1,98	0,21	7,09E-02	3,73E-02	96,41	82,57
40	1,72E-05	1,12E-05	2,01	0,21	8,97E-02	1,85E-02	95,54	91,02
50	4,35E-05	1,18E-05	2,02	0,21	1,33E-01	2,15E-02	93,41	89,81
60	7,93E-05	1,41E-05	2,06	0,23	2,27E-01	3,53E-02	88,97	84,67
70	1,41E-04	1,95E-05	2,02	0,22	2,87E-01	3,09E-02	85,77	86,01
80	2,22E-04	2,86E-05	2,01	0,24	4,18E-01	6,07E-02	79,24	74,53
90	3,47E-04	4,68E-05	2,09	0,24	6,20E-01	6,94E-02	70,40	71,31
100	5,38E-04	7,16E-05	2,19	0,26	8,15E-01	9,87E-02	62,72	62,43
110	7,31E-04	1,43E-04	2,27	0,34	1,14E+00	1,89E-01	49,74	44,35

Table S6 : Creep rate, maximum elongation, residual elongation and creep recovery for C-FT-1% and C-BT-5% at several temperatures