Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Incorporation of fillers to modify the mechanical performance of inverse vulcanised polymers

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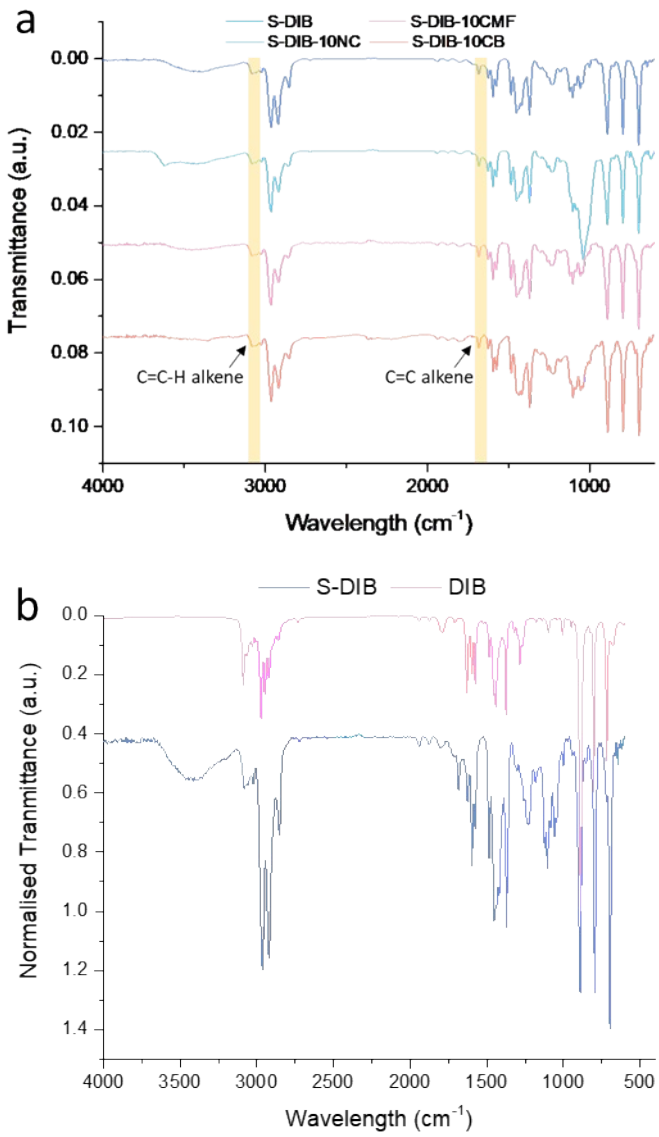

Fig. S1 FT-IR spectra of (a) S-DIB composites with fillers at 10 wt.% loading; (b) S-DIB and DIB. Stretching vibrations of alkene C=C-H and C=C bonds at 3093 cm^{-1} and 1681 cm^{-1}, indicate that some C=C bonds have been left unreacted. This was expected as the sample was only partially cured for 30 min.

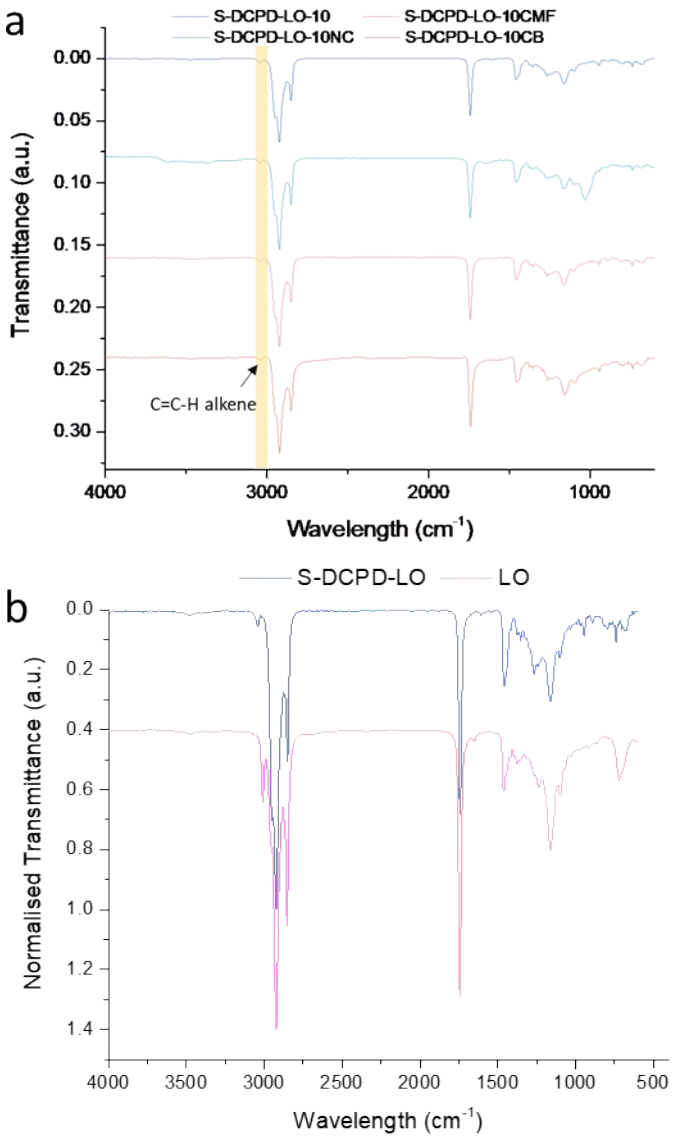

Fig. S2 FT-IR spectra of (a) S-DCPD-LO composites with fillers at 10 wt.% loading; (b) S-DCPD-LO and LO. C=C-H bond stretching vibration at 3059 cm^{-1} indicates that not all C=C bonds have been consumed, however, the low intensity suggests very few C=C bonds remain.

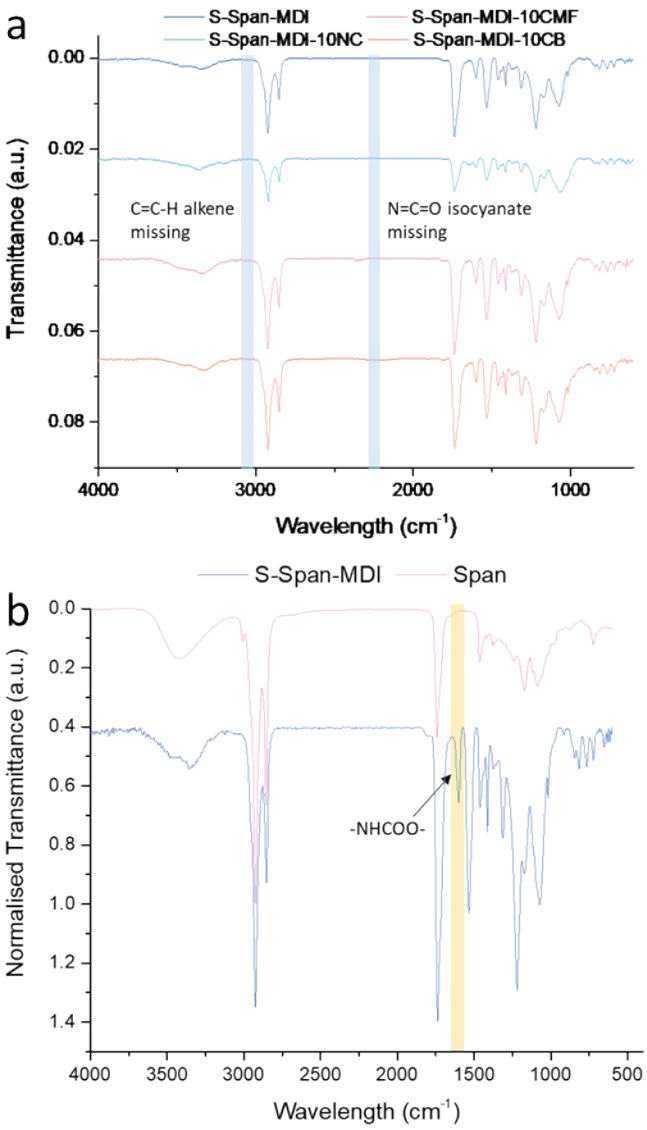

Fig. S3 FT-IR spectra of (a) S-Span-MDI composites with fillers at 10 wt.% loading; (b) S-Span-MDI and Span. In (a) C=C-H stretching vibration is missing indicating all C=C bonds have been consumed. N=C=O isocyanate stretching vibration is also missing indicating the isocyanate groups of MDI have fully reacted with Span to form –NHCOO- groups. In (b) a new peak resulting from –NHCOO- stretching vibration in S-Span-MDI is not present in Span.

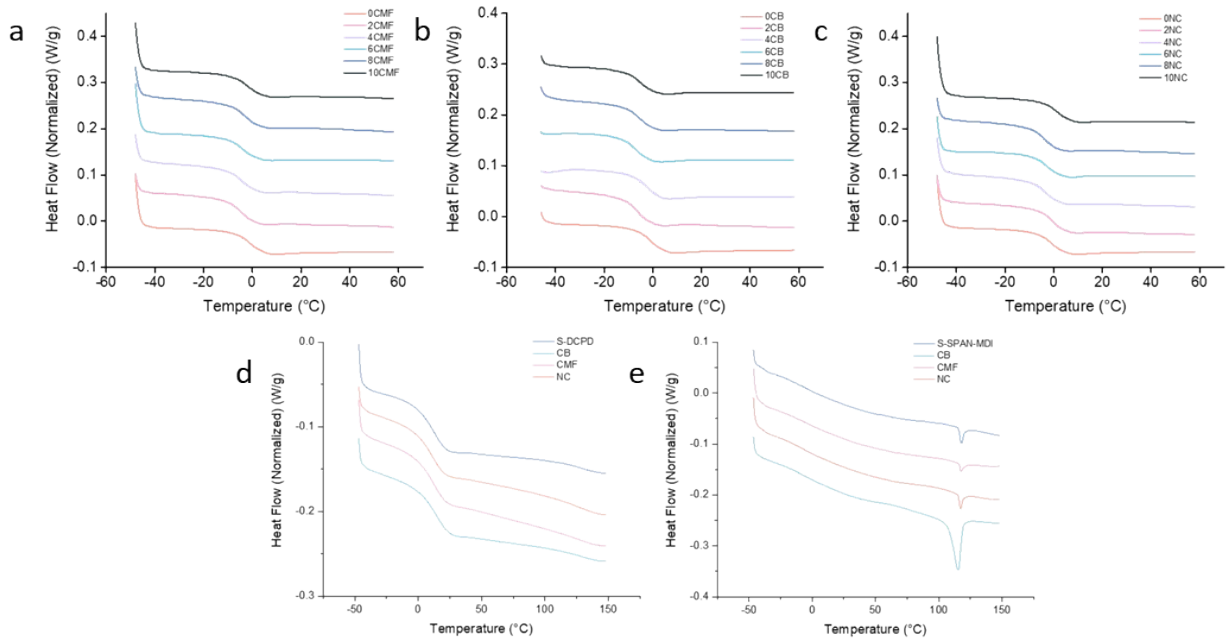

Fig. S4 DSC thermograms of (a) S-DIB composites with CMF at 0-10 wt.% loadings; (b) S-DIB composites with CB at 0-10 wt.% loadings; (c) S-DIB composites with NC at 0-10 wt.% loadings; (d) S-DCPD-LO composites with different fillers at 10 wt.% loading; (e) S-Span-MDI composites with different fillers at 10 wt.% loading.

Table S1 T_g values of unfilled and filled S-DIB, S-DCDP-LO, and S-Span-MDI and time taken to hot-press each sample into a film.

Sample	Hot-press time (min)	T_g (°C)
S-DIB PB1[a]	-	-1.1
S-DIB PB2[b]	-	-6.3
S-DIB B1[c]	10	-0.08
S-DIB B2[d]	15	-0.9
S-DIB-2CB	15	-5.9
S-DIB-4CB	10	-1.7
S-DIB-6CB	15	-5.8
S-DIB-8CB	15	-3.6
S-DIB-10CB	10	-4.0
S-DIB-2CMF	10	-3.6
S-DIB-4CMF	10	-3.4
S-DIB-6CMF	10	-3.0
S-DIB-8CMF	15	-2.4
S-DIB-10CMF	10	-0.8
S-DIB-2NC	10	0.1
S-DIB-4NC	10	-2.4
S-DIB-6NC	10	-2.3
S-DIB-8NC	15	-3.2
S-DIB-10NC	10	2.0
S-DCPD-LO	10	11.0
S-DCPD-LO-10CB	10	13.4
S-DCPD-LO-10CMF	10	11.3
S-DCPD-LO-10NC	10	10.3
S-Span-MDI	10	3.6
S-Span-MDI-10CB	10	3.8
S-Span-MDI-10CMF	10	5.0
S-Span-MDI-10NC	10	1.8

[a]PB1 = polymer powder batch 1.
[b]PB2 = polymer powder batch 2.
[c]B1 = batch 1 – higher T_g than batch 2; therefore, required less time on the hot-press.
[d]B2 = batch 2 – required more curing time on the hot-press to obtain similar T_g to batch 1 in order to achieve reproducible tensile tests.

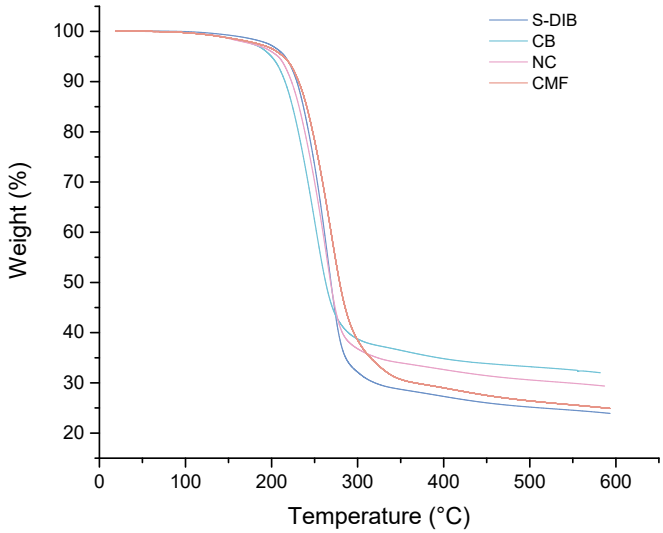

Fig. S5 TGA thermogram of unfilled S-DIB and S-DIB composites containing different fillers at 10 wt.% loading.

Table S2 Onset and end temperatures, and weight loss of the samples from TGA.

Sample	Onset temperature (℃)	End temperature (℃)	Weight loss (%)
S-DIB	237	280	65
S-DIB-10NC	235	285	62
S-DIB-10CMF	238	293	67
S-DIB-10CB	229	280	59

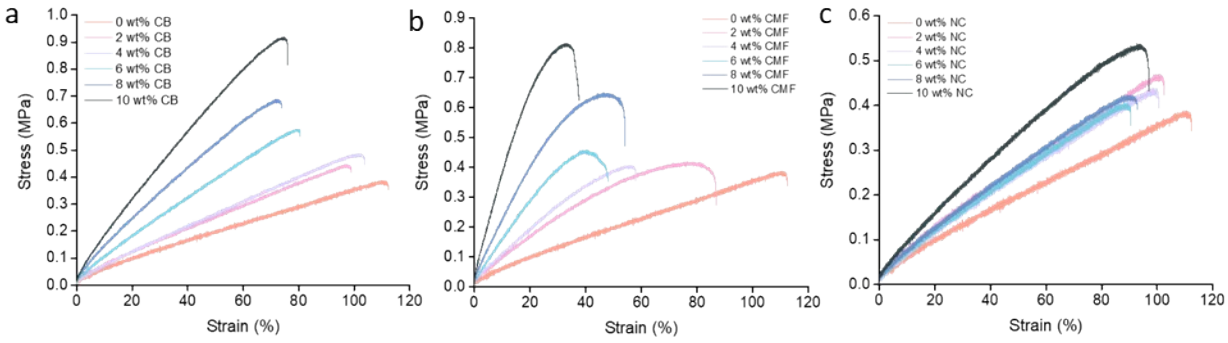

Fig. S6 Stress-strain curves of S-DIB composites with (a) CB at 0-10 wt.% loadings; (b) CMF at 0-10 wt.% loadings; (c) NC at 0-10 wt.% loadings.

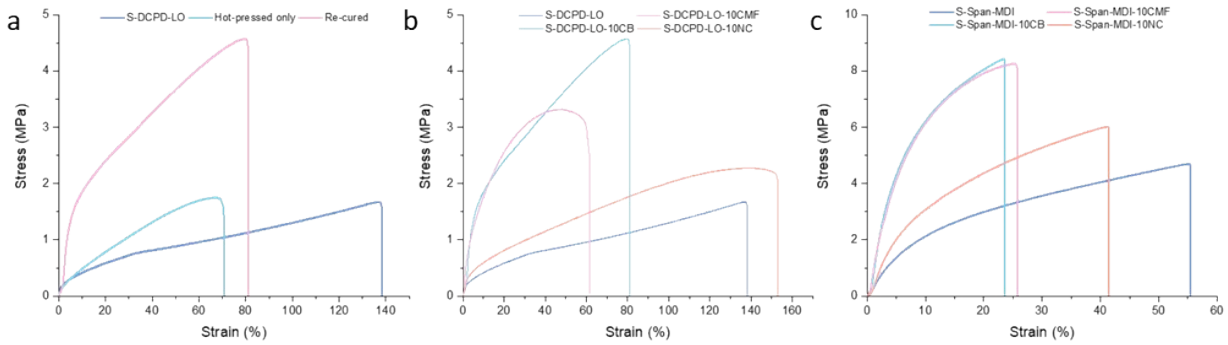

Fig. S7 Stress-strain curves of (a) incorporating CB into S-DCPD-LO by hot-pressing only vs hot-pressing and re-curing vs unfilled S-DCPD-LO; (b) unfilled S-DCPD-LO and S-DCPD-LO composites containing different fillers at 10 wt.% loading; (c) unfilled S-Span-MDI and S-Span-MDI composites containing different fillers at 10 wt.% loading.

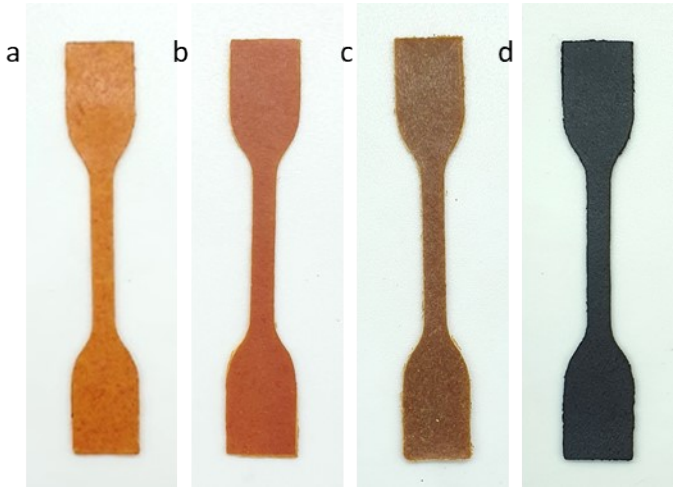

Fig. S8 Photos of dog bones of (a) S-DIB; (b) S-DIB-6NC; (c) S-DIB-10CMF; (d) S-DIB-10CB.

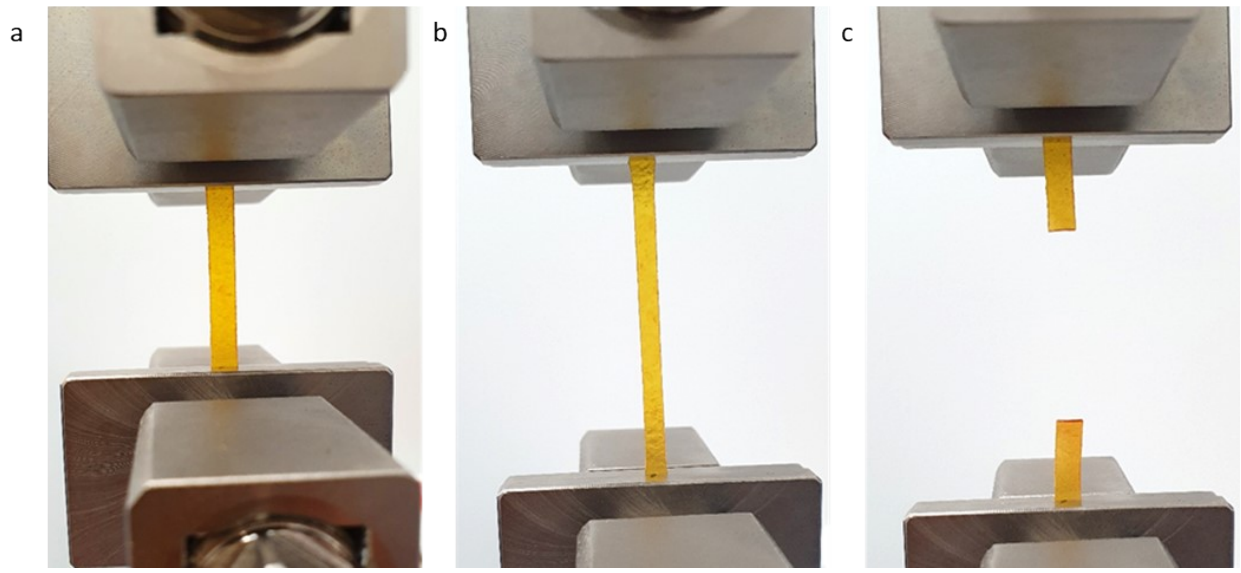

Fig. S9 Tensile tests of S-DIB where (a) is the original length; (b) is the dog bone after elongation, close to the fracture point; (c) is the dog bone after fracture.

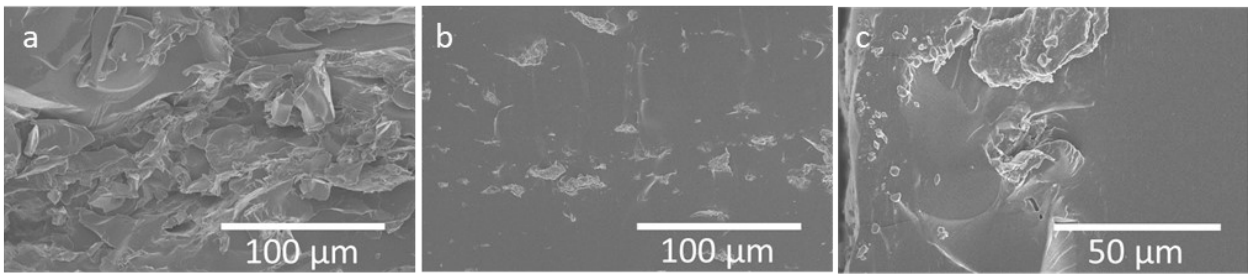

Fig. S10 Micrographs of the cross-sections of (a) S-DCPD-LO-10CMF; (b) S-DCPD-LO-10NC; (c) S-DCPD-LO.

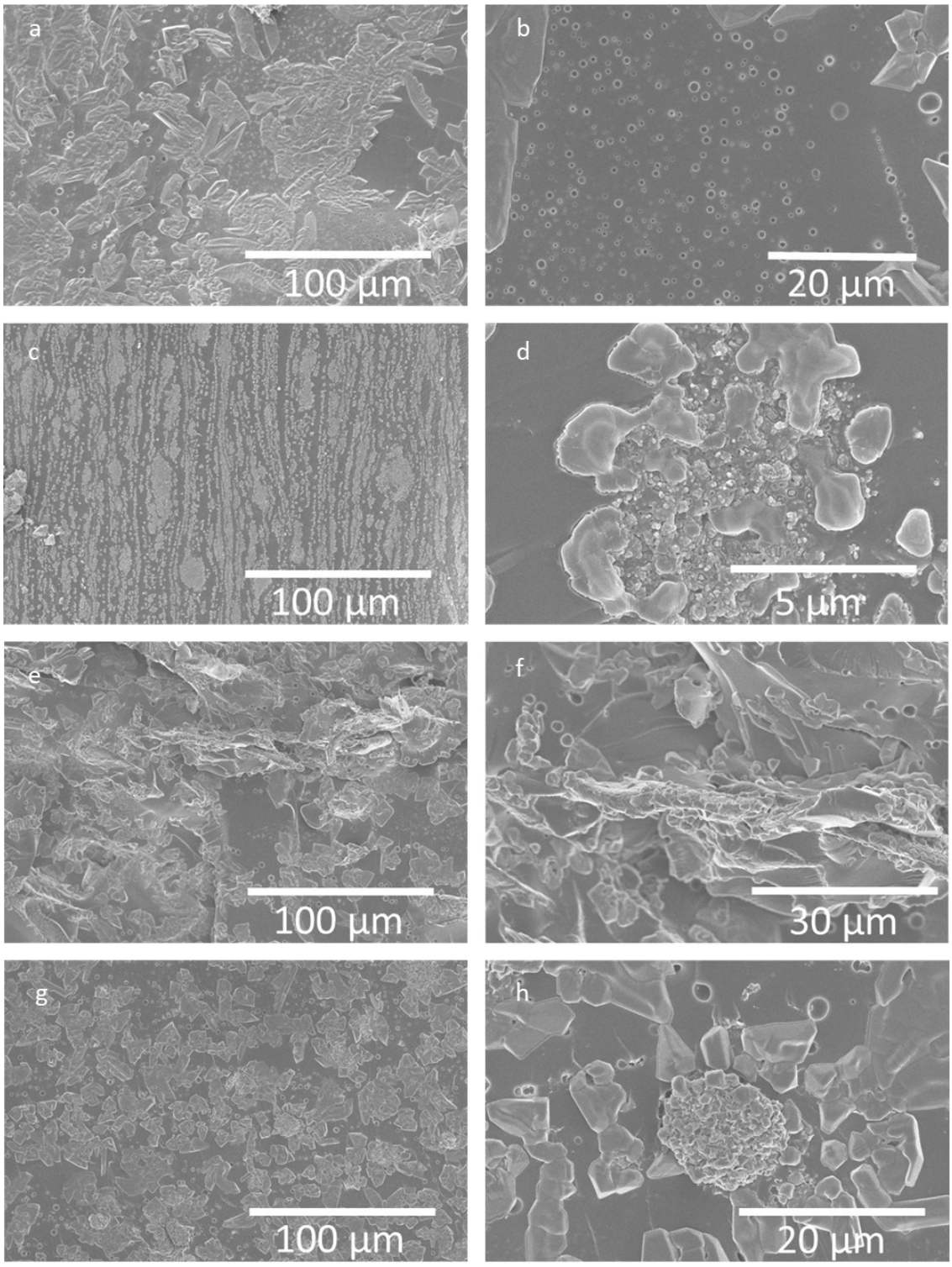

Fig. S11 Micrographs of the cross-sections of (a) unfilled S-Span-MDI; (b) unfilled S-Span-MDI at higher magnification; (c) S-Span-MDI-10CB; (d) S-Span-MDI-10CB at higher magnification; (e) S-Span-MDI-10CMF (f) S-Span-MDI-10CMF at higher magnification; (g) S-Span-MDI-10NC; (h) S-Span-MDI-10NC at higher magnification.

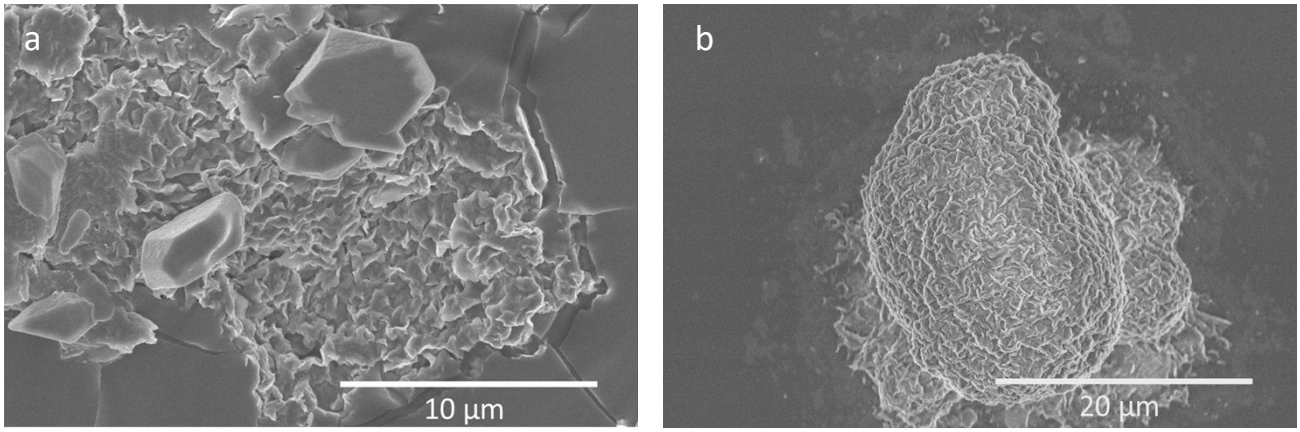

Fig. S12 Micrograph of (a) NC aggregate in S-DIB-10NC cross-section; (b) Neat NC aggregate. Consistent morphology is seen in both micrographs, confirming the presence of an NC aggregate in (a).

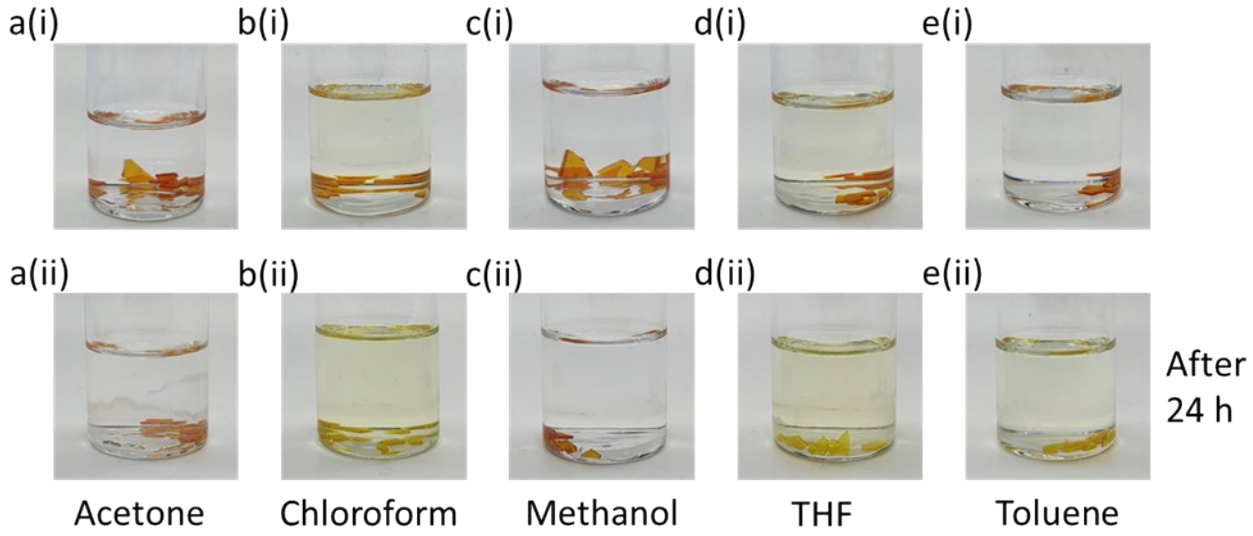

Fig. S13 Solubility studies of S-DIB in (a) acetone; (b) chloroform; (c) methanol; (d) tetrahydrofuran (THF); (e) Toluene. These demonstrate the partial solubility of S-DIB in chloroform, THF, and toluene, indicating that the S-DIB sample is not fully crosslinked.

Table S3 CHNS analysis of unfilled and filled S-DIB, S-DCPD-LO, and S-Span-MDI compared to calculated values.

	Calculated				Analysis			
Sample	%C	%H	%N	%S	%C	%H	%N	%S
S-DIB	31.90	3.10	-	65.00	25.91	2.97	-	71.00
S-DIB-2CB	33.20	3.10	-	63.70	27.87	2.72	-	69.80
S-DIB-4CB	34.60	3.00	-	62.40	29.23	2.65	-	68.30
S-DIB-6CB	36.00	2.90	-	61.10	30.44	2.76	-	66.80
S-DIB-8CB	37.30	2.90	-	59.80	32.04	2.61	-	65.50
S-DIB-10CB	38.70	2.80	-	58.50	33.68	2.56	-	64.00
S-DIB-2CMF	32.10	3.20	-	63.70	26.59	2.95	-	68.50
S-DIB-4CMF	32.40	3.10	-	62.40	27.62	3.26	-	68.20
S-DIB-6CMF	32.60	3.30	-	61.10	26.98	2.88	-	67.30
S-DIB-8CMF	32.90	3.40	-	59.80	27.18	3.15	-	66.50
S-DIB-10CMF	33.10	3.40	-	58.50	27.97	3.14	-	64.00
S-DIB-2NC	31.20	3.10	-	63.70	25.75	2.85	-	69.10
S-DIB-4NC	30.60	3.00	-	62.40	25.06	2.65	-	68.70
S-DIB-6NC	30.00	3.00	-	61.10	24.61	2.73	-	67.30
S-DIB-8NC	29.30	2.90	-	59.80	24.25	2.81	-	66.30
S-DIB-10NC	28.70	2.90	-	58.50	22.03	2.89	-	59.70
S-DCPD-LO	42.20	5.10	-	50.00	41.36	5.13	-	49.10
S-DCPD-LO-10CB	48.00	4.60	-	45.00	45.37	4.49	-	46.20
S-DCPD-LO-10CMF	42.40	5.20	-	45.00	40.55	4.99	-	45.40
S-DCPD-LO-10NC	38.00	4.60	-	45.00	36.96	4.59	-	45.80
S-SPAN-MDI	38.50	5.00	1.40	43.60	48.08	6.20	2.08	33.00
S-SPAN-MDI-10CB	44.7	4.5	1.3	39.3	52.64	5.72	1.69	32.2
S-SPAN-MDI-10CMF	39.1	4.5	1.3	39.3	50.46	6.65	2.32	26.45
S-SPAN-MDI-10NC	34.7	4.6	1.3	39.3	45.28	6.18	1.82	28.2

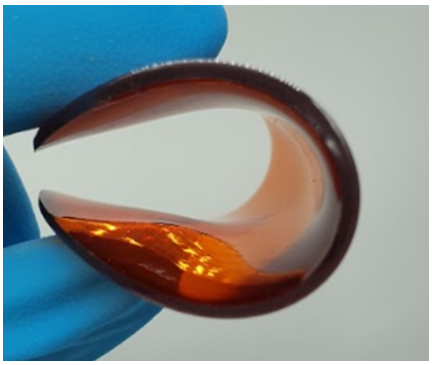

Fig. S14 Photo of S-DIB to demonstrate its flexibility.