Electronic Supplementary Information

A New Class of Moisture-cured Solvent free Silylated Poly(ether-urea) Pressure-Sensitive Adhesives for use in Adhesion to Skin and in Transdermal Drug Delivery (TDD)

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1 Supplementary pictures

Figure S1. Rolling Ball ramp used to evaluate the tackiness of the cured adhesives.

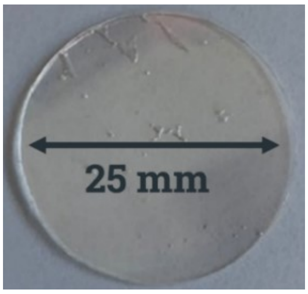

Figure S2. 25 mm cured adhesive disc between two release liners used for rheology analysis.

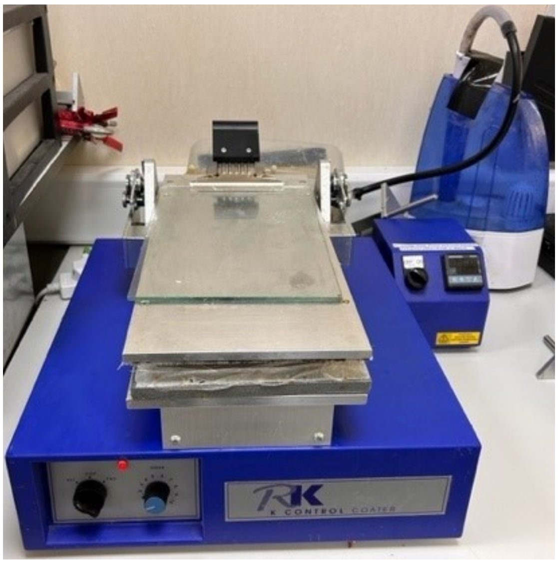

Figure S3. The setup of coater and humidifier used for curing adhesives.

2 Supplementary analysis and experimental data

2.1 Characterisation of commercial polyetheramines

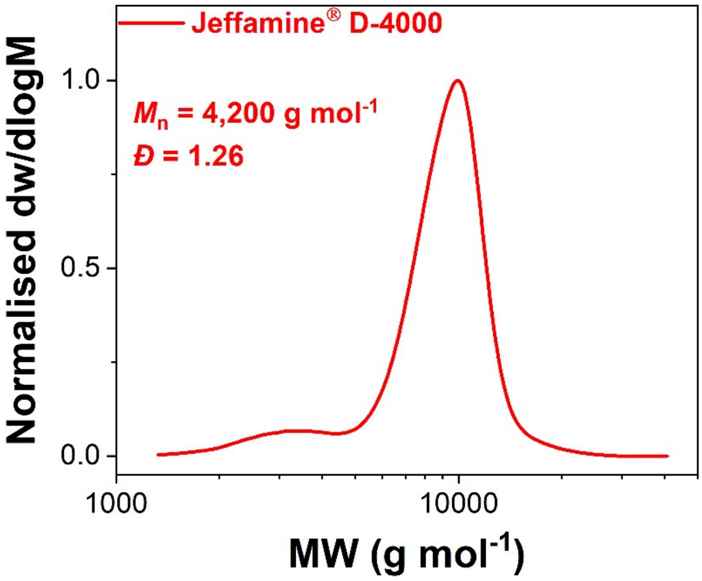

Figure S4. Molecular weight distribution traces of commercial Jeffamine® D-4000 as determined by SEC with DMF as eluent.

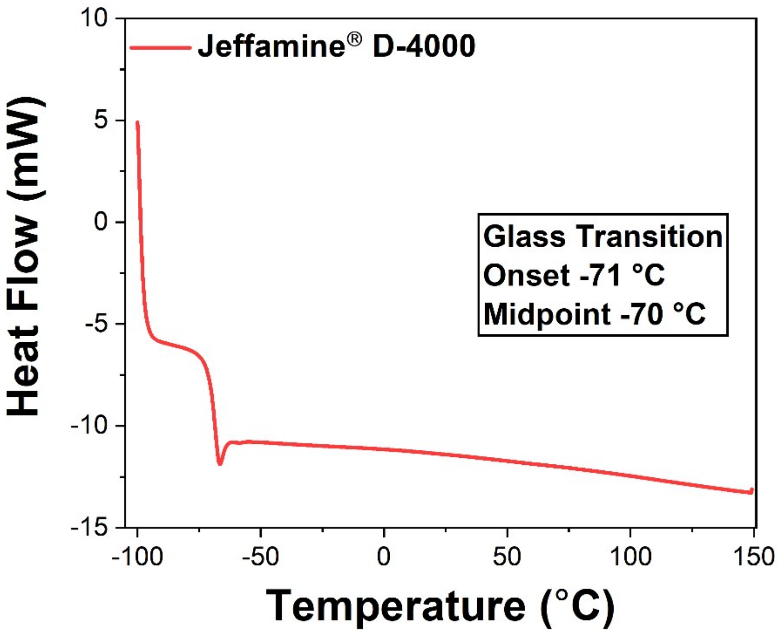

Figure S5. DSC thermogram of commercial Jeffamine® D-4000 using a heating rate of 10 °C min^{-1} (exo up) during the second thermal cycle.

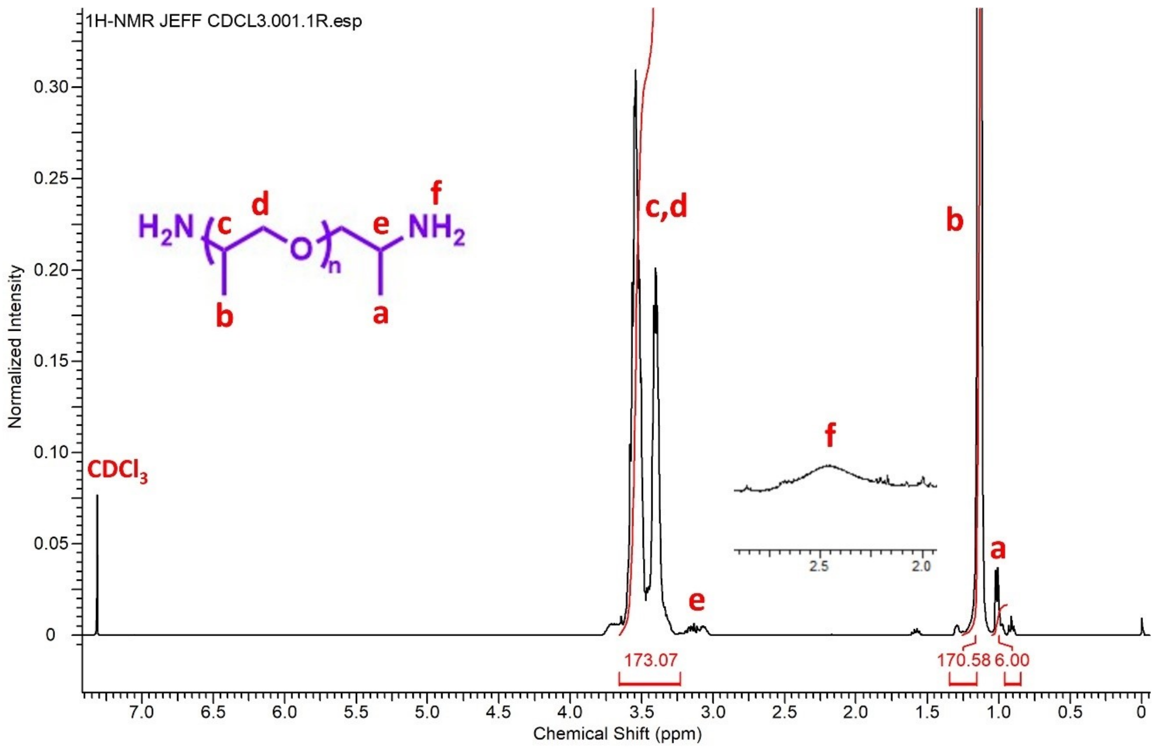

Figure S6. ^{1}H-NMR (400 MHz, $CDCl_3$) of Jeffamine® D-4000.

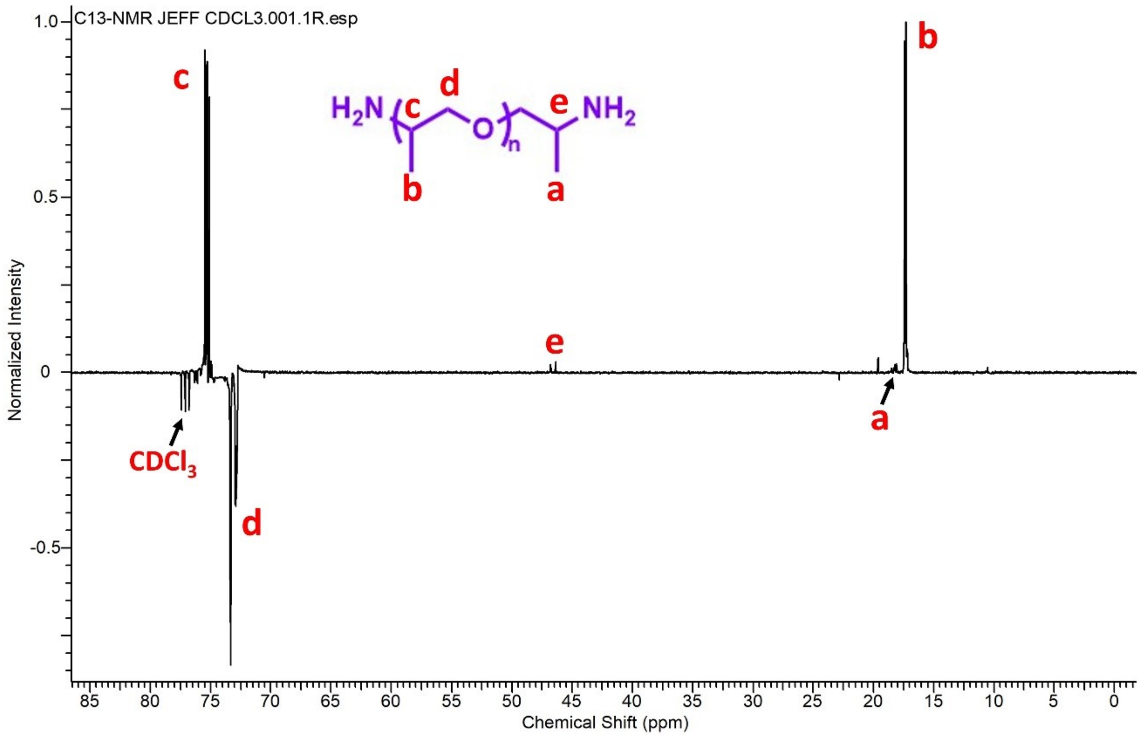

Figure S7. ^{13}C-NMR (400 MHz, $CDCl_3$) of Jeffamine® D-4000.

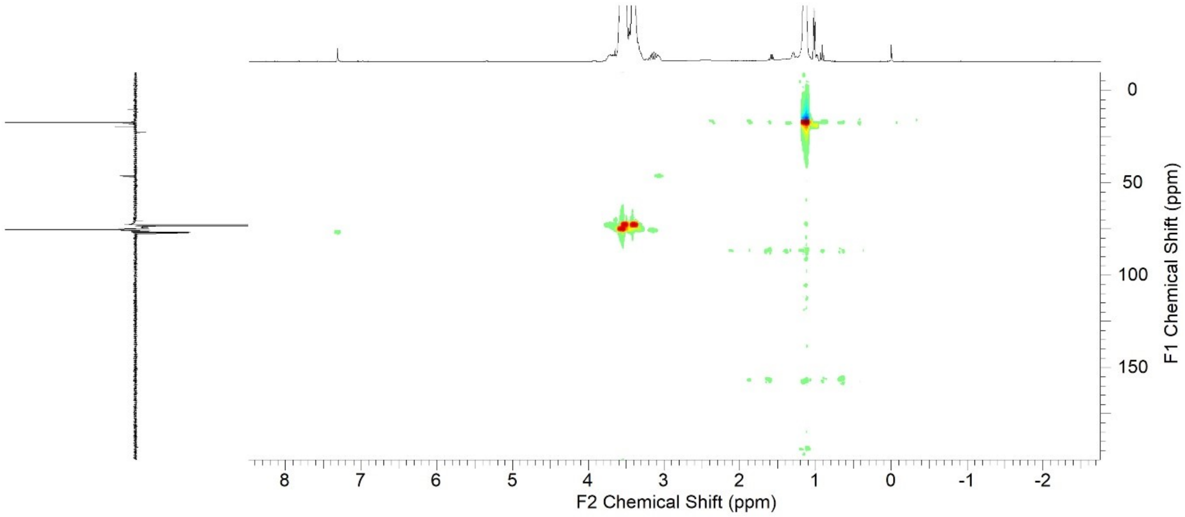

Figure S8. HSQC (400 MHz, $CDCl_3$) spectrum of Jeffamine® D-4000.

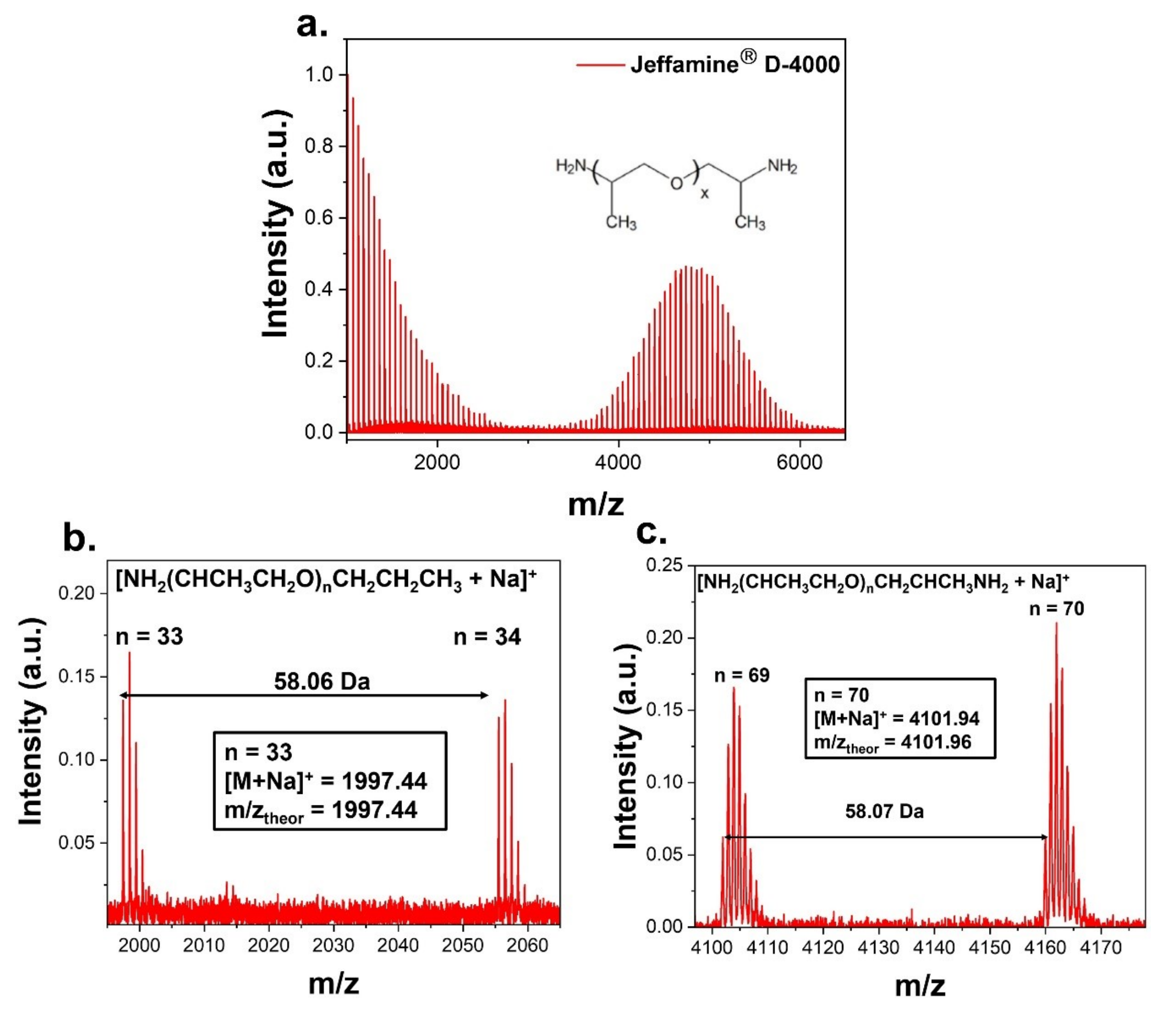

Figure S9. MALDI-ToF analysis of commercial Jeffamine® D-4000 (a) MALDI spectra along with (b) zoomed region for the monofunctional species and (c) zoomed region for the difunctional species.

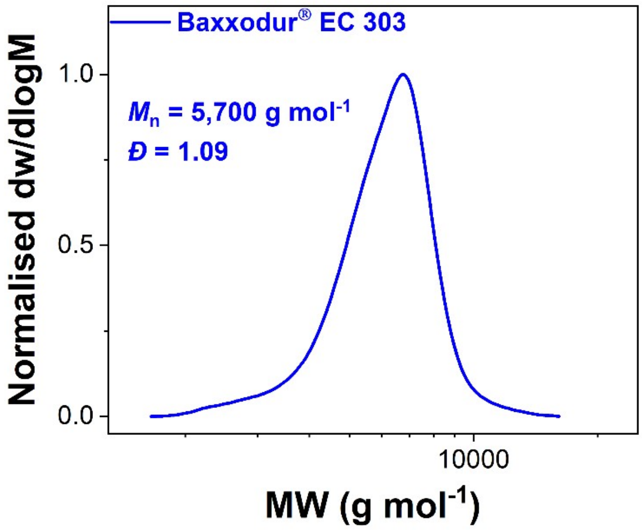

Figure S10. Molecular weight distribution traces of commercial Baxxodur® EC 303 as determined by SEC in DMF.

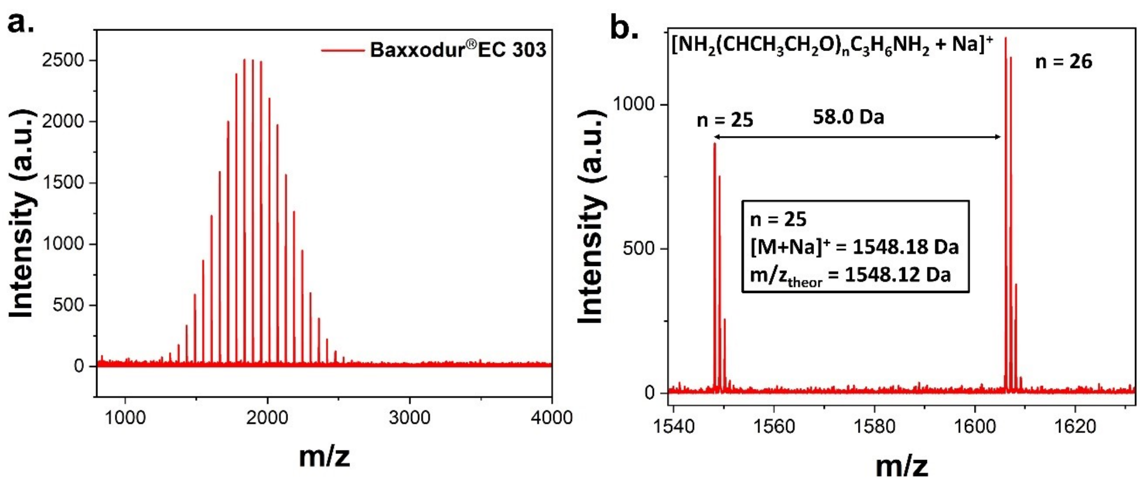

Figure S11. MALDI-ToF analysis of commercial Baxxodur® EC 303 (a) MALDI spectra along with (b) zoomed region.

2.2 Additional data from the synthesis of the PUXL PSA adhesives

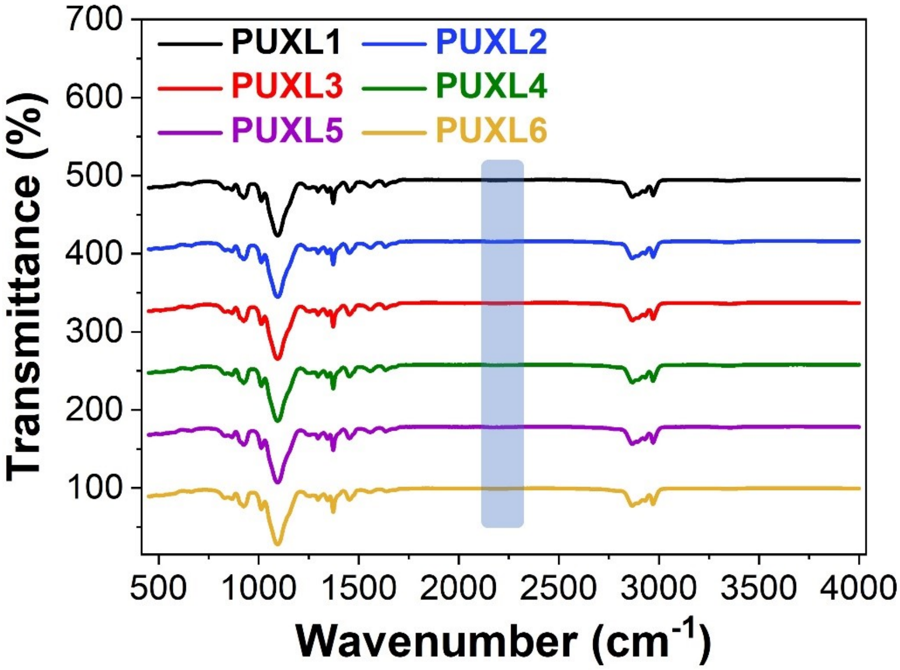

Figure S12. FT-IR spectra from the synthesis of the PUXL prepolymer variants. The absence of -CNO groups after the end of each step is highlighted.

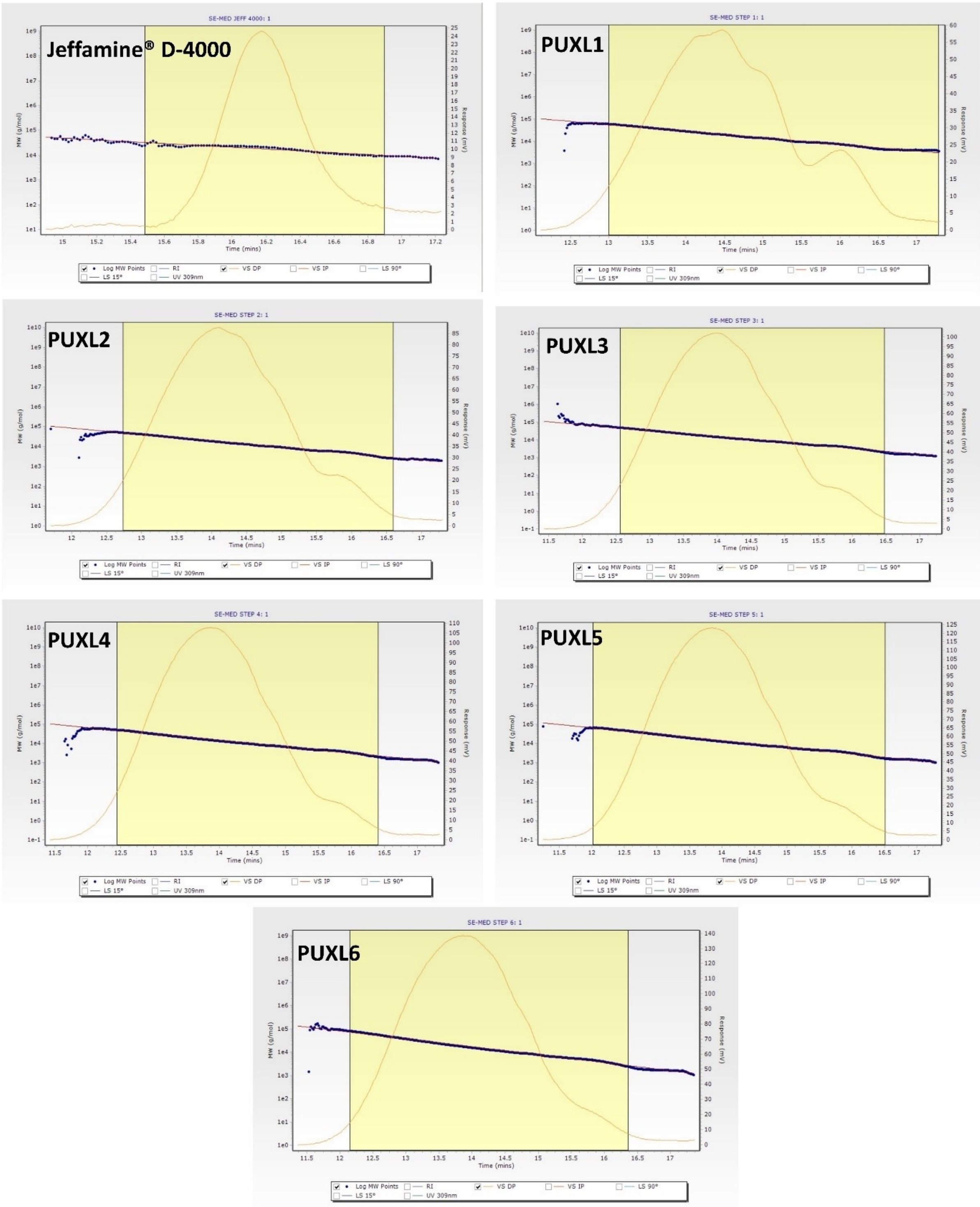

Figure S13. Mark Houwink plots fitting curves utilising the VS DP data.

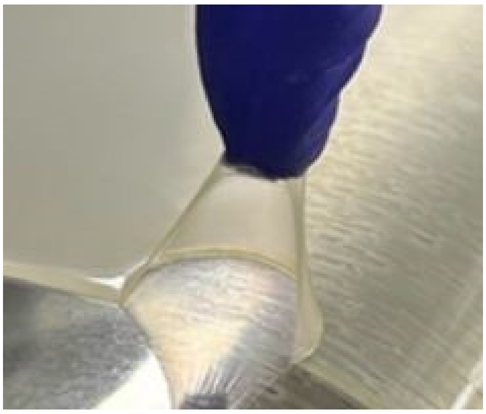

Figure S14. Finger tack test demonstrating a cured PUXL formulation. No cohesion failure was noticed upon peeling.

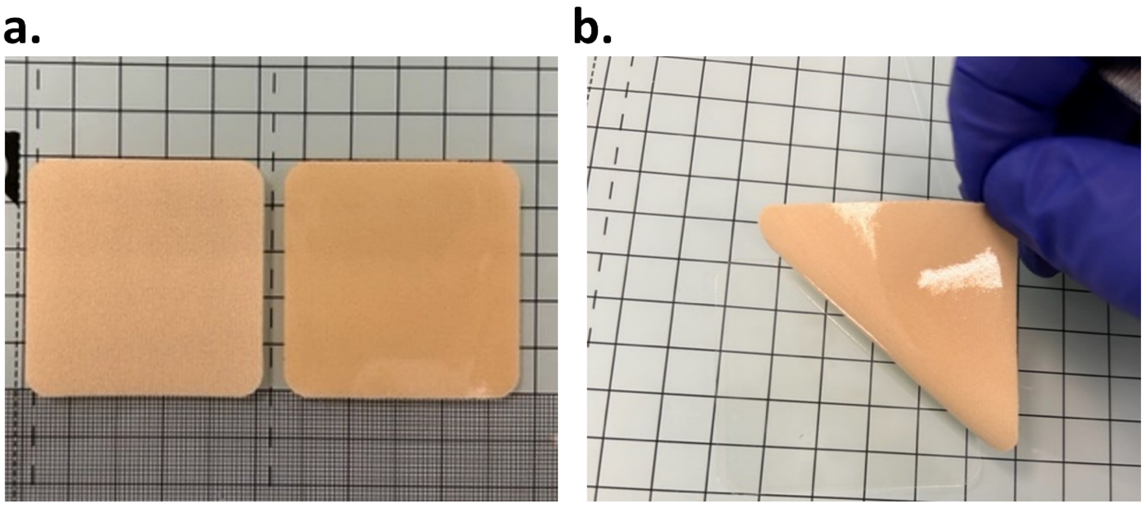

Figure S15. (a) Cured PUXL5 adhesive in a fabric backing liner, (b) clean removal of the cured adhesive from the release liner.

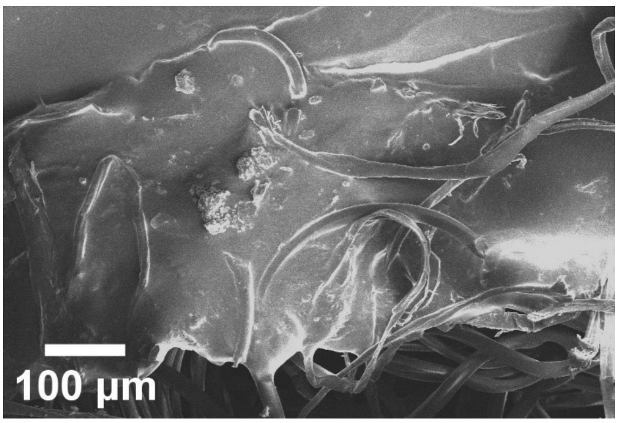

Figure S16. SEM image of the PUXL5 adhesive coated in a fabric backing liner.

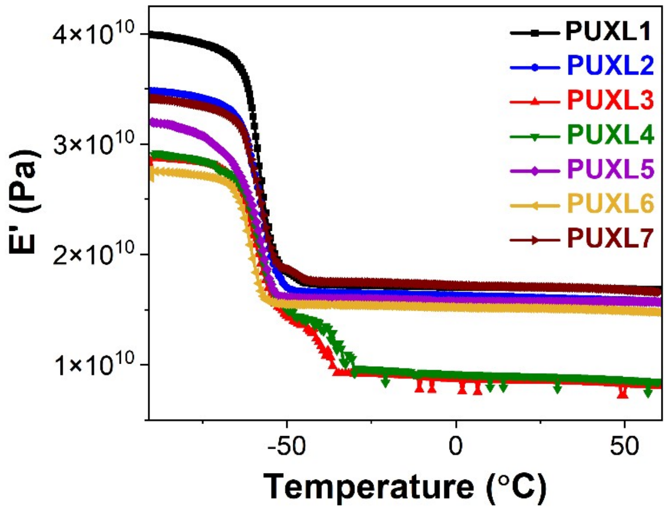

Figure S17. DMA curves of elastic modulus (E') evolution with temperature for all PUXL cured variants.

Entry	TGA		DSC	DMA
	T_d (°C)	Mass Loss (%)	$T_{g,\ mid}$ (°C)	$T_{g,\ DMA}$ (°C)
Jeffamine® D-4000	-	-	-70	-
PUXL1	~ 380	97	-69	-56
PUXL2	~ 380	99	-68	-55
PUXL3	~ 380	98	-68	-56
PUXL4	~ 380	97	-68	-56
PUXL5	~ 380	98	-69	-56
PUXL6	~ 380	99	-68	-59
PUXL7	~ 380	98	-68	-56

Table S1. Thermal data of the PUXL variants as analysed by TGA, DSC and DMA.

Table S2. Rheological data of cured PUXL variants for ω = 0.01 and 100 rad s^{-1} measured at 25 °C using plate-plate oscillatory rheology. Values were used for Chang's windows graphs.

Entry	$G'_{0.01}$ (Pa)	$G''_{0.01}$ (Pa)	G'_{100} (Pa)	G''_{100} (Pa)
PUXL1	7,930 ± 660	1,150 ± 460	40,950 ± 16,850	22,750 ± 8,200
PUXL2	2,250 ± 47	161 ± 93	17,100 ± 950	3,260 ± 400
PUXL3	563 ± 18	29 ± 2	22,300 ± 8,300	18,900 ± 5,150
PUXL4	315 ± 30	36 ± 7	24,720 ± 13,020	19,500 ± 2,040
PUXL5	275 ± 47	17 ± 3	14,030 ± 350	11,670 ± 380
PUXL6	197 ± 50	74 ± 16	4,750 ± 370	5,900 ± 890
PUXL7	309 ± 11	30 ± 8	20,810 ± 3,250	18,390 ± 3,180

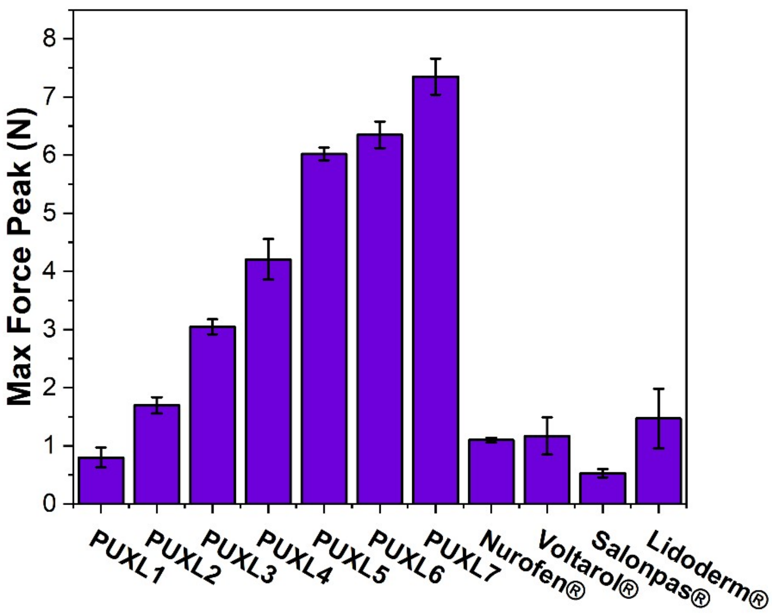

Figure S18. Max Force peak of all analysed adhesives attained from the 90° peel tests.

Table S3. Cold flow results for different PUXL variants in triplicates as determined at ambient temperature, 32 °C and 40 °C.

Variant	Temp	Initial Size (mm)			Size after 72 hrs (mm)			% difference after 72 hrs			
		R1	R2	R3	R1	R2	R3	R1	R2	R3	Average
PUXL1	Room Temp	9	9	9	9	9	9	0	0	0	0.00
PUXL1	32 °C	9	9	9	9	9	9	0	0	0	0.00
PUXL1	40 °C	9	9	9	9	9	9	0	0	0	0.00
PUXL2	Room Temp	9	9	9	9	9	9	0	0	0	0.00
PUXL2	32 °C	9	9	9	9	9	9	0	0	0	0.00
PUXL2	40 °C	9	9	9	9	9	9	0	0	0	0.00
PUXL3	Room Temp	9	9	11	9	9	11	0	0	0	0.00
PUXL3	32 °C	9	9	9	9	10	9	0	11.1	0	3.70
PUXL3	40 °C	10	9	9	10	9	9	0	0	0	0.00
PUXL4	Room Temp	9	9	9	9	9	9	0	0	0	0.00
PUXL4	32 °C	9	10	9	9	10	9	0	0	0	0.00
PUXL4	40 °C	9	9	9	9	9	9	0	0	0	0.00

PUXL5	Room Temp	9	9	9	9	9	9	0	0	0	0.00
PUXL5	32 ℃	9	9	9	9	9	10	0	0	11.1	3.70
PUXL5	40 ℃	9	10	9	9	10	9	0	0	0	0.00
PUXL6	Room Temp	11	9	9	11	9	9	0	0	0	0.00
PUXL6	32 C	9	9	9	9	9	9	0	0	0	0.00
PUXL6	40 C	9	9	9	9	9	9	0	0	0	0.00
PUXL7	R.T.	10	9	9	10	9	9	0	0	0	0.00
PUXL7	32 C	9	9	10	9	9	10	0	0	0	0.00
PUXL7	40 C	9	9	9	9	9	9	0	0	0	0.00