Electronic Supplementary Information

A Mesh Reinforced Pressure Sensitive Adhesive for Linerless Label Design

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List of Figures

1 Experimental

Figure S1: The set up used for peel testing using a Shimazdu EZ-LX universal testing machine with a 500 N tensile jig in the upper position and a peel rolling jig in the lower position.

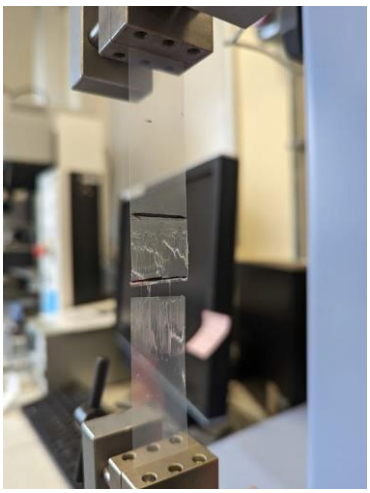

Figure S2: The set up used for shear strength testing using a Shimazdu EZ-LX universal testing machine with with two 500 N tensile jigs.

Figure S3: The setup utilized for blocking tests involved placing two strips of Film 3 with adhesive sides facing each other underneath a metal bar. This ensured that the weight applied was evenly distributed across the adhesive-adhesive interface.

Figure S4: The custom metal template made to hold 8 mm diameter rheometer parallel metal plates. This enabled thin films to be cast over the rheometer plates with a homogeneous thickness. The numbers quoted on the plate is the error between the height of the template and parallel plates in mm.

2 Results and Discussion

2.1 Colloid synthesis and properties

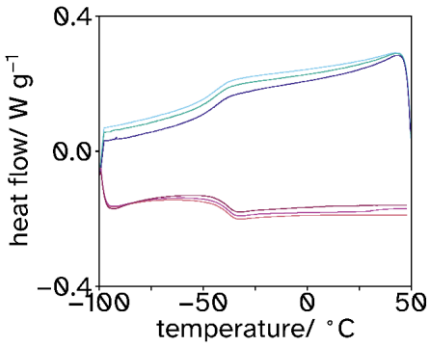

Figure S5: DSC thermogram with three heating (—, —, —) and cooling (—, —, —) cycles for a dried PSA-latex sample

. The T_g was determined as -39.8 °C (using the half height method).

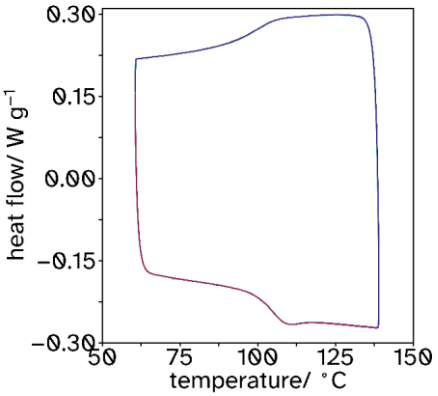

Figure S6: DSC thermogram with three heating (—, —, —) and cooling (—, —, —) cycles for a dried PS-latex sample. The T_g was determined as 102.7 °C (using the half height method).

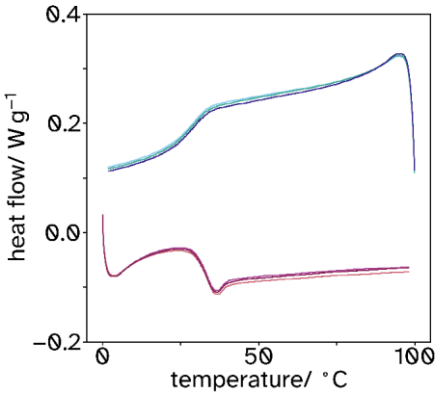

Figure S7: DSC thermogram with three heating (—, —, —) and cooling (—, —, —) cycles for a dried PVAc-latex sample. The T_g was determined as 27.4 °C (using the equal areas method to account for enthalpic recovery).

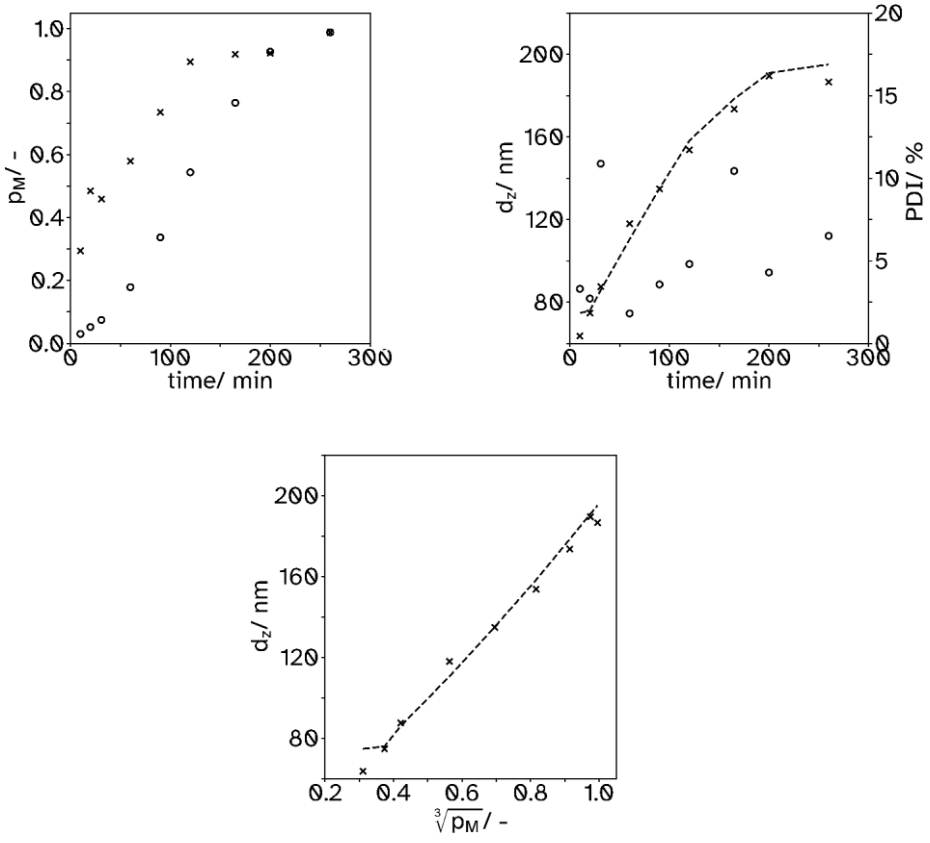

Figure S8: Data from the PS-latex synthesis. Instantaneous, crosses, and cumulative monomer conversion, open circles, against time, top left. Average hydrodynamic diameter, d_z, crosses, and dispersity, PDI, open circles, over time, top right. d_z against the cube root of cumulative conversion, bottom. The dashed line signifies the theoretical particle size based on the seed diameter and instantaneous conversion, see Equation S1.

$$r = \sqrt[3]{\frac{FR r_s^3 (t - FS) X_{m,inst,t}}{m_{c,pol} X_{c,inst}} + r_s^3} \tag{S1}$$

For Equation S1, FR is the monomer feed rate in $g\ min^{-1}$, r_s is the average radius of the seed particles measured by DLS at the time the feed began, t is the time in min, $X_{m,inst,t}$ is the instantaneous conversion at time t as a fraction, FS is the feed start time in min, $m_{c,pol}$ is the mass of the charged monomer in g, and $X_{c,inst}$ is the instantaneous conversion of the charge at FS.

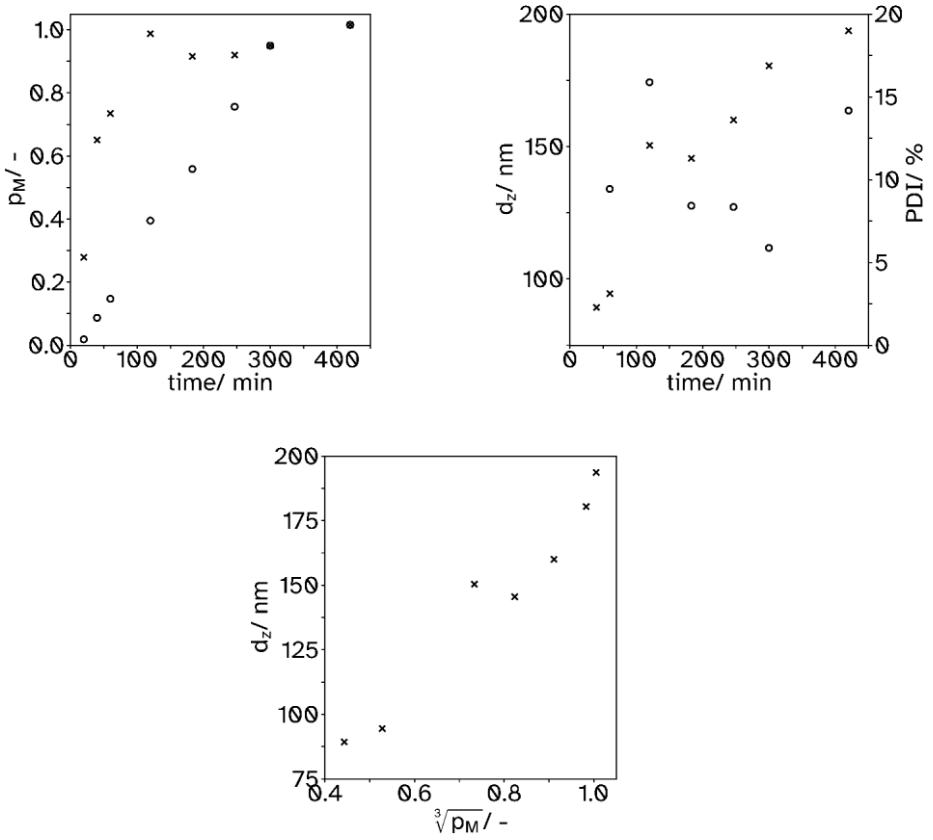

Figure S9: Data from the PVAc-latex synthesis. Instantaneous, crosses, and cumulative monomer conversion, open circles, against time, top left. Average hydrodynamic diameter, d_z, crosses, and dispersity, PDI, open circles, over time, top right. d_z against the cube root of cumulative conversion, bottom. The particle size cannot be predicted using Equation S1 as there is a continuous monomer feed during the reaction so there is no suitable r_s.

2.2 Film formation and film structure analysis

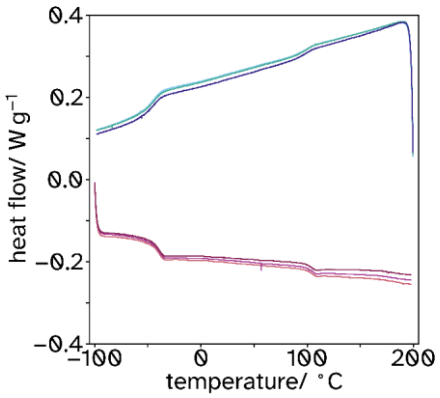

Figure S10: DSC thermogram with three heating (—, —, —) and cooling (—, —, —) cycles for for a 34.6 *vol%* PS and 65.4 *vol%* PSA dried blend. The T_g's were determined as -40.6 and 102.0 °C (using the half height method).

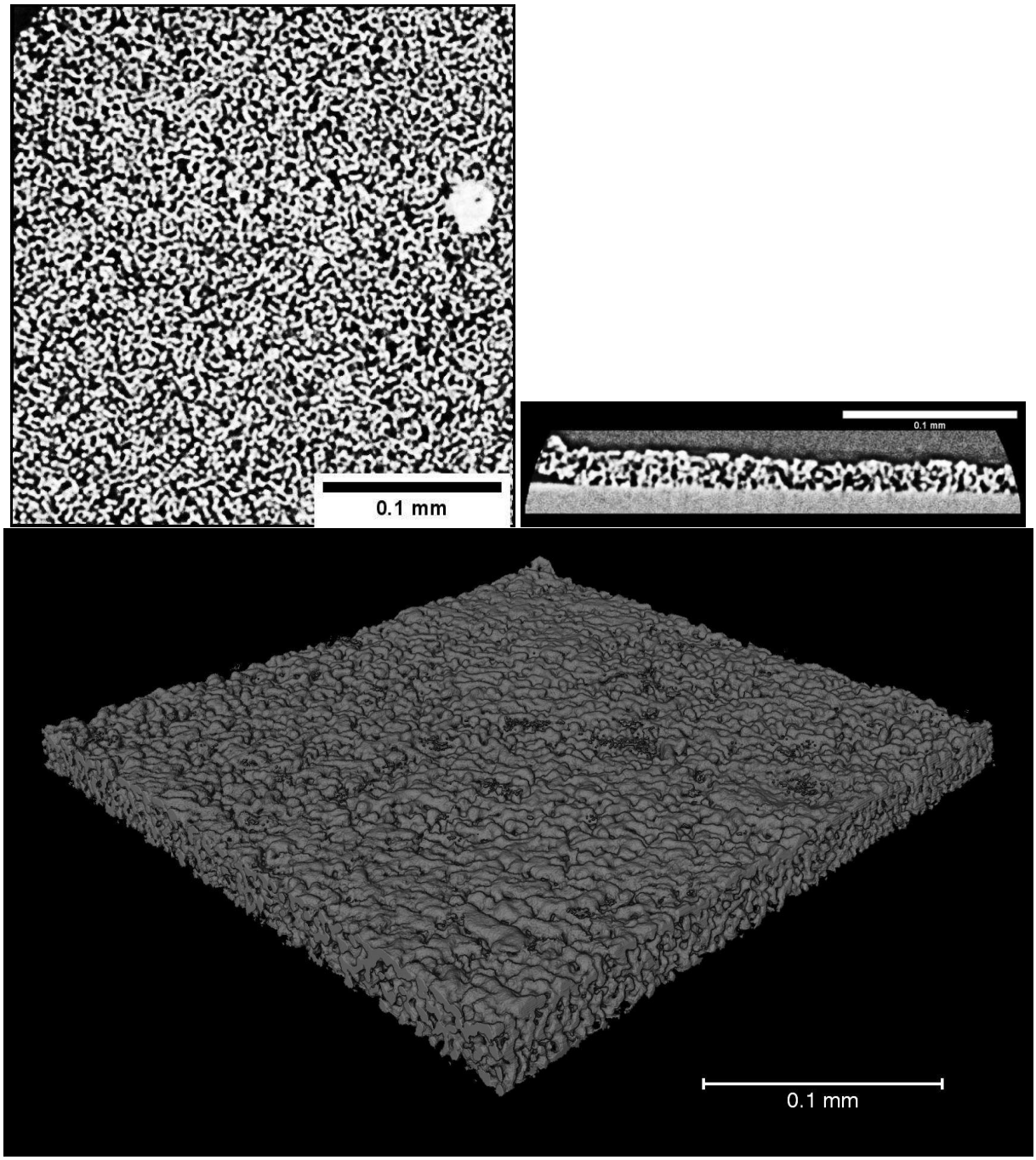

Figure S11: 2D horizontal and vertical slices from the microCT of a 34.6 *vol%* PS and 65.4 *vol%* PSA system (etched Film 1), top, and the full 3D render of the film obtained via xray tomography, bottom. For a full cross section flythrough of the 3D scan see Video S1.

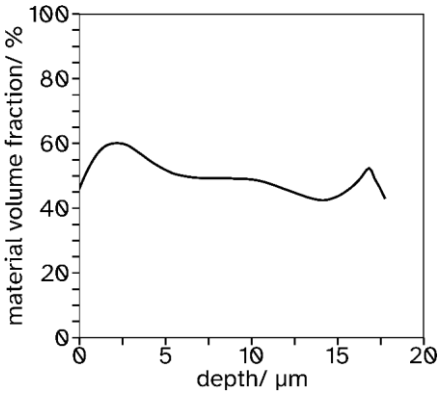

Figure S12: Material volume fraction as a function of depth (from top to bottom) through the etched Film 1 imaged using microCT, Figure S11.

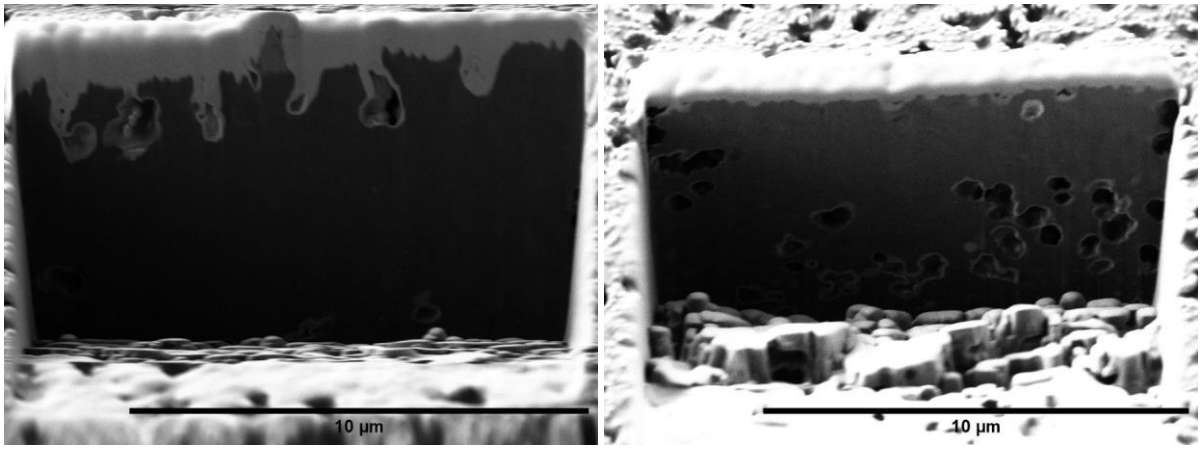

Figure S13: PS (34.3 *vol%*) and PSA (65.7 *vol%*) film, Film 2, where a trench is dug using FIB-SEM. The voids seen are air bubbles with unusal shapes supporting the hypothesis that there is structure to the PS-PSA film after annealing.

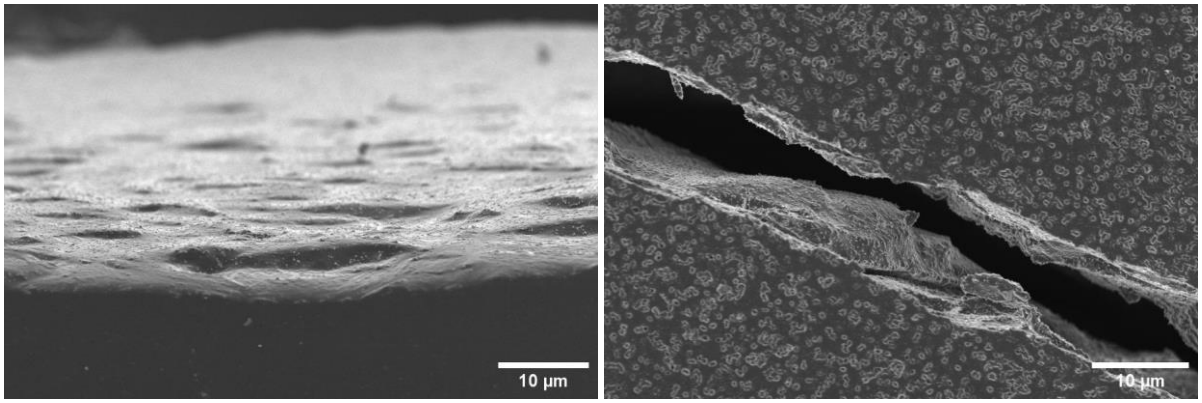

Figure S14: PS (34.3 *vol%*) and PSA (65.7 *vol%*) film, prepared similarly to Film 2 but with no annealing (left) and 120 *min* annealing (right). There is no clear structure when the sample is not annealed but after annealing for as little as 19 *min* (Figure 3e) to as long as 120 *min* structure appears on the top surface.

2.2.1 Determination of PVAc etching percentage using TGA

It is important to consider how much of the PVAc has been etched after 60 minutes. After etching and drying Film 1, the remains were scrapped from the Mylar ® A PET substrate and analysed via thermal gravimetric analysis (TGA). This is possible due to the degradation of PVAc resulting in two characteristic curves, Figure S15. The initial mass loss, w_1, starting at 270 °C corresponds to the deacetylation of the vinyl acetate units that releases acetic acid. The second degradation starting at 400 °C, w_2, corresponds to the degradation of the polymer backbone. The percentage of PVAc in the film, w_{VAc}, can be calculated by assuming a w_1 of 73.75 (Table S1) corresponds to 100% PVAc and simply taking a ratio of the sample w_1 to the PVAc w_1.

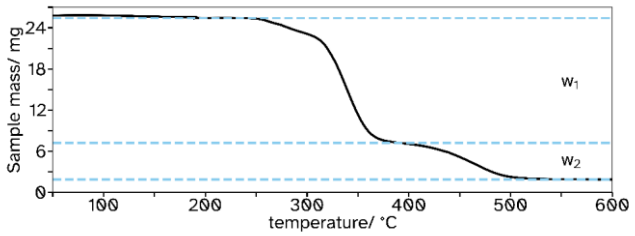

Figure S15: The degradation of a room temperature dried PVAc-latex film monitored via TGA. The two characteristic degradation curves, w_1 and w_2, are shown bounded by blue dashed lines.

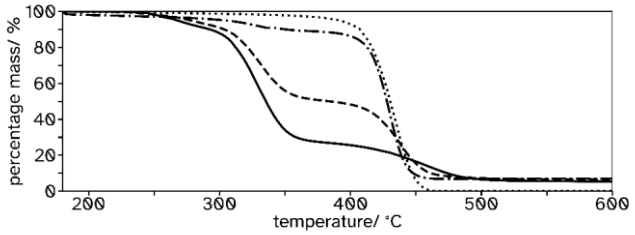

Figure S16: Percentage mass loss against temperature for a PVAc film (—), Film 1 (- - -), acetone etched Film 1 (- · - ·), and a PS-latex film (· · ·).

Table S1: The experimental (using mass data) and calculated (from TGA) w_{VAc} of various films. Those using hard-PVAc films had 34.6 *vol%* hard colloid.

Sample	Experimental w_{Vac}/ %	w_1	Calculated w_{Vac}/ %
PVAc only	100.00	73.75	assumed 100
Film 1	67.88	50.37	68.30
Etched Film 1	unknown	13.27	18.00
PS only	0	0	0

2.3 Adhesive performance

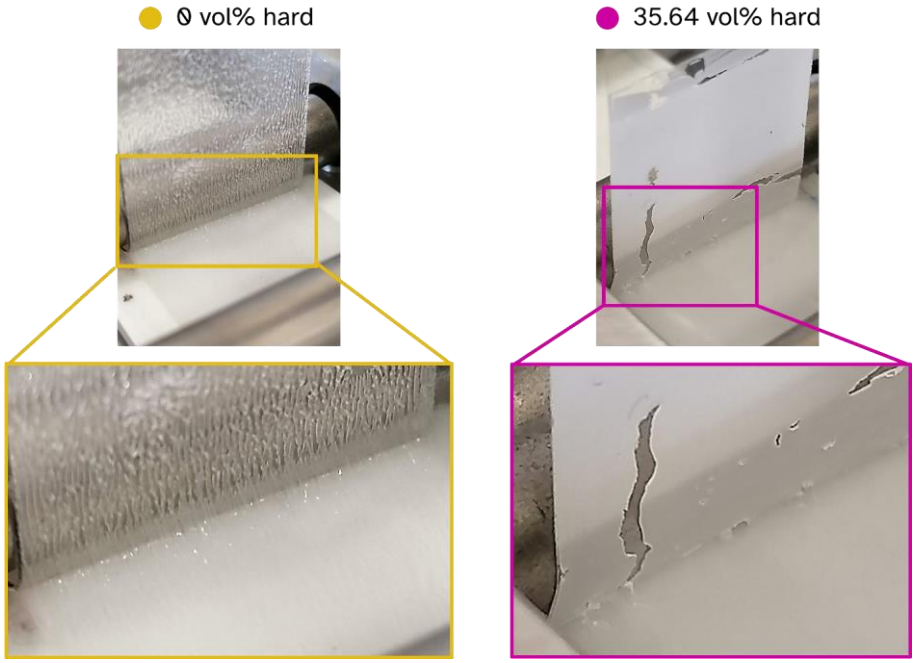

Figure S17: Example of fibrils pulled during peel testing for 0 (left) and 35.64 (right) *vol%* PS in PSA. There are longer, thicker fibrils for the soft sample and very short, thin fibrils for the PS-PSA sample as a result of the hard mesh structure.

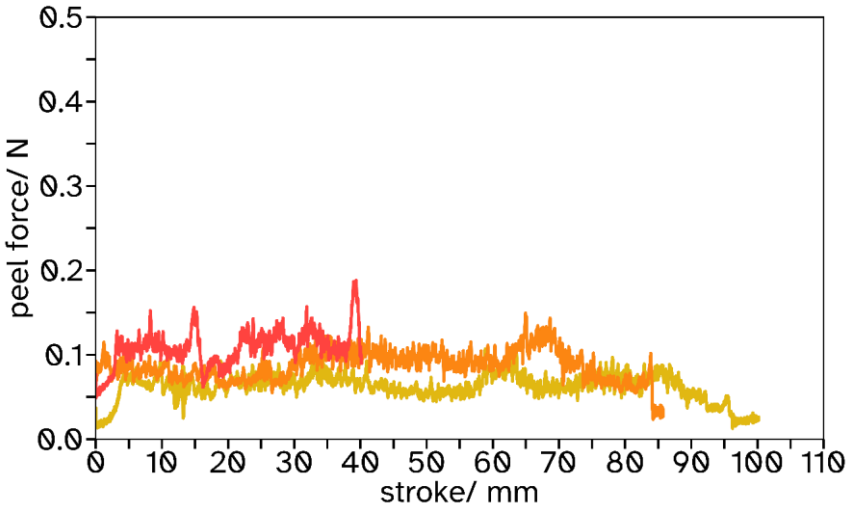

Figure S18: Peel force against stroke for the test strips of Film 3 which were not activated in the blocking ressistance test, 1.20 (—), 2.33 (—) and, 4.58 (—) *kPa*.

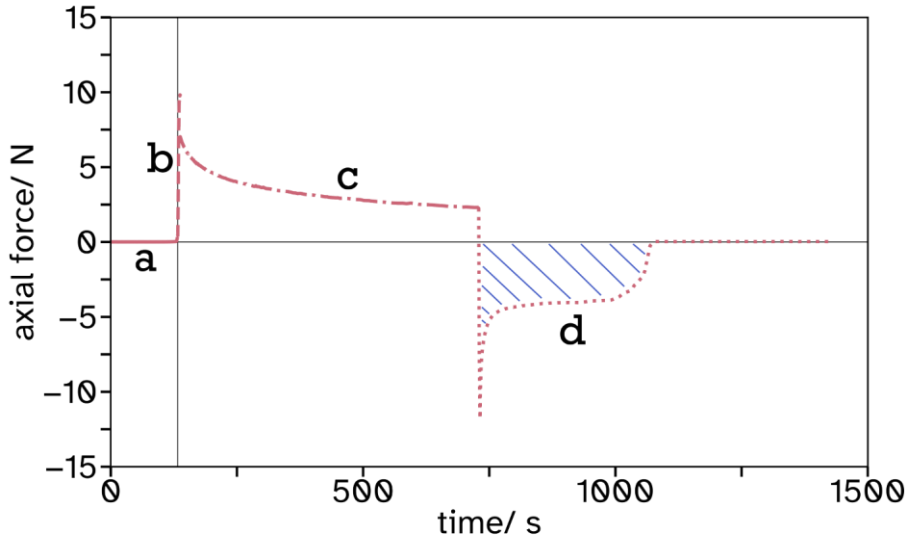

Figure S19: An example of a tack test at constant temperature. Axial force, N, against measurement time, s, is shown with 4 stages. a, the probe is lowered until the force reaches 0.1 N, the gap at this point, indicated by the vertical line, is taken to be the dry film height. b, the probe is pushed in for 5 s with the maximum force reaching 10 N. c, the sample is equilibrated for a set amount of time to enable good wetting of the adhesive on the substrate. d, the probe is pulled upwards at a constant rate and the area under the curve indicated is the adhesion energy, E_{adh}.

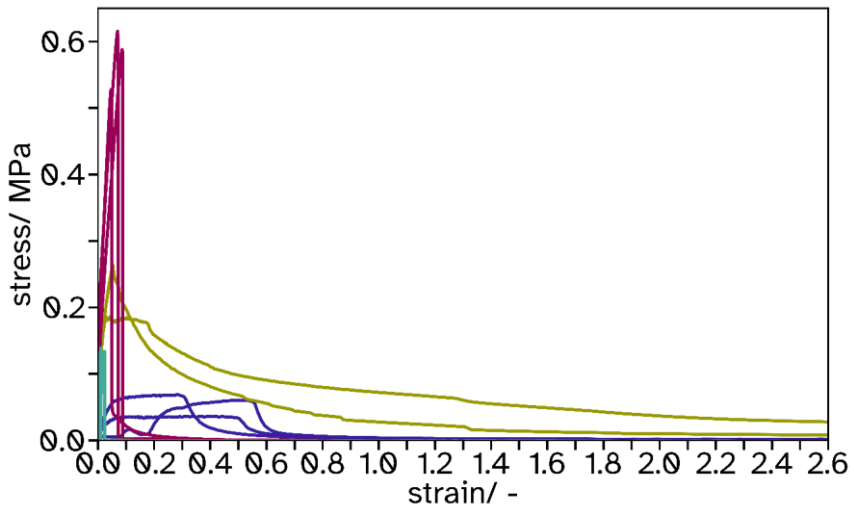

Figure S20: Zoomed out graph of Figure 10 represented as stress-strain curves (a) of ■ 0, ■ 25, ■ 34 and ■ 100 *vol%* hard PS-latex in soft PSA-latex films. The testing temperature was 65 °C, the circular area tested had a diameter of 8 mm and the film heights were $152 \pm 10, 214 \pm 93, 180 \pm 7$, and 186 ± 25 m respectively.

2.4 Rheology

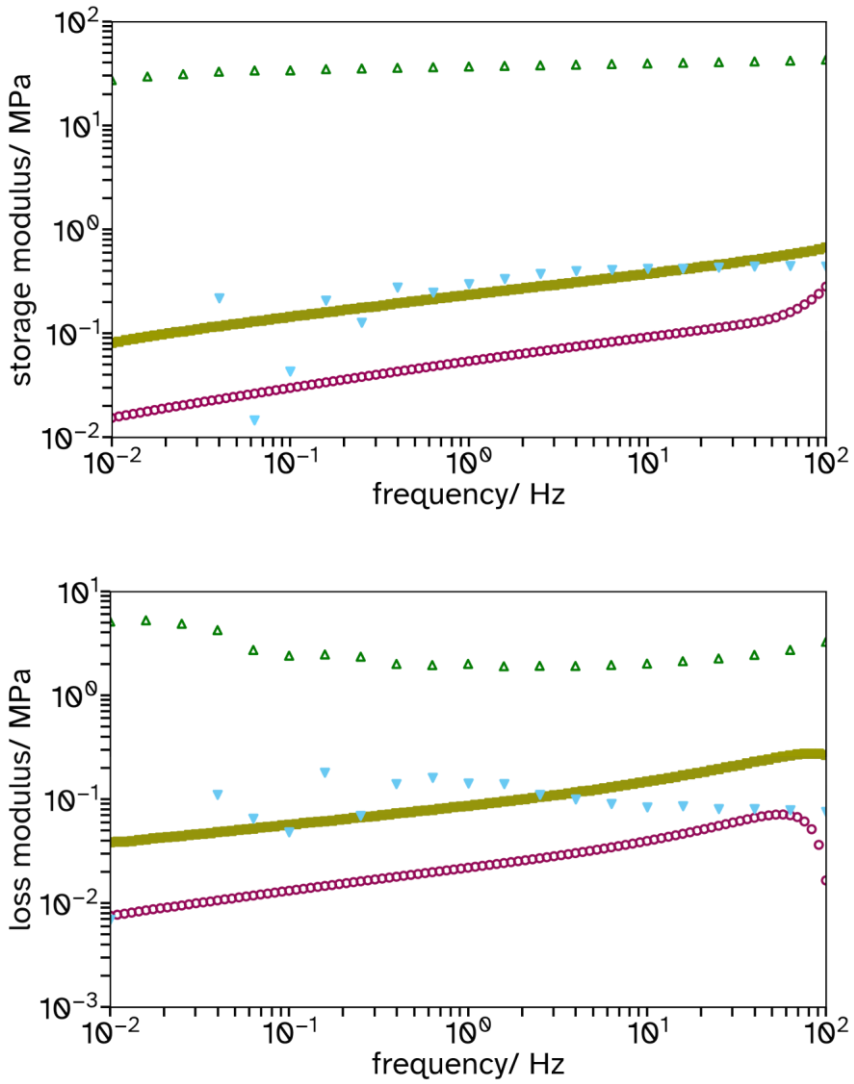

Figure S21: Frequency sweeps, at 25 °C, between 0.01 and 100 *Hz* captured on a rheometer for films made from PSA-latex, pink open circles, a non-annealed, yellow closed squares, and annealed sample, open green triangles, of a 34.3 *vol%* PS and 65.7 *vol%* PSA, and an annealed sample of the PS-latex, closed blue triangles. The PS sample does not adhear well to the plates at 25 °C and thus does not give reliable data but is shown here for completeness.

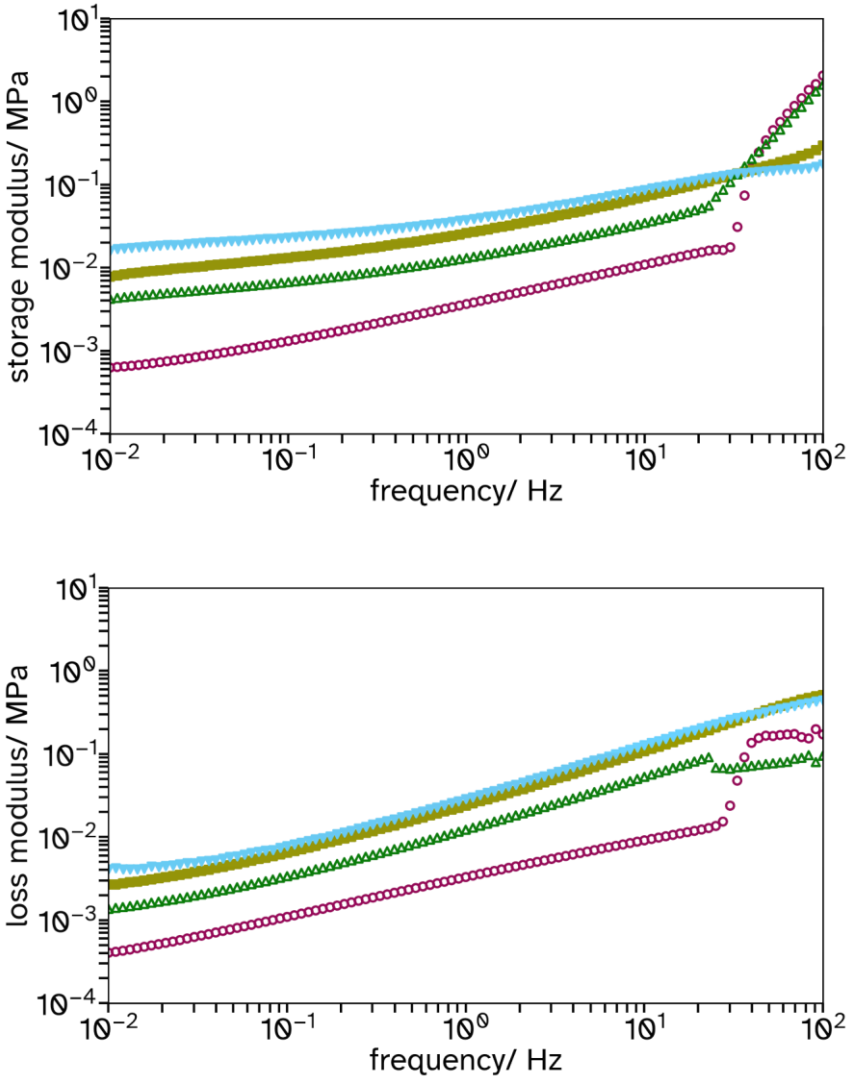

Figure S22: Frequency sweeps, at 130 °C, between 0.01 and 100 *Hz* captured on a rheometer for films made from PSA-latex, pink open circles, a non-annealed, yellow closed squares, and annealed sample, open green triangles, of a 34.3 *vol%* PS and 65.7 *vol%* PSA, and an annealed sample of the PS-latex, closed blue triangles.

Table S2: Sample and method information for frequency sweeps at 25 °C.

Sample (T=25 °C)	Film height/ *m*	Displacement/ *rad*	G' at 1 *Hz*/ MPa
PSA-latex (not annealed)	288	5e-3	0.0539
PSA-latex & PS-latex (not annealed)	329	3e-4	0.2344
PSA-latex & PS-latex (annealed)	395	2.5e-5	36.7692
PS-latex (annealed)	22	1e-5	0.2994

Table S3: Sample and method information for frequency sweeps at 130 °C.

Sample (T=130 °C)	Film height/ *m*	Displacement/ *rad*	G' at 1 *Hz*/ MPa
PSA-latex (not annealed)	309	5e-3	0.0037
PSA-latex & PS-latex (not annealed)	298	1e-3	0.0260
PSA-latex & PS-latex (annealed)	231	5e-3	0.0130
PS-latex (annealed)	174	1e-3	0.0377