

Supporting Information

Diazirine-Functionalized Polyurethane Crosslinkers for Isocyanate-Free Curing of Polyol-based Coatings

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1. General Considerations.

Chemicals and solvents were purchased from commercial suppliers and used as received. Compound **2** (2-(4-(3-(trifluoromethyl)-3H-diazirin-3-yl)phenoxy)ethan-1-ol) was synthesized according to literature.¹ Acrylic polyol (APO) was synthesized according to literature.^{2,3} Briefly, this is a butyl (meth)acrylate-based binder with (hydroxyethyl)methacrylate as its main functionality. The hydroxyl equivalent weight of this APO was determined to be 410 g mol⁻¹ (4.2 wt% based on solids). ¹H NMR spectra were acquired at room temperature on Bruker DRX 400 and 300 MHz instruments. NMR chemical shifts are reported in ppm and are referenced internally to the residual solvent peak of CDCl₃ (= 7.26 ppm). The glass transition temperature (T_g) of the polymers was determined by differential scanning calorimetry (DSC). IR spectra were recorded on a Bruker Alpha FTIR apparatus.

DSC measurements were performed on a Perkin Elmer Jade DSC. Samples were heated from 20 °C to 180 °C at a heating rate of 10°C/min followed by an isothermal step for 5 min. A cooling cycle to -20°C at a rate of 10°C/min was performed prior to a second heating run to 180°C at the same heating rate. The T_g was defined as the temperature of the midpoint of a heat capacity change on the second heating run. The Universal Analysis 2000 software was used for data acquisition.

SEC measurements were performed on a Shimadzu LC-20AD system with two PLgel 5 μm MIXED-C columns (Polymer Laboratories) in series and a Shimadzu RID-10A refractive index detector. CH₂Cl₂ was used as mobile phase at a flow rate of 1 mL/min and T = 35 °C. Polystyrene standards in the range of 760 – 1 880 000 g mol⁻¹ (Sigma Aldrich) were used for calibration.

Dynamic thermal-mechanical analysis (DMTA) was performed on a TA Instruments RSA3 in a temperature range of -60 °C to 180 °C. Samples with dimensions 15 mm x 6 mm x 0.04 mm were tested with uniaxial stretching performed with a heating rate of 5 °C min⁻¹, frequency of 10 Hz and strain of 0.03%. The storage modulus (E') and the loss factor (tan δ) were recorded as a function of temperature. In order to estimate the apparent cross-linking density (M_c), the storage modulus in the rubbery plateau region (E'_R) was extracted from the graph. Equation (1) was used to calculate the M_c,^{4,5} where M_c is the molecular weight between crosslinks, R is the gas constant, T is the absolute temperature.

$$\text{Equation (1)} \quad M_c = \frac{3RT\rho}{E'_R}$$

2. Experimental Procedures.

Thermal crosslinking procedure for GPC, gel content, DSC and IR

In a typical procedure, acrylic polyol (50 mg, 75 wt% solids in n-butyl acetate, 0.091 mmol OH) was added to a preweighed 4 mL vial together with PUR-diazirine **3** (37.5 mg, 0.091 mmol N₂, 1:1 N₂/OH ratio). Thereafter, the samples were heated to 110 °C overnight. After cooling down to room temperature, a sample (2–5 mg) was taken for DSC and IR measurements. Thereafter, the vial was weighed again before adding DCM (4 mL) to the vial. After vortexing, the vial was centrifuged to settle all solids and the supernatant was removed to analyze the soluble contents by GPC. The leftover solids were dried in vacuo and weighed to determine the gel content of the coating.

Thermal crosslinking procedure for DMTA

In a typical procedure, crosslinker 1 (0.75 g, 1.8 mmol N₂) was added to acrylic polyol (1 g in butyl acetate, 0.75 g solids, 1.8 mmol N₂) together with ethyl acetate (approximately 100 μL) to achieve the desired viscosity for film formation. Using a drawbar, 90 μM thick films were cast onto polypropylene substrates which were heated to 110 °C for 16 hours in a well-ventilated oven. After cooling down to room temperature, the films were removed using a razor and dog-bone shapes were punched for DMTA measurements.

Synthesis of PUR-diazirine crosslinker **3**

To a flame-dried 20 mL Schlenk flask under nitrogen was added Tolonate HDT-LV **1** (1.46 g, 8.0 mmol NCO, 1 eq), one drop of dibutyl tin dilaurate and dry DCM (5 mL). The mixture was cooled to 0 °C, and 2-(4-(3-(trifluoromethyl)-3*H*-diazirin-3-yl)phenoxy)ethan-1-ol **2** (2.00 g, 8.1 mmol, 1.1 eq) in dry DCM (2 mL) was added dropwise. The cooling bath was removed afterwards, and the solution was stirred overnight.

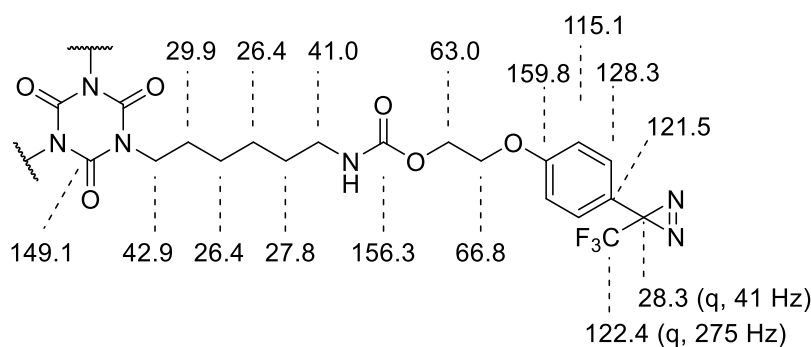
At this point the acrylic polyol (1.64 g solids, 4 mmol OH) can directly be added to provide a stock solution of 2:1 N₂/OH, for which the equivalent weight of N₂ can be calculated using ¹⁹F NMR against an internal standard (such as 3,4-dichlorofluorobenzene). This mixture can be further diluted using additional APO to the desired loading and can be cured without a difference in performance compared to the purified crosslinker.

To properly characterize the crosslinker, and evaluate the thermochemical properties, the mixture was purified by column chromatography (40% ethyl acetate in cyclohexane, R_f = 0.30) to provide the tritopic PUR-diazirine crosslinker **3** as a colorless oil (2.2 g, 1.77 mmol, 67% yield).

¹H NMR (300 MHz, Chloroform-*d*) δ 7.13 (d, J = 8.6 Hz, 6H), 6.90 (d, J = 8.9 Hz, 6H), 4.84 (s, 3H), 4.39 (t, J = 4.6 Hz, 6H), 4.13 (t, J = 4.7 Hz, 6H), 3.84 (t, 7.2 Hz, 6H), 3.15 (q, J = 6.7 Hz, 6H), 1.68 – 1.34 (m, 24H).

¹⁹F NMR (282 MHz, Chloroform-*d*) δ -65.62.

¹³C NMR (75 MHz, Chloroform-*d*) δ 159.72, 156.27, 149.10, 128.31, 122.34 (q, J = 274.7 Hz), 121.50, 115.07, 66.73, 62.99, 42.93, 41.03, 29.85, 28.33 (q, J = 40.4 Hz), 27.79, 26.36.



HRMS (ESI) *m/z* calculated [M+Na]⁺: 1265.4437, found: 1265.4386, calculated [M+NH₄]⁺: 1260.4883, found: 1260.4844.

3. Characterization of Crosslinker

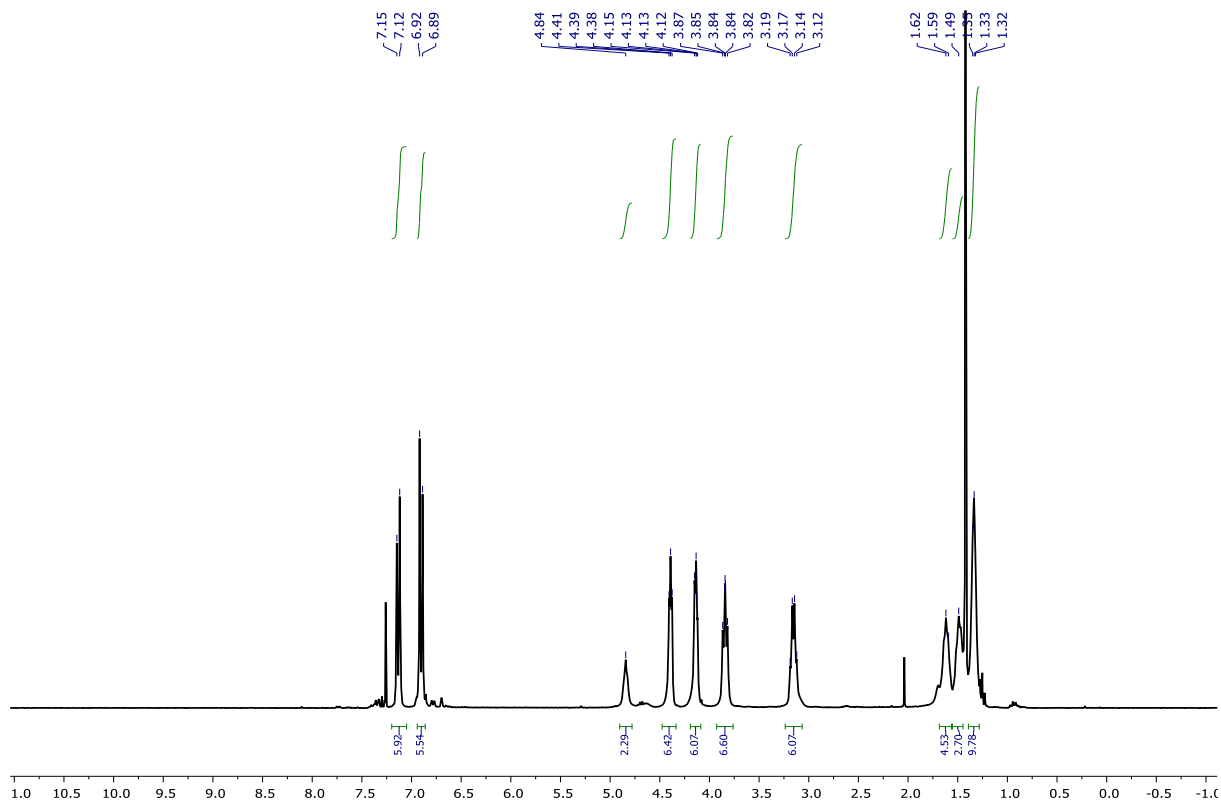


Figure S1. $^1\text{H-NMR}$ spectrum of PUR-diazirine crosslinker **3** in CDCl_3 .

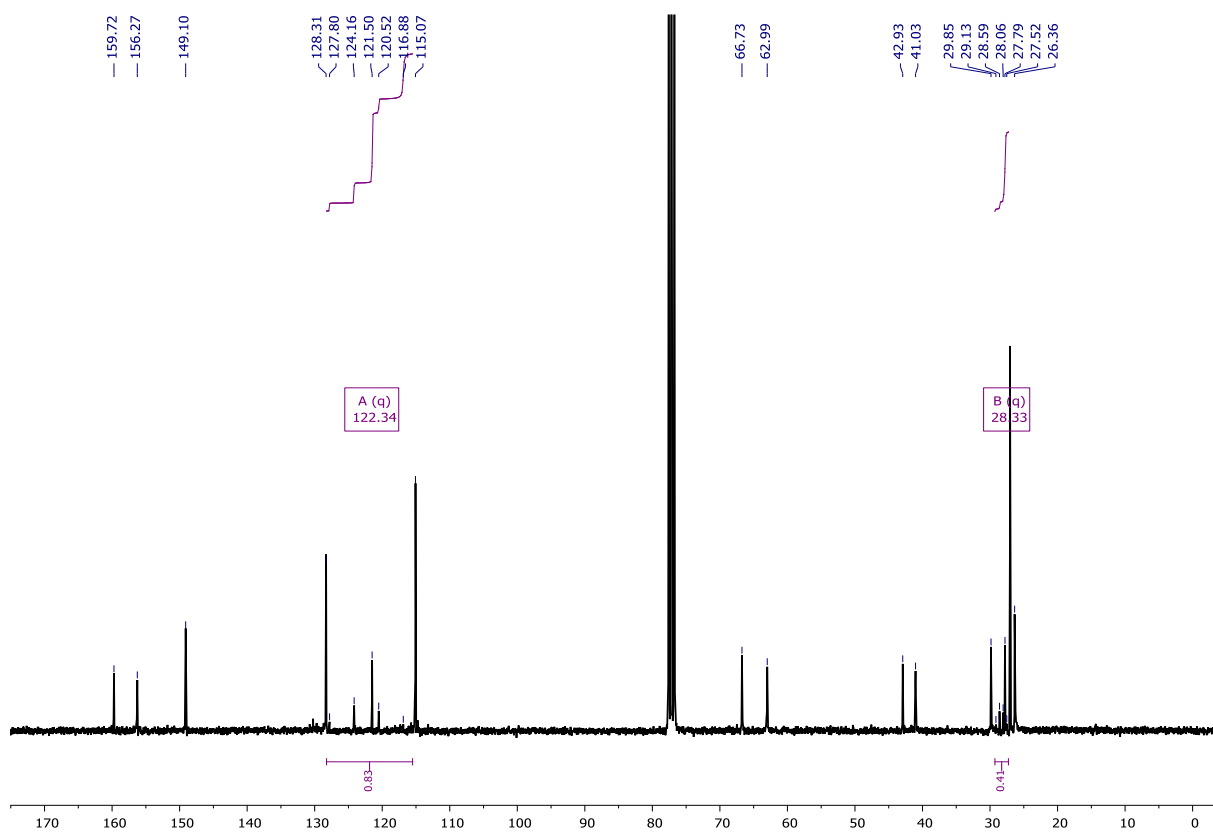


Figure S2. $^{13}\text{C-NMR}$ spectrum of PUR-diazirine crosslinker **3** in CDCl_3 .

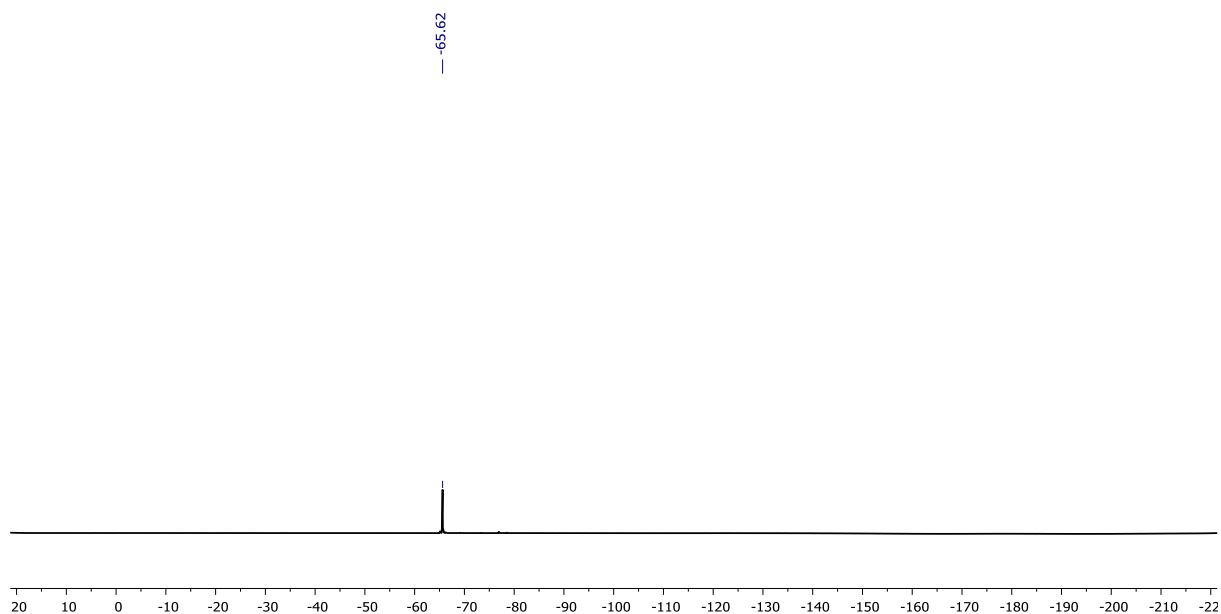


Figure S3. ^{19}F -NMR spectrum of PUR-diazirine crosslinker **3** in CDCl_3 .

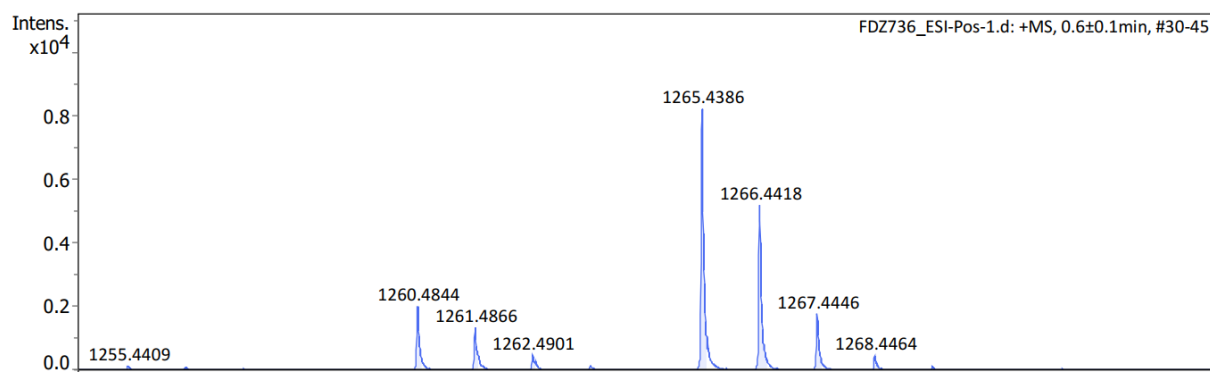


Figure S4. HRMS (ESI) spectrum of PUR-diazirine crosslinker **3**.

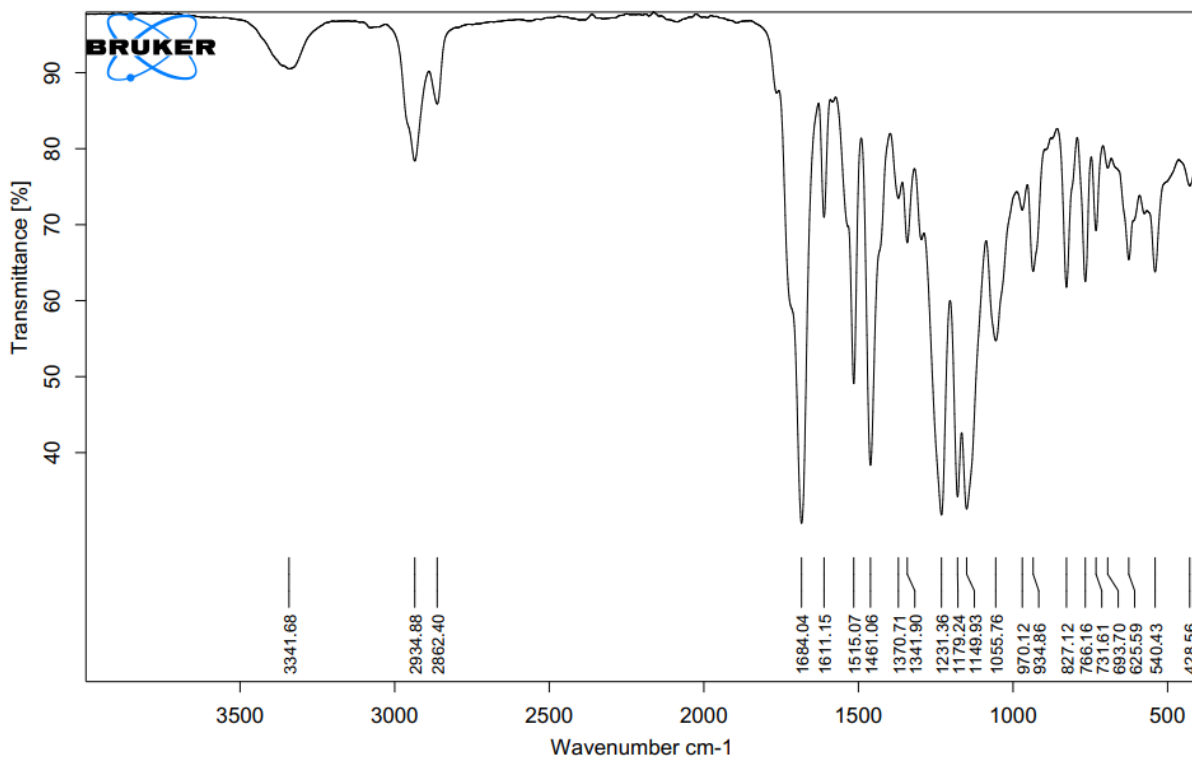


Figure S5. ATR-IR spectrum of PUR-diazirine crosslinker **3**.

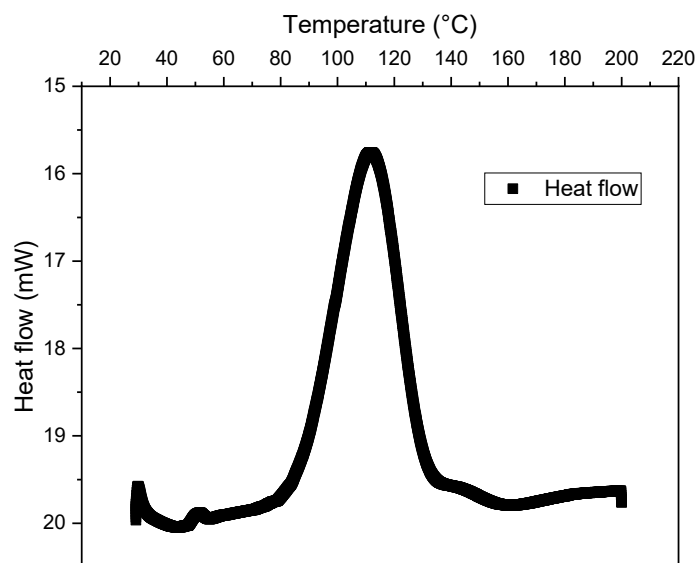


Figure S6. DSC trace of decomposition of PUR-diazirine crosslinker **3** with a 5 °C/min ramp.

4. Characterization of Coatings

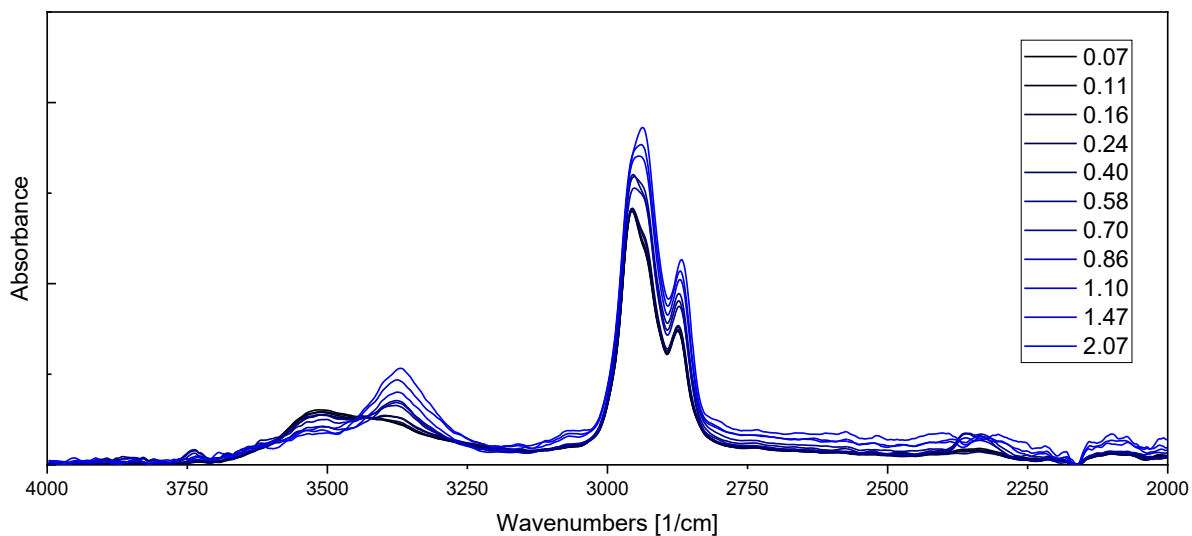


Figure S7. ATR-IR spectrum of APO with increasing amounts of PUR-diazirine crosslinker **3** (mol ratio N₂/OH in legend).

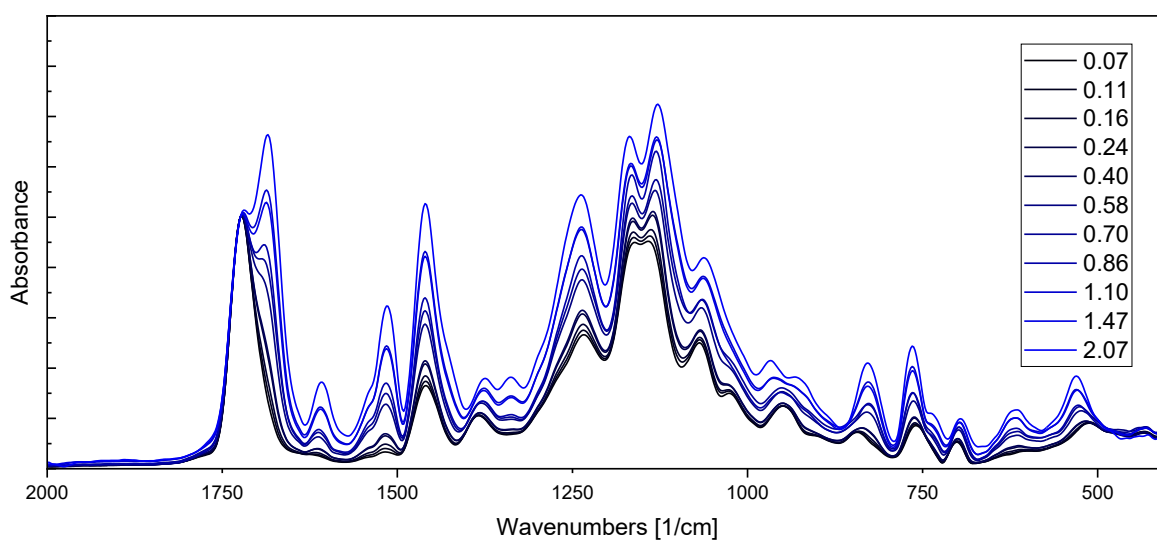


Figure S8. ATR-IR spectrum of APO with increasing amounts of PUR-diazirine crosslinker **3** (mol ratio N₂/OH in legend).

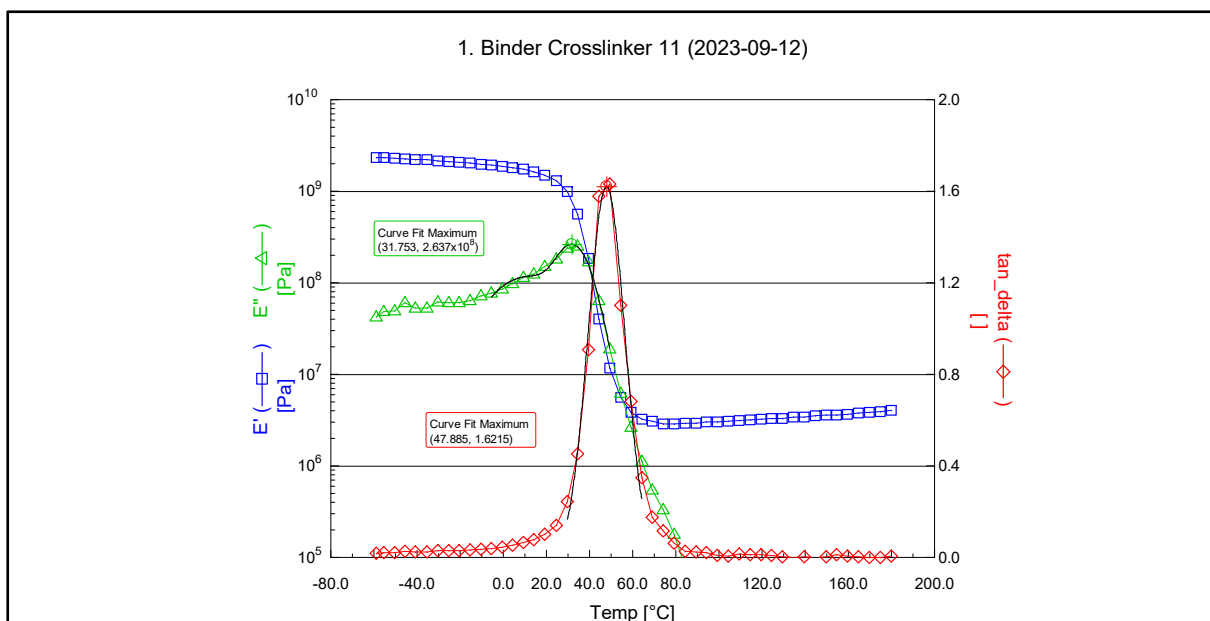


Figure S9. DMTA of PUR/APO coating containing a 1:1 ratio of N_2/OH .

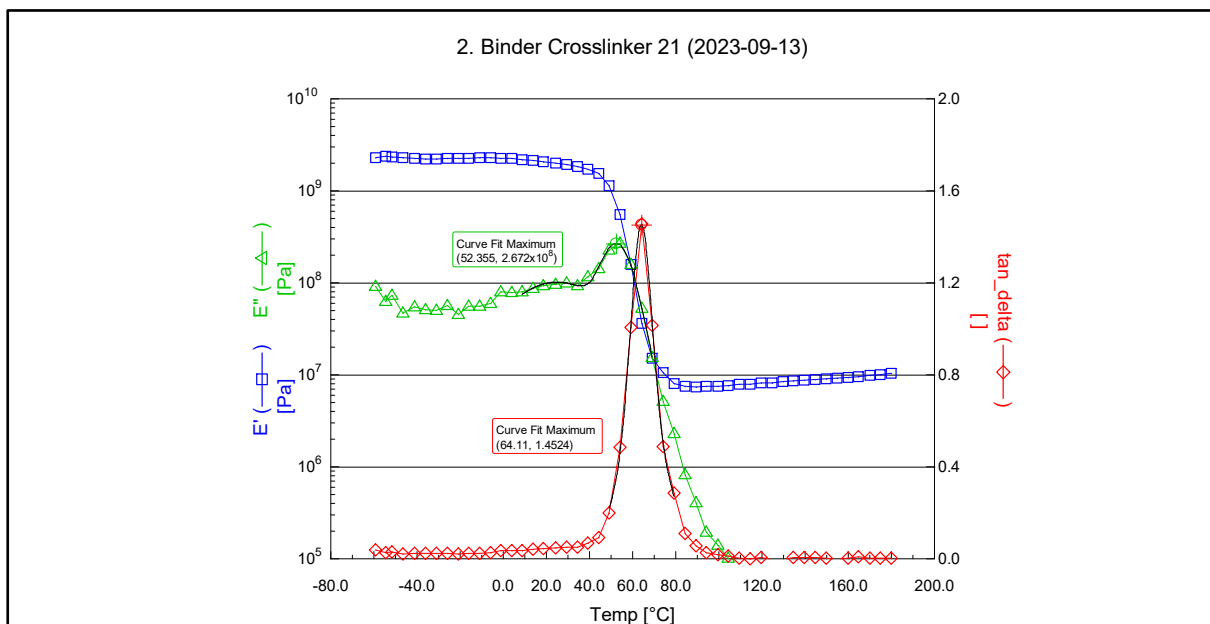


Figure S10. DMTA of PUR/APO coating containing a 2:1 ratio of N_2/OH .

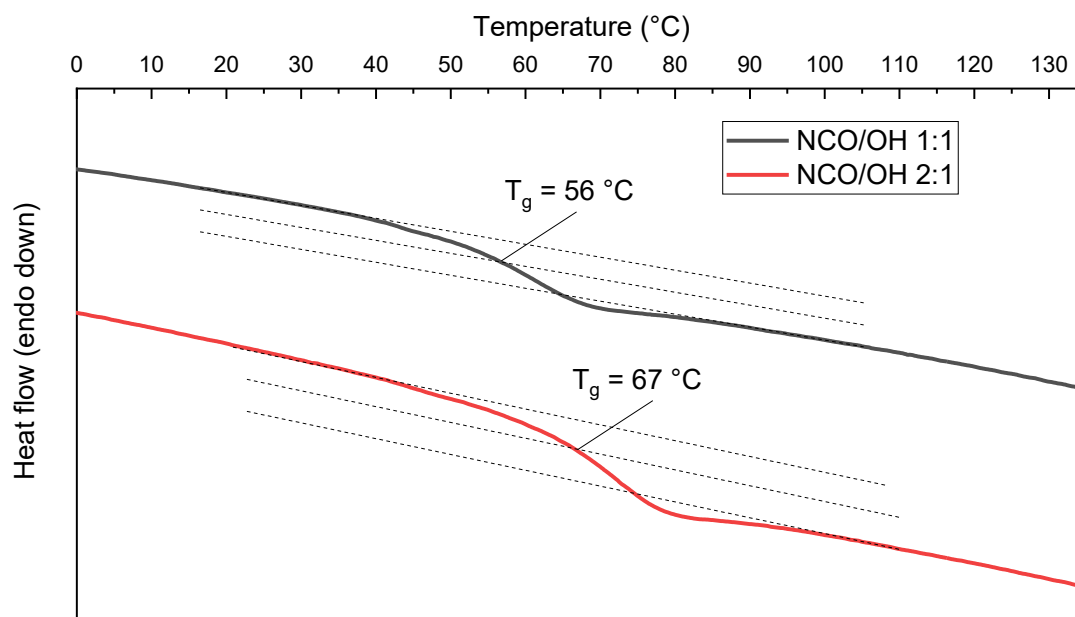


Figure S11. DSC trace of isocyanate/APO coating containing a 1:1 (black) or 2:1 (red) ratio of NCO/OH.

References

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