Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Material

Linking interfacial work of deformation from deconvoluted macro-rheological spectrum to early stage healing in selected polyurethanes

Vincenzo Montano*, Michele Senardi, Sybrand van der Zwaag and Santiago J. Garcia

Novel Aerospace Materials group, Faculty of Aerospace Engineering, Delft University of Technology, Kluyverweg 1, 2629 HS, Delft, The Netherlands

*Contact e-mail: v.montano@tudelft.nl

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1. Synthesis of self-healing segmented polyurethanes

PPDI-p

CroHeal™ 2000 was heated for 1 hour at 90 °C to reduce the intrinsic viscosity of the monomer, melting crystalline domains. Subsequently 90.0 grams (45.0 mmol) were transferred to a 300 mL polypropylene cup. 3.19 g of EHD (27.0 mmol) were then added to the cup. 12.68 g (79.20 mmol) of PPDI were weighted in a separate 25 mL polypropylene cup, purged under nitrogen inert environment and heated 1 hour at 120°C to reduce its intrinsic viscosity, melting crystalline domain. The PPDI was rapidly poured into the main reaction cup (containing CroHeal 2000 and EHD). The mixture was sheared under vacuum at 2300 rpm for 130 seconds using a vacuum assisted speed mixer (SpeedMixer™ DAC 400.2 VAC-P). The application of high vacuum (pressure below 100 mbar) turned out to be critical for the formation of bubble-free polymers. The mixture was then transferred to a 20x20 cm PTFE mold, equilibrated for 30 minutes at ambient conditions and subsequently cured overnight at 60 °C. The bulk polymers were equilibrated for 1 week at ambient condition before testing.

HMDI-p

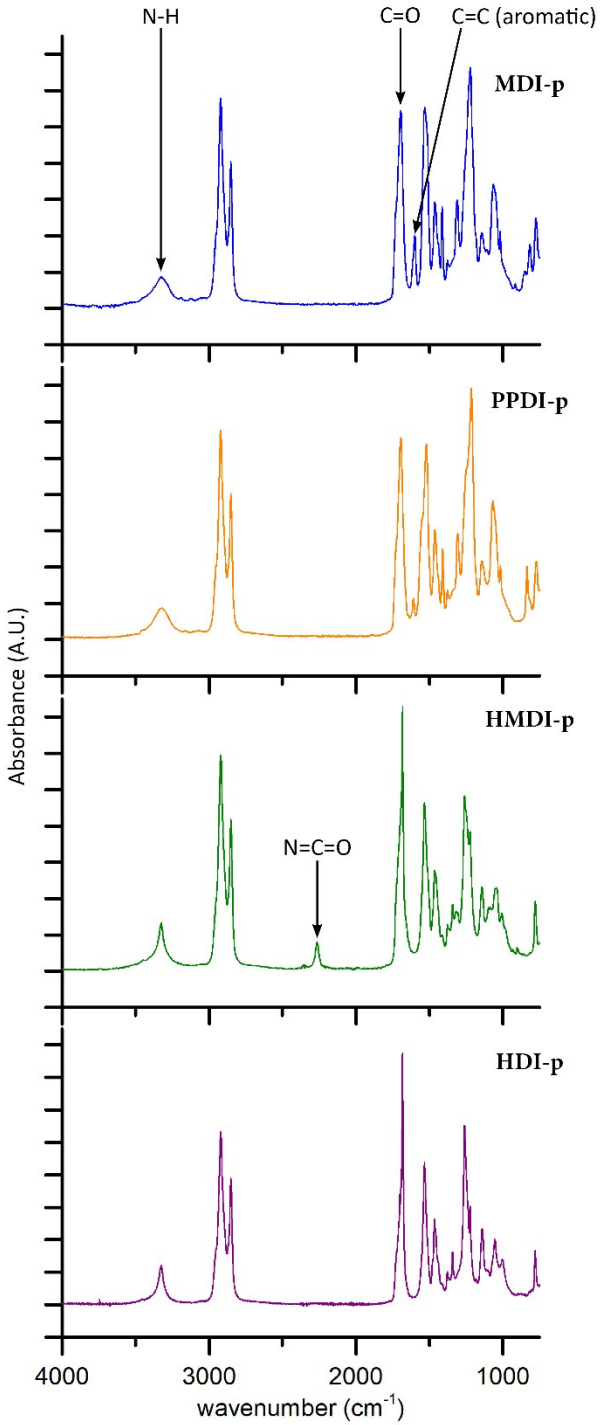
CroHeal™ 2000 was heated for 1 hour at 90 °C to reduce the intrinsic viscosity of the monomer, melting crystalline domains. Subsequently 90.0 grams (45.0 mmol) were transferred to a 300 mL polypropylene cup. 3.95 g of EHD (27.0 mmol) were then added to the cup. 20.78 g (79.20 mmol) of HMDI were weighted in a separate 25 mL polypropylene cup and purged under nitrogen inert environment. The HMDI was injected into the main reaction cup (containing CroHeal 2000 and EHD) using a syringe. The mixture was sheared under vacuum at 2300 rpm for 180 seconds using a vacuum assisted speed mixer (SpeedMixer™ DAC 400.2 VAC-P). The application of high vacuum (pressure below 100 mbar) turned out to be critical for the formation of bubble-free polymers. The mixture was then transferred to a 20x20 cm PTFE mold, equilibrated for 30 minutes at ambient conditions and subsequently cured overnight at 50 °C. The bulk polymers were equilibrated for 1 week at ambient condition before testing.

HDI-p

CroHeal™ 2000 was heated for 1 hour at 90 °C to reduce the intrinsic viscosity of the monomer, melting crystalline domains. Subsequently 90.0 grams (45.0 mmol) were transferred to a 300 mL polypropylene cup. 3.95 g of EHD (27.0 mmol) were then added to the cup. 13.32 g (79.20 mmol) of HDI were weighted in a separate 25 mL polypropylene cup and purged under nitrogen inert environment. The HDI was injected into the main reaction cup (containing CroHeal 2000 and EHD) using a syringe. The mixture was sheared under vacuum at 2300 rpm for 180 seconds using a vacuum assisted speed mixer (SpeedMixer™ DAC 400.2 VAC-P). The application of high vacuum (pressure below 100 mbar) turned out to be critical for the formation of bubble-free polymers. The mixture was then transferred to a 20x20 cm PTFE mold, equilibrated for 30 minutes at ambient conditions and subsequently cured overnight at 60 °C. The bulk polymers were equilibrated for 1 week at ambient condition before testing.

2. ATR-FTIR

Figure S1. ATR-FTIR spectra of the synthesized PU. Synthesis completion was followed through disappearance of N=C=O stretching band at 2270 cm^{-1} and appearance of absorption peaks at 1170 cm^{-1} (C=O bond) and 2270 cm^{-1} (N-H bond). A small peak of unreacted isocyanate is observed for HMDI-p attributed to the monomer low reactivity.



3. Macro-rheology deconvolution protocol

The mechanical relaxation spectrum was deconvoluted following the procedure introduced elsewhere [1]. Herein we reports some principal highlights and the procedure to compute the average stored work of deformation associated to individual relaxation process.

To fit the relaxation spectrum the infinite Maxwell-Weichert model was chosen

$$H_{Model}(\ln \tau) = \sum_{i=1}^{n} A_i exp\left(- \frac{\left(\ln (\tau) - \ln \left(\tilde{\tau}_i\right)\right)^2}{2\sigma_i^2} \right)$$

The model entails an infinite number of Maxwell elements (a compliance and a dashpot in series) connected in parallel. The choice of this model allows us to approach the problem in the most general and unbiased way.

The experimental $H(\tau)\ exp.$ is fitted with a user-defined initial number of relaxation elements i. the optimal number of Maxwell elements and the set of best fitting parameter values is identified based on the minimization of the coefficient of determination (r^2) obtained by comparing the model storage and loss moduli with experimental moduli. The model storage and loss moduli are calculated as:

$$G^{'}(\omega) = \int_{-\infty}^{\infty} \left[\frac{H(\ln \tau)\omega^2\tau^2}{1+\omega^2\tau^2} \right] d\ln \tau$$

$$G^{''}(\omega) = \int_{-\infty}^{\infty} \left[\frac{H(\ln \tau)\omega\tau}{1+\omega^2\tau^2} \right] d\ln \tau$$

The average stored work of deformation is defined as [2]:

$$W_s(\omega)_{average} = \left(\frac{\omega}{2\pi}\right) \int_{\frac{2\pi(n-1)}{\omega}}^{\frac{2\pi n}{\omega}} W_s(t)dt = (\varepsilon_0^2/4)G^{'}(\omega)$$

Substituting the expression of $G^{'}(\omega)$

$$W_s(\omega)_{average} = (\varepsilon_0^2/4) \int_{-inf}^{+inf} H(\tau) \frac{\omega^2\tau^2}{1+\omega^2\tau^2} dln(\tau)$$

The individual stored work of deformation are then obtained substituting in this relation the single components of the deconvoluted relaxation spectrum.

3. Extensional DMA data

Figure S2. MDI-p Temperature Sweep

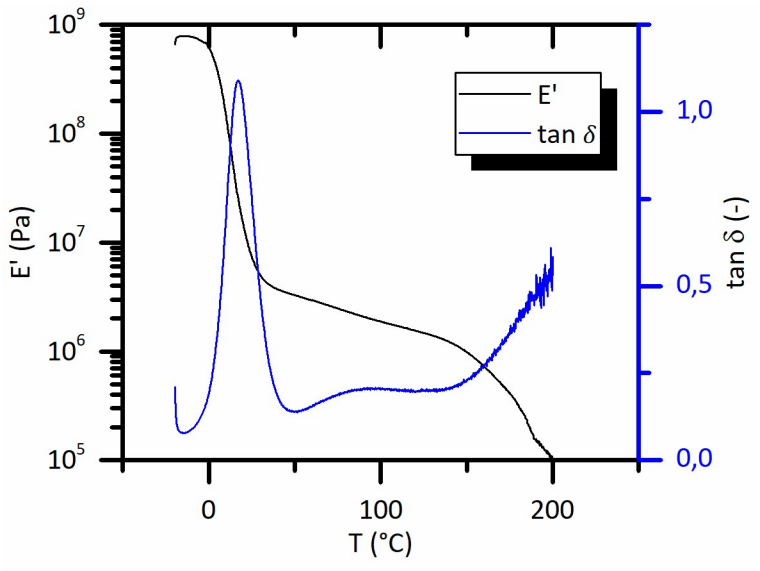


Figure S3. PPDI-p Temperature Sweep

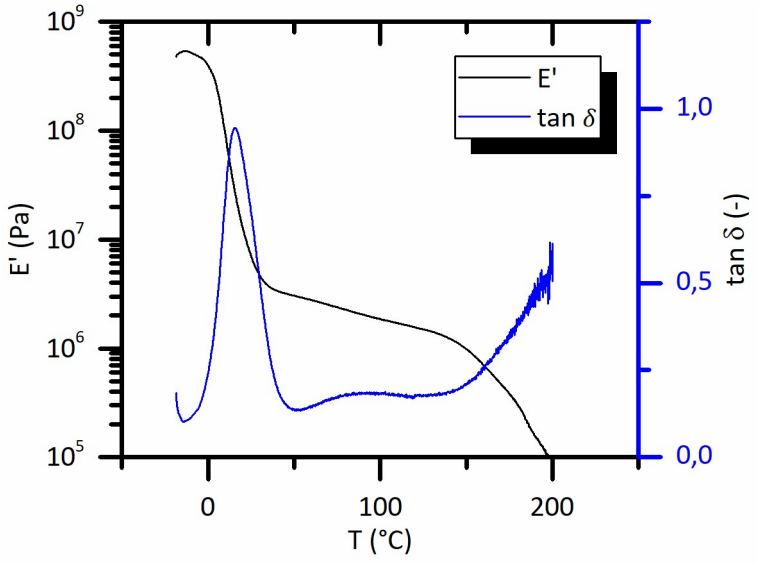


Figure S4. HMDI-p Temperature Sweep

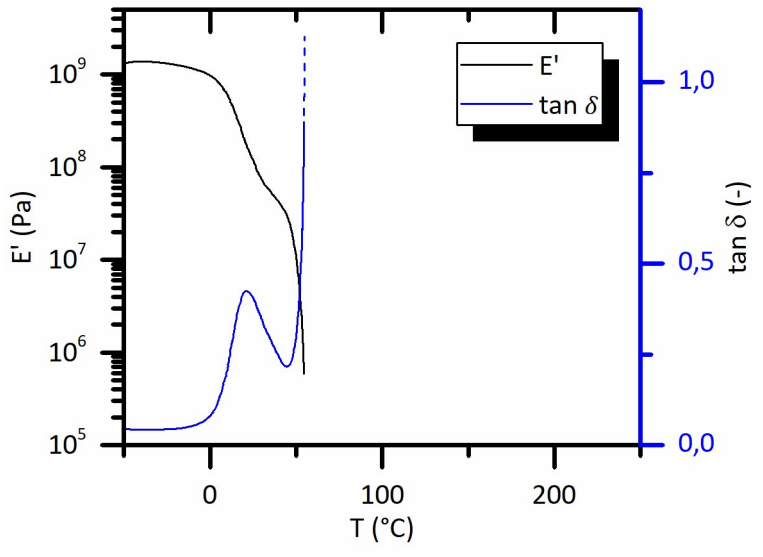
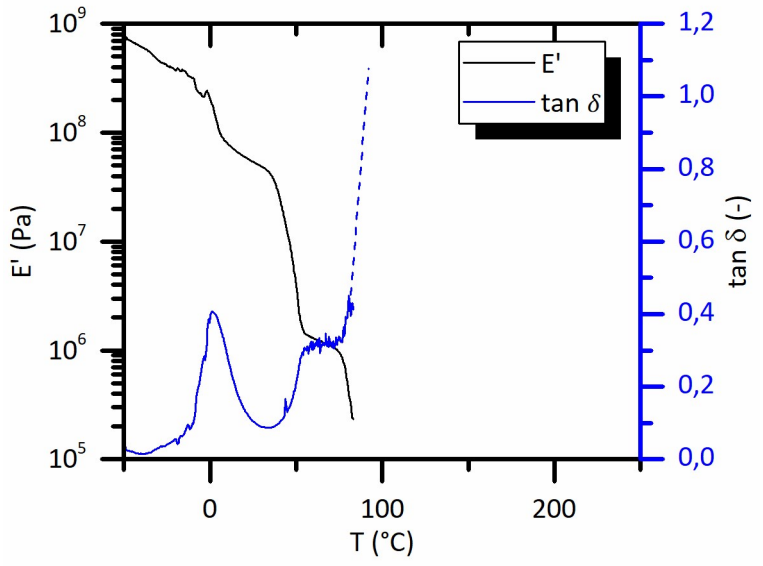


Figure S5. HDI-p Temperature Sweep



4. SENT raw data

Figure S6. MDI-p SENT raw data. The figure shows the initial and final frames of the mechanical test and the load-displacement curve. From up to down: Pristine, Healing 3.6 x 10^3 s (1 hour) at 30 °C, Healing 8.64 x 10^4 s (1 day) at 30 °C, Healing 1.2 x 10^6 (2 weeks) at 30 °C.

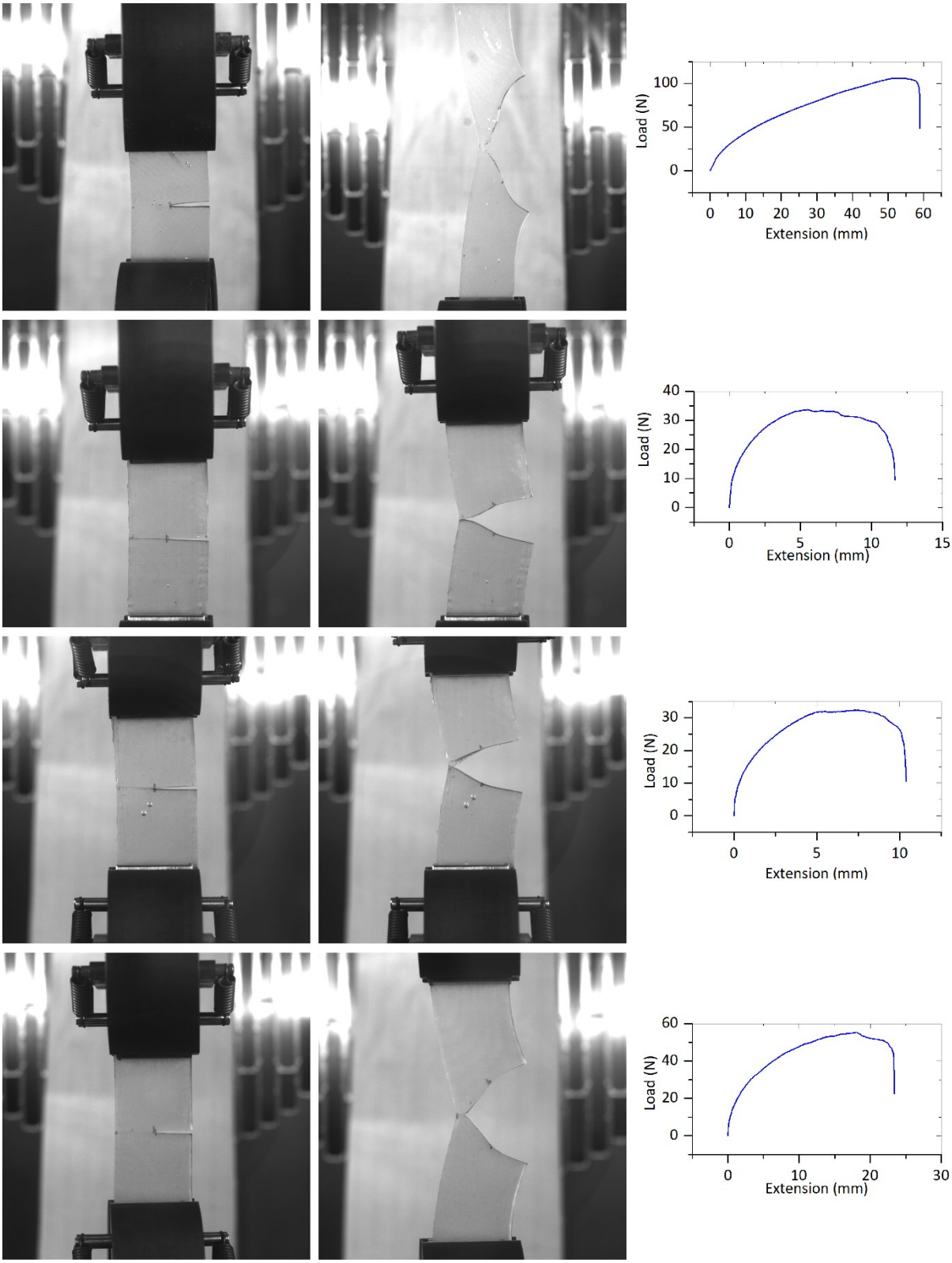


Figure S7. PPDI-p SENT raw data. The figure shows the initial and final frames of the mechanical test and the load-displacement curve. From up to down: Pristine, Healing 3.6 x 10^3 s (1 hour) at 30 °C, Healing 8.64 x 10^4 s (1 day) at 30 °C, Healing 1.2 x 10^6 (2 weeks) at 30 °C.

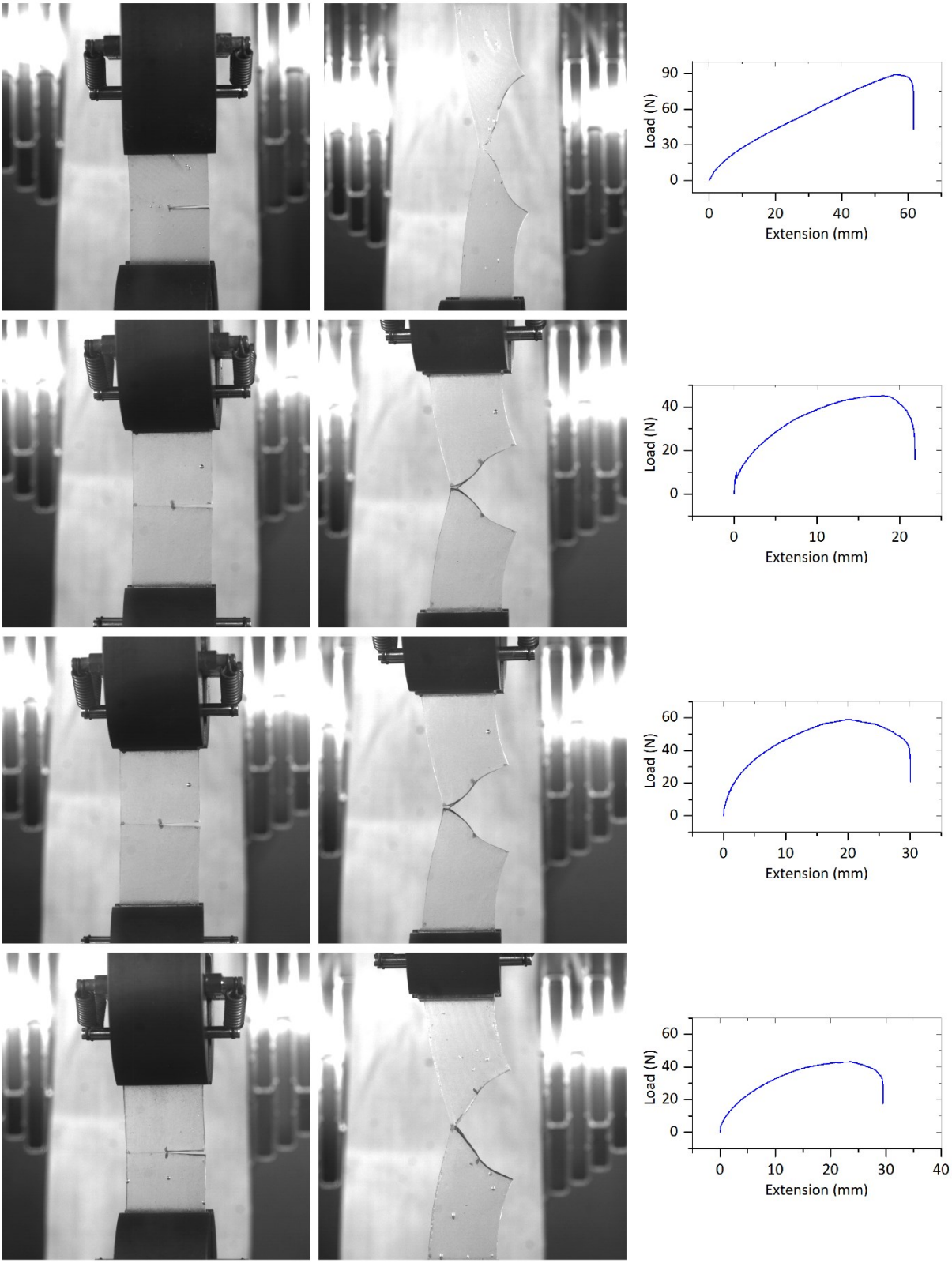


Figure S8. HMDI-p SENT raw data. The figure shows the initial and final frames of the mechanical test and the load-displacement curve. From up to down: Pristine, Healing 3.6 x 10^3 s (1 hour) at 30 °C, Healing 8.64 x 10^4 s (1 day) at 30 °C, Healing 1.2 x 10^6 (2 weeks) at 30 °C.

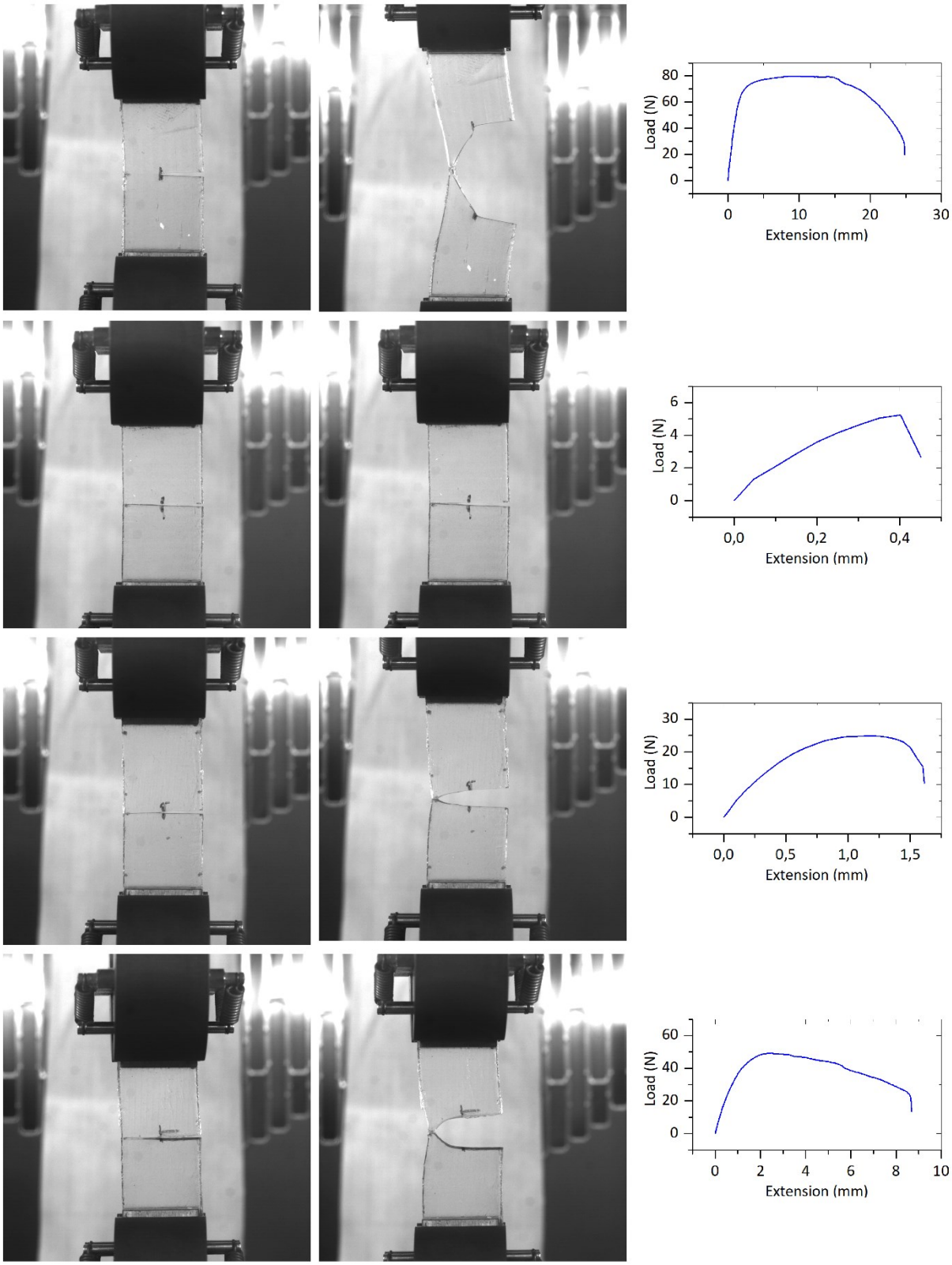
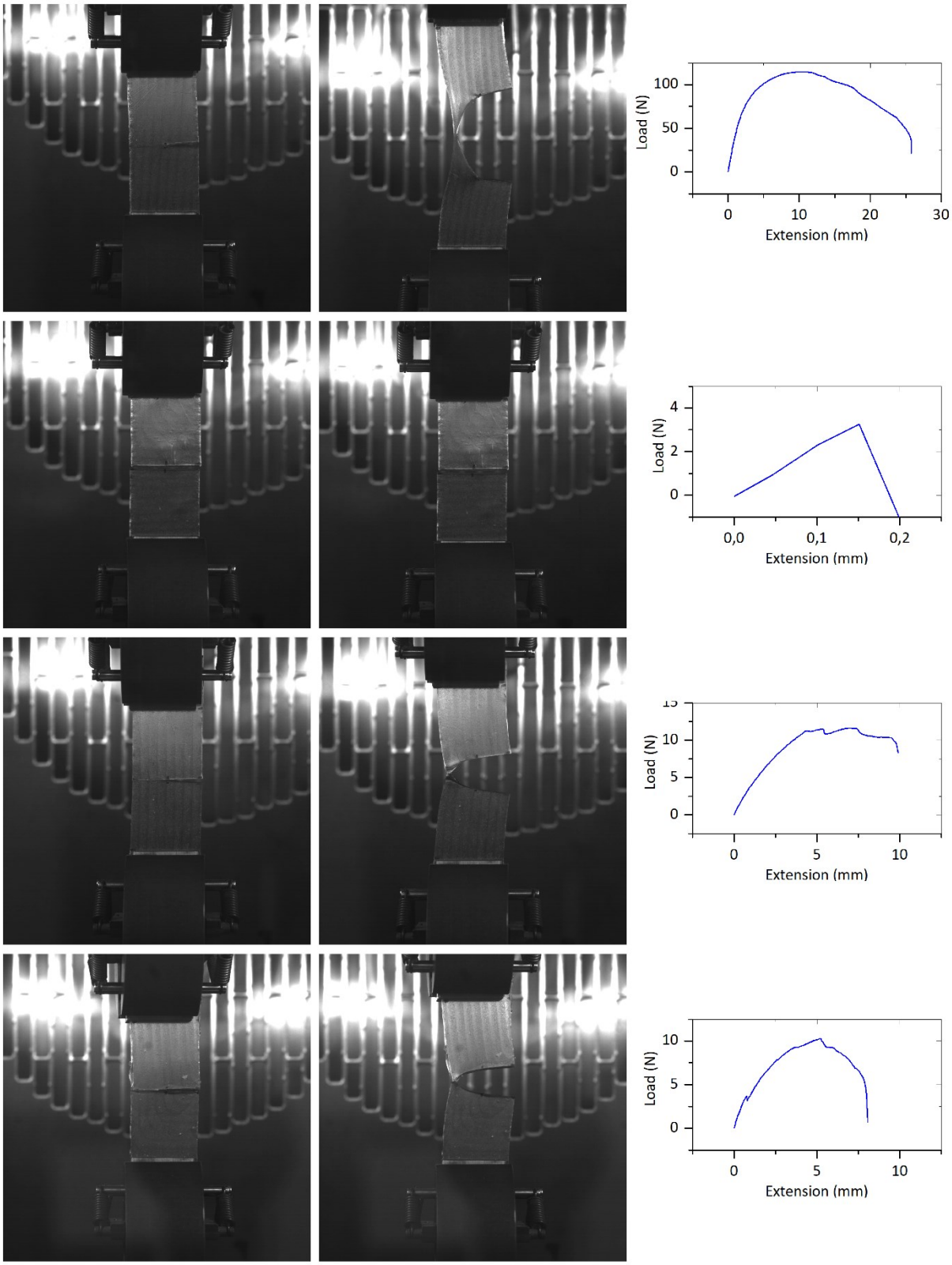


Figure S9. HDI-p SENT raw data. The figure shows the initial and final frames of the mechanical test and the load-displacement curve. From up to down: Pristine, Healing 3.6 x 10^3 s (1 hour) at 30 °C, Healing 8.64 x 10^4 s (1 day) at 30 °C, Healing 1.2 x 10^6 (2 weeks) at 30 °C.



5. µFTIR-ATR mapping

Table S1. **Amount of microscopic segregated phase for PU systems.** The segregated phase content is quantified by µFTIR-ATR via principal component analysis.

Polymer	Segregated phase (PCA%)
MDI-p	4.7 ± 0.4
PPDI-p	2.3 ± 0.35
HMDI-p	< 0.5
HDI-p	< 0.5

References

[1] Montano V, Picken S J, van der Zwaag S, Garcia S J. A deconvolution protocol of the mechanical relaxation spectrum to identify and quantify individual polymer feature contributions to self-healing. *Phys. Chem. Chem. Phys.* 2019;**21**:10171–84

[2] Tschoegl N W. The pheonomenological theory of linear viscoelastic behavior: an introduction. Springer Science & Business Media. 2012