Supporting Information

Frontal Polymerization of Thiol-Acrylate Covalent Adaptable Networks

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Materials

All materials were used without further purification. Trimethylolpropane triacrylate (**TMPTA**), glycerol 1,3-diglycerolate diacrylate (**GDGDA**), trimethylolpropane tris(3-mercaptopropionate) (**TMPMP**), 1,1,2,2-tetraphenyl-1,2-ethanediol (**TPED**), phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (**BAPO**), bis[2-(methacryloyloxy)ethyl] phosphate (**DMAP**), were acquired from Sigma Aldrich. The structures of the used chemicals are shown in **Figure 1**.

Experimental Section

Resin preparations

The resin formulation was prepared by dissolution of the photoinitiator BAPO (3 mol%) as well as the thermal initiator TPED (1.5 mol%) in a mixture of the acrylates TMPTA and GDGDA in their respective ratios. The resin was heated to 80 °C until the initiators were fully dissolved. Subsequently, the respective amount of the thiol TMPMP and the phosphate ester DMAP were added. The exact mixing ratios can be seen in **Table 1 SI**.

Table 1 SI Used resin with a constant BAPO (3 mol%) and TPED (1.5 mol %) content

Component	Reference	SH15	SH20	SH25	PH15	PH20	PH25
TMPTA [eq.]	5	4.25	4	3.75	4.25	4	3.75
GDGDA [eq.]	4	3.25	3	2.75	3.25	3	2.75
Phosphate [eq.]	1	1	1	1	1.5	2	2.5
TMPMP [eq.]	-	1.5	2	2.5	1	1	1

Fro ntal pol

ymerization

The resin was poured into a silicone mould with the dimensions of 5x10x50 mm. Subsequently, the resin was irradiated using UV-light from an Omnicure Series 2000 lamp (Excelitas, USA) with an intensity of 2 W/cm² at a distance of a 5 mm for 20 s. The front was monitored using an FLIR E54 infrared camera (Teledyne Technologies, USA) to obtain the maximum frontal temperature. The frontal velocity was calculated from the resulting video.

Curing kinetics

FT IR Spectroscopy

Thin films were drop casted on silicon wafers and subsequently irradiated with the Omnicure S2000 lamp using an intensity of 0.5 W/cm² at a distance of 20 cm. Fourier transform infrared spectroscopy measurements were performed after defined exposure times with a Bruker Advance P spectrometer (Bruker, USA). The spectra were recorded in transmission mode at a resolution of 4 cm^{-1} with 24 scans per measurements in a range from 4000-900 cm^{-1}. The spectra were analysed for calculation of the carbon double bond conversions using SpectraGryph software.

Photo-Differential Scanning Calorimetry

Resin formulations were mixed according to Table 1 SI with a total weight for the measurements of around 10 mg. Reaction enthalpies were measured using a NETZSCH 204 F1Phoenix Photo-DSC (Netzsch, Germany). The experiments were conducted at 1% of lamp intensity at room temperature for an irradiation time of 15 min (twice per formulation).

Mechanical properties

Swelling Test

Samples were drop casted on a glass slide and irradiated with an Omnicure Series S2000 lamp at 2 W/cm² for 10 min. Subsequently, the samples were post-cured at 140 °C for 20 min, weighed and emerged in dichloromethane for 48 h. After swelling, the samples were weighed again and dried for one week at 100 °C in a vacuum oven, before weighing them again. The degree of swelling was calculated by dividing the swollen sample weight by the original sample weight. The gel content was calculated by dividing the dried sample weight after swelling by the original weight.

Thermogravimetric analysis

Samples were prepared as described in the previous section for swelling measurements. For TGA analysis a Perkin Elmer TGA 8000 (Perkin Elmer, USA) was used measuring from 40 to 550 °C at a heating rate of 20 °C/min under a nitrogen flow of 20 mL/min.

Dynamic mechanical analysis

For sample preparation, the resins were poured into silicone moulds with the dimensions of 30x2x4 mm, frontally cured with UV-light using the Omnicure Series S2000 lamp (intensity of 2 W/cm² at a distance of 10 cm). Post-curing was done at 140 °C for 20 min in an oven. To determine the glass transition temperatures of the networks, a Mettler Toledo DMA/STDA 1 (Mettler Toledo, USA) was used. Samples were measured between 0 and 150 °C at a frequency of 1 Hz, 1% strain and with a heating rate of 2 K/min.

Stress relaxation test

For sample preparation, the resins were poured into silicone moulds with the dimensions of 15x5x1 mm following the same process as for the DMA-samples. The samples were measured in DMA mode with an Anton Paar Physica MCR501 (Anton Paar, Austria) rheometer by applying a deformation of 1% and a normal force of 0.1 N at 200 °C.

The curves at varying temperature were modelled using the Kohlrausch-Williams-Watts function (KWW) with σ_t/σ_0 as the normalized relaxation modulus, t the time in [s], τ as the relaxation time in [s] and β as the exponential coefficient. The resulting data from the KWW model was fitted to an Arrhenius model, where τ is the relaxation time at 1/e in [s], E_a is the activation energy in [Jmol⁻¹], R the ideal gas constant in [JK⁻¹mol⁻¹] and T represents the absolute temperature in [K]

Equation 1 SI KWW function used for modelling

$$\frac{\sigma_t}{\sigma_0} = e^{-\left(\frac{t}{\tau}\right)^{\beta}}$$

Equation 2 SI Arrhenius model for temperature dependency of relaxation

$$\ln(\tau) = \frac{E_a}{R} * \frac{1}{T} + c$$

Reshaping and reprocessing

Reshaping

A bar-like sample of frontally cured SH20 was prepared akin to the process used for DMA samples. The sample was shaped over T_g at 100 °C in an oven and fixed in its reprogrammed shape with aluminium foil at 180 °C for 2 h. Subsequently, the programmed sample was heated over T_g again and reshaped into its original shape, however without an additional fixation step over T_v, in order to check the shape recovery.

Reprocessing

The frontally cured test specimen of SH20 (prepared as described in the DMA section) were milled in two subsequent milling steps (each 30 s) using a Retsch CryoMill (Retsch, Germany) with liquid nitrogen cooling. In cooperation with Meltprep (Graz, Austria), powders of the sample were pressed in a Meltprep vacuum compression moulding device at 10 MPa at 200°C for 30 min. The resulting samples were further investigated measuring their Shore-D-Hardness and optical microscopy with an Olympus DSX 1000 (Olympus, Japan).

Recovery of glass fibres

A polymeric composite was prepared by mixing resin SH20 with 5 wt% of glass fibres, obtained from a glass fibre mat (R&G GmbH, Germany) with a weight of 300 g/m², a fibre length of 50 mm and a yarn titer of 30 tex. The glass fibre mat was placed in a silicon mould and the resin was poured onto it. Frontal polymerization was thermally triggered at 250 °C with a solder iron. Once cured, the composite was emerged in ethylene glycol for 72 h at 200 °C. The fibres were recovered via filtration, dried and subsequently investigated via optical microscopy using an Olympus DSX 1000.

Results and Discussion

Figure 1 SI frontally polymerized a.) reference sample; b.) PH20 sample; c.) SH20 sample

Curing kinetics

Table 2 SI Frontal velocities and maximum temperatures of the resins under investigation

Formulation	T_{max} [°C]	Velocity [cm/min]
Reference	239 ± 11	4.01 ± 0.22
SH15	218 ± 13	2.81 ± 0.06
SH20	205 ± 6	2.46 ± 0.06
SH25	172 ± 4	1.63 ± 0.08
PH15	217 ± 8	2.65 ± 0.06
PH20	208 ± 4	2.00 ± 0.08
PH25	207 ± 3	2.04 ± 0.04

Table 3 SI Carbon double bond conversions of resins under investigation acquired with IR-kinetics prior to and after a heating step at 100 °C for 20 min

Formulation	Maximum Conversion at 25 °C [%]	Maximum Conversion at 100 °C [%]
Reference	67.4	77.1
SH15	76.3	83.3
SH20	82.0	88.5
SH25	91.1	95.1
PH15	71.0	84.3
PH20	66.5	74.1
PH25	58.5	68.5
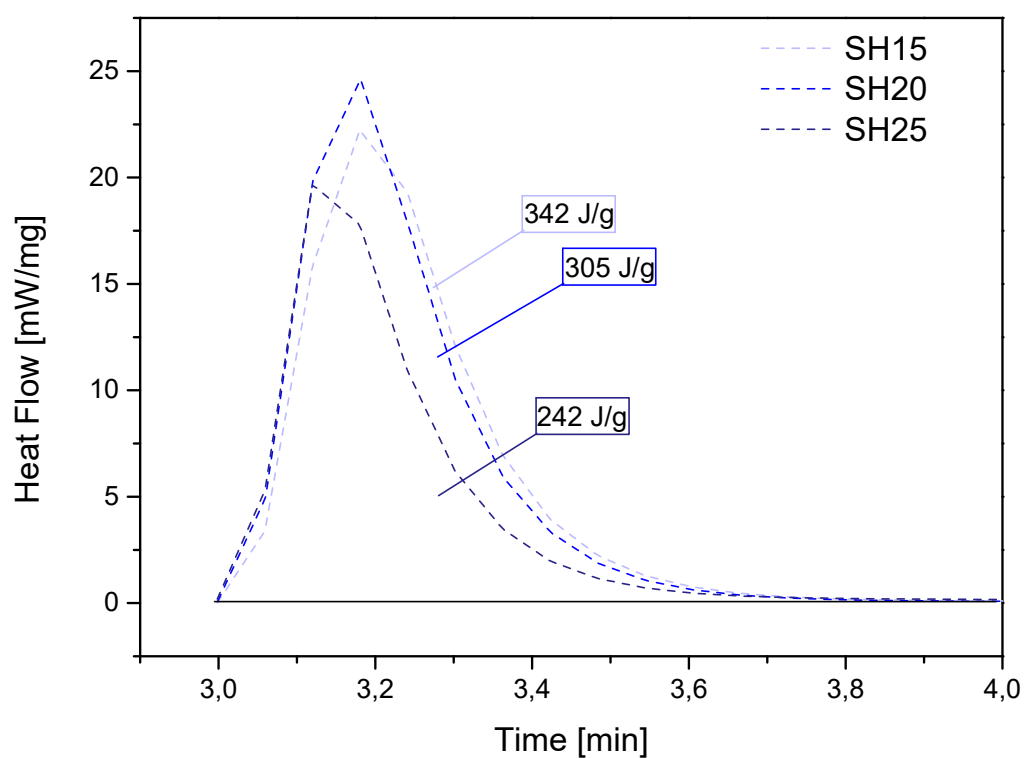
Figure 2 SI Photo-DSC curves of resins with varying thiol content

Mechanical and thermal properties
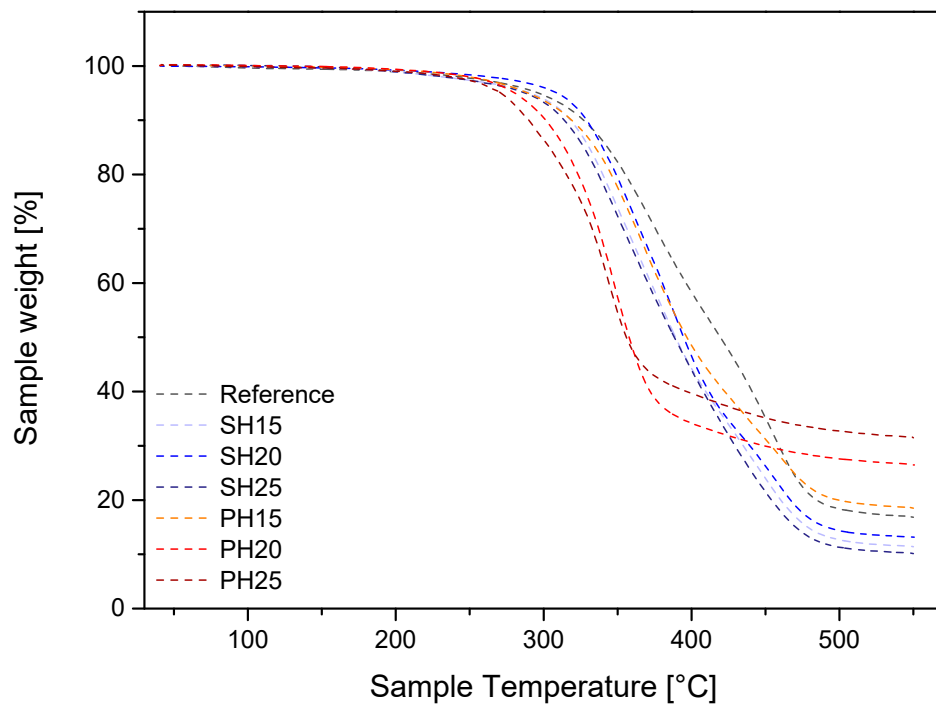
Figure 3 SI TGA curves of the frontally cured resins under investigation

Table 4 SI Values measured for DMA of the frontally cured resins under investigation

Formulation	Onset [°C]	T_g [°C]	Offset [°C]
Reference	34	94	141
PH15	44	88	125
PH20	46	89	126
PH25	46	88	125
SH15	37	75	111
SH20	34	56	90
SH25	24	40	65
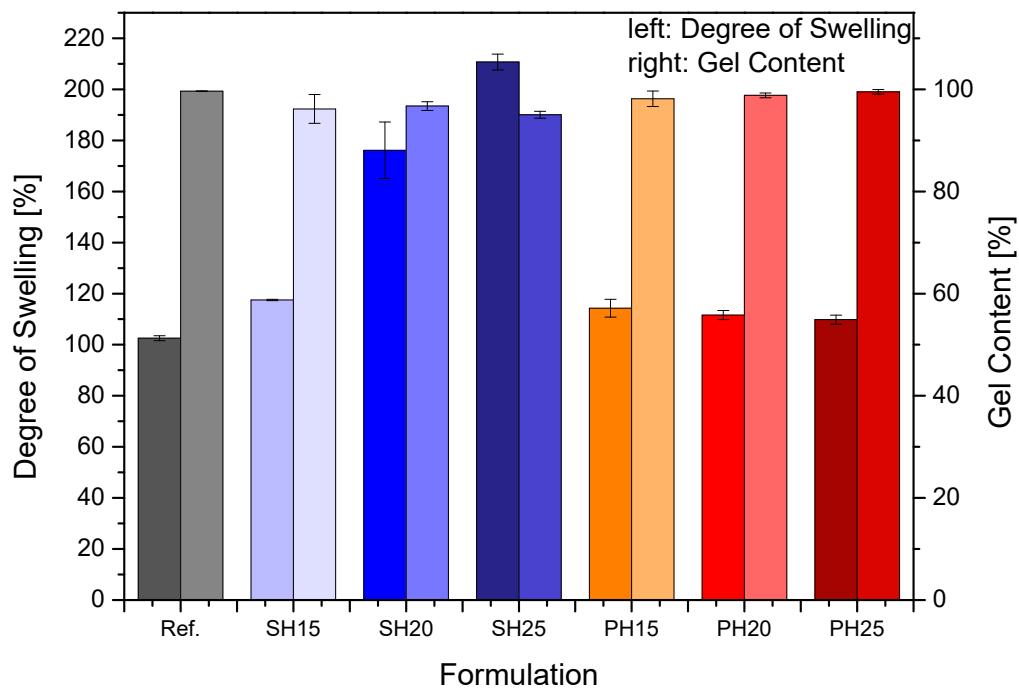
Figure 4 SI Swelling tests of frontally cured resins under investigation

Table 5 SI Swelling tests of frontally cured resins under investigation

Formulation	Degree of swelling [%]	Gel content [%]
Reference	102.6 ± 0.9	99.6 ± 0.1
SH15	117.5 ± 0.3	96.2 ± 2.8
SH20	176.1 ± 11.1	96.7 ± 0.9
SH25	210.7 ± 3.1	95.0 ± 0.7
PH15	114.3 ± 3.5	98.1 ± 1.5
PH20	111.6 ± 1.8	98.8 ± 0.5
PH25	109.8 ± 1.8	99.5 ± 0.5
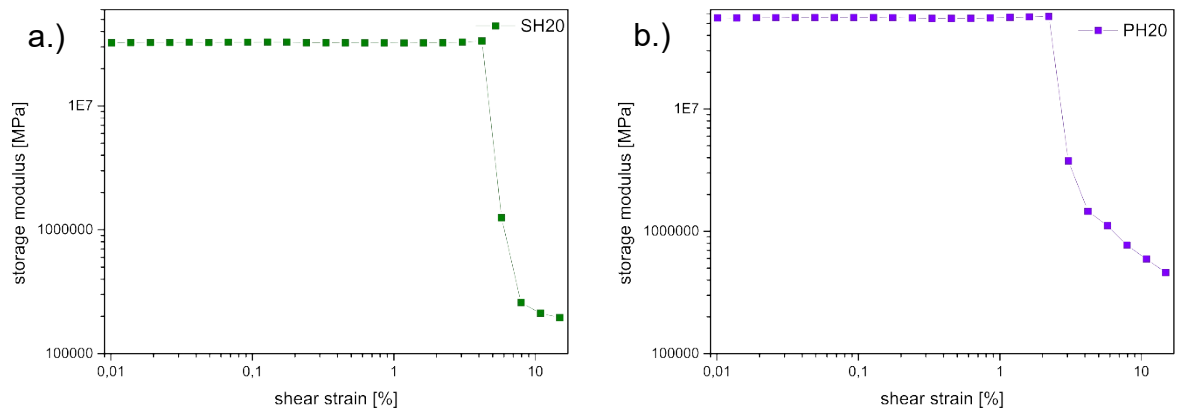
Figure 5 SI Amplitude Sweep Experiments for a.) SH20 and b.) PH20
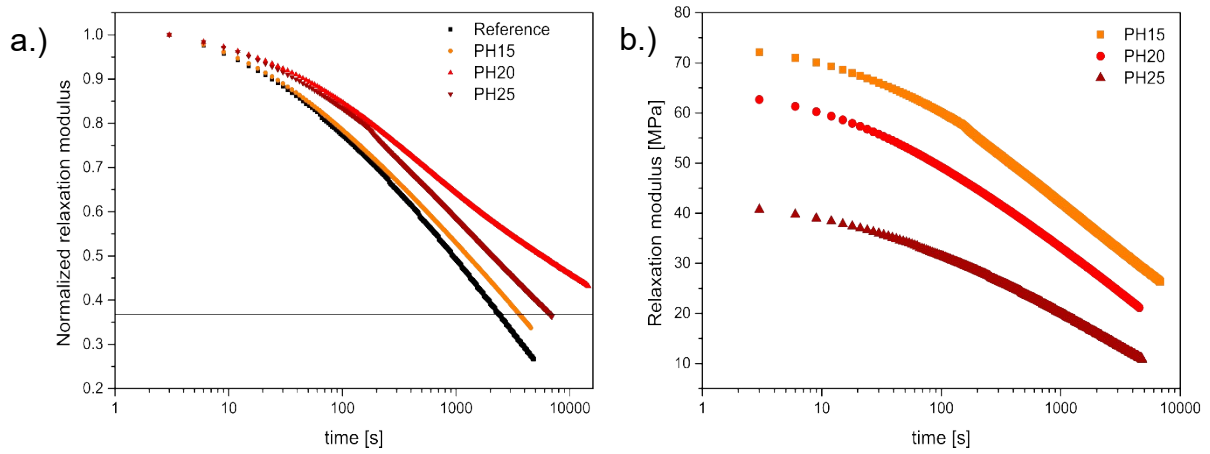

Figure 6 SI Stress relaxation measurements of frontally cured samples with varying phosphate content with a.) a normalized relaxation modulus and b.) a non-normalized relaxation modulus
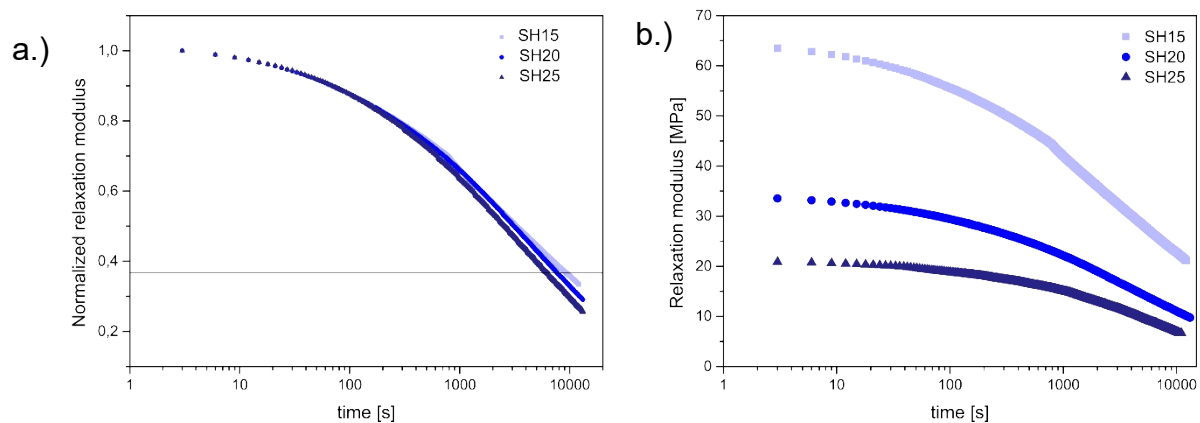
Figure 7 SI Stress relaxation measurements of frontally cured samples with varying thiol content with a.) a normalized relaxation modulus and b.) a non-normalized relaxation modulus

Table 6 SI Relaxation times of the frontally cured networks under investigation

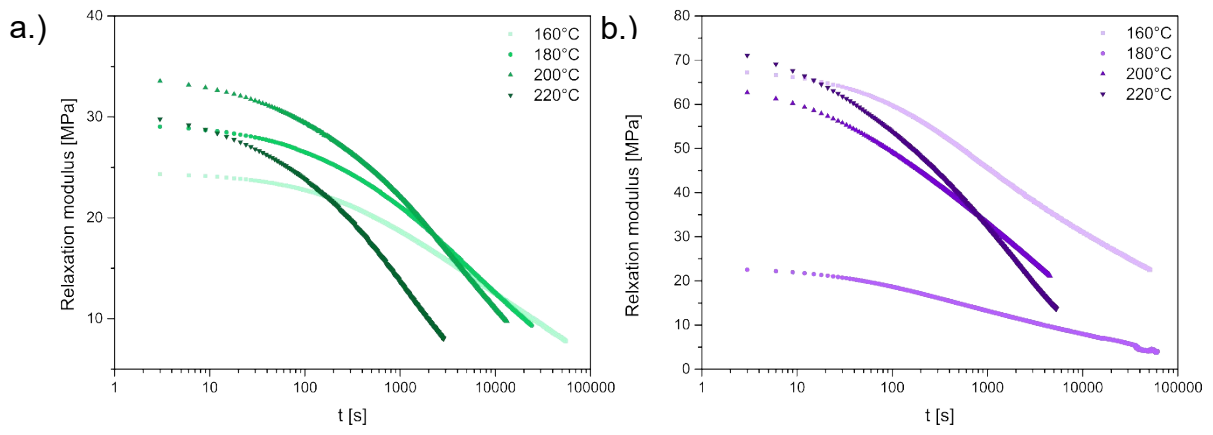| Formulation	time at 1/e at 200°C [s]
Reference	35808
SH15	9021
SH20	7635
SH25	6225
PH15	6684
PH20	3612
PH25	2391

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Figure 8 SI Non-normalized stress-relaxation measurements at varying temperature for a.) SH20 and b.) PH20
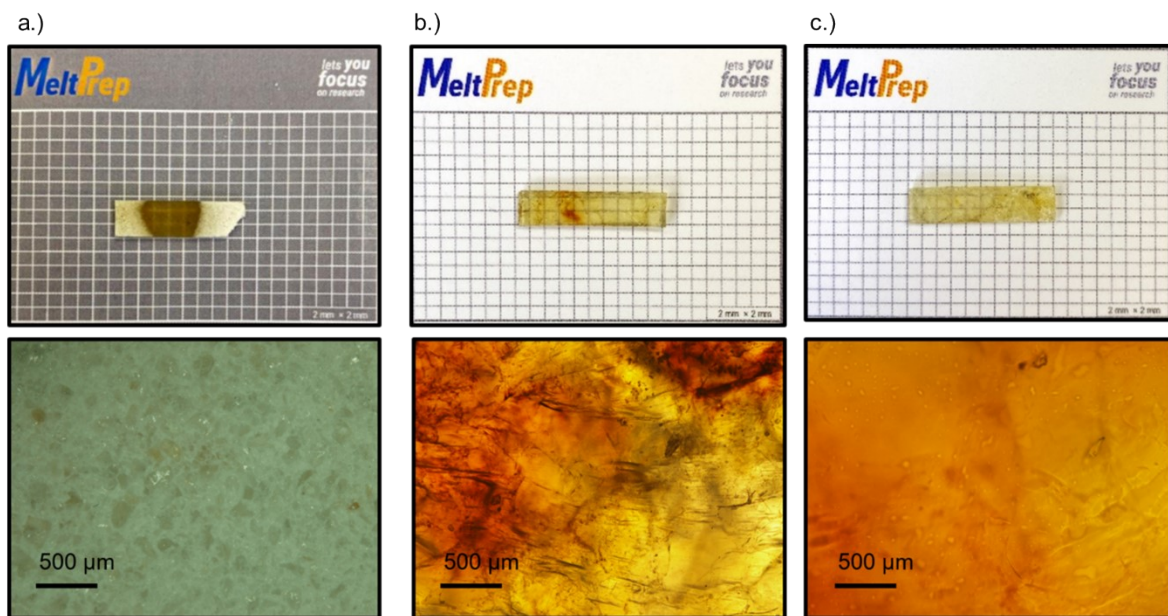
Reshaping and reprocessing

Figure 9 SI Remolding of frontally cured a.) PH20, b.) SH20 and c.) SH25 sample with VCM device sample and microscopy image of surface at 5-fold magnification.