Supporting Information for:

Additive manufacturing of highperformance polycyanurates via photoinduced catalytic poly-trimerization

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Materials and Experimental Methods

Materials

Cyanate ester novolac PT-30 was kindly gifted from Arxada AG.4- Nonylphenol, Phenyl cyanate (both abcr GmbH), Irgacure 261 (Ciba Geigy special chemicals), acetonitrile, chloroform HPLC grade, methanol HPLC grade and potassium bromide FT-IR grade (both Merck KGaA) were purchased from the respective companies. All reagents and monomers were used without further purification.

Reaction Phenyl-OCN



Scheme S1: Schematic reaction mechanism of the monofunctional phenyl cyanate.

A formulation containing 94 wt% Phenyl cyanate, 5 wt% NP and 1 wt% I261 was prepared. The formulation was homogenized by means of ultrasonic bath. After mixing, the formulation was analyzed directly by photo-DSC and subsequently with NMR. After irradiation at elevated temperature, the weight loss was documented.

Phenyl cyanate:

¹H-NMR: (600 MHz, CDCl₃) δ (ppm): 7.45-7.20 (m, 5H, aromat. H).

¹³C-NMR: (600 MHz, CDCl₃) δ (ppm): 109 (cyanate), 115, 126, 130, 153 (phenolic).

2,4,6-Triphenoxy-1,3,5-triazine:

¹H-NMR: (600 MHz, CDCl₃) δ (ppm): 7.40-7.05 (m, 5H, aromat. H).

¹³C-NMR: (600 MHz, CDCl₃) δ (ppm): 121, 126, 129, 151 (phenolic), 174 (triazine).



Figure S1: ¹H-NMR of phenyl cyanate (CDCl₃, 600 MHz) δ: 7.45-7.20 (m, 5H, aromat. H).



Figure S2: ¹H-NMR of 2,4,6-triphenoxy-1,3,5-triazine (CDCl₃, 600 MHz) δ: 7.40-7.05 (m, 5H, aromat. H).





195 190 185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 % f1 (ppm)

Figure S4: ¹³C-NMR of 2,4,6-triphenoxy-1,3,5-triazine (CDCl₃, 600 MHz) δ: 121, 126, 129, 151 (phenolic), 174 (triazine).

Formulation and sample preparation of PT-30

A formulation containing 94 wt% PT-30, 5 wt% NP and 1 wt% I261 was prepared. The formulation was homogenized by means of ultrasonic bath and kept at least 0.5 h at 80 °C in the vacuum oven. After that, the formulation was used directly for further tests. The specimens for mechanical testing were prepared by thermal curing of the formulations in silicon molds (for DMTA: 5 x 2 x 40 mm³) The PT-30 formulation were preheated to 90 °C and filled into a preheated silicon-mold (90 °C) and put in the oven for 24 h at 120 °C. The preparation of the specimens was completed with a post-processing program in an oven (Figure S5).

Photo-DSC

Photo-DSC measurements were conducted on a Netzsch DSC 204 F1 with autosampler. All measurements were performed isothermally between 80 and 100 °C under N₂ atmosphere. The formulations (11 ± 1 mg) were irradiated twice with filtered UV-light (320–500 nm) via an Exfo OmniCureTM series 2000 broadband Hg lamp under constant N₂ flow (20 mL/min). The light intensity was set to 1.0 Wcm⁻² at the tip of the light guide corresponding to ~60 mWcm⁻² on the surface of the sample. The heat flow of the polymerization reaction was recorded as a function of time. The times when the maximum of heat evolution was reached (t_{max}) as well the peak height (h) was used as indicators for the reactivity of a formulation. All measurements were performed in triplicates.

HPLC

HPLC was measured on was measured on a Hewlett-Packard Agilent 1100 Series HPLC Value System using a normal phase LiChrosorb CN-5µ, 4.6 x 150mm column. A UV detector was used for signal recording. The solvent mixture used was chloroform-methanol. Quantitative evaluation was performed by integration based on a calibration line of the monomer used.

STA

A Netzsch Jupiter STA 449 F1 thermal analysis instrument with autosampler was used to conduct combined TGA and DSC experiments, which were used to assess the volatility and thermal stability of the investigated formulations. One set of measurements was performed with a temperature ramp from 25 to 500 °C under N₂ atmosphere (10 K/min), and the second set was conducted isothermally under N₂ atmosphere at 100 °C (2 h). All samples were accurately weighed into aluminum DSC pans (10 ± 2 mg) and measured at a constant gas flow rate (40 mL/min). The mass loss and DSC signal were recorded.

IR

Transmission infrared spectra were recorded on a Perkin Elmer Spectrum 65. For the measurements, the samples were ground and pressed with 50 times the amount of KBr. The

spectra were collected in a range between 4000-500 cm⁻¹ and 16 scans were made for each spectrum. For the analysis of the results, the software Spectrum from Perkin Elmer in version 10.03.07.0112 was used.

Hot Lithography

3D-structuring via Hot Lithography was performed on a Caligma 200 UV printer. The Hot Lithography printer setup uses a 375 nm diode laser source. This beam is scanned over a 2-dimensional plane using a galvanometer scanning system. All parts that had direct contact with the formulation were heated to 90 °C; this includes the material vat, the building platform, and the recoating unit. All specimens were printed with a scan speed of 1 m/s, 10 repetitions per layer, an energy intensity of 5800 mJ/cm² and a layer thickness of 50 μ m with fresh coated resin. The laser spot on the surface of the material vat has a diameter of 18 μ m. The preparation of the specimens was completed with a post-processing program in an oven (Figure S5).



Figure S5: Post-processing program for the specimen with a heating rate of 1 K/min.

Stability Tests and Viscosity

The prepared formulations have been kept at 100 °C for the specific time. Rheology tests of the mixtures were conducted on a modular compact rheometer (MCR 300, Physica Anton

Paar). The viscosity of the formulations was measured above the printing temperature of 90 °C at 100 °C (5 min acclimatization time before measurement) with a PP-25 measuring system (diameter 25 mm). A distance of 100 μ m between Peltier plate and stamp plate was set. Measurements were conducted in rotation mode with a constant shear rate of 100 s⁻¹.

SEM

To determine layer quality, the 3D printed parts were characterized via scanning electron microscopy (SEM). The sample morphology was imaged with a Phillips XL-30 after sputtering with a thin gold layer.

Dynamic mechanical analysis

Dynamic mechanical analysis was performed in a three-point bending setup with a support span length of 40 mm (test specimens dimensions of $20 \times 6 \times 1.5$ mm³) at 1 Hz and 0.06 % dynamic strain (TA Instruments, DMA Q800), and the temperature was varied from -100 °C to 400 °C at a heating rate of 3 K/min. All samples were polished with sandpaper to reach uniform geometries and to remove defects from the photopolymer surface.

Creep Tests

Short-time creep tests were done at a TA Instruments DMA 850 in bending mode at a bending stress of 5 MPa. Support span was 10 mm, the specimens had a thickness of 0.8 mm and a width of 5 mm.

Results

Conversion determined via Photo-DSC

The conversion via photo-DSC was based on the monofunctional system. By means of Photo-DSC, the released energy of the system was determined (ΔH = 610 J/g). The samples were weighed before and after the measurement to determine the average weight loss (m_{Loss} = 17.5 %). Furthermore, the monofunctional samples were analyzed for their conversion by HPLC (α_{HPLC} = 86 %). With the molecular weight of M_{PhenylOCN} = 119 g/mol and the mass fraction in the mixture ($m_{PhenylOCN}$ = 94 %), the following Equation S1 is obtained for the theoretical enthalpy per cyanate group

$$\Delta H_{0} = \left(\frac{\Delta H \times (1 - m_{Loss})}{\frac{m_{PhenylOCN} \times M_{PhenylOCN}}{1000}}\right) \times a_{HPLC}^{-1}$$

Equation S1: Calculation of the theoretical enthalpy per cyanate group.

Based on this, the photo-DSC values from the measurements (Figure S6) of the PT-30 formulation could now be used to calculate the conversion at the various temperatures (Table S1), taking into account the proportion of monomer ($m_{PT-30} = 94$ %) as well as the molecular mass of the repeating unit ($M_{PT-30} = 131$ g/mol). A loss of mass could not be observed here.

$$a_{PT-30} = \left(\frac{\Delta H \times M_{PT-30}}{m_{PT-30}}\right) \times 10^{-1} \times \Delta H_0^{-1}$$

Equation S2: Calculation of the conversion for the PT-30 formulation.

The height of the peak from the photo-DSC correlates with the rate of polymerization (Rp) which in turn correlates with the speed of curing. Rp is calculated as follows with $\rho = 1.2^{[1]}$

$$Rp = \left(\frac{h \times \rho}{\Delta H_0}\right)$$

Equation S3: Calculation of the rate of polymerization Rp.

Table S1: Photo-DSC values and calculated conversion via Photo-DSC of the PT-30 formulation at different temperatures.

	PT-30 cured 80 °C	PT-30 cured 90 °C	PT-30 cured 100 °C
ΔΗ [J/g]	240 ± 10	260 ± 10	300 ± 20
Conversion [%] without post-curing	45 ± 2	48 ± 2	55 ± 3



Figure S6: Temperature dependence of photo-DSC results for the PT-30 formulation: enthalpy change (Δ H black) and time until maximal heat is released (t_{max} green).Conversion determined via AT-IR

As described in the main section, the integrals of the stretching vibration of the C \equiv N bond at 2270 and 2235 cm⁻¹ were evaluated against a reference vibration at 2970 cm⁻¹ to calculate the conversion α_{IR} according to Equation S4 where A_t is the relative cyanate concentration in time t and A_0 is the initial relative cyanate ester concentration.

$$a_{IR} = 1 - \frac{A_t}{A_0}$$

Equation S4: Calculation of conversion α via IR.

Table S2: Calculated conversion of the cyanate ester groups..

	PT-30 cured	PT-30 cured	PT-30 cured	PT-30 thermally
	80 °C	90 °C	100 °C	cured at 120 °C
Conversion [%] without post- curing	50 ± 2	53 ± 2	58 ± 2	51 ± 2
Conversion [%]	83 ± 2	85 ± 2	86 ± 2	82 ± 2

with post-curing
Creep Tests

In order to test the durability of the samples without or with post-curing, creep tests were carried out at room temperature so that no post-curing takes place during the experiment (Figure S7). This results in the creep modulus over time (Figure S8).



Figure S7: Stress-time behavior for the materials with (green) and without post-curing (black).



Figure S8: Creep modulus over time for the materials with (green) and without post-curing (black).

Volatility

For 3D printing via Hot Lithograhpy, the formulation must be non-volatile at the selected printing temperature. Therefore, the pure formulation over 2 h at 100 °C was analyzed by STA (Figure S9).



Figure S9: STA of the plain PT-30 formulation at 100 °C.

Stability Tests

Further, the formulation must also be temperature stable over a longer period of time, to the extent that no or little thermal polymerization proceeds. For this purpose, the samples were kept in the oven and their viscosity was monitored at regular intervals by rheology measurements. As long as a value below 20 Pas is maintained, the formulation is printable. The main formulation is stable over 3 days and theoretically still printable on day 4. In contrast, formulations without a catalyst or co-catalyst do not show any increase in viscosity.



Figure S10: Stability Tests at 100 °C by means of viscosity measurements.

References

[1] Arxada, Primaset [™] PT-30 A Multifunctional Cyanate Ester Delivering High Tg and Inherent Flame Retardancy, **2017**.