Supporting Information

Approaches of combining a 3D-printed elastic structure and a hydrogel to create models for plant-inspired actuators

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1 Materials and Method

1.1 Materials

2,2'-azobis(2-methyl-propionitile) (AIBN) (Honeywell Fluka, Berlin, Germany) was recrystallized from ethanol before use. The poly(ethylene glycol) di-methacrylate (PEG-DM, $\overline{M_n}$ = 550 g·mol^{-1}), *N*-vinyl-2-pyrrolidone (NVP), di(ethylene glycol) vinyl ether (DEG-VE), poly(ethylene glycol) methacrylate (PEG-M, $\overline{M_n}$ = 360 g·mol^{-1}), poly(ethylene glycol) methyl ether methacrylate (PEG-MEM, $\overline{M_n}$ = 1100 g·mol^{-1}), sodium hydroxide (NaOH), ethanol, and chloroform were purchased at Sigma-Aldrich (Taufkirchen, Germany), 1,4-dioxane was purchased at Carl Roth (Karlsruhe, Germany), 1,2-dichloroethane was purchased at Acros Organics (Geel, Belgium) and were all used as received. Model materials and support material for the 3D-printer were purchased from Stratasys (Frankfurt, Germany).

1.2 Determination of T_g and T_m

Glass transition temperature and melting transition temperature were determined by differential scanning calorimetry (DSC) experiments using Netzsch DSC 204 Phoenix (Netzsch, Selb, Germany). The temperature program was set between -100 to +100 °C with heating and cooling rates of 10 K·min^{-1}. Samples were placed in sealed aluminium pans. Samples were heated twice and T_g and T_m were determined from the second heating run in order to remove influence from material history.

1.3 3D-Printing

3D-printing was performed using Object 260 Connex (Stratasys, Eden Prairie, MN, USA). Printed materials were immersed into different solvents at room temperature and 60 °C for 24 hours to investigate compatibility between 3D-printed materials and hydrogel synthesis conditions.

1.4 Immersion Tests

Printed materials were immersed into different solvents at room temperature and 60 °C for 24 hours to investigate compatibility between material and hydrogel synthesis conditions. Their aspect and mechanical properties were qualitatively evaluated. In addition, mass degree of swelling ($Q_{w,print}$ in weight percentage) was calculated according to equation 1, where m_{final} is the mass of the material after immersion and $m_{initial}$ is the mass of the material after printing. Before weighing, solvent from surfaces was carefully removed.

$$Q_{\mathrm{w,print}} = \frac{m_{\mathrm{final}}}{m_{\mathrm{initial}}} \times 100 \quad (1)$$

1.5 Extraction and Gel Content

Hydrogels were extracted in distilled water over 24 hours by changing solvent every hour. Then hydrogels were dried under vacuum at 25 °C until constant weight was achieved. Gel content was calculated according to equation 2, where G is the gel content in weight percentage, $m_{extracted}$ is the mass of the extracted and dried hydrogel and $m_{initial}$ is the mass of the hydrogel after gelification.

$$G = \frac{m_{\mathrm{extracted}}}{m_{\mathrm{initial}}} \times 100 \quad (2)$$

1.6 Mass Degree of Swelling

Hydrogels were swollen in distilled water until constant weight was achieved. Before weighing, water from the hydrogel surfaces and pores was carefully blotted with filter paper. Mass degree of swelling was calculated according to equation 3, where Q_w is the mass degree of swelling in weight percentage, $m_{swollen}$ is the mass of the swollen hydrogel and m_{dry} is the mass of the dry hydrogel after the extraction process.

$$Q_{\mathrm{w}} = \frac{m_{\mathrm{swollen}}}{m_{\mathrm{dry}}} \times 100 \quad (3)$$

1.7 Swelling Kinetics

In order to determine swelling kinetics, dry hydrogels were weighted and swollen in excess amount of distilled water. At selected intervals of time, the hydrogels were removed from the swelling agent, water from surfaces and pores was carefully blotted with filter paper, and the hydrogels were weighted. Swelling equilibrium was determined by swelling the hydrogels in excess amount of distilled water until constant weight was achieved. Swelling kinetic curves were obtained by plotting the difference, before and after swelling, in hydrogel weight as a function of time.

1.8 Tensile Tests

In order to determine elastic modulus (E) and elongation at break (ε_b), printed materials underwent tensile tests at room temperature using Zwick 2.5 (Zwick, Ulm, Germany). The samples were cut into standard samples (ISO-527-2/1BB) and the thickness of the samples was 1.4 mm. The load cell was 20 N. The deformation rate was 10 mm·min^{-1}.

Table S1. Reactant (X) and mole of X and PEG-DM (n_X, $n_{PEG\text{-}DM}$) used for synthesis of hydrogels.

X	n_X (mol%)	$n_{PEG\text{-}DM}$ (mol%)
NVP	99.5	0.5
	3	97
	30	70
	50	50
DEG-VE	90	10
	85	15
	80	20
	70	30
	50	50
PEG-ME	90	10
PEG-MEM	90	10

Table S2. E-modulus (E) and elongation at break (ε_b) of samples pulled along x-axis (E_x, $\varepsilon_{b,x}$), y-axis (E_y, $\varepsilon_{b,y}$), or z-axis (E_z, $\varepsilon_{b,z}$) directions, and glass transition temperature (T_g) of printed Agilus30 and TangoBlackPlus materials.

		Agilus30	TangoBlackPlus
E (MPa)	E_x	0.59 ± 0.05	0.51 ± 0.06
	E_y	0.62 ± 0.03	0.49 ± 0.02
	E_z	0.31 ± 0.06	0.09 ± 0.16
ε_b (%)	$\varepsilon_{b,x}$	223 ± 8	151 ± 9
	$\varepsilon_{b,y}$	223 ± 9	157 ± 9
	$\varepsilon_{b,z}$	186 ± 9	110 ± 12

Table S3. Mole of PEG-DM and DEG-VE ($n_{PEG\text{-}DM}$, $n_{DEG\text{-}VE}$), gel content (G), and mass degree of swelling (Q_w) of hydrogels.

$n_{PEG\text{-}DM}$ (mol%)	$n_{DEG\text{-}VE}$ (mol%)	G (wt%)	Q_w (wt%)
10	90	0.45 ± 0.02	249 ± 4
15	85	0.58 ± 0.00	195 ± 7
20	80	0.56 ± 0.00	180 ± 22
50	50	0.61 ± 0.05	151 ± 2

a) b)

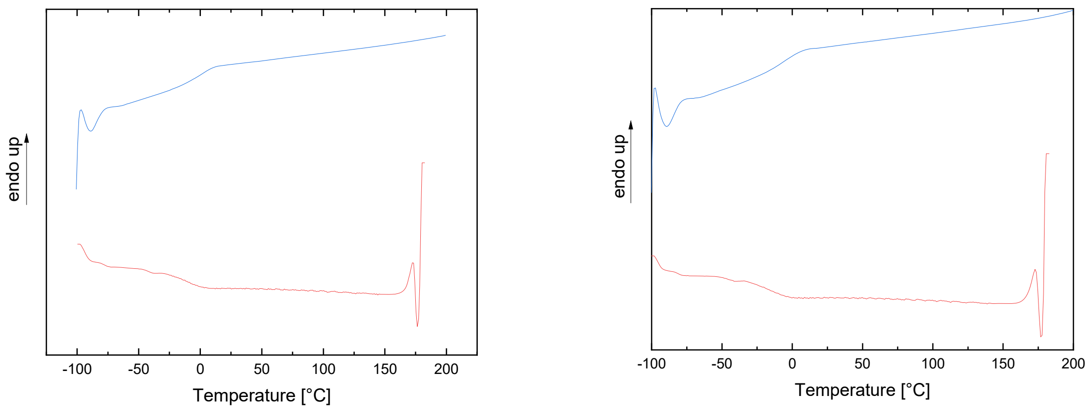

Figure S1. DSC thermogram of (a) AG and (b) TBP in blue heating and red cooling direction.

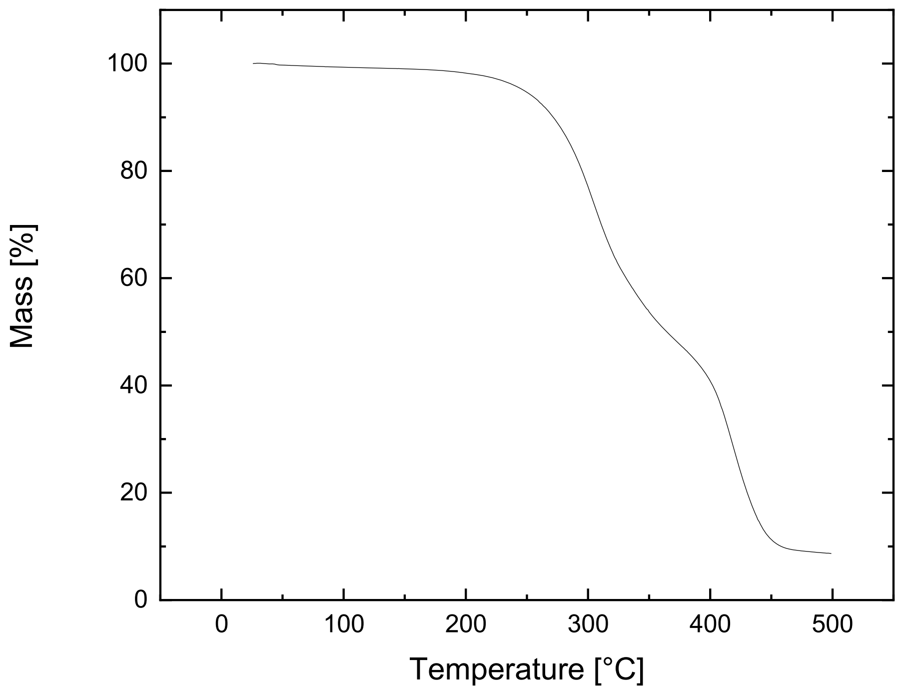

Figure S2. Thermogravimetric analysis of AG

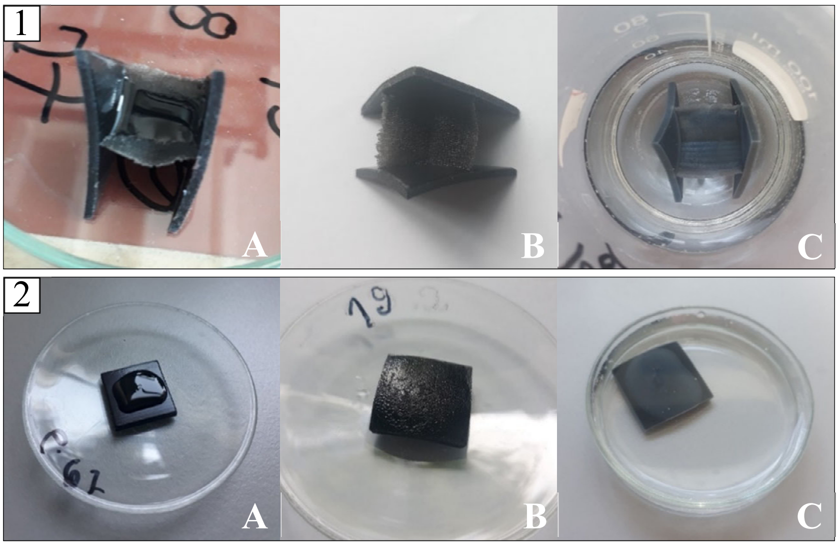

Figure S3. Moulding of hydrogel solution (A), multi-material after gel polymerization (B) and swelling of hydrogel (C) onto skeleton (1) and surface from xy-axis (2) made of TangoBlackPlus.

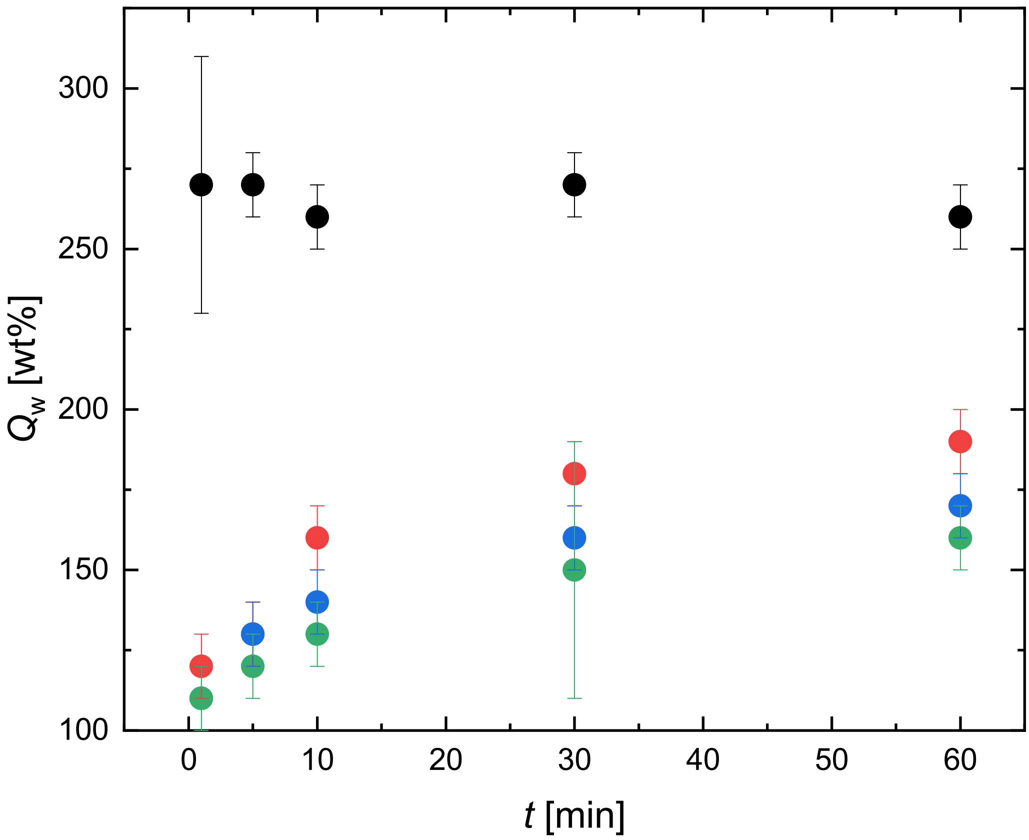

Figure S4. Mass degree of swelling of hydrogels based on DEV-VE and PEG-DM at different ratio (Q_w) as a function of time of immersion (t); the bar gives the standard deviation value; black: 10 mol%, red: 15 mol%, blue: 20 mol%, green: 50 mol%.