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Robust thermostable polymer composition based on poly[*N*,*N*′-(1,3-phenylene)isophthalamide] and 3,3-bis(4-acrylamidophenyl)phthalide for laser 3D printing

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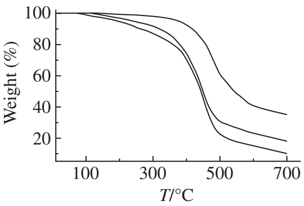
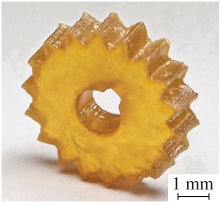
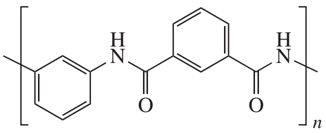
A photopolymer composition based on poly[*N*,*N*′-(1,3-phenylene)isophthalamide] and 3,3-bis(4-acrylamidophenyl)phthalide was developed and utilized for the formation of 3-dimensional structures using the laser stereolithography method with a high reproducibility and the absence of any autopolymerization effects. The obtained 3D structures were mechanically strong and characterized by a high thermal stability (up to 415 °C), which makes them promising as high-tech plastics for constructional purposes.





Laser 3-dimensional (3D) printing allows one to significantly reduce production expenses, speeds up manufacturing process, and can provide complex geometrical structures.[1–4] It is increasingly being introduced into high-tech manufacturing, *e.g.*, aircraft construction.[1] One of the most accessible methods of laser 3D printing is the laser stereolithography (SLA). This process includes a directional, layer-by-layer photoinduced cross-linking of the liquid photopolymer composition (PPC) according to the computer designed 3D model. Thus, 3D objects possessing complicated geometric shapes with specific architectonics can be formed at the resolution of tens of microns. However, only a limited number of commercial PPCs based mainly on methacrylate aliphatic derivatives has been developed for the SLA technology.[1] In addition, the 3D objects built from such compositions cannot be utilized under harsh operating conditions (*e.g.*, aggressive media, elevated temperatures, *etc.*), which significantly limits the practical application of the SLA method.



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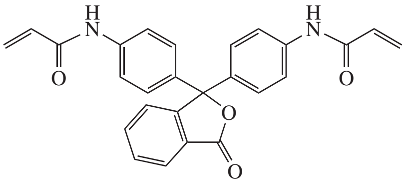

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We have previously reported[5] that thermally stable and mechanically strong 3D structures can be produced using PPC based on poly[*N*,*N*′-(1,3-phenylene)isophthalamide] **1**[†] and 4-acrylamidophenyl ether. However, the poor solubility of the latter in the composition resulted in relatively low values of Young's modulus for the obtained 3D structures, which was due to the low density of cross-linking of polymer chains. To solve that problem, this work was aimed at the utilization of 3,3-bis(4-acrylamidophenyl)phthalide **2** as the cross-linker instead of 4-acrylamidophenyl ether. Compound **2** contains a cardo phthalide group and thus exhibits a good solubility in various organic solvents. It was obtained in a high yield by condensation of two equivalents of acryloyl chloride and 3,3-bis(4-aminophenyl)phthalide.[‡] Compound **1** was selected as the matrix polymer due

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[†] The IR spectra were recorded on an Alpha (BrukerOptik GmbH) spectrometer in the range of 4000–400 cm^{-1} in KBr pellets. The NMR spectra were recorded on Bruker WP-200 SY (200.13 MHz) and Varian VXR-500S (500 MHz) spectrometers in DMSO-d_6 using TMS as the internal standard.

Polymer **1** was prepared *via* polycondensation of equimolar amounts of *m*-phenylenediamine and isophthaloyl chloride in a *N*,*N*-dimethylacetamide solution at –10 °C for ~1.5 h. Once the reaction was completed, the solution was poured into ethanol (excess). The yield of polymer was quantitative. η_{inh} = 1.5 dl g^{-1} (*N*,*N*-dimethylacetamide, 20 °C). IR (ν/cm^{-1}): 3380 (N–H), 1653 (C=O). ^{1}H NMR, δ: 10.3 (N–H). ^{13}C NMR, δ: 164.83 (C=O). Found (%): C, 69.81; H, 4.58; N, 11.64. Calc. for $C_{14}H_{10}N_2O_2$ (%): C, 70.59; H, 4.20; N, 11.76.

[‡] *3,3-Bis(4-acrylamidophenyl)phthalide* **2** was prepared *via* condensation of a two-fold molar excess of acryloyl chloride and 3,3-bis(4-aminophenyl)phthalide in a solution of *N*-methyl-2-pyrrolidone at –20 °C for 30 min and at 20 °C for 30 min. The reaction product was separated by

to its high thermal stability, good physicomechanical characteristics, and solubility in solvents of amide type.

Since the obtained substances are solids, it seemed reasonable to use an active amide type solvent, *N*,*N*-dimethylacrylamide (DMAA), which was chosen due to its good dissolving power towards compounds **1** and **2**. Furthermore, it is not only the diluent of polymer systems, but it can also participate in photo(co)polymerization processes. The PPC composition was predetermined, first of all, by the solubility of compounds **1** and **2** in this active solvent.[§] A mixture of Irgacure 369 and Irgacure 819 was employed as the photoinitiator. As it was shown earlier,[6] the mixture of several photoinitiators can substantially increase the efficiency of the photoinduced polymerization process. To determine the effectiveness of the photoinitiated cross-linking process, we have investigated materials obtained by curing this composition under the irradiation by a DRT-500 lamp for 5 (CPPC-5), 10 (CPPC-10) and 20 (CPPC-20) min.[¶]

The uncured part of PPC was extracted by DMAA for the determination of the cross-linking degree. It was found that a sequential increase in the irradiation duration leads to a significantly increased content of the insoluble residue. CPPC-5 retained only 73% of the initial mass, while CPPC-20 was practically insoluble in DMAA (its weight loss did not exceed 5% after the extraction). Note also that the extraction was accompanied by a linear swelling of the samples with an increase in size by 15–40%. The largest swelling was in the case of CPPC-5, and the least one was observed for CPPC-20, indicating a more homogeneous process of photoinduced cross-linking. Drying of the swelled CPPC-20 sample *in vacuo* upon a gradual increase in temperature from 30 to 80 °C has completely restored the initial size of the original film. Thus, it was shown that the degree of cross-linking in the composition depends on the irradiation duration. Moreover, the presented results indicate the formation of semi-interpenetrating polymer networks consisting of chemically unconnected and inseparable chains of the 3D polymer formed by DMAA and compound **2** (shown below) and linear polymer **1** during the photocuring process.[7]

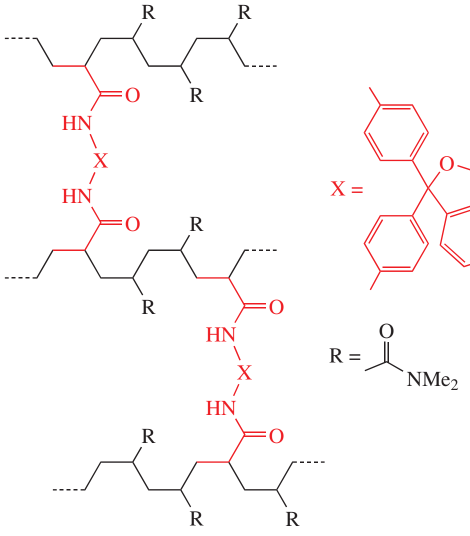

Table 1 Thermal and mechanical properties of the photocured materials.

Sample	$T_{10\%}$/°C	σ/MPa	ε (%)	Young's modulus/GPa
CPPC-5	260	35.2 ± 1.3	56.7 ± 4.4	1.84 ± 0.21
CPPC-10	320	58.1 ± 2.9	48.4 ± 3.9	2.46 ± 0.58
CPPC-20	415	102.3 ± 3.6	9.2 ± 2.1	4.07 ± 0.67

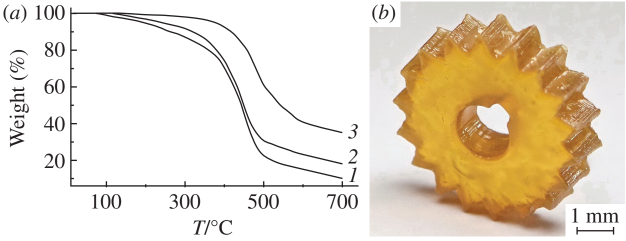

Figure 1 (*a*) TGA curves of (*1*) CPPC-5, (*2*) CPPC-10, and (*3*) CPPC-20; (*b*) micrograph of the 3D structure (a gear wheel) formed by the SLA method.

The mentioned differences in the degree of cross-linking cause a significant effect on the thermal characteristics of the prepared materials [Table 1, Figure 1(*a*)].[††] For example, the temperature of 10% weight loss for CPPC-5 and CPPC-10 is 260 and 320 °C, respectively. At 700 °C, the weight loss exceeds 80% in both cases. In contrast, the temperature resistance of CPPC-20 is 415 °C, and the coke residue at 700 °C is above 35%. Thus, all obtained CPPCs demonstrate a high temperature resistance despite the presence of aliphatic moieties, while the cross-linking degree is maximal for the CPPC-20 composition.

Mechanical properties of the obtained materials were also evaluated (see Table 1). The tensile strength (σ) and Young's modulus increased with raising the irradiation time, while the tensile elongation (ε) decreased. For CPPC-20, these values were 102.3±3.6 MPa, 4.07±0.67 GPa, and 9.2±2.1%, respectively. Thus, mechanical characteristics of these samples were significantly improved in comparison with those observed for PPC previously reported.[5]

The acquired data have preliminary demonstrated that the developed PPC was capable of forming mechanically strong and thermally stable materials *via* the photoinduced polymerization. The next step was to explore the possibility of forming 3D structures using the SLA method.[‡‡] Figure 1(*b*) shows an example of the 3D gear wheel structure formed by this method which allowed us to reproduce the original model with a high accuracy. The selected ratio of the PPC components excluded the diffusion-driven polymerization, where the formed radicals diffuse from an irradiated zone, so the polymerization also occurs outside

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precipitating in water. The yield was 96%, mp 220.2–222.6 °C. IR (ν/cm^{-1}): 3273 (N–H), 1658 (amide C=O). ^{1}H NMR, δ: 12.0 (N–H). ^{13}C NMR, δ: 166.20 (amide C=O). Found (%): C, 73.33; H, 4.84; N, 6.54. Calc. for $C_{26}H_{20}N_2O_4$ (%): C, 73.58; H, 4.72; N, 6.60.

[§] To obtain the PPC, separately prepared solutions of compounds **1** and **2** in DMAA were combined under vigorous stirring and the addition of photoinitiators Irgacure 369 and Irgacure 819. The mixture was additionally stirred for 24 h until complete homogenization. The obtained PPC contained **1** (10 wt%), **2** (10 wt%), Irgacure 369 (1 wt%), and Irgacure 819 (0.8 wt%).

[¶] To obtain CPPC, the PPC was placed between two glass plates (d = = 300 μm) and irradiated with a DRT-500 lamp for the indicated time intervals (5–20 min).

[††] The thermal stability of the obtained materials was estimated by the TGA method using a synchronous thermal analyzer STA 449 F3 (Netzsch) in air atmosphere at a heating rate of 5 K min^{-1}.

The mechanical characteristics were studied using an Instron 4465 test machine at 20 °C under a humidity of approximately 50% at a 2 mm min^{-1} stretching rate. The specimen dimensions were 50 × 5 × 0.3 mm^3 and the number of parallel measurements was 5.

[‡‡] The formation of 3D structures was carried out on a laser stereolithography setup reported previously.[5] CNI-Laser MDL-III-405 diode laser (λ = 405 nm and a maximum radiation power of 100 mW) was used as a laser source. PPC was placed in a metal cuvette (diameter of 50 mm), where a thin (200 nm) fluoroplastic film was used as the bottom. Thin PPC layers, which were formed on a movable substrate fixed on a vertical motorized movement, were irradiated providing a layer-by-layer formation of the 3D model. The radiation was administered from the bottom through a fluoroplastic film. The laser beam was moved using

that zone.[8] Thus, the SLA method employing the developed PPC makes it possible to relatively easy form the required size of the key fragments of desired structure and therefore to avoid the currently laborious process of material removal. Once the object was formed, it was additionally exposed to irradiation using a DRT-500 lamp for 20 min. This irradiation regime contributes to the formation of the most heat-resistant and mechanically strong materials. It was also found that the obtained model possesses a thermal stability similar to the test samples.

In conclusion, this work revealed that aromatic heterochain polymers can be used for the preparation of PPC, which is suitable for creation of mechanically strong and thermally stable 3D structures using the SLA method.

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an Ateko-TM LScanH-XY single-mirror galvanometer at the maximum scanning speed of 1 m s^{-1} in combination with the Ronar-Smith SL-405-100-160 F-theta lens, which allowed the laser to spot the required size (about 100 μm) on the whole working plane of the bottom of the cuvette. Ateko-TM LDesignerSLS software was used for the system management, allowing us to prepare the control program for the 3D model and to carry out the process of its manufacturing. After the completion of 3D printing and the removal of the residual material, the model was additionally exposed to irradiation using a DRT-500 lamp for 20 min to complete its curing.