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Hot-lithography SLA-3D printing of epoxy resin

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Abstract: The Hot-lithography SLA 3D printing technology has been used to print epoxy resins with high reactivity in order to achieve 3D printed structures. Different hydroxyl containing compounds were investigated as chain transfer agents, and the viscoelastic properties of UV-cured materials were fully characterized. The most promising formulations were studied at a high temperature, the 3D printing process parameters were defined, and the printed object was fully characterized. By combining the suitable precursor materials in the photocurable formulation with the advanced hot-lithography process, it is possible to produce 3D printed structures that are characterized by outstanding thermo-mechanical properties and good printability precision.

Keywords: hot-lithography, 3D printing, epoxy resin, chain transfer agent.

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1. Introduction

The development of suitable functional polymeric materials for exploitation of the 3D printing technology is becoming more and more attractive for both academia and industrial applications [1, 2]. The additive manufacturing technology permits fully customized objects to be fabricated with a high level of geometrical complexity, but at reduced fabrication times and costs. In 3D printing methods, an object is fabricated through the layer-by-layer deposition of a material, using a printing head, nozzle or another printer technology. Among the different 3D printing approaches, those based on light induced polymerization e.g. Stereolithography (SLA) and Digital Light Processing (DLP) are becoming particularly interesting. These technologies allow 3D objects to be produced through the spatially controlled solidification of a liquid resin, while exploiting the fast photopolymerization process [3-6], and they have undergone a huge development in the last few years.

The recent introduction of a heated printing chamber in commercial printers – the so-called Hot-lithography – allows 3D printing to be performed at high temperatures with the aim of studying the temperature-dependent effects within the printing process [7] as well as exploiting the use of highly viscous resins, which can be processed more easily at higher temperatures.

Conventional SLA systems operate at room temperature with low viscous resins and a very low molecular weight, and they are used as photocurable precursors. This leads to highly crosslinked networks in the printed parts, which in turn leads to low levels of toughness and poor dimensional stability under heat [8]. On the contrary, the hot-lithography developed heated coating mechanism, which is capable of processing high viscous resins, leads to significantly tougher materials. The purpose of the coater is to apply a continuous resin layer onto the transparent vat. This replaces the conventional material reservoir and enables the printer to process highly viscous resins.

The possibility of performing a 3D printing process at elevated temperatures not only affects the viscosity of a resin, but also its reactivity, and it makes it possible to process new types of resins which are not sufficiently reactive when processed at room temperature (r.t.). The use of hot-lithography could expand the printable material portfolio, which is one of the limits of all additive manufacturing processes, and especially of stereolithography.

Although the cationic photocurable process of epoxy resin may be used for important SLA technology applications to achieve 3D printing structures characterized by low shrinkage, as well as high modulus and high thermo-mechanical properties, the viscosity of bisphenol-A-diglycidyl ether (BADGE) is very high and this makes it unsuitable for many printing processes. Moreover, the reactivity of epoxy resin is much slower than that of acrylates or methacrylates. Furthermore, while

radical polymerization is affected less by temperature, it is well known that cationic polymerization is strongly temperature dependent.

The reactivity of epoxy toward cationic photopolymerization could also be enhanced by using suitable additives. The important acceleration effect of epoxy resins in cationic ring-opening polymerization, due to the presence of hydroxyl-containing compounds in cationic photocurable formulations, has been well documented in literature. The presence of alcoholic additives can influence the kinetics of photopolymerization and the properties of the cured materials. This is a consequence of the activated monomer (AM) propagation mechanism described by Kubisa and Penczek [9, 10], which competes with the activated chain end (ACE) mechanism for the ring opening polymerization process.

A decrease in crosslinking density is induced by this chain transfer reaction, with a delay of vitrification and therefore an enhancement of the epoxy group conversion and of the polymerization rate. As a consequence, significantly tougher but also more flexible polymeric networks are achieved [11-17]. Nevertheless, it is important to accurately balance the additive content in order to enhance the cationic ring-opening polymerization rate without significantly affecting the very high T_g and good thermo-mechanical properties of UV-cured epoxy networks.

For this reason, in this work, we have investigated the efficiency of using a hydroxyl containing chain transfer agent in a BADGE resin during 3D printing, coupling with the curing of the layer at high temperatures using the hot-lithography technology. Different hydroxyl containing compounds were investigated as chain transfer agents and the viscoelastic properties of UV-cured materials were fully characterized. The most promising formulations were studied at high temperatures, the 3D printing process parameters were defined, and the printed object was fully characterized. By combining the suitable precursor materials in the photocurable formulation with the advanced hot-lithography process, it has been possible to produce 3D-printed structures characterized by outstanding thermo-mechanical properties and good printability precision.

2. Material and methods

2.1 Materials

The considered epoxy resin was the diglycidyl ether of bisphenol-A (**BADGE**), the cationic photoinitiator (**PI**) was triarylsulfonium hexafluoroantimoniate salt, which was added to each formulation at 3% in weight. The resin and the photoinitiator were both provided by Aldrich. Trimethylolpropane (**TMP**), and polypropylenglycole 425 g/mol (**PPG**) and polytetrahydrofuran 2000 g/mol (**PTHF**) were also purchased from Aldrich. Anthracene was added as a photosensitizer during the printing process of the resin.

2.2 Sample preparation

An aliquot of 3 wt% of the photoinitiator was generally added to the pristine BADGE epoxy resin. Different chain transfer agents were added to the BADGE-base formulations: trimethylolpropane, polypropylenglycole and polyTHF in the 5 to 30 mol % range with respect to the epoxy resin. The formulations were either photocured in a silicon mold or used for hot-lithography 3D printing.

2.3 Mechanical tests

The obtained photocured materials were mechanically tested by performing tensile tests, stress relaxation analyses and dynamic-mechanical thermal analyses (DMTA).

Various 30 mm long, 5 mm wide, and 1.8 mm thick specimens were prepared for DMTA. The shape of the tensile samples was based on the standard 5B tensile specimen.

An RSA-G2 TA instrument was used for the stress relaxation analysis performed in humid environments (in order to evaluate the usability of the material in ambient conditions similar to the human body): the test configuration was that of a three-point bending type in water at 37 °C. In such a test, a metal cylinder surrounds the samples and the clamps, the object is sealed with screws and in this way the system can be immersed in water to start the measurement. The samples were soaked in water at a temperature of 37°C for 30 minutes before starting the test. The test lasted 2 hours and the strain applied to the sample was 2%.

The tensile tests were conducted at a speed of 5 mm min⁻¹ with a 1 kN load cell.

The instrument used for the DMTA analysis was a DMA-2980 TA Instrument and a three-point bending type measurement configuration was adopted. The test parameters were: an amplitude of 10 µm, a preload force of 0.05 N and a frequency of 1 Hz. The test was started at a temperature of -50°C, and an isothermal step was then applied at this temperature for 5 minutes in order to equilibrate the sample and, finally, a temperature ramp was applied at a heat rate of 3 °C/min up to 180 °C.

2.4Photo-DSC

Photo-Differential Scanning Calorimetry experiments were conducted on Netzsch Photo-DSC 204 F1 Phoenix equipment endowed with an autosampler. The light sources for UV LED curing were used in combination with a glass-fiber filled double-core light guide (3 mm fiber diameter). All the measurements were conducted under an inert atmosphere (N₂ flow of 20 mL/min). The power of the UV lamp was calibrated at 1 W. The polymerization reaction heat flows were recorded over time, and the temperature was maintained at a constant value. Proteus-Thermal Analysis software by

Netzsch was used for the data analysis. The UV source was an Exfo OmniCure™ 2000 device with a broadband Hg-lamp (320-500 nm, 3 W cm⁻² at the tip of the light guide) coupled with the DSC.

2.5 Photo-Rheology

RT-NIR-photorheology measurements were performed on an Anton Paar MCR 302 WESP, with a P-PTD 200/GL Peltier, borosilicate glass plate (60 mm diameter, 6 mm thickness) and a PP25 measuring system. Additionally, the rheometer was coupled with a Bruker Vertex 80 FTIR spectrometer with external mirrors to guide the IR beam through the sample during the rheology measurement. The IR beam passes through the glass plate and is reflected by the PP25 measuring system before returning to the MCT-detector. An Exfo OmniCure™ 2000, with a broadband Hg-lamp (320-500 nm, 3 W cm⁻² at the tip of the light guide), was used for UV curing. The IR chamber was continuously purged with dry air. Spectra were recorded from 7000-4000 cm⁻¹ at a resolution of 8 cm⁻¹ and a frequency of 4 Hz.

2.6 Hot Lithography printer

The printer used in this work essentially has a bottom exposure SLA setup: the vat, the building platform and the coating unit may be heated up to 100 °C (80°C for the building platform). It has a laser power of 70 mW/cm² at a wavelength of 375 nm, while the laser spot diameter is set at 25 µm during printing. The setup of the machine is visible in Figure 1.

Insert Figure 1

3. Results and discussions

3.1. Selection of the photocurable formulation

As a preliminary step, the effect of different hydroxyl containing chain transfer agents were investigated on the final thermo-mechanical properties of a BADGE-based formulation. The aim was to enhance the reactivity of the cationic UV-curing process by decreasing the viscosity of the photocurable formulations, without affecting the thermo-mechanical properties of the crosslinked polymer network to any great extent. The investigated chain transfer agents (CTA) were: TMP, PPG and PTHF, and they were investigated in the 5 and 30 mol percentage range. The cured materials were characterized by means of DMTA analysis, which allows the elastic and viscous components of the material modulus to be evaluated over a very large temperature range. The tanδ-curve (tanδ = E''/E': ratio loss modulus/storage modulus) showed a maximum in the T_g region, and this was assumed as the T_g of the cured material. The tanδ-curves for the investigated photocurable

formulations are reported in Figure 2. It is evident that a linear decrease in T_g occurs for all the investigated chain transfer agent as the CTA content in the photocurable formulation increases. This is due to the chain transfer reaction involving the OH groups in the AM mechanism, with a consequent decrease in crosslinking density and an increase in polymer network mobility. The addition of TMP induced a decrease in T_g from 163 °C, for the pristine photocured BADGE, down to 137 °C for the BADGE-based formulation containing 30 mol% of TMP. The addition of PPG induced an even higher flexibilization of the crosslinked network, which reached a T_g of 72 °C for the photocured material obtained in the presence of 20 mol% of PPG. Finally, PTHF is the CTA that induced the highest flexibilization of the polymeric network, with a T_g of – 4°C for the crosslinked formulation containing 20 mol% of PTHF.

Insert Figure 2

After considering all these data, TMP was selected as the CTA in order to avoid extreme flexibilization of the crosslinked epoxy network and to maintain the good thermo-mechanical properties of the printed structure.

The next step was the photo-DSC investigation of the BADGE-based formulation containing TMP at different temperatures, with the aim of defining the best processing performance for hot-stereolithography. The PHOTO-DSC curves are reported in Figure 3 for the BADGE formulation containing TMP in the 10 to 30 molar% range at different temperatures: 25, 50 and 80 °C.

Insert Figure 3

The formulation containing 5 mol% of the CTA did not show any significant change in photoreactivity. The presence of the CTA at r.t. induced a delay in the cationic photocuring process, with a shift of the exothermicity starting time, which could be attributed to the opening polymerization of the epoxy ring, albeit a with a similar conversion (total heat of the reaction) to that of the pristine BADGE resin. When the cationic photopolymerization was investigated at 50 °C, all the formulations showed comparable reactivity, which was higher at r.t., and a higher conversion when the TMP content was increased. The formulation containing the 20 mol% of TMP showed the highest reactivity and conversion at 80 °C.

After considering all these data, the temperature of 80 °C was selected for the photorheology characterization. The photorheology analyses were coupled with FT-IR, and it was thus possible to collect conversion curves in real-time, the epoxy group conversion at gelation (C_g) and the final epoxy

group conversion (C_{final}), as well as the rheological data, that is, the time to gel point (t_g), the storage module (G'), the loss module (G'') and the shrinkage force (F_N). All these important data are shown in Table 1. The conversion curves, as a function of the irradiation time, obtained from the RTFT-IR analysis are reported in Figure 4.

Insert Table 1

Insert Figure 4

The conversion curves are in good agreement with the photo-DSC data, and show an enhancement of the photoactivity of BADGE in the presence of TMP, when photopolymerization takes place at 80 °C.

From the data shown in Table 1, it is possible to observe that the final conversion and the conversion at gel point increase for the BADGE formulation containing 20 mol% of TMP, and for this reason the recorded G' is the highest of the all the formulations. The time needed to reach gelation (t_g) explains the reactivity of the formulations; lower values mean higher reactivity of the resin. The mechanical behavior of the photopolymer is related to the value of G'_{max} , which reaches a plateau for a high conversion of resin. The shrinkage stress, expressed by the value of F_n , is lower than the pristine BADGE, but higher than the crosslinked formulation containing 10 wt% of TMP.

Lower values of t_g of the modified formulations are crucial for 3D-printing at a proper speed for the SLA printing process, while a high conversion at gel point and high G' give a good green strength to the resin that will be used to form the layer. In the end, lower shrinkage means a better resolution and dimensional control of the layer formation: the ring-opening reaction, due to the cationic photopolymerization of epoxy resin, leads to a higher dimensional stability of the products than radical photocured materials. Taking all these data into consideration, the BADGE-based formulation containing 20 mol% of TMP was selected for the printing process at 80 °C, since all these parameters give the best balance between higher thermal reactivity at 80 °C and the mechanical properties of the photocured material.

3.2. Hot-lithography of the epoxy formulation

The BADGE formulation containing 20 mol% of the TMP was selected for the hot-SLA printing process. The thermo-mechanical properties of the printed materials were characterized and compared with the UV-cured formulations; both curing processes were conducted at 80 °C. The $\tan\delta$ curves for the UV-cured formulations are reported in Figure 5a and compared with the same formulations

obtained by means of hot-SLA. The printed formulations showed similar T_g values, as measured by means of DMTA, to those of the UV-cured formulation. Moreover, the mechanical properties measured in the tensile test (Figure 5b) of the printed formulation resulted comparable with the UV-cured ones.

Insert Figure 5

These data show that the hot-lithography process does not in general affect the final properties of the UV-cured material when crosslinked at the same temperature.

A more complex geometry was printed with the same formulation, thereby showing the possibility of reaching a good resolution for such geometries. The small object shown in Figure 6 was printed to prove the printability of the epoxy-based resin: 100 μm was chosen as the layer thickness and the selected laser speed was 200 mm/s, while the process temperature was at 80 °C.

Insert Figure 6

This preliminary printed structure clearly demonstrates the possibility of exploiting the hot-SLA technique for the 3D printing of epoxy-based formulations. It is possible to print structures using epoxy resin, with high CAD fidelity, which show a good thermo-mechanical performance.

4. Conclusions

In this paper, we have investigated the importance of coupling the use of chain transfer agents with an elevated temperature to enhance the reactivity of BADGE resins in order to make them suitable for 3D printing technologies. In this way, we were able to achieve 3D-printed structures characterized by high thermo-mechanical properties.

Different chain transfer agents were investigated: TMP, PPG and PTHF. A linear decrease in T_g was observed as the CTA content in the photocurable formulation increased, due to a chain transfer reaction involving the OH groups in the AM mechanism, with a consequent decrease in the crosslinking density and an increase in the polymer network mobility. TMP was selected as the CTA in order to avoid extreme flexibilization of the crosslinked epoxy network. Subsequently, the effect of the CTA on the curing kinetics was evaluated as a function of temperature. Although the presence of the CTA did not significantly influence the photopolymerization rate at r.t., all the formulations

containing the CTA showed comparable reactivity when the cationic photopolymerization was investigated at 50 °C, and this reactivity was higher for the same formulations at r.t.. A higher conversion was achieved by increasing the TMP content. The formulation containing 20 mol% of TMP showed the highest reactivity and conversion at 80 °C. Finally, the photorheology test, coupled with FT-IR analysis, showed that

a high conversion at gel point and high G' were achieved when TMP was added to the BADGE formulation at 20 mol%. Taking all these data into consideration, the BADGE-based formulation containing 20 mol% of TMP was selected for the printing process at 80 °C, since all these parameters lead to the best balance between the higher thermal reactivity at 80 °C and the mechanical properties of the photocured materials. The printed formulations showed similar T_g, as measured by means of DMTA, of the UV-cured formulation in the mold. The mechanical properties, measured by means of the tensile test of the printed formulation, were comparable with the UV-cured ones. Therefore, by carefully selecting the starting materials and by exploiting the use of the hot-lithography technique at 80 °C, we were able to print epoxy resins with high reactivity and achieve 3D-printed structures characterized by very good thermo-mechanical properties. Therefore, by using epoxy resin, it is possible to print structures, with high CAD fidelity, which show good thermo-mechanical performances.

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Figure 1: The stereolithography setup used in this work to print the BADGE resin (1. Building platform; 2. Heatable coater, 3. Transparent vat; 4. Part; 5. Laser; 6. Mirror scanner)

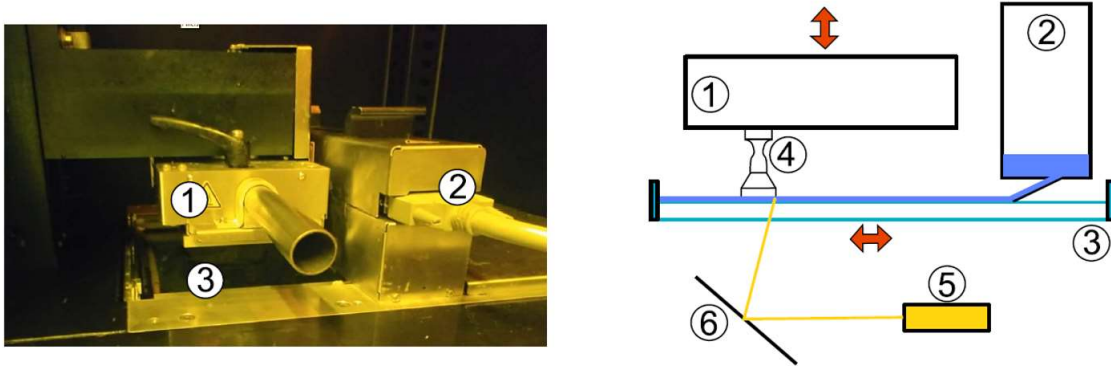


Figure 2: Tan delta vs temperature curves of the formulations containing different mol percentages of TMP (a), PPG (b) and PTHF (c) , compared with the $\tan\delta$ -delta curve of pure BADGE (the black curve).

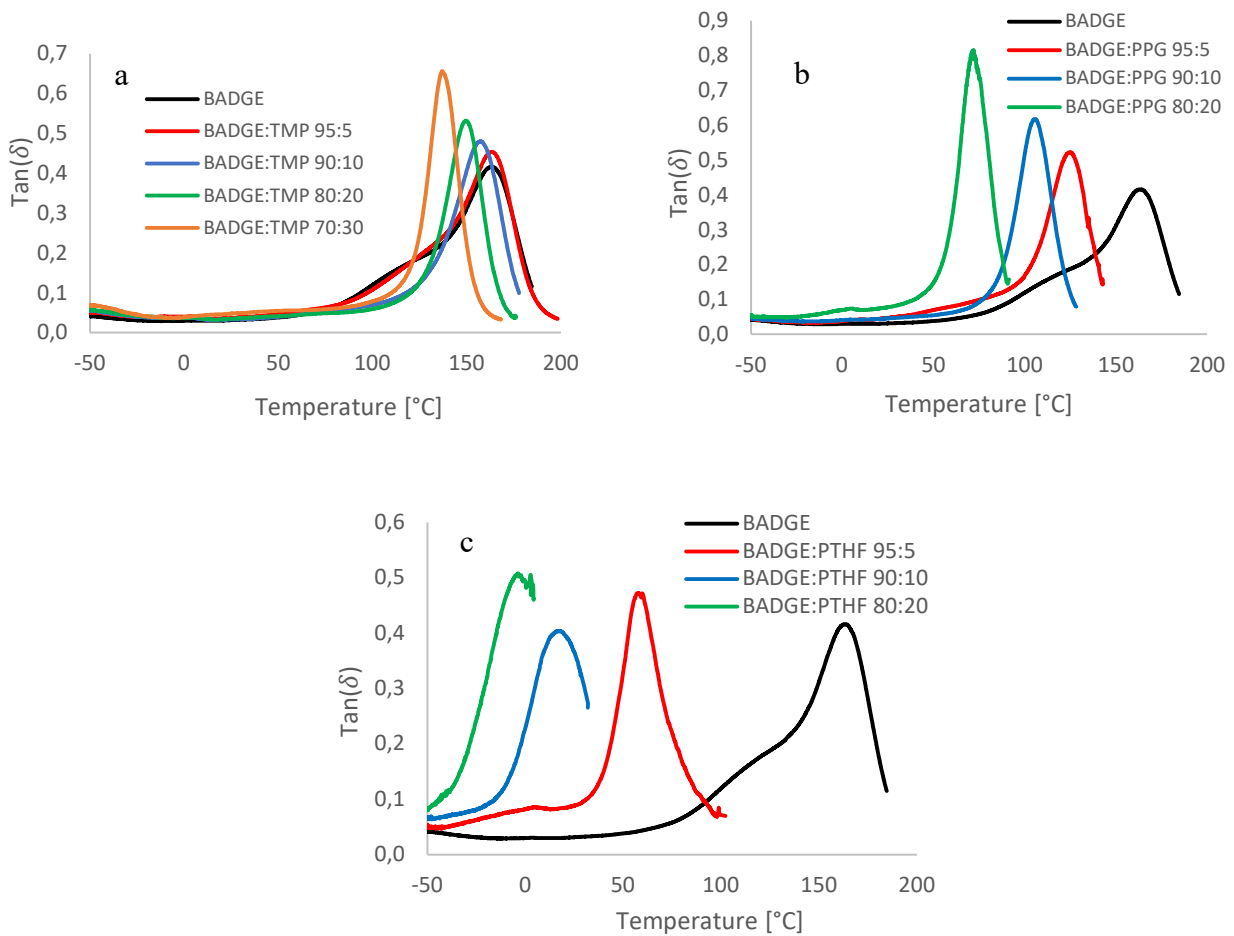


Figure 3: Photo-DSC of the BADGE and BADGE:TMP (10 mol%, 20 mol%, 30 mol%) formulations at 25 °C (a), 50 °C (b) and 80 °C (c).

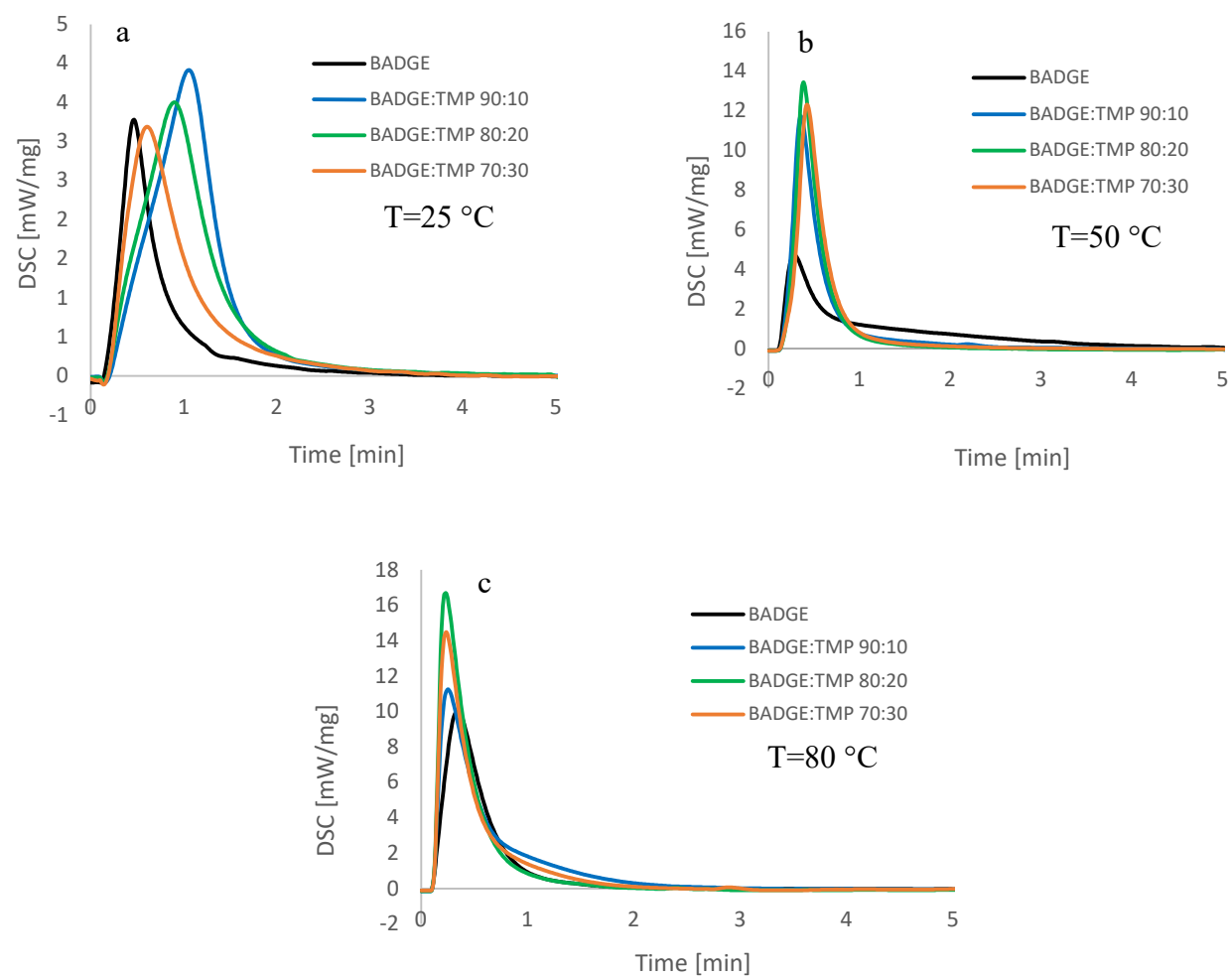


Figure 4: Conversion curves of the epoxy ring-opening for the BADGE-based formulation containing TMP at 10 and 20 mol%, recorded at 80 °C.

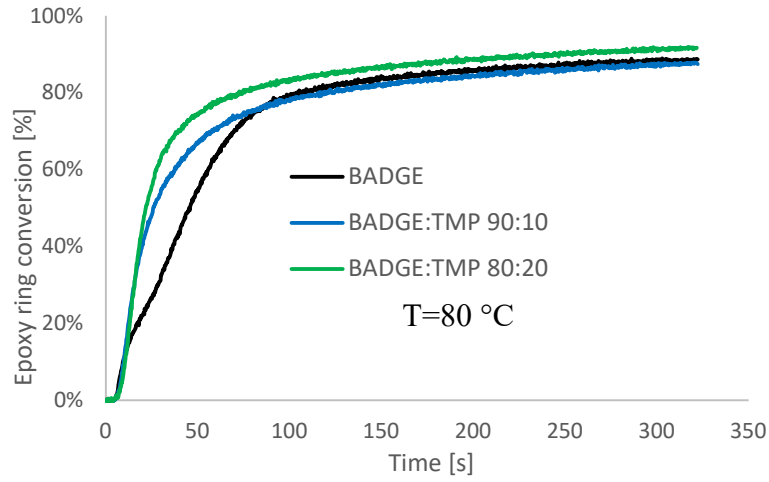


Figure 5: Tan delta curves of the BADGE:TMP 80:20 printed object compared with the BADGE:TMP 80:20 UV-cured object (a); the stress-strain plot of the BADGE:TMP 80:20 printed object compared with the BADGE:TMP 80:20 UV-cured one (b).

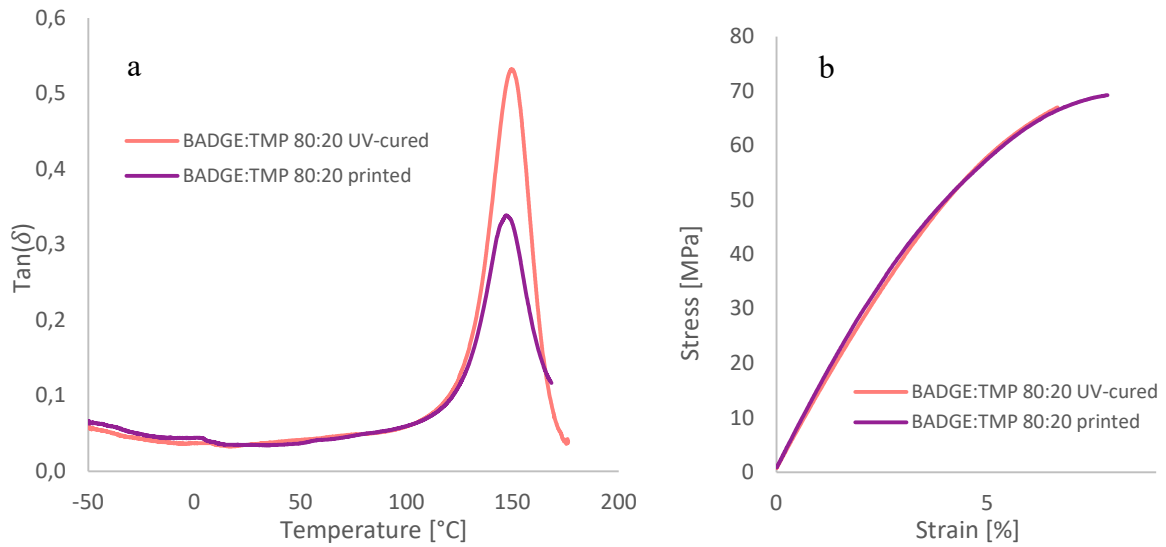


Figure 6: Printed object processing the BADGE:TMP 80:20 photocurable formulation in the hot-lithography printer: dimension (left), inner structure (middle) and starting CAD model (right).

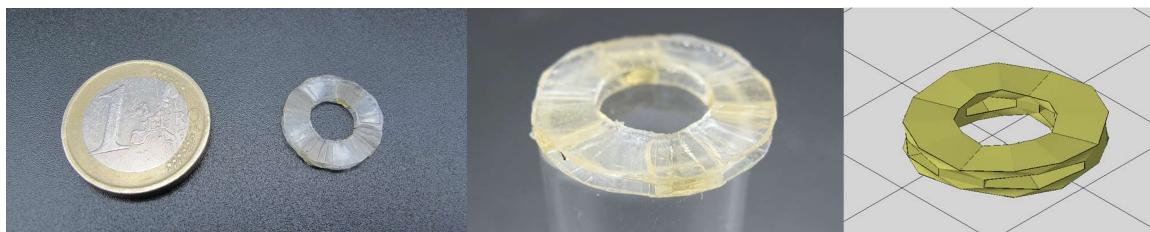


Table 1: Properties of the BADGE-based formulation containing TMP at 10 and 20 wt%, crosslinked at 80 °C.

Formulation	t_g [s]	C_g [%]	C_{final} [%]	G'_{max} [kPa]	F_n [N]
BADGE	23,4	27	89	140	-5,0
BADGE-TMP 90:10	16,8	34	88	150	-2,5
BADGE-TMP 80:20	17,4	37	92	214	-3,4

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The hot-lithography SLA-3D printing technology is used to print epoxy resins. By carefully selecting the starting materials and by exploiting the use of the hot-lithography technique at 80 °C, it is possible to print epoxy resins with high reactivity and thus to achieve 3D-printed structures characterized by very good thermo-mechanical properties.

