

Photocurable resins for 3D printing: chemical and materials engineering aspects

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Abstract

The development of functional photopolymer resins for additive manufacturing requires a combined materials and chemical engineering approach that addresses both resin formulation and the interactions between photocurable systems and 3D printing technologies. Herein, a series of investigations was conducted to rigorously delineate the influence of titanium dioxide (TiO₂) as an additive on the kinetics of the photopolymerization process and on the resulting quality parameters of photocurable resin prints. TiO₂ was incorporated at concentrations of 0.1–30 wt.%, and the resins were studied using Real-Time FT-IR, photo-DSC, photo-rheology and Jacobs curves. Low-to-medium additive concentrations accelerated early polymerization due to enhanced light scattering, whereas higher concentrations reduced light penetration and delayed curing. In addition to material performance, the chemical engineering aspects of additive manufacturing were examined by fabricating printouts on two 3D printers employing different technologies. Printouts from two 3D printers with different technologies, LCD and DLP, revealed a strong dependence on printer technology: the LCD system successfully printed only the base and 0.1 wt.% TiO₂ formulations, but with higher quality, while the higher-intensity DLP system processed all formulations. These results demonstrate that both titanium dioxide content and printing technology influence curing efficiency and final print quality, which are critical for the development of photopolymer resins.

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1. INTRODUCTION

Additive manufacturing, also known as 3D printing, has rapidly evolved into a widely used technology in fields like engineering (Iftekar et al., 2023; Jayakrishna et al., 2023; Sharma et al., 2025), medicine (Aimar et al., 2019; Hellman et al., 2023; Paul et al., 2018), and dentistry (Jeong et al., 2023; Tian et al., 2021), as a way to create 3D objects. Among the diverse techniques, photochemical resin 3D printing is especially interesting as a topic of research because of its material versatility, high object resolution, fast fabrication time and relatively low cost of the materials, as well as the 3D printers (Gauci et al., 2024; Hobich et al., 2023; Petko et al., 2023; Topa-Skwarczyńska et al., 2025). Techniques such as Stereolithography (SLA), Liquid Crystal Display (LCD), and Digital Light Processing (DLP) are among the most prominent (Chaudhary et al., 2023; Dilberoglu et al., 2017). To expand the functionality of photocurable materials, significant research efforts are now focused on incorporating various inorganic additives into the printing matrices (Chopra et al., 2025; Maher et al., 2021; Martins de Sousa et al., 2023; Zhong et al., 2025). They can enhance mechanical, optical, thermal or biological properties of the final printout.

In the vast group of the studied fillers, titanium dioxide, TiO₂, stands out as a promising one, especially for biomedical and dental photopolymers (Anselmo and Mitragotri, 2015; Bayda et al., 2020; Bobo et al., 2016; Mohammadi et al., 2025; Priyadarsini et al., 2019; Puckett et al., 2007; Tan and Lyu, 2023; Veljović and Miletic, 2023).

TiO₂ is an inorganic metal oxide, white in color, widely used as a pigment and a filler in polymer materials. It occurs in 2 common crystal structures, anatase and rutile, which differ in the spatial orientation of molecules within the crystal lattice (Stanford Advanced Materials, 2026). Because of its high refractive index, about 2.5 for both forms, it exhibits strong scattering of UV and visible light, making it valuable in applications requiring light propagation, such as photochemical 3D printing (Kaur et al., 2025). TiO₂ is inert under typical conditions and is not biodegradable. It exhibits high chemical stability, resistance to corrosion and hardness (O'Byrne et al., 2024).

In the context of resin-based additive manufacturing, TiO₂ can significantly influence the curing behavior of resins (Bao et al., 2022). It can improve it by enhancing layer formation and the uniformity of the photopolymerization process, mainly due to its scattering properties, which help distribute light



energy. At the same time, TiO_2 particles can absorb or reflect light, altering the overall kinetics of photopolymerization and making it less favourable. These effects have been shown to influence mechanical performance and print resolution (Abd Elhamid Abo Salh et al., 2025; Aktas et al., 2024; Al Rashid et al., 2021; Ijaz and Zafar, 2021; Pai et al., 2023).

Extensive literature confirms the biocompatibility and mechanical effects of TiO_2 as an additive in 3D printing, supporting its use in biomedical contexts. When incorporated into pigment form at the macro or micro scale, TiO_2 is generally regarded as safe and non-toxic. TiO_2 has been reported to exhibit antibacterial properties under light irradiation due to its photocatalytic activity and the generation of reactive oxygen species. It is also characterized by high chemical stability and corrosion resistance in physiological environments, which further supports its suitability for biomedical applications, although such effects were not investigated in the present study (Almeshari et al., 2024; Altarazi et al., 2023; Altarazi et al., 2024; Billings et al., 2021; Mansoor et al., 2022; Noworyta et al., 2023; Remaggi et al., 2023; Serov et al., 2024; Sztorch et al., 2022; Wang et al., 2025; Wu et al., 2024; Yilmaz and Kapusuz Yavuz, 2025).

Two main factors determine the impact of TiO_2 as an additive in a photocurable resin: filler concentration and the printing technology used. What fundamentally differentiates these printing methods is the way they deliver light to the resin. Intensity, distribution and uniformity are crucial. SLA systems provide localised point exposure via a laser; DLP printers utilise high-intensity light from digital micromirrors in a single projector; and LCD printers rely on masked UV emission from multiple LEDs simultaneously (Taormina et al., 2018).

Therefore, understanding the interaction between resins and TiO_2 as an additive, as well as the specific light sources in 3D printers, is essential for designing functional composites. In this study, for the first time, the influence of TiO_2 additions at concentrations of 0.1, 1, 5, 10, and 30 wt.% on a methacrylate UDMA/TEGDMA resin system was investigated. The modified resins were evaluated on two representative 3D printers, a commercial-grade LCD Anycubic Photon Mono M7 PRO and the lab-grade DLP Lumen XTM Gen 3 to assess how printer type and additive concentration affect curing behavior and overall quality of the enhanced photopolymer material.

2. EXPERIMENTAL

2.1. Materials

In this study, the monomer mixture that was the basis of the resin matrix consisted of urethane dimethacrylate (UDMA, Sigma Aldrich) combined with triethylene glycol dimethacrylate (TEGDMA, Sigma Aldrich) in a 7 : 3 proportion. Titanium dioxide was used in the form of powder with 99.8% purity, in the anatase form, with an average particle size of

25 nm, as stated by the manufacturer (TiO_2 , Sigma Aldrich) (Table A2). The resin underwent radical photopolymerization, where exposure to light generated reactive free radicals, initiating a chain reaction that converted the monomers into a solid polymer network. The photoinitiator used was an iodonium salt, (7-methoxy-4-methylcoumarin-3-yl)phenyliodonium hexafluorophosphate (Sylanto 7MP), in combination with ethyl 4-(dimethylamino)benzoate (EDB, Sigma Aldrich) as an amine co-initiator. The Sylanto 7MP/EDB system has been previously described and characterized in detail in the literature (Jankowska et al., 2025). It was chosen in this study because of its absorbance near 405 nm (Fig. 1), which is the standard range for commercial 3D printers.

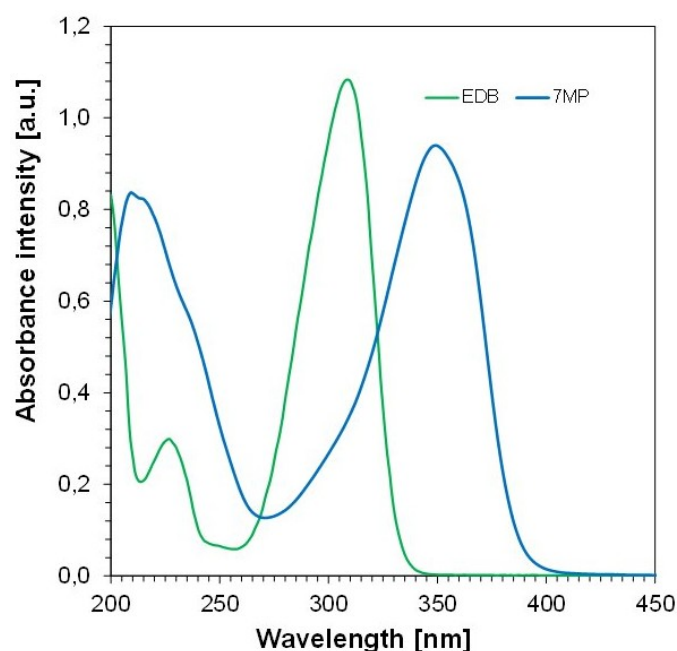


Figure 1. Absorbance of the photoinitiating system (EDB amine co-initiator and initiator Sylanto 7MP).

The dispersion protocol for titanium dioxide nanoparticles in the resin matrix was designed to ensure homogeneous distribution prior to experimental use. The required mass of nanopowder was directly added to the prepared resin mixture, after which the suspension was sealed in a glass vial containing a magnetic stir bar. The mixture was subjected to continuous magnetic stirring at 500 rpm for 12 hours at room temperature in a dark box to promote deagglomeration of the nanoparticles within the medium. Immediately before use, the suspension was sonicated for 15 seconds to re-disperse any agglomerates. This short sonication time was sufficient due to the relatively small resin volume employed. It was observed that sedimentation occurred after approximately 4 hours for nanoparticle loadings above 5 wt% and it was observed in the form of phase separation of the clear resin and the TiO_2 -packed resin.

2.2. Real-time-FT-IR analysis

Photopolymerization kinetics were examined for mixtures containing photoinitiating systems dissolved in UDMA/TEGDMA monomers with a specific wt% of titanium dioxide. Real-time infrared spectra were collected using a Nicolet i10 FT-IR spectrometer (Thermo Scientific, Waltham, MA, USA) (Fig. A1). For each measurement, a small droplet of the resin mixture was deposited onto a 25 μm polypropylene (PP) film using a glass pipette. A second PP film of identical thickness was placed on top to form a thin laminate. Gentle pressure was applied to ensure a reproducible sample layer of 25 μm ($\pm 10\%$). All prepared laminates were placed into a metal sample holder mounted horizontally in the FT-IR spectrometer. Measurements were conducted for up to 600 s in a dark environment illuminated only with red light ($\lambda_{\text{max}} \approx 650\text{ nm}$) to prevent premature photoinitiation. Sample exposure was carried out using UV/Vis LEDs from Thorlabs (USA) with an emission wavelength of 405 nm. The LEDs were powered by a Thorlabs DC2200 supply and positioned 2.1 cm from the sample surface. Illumination began 10 s after spectral acquisition commenced. The progress of curing was tracked by monitoring the reduction of the characteristic absorbance band of the reactive double bonds, around 1634 cm^{-1} for UDMA/TEGDMA methacrylate systems. Because the decrease in peak area corresponds to the consumption of functional groups, the degree of conversion was calculated from the ratio of initial and final absorbance values, using Eq. (1).

$$C_{\text{FT-IR}}[\%] = \left(1 - \frac{A_{\text{After}}}{A_{\text{Before}}}\right) \cdot 100\% \quad (1)$$

where: A_{Before} – area of the absorbance peak characteristic for appropriate monomer and type of photopolymerization before curing; A_{After} – area of the same absorbance peak after the polymerization process.

2.3. Photo-DSC analysis

Photo-DSC experiments were carried out using a Photo-DSC 204 F1 Phoenix[®] instrument (Netzsch Gerätebau GmbH, Germany). The calorimeter was equipped with a Bluepoint LED eco light-curing system (Hönle UV Technology, Germany) using LEDs with a peak emission at 405 nm (Fig. A2). The light intensity at the sample position was adjusted to approximately $18.67\text{ mW}\cdot\text{cm}^{-2}$ and verified with an Omni-Cure R2000 radiometer (Excelitas Technologies[®], Ontario, Canada). All measurements were performed isothermally at 25°C under an inert gas atmosphere.

Each sample ($2 \pm 0.5\text{ mg}$) was placed inside an aluminum crucible, covered with a thin quartz plate, and preconditioned isothermally for 10 s before irradiation. A reference crucible containing only the base monomers was used to establish baseline heat flow.

Heat evolution during polymerization was recorded continuously. Since the released heat is directly proportional to the number of reacted double bonds, both polymerization rate (R_p in Eq. (2)) and functional-group conversion ($C_{\text{photo-DSC}}$ in Eq. (3)) were derived from the integrated exotherm and the known thermochemical parameters of the monomers (molar mass, functionality, enthalpy per mole of reactive groups, and compositional ratios). These calculations followed standard procedures commonly applied in photo-DSC kinetic analysis.

$$R_p \approx 1000d_m \left(\frac{H}{m_p}\right) \frac{\sum \left(f_i \frac{w_i}{M_i}\right)}{\sum \left(f_i \frac{w_i}{M_i} \Delta H_0\right)} \quad (2)$$

where: d_m – density of monomer composition [$\text{g}\cdot\text{cm}^{-3}$]; ΔH_0 – enthalpy of polymerization the used monomers [$\text{J}\cdot\text{mol}^{-1}$] (per one functional group); H – heat flow [W]; M_i – molecular mass of i -monomer [$\text{g}\cdot\text{mol}^{-1}$]; f_i – functionality of i -monomer; w_i – percentage of i -monomer; m_p – sample mass [g].

$$C_{\text{photo-DSC}} = \frac{1}{\sum \left(f_i \frac{w_i}{M_i} \Delta H_0\right)} \int_{t_0}^t \frac{H(t)}{m_p} dt \quad (3)$$

where: M_i – molecular mass of i -monomer [$\text{g}\cdot\text{mol}^{-1}$]; f_i – functionality of i -monomer; w_i – percentage of i -monomer; ΔH_0 – enthalpy of polymerization of used monomers [$\text{J}\cdot\text{mol}^{-1}$] (per functional group); H – heat flow [W] and m_p – sample mass [g].

2.4. Photo-rheological studies

Photo-rheological measurements were performed to characterize the kinetics of photocuring by tracking changes in viscosity during UV exposure. Experiments were carried out on an MCR302e rotational rheometer (Anton Paar, Poland) equipped with a dedicated optical module for in-situ photorheology (Fig. A3). All measurements were conducted at 25°C with temperature control provided by an integrated thermostat.

Samples were irradiated using LEDs operating at 405 nm, with an incident intensity of approximately $19.82\text{ mW}\cdot\text{cm}^{-2}$. LED output was supplied and regulated via a DC2200 current controller (Thorlabs Inc., Tampa, FL, USA). To allow the system to stabilize before polymerization began, illumination was triggered 10 s after the start of each rheological test.

Polymerization shrinkage was quantified by comparing the gap between the upper glass plate and the lower aluminium plate before and after curing. The percentage change in this distance was used to calculate volumetric shrinkage using the standard relationship between the initial and final gap thicknesses (Eq. (4)).

$$\text{Shrinkage} [\%] = \left(1 - \frac{d_{\text{After}}}{d_{\text{Before}}}\right) \cdot 100\% \quad (4)$$

where: d_{After} – the distance between the glass plate and the aluminum plate after the photopolymerization [mm]; d_{Before} – the distance between the glass plate and the aluminum plate before the photopolymerization [mm].

2.5. 3D printing experiments

Two photopolymer 3D printers, representing different printing technologies, were used to evaluate the printability of a resin modified with TiO_2 at 0.1, 1, 5, 10, and 30 wt.%. The LCD Anycubic Photon Mono M7 Pro (Anycubic, China) and the DLP Lumen X™ Gen 3 (CellInk Inc., USA) served as the fabrication platforms. Both systems operated with UV irradiation at 405 nm, but differed in how light was delivered to the resin vat. The LCD printer employed pixel masking in the print matrix to form the printed layers, whereas the DLP printer projected patterned illumination, which enabled assessment of how printer build influences curing behavior and print resolution. The digital model in Fig. 2 was designed in Autodesk Fusion 360. The same resin formulations were used on both printers to enable direct comparison between the two technologies. Printing parameters such as exposure time and light intensity were adjusted to the specific needs of the resin composites (Table A3), to achieve printing with the highest possible accuracy (Fig. 2).

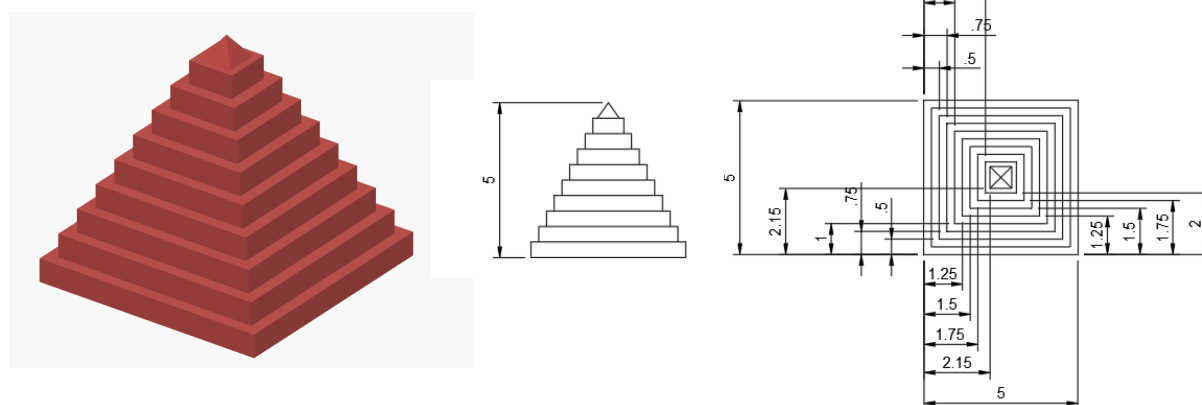


Figure 2. Printing model consisting of the 3D view of the pyramid and its dimensions (in millimeters).

Table 1. Kinetic results for the studied systems, final degree of conversion rate of acrylate monomers, slope of the polymerization process and the induction time from the Real Time FT-IR measurements.

Composition	Degree of conversion (α) [%]	$d\alpha \cdot dt^{-1}$	Induction time [s]
Base	37.7	2.99	7.48
0.1 wt.% TiO_2	34.2	3.79	5.07
1 wt.% TiO_2	34.1	4.60	2.90
5 wt.% TiO_2	29.3	3.71	2.33
10 wt.% TiO_2	31.5	4.94	2.21
30 wt.% TiO_2	41.6	2.72	2.01

3. RESULTS AND DISCUSSION

3.1. Kinetic studies using Real-Time FT-IR

Real-Time FT-IR spectroscopy was used to evaluate the photopolymerization kinetics of UDMA/TEGDMA resin containing different concentrations of TiO_2 . The progress of radical photopolymerization was tracked by monitoring the decrease of absorbance at approximately 1634 cm^{-1} , which is the characteristic $\text{C}=\text{C}$ bond band of the methacrylate compounds (Figs. A5–A10). Kinetic curves for the conversion rates obtained in Fig. 3 illustrate how the presence of the additive influences the rate of curing. In Table 1, the slope of the kinetic curves and the induction times were presented. From these, a clear acceleration of the early stages of polymerization were observed. As the concentration of TiO_2 increased, the resin exhibited shorter induction times and steeper initial slopes compared to the base resin, indicating faster radical polymer network formation after irradiation. It can be attributed to light scattering ability of TiO_2 particles, which promotes rapid initiation of the process in the early stages.

As the TiO_2 concentration increased, a slight decrease in the final degree of conversion was observed, due to limited light penetration into the depth of the composite. Nevertheless, in

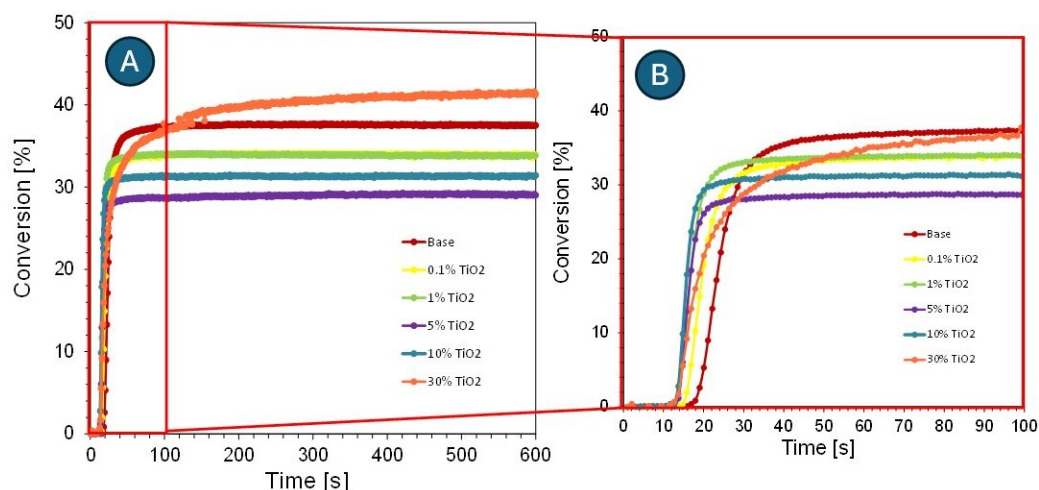


Figure 3. Kinetic profiles presenting the photopolymerization process of the UDMA/TEGDMA monomers in a 7 : 3 ratio, with a specific concentration of TiO_2 added; under LED@405 nm irradiation (and an intensity on the sample of $19.8 \text{ mW}\cdot\text{cm}^{-2}$) continuously for 600 seconds. A) the whole process, B) the first 100 seconds. The sample thickness was $25 \mu\text{m}$.

all cases, the degree of conversion levels remained acceptable for 3D printing applications. All compositions with an additive concentration of 1 wt.% or greater reached induction times below 3 s, demonstrating titanium dioxide's excellent ability to scatter light and aid the polymerisation process.

The formulation with 30 wt.% TiO_2 presented behavior distinct from the lower concentration trend. Its initial polymerization rate was lower, even below that of the base sample. It can be attributed to the very strong light scattering at such a high concentration. Although the reaction progressed slowly, requiring about 150 s to reach a plateau, compared to about 30 s in the other samples, the system achieved a higher final degree of conversion. This can be attributed to prolonged activity of the network, as the slower polymerization rate allows the systems to remain in the fluid state for longer and distribute the energy more evenly, as opposed to in the rigid solid state network, enabling continued propagation and finally yielding a higher degree of conversion.

3.2. Kinetic studies using Photo-DSC

Photo-DSC analysis was performed as an alternative and complementary method for determining photopolymerization kinetics in relation to Real Time FT-IR. Unlike the previous one, photo-DSC measured the heat released during photocuring, allowing degree of conversion to be calculated from the total reaction enthalpy. Despite the differences in the methodology of those two techniques, the same general trends were observed. Increasing TiO_2 concentration altered the rate of polymerization (Fig. 4).

At the lower TiO_2 loadings ($\leq 5 \text{ wt}\%$), the resin exhibited a lower induction time of the heat-flow and its intensity decreased, indicating a faster initialization of the polymer network formation but to a lesser extent. This behavior can be attributed to the strong light scattering ability of TiO_2 , which increases the effective optical path length within the resin and enhances light absorption, thus promoting radical

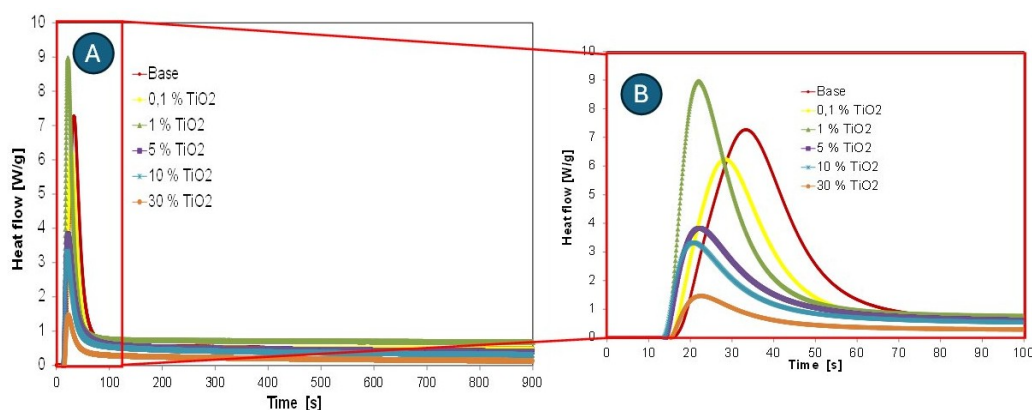


Figure 4. Photo-DSC results obtained when monitoring samples based on UDMA/TEGDMA for 900 s with an LED@405 nm light source with a sample light intensity of $18.67 \text{ mW}\cdot\text{cm}^{-2}$. Heat flow results A) for the whole experiment's time, B) for the first 100 s.

generation. Similar acceleration effects were also detected in the photo-rheological measurements, confirming the consistency of these observations across techniques. However, for the 10 and 30 wt.% filler contents, the dominant filter and shadowing effects became increasingly pronounced, leading to reduced light penetration into the material. As a result, the overall heat flow intensity decreased, and the polymerization process was prolonged. Although curing still occurred, it was less efficient. These observations demonstrate that photo-DSC is an effective tool for capturing the influence of TiO_2 concentration on photopolymerization of the resin.

3.3. Rheological studies

Photo-rheological measurements provided complementary insights into the viscoelastic evolution of the resin during curing, allowing assessment of gelation behavior, the mechanical development of the polymer network, and polymerization-induced shrinkage. Monitoring the increase in storage modulus (G') as well as the loss modulus (G'') under UV exposure revealed how TiO_2 concentration influenced the transition from liquid to solid (Figs. A11–A16). Gelling time was found to be the time at which the storage and loss moduli reached the same value and their graphs crossed (Fig. 5).

Polymerization shrinkage, estimated from Eq. (4), decreased with higher additive content. This behavior is expected, as inorganic particles limit contraction during network formation. Reduced shrinkage is advantageous for dimensional accuracy in 3D printing, as it may enhance interlayer adhesion during fabrication. Formulations with low to medium TiO_2 concentrations (from 0.1 to 5 wt.%) exhibited earlier gel points compared to the reference base, reflecting the initially accelerated polymerization observed in both Real Time FT-IR and photo-DSC. However, increasing the concentration of TiO_2 in the samples to 10 and 30 wt% led to longer gelling times, which can be explained by restricted polymer network

formation due to diminished light penetration. The 30 wt.% concentration displayed the longest gel point, which aligned with its delayed polymerization profile in Real Time FT-IR.

3.4. 3D printing

To assess the practical applicability of the resin with added TiO_2 , all resin variants were subjected to 3D printing using two different 3D printers, a commercial-grade LCD Anycubic Photon Mono M7 PRO and the lab-grade DLP Lumen X™ Gen 3. Evaluating both made it possible to determine how the method of light projection influences the printability of resins containing increasing TiO_2 concentrations. Each print was printed out in a 50 μm layer thickness, with irradiation times and light exposure power specific to the studied resin composition (Table A3). All specimens were printed in identical geometry and orientation, such that the base face of the pyramid was directly attached to the printing platform to ensure consistent fabrication conditions. After printing, the samples were rinsed in an isopropanol bath for 10 minutes to remove uncured resin, followed by post-curing under 405 nm irradiation for 5 minutes to ensure complete polymerization.

In the LCD printer, only formulations containing up to 0.1 wt% TiO_2 could be printed successfully (Fig. 7). At higher concentrations, curing was incomplete even with extended exposure times, preventing proper layer formation. However, prints obtained from the 0.1 wt% formulation exhibited excellent surface quality, sharp feature definition, and smooth layers. The high resolution of the LCD screen and its uniform light distribution likely contributed to this precision. Nevertheless, the LCD system provided lower irradiance per pixel compared to DLP projector that provided higher power. When TiO_2 concentration increased, pronounced light scattering occurred, preventing sufficient energy from reaching deeper regions of each layer, ultimately exceeding the curing capacity of the LCD system.

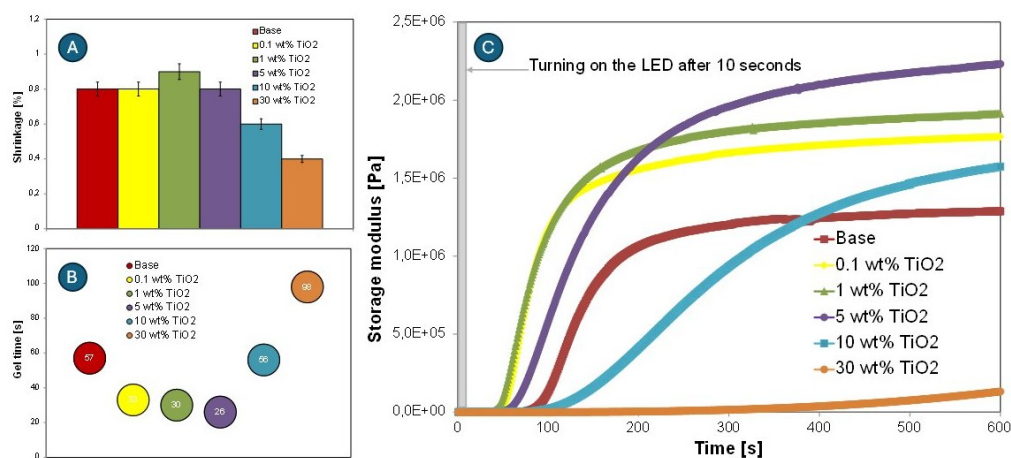


Figure 5. Photo-rheology results obtained for photo-curable compositions based on UDMA/TEGDMA and TiO_2 in various concentrations during sample monitoring for 600 s and LED@405 nm irradiation with a light intensity on the sample of $19.8 \text{ mW} \cdot \text{cm}^{-2}$. In A) photopolymerization shrinkage, B) gelling times, C) storage modulus.

In contrast, the DLP printer was able to successfully polymerize all resin variants, including the highly filled 30 wt% TiO_2 formulation (Fig. 6). At additive contents above 5 wt%, however, it was necessary to first print a thin base platform layer using the base resin to ensure adequate adhesion of the subsequent layers. DLP projector emitted a more concentrated light beam, with significantly higher irradiance than LCD panels (3 to 4 times higher). This provided a stronger curing capability that could overcome scattering losses caused by dense TiO_2 particles. As a result, complete layer formation and solidification were achieved across the entire concentration range. However, the overall print resolution and surface finish were slightly inferior to those obtained with the LCD system. This likely results from differences in optical configuration and pixel size between the systems, as DLP projector discretized light into larger pixels, which may yield more noticeable edges or

curing failures compared to high-resolution monochrome LCD screens. Both printers were operated at a 50 μm layer height, however, the LCD printer offers a finer XY plane resolution of 17 μm per pixel, compared to 35 μm in the DLP system. Additionally, at high TiO_2 loadings, increased scattering likely blurred projected pixels, reducing feature definition. As a result, the LCD system provided superior surface resolution, whereas the DLP system offered greater curing capability at high filler loadings.

The dimensions of the printouts in both LCD (Fig. 7) and DLP (Fig. 6) systems matched those of the CAD model (Fig. 2). However, they were slightly reduced due to photopolymerization shrinkage. The magnitude of this change in dimensions correlated well with the shrinkage behavior observed in the rheological measurements.

Scanning electron microscopy (SEM) was performed to evaluate the surface morphology and microstructural fidelity of the printed specimens. For the base resin and low filler concentration, LCD samples (Fig. 9) exhibited relatively smooth and homogeneous surfaces, with well-defined edges corresponding to the designed geometry, while the DLP ones (Fig. 8) retained the original outline of the finer details. With increasing TiO_2 content, however, a progressive increase in surface roughness was observed. The surface became more irregular, with visible micro protrusions that can be attributed to the presence of dispersed TiO_2 particles and their partial agglomeration. At higher magnifications, distinct clusters of TiO_2 were present, confirming that the inorganic powder was not exclusively embedded within the polymer bulk but was at least partially exposed at the surface. This observation supports the assumption that TiO_2 is present on the surface, which may be relevant for potential uses.

Despite increased roughness at higher filler loadings, the reproduction of smaller structural details remained consistent with DLP technology; however, geometric deformation

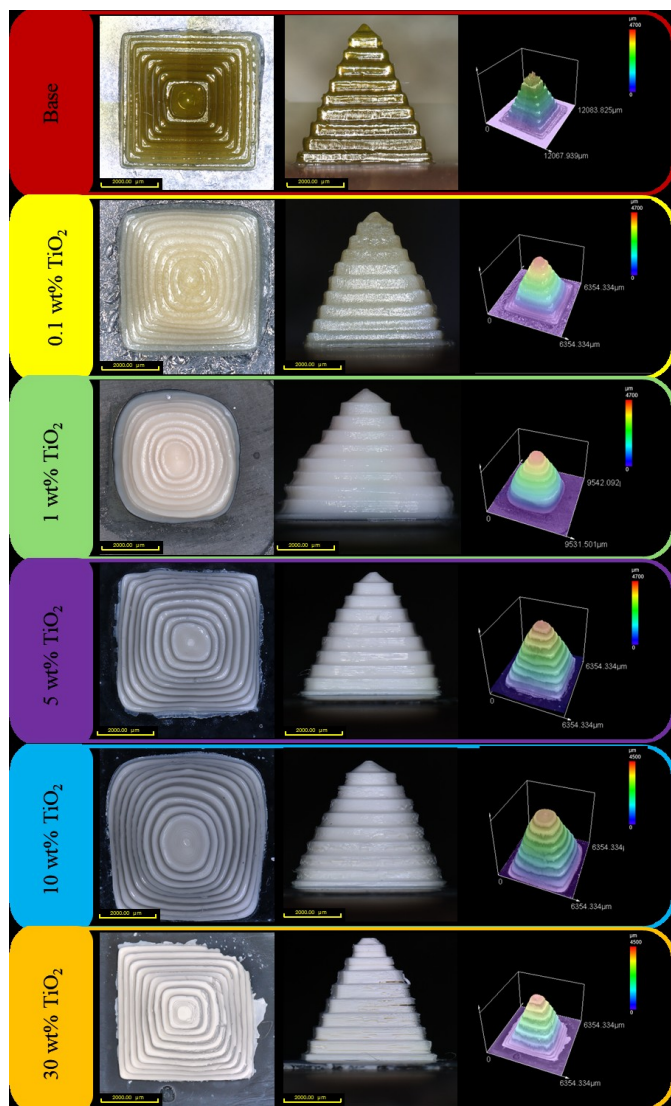


Figure 6. Optical microscope photos of the model printed from a composition consisting of UDMA/TEGDMA and various amount of TiO_2 wt% on a DLP LumenXTM Gen 3 printer using different curing parameters.

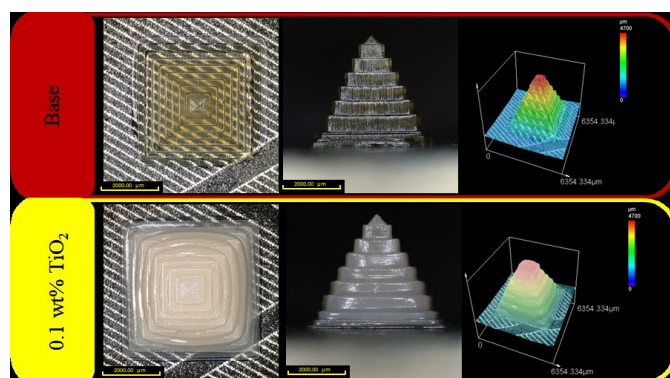


Figure 7. Optical microscope photos of the model printed from a composition consisting of UDMA/TEGDMA, and various amount of TiO_2 wt% on an LCD Anyubic Photon Mono M7 PRO printer using different curing parameters.

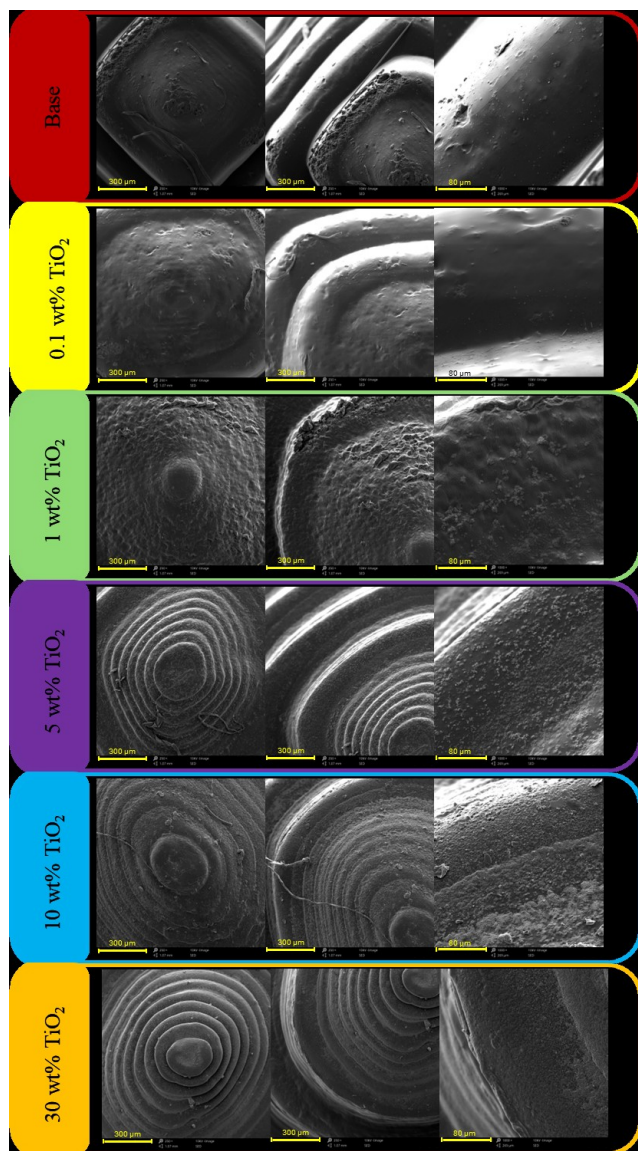


Figure 8. SEM photos of the model printed from a composition consisting of UDMA/TEGDMA and various amount of TiO_2 wt.% on a DLP LumenX™ Gen 3 printer using different curing parameters.

became more pronounced. In particular, at high TiO_2 concentrations (5 wt% and above), DLP-printed objects exhibited noticeable distortion from the designed square shape toward a more oval or rounded shape. This effect likely results from enhanced light scattering within the highly filled composite, leading to overcuring and partial blurring of projected pixel boundaries. In contrast, samples fabricated using the LCD system retained a more square-like geometry, although minor edge rounding was still detectable. The difference between the two systems may be attributed to their distinct optical systems. Overall, SEM analysis confirms that increasing TiO_2 concentration affects surface quality and dimensional accuracy rather than eliminating fine structural features altogether, with deformation effects being more pronounced in the DLP system at elevated loadings.

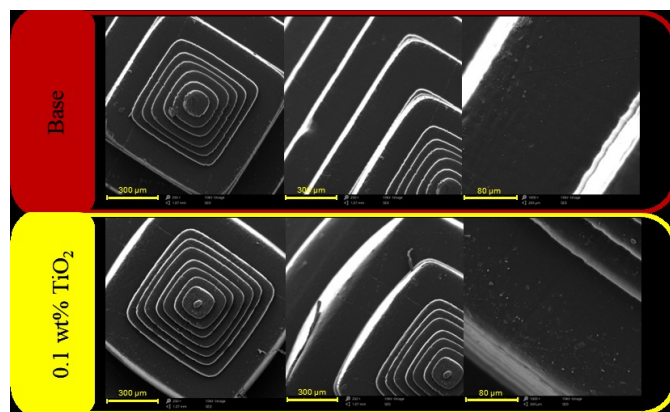


Figure 9. SEM photos of the model printed from a composition consisting of UDMA/TEGDMA, and various amount of TiO_2 wt.% on an LCD Anycubic Photon Mono M7 PRO printer using different curing parameters.

3.5. Jacobs working curves

The light penetration behavior of the investigated systems was further analyzed using the Jacobs working curve approach, which correlates the cured layer thickness, C_d , with the applied exposure dose, E_0 . Experimentally, the working curves were obtained by exposing the resin directly on the vat film without the build platform attached, to avoid influencing the cured thickness. After exposure at different controlled energy doses, the isolated polymerized layers were carefully removed and their thickness measured using micrometer screw gauge. Plotting the measured layer height as a function of exposure dose enabled determination of the penetration depth (D_p) from the slope of the linear fit and the critical exposure (E_c) from the intercept.

For the DLP Lumen X™ Gen 3 system, the base resin exhibited a steep working curve, indicating a high penetration depth and efficient energy transfer through the resin (Fig. 10). Interestingly, the addition of 0.1 wt.% TiO_2 initially resulted in a slight increase in cured layer thickness at comparable exposure doses, suggesting enhanced light energy utilization. However, at higher TiO_2 concentrations, both the slope of the working curve and the maximum achievable layer thickness decreased. The reduced steepness indicates a lower effective penetration depth, while the overall downward shift reflects a decrease in critical exposure, consistent with intensified light scattering caused by the nanoparticles. In parallel, the measured cured thickness increased from the base formulation to 0.1 wt.% TiO_2 but progressively declined at higher loadings in the DLP system, confirming the detrimental effect of excessive filler on curing efficiency. A comparable trend was observed for the LCD Anycubic Photon Mono M7 PRO with the base resin and the 0.1 wt.% TiO_2 formulation, where sufficient cured thickness was still achieved. At higher concentrations, the printer either failed to produce a photopolymer or produced a severely undercured polymer, making it impossible to measure its thickness. Thus, the Jacobs working

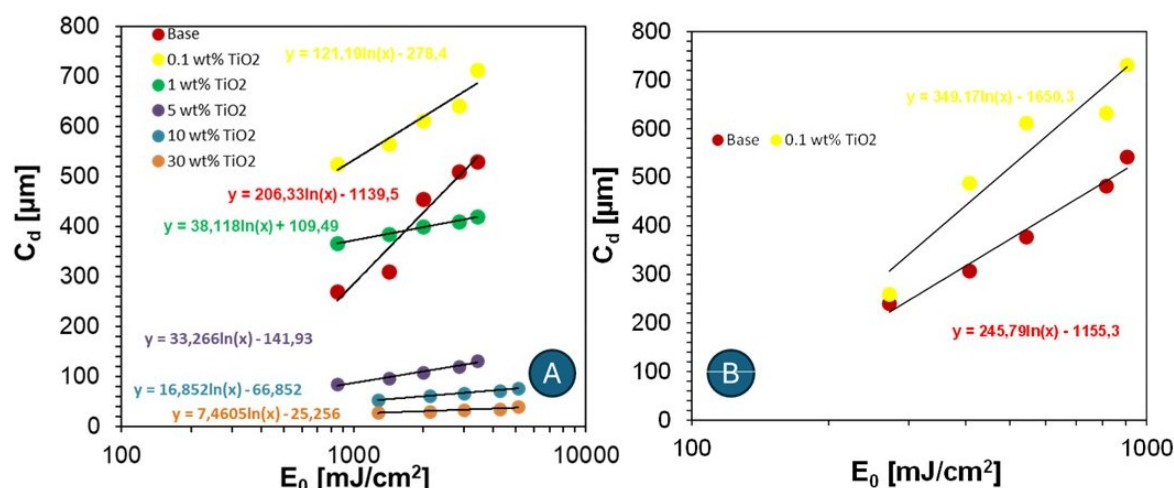


Figure 10. Jacobs working curves for the used resin formulations. Done on the A) DLP LumenX™ Gen 3; B) LCD Anycubic M7 PRO.

curve analysis provides quantitative support for the observed printability limits and further concludes that the DLP system maintains superior curing power under optical hurdles.

4. CONCLUSIONS

This study provides a comprehensive evaluation of methacrylate UDMA/TEGDMA photocurable resins with added TiO₂ in various concentrations. It examined photopolymerization behavior and printability across two different 3D printing technologies. By combining Real-Time FT-IR, photo-DSC, photo-rheology, and practical printing tests, the influence of TiO₂ concentration and printer type on curing efficiency and final material quality was clearly demonstrated.

Kinetic analyses revealed that low and medium TiO₂ concentrations (≤ 5 wt%) accelerate the early stages of photopolymerization due to enhanced scattering and redistribution of light, leading to shorter induction times and steeper polymerization slopes. However, increasing the additive level reduced light penetration, resulting in gradually lower final degrees of conversion. The 30 wt% formulation behaved differently, its high opacity caused a slower initiation rate, but the delayed polymerization allowed the network to continue reacting longer, ultimately reaching the highest overall degree of conversion. Photo-DSC confirmed these trends, demonstrating that both methods lead to consistent conclusions regarding the role of TiO₂ in curing kinetics. Photo-rheology further showed that higher filler contents delayed gelation and reduced polymerization shrinkage, suggesting improved dimensional stability for highly filled formulations.

The 3D printing experiments demonstrated that TiO₂ concentration and printer build greatly influence printability. The LCD printer, characterized by high pixel resolution but lower irradiance, could successfully process only the 0.1 wt% formulation. These prints exhibited excellent surface quality but were limited by insufficient curing power at higher

titanium dioxide loadings. In contrast, the DLP printer with its significantly greater light intensity could print all TiO₂ concentrations, including the 30 wt% formulation. For above 5 wt% TiO₂, a base platform layer of base resin was required for reliable adhesion. Although the DLP prints showed slightly lower quality, the ability to fabricate highly filled, optically demanding materials highlights the robustness of high intensity projection DLP curing.

Jacobs working curve analysis further quantified these differences, showing a decrease in penetration depth and in critical exposure with increasing additive loading. The steep working curves observed for the base and 0.1 wt% formulations explain why only these compositions could be reliably processed on the LCD printer.

SEM and microscope analysis revealed progressive surface roughening and partial exposure of TiO₂ particles at higher loadings, confirming that the inorganic nanoparticles influenced not only curing behavior but also surface topography and dimensional fidelity. The more pronounced geometric deformation observed in DLP prints at elevated concentrations supports the hypothesis of intensified light scattering and pixel blurring in highly filled systems.

Overall, this work demonstrates that TiO₂ can be used to tailor the photopolymerization behavior and functional properties of radical resins, but its successful application in 3D printing depends strongly on printer technology and concentration. These findings provide practical guidelines for designing composite resins and selecting appropriate printing conditions for advanced biomedical, dental, and engineering applications.

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SYMBOLS

A_{After}	Area of the same absorbance peak after the polymerization process, cm^{-1}
A_{Before}	Area of the absorbance peak characteristic for appropriate monomer and type of photopolymerization before curing, cm^{-1}
C_d	Cured layer thickness, μm
$C_{\text{FT-IR}}$	Degree of conversion, %
$C_{\text{photo-DSC}}$	Functional-group conversion, %
d_{After}	The distance between the glass plate and the aluminum plate after the photopolymerization, mm
d_{Before}	The distance between the glass plate and the aluminum plate before the photopolymerization, mm
d_m	Density of monomer composition, $\text{g}\cdot\text{cm}^{-3}$
$d\alpha \cdot dt^{-1}$	Slope of polymerization process
E_0	Applied exposure dose, $\text{mJ}\cdot\text{cm}^{-2}$
f_i	Functionality of i -monomer
H	Heat flow, W
M_i	Molecular mass of i -monomer, $\text{g}\cdot\text{mol}^{-1}$
m_p	Sample mass, g
R_p	Polymerization rate
w_i	Percentage of i -monomer, %
ΔH_0	Enthalpy of polymerization the used monomers, $\text{J}\cdot\text{mol}^{-1}$ (per one functional group)
λ_{max}	Maximum absorption, nm

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APPENDICES

A1. Materials used for testing

Table A1. Quantities of compounds and measurement conditions used in this article.

Initiating system	Number of moles	Percentage by moles	Monomer	Measurement conditions
Sylanto 7MP EDB	$2.9 \cdot 10^{-5}$ $5.2 \cdot 10^{-5}$	1.1 mol% 2.0 mol%	UDMA/TEGDMA in weight ratio 7 : 3	405 nm $19.8 \text{ mW} \cdot \text{cm}^{-2}$ 25 μm
Sylanto 7MP EDB Titanium (IV) oxide (TiO ₂)	$2.9 \cdot 10^{-5}$ $5.2 \cdot 10^{-5}$ $1.3 \cdot 10^{-5}$	1.1 mol% 2.0 mol% 0.51 mol%	UDMA/TEGDMA in weight ratio 7 : 3	405 nm $19.8 \text{ mW} \cdot \text{cm}^{-2}$ 25 μm
Sylanto 7MP EDB Titanium (IV) oxide (TiO ₂)	$2.9 \cdot 10^{-5}$ $5.2 \cdot 10^{-5}$ $1.3 \cdot 10^{-4}$	1.1 mol% 2.0 mol% 4.9 mol%	UDMA/TEGDMA in weight ratio 7 : 3	405 nm $19.8 \text{ mW} \cdot \text{cm}^{-2}$ 25 μm
Sylanto 7MP EDB Titanium (IV) oxide (TiO ₂)	$2.9 \cdot 10^{-5}$ $5.2 \cdot 10^{-5}$ $6.3 \cdot 10^{-5}$	1.1 mol% 2.0 mol% 20 mol%	UDMA/TEGDMA in weight ratio 7 : 3	405 nm $19.8 \text{ mW} \cdot \text{cm}^{-2}$ 25 μm
Sylanto 7MP EDB Titanium (IV) oxide (TiO ₂)	$2.9 \cdot 10^{-5}$ $5.2 \cdot 10^{-5}$ $1.3 \cdot 10^{-3}$	1.1 mol% 2.0 mol% 34 mol%	UDMA/TEGDMA in weight ratio 7 : 3	405 nm $19.8 \text{ mW} \cdot \text{cm}^{-2}$ 25 μm
Sylanto 7MP EDB Titanium (IV) oxide (TiO ₂)	$2.9 \cdot 10^{-5}$ $5.2 \cdot 10^{-5}$ $3.8 \cdot 10^{-3}$	1.1 mol% 2.0 mol% 60 mol%	UDMA/TEGDMA in weight ratio 7 : 3	405 nm $19.8 \text{ mW} \cdot \text{cm}^{-2}$ 25 μm

Table A2. Formulas, names, CAS, acronyms and manufacturers of reagents used.

Name/Acronym	Structural formula	CAS	Manufacturers
Urethane dimethacrylate / UDMA		72869-86-4	Sigma Aldrich
Triethylene glycol dimethacrylate / TEGDMA		109-16-0	Sigma Aldrich
Titanium (IV) oxide / TiO ₂	—	1317-70-0	Sigma Aldrich
(7-methoxy-4-methylcoumarin-3-yl) phenyliodonium hexafluorophosphate / Sylanto 7MP		Sylanto 7MP was obtained following the recently published procedure Pol. Pat. Appl. P-393 501 2010, Pol. Pat. Appl. P-395 515 2011.	
Ethyl 4-(dimethylamino)benzoate / EDB		10287-53-3	Sigma Aldrich

A2. Measurement setups

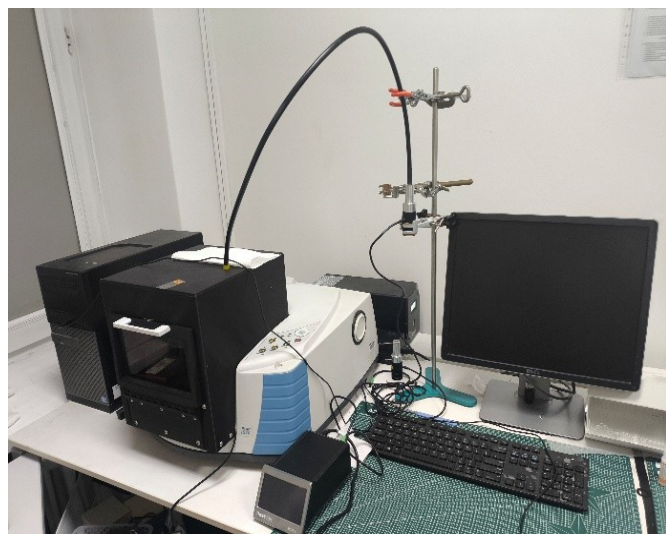


Figure A1. Nicolet i10 FT-IR spectrometer with a horizontal sample mount; samples irradiated with 405 nm Thorlabs LED ($\approx 19.8 \text{ mW}\cdot\text{cm}^{-2}$) positioned 2.1 cm from the sample and powered by a DC2200 controller.

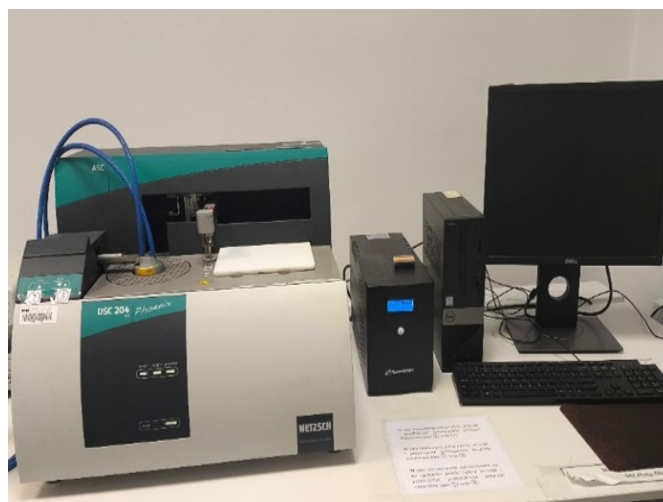


Figure A2. Photo-DSC 204 F1 Phoenix[®] system with Bluepoint LED eco light source at 405 nm ($\approx 18.67 \text{ mW}\cdot\text{cm}^{-2}$), calibrated using an OmniCure R2000 radiometer; samples sealed in aluminum crucibles with quartz covers and measured isothermally at 25 °C.



Figure A3. MCR302e rheometer equipped with an optical curing module; samples irradiated with 405 nm LEDs ($\approx 19.8 \text{ mW}\cdot\text{cm}^{-2}$) controlled by a DC2200 supply; temperature maintained at 25 °C.



Figure A4. Thermo Scientific Phenom XL G3 Desktop SEM; accelerating voltage 5–20 kV; CeB₆ source; max. magnification 200000 $\times$.

A3. Kinetic studies using the FT-IR method

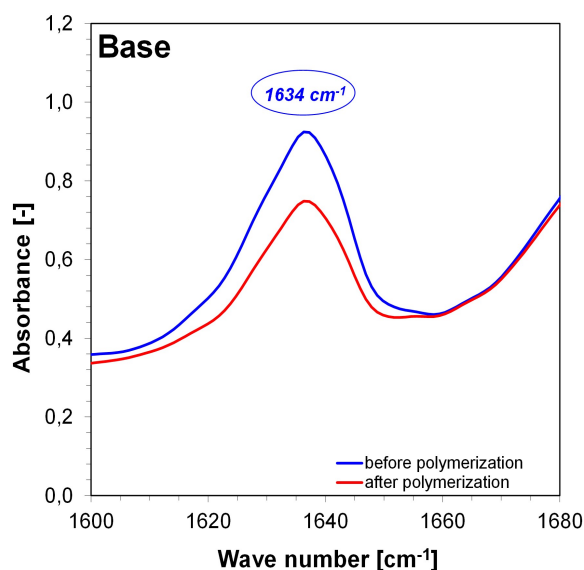


Figure A5. Before and After irradiation absorbance spectra obtained for photo-curable compositions based on UDMA/TEGDMA monomers in weight ratio 7 : 3 and one component photoinitiating systems (only photoinitiator ~ 1 wt%) during sample monitoring for 600 s and LED@405 nm irradiation with a light intensity on the sample of $19.8 \text{ mW}\cdot\text{cm}^{-2}$.

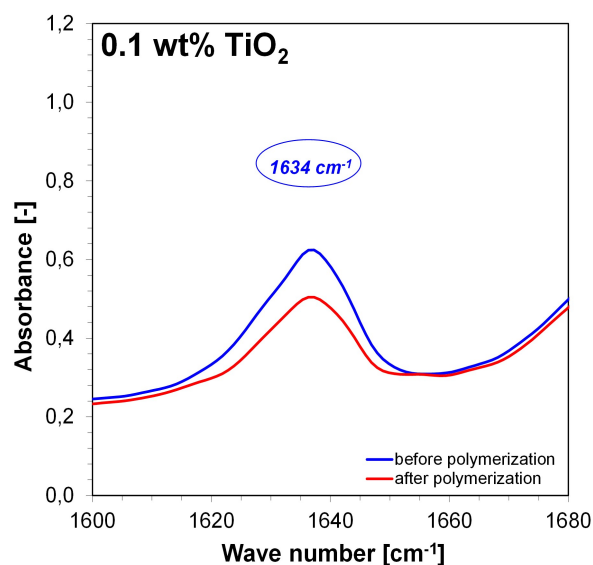


Figure A6. Before and After irradiation absorbance spectra obtained for photo-curable compositions based on UDMA/TEGDMA monomers in weight ratio 7 : 3 and one component photoinitiating systems (only photoinitiator ~ 1 wt%) and **0.1 wt% TiO_2** during sample monitoring for 600 s and LED@405 nm irradiation with a light intensity on the sample of $19.8 \text{ mW}\cdot\text{cm}^{-2}$.

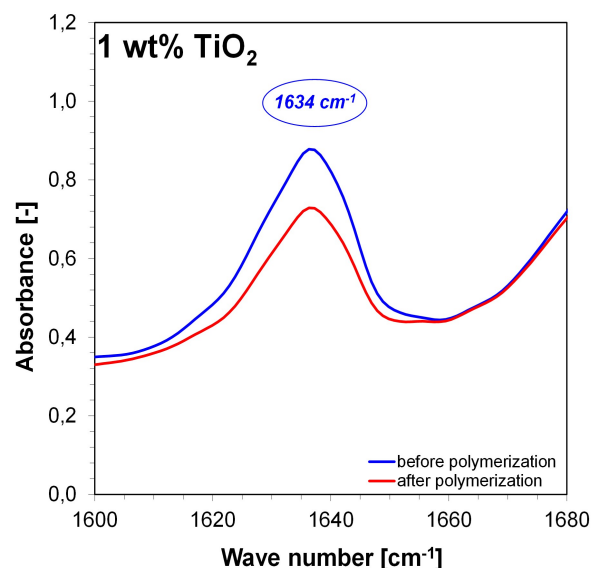


Figure A7. Before and After irradiation absorbance spectra obtained for photo-curable compositions based on UDMA/TEGDMA monomers in weight ratio 7 : 3 and one component photoinitiating systems (only photoinitiator ~ 1 wt%) and **1 wt% TiO_2** during sample monitoring for 600 s and LED@405 nm irradiation with a light intensity on the sample of $19.8 \text{ mW}\cdot\text{cm}^{-2}$.

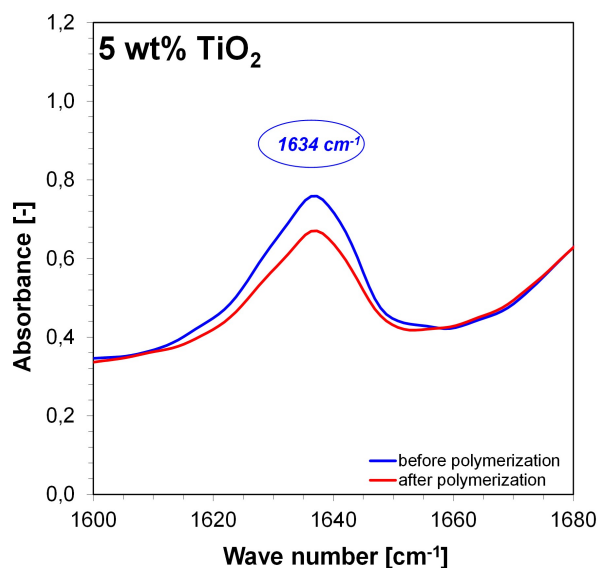


Figure A8. Before and After irradiation absorbance spectra obtained for photo-curable compositions based on UDMA/TEGDMA monomers in weight ratio 7 : 3 and one component photoinitiating systems (only photoinitiator ~ 1 wt%) and **5 wt% TiO_2** during sample monitoring for 600 s and LED@405 nm irradiation with a light intensity on the sample of $19.8 \text{ mW}\cdot\text{cm}^{-2}$.

A4. Kinetic studies using the Photo-DSC method

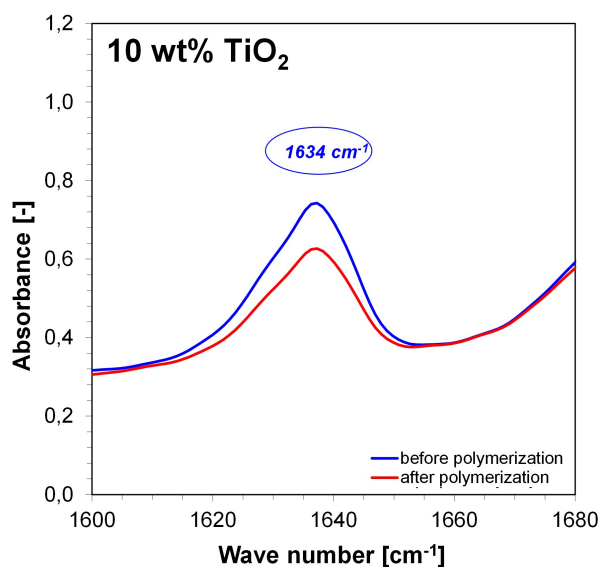


Figure A9. Before and After irradiation absorbance spectra obtained for photo- curable compositions based on UDMA/TEGDMA monomers in weight ratio 7:3 and one component photoinitiating systems (only photoinitiator ~ 1 wt-%) and **10 wt% TiO_2** during sample monitoring for light intensity on the sample of $19.8 \text{ mW}\cdot\text{cm}^{-2}$.

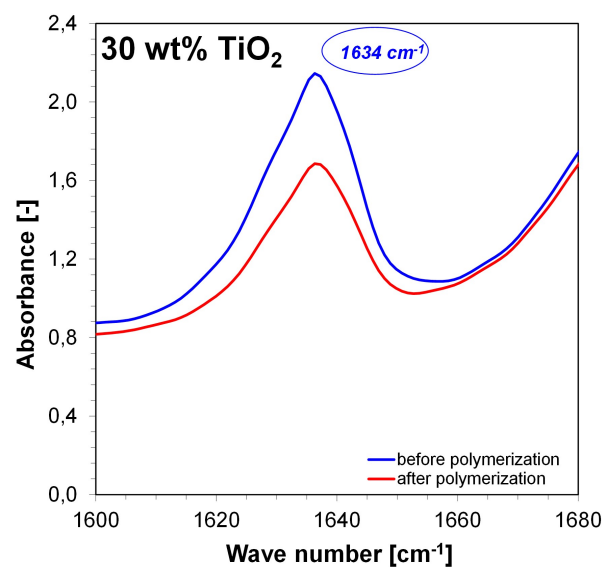


Figure A10. Before and After irradiation absorbance spectra obtained for photo- curable compositions based on UDMA/TEGDMA monomers in weight ratio 7:3 and one component photoinitiating systems (only photoinitiator ~ 1 wt-%) and **30 wt% TiO_2** during sample monitoring for 600 s and LED@405 nm irradiation with a $19.8 \text{ mW}\cdot\text{cm}^{-2}$.

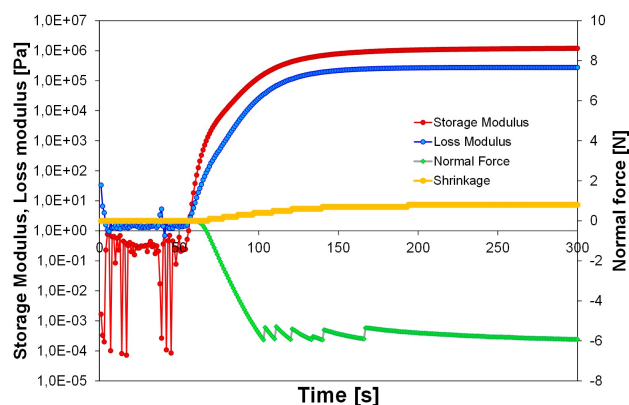


Figure A11. Photo-rheology profiles obtained for photo-curable compositions based on UDMA/TEGDMA monomers in weight ratio 7:3 and one component photoinitiating systems (only photoinitiator ~ 1 wt-%) during sample monitoring for 590 s and LED@405 nm irradiation with a light intensity on the sample of $19.8 \text{ mW}\cdot\text{cm}^{-2}$, the dark period was 10 s before the process of photopolymerization.

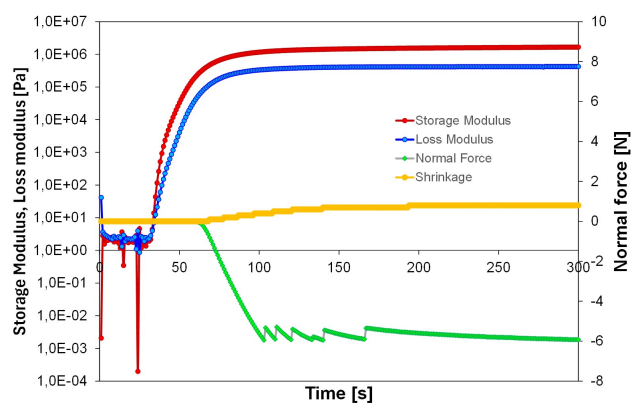


Figure A12. Photo-rheology profiles obtained for photo-curable compositions based on UDMA/TEGDMA monomers in weight ratio 7:3 and one component photoinitiating systems (only photoinitiator ~ 1 wt-%) and **0.1 wt% TiO_2** during sample monitoring for 600 s and LED@405 nm irradiation with a light intensity on the sample of $19.8 \text{ mW}\cdot\text{cm}^{-2}$, the dark period was 10 s before the process of photopolymerization.

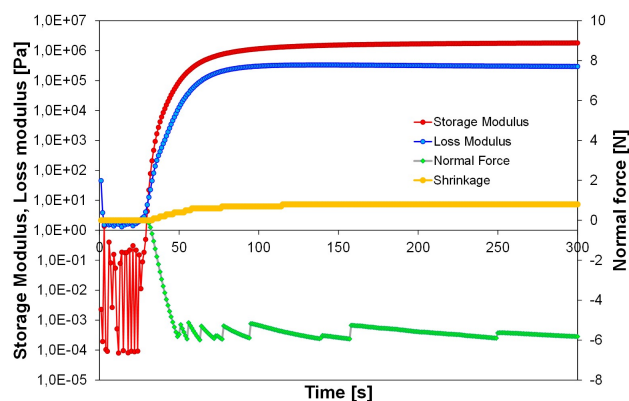


Figure A13. Photo-rheology profiles obtained for photo-curable compositions based on UDMA/TEGDMA monomers in weight ratio 7:3 and one component photoinitiating systems (only photoinitiator ~ 1 wt%) and **1 wt% TiO_2** during sample monitoring for 600 s and LED@405 nm irradiation with a light intensity on the sample of $19.8 \text{ mW}\cdot\text{cm}^{-2}$, the dark period was 10 s before the process of photopolymerization.

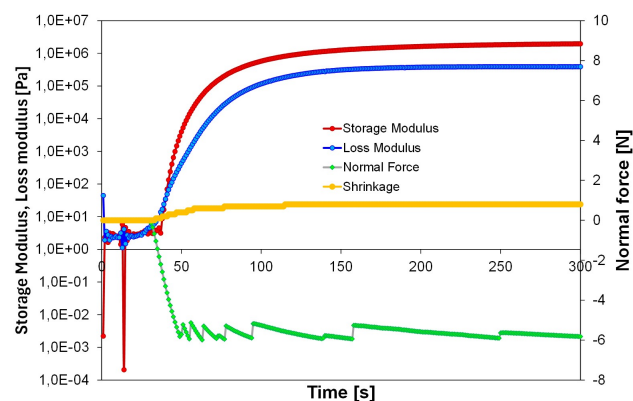


Figure A14. Photo-rheology profiles obtained for photo-curable compositions based on UDMA/TEGDMA monomers in weight ratio 7:3 and one component photoinitiating systems (only photoinitiator ~ 1 wt%) and **5 wt% TiO_2** during sample monitoring for 600 s and LED@405 nm irradiation with a light intensity on the sample of $19.8 \text{ mW}\cdot\text{cm}^{-2}$, the dark period was 10 s before the process of photopolymerization.

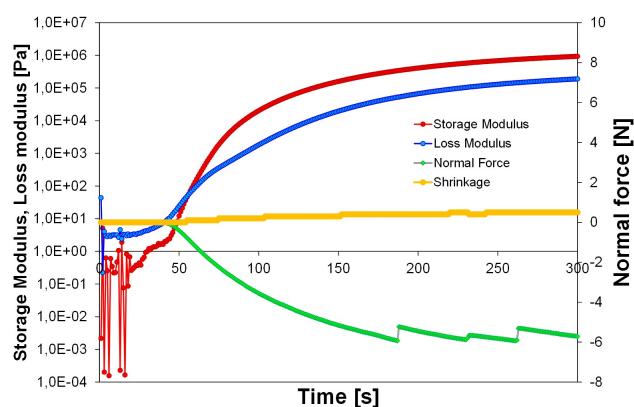


Figure A15. Photo-rheology profiles obtained for photo-curable compositions based on UDMA/TEGDMA monomers in weight ratio 7 : 3 and one component photoinitiating systems (only photoinitiator ~ 1 wt%) and **10 wt% TiO_2** during sample monitoring for 600 s and LED@405 nm irradiation with a light intensity on the sample of $19.8 \text{ mW}\cdot\text{cm}^{-2}$, the dark period was 10 s before the process of photopolymerization.

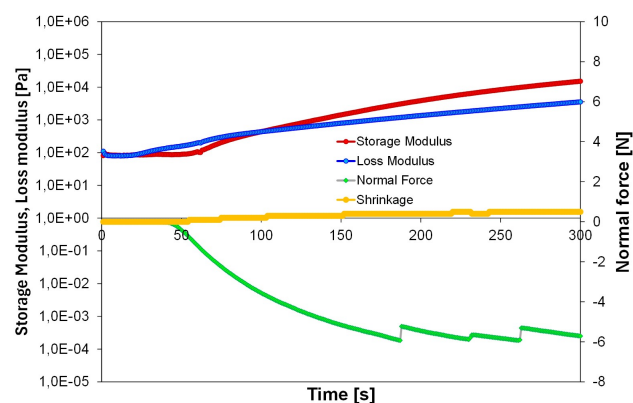


Figure A16. Photo-rheology profiles obtained for photo-curable compositions based on UDMA/TEGDMA monomers in weight ratio 7 : 3 and one component photoinitiating systems (only photoinitiator ~ 1 wt%) and **30 wt% TiO_2** during sample monitoring for 600 s and LED@405 nm irradiation with a light intensity on the sample of $19.8 \text{ mW}\cdot\text{cm}^{-2}$, the dark period was 10 s before the process of photopolymerization.

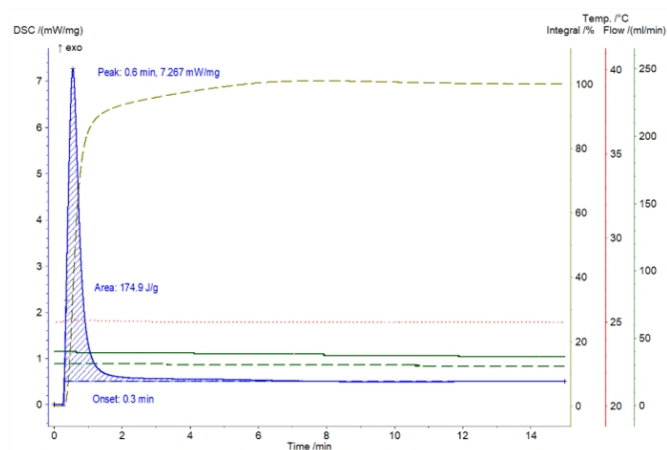


Figure A17. Photo-DSC heat profiles obtained for photo-curable compositions based on UDMA/TEGDMA monomers in weight ratio 7 : 3 and one component photoinitiating systems (only photoinitiator ~ 1 wt%) during sample monitoring for 900 s and LED@405 nm irradiation with a light intensity on the sample of $18.67 \text{ mW}\cdot\text{cm}^{-2}$.

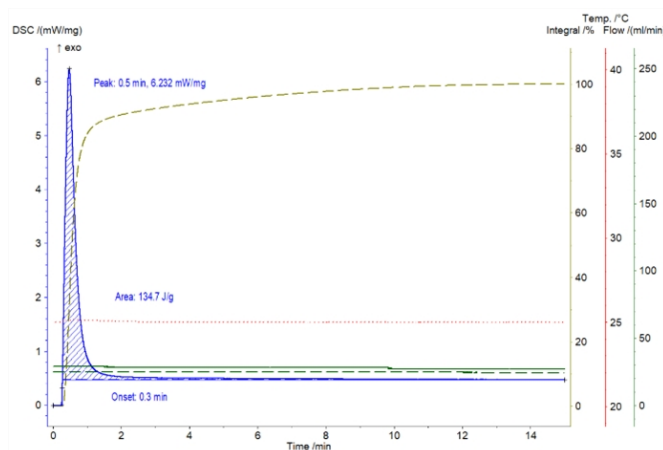


Figure A18. Photo-DSC heat profiles obtained for photo-curable compositions based on UDMA/TEGDMA monomers in weight ratio 7 : 3 and one component photoinitiating systems (only photoinitiator ~ 1 wt%) and $0.1 \text{ wt}\%$ TiO_2 during sample monitoring for 900 s and LED@405 nm irradiation with a light intensity on the sample of $18.67 \text{ mW}\cdot\text{cm}^{-2}$.

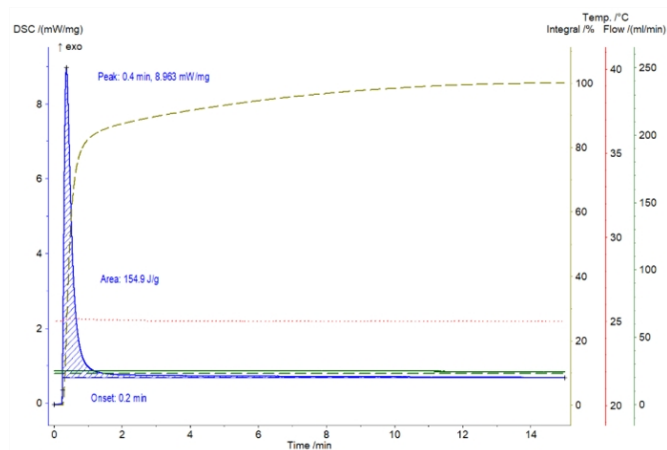


Figure A19. Photo-DSC heat profiles obtained for photo-curable compositions based on UDMA/TEGDMA monomers in weight ratio 7 : 3 and one component photoinitiating systems (only photoinitiator ~ 1 wt%) and $1 \text{ wt}\%$ TiO_2 during sample monitoring for 900 s and LED@405 nm irradiation with a light intensity on the sample of $18.67 \text{ mW}\cdot\text{cm}^{-2}$.

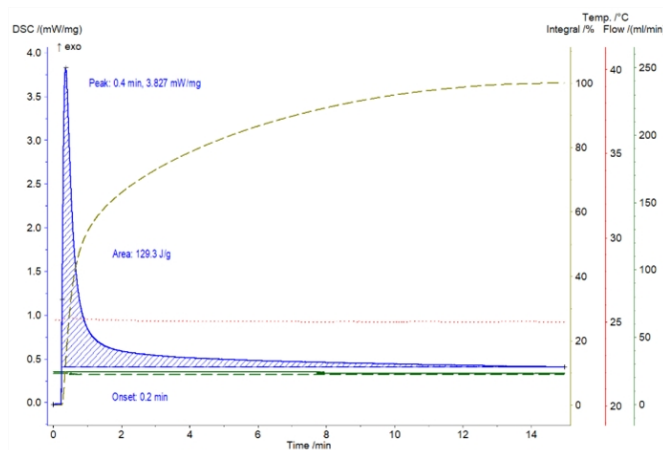


Figure A20. Photo-DSC heat profiles obtained for photo-curable compositions based on UDMA/TEGDMA monomers in weight ratio 7 : 3 and one component photoinitiating systems (only photoinitiator ~ 1 wt%) and $5 \text{ wt}\%$ TiO_2 during sample monitoring for 900 s and LED@405 nm irradiation with a light intensity on the sample of $18.67 \text{ mW}\cdot\text{cm}^{-2}$.

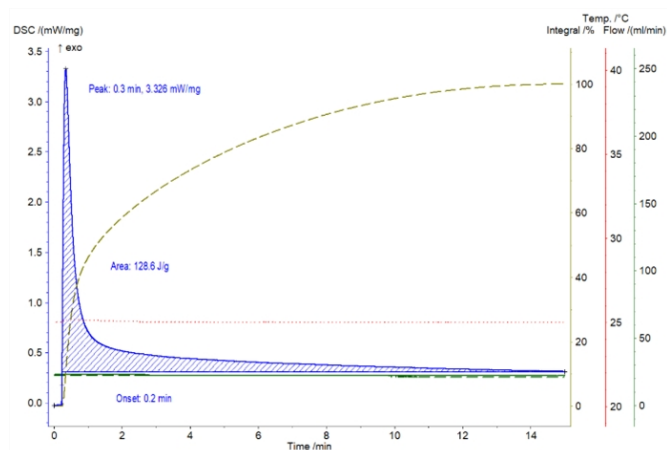


Figure A21. Photo-DSC heat profiles obtained for photo-curable compositions based on UDMA/TEGDMA monomers in weight ratio 7 : 3 and one component photoinitiating systems (only photoinitiator ~ 1 wt%) and 10 wt% TiO₂ during sample monitoring for 900 s and LED@405 nm irradiation with a light intensity on the sample of 18.67 mW·cm⁻².

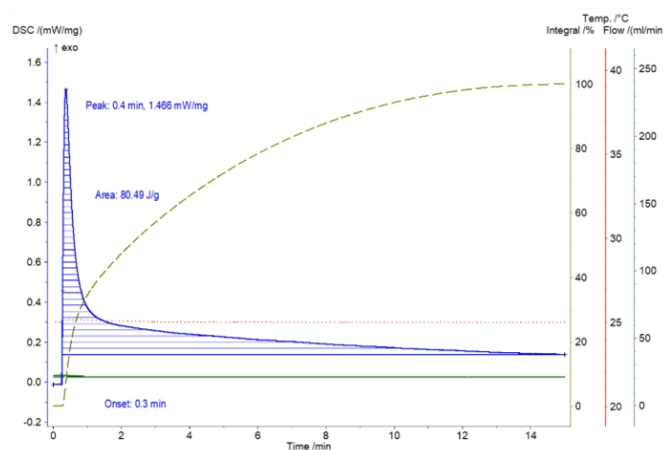


Figure A22. Photo-DSC heat profiles obtained for photo-curable compositions based on UDMA/TEGDMA monomers in weight ratio 7 : 3 and one component photoinitiating systems (only photoinitiator ~ 1 wt%) and 30 wt% TiO₂ during sample monitoring for 900 s and LED@405 nm irradiation with a light intensity on the sample of 18.67 mW·cm⁻².

Table A3. Printing parameters for the 3D printers used.

DLP LumenX™ Gen 3 (UDMA/TEGDMA 7:3, One component photoinitiating system)					
Sample	Irradiation power [mW·cm ⁻²]	Energy dose [mJ·cm ⁻²]	Exposure time [s]	Base exposure time [s]	Layer height [μm]
Base	20.5	513	25	75	50
0.1 wt% TiO ₂	20.5	513	25	75	50
1 wt% TiO ₂	25.9	777	30	80	50
5 wt% TiO ₂	25.2	907	35	75	50
10 wt% TiO ₂	29.6	1480	50	85	50
30 wt% TiO ₂	28.9	1387	48	90	50

LCD Anycubic Photon Mono M7 PRO (UDMA/TEGDMA 7:3, One component photoinitiating system)					
Sample	Irradiation power [mW·cm ⁻²]	Energy dose [mJ·cm ⁻²]	Exposure time [s]	Base exposure time [s]	Layer height [μm]
Base	7	490	70	120	50
0.1 wt% TiO ₂	7	525	75	130	50