

Study of the photopolymerization process of luminescent-labeled photocurable compositions in liquid and gas media

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Abstract

Although photocurable compositions are widely used in 3D printing, protective coatings and biomedical materials, their polymerization in oxygen-containing environments is strongly hindered by oxygen inhibition, which prolongs the reaction time and reduces the conversion rate of monomers. This study investigated the effect of the reaction environment (argon atmosphere and liquid media: distilled water and CuSO₄ solutions) on the kinetics of free-radical photopolymerization of four acrylic compositions (Bis-GMA with TMPTA or EBECRYL 45, 130, 3300 oligomers). The kinetics were monitored using Fluorescence Probe Technology (FPT) with a coumarin 102 fluorescence probe and photorheology under 365 nm UV-LED irradiation. The results showed that in an argon atmosphere, oxygen inhibition is eliminated, resulting in the shortest induction times. In liquid environments, induction times are longer, but initial polymerization rates are higher than in the gas phase due to multiple reflections of UV radiation and a higher effective dose. The addition of Cu²⁺ ions partially suppresses this effect by absorbing light. The work provides new data on the design of photopolymerizable systems with increased oxygen resistance, which is important for applications in VPP photopolymerization 3D printing.

Keywords

photopolymerization, luminescence, light cured

1. INTRODUCTION

Photopolymerization is a chemical process involving the initiation and progression of polymerization under the influence of electromagnetic radiation, most commonly in the UV or visible light range. The absorption of photons by photoinitiators results in the formation of reactive radicals or cations, which initiate the formation of long polymer chains from monomers (Corrigan et al., 2019; Jandt and Mills, 2013). This mechanism allows for precise control of the reaction process both in terms of time and space, making photopolymerization an energy-efficient and more environmentally friendly process than techniques based on elevated temperatures (He et al., 2023). It has found wide application in coating technology, dental materials, 3D printing, biomedicine (including the production of hydrogels that imitate tissues) and electronics, particularly in the production of flexible functional components (Chiulan et al., 2021; Fiedor et al., 2020; Lu et al., 2022; Ribas-Massonis et al., 2022; Schneider et al., 2010; Tezel et al., 2025; Topa and Ortyl, 2020; Wang et al., 2023). In recent years, there has been intensive development of photoinitiators activated by visible light and near-infrared light, which significantly increases the safety of processes carried out in biological environments, e.g., in regenerative medicine (Gao et al., 2025; Xiao et al., 2025; Xu et al., 2025). At the same time, hybrid systems combining radical and cationic mechanisms, composites reinforced with nanomaterials such as graphene

and smart formulations enabling process monitoring thanks to built-in luminescent probes are also being developed (Chen et al., 2025; Hola et al., 2021; Mohd Shuhairi et al., 2025).

Photopolymerization can be carried out in various phases, which significantly affects its kinetics and efficiency. In liquid systems, such as aqueous solutions, the process is easy to carry out, but its efficiency may be limited by light absorption by the solvent and slower diffusion of molecules. In gaseous systems, especially in an atmosphere of inert gases (argon, nitrogen), these limitations are minimal, resulting in faster reactions and high monomer conversion (Bowers et al., 2022; Hsieh and Zellers, 2002; Liz-Basteiro et al., 2023; Luo et al., 2024; Yang et al., 2023).

The most serious challenge in free radical photopolymerization remains oxygen inhibition. Oxygen, which dissolves easily in many solvents, reacts with radicals to form less reactive oxyradicals that inhibit polymer chain propagation. This phenomenon leads to longer induction times, reduced polymerization rates and lower conversion rates, resulting in materials with poorer mechanical properties and the presence of residual monomers. This problem is particularly important in open-air processes such as 3D printing and in biomedical applications. Inhibition is more intense in liquid systems where oxygen solubility is higher, while in gaseous systems under an inert atmosphere, this effect practically disappears. Strategies to reduce inhibition include the use of protective atmospheres,



oxygen scavenger additives (e.g., triphenylphosphine), enzymatic oxygen removal systems (glucose/glucose oxidase), the use of thiol-ene or cationic mechanisms and increasing light intensity (Andrzejewska, 2001; Belon et al., 2010; O'Brien and Bowman, 2006; Cai et al., 2021; Li et al., 2024; Llorente et al., 2021; Müller et al., 2022; Zhang et al., 2025).

Optimizing photopolymerization requires advanced methods for monitoring reaction kinetics. Photo-DSC enables analysis of reaction heat and determination of the rate and activation energy of the process. Real-time FT-IR spectroscopy allows direct tracking of the disappearance of characteristic bonds, such as C=C bonds. Techniques based on luminescent probes (FPT), which use dyes sensitive to changes in viscosity and polarization of the environment, are of particular importance. The intensity or wavelength of the emitted light changes as polymerization progresses, enabling non-invasive monitoring of the process with high temporal and spatial resolution (Camposo et al., 2022; Hu et al., 1998; Jiang and Drummer, 2020; Lang et al., 2022; Li et al., 2020; Szymaszek et al., 2023).

The use of luminescently labeled photopolymerizing compositions in liquid and gaseous environments allows for an in-depth understanding of the effect of oxygen on the kinetics of the process in different phases. Comparing reactions carried out in water, where oxygen inhibition is particularly strong, with reactions in an argon atmosphere, where this effect is almost completely absent, provides mechanistic insight into oxygen-related effects and can guide the rational design of oxygen-resistant photopolymer systems. This opens up new avenues of development in the areas of 3D printing, smart coatings and advanced polymer materials, making photopolymerization a key technology for sustainable innovation in science and industry.

2. EXPERIMENTAL PART

2.1. Materials

The study used systems consisting of 2,2-bis[4(2-hydroxy-3-methacryloxypropoxy)phenylene]propane (Bis-GMA, Sigma-Aldrich), trimethylolpropane triacrylate (TMPTA, Sigma-Aldrich), four-functional acrylated oligomer EBECRYL 45 (E45, Allnex), aliphatic diacrylate EBECRYL 130 (E130, Allnex), modified bisphenol-A-based epoxy acrylate oligomer EBECRYL 3300 (E3300, Allnex) and the photoinitiator diphenyl (2,4,6-trimethylbenzoyl) phosphine oxide (TPO, Allnex). In addition, 2,3,6,7-tetrahydro-9-methyl-1H,5H-quinolizino(9,1-g) coumarin (coumarin 102) was used as a fluorescent probe to monitor the kinetics of the photopolymerization process.

2.2. Instrumentation

2.2.1. Rheometer

A Physica MCR 302 rheometer (Anton Paar) was used to determine the viscosity of the tested composites. For photorheological measurements, the device was equipped with a special attachment enabling the samples to be exposed to UV radiation using parallel plate geometry. The attachment was fitted with a Thorlabs M365L2 UV (30 mA, 8 mW/cm²) diode with a wavelength of 365 nm. The rheometer operated under controlled temperature conditions thanks to the use of a thermostat.

2.2.2. UV-Vis apparatus (Fluorescence Probe Technology)

A set of equipment included a SILVER fiber optic spectrophotometer -Nova 200 TEC fiber optic spectrophotometer from StellarNet Inc. with a spectral range of 190–1100 nm and a Roithner Laser Technik RLT365-10E UV-LED emitting radiation with a wavelength of $\lambda_{\max} = 365$ nm, with a diode power

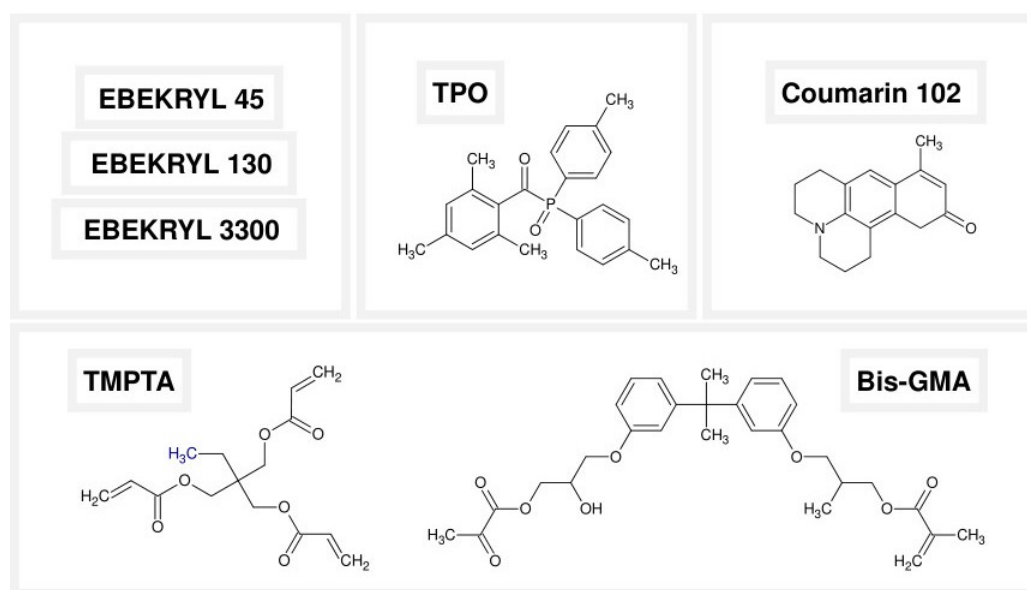


Figure 1. Compounds used for research.

of 22.5 mA (6 mW/cm²). These components were connected using Fibrochem fiber optics and the diode was powered by a dedicated power supply controlled by a computer equipped with software enabling both UV source control and analysis of recorded data. The temperature of the system was stabilized by a Thorlabs ITC4020 thermostat working in conjunction with a Peltier module equipped with a heat sink. The sample was irradiated perpendicular to its surface using a UV-LED diode, while the optical fiber connected to the spectrophotometer was set at an angle of 30° to the diode axis.

2.3. Measurement methodology

2.3.1. Rheological and photorheological measurements

Rheological tests of photopolymerizable compositions were performed at 25 °C, setting the zero gap at 0.2 mm using a spindle with a diameter of 25.019 mm. The procedure began with applying the sample to the rheometer base and setting the appropriate distance between the spindle and the substrate. Once this was achieved, excess material was removed and the actual measurement started. The analysis was carried out at variable spindle speeds (shear rates) ranging from 1 s⁻¹ to 100 s⁻¹ for 550 seconds. A spindle with a diameter of 20 mm was used for photorheological tests. During photorheological measurements, after temperature stabilization, the composition was evenly spread on a UV-transmitting glass plate, the zero gap was set and the excess was removed. The total measurement time was 10 minutes and the UV source was activated simultaneously with its start. Irradiation began 10 seconds after the start of the measurement, which is reflected in the rapid increase in both mechanical moduli after this time. The total recording time was 600 seconds, but due to the rapid transition of the composition from sol to gel, the graphical analysis was limited to the first 150 seconds of the measurement.

2.3.2. Kinetic studies using the FPT technique

The composition prepared for testing was dripped onto a holder consisting of a microscope slide and a 0.1 mm thick ring glued to it. The tests were conducted in four environments: argon, distilled water, saturated copper sulphate solution and saturated copper sulphate solution with the addition of sulfuric acid at a concentration of 1 mol/dm³. The selection of media allowed for the simultaneous assessment of the influence of oxygen content, optical properties and rheological characteristics on the course of photopolymerization. In order to conduct the tests in an aqueous environment, the prepared sample was placed on a polystyrene dish and then the dish was placed in the measuring chamber. For measurements in an argon environment, the measuring chamber was connected to an argon cylinder using a silicone hose before thermostating began. The measuring chamber was purged with argon for 2 minutes to ensure the removal of oxygen.

Based on previous investigations, a purging time of 1 minute was found to be sufficient to reduce the oxygen concentration below the limit of detection. Therefore, a 2-minute purging period was applied, corresponding to an adopted safety factor of 2. For measurements in the remaining three environments, the sample was covered with the liquid before thermostating, to a depth of 5 mm below the surface. The tests were carried out in two modes: fast and slow data collection. In fast mode, the program collected the emission spectrum of the sample every 3 seconds and in the next stage, in slow mode, every 32 seconds. The program was set to 150 fast scans and 100 slow scans. The measurement of one sample in a given environment took a total of 80 minutes, of which 60 minutes were spent measuring the kinetics of photopolymerization and 20 minutes were spent thermostating the measuring chamber to stabilize the temperature at 25 °C.

The aim of the study was to determine the influence of the reaction environment on the kinetics of photopolymerization, analyzed by measuring changes in the *R* parameter using the FPT (Fluorescence Probe Technology) method. This technique enables real-time monitoring of the cross-linking process based on changes in the emission characteristics of a luminescent fluorescent probe placed in a photopolymerizable composition. With increasing monomer conversion and growing stiffness of the resulting polymer network, systematic modifications in the probe emission spectrum are observed (Fig. 2), reflected by the *R* parameter, defined as the ratio of the recorded emission spectrum at time *t* to the emission spectrum before polymerization. Analysis of the *R(t)* function allows the determination of key kinetic parameters: the induction time *t*_{ind} and the initial polymerization rate $(\frac{dR}{dt})_0$, which is a measure of the reaction dynamics in the early stage of crosslinked structure formation.

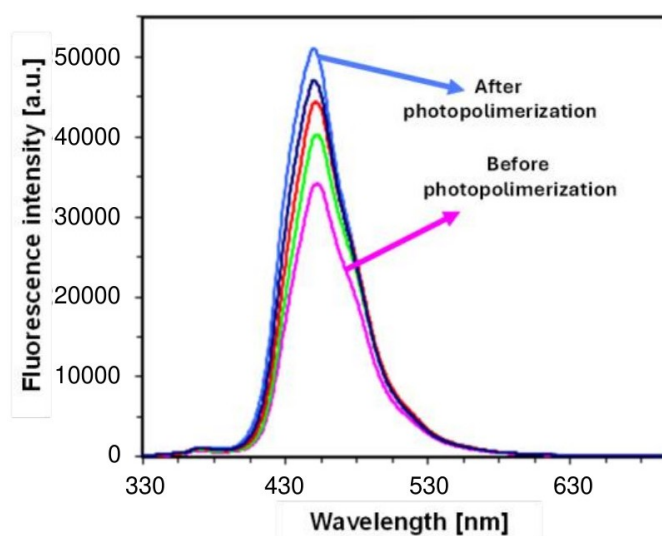


Figure 2. Changes in the emission spectrum of a fluorescent probe during the polymerization process for sample E45+BisGMA in a saturated copper(II) sulfate solution.

2.4. Sample preparation

For rheological and photorheological studies, four samples were prepared consisting of TPO photoinitiator added to the composition at a concentration of 1% by weight and E45+BisGMA, E130+BisGMA, E3300+BisGMA and TMPTA+BisGMA monomers in a 1:1 weight ratio for each composition. The compositions for testing the kinetics of photopolymerization using the FPT method were prepared with the addition of 0.1% by weight of a fluorescent probe (coumarin 102).

3. RESULTS

3.1. Rheological and photorheological studies

Figures 3–6 present the dependence of viscosity on shear rate for four compositions: E45 + BisGMA, E130 + BisGMA, E3300 + BisGMA and TMPTA + BisGMA. All tested systems exhibit shear-thinning behavior typical of non-Newtonian fluids, with viscosity decreasing as the shear rate increases. The most pronounced effect is observed in the case of the E45+BisGMA mixture, for which the viscosity initially reaches very high values, then decreases rapidly, stabilizing only at higher shear rates. This indicates a strong susceptibility of this system to liquefaction under the influence of deformation. The E130+BisGMA mixture is characterized by significantly higher rheological stability. Over the entire shear-rate range, the viscosity changes only slightly and remains close to approximately 16362 mPa·s. A similar trend, albeit with significantly

higher viscosity values, is observed in the E3300+BisGMA system, in which the viscosity gradually but slightly decreases from approximately 48424 mPa·s. The lowest viscosity values were recorded for the TMPTA+BisGMA mixture, where, despite a slight decrease in viscosity with increasing shear, it remains relatively stable at around 10084 mPa·s. All graphs indicate the shear-rate ranges used to calculate the average viscosity, corresponding to regions of relatively stable viscosity behavior for each composition.

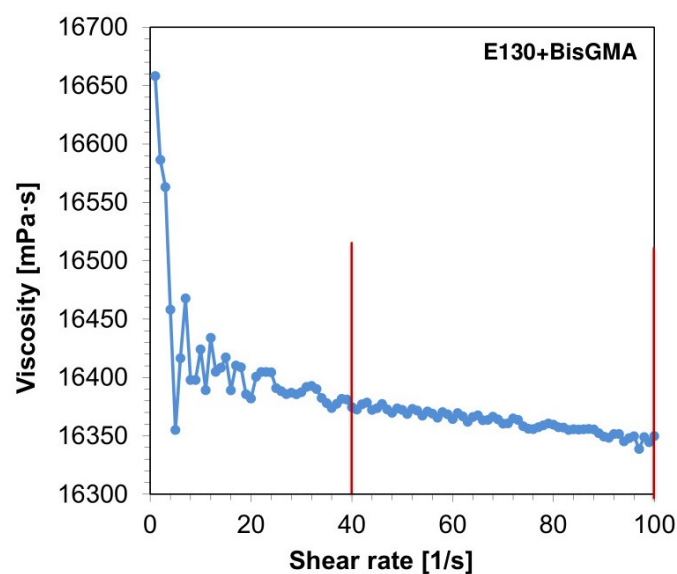


Figure 4. The dependence of viscosity on the shear rate of the E130+BisGMA sample, with the area from which the average viscosity of the composition was calculated marked.

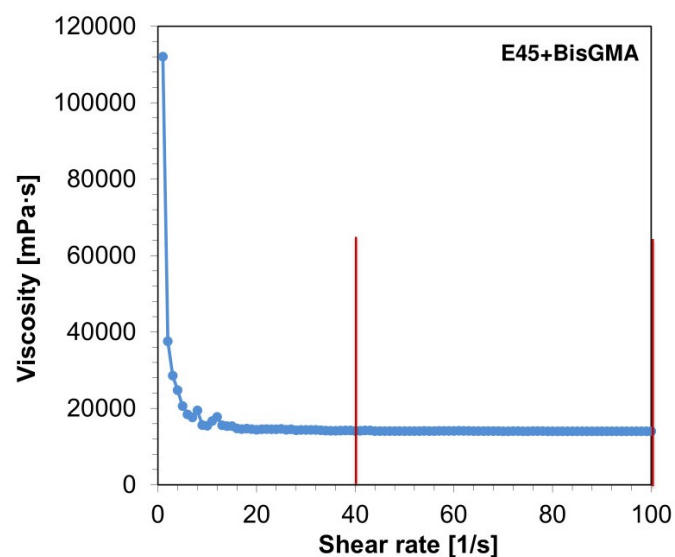


Figure 3. The dependence of viscosity on the shear rate of the E45+BisGMA sample, with the area from which the average viscosity of the composition was calculated marked.

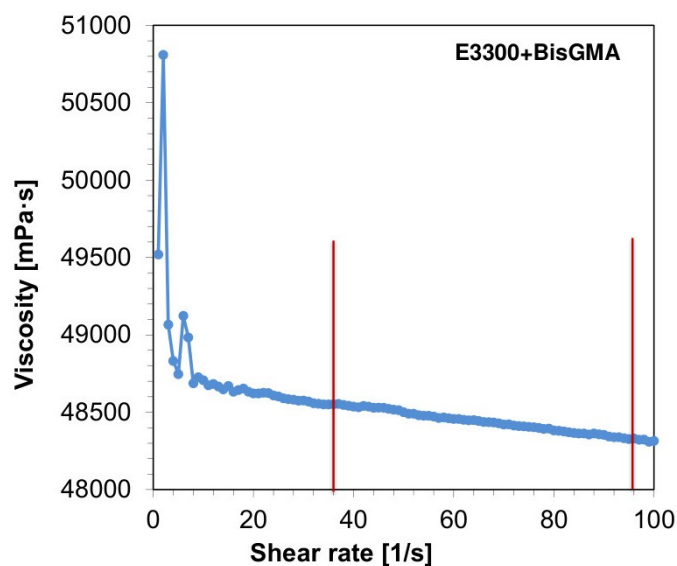


Figure 5. The dependence of viscosity on the shear rate of the E3300+BisGMA sample, with the area from which the average viscosity of the composition was calculated marked.

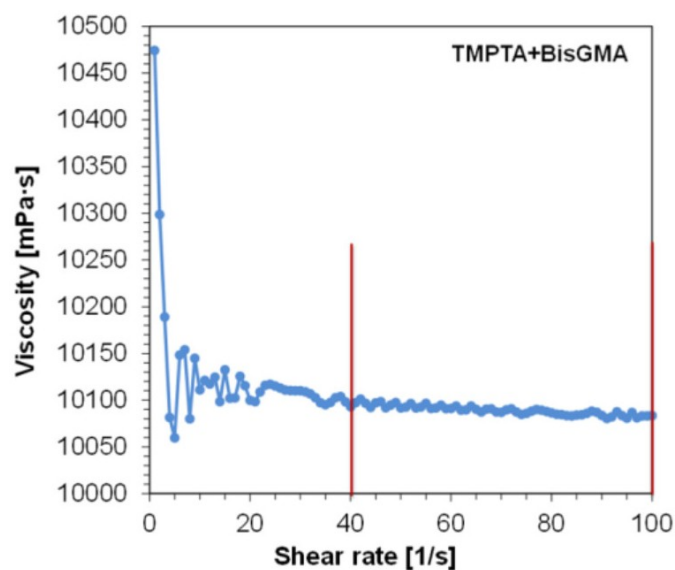


Figure 6. The dependence of viscosity on the shear rate of the TMPTA+BisGMA sample, with the area from which the average viscosity of the composition was calculated marked.

Based on rheological tests, changes in the conservative modulus, loss modulus and normal force were presented for four photopolymerizable compositions (Figs. 7–10) exposed to UV. In rheological studies, the gelation time, which corresponds to the moment of intersection of the conservative modulus and the loss modulus, was considered a key parameter. At this point, the material begins to behave like an elastic body, which indicates the formation of a three-dimensional polymer network. Analysis of the graphs and numerical data clearly shows that the individual compositions differ both in the rate of polymerization and in the amount of shrinkage accompanying the cross-linking process.

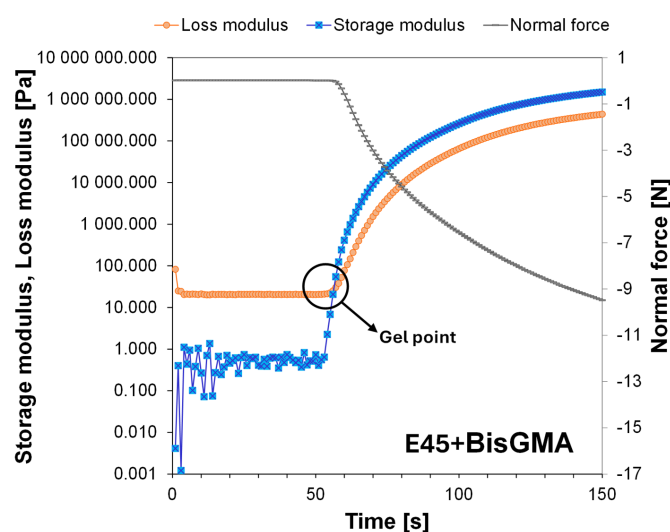


Figure 7. The relationship between the retention modulus, loss modulus and normal force over time, with the gel point marked for sample E45+BisGMA.

The E45+BisGMA sample reaches the gelation point 56 seconds after the start of the measurement, which indicates a moderate rate of network structure formation. The polymerization shrinkage calculated from Equation (1) for this composition is 1.40%, which is the highest value among all the materials tested. Analysis of the normal force curve confirms more intense shrinkage deformation after gel formation. The E130+BisGMA composition has one of the fastest polymerization processes, reaching the gel point after only 50 seconds. At the same time, the polymerization shrinkage of this sample is 1.00%, which is an intermediate value. The combination of a short gelation time and moderate shrinkage indicates a favorable balance between reactivity and dimensional stability during cross-linking.

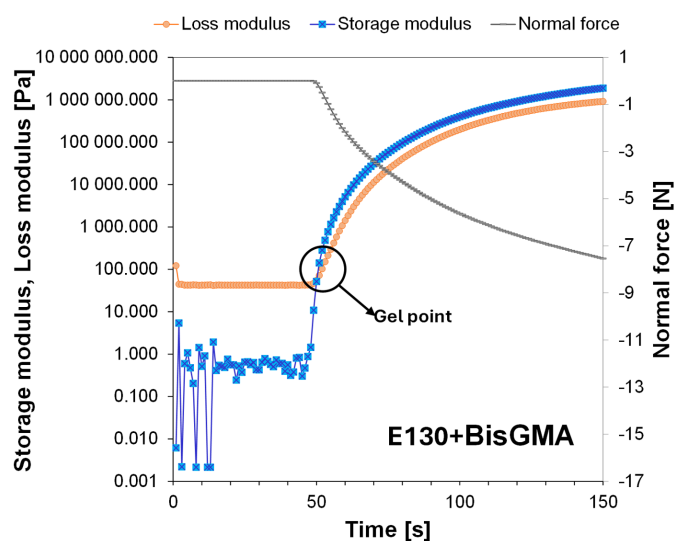


Figure 8. The relationship between the retention modulus, loss modulus and normal force over time, with the gel point marked for sample E130+BisGMA.

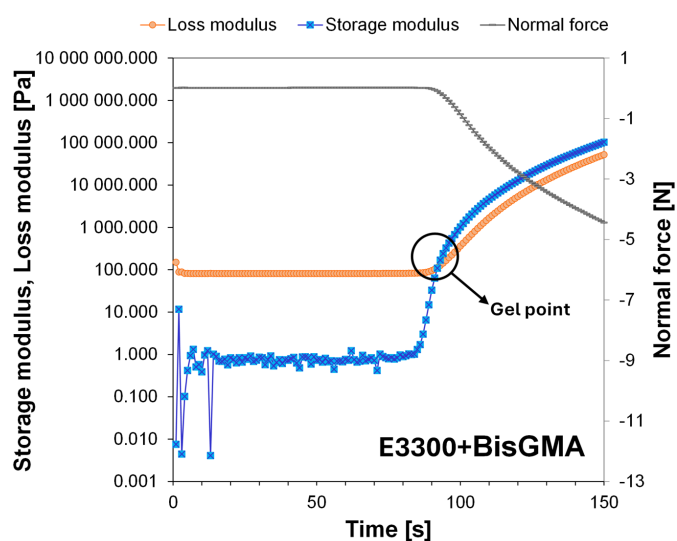


Figure 9. The relationship between the retention modulus, loss modulus and normal force over time, with the gel point marked for sample E3300+BisGMA.

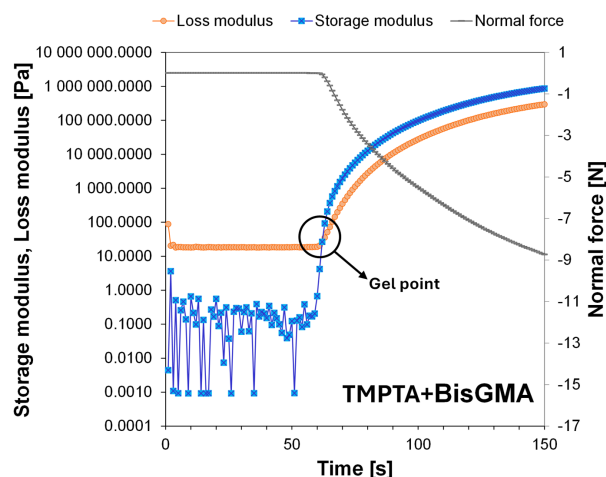


Figure 10. The relationship between the retention modulus, loss modulus and normal force over time, with the gel point marked for sample TMPTA+BisGMA.

The E3300+BisGMA composition exhibits the slowest polymerization kinetics, reaching the gel point only after 92 s — the longest gelation time among all tested samples. The slow transition from the viscous to the elastic phase is reflected in the lowest polymerization shrinkage of only 0.80%. The last of the tested compositions, TMPTA+BisGMA, reaches the gelation point after 62 seconds, which indicates a fast, but not the fastest, polymerization rate. The polymerization shrinkage value for this sample is also 1.00%. The presence of the trifunctional TMPTA monomer promotes the dynamic development of the cross-linked network, which is confirmed by the rapid increase in the conservative modulus and clear changes in normal force after reaching the gelation point. The data obtained during photorheological measurements are summarized in Table 1.

$$\text{Polymerization shrinkage [\%]} = \left(1 - \frac{d_{\text{before}}}{d_{\text{after}}}\right) \cdot 100\% \quad (1)$$

where: d_{after} — distance between the aluminum spindle and the glass base after completion of the polymerization process [mm], d_{before} — distance between the aluminum spindle and the glass base before the start of the polymerization process [mm].

Table 1. Photorheology measurement results.

Composition	Medium	Gel time [s]	Polymerization shrinkage [%]	Average viscosity [mPa·s]
E45+BisGMA	UV Light	56	1.40	—
E130+BisGMA	UV Light	50	1.00	16362
E3300+BisGMA	UV Light	92	0.80	48424
TMPTA+BisGMA	UV Light	62	1.00	10084

3.2. Kinetic measurements using the FPT method

Analysis of induction times (Table 2) showed that the shortest t_{ind} values occurred in an argon atmosphere, longer ones in water, even longer ones in a CuSO_4 solution and the longest ones in a $\text{CuSO}_4\text{--H}_2\text{SO}_4$ solution. This trend was fully confirmed by the $R(t)$ curves (Figs. 11–14). The mechanism behind the observed sequence is mainly due to oxygen inhibition. Under anaerobic conditions (argon), the quenching of radicals by oxygen is negligible, allowing propagation to start almost immediately. In an aqueous environment, however, dissolved oxygen is present, resulting in a short-term inhibition

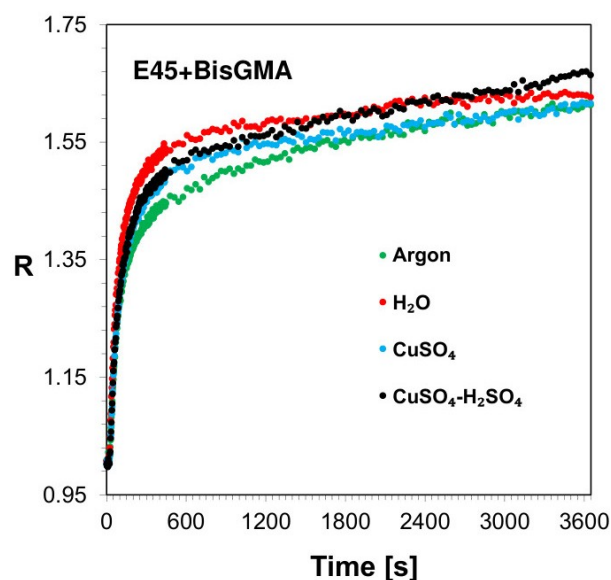


Figure 11. Graph showing the dependence of the r parameter on time for the composition named e45+bisigma in different environments.

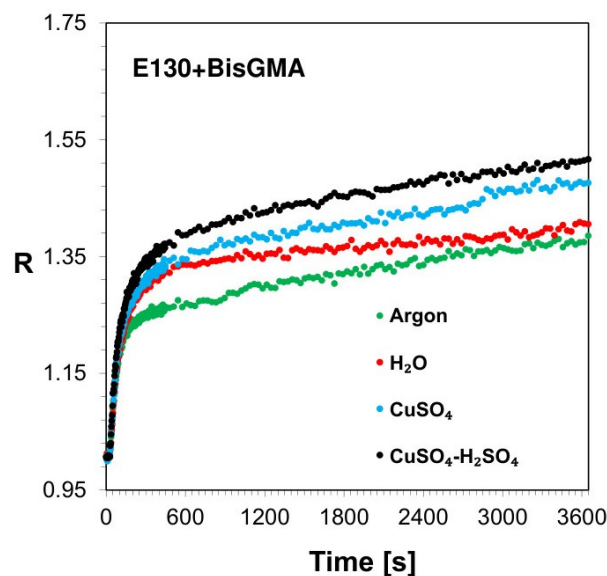


Figure 12. Graph showing the dependence of the r parameter on time for the composition named e130+bisigma in different environments.

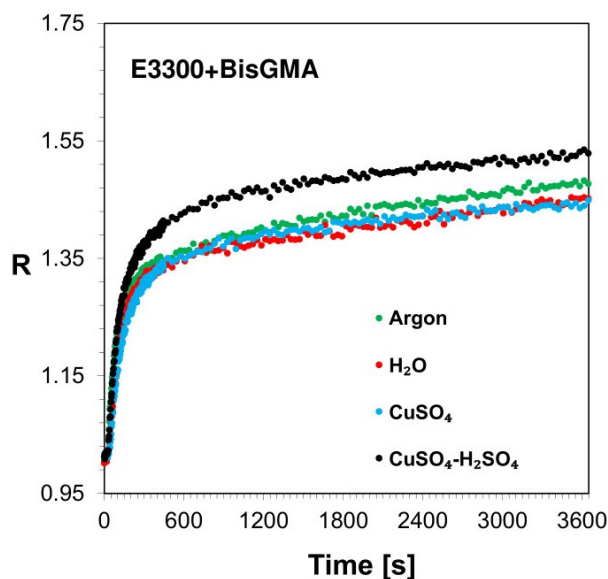


Figure 13. Graph showing the dependence of the r parameter on time for the composition named e3300+bisgma in different environments.

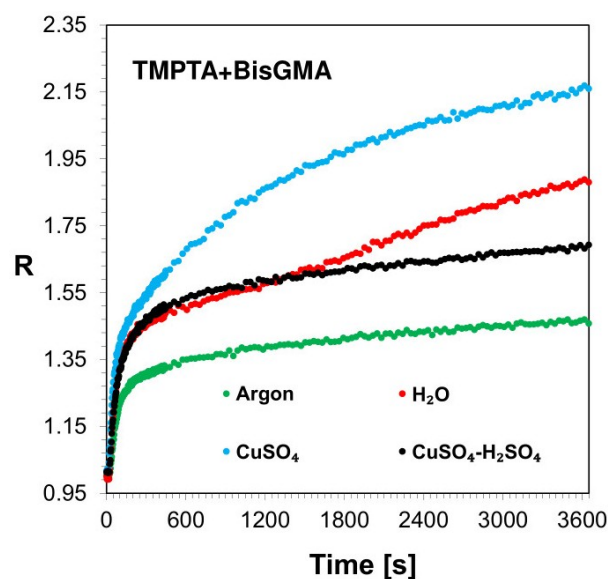


Figure 14. Graph showing the dependence of the r parameter on time for the composition named tmpta+bisgma in different environments.

of initiation. In the CuSO_4 solution, oxygen inhibition persists longer despite the presence of Cu^{2+} ions capable of reducing oxygen, because some oxygen remains available and, in addition, the liquid limits the diffusion of radicals. The strongest delay in initiation was observed in the $\text{CuSO}_4\text{--H}_2\text{SO}_4$ solution, where strongly hydrated copper(II) ions have a limited ability to reduce oxygen, which prolongs the time it takes to remove it from the reaction environment.

The values for the initial polymerization rates $\left(\frac{dR}{dt}\right)_0$ in liquid media, especially in water, were higher than in argon. This is due to fundamental optical differences between the gas and

Table 2. Results of kinetic studies using the FPT technique.

Composition	Medium	t_{ind} [s]	$\left(\frac{dR}{dt}\right)_0$
E45+BisGMA	Argon	18.15	$4.34 \cdot 10^{-3}$
	Distilled water	19.55	$6.26 \cdot 10^{-3}$
	CuSO_4	20.30	$4.72 \cdot 10^{-3}$
	$\text{CuSO}_4\text{--H}_2\text{SO}_4$	21.28	$4.75 \cdot 10^{-3}$
E130+BisGMA	Argon	25.09	$3.05 \cdot 10^{-3}$
	Distilled water	27.50	$3.15 \cdot 10^{-3}$
	CuSO_4	27.48	$3.16 \cdot 10^{-3}$
	$\text{CuSO}_4\text{--H}_2\text{SO}_4$	27.17	$4.00 \cdot 10^{-3}$
E3300+BisGMA	Argon	18.78	$3.20 \cdot 10^{-3}$
	Distilled water	24.73	$2.18 \cdot 10^{-3}$
	CuSO_4	27.18	$2.16 \cdot 10^{-3}$
	$\text{CuSO}_4\text{--H}_2\text{SO}_4$	27.51	$3.61 \cdot 10^{-3}$
TMPTA+BisGMA	Argon	15.07	$2.86 \cdot 10^{-3}$
	Distilled water	14.73	$5.34 \cdot 10^{-3}$
	CuSO_4	16.45	$7.45 \cdot 10^{-3}$
	$\text{CuSO}_4\text{--H}_2\text{SO}_4$	18.02	$4.59 \cdot 10^{-3}$

liquid phases. In argon, the UV beam penetrates the sample and is reflected to a minimal extent. In liquid media, however, multiple reflections occur at the phase boundary, leading to secondary irradiation of the sample and, consequently, an increase in the effective radiation dose. The higher photon flux results in more intense radical generation and a higher initial rate of increase of the R parameter.

In CuSO_4 and $\text{CuSO}_4\text{--H}_2\text{SO}_4$ solutions, there is an additional effect of UV radiation absorption by Cu^{2+} ions, reducing the intensity of radiation reaching the interior of the sample. This has a dampening effect on the propagation rate, making $\left(\frac{dR}{dt}\right)_0$ in these media greater than in argon, but lower than in water. These trends are shown in the $R(t)$ curves (Figs. 11–14).

4. CONCLUSIONS

The investigated resin systems exhibited non-Newtonian shear-thinning behavior with viscosity and gelation characteristics strongly dependent on composition. Photorheological analysis confirmed that resin formulation governed polymerization rate and shrinkage, directly influencing network formation and dimensional stability. Kinetic studies using the FPT technique demonstrated a pronounced influence of the reaction environment on photopolymerization. The shortest induction times were observed under argon, confirming the role of oxygen inhibition, whereas aqueous and metal-ion-containing media prolonged the induction period. In contrast, the initial polymerization rate $\left(\frac{dR}{dt}\right)_0$ was higher in liquid environments, indicating the additional contribution of optical effects to the

reaction kinetics. Overall, the results highlight the combined impact of chemical and optical factors on photopolymerization and provide guidance for the development of oxygen-tolerant photopolymer systems.

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REFERENCES

- Andrzejewska E., 2001. Photopolymerization kinetics of multi-functional monomers. *Prog. Polym. Sci.*, 26, 605–665. DOI: [10.1016/S0079-6700\(01\)00004-1](https://doi.org/10.1016/S0079-6700(01)00004-1).
- Belon C., Allonas X., Croutxé-Barghorn C., Lalevée J., 2010. Overcoming the oxygen inhibition in the photopolymerization of acrylates: a study of the beneficial effect of triphenylphosphine. *J. Polym. Sci., Part A: Polym. Chem.*, 48, 2462–2469. DOI: [10.1002/pola.24017](https://doi.org/10.1002/pola.24017).
- Bowers L.N., Stefaniak A.B., Knepp A.K., LeBouf R.F., Martin S.B. Jr., Ranpara A.C., Burns D.A., Virji M.A., 2022. Potential for exposure to particles and gases throughout vat photopolymerization additive manufacturing processes. *Buildings*, 12, 1222. DOI: [10.3390/buildings12081222](https://doi.org/10.3390/buildings12081222).
- Cai W.-B., Liu D.-D., Chen Y., Zhang L., Tan J.-B., 2021. Enzyme-assisted photoinitiated polymerization-induced self-assembly in continuous flow reactors with oxygen tolerance. *Chin. J. Polym. Sci.*, 39, 1127–1137. DOI: [10.1007/s10118-021-2533-z](https://doi.org/10.1007/s10118-021-2533-z).
- Campos A., Arkadii A., Romano L., D'Elia F., Fabbri F., Zussman E., Pisignano D., 2022. Impact of size effects on photopolymerization and its optical monitoring *in-situ*. *Addit. Manuf.*, 58, 103020. DOI: [10.1016/j.addma.2022.103020](https://doi.org/10.1016/j.addma.2022.103020).
- Chen Y., Li L., Han G., Liu R., An G., Zhu Y., 2025. Macromolecular coumarin sulfonium salt with side chain effect constructed by copolymerization strategy for free radical, cationic and hybrid photopolymerizations. *Chin. Chem. Lett.*, 36, 110458. DOI: [10.1016/j.cclet.2024.110458](https://doi.org/10.1016/j.cclet.2024.110458).
- Chiulan I., Heggset E.B., Voicu Ş.I., Chinga-Carrasco G., 2021. Photopolymerization of bio-based polymers in a biomedical engineering perspective. *Biomacromolecules*, 22, 1795–1814. DOI: [10.1021/acs.biomac.0c01745](https://doi.org/10.1021/acs.biomac.0c01745).
- Corrigan N., Yeow J., Judzewitsch P., Xu J., Boyer C., 2019. Seeing the light: Advancing materials chemistry through photopolymerization. *Angew. Chem. Int. Ed.*, 58, 5170–5189. DOI: [10.1002/anie.201805473](https://doi.org/10.1002/anie.201805473).
- Fiedor P., Pilch M., Szymaszek P., Chachaj-Brekiesz A., Galek M., Ortyl J., 2020. Photochemical study of a new bimolecular photoinitiating system for vat photopolymerization 3D printing techniques under visible light. *Catalysts*, 10, 284. DOI: [10.3390/catal10030284](https://doi.org/10.3390/catal10030284).
- Gao T., Liu Z., Yin J., Feng J., Dietlin C., Morlet-Savary F., Schmitt M., Petithory T., Pieuchot L., Zhang J., Dumur F., Lalevée J., Xiao P., 2025. Novel low-cytotoxic and highly efficient type I photoinitiators for visible LED-/sunlight-induced photopolymerization and high-precision 3D printing. *Angew. Chem. Int. Ed.*, 64, e202425598. DOI: [10.1002/anie.202425598](https://doi.org/10.1002/anie.202425598).
- He X., Zang L., Xin Y., Zou Y., 2023. An overview of photopolymerization and its diverse applications. *Appl. Res.*, 2, e202300030. DOI: [10.1002/appl.202300030](https://doi.org/10.1002/appl.202300030).
- Hola E., Gruchała A., Popielarz R., Ortyl J., 2021. Non-destructive visual inspection of photocurable coatings based on fluorescent response of naked-eye visible colorimetric and fluorescent sensors. *Eur. Polym. J.*, 160, 110802. DOI: [10.1016/j.eurpolymj.2021.110802](https://doi.org/10.1016/j.eurpolymj.2021.110802).
- Hsieh M.-D., Zellers E.T., 2002. In situ UV-photopolymerization of gas-phase monomers for microanalytical system applications. *Sens. Actuators, B: Chem.*, 82, 287–296. DOI: [10.1016/S0925-4005\(01\)01011-5](https://doi.org/10.1016/S0925-4005(01)01011-5).
- Hu S., Popielarz R., Neckers D.C., 1998. Fluorescence probe techniques (FPT) for measuring the relative efficiencies of free-radical photoinitiators. *Macromolecules*, 31, 4107–4113. DOI: [10.1021/ma971390l](https://doi.org/10.1021/ma971390l).
- Jandt K.D., Mills R.W., 2013. A brief history of LED photopolymerization. *Dent. Mater.*, 29, 605–617. DOI: [10.1016/j.dental.2013.02.003](https://doi.org/10.1016/j.dental.2013.02.003).
- Jiang F., Drummer D., 2020. Curing kinetic analysis of acrylate photopolymer for additive manufacturing by photo-DSC. *Polymers*, 12, 1080. DOI: [10.3390/polym12051080](https://doi.org/10.3390/polym12051080).
- Lang M., Hirner S., Wiesbrock F., Fuchs P., 2022. A review on modeling cure kinetics and mechanisms of photopolymerization. *Polymers*, 14, 2074. DOI: [10.3390/polym14102074](https://doi.org/10.3390/polym14102074).
- Li J., Li S., Li Y., Li R., Nie J., Zhu X., 2020. In situ monitoring of photopolymerization by photoinitiator with luminescence characteristics. *J. Photochem. Photobiol., A: Chem.*, 389, 112225. DOI: [10.1016/j.jphotochem.2019.112225](https://doi.org/10.1016/j.jphotochem.2019.112225).
- Li X., Bian F., Huang R., Wei J., Gui X., Hu J., Li W., Lin S., 2024. Preparation of free radical/cationic hybrid UV-cured silicone materials with reducing oxygen inhibition via silyl radicals. *Eur. Polym. J.*, 221, 113582. DOI: [10.1016/j.eurpolymj.2024.113582](https://doi.org/10.1016/j.eurpolymj.2024.113582).
- Liz-Basteiro P., Sanz-Horta R., Reviriego F., Martínez-Campos E., Reinecke H., Elvira C., Rodríguez-Hernández J., Gallardo A., 2023. High resolution molds, sacrificial in aqueous media, obtained by vat photopolymerization 3D printing. *Addit. Manuf.*, 75, 103758. DOI: [10.1016/j.addma.2023.103758](https://doi.org/10.1016/j.addma.2023.103758).
- Llorente O., Agirre A., Calvo I., Olaso M., Tomovska R., Sardon H., 2021. Exploring the advantages of oxygen-tolerant thiol-ene polymerization over conventional acrylate free radical photopolymerization processes for pressure-sensitive adhesives. *Polym. J.*, 53, 1195–1204. DOI: [10.1038/s41428-021-00520-z](https://doi.org/10.1038/s41428-021-00520-z).

- Lu G., Yuan H., Zhou J., Chen F., Li C., Xue T., Shu X., Zhao Y., Nie J., Zhu X., 2022. Patterned magnetofluids via magnetic printing and photopolymerization for multifunctional flexible electronic sensors. *ACS Appl. Mater. Interfaces*, 14, 30332–30342. DOI: [10.1021/acsami.2c04755](https://doi.org/10.1021/acsami.2c04755).
- Luo J., Ruta V., Kwon I.S., Albertazzi J., Allasia N., Nevskiy O., Busini V., Moscatelli D., Vilé G., 2024. Fabricating a structured single-atom catalyst via high-resolution photopolymerization 3D printing. *Adv. Funct. Mater.*, 34, 2404794. DOI: [10.1002/adfm.202404794](https://doi.org/10.1002/adfm.202404794).
- Mohd Shuhairi D.N., Abdul Malek N.S., Mohd Ghazali M.I., Sin N.D.M., Bonnia N.N., Yamada K., Rosman N., Hajar N., Omar H., Asli N.A., 2025. Nanofillers in vat photopolymerisation additive manufacturing: Mechanical properties of graphene and acrylate-based composites. *Prog. Addit. Manuf.*, 10, 11319–11341. DOI: [10.1007/s40964-025-01289-w](https://doi.org/10.1007/s40964-025-01289-w).
- Müller S.M., Schlögl S., Wiesner T., Haas M., Griesser T., 2022. Recent advances in type I photoinitiators for visible light induced photopolymerization. *ChemPhotoChem*, 6, e202200091. DOI: [10.1002/cptc.202200091](https://doi.org/10.1002/cptc.202200091).
- O'Brien A.K., Bowman C.N., 2006. Impact of oxygen on photopolymerization kinetics and polymer structure. *Macromolecules*, 39, 2501–2506. DOI: [10.1021/ma051863l](https://doi.org/10.1021/ma051863l).
- Ribas-Massonis A., Cicujano M., Duran J., Besalú E., Poater A., 2022. Free-radical photopolymerization for curing products for refinishing coatings market. *Polymers*, 14, 2856. DOI: [10.3390/polym14142856](https://doi.org/10.3390/polym14142856).
- Schneider O.D., Stepuk A., Mohn D., Luechinger N.A., Feldman K., Stark W.J., 2010. Light-curable polymer/calcium phosphate nanocomposite glue for bone defect treatment. *Acta Biomater.*, 6, 2704–2710. DOI: [10.1016/j.actbio.2010.01.033](https://doi.org/10.1016/j.actbio.2010.01.033).
- Szymaszek P., Tomal W., Świergosz T., Kamińska-Borek I., Popielarz R., Ortyl J., 2023. Review of quantitative and qualitative methods for monitoring photopolymerization reactions. *Polym. Chem.*, 14, 1690–1717. DOI: [10.1039/D2PY01538B](https://doi.org/10.1039/D2PY01538B).
- Tezel Ö., Kahraman M.V., Ceylan R., Açıkşarı A., Demir E., Çetinel S., 2025. Usage of 3D-printed scaffolds manufactured with bio-based photopolymer resin via 3D DLP in tissue engineering. *J. Polym. Environ.*, 33, 3013–3028. DOI: [10.1007/s10924-025-03592-7](https://doi.org/10.1007/s10924-025-03592-7).
- Topa M., Ortyl J., 2020. Moving towards a finer way of light-cured resin-based restorative dental materials: recent advances in photoinitiating systems based on iodonium salts. *Materials*, 13, 4093. DOI: [10.3390/ma13184093](https://doi.org/10.3390/ma13184093).
- Wang P., Li J., Yang J., Wang G., He L., Zhang H., 2023. Enabling 3D multilayer electronics through the hybrid of vat photopolymerization and laser-activated selective metallization. *Addit. Manuf.*, 74, 103717. DOI: [10.1016/j.addma.2023.103717](https://doi.org/10.1016/j.addma.2023.103717).
- Xiao X., Huang Z., Duan H., Yang L., Yang Y., Lai Y., Li C., Feng L., 2025. Enhanced near-infrared light-mediated hydrogel curing using photoinitiator integrated upconversion particles as nano initiator for 3D bioprinting. *Biomacromolecules*, 26, 3364–3379. DOI: [10.1021/acs.biomac.4c01775](https://doi.org/10.1021/acs.biomac.4c01775).
- Xu M., Liu M., Wang F., Chi H., 2025. Strategies to improve water solubility of photoinitiator for photopolymerization-based 3D printing in biomedical applications. *ACS Appl. Polym. Mater.*, 7, 4077–4092. DOI: [10.1021/acsapm.5c00184](https://doi.org/10.1021/acsapm.5c00184).
- Yang S., Chen T., Bu Z., Tuo X., Gong Y., Guo J., 2023. Thermal responsive photopolymerization 3D printed shape memory polymers enhanced by heat transfer media. *J. Appl. Polym. Sci.*, 140, e53514. DOI: [10.1002/app.53514](https://doi.org/10.1002/app.53514).
- Zhang Y., de Haan H., Houlahan K., Sampson K.L., Webber D., Orth A., Lacelle T., Gaburici L., Lam R., Deore B., Paquet C., 2025. Impact of oxygen inhibition on (meth)acrylate photopolymerization in tomographic volumetric printing. *Addit. Manuf.*, 109, 104844. DOI: [10.1016/j.addma.2025.104844](https://doi.org/10.1016/j.addma.2025.104844).