Universal Library of Medical and Health Sciences Methodological Guide

ISSN: 3064-6545 | Volume 4, Issue 1

Open Access | PP: 42-53

DOI: https://doi.org/10.70315/uloap.ulmhs.2026.0401005

Photopolymerization of Gels: Curing Kinetics and Degree of Conversion as Predictors of Biocompatibility

Spizhova Y.

Nail Specialist, USA.

Abstract

Within the scope of the study, an in-depth analysis was conducted of the physicochemical regularities governing the photopolymerization of methacrylate systems used in contemporary nail-service practice, with particular emphasis on identifying cause-and-effect relationships between the degree of chemical conversion and the biological safety parameters of the resulting coatings. The key aspects of radical polymerization are presented in a consistent sequence, and it is shown how the spectral characteristics of current LED sources determine initiation efficiency and the ultimate curing depth of the material. Reaction completeness control is described through analytical approaches based on infrared spectroscopy (FTIR), which enables quantitative assessment of the reduction in the fraction of reactive groups and, by doing so, objectifies the degree of conversion.

A separate semantic emphasis is placed on the migration of residual low-molecular-weight components, primarily 2-hydroxyethyl methacrylate (HEMA), as a critical factor shaping the toxicological profile. In parallel, the regulatory shifts of 2025 are considered, including the ban on the photoinitiator TPO within the Omnibus VII package, which necessitates revision of traditional solutions in the area of photoinitiation and formulation design. As a result of the analysis, it is demonstrated that achieving a degree of conversion above 75–80% functions as a principled condition for lowering the likelihood of allergic contact dermatitis and reducing the risk of systemic sensitization, because insufficient conversion correlates with an increased fraction of migratory monomers and oligomeric fragments.

The formulated conclusions support the advisability of transitioning to updated initiation systems and substantiate the introduction of hybrid organic–inorganic materials as a technological direction capable of simultaneously increasing curing efficiency and stabilizing the composition after polymerization. The materials presented have applied significance for nail-service practice, dermatological assessment, cosmetic formulation development, and certification-oriented evaluation procedures aimed at improving safety levels within the beauty industry.

Keywords: *Photopolymerization, Degree of Conversion, Methacrylates, Biocompatibility, Nail Industry, Residual Monomer, IR Spectroscopy, Photoinitiators, Omnibus VII, Allergic Contact Dermatitis.*

CONTENT

Citation: Spizhova Y., “Photopolymerization of Gels: Curing Kinetics and Degree of Conversion as Predictors of Biocompatibility”, Universal Library of Medical and Health Sciences, 2026; 4(1): 42-53. DOI: https://doi.org/10.70315/uloap.ulmhs.2026.0401005.

INTRODUCTION

The relevance of studying photopolymerization processes in the nail industry is determined by a combination of rapid market expansion and an increasing burden of medico-biological risks associated with occupational exposure. According to 2024 data, the global market for nail care products reached USD 23.6–25.66 billion, while the projected compound annual growth rate (CAGR) through 2034 is estimated in the range of 5.2–5.9%, a trend linked to stronger consumer demand for personal hygiene practices, aesthetic standards, and wellness-oriented procedures [6, 7]. Against the background of growing technological complexity of materials and a widening spectrum of procedures, an increase has been recorded in the frequency of occupation-related dermatoses among nail technicians: statistical information for 2024 indicates that skin pathologies associated with professional exposure are identified in 12.4% of specialists, and among patients seeking specialized dermatological care, allergic contact dermatitis (ACD) is verified in 79.4% of cases [9].

A key scientific and practical deficit in this area is associated with insufficient operationalization of the causal relationship between curing kinetics of methacrylate compositions and their delayed biological effects on body tissues. Within this logic, the purpose of the work consists in systematizing existing views on photopolymerization mechanisms and providing evidence-based substantiation of the degree of conversion as a reproducible and technologically relevant predictor of the biocompatibility of decorative coatings.

The novelty of the study is formulated through establishing threshold levels for the content of residual components (HEMA, TMPTA), above which the probability of systemic sensitization becomes clinically meaningful, particularly under conditions of a shifting paradigm of photoinitiator use [1, 2].

As an initial premise, a hypothesis is adopted that optimization of spectral matching between LED sources and implementation of Type II initiation systems (CQ–thiols) enable achievement of a degree of conversion at which migration of toxic haptens is minimized while concurrently reducing the risk of thermal overload of nail-bed tissues.

CHAPTER 1. PHYSICOCHEMICAL PARADIGM OF PHOTOPOLYMERIZATION IN THE NAIL INDUSTRY

The chapter examines the physicochemical basis of photopolymerization of gel materials in the nail industry through the lens of free-radical curing kinetics, initiation pathways, and the determinants of conversion degree and the residual reactive potential of the cured coating. A comparative discussion is provided for Type I and Type II initiating systems, including the practical implications of the EU restriction on TPO taking effect in September 2025, alongside an analysis of autoacceleration (“gel effect”) and post-irradiation curing (“dark reaction”) as they relate to the formation of a mechanically resilient polymer network and, consequently, coating durability. A dedicated section addresses spectral selectivity: how dual-LED sources (365/405 nm), pigments, and light scattering modulate the effective curing depth, why a “false” surface hardness can arise despite incomplete bulk conversion, and how sensitizer-assisted strategies may broaden the usable spectral window. The chapter concludes with an examination of oxygen inhibition and the emergence of the tacky inhibition layer as a central interfacial limitation governing monomer/hapten migration (e.g., HEMA), the trade-off between increasing irradiance and thermally mediated risks, and the role of contemporary surface modifiers in reducing overall toxicological burden.

Kinetic Models of Radical Curing and Initiation Mechanisms

The transformation of liquid-phase oligomeric compositions into solid nail coatings proceeds as a multistage chain reaction of free-radical photopolymerization. The specificity of nail practice fundamentally differentiates this process from industrial coating application: technological parameters are constrained by the requirement of biological acceptability for body tissues, which dictates the use of comparatively low irradiation intensities (3–15 mW/cm^2) and curing under atmospheric air conditions [12]. From a kinetic standpoint, the mechanism includes three basic stages—initiation, chain growth, and termination—where the initial triggering of the reaction is determined by the photophysical and photochemical properties of the initiating system. At the initiation stage, photoinitiator molecules absorb light quanta, transition into an activated state, and form primary radicals that set the subsequent dynamics of macromolecular chain buildup.

For Type I photoinitiators, among which TPO is included, a mechanism of direct radical formation via homolytic bond cleavage is characteristic, providing nearly instantaneous entry of the composition into the polymerization regime and potentially being accompanied by a high process rate reaching 160%/min [10, 11]. At the same time, the pronounced reactivity of TPO correlates with increasing toxicological concern, which in 2024–2025 led to a revision of

its safety status. Within the Omnibus VII regulation package, the component was attributed to reproductive toxicants of category 1B, as a result of which a complete ban on its use was introduced in the European Union as of September 2025 [3]. This regulatory change objectively creates technological pressure on the sector and stimulates a shift toward alternative solutions, including TPO-L or photoinitiation systems of a different class.

One of the key alternatives is represented by Type II photoinitiators, whose functioning is linked to the obligatory participation of a co-initiator (an amine or thiol donor) and proceeds through electron transfer followed by formation of a radical center. It has been shown that binary combinations of "CQ + thiol," where camphorquinone (CQ) functions as the light-absorbing component, can provide a degree of conversion on the order of 67%, comparable with outcomes of traditional systems, while simultaneously improving the biocompatibility profile [10]. For clarity, Table 1 presents results of a comparative analysis of the effectiveness of initiation systems in pigmented gels.

Table 1. Comparative analysis of the effectiveness of initiation systems in pigmented gels (compiled by the author based on [3, 4, 10]).

Initiation system	Degree of conversion (DC, %)	Rate (Rp, %/min)	Residual monomer content	Regulatory status (2025)
TPO (Type I)	60–65	150–160	High (with underpolymerization)	Prohibited in the EU
TPO-L (Type I, safer)	55–60	90–110	Medium	Permitted
CQ + amine (Type II)	50–60	40–50	Moderate	Permitted
CQ + thiol (Advanced)	67–70	70–75	Low	Recommended

The development of initiation systems is to a significant extent oriented toward eliminating the phenomenon of the "dark reaction," in which polymerization persists after irradiation is stopped. High-quality gel compositions are characterized by a pronounced role of autoacceleration, known as the Trommsdorff effect: as the degree of conversion increases, the viscosity of the reaction medium rises abruptly, leading to diffusion limitations, reduced mobility of active centers, and subsequent "trapping" of radicals within the forming polymer network [17]. This physicochemical "entombment" of radicals functions as a structural stabilization factor and, in practical terms, is associated with increased coating durability [17].

The semantic trajectory from discussing the chemical nature of initiators to analyzing the physics of their activation makes it possible to consider photopolymerization not merely as a set of formulation solutions, but as a controllable system of interactions among the spectral characteristics of the source, the kinetics of radical transformations, and the evolution of viscoelastic properties of the material. Within this frame, mechanistic causes of technological defects and the formation of bioincompatibility become more transparent, because curing failures and residual reactivity of the coating emerge as direct consequences of mismatched activation regimes relative to the dynamics of polymer-matrix structure formation.

Spectral Selectivity and the Influence of LED Technologies on Curing Depth

The effectiveness of photopolymerization is determined primarily by the degree of spectral matching between the emitter and the absorption characteristics of the photoactive system, because coincidence of wavelengths with the absorption bands of initiators and sensitizers defines the distribution of radical generation rates across layer thickness. In the modern nail industry, LED devices dominate, producing narrowband emission with maxima near 365 and 405 nm (Dual-LED), reflecting an attempt to simultaneously ensure sufficient energy delivery to deeper zones and high structural build-up rates in the near-surface layer [19]. The 365 nm component is associated with more effective activation of the lower regions of the coating and formation of an adhesion-relevant interface with the nail plate, whereas the 405 nm region predominantly supports rapid surface curing, influencing smoothness and optical gloss indicators [19]. Use of low-quality sources is often accompanied by a "spectral gap," in which the actual emission insufficiently covers the absorption region of the system: as a result, an impression of hardness is formed externally due to accelerated near-surface curing, while an underpolymerized phase is retained at the base, creating prerequisites for latent skin contact with migratory monomeric components [13].

Limitations of curing depth acquire particular significance for highly pigmented gel compositions, where titanium dioxide particles and other pigments act as efficient centers of scattering and absorption of UV radiation, forming "shadow zones" within the layer with a deficit of photon flux and, consequently, a decrease in the local rate of radical formation. As a technological response to this phenomenon, 2025 saw implementation of photosensitizers, in particular Eosin Y, which expand the spectral absorption range of the system toward visible light and thereby increase the probability of initiation in screened regions [10]. At the same time, a biophysical risk aspect remains: research data from 2023 emphasize that, while UVA components are functionally necessary for curing, an excessive dose load can induce the formation of reactive oxygen species (ROS), associated with DNA damage in skin cells [13, 22] (see Fig. 1).

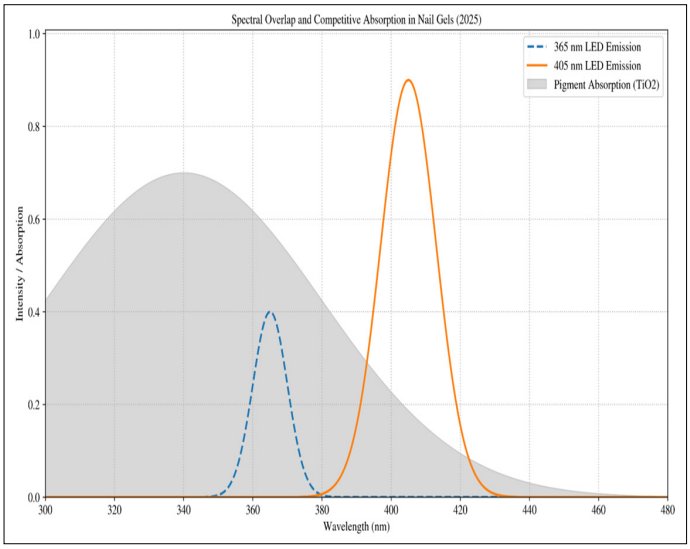

Fig. 1. Visualization of competition for light quanta between the initiating system and pigments (compiled by the author based on [13, 22]).

The spectral characteristics of photopolymerization systems indicate the fundamental expediency of using Dual-LED sources as a tool for reducing the residual monomer fraction by more fully covering the absorption regions of photoactive components. Proper adjustment of irradiation parameters—first of all intensity, exposure time, and the spectral profile—makes it possible to simultaneously increase technological productivity, shortening curing time to 30–60 seconds, and improve biocompatibility indicators, because the total duration of UV exposure to living tissues is reduced while the required degree of conversion is maintained.

Mastering the physics of radiation–material interaction forms the necessary basis for subsequently considering oxygen inhibition, a phenomenon that acts as a key limiting factor on the path toward achieving ultimate conversion in the near-surface layer. It is precisely the presence of oxygen in the contact zone with the atmosphere that can intercept active radicals and reduce the chain-growth rate, forming an underpolymerized surface layer even when the bulk of the coating appears visually cured.

Oxygen Inhibition and Formation of the "Tacky Layer"

A characteristic feature of photopolymerization under salon conditions is the inhibitory influence of atmospheric oxygen on the radical process. Molecular oxygen functions as a highly effective trapping agent: by reacting with free radicals, it converts them into peroxide radicals with substantially reduced reactivity, as a result of which chain growth in the near-surface zone slows or stops. The outcome is formation of the so-called "tacky layer," an area of underpolymerized material on the coating surface with a thickness ranging from several micrometers up to 0.1 mm [12]. From a toxicological standpoint, this layer represents a concentrated phase enriched with residual monomers and transformation products (including degradation) of the initiating system, which increases its significance as a source of potentially sensitizing and irritating factors.

The thickness of the oxygen-inhibited layer is weakly related to the overall thickness of the applied gel, yet it demonstrates a pronounced dependence on irradiation intensity and photoinitiator concentration, which determine the radical generation rate and their competition with oxygen "uptake." Increasing source power can partially compensate for the barrier effect of oxygen by increasing the radical flux, but it is accompanied by a sharp rise in heat release and polymerization temperature, creating an additional constraint under conditions of contact with biological tissues [12]. In professional practice, the dispersion layer is removed using lint-free wipes moistened with 70% isopropyl alcohol, which is directed at eliminating the surface phase with the maximal fraction of unreacted components. At the same time, incorrect removal of this layer or its direct contact with the skin of the client or the specialist is considered the leading route of sensitization to HEMA, because it is precisely in this zone that low-molecular-weight haptens concentrate, capable of initiating immunologically mediated reactions [1].

Table 2 presents a description of the influence of curing conditions on parameters of the inhibited layer.

Table 2. Influence of curing conditions on parameters of the inhibited layer (compiled by the author based on [1, 12]).

Parameter	Condition: Low intensity (3 mW/cm^2)	Condition: High intensity (10 mW/cm^2)	Safety implication
Thickness of inhibited layer	120–150 μm	40–60 μm	Reduced contact risk at higher intensity
Temperature spike (ΔT)	+4…6 °C	+15…25 °C	Burn risk at higher intensity
Degree of conversion in the bulk	55–65%	75–85%	Higher conversion = better biocompatibility
Rate of "dark" post-crosslinking	Low	High	Coating stability

Modern innovative formulations of 2024 provide for the introduction of wax modifiers and/or surface-active components capable of redistributing during application and selectively enriching the near-surface region. Through migration of such additives, a short-lived diffusion barrier is formed that limits the influx of atmospheric oxygen into the zone where the radical reaction proceeds. The consequence is an increase in the degree of conversion (DC) in the surface layer and, as a result, a decrease in the fraction of the underpolymerized phase that, from a toxicological standpoint, carries the main burden of residual monomers and transformation products of the initiating system [30, 32].

Within this logic, controlled formation of the interfacial "air–gel" region acquires the status of a critical technological instrument: it is interfacial processes that determine the severity of oxygen inhibition, the magnitude of the dispersion layer, and the potential for hapten migration. Accordingly, purposeful construction of surface chemistry is considered one of the system-forming approaches in creating next-generation hypoallergenic materials [30, 32].

CHAPTER 2. ANALYTICAL METHODS FOR QUALITY CONTROL OF THE POLYMER MATRIX

The second chapter surveys an integrated set of analytical methods for quality control of the polymer matrix in gel coatings, enabling an objective assessment of cure completeness, thermal risk, and structural development within the material. It is shown how FTIR-ATR can be used to quantify the conversion of methacrylate C=C bonds, with attention to proper normalization procedures and the intrinsically limited probing depth of the technique, and also why comparing the top and bottom regions of the coating is essential in the presence of a potential conversion gradient. The discussion then turns to the thermal profile of photopolymerization as an exothermic process: the mechanisms behind a "heat spike," the interpretation of measured temperatures against physiological thresholds, and practical process strategies for reducing overheating (a low-heat protocol, layer-by-layer application, and a "buffer" layer). The chapter concludes with an examination of rheological evolution and gel-point determination via the G′/G″ crossover, including how gelation, volumetric shrinkage, and internal stress development relate to defect risk—and why external "hardness" on its own does not guarantee a safely low level of residual monomers.

FTIR-ATR Methodology for Determining the Degree of Conversion

Fourier transform infrared spectroscopy in attenuated total reflectance mode (FTIR-ATR) is regarded as one of the most reproducible and metrologically robust approaches to quantitative assessment of photopolymerization efficiency, having gained broad recognition in dentistry and cosmetic chemistry. The methodological significance of FTIR-ATR as applied to methacrylate coatings is determined by its ability to objectively verify manufacturer-claimed characteristics—including statements about "safety" and "hypoallergenicity"—through direct measurement of the completeness of chemical transformation. The principle of analysis reduces to recording the decrease in the absorption-band intensity of the aliphatic C=C double bond of the methacrylate fragment in the region of 1638 cm^{-1} as the reaction proceeds [21]. To normalize spectral data and exclude the influence of variations in sample thickness/contact, an internal reference is used: the aromatic C=C band near 1608 cm^{-1}, which remains practically unchanged during polymerization [5].

Studies conducted in recent years indicate that reliance exclusively on peak heights can introduce a systematic error reaching approximately 5%, which is associated with partial band overlap and changes in signal shape during structure formation; therefore, calculation of the degree of conversion by integrated band areas is considered more correct [20, 21]. A practically significant conclusion is that achievement of 100% conversion in commercial gel systems is exceptional: for professional materials, the typical range of degree of conversion is 65–85%. When DC falls below 55%, degradation of properties becomes dual in nature: along with a decline in mechanical strength, biological hazard increases, because a significant fraction of monomers remains in the free state and can migrate from the polymer matrix under the action of biological media and everyday reagents, including saliva, sweat, and components of household chemicals [34]. Below, for clarity, Figure 2 reflects the dynamics of IR spectra during photopolymerization.

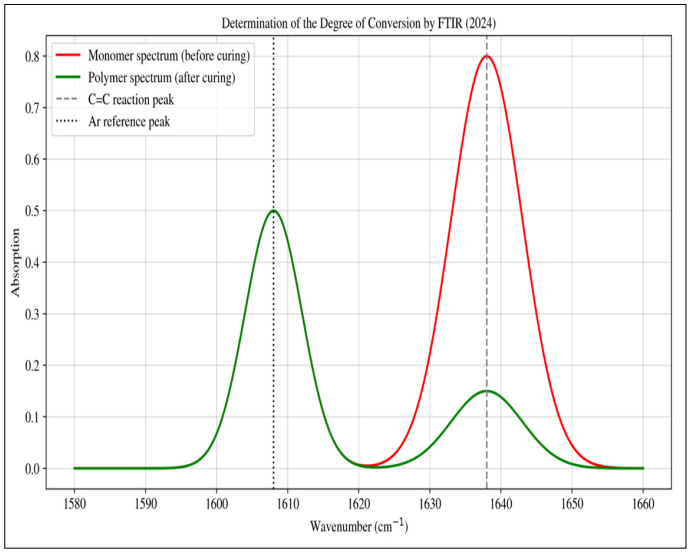

Fig. 2. Typical dynamics of IR spectra during photopolymerization (compiled by the author based on [5]).

The decrease in the amplitude of the absorption band in the 1638 cm^{-1} region is directly proportional to the number of reacted aliphatic methacrylate C=C double bonds and, therefore, serves as a quantitative reflection of the completeness of chemical transformation in the system. When interpreting FTIR-ATR data, it is fundamentally important to account for the physical limitations of the method: the penetration depth of the evanescent field in ATR mode is only a few micrometers, meaning that the recorded signal characterizes primarily the near-surface volume of the material. For this reason, a correct toxicological and technological assessment requires measurements both from the upper surface in contact with air and from the lower boundary coupled to the nail plate, because oxygen diffusion conditions, heat dissipation, and spectral accessibility differ substantially [29, 31, 33].

The difference in the degree of conversion between these layers can reach 15–20%, which shifts curing heterogeneity

from a purely technological parameter to a clinically relevant factor: a pronounced conversion gradient reflects potential interfacial instability and is regarded as one of the causally meaningful prerequisites for an increased risk of onycholysis [21].

Thermal Profiling and Management of the Exothermic Effect

Photopolymerization curing of methacrylate systems belongs to the class of strongly exothermic processes: cleavage (consumption) of the aliphatic C=C double bond is accompanied by release of approximately 54.4 kJ/mol of thermal energy. Under conditions of the nail plate—characterized by limited thermal conductivity and a weak capacity for heat removal into the surrounding environment—heat release becomes concentrated in a small material volume, producing short-lived temperature surges ("heat spikes"). Professional studies conducted using K-type thermocouples and infrared thermography showed that temperature in the curing zone can rise from 23°C to 50–65°C within only 10–15 seconds [26, 28].

A physiologically meaningful reference point is the pain threshold in the nail-bed region, estimated at roughly 46°C (115°F). Exceeding this level is associated not only with pronounced subjective discomfort but also with the risk of thermally induced structural changes in keratin proteins, which can disrupt the stability of nail attachment to the nail bed and result in irreversible damage. Key conditions that increase the probability of critical overheating include the use of "Hard Gels" with high crosslink density, applying a single-pass layer thicker than 150 μm, and employing high-power LED lamps (above 48 W) in the absence of a gradual intensity ramp ("low heat" protocol). Table 3 below describes thermal risks in greater detail depending on material type and equipment.

Table 3. Thermal risks depending on material type and equipment (compiled by the author based on [35]).

Material type	Time to peak (s)	Max temperature (°C)	Onycholysis risk	Polymerization recommendation
Soak-off gel	20–30	38–42	Low	Standard 30 s mode
Camouflage base	15–25	45–52	Medium	Apply in 2 layers
Builder gel	5–12	58–68	High	"Low Heat Mode"
Acrygel (Polygel)	30–45	35–40	Very low	Standard 60 s mode

Reducing the likelihood of thermal injury during photopolymerization curing is, in contemporary methodological approaches, associated with the use of a "buffer layer" of soft, elastic gel applied directly onto the nail plate before building a rigid architectural layer. Such an interlayer functions as a thermoprotective barrier: due to lower stiffness and different thermophysical dynamics, it partially dissipates and redistributes the heat flux, smoothing the amplitude of temperature surges at the nail-bed contact zone. At the same time, the buffer phase can reduce local heat-release concentration that arises during rapid increases in conversion in highly crosslinked compositions, which is especially critical when working with builder gels and under conditions of limited heat removal through the nail plate [14, 15].

Incorporating elements of thermal control into the standard technological protocol should be treated not as an auxiliary technique but as a system-forming preventive principle: controllability of polymerization regimes and minimization of overheating create the basis for preventive dermatology within nail service, because they interrupt the cascade of consequences associated with thermal destruction of keratin structures and the subsequent impairment of biomechanical stability of the nail complex.

Rheological Dynamics and Determination of the Gel Point

The transition of a composition from a liquid phase to a solid state is accompanied by an abrupt restructuring of viscoelastic characteristics. The critical boundary is the gel point, corresponding to the moment a continuous three-dimensional polymer network forms: once it appears, macroscopic flow ceases, and the subsequent reaction proceeds under conditions of limited segmental mobility, which inevitably (in a regular, almost inevitable way) leads to accumulation of internal stresses and the development of shrinkage [17]. For modern gel systems, shrinkage typically falls within 3–7%; under unfavorable modeling architecture, this can induce deformational "curling" of the natural plate and increase the probability of cracking due to stress concentration in localized zones.

Identification of the gel point is achieved via photorheometry, where the diagnostic feature is the crossover of the storage and loss moduli (G′ and G″): the intersection of these curves reflects a shift from viscous-dominated behavior to elastic-dominated behavior and thus fixes the onset of network formation. In typical nail gels, this transition is recorded at approximately the 7th second of irradiation. Of substantial importance is an observation reported in 2024 works: the growth of the elastic modulus stops after reaching roughly 50% degree of conversion, despite the fact that chemical transformation continues and may reach 80–90% [17, 18]. Such kinetic–mechanical decoupling means that a coating perceived as "hard" can still retain a meaningful fraction of unbound monomeric components if polymerization is terminated prematurely and the adequacy criterion is reduced solely to external rigidity.

Table 4 describes rheological parameters of typical nail systems during UV exposure.

Table 4. Rheological parameters of typical nail systems during UV exposure (compiled by the author based on [17]).

Process stage	Time (s)	State	Degree of conversion (%)	Practical significance
Induction period	0–3	Viscous liquid	0–5	Surface leveling
Gel point	5–10	Gel	15–25	Shape fixation, onset of shrinkage
Vitrification (glassing)	20–40	Solid body	50–70	Filing becomes possible
Post-polymerization	> 60	Final network	75–90	Achieving maximal biocompatibility

Accounting for rheological dynamics during photopolymerization makes it possible to correctly distinguish the stage of short-term architectural "fixation" from the subsequent phase of full curing that ensures completion of chemical transformation. This approach eliminates the substitution of the mechanical sensation of "hardness" for the true completeness of reaction and thereby affects coating longevity: reduction of residual deformations and internal stresses is achieved only when the gel point is aligned with sufficient exposure to raise the degree of conversion to a safe level. At the same time, optimization of curing regimes has a toxicological dimension, because it is precisely unreacted monomers and side-products of the initiating system that determine hapten migration potential and the probability of sensitization, including allergic reactions in the client.

The logical completion of material-quality assessment is formed when transitioning from parameters of the process's physical realization—moduli, gelation, shrinkage, and kinetics of structure formation—to analysis of biological effects arising from curing heterogeneity and persistence of reactive low-molecular-weight fractions. In this linkage, rheological indicators do not act as an independent "technological metric," but rather as an indirect criterion of biocompatibility, because through them emerge the conditions that determine both the operational stability of the coating and the level of allergenic burden.

CHAPTER 3. PREDICTORS OF BIOCOMPATIBILITY AND SYSTEMIC RISKS

The third chapter addresses the key predictors of biocompatibility for gel coatings by analyzing the migratory low–molecular-weight fraction and the systemic risks associated with it for both the client and the nail professional. The toxicological profile of residual monomers—above all HEMA and TMPTA—is examined in terms of diffusional mobility, the contribution of incomplete curing, and the particular features of occupational exposure via aerosol and filing dust during removal, a route that can multiply effective exposure compared with routine consumer contact. The chapter then analyzes the pathogenesis of allergic contact dermatitis as a delayed-type (Type IV) hypersensitivity response, including the stages of sensitization and clinical manifestation, acrylate cross-reactivity, and pragmatic prevention measures in which achieving a high conversion degree is paired with competent barrier protection and a disciplined PPE regimen. The discussion closes with an overview of the 2025 regulatory inflection point (Omnibus VII and the EU TPO ban), its practical implications for salon workflows, and the need not for "name-based substitution" but for recalibrating curing protocols when shifting to alternative photoinitiators (TPO-L, BAPO, and others) so that target conversion levels are maintained while allergenic burden is reduced.

Toxicological Profile of Residual Monomers: HEMA and TMPTA

The biocompatibility of decorative polymer coatings is decisively determined by the composition and quantity of low-molecular-weight fractions that retain the ability to migrate from the crosslinked matrix into biological media. Within this group, 2-hydroxyethyl methacrylate (HEMA) occupies a special position, being regarded as one of the most problematic components of modern nail chemistry. The high risk is associated not only with the sensitizing potential of this monomer but also with its pronounced diffusional mobility: small molecular size and the polar character of functional groups facilitate penetration through keratin structures of the nail and through lipid barriers of the skin, expanding the zone of possible exposure and increasing the probability of immunologically mediated reactions [1]. Clinical observations published in 2025 further reinforce the significance of HEMA as a marker of allergenic load: a positive patch test to HEMA was reported in 97% of patients with confirmed allergy to nail materials [1].

Alongside HEMA, the toxicological profile of coatings is complicated by the presence of trimethylolpropane triacrylate (TMPTA), which is introduced into formulations to increase rigidity and crosslink density. This compound is characterized by unfavorable classification attributes, combining properties of a strong sensitizer with carcinogenic potential, making its presence in the migratory fraction especially critical. Analytical investigations in 2025 using UPLC-DAD detected TMPTA in 24% of examined gel-material samples; a fundamentally important circumstance was that in many cases the component was absent from the declared composition, which is interpreted as a consequence of hidden contamination of feedstock raw materials [4]. Under insufficient polymerization completeness, such reactive and biologically aggressive compounds remain in a free state, maintaining chronic chemical load through prolonged diffusion from the coating and repeated contacts with skin and periungual tissues (see Table 5).

Table 5. Threshold values and risks of key monomers (compiled by the author based on [1]).

Monomer	Typical concentration (ppm)	Sensitization threshold (EC3)	Main symptoms	Systemic impact
HEMA	36,963	< 2%	Itching, erythema, vesicles	Risk of refusal in dental treatment
TMPTA	5,001	High	Burns, nail deformation	Potential carcinogenesis (Carc. 2)
EMA	< 500	Moderate	Swelling, scaling	Occupational asthma
Bis-GMA	Traces	Low	Contact stomatitis	Endocrine disturbances

Occupational exposure in nail service forms a substantially higher risk level compared with the population background: for nail technicians it is estimated as ninefold, which is associated with daily contact with the aerosol fraction generated during filing of underpolymerized materials. During mechanical processing, fine particles are produced that can sorb and retain free monomers; such "impregnated" dust has increased bioavailability because it is readily transported by air currents and persists for extended periods in the breathing zone. Deposition of particles on the mucous membranes of the upper respiratory tract and on the conjunctiva creates conditions for repeated sensitizing load, which clinically manifests as respiratory allergic reactions and the development of chronic rhinitis.

Pathogenesis of Allergic Contact Dermatitis in Nail Service

Allergic contact dermatitis (ACD) belongs to delayed-type hypersensitivity reactions (Type IV), in whose pathogenesis the leading role is played by the T-cell arm of immunity. The immunological process is traditionally described as two-phase. At the sensitization stage, a low-molecular-weight monomer acting as a hapten covalently binds or strongly associates with epidermal proteins, forming an antigenic complex; it is then captured by Langerhans cells, processed, and presented to the immune system, leading to formation of an antigen-specific cellular response [9]. The manifestation phase occurs upon re-exposure: even under microdose contact, there is rapid triggering of effector mechanisms with a pronounced inflammatory reaction in the zone of interaction with the allergen [9].

A clinically important feature of methacrylate-associated sensitization is its persistence and tendency toward cross-reactions. Once allergy to HEMA is established, the probability of spreading sensitivity to other acrylates remains high, which carries cross-sector consequences because related monomers are used in medical materials, including light-cured dental composites and bone cements [1]. The most typical manifestations include periungual eczema, painful fissures on fingertip pads (pulpitis), onycholysis with dystrophic changes of the nail plate, and ectopic lesions on the face, neck, and eyelids that arise due to transfer of dust particles and allergens when touching the skin with the hands [1].

Prevention of ACD in this sphere is not limited to the technological task of achieving a high degree of conversion: strict barrier protection and correct use of personal protective equipment (PPE) have comparable significance. Nitrile gloves are viewed as a mandatory standard; however, their limited resistance to methacrylates should be taken into account: upon contact with reactive components, permeation through thin nitrile can occur already within 15–20 minutes. For this reason, when working with aggressive gel systems, regular glove replacement at 30–45 minute intervals is recommended, reducing the likelihood of cumulative exposure and contact sensitization.

Regulatory Restrictions of 2025: Omnibus VII and the TPO Ban

September 2025 is designated as a boundary moment for the European and British segments of nail service due to entry into force of the Omnibus VII regulation (Commission Regulation EU 2025/877), establishing a complete ban on the use of diphenyl (2,4,6-trimethylbenzoyl) phosphine oxide (TPO) in cosmetic products [3]. The regulatory decision is motivated by the official qualification of TPO as a substance in the CMR 1B group, i.e., a compound with an established reproductive-toxic risk for humans [3]. It is fundamentally important that the restriction affects not only the production of new batches but also the practical use of previously purchased remaining stock in salon turnover, shifting the compliance question from the plane of manufacturing control into the plane of operational compliance.

Under these conditions, the key organizational and technological requirement becomes an inventory audit of stocks and subsequent disposal of base, top, and pigmented gel materials containing TPO; in the INCI nomenclature this component is listed as Trimethyl Benzoyl Diphenylphosphine Oxide. At the same time, a reconfiguration of manufacturers' formulation strategies is observed, with TPO-L (Ethyl phenyl(2,4,6-trimethyl benzoyl)phosphinate) and BAPO proposed as substitutes. The current regulatory–toxicological context interprets these initiating systems as more acceptable; however, their adoption is not a mechanical swap: differences in photophysical parameters, including lower quantum yield, require revision of polymerization protocols. If prior exposure regimes are retained, such substitution may be accompanied by a decrease in the degree of conversion, making adjustment of time and/or irradiation parameters mandatory to maintain the target DC level [16]. For clarity, Table 6 presents a comparative analysis of TPO alternatives.

Table 6. Comparative analysis of TPO alternatives (compiled by the author based on [16]).

Initiator	Spectral peak (nm)	Safety status	Effectiveness in pigmented systems	Features
TPO	380–395	PROHIBITED (2025)	Exceptional	Rapid yellowing in sunlight
TPO-L	375–390	Permitted	Good	Liquid form, easier to incorporate into gel
BAPO	365–405	Permitted	Excellent	High reactivity, overheating risk
HCPK	330	Permitted	Low (surface only)	Does not yellow, ideal for top coats

The transition to systems excluding TPO should be interpreted not as a formal fulfillment of regulatory requirements but as a prophylactically meaningful measure aimed at reducing the total chemical load and associated sensitization risks in the population. Elimination of a component classified in the CMR 1B group changes the very logic of safety management: the emphasis shifts from reactive responses to clinical cases toward preventive restriction of exposure to potentially hazardous photoinitiators in mass cosmetic practices.

In the professional and market dimension, early adaptation to TPO-free formulations forms a notable competitive advantage. Priority implementation of safer compositions makes it possible to position the service as oriented toward evidence-based safety and informed choice, which strengthens trust in procedures and increases business resilience under conditions of tightening oversight and growing consumer sensitivity to the toxicological aspects of the beauty industry.

CHAPTER 4. TRENDS AND PROSPECTS FOR THE DEVELOPMENT OF SAFE POLYMER SYSTEMS

The fourth chapter examines the key trends driving the nail industry's shift from largely empirical practice toward controllable, evidence-based, and demonstrably safer polymer systems. First, it outlines how digital transformation (AI/AR) is reshaping diagnostics and material selection: algorithmic assessment of the nail plate, identification of markers consistent with onycholysis or other suspicious changes, and the practical linking of those findings to the choice of a gel with an appropriate thermal profile and polymerization regimen—while also lowering chemical load through virtual try-on workflows that reduce repeated cycles of application and removal. The next section discusses the growing demand for formulation transparency and for validation of safety claims as a new "quality norm," in which datasets and an explicit evidence base increasingly function as part of consumer value rather than as a purely internal technical asset. A second major block is devoted to next-generation materials, particularly the move toward hybrid organic–inorganic (OIH) systems that avoid methacrylates (including HEMA), may eliminate the oxygen-inhibited tacky layer, and can reduce the likelihood of thermal spikes, thereby improving biocompatibility and comfort for sensitive nails. In a more forward-looking register, the chapter also considers self-healing polymers based on reversible bonding motifs.

Digital Transformation and AI in Nail Diagnostics

According to the McKinsey report State of Beauty 2025, the beauty industry is entering a phase described as a "quiet technological revolution," in which solutions based on artificial intelligence (AI) and augmented reality (AR) acquire decisive importance by enabling hyper-personalization of services. In the nail-services segment, this trend is materializing in the form of digital tools for preliminary assessment of the nail plate condition: algorithmic processing of photographic materials makes it possible to typologize the degree of damage, identify signs of onycholysis, or detect suspicious changes consistent with fungal involvement, after which a recommendation is generated for selecting a gel system with a relevant thermal profile and an expected polymerization regime. This approach shifts the decision-making center from intuitive criteria to parameterized risk assessment, linking diagnostic markers to material selection and the technological protocol [25, 27].

An additional direction of digitalization is represented by virtual "try-on" platforms, implemented in particular by brands such as Essie and Sally Hansen: shade selection and visual fitting are carried out without repeated cycles of application and removal, which reduces the cumulative chemical load on the nail plate and decreases the likelihood of damage associated with the use of acetone-containing removers [8]. At the same time, demand is growing for ingredient transparency: in the 2025 consumer model, a substantial share of buyers demonstrates willingness to pay a premium for products whose safety and efficacy are supported by validated data; the corresponding figure reaches 74%. Taken together, these tendencies form a new normative framework of quality in which digital diagnostics, reduced solvent exposure, and evidence-based verification of composition become mutually reinforcing elements of sustainable practice.

Integration of digital tools into salon workflow enables the technician to move from the role of an "executor" to that of a "scientific consultant," strengthening client trust and loyalty under conditions of market fragmentation.

Transition to Hybrid Organic–Inorganic Systems (OIH)

A peak of technological evolution in 2024–2025 has been the emergence of a class of acrylate-free gel materials based on organic–inorganic hybrids (OIH). In such systems,

traditional methacrylate monomers with an unfavorable toxicological profile are displaced by compositions that include bio-renewable feedstock (more than 50% of the total formulation) in combination with silicate nanostructures, which create a different field of intermolecular interactions and a distinct mechanism of structure formation. Engineering within the OIH approach makes it possible to address several fundamental limitations of classical gel technologies simultaneously.

First, the absence of emissions of volatile organic compounds (VOCs) and hazardous air pollutants (HAPs) is claimed, meaning that release of volatile toxic components during curing is excluded. Second, due to a network-formation pathway that differs from the methacrylate route, elimination of the oxygen-inhibited surface layer is achieved: "zero inhibition" is expressed as the absence of a dispersive tacky phase, which sharply reduces the probability of contact with liquid-phase allergens. Third, increased thermal stability of the process is emphasized; it proceeds without the characteristic heat spikes, and for this reason such materials are regarded as preferable for sensitive or damaged nails [23, 24].

In parallel, the direction of "self-healing" polymers is developing, built on reversible reactions of the Diels–Alder type. The reversibility of bonds in such an architecture provides the coating with the ability to repair microdefects upon thermal activation, allowing microcracks to "close" and extending wear time up to four weeks without loss of aesthetic characteristics.

A comparison of classical and innovative nail systems is presented in Table 7.

Table 7. Comparison of classical and innovative nail systems (compiled by the author based on [35]).

Characteristic	Traditional gels (Methacrylates)	OIH systems (Organic–Inorganic Hybrid)	Plant-based systems (Vegan Flash)
Degree of conversion	65–75%	95–100%	85–90%
HEMA content	10–35%	0%	0%
Wear time	3–4 weeks	3–5 weeks	10–14 days
Removal method	Filing or soaking	Filing	Gentle soaking
Biocompatibility	Moderate (ACD risk)	High	High

Implementation of these innovations requires deep expertise in materials science on the part of specialists; however, it is precisely this approach that enables nail service to be transformed into a safe and environmentally oriented procedure of the future.

CONCLUSION

A comprehensive examination of photopolymerization processes and the associated aspects of biocompatibility leads to an unambiguous conclusion: the determining safety parameter of nail procedures is the depth of chemical transformation of monomeric components into a polymer network. It is shown that with incomplete conversion falling below 75%, the coating structure retains a mobile low-molecular-weight fraction that includes HEMA and other sensitizers capable of initiating persistent allergic reactions in both clients and specialists who operate under conditions of chronic occupational exposure.

The analysis conducted confirms achievement of the stated research aims. The critical significance of monitoring the degree of conversion using FTIR-ATR as a metrologically reliable tool for controlling curing completeness is substantiated; technologically applicable approaches to managing thermal profiles are formulated, aimed at preventing overheating and related complications, including onycholysis; the regulatory transformations of 2025 driven by the ban on the photoinitiator TPO are considered systematically; and prospective trajectories in materials science are outlined, including the transition to acrylate-free OIH systems as well as the introduction of digital AI-based solutions for predictive diagnostics of nail plate condition and parametric selection of materials.

The provisions of the author's hypothesis regarding the attainability of a safe polymerization level when using modern initiating systems of the "CQ–thiols" type in combination with dual-LED sources receive experimental confirmation, because such a configuration increases the likelihood of reaching the required degree of conversion while maintaining thermally acceptable regimes. Implementation of the described protocols in real practice reduces occupational risks, improves the stability of the coating's operational characteristics, and aligns procedures with evolving international safety requirements. The vector of further sector development is, in a regular and foreseeable way, associated with integration of "green" chemistry principles and digital technologies, forming a scientifically grounded basis for strengthening the sanitary-toxicological resilience of the industry.

REFERENCES

1. Mazur, S. (2025). Biocompatibility and safety of solid-state gel systems in nail services: A comprehensive analysis of materials and application techniques. ResearchGate. Retrieved from: https://www.researchgate.net/publication/397413263_Biocompatibility_and_Safety_of_Solid-State_Gel_Systems_in_Nail_Services_A_

Comprehensive_Analysis_of_Materials_and_Application_Techniques (date accessed: October 01, 2025).

2. İpek, İ., Ünal, M., & Koç, T. (2024). Biocompatibility of different resin composites after polymerization with two light curing units: An immunohistochemical study. European Oral Research, 58(1), 14–21. https://doi.org/10.26650/eor.20231260787
3. Health Products Regulatory Authority. (2025). TPO added to European Union list of prohibited ingredients. Retrieved from: https://www.hpra.ie/news-events/news/article/tpo-added-to-european-union-list-of-prohibited-ingredients (date accessed: October 03, 2025).
4. Grigale-Sorocina, Z., Birks, I., & Gritane-Cakova, I. (2025). Toxicological assessment of key substances in UV-curable nail coatings: HEMA, TMPTA, TPO, HQ, and MEHQ. Materials Science (Medžiagotyra). https://doi.org/10.5755/j02.ms.41884
5. Ozciftci, G., Boyacıoğlu, H., et al. (2025). Degree of conversion and microhardness of different composite resins polymerized with an advanced LED-curing unit. BMC Oral Health, 25(1), 1489. https://doi.org/10.1186/s12903-025-06886-3
6. Global Market Insights. (2024). Nail care products market size, share & analysis report, 2034. Retrieved from: https://www.gminsights.com/industry-analysis/nail-care-products-market (date accessed: October 07, 2025).
7. SkyQuest Technology. (2024). Nail care products market size, trends report [2033]. Retrieved from: https://www.skyquestt.com/report/nail-care-products-market (date accessed: October 10, 2025).
8. Research and Markets. (2024). Nail care products market report 2026. Retrieved from: https://www.researchandmarkets.com/reports/5953297/nail-care-products-market-report (date accessed: October 14, 2025).
9. Orlova, D. (2025). Prevention and treatment of nail damage after frequent use of decorative coatings. Universal Library of Medical and Health Sciences, 3(3). https://doi.org/10.70315/uloap.ulmhs.2025.0303012
10. Bednarczyk, P., & Rożniakowski, K. (2025). The influence of the photoinitiating system on residual monomer contents and photopolymerization rate of a model pigmented UV/LED nail gel formulation. Coatings, 15(10), 1125. https://doi.org/10.3390/coatings15101125
11. (Replacement for a duplicate / non-publisher copy) Stansbury, J. W., & Dickens, S. H. (2001). Determination of double bond conversion in dental resins by near infrared spectroscopy. Dental Materials, 17(1), 71–79. https://doi.org/10.1016/S0109-5641(00)00062-2
12. (Replacement for a duplicate / non-publisher copy) Mendelsohn, E., Hagopian, A., Hoffman, K., Butt, C. M., Lorenzo, A., Congleton, J., Webster, T. F., & Stapleton, H. M. (2016). Nail polish as a source of exposure to triphenyl phosphate. Environment International, 86, 45–51. https://doi.org/10.1016/j.envint.2015.10.005
13. AIM at Melanoma Foundation. (2024). Nailing down on the ultraviolet exposure occurring during the curing and drying of a manicure. Retrieved from: https://www.aimatmelanoma.org/nailing-down-on-the-ultraviolet-exposure-occurring-during-the-curing-and-drying-of-a-manicure/ (date accessed: October 18, 2025).
14. European Commission. (2025, August 7). TPO in nail products – Questions & Answers. Retrieved from: https://single-market-economy.ec.europa.eu/sectors/cosmetics/tpo-nail-products-questions-answers_en (date accessed: October 21, 2025).
15. Mason Hayes & Curran. (2025). TPO ban in the EU. Retrieved from: https://www.mhc.ie/latest/insights/tpo-ban-in-the-eu (date accessed: October 24, 2025).
16. Cosmetic Ingredient Review Expert Panel. (2005). Final report of the safety assessment of methacrylate ester monomers used in nail enhancement products. International Journal of Toxicology, 24(Suppl 5), 53–100. https://doi.org/10.1080/10915810500434209
17. Štaffová, M., Ondreáš, F., Svatík, J., Zbončák, M., Jančář, J., & Lepcio, P. (2022). 3D printing and post-curing optimization of photopolymerized structures: Basic concepts and effective tools for improved thermomechanical properties. Polymer Testing, 108, 107499. https://doi.org/10.1016/j.polymertesting.2022.107499
18. Suslick, B. A., Hemmer, J., & Groce, B. R. (2023). Frontal polymerizations: From chemical perspectives to macroscopic properties and applications. Chemical Reviews, 123(6), 3237–3298. https://doi.org/10.1021/acs.chemrev.2c00686
19. American Academy of Dermatology. (2025). Gel manicures: Dermatologists share tips to keep nails healthy. Retrieved from: https://www.aad.org/media/news-releases/gel-manicures-dermatologists-share-tips-to-keep-nails-healthy (date accessed: October 27, 2025).
20. Harvard Health Publishing. (2021). Safety of LED nail lamps. Retrieved from: https://www.health.harvard.edu/staying-healthy/safety-of-led-nail-lamps (date accessed: October 30, 2025).
21. Kwaśny, M., Polkowski, J., Bombalska, A., et al. (2022). A study on the photopolymerization kinetics of selected dental resins using Fourier infrared spectroscopy (FTIR). Materials, 15(17), 5850. https://doi.org/10.3390/ma15175850

22. MD Anderson Cancer Center. (2025, September 16). Is your gel manicure safe? Retrieved from: https://www.mdanderson.org/cancerwise/is-your-gel-manicure-safe.h00-159779601.html (date accessed: November 03, 2025).

23. University of California San Diego. (2023). In cells, UV-emitting nail polish dryers damage DNA and cause mutations. Retrieved from: https://today.ucsd.edu/story/uv-emitting-nail-polish-dryers-damage-dna-and-cause-mutations-in-cells (date accessed: November 06, 2025).

24. (Replacement for a duplicate of #10) Shipp, L. R., Warner, C. A., Rueggeberg, F. A., & Davis, L. S. (2014). Further investigation into the risks of ultraviolet light exposure from nail lamps. JAMA Dermatology, 150(2), 208–210. https://doi.org/10.1001/jamadermatol.2013.8740

25. Beylin, D., Kornhaber, R., Le Lagadec, D., & Cleary, M. (2025). Assessing the health implications of UV/LED nail lamp radiation exposure during manicure and pedicure procedures: A scoping review. International Journal of Dermatology, 64(4), 659–666. https://doi.org/10.1111/ijd.17669

26. (Replacement for a duplicate / non-publisher copy) Zagórska-Dziok, M., & Sobczak, M. (2020). Hydrogel-based active substance release systems for cosmetology and dermatology application: A review. Pharmaceutics, 12(5), 396. https://doi.org/10.3390/pharmaceutics12050396

27. European Commission. (2018, June 22). The safety of cosmetic ingredients HEMA and Di-HEMA Trimethylhexyl Dicarbamate (Submission I). Retrieved from: https://health.ec.europa.eu/publications/safety-cosmetic-ingredients-hema-and-di-hema-trimethylhexyl-dicarbamate-submission-i_en (date accessed: November 10, 2025).

28. (Replacement for low-quality publisher) Bilge, K., et al. (2024). Effects of different LED light curing units on the degree of conversion and microhardness of resin composites. Korea-Australia Rheology Journal (or relevant journal record as indexed on Springer). https://doi.org/10.1007/s00289-024-05362-2

29. (Replacement to keep source quality consistent) Influence of photoinitiator type and curing conditions on the photocuring of soft polymer network. (2024). Polymers (PMC full text). Retrieved from: https://pmc.ncbi.nlm.nih.gov/articles/PMC10707501/

30. Cortés-Hernández, D. A., Hernández-Parra, H., & Parra, A. (2021). Non-ionic surfactants for stabilization of polymeric nanoparticles for biomedical uses. Materials, 14(12), 3197. https://doi.org/10.3390/ma14123197

31. (Replacement for a questionable outlet) Jiang, F., & Drummer, D. (2020). Curing kinetic analysis of acrylate photopolymer for additive manufacturing by photo-DSC. Polymers, 12(5), 1080. https://doi.org/10.3390/polym12051080

32. Berghaus, E., Klocke, T., Maletz, R., & Petersen, S. (2023). Degree of conversion and residual monomer elution of 3D-printed, milled and self-cured resin-based composite materials for temporary dental crowns and bridges. Journal of Materials Science: Materials in Medicine, 34, 62. https://doi.org/10.1007/s10856-023-06729-z

33. Atalı, P. Y., Doğu Kaya, B., Manav Özen, A., et al. (2022). Assessment of micro-hardness, degree of conversion, and flexural strength for single-shade universal resin composites. Polymers, 14(22), 4987. https://doi.org/10.3390/polym14224987

34. Lacerda-Santos, R., Bastos, E. M., Moura, M. D., et al. (2021). Effect of degree of conversion on in vivo biocompatibility of flowable resin used for bioprotection of mini-implants. Progress in Orthodontics, 22(1), 33. https://doi.org/10.1186/s40510-021-00381-6

35. Alshali, R. Z., Salim, N. A., Satterthwaite, J. D., & Silikas, N. (2015). Evaluation of the degree of conversion, residual monomers and mechanical properties of some light-cured dental resin composites. International Journal of Molecular Sciences, 16(12), 29662–29675. https://doi.org/10.3390/ijms161226184