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Investigation of green light-activated dental dimethacrylate resins containing a new type of photoinitiator and gold nanoparticles

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Introduction

The introduction of photopolymerization and light-initiated polymers has revolutionized dentistry. A good example is the application of light-initiated composite filling materials in dentistry. A major advantage of the technology is that photopolymerization shortens the process of filling the tooth and improves the handling of the filling material. It gives chance to take a relatively longer time to place and shape the aesthetic polymer-based filling material in a pre-prepared cavity, and then the material polymerizes under a few seconds of illumination, forming a strong cross-linked structure, which allows the chewing surface to be loaded almost immediately after the filling is placed [1]. These filling materials are in great demand as they are aesthetic and, since their introduction, they have been the subject of numerous developments resulting in excellent mechanical, biocompatibility and chemical properties, which are determined by the components that make up the composite; the high cross-linked copolymer matrix and the dimethacrylate monomers that form it, the inorganic filler, usually silica, and the coupling molecule, most often silane (gamma-

methacryloxypropyl trimethoxy silane), which modifies the surface of the filler, have an important influence.

Nowadays, newer components are also appearing among the ingredients to create an intelligent material that can react to the effects of the environment (self-healing composites, anti-bacterial agents, metal nanoparticles within the material), which further improve the basic properties or add new capabilities to the material [2, 3, 4]. If we follow the path of light when illuminating a filling material, the first phenomenon we experience is the reflection of light from the surface of the restoration. Subsequently, the light entering the material is absorbed by the initiator molecules and pigments and scattered on the surface of the filler particles. In the meantime, photopolymerisation takes place in the matrix of the material, which results in a change in the refractive index of the matrix and affects the amount of light scattering [5, 6]. The scattering of light on the surface of the filler particles can be described in most cases by the Rayleigh scattering laws based on the filler particle size of today's composites and the wavelength range of the light used for polymerisation [7, 8]. In the deeper zones of the filling,

the reduced intensity of curing light is no longer able to induce polymerization with sufficient efficiency, leading to a deterioration of the material quality and limiting the amount of composite that can be inserted into the cavity in one layer (depth of cure). Below a critical intensity value, the degree of polymerization in a deeper layer becomes insufficient, resulting in a deterioration of the material quality. The “depth of cure” depends on the intensity of the curing light, the time of irradiation and the content of composite (pigments, type and amount of filler, its distribution), its light transmission and the light scattering by the filler surface [8, 9, 10].

Modern research on dental composites has taken a new direction and is looking for the possibility to develop several properties according to the concept of functional fillers [4]. The use of silver and gold nanoparticles in experimental composites has been reported in the literature mainly for the development of antibacterial properties [11, 12, 13]. However, by exciting these metal nanoparticles with light of appropriate wavelengths, they have an untapped plasmonic effect in dentistry. The surface plasmon resonance is the wave-like motion,

collective oscillation, of conductive electrons in the metal close to the surface excited by the electromagnetic field. The oscillation of the electrons creates an electromagnetic field around the nanoparticles, the surface of the particle becomes a kind of energy storage surface, some of the particle's energy is emitted as light to its surroundings, while some is absorbed by the particle and generates heat. Both processes are related to the diameter of the particle [14, 15].

It is envisioned that the interference in the wave space between the filler particles may result in the waves cancelling each other out, in certain regions, and therefore the filler particle and the clusters (that form from them due to their high specific surface area) may have a shielding/shadowing effect. The polymerization efficiency may deteriorate in the space between or behind of the filler particles. Research on the development of functional fillers has shown that additives can be used in dental composites to add new functionalities or to improve existing properties. By studying the literature on the application of gold nanoparticles in polymers, we found data that gold nanoparticles excited by light of appropriate

wavelength could induce polymerization in methacrylate and epoxy resins by thermo-plasmonic and/or plasmon-induced photopolymerization ability [16, 17].

Literature review

Knowing the difficulties and the efficiency of polymerization of dimethacrylate resins for dental composites, we came up with the idea of using gold nanoparticles to compensate the shielding effect of the filler and the matrix conversion reduction by thermoplasmonic and plasmon induced polymerization of excited gold nanoparticles. The photopolymerization technology currently used in dentistry is based on camphorquinone initiator, tertiary-aromatic-amine co-initiator technology and light sources (mostly LEDs emitting in the high energy blue light range) used for photoinitiation [18]. The green light range is required for the excitation of the gold nanoparticles we envision. Accordingly, we searched for an initiator (Irgacure 784) sensitive to the same green light range used to excite the gold nanoparticles and designed a new light source

capable of exciting both the new initiator and the gold nanoparticles with light of the appropriate wavelength (green LED) [19, 20].

Objective

The aim of our work was to prepare an experimental dimethacrylate-based photopolymer in which functionalized gold nanoparticles are dispersed. Plasmon resonance connected to the surface of the nanoparticles was studied through its effect on the chemical and physical properties of the resin. The polymerization processes and their efficiency have been investigated to eliminate the shielding effect of the filler in the light propagation path and the light intensity reducing effects associated with it. To this end, a green-emitting LED light source has been prepared for the excitation of gold nanoparticles and a new green-light sensitive photoinitiator (Irgacure 784) has been used. The aim of the first phase of our work was to study the chemical properties of the resin without gold nanoparticles; reaction kinetics, polymerization efficiency, leaching, density, and mechanical properties;

hardness, compressive strength, flexural strength and diametral tensile strength. Our further aim was then to observe the thermoplasmonic effect of gold nanoparticles in the experimental resin. We investigated the optimal gold concentration and irradiation intensity for which we monitored the variation of conversion and mechanical parameters and monitored the refractive index. Furthermore, we observed the presence and distribution of gold nanoparticles in the samples.

Material and Method

Our studies were carried out in two steps. In the first step, we created an experimental resin containing a new photo initiator and frequently used dimethacrylate monomers, and a green LED light source suitable for operating this resin and investigated the properties and functionality of this model system. Then, in the second phase of the experiments, functionalized gold nanoparticles were mixed with the experimental resin in order to study the thermoplasmonic and plasmon-induced polymerization

effect of the gold nanoparticles and to optimize the amount of gold and the required irradiation intensity.

Production of experimental resins

For the preparation of the photocurable resin matrix was a mixture of bisphenol-A glycidyl dimethacrylate (Bis-GMA) (Sigma-Aldrich Co., St. Louis, MO, USA), triethylene glycol dimethacrylate (TEGMA) (Sigma-Aldrich Co., St. Louis, MO, USA) and diurethane dimethacrylate (UDMA) (Sigma-Aldrich Cheme GmbH, Steinheim, Germany) monomers in the order 21.4: 25.4: 53.3 w/w %, in which Irgacure 784 (BASF Hungary Ltd., Budapest, Hungary) photoinitiator was mixed at 2 w/w %. High Performance Liquid Cromatography (HPLC) purified dimethylformamide (DMF) (Sigma-Aldrich Cheme, GmbH, Steinheim, Germany) was used for the extraction. The materials were used without further purification. In the second phase, spherical gold nanoparticles (AuNP) with a diameter of 5 nm and functionalized with dodecane thiol (Nanoprobes Ink., Yaphank, NY, USA) were prepared as a stock solution at a concentration of 1 mg/ml using HPLC graded toluene

(VWR International LLC, Debrecen, Hungary). From this stock solution, a different amount was mixed with the measured UDMA monomer in order, to prepare experimental composites with different gold nanoparticle concentrations (Au1:0.0208, Au2:0.0416, Au3: 0.0833, Au4:0.1665, Au5: 0.3330, Au6:0.6660 m/m%). The nanoparticles were uniformly dispersed in the resins by ultrasonic bath. Toluene was then removed from the samples using a rotary vacuum distillation unit (Heidolph Hei-VAP Precision, Heidolph, Schwabach, Germany) at 55°C under 3 mbar pressure until constant mass was achieved.

Description of the polymerization unit used in the sample preparation

In our work, the polymerization of the samples was carried out using a custom-made apparatus. The emission range of the green LED light source (Megaled 3 W, Hungary) is centered at wavelength of 531 nanometers. The full width of the emission spectrum at half of the maximum value is 32 nm (Figure 3). The polymerization unit was designed

to illuminate a 3cm x 3cm surface adequately. To this end, a square-section light guide tube, open at both ends and surface-treated with highly reflecting coating on its inner surface, was fixed under the light source to produce a homogeneous irradiation. The optical spectrum of the light source was determined using a fiber optical spectrophotometer (Ocean Optic, USB 650, US) and its intensity was measured with power meter setup (ThorLabs, PM 100, US). The spectral irradiance distribution of the light source was measured with a spectroradiometer (EKO Instruments, LS-100, Japan). The UV-vis spectra of the photoinitiator in toluene under UV-visible light was recorded on an Agilent Cary 60 spectrophotometer (Agilent, Santa Clara, CA, USA) in a quartz cuvette with an optical length of 1.00 cm in which 3 cm^3 of solution was tested.

Preparation of samples for the study of the experimental resin

The samples were fabricated in Teflon moulds, covered with a translucent polyester strip to prevent oxygen

inhibition from the direction of irradiation. Light activation was performed for 30 seconds with a green LED light source at light intensities of 0.7, 1.0, 1.2, 1.4, 2.0, 4.0 and 6.0 mW/cm^2. The photoplymerizations were done in dark room. The specimen disks were 2mm thick and 10 mm in diameter for hardness, extraction water swelling and density tests.

Investigation of resin density, Extraction and Water Swelling

The *density* of the cured samples was determined in a pycnometer at 25°C, using water as the medium. For *swelling studies*, three specimens were used at each light intensity (0.7, 1.0, 1.2, 1.4, 2.0, 4.0 and 6.0 mW/cm2). The test specimens were stored in deionized water at 25^{o}C for one week until they reached equilibrium. The specimens were then wiped, dry and their mass was immediately measured. For the *extraction tests*, 24 hours after the polymerization, the prepared samples were placed in a Soxhlet-type extractor in dimethylformamide (DMF) overnight after mass measurement. The extracted samples

were then dried under vacuum at 50°C for 2 days and finally reweighed.

Investigation of the polymerization kinetics of experimental resins prepared under different light intensities by Raman spectroscopy

The Raman spectra were recorded using a spectrophotometer (Ocean Optics QE 6500, US) with a CW (Continuously operated Wave) laser operating at 785 nm, as this value was out of the absorption range of the photoinitiator, so that the laser light did not affect the photopolymerization process. The study was carried out, in a polystyrene cuvette (in which the liquid monomer was placed). Spectrums were recorded both before and after polymerization. Polymerization was also studied in situ. Raman spectra were recorded every second while the samples were irradiated, which also allowed the analysis of the polymerization kinetics at different intensities (0.7-10 mW/cm2). The laser was focused to the center of the cuvette, so the spectral information was collected from the volume of the sample and not from the surface. The

polymerization was performed for 250 seconds to ensure that the front of the polymerizing material reached the Raman light source. The images wich display changes in composition and degree of conversion were generated with OriginPro 8.0TM software.

Vickers microhardness measurement

Samples 2 mm thick and 10 mm in diameter were prepared as described previously and stored at room temperature (25^{o}C) for 24 hours before testing. At each light intensity used, 3 samples were prepared and 5 microhardness measurements per sample were taken. For hardness measurements, a microhardness measuring device (Buehler Vickers Microhardness, Micromet 5103, US) was used. We applied 100g load for 20 seconds. The purpose of these tests, was to determine the optimum light intensity for the subsequent manufacturing of the mechanical tests specimens at the selected intensity value.

Diametral tensile strength measurement

The unpolymerised resin was placed in a Teflon mould and covered with a translucent polyester foil. The samples were illuminated with a green LED light of 1.4 mW/cm2 intensity for 30 seconds. The cylindrical samples obtained had a thickness of 3 mm and a diameter of 6 mm. The diametral tensile strength test was carried out using a universal test apparatus (INSTRON 5544, US). A 2 kN load cell was used for the tests with a crosshead speed of 1 mm/min. The diametral tensile strength (δ) was calculated at the maximum measured compressive load (F) ($\delta=2F/hd\pi$) at which the specimen fractured (h is the height of the specimen, d is the diameter of the specimen π constant: 3.14.

Flexural strength measurement

The flexural strength of the experimental resin samles was investigated with a mechanical testing device (INSTRON 5544, US) equipped with 100N load cell at a crosshead speed of 1mm/min. The span distance was 18 mm. The three-point bending test specimens were 25 mm long and

2mm x 2mm in cross section. During fabrication, the specimens were illuminated with green LED light of 1.4 mW/cm^2 intensity for 30 seconds. The samples were prepared in Teflon moulds covered with polyester strips and stored at room temperature for 24 hours before testing. Flexural strength and elastic modulus of elasticity were calculated according to MSZ EN ISO 178.

Compressive strength measurement

The measurements were performed using a mechanical testing analyser (INSTRON 8874, High Wycombe, UK) with a 25 kN load cell at a crosshead speed of 1 mm/min. The 15 cylindrical specimens (n=15) were each 6 mm high and 3 mm in diameter. During specimen preparation, green LED light of 1.4 mW/cm^2 intensity was applied for 30 seconds.

Investigation of the Progress of Photopolymerization of Gold Nanoparticle (AuNP)-Doped Nanocomposites—Surface Plasmon Resonance Imaging (SPRi) and Ellipsometry Measurements

These measurements helped us to choose the optimal AuNPs concentration for further analysis of physical properties. The photopolymerization process was studied by measuring the change of the refractive index during irradiation. The refractive index change caused by a green LED light source (output P = 1.0 mW/cm^2, 1.4 mW/cm^2 and 2.0 mW/cm^2) was measured by surface plasmon resonance imaging (SPRi). For the measurements, a custom-built SPRi instrument was used, which utilizes Kretschmann optical configuration with a 680 nm super luminescent light source and a 1 MP charge-coupled device (CCD) camera with a 25° range of incident angle. In this configuration, the positions of the light source and the camera are fixed, and only the prism holder platform can be rotated to scan and find the inflection point of the SPR peak to maximize the sensitivity. There are no moving parts during the measurements. Although the SPRi

instrument was designed and adjusted to measure primarily in aqueous environments, we re-calibrated the device to be able to measure the much higher refractive indexes of polymers, such as those of the investigated nanocomposites. For SPRi measurements, the investigated nanocomposites were placed onto an SPRi chip (50 nm gold deposited on a glass substrate, purchased from Mivitec, Germany), then a thin layer was formed by pressing an ultraviolet–visible (UV–VIS) transparent polyester film on the top of the nanocomposites. Real-time changes in the refractive index of the media were monitored during the whole illumination. SPRi results (kinetics) are always given as absolute changes in the refractive index of the nanocomposites with time. Due to the nature of the SPRi measurements, only kinetics measured simultaneously on sample-pairs—on the same chip, at the same time—can be compared with each other, which is true for all the kinetics curves presented in our figures. No comparison between the individual measurements (e.g., comparison of kinetic curves from separate measurements) was made. Based on SPRi measurement (causing the largest refractive index

change), two nanocomposites were chosen for further investigation. The refractive index, before and after photopolymerization of the Ref, the Au1, and Au2 samples were measured by ellipsometry (Woollam M-2000DI, Lincoln, NB, USA). For the irradiation, the same light source and parameters were used for the SPRi measurements. The obtained data with ellipsometry was used to normalize the SPRi kinetics and to obtain an absolute change in the refractive index. All the samples were irradiated for 180 s. The largest change of the refractive index was obtained after 120–135 s. In the case of the refractive index measurement for each sample and light intensity, $n = 5$ samples were investigated. In the case of the SPRi measurements for each sample and light intensity, $n = 3$ samples were studied.

Analysis of the Plasmonic Effect and Dispersion of AuNPs in Polymer Nanocomposites—Optical Transmission Measurements and Transmission Electron Microscopy (TEM) Analysis

Based on the SPRi measurements, two AuNP concentrations were chosen for further analysis. The optical transmission measurements helped us to present the plasmonic effect of nanoparticles by light absorption. The TEM records can certify the distribution of AuNPs in the cured matrix. The optical transmission of the reference sample, the nanocomposite containing AuNPs, and AuNPs in toluene were measured by spectrophotometer (Shimadzu UV-3600, Kyoto, Japan), while the spectral irradiance distribution of the light sources were detected with a spectroradiometer (EKO Instruments, LS-100, De Haag, Netherlands). The measured data were normalized to reference sample data. In our experiments, we used an LED light source (Megaled, 3W green power LED, Budapest, Hungary) to polymerize the resin matrix. The optical spectra of the light source were measured by fiber optical spectrophotometer (Ocean Optics, USB650,

Dunedin, FL, USA). It was found that the peak of the LED light source was at 532 nm. The intensity of the light sources was measured by the power meter setup (ThorLabs, PM100, Newton, NJ, USA).

The AuNPs distribution in the polymerized resin was investigated with Transmission Electron Microscopy (TEM, Jeol-2000FX-II, Tokyo, Japan) equipped with a Bruker EDS system. The TEM samples were produced by ultramicrotomy (LKB Ultrotome 4801A Stockholm-Bomma, Sweden) from the cured polymer blocks containing Au NPs. The sections were floated onto copper microgrids. Samples were investigated at 200 kV accelerating voltage.

Investigation of the Physical Properties of the Polymer Nanocomposites—Diametral Tensile Strengths (DTS) and Degree of Conversion Measurements (DC)

The reference resin and resins containing AuNPs were polymerized for 3 min in a Teflon mold covered by a polyester strip at green LED light intensities of 1.0, 1.4, and 2.0 mW/cm^2. The polymerization was performed in a

dark room. The dimension of specimens was 3 mm in height and 6 mm in diameter for mechanical testing. Before mechanical testing and Raman measurements, the specimens were stored at room temperature for 24 h.

Diametral tensile strength (DTS) was measured on polymerized specimens of reference resin (n = 10) and AuNPs doped resins (Au1 (n = 10) and Au2 (n = 10)) with the help of a mechanical testing device (INSTRON 8874, High Wycombe, UK) equipped with 25 kN load cell. The crosshead speed was 1.00 mm/min. The DTS strength data were calculated based on MSZ EN ISO 604:2003

Characterization of the degree of conversion (DC) was studied with Raman Microscopy at different depths. The degree of conversion of specimens (n = 3) (3 mm in height and 6 mm in diameter) was measured by confocal Raman spectroscopy (Horiba LabRam HR Evo, Palaiseau, France). On the sample surface, 6 measurements were performed on different points. During the work, a 633 nm laser was used as an excitation source, and the measurement time for each sample was 20 s, the

accumulation was 10. The excitation beam was focused onto the sample surface with a 10× lens, while the 600 line/mm grating was used for the measurement. The intensity of the laser was reduced to <1 mW at the sample surface to avoid damages and light-induced transformation of the samples. Spectra were baseline-corrected with the built-in algorithm of the Raman spectrometer software, then normalized and fitted with a set of Gaussians to obtain the Raman peak parameters. The error of the fitting and calculation of the investigated peaks, their parameters, and the estimation of the degree of conversion was about 0.5–1%. For the Raman spectrum, the analyte was placed on a bare glass slide under the same conditions, and in the same amount. The degree of conversion was calculated based on this equation:

$$\mathrm{DC}\ (\%) = 100\ \mathrm{x} \left[1 - \left(\frac{\frac{\mathrm{I}_{2\mathrm{polimerizált}}}{\mathrm{I}_{1\ \mathrm{polimerizált}}}}{\frac{\mathrm{I}_{2\ \mathrm{polimerizálatlan}}}{\mathrm{I}_{1\ \mathrm{polimerizálatlan}}}} \right) \right]$$

Where I_1 and I_2 correspond to the area under the peaks at 1610 cm^{-1} and 1640 cm^{-1}, respectively.

Statistical Analysis for Diametral Tensile Stress (DTS) and Degree of Conversion (DC)

Statistical analysis for DTS and DC Data was performed using Student's t-test with SPSS 17.0 software (IBM, Armonk, NY, USA). All of the tests' accuracies were set at a significance level of 0.05. The Kolmogorov–Smirnov Test revealed that the data showed normal distribution and variances are equal across groups based on homoscedasticity Bartlett's Test.

Results and Discussion

Effect of the ratio of the basic components of the experimental resin on the conversion. Irgacure 784 photoinitiator absorption spectrum green LED light source spectral power distribution correlations

In our experiments, the reference resin we used contained Bis-GMA, TEGDMA and UDMA matrix-forming monomers in the order of 21.4:25.4:53.3 wt%. Literature data show that the stereochemistry of the matrix-forming monomer molecules and the flexibility of the monomers

strongly influence the conversion as well as the mechanical properties [21]. We have found literature data which have highlighted that the matrix properties are more ideal when the monomer ratio in the resin is adjusted to contain less Bis-GMA and more TEGDMA and UDMA, which is more conducive to increase the conversion and favourably affect the mechanical properties of the copolymer, and which is matched by our monomer ratio.

The new initiator used in resins, Irgacure 784, is reported in the literature to be a very efficient radical-forming molecule that absorbs photons in the green range of visible spectra (λ=532nm). One of the main requirements for the effective functioning of dental dimethacrylate photopolymers is that the emission spectrum of the light source overlaps with the absorption spectrum of the photoinitiator. The absorption capability of the initiator molecule is described by the molar extinction coefficient (ε), which provides information on the molecule's ability to absorb light (photons) efficiently at a given wavelength. For the initiator, the higher the ε value at a given wavelength, the more optimal it is, while for the light

source, the number of photons available to be emitted is important for the interaction between the two systems. The absorption and emission spectra of our Irgacure 784 - Green LED light source system show an overlap. The extinction coefficient of the Irgacure 784 initiator is ε=90 1/Mcm. If we compare this value with the values of other iniciators found in the literature (PPD ε=150 $\frac{1}{Mcm}$, Lucirin ε=520 $\frac{1}{Mcm}$, Irgacure 819 ε=300 $\frac{1}{Mcm}$, CQ ε=28 $\frac{1}{Mcm}$) we see that the most commonly used photoinitiator in dentistry, camphorquinone, has a value of ε=28 $\frac{1}{Mcm}$) less than one third of that of Irgacure 784. At the same time, the values of the other iniciators are an order of magnitude higher [22].

If we look at the spectral irradiance of our light source at the maximum wavelength E_{532nm}=8,99 x10^{-3} mW/cm^2nm. This value is considerably lower than the spectral irradiance of first, second and third generation dental LED light sources found in the literature (2-21 mW/cm2/nm) [18]. From these literature data, we conclude that our system can work with an initiator with acceptable photon

absorption (Irgacure 784) together our green LED with significantly lower spectral irradiance.

Kinetics of photopolymerisation and its relationship with the monomers used

The polymerization processes of our pilot resins were investigated by Raman spectroscopy, which is the method used in the literature for this type of measurements. The application of Irgacure 784 initiator to dimethacrylate resins has not yet been found in the literature [23]. The simple model proposed by Maffezioli and Terzi for the characterisation of the overall photopolymerisation kinetics of acrylates [24]. This model could be fitted well to the curve of the rate data calculated from the Raman results and plotted against the applied intensity values. Here, the applicability of the model describing the general kinetic behaviour was tested by comparing theoretical rate data with experimental data. Calculated conversion data were obtained using the two-frequency technique (1) based on Raman spectra [23, 25]. Maximum conversion values of 70-80% were observed after 150 s irradiation

time at light intensities of 6-10 mW/cm^2. It was found that the conversion characteristic of photopolymerization is light intensity dependent. Using a low value of 1.4 mW/cm^2, only 50% conversion was achieved and more than 200 s were needed to reach the final value. However, there was little difference between the values of 6 and 10 mW/cm^2 I_o, at which intensities conversion values of more than 70% were measured after 150 s. By studying the dimethacrylates in the literature, (Bis-GMA, Bis-EMA, UDMA, TEGDMA) we found that their reaction kinetics and the maximum conversion value obtained strongly depend on the stereochemical structure of the molecule and the cross-linking capacity of the monomer to stabilize the cross-link [26, 27]. It has been found that the experimental resins behave according to the kinetic model used, in which the type and ratio of monomers used is the determining factor. Furthermore, our resins exhibit good polymerization efficiency, which is likely to be due to the monomers and their ratios used, as well as to the intensity of irradiation and the efficiency of the initiator.

Discussion of density, water absorption and extraction data of the experimental resin

During polymerization, a three-dimensional polymer structure is built up from the original monomer solution that reach in cross-linkage which is much more compact than the initial state. A good indicator of this process is the increase in system *density*. In our case, the density of the initial monomer solution increased from 1.121± 0.001 g/cm3 to 1.18 g/cm3. The density values of each sample do not show significant differences, indicating that the cross-linked structure of the polymer and the conversion of the monomers in our samples are the same. *The water uptake* in none of the samples exceeded 1 m/m%, which is favorable for dimensional stability and potential application in wet, aqueous environments like oral cavity. Data from the literature show values of the same order of magnitude as our values (1 m/m%), but slightly higher (TEGDMA (6.33 m/m%) > Bis-GMA (2.93 m/m%)> UDMA (2.59 m/m%) > bis-EMA (1.79 m/m%)). The difference may also be due to the use of different initiators and light sources. Furthermore, the uptake of water by

such systems is not only explained by the hydrophilicity of the monomers, but rather by density of the cross-linking formed, the heterogeneous structure of the polymer and the flexibility of the monomers [28, 29]. We think that the explanation for our lower values lies not only in the chemical properties of the ingredients (molecular flexibility, hydrophilicity) but also in the ratio of monomers used and the polymerization process associated with the new ingredient-initiator (Igacure 784) and new polymerization unit.

Extraction studies in DMF are well suited to assess the degree of conversion. The loss in mass after leaching in our samples was 9-10%. Conversion was close to 90%, even at the lowest irradiance of 1 mW/cm2, confirming the efficient operation of the Irgacure 784 initiator with our narrow emission spectrum green LED light source.

Discussion of the experimental resin Vickers Microhardness data

Hardness is a surface property of the material but is also a factor influenced by internal material properties. The

hardness of a solid polymer is also influenced by the size of the molecules that make up the polymer. Generally, the harder a polymer is, the larger the polymer molecules that make it up. Thus, the degree of conversion (DC), strongly influences the measured hardness value [30/31/69, 31/32/70]. The measured Vickers microhardness value was maximum at an intensity of 1.4 mW/cm^2 at one day (25.02 kgf/mm^2) and one week (26.5357 kgf/mm^2) later. In relation to post-polymerization and hardness tests, there are differences in the assessment of how long this process continues and how it affects the properties of the material, its hardness. This time interval is likely to be from one hour after the light initiation to 12 days. This process is also influenced by the value of the conversion achieved in the preceding polymerization, the composition of the dimethacrylate copolymer resin, the availability of free radicals and the ambient temperature [30, 31, 32, 33] In view of the above, we also took our hardness measurements at two times; one day after polymerization and one week later. We found that the hardness data for each intensity value do not show a large variation, so that even at low intensity values our resin shows efficient

polymerization and therefore good hardness properties even at 1 mW/cm^2, which agrees with the leaching data. It can be said that after one week there is no significant difference compared to the one-day hardness data, so polymerisation is highly efficient even within one day after illumination. In our experience, the hardness data were invaluable at intensity values above 6mW/cm^{2,} which we attributed to the higher concentration of photoinitiator 2 m/m%. The concentration of Irgacure 784 was chosen based on the use of 1.5-2 m/m% of Camphorquinone [34]. However, at this concentration Irgacure 784 is much more efficient and at higher light intensities the resulting polymer structure is too inhomogeneous, which affects the quality of the cross-linked polymer nettwork. For the further investigation of mechanical properties, the light intensity value (1.4 mW/cm^2) was used where the highest hardness data were measured.

Measurement results and discussion of mechanical properties

The experimental resin has an *elastic modulus* of 876.4 MPa and a flexural strength of 61.7 MPa. According to literature data, the modulus of elasticity of dentin is 11-20 GPa, while that of enamel is 40-90 GPa [35, 2]. The average modulus of elasticity of currently available composites is 3-17 GPa, and the flexural strength is 60-180 MPa, which varies depending on the type of composite [36, 37]. Several factors can influence the measured values. The first is the microstructure of the composite; this includes the spatial distribution of the filler, the shape of the filler and the effect of any defects and cracks that may be present. The character of the resin; the ratio and chemical structure of the monomer, the degree of conversion and, under oral conditions, the water absorption and solubility also play a role in the mechanical properties. However, in the literature, the filler content is the most important factor influencing the elastic parameters of the material [38]. Our resins did not contain inorganic fillers and therefore the average elastic modulus

values are below the average elastic modulus values of composites. This fact is supported by several literature data. However, our elasticity parameters are in agreement with values published in a previous study (flexural strength of the reference resin: 54.814 MPa), in which resins with similar basic compositions were tested using camphorquinone initiator and blue light unit [39]. *The compressive strength* of human enamel can vary between 363-505 MPa, depending on the test design, while the compressive strength of dentin can vary between 454-585 MPa. According to older sources, the compressive strength of dentin is around 297 MPa, while that of enamel is around 382 MPa [40, 41]. Considering the average compressive strength of our resins (348.8 MPa), the value is higher than the average compressive strength of dentin, but lower than that of enamel. We found data for the compressive strength of experimental composite resins (190 MPa), which could be increased by increasing the filler content (290 MPa), but for this the filler content must exceed a ratio of 40-50 v/v % [42]. The compressive strength of our resins (348.8 MPa) exceeds that of resins without filler (190 MPa). Other authors have investigated

the mechanical properties of modern composites, where the average compressive strength values varied in the range 409.6-226.5 MPa [43]. Our measured compressive strength value without the use of filler fits into this range. The reason for this, according to the literature, is that our resin undergoes plastic deformation during the compressive strength test, which may result in higher compressive strength values.

The *diametral tensile strength* test is mainly used to characterise brittle materials and can also be applied to dental composites. Several comparative studies were found in which it was described that the control resin showed higher plastic deformation under load compared to the tested composites [44]. In general, the difference in DTS measured between composites is explained by the resin composition, the type of matrix-forming dimethacrylates, the filler size, the filler-matrix relationship/connection and the ratio of the constituent dimethacrylates [21]. Our average DTS of 46.1 MPa (with minimum values of 33.1 MPa and maximum values of 64.1 MPa) was in agreement with the literature.

Analysis of Ellipsometry and Surface Plasmon Resonance Imaging (SPRi) data

The role of refractive index growth in the formation of cross-linked structures of dimethacrylate resins has been extensively studied in the literature. The increase in refractive index during polymerization of the resin is due to an increase in cross-link density during polymerization and an increase in the viscosity of the copolymer (gelation, vitrification) [6]. For dimethacrylate-based composites, the refractive index varies linearly with the change in conversion during polymerization. Thus, it is possible to study the polymerization processes of our experimental resin through the refractive index variation [5, 45]. The increase in refractive index with increasing polymerization light intensity (1; 1.4; 2 mW/cm2) observed in our reference resin is explained by the increase in conversion due to the increase in intensity detected in the first phase of the experiments, in the order 1.483; 1.490; 1.494. Based on the refractive index variation of the gold nanoparticle-filled resins, we can say that for all three illumination intensities, the refractive index variation of Au1 and Au2

samples is the highest at an intensity of 1.4 mW/cm2 (Au_1: 0. 0326, Au_2: 0.0304), followed by values measured at 2.0 mW/cm^2 (Au_1: 0.0309, Au_2: 0.0296) and finally at 1.0 mW/cm2 (Au_1: 0.0202, Au_2: 0.0182). No significant differences were found between the changes in the refractive index. Based on the SPRi curves, it was found that the addition of gold nanoparticles affects the rate of photopolymerization. Which is due to the thermoplasmonic and plasmon induced polymerization effect of the particles. Based on experimental studies with uncharged dimethacrylate, blue light sensitive photopolymers found in the literature, it was described that the change in refractive index of the resins was linear in time with the change in conversion. Furthermore, the value of the refractive index developed depended on temperature and conversion. At the same time, the intensity of the irradiating light and the concentration of the initiator had no effect on the refractive index values [6]. When a plasmonically excited nanoparticle is illuminated, part of the light is scattered by the particle and absorbed by its surroundings, the other part is absorbed by the particle and radiated as heat. It has been shown in the literature that for

gold nanoparticles, the extent to which these two phenomena characterise the behaviour of the particle is size dependent. Particles smaller than 10 nm tend to emit heat, while particles around 50 nm tend to scatter light incident on them [15]. Based on these results, we hypothesize that in our system, gold nanoparticles mainly exhibited thermo-plasmonic and, in addition or to a lesser extent, plasmon-induced polymerization effects.

Discussion of the diametric tensile strength (DTS) and conversion (DC) data of an experimental gold nanoparticle-filled resin

The average values of the tensile strength of our reference resin DTS Ref (67.171 MPa, 74.464 MPa, 75.112 MPa) are in agreement with the values measured in the first phase of our experiments (33.1-64.4 MPa). Our samples Au_1, Au_2, containing gold nanoparticles, are capable of higher DTS (Au_1: 75. 811 MPa, 86.392 MPa, 80.454 MPa, Au_2: 70.554 MPa, 79.524 MPa, 74.389 MPa) and DC (Au_1: 58.071%, 64.137%, 59.113% Au_2: 56.154%, 60.020%, 58.057%) values. It is believed that the

thermoplasmonic effect of the gold nanoparticles increased the temperature of their environment and consequently the green light triggered photopolymerization was more efficient, resulting in higher polymerization efficiency (DC) and DTS values. Considering the monomer ratios of our resin, the number of hydrogen cross-links in the matrix is presumably high, and the necessary polymerization efficiency is ensured [46, 47]. Our measured DC data ($DCAu_{1-2}$: 56.154-64.137%, DC_{Ref}: 54.098-60.056%) are in agreement with literature data on composites and experimental dimethacrylate resins [48, 47]. The highest DC and DTS data were obtained for the Au_1 sample at light intensity of 1.4 mW/cm2. This means that the ideal gold nanoparticle concentration is found in the Au_1 sample. The lower DTS (79.524 MPa) and DC (60%) values of the Au_2 sample compared to the Au_1 sample compared to the Au_1 sample are also explained by the optical properties of the gold nanoparticles and the clusters formed from them, which inhibit the propagation of light in the material [49].

Transmission Electron Microscopy (TEM) images

The TEM images showed that gold nanoparticles are present in isolation in the resin and, due to their high specific surface area, they clump together and form clusters. Studies on models in the literature have shown that the more pronounced the clustering of particles, the higher the temperature in the agglomeration environment and the longer the time required to reach thermal equilibrium. The size and spatial arrangement of the agglomerating particles is also an important parameter for the heat produced. On this basis, it is believed that the agglomeration of nanoparticles in our resins is not ideal for uniform heat distribution but does not hinder the evolution and release of heat **[50**].

Evaluation of transmittance curves

In the first phase of our experiments, we have demonstrated that the emission spectrum of the green LED light source overlaps well with the absorption spectrum of the Irgacure 784 initiator. On the transmittance curve of the Au1 sample, we observed that the first peak of the

curve appears at 460 nm due to the photoinitiator, followed by a second peak (between 520-550 nm) due to the excited gold nanoparticles, which is confirmed by the characteristics of the transmittance curve of the gold nanoparticles dissolved in toluene, where an enhancement of the plasmonic region is observed. Based on the transmittance analysis, it can be said that our light source emits in the range of wavelength where it is absorbed by the gold nanoparticles dispersed in toluene and the gold nanoparticles in the Au_1 sample.

Summary

In our work, we developed a dimethacrylate copolymer using a new initiator (Irgacure 784) not yet used in dentistry. For the operation of this system, we have prepared a unique green LED light source, also not yet used in dentistry. The analysis of the optical spectrum of the light source and the spectral irradiance of the emitted light, as well as the absorption spectrum of the initiator, and molar extinction coefficient showed that our system is capable of working, as confirmed by the resin conversion,

density, leaching and swelling data. The polymerization kinetic curve of the experimental resin fitted well the literature model proposed by Maffezioli and Terzi for the characterization of the photopolymerization kinetics of acrylates. The conversion data varied between 50-80% and showed an intensity dependence. The mechanical properties coincide with or explained by the literature data. We then investigated the thermoplasmonic and plasmon induced polymerization effects of green light excited gold nanoparticles in our system. It was found that the application of spherical gold nanoparticles with a diameter of 5 nm functionalized with dodecanethiol had effect on the polymerization properties of the resin. Based on the refractive index change data of gold-containing samples/resins and SPRi kinetic study, we selected the intensity value (1.4 mW/cm2) at which we continued our investigations with the two gold-containing samples (Au1, Au2), which also showed the highest refractive index change. The results of the performed diametral tensile strength (DTS) and conversion (DC) measurements clearly showed that both samples have higher DTS and DC values compared to the reference resin data. Moreover, the

measured data are in agreement with and can be explained by the literature data. Finally, we were able to select Au_1 sample, that contained the optimal gold nanoparticle concentration (0,0208 wt%). Transmission spectrophotometry measurements showed that the gold nanoparticles used in our resins can be excited by our green LED light source in the irradiation range of 520-550 nm. Moreover, we confirmed the presence and characteristics of gold nanoparticles by elemental analysis and transmission electron microscopy images and showed that the particles form clusters, which does not prevent their thermo-plasmonic or plasmon-induced photopolymerization in the resins.

- Based on the analysis of dimethacrylate resin without gold nanoparticles, we found that the emission peak of the new green LED light source is located at 531nm and emits in a narrow spectrum (490-590nm), where the molar extinction coefficient of Irgacure 784 initiator $\varepsilon = 90 M^{-1} cm^{-1}$, which makes the light source functional.

- The conversion data calculated from the Raman measuremets and their variation with time were consistent with the behaviour of the kinetic model based on Maffezolli's modified equation. The maximum conversion was 70-80% after irradiation of the samples with green light of intensity 6-10 mW/cm^2 and irradiation time 150s.
- The density of the test samples increased to the same value ($\rho \sim 1{,}17 - 1{,}19 \frac{g}{cm^3}$) regardless of the irradiation intensity. DMF extraction samples showed a 10% mass loss, which assumes a 90% conversion at all intensity values tested. The polymerized samples showed little swelling in water (less than 1% water uptake over 1 week), which is conducive for dental applications.
- Favourable hardness values (20-25 kgf/mm^2) were obtained at irradiance levels one order of magnitude lower than those typical for dental illumination, although below I=6 mW/cm^2 the quality/hardness of the samples deteriorated rapidly due to the high initiator concentration.

- The mechanical properties of the samples at an illumination value of 1.4 mW/cm^2 correlated well with the literature data.
- In the dimethacrylate resin, dodecane thiol functionalised gold nanoparticles of 5 nm size was successfully used.
- Using Surface Plasmon Resonance imaging (SPRi) measurements and confocal Raman spectroscopy, we were able to study the conversion and polymerization process in our experimental resin.
- The use of gold nanoparticles also improved the diametral tensile strength and conversion of the resins compared to the reference resin. In our system, we found the optimal irradiation intensity (1.4 mW/mm^2) and gold nanoparticle concentration (0.0208 vol %). Based on our results, we have synthesized a workable green light polymerizable dimethacrylate based resin containing functionalised gold nanoparticles and a new type of initiator (Irgacure 784) was used, which can be the basis for a future experimental dental composite containing inorganic filler.

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Subject: PhD Publication List

Candidate: Katalin Bukovinszky
Doctoral School: Doctoral School of Dental Sciences

List of publications related to the dissertation

1. **Bukovinszky, K.**, Szalóki, M., Csarnovics, I., Bonyár, A., Petrik, P., Kalas, B., Daróczi, L., Kéki, S., Kökényesi, S., Hegedűs, C.: Optimization of Plasmonic Gold Nanoparticle Concentration in Green LED Light Active Dental Photopolymer.
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List of other publications

3. **Bukovinszky, K.**, Molnár, L., Bakó, J., Szalóki, M., Hegedűs, C.: Folyékony kompozitok és töltetlen kompozit gyanta polimerizációs zsugorodásának összehasonlító vizsgálata.
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