



Influence of gold nanoparticles in polymer nanocomposite on space-temporal-irradiation dependent diffraction grating recording

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ARTICLE INFO

Keywords:

Polymer nanocomposite
Photopolymerization processes
Gold nanoparticles
Plasmon fields
Diffraction gratings

ABSTRACT

Following the modern and extremely useful direction of research and development of polymer nanocomposites with combined effects of photopolymerization superimposed by plasmon-induced processes, we investigated acrylate-based nanocomposites with broadband sensitive Irigaure784 initiator and silicon oxide as well as gold nanoparticles in different regimes of illumination. The details of initiator photodecomposition and polymer chain formation mechanisms at the presence of the gold nanoparticles' (GNPs) plasmon fields and different combinations of irradiation wavelengths or intensities are discussed. These are related to the mechanism and efficiency of holographic volume and surface grating recording based on photopolymerization and mass-transport, diffusion processes of the organic matrix, and nanoparticles. GNP's presence in a monomer nanocomposite influences the recording parameters in a combined way, making preferable the double-wavelength irradiation mode, which may increase the efficiency of the recorded gratings up to two times at decreased exposures. Results may be used for planning fabrication processes of more complex, multifunctional photonic elements.

1. Introduction

Research and development of polymer composites in general and nanocomposites, in particular, became an important part of modern materials science and different industrial applications [1,2]. Special interests are connected with multifunctional, versatile nanocomposites for optics, photonics, information technology, sensors, and biomedicine, where thin, flexible elements and structures can replace robust inorganic materials with high efficiency and cheap fabrication processes [3,4]. Typical examples may be lenses or lens matrices, diffractive and nonlinear optical elements, photonic crystals, and metasurfaces widely used in photonics for light manipulation [4–6]. One basic advantage of light-sensitive nanocomposites is the possibility of *in situ* creating required optical elements in a necessary place, which also can be used as molds for replication. Not less important is the possibility to combine functions of such elements, like irreversible or reversible optical memory, luminescence, optical non-linearity, sensing different signals. These characteristics may be combined in nanocomposites by proper selection of matrix monomer components, initiators as well as different organic or inorganic fillers-nanoparticles, which provide the necessary functionality. As far we are interested in optical applications, the optical

parameters (absorption, reflection, scattering, refractive index) and the optically recorded elements' stability should satisfy the actual conditions.

The development of polymer nanocomposites for photonics with a required set of parameters consists of monomer selection, combining it with proper initiator and nanoparticles, which allows optical processing, recording elements with necessary optical parameters. Besides the final parameters of the element, nanoparticles can affect the polymerization, spatial and temporal parameters of the recording process [7,8]. One of the most interesting and versatile nanoparticles is gold (GNPs), because of their stability and specific property of plasmon resonance, which appears under light excitation, usually in a green-yellow spectral region [9] and essentially influences ongoing processes in its surroundings. Plasmon-mediated processing is an important field of research and development in which polymer nanocomposites as plasmonic nanomaterials possess new functions as mediators to redistribute and convert photon energy into a localized photon, electron, and/or thermal energies, enhance sensing functions of an element in biomedicine.

Polymer nanocomposites are comparatively homogeneous mixtures of organic and/or inorganic nanoparticles in a polymer matrix. The mechanism of optical recording processes in such materials is actively

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<https://doi.org/10.1016/j.polymer.2020.123240>

Received 31 August 2020; Received in revised form 2 November 2020; Accepted 14 November 2020

Available online 18 November 2020

0032-3861/© 2020 The Author(s).

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investigated [10–13]. It consists of two main components: photo-stimulated polymerization and diffusion of monomers and nanoparticles in the in-homogeneously irradiated volume. Usually, in a simple case of spatially inhomogeneous illumination by light interference fringes, monomers' polymerization starts in bright regions that influence the chemical potentials and stimulates diffusion of specific components from dark to bright regions. In its turn, the nanoparticles which do not take part directly in polymerization diffuse from bright to darker regions. As a result, a certain spatial distribution of material composition, refractive index, and other parameters appears, photonic elements like diffraction gratings or more complex structures can be created. The introduction of different inorganic nanoparticles influences different properties of nanocomposites like linear and nonlinear parts of the refractive index, enhanced luminescent, photosensitive characteristics, to say only about optical characteristics [14]. Metallic nanoparticles with plasmon resonance effects, especially silver and gold are in the focus of interest as fillers because of their stability, biocompatibility, resonance excitation in a visible optical spectral range [15].

Important problems related to the GNPs-polymer light-sensitive nanocomposites for photonics are the preparation technology, including the selection of monomers and initiators with a certain set of parameters, the possible combination of different compatible nanoparticles regarding the photopolymerization process and homogeneity of the initial mixture, the stability of the resulting structure with given optical or others parameters [16,17]. Several strategies have been reported for the preparation of GNPs - polymer composites with different polymerization paths [18–21].

The influence and role of nanoparticles, especially of GNPs, in the photopolymerization process during optical pattern creation may be investigated by known optical methods of absorption, reflection, and transmission measurements, as well as using optical, holographic recording-readout methods. The last ones give us possibilities of direct measurements of optical and complement geometrical reliefs, for example, Bragg gratings, serving the basis of different, one-two-dimensional photonic structures formation like it was reported in Ref. [22], or even of more complex ones. Despite some researches on the role of GNPs in hologram recording processes [23–25], the essential details like the influence of GNP on the dissociation of the given initiator and the breakup of double bonds in monomer, the effects of excitation intensities at different or combined wavelengths are not cleared. In the present paper, we describe these investigations using selected monomer composites with improved stability parameters [26].

Here we used Bragg grating recording, as well as some other optical experimental technics for investigation of acrylate-based polymer nanocomposites with selected Irgacure 784 initiator and SiO₂ nanoparticles, with and without GNPs to determine the influence of GNPs, its plasmon fields on polymerization processes, complemented by formation of geometrical surface reliefs during holographic Bragg grating recording at different combinations of 408 nm UV and 442 or 532 nm laser excitation wavelengths and intensities. Surface plasmon resonance imaging (SPRI) was used to measure the real-time variations in the refraction index during polymerization, while infrared spectroscopy measurements allowed us to follow the decomposition of the initiator and double bonds of monomers.

All these results should be useful for selecting functional polymer nanocomposites and regimes of different photonic elements, structures fabrication on their basis.

2. Experimental

2.1. Materials

- Diurethane dimethacrylate, a mixture of isomers(UDMA, 436909 ALDRICH)
- *Isodecyl acrylate* (IDA, 408956 ALDRICH),
- *2-carboxyethyl acrylate* (2Car, 552348 ALDRICH)

- the monomers mixture was used with *Bis(.eta.5-2,4-cyclopentadiene-1-yl)-bis(2,6-difluoro-3-(1H-pyrrol-1-yl)-phenyl) titanium* (Irgacure784) initiator as basic matrix components.
- SiO₂ nanoparticles with diameter 7 nm (Aldrich N^o066K0110)
- Gold nanoparticles, surface modified by dodecanethiol, 5 nm in diameter (AuNPs No. 3014, Nanoprobes) were used for the nanocomposites.

2.2. Preparation of the nanocomposites and investigated samples

Two types of nanocomposites were created and studied: structures without and with GNPs (abbreviated in the following as SiO₂-NC and SiO₂-GNP-NC). The mixture of monomer materials (UDMA/2Car/IDA = 75/18/7 wt%) was stirred together for 3 h. In the next step, 13.5 wt% SiO₂NPs were added to the prepared monomer mixture by magnetic stirring (24 h). Furthermore, GNPs dissolved in toluene may be added in the amount of 0.08 or 0.15 wt%. Finally, 0.5 wt% photoinitiator was added, and the prepared nanocomposites were stirred for another 5 h. Evaporation of solvents was made done until the weight of the liquid nanocomposite remained constant. It should be mentioned that the used 5 nm GNPs were dodecanethiol-modified, and the addition of SiO₂ nanoparticles (7 nm) was necessary to avoid aggregation of GNPs in the given mixture of monomers at their concentrations above 0.05 wt%, as it was established experimentally in our previous work [31]. So SiO₂NPs are important components of investigated nanocomposites. This way, at the given concentrations, we had homogeneous, optically transparent monomer-polymer nanocomposites with plasmon resonance effects on separated GNPs, low level of light scattering, and usable for optical recording of micrometer-sized structures [31].

To prepare acrylate-urethane monomer based nanocomposite sample layers, a droplet of liquid nanocomposite was placed onto the microscope glass substrate. It was covered from the top by mylar film since the oxygen inhibits the polymerization process. The thickness of the layered sample was determined by the spacer ring located between the substrate and the cover film, and it was usually 100 μm thick. Such samples were used for optical, holographic experiments.

2.3. Investigation of the decomposition rate of the initiator and the C = C double bonds in monomers

To measure the decomposition rate of the Irg784 initiator, nanocomposite layer samples were irradiated by light with a certain wavelength (408 nm, 532 nm, or [408 + 532] nm) and UV-VIS optical transmission spectra were measured during polymerization. To investigate the illumination-induced processes, the prepared nanocomposites were also irradiated with light-emitting diodes (MPL-F, 408 nm) or with a green laser setup (diode-pumped solid-state laser (DPSS), 532 nm). The use of UV LED for measurements of polymerization-related processes was more suitable in comparison with 442 nm emitting laser, used for hologram recording, moreover, the sensitivities of Irgacure784 initiator are almost similar at these wavelengths. During the measurements under illumination, the initially liquid nanocomposites were placed between quartz glass plates separated by spacers. The whole surface area of the tested samples was irradiated. The decomposition rates of initiator were measured at power densities 0.4 mW/cm², the measurements of C=C decomposition rates were measured at power densities 2 mW/cm². During the decomposition process of Irgacure784 under irradiation, optical spectra were measured by a Shimadzu UV-1800 spectrophotometer. The kinetics of Irg784 photoinitiator's dissociation upon light irradiation was determined by measuring the decrease of the absorption peaks at 396 nm, which is characteristic of these materials. The rate of initiators decomposition due to the irradiation was measured as the slope of the curve, which describes the decrease of the initiator's absorption with irradiation time. To make a comparison of initiator decomposition rate without and with GNPs, data were transformed to percentages, where 100% was the absorption pike intensity at

the beginning of the process.

IR spectroscopy was used for measuring the conversion degree in the nanocomposite with and without GNPs. The decomposition rate of double C=C bonds in acrylate-urethane monomers in nanocomposite layers under irradiation by light (408, or 532, or 408 + 532 nm) was determined from IR spectra by measuring 1637 cm^{-1} IR line intensity before and every 10 s of irradiation on Bruker Tensor 37 spectrophotometer. Deconvolution (Lorentz approximation of pikes) was performed by the Opus program for the peak at 1637 cm^{-1} . The degree of conversion of the monomers' (K) was calculated as Eq. (1).

$$K = \frac{A - B}{A} * 100\% \quad (1)$$

Where A is the normalized intensity of the 1637 cm^{-1} peak before polymerization, B is the normalized intensity of the peak at the given time stage of polymerization.

2.4. SPRi measuring the refractive index variations in the nanocomposites during polymerization

The photopolymerization process was also investigated by measuring the changes in the refractive index during the irradiation of monomers. The refractive index change caused by UV source radiation (output $P = 1\text{ W}$, operating wavelength: 408 nm) and green light-emitting DPSS laser (output $P = 14\text{ mW}$, operating wavelength 532 nm) was measured by surface plasmon resonance imaging (SPRi). The light beam of the sources was defocused, so the intensity of illumination on the sample was $0.5\text{--}7\text{ mW/cm}^2$ for the green laser diode and $2\text{--}7\text{ mW/cm}^2$ for the UV source. For the measurements, a custom-built SPRi instrument [27] was used, which utilizes Kretschmann optical configuration with a 680 nm superluminescent light source and a 1 MP CCD camera with 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 inflexion point of the SPR peak to maximize the sensitivity. There are no moving parts during the measurements. Although the SPRi instrument was designed to measure primarily in aqueous environments, the device was re-calibrated to be able to measure polymers with much higher refractive indexes, such as the investigated nanocomposites. For SPRi measurements, the investigated nanocomposites were dispersed onto an SPRi chip (50 nm gold deposited on a glass substrate, purchased from Xantec, Germany), then a thin layer was formed by pressing a UV transparent polyester film on top of the nanocomposites. Real-time changes in the refractive index of the media were monitored during the whole duration of the 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 presented kinetics comparisons in our figures. No comparison between the individual measurements (e.g., comparison of kinetic curves from separate measurements) was made.

2.5. Optical recording by two-beam interference

Optical recording of the diffraction gratings was performed by a He–Cd laser emitting 442 nm light. The laser beam was polarized, its intensity was varied by graded optical filters. The beam was expanded, divided, and reflected the sample, so the interference pattern of two s-polarized beams was projected onto the sample. The principal scheme is presented in Fig. 1.

The above-described SiO_2 -nanocomposites or SiO_2 – GNPs-nanocomposites were used as light-sensitive media for the holographic recording of diffraction gratings. The holographic recording was usually conducted in an interference field with a period of $2\text{ }\mu\text{m}$. The diffraction efficiency was determined by another laser at 633 nm wavelength as a ratio of the first-order diffraction intensity to the incident radiation intensity.

3. Results

One of the essential tasks in the development of light-sensitive polymer nanocomposites consists of the selection of the proper initiator for the given monomer or their mixture, which in our case can be influenced by the plasmon field of added GNPs as well and so should be sensitive in the spectral range of plasmon excitation besides the UV-blue region, usual for efficient photopolymerization (it is necessary for understanding the possible influence of plasmon fields on photodecomposition of initiator and so on the polymerization process in the whole). Our basic nanocomposite for hologram recordings was made from a mixture of urethane-acrylates, like in Ref. [26], consisting of SiO_2 NPs. It contains an Irgacure 784 initiator, which has a sensitivity spectrum complementary to the emission of the light source, used for gratings recording (442 nm), and partially in the 532 nm range, where plasmon resonance generation was observed as well if GNPs are present in the composite. The absorption spectra presented in Fig. 2 support these statements.

Based on these starting points of irradiation-composition variation possibilities for our nanocomposites, we used three holographic grating recording regimes to investigate the role of GNPs in grating formation processes.

The first was recording only by 442 nm light, i.e., out of GNP plasmon resonance frequency (near 530 nm, as visible in Fig. 2).

The second was recorded only by a 532 nm laser beam, i.e., in the spectral range of resonant excitation of our GNPs.

The third regime consists of holographic grating recording by 442 nm laser irradiation, at simultaneous irradiation at 532 nm for plasmon excitation.

These regimes of holographic recording were based on the details of photopolymerization processes, which were investigated using the same light sources plus one, non-coherent light source emitting at 408 nm, where the sensitivity of Irgacure784 is higher.

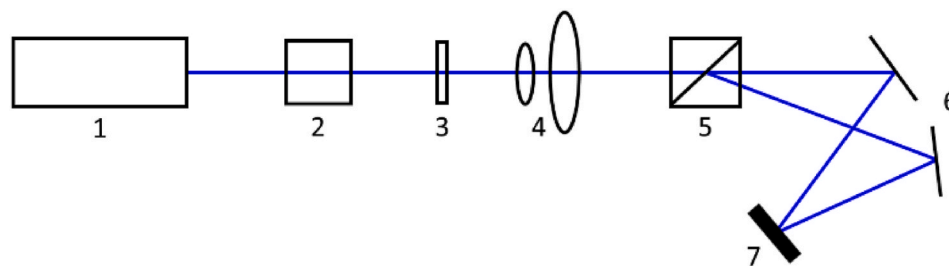


Fig. 1. Illustration of the equipment used for the hologram recording experiment. 1 – laser, 2 – polarizer, 3 – optical filter, 4 – lenses, 5 – beam splitter, 6 – mirrors, 7 – sample.

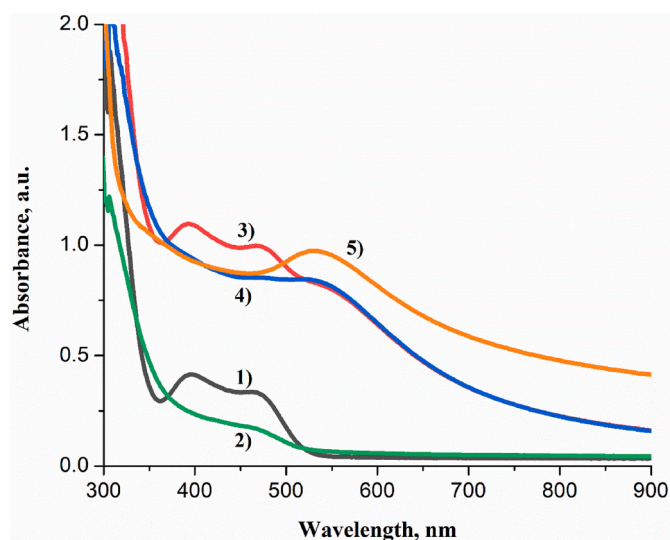


Fig. 2. Optical absorption spectra of the nanocomposite, irradiation 408 nm: 1- SiO₂ -nanocomposite with Irgacure784 started polymerization; 2- SiO₂ -nanocomposite with Irgacure784, finished polymerization; 3- SiO₂ - GNPs - nanocomposite with Irgacure784 started polymerization; 4- SiO₂ - GNPs-nanocomposite with Irgacure784, finished polymerization; 5- SiO₂ -nanocomposite + GNPs without Irgacure784 before and after irradiation.

3.1. Influence of GNPs on the holographic recording process and its parameters

The next part of investigations and results relates the influence of irradiation intensities on the grating recording process and on its' resulting diffraction efficiency, which is a well-defined parameter and adumbrate the underlying polymerization, mass-transport processes.

Two basic processes determine the final type, form, and efficiency of the recorded holographic grating in our nanocomposites: polymerization (its' rate, interconnected with initiator dissociation and double-bond breaking) and mass-transport, diffusion of monomer and nanoparticle components in a non-homogeneously irradiated nanocomposite. The ratio of these processes may essentially influence the whole recording and the form, optical and geometrical profile, resulting in optical parameters of the grating or more complex relief. Both processes may be dependent on irradiation intensities, irradiation wavelength. At the same time, such measurements can give us additional information about the mechanism of light-induced processes in nanocomposites.

The influence of irradiation intensity (power density P) variations at three above mentioned recording configurations on the resulting diffraction efficiency (DE) of gratings, which were recorded during the same time (8 min) are presented in Table 1. But intensities P are different: P of only blue or green light varies between 3 and 11 mW/cm², in nanocomposites with SiO₂ NPs, Irgacure784 without and with GNPs (at their concentration 0.15 wt%), but in combined regime (442 + 532 nm) the additional uniform green irradiation intensity was stable 2.3

Table 1
Diffraction efficiencies of gratings recorded at different conditions. Errors are within 5%.

P (mW/cm ²) of grating recording	DE [%], SiO ₂ -nanocomposite			DE [%], SiO ₂ - GNPs- nanocomposite		
	Recording conditions			Recording conditions		
	442 nm	532 nm	442 nm + 532 nm ($P+2.3$ mW/cm ²)	442 nm	532 nm	442 nm + 532 nm ($P+2.3$ mW/cm ²)
3.3	24.0±1.2	5.0±0.3	37.0±1.9	75.0±3.8	12.5±1.2	85.0±4.2
4.8	62±3.1	12.0±0.6	75.0±3.8	62.0±3.1	2.5±0.1	76.0±3.8
6.2	40±2.0	5.0±0.3	54.0±2.7	35.0±1.8	6.0±0.3	74.0±3.7
10	15±0.8	5.0±0.3	58.0±2.9	16.0±0.8	3.0±0.2	75.0±3.8

mW/cm².

It can be seen based on Table 1 that in the nanocomposites without GNPs the diffraction efficiency (DE) of gratings recorded with 442 nm or 442 + 532 nm irradiation always has an increasing and decreasing part with increasing intensities. Maximum DE, equal to 62% (recording at 442 nm) and 75% (442 + 532 nm) were obtained at $P = 4.8$ mW/cm² of blue light. Further P increase of 442 nm irradiation leads to the DE smooth decrease, to 15%, while in the case of 442 + 532 nm irradiation, the DE does not decrease necessarily and reaches a plateau. Recording only with a 532 nm light beam resulted in the lowest DE values.

Introduction of GNPs into the mixture of monomers with SiO₂NPs and Irgacure 784 causes higher DE (75%) of gratings recorded with 442 nm irradiation yet at lower power densities ($P = 3.3$ mW/cm²). But at higher P the DE values decrease in a monotonous way, and they are comparable with DE in nanocomposites without GNPs. Recording at 442 + 532 nm conditions in the nanocomposite with GNPs also results in high DE values (85% at lower $P = 3.3$ mW/cm²). But the further increase of P to 10 mW/cm² causes a small decrease of DE to 77% stable value. Recording with only at 532 nm in nanocomposites with and without GNPs results in lower DE in comparison with other variants.

Summarizing results on grating recordings, it can be concluded that recording in (442 + 532 nm) regime always results in higher DE in comparison with 442 nm only; and increasing the power density above 4.8 mW/cm² always yields that DE does not more depend on recording power density. The presence of GNPs in the nanocomposite results in increasing of DE at decreased P of 442 nm. Independently on the presence of GNPs the recording only at 532 nm always results in gratings with lower DE in comparison with other regimes. Based on the data shown in Table 1 and other experiments allow us to conclude that the presence of GNPs in a monomer nanocomposite influences the holographic grating formation, and this influence depends on recording parameters (wavelength, intensity) in a combined way. Using 532 nm extra irradiation plasmon fields of the given size GNPs can be excited, which influences not only the pure polymerization processes but the alignment of polymerization and diffusion, spatial mass-transport processes, which define the formation of amplitude-phase optical as well as geometrical relief in the layer. Since the diffusion processes depend on viscosity, what in turn depends on initiator decomposition and bond breaking, we should study the direct effects of light influence on polymerization.

3.2. Influence of GNPs on the initiator decomposition

In the present work, we have investigated two main stages of polymerization: initiation and chain growth. Initiation was studied by measuring the rate of Irgacure 784 initiator decomposition (photolysis) by UV-VIS spectroscopy. The chain growth stage of polymerization was characterized by the rate of C=C bonds breaking (photolysis) by the IR spectroscopy method. Additional data on polymerization were obtained by SPRi measurements.

To analyze the first, initialization step of polymerization at the presence of GNPs, which may influence the decomposition (photolysis) of Irgacure 784 in the given nanocomposite, we have measured UV-VIS absorption spectra during the whole time of irradiation (polymerization)

of the nanocomposite at different irradiation conditions. In these measurements for all irradiation regimes (408, 532, 408 + 532 nm) we used decreased intensities 0.4 mW/cm^2 for better resolution of process kinetics and comparisons.

Typical absorption spectra before and after irradiation/polymerization of different nanocomposites are presented in Fig. 2. One can see that the excited plasmon peak in our composite with given GNP size is localized near 530 nm (curve 5), as it was observed earlier in our nanocomposites with the same type of GNPs, selected for work with green laser sources [25]. Since this plasmon peak is overlapping with the Irgaquare784 absorption tail, the possible small peak shift due to the polymerization of the surrounding matrix has no noticeable influence on the whole process and was not separately investigated, the more so, that no polymerization occurs without an initiator.

What is more, the possible situation with the aggregation of separate GNPs in a variable matrix is changing in our case since GNPs are distributed without aggregation in the given mixture of monomers and SiO_2 NPs, as it was established experimentally in our work [31].

At the same time, GNPs may form a stable complex with Irgaquare784, as it was described in our paper [25]. Formation of Irgaquare784/GNP - complex is possible because donor-acceptor bonds can be created between phenyl and/or pyrrole rings of Irgaquare784 initiator and the positively charged gold nanoparticle surface, which are acceptors of negative particles [25].

The decrease of the Irgaquare784 initiator's maximum at 398 nm during irradiation was used for plots of photodissociation in nanocomposite with and without GNPs for all regimes of irradiation (Fig. 3). The change of slopes characterizes the initiator's photo-decomposition

rate. It follows from the data of Fig. 3 that the photolysis rate is changing in the function of the irradiation regime and the presence of GNPs. Under 408 nm and 408 + 532 nm irradiations, the introduction of GNPs decreases the initiator's photo-decomposition rate. At the same time, under only 532 nm irradiation, the decomposition rate increases, as explained later.

Such influence of GNPs on the initiator's decomposition may be explained by the (due to the) presence of Irgaquare/GNP complexes. Decrease of the Irgaquare784 photo-decomposition rate at the presence of GNPs under 408 nm irradiation may be explained by the formation of donor-acceptor bonds, as shown in Ref. [25] between GNPs and Irgaquare784 molecule. This makes Irgaquare784 molecules more stable to irradiation and results in the decrease of dissociation rate. But under 532 nm irradiation, the influence of GNPs on Irgaquare decomposition is different. It is visible from Fig. 3, that the same initial rate essentially increases during further irradiation in comparison with GNP-free composite. Distance between GNPs and initiator molecules is within the action of the GNP plasmon field since the average distance between GNPs at the given concentrations is within 100 nm so at 532 nm plasmon resonance-close excitation, these influence the initiator molecule. At this condition, the stabilizing influence of the GNP/Irgaquare784 complex is exceeded by the destructive influence of GNPs plasmon field on the initiator molecules, which results in the increased dissociation rate. At the same time, it is more pronounced at high excitation intensities, like it was shown in our paper [25] for higher, 4 mW/cm^2 excitation intensities, or prolonged irradiation at 0.4 mW/cm^2 , as in the present case (see Fig. 3b). Here the effect of irradiation intensity increase may increase initiator decomposition rate like it was described in Ref. [32], but

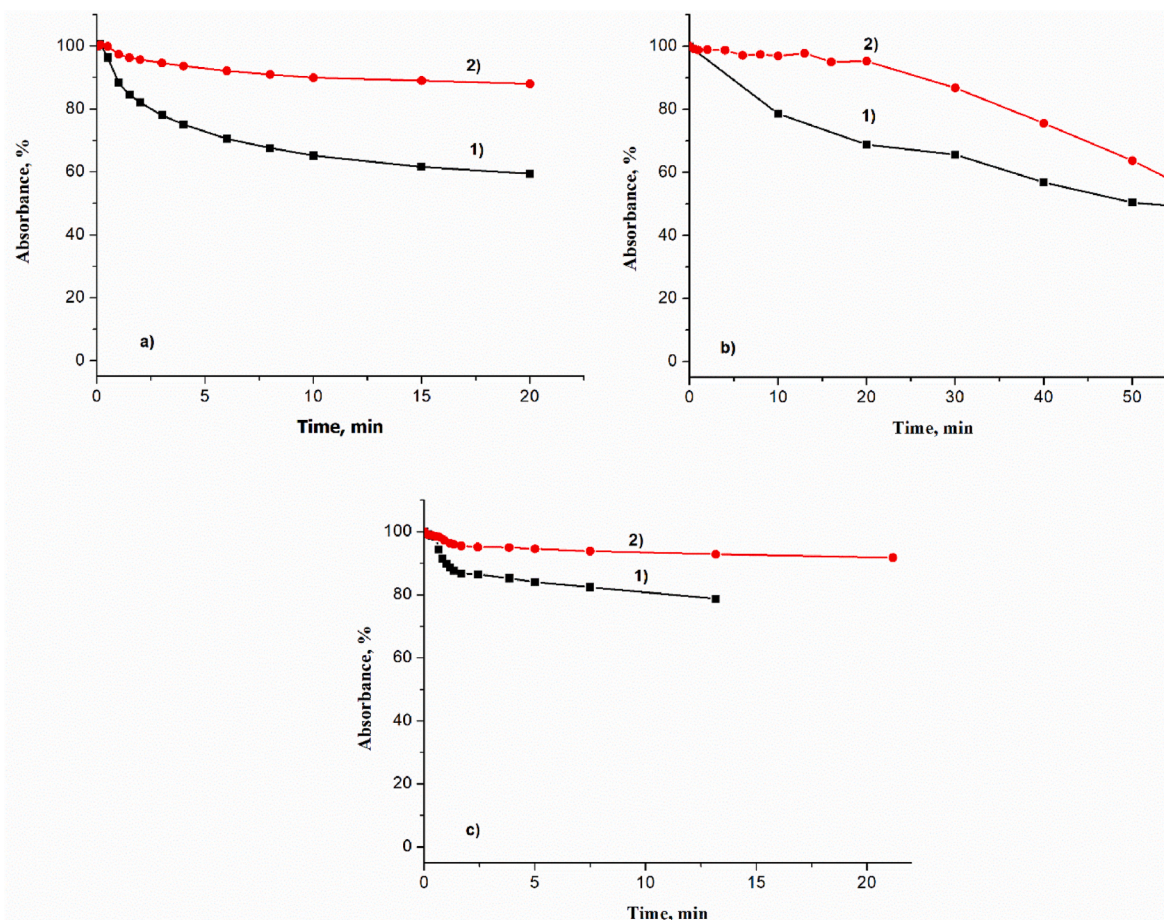


Fig. 3. Decrease of the 398 nm absorption peak of Irgaquare 784 (in the percentage of initial height). Data for SiO_2 -nanocomposites (1) and SiO_2 -GNPs-nanocomposites (2) at irradiations: a-408 nm, b-532 nm, c- 408 + 532 nm. The intensity of the basic blue irradiation was 0.4 mW/cm^2 . (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

the influence of GNPs on the whole recording processes, which involves changes in the initiator, seems to be the same.

These spectra show us the presence and localization of plasmon resonance excitation if GNPs are added, so they may influence the polymerization and the recording processes in our nanocomposites at the presence of 532 nm excitation. The role of the plasmon electric fields in the above-mentioned processes seems to be essential [28–30], but some influence of cumulative thermal effects due to the light absorption by metallic GNPs may also be supposed [31]. The possible influence of thermal effects on the dissociation of the initiator should also be mentioned since metallic GNPs actively absorb energy at 532 nm irradiation and transform it to heat besides the plasmon field. This aspect of the processes was not analyzed here, while it should not be excluded despite the fact that Irqaure 784 is considered as a thermally stable initiator [33].

3.3. Influence of GNPs on the degree of conversion of the monomers

As the decomposition of the photoinitiator during the photopolymerization process is only one element which can influence the optical recording, so on the parameters of the created surface structures, other elements should be investigated to clear the complex mechanism of this process. At this step, the influence of GNPs on the chain growth should be analyzed during the photopolymerization process, which possibly influences the material transport in periodically illuminated nanocomposites, and so the parameters of created photonic elements.

To investigate the influence of GNPs on the second part of polymerization (chain growth) we used the measurements of C=C double bonds' dissociation kinetics and calculations of the degree of conversion.

So during the photopolymerization process, the IR absorption spectra of nanocomposites with and without GNPs were measured under different irradiation conditions. Based on the decrease of 1637 cm^{-1} band maximum, which characterizes vibrations of C=C double bond [34], the kinetics of C=C double bond dissociations were estimated (see Fig. 4).

The deconvolution method was used to eliminate the influence of lines neighboring the maxima at 1637 cm^{-1} , and further, the conversion degree was calculated (see the results in Table 2). The rate of C=C bond breaking for the nanocomposite with SiO_2 NPs may be determined by the concentration of free radicals, and so will indirectly depend on the sensitivity of the initiator on the given wavelength and intensity of irradiation. It follows from Fig. 4, that the rate and percentage of C=C bond breaking in the SiO_2 -nanocomposite depend on the irradiation wavelength. The largest rate is observed under 408 nm irradiation. Under 532 nm irradiation, the breaking process is much slower, which is in agreement with the smaller sensitivity of initiator in this spectral region, and the concentration of radicals is low. Under two-wavelength (442 + 532 nm) irradiation, the C=C bond-breaking rate increases in comparison with only 532 nm irradiation, but still is less as under 408 nm irradiation. Under 408 nm irradiation, up to 35% of double bonds are not broken during the given exposition time, while under 532 nm and (408 + 532) nm irradiation these values are 55% and 50%. The calculated conversion degrees, 66%, 49%, and 53% are in good accordance with graphical analysis. Small deviations in the number of preserved double bonds determined by calculation and graphically by comparison of areas may be explained by the application of the deconvolution method, which takes into account the influence of adjacent lines.

The inclusion of GNPs always results in the increase of the C=C bond-breaking rate in comparison with nanocomposite without GNPs, as

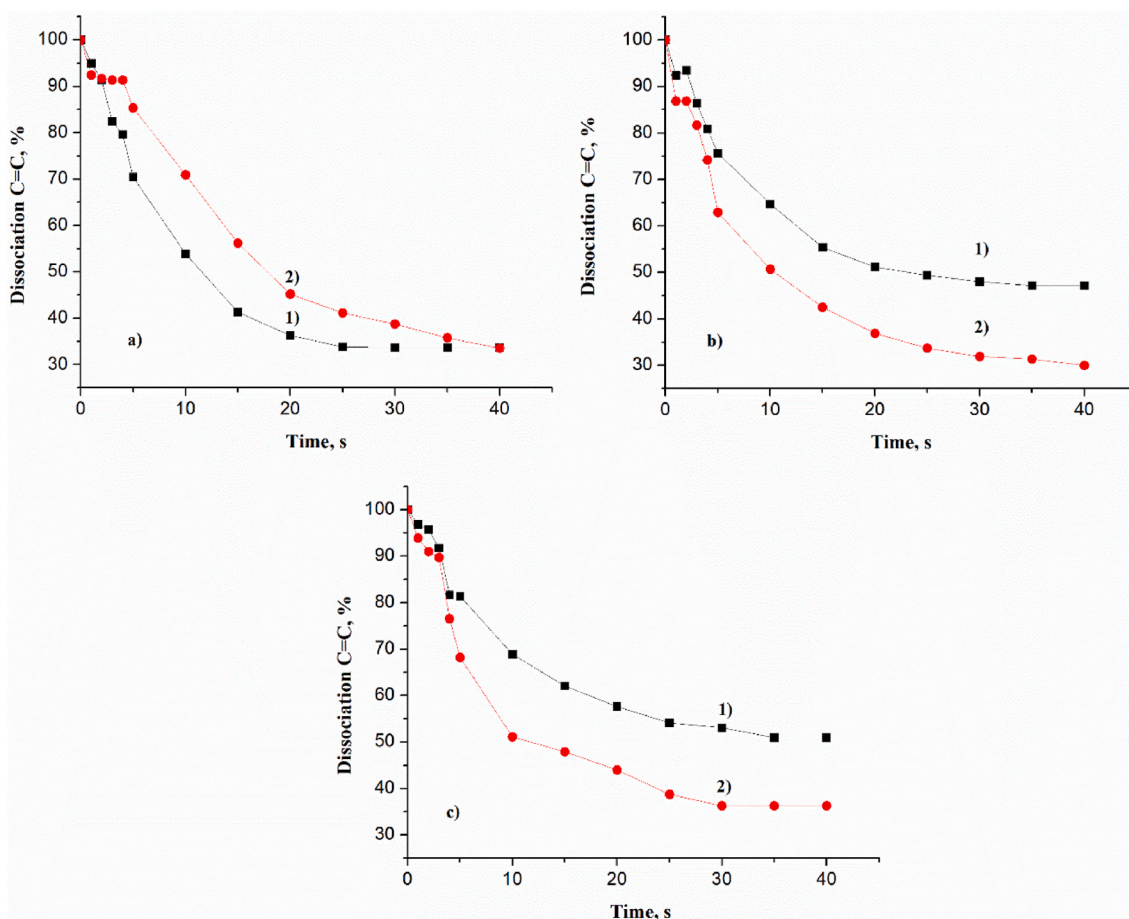


Fig. 4. Dissociation of C=C bonds at different irradiation regimes. Data for SiO_2 -nanocomposites (1) and SiO_2 -GNPs-nanocomposites (2) at irradiations: a-408 nm, b-532 nm, c- 408 + 532 nm.

Table 2

Conversion degree in nanocomposites under different irradiation conditions (regimes). Errors are within 5%.

Nanocomposite	SiO ₂ - Nanocomposite			SiO ₂ - GNP- Nanocomposite		
	408	532	408 + 532	408	532	408 + 532
Irradiation wavelength, [nm]						
Conversion degree, [%]	66.0±3.3	49.0±2.5	53.0±2.7	66.0±3.3	64.0±3.2	71.0±3.6

well as an increase of conversion degree at all irradiation regimes. It can be seen from Fig. 4b that the most substantial C=C bond breaking rate takes place under 532 nm irradiation, not at 408 nm irradiation, as it is in the nanocomposite without GNPs. The same relates to the conversion degrees (64%) in the nanocomposite with GNPs in comparison with 49% in the composite without GNPs. It is also interesting that under double irradiation (408 + 532 nm) the C=C bond breaking rate is slightly less as under 532 nm irradiation only, but the conversion degree was the largest, 71%.

It may be concluded that at the presence of 532 nm irradiation, the GNPs influence the kinetics of C=C bond breaking and the resulting conversion degree, not only the decomposition of the initiator. Three effects may be involved for explanation: influence of plasmon fields of excited GNPs, the role of possibly emitted hot electrons, and local thermal effects caused by heating of GNP under irradiation [28,35,36].

The more precise separation of these effects in the given type of nanocomposites needs additional investigations. At the present stage of investigations, it may be concluded that more efficient can be the process of polymerization, and so the hologram recording in our nanocomposites with SiO₂ and GNPs at double-wavelength irradiation: one for interference relief formation and recording, the second for plasmon excitation and enhancement of recording process efficiency.

3.4. Influence of GNPs on the refractive index change during nanocomposite polymerization

Additional experimental investigations based on SPRI were performed to establish the influence of GNPs on the polymerization of nanocomposites with SiO₂ nanoparticles in more detail. The surface plasmon resonance imaging method allowed us to determine the rate of the refractive index change under polymerization at different irradiation regimes.

It is visible from Fig. 5 that the introduction of GNPs to the monomer mixture promotes polymerization with a higher resulting refractive index under all irradiation regimes, compared with compositions without GNPs. Also, the refractive index increase rates are higher in the presence of GNPs. The highest difference of the refractive index increase between the nanocomposites without and with GNPs occurs under the 442 + 532 nm irradiation regime. This result correlates with our data on polymerization in nanocomposites [37], which shows the refractive index increase connected with an increase of nanocomposite density and microhardness during the photopolymerization at the presence of GNP.

4. Discussion

The above-presented investigation results allow us to propose the possible mechanisms of GNP's influence on the polymerization of SiO₂

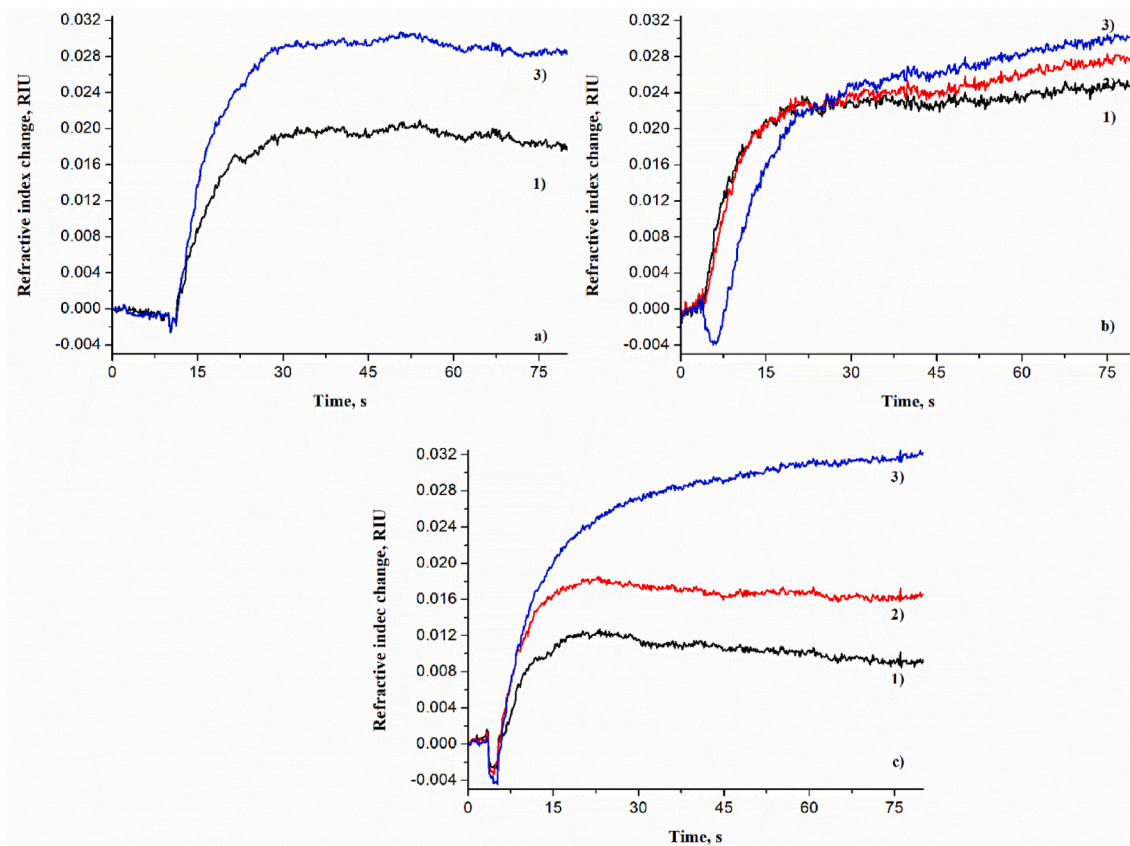


Fig. 5. Refractive index change during the polymerization of SiO₂-nanocomposite (1) and with SiO₂- GNPs-nanocomposite (2 - concentration of GNPs 0.08 wt%; 3- concentration of GNPs 0.15 wt%) under different irradiation regimes: a-408 nm, b-532 nm and c- 408 + 532 nm.

NPs containing acrylate-urethane nanocomposite.

In the composite of monomers, GNPs create complexes with Irgacure784, which increases the irradiation stability of the initiator, decreases the speed of photolysis, except for the irradiation with single 532 nm light, which excites SPRI in GNPs and increases the photolysis rate in comparison with GNP-free case. At these conditions, the quantity of initiator in the volume of polymerizable material is preserved for a longer time, that keeps up the active role of initiator for a longer time at the decreased viscosity conditions, as well as supports longer polymerization process, which is desirable for the diffusion of components at the non-uniform irradiation pattern, i.e., holographic recording, etc.

At the stage of polymer chain growth, the plasmon fields of introduced GNPs cause an increased rate of C=C bonds breaking and promote higher conversion degrees, especially in the case of 408 + 532 nm irradiation condition. This is important for increasing the DE, recording efficiency of different optical reliefs, elements. If the conversion degree is low and a high amount of monomers remains after the recording, the stability of the recorded reliefs, for example, surface waves, decreases due to the diffusion processes. In our case of increased conversion, the stability is higher.

Here we should also keep in mind the possible thermal effects near the GNPs, as mentioned above. Heating may stimulate some decrease in the viscosity and increase of conversion degree, which in our case also may be useful for recording. Calculations made in Ref. [37] showed the possibility of thermal effects under 640 nm irradiation power density P higher as 2 mW/cm^2 . Here the type of substrate, the thickness of layers also is influencing factors. At the same time, the increase of irradiation density is not always useful: as it also follows from Table 1, the increase of P to a certain level causes fast polymerization of the whole volume, which limits the segregation of components. Estimation of these limits needs further experiments at different temperatures.

Now, the results of holographic grating recordings, presented in Table 1, maybe commented on as follows. Recording only with 532 nm radiation, we always got gratings with the smallest DE, which may be explained by the low sensitivity of Irgacure784 initiator and the nature of the monomers used, which results in low conversion rates. Introduction of GNPs to the composite fasts photolysis of initiator and C=C bond breaking occurs, so the whole volume of nanocomposite polymerizes rapidly and the interdiffusion of components, segregation of monomers and nanoparticles is not optimal.

At the same time, the positive effect of GNPs introduction to the light-sensitive nanocomposite develops in the case of properly regulating the initialization and chain growth, the polymerization rate, and the interdiffusion of components. These results in the optimization of the diffraction grating recording, formation of other elements with optical and geometrical reliefs. It is more efficient to make a holographic recording with two light sources: one monochromatic for interference pattern formation in the spectral region of initiators' sensitivity but out of plasmon resonant frequency of GNPs, and the other with proper intensity just for localized plasmon generation in the GNPs. Further combinations may include the variation of light beam polarizations.

The possible presence of local thermal effects due to the heating of GNPs at certain recording irradiation densities (probably near $2\text{--}3 \text{ mW/cm}^2$ for our compositions, according to Table 1) may influence, decrease the viscosity of the material and increase the time necessary for components separation. The upper limit of recording light intensities relates to the stage of fast polymerization in the volume of nanocomposite and may limit the segregation of components. Data of Table 1 gave us optimal values near $3\text{--}4 \text{ mW/cm}^2$ for our compositions.

Besides the influence of GNPs on proper irradiation regimes, the efficiency of the recorded holograms will depend on the resulting spatial distribution of these NPs, since the refractive index of polymer with higher GNPs concentration is higher, even at such comparatively low concentrations, what in turn ensure low scattering levels. So additional phase modulations are introduced into the recorded element, increasing its efficiency, as well as mechanical stability, together with excellent

optical quality.

5. Conclusion

Combined effects of photopolymerization superimposed by plasmon-induced processes in acrylate-based nanocomposites with broadband sensitive Irgacure784 initiator and silicon oxide as well as gold nanoparticles, were investigated in different regimes of illumination and analyzed from chemical mechanisms and related spatial structure formation.

The details of holographic diffraction grating recordings with the highest diffraction efficiency are connected with Irgacure784 initiator photodecomposition and polymer chain formation mechanisms at the presence of gold nanoparticles plasmon fields and different combination of irradiation wavelengths (408, 442, 532 nm) or intensities with optimum near $2\text{--}3 \text{ mW/cm}^2$. The presence of GNPs in a monomer nanocomposite influences the holographic grating formation, and this influence depends on recording parameters (wavelength, intensity) in a combined way: the recording in (442 + 532 nm) regime always results in higher DE in comparison with 442 nm only; increasing the power density above 4.8 mW/cm^2 always yields that DE does not more depend on recording power density, and the presence of GNPs in the nanocomposite results increasing of DE at a decreased intensity. These relate to the mechanism and efficiency of holographic volume and surface grating recording based on photopolymerization and mass-transport, diffusion processes of the organic matrix, and nanoparticles.

The effect of GNPs introduction to the light-sensitive nanocomposite develops in the case of properly regulating the initialization and chain growth, the polymerization rate, and the interdiffusion of components. Further combinations may include the variation of light beam polarization, adding luminescent or anisotropic nanocrystalline components what is interesting for the fabrication of more complex, multifunctional optical elements of photonics.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was financially supported by the grant GINOP-2.3.2-15-2016-00041. The project is co-financed by the European Union and the European Regional Development Fund. The support given by the scientific cooperation agreement between ITMO University and University of Debrecen is acknowledged. Attila Bonyár acknowledges the support of the NRD Fund (TKP2020 IES, Grant No. BME-IE-BIO) based on the charter of bolster issued by the NRD Office under the auspices of the Ministry for Innovation and Technology. István Csarnovics acknowledges the support of the János Bolyai Research Scholarship of the Hungarian Academy of Sciences (BO/348/20) and the support through the New National Excellence Program of the Ministry of Human Capacities (ÚNKP-20-5-DE-107).

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