Improving the mechanical, spectroscopic and laser ablation characteristics of UDMA-MMA copolymers using a titanocene photoinitiator

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ABSTRACT

We have shown that the Irgacure 784 titanocene photoinitiator can be advantageously used to improve the light absorption, mechanical and nanosecond-regime laser ablation properties of urethane dimethacrylate (UDMA)-methyl methacrylate (MMA) polymer blends with photopolymerization using curing with green (520–525 nm) light. The hardness was found to be significantly higher (0.25–0.29 GPa) than that of other UDMA polymer blends photopolymerized using other initiator systems. The established 48–63 % degree of conversion is also comparable to that of similar other blends and is useful in many applications. The laser ablation and laser-induced breakdown spectroscopy (LIBS) properties of these polymers were studied at 266 and 532 nm laser wavelengths. The polymers showed consistently good laser ablation characteristics (reproducible, well-defined, shallow craters) at 266 nm wavelength, whereas at 532 nm, extensive carbonization and strong photothermal effects were observed. LIBS spectra of the blend shows lines of C, H, O, N and Ti as well as C_2 and CN bands, but provide many spectral windows for interference-free analytical measurements. Our findings indicate that UDMA-MMA polymer blends can be good candidates as target matrices for laser ablation-based measurements in the UV or Vis range, in applications like analytical spectroscopy or laser-initiated fusion research.

1. Introduction

It is hard to overestimate the importance of synthetic polymers and plastics in modern industry and science. Synthetic polymers are being developed for and are employed in a range of applications, including biomedicine, sensing, packaging, automotive, clothing and more. The main appeal of synthetic polymers is their controllable chemical and physical properties such as modulus strength, elasticity, resistance against chemicals/corrosion, electrical and heat conductivity, functionalization and doping possibilities, etc. However, they are also highly valuable for the industry considering their low density/weight, recyclability, low melting point (cost-efficient thermal processing), etc. Synthetic polymers are also important raw materials for 3D printing, which is an efficient upcoming tool for prototyping and manufacturing [1].

Urethane dimethacrylate (UDMA) resins are used in a spectrum of applications ranging from dentistry over engineering to 3D-printing industries [2–4]. Its polymerization gives rise to extensive crosslinking due to that two carbon double bonds are present in the monomer. By functionalizing the monomer and via the addition of other crosslinking agents, the properties of UDMA resins can be adjusted in a wide range. Another commonly used monomer in the bonding industry is methyl methacrylate (MMA), due to its flexibility, high strength, high cure speed and low toxicity [5,6]. However, MMA is a low molecular weight monomer, which easily evaporates and its polymer tends to shrink. Mixing the high molecular weight UDMA and low molecular weight MMA monomers for polymerization has recently been proposed to improve the mechanical properties of the blend [6]. MMA is a good solvent for high molecular weight monomers in general, but it mixes especially well with the basic UDMA monomer, due to their similar

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chemical structure. UDMA and MMA polymers are optically clear materials that have high transmission in the Vis-NIR range [7]. Poly-methyl methacrylate (PMMA) is an especially popular optical material, often used to make lenses or optical fibers [8].

Both UDMA and MMA polymers, being acrylates, are often synthesized via photopolymerization by using the free radical mechanism [1]. There are a variety of photoinitiators (or photoinitiator systems) in use for this reaction, typically to be excited in the UV range. Example photoinitiators include EDAB (ethyl-4-dimethylamino-benzoate) H-Nu 535 (2,4,5,7-tetraiodo-3-hydroxy-6-fluorone) or TPO-L (Ethyl (2,4,6-trimethylbenzoyl) phenyl phosphinate) [9]. A newer photoinitiator is Irgacure 784 (also known as Omnirad 784 or Sinocure 784), a titanocene compound, which has been proposed to be used in imaging and information storage applications [10]. This photoinitiator has an orange colour and has a strong absorption at 488 nm and 532 nm laser wavelengths.

The first reports on polymer laser ablation were published around 1980 [11–13]. By today, laser ablation has become an important subtractive (top-down) tool of polymer material processing and nano-/microfabrication. Advances in the field were reviewed recently by Ravi-Kumar et al. [14]. During laser ablation, also called ablative photodecomposition, complex chemical and photonic processes occur in the polymers, for the description of which various photochemical, photothermal and photophysical models were developed in the literature [15]. Conditions that play a fundamental role in the pulsed laser ablation of polymers are the light absorption of the polymer at the laser wavelength, the duration of the laser pulse, and the intensity (irradiance, power density). A higher light absorption coefficient of the polymer at the laser wavelength results in a lower laser ablation intensity threshold. Orders of magnitude changes in the duration of the laser pulse cause a significant change in the mechanism of the laser-polymer interaction. Consequently, for optical polymers, like UDMA or PMMA, the laser ablation typically requires excimer UV lasers [14], unless the polymer is colored with an additive that increases its light absorption in the Vis or NIR range.

Laser ablation of polymers also bears importance in analytical spectroscopy. For example, epoxy embedding of biological specimens or geological samples is a common sample preparation approach for elemental mapping by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and laser-induced breakdown spectroscopy (LIBS) [16]. Embedding resins were also found useful as calibration standards for LA-ICP-MS measurements. Reifschneider et al. prepared a hydroxyethyl methacrylate (HEMA) polymer and spiked it with platinum acetylacetonate prior to curing in order to create Pt calibration standards for quantitative bioimaging [17]. Fitzpatrick proposed the use of xerogels prepared by the sol-gel process (by the polymerization of tetraethyl orthosilicate) and spiked with a multielemental solution for the same purpose [18]. Gold nanorod-doped polymers have also been proposed and used most recently as targets in fs laser-induced plasmonic fusion experiments [19,20].

Today, most LIBS and LA-ICP-MS experiments are still performed with ns laser pulses and in this case, the light absorption of the embedding resin has to be sufficient at the laser wavelength. This is especially important when biological samples are embedded in a relatively thick (in excess of 50 μm) resin layer and depth-resolved LIBS elemental mapping is performed [16]. Best analytical results can be obtained if either the laser wavelength is tuned to that of the resin (e.g. 213 nm is ideal for HEMA ablation [17], 266 nm is suitable for many acrylate resins) or the absorption peak of the resin can be shifted to the vicinity of the laser wavelength by the addition of a dye to the resin during synthesis. Since the laser wavelength is typically fixed in an ablation system, the latter approach can be more practical.

In the present work, we prepared UDMA-MMA polymer blends with the intention of their future application as laser ablation targets in analytical spectroscopy at UV and Vis wavelengths. The photopolymerization of the blend was done using the Irgacure 784 initiator,

Table 1
The full list of polymer sample variations prepared with their sample identifiers.

Sample identifier (ID)	Monomer mass ratio (UDMA:MMA)	Photoinitiator concentration (m/m%)	Curing time (min:sec)
U3I1	3:1	2	2:00, 2:30, 3:00, 3:30, 4:00
U3I2	3:1	4	2:00, 2:30, 3:00, 3:30, 4:00
U5I1	5:1	2	2:00, 2:30, 3:00, 3:30, 4:00
U5I2	5:1	4	2:00, 2:30, 3:00, 3:30, 4:00

which also served as a light absorber, thereby allowing the ablation of the acrylate polymer blend also at the 532 laser wavelength. We also found that the use of this titanocene photoinitiator improved the mechanical properties of the prepared polymer blend. Laser ablation and LIBS spectroscopy characteristics using 266 nm and 532 nm ns pulsed laser sources were also studied.

2. Materials and methods

2.1. Preparation of MMA and UDMA copolymers

The co-polymer was synthesized using methyl methacrylate and urethane dimethacrylate monomers (both obtained from Sigma-Aldrich Chemie, Germany) in 99 % purity. The synthesis was photoinitiated by Irgacure 784 (BASF Hungária Kft., Hungary).

Monomer test mixtures with MMA:UDMA compositions of 1:5, 1:3, 1:1, 3:1 and 5:1 were prepared gravimetrically in 10 mL screw-cap glass vials. The calculated amount of the photoinitiator was added to the mixture to set its concentration at 2 m/m% or 4 m/m% in the mixture and then a PTFE-coated magnetic stir bar was also added and the vials were closed. Prior to use and also before closing, each vial was rinsed and filled with argon gas (99.995 % purity, Messer Hungarogáz, Hungary) in order to keep the oxygen out of the reaction vessel. The mixture was then magnetically stirred overnight with a speed of 300 min^{-1} to homogenize it and to promote the dissolution of the photoinitiator. A tight aluminum foil wrapping was employed to keep the contents of the vials in dark during the whole mixing time.

Immediately prior to the illumination, the monomer mixture was spread on a glass microscope slide and covered with another glass slide. A ring-shaped PTFE spacer with a thickness of 2.0 mm was used to control the thickness of the produced polymer discs, which had a diameter of 10 mm. The illumination of the monomer mixture was done using a green LED source with a duration varying between 2 and 4 min.

It was observed that under the conditions used here, only the UDMA-rich 3:1 and 5:1 compositions produced solid copolymer products reproducibly, therefore experimental results will be reported only for these compositions (Table 1). Fig. 1 shows the photo of some of the polymer samples prepared, as an illustration.

2.2. Equipment and software

All reagents were dosed out using an analytical balance or precision micropipettes. The illuminating source used during the photopolymerization was a 3W light-emitting diode (Megaled, Hungary) that emitted light in the 520–525 nm wavelength range. The light was directed onto the monomer mixture by using a reflective cylindrical light guiding tube.

Raman spectroscopy data was collected using an inVia (Renishaw, UK) micro-Raman spectrometer integrated with a Leica DM2700 microscope, operating in the backscattering measurement mode. Stokes

Fig. 1. Photo of some of the polymer samples prepared (from left to right: U3I1 2:00, U5I1 2:00 and U3I2 3:30). Please note the slightly deeper color of the I2 sample compared to I1 samples, caused by the higher photoinitiator concentration in the composition. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Raman spectra were collected using solid state laser excitation at the 532 nm wavelength.

The UV–Vis absorption spectra of the polymer samples were recorded on a PG85+ double beam UV–VIS spectrometer (PG Instruments, UK), in the spectral range of 200–1100 nm, with a 1.0 nm resolution.

Mechanical properties of the polymer samples were investigated by depth-sensing indentation (DSI) measurements using a UMIS type instrument (CSIRO, Australia). Indentations were carried out with a Vickers indenter tip for maximum loads of 10 and 50 mN. Five repeated measurements, on different locations, were carried out on each sample. The hardness and Young modulus values were evaluated using the well-known Oliver-Pharr method [21,22].

Laser ablation properties of the polymer samples were tested using two Nd:YAG Ultra 100 stable laser sources (Lumibird/Quantel, France), equipped with second harmonic generation modules to produce 532 nm and 266 nm emission with a pulse duration of 10 ns. In laser ablation and LIBS experiments involving 266 nm laser irradiation, a J-200 tandem LA-LIBS (Applied Spectra Inc, USA) instrument, whereas for 532 nm experiments, a standalone laser was used. Focusing the laser light on the samples was achieved using microscope objectives. The pulse energy (ca. 17 mJ) and focal spot size (ca. 140 μm diameter) was tuned to values as close as possible on the two systems, thereby keeping the fluence and laser ablation conditions comparable. LIBS spectra recording was achieved using fiber optics coupled multichannel CCD spectrometers (Avantes, NL), in the full UV–Vis spectral range, with a resolution better than 100 p.m. The gate delay was 1 μs and the integration time 2 ms.

Laser ablation craters created were studied with light microscopy by using a BL-600TiFL microscope (Optika, Italy) equipped with a 1.4 MP color digital camera (Tucsen, China), and contact profilometry by using a Dektak 8 (Veeco/Bruker, USA) instrument. In profilometry experiments, a constant force of 30 μN was applied to the tip (radius: 2.5 μm, angle: 30°). The 3D maps generated had a lateral step resolution of 0.333 μm and 6.35 μm, and 4 nm in the z direction.

All measurement data was processed and evaluated in Origin 8.0 (OriginLab, USA) software.

3. Results and discussion

3.1. Degree of conversion

The degree of conversion (DC) for the polymerization reaction was estimated by Raman spectroscopy, using the methodology described for

Table 2
Degree of conversion data for the UDMA-MMA polymers prepared.

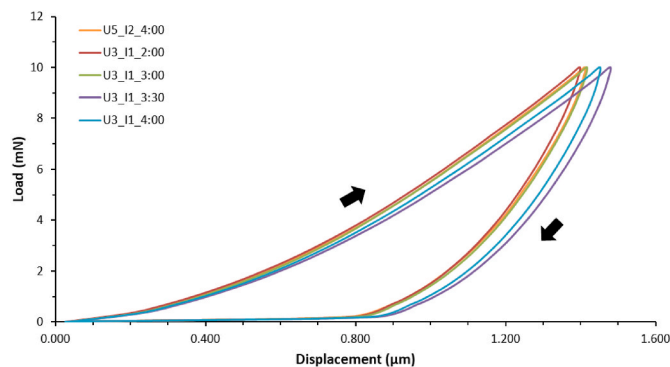| DC (%)	Curing time (min:sec)				
	2:00	2:30	3:00	3:30	4:00
U3I1	61	56	63	55	54
U3I2	53	49	51	43	50
U5I1	49	53	50	48	54
U5I2	58	51	52	62	61

Fig. 2. Dynamic hardness (load – displacement) curves of some prepared polymer blends.

acrylate-type polymers in the literature [6,23]. This methodology is based on the decrease of the intensity of the C=C peak (at 1637 cm^{-1} in acrylates) in the mixture measured before and after photopolymerization. For signal normalization, the C=O peak (at 1717 cm^{-1}) which does not change during the reaction, was used as an internal standard.

We determined the DC for all initiation and mixing conditions used. The results can be seen in Table 2. All DC values fit in the range of 48–63 %. Differences were not significant or trendlike, especially when the scatter of Raman signal intensities or typical photopolymer reproducibility, both of which amount to 5–10 % rel., are also factored in. These DC values are lower than optimal, but are similar in range to literature values (50–75 %) for other photopolymerized UDMA dental resin mixtures (e.g. Refs. [6,24,25]. The lack of clear trends rules out the possibility for a serious optimization with the DC as objective function.
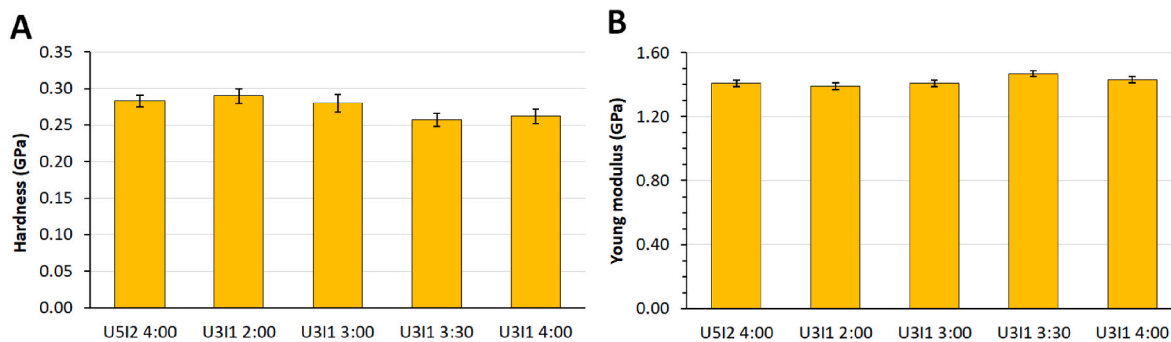
Fig. 3. Measured (a) hardness and (b) Young modulus values for some prepared polymer blends. Error bars refer to five repeated measurements.
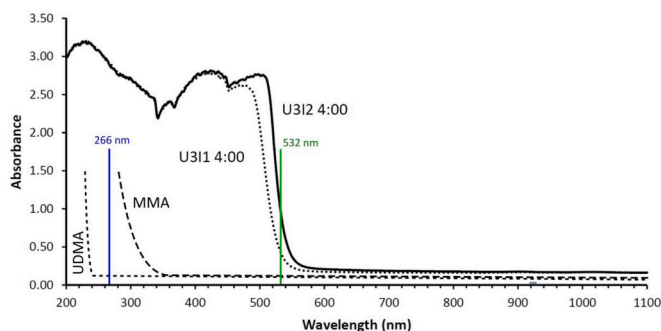

Fig. 4. UV–Vis absorption spectra of 2 mm thick polymer blend samples (U3I1 4:00 and U3I2 4:00) prepared using 2 and 4 m/m% photoinitiator concentrations, respectively. The graph also indicates the spectra of MMA and UDMA, as well as the two laser wavelengths used in this study.

3.2. Mechanical properties

Dynamic hardness measurement data were also collected on the prepared polymer blends. Only five representative samples were included in this part of the study as DC values have not revealed a large sample variability, thus a great variation of mechanical properties was

also not expected. Some typical depth-load indentation curves can be seen in Fig. 2. The obtained hardness and Young modulus values are shown in Fig. 3. All measurements were carried out in five replicates on different sample locations.

Experimental results show that both the loading and unloading sections of the load-depth curves (Fig. 2.) reveal nonlinear deformation. The slope of the curves, which were recorded for up to a 10 mN limit load, is relatively large compared to other polymers [26]. The slope increases along with the increase of UDMA weight ratio and decrease of the duration of illumination, in accordance with the static hardness and Young modulus data (Fig. 3b.).

As shown in the graphs of Fig. 3., the hardness of our Irgacure 784 photoinitiated UDMA-MMA photopolymer blends was found to be significantly higher (0.25–0.29 GPa) than that of other UDMA polymer blends photopolymerized using other initiator systems. Hardness values for camphorquinone (CQ)/EDAB [6,24] and CQ/2-(dimethyloamino) ethyl methacrylate (DMAEMA) [25] initiator systems were reported to be in the 0.15–0.24 GPa range only. The repeatability of our hardness data was also found to be very good, indicating a homogeneous composition, which allowed the observation of some trends as well. For example, similarly to the observation of Alabdali et al. [6] and Li et al. [24], we also found that increasing the UDMA content in the blend increases the hardness. At the same time, the increase in the illumination time causes a slight decrease in the hardness.
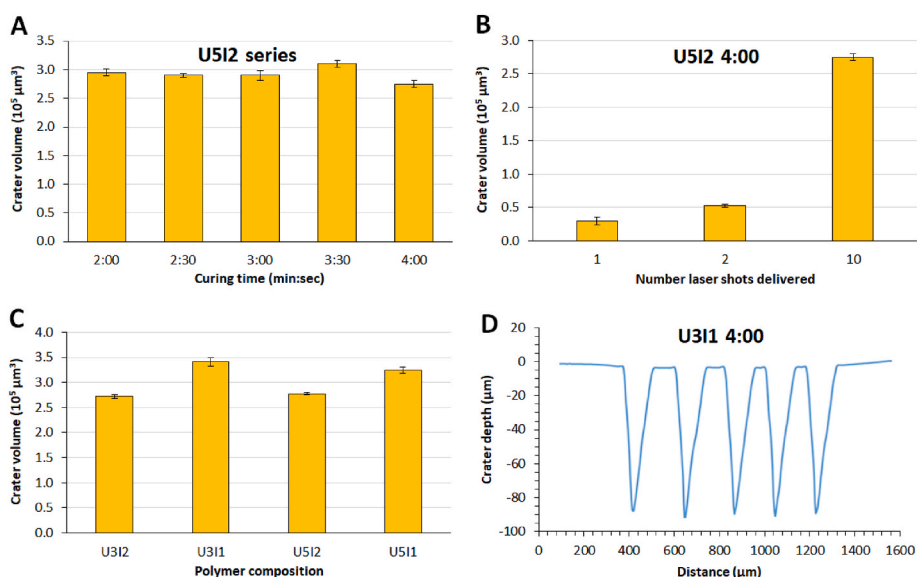

Fig. 5. Illustrative profilometry data on the laser ablation behaviour of the polymer samples at 266 nm. (a) ablation crater volume as a function of curing time (U5I2 series), (b) ablation crater volume as a function of the number of pulses (U5I2 4:00), (c) ablation crater volume versus polymer composition (curing time 4:00), (d) shape and depth of cross-sectional crater profiles (U3I1 4:00). Crater volume and depth data are based on ten laser shots delivered to the same spot except in B). Error bars refer to three repeated profilometry measurements.
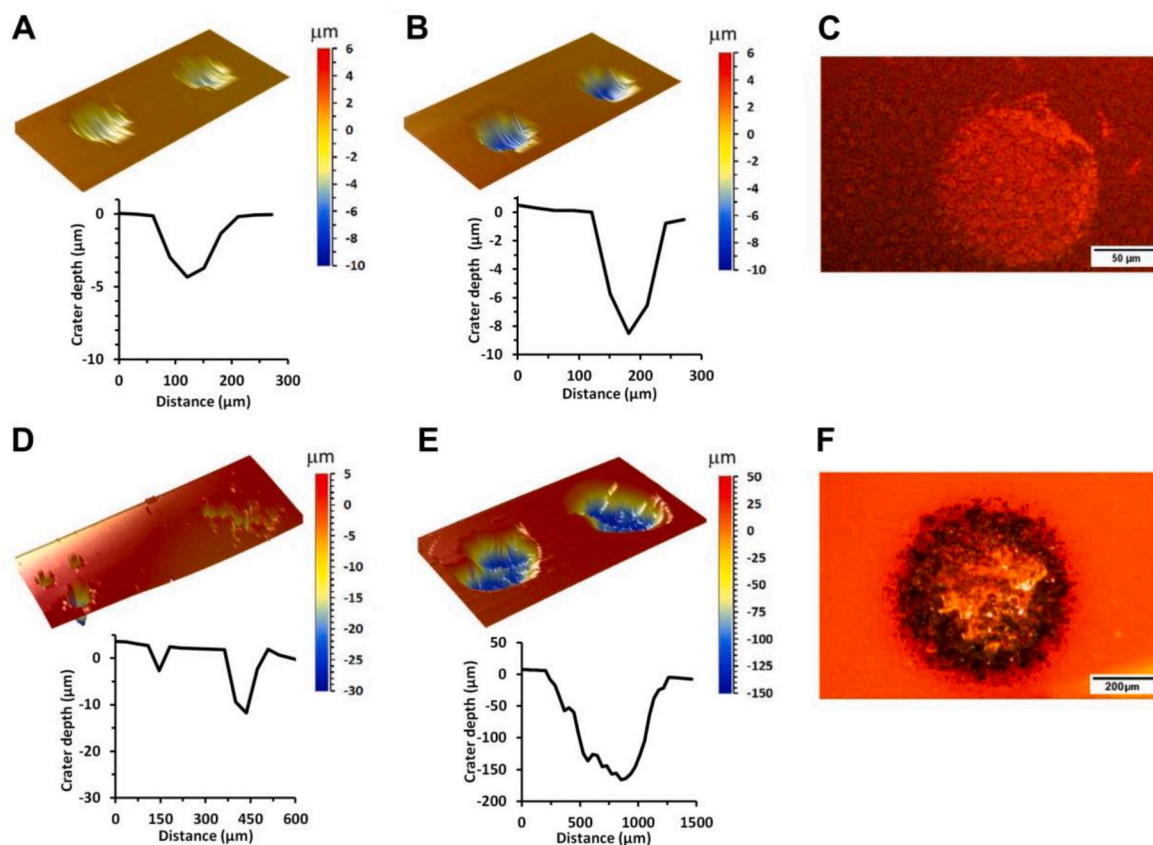
Fig. 6. Illustrative crater images produced by laser pulses delivered to UDMA-MMA polymers. Images (a), (b), (d) and (e) were recorded using contact profilometry, whereas (c) and (f) are transmission light microscope images. Ablation craters were produced by (a) a single 266 nm pulse, (b) two 266 nm pulses, (c) a single 266 nm pulse, (d) a single 532 nm pulse, (e) two 532 nm pulses, (f) a single 532 nm pulse. Each 3D profilometry image shows two ablation craters next to each other and color scales referring to the z-direction. Inserts are representing cross sections of single ablation craters. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

3.3. UV–Vis spectroscopic characterization

The light absorption of the polymers in the UV–Vis or NIR range is highly important in consideration of the intended application as laser ablation targets. One of the reasons for this is that the correct adjustment of the lens-to-target distance (focusing the laser beam onto the surface of the target) is very difficult, if the target is transparent in the Vis range, where the autofocus subsystem of most analytical laser ablation instruments (e.g. LIBS or LA-ICP-MS) work. The other reason is that in the case of nanosecond-range pulse duration, the short penetration depth of the laser light is essential for an efficient laser ablation (LA-ICP-MS application) or breakdown plasma production (LIBS application).

As is known, both MMA [7] and UDMA [27] have weak light absorption in the Vis-NIR range. Their absorption only starts to increase in the UV, more precisely below ca. 240 nm for UDMA and ca. 350 nm for MMA. The Irgacure 784 photoinitiator however strongly absorbs at UV and Vis wavelengths, up to around 550 nm [10]. This is also reflected in Fig. 4., as our synthesized UDMA-MMA copolymer samples produced several units of absorbance in a 2 mm thickness for wavelengths downwards from around 520 nm. At 532 nm, the absorbance was around 0.98 for the higher (4 m/m%) photoinitiator concentration and slightly less than half of this (0.44) for the lower (2 m/m%) concentration. The approximate proportionality of the absorbance with the concentration also indicates that the photoinitiator serves mainly as the absorber. At longer wavelengths, the absorption is very low and completely flat up to 1100 nm. These observations suggest that our Irgacure 784-doped polymer blends may have suitable light absorption for analytical purposes at frequency quadrupled and doubled harmonic

wavelengths (266 nm and 532 nm, respectively) of Q-switched Nd:YAG lasers. At the fundamental wavelength (1064 nm) however, the light absorption does not appear to be sufficient for ablation or plasma production.

3.4. Laser ablation behaviour

Laser ablation targets must produce well-defined, reproducible crater sizes and volumes in order to provide stable LA-ICP-MS or LIBS analytical signals, thus we also tested the ns pulsed laser ablation behaviour of our polymer samples. We carried out the experiments at both 266 and 532 nm laser wavelengths, under argon atmosphere. One, two and ten laser shots were delivered to the polymers at multiple locations and the crater characteristics were studied by contact profilometry and light microscopy.

In general, the 266 nm laser pulses were found to produce well-defined, clean craters, in both the single-shot and multi-shot scenarios. Under constant conditions, the crater depths and volumes were quite reproducible. The single shot craters already were well-formed, although of course shallower than multi-shot craters. Illustrative images and descriptive data about these craters are shown in Fig. 5a-d and **5(a–c)**. As can be seen, crater data was found to be fairly independent of the curing time or blend composition, however an increase of the absorber (photoinitiator) concentration lowered the crater volume, as expected. The crater volume is reasonably proportional with the number of pulses delivered. These observations are in line with those of laser ablation studies of pure acrylate polymers [15,28].

The polymers' laser ablation behavior was very different at 532 nm.
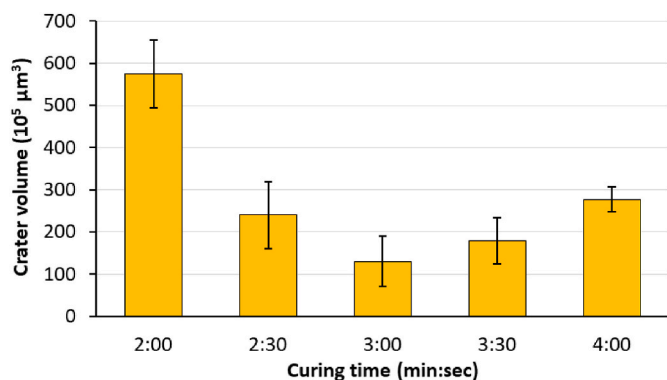
Fig. 7. Double-pulse 532 nm laser ablation crater volumes produced in UDMA-MMA polymer samples (U5I2 series). Error bars refer to three repeated profilometry measurements.

Due to the several times lower light absorption of the material at this wavelength, single laser shots produced only a small damage to the polymer, in multiple „hot spots" within the focal spot region (see Fig. 6d.). Only after the second and later laser shots delivered to the same spot did the ablation craters become observable (Fig. 6e.). It was also noted that the crater diameters were substantially larger than at 266 nm and that the laser pulse created microscopic black particles within the polymer material in the laser focal spot area, especially around the edges of the crater, noticeable under a microscope (Fig. 6f.). This effect was most pronounced in single-shot experiments, later shots delivered to the same spot basically ablated away this material. This suggests an incubation-like phenomenon. The formation of this blackening can be due to either the carbonization of the polymer or the pyrolysis of the Irgacure 784 molecule. Extensive carbonization of certain polymers, among them acrylates, has been observed and described in the literature, which ascribed it to photothermal effects, more pronounced at longer wavelengths (e.g., 532 nm and 1064 nm as opposed to UV) [15, 28]. On the other hand, Irgacure 784 is a titanocene compound, and the photolysis or thermal treatment of such compounds has been found to produce TiC [29,30]. In general, the reproducibility of the crater formation was poor and the larger penetration depth created significantly larger crater volumes than at 266 nm. The 10-pulse craters were too deep and steep for contact profilometry measurements, so Fig. 7 shows the volumes for double-pulse craters as an illustration. The poor reproducibility of crater parameters did not allow for studying the same composition and curing time correlations as at 266 nm.

3.5. Laser-induced breakdown spectroscopy

We have also recorded the LIBS spectra of the polymers under the same laser conditions as the ones used in laser ablation experiments. No photobleaching (fading of color) of the polymer was observed outside the laser focal spot, even when ten laser shots were delivered to the same spot, which indicates that the polymer and the photoinitiator itself are fairly photostable under the impact of the UV–Vis radiation from the breakdown plasma. LIBS spectra were collected from ten different locations in the samples and averaged.

Only the 266 nm laser wavelength produced meaningful LIBS spectra with good repeatability. The spectra are illustrated in Fig. 8. As can be seen, the spectra are eventful and intense with good signal-to-noise ratios. Lines appearing can be well assigned to the component elements of the polymer and photoinitiator (C, H, O, N, Ti), as well as to the gas atmosphere (Ar). C_2 and CN molecular bands result from recombinations occurring during the decaying stage of the plasma. As expected, the spectra showed no significant variations as a function of blend composition or curing time. The only difference seen was caused by the change of the titanocene photoinitiator concentration; understandably, 4 m/m% samples produced approximately twice as high Ti line intensities as 2 m/m% samples. In each sample, the signal intensities were quite stable; even for Ti, which indicates that the Irgacure 784 distribution in the polymer is fairly homogeneous. The spectrum is quite free from strong spectral lines in the 180–300 nm range, as well as around 600 nm. In addition, in the absence of argon atmosphere, the NIR wavelength range is also available for analytical lines.

4. Conclusion

We have shown that the Irgacure 784 titanocene photoinitiator can be advantageously used to improve the light absorption, mechanical and nanosecond-regime laser ablation properties of UDMA-MMA polymer blends. The hardness was found to be significantly higher (0.25–0.29 GPa) than that of other UDMA polymer blends photopolymerized using other initiator systems. The established 48–63 % degree of conversion is also comparable to that of similar other blends and is useful in many applications. It was found that although the light absorption of the polymer greatly improved at wavelengths downwards from about 550 nm, the samples only showed consistently good laser ablation characteristics at 266 nm wavelength. At 532 nm, extensive carbonization and strong photothermal effects were observed. The samples also produced strong laser-induced breakdown spectra with 266 nm laser excitation.

Our observations indicate that UDMA-MMA polymer blends prepared with Irgacure 784 are good candidates as target matrices for laser ablation-based analytical spectroscopy measurements. If a 266 nm, or
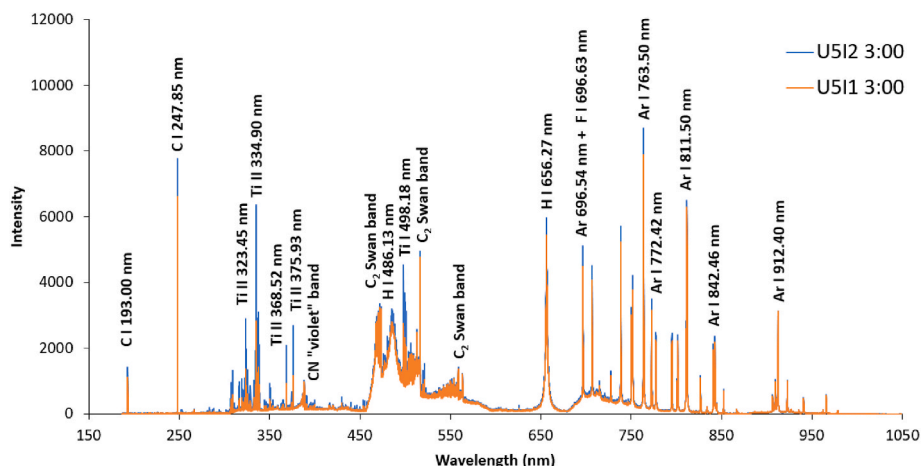

Fig. 8. Illustrative LIBS spectra of polymer blends with different Irgacure 784 content (averages from 10 repeated measurements recorded in Ar atmosphere).

shorter, laser wavelength is used, these polymers can potentially be used in LA-ICP-MS or LIBS spectroscopy as an embedding material for e.g. biological tissues in elemental mapping studies or to prepare calibration standards by doping them with stock solutions of the analyte. The spectrum of the polymer blend leaves practically wide-open windows in the UV, Vis and NIR range for analyte lines in LIBS spectroscopy.

We would also like to mention that we see an additional unique benefit of using MMA in an acrylate resin blend in laser ablation applications. A commercially available deuterated MMA monomer can also be used to prepare the UDMA-MMA copolymer, which allows the direct control of the deuterium content of the polymer. Such blends can potentially serve as calibration standards for deuterium determination in polymers (or other solids) by LIBS or LA-ICP-MS, since they would contain D in a covalently bound, stable form. Another application possibility for such deuterated polymer blends is their use as targets in high intensity laser-initated fusion experiments. Our team is involved in larger research projects progressing in both these directions and is currently exploring the above novel applications.

CRediT authorship contribution statement

D.J. Palásti: Investigation, Data curation. **O. Urbán:** Visualization, Investigation, Data curation. **F.A. Casian-Plaza:** Visualization, Funding acquisition. **J. Kámán:** Resources, Investigation, Conceptualization. **I. Rigó:** Resources. **M. Szalóki:** Resources, Methodology. **A. Bonyár:** Writing – review & editing, Resources, Methodology. **N.Q. Chinh:** Writing – review & editing, Investigation. **Z. Galbács:** Methodology. **M. Veres:** Writing – review & editing, Writing – original draft, Supervision, Funding acquisition, Conceptualization. **G. Galbács:** Writing – review & editing, Writing – original draft, Supervision, Funding acquisition, Conceptualization.

Declaration of competing interest

We have no competing interests to report. All funding sources received are acknowledged in the manuscript.

Data availability

Data will be made available on request.

Acknowledgments

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