Hydrogels photo-crosslinking by 266 nm pulsed laser radiatio

Tozar Tatiana*, Boni Mihai, Nistorescu Simona, Pascu Mihail Lucian, Staicu Angela

National Institute for Laser, Plasma and Radiation Physics, Laser Department, Magurele, Romania

**E-mail: tatiana.alexandru@inflpr.ro*

Abstract

- This study is addressing the hydrogel formation by photo-crosslinking gelatin chains functionalized with methacrylate groups when Irgacure 2959 was used as photoinitiator.
- The solution was exposed to the fourth harmonic of a Nd:YAG laser at energies between 0.25 and 1 mJ.
- The crosslinking process was monitored in real-time by laser-induced fluorescence and offline by UV-Vis and FTIR absorption spectroscopy.
- The dimerization reaction was evaluated at intermediate times and the changes from dilute to semi-dilute polymer solution and to a fully crosslinked hydrogel was observed.

Introduction

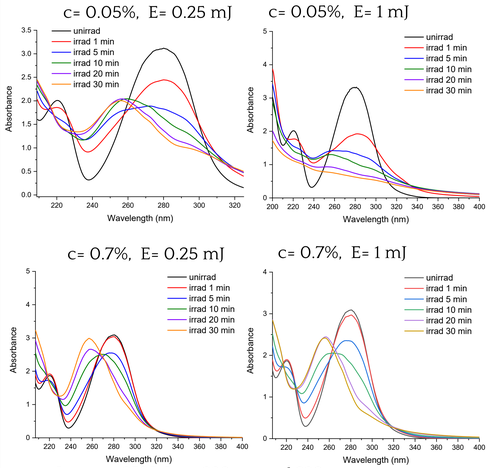
- Conventional drug delivery methods are overwhelmed by repeated application of drugs and their systemic toxicity.
- An alternative are hydrogels that offer optimized therapeutic action of the drug and minimize disadvantages of classical delivery methods, emerging as very efficient in drug protection from degradation, and in controlling the drug release.
- The photopolymerization through laser irradiation offers the following advantages: chemical additives are not used and simultaneously, sterilization, temporal and spatial control, negligible heat production are obtained .
- Irgacure 2595 is one of the few water-soluble photoinitiator used in hydrogel formation when irradiated, cleaves into two radicals, benzoyl and alkyl, which can both initiate a polymerization reaction.
- The hydrogels obtained by polymers exposure to UV radiation offer the advantages of temporal and spatial control, free of chemical additives, and simultaneously sterilization is obtained.

Methodology

- Irgacure 2595, (2-hydroxy-1-[4-(2-hydroxyethoxy) phenyl]-2-methyl-1-propanone), dissolved in ultrapure water at 0.05 % and 0.7% (w/v), V= 35 µL.
- Photodegradation conditions:
  - 266 nm pulsed laser Nd:YAG (10 Hz repetition rate, 6 ns FWHM),
  - E= 0.25 and 1 mJ, I= 6.58 and 26.32 mW/cm2, P= 2.5 and 1 mW,
  - exposure time=1, 5, 10, 20, and 30 min.
- Mold: 3D printed, Ø=0.7 cm, h =1 mm, material = polylactic acid.
- Characterization: real-time laser-induced fluorescence (LIF), UV-Vis absorption spectroscopy, FTIR absorption spectroscopy.
- LIF: optical fiber positioned at 45° with respect to beam propagation direction; average of the fluorescence spectra collected for 50 pumping laser pulses;
- FTIR spectra: range 3,700-850 cm^{-1}, resolution 4 cm^{-1};
- UV-Vis spectra: 200-350 nm;

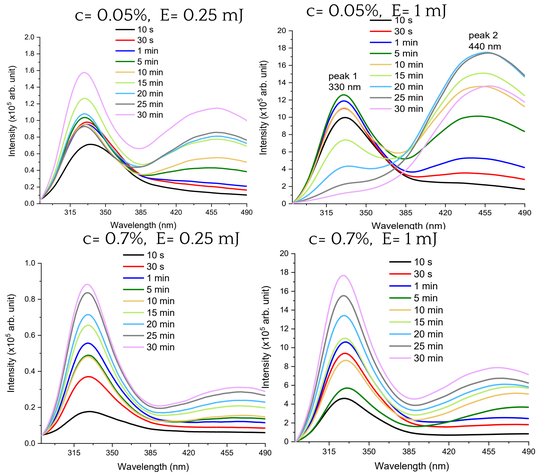
Results

Absorption spectra of Irgacure 2959 exposed to 266 nm pulsed laser beam



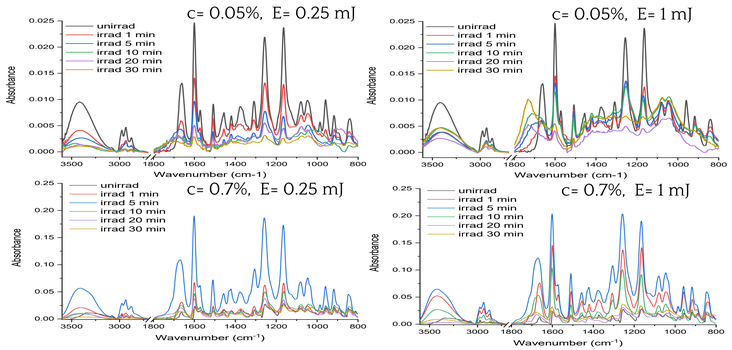
- Irgacure 2595: λ_{max}=280 nm and 220 nm
- low concentration:
  - the absorbance bands start to decrease and after 5 min irradiation a broad band appears (270 nm);
  - after 10 min of irradiation a new band with peak at 256 nm appears and the 280 nm peak disappears;
  - the 256 nm peak disappears after 30 min irradiation at 1 mJ;
- high concentration:
  - the absorbance bands start slightly to decrease and after 10 min of irradiation a broad band appears (270 nm);
  - after 20 min of irradiation a new band with peak at 256 nm appears and the 280 nm peak disappears;
  - at 0.25 mJ the band with peak at 265 nm presents the highest absorbance for 30 min irradiation ;
  - at 0.25 mJ the band with peak at 265 nm presents the highest absorbance for 20 and 30 min irradiation ;

LIF spectra of Irgacure 2959 exposed to 266 nm pulsed laser beam



- Irgacure 2595: λ_{max}=330 nm
- low concentration:
  - a new band with peak at 440 nm appears after 5 min for 0.25 mJ and after 30 s for 1 mJ;
  - 440 nm peak has the highest fluorescence intensity after 30 min irradiation with 0.25 mJ and after 20 min irradiation with 1 mJ;
  - Irgacure 2595 is not fully photo-fragmentated after 30 min irradiation at 0.25 mJ and is fully photo-fragmentated after 30 min irradiation at 1 mJ;
- high concentration:
  - 440 nm and 330 nm peaks have the highest fluorescence intensity after 30 min irradiation at 0.25 mJ and 1 mJ;
  - Irgacure 2595 is not fully photo-fragmentated after 30 min irradiation at 0.25 mJ and 1 mJ;

FTIR spectra of Irgacure 2959 exposed to 266 nm pulsed laser beam



- low concentration:
  - at 0.25 mJ: 1660 cm^{-1}, 1375 cm^{-1}, and 840 cm^{-1} disappear after 10 min and a new band with peak at 1725 cm^{-1} is formed;
  - at 1 mJ: 1660 cm^{-1} and 1375 cm^{-1} disappear after 5 min and a new band with peak at 1725 cm^{-1} is formed; 840 cm^{-1} disappears after 20 min;
- high concentration:
  - at 0.25 mJ: 1660 cm^{-1} is present after 30 min and a new band with peak at 1725 cm^{-1} is formed; 1375 cm^{-1} becomes a broad band after 5 min;
  - at 1 mJ: 1660 cm^{-1} disappears after 5 min and a new band with peak at 1725 cm^{-1} is formed; 1375 cm^{-1} disappears after 20 min; 840 cm^{-1} disappears after 20 min;

Conclusion

- Absorption, LIF and FTIR confirmed the photo-fragmentation of Irgacure 2952 exposed to 266 nm pulsed laser beam into the two radicals, benzoyl and alkyl.
- By monitoring the optical characteristics of Irgacure 2959 during irradiation one can determine when the hydrogel is fully cross-linked.

Acknowledgements

ACKNOWLEDGMENTS: This research was funded by Ministry of Research, Innovation and Digitization, CNCS/CCCDI-UEFISCDI, project PN-III-P1-1.1-PD-2019-1117, NUCLEU Program 16N/08.02.2019.