DOI: https://doi.org/10.33216/1998-7927-2025-291-5-59-63

UDC 678.743

STUDY OF THE INFLUENCE OF LASER RADIATION ADSORBERS ON THE ABLATION OF CARBON FIBER-REINFORCED PLASTIC BY FEMTOSECOND LASER PULSES

Baklan D.V., Myronyuk O.M., Bilousova A.O., Vanagas E.

ДОСЛІДЖЕННЯ ВПЛИВУ АДСОРБЕРІВ ЛАЗЕРНОГО ВИПРОМІНЮВАННЯ НА АБЛЯЦІЮ ФЕМТОСЕКУНДНИМИ ЛАЗЕРНИМИ ІМПУЛЬСАМИ АРМОВАНОГО ВУГЛЕЦЕВИМ ВОЛОКНОМ ПЛАСТИКУ

Баклан Д.В., Миронюк О.В., Білоусова А.О., Ванагас Е.

Carbon fiber-reinforced plastics (CFRPs) have gained popularity due to their advantageous properties, including a high strength-to-weight ratio, resistance to chemicals, and design flexibility. However, the processing of these composite materials remains challenging due to the heterogeneity between carbon fibers and the polymer matrix. Laser ablation, particularly with ultrafast femtosecond lasers, has emerged as a promising technique for the precise machining of CFRPs. Advantages of this technique include minimal thermal damage and improved ablation precision. However, disparities in ablation rates between the epoxy matrix and carbon fibers frequently impede process efficiency. The present study investigates the use of hydroxyapatite-based additives to enhance laser–material interaction and optimize the ablation behavior of CFRP systems. Specifically, copper-substituted hydroxyapatite (Cu-HAp) microparticles, which are known for their strong absorption in the near-infrared (NIR) region around 1030 nm, were synthesized and introduced into the epoxy matrix. Calcium hydroxyapatite (Ca-HAp), a thermally stable and biocompatible ceramic with low NIR absorption, was utilized as a reference to assess the specific contribution of copper ions. Epoxy composites with 5 wt.% of various filler compositions (100% Cu-HAp, 75% Cu-HAp/25% Ca-HAp, and 50% Cu-HAp/50% Ca-HAp) were prepared and incorporated into CFRP laminates. Femtosecond laser ablation at 1030 nm was performed under optimized conditions for each sample type, followed by evaluation of the resulting surface morphology using optical profilometry and SEM. The findings indicated that the incorporation of Cu-HAp fillers promoted enhanced energy absorption, thereby facilitating more efficient ablation with reduced thermal damage in comparison to unmodified epoxy and Ca-HAp-filled systems. Replacing Cu-HAp with Ca-HAp increased the required laser fluence and energy input. This indicates that copper ions enhance localized heating and energy coupling. SEM imaging showed that Cu-HAp particles had a porous, aggregated morphology that redistributed thermal energy, while Ca-HAp had denser, more homogenous filler structures with reduced porosity. This work shows the potential of Cu-HAp as a functional additive to adjust how femtosecond laser radiation interacts with composite materials and improve micromachining outcomes. The findings support the feasibility of using NIR-absorbing ceramic fillers to deal with common issues associated with laser processing of CFRPs, including heat-affected zones and ablation inhomogeneity.

Ключові слова: *CFRP; carbon fiber; laser processing; femtosecond laser; cutting; ablation.*

Introduction. Carbon fiber reinforced plastics (CFRPs) have properties that make them ideal for use in aerospace, automotive, and marine applications. These properties include lightness, strength, ease of formation, ease of scaling, and resistance to aggressive environments. However, processing such materials is challenging due to the heterogeneous phases (fiber and polymer), which require more operations [1]. One promising processing method is laser processing. For CFRP, however, laser processing is associated with several problems, particularly the formation of heat-affected zones (HAZs), which can negatively impact structural integrity [2].

This method uses continuous or pulsed laser exposure. However, this approach is energy-intensive and often results in significant thermal damage at the cut edge, particularly with conventional nanosecond or picosecond pulses [3]. Using ultrafast (femtosecond) laser pulses has several advantages, including minimal thermal diffusion, higher precision, and reduced HAZ due to ultra-short interaction times and nonlinear absorption processes [4, 5]. Another advantage of femtosecond laser processing is equalizing the ablation rate of the polymer part (epoxy matrix) and the reinforcing fibers (carbon fiber) in the composite material. In conventional laser cutting, epoxy degrades faster than carbon fiber under laser irradiation, resulting in uneven and inefficient ablation [6].

One strategy to address this imbalance involves modifying the polymer matrix with additives that increase its absorption in the laser wavelength range and improve the resin's thermal resistance. Using adsorbing fillers that enhance interaction with the laser beam and redistribute thermal energy locally can be an effective solution [7].

Recently, copper-substituted hydroxyapatites have attracted attention due to their strong absorption in the near-infrared (NIR) region, particularly at around 1030 nm wavelengths [8]. Their hierarchical structure and surface morphology suggest potential applications in enhanced heat dissipation and localized energy management. In this context, copper hydroxyapatite (Cu-HAp) microparticles were selected as functional additives. In addition to Cu-HAp, this study utilizes calcium hydroxyapatite (Ca-HAp) as a reference material. Ca-HAp is a well-known, thermally stable, biocompatible ceramic with limited absorption in the NIR region [9]. Including it allows for a comparative analysis that isolates the specific contribution of copper ions to laser absorption efficiency and ablation behavior. Ca-HAp was also chosen because of its structural similarity to Cu-HAp and its widespread use in materials science as a baseline material in studies of substitution effects [10, 11].

Task setting. The present work is aimed at investigating the influence of hydroxyapatite-based fillers on the efficiency and precision of femtosecond laser ablation of CFRP systems. The study includes: the synthesis and morphological characterization of copper hydroxyapatite (Cu-HAp) and calcium hydroxyapatite (Ca-HAp) microparticles; preparation of modified epoxy resins and CFRP systems incorporating these additives; laser ablation of the modified systems using a femtosecond laser with a wavelength of 1030 nm; comparative analysis of the ablation quality, morphology, and uniformity for the reference and modified systems.

The aim of the work is to evaluate the potential of hydroxyapatite-based additives, particularly Cu-HAp, as effective NIR absorbers for enhancing the femtosecond laser ablation of CFRP materials. A comparative analysis with Ca-HAp is conducted to determine the role of copper substitution in modulating laser-matter interaction, minimizing heat-affected zones, and improving ablation precision and uniformity.

Presentation of the main research material. The required amounts of copper nitrate and ammonium dihydrogen phosphate in a 2:1 ratio were dissolved in water to form a 0.2 M solution. The pH was increased to 7 with ammonia solution. The solution was left to stir at room temperature for 16 hours. After that, it was filtered, washed with distilled water, and centrifugated at 20,000 rpm. The powder was then dried in an oven at 80 °C for 3 hours. The copper hydroxyapatite powder was additionally calcined in an oven at 400 °C for 1 hour. To prepare calcium hydroxyapatite powders, the required amount of calcium nitrate was substituted for copper nitrate and synthesized. As a result, 3 samples of adsorbers were obtained: 1) 100%Cu-HAp, 2) 75%Cu-HAp + 25%Ca-HAp, 3) 50%Cu-HAp + 50%Ca-HAp.

To evaluate the effect of the obtained hydroxyapatite fillers on laser ablation, epoxy composites were prepared by dispersing the synthesized Ca-HAp and Cu-HAp particles in epoxy resin (CHS-Epoxy 520, Spolchemie). The filler loading was set at 5 wt. % for both types of particles. The fillers were dispersed in the epoxy resin for a duration of 30 minutes by means of a high-speed disperser (WiseTis HG 15A). Subsequently, the hardener was incorporated in accordance with a stoichiometric ratio (TELALIT 0600, Spolchemie), and the mixture was manually agitated. Following this, the mixture was subjected to homogenization and degassing under vacuum. The resulting composition was subsequently poured into molds to form plates with a thickness of approximately 2 mm. The plates were then cured at room temperature for a period of 24 hours, followed by a curing process at 50 °C for 3 hours. The modification of CFRP entailed a procedure analogous to the one employed to prepare a thin layer between the carbon fiber layers (3K twill, 220 g/m^2). The modified epoxy compositions (with 5 wt. % filler) were applied between the CFRP sheets and cured under the same conditions to obtain samples with the fillers incorporated into the matrix.

The laser ablation procedure was executed using a femtosecond laser system (Fig. 1), which operates at a wavelength of 1030 nm, achieves a maximum output power of 6 watts, and can generate up to 200 kHz of repetition rate. The beam exhibited a Gaussian profile, with a diameter of 4,1 mm (at an intensity level of 1/e^2), and was formed using a half-wave plate (HWP), a polarizer (Pol), and a quarter-wave plate (QWP) for circular polarization. The focusing process utilized a 10x Mitutoyo Plan Apo NIR objective, yielding a focal spot of approximately 3,9 µm (1/e^2). The samples were mounted on a high-precision XY table (Aerotech ANT130-XY). The laser scanning procedure was conducted over an area measuring 0,5×0,5 mm, with a scanning step size of 2,5 micrometers. To ascertain the most efficacious overlap values, a series of trials were conducted. After processing, the samples were rinsed with distilled water in an ultrasonic bath to remove any extraneous particulate matter.

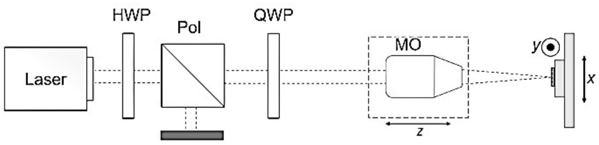
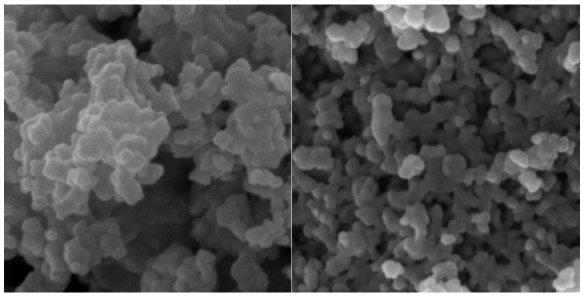


Fig. 1. Optical setup for CFRP laser ablation

The processed samples were analyzed using optical profilometry (SensoSCAN 6 profilometer with an EPI 20X v35 lens and SensoVIEW 1.8.0 software, Sensofar metrology).

SEM image (Fig. 2. a) shows that copper hydroxyapatite (Cu-HAp) particles have a highly aggregated morphology, consisting of nanoscale primary particles forming larger porous clusters. The surface is rough with significant texture and irregular growth pattern. The 1:1 mixture of Cu-HAp and Ca-HAp has a more homogeneous and densely packed structure (Fig. 2. b). The presence of Ca-HAp reduces the degree of agglomeration and promotes denser packing of particles. The particle size distribution becomes narrower, and the overall morphology becomes less porous compared to pure Cu-HAp.

The samples were analyzed using optical profilometry to evaluate the effect of calcium hydroxyapatite (Ca-HAp) on the laser ablation behavior of epoxy composites. Optimal laser parameters were selected for each composite type to achieve clean and controlled ablation with minimal thermal damage (Table 1). This was done for an equivalent ablation volume at 10 µm deep.



a b

Fig. 2. SEM of synthesized particles
(5 µm field of view):
a – Cu-HAp, b – 50%Cu-Hap+ 50%Ca-HAp

The addition of hydroxyapatite-based fillers significantly impacted on the optimal laser fluence, energy, and power required for effective ablation. The neat epoxy (without additives) required the lowest energy input (2,5 µJ) and fluence (10,3 J/cm^2). Incorporation of 100% Cu-HAp slightly increased these values to 2,75 µJ and 11,4 J/cm^2, respectively, indicating some enhancement of energy absorption due to the presence of copper ions, which likely contribute to increased local heat generation and absorption of the laser radiation.

With the progressive substitution of Cu-HAp by Ca-HAp, the energy thresholds increased noticeably. For the 75% Cu-HAp + 25% Ca-HAp composite, the optimal energy rose to 3,25 µJ, and for the 50% Cu-HAp + 50% Ca-HAp composition, it further increased to 3,75 µJ, along with a fluence of 16,0 J/cm^2 and power of 0,75 W. This trend suggests that the introduction of Ca-HAp, which is less absorbing power than Cu-HAp, modifies the thermal and optical properties of the composite, requiring higher laser input to initiate effective ablation. These findings indicate that not only the type of filler but also its ratio strongly influences the interaction of the material with femtosecond laser pulses.

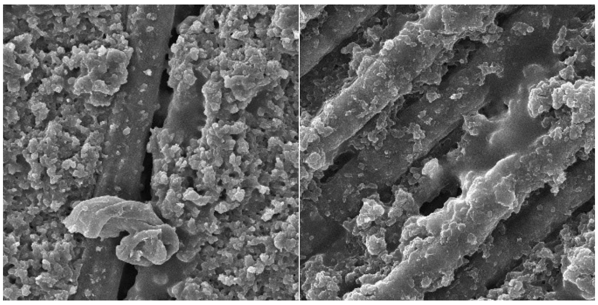
Table 1

Optimal femtosecond laser parameters

Sample	Fluence, J/cm^2	Energy, uJ	Power, W
Without additive	10,3	2,5	0,5
100% Cu-HAp	11,4	2,75	0,55
75%Cu-Hap +25%Ca-HAp	14,0	3,25	0,65
50%Cu-Hap +50%Ca-HAp	16,0	3,75	0,75

Increasing the power to ablate the same amount of material uses more energy, but it allows better control of the process to minimize damage. The results show that the Cu-HAp additive is best at absorbing laser radiation at 1030 nm.

To analyze the effect on surface morphology of the treated areas, an additional SEM photo was made (Fig. 3).



a b

Fig. 3. SEM CFRP surface after laser ablation (50 µm field of view): a – neat epoxy carbon fiber composite, b – CFRP with Cu-Hap additive

The CFRP surface after ablation is rough and irregular with extensive debris and signs of thermal degradation (Fig. 3 a). The polymer matrix is partially decomposed, forming amorphous structures, and the exposed carbon fibers are poorly defined, with signs of burning and delamination. This morphology indicates inefficient ablation, where excessive thermal energy leads to melting and resolidification rather than precise removal. The composite containing Cu-HAp (Fig. 3 b) demonstrates a smoother ablation pattern. The carbon fibers are cleaner and more distinct, with minimal surrounding debris. This improvement is due to the enhanced laser energy absorption and heat conductivity provided by the Cu-HAp additive. These observations suggest that the inclusion of Cu-HAp alters the thermal response of the material during laser exposure.

Conclusion. This study shows that hydroxyapatite-based fillers can effectively tailor the interaction of femtosecond laser radiation with CFRP composites. Copper-substituted hydroxyapatite (Cu-HAp) enhances near-infrared (NIR) absorption, improving the coupling efficiency between laser energy and the polymer matrix. The incorporation of Cu-HAp into the epoxy matrix enabled uniform and controlled ablation, with minimal heat-affected zones and smoother ablation profiles. In contrast, gradual substitution of Cu-HAp with calcium hydroxyapatite (Ca-HAp), a less absorptive but structurally similar filler, increased the energy thresholds required for effective ablation. This indicates that copper ions modulate local heat generation and enhance NIR absorption. The combination of femtosecond laser processing with NIR-absorbing additives such as Cu-HAp offers a strategy for improving the precision and efficiency of CFRP micromachining. These findings optimize laser-based manufacturing techniques for composite materials, particularly in applications where thermal damage must be minimized.

Funding. This research was funded by the Research Council of Lithuania, grant number P-LU-24-46, and by the Ministry of Education and Science of Ukraine, agreement number M/50-2024, reg. number 0124U003362.

References

1. Machining of carbon fibre reinforced plastics / E. Uhlmann et al. Procedia CIRP. 2014. Vol. 24. P. 19–24. URL: https://doi.org/10.1016/j.procir.2014.07.135
2. Analysis and optimization of the heat affected zone of CFRP by femtosecond laser processing / M. Chen et al. Optics & laser technology. 2023. Vol. 167. P. 109756. URL: https://doi.org/10.1016/j.optlastec.2023.109756
3. Study on the CFRP nanosecond laser cutting damage and efficiency by aspiration system assisted method / C. Chen et al. Journal of manufacturing processes. 2023. Vol. 102. P. 95–105. URL: https://doi.org/10.1016/j.jmapro.2023.07.031
4. Femtosecond laser drill high modulus CFRP multidirectional laminates with a segmented arc-based concentric scanning method / C. Zhao et al. Composite structures. 2023. P. 117769. URL: https://doi.org/10.1016/j.compstruct.2023.117769
5. Mechanism of selective texturing of CFRP by femtosecond laser / K. Li et al. Composites part B: engineering. 2024. P. 112000. URL: https://doi.org/10.1016/j.compositesb.2024.112000
6. Comparison of the effects of femtosecond and nanosecond laser tailoring on the bonding performance of the heterojunction between PEEK/CFRP and Al–Li alloy / J. Chen et al. International journal of adhesion and adhesives. 2023. P. 103483. URL: https://doi.org/10.1016/j.ijadhadh.2023.103483
7. Absorbance study of powder conditions for laser additive manufacturing / B. Brandau et al. Materials & design. 2022. Vol. 216. P. 110591. URL: https://doi.org/10.1016/j.matdes.2022.110591
8. Nishiyama H., Nara H., Kawabe H. Direct laser microprinting of hydroxyapatite-clad structures by photoreduction-triggered nanomaterial deposition. Optical materials express. 2023. URL: https://doi.org/10.1364/ome.506246
9. Kolmas J., Marek D., Kolodziejski W. Near-Infrared (NIR) spectroscopy of synthetic

hydroxyapatites and human dental tissues. Applied spectroscopy. 2015. Vol. 69, no. 8. P. 902–912. URL: https://doi.org/10.1366/14-07720
10. Exploring the various effects of Cu doping in hydroxyapatite nanoparticle / A. Noori et al. Scientific reports. 2024. Vol. 14, no. 1. URL: https://doi.org/10.1038/s41598-024-53704-x
11. Pérez-Barrado E., Darton R. J., Guhl D. Synthesis and applications of near-infrared absorbing additive copper hydroxyphosphate. MRS communications. 2018. Vol. 8, no. 03. P. 1070–1078. URL: https://doi.org/10.1557/mrc.2018.144.

Баклан Д.В., Миронюк О.В., Білоусова А.О., Ванагас Е., Дослідження впливу адсорберів лазерного випромінювання на абляцію фемтосекундними лазерними імпульсами армованого вуглецевим волокном пластику

Армовані вуглепластики (CFRP) набули популярності завдяки своїм переважним властивостям, зокрема високому співвідношенню міцності до ваги, стійкості до хімічних речовин та гнучкості конструкції. Однак обробка цих композитних матеріалів залишається складним завданням через неоднорідність вуглецевих волокон і полімерної матриці. Лазерна обробка, особливо за допомогою надшвидких фемтосекундних лазерів, стала багатообіцяючою технологією для точної обробки вуглепластиків. Перевагами цього методу є мінімальне термічне пошкодження та підвищена точність абляції. Однак різниця у швидкості абляції між епоксидною матрицею та вуглецевими волокнами часто перешкоджає ефективності процесу. У цьому дослідженні вивчається використання добавок на основі гідроксиапатиту для покращення взаємодії лазера з матеріалом та оптимізації поведінки при абляції систем з вуглепластику. Зокрема, мікрочастинки коп-пер-заміщеного гідроксиапатиту (Cu-HAp), які відомі своїм сильним поглинанням в ближній інфрачервоній області (NIR) близько 1030 нм, були синтезовані і введені в епоксидну матрицю. Гі-дроксиапатит кальцію (Ca-HAp), термічно стабільна і біосумісна кераміка з низьким поглинанням в ближній інфрачервоній області, був використаний як еталон для оцінки питомого внеску іонів міді. Епоксидні композити з 5 мас. % різних композицій наповнювачів (100% Cu-HAp, 75% Cu-HAp/25% Ca-HAp та 50% Cu-HAp/50% Ca-HAp) були підготовлені та інкорпоровані в ламінати CFRP. Фемтосекундну лазерну абляцію при 1030 нм проводили в оптимізованих умовах для кожного типу зразків, після чого оцінювали морфологію поверхні за допомогою оптичної профілометрії та СЕМ. Результати показали, що включення наповнювачів Cu-HAp сприяло підвищеному поглинанню енергії, тим самим сприяючи більш ефективній абляції зі зменшеним термічним пошкодженням порівняно з немодифікованою епоксидною смолою і системами, наповненими Ca-HAp. Заміна Cu-HAp на Ca-HAp збільшила необхідну інтенсивність лазерного випромінювання та енергоспоживання. Це вказує на те, що іони міді посилюють локалізоване нагрівання та зв'язок енергії. SEM-зображення показали, що частинки Cu-HAp мають пористу, агреговану морфологію, яка перерозподіляє теплову енергію, в той час як Ca-HAp має щільнішу, одноріднішу структуру наповнювача зі зменшеною пористістю. Ця робота показує потенціал Cu-HAp як функціональної добавки для регулювання взаємодії фемтосекундного лазерного випромінювання з композитними матеріалами та покращення результатів мікрообробки. Отримані результати підтверджують доцільність використання керамічних наповнювачів, що поглинають інфрачервоне випромінювання, для вирішення загальних проблем, пов'язаних з лазерною обробкою вуглепластиків, включаючи зони термічного впливу та абляційну неоднорідність.

Ключові слова: *CFRP; вуглецеве волокно; лазерна обробка; фемтосекундний лазер; різання; абляція.*

Баклан Денис Віталійович – доктор філософії, асистент, кафедри хімічної технології композиційних матеріалів, хіміко-технологічний факультет Національний технічний університет України "Київський політехнічний інститут імені Ігоря Сікорського", d.baklan@kpi.ua.
Миронюк Олексій Володимирович – доктор технічних наук, доцент, завідувач кафедри хімічної технології композиційних матеріалів, хіміко-технологічний факультет Національний технічний університет України "Київський політехнічний інститут імені Ігоря Сікорського", o.myronyuk@kpi.ua.
Білоусова Анна Олегівна – аспірант, асистент кафедри хімічної технології композиційних матеріалів, хіміко-технологічний факультет Національний технічний університет України "Київський політехнічний інститут імені Ігоря Сікорського", a.bilousova@kpi.ua.
Ванагас Егідіюс – доктор філософії, головний науковий співробітник лабораторії когерентної оптики, відділ фундаментальних досліджень, Центр фізичних наук і технологій (Вільнюс, Литва), egidijus.vanagas@ftmc.lt

Стаття подана 10.05.2025.