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# Interaction between laser radiation and antifouling coating underwater

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**Abstract**

Biofouling on a ship´s hull has an enormous economic impact on its operation. Increasing biofouling leads to the introduction and spread of invasive species, an elevated frictional drag in the water, an increased fuel consumption and thus an additional emission of greenhouse gases. In this context, the prevention or removal of biofouling is essential. Conventional, mechanical in-water-cleaning methods have several ecological and regulatory disadvantages. In the context of a laser-based underwater ship cleaning, which is currently under development, we investigated the interaction between laser radiation and a self-polishing copolymer antifouling coating. Important process parameters were investigated to determine the laser power damage threshold of the SPC coating. This includes the measurement of the reflection- and the surface properties of the SPC coating.

Keywords: laser; water; ship hull; biofouling; cleaning; ecofriendly

## 1. Introduction

The term "biofouling" describes the unwanted formation of biological layers on technically relevant surfaces under water. If a surface is exposed to seawater under natural conditions, a biofilm develops after a short time. This leads to considerable problems, especially in shipping. The fouling of the ship's hull increases

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the total weight of the ship and the roughness along with an increase in water resistance. As a result, transport times are longer and the energy consumption is higher. In summary, the economic and commercial consequences of biofouling are immense (Bader-Eldin, 2008; Callow, 1990; Candries, 2001; Quijada Cordova, 2019).

Special coatings are used on the hull of ships to prevent biofouling. In general, the commercial coatings can be divided into two different groups concerning their working mechanisms. These include biocide-free and biocide-containing coatings. With a market share in the range of 90% in 2016, biocide-containing coatings account for the highest percentage of commercially sold products (Quijada Cordova, 2019). This type of coating also includes the so-called self-polishing copolymers (SPC). The mechanism of SPC coatings is based on a chemical reaction, which results in a constant release of biocide-containing compounds from the uppermost layers. This achieves a high level of fouling protection and, in addition, the uniform chemical dissolution of the uppermost layers results in a self-polishing effect of the surface (Bader-Eldin, 2008; Candries, 2001).

In the literature, previous approaches focus on the basic damage to organisms in a water environment but do not consider a combination of the effectiveness of high-power lasers and the protection of existing antifouling layers, which is of particular interest for industrial applications. Studies are currently being carried out on laser-induced ablation of surface layers underwater (Bykanova, 2020; Kostenko, 2019). However, there are fundamental differences in the actual research objective, as the results show that complete ablation of all layers down to the bare metal takes place.

The investigations in this paper deals with a new laser-based cleaning process for biofouling, which is currently under development in the "FoulLas"-project. For the full understanding of the new cleaning process, knowledge of the actual fundamental interactions between the laser radiation and the SPC coating are essential.

## 2. Experimental setup

Within the scope of the investigations, glass slides with a red SPC coating were analysed to determine the damage thresholds, reflection measurements and microscopic examinations. To investigate an ageing effect of the coating in relation to the reflectance properties, some samples were aged in seawater under natural conditions and then manually cleaned from biofouling for analysis. The experiments were carried out according to the setup in figure 1.

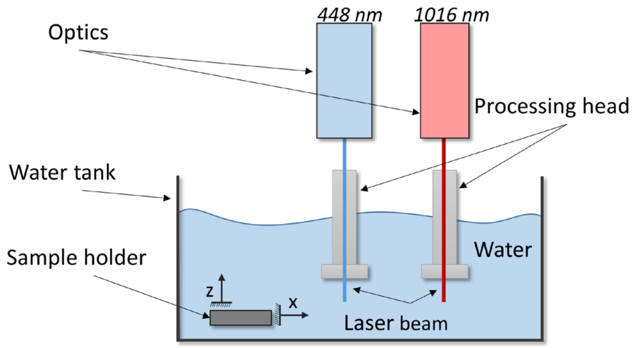


Fig. 1. Schematic experimental setup

The samples were moved with a sample holder inside the water tank in z- and x-direction. Two diode lasers were used as laser sources. The blue laser source emits radiation at a wavelength of 448 nm with a maximum power of 1.5 kW, while the infrared laser emits radiation at 1016 nm and has a maximum power of 3.5 kW. In the irradiation experiments, only one laser source was used at a time to irradiate the respective samples. To couple the laser beam from the air into the water, processing heads with a protection window were used. The processing optics form line-shaped foci with adjustable line widths from the laser radiation to generate different power densities. The working distance between the processing head and the sample surface correspond to the distance the laser passes through the water. This value of 20 mm was the same for all experiments.

The reflection measurements of the SPC coating were carried out with an integrating sphere. To cover a broad wave spectrum, two different light sources were chosen. A deuterium lamp was used for the UV radiation and a halogen lamp for the VIS-IR wavelength range. The spectrometer for the measurement of the reflected radiation was the Perkin Elmer Lambda 1050.

The microscope images and the topography measurements were carried out with a laser-scanning-microscope (LSM), the Keyence VK-X1100. Within the measurement area, lines were defined for the determination of the roughness values, based on which the corresponding line profile was derived. In total, each measurement of the roughness values was based on 60 individual measurement lines, which are combined to calculate the average value. No filters were used for the calculation and evaluation of the line profiles, as only the comparability within the same measuring range before and after irradiation was investigated.

## 3. Results

### *3.1. Reflection measurements*

The graph in Figure 2 a) illustrates the reflective properties of the SPC coating. The solid black line represents the characteristic reflectance behaviour in the initial state of the reference sample. Almost identically, the dotted red line runs on top of the black line, which represents an irradiated coating sample below the destruction threshold. In contrast, the dashed blue line of an aged sample shows a different curve. Specifically, it has a higher reflectance at a wavelength of 550 nm than the other samples. In addition, the lighter colour of the coating after ageing is visible, as shown in Figure 2 b). All samples generally behave similarly. The reflectance properties are not constant over the entire wavelength range investigated from 300 nm to 1200 nm. In the blue wavelength range from 300 nm to 550 nm, the reflectance of the coating is low and well below 10 %. With increasing wavelength, the curves take a saddle-shaped course and reach their maximum in the infrared wavelength range at a reflection of about 45 %.

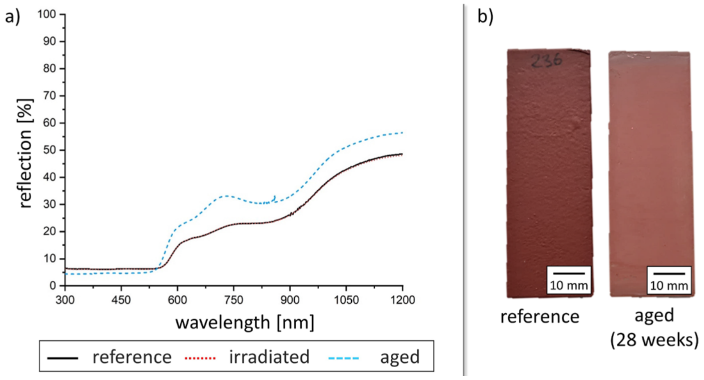


Fig. 2. (a) Reflection measurements of SPC coating; (b) Ageing effect of the coating after 28 weeks of immersion in natural seawater, the biofouling was removed by hand

### *3.2. Definition and measurement of the destruction threshold*

An essential goal of laser-based cleaning of antifouling coatings is to ensure that the coating is not negatively affected or damaged. For this reason, the definition and determination of the destruction thresholds is an important factor. Figure 3 a) shows the effects on the coating using the IR laser and a uniform power variation. An SPC sample in the initial state was irradiated with a constant feed rate and a continuously increasing laser power.

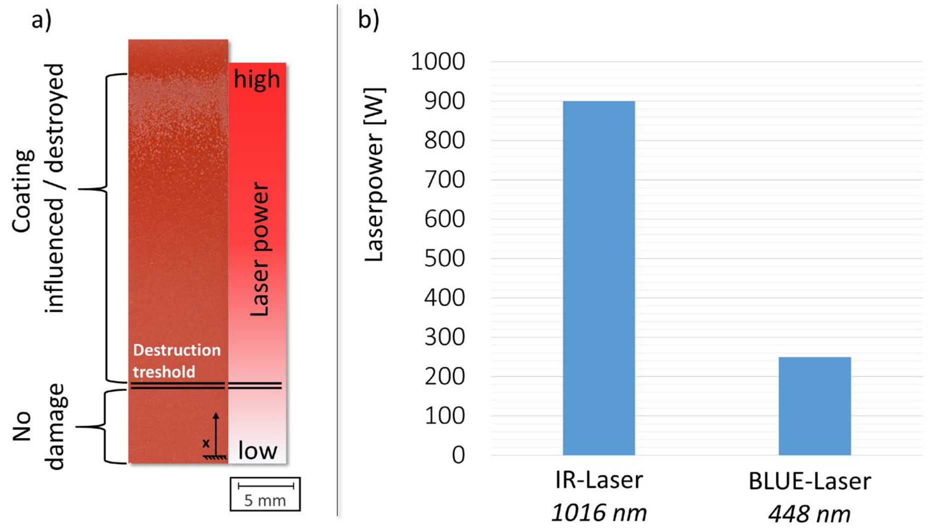


Fig. 3. (a) Power ramp for determining and defining the destruction threshold, irradiated by IR laser; (b) results of the determined damage threshold of laser power in relation to the laser source

The damage pattern of the coating changes from a slightly darker discolouration to increasing blistering as the laser power rises. As soon as an optical change was visible in the macroscopic area of the coating, the applied laser power is defined as the destruction threshold. Based on these observations, the destruction threshold was then determined as a dependence of the two laser sources. The results from the bar chart in Figure 3 b) show that there are clear differences in the laser power. For the blue laser, the destruction threshold of 250 W was reached significantly earlier than with the IR laser at 900 W. The data of the determined destruction thresholds correlate with the results of the reflection measurements.

### *3.3. Roughness analyses*

In order to be able to completely exclude a negative influence of the coating by the irradiation process, the surface was additionally examined with an LSM. No changes could be detected optically below the destruction threshold. During the investigations, however, the following effect was observed. By slightly exceeding the destruction threshold, changes in the microtopography became visible. Figure 4 compares two microscope images of the non-irradiated reference area with the same section after laser irradiation. The left image shows that micro-roughness was present in the binding material between the particles. This microscopic surface roughness was smoothed by the laser irradiation, as shown in the right image.

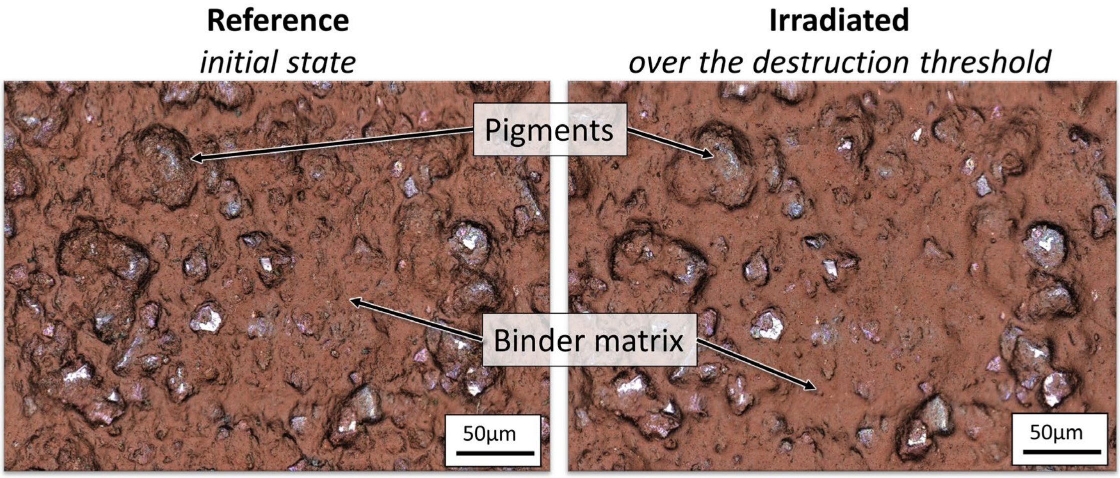


Fig. 4. Comparison of the SPC coating microstructure in the initial state and after irradiation above the destruction threshold power, 50x magnification

The effect was not only optically observable but could also be measured in the roughness values, as seen in Figure 5. In terms of roughness values, the average roughness of all samples after irradiation above the destruction threshold decreased by (3.15 ± 1.00) % for the $R_a$ value, while the $R_z$ value also decreased by (4.11 ± 1.08) %.

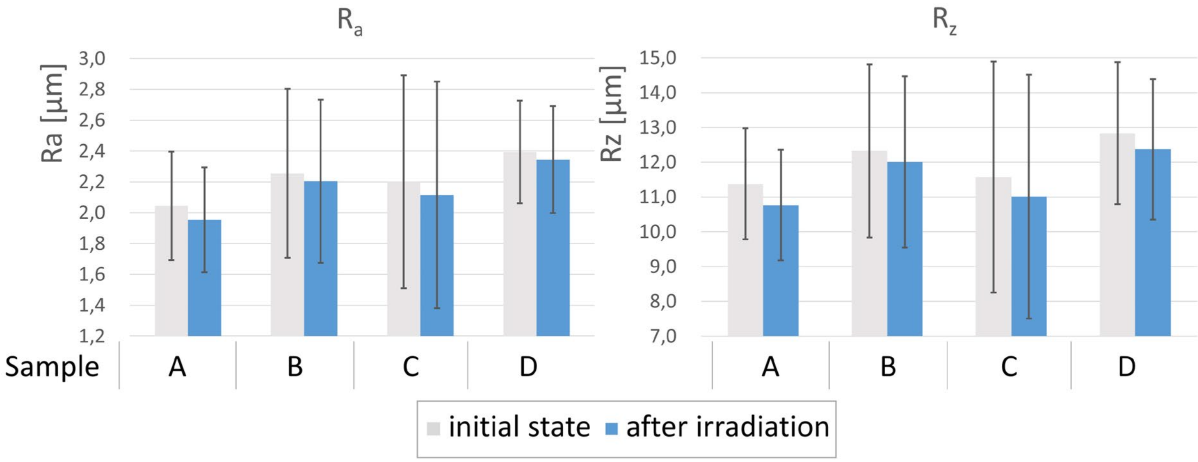


Fig. 5. Roughness values determined using LSM in comparison between the initial state and an irradiation above the destruction threshold

## 4. Discussion

The destruction threshold of the laser power is mainly influenced by the absorption properties of the SPC coating and by the reduction of the laser radiation by the water. The results of the reflection measurements allow an indirect statement about the absorption behaviour of the SPC coating. A higher reflection also means that less radiation is absorbed and thus a higher destruction threshold laser power is achieved. The determination of the reflection properties has shown that due to the strong dependence on the wavelength, a high reflection of 46.4% is achieved at a wavelength equivalent to the infrared laser radiation of 1016 nm, whereas at a wavelength of 448 nm significantly less radiation, namely 6.3%, is reflected. The results of the reflection measurements correlate with the destruction threshold of the laser powers measured. In numbers, the destruction threshold of the laser power for the infrared wavelength exceeds that of the laser power of the blue wavelength by a factor of 3.6. The characteristic absorption coefficient of water has a significant influence on this, as it is 1175 times smaller at a laser wavelength of 500 nm than at a wavelength of 1000 nm. (Irvine, 1968).

Irradiation of the SPC coating below the destruction threshold does not influence the reflection properties. The microscopic analysis using LSM also supports this conclusion. In contrast, the ageing of the coating samples in seawater has a different effect with an increase in reflection. A possible reason for this observation is the self-polishing effect of the SPC coating. Optically, the aged SPC samples have a significantly lighter colour than the reference samples in their initial state. Among other things, a lighter colour also indicates a higher reflection, which in turn corresponds to the measurement results.

Furthermore, an effect could be observed after slightly exceeding the destruction threshold of the laser power. The roughness peaks are flattened and micro-roughness is reduced. A possible reason for this effect could be the local melting of the top surface layer.

## 5. Conclusions

In this study, samples with an SPC coating were irradiated by laser radiation under water to evaluate essential process parameters for a laser-induced cleaning process of coatings from biofouling. The focus was on the fundamental interactions between laser radiation and an SPC coating. This includes the definition and identification of the destruction threshold of the laser power, measurements of the wavelength-specific reflection properties and an analysis of the microscopic surface roughness. Furthermore, two different laser sources with respective wavelengths of 448 nm and 1016 nm were used for the irradiation tests in order to map the influences of the two laser wavelengths. The following findings were achieved in detail:

- The results of the reflection measurements show clear differences with regard to the wavelength. It can be noted that less radiation is reflected at shorter wavelengths than at longer wavelengths. The absorption of the coating can be derived from the determined reflection, which ultimately has an essential influence on the damage threshold of the laser power.
- The determined damage thresholds of the laser powers related to the infrared and blue laser source vary by a factor of 3.6 from 900 W (infrared laser) in relation to 250 W (blue laser). The reason for the large difference can be attributed to the reflection properties of the SPC coating and the characteristic absorption coefficient of the water.
- The definition and classification of the destruction threshold of the laser power according to optical scales on a macroscopic level could be confirmed based on the reflection measurements and with the aid of microscope images.
- A slight exceeding of the destruction threshold of the laser power leads to a change in the microtopography of the SPC coating. The effect can be observed optically and confirmed by roughness measurements. This effect reduces micro-roughness.

## 6. Acknowledgments

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