ORNAMENTS IN RADIATION TREATMENT OF CULTURAL HERITAGE: COLOR AND UV-VIS SPECTRAL CHANGES IN IRRADIATED NACRES

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Abstract

Cultural heritage objects that are radiation treated in order to stop their biodegradation often contain ornamenting materials that cannot be removed. Radiation may produce unwanted changes to such materials. Nacre is a common ornamenting material so this is an attempt to assess the impact of gamma-radiation on its optical properties. Two types of nacre (yellow and white) were obtained from a museum and subjected to different absorbed doses of Co-60 gamma irradiation under the same conditions. The radiation induced changes of nacres color were investigated with fiber optic reflectance spectroscopy (FORS). Colorimetry in CIE Lab space revealed that in both nacres the lightness shifted to darker grey hues at high doses while the color component's (red, green, yellow and blue) behavior depended on the nacre type. Observable changes occurred at doses much above the dose range needed for radiation treatment of cultural heritage objects that are often ornamented with nacre.

In UV-Vis reflectance spectra of samples irradiated to high doses carbonate radical anion absorption appeared.

Keywords: gamma irradiation; fiber optics reflectance spectroscopy (FORS); CIE Lab colorimetry; UV-Vis spectroscopy; cultural heritage; nacre

1. Introduction

Cultural heritage (CH) objects of organic origin such as wood, leather, paper and textiles, are subject to biological attack and subsequent degradation. Radiation methods have been proven to be very effective in saving CH objects [Katušin-Ražem et al. 2009]. The dose ranges for treatment are based on experience in radiation treatment of food, pharmaceutics and medical devices and they are selected according to the biodegradant type. This is the reason why most of the published research on the subject of CH treatment using gamma irradiation has also been done from the microbiological point of view [Bletchly et al. 1957, Briški et al. 2001, Petushkova et al. 1988]. To comply with restores criteria it is necessary to confirm no irreversible change occurred in the treated object. Considering the constituent materials radiation effect on wood [Despot et al. 2012, Divos et al. 2006, Pointing et al. 1998] and wood consolidation are mainly studied. Recently an increased number of publications appeared on the research on the influence of irradiation on pigments [Manea et al. 2012, Negut et al. 2012, Rizzo et al. 2002]. To our best knowledge no research has been published on the influence of gamma irradiation on various properties of materials that by themselves need not be irradiated but are decorating CH objects and cannot be removed. In that case the personnel of the radiation facilities are compelled to work according to their own judgment and expertise if they have one. The experience gathered on radiation treatment of various CH objects that is performed at the Radiation Chemistry and Dosimetry Laboratory, Ruđer Bošković Institute for over 30 years [Katušin-Ražem et al. 2009] prompted us to investigate some of the materials that may be found on CH objects.

Nacre or mother-of-pearl is a tough biomineral produced by numerous kinds of mollusks. Like pearls it consists of about 95% of highly oriented aragonite crystals embedded in an organic matrix composed of proteins and chitin that forms a lamellar structure [Xie et al. 2011] giving it its special optical properties. The colors of nacre vary naturally and may be enhanced by one of the common treatments like bleaching and heating [Elen 2001]. It can be found in a variety of colors and practically no two samples of nacre look the same. It is commonly used for decoration of various CH objects, particularly those made of wood that are often radiation treated. Removing the ornaments is rarely feasible so the question arises whether it is acceptable to irradiate nacre-containing CH objects at all and if yes up to which doses. Because of that this study focuses on how nacre's color is affected by irradiation. There is a study on changes in pearls irradiated to modify their color [Kim et al. 2012] but without colorimetric and/or spectroscopic analysis but no research on irradiation effects on nacre color was published. Because of that this study focuses on how nacre's color is affected by irradiation.

2. Experimental

2.1. Test material and samples

The nacre samples have been obtained from the conservation stock of Museum of Arts and Crafts in Zagreb since such are likely to occur on CH objects. The origin of nacres is unknown as well whether they were treated in any way. In Fig. 1 two types of nacre that were studied are shown, a white one (in text referred as "white nacre") and the other with a yellowish tone (referred as "yellow nacre"). Relatively large pieces were cut to appropriate dimensions for FORS measurements, i.e. roughly 1x1 cm^2 (thickness 2-3 mm).

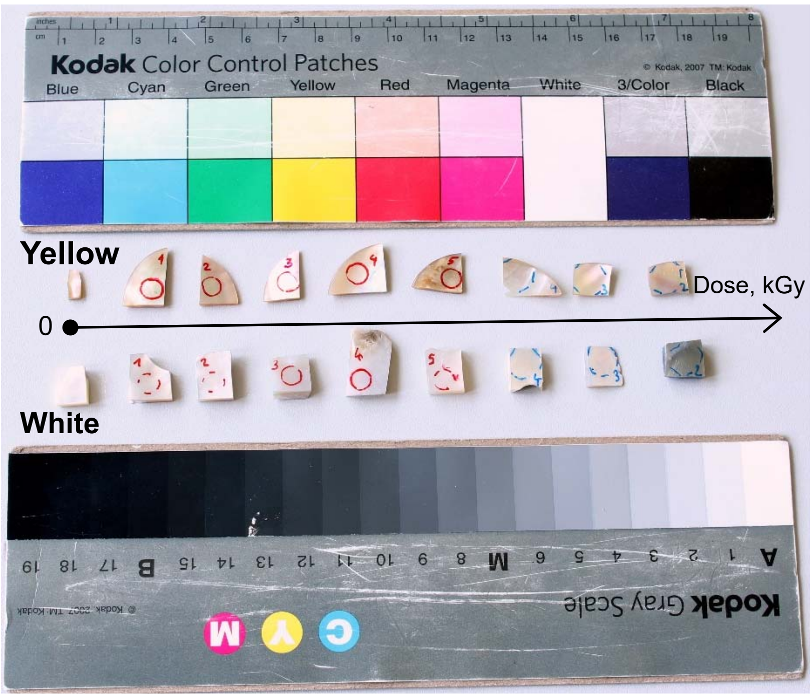


Fig. 1. Unirradiated and irradiated samples of nacre arranged according to the increasing absorbed dose: 0, 0.5, 1, 2, 6, 10, 22 and 54 kGy in comparison with color and gray scales. The marks on samples indicate positions for FORS measurements.

2.2. Gamma irradiation

Irradiation was performed at a Co-60 γ-source of Radiation Chemistry and Dosimetry Laboratory, Division of Materials Chemistry, Ruđer Bošković Institute at room temperature, in contact with air, the dose rate was 0.32 kGy/h.

A separate sample of each nacre and an ECB-system dosimeter (to confirm the dose) were irradiated to a selected absorbed dose. The dose range included doses common in CH treatment: 0.5, 1, 2, 6, 10 kGy; and much higher doses: 22 and 54 kGy to ensure development of radiation induced effects (all doses are expressed as absorbed dose in water). During the post-irradiation period the samples were kept in the dark at room temperature. A reference sample of each type of nacre was left unirradiated.

2.3. Methods and analysis

Fiber optic reflectance spectroscopy (FORS) measurements were done under a 45°/45° geometry using Ocean Optics USB4000 spectrometer with a HL-2000 halogen source connected via fiber optics. Before each set of measurements calibration of the spectrometer was performed using a PTFE optical diffuse reflectance standard. The exact position and orientation were marked on each sample (Fig. 1) and the measurements were performed the same way each time. The colorimetric properties and reflectance spectra of each sample were taken prior to irradiation (referred as "unirradiated"), the day after irradiation ("immediately"), 30 days after irradiation ("one month") and 60 days after irradiation ("two months"). To ensure reproducibility the spectra of unirradiated reference samples of each nacre were taken each time the radiation effects were monitored.

The radiation induced color change in studied nacres was monitored using CIE colorimetry, in the CIE 1976 Lab $L^*a^*b^*$ [CIE 1978] system. CIE Lab is a color specification system for quantitative interpretation of the color developed by the Commission Internationale de l'Eclairage (CIE). It provides a standard method for describing the stimulus of a color, under controlled light and viewing conditions, based on the average known response of the human visual system [Schanda 2007]. Parameter L^* represents the lightness of a color, known as the CIE 1976 psychometric lightness. The scale of L^* is from 0 (black) to 100 (white). The chromaticity of a color is represented in a two-dimensional diagram where axis a^* determines the ratio of green (negative) to red (positive), and axis b^* specifies the ratio of blue (negative) to yellow (positive).

Widely used measure for overall color change is the CIE 1976 $L^*a^*b^*$ color difference, that is simply calculated as the Euclidean distance in CIELAB space. For colors specified by [L_1^*, a_1^*, b_1^*] and [L_2^*, a_2^*, b_2^*] parameters the difference, ΔE^*, is calculated as follows:

$$\Delta E^*{}_{a,b} = \sqrt{(L_1^* - L_2^*)^2 + (a_1^* - a_2^*)^2 + (b_1^* - b_2^*)^2} \quad (1)$$

The interpretation of color differences is not straightforward. The observer will perceive a difference in color only after a certain amount, equal to the Just Noticeable Difference (JND). The JND value varies for different materials that are observed and thus different values are found in literature [Hardeberg 2001]. The value of JND $\Delta E^*{}_{a,b}$ =1 is often mentioned in literature [Kang 1997], but Mahny et al. introduced the value $\Delta E^*_{a,b}$ =2.3 [Mahy et al. 1994] since this is the value below which not even a trained observer's eye can notice the difference.

When two colors are shown side by side $\Delta E^*_{a,b}$ is according to Hardeberg [Hardeberg 2001] interpreted as: $\Delta E^*_{a,b} < 3$ the effect is *hardly perceptible*, $3 < \Delta E^*_{a,b} < 6$ *perceptible, but acceptable* and $6 < \Delta E^*_{a,b}$ *not acceptable*.

3. Results and discussion

Several factors contribute to nacre color appearance. Diffraction of the light on its lamellar structure [Liu et al. 1999] and iridescence [Snow et al. 2004] give it its structural colors. Depending on the mollusk type and origin, pigments like carotenoids and melanin may contribute to the color [Karampelas et al. 2007] that may be artificially enhanced.

3.1. Color characteristics of non-irradiated nacre

The non-homogeneity of a natural material caused slight variations of measured colorimetric parameters even in non-irradiated nacres as can be seen in Figs. 2, 3 and 4. The surface of nacre is not perfectly flat what makes very small shifts in the measuring position and angle inevitable what predominantly impacted the lightness, L^*. If nacres were grounded into powder instead of being cut into pieces such problems could have been avoided but much of the information on optical properties would have been lost.

Lightness, L^*, is in both nacres below 50 % (yellow nacre 37.5% and white 43.2%) meaning that both are grey leaning more to the black direction than the absolute white one. The values of both a^* and b^* parameters are close to 0 (in theory there are no maximum values of a^* and b^*, but in practice they are usually numbered from -128 to +127) indicating that the colors are present only as soft tones. A slightly yellow tone is confirmed in the yellow nacre, while the white one has a somewhat more pronounced blue tone.

There is a significant shift of b^* parameter toward yellow color in both nacres subjected to the highest dose, i.e. 54 kGy, that remained after the post-irradiation period, while parameter a^* was unaffected by irradiation (Fig. 2b).

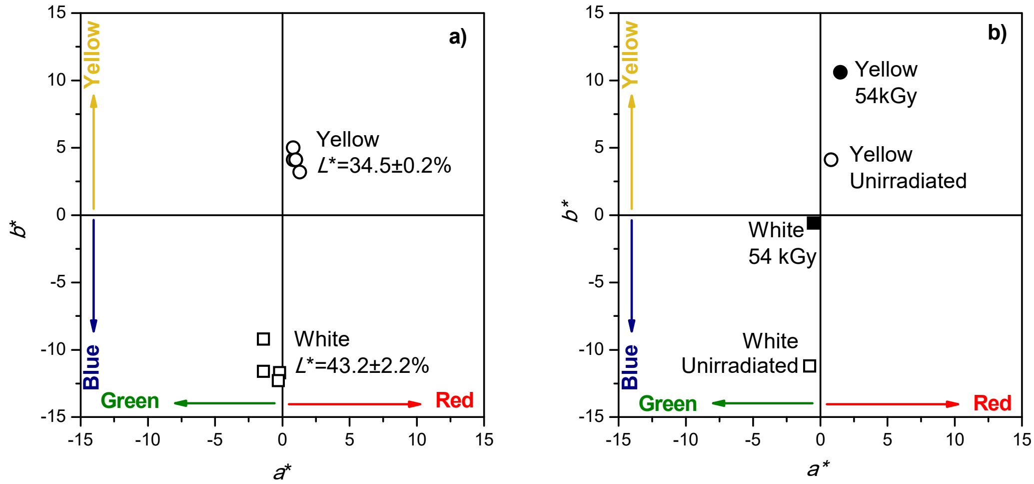
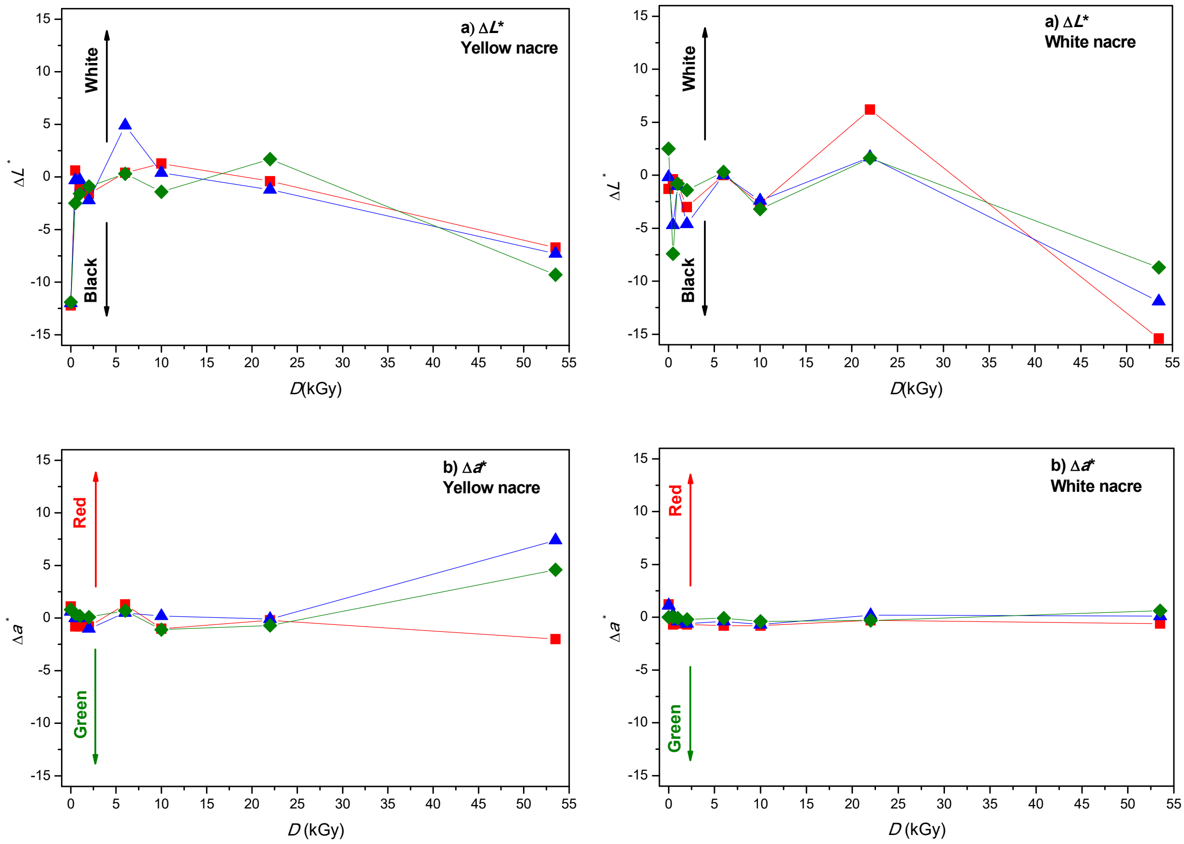


Fig. 2. Color characteristics of the studied nacres: a) scattering of the a^* and b^* parameters in unirradiated samples of nacre and b) comparison of the unirradiated samples and the samples subjected to the highest applied dose.
Yellow/white nacre: ○/□ - prior to irradiation and ●/■ - 2 months after irradiation with 54 kGy.

3.2. Color change in irradiated nacres



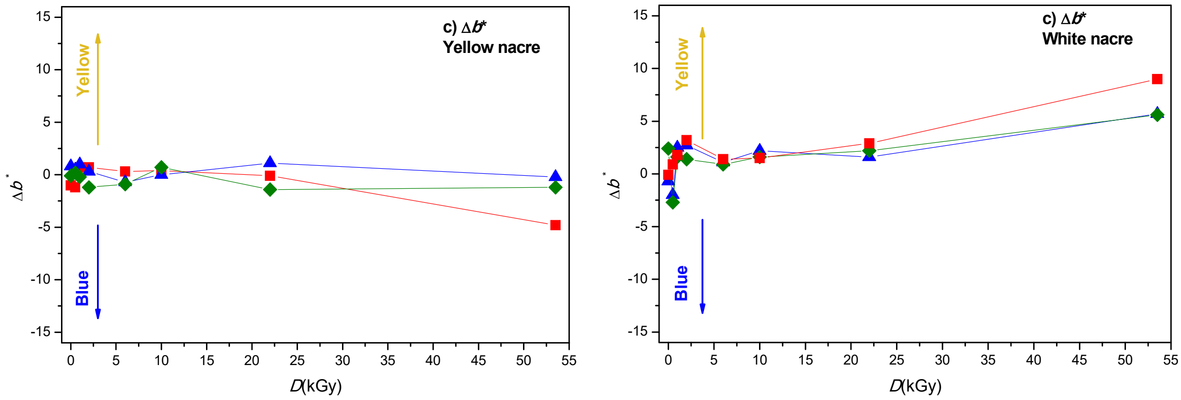


Fig. 3. The change in colorimetric CIE-$L^*a^*b^*$ system parameters of the nacre samples irradiated to selected doses immediately after irradiation and during post-irradiation period.

■ - immediately after irradiation; ▲ - after 1 month; ♦ - after 2 months.

The parameter values were compared to those for the same samples obtained prior to irradiation.

Irradiation up to 22 kGy including the post-irradiation period resulted in only slight changes of colorimetric parameters L^*, a^* and b^* of both nacres (Fig. 3). A significant change that can also be visually observed occurred only in samples that were subjected to a dose of 54 kGy.

The most irradiation-affected colorimetric parameter (also with the largest scattering) in both nacres is again lightness, L^* (Fig. 3a). Still, the changes at low doses that are commonly applied in treatment of CH objects are relatively insignificant. In the samples irradiated to 54 kGy ΔL^* is negative (yellow: ΔL^* = -7 to -9; white: ΔL^* = -15 to -9) confirming that the samples darkened. The main difference between nacre types appeared during the post-irradiation period. L^* values of yellow nacre slightly decreased further and the nacre became even darker (from -7 immediately after irradiation to -9 after 2 months). The ΔL^* value of the white nacre is greater immediately after irradiation (from -15 to -9) than that of the yellow one, but ΔL^* decreased with time and white nacre samples became lighter.

Except at the largest dose a^* values of both nacres were almost constant and not affected by irradiation (Fig. 3b) and the variations in b^* values were small (Fig. 3c). In yellow nacre samples irradiated to the highest dose of 54 kGy the a^* value slightly decreased (shifted towards green color) immediately after irradiation but increased during post-irradiation period. That indicates appearance of a reddish tone (Δa^* = 7) after one month. Simultaneously b^* values decreased and a slightly bluish tone appeared (Δb^* = -5) but it faded away in the post-irradiation period. White nacre obtained a yellowish tone (Δb^* = 9) immediately after irradiation. This tone somewhat decreased during the post-irradiation period and stabilized at around Δb^* = 5.5.

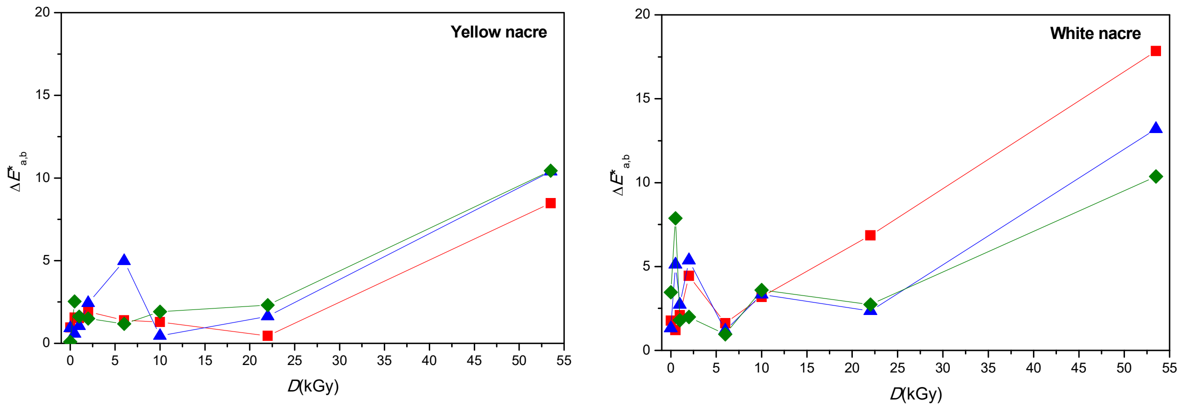


Fig. 4. The total color difference of the nacre samples irradiated to selected doses immediately after irradiation and during post-irradiation period.

■ - immediately after irradiation; ▲ - after 1 month; ♦ - after 2 months.

Fig. 4 presents the total color difference, $\Delta E^*{}_{a,b}$, calculated according to eq. (1). For all the yellow nacre samples irradiated up to 22 kGy the $\Delta E^*{}_{a,b}$ values are more or less similar and below 2.3 (if disregarding the scattering). A large increase of $\Delta E^*{}_{a,b}$ is noticed only for the sample irradiated to the dose of 54 kGy, $\Delta E^*{}_{a,b}$ being greater than 8 and it increased further during the post-irradiation period.

The white nacre's color is apparently more susceptible to irradiation. Even at the lowest dose of only 0.5 kGy $\Delta E^*{}_{a,b}$ becomes greater than 2.3 (JND) and all samples irradiated up to 10 kGy fall in the range *perceptual but acceptable* [Hardeberg 2001]. The color change decreased particularly during the first month and somewhat less after two months. The values of $\Delta E^*{}_{a,b}$ in the case of the sample irradiated with 22 kGy have actually decreased to 2.3-2.7 and thus fall back into Hardeberg's *hardly perceptible* category.

Although Δ*E** is commonly used to assess color change it should be noted that it gives only an estimate of the change in the appearance and should be considered with caution. To gain a real picture of the change in appearance each of the *L**, *a**, *b** parameters should be studied individually.

3.3. UV-Vis reflectance spectroscopy

The color of an object strongly depends on its spectral reflectance, that is, the amount of incident light that is reflected from the surface at different wavelengths. Plots in Fig. 5 present UV-VIS reflectance spectra of each sample prior to and immediately after irradiation including the spectra recorded during the post-irradiation period.

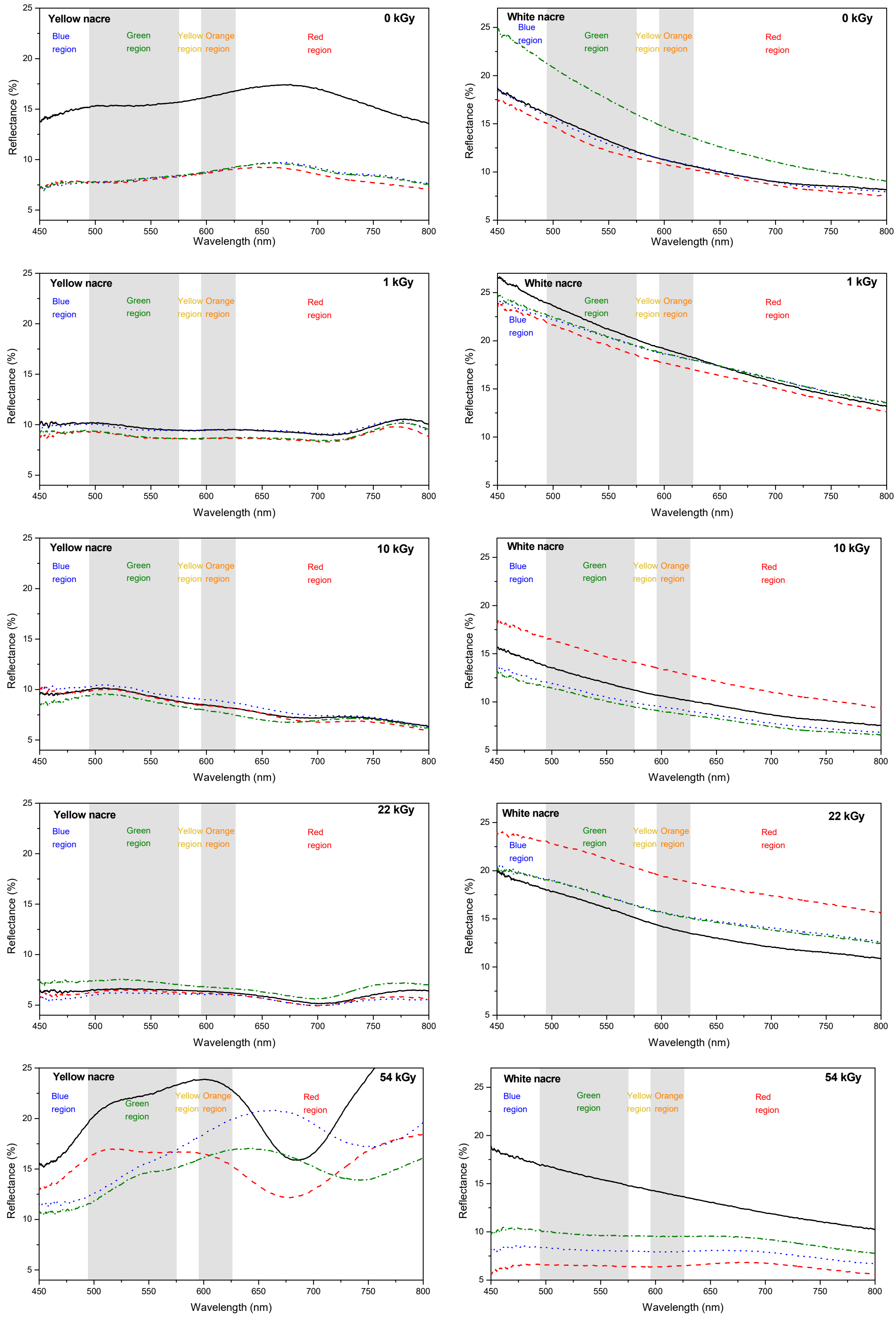


Fig. 5. Change of the reflectance of each sample after irradiation and with time.

Solid (——) - before irradiation; **Dash (- - - -)** - immediately after irradiation;

Dot (·····) - after 1 month; **Dash-dot** (-·-·-) - after 2 months.

(The UV-VIS spectra of non-irradiated sample, indicated as "0 kGy" were taken repeatedly each time spectra of irradiated samples were recorded.)

The variation of properties of natural nacres is also obvious from the differences of the UV-VIS reflectance spectra. Like the colorimetric parameter L^* the reflectance is sensitive to slight changes in the position when readings were taken. The spectra of non-irradiated white nacre are featureless with significantly greater reflectance in the blue part of the spectrum because of which they appear white. Comparison with spectra of the irradiated samples to the spectra of the same sample prior to irradiation mostly reveals changes in the curve slopes that may be tailings of some absorptions beyond the measured wavelength range. Slight and wide absorptions in the ranges between 500 nm to 550 nm and 680 to 720 nm are visible in UV-VIS spectra of all yellow samples what is characteristic for yellow pearls [Karampelas et al. 2011], particularly those heat-treated [Elen 2001]. At lower doses only slight increase of the absorption at the red end of the spectrum is observed.

In the spectra of the white nacre irradiated to 54 kGy a weak wide absorption peak appeared at around 600 nm, in the yellow and orange region. According to Behar et al. [Behar et al. 1970] this peak can be attributed to a carbonate radical anion that seems to be one of the species responsible for color change. The same peak can be observed in the spectrum of the sample irradiated to 22 kGy at somewhat lower wavelength, in the yellow region. That complies with the observed changes of the b^* color parameter. The same absorption appeared as a shoulder of the peak in the red region, at around 670 nm in the spectrum of the yellow nacre irradiated to 54 kGy. This is also in accordance with the results of a^* color parameter changes. In the post-irradiation period this band shifted to larger wavelengths, to the red region.

Significant reduction in reflectance can only be observed at 54 kGy immediately after irradiation. During the post-irradiation period the changes in the spectra decrease due to the so called “bleaching” of color centers that was taking place.

4. Conclusions

Our results show that the commonly used total color difference $\Delta E^*_{a,b}$ is not the best parameter to assess the color change that is a result of irradiation and that each of the L^*, a^*, b^* parameters should be studied individually.

The main radiation induced change in color properties of studied nacres is the change in brightness (L^*). Both types of nacre darken after irradiation. The results indicate that only at doses much above the dose range for CH object treatment of unacceptable long term color change occurred. The post-irradiation changes depend on the nacre type - in the case of yellow nacre the color change increased with time, while in the white nacre’s case it decreased with time. Overall the results indicate that nacre can be safely radiation treated for insects (up to 2 kGy). It should be treated with caution for fungi and molds, especially if doses above 10 kGy have to be applied but high doses are seldom needed in CH treatment since sterility is not the goal.

A carbonate radical anion absorption detected in UV-VIS reflectance spectra of nacres irradiated to high doses indicates that radical species are at least partly responsible for appearance of color centers. Further study on radiation induced color formation is planned.

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