Effects of Light Irradiation on Fluorescence and Optical Reflectance of Pearls

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Abstract

Color of cultured pearls of *P. fucata* (Akoya oyster) can be changed by light irradiation, which has been applied to pearl processing. The effects of light irradiation on fluorescence and optical reflectance of pearls have been investigated experimentally. Changes in the fluorescence and reflectance spectra have been observed. These changes depend on the wavelength of light and are considered to be due to degradation of conchiolin (a kind of scleroprotein) and discolouration of pigments contained in the nacre (the surface layer around the core of a pearl).

1. Introduction

Pinctada fucata (Akoya oyster) is the most famous and important shellfish for pearl culturing. Artificial processing techniques have been introduced to increase the commercial value of cultured pearls. For instance, the gamma-ray irradiation on low grade pearls is one method for changing their color to bluish-grey.

Although the effect of gamma-ray irradiation on the reflectance and fluorescence of pearls has already been studied,[1,2] that of light irradiation has not yet been reported. The effect of light irradiation is important from a viewpoint of deterioration of pearls caused by light. In previous papers,[3-7] we have clarified experimentally that fluorescence from cultured pearls can be characterized with various organic components contained in the nacre (the surface layer around the core of a pearl), and have briefly mentioned that light affects fluorescence from pearls; some of spectral charactristics partly disappear with exposure to light.[3] In this paper, we discuss the effect of light irradiation on fluorescence and optical reflectance of pearls of *P. fucata*.**

2. Experimental Procedure

The materials used in this study were yellow pearls from *P. fucata* without any

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**While coloring of the nucleus (the core of a pearl) is observed for gamma-ray irradiation, it is not for light irradiation. This result indicates that the effect of nucleus on reflection spectra of pearls is negligible for light irradiation. Moreover, we have found that the fluorescence from pearls is hardly affected by the nucleus.[2] Thus this paper does not report the effect of light irradiation on the fluorescence and reflectance of the nucleus.

preliminary chemical or physical treatment. These pearls had a spherical shape with a diameter of about 6 mm. Pearls were irradiated in air at room temperature. Five pearls were examined for the following light sources: a low-pressure Hg lamp (Ushio ULM-50; electric power P=50 W), a high-pressure Hg lamp (Irie; P=100 W), a carbon arc lamp (this lamp is enclosed within a UV fademeter, Suga Test Instruments FAL-AU; lamp current=16 A, lamp voltage=135 V), six fluorescent lamps (Toshiba FL20S-WW-SF; P=20 W× 6), a halogen lamp (Ushio; P=100 W), a Xe arc lamp (Irie HX-500W; P=500 W), and in addition, the sunlight.

It is difficult to choose an appropriate exposure time for such light sources, since they have different light powers as well as wavelength distributions. We measured the light power using a thermopile-type power meter (Scientech 36-0001). The results are listed in Table 1. It seems reasonable that exposure time is determined to be inversely proportional to the light power. However, longer wavelength light may be ineffective for photo-chemical reactions. In this experiment, the blue scale (JIS L-0841: Testing Method for Color Fastness to Sunlight and Daylight) was used to determine the exposure time for respective light sources. The blue scale and samples were exposed to respective light sources simultaneously under the same condition. When the 3rd grade of the blue scale was faded completely at each experiment, irradiation was stopped.

For sunlight irradiation, pearls were put horizontally on a rooftop and were exposed to direct sunlight during the daytime from February to April, 1988. Exposure time was not measured in this case.

Spectral reflectance curves were measured with a double beam spectrophotometer equipped with an integrating sphere (Japan Spectroscopic UVIDEC-610C); a small plate made of Al_2O_3 was used as a reference.

Laser-induced fluorescence spectra of pearls were measured before and after irradiation with the following apparatus at 300 K. The excitation source was a pulsed N_2

Table 1 Light power and exposure time for various light sources.

Light source	Light power	Exposure time
Low-pressure Hg lamp	20mW/cm²	5.5h
High-pressure Hg lamp	200	15
Carbon arc lamp	100	20
Fluorescent lamp	1	400
Sunlight	50	
Halogen lamp	140	76
High-pressure Hg lamp with a filter[1)]	3	96
Xe arc lamp with filters[2)]	0.5	192

1) A filter is UV-D25.

2) Filters are L-39, KL-43 and CS-4-94.

laser (NDC JS-1000L; wavelength=337.1 nm, pulse duration= 5 ns, repetition rate= 4 Hz). The laser beam was set at an angle of about 40°off the normal incidence to the surface of the sample and was focused on a spot about 1 ㎟ in area with a quartz lens (focal length f=150㎜). The peak intensity of the laser light on the sample was about 50kW/㎠. The fluorescnece was collected normal to the sample surface, focused on the end of an optical fiber with a glass lens (f=70㎜), and led to the entrance slit of a 27㎝ monochromator (Jarrell-Ash Monospec 27). Fluorescence spectra were measured with an optical multichannel analyser (Princeton Instruments D/SIDA-700).

Excitation spectra were measured using a spectrofluorophotometer (Japan Spectroscopic FP-770).

3. Results and Discussion

Figure 1 shows typical fluorescence spectra of light irradiated and unirradiated pearls. The fluorescence peak is at 460 nm before irradiation, and it is at shorter wavelengths after irradiation. As reported in a previous paper,[2] the blue shift of the fluorescence is attributable to degradation of conchiolin (a kind of scleroprotein). In addition to this, fluorescence of pearls is associated with certain pigments contained in the nacre.[3] Therefore, change in the fluorescence of pearls is considered to be due to not only degradation of the conchiolin but also discoloration of the pigments.

In order to investigate the origin of the luminescence change, optical reflection spectra were measured. Figure 2 shows spectral reflectance curves of pearls before

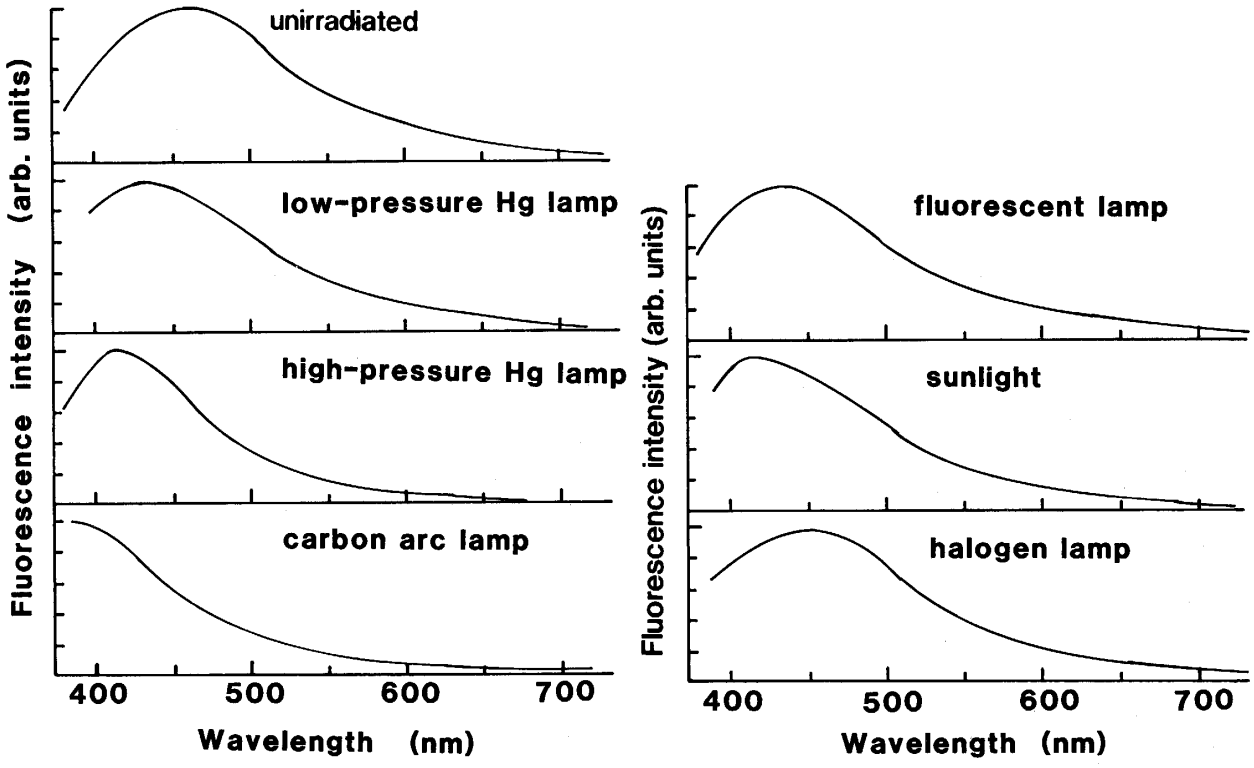

Fig. 1 Fluorescence spectra of pearls before and after irradiation. Peak intensity ratios are as follows: 1 (unirradiated), 2.4 (low-pressure Hg lamp), 2 (high-pressure Hg lamp), 0.8 (carbon arc lamp), 1 (fluorescent lamp), 1 (sunlight), 1 (halogen lamp).

(solid curves) and after (dashed curves) exposure to light. A peculiar absorption at 280 nm caused by protein decreases after exposure. This result indicates that the conchiolin is degraded with light irradiation. Moreover, three dips at 407 nm, 430 nm and 460 nm are slightly changed after exposure. These dips may be due to pigments in the nacre and characterize Akoya pearl. Pigments in the nacre are known to be discolored with light irradiation. Thus, the above results indicate that the change in the fluorescence spectrum is caused by the degradation of the conchiolin and discoloration of the pigments.

The fluorescence and reflection spectra of light irradiated pearls vary with the light sources. These differences depend probably on the difference in spectral distribution of light sources as shown in Fig. 3 . Main peak depends on light sources; from 253.7 nm (low-pressure Hg lamp) to 852 nm (halogen lamp).

The spectral behavior for the low-pressure Hg lamp irradiation, which is distinctive from others, is explained as follows. Short-wavelength light in UV region is effective for photo-chemical reactions. Thus the 280 nm absorption in reflection spectrum decreases. The degradation of the conchiolin yields decomposition products. These

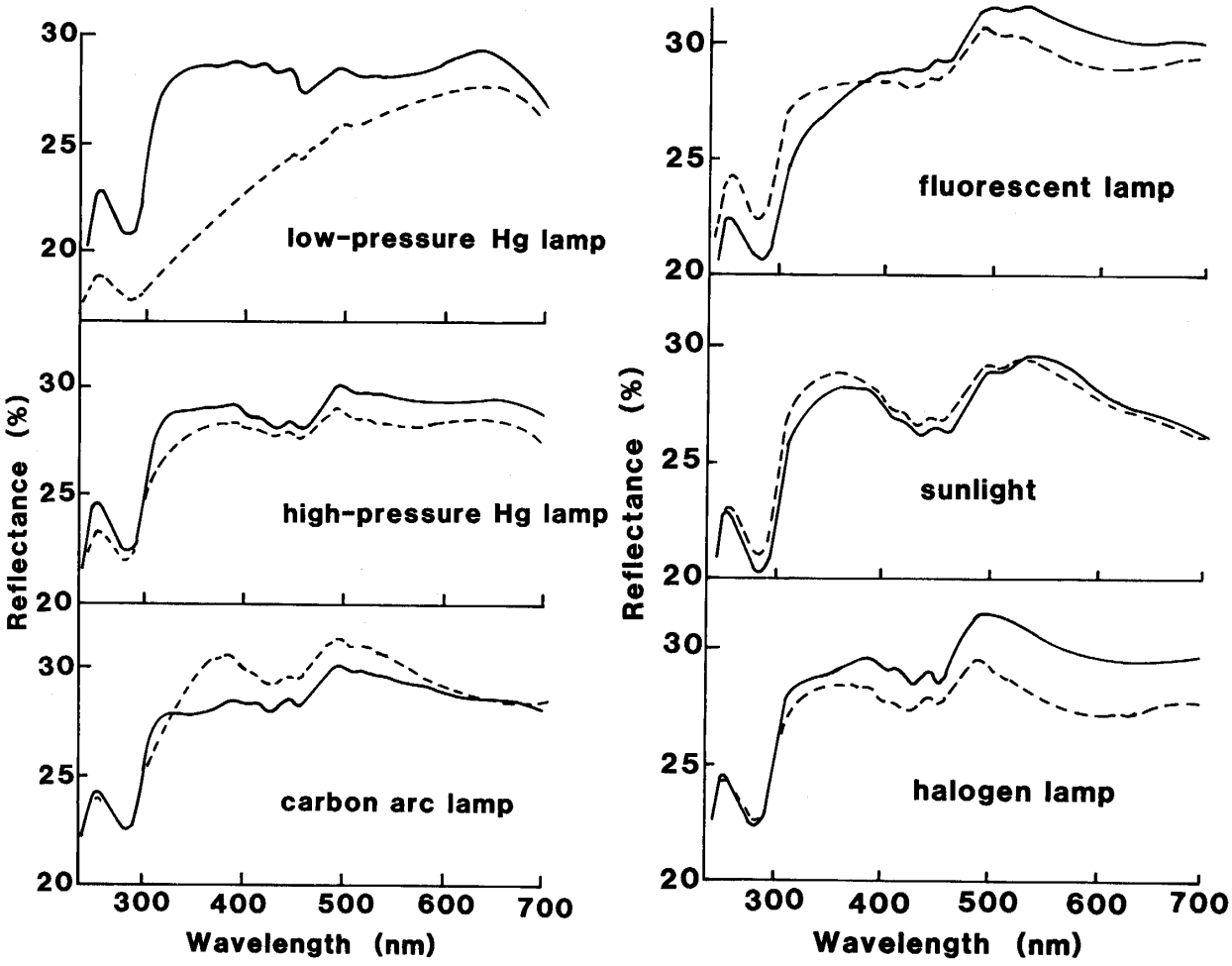

Fig. 2 Reflection spectra of pearls before (solid curves) and after (dashed curves) irradiation.

products show fluorescence at about 430 nm, so that fluorescence intensity increases as shown in Fig. 1 . These products cause decrease in reflectance shorter than about 500 nm.

The high-pressure Hg lamp yields short wavelength light (around 250 nm). However, the short-wavelength light is not the main component, so that change in reflectance is less than that for the low-pressure Hg lamp.

The fluorescence spectrum for the carbon arc lamp irradiation is distinctly different from those for other light sources. The main peak of the carbon arc lamp is 380 nm. The 380 nm light is probably effective for discoloration of pigments. Since these pigments show fluorescence at longer wavelength, the fluorescence peak shifts to shorter wavelength and reflectance in visible region increases after irradiation. The 380 nm light is ineffective for degradation of conchiolin, so that decrease in the 280 nm absorption is slight.

The fluorescent lamp, the sun and the halogen lamp yield light near 380 nm. However, this light is not the main component, so that the pigments are partly discolored and the peak shift of fluorescence is less than that for the carbon arc lamp.

In order to examine the effect of wavelength of light, pearls were irradiated with monochromatic light using the Xe arc lamp with filters : L-39, KL-43 (Toshiba) and CS-4-94 (Corning). Peak wavelength of the filtered light is about 440 nm and full width at half maximum is about 20 nm. The fluorescence and reflection spectra are shown in Figs. 4 and 5 . These spectra are similar to those for the carbon arc lamp though change in spectral shapes are not so prominent as those for the carbon arc lamp. Pearls were also irradiated with light using the high-pressure Hg lamp with a filter: UV-D25 (Toshiba). Peaks of the light are at 312.5 nm, 334.1 nm and 365.5 nm.

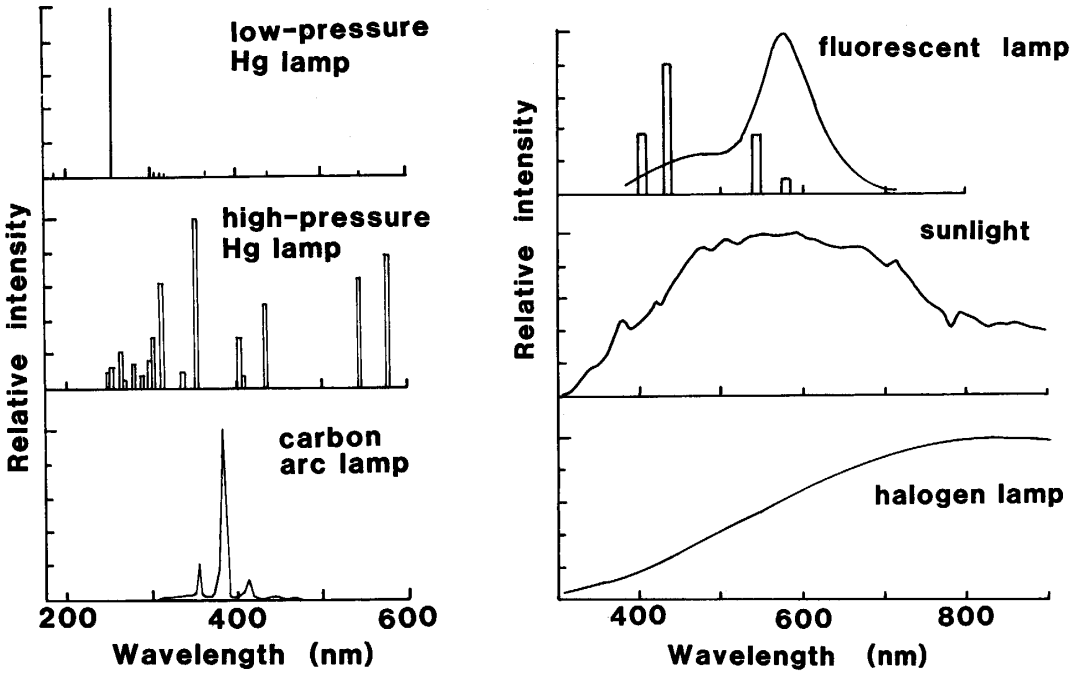

Fig. 3 Spectral distribution of light sources. These data are quoted from catalogues by manufacturers.

The fluorescence and reflection spectra are shown in Figs 4 and 5 . They are similar to those for the low-pressure Hg lamp. These results indicate that the light near 400 nm is effective in discoloring the pigments and the light shorter than about 330 nm is effective in degrading the conchiolin in pearls.

Since the longer-wavelength fluorescnece is attributable to the pigments, the excitation spectrum is measured with the spectrofluorophotometer to examine the properties of the materials. Figure 6 shows the excitation spectra of the 480 nm fluorescence. In the excitation spectrum, the observed wavelength was fixed at 480 nm and the excitation wavelength was scanned. A peak was observed at 380 nm for

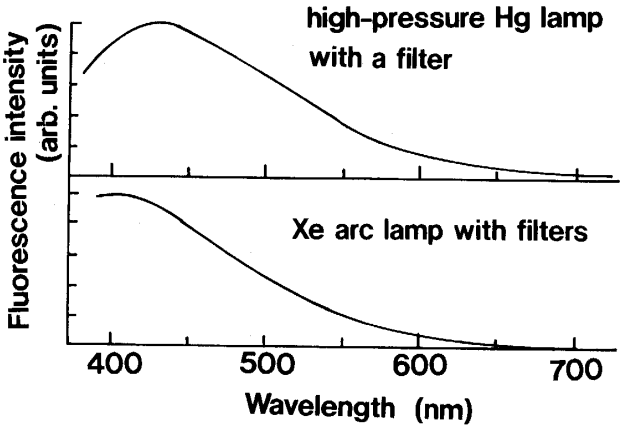

Fig. 4 Fluorescence spectra of pearls after irradiation. Peak intensity ratios are as follows: 2 (high pressure Hg lamp with a filter), 1 (Xe arc lamp with filters).

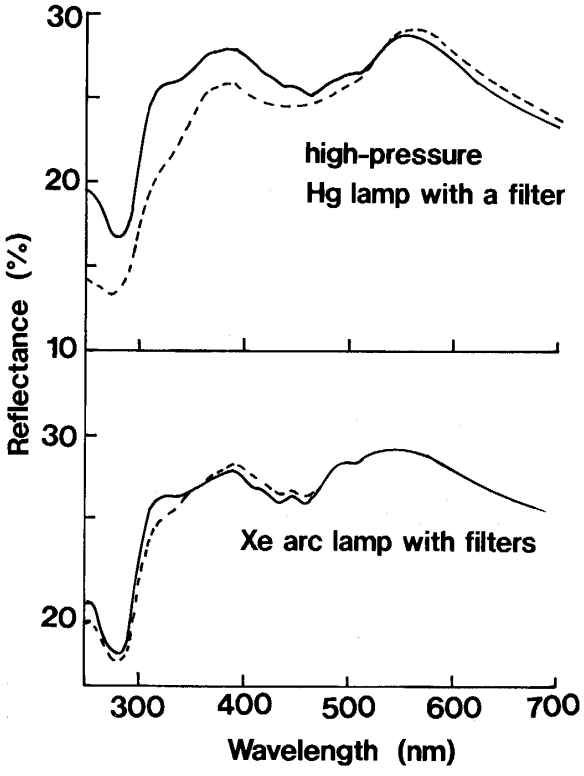

Fig. 5 Reflection spectra of pearls before (solid curves) and after (dashed curves) irradiation.

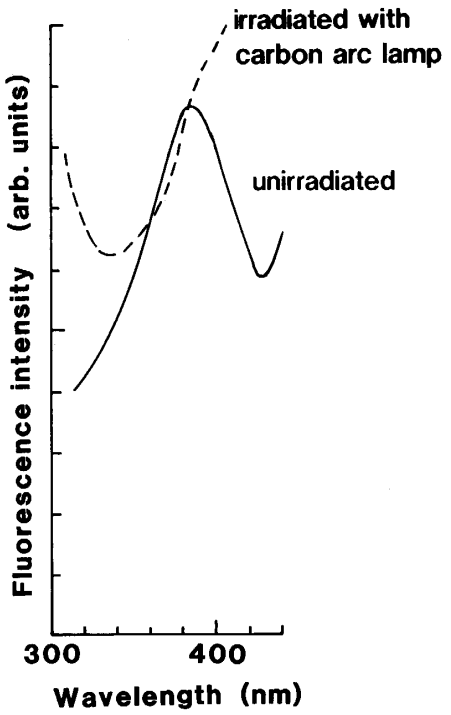

Fig. 6 Excitation spectra of the 480 nm fluorescence of pearl before (solid curve) and after (dashed curve) irradiation with the carbon arc lamp.

the unirradiated pearl (solid curve). This result indicates that the pigments have an absorption peak at 380 nm. Since the 380 nm light is strongly absorbed by the pigments, these materials are effectively discolored with the 380 nm light. The 380 nm peak disappears after irradiation with the carbon arc lamp (dashed curve). This result indicates that the pigments are discolored with light irradiation. The disappearance of the 380 nm peak was not observed for other light sources.

4. Conclusion

Effects of light irradiation on fluorescence and optical reflectance of pearls were examined. It was found that peak wavelength of fluorescence from pearls shifts to shorter wavelength region after exposure to light. Furthermore, change in spectral shape of reflectance was also observed. These changes in spectra are due to degradation of the conchiolin and discoloration of the pigments contained in the nacre. The degree of degradation and discoloration depends on wavelength of light.

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