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Depth-distribution of Fluorescent Species in Silk Fabrics as Revealed by Total Internal Reflection Fluorescence Spectroscopy

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Fluorescence spectra of silk woven fabrics with and without dyes, carthamin and berberin, were measured by using an excimer laser as an excitation pulse. Examining the results obtained with excitation under total internal reflection and normal conditions, a depth-distribution of fluorescent dyes in the silk was considered.

Surface structure and reactivity of solid materials have been studied by various kinds of electron spectroscopy,[1] attenuated total reflection infrared spectroscopy,[2] and Raman scattering measurement under total internal reflection (TIR) condition.[3] Recently, we have demonstrated for the first time a high potential of time-resolved TIR fluorescence spectroscopy for surface photophysics studies.[4,5] This new methodology has the following characteristics. The first is its high time-resolution which makes it possible to measure electronic processes directly in ns ~ ps time region. The second is that fluorescent minor components contained in the materials can be detected, because fluorescence measurement has a high sensitivity and an efficient energy migration to minor fluorescent traps is often involved. As one of the applications of this method, we studied a triply-layered model film composed of 12-(1-pyrenyl)-dodecanoic acid (15 nm thickness), stearic acid (150 nm), and perylene (100 nm).[6] Under TIR condition, a contribution of 12-(1-pyrenyl)dodecanoic acid to fluorescence spectrum was enhanced compared to that of perylene at some delay times, although this layer was thin. In the present work, silk fabrics containing some fluorescent dyes were studied as the second application and their depth-distribution was considered.

Silk woven fabrics was purchased from Tanaka Nao Co. Ltd. Test pieces were dyed with carthamin and berberin according to the literature.[7,8] A piece of dyed silk fabrics was pressed firmly to a sapphire plate ($30 \times 10 \times 2$ mm^3) whose optical alignment is schematically shown in Fig. 1. Under TIR condition, a laser beam penetrates into a fabric with smaller refractive index from the sapphire with a higher value. This is called an evanescent wave and excites the surface area of the attached sample. The details of the TIR fluorescence measurement were the same as reported before.[4,5] This silk-sapphire combination was fixed on a goniometer (Tokyo Kodenshi Co. Ltd.) by which an incident angle was adjusted. In the present work, an incident angle was set to 60°.

Lumonix TE 430T-2 excimer laser (308 nm, 6 ns, 10 mJ) was used as an excitation light source, and its effective diameter was reduced to 1 mm with an aperture. Time-resolved fluorescence spectra at a fixed delay time and time variation of fluorescence intensity were measured by using Jovin Yvon H-10 monochromator, HTV 1P28 photomultiplier, and Iwatsu SAS 601B sampling oscilloscope. Here, fluorescence spectra measured at 10 ns after the beginning of a laser oscillation were analysed.

As shown in Fig. 2 (A), a fluorescence spectrum of silk fabrics consisted of a peak at 340 nm, a shoulder below 400 nm and a descending tail in the longer wavelength region. This spectral shape was independent of the excitation condition, indicating that the silk fabrics has a homogeneous structure along the depth of the yarn.

Fluorescence spectra of a silk dyed with carthamin are shown in Fig. 2 (B). In addition to the fluorescence bands of the silk, a new band due to carthamin was observed around 585 nm. Their relative intensity was sensitive to the excitation condition, namely, the ratio of the dye fluorescence intensity to the silk one under TIR condition was smaller than that under the normal condition. This means that the carthamin concentration in the surface is lower than that in the bulk.

A similar experiment was performed for a silk dyed with both carthamin and berberin. The result is given in Fig. 3 where their concentrations were larger than the concentration of carthamin of Fig.2 (B). A band around 500 nm was assigned to berberin and the band of carthamin was detected as a shoulder in the longer wavelength region. As in Fig. 2 (B) the silk fluorescence was more intense than dye emissions under TIR condition, while the former is negligibly small compared to the latter in the case of normal excitation. These results indicate that a distribution of berberin is also less in the surface area compared to in the bulk and almost similar to that of carthamin.

In conclusion, we have made clear that the fluorescent dyes contained in the silk fiber are not homogeneously distributed along the depth from the surface. This suggests a depth-distribution of chemical reactions such as dyeing, oxidation, photodegradation etc., which have an important role in determining physical and chemical properties of silk fabrics. As far as we know, there is no report on such a depth-profiling of chemical species of the silk yarn. Although a more quantitative analysis is strongly required, there is an experimental difficulty. Namely, the fabric consists of a lot offibers, so that the penetration depth of the evanescent wave is various for each fiber. One of the possible solutions is to measure TIR fluorescence spectra of the silk fabrics with use of a fluorescence microscope, which will

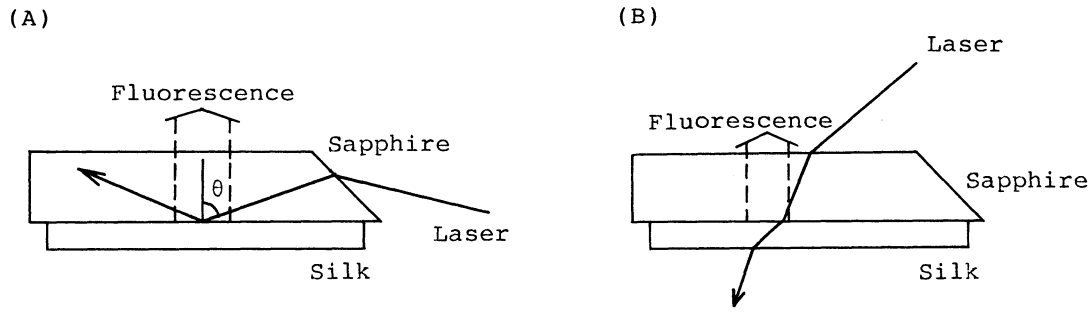

Fig. 1. Optical sets. (a) Total internal reflection condition. (B) Normal excitation condition. θ: Incident angle.

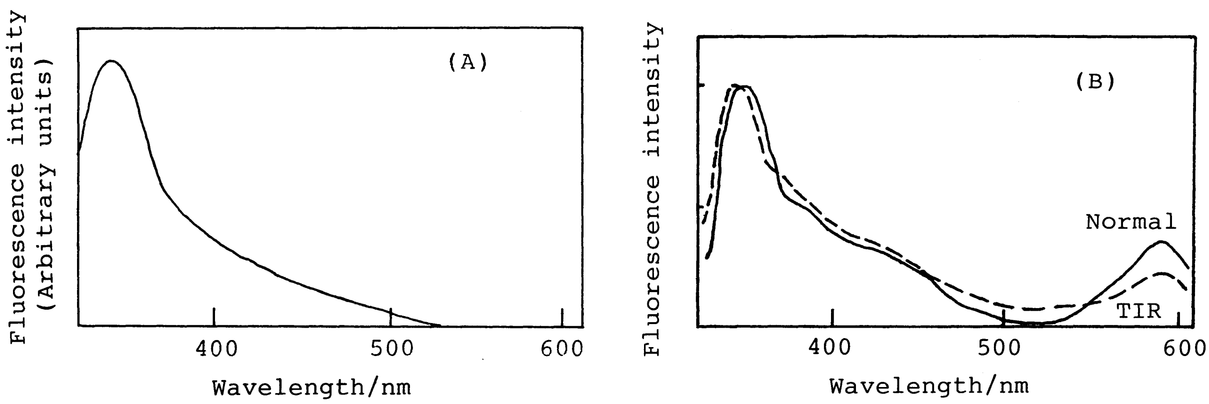

Fig. 2. (A) Fluorescence spectrum of a silk measured under the normal excitation condition.
(B) Normalized fluorescence spectra of a silk dyed with carthamin, measured under total internal reflection and normal excitation conditions.

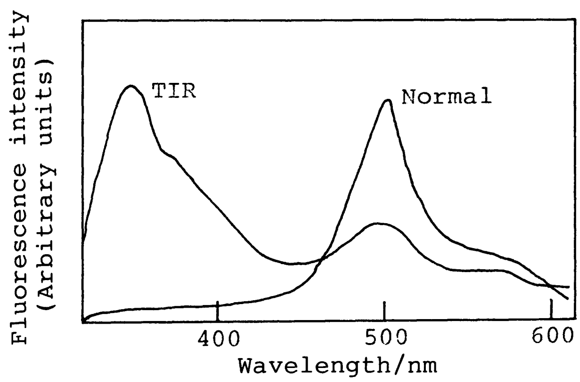

Fig. 3. Fluorescence spectra of a silk dyed with carthamin and berberin, measured under total internal reflection and normal excitation conditions.

be published shortly.[9] This will make it possible to elucidate molecular aspects of fluorescence species in the silk yarn as a function of the depth.

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