Measurement of Translucency of Porcelain Bodies

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磁器素地の透光性測定

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Two methods for evaluating absorption coefficients of porcelain bodies in the visible wavelength range were proposed and applied to Japanese porcelain. The comparative merits of the methods were discussed. Apparent absorption coefficients could be obtained more precisely than conventional ones by measuring the transmittances for different sample thicknesses. Variations in translucency due to compositional change of the porcelain bodies could be explained quantitatively using these coefficients. The scattering and absorption coefficients of bodies were calculated from their reflectances and transmittances using the Kubelka-Munk equations. The accuracy of these coefficients was lower than that of the apparent absorption coefficient because of difficulties in the transmittance measurements. Nevertheless these coefficients were very useful for understanding the optical properties of porcelain bodies. The relationship between the reflectance and scattering coefficient of bodies was also discussed.

[Received December 26, 1995; Accepted June 5, 1996]

Key-words: Absorption coefficient, Transmittance, Porcelain body, Scattering coefficient, Reflectance

1. Introduction

Translucency is one of the most important characteristics to be taken into consideration when developing porcelain bodies by changing their chemical or mineral compositions. The relationship between the translucency and microstructure of a porcelain body was studied in detail by Noguchi and Hamano.^{1,2)} Several studies were also carried out with the aim of increasing the translucency of porcelain.³⁻⁷⁾ Conventional methods for measuring translucency, however, have not been fully validated. The evaluation of translucency by measuring the transmittance of a sample of constant thickness (1 mm) is inadequate.⁸⁾ It should be noted that the transmittance includes not only transmission but also reflection at the surface (Fig. 1). The importance of spectral absorption coefficients in studying the optical properties of porcelain bodies has been emphasized,⁹⁾ although these coefficients have been discussed in only a few studies.⁹⁻¹¹⁾ Absorption coefficients can be obtained in two ways: (1) by measuring the transmittance of the same sample at different thicknesses or (2) by measuring the transmittance and reflectance of a single piece and calculating the coefficients using the Kubelka-Munk equations. The former method has the advantage of giving precise values

and the latter has that of obtaining scattering and absorption coefficients independently. The spectral absorption coefficients of porcelain bodies were obtained only by the latter method.⁹⁻¹¹⁾ Moreover, the measurements of spectral absorption coefficients were incomplete.

In this study, the methods for evaluating translucency were investigated by measuring the absorption coefficients of Japanese porcelain bodies. The comparative merit of the former method in evaluating translucency was also discussed.

2. Theory

The basic theory for analyzing the optical properties of turbid media was reported by Kubelka and Munk¹²⁾ and Ryde.¹³⁾ The application of this theory to the study of porcelain bodies was proposed by Dinsdale⁹⁾ and Hogg.¹⁰⁾

For a dense sample in which incident light is highly scattered before being transmitted through a very short distance compared to the sample thickness, the experimentally observed transmittance (t) and reflectance (r) can be expressed in terms of absorption and scattering coefficients (K and S) as follows:^{12,13)}

$$t = \frac{(1-r_1)(1-r_2)T}{(1-r_2R)^2 - r_2^2T^2} \quad (1)$$

$$r = r_1 + \frac{(1-r_1)(1-r_2)\{R(1-r_2R) + r_2T^2\}}{(1-r_2R)^2 - r_2^2T^2} \approx r_1 + \frac{(1-r_1)(1-r_2)R}{1-r_2R} \quad (2)$$

$$T = \frac{k}{(K+S) \sinh(kd) + k \cosh(kd)} \quad (3)$$

$$R = \frac{S}{K+S+k \coth(kd)} \quad (4)$$

$$k = \{K(K+2S)\}^{1/2} \quad (5)$$

where r_1 , r_2 , and d are the reflection coefficients of the front and back surfaces and the thickness of the specimen, respectively.

The translucency of porcelain bodies can be determined

Fig. 1. Schematic diagram of passage of light through a porcelain body.

from the absorption and scattering coefficients obtained from transmittance and reflectance measurements using these equations. There are, however, some difficulties in obtaining accurate coefficients by this method as described below.

Another method for evaluating the translucency is to obtain the apparent absorption coefficient from transmittance measurements based on Lambert's law. If kd in Eqs. (3) and (4) is large, $\exp(-kd)$ is negligible compared to $\exp(kd)$ and the expression for T can be reduced to the simple form

$$T = (2k/K + S + k) \exp(-kd)$$

(3')

Furthermore, if the attenuation rate of nonscattered light and the thickness of the specimen are sufficiently large that duplicative reflection between the two surfaces can be neglected, then Eq. (1) is rewritten as

$$t = (1 - r_1)(1 - r_2)T$$

(1')

In the higher thickness range, therefore, the transmittance varies with the thickness according to Lambert's law. The absorption coefficient k is obtained from the linear relationship $\log(t)$ vs. d . For a material in which light scattering occurs extensively, the observed absorption coefficient is referred to as the "apparent absorption coefficient". The transmitted light is attenuated by backscattering in the specimen and absorption during multiple scattering; therefore, the effective path length is greater than the sample thickness.

Two methods are used in this study; one based on the Kubelka-Munk equations which are used to understand the optical properties of porcelain bodies semiquantitatively and the other based on Lambert's law for quantitative evaluation of translucency.

3. Experimental

Three types of porcelain bodies were prepared by mixing siliceous stone, Ohira feldspar, and Seto Gaerome clay in weight ratios of (a) 30 : 35 : 35, (b) 30 : 50 : 20 and (c) 30 : 20 : 50 in a ball mill for 24h. Body (a) has a mineral composition typical of porcelain mass-produced in Tokai districts (central Japan). The compositions of bodies (b) and (c) are rich in feldspar and clay, respectively. The chemical compositions of the raw materials and prepared bodies were determined by X-ray fluorescence analysis. A mixed slip was dried and formed into discs (44 mm in diameter and about 2 mm or 10 mm thick) by dry pressing using a metal mold at a pressure of 80 MPa. The specimens were fired at 1300°C under a reducing atmosphere using a gas kiln, at a heating rate of about 100°C/h. The concentrations of CO and CO₂ in the kiln were measured using a gas infrared analyzer. The reducing atmosphere was controlled by keeping the CO/CO₂ ratio at 0.4 after the firing temperature reached 900°C.

The surfaces of the fired specimens were polished using #2000 polishing powder. The particle size of the powder

has been reported to have little influence on the measured transmittance and reflectance values, if it ranges between #2000 and #600 mesh.¹⁴⁾ The specimen had an initial thickness of 2 mm which was reduced by polishing to a thickness of about 0.7 mm (stepwise). The hemispherical diffuse spectral transmittance of several different thicknesses was measured after each polishing step. Diffuse spectral reflectance measurements were carried out using specimens about 10 mm thick and 1 mm thick. In all experiments the samples were backed on to a black box to absorb any transmitted light. The transmittance and reflectance in the visible wavelength range were measured using a Hitachi Color Analyzer 307 double-beam spectrometer fitted with an integrating sphere (JIS Z8722). The surface roughness, R_a , of specimens was measured using a tracer method.¹⁵⁾ To evaluate the degree of vitrification, the shrinkage after firing and the amount of water absorbed were measured and the microscopic structures were observed by scanning electron microscopy (SEM). The crystal phases of the fired bodies were investigated by X-ray diffraction using Cu K α radiation.

4. Results and discussion

4.1 Chemical compositions and microstructures of specimens

The chemical compositions of the prepared bodies were approximately equal to those calculated from the mixing ratios and compositions of the raw materials (Table 1). The iron content of the bodies varied depending mainly on the clay content. A slight increase in the SiO₂ content and a decrease in the Al₂O₃ content were observed, which were considered to result from silica contamination from the porcelain balls or pot used for milling.

Water absorption in all three bodies was less than 0.01%, and hence they were considered to be sufficiently vitrified after firing. The firing shrinkages of bodies (a), (b) and (c) were 8.4%, 9.2% and 8.4%, respectively. Peaks attributed to quartz, mullite and cristoballite were observed in the X-ray diffraction spectra for all bodies. A broad peak at around $2\theta=22^\circ$, which indicates an abundant glassy phase was observed in the spectrum for the body with high feldspar content. Large crystals of quartz or cristoballite and small mullite crystals were observed by SEM. These results show that the three bodies had the same microstructures as those generally observed in conventional porcelain bodies.

The surface roughnesses of specimens after polishing generally vary due to differences in the hardness and microstructures, even when they are polished under the same conditions. The roughnesses, R_a , of bodies (a), (b) and (c) were 0.145, 0.154, and 0.148 μm , respectively, which were small compared to the wavelength of visible light. Therefore, the influence of surface roughness on the optical measurements was considered to be negligible.

Table 1. Chemical Compositions of Raw Materials and Prepared Bodies

Sample	Composition / mass %										
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	Na ₂ O	K ₂ O	MnO	P ₂ O ₅	Ig.loss
siliceous stone	99.80	0.00	0.00	0.02	0.11	0.00	0.00	0.00	0.01	0.00	0.06
feldspar	72.03	15.54	0.10	0.03	1.40	0.00	3.93	6.84	0.01	0.01	0.11
clay	48.48	35.48	1.30	0.74	0.25	0.27	0.18	0.83	0.02	0.03	12.42
body (a)	73.87	16.36	0.39	0.23	0.62	0.05	1.39	2.90	0.01	0.01	4.23
body (b)	75.40	15.35	0.28	0.16	0.76	0.06	1.75	3.74	0.01	0.01	2.50
body (c)	69.89	20.02	0.61	0.34	0.44	0.05	0.66	1.90	0.01	0.01	6.07

Fig. 2. Spectral transmittances of body (a) (solid lines) at thicknesses of 0.86, 1.03 and 1.26 mm, body (b) (dotted lines) at thicknesses of 1.04 and 1.19 mm, and body (c) (dashed lines) at thicknesses of 0.81, 0.96 and 1.21 mm.

4.2 Spectral transmittance

The hemispherical diffuse spectral transmittance of bodies of various thickness was measured; some of the data are shown in Fig. 2.

The thickness of each specimen was measured with an accuracy of 0.001 mm. The maximum difference in thickness within the irradiated area (about 40 mm²) was 0.01 mm. Therefore, the error in thickness was less than 1.5%. The accuracy of the apparatus used to measure transmittance was within 0.002 of the absolute value.

A large transmittance correction is necessary in the case of nonideal contact of the specimen with the integrating sphere because of the thickness (3 mm) of the shell of the integrating sphere. The size of the correction estimated from the transmitted light intensities measured by changing the distance between the specimen and the integrating sphere several times (Fig. 3) was considerable. More precise estimation requires measurement of the angular distribution of the transmitted light. The ratios of the correction to the observed values were almost constant for three bodies with different thicknesses, as expected from angle-dependent calculations in which it was assumed that the light in the specimen is fully scattered. The error due to this correction has no influence on the apparent absorption coefficient calculated using Lambert's law, because it is proportional to the observed value and thus can be canceled out. In this study, the transmittance was not corrected as in other studies,⁹⁾⁻¹¹⁾ although the transmittance error had a direct influence on the absorption and scattering coefficients calculated using the Kubelka-Munk equations.

The actual appearance of a translucent porcelain body can be represented by the spectral transmittance at a cer-

Fig. 3. Observed transmittances of specimens at a distance from the integrating sphere.

○ body (a), □ body (b), △ body (c).

tain constant thickness. The total transmittances of bodies (a), (b) and (c) with a thickness of 1 mm irradiated using a standard illuminants C (CIE) could be calculated from the measured values as 18.9%, 27.4% and 10.2%, respectively. The color of light transmitted by bodies (a), (b) or (c) with a thickness of 1 mm was expressed as 3.4Y 4.90/1.9, 3.7Y 5.77/0.9, or 0.7Y 3.71/3.8 using the Hue Value/Chroma notation in the Munsell Renotation system (JIS Z8721).

4.3 Apparent absorption coefficient obtained in terms of Lambert's law

The log(transmittance)-thickness relation at each wavelength can be regarded as linear in the range of thickness measured (Fig. 4). This result indicates that the relationship can be expressed by Eqs. (1') and (3'). The extrapolated transmittance at zero thickness is mainly due to surface reflection which is slightly different in each body.

The absorption coefficients can be obtained from the slopes of these graphs. Absorption coefficients obtained by this method are not affected by systematic errors proportional to the observed transmittance which originate from imperfections in the preparation of the specimen and in the optical system. Furthermore this method requires only the measurement of transmittance which does not require a standard material. The apparent absorption coefficients for the visible wavelength range from 380 nm to 780 nm were calculated at intervals of 5 nm from the observed transmittance.

Fig. 4. Variation of transmittance with sample thickness for light with wavelengths of 450, 550 and 650 nm.

○ body (a), □ body (b), △ body (c).

Fig. 5. Apparent absorption coefficients of porcelain bodies. solid line : body (a), dotted line : body (b), dashed line : body (c).

tance values (Fig. 5). The error in the coefficients obtained in this study was estimated to be about 5%, which stems from a combination of the errors in thickness and transmittance measurements. This method has advantages in the evaluation of translucency because reliable data can easily be obtained experimentally.

The apparent absorption coefficients of body (b) were about 1.0 mm^{-1} in the wavelength range from 500 to 750 nm, whereas those of the body with higher feldspar content were lower and almost constant over the entire visible wavelength range. The coefficients in the short wavelength range (380–600 nm) increased markedly with increasing clay content. These results are consistent with the empirically established fact that increased feldspar content enhances the translucency of a porcelain body. The apparent absorption coefficients obtained in this study expressed quantitatively the variations in translucency with composition.

The minimum values of the absorption coefficients of bodies (a), (b) and (c) were 0.89 mm^{-1} at 640 nm, 0.58 mm^{-1} at 600 nm and 1.50 mm^{-1} at 650 nm, respectively. The minimum value appears to determine the actual translucency of a porcelain body in daylight. The total absorption coefficients of bodies (a), (b) and (c) for incident light of standard illuminants C were 0.95, 0.61 and 1.90 mm^{-1} , respectively.

4.4 Absorption and scattering coefficients

The absorption and scattering coefficients of the three bodies (Figs. 6 and 7) were calculated from the observed transmittance and reflectance using the Kubelka-Munk equations. In this calculation, the boundary reflection coefficients for parallel light incident normally on the front surface and scattered light incident on the inside surface were assumed to be 0.06 and 0.5 as was assumed by Hogg.¹⁰ The Kubelka-Munk equations are based on the assumption that light in the sample is completely scattered.¹³ The accuracy of the calculated coefficients is reduced due to these assumptions. Nevertheless absorption and scatter-

Fig. 6. Absorption coefficients of porcelain bodies.
solid line : body (a), dotted line : body (b), dashed line : body (c).

Fig. 7. Scattering coefficients of porcelain bodies.
solid line : body (a), dotted line : body (b), dashed line : body (c).

ing coefficients are very useful in understanding the optical properties.

The variation of the absorption coefficients with wavelength showed almost the same tendency as that of the apparent absorption coefficients: a marked increase at the blue end of the spectrum and slight increase at the red end if the body has a large clay content. The variation of absorption coefficients in the short wavelength range was proportional to the iron content. The relationship between the absorption coefficient and the iron content could be obtained quantitatively by measuring the coefficients of bodies with widely varied compositions. The profiles of the absorption coefficients of bodies (a) and (b) were similar to that of English hard porcelain,¹⁰ although the firing temperature and composition of hard porcelain are quite different from those of bodies (a) and (b). The scattering coefficients of the three bodies were smaller than that of hard porcelain.

These variations of absorption and scattering coefficients are strongly related to the chemical compositions and microstructures of the bodies. Absorption in porcelain bodies is mainly due to absorption by transition metal ions in the crystalline or glassy phase.¹⁰ The factors controlling the scattering coefficient are considered to be the distributions of crystalline substances, glassy phases and pores and their refractive indices.⁸ Absorption and scattering coefficients obtained using the Kubelka-Munk equations are considered to be very useful in studying the relationship between translucency and these factors.

The apparent absorption coefficient is related to the absorption and scattering coefficients by Eq. (5). The calculated apparent absorption coefficients of the three bodies were different by $\pm 20\%$ from the observed values. This disagreement is considered to be due to errors in the assumed reflection coefficients of the surfaces and the simplified equations used to calculate the absorption and scattering coefficients. In order to obtain more precise values for the scattering and absorption coefficients using the Kubelka-Munk equations, precise values for the transmittance and reflectance of many specimens with different thicknesses and the application of more complex equations¹³ are necessary.

The apparent absorption coefficients were, therefore, more appropriate for quantitative evaluation of translucency. Nevertheless, scattering and absorption coefficients obtained independently are very useful in understanding the optical characteristics of porcelain bodies.

4.5 Reflectance and optical characteristics of porcelain bodies

The diffuse spectral reflectances of bodies with thicknesses of about 10 mm and about 1 mm were measured for normal incidence (Fig. 8). The reflectances of bodies (a) and

Fig. 8. Reflectances of thick specimens (solid lines) and thin specimens (dotted lines).

(b) varied depending on their thickness, while in the case of body (c), there was little variation. The refractive index and the reflectances of the front and back surfaces (r_1 and r_2) were calculated using Eqs. (1), (1'), (3') and the Fresnel formula.¹⁶⁾ The calculated refractive indices of the three bodies were in the range of 1.15–1.4, and were smaller than expected from refractive indices of feldspathic glass in porcelain.²⁾ More accurate values for the refractive indices could be obtained by measuring (1) the absorption and scattering coefficients more precisely and (2) the angular distribution of the scattered light in the specimens. The reflectivity of the front surface is, however, calculated as being in the range of 0.002–0.05 corresponding to a refractive index in the range from 1.1 to 1.6. Most of the reflected light was considered to be back-scattered from the interior of the specimen. The similarity between the scattering coefficient (Fig. 7) and the reflectance of the thin bodies (Fig. 8) was consistent with this assumption. The difference between the reflectances of the thick and thin specimens indicated that the light reflected by the thick specimen included light scattered from regions in the specimen deeper than 1 mm from the front surface. This difference was smaller in the wavelength region of 500–650 nm for which the absorption coefficient was larger.

These results indicate that reflectance, which is strongly related to whiteness, was influenced only by scattering in the case of thin porcelain bodies while in the case of thick porcelain bodies, it was also influenced by absorption.

A new method of characterizing the optical properties of porcelain bodies by simple measurements has been developed.⁸⁾ In this method, the optical characteristics are related to the transmittance and reflectance of a sample 2 mm thick. The total transmittance and reflectance of body (a) with a thickness of 2 mm calculated from the observed values were 7.3% and 70%, respectively. Body (a) had characteristics more similar to those of American porcelain than those of continental porcelain.⁸⁾ Improvement in this method such that variations in transmittance and reflectance with thickness are taken into account is expected.

Reflectances of bodies for normal incidence were measured in this study. The actual appearance of porcelain must be evaluated precisely by measuring the reflectance for diffuse incidence. Nevertheless, the experimental results indicate that absorption and scattering strongly influence the appearance of porcelain. The absorption and scattering coefficients are also important characteristics in the study of reflectance.

5. Conclusions

Two methods for obtaining spectral absorption coefficients were applied to Japanese porcelain bodies.

The absorption coefficients could be measured precisely by evaluating the transmittance of a sample of variable thickness at a number of different points. The differences between the translucencies of three bodies with different compositions could be quantitatively represented in terms of these coefficients.

The absorption and scattering coefficients calculated using the Kubelka-Munk equations were very useful as characteristics of translucency, although there were errors in the data used to calculate these coefficients, as indicated by measuring several specimens at different distances from the aperture of the integration sphere.

For the purpose of practical evaluation of the translucency of porcelain bodies, the "apparent absorption coefficient" is appropriate because of it is reliable and easy to measure precisely. However, few values for the apparent absorption coefficients of porcelain bodies have been reported. The spectral apparent absorption coefficients reported in this study will be useful in developing porcelain bodies with improved optical properties.

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