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Color and Luminescence Stability of Selected Dental Materials In Vitro

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Abstract

Purpose: To study luminescence, reflectance, and color stability of dental composites and ceramics.
Materials and Methods: IPS e.max, IPS Classic, Gradia, and Sinfony materials were tested, both unpolished (as-cast) and polished specimens. Coffee, tea, red wine, and distilled water (control) were used as staining drinks. Disk-shaped specimens were soaked in the staining drinks for up to 5 days. Color was measured by a colorimeter. Fluorescence was recorded using a spectrofluorometer, in the front-face geometry. Time-resolved fluorescence spectra were recorded using a laser nanosecond spectrofluorometer.
Results: The exposure of the examined dental materials to staining drinks caused changes in color of the composites and ceramics, with the polished specimens exhibiting significantly lower color changes as compared to unpolished specimens. Composites exhibited lower color stability as compared to ceramic materials. Water also caused perceptible color changes in most materials. The materials tested demonstrated significantly different initial luminescence intensities. Upon exposure to staining drinks, luminescence became weaker by up to 40%, dependent on the drink and the material. Time-resolved luminescence spectra exhibited some red shift of the emission band at longer times, with the lifetimes in the range of tens of nanoseconds.
Conclusions: Unpolished specimens with a more developed surface have lower color stability. Specimens stored in water develop some changes in their visual appearance. The presently proposed methods are effective in evaluating the luminescence of dental materials. Luminescence needs to be tested in addition to color, as the two characteristics are uncorrelated. It is important to further improve the color and luminescence stability of dental materials.

Appearance affects a person's quality of life, status, and self-assessment. Thus, healthy-looking teeth are an important and desired attribute affecting self-esteem and self-assurance. Therefore, the aesthetic aspect of dental care has an ever-increasing importance. An important practical problem is to produce dental materials in a hue matching that of natural tooth tissue and capable of maintaining it in the oral cavity for years. Materials with improved adhesion to hard tooth tissue and improved physical, chemical, and aesthetic properties are becoming increasingly available. Still, most of these materials suffer deterioration to some degree: they get dark and lose transparency and luster.[1] Factors responsible for the deterioration include staining drinks and elevated temperatures.[2,3] These external influences make the proper choice of the material hue more difficult.[4] Most often the choice is made by comparison to standards (a color key), as color perception depends on lighting conditions and surroundings, with some individual variability. Thus, a rigorous method, color mixing, based on spectral techniques has been introduced.[5,6] In the 1980s Yamamoto began studying material color in dentistry.[7,8]

Usually color is described in terms of the L*, a*, b* coordinates, as defined by CIE (Commission Internationale de l'Eclairage).[9] Another set of color parameters we shall use includes hue (H), chroma, (C), and lightness (L) and is more directly related to human perception of color.[10]

Recently, composite materials began to be additionally characterized by the so-called optical properties, including luminescence; this term describes emission of light by a material that absorbs UV or visible light. Ideally, a restorative material should have luminescence similar to that of natural tooth tissue. There is some understanding that luminescence can be used as a tool to identify a restorative material, distinguish it from natural tooth tissue, and allow it to be examined after staining.[11-20] In fact, luminescence is becoming more important due to widespread use of artificial lighting with blue or UV contributions. Thus, our present objective is to evaluate the changes in luminescence of selected composite materials due to staining drinks.

Materials and methods

As a natural way to study luminescence, spectral measurements using the diffuse reflectance method were performed to monitor the effects of staining treatment. In addition to the usual spectral measurements, we performed colorimetric measurements to evaluate the in vitro color stability of dental composites exposed to staining agents such as coffee, tea, and red wine.

Coffee, tea, red wine, and distilled water were used as staining liquids. Staining liquids were prepared once, with the same portion used for each specimen during the entire soaking time. Disk-shaped specimens were soaked in the staining liquids for up to 5 days, with the same specimen of each material used in all immersion intervals. One specimen of each material was immersed into each of the staining liquids. The study was performed on four materials for aesthetic dental restoration in A.2 shade, using both unpolished (as-cast) and polished specimens. Two ceramic materials, IPS e.max and IPS Classic (Ivoclar Vivadent AG, Schaan, Lichtenstein, Germany), and two composite materials used in prosthetics, Gradia (GC Europe, Leuven, Belgium) and Sinfony (3M ESPE, Seefeld, Germany) were chosen for study. Solid specimens (6 mm diameter, 1.5 mm thick) were prepared in a special mold, giving all specimens the same size and shape. A GC Labolight LV-III fluorescent light-curing unit was used for 4 minutes to polymerize Gradia specimens. Sinfony specimens were polymerized using a Visio^{TM} Beta Vario (Vita, Bad Säckingen, Germany) light unit for 4 minutes. Specimens of ceramic materials had one layer, and were fired at 750°C for IPS e.max and 920°C for IPS Classic. After polymerization, the specimens were polished on the two main surfaces with Polityp P rubber (Ivoclar Vivadent AG) and washed with distilled water. Unpolished specimens were also examined to verify the importance of proper polishing for color stability.

Staining liquids

The tests on the materials studied were performed using the following liquids.

Coffee: 60.0 g of coffee (Jacobs Kronung, Kraft Foods, Warsaw, Poland) was added to 1.00 dm^3 of distilled water and boiled for 10 minutes; the liquid obtained was filtered through a paper filter and supplemented with distilled water to 1.00 dm^3.

Tea: 10.0 g of black tea (Lipton Tea, Lipton, Warsaw, Poland) was added to 1.00 dm^3 of distilled water and boiled for 5 minutes; the liquid obtained was filtered through a paper filter and supplemented with distilled water to 1.00 dm^3.

Red wine: was used as commercially available (Tio de la Bota, Spain).

Distilled water: was used for control to soak the control specimens.

Tests

Prior to the tests, the specimens of the composites tested were subjected to color determination. Next, the specimens were immersed individually in 40 ml of the staining liquids in Petri dishes and stored at 37°C for 0.5, 1.5, 3.0, 6.0, 12, 24, 48, 70, and 116 hours. The practical relevance of the exposures to staining liquids for periods of days follows from the following estimate: 3 coffees per day times 1 minute of exposure per cup times 365 days per year, for a total of 1095 minutes, or more than 18 hours of exposure per year.

After each of these time intervals, the specimens were washed by making 10 immersions in distilled water, dried with a paper towel, and subjected to color determination on the two main surfaces. The luminescence of all of the specimens was measured after the respective immersion time followed by washing and drying. After the color measurements, all specimens were immersed again in the staining liquids, and the same procedure was repeated after the next time interval. Luminescence was measured for one specimen of each material and each shade before the immersion in the staining liquids and after 5 days of their storage in these liquids.

The luminescence spectra were measured on a Fluorolog 3–11 Spex spectrofluorometer (Horiba Jobin Yvon Inc., Kyoto, Japan). The measuring system of the spectrofluorometer was interfaced to the system for data collection and analysis using the DataMAX software working in the MS Windows environment. Fluorolog 3–11 was equipped with individual monochromators at the input and output of the optical signal, a 450 W xenon lamp and an R928 photomultiplier detector. The xenon lamp was warmed up for about 45 seconds for stable performance. An attachment for solids was used to mount the specimens. To determine the total luminescence spectra of the specimens, the luminescence measurements were repeated as the excitation wavelength was changed at the 10 nm step. Such measurements permitted us to obtain 3D spectra in the coordinates of excitation wavelength, emission wavelength, and luminescence intensity. Contour maps were produced from the 3D spectra, to facilitate their visual presentation.

Reflectance measurements

Reflectance spectra were measured using a Specord M-42 spectrophotometer (Carl Zeiss Inc., Thornwood, NY), equipped with a Labsphere integrating sphere. The remission function F(R) was obtained by calculating the Kubelka–Munk function for an ideal diffuse scatterer, which is optically thick at the

wavelength of interest, assuming a homogeneous distribution of absorbers throughout the specimen[21]

$$F(R) = \frac{(1-R)^2}{2R} = \frac{K}{S} \quad (1)$$

where R represents the observed diffuse reflectance from the specimen surface, and K and S are absorption and scattering coefficients, respectively, both measured in (distance)$^{-1}$ units.[22,23] For an ideal diffuser, where the radiation is isotropic, the F(R) value is proportional to K, which in turn is proportional to the absorber concentration.

Color measurements were made using a Konica Minolta CM-2600d spectrocolorimeter (Konica Minolta Sensing Inc., Ramsey, NJ). The D65 illuminant was used in all experiments. The location of a color in the CIE LAB color space is defined using a 3D Cartesian coordinate system. The lightness value (L^*) indicates how light or dark a color is. The a^* and b^* values indicate the location on the green(−)/red(+) and blue(−)/yellow(+) axes, respectively. Tables 1 to 3 list the measured color parameters (L^*, a^*, b^*) for Sinfony, and representative data for all materials. The L^*, a^*, and b^* data were also used to calculate other parameters, which directly correlate to the visually perceived color attributes: the hue angle, h°, and chroma, C. The latter two are related to the color attributes, hue and color saturation, respectively. By definition, the hue angle is $h^o = \text{arc tan } (b^*/a^*)$, and chroma is $C = [(a^*)^2 + (b^*)^2]^{1/2}$. The CIELAB color difference values (ΔE_{ab}) were calculated to provide a quantitative measure of color changes, as

$$\Delta E_{ab} = [(L_0 - L)^2 + (a_0^* - a^*)^2 + (b_0^* - b^*)2]^{1/2} \quad (2)$$

where L_0, a_0^*, b_0^* are the respective color parameters of the starting specimens, $\Delta L^* = L_0 - L$ is the difference in lightness, $\Delta a^* = a_0^* - a^*$ is the difference in red-green coordinate and $\Delta b^* = b_0^* - b^*$ is the difference in yellow-blue coordinate. According to some authors, these values have been found to correlate well with average visually perceived color differences.[24] The color difference ΔE_{ab} is simply the Euclidian distance between points in the CIELAB color space; however, CIELAB is not without its problems. For example, a number of researchers have conducted visual experiments that show color differences perceived by humans are not uniform across the CIELAB color space. Thus, in 2000 CIE recommended a new CIEDE2000 color difference formula, to be used mainly for evaluating small color differences (fewer than 5 ΔE_{ab} units). Color difference, ΔE_{00}, is defined according to this formula as[10]

$$\Delta E_{00} = [[\Delta L'/(k_L S_L)]^2 + [\Delta C'/k_C S_C)]^2 + \Delta H'/(k_H S_H)]^2 + R_T[\Delta C'/(k_C S_C) \times \Delta H'/(k_H S_H)]]^{1/2} \quad (3)$$

Here, ΔL', ΔC', and ΔH' are the differences in lightness, chroma, and hue; for a detailed definition the reader is referred to the original paper by Luo et al,[10] especially for the formula to calculate the hue difference, which is not a simple absolute value of the difference, an error often encountered on the Internet. Additionally, S_L, S_C, and S_H are the weighting functions for the lightness, chroma, and hue components, respectively, while k_L, k_C, and k_H are the parametric factors to be adjusted according to different viewing parameters. Still, despite its advantages, equation (3) is a more complex formula than equation (2), therefore, its usage is more limited.

Table 1 Color parameters of unpolished specimens of Sinfony soaked in coffee, tea, wine, and distilled water (control)

Liquid/time (hours)	L*(D65)	a*(D65)	b*(D65)	ΔE_{ab}(D65)	ΔE_{00}(D65)
0 (mean)[1]	72.26	0.22	12.07	0.36	0.26
Water					
0.5	71.79	0.34	12.73	0.97	0.66
1.5	71.6	0.16	12.37	0.72	0.50
3	72.05	−0.02	12.33	0.56	0.43
6	70.76	0.06	12.02	1.30	0.99
12	70.69	−0.02	11.96	1.36	1.05
24	70.83	−0.16	11.72	1.24	1.01
48	71.07	−0.22	11.10	1.25	1.00
70	70.01	−0.14	11.76	2.04	1.59
116	69.59	−0.09	11.77	2.45	1.90
Coffee					
0.5	71.02	−1.30	13.76	2.65	2.35
1.5	70.22	−0.95	15.79	4.52	3.13
3	69.53	−0.66	16.87	5.72	3.76
6	68.50	−0.60	16.88	6.23	4.22
12	67.14	−0.30	18.03	7.94	5.36
24	66.71	−0.28	17.72	7.98	5.50
48	65.37	0.45	19.86	10.46	7.04
70	67.11	−0.60	14.17	5.52	4.22
116	66.34	−0.09	18.48	8.78	5.97
Tea					
0.5	71.59	−0.77	10.95	1.34	1.41
1.5	70.88	−0.42	12.49	1.47	1.25
3	70.19	−0.02	13.16	2.29	1.67
6	68.65	0.07	12.60	3.48	2.66
12	68.36	0.04	14.01	4.29	3.17
24	68.14	0.02	13.96	4.46	3.31
48	67.51	0.24	13.15	4.72	3.61
70	65.91	0.82	16.16	7.54	5.54
116	67.74	−0.04	12.16	4.31	3.35
Wine					
0.5	71.93	0.30	12.60	0.82	0.55
1.5	70.04	0.44	14.05	3.02	2.11
3	70.22	0.82	14.74	3.51	2.43
6	68.10	0.20	15.27	5.25	3.73
12	66.55	0.56	17.67	8.04	5.56
24	65.35	0.09	16.78	8.33	6.06
48	67.65	0.17	13.09	4.57	3.49
70	69.47	−0.16	13.40	3.04	2.26
116	68.31	−0.45	15.32	5.16	3.69

[1] Average values, calculated for 12 starting specimens. The respective ΔE_{ab} and ΔE_{00} characterize variation within the set of the starting specimens and can be used as standard deviations to estimate the significance of measured changes.

Luminescence is a generic term describing both the short-lived emission from singlet excited states, fluorescence, and the long-lived emission from triplet excited states, phosphorescence. A given specimen may exhibit either fluorescence, or phosphorescence, or both. The laser-induced luminescence (LIL) setup uses short laser pulses to excite luminescent species

Table 2 Color parameters of unpolished specimens of the dental composites and ceramics soaked in coffee, tea, wine, and distilled water (control)

Liquid/time	IPS e.max					IPS Classic					Gradia					Sinfony				
(hours)	L*	a*	b*	ΔE_{ab}	ΔE_{00}	L*	a*	b*	ΔE_{ab}	ΔE_{00}	L*	a*	b*	ΔE_{ab}	ΔE_{00}	L*	a*	b*	ΔE_{ab}	ΔE_{00}
0 (mean)[1]	85.12	1.25	18.62	0.16	0.09	85.59	0.55	19.38	0.19	0.14	82.96	1.36	18.17	0.15	0.11	83.60	2.74	22.80	0.25	0.26
Coffee																				
24	83.58	1.66	19.43	0.98	0.64	84.49	1.02	19.19	0.73	0.51	68.44	8.04	32.51	22.02	13.94	66.71	−0.28	17.72	9.71	5.50
70	83.71	1.82	19.76	0.77	0.59	85.10	0.73	17.55	2.14	1.33	67.15	8.31	32.39	22.98	14.83	76.65	5.33	29.04	9.58	4.22
Tea																				
24	82.29	2.09	19.17	2.31	1.62	83.38	1.54	18.84	0.63	0.53	64.83	10.07	28.71	23.59	16.64	68.14	0.02	13.96	9.74	3.31
70	82.46	2.26	19.0	2.25	1.65	83.49	1.69	19.23	0.59	0.60	64.88	10.15	28.87	23.64	16.64	74.94	6.35	28.94	11.09	5.54
Wine																				
24	84.75	1.49	18.84	1.57	0.93	86.79	0.56	13.18	1.83	1.10	76.04	5.78	18.83	11.52	9.34	80.30	3.41	25.68	5.43	5.06
70	83.81	1.85	19.87	0.67	0.55	84.54	0.91	17.45	1.90	1.10	74.14	5.57	19.12	11.13	8.67	78.61	3.73	26.84	6.41	2.26
Distilled water																				
24	85.32	0.70	18.01	1.81	1.19	86.67	0.64	12.93	1.59	0.89	84.61	0.82	18.90	0.32	0.22	82.03	3.15	22.85	1.78	1.01
70	84.64	0.89	19.40	0.88	0.72	83.75	1.25	18.00	1.18	0.65	83.58	0.99	18.41	0.88	0.55	81.62	3.18	22.49	1.92	1.59

[1] Average values, calculated for 12 starting specimens. The respective ΔE_{ab} and ΔE_{00} characterize the variation within the set of the starting specimens and can be used as standard deviations to estimate the significance of measured changes.

Table 3 Color parameters of polished specimens of the dental composites and ceramics soaked in coffee, tea, wine, and distilled water (control)

Liquid/time	IPS e.max					IPS Classic					Gradia					Sinfony				
(hours)	L*	a*	b*	ΔE_{ab}	ΔE_{00}	L*	a*	b*	ΔE_{ab}	ΔE_{00}	L*	a*	b*	ΔE_{ab}	ΔE_{00}	L*	a*	b*	ΔE_{ab}	ΔE_{00}
0 (mean)[1]	74.93	0.95	14.34	0.16	0.13	75.4	0.43	13.77	0.17	0.13	78.39	0.48	16.31	0.12	0.09	73.08	0.32	12.88	0.03	0.03
Coffee																				
24	73.75	0.81	13.35	1.53	1.06	76.71	0.47	11.89	0.68	0.47	74.78	1.01	18.06	3.48	2.46	68.85	0.46	16.99	7.21	4.82
70	73.51	0.89	13.64	1.71	1.22	75.56	0.69	13.49	0.54	0.48	74.34	1.23	18.74	4.75	3.29	68.90	0.57	15.91	5.18	3.70
Tea																				
24	74.49	0.99	14.02	0.68	0.49	73.37	0.96	13.72	2.10	1.66	76.14	0.81	16.78	2.12	1.57	69.58	0.57	13.62	4.57	3.46
70	74.08	1.14	14.07	1.02	0.75	72.54	1.32	13.60	2.85	2.31	75.48	1.06	16.90	2.97	2.18	68.51	0.74	13.80	4.68	3.59
Wine																				
24	73.45	1.06	13.80	1.73	1.26	73.67	0.67	12.80	2.75	2.00	74.71	3.69	13.03	6.35	5.86	69.63	0.58	12.53	5.70	4.47
70	72.46	1.22	14.03	2.59	1.92	72.60	0.97	11.96	3.28	2.41	73.04	4.42	12.22	7.72	7.05	68.93	0.24	12.21	4.21	3.21
Distilled water																				
24	74.32	0.79	13.54	0.63	0.47	75.38	0.30	13.52	0.80	0.59	77.17	0.35	15.18	1.54	0.98	71.54	0.07	12.31	1.34	1.04
70	74.14	0.86	14.06	0.97	0.71	75.22	0.27	13.31	0.53	0.36	76.75	0.26	14.55	2.30	1.50	70.43	0.02	11.59	2.97	2.22

[1] Average values, calculated for 12 starting specimens. The respective ΔE_{ab} and ΔE_{00} characterize the variation within the set of the starting specimens and can be used as standard deviations to estimate the significance of measured changes.

existing in the specimen and obtains their detailed characteristics by recording time- and spectrally resolved emission. All measurements were performed at room temperature in the front-face arrangement on a system built in Lisbon. A detailed description together with a diagram of the system was presented by Botelho do Reso et al.[25] Briefly, the system uses the 337.1 nm pulse of a N_2 laser (Photon Technology Instruments, London, Ontario, Canada, Model PL-2300, ca. 600 ps FWHM, ~1.3 mJ/pulse) as the excitation source. At the detection site a gated intensified charge-coupled device (ICCD, Oriel model Instaspec V, Newport, Irvine, CA) is used to collect light arising from the specimens and provide the required time resolution. The ICCD is coupled to a fixed compact imaging spectrograph (Oriel, model FICS 77441) providing spectral resolution. The system can be used either by capturing all light emitted by the specimen or in the time-resolved mode by using a delay generator (model DG535, Stanford Research Systems, Sunnyvale, CA) producing a gate pulse of suitable width to select the time interval of interest. The ICCD has high-speed (2.2 ns) gating electronics and covers the 200 to 900 nm wavelength range. Time-resolved emission spectra are thus available in the nanosecond to second time range.[25-27] Because in the majority of cases, luminescent properties are independent of the type of excitation, the present LIL setup adequately characterizes the luminescent properties of the specimens, discriminating the nature of the respective excited states by the time-resolved information provided.

Results

Reflectance spectra

Ground-state diffuse reflectance spectra were collected together with spectrocolorimetric data for all of the dental materials studied before and after immersion in test liquids. Figure 1 shows reflectance spectra of the IPS e.max, IPS Classic, Gradia, and Sinfony dental materials in A.2 shade, and reflectance spectra of Gradia (unpolished) and IPS Classic (polished) after representative times of immersion in tea. The diffuse reflectance spectra are plotted in terms of the remission function F(R) versus wavelength. The two materials selected illustrate the two extreme cases: Gradia, representing an example of a clear effect of immersion on diffuse reflectance spectra, and IPS Classic, representing only a very slight effect of immersion on the spectral properties of dental materials.

Color parameters

Changes in the reflectance properties of the material imply changes both in the visually perceived color and the instrumentally measured color parameters, L^*, a^*, and b^*. The detailed values of color parameters of unpolished specimens of Sinfony soaked in coffee, tea, wine, and distilled water are given in Table 1. The effect of immersion time and staining fluid on color differences in some representative materials is presented in Figure 2. The representative data in function of time are presented in Tables 2 and 3 for all materials and experiments with immersion, for unpolished and polished materials, respectively.

Luminescence contour maps

The characteristics of tooth autofluorescence, and those of dental materials mimicking them, are expected to be quite complex due to overlapping emissions from numerous species, high concentration of fluorophores, and the opaque nature of the materials involved. Therefore, it is necessary to apply multidimensional fluorescence techniques to obtain a comprehensive description of the fluorescent components; otherwise luminescence will be difficult to interpret, for example, because of its apparent dependence on the excitation wavelength. The so-called excitation–emission matrices or total luminescence spectra are 3D spectra, in which one axis represents the excitation wavelength, another the emission wavelength, and the third the intensity (Fig 3, top panel). Alternatively, 3D spectra may be transformed into 2D contour maps (Fig 3A), in which one axis represents the emission and another the excitation wavelength. The contours are plotted by linking points of equal fluorescence intensity. Such a presentation is more practical for visual analysis of the fluorescence patterns. Thus, contour maps were produced to examine the total luminescence emission of the materials studied, with typical examples shown in Figures 4 and 5.

A total luminescence spectrum gives a comprehensive description of a fluorescent material, incorporating the complete information present both in the fluorescence spectra (Fig 3B) and excitation spectra (Fig 3C) of all of the fluorescent constituents. Due to these features, the total luminescence contour map may serve as a unique fingerprint for identification and characterization of the materials. The spectral resolution of an excitation–emission matrix depends on the number of conventional emission scans at different excitation wavelengths used to construct the contour plot. Acquisition of contour maps on conventional spectrofluorometers at sufficient resolution requires a large number of emission scans for each specimen. The analysis may be speeded up with CCD or video-spectrofluorometers; however, such instruments are not widely accessible in laboratories yet.

Laser-induced luminescence (LIL)

The emission spectra of all dental materials excited at 337 nm show a single band with the maximum at about 435 nm for the composite materials and 410 nm for the ceramic materials (Fig 6); however, the most pronounced differences are in the luminescence lifetime, relatively short for composite materials, and much longer for both ceramic materials. Another difference is the luminescence intensity, the luminescence being very weak for Sinfony. The effect of immersion time on the luminescence lifetime was also recorded and is shown in Figure 7.

Discussion

Reflectance spectra

Although all of the presently studied materials were of the A.2 shade, their reflectance spectra show important differences in the long-UV range, being of course very similar in the visible range, responsible for our color perception. As might be

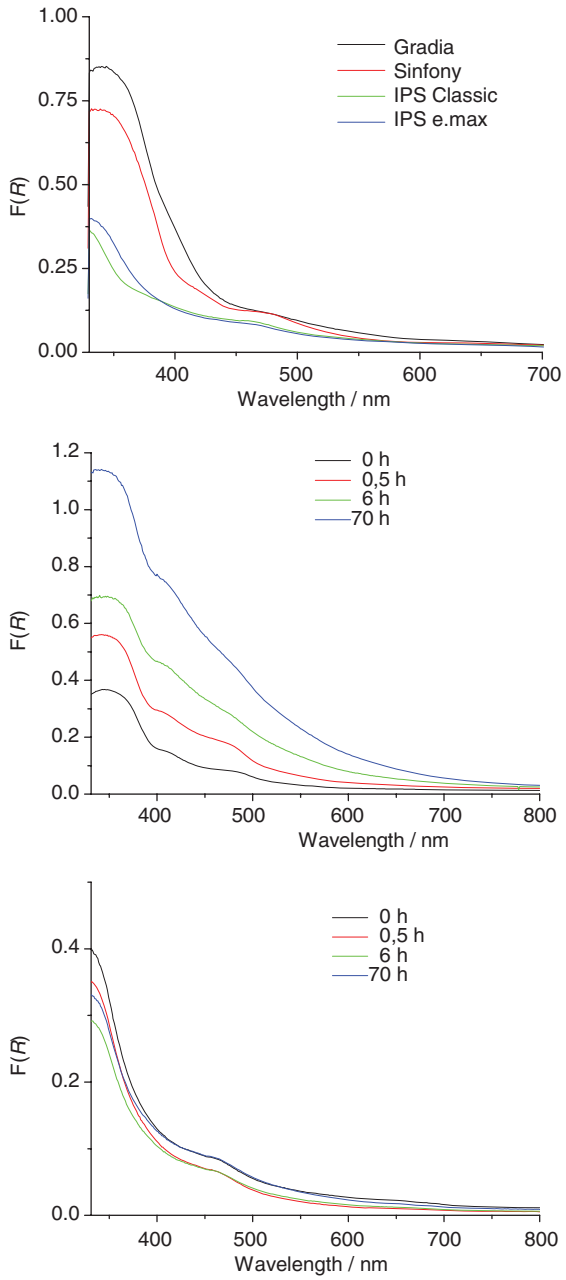

Figure 1 Top panel—reflectance spectra of selected dental materials in A.2 shade: IPS e.max, IPS Classic, Gradia, and Sinfony (all polished) before immersion; middle panel—reflectance spectra of Gradia (unpolished) after representative times of immersion in tea; bottom panel—reflectance spectra of IPS Classic (polished) after representative times of immersion in tea.

expected, IPS materials seem to have lower absorption in the entire spectral range, also including the short-wavelength region. The composite materials have significantly higher absorption at shorter wavelengths, compared to ceramic materials, probably due to their polymeric matrix. The spectra also show some variations in function of the material in the visible range, although, being of the same enamel shade, they are predictably

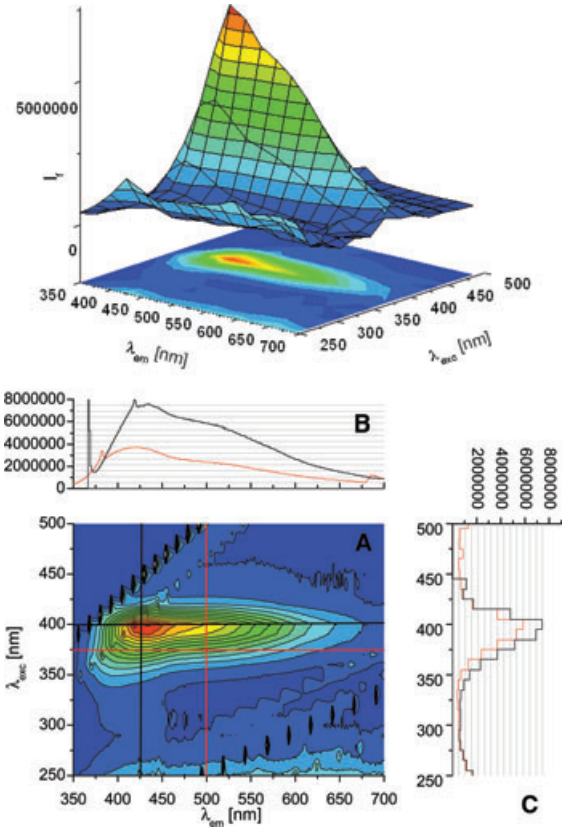

Figure 3 Total luminescence spectra of Sinfonia A.2 after soaking for 116 hours in water (top panel). Bottom panel—the corresponding contour map showing the intensity of luminescence of the same material (A), together with (B) luminescence spectra and (C) excitation spectra extracted from the contour map (A).

similar at longer wavelengths (Fig 1, top panel). The spectra of untreated materials exhibit a broad spectral absorbance band with an intensity increasing toward the shorter wavelengths and an apparent absorption maximum at about 350 nm.

Figure 1 (middle and bottom panels) also shows the reflectance spectra obtained for differently stained dental materials. Gradia soaked in tea is shown as a typical case; the changes in the diffuse reflectance spectrum are easily detected, with the effect similarly evident in both composite materials and even larger in unpolished specimens (data not shown). In contrast, the two ceramic materials were resistant to the staining fluids, with moderate spectral changes at different immersion times. A typical example is presented by the diffuse reflectance spectra of IPS Classic soaked in tea (Fig 1, bottom panel). Polishing of ceramic materials did not make much difference, either for IPS Classic or IPS e.max, which appear to be relatively resistant to staining, even after 5 days of immersion.

Color parameters

Color saturation shows the most pronounced changes for the composite materials Gradia and Sinfony (Tables 1 to 3). In

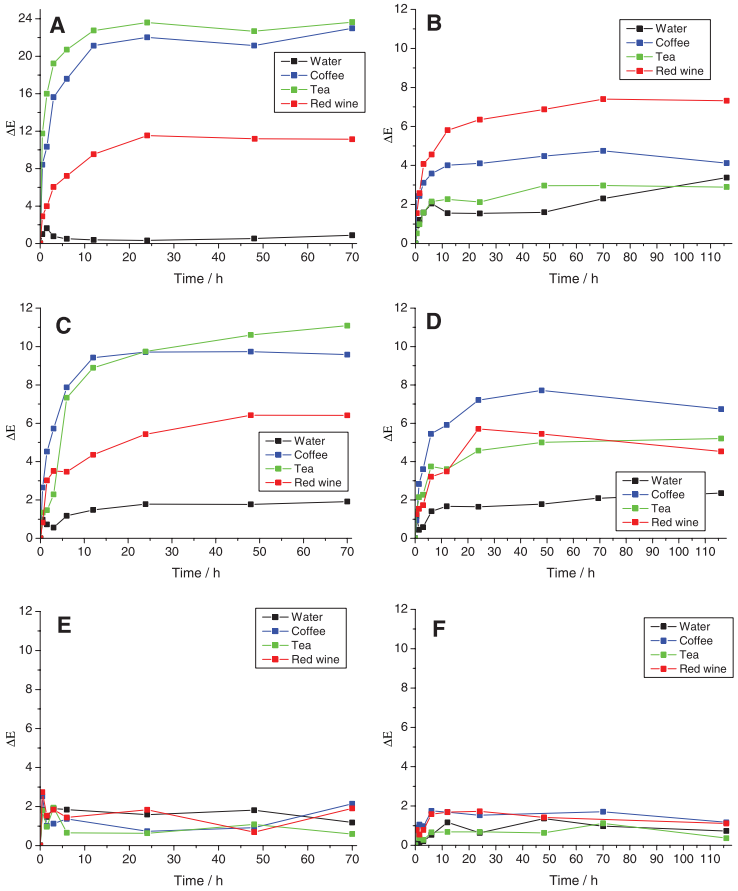

Figure 2 Color changes in: Gradia unpolished (A) and polished (B); Sinfony unpolished (C) and polished (D); IPS Classic unpolished (E); and IPS e.max polished (F). All materials in A.2 shade were kept in staining fluids as indicated.

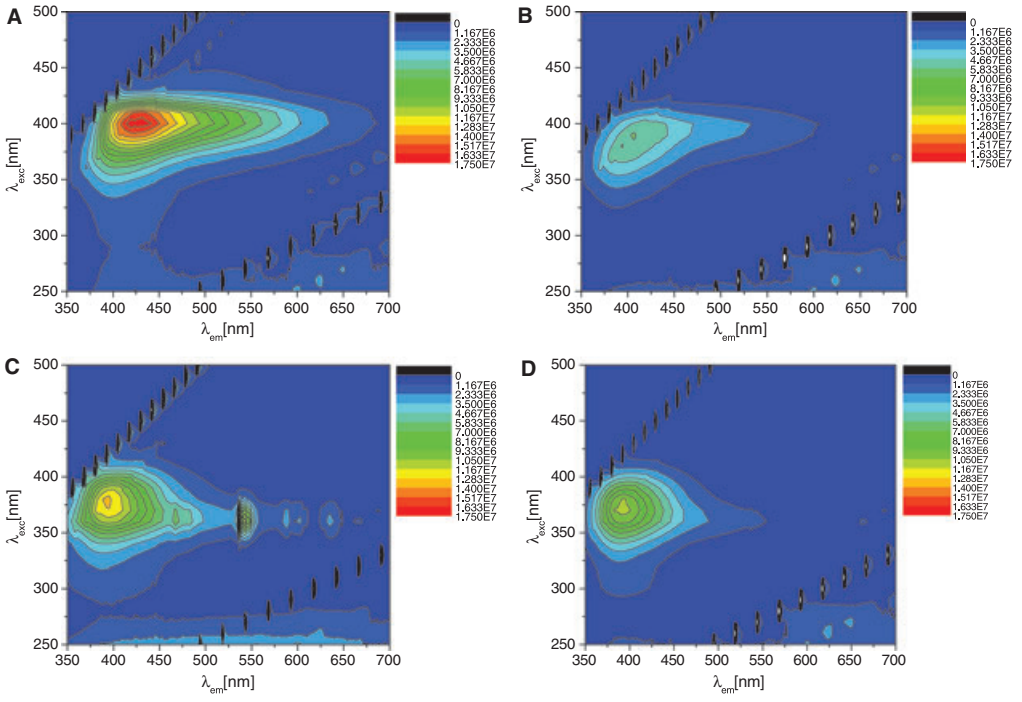

Figure 4 Contour maps presenting the intensity of luminescence of control specimens in A.2 shade of the following polished materials: (A) Gradia, (B) Sinfony, (C) IPS Classic, and (D) IPS e.max.

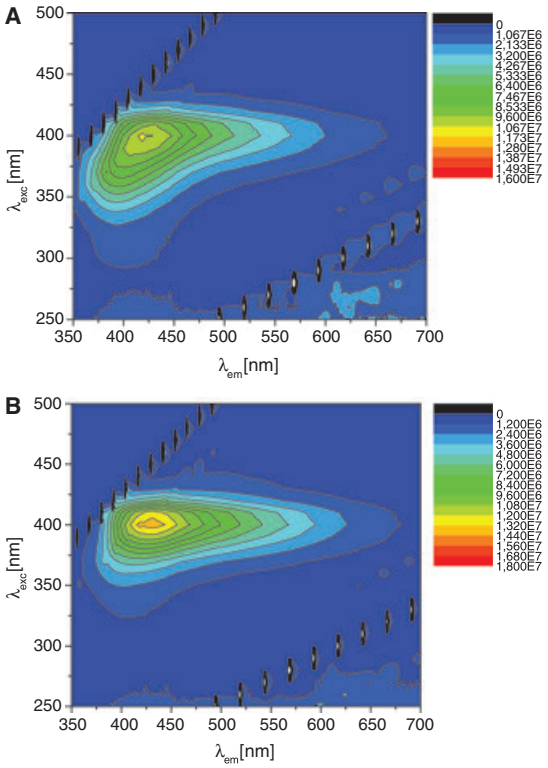

Figure 5 Contour maps illustrating the intensity of luminescence of A.2 specimens of Gradia after 5 days of experiment: (A) soaked in tea and (B) soaked in red wine.

contrast, ceramic materials were not affected significantly by staining fluids.

It is commonly assumed that a change in each of the CIELAB color coordinates by one unit is a threshold of color difference perception by an average, although trained, observer. According to CIE, the threshold value of color perception or color difference is $\Delta E_{ab} = \sqrt{3} \approx 1.7$ in the space of the coordinates L*, a*, b*. However, in recent publications the threshold of color difference perception has been variously defined in a wide range from $\Delta E_{ab} = 1$ to $\Delta E_{ab} = 3.7$. Some examples include Knispel[28] and Tung et al[29] who have defined this threshold as $\Delta E = 1 \div 2$. Haselton et al[30] suggested that $\Delta E_{ab} = 3.7$, whereas Kolbeck et al[31] assumed it as $\Delta E_{ab} = 1.5$. According to some other researchers the threshold is $\Delta E_{ab} = 1$.[32–34] However, in contrast, Guan et al[35] and Tung et al[29] assume that the maximum color difference acceptable in dental materials is $\Delta E = 2$, while others claim that this value is $\Delta E_{ab} = 3.3$.[33,36] According to some more liberal approaches to this problem, this value is $\Delta E_{ab} = 3.5$[37] or even $\Delta E_{ab} = 3.7$, as proposed by Ertas et al[2] and Guler et al[38] and by Haselton et al.[30] Another subject of study has been the effect of potentially discoloring diet elements (such as tea, coffee, and red wine) on the color of dental materials.[30,31,34,38,39] The general outcome of the works of these authors was that the largest color difference was caused by exposure to red wine, irrespective of the type of dental material studied, while coffee and tea lead to a similar and lower degree of discoloring.

As known in dentistry, discoloration becomes perceptible with a total color difference ΔE_{ab} exceeding 1.0. The value $\Delta E_{ab} = 3.3$ is the upper limit of acceptability in the subjective visual color perception, as discoloration above this level is commonly considered unacceptable. According to these criteria, the immersion of the studied composite materials in tea, coffee, and wine leads to a distinct discoloration after 5 days of treatment, for both polished and unpolished composite materials; however, the color changes observed in ceramic materials soaked in tea, coffee, or red wine did not exceed the acceptability limits even after 5 days of soaking in these drinks.

Until now we have only considered ΔE_{ab} as the color comparison criterion; however, this value may not always be the

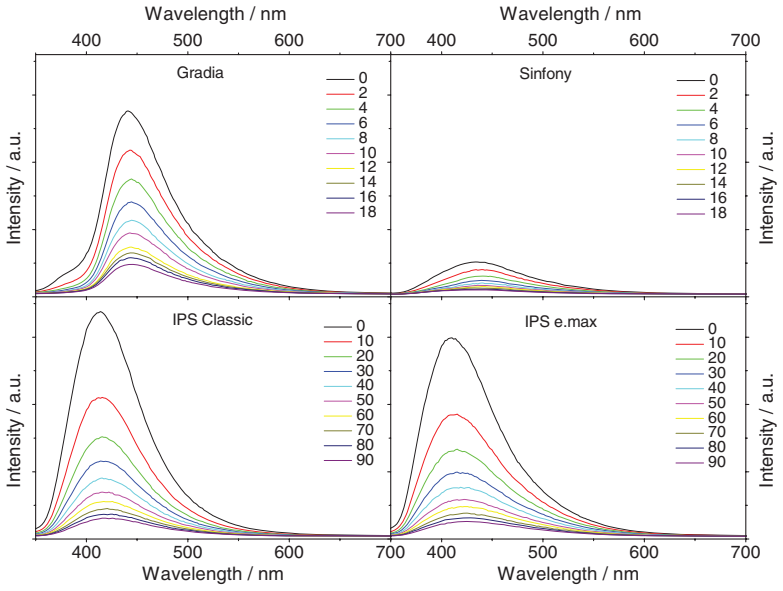

Figure 6 Time-resolved fluorescence spectra of polished specimens of dental materials: Gradia, Sinfony, IPS Classic, and IPS e.max. Excitation was at 337 nm for all specimens; the spectra were recorded with the time delays (ns) indicated on the respective panels.

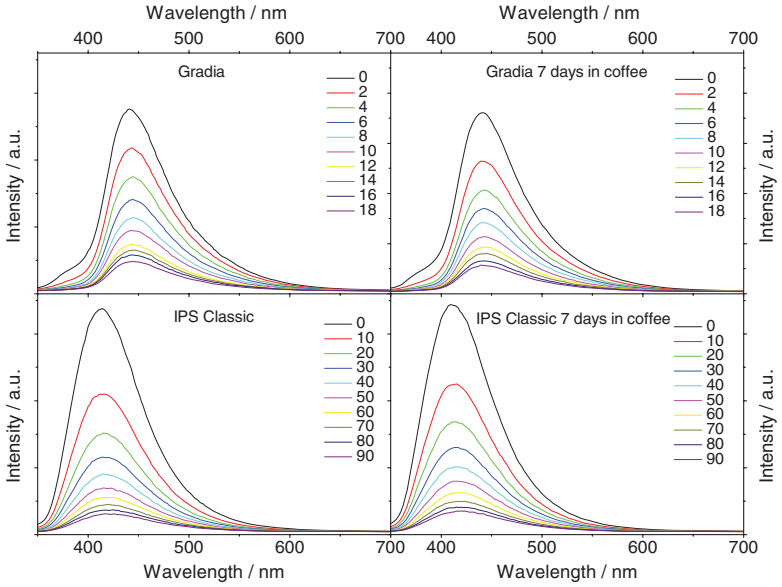

Figure 7 Time-resolved fluorescence spectra of polished dental materials: Gradia and IPS Classic. Excitation was at 337 nm in all specimens; the spectra were recorded with the time delays (ns) indicated on the respective panels. All materials (A.2 shade) in the right panels were subject to immersion in coffee for 7 days; the specimens before immersion are shown in the left panels for comparison.

most appropriate one, keeping in mind all possible values of the L^*, a^*, b^* coordinates, and the visual inspection of color change as the ultimate criterion. Indeed, the new CIEDE2000 color difference formula reproduces our visual perception of color difference much better; however, being relatively new, the CIEDE2000 formula and its ΔE_{00} criterion have not been used very often, thus its usage may preclude comparisons to previous studies. On the other hand, the ΔE_{ab} values usually indicate larger color differences as compared to ΔE_{00}, with the differences between the two formulas becoming significant for values exceeding 2. Therefore, we present both values.

We see that the composite materials studied are less color-stable than the ceramic materials. This may be explained by a conjunction of at least two fundamental reasons: first, the polymers that make the base of the composites, being more hydrophobic than ceramics, have larger affinities to the organic dyestuffs present in the staining fluids and thus adsorb those dyestuffs stronger at their surface; second, polymers as opposed to ceramics have generally larger diffusion coefficients and higher porosities, facilitating penetration of the dyestuffs into their bulk. Additionally, unpolished specimens are easier to stain than polished specimens, due to their more developed surface, with more sites adsorbing the dyes.

Typical luminescence contour maps

Figure 4 presents the contour maps of the total luminescence of the materials of A.2 shade, control specimens. A relatively intense band was observed in each of the materials, except Sinfony. The excitation band was at ca. 375 to 425 nm and the emission band at ca. 425 to 650 nm. The strongest luminescence was recorded for Gradia, with the two ceramic materials presenting slightly weaker luminescence, and Sinfony the weakest (Fig 2). Thus, the EEM measured using the front-face geometry exhibits a relatively intense band with excitation centered at about 375 nm and emission at 400 nm in all materials (Fig 4). Note that the features grouped along sloping straight lines, in this figure and elsewhere, are artifacts and thus should be disregarded.

Figure 5 shows the intensity of luminescence emitted by A.2 shade specimens of Gradia specimens, after 5 days soaked in tea (panel A), and after 5 days soaked in red wine (panel B). Similar to what is observed for color stability, the luminescence of composites degrades more readily upon staining than that of ceramics. Assuming that the changes are caused by absorption of both incident and emitted light by the dyestuffs accumulated at the specimen surface and in the bulk, luminescence stability should be correlated to color stability, as indeed happens. An alternative hypothesis stating that the luminescence changes are caused by specific interactions of the luminescent components with the adsorbed dyestuffs is contradicted by the luminescence lifetimes being independent on staining—see the following section.

Note also that the excitation band in the two ceramic materials (Figs 4C and D) is centered at ca. 375 nm, and thus the fluorescent components, absorbing in the near-UV, will not affect the color of the respective materials to a noticeable extent. On the other hand, the excitation band in Gradia (Fig 4A), centered at ca. 400 nm, exhibits a stronger absorbance in the visible range, and thus will contribute to the color of the respective material, apart from providing the fluorescence. The luminescent component in the Sinfony composite (Fig 4B) has its excitation maximum at an intermediate location, ca. 385 nm, and therefore may also provide a noticeable contribution to the color of this material.

LIL and lifetime studies

Figures 6 and 7 present time-resolved fluorescence spectra of the four dental materials studied (Gradia, Sinfony, IPS Classic,

and IPS e.max). The excitation was at 337 nm in all specimens, and the spectra were recorded in the nanosecond time range in all LIL experiments. Most striking is the difference observed in the luminescence lifetime between composite and ceramic materials. The lifetimes determined for the composite materials, Gradia and Sinfony, were 9.4 ± 0.3 ns and 7.4 ± 0.2 ns, respectively, while for the ceramic materials, IPS Classic and IPS e.max, we determined lifetimes of 33.1 ± 0.5 ns and 31.7 ± 0.4 ns, respectively. Another interesting fact is that there is no effect of staining fluid on the luminescence lifetime (Fig 7). Indeed, no difference was detected within experimental errors after about 1 week of contact with coffee or tea. As already noted, the independence of the emission lifetimes upon the degree of staining excludes any contribution of the eventual excited state quenching effects by the absorbed dyestuffs to the degradation of luminescence intensity observed upon staining.

It is somewhat surprising that the longest lifetimes were obtained for the materials less subject to color changes, that is, the ceramic materials, as longer lifetimes should originate stronger quenching by any dissolved or absorbed species. Clearly, this is not the case, the reason probably being low diffusion coefficients in all materials that exclude any noticeable effects of quenching upon their luminescence, as once again supported by the stability of the luminescence lifetimes, unaffected by staining.

Conclusions

The color of the studied composite materials changes much easier than that of the ceramic materials, when subject to staining drinks. The color changes saturate in about 20 hours of exposure to staining drinks, being stronger in unpolished as compared to polished specimens, illustrating the importance of surface quality for color stability, which is also related to scratch resistance of the materials, not addressed presently, but predictably better in ceramics. The lower color stability of the unpolished specimens is explainable by their more developed surface, with more sites that may absorb dyestuffs. Note also that soaking in distilled water also causes perceptible color changes in most materials; therefore, it is the color of water-saturated rather than dry specimens that should be compared to that of the tooth tissue.

Luminescence intensity of stained specimens may be significantly lower than that of control specimens. Once more, the changes are most notable in the composite materials as compared to ceramic materials. Conjugating these results with the fact that the luminescence lifetimes remain unchanged upon staining, we conclude that the luminescence intensity changes are most probably due to extinction of both the incident excitation photons and the emitted luminescent photons by the absorbed dyestuffs, rather than to any specific energy-transfer phenomena between the luminescent components of the dental materials and the absorbed dyestuffs.

Additionally, both the absorption and the emission spectra offer some clues to the composition of the dental materials studied. In particular, we may note that the luminescent components differ between materials, having differing total emission spectra and significantly different emission lifetimes. The diffuse reflectance spectra demonstrate that although all of the materials were programmed to have the same color shade, in practice, slight color differences remain, some materials being more intensely colored than others.

One limitation of this study is that we were working in vitro, instead of in vivo. Although the relative behavior of the dental restoration material versus the tooth tissue toward various staining agents is an important issue, it should be largely reducible to the problem currently addressed. Indeed, assuming that most patients regularly use toothpaste to clean their teeth, and some resort to whitening procedures from time to time, the probability of permanent staining of the live tooth tissue should be relatively low. On the other hand, the logistical difficulties and additional costs of the in vivo studies would preclude the possibility of obtaining statistically pertinent data sets, allowing the achievement of definite conclusions, as very often happens in clinical studies.

We believe that the future of such luminescence studies lies in a combination of total luminescence studies with time-resolved techniques, combining the possibility to record the steady-state excitation–emission matrix together with its time-resolved characteristics. To do so, it is necessary to apply new CCD devices with the possibility of timing of the luminescence signals on at least the nanosecond time scale. Such combination will bring new possibilities in rapid and adequate determination of all luminescence parameters, while still retaining all advantages of steady-state measurements. Attention should be given to eliminating disadvantages and possible artifacts caused by doing measurements for strongly absorbing or opaque specimens, by using the front-face arrangement, while capitalizing on all advantages of the time-resolved techniques.

References

1. Schulze KA, Tinschert J, Marshall SJ, et al: Spectroscopic analysis of polymer-ceramic dental composites after accelerated aging. Int J Prosthodont 2003;16:355-361
2. Ertas E, Guler AU, Yucel AC, et al: Color stability of resin composites after immersion in different drinks. Dent Mater J 2006;25:371-376
3. Cho MS, Lee YK, Lim BS, et al: Changes in optical properties of enamel porcelain after repeated external staining. J Prosthet Dent 2006;95:437-443
4. Douglas RD, Steinhauer TJ, Wee AG: Intraoral determination of the tolerance of dentists for perceptibility and acceptability of shade mismatch. J Prosthet Dent 2007;97:200-208
5. Braun A, Jepsen S, Krause F: Spectrophotometric and visual evaluation of vital tooth bleaching employing different carbamide peroxide concentrations. Dent Mater 2007;23:165-169
6. Cho BH, Lim YK, Lee YK: Comparison of the color of natural teeth measured by a colorimeter and Shade Vision System. Dent Mater 2007;23:1307-1312
7. Yamamoto M: Value conversion system: a new procedure for modification of ceramic color under special conditions of color brightness (2). Die Quintessenz der Zahntechnik 1991;17:1067-1087
8. Yamamoto M: Value conversion system: a new procedure for modification of ceramic color under special conditions of color brightness (1). Die Quintessenz der Zahntechnik 1991;17:929-962
9. CIE: Colorimetry CIE Publ. No. 15.2. (ed 2). Vienna, Central Bureau of the CIE, 1986

10. Luo MR, Cui G, Rigg B: The development of the CIE 2000 color-difference formula: CIEDE2000. Color Res Appl 2001;26:340-350
11. Spitzer D, ten Bosch JJ: Total luminescence of bovine and human dental enamel. Calcif Tissue Res 1976;20:201-208
12. Monsenego G, Burdairon G, Clerjaud B: Fluorescence of dental porcelain. J Prosthet Dent 1993;69:106-113
13. Taubinsky IM, Alexandrov MT, Kozma SY, et al: Prospects for applying fluorescence spectroscopy to diagnose the hard tissues of a tooth. Crit Rev Biomed Eng 2000;28:137-144
14. Amaechi BT, Higham SM: Quantitative light-induced fluorescence: a potential tool for general dental assessment. J Biomed Optics 2002;7:7-13
15. Tani K, Watari F, Uo M, et al: Fluorescent properties of porcelain-restored teeth and their discrimination. Mater Transact 2004;45:1010-1014
16. Dos Reis RSA, Casemiro LA, Carlino GV, et al: Evaluation of fluorescence of dental composites using contrast ratios to adjacent tooth structure: a pilot study. J Esthet Rest Dent 2007;19:199-206
17. Lim YK, Lee YK: Fluorescent emission of varied shades of resin composites. Dent Mater 2007;23:1262-1268
18. Park MY, Lee YK, Lim BS: Influence of fluorescent whitening agent on the fluorescent emission of resin composites. Dent Mater 2007;23:731-735
19. Lee YK, Lu H, Powers JM: Changes in opalescence and fluorescence properties of resin composites after accelerated aging. Dent Mater 2006;22:653-660
20. Mazur-Koczorowska A, Sikorska E, Krawczyk A, et al: Luminescence of selected dental composites in vitro. Dent Mater 2008;24:1329-1335
21. Wendlandt WW, Hecht HG: Reflectance Spectroscopy. New York, Wiley, 1966
22. Wilkinson F, Kelly G: Diffuse reflectance flash photolysis. In Scaiano JC (ed): Handbook of Organic Photochemistry. Boca Raton, CRC Press, 1989, pp. 293-314
23. Kubelka P, Munk F: Ein beitrag zur optik der farbanstriche. Z Tech Phys 1931;12:593-601
24. Gross MD, Moser JB: A colorimetric study of coffee and tea staining of four composite resins. J Oral Rehabil 1977;4:311-322
25. Botelho do Rego AM, Ferreira LFV: Photonic and electronic spectroscopies for the characterization of organic surfaces and organic molecules adsorbed on surfaces. In Nalwa HS (ed): Handbook of Surfaces and Interfaces of Materials. New York, Academic Press, 2001, pp. 275-315
26. Ferreira LFV, Machado IF, Da Silva JP, et al: A diffuse reflectance comparative study of benzil inclusion within microcrystalline cellulose and beta-cyclodextrin. Photochem Photobiol Sci 2004;3:174-181
27. Ferreira LFV, Machado IF, Oliveira AS, et al: A diffuse reflectance comparative study of benzil inclusion within p-tert-butylcalix[n]arenes (n = 4, 6, and 8) and silicalite. J Phys Chem B 2002;106:12584-12593
28. Knispel G: Factors affecting the process of color matching restorative materials to natural teeth. Quintessence Int 1991;22:525-531
29. Tung FF, Goldstein GR, Jang S, et al: The repeatability of an intraoral dental colorimeter. J Prosthet Dent 2002;88:585-590
30. Haselton DR, Diaz-Arnold AM, Dawson DV: Color stability of provisional crown and fixed partial denture resins. J Prosthet Dent 2005;93:70-75
31. Kolbeck C, Rosentritt M, Lang R, et al: Discoloration of facing and restorative composites by UV-irradiation and staining food. Dent Mater 2006;22:63-68
32. Ertan AA, Ahin E: Colour stability of low fusing porcelains: an in vitro study. J Oral Rehabil 2005;32:358-361
33. Janda R, Poulet JF, Latta M, et al: Color stability of resin-based filling materials after aging when cured with plasma or halogen light. Eur J Oral Sci 2005;113:251-257
34. Um CM, Ruyter IE: Straining of resin-based veneering materials with coffee and tea. Quintessence Int 1991;22:377-386
35. Guan YH, Lath DL, Lilley TH, et al: The measurement of tooth whiteness by image analysis and spectrophotometry: a comparison. J Oral Rehabil 2005;32:7-15
36. Ikeda T, Sidhu SK, Omata Y, et al: Colour and translucency of opaque-shades and body-shades of resin composites. Eur J Oral Sci 2005;113:170-173
37. Reich S, Hornberger H: The effect of multicolored machinable ceramics on the esthetics of all-ceramic crowns. J Prosthet Dent 2002;88:44-49
38. Guler AU, Yilmaz F, Kulunk T, et al: Effects of different drinks on stainability of resin composite provisional restorative materials. J Prosthet Dent 2005;94:118-124
39. Villalta P, Lu H, Okte Z, et al: Effects of staining and bleaching on color change of dental composite resins. J Prosthet Dent 2006;95:137-142