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Surface characteristics and staining of experimental visible light-cured unfilled resins

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This experiment was designed to study the internal colour change of five experimental visible light-cured (VLC) resins and to deduce the relationship between staining and the physicochemical properties of the resins and a glass. The staining of the materials was measured colorimetrically, with immersion in two types of staining solution (Oil Orange or Food Red 3) for 70 days at 37 °C. The water sorption, contact angle and zeta-potential of these samples were also measured. With the Oil Orange dye a positive relationship was observed only between staining and the contact angles, whereas with Food Red 3 dye a positive relationship was observed between staining and the zeta-potential and between staining and the water sorption. The results could allow a comparison of the relative contributions to staining made by physicochemical forces for the samples tested.

1. Introduction

There are many factors that contribute to the colour change of dental composite resins in clinical service [1]. Since colorimetric measurements permit both a quantitative study and a comparison of the colour changes of materials, the colour change of chemically cured composite resins were studied by this method [2–4]. Those reports indicated that the colour change of chemically cured composite resin differed from resin to resin. On the other hand, the endogenous colour change of chemically cured composite resin is dependent, at least partly, on the ratio of amine to BPO [5]. It is considered that the colour change of VLC composite resins is greatly reduced when the polymerization mechanism does not involve an aromatic amine [1] and in the absence of porosity [6]. However, marked discoloration of VLC composite resins, which were mainly composed of Bis-GMA monomer {2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy)phenyl] propane} occurs in the clinical situation.

In this experiment an attempt was made to study the internal colour change of five experimental VLC composite resins and the staining of these resins and a glass. These components were separated into base resins and filler (glass) to simplify the experimental system and the staining by two types of organic dye. The value of staining was correlated with the values of surface hydrophobicity, water sorption and zeta-potentials of the resins and glass. The relative contributions of the hydrophobic interaction, water sorption and electrostatic interaction to the adsorption of staining on the surface of materials tested were thus assessed.

2. Materials and methods

Five VLC resins without fillers and one glass material were used, as indicated in Table I. The amounts of monomer compositions used (wt %) were as follows: code A, 63.4% Bis-GMA (Epoxylite Co., USA) + 34.1% triethyleneglycol dimethacrylate (TEGDMA; Tokyo Kasei Co., Tokyo, Japan); code B, 68.3% Bis-GMA + 29.2% glycerol-1,3-dimethacrylate (GDMA; Tokyo Kasei Co., Tokyo, Japan); code C, 67.2% Bis-GMA + neopentylglycol dimethacrylate (NPGDMA; Tokyo Kasei Co., Tokyo, Japan); code D, 65.7% 2,2-bis[4-(methacryloxypolyethoxy)phenyl] propane (Bis-MPEPP; Shin Nakamura Co., Wakayama, Japan) + 31.8% NPGDMA; and code E, 97.5% 7,7,9-trimethyl-4,13-dioxo-5,12-diazohexadecane-1,16-diyldimethacrylate (IUPAC; Shin Nakamura Co., Wakayama, Japan). All resins contain 0.5% camphoroquinone (CQ; Tokyo Kasei Co., Tokyo, Japan) as a photosensitizer, 1.95% dimethylaminoethylmethacrylate (DMAEMA; Tokyo Kasei Co., Tokyo, Japan) as a tertiary amine for polymerization promoter and 0.05% butylated hydroxytoluene (BHT; Tokyo Kasei Co., Tokyo, Japan) for polymerization prohibitor.

Each resin disc (diameter 20.0 ± 1.0 mm × 1.0 ± 0.05 mm thickness) was prepared against washed glass slides which produced an optically smooth surface and were cured by visible light for 30 min [7]. Glass samples (Code 7740: SiO_2 80.9%, B_2O_3 12.7%, Na_2O 4%, Al_2O_3 2.3%, K_2O 0.04% and Fe_2O_3 0.03%; Iwaki Glass Co., Tokyo, Japan) were cut to the same size as the resin samples.

2.1. Determination of colour change

Two types of solutions, Oil Orange solution [5 g Oil Orange ($C_{16}H_{12}N_{20}$) dissolved in 500 ml olive oil] and Food Red 3 solution [5 g Erythrosine B

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TABLE I Samples used and the internal colour change

Code	Main monomer (wt %)	Diluent monomer (wt %)	Colour change
A	Bis-GMA, 63.4	TEGDMA, 34.1	2.37 ± 0.52
B	Bis-GMA, 68.3	GDMA, 29.2	2.67 ± 0.67
C	Bis-GMA, 67.2	NPGDMA, 30.3	2.60 ± 0.50
D	Bis-MPEPP, 65.7	NPGDMA, 31.8	3.29 ± 0.90
E	IUPAC, 97.5		3.20 ± 0.92
F	Glass		

The residues (2.5%) were included in the materials tested. Means ± SD, sample size $n = 10$.

($C_{20}H_6O_5I_4Na_2$) dissolved in 500 ml distilled water] were prepared. Oil Orange is an oil-soluble hydrophobic dye, whereas Food Red 3 is a water-soluble hydrophilic dye.

As described above for each, 30 specimens were prepared, making a total of 180 samples, which were divided into three groups. The first two groups of specimens were immediately placed at the bottom of a glass container to which each staining solution was added to immerse the specimens. The glass container was then covered with Scotch tape and placed in an oven maintained at 37 °C. The colour change vector obtained from L*a*b* [8] was measured by a colour and colour difference meter (model 1001 DP; Nippon Densyoku Kogyo Co., Tokyo, Japan) before and after 10, 30, 50 and 70 days immersion. The other group was placed at the bottom of a glass container filled with distilled water, followed by covering the container with tape and placing it in an oven maintained at 60 °C for 30 days. The colour change was measured before and after immersion. All numerical data obtained were analysed by Student's t-test.

2.2. Physicochemical properties

In six samples of each material the volume (V_0) of each sample was calculated by measuring the thickness and diameter with a micrometer. The samples were placed in a desiccator until a constant weight (W_0) was obtained before immersion in distilled water maintained at 37 °C. After immersion for 10, 30, 50 or 70 days, specimens were then reweighed (W_1). The difference in weight between W_1 and W_0 was considered as the volume of water uptake:

$$\text{water sorption (v/v)} = (W_1 - W_0)/V_0$$

The surface hydrophobicity of samples was determined by measuring the contact angle of distilled water on the sample plates, which was measured by the horizontal projection technique with a contact-angle meter (model CA-A; Kyowa Co., Tokyo, Japan) at 20 °C [9] and at three separate points on 10 plates of each type of materials.

The samples were crushed in a mortar, sieved through a mesh (size 2–5 μm). The particles were suspended in 0.05 mol/l tris(hydroxymethyl)aminomethane (Tris)–HCl buffer (pH 7.2). The electrophoretic mobility of each type of resin and glass particle was measured 10 times by using a Face zeta-potential meter (ZP-OM; Kyowa Kaimenkagaku Co., Tokyo, Japan). The zeta-potential was calculated from the Heimholtz–Smoluchowski formula [10] $\zeta = 4\pi\eta U/D$, where U is the electrophoretic mobility or velocity at unit potential gradient, η is the viscosity of the liquid and D is the dielectric constant.

3. Results

Internal colour change values after 30 days at 60 °C by accelerated test are listed in Table I. Code A had the lowest and code D had the highest value, although no significant difference was observed among all the resins ($P < 0.05$). The colour change value of staining was measured after 10, 30, 50 and 70 days immersion

TABLE II Colour change values of resins and a glass discoloured with Oil Orange and Food Red 3 solutions

Code	10 days	30 days	50 days	70 days
Colour change with Oil Orange				
A	3.2 ± 0.6	4.8 ± 0.6	6.0 ± 0.6	6.3 ± 0.8
B	4.0 ± 0.5	5.5 ± 0.6	6.5 ± 0.7	6.7 ± 0.6
C	4.6 ± 0.7	6.4 ± 0.9	7.8 ± 1.1	8.0 ± 1.0
D	5.3 ± 0.8	10.6 ± 1.2	12.0 ± 1.4	12.0 ± 1.2
E	4.0 ± 0.6	5.6 ± 0.7	6.4 ± 0.9	6.7 ± 0.7
F	1.5 ± 0.4	1.5 ± 0.5	1.5 ± 0.4	1.6 ± 0.2
Colour change with Food Red 3				
A	5.0 ± 0.6	7.2 ± 0.8	9.8 ± 1.1	10.0 ± 1.3
B	6.5 ± 0.9	10.1 ± 1.0	13.0 ± 1.8	13.0 ± 1.4
C	4.9 ± 0.6	7.5 ± 1.0	9.9 ± 0.9	10.1 ± 1.4
D	4.2 ± 0.6	6.5 ± 0.8	8.8 ± 0.5	9.0 ± 0.9
E	4.5 ± 0.5	6.3 ± 0.7	8.6 ± 0.7	8.8 ± 0.8
F	0.9 ± 0.3	1.0 ± 0.2	1.2 ± 0.3	1.3 ± 0.2

Means ± SD ($n = 10$).

in two types of staining solution. For both solutions, values reached a plateau at 50 days (Table II). For the Food Red 3 solution, code B showed the highest value after 70 days immersion, followed by codes C, A, D and E, whereas the glass sample showed the lowest value ($P < 0.05$). For Oil Orange solution, code D showed the largest value after 70 days immersion, followed by codes C, B, E and A, and the glass sample showed the smallest value, showing that significant differences existed between the materials ($P < 0.05$).

The results of water sorption for 70 days are shown in Table III. Code B showed the highest value, followed by codes A, E, C, D and F. No significant differences were observed between codes A, C and E ($P < 0.05$).

The values of the contact angle of samples for 70 days immersion are shown in Table IV. Code D showed the highest angle, followed by codes C, E, A and B, and glass showed the lowest angle ($P < 0.05$).

The zeta-potential as an index of the surface electric charge is given in Table V. Glass showed the lowest value ($P < 0.05$). Among the resin samples, the zeta-potentials of the Bis-GMA groups (codes A, B and C) were lower than those of codes D and E resins ($P < 0.05$).

The correlation coefficients among the zeta-potential, contact angle or water sorption and the colour

TABLE VI Correlation coefficient among the colour change value and water sorption, contact angle and zeta-potential

Physico-chemical property	Period (days)	Colour change with	
		Food Red 3	Oil Orange
Water sorption	10	0.8770*	0.2839
	30	0.8279*	− 0.0394
	50	0.7759	− 0.0335
	70	0.7848	0.0173
Contact angle	10	0.7680	0.9447***
	30	0.7670	0.8362*
	50	0.7684	0.8926**
	70	0.7902	0.9009**
Zeta-potential	10	0.9501***	0.7986
	30	0.9449***	0.6372
	50	0.9579***	0.6975
	70	0.9637***	0.7169

* $P < 0.05$, **$P < 0.02$ and ***$P < 0.01$.

TABLE III Water sorption of resins and glass

Code	Water sorption (v/v)			
	10 days	30 days	50 days	70 days
A	0.34 ± 0.04	0.37 ± 0.04	0.34 ± 0.02	0.30 ± 0.02
B	0.55 ± 0.02	0.58 ± 0.02	0.54 ± 0.02	0.49 ± 0.02
C	0.32 ± 0.01	0.33 ± 0.01	0.25 ± 0.03	0.24 ± 0.03
D	0.12 ± 0.01	0.12 ± 0.03	0.09 ± 0.02	0.09 ± 0.01
E	0.33 ± 0.02	0.35 ± 0.02	0.29 ± 0.03	0.27 ± 0.04
F	0.05 ± 0.01	0.09 ± 0.02	0.08 ± 0.01	0.07 ± 0.01

Means ± SD ($n = 6$).

TABLE IV Contact angles of resins and glass

Code	Contact angle (degrees) at			
	10 days	30 days	50 days	70 days
A	60.8 ± 3.7	60.4 ± 1.2	61.2 ± 1.3	60.6 ± 1.5
B	59.8 ± 3.5	59.6 ± 1.8	59.7 ± 1.1	60.0 ± 1.0
C	64.6 ± 2.5	64.7 ± 1.5	64.7 ± 1.4	64.6 ± 1.1
D	66.5 ± 1.8	66.4 ± 2.3	67.2 ± 1.0	66.6 ± 1.3
E	62.5 ± 1.5	63.5 ± 1.9	63.5 ± 1.5	63.6 ± 1.2
F	43.3 ± 3.7	41.3 ± 3.3	44.3 ± 2.6	44.9 ± 2.4

Means ± SD ($n = 10$ at three separate points).

TABLE V Zeta-potentials of resins and glass

Code	Zeta-potential (mV)			
	10 days	30 days	50 days	70 days
A	− 26.8 ± 1.9	− 26.3 ± 1.5	− 26.0 ± 1.3	− 26.0 ± 2.0
B	− 21.9 ± 2.0	− 22.9 ± 1.3	− 22.0 ± 1.7	− 21.4 ± 1.9
C	− 20.7 ± 1.9	− 22.1 ± 2.1	− 21.0 ± 2.3	− 20.2 ± 1.3
D	− 29.8 ± 2.0	− 28.9 ± 2.3	− 28.3 ± 2.5	− 28.1 ± 2.1
E	− 30.8 ± 3.0	− 31.2 ± 2.2	− 30.7 ± 1.9	− 30.5 ± 1.9
F	− 59.4 ± 7.3	− 59.9 ± 4.3	− 60.3 ± 6.0	− 61.5 ± 8.1

Means ± SD ($n = 10$).

change of staining are summarized in Table V. With Food Red 3 solution a positive relationship was observed between the colour change value and the zeta-potential throughout the experimental periods, and a positive relationship was observed between the colour change and water sorption for 10 and 30 days immersion. No significant correlation existed between the colour change value and the contact angle. On the other hand, with Oil Orange solution a positive relationship was observed between the colour change value and the contact angle at all times, although there was no significant relationship between the colour change value and water sorption or the zeta-potential.

4. Discussion

Five types of VLC resins were used, and a glass which was substituted for filler. In VLC resins the internal colour change was found to be slight and less than the staining, which indicates that the internal colour change of VLC resin had been reduced. In time VLC resins were stained by oily foods, cigarettes, tannin from tea or synthetic dyestuffs. Dental composite resins were stained easily by mechanical adsorption owing to its surface roughness [4], caused by irregularly arranged filler particles in its components [11]. It was reported that the surfaces of the resins produced by the celluloid matrix alone discoloured more than polished surfaces [3], which indicated adsorption of soiled substances to the resin surface.

In this experiment the contact angle, water sorption and zeta-potential of these materials were measured to study the relationship between these characteristics and staining by using different types of dyes. Oil Orange solution was used for the staining test of composite resins, owing to its similarity to clinical discoloration as an oily food [3, 4, 12, 13]. Food Red 3, which is prepared from Erythrosin B, is used as dental disclosing solution (Red-Cote, Butler Co., USA), and is one of the 11 kinds of synthetic dyestuffs permitted to be used as a food dye in Japan, and it has the largest adsorption index among the 11 synthetic dyes.

The colour change in a glass sample was slight in two solutions due to the physicochemical properties. This suggests that the colour change value in VLC resins with a large amount and size of inorganic fillers should be negligible; nevertheless, such discolorations occur along the bonding between the filler and the resin matrix. The colour change value of these samples correlated significantly with the contact angles in the case of staining by Oil Orange solution. Since the contact angle is an index of hydrophobicity, it is suggested that hydrophobic interaction plays an important role in the staining of VLC resins by hydrophobic solutions. This is consistent with the theory based on thermodynamic studies [14, 15]. With Food Red 3 dye, which is hydrophilic, hydrophobic interaction did not seem to contribute significantly to the staining of the materials tested. The staining by Food Red 3 solution seems to be due to electrostatic interaction, because the zeta-potential and the colour change value showed a statistically positive relationship. These findings indicate that hydrophobic interaction plays a more important role than electrostatic interaction in the staining of composite resins with high hydrophobic surface properties. This seems reasonable, since hydrophobic interaction occurs between two hydrophobic surfaces.

Adsorption of oily foods and cigarette tar by resin surfaces seemed to occur by hydrophobic interactions, since both the composite resins, oily foods and tar are hydrophobic. It is considered that staining by a hydrophilic organic dye (e.g. tea or coffee) may occur along with other physicochemical forces such as electrostatic forces, hydrogen bonding or water sorption. In fact, the colour change value with Food Red 3 solution correlated with the zeta-potential, indicating that electrostatic interaction plays an important role in staining by hydrophilic solution. Thus, in staining by hydrophobic organic dyes, the hydrophobic interaction would play an important role, whereas in staining by organic dye of lower hydrophobicity and high negative zeta-potential, electrostatic interaction seems to be important. The staining phenomenon is similar to that of bacterial adhesion to solid substances found in our previous studies [9, 16], which indicated that neither electrostatic forces nor hydrophobic interactions alone determine the adherence of bacteria. However, colour change of VLC resins was also affected by water sorption. Since the colour change with Food Red 3 solution correlates with the water sorption particularly, during the earlier period, it is likely to contribute to the process of staining.

On the other hand, the colour change value of a glass sample by two organic dyes was the smallest among all samples tested. These results might be explained by its repulsive force, such as in electrostatic forces arising from its highly negative charge, in hydrophobic interactions from its low hydrophobicity and in hydrogen bonding due to its low water sorption.

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