JOURNAL OF MATERIALS SCIENCE: MATERIALS IN MEDICINE 6 (1995) 620–623

Effect of TEGDMA content on staining of experimental bis-GMA-based resins

I. MATSUMAE, K. WAKASA*, N. SATOU, H. URABE, H. SHINTANI, M. YAMAKI*
Hiroshima University, School of Dentistry, Department of Operative Dentistry, and
** Department of Dental Materials, Kasumi 1 chome, Minamiku, Hiroshima City, 734 Japan*

This study was to examine water uptake, contact angle and colour change vector in relation to the staining on the optically smooth surface in five experimental visible light-cured (VLC) bis-GMA-based resins. They were formulated from bis-GMA-based resins including 25 to 45 wt% TEGDMA which were accelerated by CQ/DMAEMA/BHT = 0.5/2/0.05 (wt%) to bis-GMA/TEGDMA resin matrix. Of the set resins including more than 25 wt% of TEGDMA, the resins including 30 to 45 wt% had less than 1.0% as bis-GMA residual monomer. Water uptake and solubility in bis-GMA-based resins including 35 wt% TEGDMA were the minimum of the resins tested. Contact angle decreased with increasing time over 70 days, from 67 to 62 degrees. Using the hydrophilic staining solution (food red 3), the values of colour change vector were 6 to 9 after immersing them for 70 days at 37 °C, whereas hydrophobic oil orange staining test had a range of 12 to 19. The change of water uptake with time of immersion correlated with that of the colour change vector. With the accelerated test, the minimum value was 4.55 in 65/35 (bis-GMA/TEGDMA) resin. Of the bis-GMA-based resins (25 to 45 wt% fraction of TEGDMA) the minimum value of water uptake and contact angle were obtained.

1. Introduction

Staining is important clinically in operative dentistry [1–3], and the value of the colour change vector determined by colourimetric measurement depended on the amine-to-BPO ratio in chemically cured resins [2]. In VLC composite resins which were cured by a visible light source, an aromatic amine in the set composite affected the colour change vector [2]. They were also stained because of physical adsorption which was caused by irregularly arranged filler particles in the composites [4, 5]. Because the staining of dental composite resins was caused by physical adsorption, the surface characteristics (contact angle, water uptake and colour change vector) were investigated. Shintani *et al.* [5] reported that the effect of surface roughness on the staining and bacteria accumulation varied with the substance adsorbed and the nature of resins. Clayton *et al.* [6] reported that there was no particular difference in bacterial accumulation between ceramics, alloys and resins which had approximately the same smoothness. These results clarified that staining was influenced by surface characteristics of the composite resins. With the use of diluent monomers, such as TEGDMA (triethylene glycol dimethacrylate), GDMA (glycerol-1,3-dimethacrylate) and NPGDMA (neopentylglycol dimethacrylate), the staining of bis-GMA-based resin (bis-GMA content = 63.4 wt %, TEGDMA = 34.1 wt %, reducing agents = 2.5 wt %) had smaller values of colour change vector [5]. Thus, to examine the staining of experimental bis-GMA-based resins in two types of staining solutions, colour change vector measurements were carried out on the optically smooth surface. Residual monomers in the set resins, water uptake and contact angle on the smooth surface of the resins were also analysed.

2. Materials and methods

The five VLC unfilled resins tested are indicated in Table I. The amounts of monomers (wt %) were as follows: Code A1, 75% bis-GMA (Epoxylite Co, USA)/25% triethyleneglycol dimethacrylate (TEGDMA, Tokyo Kasei Co, Tokyo); code A2, 70/30 = bis-GMA/TEGDMA; code A3, 65/35; code A4, 60/40; code A5, 55/45. All resins contained 0.5 wt % CQ (camphorquinone, Tokyo Kasei Co) and 2 wt % DMAEMA (dimethylaminoethyl methacrylate, Tokyo Kasei Co) as photo-initiators and 0.05 wt % BHT (butylated hydroxytoluene, Tokyo Kasei Co) as a polymerization inhibitor, which were added to the bis-GMA/TEGDMA base resins.

Residual monomers in the set resins (rod; 3 mm in diameter and 6 mm long) were measured according to the conditions indicated in Table II. A small portion of the uncured (residual) resin in the set resins was dissolved in acetone, and the solution was then centrifuged. The aliquot was injected into the

0957–4530

TABLE I Materials used in this study (for key see text)

Code	Resin monomer (wt %) bis-GMA	TEGDMA
A1	75	25
A2	70	30
A3	65	35
A4	60	40
A5	55	45

CQ/DMAEMA/BHT = 0.5/2/0.05

TABLE II Measurement conditions for residual monomers using HPLC analysis

Apparatus	:TWINCLE (Japan Spectroscopic Co. Ltd)
Detector	:UVIDEC-100-IV
Column	:Inatosil ODS II
Mobile phase	:70% Acetonitrile-H_2O
Flow rate	:0.5 ml/min
Wavelength	:254 nm
Range	:0.16 O.D.
Integrator	:Chromatopac CR-3A
Temperature	:Constant 30 °C

chromatographic column for qualitative confirmation of the peaks of monomers.

Water uptake, contact angle and colour change vector were measured using a specimen 20 mm in diameter and 1.0 mm long (stainless steel mould), which was prepared on a washed glass surface to obtain an optically smooth flat surface with less than 0.7 μm surface roughness.

The ten samples for each test were irradiated for 30 s on the top and bottom surfaces (Quick Light II, J. Morita Co, Kyoto).

Water uptake in the samples was calculated by the following equation:

$$\text{water uptake (\%)} = ((W_a - W_0)/W_0) \times 100$$

where W_a is the weight (mg) after immersion for 3, 5, 10 and 70 days in distilled water (37 °C) and W_0 the constant weight (mg) after placing in a dessicator at 23 ± 2 °C before the measurement. Also the corrected magnitude (W_c) was calculated as follows:

$$W_c\,(\%) = ((W_{3mw} - W_{3md})/W_{3md}) \times 100$$

where W_{3mw} is the weight after 3 months immersion and W_{3md} the weight at the dry state (3 months).

Using the weight of resins after immersing them in distilled water for 3 months at 37 °C, the following equation was defined as the solubility (S) in this study:

$$S\,(\%) = ((W_0 - W_{3md})/W_0) \times 100$$

The samples were stored in a dessicator after 3 months immersion, and placed in air at 37 °C until constant (W_{3md}) was obtained.

The initial contact angle of distilled water on the sample surface was measured by the horizontal projection technique with a contact-angle meter (Model CA-A; Kyowa Co, Tokyo) at 18 °C (50% wettability). The angle was also measured after immersing the sample for 3, 5, 10 and 70 days at 37 °C in distilled water. The samples were measured at three separate points on 10 plates of each type of material.

Two types of staining 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 ($C_{20}H_6O_5I_4Na_2$) dissolved in 500 ml distilled water) were prepared. The former is an oil-soluble hydrophobic dye, and the latter a water-soluble hydrophilic dye. Ten samples were immersed in each staining solution at 37 °C, their values being measured after immersing them for 1, 3, 5, 10 and 70 days. First, L_0^*, a_0^*, b_0^* in the sample before immersion was measured using a colour difference meter (Model MMP-1001 DP, Nippon Denshoku Kougyou Co, Tokyo). Second, the colour change vector from the initial value (L_0^*, a_0^*, b_0^*) in the chromaticity coordinate C.I.E.–$L^*a^*b^*$ [7] was also obtained after measuring the values (L^*, a^*, b^*) in immersed samples (measured area = 0.4 mm diameter).

$$\Delta E = ((\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2)^{1/2}$$

where, $\Delta L = L^* - L_0^*$, $\Delta a = a^* - a_0^*$ and $\Delta b = b^* - b_0^*$.

An accelerated test was carried out according to the method recommended by Asmussen, which determined the colour change vector in distilled water on the surface [8]. After irradiation by a visible light source, samples were stored for 1 day at room temperature in a dessicator, and the initial values of L_0^*, a_0^*, b_0^* were measured. After measuring these values, one sample was stored for 30 days at 60 °C in a glass container covered with aluminium foil in distilled water and the colour difference was calculated as ΔE.

All data were analysed by student's t-test.

3. Results

Residual monomer data for bis-GMA and TEGDMA is shown in Fig. 1. TEGDMA residual monomer was less than 0.2 wt %, and residual bis-GMA monomer varied from 2 to 0.3%, as the TEGDMA increased from 25 to 45%. However the major decrease was between 30 and 45% TEGDMA. There appeared to be a significant difference between total residual monomers A1 and A2 to A5 ($p < 0.05$).

Water uptake results for 70 days in distilled water are shown in Fig. 2, indicating that the amount increased with increasing time. The A3 resin (2.77%) had a smaller uptake than the other resins (3.09 to 3.67%), and the solubility of A3 (TEGDMA = 35 wt %) was much smaller than those of the others (Fig. 3). The difference was statistically significant ($p < 0.05$).

The values of contact angle at each immersion time are shown in Fig. 4, indicating that the values decreased with increasing time (from 67 to 62 degrees as average values). A1 and A3 resins had smaller values than those in A2, A4 and A5.

The colour change vector as colour difference (ΔE) in food red 3 and oil orange is shown in Fig. 5a and 5b, respectively. The values increased with increasing

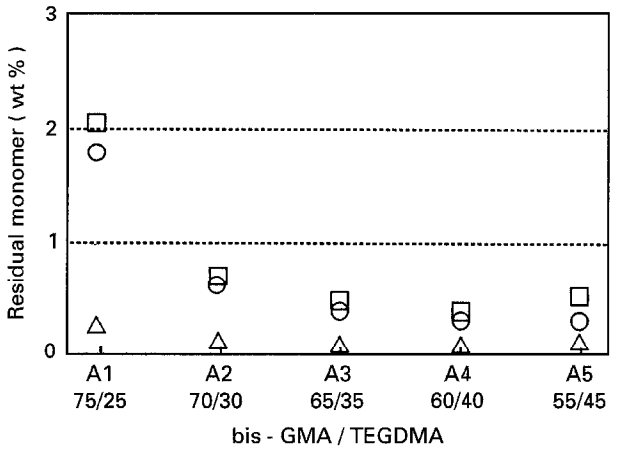

Figure 1 Residual monomers of bis-GMA (○) and TEGDMA (△). Total amount indicated by □.

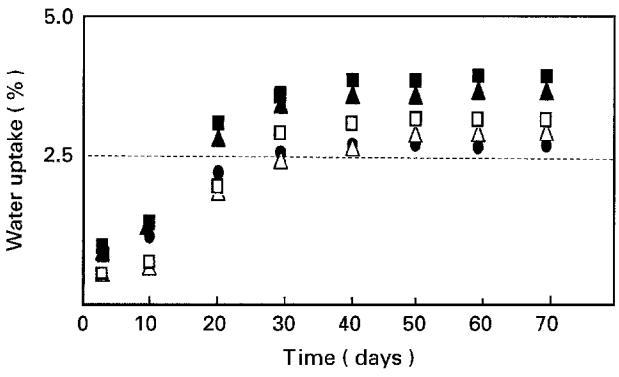

Figure 2 Water uptake after 70 days immersion: A1 (□); A2 (▲); A3 (●); A4 (Δ); A5 (■).

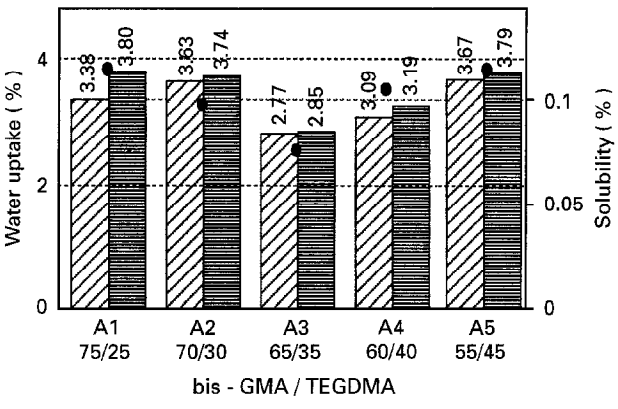

Figure 3 Water uptake (▨), corrected water uptake (≡) and solubility after 70 days immersion (●).

time and reached constant values for each material. Staining due to ΔE occurred for all resins tested, showing that ΔE in food red 3 was from 6 to 9 and ΔE in oil orange from 12 to 19.

The accelerated test recommended by Asmussen [8] is shown in Figs 6 and 7. The results measured by the colour difference meter (L^*, a^*, b^*, L_0^*; a_0^*, b_0^*) are given in Fig. 6, and the ΔE values had the minimum value (4.55) for A3 (TEGDMA = 35 wt %) compared with the resins tested.

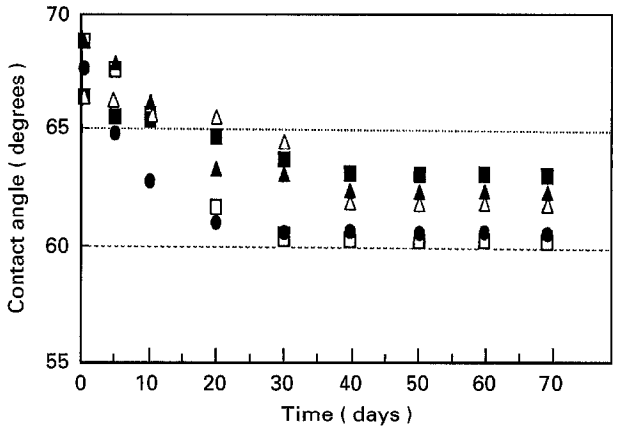

Figure 4 Contact angle with respect to immersing time. Symbols as Fig. 2.

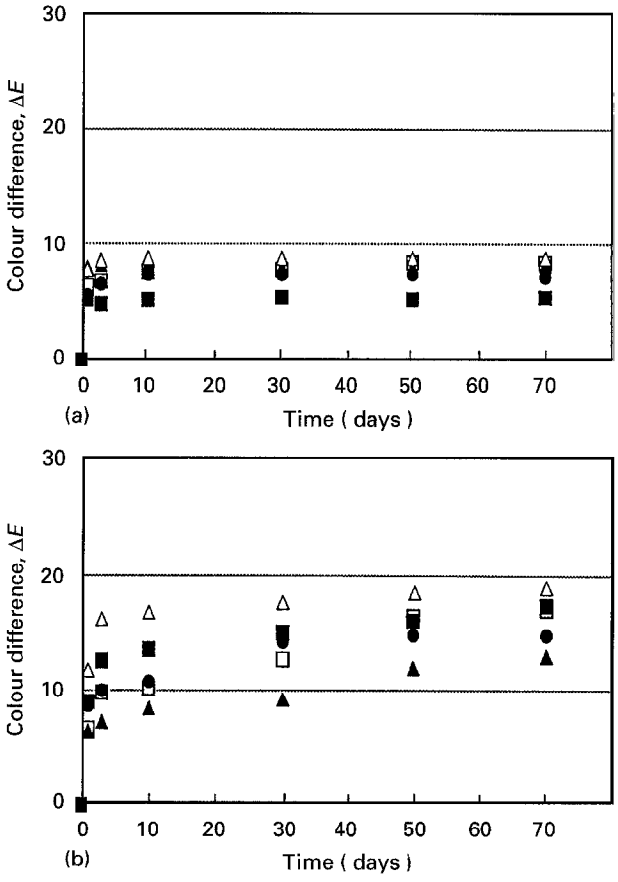

Figure 5 ΔE as colour difference over 70 days: (a) food red 3; (b) oil orange. Symbols as Fig. 2.

4. Discussion

Since the colour change vector is determined by the surface characteristics of dental composite resins, the unfilled resins without filler should be tested in relation to physical adsorption. The characteristic staining tendencies of dental composite resins to tobacco smoke solution or oil orange solution depends on the surface roughness and water uptake change with time [5]. In this study the resin surface for the colour change vector measurement was optically smooth. Also, the staining test of the composite resins was carried out using two types of dyes which are similar to those causing clinical discolouration. As indicated

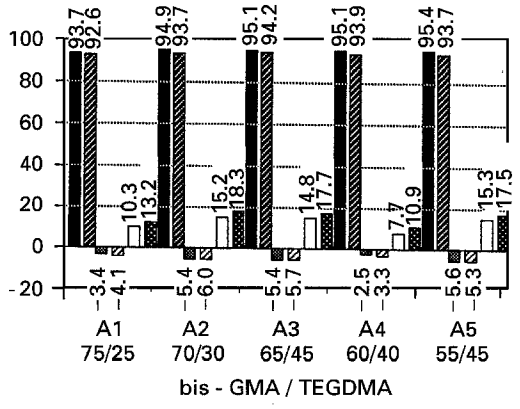

Figure 6 L^*(▨), a^*(▨), b^*(■) and L_0^*(■), a_0^*(▨), b_0^*(□) values at accelerated test.

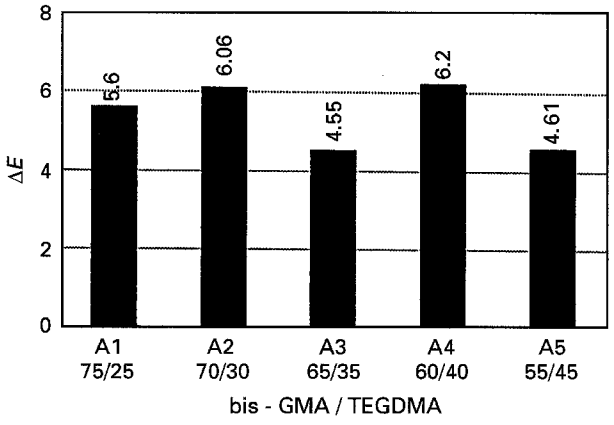

Figure 7 ΔE value at accelerated test.

in this study, oil orange and food red 3 were typically used as an oily food and a synthetic dyestuff (food dye in Japan), respectively.

The staining was evaluated by the colour change vector (Figs 5, 6 and 7). Because the contact angle is an indication of hydrophobicity, A1 (TEGDMA = 25 wt %) and A3 (TEGDMA = 35 wt %) had a hydrophobic effect on its value and its related staining. As shown in Fig. 5a, the magnitude of ΔE (6 to 9) was much smaller than with oil orange (12 to 19) at 70 days immersion. These results mean that hydrophobic interaction is important with respect to the staining in oil orange. On the contrary, in the case of food red 3, the hydrophobic interaction effect might not be important, because the ΔE value was less.

Because the staining mechanism is mainly explained by physical adsorption [9, 10], the following interactions are deduced. In oil orange solution (hydrophobic) with $\Delta E > 10$, hydrophobic interaction seems to contribute to the staining. In food red 3, its electrostatic interaction acted on the resin surface when immersed in the hydrophilic staining solution, as suggested by the finding of electrostatic interaction [11], because the zeta-potential correlated positively with ΔE values.

As shown with water uptake (Fig. 2) and ΔE (Fig. 5), the change of the values with the immersion time was similar, showing that they increased with time. This means that the staining during immersion in those solutions is related to water uptake. Also, the accelerated test in distilled water suggests that TEGDMA content in bis-GMA/TEGDMA base resin controls the colour change vector as determined by ΔE.

It is concluded that the TEGDMA content affects the staining of experimental bis-GMA/TEGDMA-based resins in solutions. With use of different amounts of TEGDMA in bis-GMA/TEGDMA resin, smaller water uptake and also smaller contact angles were obtained on the resin surface. Together with the staining tests using two types of staining solutions, the accelerated test demonstrated that the TEGDMA content as a diluent monomer to bis-GMA determined their surface characteristics.

References

1. M. D. GROSS and J. B. MOSER, *J. Oral Rehabil.* **4** (1977) 311.
2. W. H. DOUGLAS and R. G. CRAIG, *J. Dent. Res.* **61** (1982) 41.
3. Y. HACHIYA, M. IWAKU, H. HOSODA and FUSAYAMA, *J. Prosthet. Dent.* **6** (1984) 811.
4. L. N. JOHNSON, R. E. JORDAN and J. A. LYNN, *J. Amer. Dent. Assoc.* **83** (1971) 321.
5. H. SHINTANI, J. SATOU, N. SATOU, H. HAYASHIHARA and T. INOUE, *Dent. Mater.* **1** (1985) 225.
6. J. A. CLAYTON and E. GREEN, *J. Prosthet. Dent.* **23** (1970) 407.
7. Commission Internationale de l'Eclairage (C.I.E.), *supplement No. 2 of Publication C.I.E. No. 5* (*E*-1.3.1), Bureau Central de la C.I.E., Paris, France.
8. E. ASMUSSEN, *Acta Odontol. Scand.* **41** (1982) 11.
9. N. SATOU, J. SATOU, H. SHINTANI and K. OKUDA, *J. Gen. Microbiol.* **134** (1988) 1299.
10. J. SATOU, A. FUKUNAGA, N. SATOU, H. SHINTANI and K. OKUDA, *J. Dent. Res.* **67** (1988) 588.
11. N. SATOU, I. MATSUMAE, A. M. KHAN, J. SATOU, H. SHINTANI, K. WAKASA and M. YAMAKI, *J. Mater. Sci. Mater. Med.* **4** (1993) 66.

Received 1 June 94
and accepted 6 June 95