Optical and thermal properties in experimental Bis-GMA-based resins influenced by filler characteristics

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The optical and thermal properties were examined in experimental 2,2-Bis-[4-(3-methacryloxy-2-hydroxypropoxy)phenel]propane (Bis-GMA)-based composite resin systems, each of which contained silica, silica–alumina and alumina filler particles. The filler particles were surface-treated by 1% γ-methacryloxypropyl trimethoxy silane and directly dispersed into the visible-light-cured Bis-GMA-based resin matrix. The average particle size was from 0.012 to 70 μm (silica filler), 2.4 to 8.4 μm (silica–alumina) and 0.02 μm (alumina). The analyses indicated that the filler-containing resin had a larger value of light transmittance when the difference in refractive index between comonomer and filler was smaller. In selected properties such as light transmittance, refractive index and depth of cure, the transmittance and the refractive index difference were important in the increased depth of cure in the Bis-GMA-based resins.

1. Introduction

The effect of filler characteristics on the properties of composite resins had been studied in the dental field [1–7]. The filler affected tooth–brush abrasion, *in vitro* wear and the mechanical properties of dental composite resins which were composed of different kinds of fillers and matrices. In the fillers investigated the diameter ranged from 20 to 40 nm as a very small silica particle [5], and borosilica glass particles of larger size (2 to 15 μm in diameter) were also applied to dental composite resin [6]. The filler content in the composite resin ranged from 10 to 65 wt % for the resin base, and the larger volume of filler in the resin was obtained by using a larger size of filler [6]. However, much of the work was done with commercial dental composite resins where the base monomers and fillers may well differ. Therefore, it is desirable to examine the properties of filled resin systems where the different types of fillers were prepared in the same resin matrix.

The present study was to examine visible-light-cured Bis-GMA-based resins with respect to filler characteristics (chemical composition, diameter, light transmittance and surface treatment). Each resin system contained a different filler material (silica, alumina and silica–alumina particles) incorporated in appropriate amounts into the Bis-GMA-based resin base. The properties investigated were the refractive index, light transmittance, hardness, thermal properties (activation energy) and depth of cure.

2. Materials and methods

The resin matrix was a visible-light-cured system composed of Bis-GMA ((Epoxylite Co., USA) and triethylene glycol dimethacrylate (3G; Tokyo Kasei Co., Tokyo, Japan), 60 and 40 wt %, respectively, according to [8]. Camphorquinone (CQ, 0.5 wt %; Tokyo Kasei Co., Tokyo, Japan) and dimethyl aminoethyl methacrylate (DMAEMA, 0.5 wt %; Tokyo Kasei Co., Tokyo, Japan) were used for the resin, each of which was filled with four types of silica particles (0.012 to 70 μm in diameter), four silica–alumina particles (2.4 to 8.4 μm in diameter) and two alumina particles (0.020 μm; RX was RM surface-treated by hexamethyl disilazane). The fillers used are shown in Table I. The filler was treated for 2 h at 80° C with 1% γ-methacryloxypropyl trimethoxy silane (MPTS;

TABLE I Fillers used in this study (RX filler was RM filler treated with hexamethyl disilazane)

Brand name	Manufacturer	Size (μm)	Main ingredient	Code
Silicic anhydride	Wako Pure Chemicals	7 to 70	SiO_2	SA
Spherical silica	Micron	3.0	SiO_2	SS
RM50	Nippon Aerosil	0.040	SiO_2	R5
Aerosil 200	Nippon Aerosil	0.012	SiO_2	A2
BD	NEG	8.4	SiO_2, Al_2O_3	BD
EF	NEG	4.5	SiO_2, Al_2O_3	EF
BX-38	NEG	4.2	SiO_2, Al_2O_3	B3
BO-9	NEG	2.4	SiO_2, Al_2O_3	B9
RMC	Nippon Aerosil	0.020	Al_2O_3	RM
RXC	Nippon Aerosil	0.020	Al_2O_3	RX

0957–4530/90 $03.00 + .12

TABLE II Amounts of fillers contained in Bis-GMA-based resin

Code	Filler content (wt %)		
	*	**	***
SA	10		35
SS	10	50	90
R5	10	50	50
A2	10		30
BD	10	50	78
EF	10	50	80
B3	10	50	80
B9	10	50	85
RM	10	50	50
RX	10		40

TABLE IV The values of the refractive index when each filler was untreated or treated with 1% γ-MPTS

Code	Refractive index	
	Untreated	Treated
SA	1.4497	1.4562
SS	1.4562	1.4657
R5		1.4750
A2	1.4562	1.4657
BD	1.4960	1.4901
EF	1.5600	1.5521
B3	1.4800	1.4750
B9	1.4630	1.4680
RM		1.5521
RX		1.5619

Shinetsu Silicone Co., Tokyo, Japan) and dried for 3 h at 100° C. The resin specimens were light-cured for 40 sec by means of Quick Light (J. Morita Co., Kyoto, Japan). In Table II the contents (in wt %) of fillers used are indicated, which were 10 wt % (*) for light transmittance measurements, and 50 wt % (**) and 35 to 90 wt % (***) for hardness and thermal properties.

2.1. Optical properties (refractive index and light transmittance)

The refractive index of resin monomer and organic solution was measured by Abbe refractometer (Olympus Co., Tokyo, Japan) at 20° C. The value of fillers used was measured by an indirect method due to immersed solutions which had many known refractive indices of mixtures (isobutyl alcohol, refractive index 1.3953, Katayama Chemicals, Osaka, Japan; trycrolobenzene, 1.5710, Wako Pure Chemicals, Osaka, Japan). The light transmittance of the filler immersed in their mixtures was measured at 467.0 nm according to Table III, because the value (467.0) was equivalent to the absorption peak of CQ. The refractive index of fillers was considered to be the value at which the transmittance had the maximum value [9]. The amount of filler which was added to the Bis-GMA-based resin was determined to be 10 wt %, because the consistency of the resin was obtained at the same rate for all cases. The measurement of Bis-GMA-based resins containing fillers was done for the conditions of Table II. The resin paste was inserted into Teflon rings 6 mm in diameter and 0.5 mm high for the light transmittance measurement. The plastic film (Hawe-Neos Dental Co., Tokyo, Japan; No. 687, thickness 0.5 mm) was set on the upper surface of the resin paste by 40 sec irradiation of Quick Light. The measurement was repeated three times.

2.2. Cure performance

The Knoop hardness and thermal properties were obtained for resins containing different amounts of fillers as indicated in Table II. The former value was measured using microhardness apparatus (Akashi Co., Osaka, Japan; MVK type, loading 50 g for 30 sec). At intervals of 0.5 mm from the upper surface of the specimen, measurements were made three times at each depth for the three pieces of specimen [10, 11].

The activation energy for curing was calculated using differential scanning calorimetry (DSC; Shimadzu Co., Kyoto, Japan; DT-30), similarly to the study reported in [12]. At the apparatus the distance between the aluminium cell (sample weight 10 ± 0.1 mg) and the outlet of the visible-light unit was 3 mm. A cell without alumina powder was used at a reference side in the apparatus. The environmental temperatures selected were 10, 30 and 50° C. The activation energy for visible-light polymerization was obtained according to the Arrhenius plot [12–14].

TABLE III Measurement condition for light transmittance

Apparatus	UVIDEC 610B
Data mode	%T
Bandwidth	2.00 nm
Time constant	0.4 sec
λ scale	20 nm cm^{-1}
Scan speed	400 nm min^{-1}
Cell	Quartz

3. Results

The refractive index of Bis-GMA and 3G comonomer is shown in Fig. 1. The values for Bis-GMA and 3G monomers were, respectively, 1.5510 and 1.4602, and the value for the comonomer of 60 wt % Bis-GMA and 40 wt % 3G was 1.5138. The resin containing both

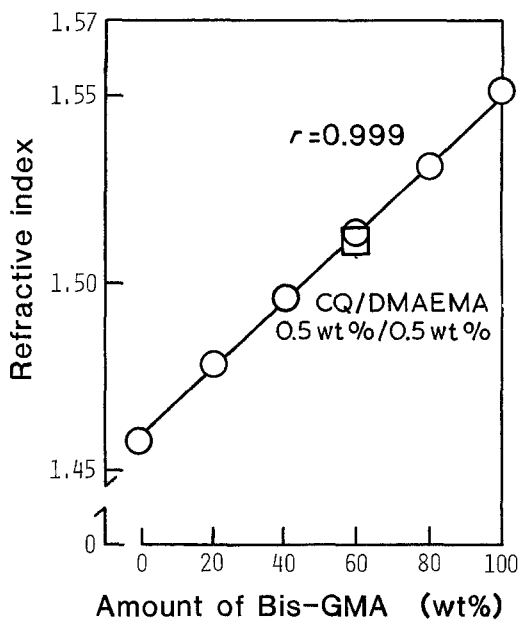

Figure 1 The change in the refractive index with amount of Bis-GMA monomer content in Bis-GMA-based resin tested (3G monomer was used as a comonomer).

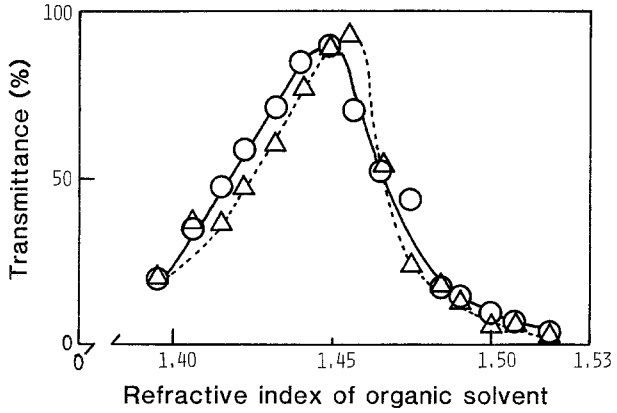

Figure 2 Typical example – the relationship between the refractive index of the organic solvent and light transmittance when the filler SA (10 wt %) was contained. (○) Untreated filler and (△) 1% γ-MPTS treated filler.

TABLE V Values of light transmittance for fillers in the resins indirectly measured by organic solvents (both uncured resin paste and visible-light-cured resin containing 10 wt % as a filler were used)

Code	Transmittance (%)			
	Paste only		Resin (10 wt % filler)	
	Untreated	Treated	Untreated	Treated
SA	11.0 ± 0.4	10.6 ± 1.0	11.1 ± 1.2	8.8 ± 1.4
SS	2.2 ± 0.2	3.3 ± 0.2	0.2 ± 0.1	0.4 ± 0.1
R5		28.1 ± 1.0		2.6 ± 0.8
A2	91.3 ± 4.1	53.2 ± 2.3	75.7 ± 1.8	45.9 ± 2.4
BD	73.1 ± 14.4	56.0 ± 3.5	13.8 ± 3.2	4.5 ± 1.4
EF	16.9 ± 4.3	11.8 ± 2.4	37.6 ± 6.2	31.9 ± 6.5
B3	37.8 ± 12.3	29.8 ± 5.0	8.7 ± 3.7	3.8 ± 0.5
B9	12.9 ± 7.2	7.7 ± 1.5	1.7 ± 1.0	1.5 ± 0.3
RM		2.1 ± 0.2		6.6 ± 1.4
RX		19.3 ± 1.4		43.8 ± 0.2

CQ (0.5 wt %) and DMAEMA (0.5 wt %) was determined to be 1.5124. From Fig. 2 (the relationship between refractive index of organic solvent and light transmittance in untreated filler SA and the 1% γ-MPTS-treated one), the peak of transmittance was found, and as a result the value of the refractive index was equivalent to that of filler investigated according to [9]. Table IV indicates the refractive index of the filled resin investigated. The approximate values were 1.45 to 1.48 (silica particles; SA, SS, A2 and R5), 1.55 to 1.56 (alumina particles; RM and RX) and 1.46 to 1.56 (silica–alumina particles; BD, EF, B3 and B9). In Table V (light transmittance) both the resin paste and light-cured resin containing 10 wt % filler for the resin base were used for measurements. The value of light transmittance was decreased by the addition of fillers to the resin base.

The Knoop hardness values for Bis-GMA-based resins are shown in Figs 3a (50 wt % content of filler for the resin base) and b (maximum content). The maximum Knoop hardness was obtained at a depth of 0.5 mm from the upper surface of the specimen. The change of hardness with depth of the specimen was found, ranging from 12 to 42.

The typical DSC curves when visible light was irradiated to the resin paste are shown in Fig. 4, which shows that the heat for curing increased at higher environmental temperature. In Fig. 5 (code BD as a filler) the relationship between $1/T$ (T being the environmental temperature) and H (heat for curing)/T_p (peak time) is plotted to obtain the activation energy for visible-light polymerization [12]. The result is indicated in Table VI. The activation energy changed from 3.3 (unfilled resin; 60 wt % Bis-GMA and 40 wt % 3G) to 2.2 as a lower value (B9 filler; 50 wt %) or 3.8 as an upper one (B9; 85 wt % filler).

4. Discussion

Experimental resin systems (60 wt % Bis-GMA and 40 wt % 3G; CQ/DMAEMA = 0.5 wt %/0.5 wt % for the resin base) which contained the inorganic fillers indicated in Table I were examined for optical and

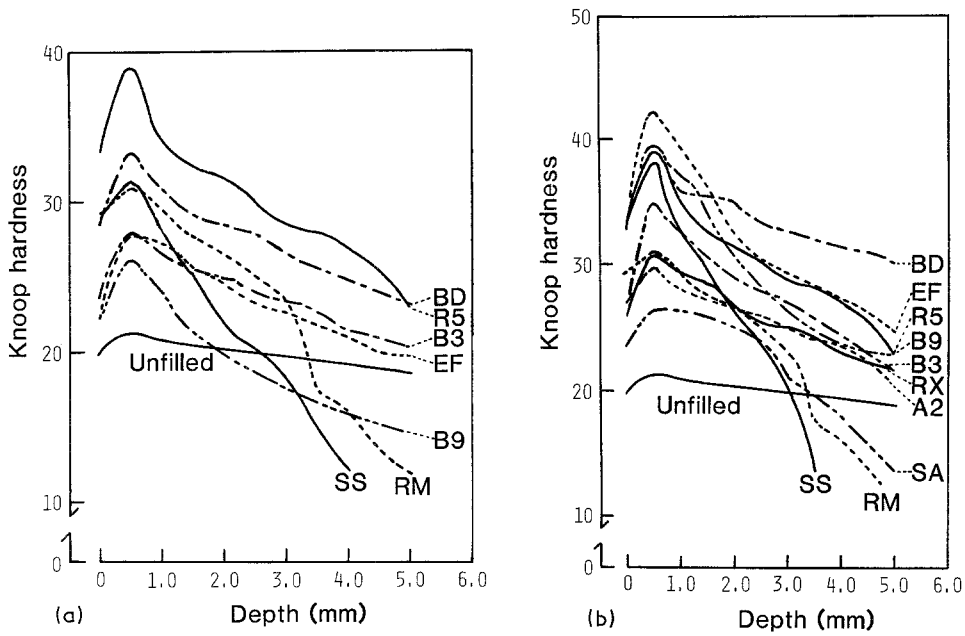

Figure 3 Knoop hardness and depth of cure from the upper surface specimen in filled Bis-GMA-based resins. (a) Filler content 50 wt % and (b) maximum content as a filler to each Bis-GMA-based resin.

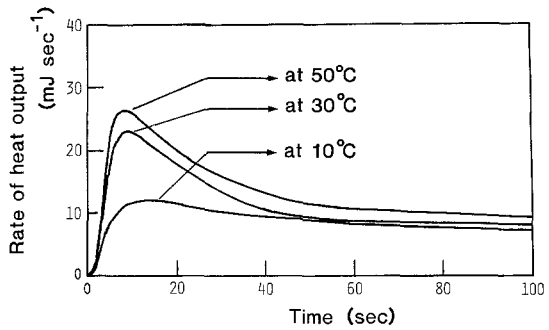

Figure 4 DSC curves at 10, 30 and 50° C for BD filler-containing Bis-GMA-based resin (78 wt % as a filler).

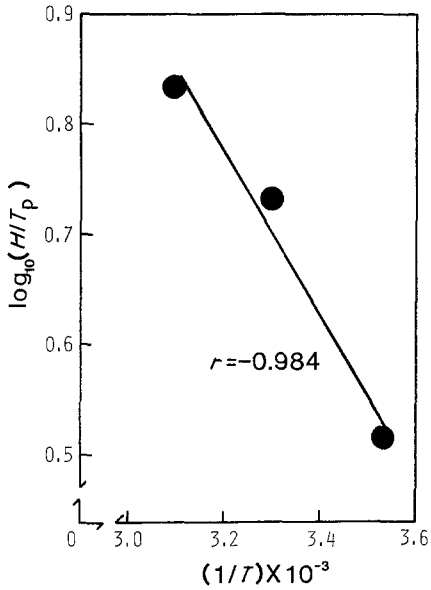

Figure 5 A plot of $1/T$ (T being the absolute isothermal temperature) against log H (heat for curing)/T_p (peak time).

thermal properties. The results indicate that the filler characteristics such as filler type and content had a significant effect on the refractive index, light transmittance and activation energy for curing in the experimental resin systems. Increased filler content (20 to 65 wt %) in polyphenylene polymethacrylate resin matrix resulted in an increase in hardness, compressive strength and stiffness [7].

The refractive index in unfilled resin (60 wt % Bis-GMA and 40 wt % 3G; 1.5138) was lower (1.5124) when the photo-initiator of CQ/DMAEMA = 0.5 wt %/0.5 wt % was added to the resin base. The effect of surface treatment of fillers on refractive index is as shown in Table IV, because a scattering at the interface of filler and treated layer due to surface treatment may occur. As indicated in Table IV, the refractive index of fillers ranged from 1.4497 to 1.5619. It would be thought that the smaller difference of refractive index between filler and comonomer would be better, because the scattering between them could be decreased. In Figs 6a and b, the relationship between light transmittance and depth of cure and also the one between depth of cure and the refractive index difference are shown. At a depth of 0.5 mm from the upper surface the maximum hardness value was found (Figs 3a and b). In this study the depth of cure was assumed to be the position where the percent of 80 to the maximum value for each hardness was equivalent [10, 11]. The depth of cure depended on the transmittance value (Fig. 6a) and the refractive index difference (Fig. 6b). The depth of cure increased with increasing light transmittance in each resin containing 50 wt % as a filler. The largest depth of cure for BD filler-containing resin was consistent with the largest transmittance value of all filler-containing resins. As the light scatter was affected by the depth of cure in composite resins [15], the very small fillers (A2, R5, RM and RX) would indicate a decreased scattering of light, compared with the large-sized fillers (BD, B3, EF, SA and SS). The difference in the refractive index between comonomer and filler was important (Fig. 6b), and the greater depth of cure was explained by the smaller difference of refractive index. Considering the activation energy for visible-light polymerization, the effect of the refractive index difference on the cure performance in experimental resin systems was observed (Table VI and Figs 6a and b). The results show that the activation energy (3.3 kcal mol^{-1}) in unfilled Bis-GMA-based resin showed a small change when the filler was contained.

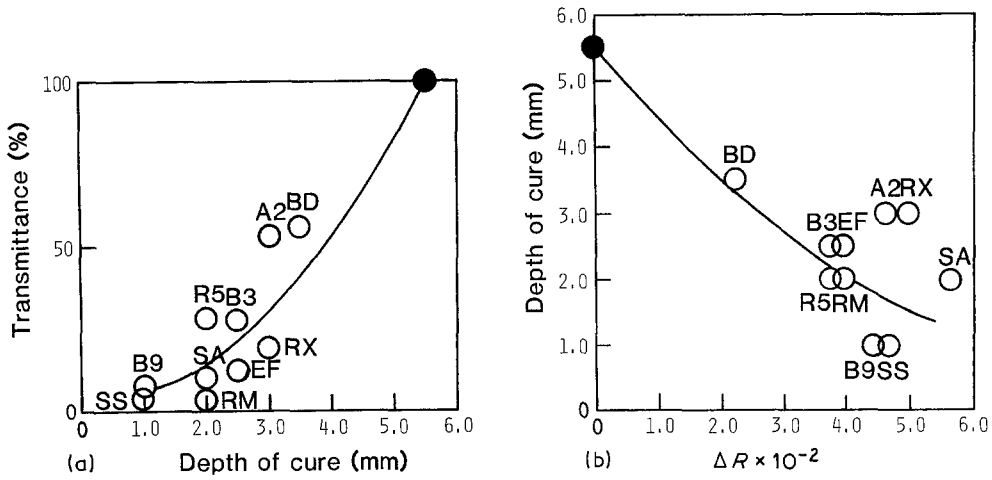

Figure 6 (a) Relationship between the depth of cure and light transmittance in the Bis-GMA-based resins (1 % γ-MPTS treated filler; 50 wt % content of the filler for resin base). (●) Unfilled resin and other symbols as in Table I. (b) Relationship between the refractive index difference and depth of cure in the resins (the difference ΔR was obtained between Bis-GMA and 3G comonomer R_B and filler R_F). For key, see Table I.

TABLE VI Values of the activation energy for filled Bis-GMA-based resins (R5, BD and B9) and unfilled Bis-GMA-based resin

Code	Activation energy (kcal mol^{-1})
R5 (50 wt %)	2.9
BD (50 wt %)	3.3
BD (78 wt %)	3.4
B9 (50 wt %)	2.2
B9 (85 wt %)	3.8
Unfilled	3.3

In each visible-light-cured Bis-GMA-based resin matrix, which was filled with different types of fillers, the optical and thermal properties were examined. The analysis data from the results shows that both the light transmittance and depth of cure were influenced by the filler and matrix refractive index difference in the Bis-GMA-based resin. The results obtained in this study for the filler characteristics may apply only to the similar type of resin matrix. It is therefore desirable that the cure performance in filled resin series with different resin matrices could be determined using the same filler material.

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Received 13 October
and accepted 19 October 1989