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Application of multifunctional base monomer to dental composite resins

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Experimental composite resin systems were prepared with visible-light-cured multifunctional matrices to which various amounts of organic composite filler were added. In comparison with the unfilled resins, the filled resin systems were tested for Knoop hardness, compressive and diametral tensile tests, thermal properties, and water sorption. Analyses of the results obtained for the unfilled resins indicate that the increased hardness and mechanical strength were dependent on the multifunctional base monomer. The effective composite resin system was the one that was filled with organic composite filler in the multifunctional comonomer having triethylene glycol dimethacrylate as a diluent monomer.

1. Introduction

2,2-Bis-[4-(3-methacryloxy-2-hydroxypropoxy)phenel] propane (Bis-GMA)-based resin matrix was examined for its optical and thermal properties [1], and that work suggests that the filler characteristics depend on the refractive index difference between the filler and the resin matrix. As both the fillers and the matrices were different among commercial dental composite resins, the filler and matrix constitution of the resin system should be controlled to clarify its effect on the properties. The resin matrices analysed were generally Bis-GMA, triethylene glycol dimethacrylate (3G) and urethane dimethacrylate [2–7]. The type (chemical composition) of fillers used was mainly silica particles of different sizes [6, 8]. Therefore, the resin formulations which contained a constant fraction of fillers to resin matrix could be investigated. The mechanical, physical and thermal properties were examined in experimental composite resins, each of which was filled by a similar organic composite filler incorporated in constant amounts into four different resin matrices. The purpose of this study was to examine the effect of resin matrices on the properties of the composite resins. The properties investigated were the refractive index of comonomers, base monomers and diluent monomers, the mechanical properties (compressive and diametral tensile strengths), a physical property (water sorption) and thermal properties (activation energy for curing, polymerization shrinkage and coefficient of thermal expansion).

2. Materials and methods

2.1. Specimen preparation

The resin base monomers investigated in this study were Bis-(1-methacryloryloxy-3-acryloryloxy-2-propanetriyl)-N,N′-hexamethylene dicarbamate (MAP-HMDC; Shin-Nakamura Chemicals, Tokyo, Japan) and Bis-GMA (Epoxylite Co., USA). The diluent monomers used were 3G (Tokyo Kasei Co., Japan), neopenthyl glycol dimethacrylate (NPG; Shin-Nakamura Chemicals, Tokyo, Japan) and diacryloyl pentylidene penta-erythrite (DAPPE; Showa High-polymer Co., Tokyo, Japan). Using the monomers with chemical structural formulae shown in Fig. 1, the experimental comonomers were cured as indicated in Table I. In this study the control resin specimen was 60 wt % Bis-GMA and 40 wt % 3G comonomer, for which it was reported that the resin matrix had better mechanical properties [9]. Camphorquinone (CQ; Tokyo Kasei Co., Tokyo, Japan) and dimethyl-*p*-toluidine (DMPT; Tokyo Kasei Co., Tokyo, Japan) contained 0.5 wt % to the experimental comonomer.

The experimental composite resin series, which were filled with organic composite filler, were prepared using resin comonomers. The filler was prepared as follows: the organic constituent was prepared from trimethylol propane trimethacrylate (TMPT; Shin-Nakamura Chemicals, Tokyo, Japan) and the inorganic filler was colloidal silica RM50 (Japan Aerosil Co., Tokyo, Japan; particle size 0.040 μm), which was surface-treated by γ-methacryloxypropyl trimethoxy silane. The amounts of inorganic and organic constituents were each 50 wt %, and the composite was cured with benzoyl peroxide (BPO; Katayama

TABLE I Experimental resin monomer compositions

Code	Monomer composition	(wt %)
T-5	MAP-HMDC · 3G	50:50
T-4	MAP-HMDC · 3G	60:40
T-3	MAP-HMDC · 3G	70:30
N-5	MAP-HMDC · NPG	50:50
N-4	MAP-HMDC · NPG	60:40
N-3	MAP-HMDC · NPG	70:30
S-5	MAP-HMDC · DAPPE	50:50
S-4	MAP-HMDC · DAPPE	60:40
S-3	MAP-HMDC · DAPPE	70:30
B-4	Bis-GMA · 3G	60:40

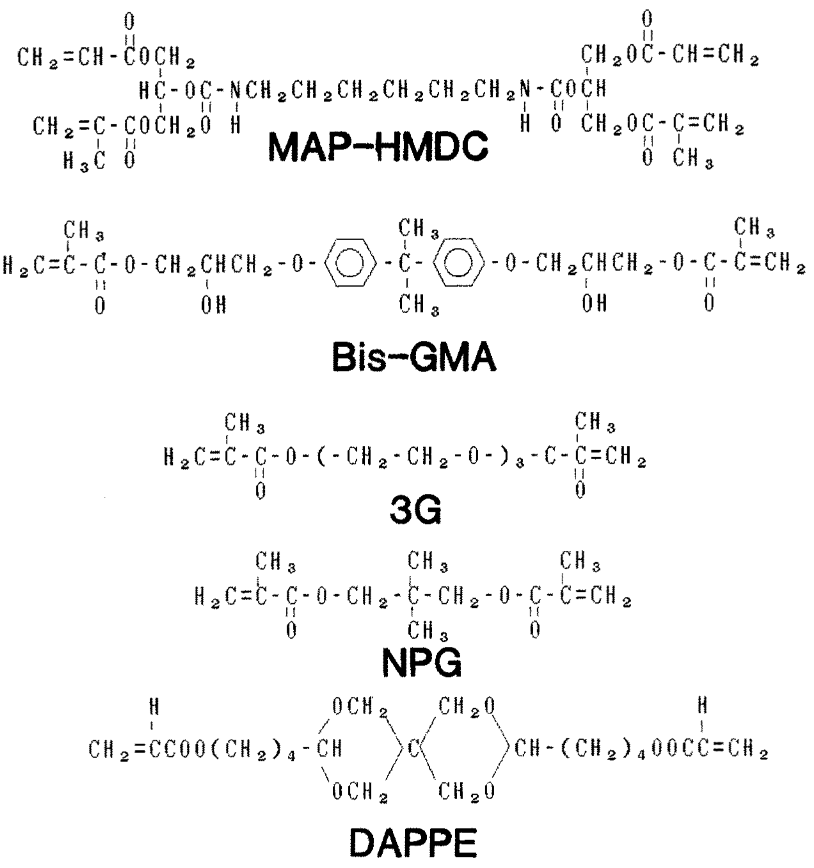

Figure 1 Structural formulae of MAP-HMDC, Bis-GMA, 3G, NPG and DAPPE.

Chemicals, Tokyo, Japan; 0.5 wt % for the resin base) for 30 min at 130° C. The cured specimens were powdered by spectro-mill (Mitamura Riken Inc., Tokyo, Japan), and the particle size used was that which passed through 325-mesh (44 μm).

2.2. Properties investigated

2.2.1. Experimental 1: comonomers

The refractive index (at 20° C) was measured by Abbe refractometer (Olympus Co., Tokyo, Japan) according to [1]. The mechanical and physical properties obtained were: Knoop hardness in the cured specimens (diameter 6 mm and height 3 mm) after water immersion at 37° C for 1, 2, 4, 7 and 30 days, compressive (diameter 3 mm and height 6 mm) and diametral tensile tests (diameter 6 mm and height 3 mm), the amount of water sorption (diameter 7 mm and height 1 mm; water immersion at 37° C for 1, 2, 4, 7, 30 and 60 days) and the amount of residual monomer (measurement condition as indicated in Table II, diameter 6 mm and height 3 mm). Water sorption has been described by the expression in weight gain to the initial weight over the test period (wt %) [10–12] or weight gain per surface area (mg cm^{-2}) [8, 13, 14]. The value of water sorption was calculated, in this study, for each specimen as follows: water sorption (mg cm^{-2}) = [weight of sample after immersion (mg) − conditioned weight (mg)]/surface area (cm^2), according to the procedure defined in [14].

TABLE II Measurement conditions for residual monomers

Apparatus	Shimadzu GC-14A
Solvent	MeOH
Liquid phase	Silicon OV-1 2%
Support	Uniport HP 60/80 mesh
Column	2.0 m
Carrier gas	Nitrogen
Column temperature	100 to 280° C
Injection temperature	300° C
Detection temperature	340° C
Temperature rate	15° C min^{-1}
Detector	FID

The thermal property of activation energy due to visible-light curing was also measured by differential scanning calorimetry (DSC) [9]. The visible light was irradiated for 40 sec (Quick Light; J. Morita Co., Kyoto, Japan). The other conditions for the measurements are detailed in [1, 9].

2.2.2. Experimental 2: composite resins

The values of Knoop hardness and mechanical strengths were measured for experimental composite resins containing organic composite filler. Experimental composite resins with optimum monomer contents obtained by adding organic composite fillers to unfilled resin comonomers, such as the T-3, N-3, S-3 and B-4 series, were investigated. The filler contents selected were 65 and 70 wt % for the resin matrices. An electron microanalyser (EPMA: Shimadzu Co., Kyoto, Japan) was used for the experimental composite resins which were visible-light-cured for 40 sec and polished using emery paper (No. 1500) and alumina powder (0.03 μm) after curing. The mechanical and physical properties were measured similarly to as described in the previous section.

Thermal expansion, the thermal expansion coefficient and the glass transition temperature (T_g) were obtained (Rigaku; TMA standard type, 5° C min^{-1} in the temperature range 20 to 150° C). For the cured specimen (diameter 5 mm and height 3 mm) the polymerization volumetric shrinkage when cured for 40

TABLE III Refractive index of comonomers, base and diluent monomers

Code	Refractive index
T-5	1.4741 ± 0.0001
T-4	1.4769 ± 0.0001
T-3	1.4791 ± 0.0001
N-5	1.4699 ± 0.0001
N-4	1.4739 ± 0.0001
N-3	1.4775 ± 0.0003
S-5	1.4845 ± 0.0001
S-4	1.4851 ± 0.0001
S-3	1.4860 ± 0.0002
B-4	1.5136 ± 0.0002
MAP-HMDC	1.4895 ± 0.0003
Bis-GMA	1.5510 ± 0.0001
3G	1.4602 ± 0.0001
NPG	1.4541 ± 0.0001
DAPPE	1.4795 ± 0.0001

and 80 sec by Quick Light light unit was calculated from the difference between both specific weights of uncured and cured specimens, using a specific gravity bottle, similarly to a graduated dilatometer tube attached to a density tube [15].

3. Results

3.1. Experimental 1

The refractive index of experimental comonomers, base monomers and diluent monomers are indicated in Table III. The value of comonomers used ranged from 1.4699 (N-5) to 1.4861 (S-3), representing a lower value than MAP-HMDC (1.4895) and Bis-GMA (1.5510). The values of the diluent monomers (3G, NPG and DAPPE) were found within the range of base monomers, showing that their selection was appropriate to make comonomers in resin formulations.

In Table IV (Knoop hardness after water immersion) a decrease of Knoop hardness with increasing period of immersion in water is found. The decrease of hardness at 30 days immersion compared with that after curing was remarkable for the comonomer systems containing DAPPE as a diluent monomer. Table V indicates the strength values at compressive and diametral tensile tests, showing that diametral tensile strength became especially large in the comonomers with 3G as a diluent monomer. The water sorption in the comonomers (Table VI) over the 60 day period indicates that there is a significant difference ($p < 0.01$) between N-series and T-series, or S-series, or B-4, and the tendency of increasing water sorption with increasing period was found.

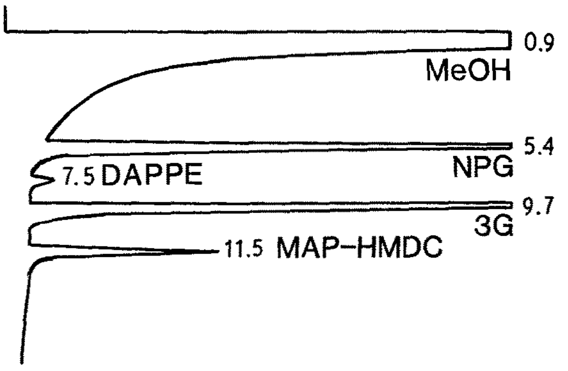

Figure 2 An example of a gas chromatograph.

In Fig. 2 (gas chromatograph showing the findings for MAP-HMDC, 3G, NPG and DAPPE) and Figs 3a to d (calibration curves for each monomer), the residual monomers were measured. The value at each peak indicates the retention time where each monomer could be detected. Fig. 4 shows the total amount of residual monomer of experimental comonomers which ranged from 1/2 to 1/5 compared with that of B-4 comonomer. For the T-series the total amount of residual monomers containing diluent and base monomers were lower than those of the other series. Table VII presents the activation energy for curing the comonomer formulations with visible light. In the experimental comonomers the values (0.4 to 2.4 kcal mol^{-1}) were smaller than that of B-4 comonomer (4.0 kcal mol^{-1}). In Fig. 5 typical DSC curves (10, 30 and 50° C; isothermal temperature) were obtained to calculate the activation energy in Table VII.

3.2. Experimental 2

The refractive index of organic composite filler (FTP), 1.4831 in this study, showed an almost identical value to S-3 comonomer (1.4860). It has been reported that the hardness value changed with the depth of the cured specimen from the upper surface [16]. The values decreased with increasing depth of cure and became less than 20 at a depth of about 5 to 7 mm. Figs 6 to 9 show typical electron micrographs of filled resins which contained 65 wt % as a filler to the resin

TABLE IV The values of Knoop hardness in experimental comonomers investigated after water immersion

Code	Period					
	After	1 day	2 days	4 days	7 days	30 days
T-5	18.3 ± 1.3	15.6 ± 0.3	17.2 ± 0.3	15.7 ± 0.4	15.6 ± 0.6	13.7 ± 1.2
T-4	19.0 ± 2.0	16.6 ± 1.3	17.1 ± 1.3	16.7 ± 0.5	16.2 ± 0.2	15.8 ± 0.2
T-3	16.4 ± 0.5	16.0 ± 0.4	15.3 ± 0.4	16.5 ± 1.0	14.0 ± 0.8	14.3 ± 0.4
N-5	17.7 ± 1.0	17.2 ± 1.1	17.7 ± 0.3	17.5 ± 0.4	17.8 ± 1.4	17.1 ± 0.5
N-4	17.6 ± 0.3	17.3 ± 0.4	18.1 ± 0.8	16.4 ± 0.1	16.1 ± 1.0	15.4 ± 0.9
N-3	16.5 ± 1.2	17.2 ± 2.4	17.8 ± 0.6	17.7 ± 0.9	16.2 ± 1.4	15.2 ± 0.3
S-5	17.0 ± 0.8	13.9 ± 0.2	16.2 ± 1.8	12.7 ± 0.9	11.6 ± 0.4	11.1 ± 0.2
S-4	19.8 ± 0.8	13.1 ± 0.3	13.7 ± 0.3	12.5 ± 1.0	11.7 ± 0.4	11.6 ± 0.4
S-3	18.8 ± 1.6	16.1 ± 0.8	14.1 ± 1.1	15.3 ± 0.6	12.4 ± 1.2	12.8 ± 1.0
B-4	19.3 ± 1.6	19.0 ± 0.2	17.5 ± 0.6	17.3 ± 1.0	16.5 ± 0.8	15.2 ± 0.5

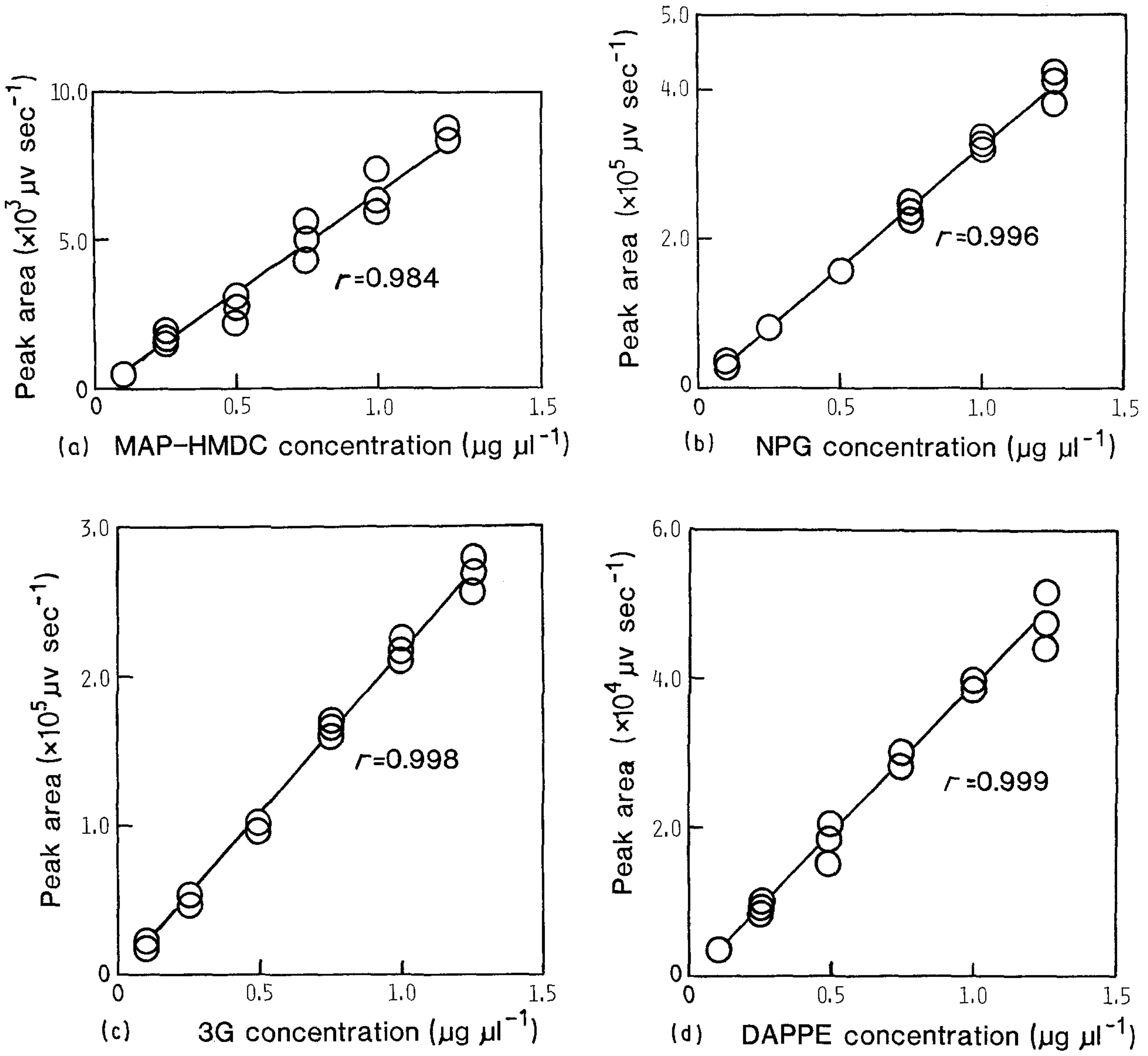

Figure 3 Calibration curves of (a) MAP-HMDC, (b) NPG, (c) 3G and (d) DAPPE.

base. Their resins contained organic composite filler of average size $44\,\mu m$. For the composites the porosity formation due to curing was not found, showing the good cure performance in the multifunctional comonomer systems investigated. In Table VIII (Knoop hardness, and compressive strength and proportional limit at compressive test) the hardness and strengths as related to filler content are presented. The values in parentheses indicate the contents of inorganic filler to the resin base within the organic composite filler. The hardness and strengths increased with increasing organic filler content from 65 to 70 wt % for a resin base.

From Table IX (thermal expansion, coefficient of thermal expansion and T_g) and Table X (polymerization shrinkage) the thermal properties in experimental

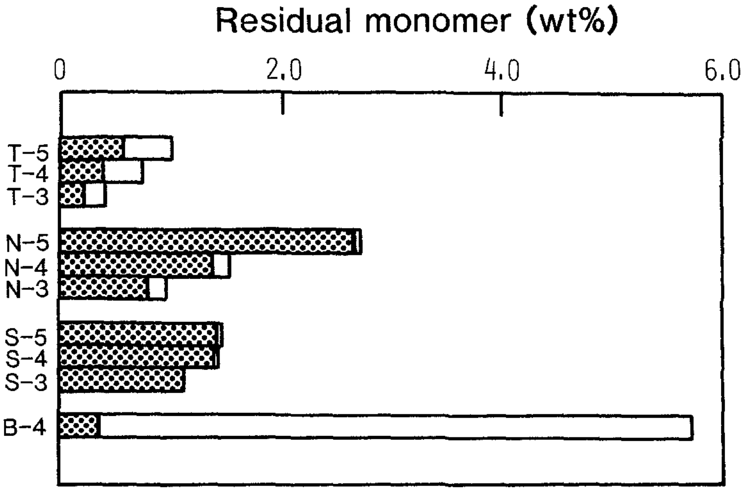

Figure 4 The amounts of (□) residual monomers of base and (▨) diluent monomers in the experimental resin systems.

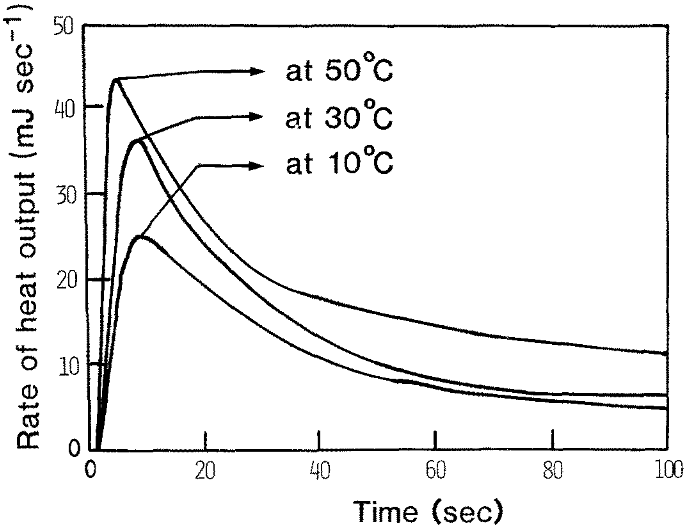

Figure 5 Examples of DSC curves at 10, 30 and 50°C (isothermal temperature).

composite resin systems were improved compared with B-4-based composite resins (B4-1 and B4-2). The polymerization shrinkage in the T-3 series was much smaller than those in the N-3 and S-3 series, and the former value was almost the same as in the B-4 series. The shrinkage value increased about 1.2 times when the irradiation time increased from 40 to 80 sec. The water sorption of experimental composite resin series over a 30 day period (Table XI) ranged from 0.94 to 1.35 (mg cm^{-2}), similarly to that in B-4 composite resins (1.09 to 1.17 mg cm^{-2}). The composite resins containing 70 wt % filler sorbed significantly less water than did the 65 wt % filler-containing resin.

4. Discussion

The results obtained in this study show that the contents of base and diluent monomers had a significant effect on the properties investigated. In particular the multifunctional monomer (MAP-HMDC) as a base monomer was used with diluent monomers such as 3G, NPG and DAPPE. The DAPPE diluent monomer developed as applied to the spilane resin system was utilized in dental composite resin [17–19]. As shown in Fig. 1, the MAP-HMDC base comonomer with hexamethylene base would be workable compared with Bis-GMA with aromatic base. The use of MAP-HMDC improved mechanical properties (Knoop hardness, Table IV; compressive and diametral tensile strengths, Table V) with the exception of those having DAPPE diluent monomer. The diametral tensile strength decreased compared with B-4 Bis-GMA-based resin.

In the base comonomer MAP-HMDC with urethane base the water sorption would be increased compared

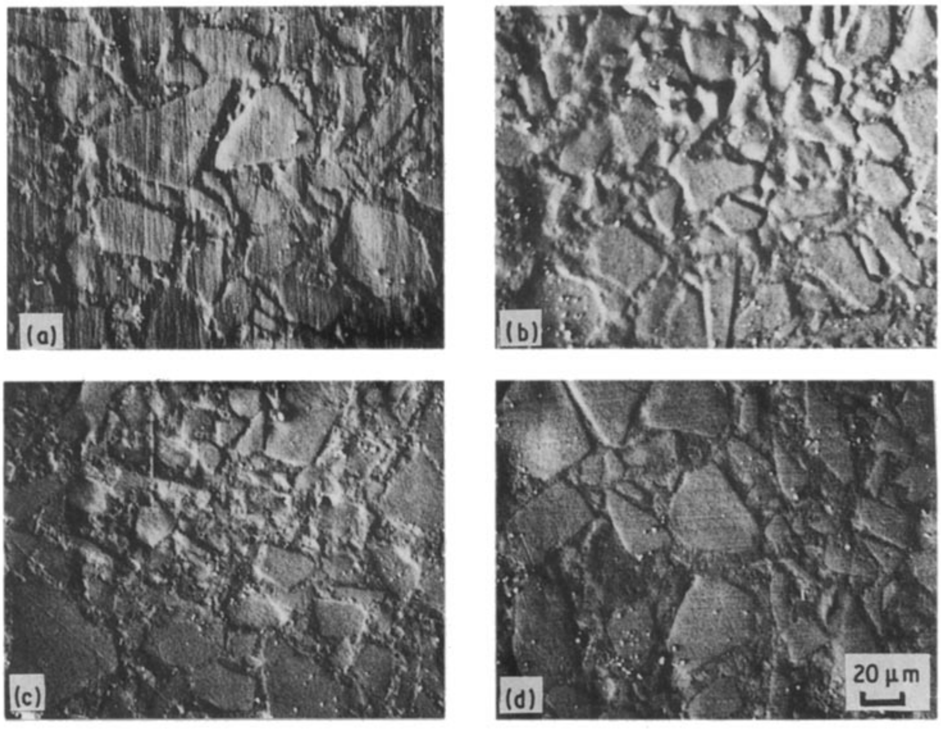

Figure 6 Electron micrographs of (a) T3-1, (b) N3-1, (c) S3-1 and (d) B4-1 composite resin systems (filler content 65 wt %): secondary electron image.

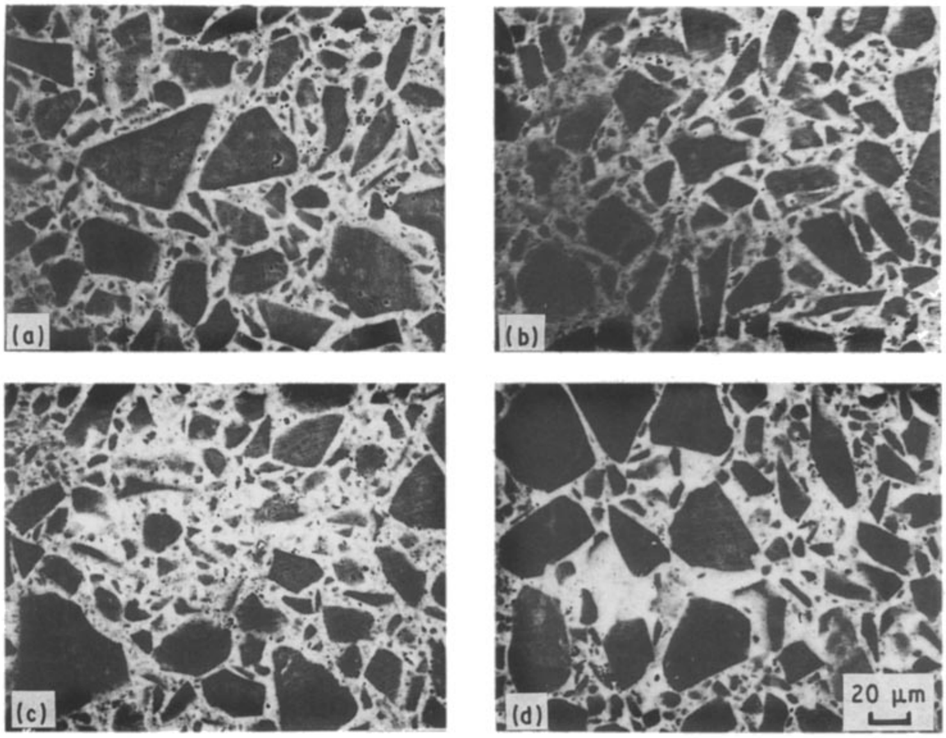

Figure 7 Specimen current image in Fig. 6.

with that with urethane base [20–22]. As a cure performance the activation energy for visible-light curing in base and diluent monomers was an important factor in the polymerization process [1, 23]. As indicated in Table VII, the multifunctional base monomer was effective in curing the unfilled resins (comonomers); the values were lower than that in Bis-GMA-based resin B-4.

In this study the analyses of the results obtained for experimental resin systems (TMPT organic composite filler) indicated that the kind of filler had an influence on the curing efficiency and refractive index, and the organic composite filler was useful for the composite resin system. Therefore, the comonomer systems MAP-HMDC. 3G (T-3), MAP-HMDC. NPG (N-3) and MAP-HMDC. DAPPE (S-3) were selected from larger values of strengths (Table V), and the composite resins containing TMPT organic filler had improved properties. The hardness changed with

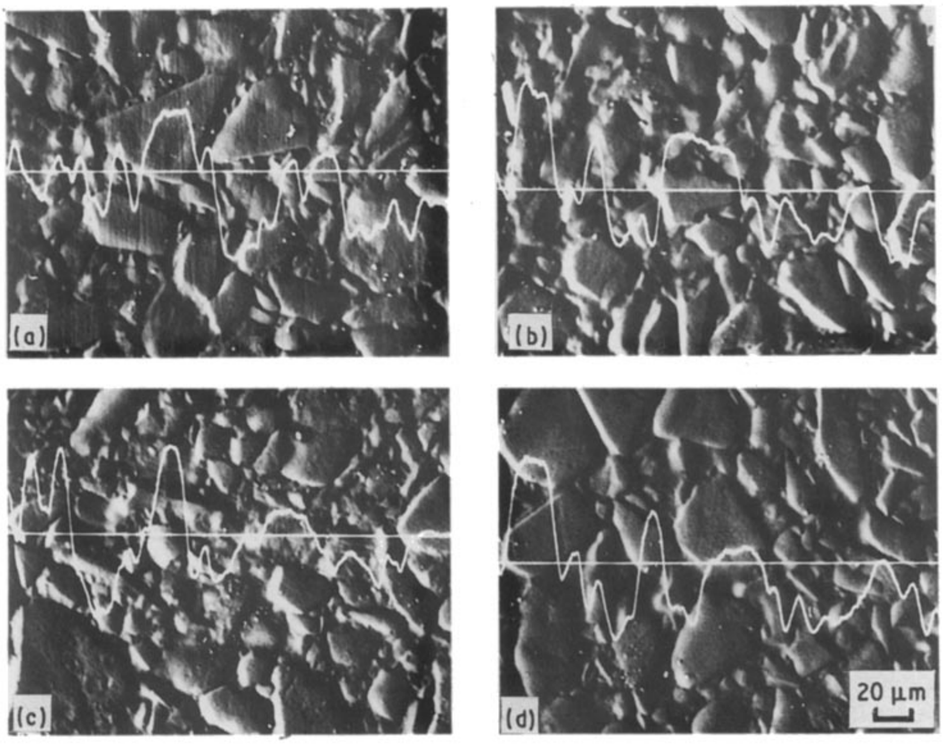

Figure 8 Line analysis of element silicon in Fig. 6. The straight line shows the portion analysed.

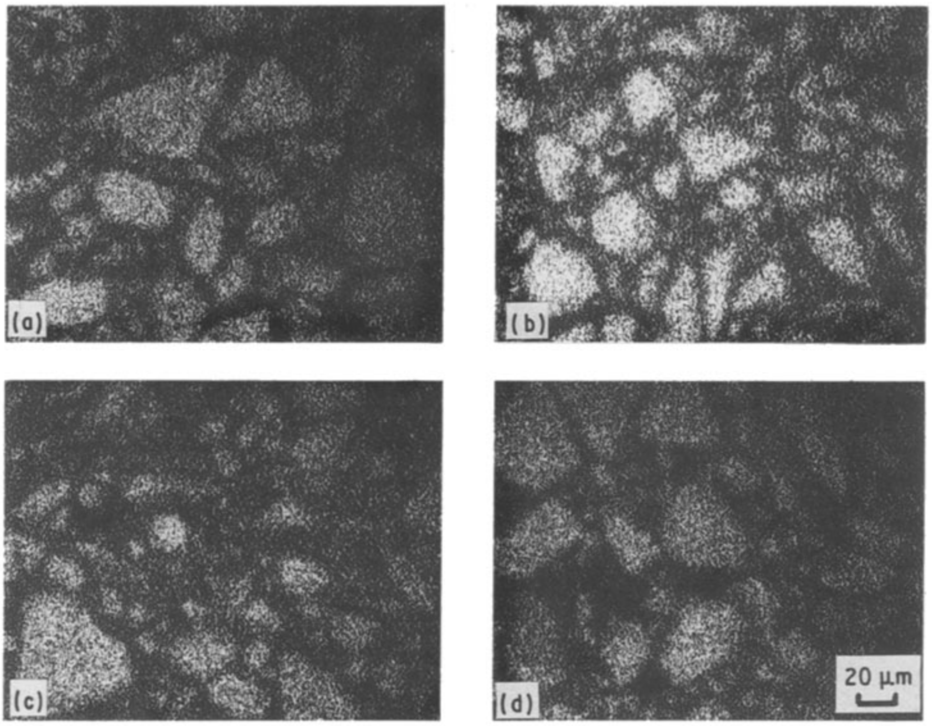

Figure 9 Silicon mapping image in Fig. 6.

increase from 65 to 70 wt %, compared with B-4 resin series filled with the organic filler. In addition the experimental composite resin series had larger values than those of B-4 ones (Table VIII). The values of T_g were larger than for B-4 and the thermal expansion coefficient decreased in the experimental resin series.

TABLE V Compressive and diametral tensile strengths

Code	Compressive strength (kg cm^{-2})	Diametral tensile strength (kg cm^{-2})
T-5	989.6 ± 413.4	503.7 ± 67.7
T-4	1172.4 ± 346.8	593.9 ± 145.7
T-3	1179.5 ± 184.7	646.4 ± 110.6
N-5	1074.0 ± 252.2	433.8 ± 97.7
N-4	1153.1 ± 84.2	391.1 ± 25.0
N-3	1179.5 ± 107.2	377.6 ± 144.0
S-5	1248.9 ± 120.3	370.0 ± 31.2
S-4	1266.8 ± 53.4	267.9 ± 35.0
S-3	1342.3 ± 195.4	222.2 ± 11.9
B-4	982.2 ± 49.6	409.7 ± 45.6

The finding for the experimental multifunctional resin systems was the increased hardness and mechanical strength with an increase of filler content. Again, this was the most pronounced in the T-3, N-3 and S-3 resin series filled with TMPT organic filler. However, the polymerization shrinkage of the resin series N-3 and S-3 was more than 5%. As the diluent monomers of NPG and DAPPE were used, the shrinkage would become large during polymerization due to visible light compared with Bis-GMA-based resin series B-4. The shrinkage value was about 3% when the 3G diluent monomer was used, and the value was similar to the B-4 ones.

The ultimate properties of dental composite resin systems are undoubtedly the result of an interaction of the properties of constituents in the systems, and this result would be applied to the filled resin containing a similar organic composite filler in similar types of matrices. The main analysis data could be useful for the development of new resin systems with multifunctional base monomer in the dental field.

TABLE VI Water sorption after water immersion (mg cm^{-2})

Code	Period					
	1 day	2 days	4 days	7 days	30 days	60 days
T-5	1.12 ± 0.16	1.33 ± 0.23	1.45 ± 0.22	1.37 ± 0.31	1.58 ± 0.22	1.44 ± 0.24
T-4	1.25 ± 0.12	1.62 ± 0.35	1.72 ± 0.15	1.87 ± 0.32	2.07 ± 0.24	2.32 ± 0.45
T-3	1.14 ± 0.34	1.12 ± 0.42	1.20 ± 0.34	1.41 ± 0.47	1.44 ± 0.42	1.65 ± 0.42
N-5	0.58 ± 0.07	0.62 ± 0.13	0.51 ± 0.13	0.40 ± 0.06	0.40 ± 0.24	0.04 ± 0.13
N-4	0.59 ± 0.42	0.95 ± 0.26	0.95 ± 0.33	0.91 ± 0.08	0.99 ± 0.31	1.21 ± 0.13
N-3	0.60 ± 0.32	0.78 ± 0.14	1.03 ± 0.14	1.00 ± 0.20	1.04 ± 0.03	1.18 ± 0.05
S-5	1.20 ± 0.60	1.30 ± 0.59	1.48 ± 0.65	1.44 ± 0.53	1.69 ± 0.37	1.65 ± 0.61
S-4	1.55 ± 0.13	1.69 ± 0.33	1.90 ± 0.12	1.80 ± 0.30	1.83 ± 0.08	2.11 ± 0.20
S-3	0.92 ± 0.37	1.24 ± 0.16	1.41 ± 0.21	1.59 ± 0.01	1.63 ± 0.30	1.69 ± 0.18
B-4	0.92 ± 0.11	1.34 ± 0.16	1.45 ± 0.36	1.48 ± 0.27	1.77 ± 0.15	1.73 ± 0.33

TABLE VII Activation energy for curing due to visible light

Code	Activation energy (kcal mol^{-1})
T-5	1.5
T-4	0.4
T-3	1.0
N-5	2.4
N-4	1.2
N-3	1.8
S-5	0.9
S-4	0.6
S-3	0.8
B-4	4.0

TABLE VIII Mechanical properties of experimental composite resins (TMPT organic composite filler code FTP).

Code	Filler content (wt %)	Knoop hardness	Compressive strength (kg cm^{-2})	Proportional limit (kg cm^{-2})
T3-1	65(39)	26.8 ± 2.0	1760.8 ± 44.2	1049.7 ± 118.3
T3-2	70(42)	34.0 ± 2.2	1800.4 ± 34.0	1090.4 ± 59.7
N3-1	65(39)	26.2 ± 1.1	1329.4 ± 79.4	1049.1 ± 211.9
N3-2	70(42)	33.3 ± 4.1	1507.1 ± 112.1	1255.2 ± 217.1
S3-1	65(39)	30.7 ± 2.3	1957.1 ± 193.0	925.7 ± 72.6
S3-2	70(42)	43.2 ± 0.3	2143.7 ± 209.7	934.2 ± 100.6
B4-1	65(39)	26.6 ± 2.1	1404.1 ± 55.8	571.8 ± 10.1
B4-2	70(42)	30.2 ± 1.6	1407.9 ± 19.9	1023.8 ± 91.0

TABLE IX Thermal properties in the resins (for codes, see Table I)

Code	Filler content (wt %)	Thermal expansion (%)	Coefficient of thermal expansion ($\times 10^{-6}$ °C^{-1})	T_g(°C)
T3-1	65(39)	0.60	35.0	126.7
T3-2	70(42)	0.62	30.0	121.6
N3-1	65(39)	0.51	25.0	129.3
N3-2	70(42)	0.53	30.0	124.7
S3-1	65(39)	0.72	40.0	120.6
S3-2	70(42)	0.66	45.0	117.4
B4-1	65(39)	0.92	50.0	109.6
B4-2	70(42)	0.87	55.0	112.1

TABLE X Polymerization shrinkage at 40 and 809 sec irradiation times

Code	Polymerization shrinkage (%)		
	Filler content (wt %)	Irradiation time	
		40 sec	80 sec
T3-1	65(39)	3.48	4.29
T3-2	70(42)	3.81	3.88
N3-1	65(39)	8.93	9.87
N3-2	70(42)	8.07	9.07
S3-1	65(39)	5.49	6.55
S3-2	70(42)	5.63	6.38
B4-1	65(39)	2.95	3.81
B4-2	70(42)	2.71	3.20

TABLE XI Water sorption (in mg cm^{-2})

Code	Filler content (wt %)	Period				
		1 day	2 days	4 days	7 days	30 days
T3-1	65(39)	0.70 ± 0.23	1.02 ± 0.07	0.86 ± 0.09	1.12 ± 0.23	1.21 ± 0.23
T3-2	70(42)	0.58 ± 0.16	0.77 ± 0.02	0.80 ± 0.05	1.00 ± 0.09	1.19 ± 0.05
N3-1	65(39)	0.62 ± 0.31	0.82 ± 0.11	0.78 ± 0.09	0.85 ± 0.14	0.98 ± 0.25
N3-2	70(42)	0.55 ± 0.30	0.61 ± 0.31	0.78 ± 0.28	0.74 ± 0.30	0.94 ± 0.35
S3-1	65(39)	0.61 ± 0.19	0.84 ± 0.05	0.87 ± 0.10	1.13 ± 0.07	1.35 ± 0.10
S3-2	70(42)	0.44 ± 0.06	0.79 ± 0.12	0.69 ± 0.05	0.91 ± 0.03	1.16 ± 0.05
B4-1	65(39)	0.55 ± 0.31	0.88 ± 0.02	0.94 ± 0.04	1.01 ± 0.04	1.17 ± 0.07
B4-2	70(42)	0.45 ± 0.12	0.64 ± 0.12	0.70 ± 0.07	0.83 ± 0.22	1.09 ± 0.17

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