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Mechanical strength of urethane-based visible-light-cured resins

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In experimental urethane-based visible-light-cured(VLC) resins containing a diluent monomer, a lower value of activation energy for polymerization than in *bis*-GMA-based VLC resin was obtained. A greater increased diametral tensile strength and slightly larger compression strength were observed. The diluent monomer in the urethane-based VLC resins gives an increase of strength, associated with lower activation energy for polymerization, compared with the *bis*-GMA-based resin.

1. Introduction

Dental resins were polymerized by an extra-oral cure involving visible light and/or heat [1]. The *bis*-GMA-based visible-light-cured (VLC) resins exhibited an increase in hardness and mechanical strength owing to an increasing degree of polymerization [1–8]. The monomer compositions and the concentration of catalyst in VLC resins were very important in the visible-light polymerization [5, 6]. By analysing the extent of polymerization of base monomer systems, the appropriate percentage of base monomers (*bis*-GMA; bisphenol A glycidyl dimethacrylate and TEGDMA; triethylene glycol dimethacrylate) was 60 and 40 wt % [5, 6]. Because dental VLC resins need a source of heat in the blue-light range of the spectrum to cure them [9, 10], differential scanning calorimetry (DSC) was necessary to determine the thermal properties of VLC resins, especially the activation energy for visible-light curing under isothermal mode [6, 11–13]. Heat-cured resins based on urethane dimethacrylate and 2-hydroxyethyl methacrylate are superior to heat-cured *bis*-GMA-based resins with respect to mechanical strength [14]. In order to develop urethane-based VLC resin, it was effective to examine the effect of a diluent monomer on activation energy for VL curing in urethane-based VLC resins, and also to evaluate mechanical strengths (diametral tensile and compression strength) in the VLC resins.

2. Materials and methods

The main monomers and percentages used in this study are given in Fig. 1 and Table I: *bis*-GMA (Shin-Nakamura Chem., Wakayama), TEGDMA (Tokyo Kasei Co., Tokyo), and neopenthyl glycol dimethacrylate (NPG; Shin-Nakamura Chem., Wakayama), and *bis*-(1-methacryloyloxy-3-acryloyloxy-2-propanetriyl)-*N*,*N*′-hexamethylene dicarbamate (MAP-HMDC), diacryloryl pentylidene penta erythrite (DAPPE) and diallylidene penta erythritol (DAPE, Showa High-polymer Co., Tokyo), and camphorquinone (CQ), dimethylaminoethyl methacrylate (DMAEMA), and dimethyl para toluidine (DMPT; Tokyo Kasei Co., Tokyo). Six resin systems were formulated by resin comonomers present within the monomers at a ratio of CQ/DMAEMA (0.5 wt %/0.5 wt %). As a control resin (CONT) *bis*-GMA-based VLC resin (60 wt % *bis*-GMA and 40 wt % TEGDMA) containing CQ/DMPT = 0.5 wt %/0.5 wt % to the matrix resin was used. In the present study, MAP-HMDC·NPG·DAPPE, or DAPE (N-2, N-3) and MAP-HMDC·TEGDMA·DAPPE, or DAPE(T-2, T-3) VLC resin systems including, either DAPPE or DAPE diluent monomer, were examined, because each MAP-HMDC·NPG (N-1; 1.2–2.4), or TEGDMA (T-1; 0.4–1.5) comonomer system had lower activation energy than *bis*-GMA-based resin (CONT; 4.0 kcal mol^{-1}) [6].

The samples were measured by illuminating them in a DSC apparatus (Shimadzu DT-30, Kyoto) with radiation from a visible light source (Quick Light, J. Morita Co., Kyoto) for 100 s at 10, 30 and 50 °C (environmental temperatures), as described previously [6].

The VLC cylindrical samples had dimensions $h = 3.0$ mm, $d = 6.0$ mm for diametral tensile strength ($2F/\pi dl$, $l =$ length and $F =$ force at fracture) and $h = 6.0$ mm, $d = 3.0$ mm for compression strength. The polymerized samples irradiated by Quick Light for 40 s were tested at a cross-head speed of 0.5 mm min^{-1} (diametral tensile strength) and 2.0 mm min^{-1} (compression strength) using an Autograph Testing Machine (Shimadzu DCS-500, Kyoto).

3. Results and discussion

Fig. 2 shows typical DSC curves for unfilled N-1 and N-2 VLC resins (isothermal modes of 10, 30 and 50 °C) during 100 s irradiation. In the curve with a peak, the time at the peak is represented by the peak, and the peak height is shown by the height at the peak time. The heat for curing is defined as the area to reach the

TABLE I Materials used for preparation of unfilled resins (N-1, N-2, N-3, T-1, T-2, T-3, CONT) and the percentages (wt %). See text for key

Code	Composition (wt %)					
	MAP-HMDC	NPG	DAPPE	DAPE	Bis-GMA	TEGDMA
N-1	50	50				
N-2	100/3	100/3	100/3			
N-3	100/3	100/3		100/3		
T-1	50					50
T-2	100/3		100/3			100/3
T-3	100/3			100/3		100/3
CONT					60	40

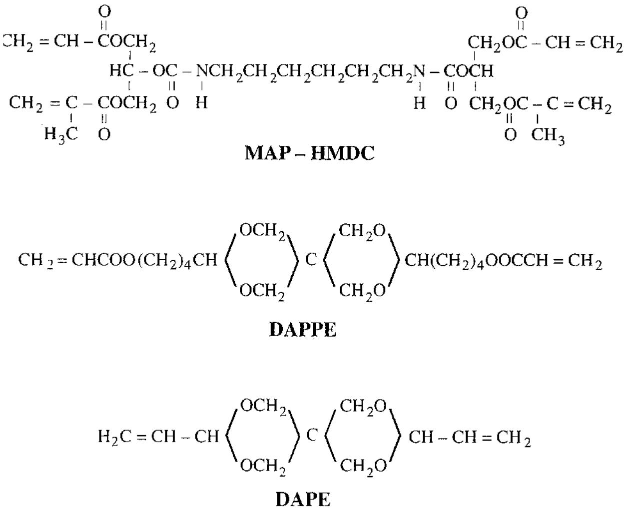

Figure 1 Structural formula of (a) urethane monomer (MAP-HMDC) and the diluent monomers (b) DAPPE and (c) DAPE. See text for key.

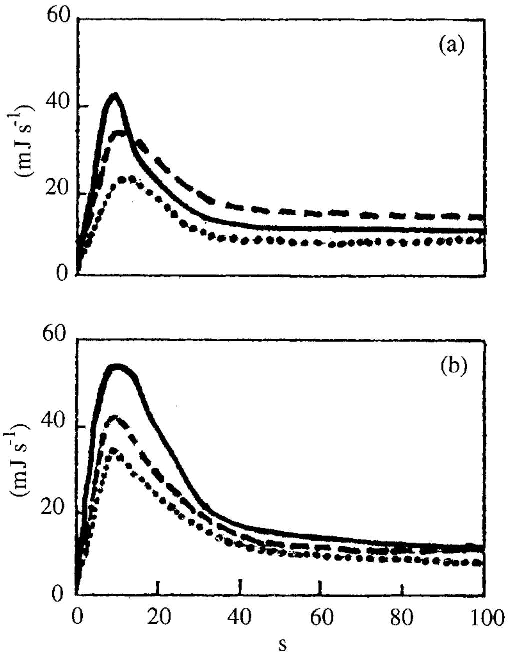

Figure 2 DSC curves of N-1 and N-2 unfilled resins; (···) 10, (– – –) 30, (——) 50 °C. Sample Size = 5.

TABLE II Unfilled resins: mean values and standard deviation of diametral tensile strength (T), and compression strength (C). See Table I for Key.

Code	T (MPa)	C (MPa)
N-1	42.5 ± 9.6	105.3 ± 24.7
N-2	50.5 ± 7.7	129.8 ± 62.2
N-3	45.1 ± 6.6	99.8 ± 45.5
T-1	49.4 ± 6.6	111.0 ± 47.9
T-2	51.0 ± 2.2	93.6 ± 15.7
T-3	42.7 ± 2.3	102.8 ± 32.9
CONT	40.2 ± 2.5	96.3 ± 4.7

Sample size = 7

horizontal line of the DSC curve (the magnitude was obtained per gram of a sample from the DSC curve). The peak height increased on adding diluent monomer DAPPE to N-1 resin. As the relation between (1/isothermal temperature) and logarithm of (heat/peak time) is obtained for N-1 and N-2, activation energy for curing is calculated from the slope according to the Arrhenius plot [6] (N-1, 2.7 kcal mol^{-1}; N-2, 2.1 kcal mol^{-1}). The magnitude of activation energy in N-2 was lower than that in *bis*-GMA VLC resin (4.0 kcal mol^{-1}), but larger than those in urethane-based VLC comonomers (MAP-HMDC·NPG, or TEGDMA).

Table II (T, diametral tensile strength; C, compression strength) gives the magnitudes of mechanical strengths in urethane-based resin and CONT. The T value (mean) ranged from 43–51 MPa for N-1 to N-3, and 49–51 MPa for T-1 to T-3, and had larger values than that in CONT. There appeared a significant difference between CONT and each urethane-based resin ($p < 0.05$). Within each group of composition (N-1 to N-3, or T-1 to T-3), T values were significantly different ($p < 0.05$), showing that N-2, or T-2 had the largest values in each group. The C value in N-1 to N-3, and T-1 and T-3 was larger than CONT(96 MPa), ranging from 100–111 MPa, but C in T-2 was very similar to CONT.

The addition of either DAPPE or DAPE to comonomers (MAP-HMDC·NPG, or TEGDMA) resulted in an increase of T value. DAPPE was more effective than DAPE, in increasing T, but both DAPPE for MAP-HMDC·NPG and DAPE for MAP-HMDC·TEGDMA gave an increase of C value. DAPPE addition to resin comonomer systems might increase the degree of polymerization and have a positive effect on mechanical strength. Therefore, DAPPE in VLC comonomers systems might lead to polymerization at lower magnitude of activation energy (curing).

With respect to mechanical strengths of heat-cured inlay/onlay materials, the range of T values was 47–58 MPa [15], and T values in the urethane-based unfilled VLC resins were 42–51 MPa. Compared with T values, the urethane-based VLC resins containing either DAPPE or DAPE exhibited a good property, even as experimental materials.

It is concluded that the urethane-based VLC resin had a greater increased diametral tensile strength than *bis*-GMA-based VLC resin on adding to either DAPPE, or on adding DAPE to urethane-based (MAP-HMDC·NPG, or TEGDMA) comonomer systems. Compression strength in experimental resin systems was slightly larger than that in the *bis*-GMA-based one, and DAPPE was more effective than DAPE as a diluent monomer to urethane-based comonomer systems. We hope that the urethane-based VLC resin systems containing DAPPE or DAPE as a diluent monomer to the urethane comonomer, will be applied to dental VLC materials.

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