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Effect of filler content on mechanical strength in bis-GMA-based resins with urethane linkages

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Bis-GMA-based visible-light-cured resins containing urethane linkages exhibited improved hardness and strength by addition of filler to the unfilled resins. The urethane monomers in the resins strengthened the resin matrix, exhibiting an increased Shore hardness value. Urethane monomer derived from 2HEMA and N3500 was more effective than that from 2HEMA and HT. The increased strength in the resin matrix occurred after storage in water at 37 °C. Addition of filler to bis-GMA-based resins increased compressive strength (110 MPa as the maximum), while diametral strength values of 20 MPa were obtained.

1. Introduction

Because of incomplete polymerization of resin composites cured by visible light, maximum mechanical strength is not attained [1–4]. The monomer compositions and the concentration of catalyst in the resins need to be optimized in 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 found to be 60 wt% and 40 wt% [5, 6]. The resins needed an additional source of heat when irradiated in the blue-light range of the spectrum to cure them [5, 6]. Differential scanning calorimetry (DSC) has been used to determine the thermal properties of bis-GMA-based resins, especially, activation energy for visible light curing under isothermal mode [7, 8]. Visible light and post-heat cured resins based on urethane dimethacrylate(UDMA) and 2-hydroxyethyl methacrylate(2HEMA) are superior to heat-cured bis-GMA/TEGDMA-based resins with respect to mechanical strength [9].

It was thus the aim of this study to test the effect of additive polyisocyanate diluted by 2HEMA on selected mechanical strength parameters of experimental bis-GMA/TEGDMA/urethane monomer-based resins which were polymerized by visible light in an attempt to improve the mechanical properties.

2. Materials and methods

Resin monomers tested in this study are as follows: bis-GMA (Shin–Nakamura Chem, Wakayama) and TEGDMA (Tokyo Kasei Co, Tokyo). Experimental urethane monomers were synthesized from 2HEMA(40 wt%) and N3500(60 wt%) (code; UA) and 2HEMA(30 wt%) and HT(70%) (code; UB) as shown in Fig. 1, by the method described previously [10, 11]. N3500 and HT are polyisocyanate and isocyanulate and its adducts (Sumitomo Bayer Co, Osaka). Camphorquinone(CQ) and dimethylaminoethyl methacrylate(DMAEMA) were used as the photo-initiators at concentrations of 0.5 wt%. The base resin monomers used are 50 wt% TEGDMA(2)/25 wt% bis-GMA(1)/25 wt% UA(1) (code U1), TEGDMA(1)/bis-GMA(1)/UA(1) (code U2) and TEGDMA(1)/bis-GMA(1)/UB(1) based resins (code U3). Following the addition of urethane monomer, the resins were loaded with silanized glass filler (SiO_2, Katayama Chem, Osaka) to a content of 75 wt%. The upper surfaces of the test samples were irradiated with visible light for 40 s (Quick Light, J. Morita Co, Kyoto). This is referred to as the top surface, the other one is termed the bottom surface.

Hardness tests were carried out using a Shore hardness tester (weight of the hammer = 36.2 g, Type D, Shimadzu Co, Kyoto) (sample dimension = 6.0 mm diameter × 3.0 mm length);

$$\text{Shore hardness} = k(h_2/h_1)$$

where $k = 140$, h_2 = height after falling (mm) and h_1 = initial falling distance, 19.0 mm.

Cylindrical samples of dimensions $l = 3.0$ mm and $d = 6.0$ mm were used for diametral tensile strength measurements:

$$T = 2F/\pi d l$$

where F = force at proportional limit and maximum limit at fracture (MPa).

The compressive strength of specimen samples (length, $l = 6.0$ mm and diameter, $d = 3.0$ mm) was determined as $4F/\pi d^2$(MPa). The polymerized samples were tested at a crosshead speed of 0.5 mm/min (diametral tensile strength) and 2.0 mm/min (compression strength) by means of an Autograph Testing Machine (Shimadzu DCS-500, Kyoto). Seven test pieces of each formulation were used for the respective tests.

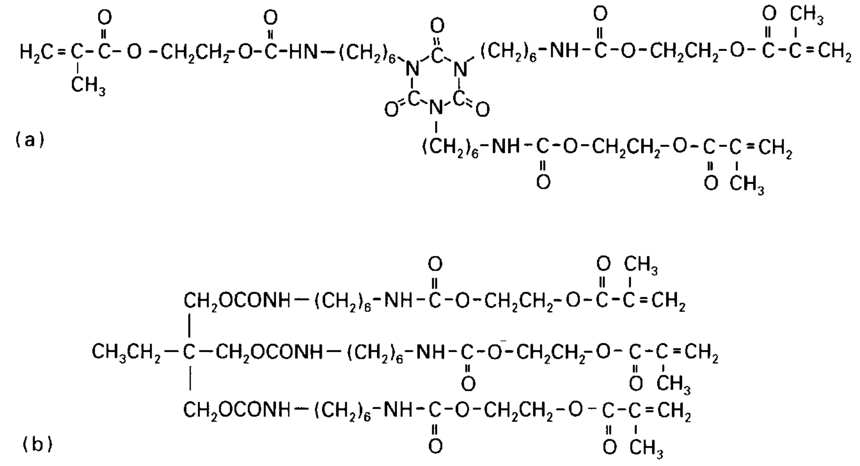

Figure 1 Structures of urethane monomers synthesized by (a) 2HEMA and N3500; (b) 2HEMA and HT.

TABLE I Mean value and standard deviation of Shore hardness value for top and bottom surfaces in wet and dry state

Sample code	Top surface Dry	Wet		Bottom surface Dry	Wet	
	1 day	7 days	30 days	1 day	7 days	30 days
U1	85.3	81.17	77.82	80.5	74.7	76.24
	(2.66)	(1.61)	(1.69)	(5.2)	(3.79)	(2.30)
U2	83.3	80.78	78.1	77.4	75.66	73.9
	(6.78)	(2.03)	(0.50)	(8.84)	(3.44)	(1.98)
U3	80.9	71.97	69.24	76.3	68.77	66.77
	(3.31)	(1.74)	(2.70)	(4.82)	(2.71)	(1.90)

TABLE II Diametral tensile strength of U1, U2 and U3 unfilled resins

Sample code	Proportional limit (MPa) Dry	Wet		Maximum limit (MPa) Dry	Wet	
	1 day	7 days	30 days	1 day	7 days	30 days
U1	22.71	18.07	14.96	47.6	50.26	15.80
	(1.51)	(1.35)	(0.25)	(4.16)	(17.36)	(0.20)
U2	23.30	18.22	14.03	47.41	36.51	15.34
	(2.22)	(3.55)	(0.09)	(14.19)	(15.83)	(1.03)
U3	17.92	10.81	9.73	45.89	23.03	15.74
	(0.22)	(0.91)	(0.24)	(18.65)	(6.15)	(0.49)

3. Results and discussion

Table I indicates the Shore hardness values of unfilled bis-GMA-based resin, showing that there are no significant differences between top and bottom surfaces in the samples.

Tables II and III (*T*, diametral tensile strength and *C*, compressive strength) gives these values in unfilled resins. *T* value (mean) ranged from 10 to 23 MPa (proportional limit) and 16 to 48 MPa (maximum limit) for U1, U2 and U3. There appeared to be a significant difference in diametral tensile strength between dry and wet conditions for each sample ($p < 0.05$). Water immersion of samples for up to 30 days reduced this value. *C* value (mean) ranged from 28 to 64 MPa (proportional limit) and 38 to 72 MPa (maximum limit). Within each group of compositions (U1, U2, U3) compressive strength and diametral tensile strengths are lower for the U3 resin. Use of UA urethane in bis-GMA-based resin resulted in an increase of *C* and *T* values, as compared with UB urethane (Tables III and IV). For *C* value the influence of UA or UB on resin monomer systems was shown clearly in wet conditions with higher *C* values for U1 and U2 resins (58 and 62 MPa). With respect to mechanical strengths of visible light and post-heat cured inlay/onlay materials, the range of *T* values (maximum limit) was 47 to 58 MPa [9].

TABLE III Compressive strength in unfilled resins

Sample code	Proportional limit (MPa)			Maximum limit (MPa)		
	Dry	Wet		Dry	Wet	
	1 day	7 days	30 days	1 day	7 days	30 days
U1	42.69	53.50	60.20	61.37	56.78	61.61
	(8.29)	(1.20)	(1.48)	(3.68)	(1.53)	(1.74)
U2	63.63	51.68	56.35	72.29	57.12	57.52
	(4.21)	(3.04)	(0.55)	(3.40)	(4.09)	(0.47)
U3	27.73	32.60	39.40	45.73	37.99	49.59
	(0)	(1.80)	(0.82)	(7.65)	(1.32)	(0.81)

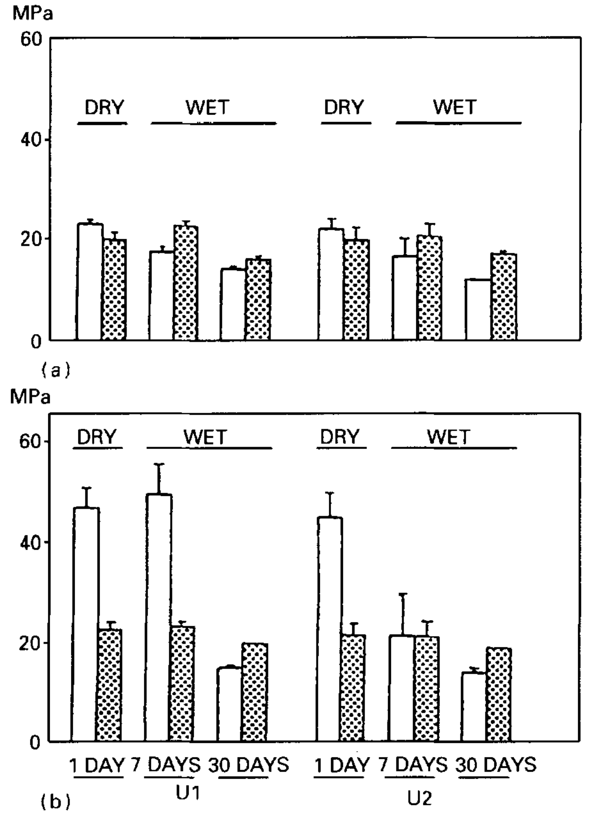

Figure 2 Diametral tensile strength in unfilled (□) and filled (▨) resins: (a) proportional limit; and (b) maximum limit.

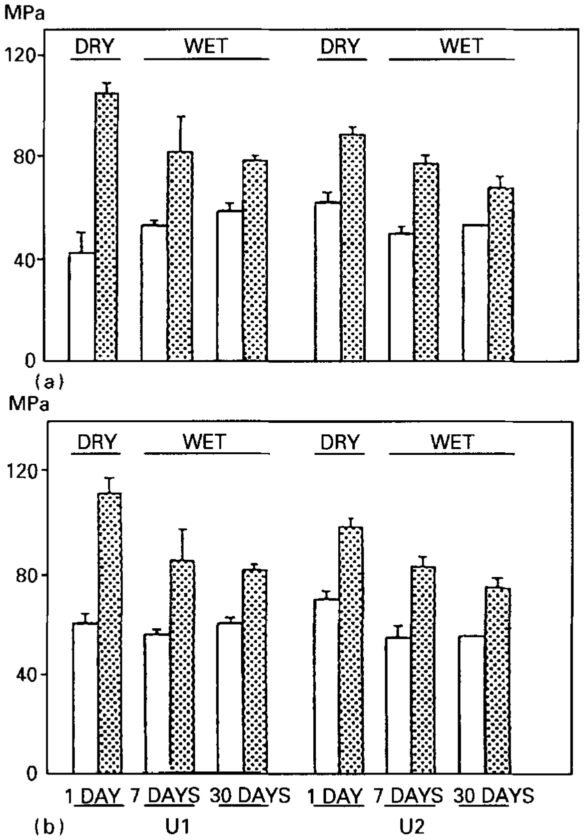

Figure 3 Compressive strength in unfilled (□) and filled (▨) resins: (a) proportional limit; and (b) maximum limit.

Fig. 2a and b show T values at the proportional limit and maximum limit, respectively, for unfilled and filled resins, showing that T ranged from 14 to 23 MPa (proportional limit), and 16 to 50 MPa (maximum limit). Water had no significant effect upon the proportional limit of either U1 or U2 resins. Fig. 3a and b show C values under the same conditions as Fig. 2, showing that C ranged from 41 to 110 MPa (proportional limit), and 58 to 110 MPa (maximum limit). However, a significant difference was found between unfilled and filled resins for each condition.

With resin composites marketed for use as inlay or crown materials, mechanical strengths in the following range were found (T, 47 to 58 MPa as the maximum limit at fracture for unfilled resins). In their filled condition T values were 20 to 23 MPa depending upon dry or wet condition. Strength values were in the range 65 to 77 MPa in visible light and post-heat cured filled resin when placed in distilled water at 37° C for 1 week prior to being tested [9]. As expected, the increased strength is probably due to the increased reactivity of the free radicals formed during irradiation [12] and the additional activation of free radicals due to post-cure heating by heat [13]. Thus, the improvement of the resin matrix due to other urethane linkages is needed because of complete polymerization in bis-GMA-based resins.

In this study a strengthening of bis-GMA-based resin matrix was produced using urethane monomer (Fig. 1), because almost the same Shore hardness values were obtained for dry and wet conditions of the matrix. It is concluded that urethane-including bis-GMA-based resin(urethane monomer; 2HEMA and N3500) has higher strength values than other bis-GMA-based resin (urethane monomer; 2HEMA and HT). Bis-GMA/TEGDMA comonomer was strengthened by containing urethane monomer linkages within the resin matrix and also the filler addition to urethane-included bis-GMA-based resin was available because of the increased strength value.

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