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Dental application of binary urethane monomer mixtures: strengthened resin matrix

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The strengthened resin matrices in six experimental binary visible light-cured (VLC) urethane monomer mixtures were examined in terms of mechanical strength. A 60 wt % bis-GMA/40 wt % binary monomer mixture was used as a control sample. A dry state (1 day in air at 37 °C) and a wet state by immersion in distilled water (7 and 30 days at 37 °C) were investigated. The compressive strength and diametral tensile strength of urethane monomer samples had values equivalent to, or greater than those of a control sample in the dry state, but had increased values in the wet state. The nano-indentation hardness values in experimental urethane monomer mixtures were greater than that in a control sample in the dry state, showing that immersion in water gave increased strength (maximum increase was about 2.5 times) in six binary urethane monomer mixtures. The compressive strength of the samples in the dry and wet states exhibited linearly increasing elastic modulus values for the resin matrix in the range about 50 to 2600 MPa. The toughened resin matrix had smaller amounts of residual monomer in the urethane monomer mixtures (0.41 to 5.03 wt %) compared with that of the binary 60bis-GMA/40TEGDMA mixture (0.71 to 6.26 wt %). This study has revealed that resin matrices are strengthened by the use of four-functional urethane monomers in experimental binary urethane monomer mixtures.

1. Introduction

Visible light-cured (VLC) resin composite materials based on polyfunctional monomers exhibit a more efficient curing performance than conventionally chemical-cured resins [1–12]. The more efficient curing performance gives resin matrices with increased mechanical strength and very small amounts of uncured monomers [8, 9, 13]. The mechanical strength values determined were compressive strength, diametral tensile strength and elastic modulus; elastic deformation energy was also measured [1–12]. Both bis-GMA/TEGDMA based and urethane based monomer mixtures are used in the dental field [1–20]. Ternary bis-GMA (bis-phenol A glycidyl dimethacrylate)/TEGDMA (triethylene glycol dimethacrylate)/urethane resins with reduced residual monomers have been shown to be toughened by the polyfunctional urethane monomers in the ternary resin matrices [5–9, 15, 16, 20–28]. Polyfunctional urethane monomers have frequently been applied to dental bis-GMA-based resins to obtain a strengthened resin matrix, enhanced curing and less residual monomer [5–9, 26–30]. The present study evaluated the strength in visible light-cured binary urethane monomer mixtures, and examined the relation between the elastic modulus and the strength as a function of the content of experimentally synthesized urethane monomer in binary mixtures.

2. Materials and methods

2.1. Sample preparation

The resins used in this study are indicated in Tables I and II: UH1, UH2, UH3 (UH series), U1, U2, U3 (U series) and a control bis-GMA (60 wt %)/TEGDMA (40 wt %) binary mixture. The resin monomer mixtures were bis-GMA (bis-phenol A glycidyl dimethacrylate ; Shin-Nakamura Chem Co, Wakayama) and TEGDMA (triethylene glycol dimethacrylate ; Tokyo Kasei Co, Tokyo). The experimentally synthesized tri-functional urethane monomer was coded as EXP3, and two commercial four-functional urethane monomers were indicated as U–4TXA and U–4HA (Fig. 1).

The experimental urethane monomer, EXP3, was synthesized using the following method. A liquid 2-HEMA (40 wt % ; 2-hydroxyethyl methacrylate ; Tokyo Kasei Co) was added to N3500 (60 wt % ; isocyanate; -NCO content =21.6 %; Sumitomo Bayer Urethane Co, Osaka), catalysed with D-n-butyltin dilaurate (0.5 wt %) and hydroquinone (0.5 wt %) at about 60 °C for 12 h in an inert atmosphere, with continuous stirring, until the reaction was essentially completed.

Camphorquinone (CQ) and dimethylaminoethyl methacrylate (DMAEMA) were added to the binary monomer mixtures as the photoinitiator and reducing agent, respectively, at concentrations of 0.5 and

TABLE I Compressive strength values of three UH series and one B6G control sample under dry and wet conditions (kept for, respectively, 1 day in an incubator and for 7 and 30 days in distilled water). The values were calculated at proportional and maximum limit

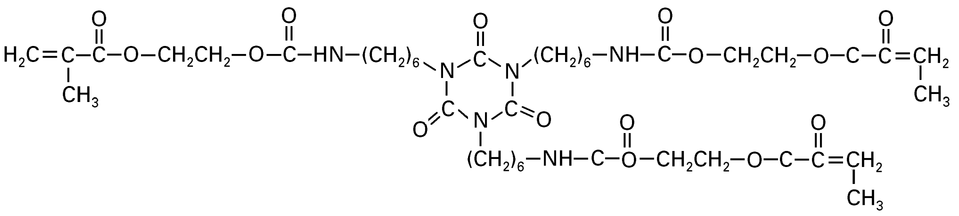
Sample code	Compressive strength Proportional limit (MPa)			Maximum limit (MPa)		
	Dry 1 day	Wet 7 days	30 days	Dry 1 day	Wet 7 days	30 days
UH1	56.41	51.32	69.32	65.65	69.36	77.22
	(7.12)	(8.06)	(1.39)	(9.02)	(9.09)	(0.80)
UH2	70.74	56.41	70.28	82.3	69.82	81.14
	(6.04)	(7.64)	(3.49)	(6.56)	(5.61)	(3.18)
UH3	66.12	67.51	83.69	73.52	83.22	110.04
	(7.64)	(7.64)	(2.12)	(4.16)	(10.83)	(6.26)
B6G	81.61	46.7	50.63	92.48	58.95	57.33
	(1.45)	(3.20)	(5.41)	(2.42)	(1.84)	(4.87)

UH1,2,3 ; EXP3/U–4HA =1/1(50 wt %/50 wt %), 2/1(66.6 wt %/33.3 wt %), 1/2(33.3 wt %/66.6 wt %)
B6G ; bis-GMA/TEGDMA =60 wt %/40 wt %

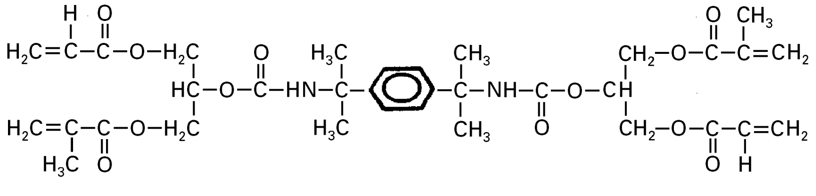
TABLE II Compressive strength values of three U series and one B6G control sample under dry and wet conditions (kept for, respectively, 1 day in an incubator and for 7 and 30 days in distilled water)

Sample code	Compressive strength Proportional limit (MPa)			Maximum limit (MPa)		
	Dry 1 day	Wet 7 days	30 days	Dry 1 day	Wet 7 days	30 days
U1	72.36	72.59	76.75	85.77	84.61	86.92
	(8.78)	(4.46)	(0.80)	(11.24)	(4.16)	(2.12)
U2	75.38	66.58	77.68	86.23	80.91	77.68
	(6.23)	(7.26)	(3.67)	(4.92)	(10.41)	(3.67)
U3	78.60	95.48	87.62	89.24	106.81	98.72
	(4.46)	(2.43)	(5.82)	(5.25)	(2.40)	(4.72)
B6G	81.61	46.7	50.63	92.48	58.95	57.33
	(1.45)	(3.20)	(5.41)	(2.42)	(1.84)	(4.87)

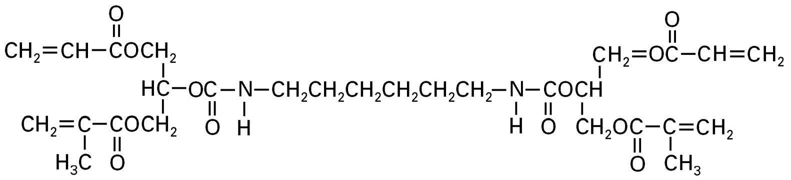
U1,2,3 ; EXP3/U–4TXA =1/1(50 wt %/50 wt %), 2/1(66.6 wt %/33.3 wt %), 1/2(33.3 wt %/66.6 wt %)



(a) EXP3



(b) U-4TXA



(c) U-4HA

Figure 1 Urethane monomers used in this study, EXP3, U–4TXA and U–4HA, which were applied to six binary urethane monomer mixtures, that is, EXP3/U–4HA (UH series) and EXP3/U–4TXA (U series).

0.5 wt %. Visible light curing from the surface was carried out for 80 s with Quick Light (J. Morita Co, Kyoto). Ten specimens were used for UH, U series and B6G samples at each test.

Six kinds of test samples (UH and U series) and a control sample (B6G) were prepared in an incubator at 37 °C for 1 day (the dry state) and immersion in distilled water at 37 °C for 7 and 30 days (the wet state).

2.2. Mechanical strength measurement

The compressive strength and diametral tensile strength were obtained at proportional limit and maximum limit, as indicated schematically in Fig. 2 (AUTOGRAPH DCS-500, Shimadzu Co, Kyoto). The crosshead speed was 2 and 0.5 mm/min for the compressive strength and diametral strength measurements, respectively (full scale =250 kgf, chart speed ratio =100). The compressive strength (*C*) value was calculated from $4L/\pi d^2$(L, load at proportional limit or maximum limit, kgf ; d, diameter (3 mm) of cylindrical specimen), and converted to MPa (SI unit). The diametral tensile strength (*DT*) value was calculated from $2L_{Dt}/\pi dl$(L_{Dt}, load at proportional limit or maximum limit, kgf ; d, diameter (6 mm) and l, thickness (3 mm) of disc-shaped sample), which was converted to MPa.

From nano-indentation test data (DUH-200, Shimadzu Co, Kyoto), the (dP/dh) and h values were calculated as indicated schematically in Fig. 3. Nanohardness (*N*) value, H_D, was calculated from $H_D = 37.838\,P/h^2$(P = applied load, kgf ; h = depth of nano-indentation), and expressed in MPa. Using the triangular pyramidal indenter, $2a$ and d values were measured (Fig. 3a). On the load/deflection curves a (dP/dh) value was measured during the loading/unloading operation as indicated in Fig. 3b.

2.3. Elastic modulus calculation

The slope of the unloading curve during nano-indentation testing together with the deflection/load curves was used as a measure of the elastic modulus of the test samples (Fig. 3). The elastic behaviour was modelled as the elastic deformation of an isotropic elastic solid. The value of (dP/dh) as the slope of the unloading curve was calculated as described in [31, 32], and is given, for a triangular pyramid indenter, by

$$(dP/dh) = (2/\pi)^{1/2}(A(3)^{1/2}\sin\beta)^{1/2}E_r \qquad (1)$$

where A is the indented contact area and E_r is Young's modulus for the resin matrix:

$$A = d^2/((3)^{1/2}\sin\beta) \qquad (2)$$

where d is the diagonal length of the indenter and β is the angle of the indenter (65°). Young's modulus can then be calculated, provided (dP/dh) and A or d are known.

2.4. Residual monomer measurement

The method was as described previously [19, 20]. The cured samples were ground to powders and analysed

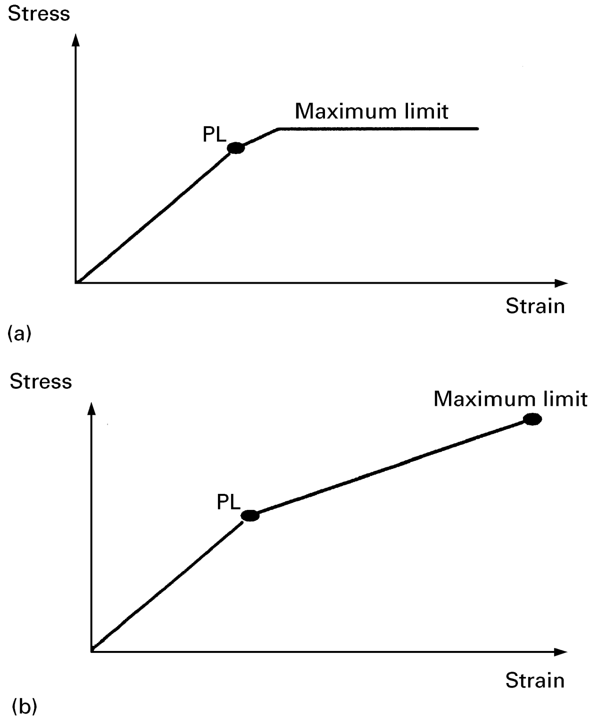


Figure 2 Schematic diagrams of (a) compressive strength and (b) diametral tensile strength, to calculate compressive and diametral tensile strength values at proportional and maximum limit.

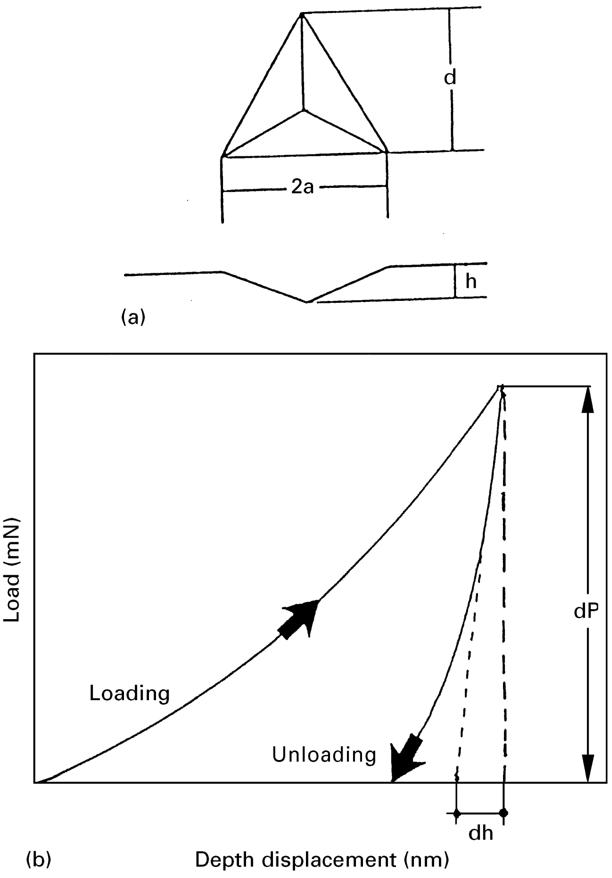


Figure 3 Schematic diagrams of (a) indented area and (b) load/deflection curves during nano-indentation testing, to determine the values $2a$, d and (dP/dh).

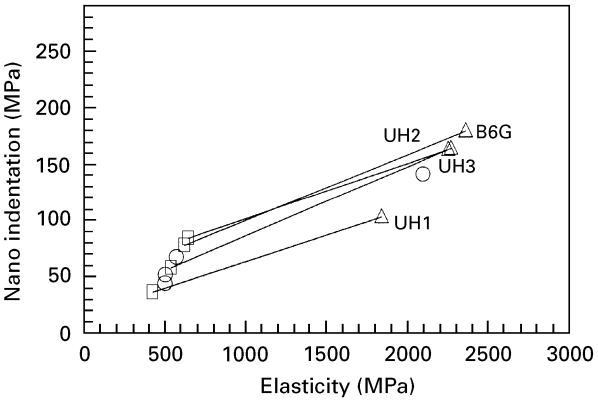


Figure 4 Elastic modulus value/nano indentation hardness relation of UH series and B6G control samples. □ Dry, 1day; ○ wet, 7 days; △ wet, 30 days.

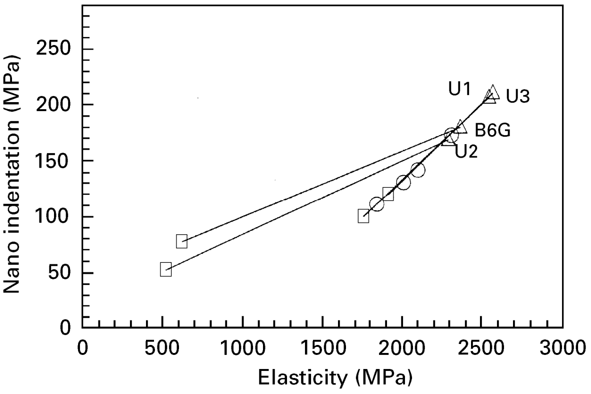


Figure 5 Elastic modulus value/nano indentation hardness relation of U series and B6G control samples. □ Dry, 1day; ○ wet, 7 days; △ wet, 30 days.

TABLE III Diametral tensile strength values of three UH series and one B6G control sample under dry and wet conditions (kept for, respectively, 1 day in an incubator and for 7 and 30 days in distilled water). The proportional and maximum limit were calculated

Sample code	Diametral tensile strength Proportional limit (MPa)			Maximum limit (MPa)		
	Dry 1 day	Wet 7 days	30 days	Dry 1 day	Wet 7 days	30 days
UH1	23.99 (3.04)	26.29 (1.00)	22.54 (3.13)	33.89 (3.13)	40.73 (3.41)	29.47 (3.97)
UH2	30.25 (6.17)	27.17 (3.28)	29.19 (0.50)	49.14 (5.66)	43.75 (5.97)	56.55 (4.50)
UH3	29.48 (0.87)	30.90 (2.50)	24.85 (5.90)	46.38 (2.12)	51.73 (6.95)	45.37 (10.84)
B6G	22.97 (1.89)	23.55 (2.23)	18.2 (0)	30.17 (2.18)	31.10 (2.57)	22.54 (0.87)

by high-performance liquid chromatograpy (HPLC) analysis (UV spectrophotometric detector SPD-6A, chromatopac C-R3A, column holder LC-8A and liquid chromatograph LC-6AD ; Shimadzu Co, Kyoto). Calibration was carried out with standard solutions of EXP3, U–4HA and U–4TXA as urethane monomers, and bis-GMA and TEGDMA in binary bis-GMA/-TEGDMA mixtures.

3. Results and discussion

Mechanical strength values are detailed in Tables I to VI. Compressive stress data is given for UH and U series samples at the proportional limit and maximum limit for samples in dry and wet conditions (Tables I and II). The UH and U series samples kept in the dry state were similar to the B6G material. Under wet conditions, the urethane resin matrix showed increased strength compared with those samples in the dry state. Diametral tensile strength values of UH and U series samples are given for the dry and wet states in Tables III and IV. The urethane UH and U series samples showed greater values than the B6G sample, but showed values in the dry state rather than in the wet state. Nanohardness values of the UH and U series samples are given for the dry and wet states in Tables V and VI. It is seen that the U series shows greater nanohardness than the UH series and that the U1 sample shows a stronger matrix than other urethane samples or the B6G control sample.

Resin matrices having different elastic moduli were obtained for the various binary monomer systems (Tables VII and VIII). The dP/dh values for the UH and U series samples had larger values than the B6G sample, and the h value in urethane UH and U series samples was more than that in the B6G sample. Elastic moduli were calculated from nanoindentation test data (Tables IX and X) (Figs 4 and 5). Of the urethane UH and U series samples, U1 and U3 had the largest values of elastic moduli, at about 2 000 MPa, compared with about 600 MPa in the B6G sample.

Tables XI and XII indicate the HPLC analysis results of extracts from the acetonitrile solvent obtained from the set (hardened) test samples. The qualities of bis-GMA and TEGDMA, or EXP3 and U–4HA or U–4TXA monomers were obtained. At holding times of 1 day (dry) and 30 days (wet), the concentration of residual monomers in UH and U series was less than in control sample B6G.

TABLE IV Diametral tensile strength values of three U series and one B6G control sample under dry and wet conditions (kept for, respectively, 1 day in an incubator and for 7 and 30 days in distilled water)

Sample code	Diametral tensile strength Proportional limit (MPa)			Maximum limit (MPa)		
	Dry 1 day	Wet 7 days	30 days	Dry 1 day	Wet 7 days	30 days
U1	30.26 (0.92)	30.92 (0.50)	24.85 (1.80)	41.26 (1.80)	57.36 (3.93)	40.17 (3.04)
U2	32.65 (1.32)	24.56 (4.28)	26.59 (2.65)	41.55 (3.04)	35.83 (5.77)	40.17 (1.18)
U3	32.94 (0.86)	19.78 (5.08)	35.54 (2.30)	40.96 (1.11)	27.16 (4.28)	47.68 (8.36)
B6G	22.97 (1.89)	23.55 (2.23)	18.2 (0)	30.17 (2.18)	31.10 (2.57)	22.54 (0.87)

TABLE V Nanohardness values of three UH series and one B6G control sample under dry and wet conditions (kept for, respectively, 1 day in an incubator and for 7 and 30 days in distilled water)

Sample code	Nano-hardness (MPa) Dry 1 day	Wet 7 days	30 days
UH1	35.87 (5.29)	42.83 (4.70)	101.82 (10.56)
UH2	83.59 (8.13)	66.05 (6.37)	162.58 (20.19)
UH3	57.62 (2.06)	50.47 (2.16)	163.66 (9.60)
B6G	77.32 (3.82)	140.04 (11.76)	178.75 (22.44)

TABLE VI Nanohardness values of three U series and one B6G control sample under dry and wet conditions (kept for, respectively, 1 day in an incubator and for 7 and 30 days in distilled water)

Sample code	Nano-hardness (MPa) Dry 1 day	Wet 7 days	30 days
U1	99.18 (15.19)	171.01 (28.13)	205.70 (20.97)
U2	52.53 (16.37)	109.47 (17.05)	167.68 (21.95)
U3	118.97 (25.38)	128.87 (9.99)	209.62 (26.85)
B6G	77.32 (3.82)	140.04 (11.76)	178.75 (22.44)

TABLE VII dP/dh and h values for UH series and B6G samples determined from nano-indentation tests. The test sample conditions were the same as in Table I

Sample code	dP/dh (N/m)	Nano-indentation		h (μm)		
	Dry 1 day	Wet 7 days	30 days	Dry 1 day	Wet 7 days	30 days
UH1	3037.68	3294.88	5119.94	3.24 (0.23)	2.98 (0.18)	1.91 (0.08)
UH2	4640.80	4125.18	6463.36	2.11 (0.10)	2.38 (0.12)	1.52 (0.09)
UH3	3885.80	3610.72	6499.01	2.54 (0.05)	2.71 (0.06)	1.51 (0.04)
B6G	4466.89	6007.58	6779.57	2.19 (0.05)	1.63 (0.07)	1.45 (0.16)

Strengthened resin matrices were achieved using polyfunctional urethane linkages in binary bis-GMA/TEGDMA monomer mixtures. Less residual monomers in toughened resin matrices were also detected. Residual monomer content in the VLC composite resins was analysed using the solvent extraction method [7, 12, 17–20]. Residual TEGDMA and bis-GMA monomers left in VLC bis-GMA/TEGDMA based resins were identified by an acetonitrile solvent method [19, 20]. The percentage of residual TEGDMA monomer left in bis-GMA/TEGDMA/urethane-based resins was very small compared with that remaining in a bis-GMA monomer [12]. A small percentage of residual monomers (urethane and TEGDMA) was observed in experimental ternary resin systems.

In this study, the use of polyfunctional U–4HA or U–4TXA to experimental urethane monomer EXP3

TABLE VIII dP/dh and h values for U series and B6G samples determined from nano-indentation tests. The test sample conditions were the same as in Table I

Sample code	dP/dh (N/m)	Nano-indentation (MPa)		h (μm)		
	Dry	Wet		Dry	Wet	
	1 day	7 days	30 days	1 day	7 days	30 days
U1	5051.36	6623.99	7288.28	1.94 (0.13)	1.49 (0.11)	1.35 (0.07)
U2	3800.47	5298.70	6564.55	2.62 (0.38)	1.86 (0.17)	1.50 (0.10)
U3	5514.77	5758.77	7348.17	1.79 (0.17)	1.70 (0.07)	1.34 (0.08)
B6G	4466.89	6007.58	6779.57	2.19 (0.05)	1.63 (0.07)	1.45 (0.16)

TABLE IX Elastic modulus values for UH series and B6G samples determined from nano-indentation tests. The test sample conditions were the same as in Table I

Sample code	Elastic modulus (MPa)		
	Dry	Wet	
	1 day	7 days	30 days
UH1	423.71	501.28	1842.44
UH2	648.00	574.72	2256.53
UH3	539.37	504.08	2273.31
B6G	623.97	2100.83	2363.39

TABLE X Elastic modulus values for U series and B6G samples determined from nano-indentation tests. The test sample conditions were the same as in Table I

Sample code	Elastic modulus (MPa)		
	Dry	Wet	
	1 day	7 days	30 days
U1	1759.72	2309.72	2542.83
U2	523.09	1842.13	2288.39
U3	1914.62	2011.61	2568.46
B6G	623.97	2100.83	2363.39

TABLE XI Concentration of residual monomers of EXP3 and U–4HA for UH series, and bis-GMA and TEGDMA for B6G samples. The test sample conditions were the same as in Table I

Sample code	Residual monomer (wt %)							
	EXP3		U–4HA		TEGDMA		Bis-GMA	
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
	1 day	30 days	1 day	30 days	1 day	30 days	1 day	30 days
UH1	1.82	0.75	2.35	0.88				
UH2	1.54	1.14	1.00	0.77				
UH3	0.70	0.41	1.43	0.79				
B6G					1.10	0.71	5.87	6.26

TABLE XII Concentration of residual monomers of EXP3 and U–4TXA for U series, and bis-GMA and TEGDMA for B6G samples. The test sample conditions were the same as in Table I

Sample code	Residual monomer (wt %)							
	EXP3		U–4TXA		TEGDMA		Bis-GMA	
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
	1 day	30 days	1 day	30 days	1 day	30 days	1 day	30 days
U1	1.23	1.09	2.75	2.71				
U2	1.77	0.91	2.92	2.03				
U3	1.77	0.59	5.03	2.61				
B6G					1.10	0.71	5.87	6.26

in binary monomer mixtures, their mechanical strength values increased (Table I to VI). The increased strength obtained for these resin matrices is assumed to be due to urethane linkages increasing the degree of crosslinking and having a positive effect on mechanical properties. Urethane dimethacrylate monomer/2-hydroxyethyl methacrylate showed better mechanical properties than bis-GMA/TEGDMA based resin [5, 8]. The positive correlation between mechanical properties and the urethane content suggests that crosslinking may occur when the amide group is part of the monomer skeleton [2]. The elastic modulus value of urethane resin matrices showed clearly increased values compared with a control sample (Tables IX and X).

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References

1. J. HUTCHISON and A. LEDWITH, *Adv. Polym. Sci.* **14** (1974) 49.
2. R. G. CRAIG, *Dent. Clin. North Amer.* **25** (1981) 219.
3. K. F. LEINFELDER, *ibid.* **29** (1985) 359.
4. H. J. WILSON, *Brit. Dent. J.* **164** (1988) 326.
5. E. ASMUSSEN and A. PEUZFELDT, *Scand. J. Dent. Res.* **98** (1990) 564.
6. J. W. OSBORNE, R. D. NORMAN and E. N. GALE, *Quint. Int.* **21** (1990) 111.
7. K. TANAKA, M. TAIRA, H. SHINTANI, K. WAKASA and M. YAMAKI, *J. Oral Rehabil.* **18** (1991) 353.
8. A. PEUZFELDT and E. ASMUSSEN, *J. Dent. Res.* **70** (1991) 1537.
9. J. W. STANSBURY, *ibid.* **71** (1992) 1408.
10. K. WAKASA, H. URABE, M. TAIRA, T. HIROSE and M. YAMAKI, *J. Mater. Sci. Mater. Med.* **4** (1993) 404.
11. K. YOSHIDA and E. H. GREENER, *J. Dent.* **22** (1994) 296.
12. N. A. CHOWDHURY, K. WAKASA. R. PRIYAWAN and M. YAMAKI, *J. Mater. Sci. Mater. Med.* **6** (1995) 400.
13. W. D. COOK and P. H. STANDISH, *Aust. Dent. J.* **28** (1983) 307.
14. G. D. STAFFORD and S. C. BROOKS, *Dent. Mater.* **1** (1985) 135.
15. T. HIROSE, K. WAKASA and M. YAMAKI, *J. Mater. Sci.* **25** (1990) 932.
16. H. URABE, K. WAKASA and M. YAMAKI, *ibid.* **26** (1991) 3185.
17. K. INOUE and I. HAYASHI, *J. Oral Rehabil.* **9** (1982) 493.
18. W. H. DOUGLAS and J. F. BATES, *J. Mater. Sci.* **13** (1978) 2600.
19. S. HIRABAYASHI, T. HIRASAWA, I. NASU and S. NAKANISHI, *J. Dent. Res.* **62** (1983) 118.
20. N. A. CHOWDHURY, K. WAKASA, R. PRIYAWAN and M. YAMAKI, *Hiroshima Daigaku Shigaku Zasshi* **28**, in press, 1996.
21. S. BAN, H. KATO, S. ITO and J. HASEGAWA, *Aichigakuin Shigaku Zasshi* **24** (1986) 383.
22. S. BAKER, S. C. BROOKS and D. M. WALKER, *J. Dent. Res.* **6** (1988) 1295.
23. A. EKFELDT and G. OILO, *J. Oral Rehabil.* **17** (1990) 117.
24. R. PRIYAWAN, K. WAKASA, N. A. CHOWDHURY and M. YAMAKI, *J. Mater. Sci. Mater. Med.* **6** (1995) 1.
25. M. TAIRA, A. M. KHAN, T. TANAKA, H. SHINTANI, K. WAKASA and M. YAMAKI, *ibid.* **6** (1995) 167.
26. M. TAIRA, A. M. KHAN, K. OHMOTO, K. TANAKA, N. SATOU, H. SHINTANI, K. WAKASA and M. YAMAKI, *Hiroshima Daigaku Shigaku Zasshi* **26** (1994) 313.
27. M. TAIRA, H. TOYOOKA, H. MIYAWAKI and M. YAMAKI, *Dent. Mater.* **9** (1993) 167.
28. T. TSUJI, K. WAKASA and M. YAMAKI, *J. Mater. Sci. Mater. Med.* **6** (1995) 396.
29. W. T. NAKAYAMA, D. R. HALL, D. E. GRENOBLE and J. L. KATZ, *J. Dent. Res.* **53** (1974) 1121.
30. K. H. CHUNG, *ibid.* **69** (1990) 852.
31. M. F. DOERNER and W. D. NIX, *J. Mater. Res.* **1** (1986) 601.
32. K. WAKASA, M. YAMAKI and A. MATSUI, *Dent. Mater. J.* **14** (1995) 152.

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