



Research article

Optimal resin monomer ratios for light-cured dental resins

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ABSTRACT

Monomer ratios play a crucial role on the performances of dental resins, the optimal monomer ratios for dental resins are determined by combining the degree of conversion (DC), rate of polymerization (Rp), and mechanical properties, based on commonly-used Bis-GMA (bisphenol A-glycidyl methacrylate), UDMA (urethane dimethacrylate), and TEGDMA (triethyleneglycol dimethacrylate) resins. The DC and mechanical properties of the dental resins are examined by NIR (Near Infrared Ray) spectroscopy and nanoindentation tests, respectively. The results indicate that the Rp increases while the DC decreases with the loading content of Bis-GMA or UDMA in dental resins (i.e., Bis-GMA/TEGDMA and UDMA/TEGDMA). Meanwhile, both elastic modulus and hardness also present a tendency to increase. Various different monomers maybe create a strong polymer matrix in proper proportions, comprehensively comparing the performances of dental resins in different monomer ratios, the cured resins containing Bis-GMA (15–35 wt%), UDMA (37–60 wt%) and TEGDMA (20–35 wt%) show better material properties. The present study offers a quantitative analysis for Bis-GMA/UDMA/TEGDMA dental resins as well as provides guidance for the research of dental resins.

1. Introduction

The application of resin matrix composites has greatly promoted the development of dental restorative materials. The light-cured dental composites possess excellent mechanical properties, superior biocompatibility and aesthetic appearance compared with traditional amalgam and ceramic materials, and have gradually occupied a major position in the field of dental restoration [1, 2]. Light-cured dental composites are mixtures containing organic matrix, photo-initiation system and inorganic fillers. The organic matrix consists of several monomers, such as Bis-GMA (bisphenol A-glycidyl methacrylate), UDMA (urethane dimethacrylate), and TEGDMA (triethylene glycol dimethacrylate). Among these, the TEGDMA is usually used as a diluted monomer combined with Bis-GMA and UDMA to improve the conversion of double bonds and win better material performances [3, 4, 5]. The degree of conversion of resins matrix plays a potentially significantly role in determining the ultimate mechanical properties of dental materials. In general, the higher the conversion of double bonds, the better the mechanical strength is [6, 7, 8, 9]. Meanwhile, the incomplete conversion of resin monomers will result in monomers residual, then form defects and lead to the formation of

residual stress, and ultimately reduce the biocompatibility, durability and mechanical properties of the dental resin materials [10, 11].

The performances of dental resins are depended on many factors, such as the conversion of double bonds, the structures and ratios of monomers, light conditions, the kind of photoinitiators and so on [4, 12]. Abundant literature published have been studying the relevant factors affecting their properties, however, not all studies on the properties of dental resins are based on fixed monomer ratio. Zeng [13] et al. studied the properties of Bis-GMA/TEGDMA (50/50, wt%/wt%) dental resins reinforced with carbon nanotubes (CNTs) modified by different amount of silane coupling agents named 3-(methacryloxy)propyltrimethoxysilane (γ -MPS). It is reported that incorporation of too much CNTs into dental resins, mechanical properties of dental resins would be impaired by the significant lower DC, and the best properties of dental resin matrix could be obtained by incorporating 0.025 wt% of CNTs and 1.0 wt% of γ -MPS. Kang [14] et al. compared the mechanical properties among the groups with distinct monomer ratios on Bis-GMA/TEGDMA (wt%/wt%) based polymer-infiltrated ceramic-network (PICN) composites, found the Bis-GMA/TEGDMA (60/40, wt%/wt%) based PICN composites would achieve higher mechanical properties, combining flexural strength,

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flexural modulus, fracture roughness, moderate hardness and other properties. Gongalves [15, 16] et al. studied the effects of different molar ratios of monomers on the properties of the cured resins. They found that the DC of the dental resins decreased systematically by 29.7% and 7.5%, as the mass fraction of the Bis-GMA and UDMA increased from 20 to 80 wt%, respectively. Contrarily, the mechanical properties such as elastic modulus increased. Floyd [17] et al. concluded that with the molar fraction of TEGDMA increased, the DC of the resins consisted of UDMA/TEGDMA and Bis-GMA/TEGDMA increased, but the mechanical properties decreased. Izabela [18, 19] et al. studied the DC and mechanical properties of the resins with different resin monomer ratios. They evaluated the mechanical properties such as flexural modulus, flexural strength and hardness of the resins with different monomer ratios. The experimental results were irregular, and none of cured resins had both excellent mechanical properties and DC.

Although generous researches on dental resins, however, there is no uniform standard for the selection of resin matrix, and various dental resins have been employed in previous studies. In addition, for pure dental resins, there is very limited concerning detailed studies on optimal monomer ratio of dental resins. Therefore, we explore the optimal monomer ratios of dental resins using Bis-GMA, UDMA and TEGDMA, so as to provide an intuitive guideline for the resin matrix application. In this work, we determine the optimal monomer ratios for dental resin compounds (Bis-GMA/TEGDMA, UDMA/TEGDMA and Bis-GMA/UDMA/TEGDMA) by combining three critical properties of the cured resins: degree of conversion, rate of polymerization and surface mechanical properties. The DC and Rp are characterized by NIR (Near Infrared Ray) spectroscopy while the surface mechanical properties is measured by nanoindentation tests. We find that the cured resins exhibit the optimal comprehensive properties when the mass fractions of Bis-GMA, UDMA, and TEGDMA are 15–35 wt%, 37–60 wt%, and 20–35 wt %, respectively. The presented study gives the optimal monomer ratios to achieve the optimal comprehensive performances for dental resins, and is expected to provide experimental basis for practical use of the dental polymers.

2. Materials and methods

2.1. Materials

The primary monomers Bis-GMA (B) (BOC Sciences Inc., USA) and/or UDMA (U) (ESSTECH Inc., USA) were combined with TEGDMA (T) (BOC Sciences Inc., USA) using various mass ratios. Among them, the binary dental resins were abbreviated according to the mass ratios of Bis-GMA or UDMA, i.e., B20 for B/T resins with 20 wt% Bis-GMA and U20 for U/T resins with 20 wt% UDMA. The photoinitiator system was composed of CQ (camphorquinone) and EDAB (ethyl 4-dimethylaminobenzoate) (both from Sigma-Aldrich, Milwaukee, WI) with 0.2 wt% and 0.8 wt%, respectively [20, 21]. The resin monomers and photoinitiator system were blended in a centrifugal mixer (DAC 150FVZ, FlackTek Inc., Landrum, SC), and stirred for about 30 min (2000r/s) to ensure the dental resin compounds were well-mixed. The monomers were stored under refrigeration and the photoinitiators were kept in the dark before used.

2.2. Degree of conversion and rate of polymerization

The DC of dental resins was measured by NIR spectroscopy that contained a NIR detector (NIR Quest 512-2.2, Ocean Optics) and an infrared (IR) light source (HL-2000, Ocean Optics) [22]. The curing light system was composed of a controller (6340 Combo Source, Arroyo Instruments) and a light-emitting diode (LED LZ1-10DB00, LED Engin). The curing light was a single blue color LED and all samples were cured for 40 s. The light intensity was firstly varied from 200 to 1400 mW/cm² to reveal the influence of light intensities for U/T and B/T dental resins.

After that, the effect of monomer ratio on the DC was studied by appropriate light intensity selected.

The uncured resins were injected into the non-tacky Teflon sleeve (the inner diameter and height are 2.5 mm and 2–3 mm, respectively) by a syringe. The change of carbon double bonds absorption peak (the methacrylate functional group centered at 6164 cm⁻¹ [23]) was monitored, and the DC is calculated according to Eq. (1):

$$DC(\%) = \frac{A_0 - A_t}{A_0} \times 100\% \quad (1)$$

where A_0 is the area of $-C=C-$ absorption peak before curing; A_t is the area of $-C=C-$ absorption peak of dental resins at time t . Each samples were measured for 3–5 times, and the DC of dental resins was determined by the average value of the test samples.

Selecting one of the DC-time curves, then fitted by Hill's 3-parameter non-linear regressions [24], the DC of dental resins as a function of time (t) is obtained by Eq. (2):

$$DC = \frac{at^b}{c^b + t^b} \quad (2)$$

where a , b and c are constants. Based on the first derivative of the real-time DC plots, the Rp is obtained by Eq. (3):

$$Rp = \frac{abt^{b-1}c^b}{(c^b + t^b)^2} \quad (3)$$

2.3. Nanoindentation tests

Firstly, the dental resins were injected into a square mold (10 mm × 10 mm × 5 mm) and cured with blue color LED (light intensity is 1000 mW/cm² and curing time is 40 s). Then the cured resins were inlaid with epoxy resins and curing agent in the mass ratio of 2:1. Finally, the samples were sanded and polished in a polisher (Ecomet 250, Buehler) to ensure the surface of samples smooth.

The mechanical properties of dental resins were investigated by the Triboindenter system (TI950, Hysitron Inc., USA) with a diamond equilateral triangular indenter (Berkovich) [25]. Samples were tested in a quasi-static force-control mode where the applied force was controlled by computer, and the displacement was monitored real-time. The load function (shown in Figure 1) selected was 5-2-5 model (i.e. 5 s loading, 2 s load holding and 5 s unloading), and the maximum load was set to 2000 μN. The load-displacement curve was obtained from nanoindentation

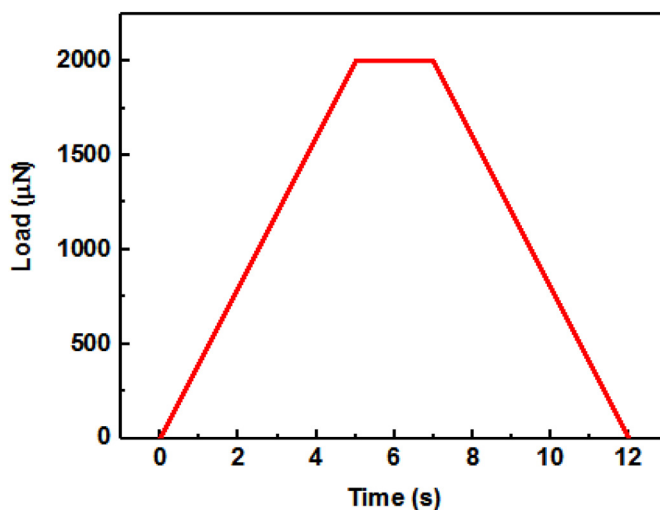


Figure 1. Schematic diagram of loading function for indentation test. Loading function of force for nanoindentation test.

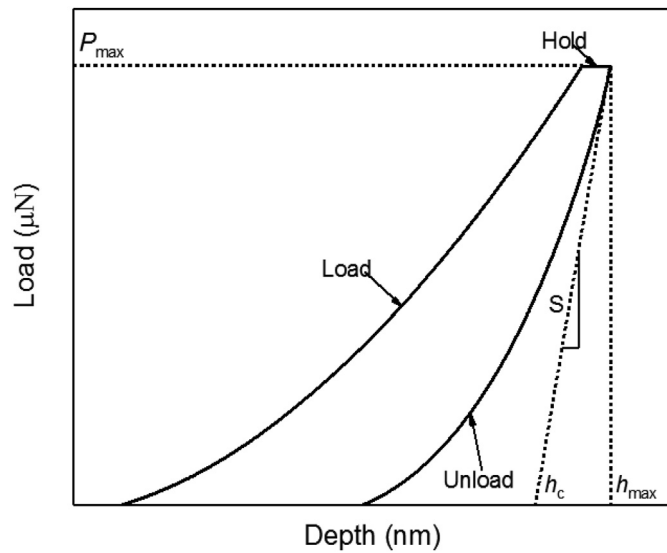


Figure 2. Typical load-displacement curve. Typical load-displacement curve in the test. P_{max} : maximum load; h_{max} : maximum displacement; h_c : residual displacement; S : contact stiffness.

tests, and the hardness and elastic modulus of materials were acquired based on Oliver and Pharr's method [26]. From Figure 2, we can obtain the maximum load (P_{max}), maximum displacement (h_{max}), and residual displacement (h_c). Eq. (4) is used to calculate the hardness (H) [27]:

$$H = \frac{P_{max}}{A_c} \tag{4}$$

where A_c is the contact area between the indenter and the sample surface. The reduced modulus E_r is obtained by using Oliver and Pharr's [27, 28] method, as shown in Eq. (5):

$$E_r = \frac{\sqrt{\pi}}{2\beta} \frac{S}{\sqrt{A_c}} \tag{5}$$

where β is a constant associated with the indenter, for the Berkovich indenter, $\beta = 1.034$ [29]. S is the contact stiffness, which can be regarded as the initial slope of the unloading curve. S and A_c can be calculated by Eqs. (6) and (7) [30]:

$$S = \left(\frac{dP}{dh} \right)_{h=h_{max}} = \frac{P_{max}}{h_{max} - h_c} \tag{6}$$

$$A_c = 24.5h_c^2 + C_1h_c + C_2h_c^{1/2} + C_3h_c^{1/4} + C_4h_c^{1/8} + C_5h_c^{1/16} + C_6h_c^{1/32} + C_7h_c^{1/64} + C_8h_c^{1/128} \tag{7}$$

where $C_1, C_2, C_3, \dots, C_8$ are the function fitting parameters of the indenter tip area of the indenter, as shown in Table 1.

The elastic modulus E_c [29] can be calculated by Eq. (8):

$$\frac{1}{E_r} = \frac{1 - \nu_c^2}{E_c} + \frac{1 - \nu_s^2}{E_s} \tag{8}$$

The E_s is the elastic modulus of the Berkovich indenter, $E_s = 1140$ GPa [29]. In this experiment, $E_s \gg E_c$, Eq. (5) is simplified to Eq. (9) as follows:

$$E_c = (1 - \nu_c^2)E_r \tag{9}$$

where ν_c is the Poisson's ratio of the material.

The schematic diagram of indentation tests is shown in Figure 3. Each samples were measured for 3–5 times, and the hardness and modulus of dental resins were determined by the average value of the test samples. The hardness and modulus of each sample were calculated as the average values of the $4 \times 3 \times 3$ indentation points.

3. Results

3.1. Degree of conversion

3.1.1. Effect of light intensity on the DC of dental resins

In general, the greater the light intensity is, the higher the DC of dental resins is. The DC of dental resins with different light intensities is shown in Figure 4. Obviously, with the increase of light intensity, the DC of dental resins increases gradually and finally tends to be stable. And when the light intensity exceeds 1000 mW/cm^2 , the light intensity has little effect on the DC. Besides, the DC of B/T resin compounds has a much greater increment than U/T resin compounds when light intensity rise from 200 mW/cm^2 to 1400 mW/cm^2 .

3.1.2. Effect of the monomer ratios on the DC of dental resins

The DC of dental resins can reflect the consumption of monomers well. Based on the previous results, the light intensity is set as 1000 mW/cm^2 and curing time is 40 s. The effects of mass fractions of monomers on DC were studied and the results are shown in Figure 5. With the increase of the mass fraction of U or B, the DC of dental resins decreases monotonically. The DC drops from 76.12% for U20 (68.97% for B20) to 60.74% for U80 (52.69% for B80), with a decrease of 20.21% (23.60%). From the results of the experiment, no matter the mass fraction of U or B increases, the DC of dental resins decreases, and the DC of U/T resin compounds is higher than B/T resin compounds at the same monomer ratios.

3.2. Rate of polymerization

The raw curves of DC with curing time are fitted by Hill's 3-parameter non-linear regression, and the rate of polymerization is determined by

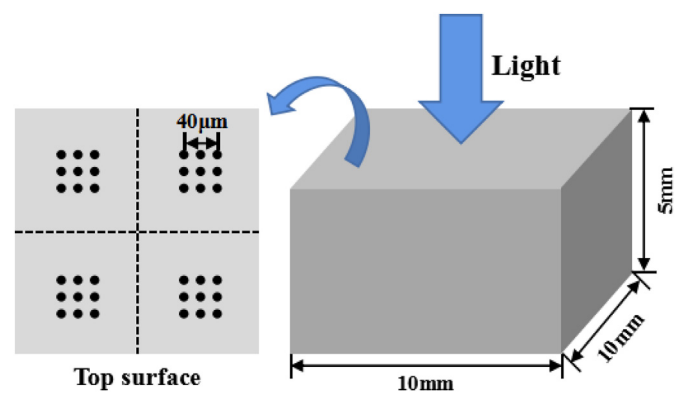


Figure 3. The schematic diagram of the indentation test. In order to ensure the accuracy of experimental data, four independent areas are selected on the sample surface for indentation test. The hardness and modulus of the sample were calculated by the average of $4 \times 3 \times 3$ indentation points.

Table 1. Function fitting parameters of indenter tip region of Nano Indenter.

C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8
3140.16	3062.75	3512.92	-2246.53	-4227.22	-5300.59	-5864.51	-6153.9

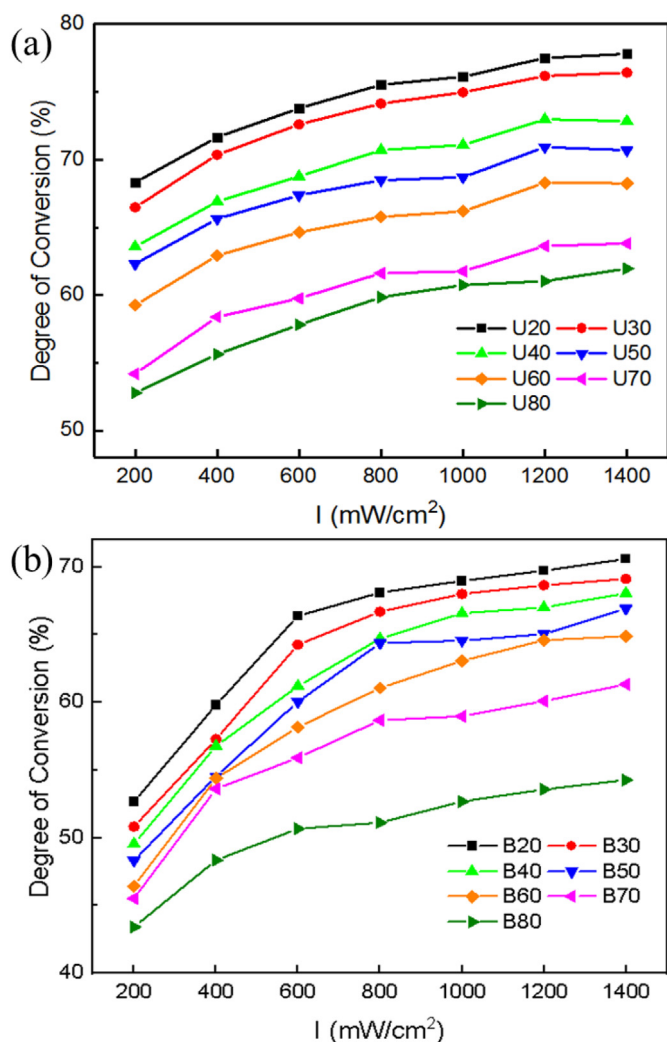


Figure 4. Variations of the degree of conversion with different light intensities: (a) U/T resin compounds and (b) B/T resin compounds. I : light intensity; U: UDMA; B: Bis-GMA; The number indicates the monomer mass fraction, i.e., U20 means the mass fraction of UDMA is 20 wt%, and B20 means the mass fraction of Bis-GMA is 20 wt%. With the increase of light intensity, the DC of dental resins increases gradually and finally tends to be stable in U/T or B/T resin compounds.

the first derivative of the curves of DC (as shown in Figure 6). When the mass fraction of the U (B) from 20 to 80 wt%, the maximum R_p increases from $3.53\% \cdot s^{-1}$ of U20 ($2.02\% \cdot s^{-1}$ of B20) to $22.49\% \cdot s^{-1}$ of U80 ($5.84\% \cdot s^{-1}$ of B80), with an increment of 84.30% (65.41%), respectively. For all samples, the higher the mass fraction of U or B, the faster the R_p increases and the corresponding maximum R_p is higher.

3.3. Mechanical properties

Variations of the hardness (H) and elastic modulus (E) with different mass fractions of monomers as shown in Figure 7. Both H and E increase monotonously with the mass fraction of U or B. H and E rise from 0.199 GPa and 3.31 GPa (0.178 GPa and 3.31 GPa) of U20 (B20) to 0.244 GPa and 4.08 GPa (0.231 GPa and 4.15 GPa) of U80 (B80), with increments of 22.6% and 23.3% (29.8% and 25.4%), respectively. Combining the DC and mechanical properties of dental resins, find that the mass fraction of monomers (U or B) is 70–80 wt%, the cured resins exhibit the optimal material properties.

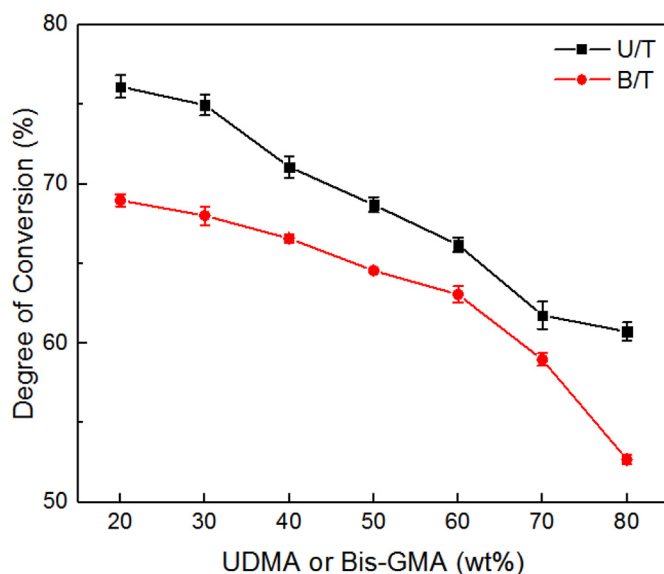


Figure 5. Variations of the degree of conversion with different monomer ratios. U: UDMA; B: Bis-GMA; T: TEGDMA; With the increase of the mass fraction of UDMA or Bis-GMA, the degree of conversion of dental resins decreases monotonically.

3.4. Comprehensive properties of cured resins with three monomers

Many researchers have discussed the properties on dental resins of mixing two monomers [15, 16, 17, 18, 19]. Based on pairwise mixing, we continue to add the third resin monomer and systematically study the DC and mechanical properties of cured resins, experimental results are shown in Figure 8. From the result, the H, E and DC of cured resins with three types of monomers can be as high as 0.44 GPa, 5.96 GPa, and 76.2%. We find that the H and E of cured resins of three types of monomers are mostly higher than the mixed resins of two types of monomers (U/T or B/T), but the DC of dental resins is without at a low level. It is important for dental resins with high DC and excellent mechanical properties (H and E), however, these requirements generate a conflict, achieve difficultly. We can find that the cured resins containing B (15–35 wt%), U (37–60 wt%) and T (20–35 wt%) achieve high DC (above 58%) and excellent mechanical strength (Where E exceeds 4.304 GPa and H exceeds 0.276 GPa).

4. Discussion

Many previous investigations studied the impact of light intensity on polymerization, mainly focusing on dental resins. Photoinitiator in resin compounds is activated by light and then produces active free radicals to initiate polymerization, the light intensity determines the number of active radicals and their activity [31]. From Figure 4, the improve of DC is attributed to the increase of light intensity. However, above a specific value (about 1000 mW/cm² here), the enhancement effect of light intensity on DC of dental resins could be ignored. Just as Lovell et al. found that when B and T were co-polymerized under various light intensities, the DC of resin compounds was enhanced with light intensity [32], but blindly increasing light intensity would improve the volume shrinkage and weaken the mechanical properties of the cured resins [33]. Meanwhile, with the light intensity increased, the collision probability of free radicals increased, leading to self-annihilation instead of participating in the polymerization process, that why the DC of dental resins is limited to a certain level [34, 35]. The DC is affected by many factors, when at a low light intensity, the viscosity of resin compounds is the dominant factor. So the high viscosity of B/T resin compounds show a low DC. However, when the light intensity increases to a certain extent, the light intensity

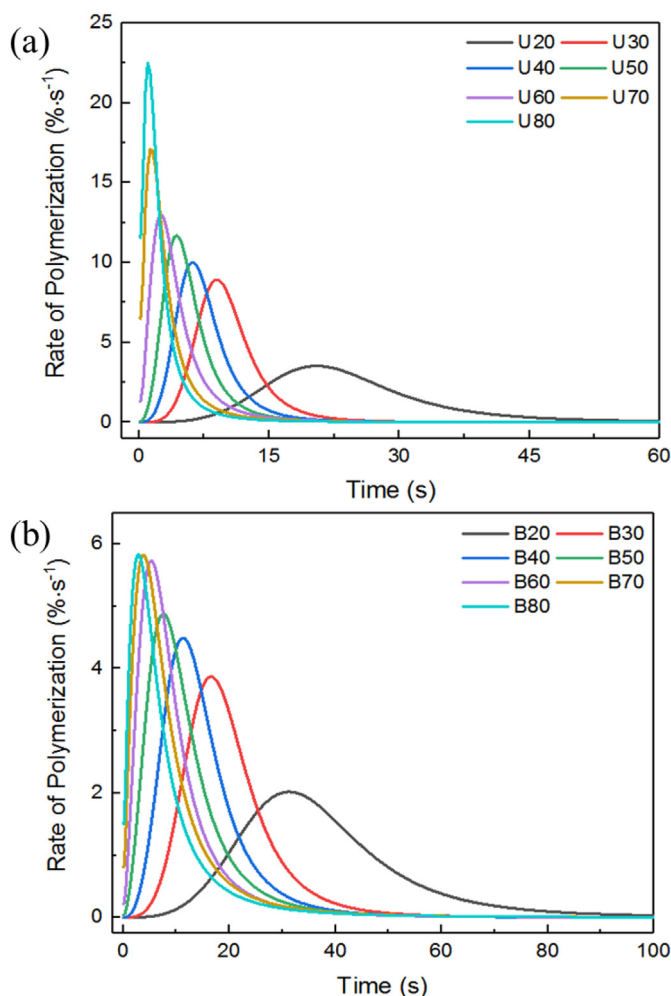


Figure 6. Real-time development of the DC rate for the various specimens with different monomer ratios: (a) U/T resins and (b) B/T resins. U: UDMA; B: Bis-GMA; The number indicates the monomer mass fraction, i.e., U20 means the mass fraction of UDMA is 20 wt%, and B20 means the mass fraction of Bis-GMA is 20 wt%. For all samples, the higher the mass fraction of UDMA or Bis-GMA, the faster the Rp increases and the corresponding maximum Rp is higher.

becomes the dominant factor, the increment of the DC of dental resins is not obvious with the increase of light intensity.

With the increase of the mass fraction of U or B, the DC of dental resins decreases gradually. This is because when the cured resins have more viscous monomers and larger molecular weight, the movement of the monomers in the polymerization process is hindered more easily, and the DC will be smaller [36]. As we all know, the polymerization of the light-cured dental resins is free radical polymerization [37, 38]. During the polymerization, the increase slightly of resins' viscosity is conducive to the growth of Rp. On the one hand, as the reaction continues, the monomers form a polymer network which leads to the viscosity of resin compounds increasing sharply, resulting in a significant decrease in the termination rate constant Kt decreases significantly, however, the chain growth rate constant Kp remains basically unchanged [39, 40]. As a result, the rate of polymerization increases significantly, as shown in Figure 6. On the other hand, the movement of active free radicals and active segments is hindered seriously and which reduces the Rp of the resins [36, 41] at the late reaction. Meanwhile, the -NH- group with high reactivity in the U molecular chain could increase the rate of polymerization substantially [6, 42]:

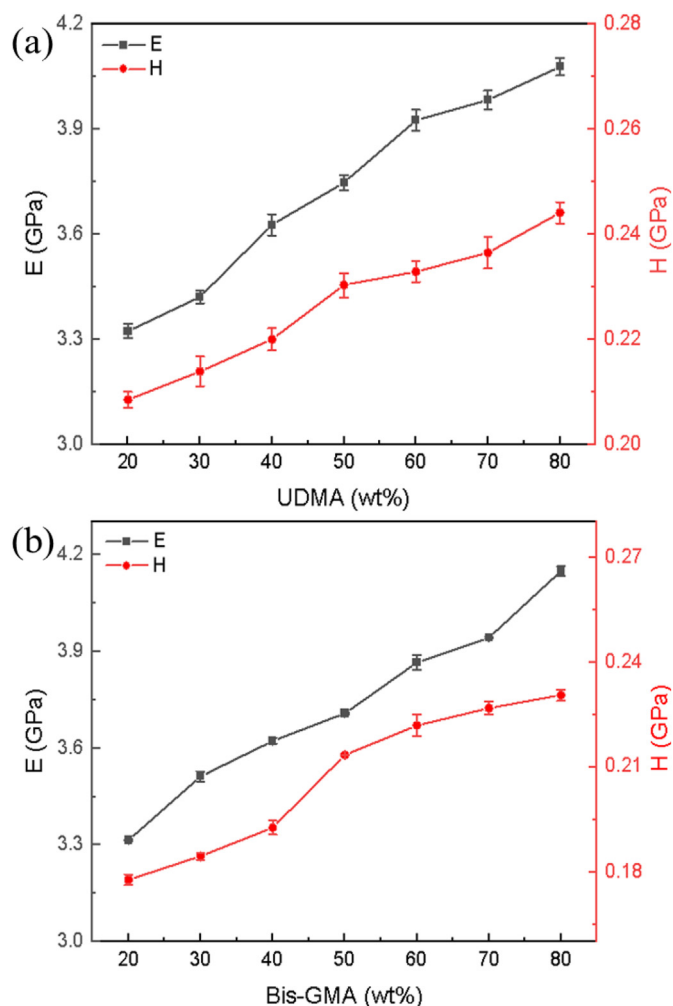
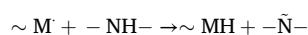


Figure 7. Variations of the hardness (H) and elastic modulus (E) with different mass fractions of monomers: (a) U/T resin compounds and (b) B/T resin compounds. H: hardness; E: elastic modulus; U: UDMA; B: Bis-GMA; Both H and E increase monotonously with the mass fraction of UDMA or Bis-GMA.



Where $\sim M'$ is an active molecular chain and the -NH- group may be part of a monomer or a polymer molecule, the newly formed radical can be an active site that can cause the initiation of polymerization or crosslink.

Many scholars studied the effect of ratios of monomers on the mechanical properties of the resins. Inagaki compared U/T (25/75, wt%/wt%) with U/T (0/100, wt%/wt%), found that the E of the U/T (25/75, wt%/wt%) is 31.7% higher than U/T (0/100, wt%/wt%), indicating that the increase of the mass fraction of U was conducive to the improvement of mechanical properties [43]. Other scholars found that with the increase of mass fraction of T, the mechanical properties of the resins decreased [15, 16, 17], which was similar to the trend of the data we obtained. Whether the resin compounds of two or three types of monomers, the addition of U or B would increase the mechanical properties of the resins and reduce the DC of the resins (Figure 5 and Figure 7). The significant increases in H and E can attribute to the difference in molecular structure between B, U, and T monomers. The hydroxyl groups and methylene groups in B and U are beneficial to the formation of hydrogen bonds between molecules to strengthen the mechanical

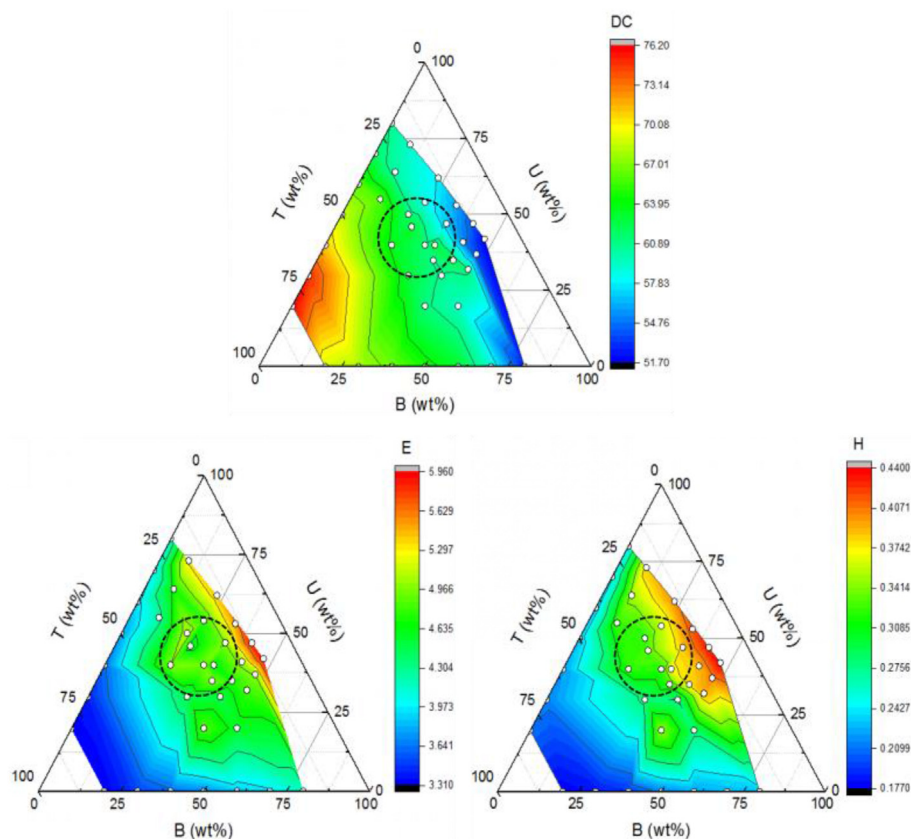


Figure 8. Degree of conversion and mechanical properties (E and H) of dental resins. DC: degree of conversion; H: hardness; E: elastic modulus; U: UDMA; B: Bis-GMA; T: TEGDMA; The degree of conversion and mechanical properties (E and H) of dental resins when Bis-GMA, UDMA and TEGDMA are mixed in different proportions. The dental resins (B/U/T) exhibit better properties when monomer ratios within the black circle area.

properties of resin compounds. Besides, the rigid benzene ring in the B molecular chain improves greatly the resins' mechanical properties.

To obtain better mechanical properties, many researchers usually mixed the polymer matrix with inorganic filler, such as silicon, barium glass, zirconium, and aluminum oxides. For example, researchers studied the effect of barium glass content on the mechanical properties of the resins, found that the E of the resins improved with the increase of filler content, and the E of the resins could be as high as 3.9 GPa [16]. That the E of the resins could reach 4.6 ± 1.8 GPa and 5.2 ± 3.9 GPa with 20 wt% silica or aluminum oxides added [44]. The E in the article is even lower than most experimental values (Figure 8) in our work which the E of most cured resins exceeds 4.6 GPa, even up to 5.96 GPa.

In this study, we characterize the degree of conversion and mechanical properties of dental resins by NIR spectroscopy and nanoindentation tests, respectively. The experimental results show that the B/U/T ternary dental resins own more excellent overall properties as compared to B/T and U/T resins, and the B/U/T ternary dental resins present the optimal performance when the mass fractions of B, U and T are 15–35 wt%, 37–60 wt% and 20–35 wt%, respectively. Meanwhile, the optimum monomer ratios of the dental resins (U/T, B/T, and B/U/T) may be affected by many factors such as the light conditions, the type of the initiators, the structure of monomers, etc. However, we believe the general method adopted here is beneficial to further studies if one wants to find the optimal ratios for resin monomers.

5. Conclusions

In this work, we have explored the optimal monomer ratios of dental resin compounds (U/T, B/T, and B/U/T) by studying such material properties as the degree of conversion (DC), rate of polymerization (R_p) and mechanical properties. The equilibrium DC of the light-cured dental

resins decreases with the increasing mass fractions of U and B, while the R_p shows the opposite trend. With the increase of the mass fractions of U and B, the elastic modulus and hardness of the dental resins increase monotonically. Combining the curing and mechanical properties, it is found that the cured resins exhibit the optimal material properties when the mass fractions of B, U, and T are close to 15–35 wt%, 37–60 wt%, and 20–35 wt%, respectively. The method reported here can help the better studying of the behavior of dental resins and also provide valuable information to braid the optimal recipe design for dental resins.

Declarations

Author contribution statement

Weideng Li: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Kun Wang: Analyzed and interpreted the data.

Zhengzhi Wang: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data.

Bei Li: Conceived and designed the experiments; Analyzed and interpreted the data.

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Data availability statement

Data included in article/supp. material/referenced in article.

Declaration of interest's statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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