

Available online at www.sciencedirect.com

journal homepage: www.intl.elsevierhealth.com/journals/dema

Resin viscosity determines the condition for a valid exposure reciprocity law in dental composites

Sri Vikram Palagummi^a, Taeseung Hong^{a,c}, Zhengzhi Wang^b,
Chang Kwon Moon^c, Martin Y.M. Chiang^{a,*}

^a Biosystems and Biomaterials Division, National Institute of Standards and Technology, Gaithersburg, MD, United States

^b Department of Engineering Mechanics, School of Civil Engineering, Wuhan University, Wuhan, Hubei, China

^c Department of Materials Science and Engineering, Pukyong National University, Busan, Republic of Korea

ARTICLE INFO

Keywords:

Photopolymerization
Exposure reciprocity law
Radiant exposure
Irradiance
Autodeceleration
Polymerization exotherm

ABSTRACT

Objective. To provide conditions for the validity of the exposure reciprocity law as it pertains to the photopolymerization of dimethacrylate-based dental composites.

Methods. Composites made from different mass ratios of resin blends (Bis-GMA/TEGDMA and UDMA/TEGDMA) and silanized micro-sized glass fillers were used. All the composites used camphorquinone and ethyl 4-dimethylaminobenzoate as the photo initiator system. A cantilever beam-based instrument (NIST SRI 6005) coupled with NIR spectroscopy and a microprobe thermocouple was used to simultaneously measure the degree of conversion (DC), the polymerization stress (PS) due to the shrinkage, and the temperature change (TC) in real time during the photocuring process. The instrument has an integrated LED light curing unit providing irradiances ranging from 0.01 W/cm² to 4 W/cm² at a peak wavelength of 460 nm (blue light). Vickers hardness of the composites was also measured.

Results. For every dental composite there exists a minimum radiant exposure required for an adequate polymerization (i.e., insignificant increase in polymerization with any further increase in the radiant exposure). This minimum predominantly depends on the resin viscosity of composite and can be predicted using an empirical equation established based on the test results. If the radiant exposure is above this minimum, the exposure reciprocity law is valid with respect to DC for high-fill composites (filler contents >50% by mass) while invalid for low-fill composites (that are clinically irrelevant).

Significance. The study promotes better understanding on the applicability of the exposure reciprocity law for dental composites. It also provides a guidance for altering the radiant exposure, with the clinically available curing light unit, needed to adequately cure the dental composite in question.

Published by Elsevier Inc. on behalf of The Academy of Dental Materials.

* Corresponding author at: National Institute of Standards and Technology (NIST), 100 Bureau Drive, MS 8543, Gaithersburg, MD 20899, United States. Official contribution of NIST; not subject to copyright in the United States.

E-mail address: martin.chiang@nist.gov (M.Y.M. Chiang).

<https://doi.org/10.1016/j.dental.2019.12.003>

0109-5641/Published by Elsevier Inc. on behalf of The Academy of Dental Materials.

1. Introduction

In photochemistry, using different combinations of irradiance (radiant flux per unit area) and exposure time is justified by the Bunsen–Roscoe reciprocity law [1] (also referred to as the exposure reciprocity law, ERL). For example, in restorative dentistry the ever-increasing demand from dentists for reducing the exposure time (i.e., reducing chairside time) in photocuring composites has led to high irradiance LED curing units (e.g., $>2\text{ W/cm}^2$) [2]. The ERL states that for a given radiant exposure (defined as the total radiant energy received per unit area = irradiance \times exposure time), the polymerization (the degree of conversion from monomers to polymers, DC) of the resin does not change with any combination of irradiance and exposure time. However, studies in the literature have debated rather inconclusively about the validity of the ERL in dentistry [3–16]. The results of these studies depended on the combination of the photocuring conditions (irradiance and radiant exposures) and materials (model dental resins/composites and commercial composites) used. The objective of this work is to address the discrepancies regarding the validity debate and, hence, promote a better understanding of the applicability of the ERL as it pertains to resin-based dental composites.

Although a few studies showed that the ERL for dental materials was valid [14,15], a majority of the studies showed that the ERL was invalid. These studies can be divided broadly into two categories. In the first category, the ERL has been demonstrated not to be valid since a higher DC was obtained using a higher irradiance in comparison to lower irradiances [5,13,17]. For example, Wydra et al. [13] showed that using a high irradiance (0.024 W/cm^2) UV-cure on a dimethacrylate resin mixture resulted in a higher DC when compared to using a low irradiance (0.003 W/cm^2). Leprince et al. [5] showed the same trend when a dimethacrylate resin and composite were cured with Lucirin-TPO as the initiator. Some theoretical arguments made in these studies, in support of their results, state that the ERL cannot be valid since the DC, derived from the classical equation for the rate of photopolymerization [18,19], is not proportional to the first order of the radiant exposure. Conversely, in the second category, a large number of studies have indicated the ERL not to be valid as a lower DC was obtained using a higher irradiance in comparison to lower irradiances [3–12,16]. For example, Hadis et al. [10] showed that DC achieved using a higher irradiance of 3 W/cm^2 was significantly lower than that using an irradiance of 0.4 W/cm^2 for a range of commercial dental composites. Similar trends were seen by Feng et al. [3,4] when they examined the validity of the ERL on a range of multifunctional acrylate resins, methacrylate resins, and commercial composites. Due to the clinical resemblance of the materials used in these studies, this study will primarily address the ERL validity in this category. Also, subsequently, results and discussion are provided regarding the first category as mentioned earlier.

In addition to exploring the validity of the ERL, some studies also discussed the effect of irradiance, at a constant radiant exposure, on other key properties of the composites. These properties involve, but are not limited to, polymerization stress (PS) due to shrinkage, the temperature change (TC)

due to the reaction exotherm and absorbance associated with the photocuring process, and the hardness. For example, it has been discussed that photocuring with high irradiance may increase PS and effectively decrease the bond strength to the tooth [20–22]. Although an increase in irradiance will increase the rate of PS, it is speculative as to whether this will lead to a higher PS [13,23–27]. The exothermic temperature increases due to the increase of irradiance, along with the temperature rise due to the absorbance. This can potentially lead to pulpal and dental tissue damage [28–30]; however, only a few studies on the validity of the ERL [17,31] have measured TC. The hardness of the composites was also evaluated, sometimes as a substitute to measuring the DC, to test the validity of the ERL [16]. As these properties are clinically relevant, in the current study they will also be measured and discussed in conjunction with the discussion of the ERL.

A systematic study involving the variation of the composition of model dental composites and the photocuring conditions has been carried out in this work to address the validity of the exposure reciprocity law (ERL) with respect to the DC. Model dimethacrylate dental resins blended of Bis-GMA (bisphenol A glycidyl methacrylate)/TEGDMA (triethyleneglycol dimethacrylate) or UDMA (urethane dimethacrylate)/TEGDMA at different ratios were used. The resin blends were mixed with a fixed mass of visible-light initiator system (camphorquinone and ethyl 4-dimethylaminobenzoate) and with varied content of a silanized micro-sized glass filler. A NIST-developed standard reference instrument (NIST SRI 6005) [32,33] coupled with NIR spectroscopy and a microprobe thermocouple, which simultaneously measures DC, PS, and TC in real time during the photocuring process, was used in this study. After the measurement of the polymerization properties, the Vickers hardness test was performed for the composites. The result from this study indicates that for every dental composite there exists a minimum radiant exposure required for adequate polymerization (i.e., insignificant increase in polymerization will be produced with any further increase in the radiant exposure). This minimum depends primarily on the resin viscosity of composite; an empirical model as a function of the resin viscosity is established and verified based on experimental results to predict it. The validity of the ERL should be discussed only if the radiant exposure used in the photocuring process is above this minimum. The ERL is valid with respect to DC for high-fill composites (filler contents $>50\%$ by mass, which are clinically relevant to dental composites) while invalid for low-fill composites. The difference between the high-fill and low-fill composites on the ERL validity is largely due to the significance of polymerization temperature effect on the resin viscosity during the photocuring process. The result of the study clarifies discrepancies reported in the literature and gives guidance on the validity of the exposure reciprocity law for dental composites. Also, the empirical model can enable one to determine the exposure time required to adequately cure a given dental composite with the available curing light unit (irradiance). More importantly, when employing a high irradiance and the corresponding exposure time, based on the law, care should be taken such that the associated temperature change in the underlying tissue is clinically acceptable. Finally, although the study is based on dimethacrylate-based resin

composites, the conclusions made in this study are applicable to other resin composite systems where the nature of the photopolymerization reaction is primarily influenced by the diffusion-controlled polymerization.

2. Materials and methods

Model composites comprising of typical commercial dental resins filled with silanized inorganic fillers were tested (Table 1). The fillers were mixed with resin blends using a centrifugal mixer (DAC 150FVZ, FlackTek Inc., Landrum, South Carolina, USA).

Uncured composite specimens of disk shape (2.5 mm diameter, 2 mm height, C-factor = diameter/(2 × height) = 0.625) were prepared. The photopolymerization properties of composites were measured using the NIST-developed cantilever beam-based instrument (NIST SRI 6005, Polymerization Stress Tensometer). The design of the instrument, comparing to its previous version [34,35], follows the first principle of mechanics that provides much higher sensitivity and accuracy to the presence of polymerization shrinkage [32]. The instrument setup is coupled with an *in-situ* near-infrared (NIR) spectrometer (NIRQuest512-2.2, Ocean Optics, Inc., Dunedin, Florida, USA) in transmission mode and a microprobe thermocouple (0.1 mm diameter, Physitemp Instruments, Clifton, New Jersey, USA), which allow simultaneous monitoring of DC (degree of conversion), PS (polymerization stress) and TC (temperature change) during the photocuring process in real time. A more detailed description about the testing mechanics and instrument setup has been reported in our previous study [33]. A compliance of 0.33 μm/N was chosen as it is comparable to the compliance of tooth cavities reported in the literature [36,37]. A curing light system including a blue LED light (sharp absorbance peak at 460 nm, LZ1-10DB00, LED Engin, Mouser Electronics, Mansfield, Texas, USA) and a controller (6340 ComboSource, Arroyo Instruments LLC, San Luis Obispo, California, USA) is integrated with the instrument. This allows the precise delivery of varying light irradiance and exposure time for the polymerization process. Several different combinations of irradiance and the exposure time were used in the study. For every combination of irradiance and exposure time, at least three replicate experiments were conducted. Regardless of the exposure time, the polymerization properties (namely, the DC/PS/TC data) were simultaneously collected in real time for 10 min unless otherwise mentioned. The experiments were performed at room temperature (21 °C–22 °C) and under a yellow light environment to minimize premature photopolymerization. Data collected were subjected to one-way analysis of variance; pairwise comparisons were done using the Holm-Sidak method with a 95% level of statistical significance (SigmaPlot version 14.0 from Systat Software Inc., San Jose, California, USA).

After the measurement of the polymerization properties, the Vickers hardness test was carried out on the composite samples. Prior to the test, the samples were stored in a dark dry environment under vacuum for two weeks. They were then polished under a sequence of SiC papers (Struers Inc., Westlake, Ohio, USA) of decreasing abrasiveness (P800, P1200, P2400 and P4000) under continuous water cooling. The sam-

Table 1 – Composition of composites^d.

Composite ^a	Resin Blends ^b	Resin mass ratio	Filler content by mass of composite ^c
7B3T-75F	Bis-GMA:TEGDMA	7:3	75%
7B3T-50F	Bis-GMA:TEGDMA	7:3	50%
7B3T-30F	Bis-GMA:TEGDMA	7:3	30%
1B1T-75F	Bis-GMA:TEGDMA	1:1	75%
1B1T-50F	Bis-GMA:TEGDMA	1:1	50%
1B1T-30F	Bis-GMA:TEGDMA	1:1	30%
3B7T-75F	Bis-GMA:TEGDMA	3:7	75%
3B7T-50F	Bis-GMA:TEGDMA	3:7	50%
3B7T-30F	Bis-GMA:TEGDMA	3:7	30%
7U3T-75F	UDMA:TEGDMA	7:3	75%
1U1T-75F	UDMA:TEGDMA	1:1	75%

^a All composites used camphorquinone (CQ), 0.2% by mass of resin, and ethyl 4-dimethylaminobenzoate (EDAB), 0.8% by mass of resin. These mass percentages corresponded to mol% of CQ from 0.39% to 0.49% and mol% of EDAB ranged from 1.34% to 1.71% for the different resin blends. They were acquired from Sigma-Aldrich, Milwaukee, Wisconsin, USA.

^b Bisphenol A glycidyl methacrylate (Bis-GMA), urethane dimethacrylate (UDMA), and triethyleneglycol dimethacrylate (TEGDMA) were donated by Esstech Inc., Essington, Pennsylvania, USA. The resins have a maximum of 600 ppm of mequinol (MeHQ) as an inhibitor.

^c The filler (donated by Dentsply-Caulk, Milford, Delaware, USA) was TPH silanized MLD glass particle with mean size of 1 μm. The mass percentage values correspond to a volume percentage ranging from 14% to 53% of the composite. The 30F and 50F composites are referred to as low-fill composites, whereas, the 75F composites are referred to as high-fill composites in this study.

^d Certain commercial materials and equipment are identified in this manuscript in order to specify adequately the experimental and analysis procedures. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology (NIST) nor does it imply that they are necessarily the best available for the purpose.

ples were further polished using a sequence of felt cloths with 3 μm and 1 μm polycrystalline diamond suspension liquids (Buehler, Lake Bluff, Illinois, USA). Afterwards, the samples were rinsed and dried with compressed air, followed by storage under a dark dry vacuum environment for 24 h before the hardness test. A microhardness testing machine (Tukon 1202, Wilson Hardness, Norwood, Massachusetts, US) with indentation loads of 1.96 N and 2.94 N (i.e., 200 gf and 300 gf) was used for the measurement. The dwell time at a peak load of 15 s was used and the indentation size was measured with a 50× objective.

3. Results and discussion

It is known that the photopolymerization of dimethacrylate-based resins exhibit autodeceleration (the rate of degree of conversion decreases) [38,39]. Also, the time of the autodeceleration occurrence is similar to that of the peak temperature change (PTC) occurrence [40], even for bulk specimens such as those used in restorative dentistry (Fig. 1a). In addition, the autodeceleration is delayed to occur at a higher degree of conversion (DC) when the irradiance is increased [41]. Accordingly, one can infer that the composite is considered as adequately

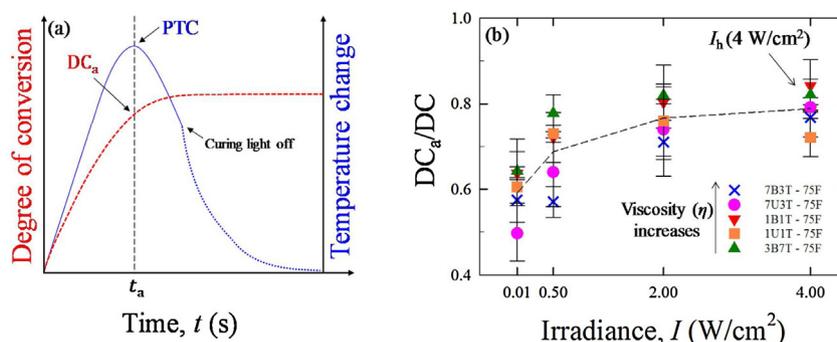


Fig. 1 – Schematic of degree of conversion and temperature change kinetics for a photopolymerization reaction (a). Normalized DC_a (at $t = t_a$) for the composites at different irradiances (0.01 W/cm^2 – 4 W/cm^2); The dashed line is the best schematic fit of results shown for visual aid (b). Vertical bars represent one standard deviation. The high irradiance of 4 W/cm^2 is more than a clinically feasible since the resultant temperature change and/or photoexcitation by the irradiance could cause irreversible damage of cells in the oral tissue [28–30].

Table 2 – Ratio DC_a/DC , t_a and PTC at different irradiances for all the 75F composites.

Composite	Photocuring condition		$DC_a/DC^{1,2}$	t_a^1	PTC ¹
	Irradiance, $I \text{ (W/cm}^2\text{)}$	Exposure time, $t \text{ (s)}$			
7B3T-75F	0.01	2000	0.57 ± 0.05	50.06 ± 16.21	1.91 ± 0.59
	0.5	40	0.57 ± 0.04	3.90 ± 0.80	10.64 ± 1.58
	2	10	0.71 ± 0.03	2.78 ± 0.14	17.53 ± 1.61
	4	5	0.77 ± 0.05	2.44 ± 0.24^3	23.67 ± 1.42
7U3T-75F	0.01	2000	0.49 ± 0.06	28.93 ± 7.93	3.27 ± 0.39
	0.5	40	0.64 ± 0.08	6.48 ± 0.85	11.02 ± 1.95
	2	10	0.74 ± 0.07	3.01 ± 0.20	21.14 ± 2.57
	4	5	0.79 ± 0.01	2.75 ± 0.23^3	26.28 ± 2.78
1B1T-75F	0.01	2000	0.64 ± 0.01	61.83 ± 12.11	2.86 ± 0.24
	0.5	40	0.72 ± 0.06	7.99 ± 1.51	10.81 ± 1.12
	2	10	0.80 ± 0.04	4.97 ± 0.55	18.45 ± 2.69
	4	5	0.84 ± 0.06	4.19 ± 0.33^3	23.70 ± 2.02
1U1T-75F	0.01	2000	0.61 ± 0.08	52.46 ± 12.23	2.86 ± 0.24
	0.5	40	0.73 ± 0.02	7.64 ± 0.89	11.43 ± 1.74
	2	10	0.76 ± 0.13	5.47 ± 0.51	19.43 ± 1.55
	4	5	0.73 ± 0.04	5.06 ± 0.11	24.02 ± 2.35
3B7T-75F	4	10^4	0.72 ± 0.06	4.67 ± 0.49^3	24.39 ± 3.68
	0.01	2000	0.64 ± 0.08	73.05 ± 15.89	2.67 ± 0.63
	0.5	40	0.78 ± 0.04	12.83 ± 0.46	10.28 ± 1.58
	2	10	0.82 ± 0.02	9.17 ± 0.82	14.78 ± 1.90
	4	5	0.64 ± 0.01	5.29 ± 0.11	15.51 ± 3.58
	4	10^4	0.82 ± 0.04	7.29 ± 0.16^3	24.84 ± 1.59

¹ Values represent mean \pm one standard deviation.

² DC was measured for 10 min for all composites and irradiances except for the irradiance of 0.01 W/cm^2 , where it was measured for 1 h. This was done to accommodate for the long exposure time at this irradiance.

³ t_a at I_h ($I = 4 \text{ W/cm}^2$) used to estimate RE_m (Fig. 2).

⁴ For the 3B7T-75F and 1U1T-75F composites, RE of 40 J/cm^2 was used for I_h (4 W/cm^2) since they were under-cured at a RE of 20 J/cm^2 .

cured (i.e., insignificant increase in the DC will be achieved with any further increase in the radiant exposure) at the onset of the autodeceleration if the irradiance is high enough. Moreover, if the time to the PTC ($t = t_a$, Fig. 1a) is obtained for a given composite cured under a high-enough irradiation (I_h), then it can be argued that the radiant exposure calculated based on the t_a (i.e., $= I_h \times t_a$) would act as the minimum (RE_m) needed for adequately curing the composite. This RE_m can be determined as follows.

Fig. 1b shows the DC at time $t = t_a$ (namely, DC_a , corresponding to the time at autodeceleration or PTC, Fig. 1a), normalized

with its respective DC recorded at the end of the experiment, as the irradiance was varied. The photocuring conditions and exact values used for the figure are listed in Table 2. The result in Fig. 1b indicates that for all the 75F composites (cf. Table 1, i.e., high-fill composites) tested the ratio of DC_a/DC increases and plateaus at a high value as the irradiance increases. This suggests that the composites irradiated with a high irradiance (i.e., $I_h = 4 \text{ W/cm}^2$) can be considered as adequately cured at the time corresponding to PTC ($t = t_a$).

The results of Table 3 indicate the DC_a/DC of the 30F and 50F composites is generally higher than that of the 75F com-

Table 3 – Ratio DC_a/DC, t_a at I_h, and PTC for all BisGMA/TEGDMA based composites.

Composite	Exposure time, t (s) at irradiance, I _h (I = 4 W/cm ²)	DC _a /DC ^{1,2}	t _a ^{1,2}	PTC ^{1,2}
7B3T-75F	5	0.77 ± 0.05 ^a	2.44 ± 0.24 ^a	23.67 ± 1.42 ^a
7B3T-50F	5	0.87 ± 0.02 ^b	2.52 ± 0.15 ^a	46.03 ± 1.38 ^b
7B3T-30F	5	0.91 ± 0.01 ^b	2.60 ± 0.12 ^a	59.02 ± 6.38 ^c
1B1T-75F	5	0.84 ± 0.06 ^a	4.19 ± 0.33 ^a	23.70 ± 2.02 ^a
1B1T-50F	5	0.91 ± 0.05 ^a	4.71 ± 0.26 ^a	41.72 ± 4.66 ^b
1B1T-30F	5	0.92 ± 0.02 ^a	4.84 ± 0.35 ^a	54.45 ± 5.48 ^c
3B7T-75F	10	0.79 ± 0.05 ^a	7.29 ± 0.16 ^a	24.84 ± 1.59 ^a
3B7T-50F	10 ³	0.88 ± 0.01 ^b	7.48 ± 0.20 ^a	43.56 ± 3.35 ^b
3B7T-30F	10 ³	0.89 ± 0.04 ^b	7.55 ± 0.42 ^a	57.03 ± 5.54 ^c

¹ Values represent mean ± one standard deviation.

² For each resin blend, values with same small letter are not statistically different at p = 0.05.

³ Like the 3B7T-75F composite, RE of 40 J/cm² was chosen at I_h for the 3B7T-50F and 3B7T-30F composites since they were under-cured at a RE of 20 J/cm² (cf. Table 2).

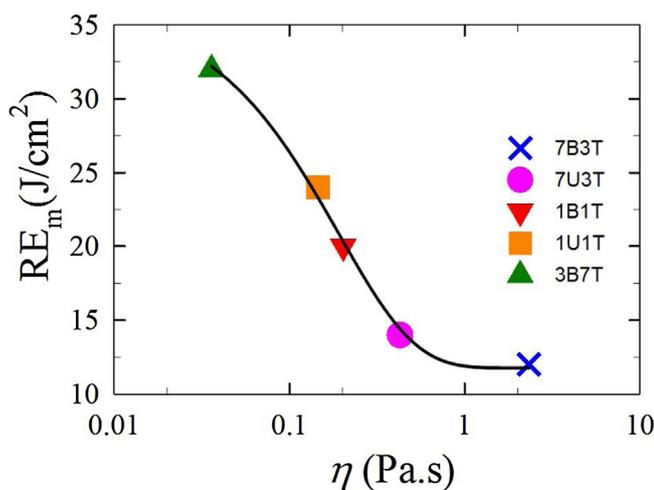


Fig. 2 – Radiant exposure (RE_m) at t = t_a, onset of autodeceleration at the irradiance I_h (4 W/cm²), vs resin viscosity (η, at room temperature) of the composites.

posites, for the same resin blend used. This can be attributed to the peak temperature change (PTC) produced in 30F and 50F, which is significantly higher than that in 75F. Thus, the increased temperature enhances the mobility of resin monomers which results in a higher DC_a/DC. Also, the results in Table 3 demonstrate there is no significant time difference in the occurrence of autodeceleration (t = t_a) among those composites with different filler contents (low-fill, 30F and 50F, and high-fill, 75F, in Table 3) and the same resin blends. However, the results indicate t_a varies with the resin blends for composites with the same filler content. A key difference between the resin blends is their viscosity. Thus, this demonstrates that the time corresponding to the PTC or autodeceleration is predominantly dependent on the resin viscosity of the composites.

Fig. 2 shows the best curve fit for the minimum radiant exposure (RE_m, J/cm²) as a function of viscosity (η, Pa.s) of resins, at room temperature, used in the study. RE_m is calculated based on the I_h (4 W/cm²) used and t_a (Table 2) experimentally obtained for the composites. As there is some uncertainty associated with the measurement of t_a, its mean value plus two standard deviations (in order to be greater than the 95% confidence interval) are used to calculate RE_m. The

Table 4 – Ratio DC_a/DC, t_a at I_h (4 W/cm²), and PTC for composites with CQ and EDAB of 0.1% and 0.4% by mass of resin respectively.

Composite	DC _a /DC ¹	t _a (s) ¹	PTC ¹
7B3T-75F	0.73 ± 0.08	2.72 ± 0.11	20.36 ± 1.61
3B7T-75F	0.78 ± 0.06	7.52 ± 0.13	21.89 ± 3.21

¹ Values represent mean ± one standard deviation.

curve fit of the data in Fig. 2 can be represented by an equation of the form as follows:

$$RE_m = 11.76 + 24.68e^{-5.27\eta} \tag{1}$$

The resin viscosity, η, is acquired from the monomer provider (Esstech Inc., Essington, PA) and literature [42,43]. Eq. (1) can be used to predict the minimum radiant exposure (RE_m) needed for any composite, whose resin viscosity falls within range tested in this study, to be adequately cured. The result in Table 5 indicates that when RE ≥ RE_m, the DC of the 75F (high-fill) composites does not change significantly comparing to the DC obtained at RE_m for the same irradiance used. This can be replicated for all the low-fill (≤50% by mass) composites shown in Table 1 as well. Hence, these results demonstrate that a RE_m exists for adequately curing the composites.

It is worthwhile to note that the increase in the rate of conversion would lead to an earlier occurrence of the autodeceleration (t_a), which implies a lower RE_m would be needed than that of Eq. (1). Four main factors that could result in a different rate of conversion than that seen in this study are, namely, the initiator type, initiator concentration, processing (ambient) temperature, and curing light bandwidth. Although most commercial composites use CQ as their only photoinitiator (type-II initiator), some commercial composites use a small amount of type-I initiator as well. These type-I initiators generally have a higher extinction coefficient than CQ and would lead to an increased rate of reaction when used with an appropriate initiator wavelength matching curing light. Studies reported in the literature have shown that the initiator concentration can vary from 0.1% to 0.4% by mass of the resin in commercial dental composites [44,45]; a CQ concentration of 0.2% was used in this study (Table 1). It is understandable that the rate of conversion would increase when the CQ

Table 5 – Degree of conversion (DC) of all 75F composites when photocured at a radiant exposure lesser than, equal to, and greater than its RE_m at three different irradiances.

Composite	RE _m (J/cm ²)	Photocuring condition			DC (%) ^{1,2}
		RE (J/cm ²)	Irradiance, I (W/cm ²)	Exposure time, t (s)	
7B3T-75F	12	10 < RE _m ³	0.5	20	58.39 ± 1.24 ^a
			2	5	58.97 ± 2.15 ^a
			4	2.5	58.50 ± 2.11 ^a
		12 = RE _m	0.5	24	59.09 ± 1.58 ^a
			2	6	59.32 ± 0.04 ^a
			4	3	59.64 ± 0.57 ^a
		20 > RE _m	0.5	40	58.13 ± 1.33 ^a
			2	10	58.33 ± 0.70 ^a
			4	5	58.18 ± 1.75 ^a
			0.5	20	73.18 ± 0.57 ^{a,b}
			2	5	73.02 ± 0.99 ^{a,b}
			4	2.5	70.07 ± 1.85 ^b
7U3T-75F	14	14 = RE _m	0.5	28	73.54 ± 1.83 ^{a,b}
			2	7	75.10 ± 0.60 ^a
			4	3.5	75.63 ± 3.24 ^a
		20 > RE _m	0.5	40	74.29 ± 1.97 ^{a,b}
			2	10	75.64 ± 1.90 ^a
			4	5	74.54 ± 1.09 ^a
		10 < RE _m	0.5	20	70.89 ± 2.41 ^a
			2	5	68.11 ± 2.42 ^{a,b}
			4	2.5	63.74 ± 1.61 ^b
			0.5	40	69.83 ± 1.82 ^a
			2	10	68.08 ± 2.23 ^a
			4	5	67.72 ± 2.03 ^{a,b}
1B1T-75F	20	20 = RE _m	0.5	80	70.51 ± 1.84 ^a
			2	20	70.01 ± 1.64 ^a
			4	10	69.86 ± 2.19 ^a
		40 > RE _m	0.5	10	75.95 ± 1.11 ^{a,b}
			2	5	72.41 ± 2.82 ^b
			4	2.5	56.24 ± 4.15 ^c
		10 < RE _m	0.5	48	76.33 ± 1.07 ^{a,b}
			2	12	77.83 ± 0.99 ^a
			4	6	75.13 ± 1.61 ^{a,b}
			0.5	80	76.39 ± 1.33 ^{a,b}
			2	20	76.19 ± 1.83 ^{a,b}
			4	10	75.72 ± 2.03 ^a
1U1T-75F	24	24 = RE _m	0.5	20	77.43 ± 3.62 ^a
			2	5	50.93 ± 2.77 ^b
			4	2.5	37.72 ± 1.35 ^c
		40 > RE _m	0.5	64	78.37 ± 2.57 ^a
			2	16	78.57 ± 0.70 ^a
			4	8	77.57 ± 2.47 ^a
		10 < RE _m	0.5	80	79.11 ± 1.70 ^a
			2	20	78.17 ± 1.31 ^a
			4	10	77.22 ± 2.31 ^a

¹ Values represent mean ± one standard deviation.

² For each composite and property, values with same small letter are not statistically different at p = 0.05.

³ The ERL was held even though 10 < RE_m due to the marginal difference between the two radiant exposures.

concentration is increased. Thus, what was needed to examine was the applicability of Eq. (1) when the concentration was lower than 0.2%. Two composites, 7B3T-75F and 3B7T-75F, were prepared with 0.1% CQ and 0.4% EDAB (reducing agent) by mass of the resin. Table 4 shows that the t_a at I_h (4 W/cm²) of these two composites occur only marginally later than those containing 0.2% CQ shown in Table 3 (i.e., they have similar rate of conversion). Regarding the processing temperature, clinically it would be higher (~37 °C) than those maintained in this study (~21–22 °C). It is known that

higher processing temperature increases the rate of conversion [46,47]. Also, this study is based upon experiments using a LED curing light with a narrow bandwidth around 460 nm wavelength. Some curing lights, such as, quartz tungsten halogen or plasma arc lamps, have broader bandwidths [48,49]. This would lead to higher rate of conversion, with similar irradiance at 460 nm wavelength, than that seen in this study. From the aforementioned discussion, one can conclude that Eq. (1) would be applicable for composites with clinically relevant initiator types, initiator concentrations, processing

Table 6 – Degree of conversion (DC) and peak temperature change (PTC) of all low-fill (-50F and -30F) composites when photocured at different irradiances and radiant exposures greater than or equal to RE_m .

Composite	RE_m (J/cm^2)	Photocuring condition			DC (%) ^{1,2}	PTC ^{1,2}
		RE (J/cm^2)	Irradiance, I (W/cm^2)	Exposure time, t (s)		
7B3T-50F	12	20	0.5	40	60.56 ± 1.06 ^a	18.89 ± 2.45 ^a
			4	5	64.53 ± 1.44 ^b	46.03 ± 1.38 ^b
7B3T-30F	12	20	0.5	40	64.98 ± 0.57 ^a	28.74 ± 2.22 ^a
			4	5	71.71 ± 0.59 ^b	56.01 ± 10.11 ^b
1B1T-50F	20	20	0.5	40	70.71 ± 0.85 ^a	22.72 ± 1.57 ^a
			4	5	70.06 ± 0.94 ^a	41.72 ± 4.66 ^b
1B1T-30F	20	20	0.5	40	69.14 ± 0.18 ^a	28.29 ± 0.29 ^a
			4	5	72.19 ± 0.83 ^b	49.45 ± 5.48 ^b
3B7T-50F	32	40	0.5	80	78.63 ± 2.08 ^a	19.74 ± 2.74 ^a
			4	10	77.79 ± 0.57 ^a	43.56 ± 3.35 ^b
3B7T-30F	32	40	0.5	80	78.33 ± 2.59 ^a	28.78 ± 0.85 ^a
			4	10	78.31 ± 1.47 ^a	57.03 ± 5.54 ^b

¹ Values represent mean ± one standard deviation.

² For each composite and property, values with same small letter are not statistically different at p=0.05.

Table 7 – BisGMA/TEGDMA based composites (Table 1) for which the ERL is valid and invalid.

Resin viscosity (η) increases ↑	Filler content increases ←		
	7B3T - 75F ✓	7B3T - 50F ✗	7B3T - 30F ✗
1B1T - 75F ✓	1B1T - 50F ✓	1B1T - 30F ✗	
3B7T - 75F ✓	3B7T - 50F ✓	3B7T - 30F ✓	

ERL valid ✓ ERL invalid ✗

temperatures, and curing lights as it generally overpredicts the required minimum radiant exposure (i.e., on the safe side).

For every dental composite, it is worthwhile to examine the validity of the exposure reciprocity law (ERL) only if the radiant exposure used is greater than (or equal to) the minimum radiant exposure (i.e., $RE \geq RE_m$), which is required for an adequate polymerization. From the results shown in Table 5, one can note that under the condition of $RE \geq RE_m$, the DC remained constant for high-fill composites cured with various irradiances, which implies the ERL is valid. However, the DC does not remain constant for some of the low-fill composites (7B3T-30F, 7B3T-50F and 1B1T-30F) cured with various irradiances, Table 6. In such a case, the ERL is invalid even when $RE \geq RE_m$. This invalidity can be attributed to the effect of the in-situ temperature rise on the mobility of reactants; this effect is not considered in the derivation of Eq. (1) as a function of resin viscosity. The in-situ temperature rise during the polymerization, due to reaction exotherm and curing light absorbance, decreases the viscosity of monomers and increases the mobility of transient polymer networks [19], resulting in a net increase in the mobility of reactants. For some low-fill composites (7B3T-30F, 7B3T-50F and 1B1T-30F), the temperature rise (i.e., increase in mobility) becomes more prominent with higher irradiances. Conversely, this temperature factor is not significant for all the high-fill (clinically relevant dental composites) and some of the low-fill composites (1B1T-50F, 3B7T-30F, 3B7T-50F) studied.

It is worthwhile to note that the DC of the 1B1T-50F composite (Table 6) does not increase with irradiance, i.e., the ERL

is valid even though its peak temperature change (PTC) is similar to that of 7B3T-50F (where the temperature factor led to an invalidity of the ERL). The 7B3T-50F has the same filler content with 1B1T-50F but higher content of BisGMA. This higher content leads to a significant temperature effect on the mobility of reactants by weakening the intermolecular hydrogen bonding [50], under similar PTC. Besides the temperature rise, the fast rate of temperature rise in the 7B3T-50F composite (Table 3) could also contribute to the reactant mobility. The invalidity of the ERL with low-fill content composites and pure resins was reported in literature as well [5,13]. Additionally, another factor that can cause a higher exothermic temperature, consequently, invalidate the ERL, is by using an initiator with a higher extinction coefficient, such as some type I initiators (e.g., Lucirin-TPO). Using such initiators was shown to lead to higher exothermic temperature due to higher rate of conversion [5,17] when compared to using a type II initiator (such as the CQ used in this study). Thus, the DC increased with irradiance when the same radiant exposure, which is believed to be greater than the RE_m , was used [5,13,17]. Theoretical arguments based on classical rate of photopolymerization equations were used in some of these studies to support the invalidity of the ERL [13]. It was claimed that since the rate of photopolymerization [18,19] is not proportional to the first order of irradiance, hence, the DC (integral of rate of photopolymerization equation) cannot be simply proportional to the first order of radiant exposure. However, in addition to the well-known limitations (e.g., steady-state assumptions) of these classical equations [19], the terms included in the equation (e.g., the rate of propagation and termination) are difficult

Table 8 – Hardness and polymerization stress (PS), at a compliance of 0.33 $\mu\text{m}/\text{N}$, of all 75F composites photocured with a radiant exposure equal to their respective minimum radiant exposure (i.e., $\text{RE} = \text{RE}_m$) at different irradiances. Degree of conversion (DC) of these composites is shown in Table 5.

Composite	Curing condition		Hardness (GPa) ^{1,2}		PS (MPa) ^{1,2}
	Irradiance, I (W/cm ²)	Exposure time, t (s)	Top ³	Bottom ⁴	
7B3T-75F	0.5 ⁵	40 ⁵	0.79 ± 0.05 ^a	0.76 ± 0.04 ^a	2.37 ± 0.12 ^{a,b}
	0.5	24	0.79 ± 0.02 ^a	0.72 ± 0.01 ^a	2.34 ± 0.02 ^a
	2	6	0.81 ± 0.05 ^a	0.72 ± 0.03 ^a	2.64 ± 0.02 ^b
	4	3	0.79 ± 0.05 ^a	0.72 ± 0.04 ^a	2.59 ± 0.16 ^{ab}
7U3T-75F	0.5 ⁵	40 ⁵	0.74 ± 0.04 ^a	0.70 ± 0.03 ^a	2.19 ± 0.27 ^{a,b}
	0.5	28	0.71 ± 0.04 ^a	0.69 ± 0.06 ^a	1.91 ± 0.06 ^a
	2	7	0.70 ± 0.03 ^a	0.68 ± 0.05 ^a	2.21 ± 0.07 ^{a,b}
	4	3.5	0.74 ± 0.04 ^a	0.70 ± 0.03 ^a	2.31 ± 0.01 ^b
1B1T-75F	0.5 ⁵	40 ⁵	0.82 ± 0.04 ^a	0.78 ± 0.05 ^a	2.88 ± 0.10 ^a
	0.5	40	0.82 ± 0.04 ^a	0.78 ± 0.05 ^a	2.88 ± 0.10 ^a
	2	10	0.73 ± 0.03 ^b	0.69 ± 0.05 ^b	2.93 ± 0.09 ^a
	4	5	0.73 ± 0.02 ^b	0.66 ± 0.02 ^b	2.42 ± 0.08 ^b
1U1T-75F	0.5 ⁵	40 ⁵	0.78 ± 0.06 ^a	0.76 ± 0.06 ^a	2.77 ± 0.24 ^a
	0.5	48	0.81 ± 0.05 ^a	0.76 ± 0.05 ^a	2.79 ± 0.02 ^a
	2	12	0.73 ± 0.02 ^b	0.69 ± 0.04 ^b	2.71 ± 0.05 ^a
	4	6	0.65 ± 0.04 ^c	0.56 ± 0.06 ^c	2.45 ± 0.21 ^a
3B7T-75F	0.5 ⁵	40 ⁵	0.84 ± 0.04 ^a	0.78 ± 0.03 ^a	3.59 ± 0.15 ^a
	0.5	64	0.85 ± 0.07 ^a	0.81 ± 0.06 ^a	3.81 ± 0.08 ^a
	2	16	0.79 ± 0.05 ^a	0.76 ± 0.04 ^a	3.83 ± 0.12 ^a
	4	8	0.57 ± 0.03 ^b	0.47 ± 0.05 ^b	2.96 ± 0.04 ^b

¹ Values represent mean ± one standard deviation.

² For each composite and property, values with same small letter are not statistically different at $p = 0.05$.

³ Top represents the side closer to the light source.

⁴ Bottom represents the side away from the light source.

⁵ Control photocuring condition.

to measure and are not constant. Hence, the determination of DC and the broad implication on the ERL from the classical equation [13] is not straightforward. Finally, it is important to note that the results of the study (summarized in Table 7) show that the ERL, when $\text{RE} \geq \text{RE}_m$, is valid for conventional dental restorative composites as they have higher filler content (such as 75F composites used in this study) and use type II initiators.

Vickers hardness test was carried out on all the 75F composites (Table 8) which were cured at their respective RE_m . The control photocuring condition shown in this table is for an irradiance of 0.5 W/cm² for 40 s. For composites of 2 mm thickness, an exposure time of 40 s is generally concerned to be excessive at a LED irradiance of 0.5 W/cm². It has to be noted that the hardness of the low resin-viscosity composites (such as 1B1T-75F, 1U1T-75F, and 3B7T-75F) photocured at the irradiance of 4 W/cm² was significantly lower than that at lower irradiances. In such a case, due to the higher content of TEGDMA molecules in these composites, the probability of primary cyclization of polymer chains increased with irradiance rather than crosslinking that can explain the lower mechanical properties albeit at similar degree of conversions [51]. Table 8 also shows the polymerization stress (PS) due to the shrinkage for all the 75F composites. For the composites with high resin viscosity (such as 7B3T-75F and 7U3T-75F), higher irradiance induced higher PS. The higher PS is likely due to higher thermal shrinkage with these irradiances. For the composites with low resin viscosity (such as 1B1T-75F, 1U1T-75F and 3B7T-75F), higher irradiance induced lower PS. The lower

PS is likely due to the lower hardness (which generally correlates with Young's modulus) of these composites discussed earlier.

4. Conclusions

This study has demonstrated that for every dental composite there exists a minimum radiant exposure for adequate polymerization (i.e., any further increase in the radiant exposure will produce no significant increase in the polymerization). This minimum predominantly depends on the resin viscosity of composite and is predicted using an empirical equation. The validity of the exposure reciprocity law (ERL) can be evaluated only if the radiant exposure is above this minimum. Afterwards, the validity of the ERL is dependent on the significance of temperature (reaction exotherm and curing light absorbance during the polymerization) that has effects on the mobility of the reactants. For clinically relevant restorative composites, where the filler content is high, this effect is negligible; thus, the ERL is valid as long as the radiant exposure (RE) is greater than (or equal to) the minimum RE (RE_m) required. However, this effect can be significant for composites having low filler content (clinically not relevant), and the ERL becomes invalid even if $\text{RE} \geq \text{RE}_m$. Finally, this study provides a guidance of altering the radiant exposure, with the clinically available photocuring unit, for an adequate cure of dental composites and promotes better understanding of discrepancies on the applicability of the ERL reported in the literature.

Acknowledgements

Financial support was provided through an Interagency Agreement between the National Institute of Dental and Craniofacial Research (NIDCR) and NIST [ADE12017-0000]. The donation of the monomers from Esstech Inc. and the filler particles from Dentsply Sirona are greatly appreciated.

REFERENCES

- [1] Bunsen R, Roscoe H. Photochemical studies. *Ann Phys* 1923;108–93.
- [2] Jandt KD, Mills RW. A brief history of LED photopolymerization. *Dent Mater* 2013;29:605–17.
- [3] Feng L, Suh BI. Exposure reciprocity law in photopolymerization of multi-functional acrylates and methacrylates. *Macromol Chem Phys* 2007;208:295–306.
- [4] Feng L, Carvalho R, Suh BI. Insufficient cure under the condition of high irradiance and short irradiation time. *Dent Mater* 2009;25:283–9.
- [5] Leprince JG, Hadis M, Shortall AC, Ferracane JL, Devaux J, Leloup G, et al. Photoinitiator type and applicability of exposure reciprocity law in filled and unfilled photoactive resins. *Dent Mater* 2011;27:157–64.
- [6] Musanje L, Darvell BW. Polymerization of resin composite restorative materials: exposure reciprocity. *Dent Mater* 2003;19:531–41.
- [7] Peutzfeldt A, Lussi A, Flury S. Effect of high-irradiance light-curing on micromechanical properties of resin cements. *BioMed Res Int* 2016;2016.
- [8] Dewaele M, Asmussen E, Peutzfeldt A, Munksgaard EC, Benetti AR, Finné G, et al. Influence of curing protocol on selected properties of light-curing polymers: degree of conversion, volume contraction, elastic modulus, and glass transition temperature. *Dent Mater* 2009;25:1576–84.
- [9] Peutzfeldt A, Asmussen E. Resin composite properties and energy density of light cure. *J Dent Res* 2005;84:659–62.
- [10] Hadis M, Leprince JG, Shortall AC, Devaux J, Leloup G, Palin WM. High irradiance curing and anomalies of exposure reciprocity law in resin-based materials. *J Dent* 2011;39:549–57.
- [11] Selig D, Haenel T, Hausnerová B, Moeginger B, Labrie D, Sullivan B, et al. Examining exposure reciprocity in a resin based composite using high irradiance levels and real-time degree of conversion values. *Dent Mater* 2015;31:583–93.
- [12] Halvorson RH, Erickson RL, Davidson CL. Energy dependent polymerization of resin-based composite. *Dent Mater* 2002;18:463–9.
- [13] Wydra J, Cramer N, Stansbury J, Bowman C. The reciprocity law concerning light dose–relationships applied to BisGMA/TEGDMA photopolymers: theoretical analysis and experimental characterization. *Dent Mater* 2014;30:605–12.
- [14] Miyazaki M, Oshida Y, Keith Moore B, Onose H. Effect of light exposure on fracture toughness and flexural strength of light-cured composites. *Dent Mater* 1996;12:328–32.
- [15] AlShaafi MM. Effects of delivering the same radiant exposures at 730, 1450, and 2920 mW/cm² to two resin-based composites. *Eur J Dent* 2017;11:22–8.
- [16] Price RBT, Felix CA, Andreou P. Effects of resin composite composition and irradiation distance on the performance of curing lights. *Biomaterials* 2004;25:4465–77.
- [17] Randolph LD, Palin WM, Watts DC, Genet M, Devaux J, Leloup G, et al. The effect of ultra-fast photopolymerisation of experimental composites on shrinkage stress, network formation and pulpal temperature rise. *Dent Mater* 2014;30:1280–9.
- [18] Terrones G, Pearlstein AJ. Effects of optical attenuation and consumption of a photobleaching initiator on local initiation rates in photopolymerizations. *Macromolecules* 2001;34:3195–204.
- [19] Andrzejewska E. Photopolymerization kinetics of multifunctional monomers. *Prog Polym Sci* 2001;26:605–65.
- [20] Price RB, Shortall AC, Palin WM. Contemporary issues in light curing. *Oper Dent* 2014;39:4–14.
- [21] Feng L, Suh BI. A mechanism on why slower polymerization of a dental composite produces lower contraction stress. *J Biomed Mater Res B* 2006;78B:63–9.
- [22] Unterbrink GL, Muessner R. Influence of light intensity on two restorative systems. *J Dent* 1995;23:183–9.
- [23] Asmussen E, Peutzfeldt A. Polymerization contraction of resin composite vs. energy and power density of light-cure. *Eur J Oral Sci* 2005;113:417–21.
- [24] Braga RR, Ferracane JL. Contraction stress related to degree of conversion and reaction kinetics. *J Dent Res* 2002;81:114–8.
- [25] Sakaguchi RL, Wiltbank BD, Murchison CF. Contraction force rate of polymer composites is linearly correlated with irradiance. *Dent Mater* 2004;20:402–7.
- [26] Bang HC, Lim BS, Yoon TH, Lee YK, Kim CW. Effect of plasma arc curing on polymerization shrinkage of orthodontic adhesive resins. *J Oral Rehabil* 2004;31:803–10.
- [27] Emami N, Söderholm KM, Berglund LA. Effect of light power density variations on bulk curing properties of dental composites. *J Dent* 2003;31:189–96.
- [28] Mouhat M, Mercer J, Stangvaltaite L, Örtengren U. Light-curing units used in dentistry: factors associated with heat development—potential risk for patients. *Clin Oral Investig* 2017;21:1687–96.
- [29] Baroudi K, Silikas N, Watts DC. In vitro pulp chamber temperature rise from irradiation and exotherm of flowable composites. *Int J Paediatr Dent* 2009;19:48–54.
- [30] Leprince J, Devaux J, Mullier T, Vreven J, Leloup G. Pulpal-temperature rise and polymerization efficiency of LED curing lights. *Oper Dent* 2010;35:220–30.
- [31] Armellini E, Bovesecchi G, Coppa P, Pasquantonio G, Cerroni L. LED curing lights and temperature changes in different tooth sites. *BioMed Res Int* 2016;2016:10.
- [32] Chiang MYM, Giuseppetti AAM, Qian J, Dunkers JP, Antonucci JM, Schumacher GE, et al. Analyses of a cantilever-beam based instrument for evaluating the development of polymerization stresses. *Dent Mater* 2011;27:899–905.
- [33] Wang Z, Landis FA, Giuseppetti AAM, Lin-Gibson S, Chiang MYM. Simultaneous measurement of polymerization stress and curing kinetics for photo-polymerized composites with high filler contents. *Dent Mater* 2014;30:1316–24.
- [34] Lu H, Stansbury JW, Dickens SH, Eichmiller FC, Bowman CN. Probing the origins and control of shrinkage stress in dental resin-composites. I. Shrinkage stress characterization technique*. *J Mater Sci Mater Med* 2004;15:1097–103.
- [35] Lu H, Stansbury JW, Dickens SH, Eichmiller FC, Bowman CN. Probing the origins and control of shrinkage stress in dental resin composites. II. Novel method of simultaneous measurement of polymerization shrinkage stress and conversion. *J Biomed Mater Res B Appl Biomater* 2004;71B:206–13.
- [36] Rodrigues FP, Lima RG, Muench A, Watts DC, Ballester RY. A method for calculating the compliance of bonded-interfaces under shrinkage: validation for Class I cavities. *Dent Mater* 2014;30:936–44.
- [37] Lee SH, Chang J, Ferracane J, Lee IB. Influence of instrument compliance and specimen thickness on the polymerization shrinkage stress measurement of light-cured composites. *Dent Mater* 2007;23:1093–100.

- [38] Leprince JG, Palin WM, Hadis MA, Devaux J, Leloup G. Progress in dimethacrylate-based dental composite technology and curing efficiency. *Dent Mater* 2013;29:139–56.
- [39] Dickens SH, Stansbury J, Choi K, Floyd C. Photopolymerization kinetics of methacrylate dental resins. *Macromolecules* 2003;36:6043–53.
- [40] Howard B, Wilson ND, Newman SM, Pfeifer CS, Stansbury JW. Relationships between conversion, temperature and optical properties during composite photopolymerization. *Acta Biomater* 2010;6:2053–9.
- [41] Lovell L, Newman S, Bowman C. The effects of light intensity, temperature, and comonomer composition on the polymerization behavior of dimethacrylate dental resins. *J Dent Res* 1999;78:1469–76.
- [42] Beun S, Bailly C, Dabin A, Vreven J, Devaux J, Leloup G. Rheological properties of experimental Bis-GMA/TEGDMA flowable resin composites with various macrofiller/microfiller ratio. *Dent Mater* 2009;25:198–205.
- [43] Silikas N, Watts D. Rheology of urethane dimethacrylate and diluent formulations. *Dent Mater* 1999;15:257–61.
- [44] Taira M, Urabe H, Hirose T, Wakasa K, Yamaki M. Analysis of photo-initiators in visible-light-cured dental composite resins. *J Dent Res* 1988;67:24–8.
- [45] Shintani H, Inoue T, Yamaki M. Analysis of camphorquinone in visible light-cured composite resins. *Dent Mater* 1985;1:124–6.
- [46] Daronch M, Rueggeberg F, De Goes M, Giudici R. Polymerization kinetics of pre-heated composite. *J Dent Res* 2006;85:38–43.
- [47] Price RB, Whalen J, Price TB, Felix CM, Fahey J. The effect of specimen temperature on the polymerization of a resin-composite. *Dent Mater* 2011;27:983–9.
- [48] Price R, Ferracane J, Shortall A. Light-curing units: a review of what we need to know. *J Dent Res* 2015;94:1179–86.
- [49] Watts DC, Kaiser C, O'Neill C, Price RB. Reporting of light irradiation conditions in 300 laboratory studies of resin-composites. *Dent Mater* 2019;35:414–21.
- [50] Lee J, Um C, Lee I. Rheological properties of resin composites according to variations in monomer and filler composition. *Dent Mater* 2006;22:515–26.
- [51] Elliott JE, Lovell LG, Bowman CN. Primary cyclization in the polymerization of bis-GMA and TEGDMA: a modeling approach to understanding the cure of dental resins. *Dent Mater* 2001;17:221–9.