Effect of curing protocols on degree of conversion and glass transition temperature of a dual-cured resin cement

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Objective: The objective of this study was to investigate the effect of light-curing protocols on degree of conversion (DC) and glass transition temperature (T_g) of a dual-cured resin cement (Variolink N). The correlation between DC and T_g was further investigated.

Materials and methods: Different light-curing protocols (no irradiation, irradiation with light tip directly contact to specimen, and irradiation with light tip positioned at 10 mm from specimen) were used investigate the influence of energy density (ED) on DC and T_g of the resin cement. 15 and 45 specimens of mixed cement were prepared for DC and T_g observation respectively, then subjected to irradiating protocols underneath a ceramic block (10 mm length x 10 mm width x 0.95 mm thickness) and light cure for 40 sec in light curing groups. DC was measured by Raman microspectroscopy and T_g was measured by differential scanning calorimetry at 5 min, 15 min and 24 hrs after post-polymerization. Data were submitted to two-way ANOVA. The DC and T_g data were subjected to linear regression analysis.

Results: Increasing of distance between light tip and specimens decreased ED. Curing protocols with different ED influenced DC (p<0.01) and T_g (p<0.01) of the cement. The increasing of ED significantly increased DC and T_g. The DC and T_g improved significantly with the extension of post-polymerization times up to 24 hrs. A significantly positive correlation was found between DC and T_g.

Conclusion: ED of curing light and post-polymerization times influenced DC and T_g of the dual-cured resin cement.

Keyword: degree of conversion, energy density, glass transition temperature, light-cure, resin cement, self-cure

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Introduction

Resin cement is commonly used for tooth restoration because of their physical and mechanical properties [1]. According to the mechanism of polymerization, this cement can be categorized into 3 types of self-cure, light-cure and dual-cure resin cement. Dual-cure resin cement is a system combining self-cure and light-cure polymerization mechanism together [2]. The light-cure polymerization is a setting mechanism of polymer via activation with blue visible light [2]. Thus, the polymerization of the dual-cure resin cement can be further occurred *via* self-cure mechanism as post-polymerization [3]. From the benefit of dual-cure mechanism, this dual-cure resin cement can be used for all clinical situations from full metal to tooth colored restoration and become mostly use in dentistry [1].

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With dual-cure polymerization mechanism of dual-cure resin cement, the influence of light cure polymerization on the final properties of dual-cured resin cement has been reported [3-6]. The mechanical properties of a dual-cured resin composite via light-cure polymerization are mainly influenced by the amount of energy delivered during irradiation [4]. The energy density (ED) or total amount of energy per unit area is the product of the power per unit area (curing light intensity) by the duration of irradiation (curing time) [4]. For a given ED, different light-curing protocols such as leaving polymerization with self-curing mode (no irradiation), curing with high intensity of curing light and curing with low intensity of light have been proposed to influence the properties of dual-cure resin cement [4,6]. Therefore, the different light-curing protocols may lead to polymers of different network structure, even though the DC is the same.

Generally, the DC of polymers is used to evaluate the conversion of double bonds to single bond while forming polymer networks [7]. However, DC of polymer could not be used as a representation of complete polymerization characterization of polymers structures because polymers of similar DC may have different extent of crosslinking or in vice versa [3,4]. This scenario may occur in dual-cure resin cements, as a result of different light-curing protocols. This may probably due to the formation of relatively fewer growth centers of self-cure mode, which may result in a more linear polymer, with decreased crosslinking. [4,8]. The increased concentration of crosslinking has been proposed to improve physical properties and stability of polymers [6,9,10].

The extent of crosslinking of a polymer may be proposed to determine by measurements of the glass transition temperature (T_g). T_g is an important parameter for polymer characterization as it marks a region of dramatic changes in the physical properties of the polymer [6,9]. The T_g value represents the temperature region at which the polymer is transformed from a glassy material into a rubberlike one. Crosslinking reduces molecular mobility and thus gives rise to increased apparent T_g [3,4,11]. Thus, the curing protocols may influence the regularity of the network and the crosslink density. This may be reflected in the T_g.

To improve the performance regarding to polymerizing characterization of dual-cured resin cement, a detailed understanding of the effects of curing protocols on DC and T_g and the correlation between Dc and T_g are necessary.

The aim of the study was to determine degree of conversion and glass transition temperature in relation with the curing protocol and post-polymerization times. The hypothesis of present study was the total energy densities caused by the different curing protocols and post-polymerization times have influence on DC and T_g properties. A further aim was to attempt to correlate the DC with T_g properties of this dual-cure resin cement.

Materials and methods

The dual-cure resin cement used in this study was Variolink N (shade yellow A3, lot NO.; U55161 (base), V03978 (catalyst), Ivoclar-Vivadent, Schaan, Liechtenstein). It is composed of base and catalyst. The compositions of base are Bis-GMA (bisphenol-A-glycidyl dimethacrylate), UDMA (Urethane dimethacrylate), TEGDMA (Triethyleneglycol dimethacrylate), inorganic filler, ytterbium tri fluoride, initiator, and stabilizer. The compositions of catalyst are Bis-GMA, UDMA, TEGDMA, inorganic filler, ytterbium tri-fluoride, benzoyl peroxide, and stabilizer.

For degree of conversion observation, the specimens were prepared by mixing the cement according to the manufacturer's instruction. The mixed cement was placed onto 1 mm thick transparent microscope glass slide and between two microscope coverslips with the thickness of 100 microns. These two coverslips were used for

controlling the cement thickness. The distance between two coverslips was 5 mm. Additional microscope coverslip was placed over the cement and pressed over to displace excessive cement. The excessive cement was then removed. This resulted equally 100- microns thickness cement specimen. The totally 15 specimens were prepared.

Specimens were further divided into 3 groups of curing protocols; self-cure mode, dual-cure mode with optimal light intensity for irradiation, and dual-cure mode with low light intensity for irradiation. Regarding to dual-cure mode, ceramic block with a dimension of 0.95 mm thickness, 10 mm width and 10 mm length was prepared from a lithium disilicate ceramic (IPS e.max CAD, LT shade A1, lot NO.; U39581, Ivoclar-Vivadent, Schaan, Liechtenstein) to simulate clinical situation. The ceramic was placed over the mixed cement covered by a coverslip. The cement was then light-cured with a light emitting diodes curing unit (Elipa S10, 3M ESPE, Seefeld, Germany) with an intensity of 1217.20 ± 32.33 mW/cm^2. For the first curing protocol, 5 specimens were kept in light-proof container for simulating self-cure mode. Remaining 10 specimens were further divided into 2 groups and subjected for light activation for 40 sec with different protocols. For the second group, the light tip directly contacted with ceramic to simulate optimal intensity of curing light. The distance between light tip and ceramic was adjusted to 10 mm to simulate low intensity of curing light for the third group. The intensity of irradiation through the ceramic was measured using a light meter (light meter 200, Rolence enterprice Inc., Taoyuan, Taiwan).

Five specimens from each curing protocol were subjected to observation of degree of conversion at 5 min after cement mixing in self-cure group and after light irradiation in dual-cure group, then after 15 min and 24 hrs of post-polymerization times.

The degree of conversion (DC) was determined using a Raman microspectroscopy (DXR Raman Microscope, Thermo Scientific, Waltham, MA, USA). The specimens were excited using 780-nm diode laser with the power of 14 mW through a microscope objective lens (x20) coupled with x10 magnification integrated microscope (Olympus) at the spatial resolution of ~1.9 μm and the spectral resolution of ~2.4–4.4 cm^{-1}. The light filter was used to protect the polymerization of cement from microscope light. The specimens were placed on the computerized XYZ stage. All Raman spectra were acquired with 60 sec exposure time and two accumulations, and then data were analyzed using OMNIC 8 software (Thermo Scientific, Waltham, MA, USA). Remaining unreacted double bond of vinyl group with absorbance intensity peak height at 1639 cm^{-1} was calculated in percentage against internal standard, which was aromatic carbon double bond with peak height at 1609 cm^{-1} before and after polymerization using the following formula.

$$DC\% = [1-(R_{curd}/R_{uncured})]\times100$$

R_{curd} is ratio of absorption peak at 1639 cm^{-1} and absorption peak at 1609 cm^{-1} of the cured specimens. $R_{uncured}$ is ratio of uncured specimens.

The glass transition temperature (T_g) was measured to identify the crosslinking density [3,4,6,11] using a differential scanning calorimetry (DSC 204 F1, Netzsch GmbH, Selb, Germany Mettler Toledo DSC 1). In self-cure group, resin cement was mixed and delivered to the sample pan. In dual-cure group, resin cement was prepared in size of 1 mm height and 3 mm in diameter, then covered with coverslip followed by ceramic block and given light irradiation through the ceramic either directly contact or 10 mm from ceramic. All samples were delivered to sample pan and weighted. Degree of cross-linking will be measured at 5 and 15 minutes after mixing of cement in self-cure group or after irradiation in light-cure group and at 24 hours of post-polymerization in every group. The T_g was measured under heating rate 10°C/min from -50°C to 100°C under nitrogen.

Data gaining from the calorimetry was analyzed with Proteus software (Netzsch GmbH, Selb, Germany). The T_g is determined from endothermic parallel transition of base line, finding T_g point at the heat flow/temperature or specific heat/temperature curve. Intersection of estimated heat flow/temperature is taken as T_g, line drawing from low temperature end, and the tangent of the slope up curve, at the inflection point.

Normal distribution and equality of variances of DC and T_g were checked using Kolmogorov-Smirnov test and Levene's test respectively. The data of DC and T_g were further statistical analysis at 95% confident interval using Two-way ANOVA and Tukey's multiple comparison. The correlation and regressive model between Dc and T_g were analysis.

Results

Light intensity and energy density of the curing unit is shown in Table 1. The light intensity measured by the light meter was reduced from 1217.20 ± 32.33 mW/cm^2 down to 570.80 ± 5.81 mW/cm^2 when irradiated through 0.95 mm of ceramic and 243.00 ± 7.31 mW/cm^2 when irradiate 10 mm above ceramic. These caused reducing in energy density from $22,832.00 \pm 232.21$ mJ/cm^2 to $9,720.00 \pm 292.57$ mJ/cm^2, respectively when curing for 40sec through ceramic.

The data of degree of conversion (DC) and glass transition temperature (T_g) are demonstrated in Table 2 and 3. The 2-way ANOVA of DC and T_g analysis demonstrated significant effect of curing

Table 1   Light intensity and energy density (mean±standard deviation)

Groups	Irradiated condition	Intensity (mW/cm^2)	Energy density (mJ/cm^2)
Group I	No irradiation	0	0
Group II	Irradiation with light tip directly contact to ceramic	570.80±5.81	22,832.00±232.21
Group III	Irradiation with light tip positioned at 10 mm from specimen	243.00±7.31	9,720.00±292.57

Table 2   Degree of conversion (%) (mean±standard deviation)

Groups		Post-polymerization times		
		5 min	15 min	24 hrs
Curing protocols	Group I	20.85±1.05[g]	49.93±1.23[f]	78.50±0.72[c]
	Group II	77.79±0.87[c, d]	78.32±1.13[c]	84.71±1.09[a]
	Group III	72.19±1.42[e]	76.21±0.80[d]	80.97±0.41[b]

Table 3   Glass transition temperature (^{o}C) (mean±standard deviation)

Groups		Post-polymerization times		
		5 min	15 min	24 hrs
curing protocols	Group I	-26.72±0.80[g]	39.07±1.03[f]	42.43±1.46[e]
	Group II	49.08±1.38[c]	49.94±1.19[c]	66.88±1.79[a]
	Group III	43.80±0.97[e]	46.50±1.01[d]	63.41±1.19[b]

protocols and post-polymerization times to DC and T_g (p<0.01). The significant interaction (p<0.01) between curing protocols and post-polymerization times was found both with DC and T_g.

The data (mean±standard deviation) with the same superscripts show no statistically significant difference (P>0.05). (Group I: no irradiation, Group II: irradiation with light tip directly contact to specimen and Group III: irradiation with light tip positioned at 10 mm from specimen)

The DC of light irradiated specimens was significantly higher than those of self-cure protocol for each post-polymerization time. Furthermore, the highest DC of each post polymerization time was observed for Group II. Increasing of post-polymerization times significantly improved DC in the same curing protocol except between 5 min and 15 min post-polymerization times of Group II, which specimens were irradiated with the curing tip contact directly to the ceramic. The highest DC (84.71%) was observed for the group II at 24 hrs post-polymerization time. Whereas, the lowest DC (20.85%) was observed for group I or self-cure protocol at 5 min post polymerization time.

The T_g of light irradiated specimens of group II was significantly higher than those of light irradiated specimens of group I and III for each post-polymerization time. Thus, the T_g of all light irradiated specimen was higher than those of specimen with self-cure protocol for each post-polymerization time. Increasing of post-polymerization times significantly improved T_g except between 5 min and 15 min post-polymerization times of Group II that specimens were irradiated with the curing tip contact directly to the ceramic. The highest T_g

(66.88 ^{o}C) was observed for the group II at 24 hrs post-polymerization time. Whereas, the lowest T_g (-26.72 ^{o}C) was observed for the group of self-cure protocol at 5 min post-polymerization time.

The correlation between DC ang T_g were calculated and demonstrated in Table 4. The high correlation between DC and T_g were observed for all groups. Regressive model for group I showed less unstandardized coefficients (1.20) than Group II (2.43) and Group III (2.14). This means that for each group within 24 hrs of post irradiation times, Group I showed lower degree of increasing of T_g than other groups. Finally, the low degree of crosslinking with the self-cure mode than other groups at 24 hrs of post irradiation times may be implied.

Discussions

In this study, a dual-cure resin cement was cured with three different protocols: no irradiation, irradiation with light tip directly contact to specimen, and irradiation with light tip positioned at 10 mm from specimen. These protocols affected different intensity of curing light caused different energy density as demonstrated in Table 1. The less energy density of curing light, the lower DC and the lower T_g was observed as showed in Table 2 and Table 3. The lowest DC and T_g were observed for the group polymerized without light curing (chemical cure mode).

The results confirm that the DC of a dual-cure resin cement which polymerization process is partially initiated by light are significantly influenced

Table 4　Correlation between DC (%) and T_g (^{o}C)

Groups	R	Regressive model
Group I	0.89	T_g = -41.51+1.20DC
Group II	0.96	T_g = -139.88+2.43DC
Group III	0.91	T_g = -112.68+2.14DC

by the amount of energy delivered to the cement during irradiation. This is in an agreement with previous studies [3-5] that showed DC increased with increasing of ED. The increasing in DC with energy density may be incorporated by the increasing in crosslinking. Thus, the significant relationship between DC and T_g was observed. This observation agrees with previous studies [4, 11, 12]. The increasing of DC and T_g influenced increasing of elastic modulus of polymers has been proposed [4]. The improvement of mechanical properties of dual-cure resin cement might be expected by light irradiation the cement with optimal intensity of light to increase DC and T_g [4]. The irradiation of the dual-cure resin cement with blue visible light might produce a higher concentration of radicals and rate of polymerization compared with the cement polymerized only with chemical cure [8]. This effect might be ED relating [4] that leads DC and T_g to increase in the groups with light activation in this study.

The characterization of polymerization such as the degree of conversion and the crosslinking network formation were observed in this study. The results of this study showed different rate of polymerization at which DC was growing with time. Therefore, the heterogeneity of polymerization was found that might be related to the mode of curing and the intensity of irradiation light as shown in Table 2 and 3. The low rate of degree of conversion was found in the group polymerized with chemical curing. The activation with blue visible light increased rate of degree of conversion that was light intensity dependence. This confirmed results of previous studies [3-5].

The apparent of unequal reactivity of polymerization to DC and T_g was observed. Even though, the same DC was observed among group I at 24 hrs (78.50%), group II at 5 min (77.79%) and group II at 15 min (78.32%) and between group II at 5 min (77.79%) and group III at 15 min (76.21%). The different of T_g among these groups

were demonstrated. The T_g of group I at 24 hrs (42.43 °C) was less than group II at 5 min (49.08 °C) and group II at 15 min (49.94 °C), and the same event was observed between group III at 15 min and group II at 5 min, which T_g were 46.33 °C and 49.08 °C respectively. The decreased T_g may be interpreted as the manifestation of a polymer structure having fewer crosslinking [3, 4, 6]. The less crosslinking network formation of group I at 24 hrs compared with group II at 5 min and 15 min, and group III at 15 min compared with group II at 5 min might be expected.

The crosslinking of polymers has been proposed that relate to a multitude of growth centers. Many growth centers will increase the tendency to form a branched polymer. On the other hand, a relatively linear polymerization will be observed with the less growth centers [4, 6]. Thus, many growth centers might be expected for dual-cure resin cement polymerized with light irradiation. The improvement of sustainability of the resin cements by increasing of crosslinking [6, 9] might be a positive effect of light curing of the dual-cure resin cement.

In conclusion, high DC and high T_g of the dual-cure resin cement could be initiated by additionally curing the cement with optimal intensity of curing light. The tip of light curing unit should be placed onto the surface of restoration as close as possible to gain high energy density of curing light that directly influence to DC and T_g. Nevertheless, it must be realized that the polymerizing characteristic of polymers is also depended on the compositions and the specific chemistry of the initiator systems too [13-15].

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