Effect of Base Monomer's Refractive Index on Curing Depth and Polymerization Conversion of Photo-cured Resin Composites

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In this study, we examined the effect of the transmitted amount of visible light through a resin composite on the curing depth and polymerization conversion. Transmitted amount of visible light was strongly dependent on the magnitude of refractive index difference that existed between the resin and silica filler. More specifically, the differences arose from the type of base monomer used. The transmitted amount of visible light exhibited a good correlation with the curing depth and Knoop hardness ratio of the bottom surface against the top surface of the resin composite. To improve the polymerization conversion of the cavity floor, it is important to reduce the refractive index difference that exists between the base resin and silica filler.

Key words: Photo-cured resin composite, Transmittance, Curing depth

INTRODUCTION

Due to significant advancements in adhesive dentistry as well as improvements in the mechanical properties of the resin composite, resin composites have been widely used as dental restorative materials. Many dentists use photo-cured resin composites since the operators can directly control their prolonged working time.

However, limited curing depth and a lower polymerization conversion of the cavity floor have emerged as major clinical problems¹⁾. These problems concern monomer-polymer conversion, because of the reported polymerization conversions ranging from 35 to 77%^{2–7)} – which affects the mechanical properties (e.g., wear resistance and susceptibility to discoloration) of the resin composite, and these problems affect the biological compatibility (local and systemic cell/tissue compatibility) of the resin composite too. In addition, the local biocompatibility of the resin composite may be impaired^{7–11)}. Generally, in cases of insufficient cavity lining, extractable residual monomers may gain access to the pulp via dentinal tubules^{9,10,13)}. Therefore, it is desirable to develop resin composites of which the bottom surface exhibits higher polymerization conversion.

Previously, to understand what kinds of parameters control the curing depth and polymerization conversion of photo-cured resin composites, the effects of different types of methacrylate monomers on curing depth were examined^{14–16)}. This is because the curing depth of a resin composite is strongly influenced by the types of base monomers. It was found that as

the refractive index of the base monomer became closer to that of the silica filler, the curing depth of the resin composite became deeper. This was possible since the degree of light scattering at the resin-silica interface was dependent on the magnitude of refractive index difference that existed between the silica and the resin.

In this study, we investigated the transmittance of visible light through the resin composite, and the curing depth and Knoop hardness of the resin composite. The effect of the transmittance of visible light through the photo-cured resin composite on the curing depth and polymerization conversion was then discussed.

MATERIALS AND METHODS

Materials

Triethyleneglycol dimethacrylate (TEGDMA, Shin-Nakamura Chemical Co., Ltd., Nagoya, Japan), dimethacryloyloxy ethyl 2,2,4-(or 2,4,4) trimethylhexamethylene diurethane (UDMA, Negami Chemical Industrial Co., Ltd., Ishikawa, Japan), and 2,2-bis(4-methacryloyloxyphenyl) propane (BMPEPP, Shinnakamura chemical Co., Ltd. Japan) were used as base monomers for the resin composite. In addition, mixed monomers, such as TEGDMA/UDMA and UDMA/BMPEPP, were also prepared. The molar ratio of the mixed monomer was 1/1. One wt% of camphorquinone (CQ, Aldrich Chemical Co., Inc., USA) was dissolved in the base monomer. In addition, 2-dimethylaminoethyl methacrylate (Wako Pure Chemical Industry, Ltd., Tokyo, Japan),

which was twice the moles of CQ, was added to the monomer.

Colloidal silica particles of $0.05\mu\text{m}$ diameter (OX 50, Nihon Aerosil Co., Ltd., Tokyo, Japan) were used as the inorganic filler. The silica was treated with 6.5 wt% of γ -methacryloxypropyltrimethoxysilane (Shin-Etsu Chemical Co., Tokyo, Japan).

To prepare the composite pastes, silane-treated silica was mixed with the monomers. The weight ratio of silica to monomer was 1:1.

Methods

1. Refractive indices of the monomers, polymers, and colloidal silica

The refractive indices of the monomers and its polymers were measured at 25°C using an Abbe's refractometer (Erma optical works, Tokyo, Japan). Polymers were obtained from bulk polymerization at 130°C for 15 minutes by using benzoyl peroxide. The additional amount of benzoyl peroxide to the monomer was 0.5 wt%. Monobromnaphthalene was used to precisely fit the polymer to the refractometer.

Non-treated silica particles were dispersed into mixed solvents of which the refractive indices had been previously determined. The suspension was then kept at a stationary state for 10 minutes. Transmittance of visible light through the suspension was observed at 468 nm by using a spectrophotometer (U best-30, JASCO, Tokyo, Japan) at 25°C . This observation was possible because CQ was excited by the absorption of visible light at 468 nm. The refractive index of the silica was determined based on the refractive index of the solvent whose suspension provided the maximum value.

2. Transmitted amount of visible light through the resin composite

Resin composite paste was injected into a brass mold ($\phi 5\text{ mm}$ inner diameter $\times 2\text{ mm}$ in depth) and both surfaces of the resin composite were then

covered with transparent plastic matrix strips. Transmittance of visible light through the resin composite was measured during light irradiation that ranged from 0 to 60 seconds by using an experimental apparatus, as shown in Fig. 1. This experimental apparatus was equipped with a light sensor that detected visible light passing through the resin composite¹⁷⁾. The Cure Master (3M, USA) was used for light irradiation. The distance between the exit window of the external light source and the top surface of the resin was 3 mm. In the absence of the sample, the transmittance of the visible light was adjusted to 100%. The obtained transmittance of visible light through the resin composite was, therefore, the ratio against the transmittance of visible light obtained in the absence of the resin composite. Three specimens were used for each experiment.

The transmitted area where the visible light had passed through the resin composite was determined by integrating the transmittance curve obtained during light irradiation from 0 to 60 seconds. The transmitted amount of visible light through the resin composite was determined by dividing the above-mentioned area by the area of the transmittance curve obtained in the absence of the resin composite.

3. Curing depth of the resin composite

Resin composite paste was injected into a brass mold ($\phi 5\text{ mm}$ inner diameter $\times 30\text{ mm}$ in depth). After the resin surfaces were covered with transparent plastic matrix strips, visible light was irradiated into the resin composite paste for 60 seconds using the Cure Master. After being ejected from the brass mold, the irradiated sample was rinsed with ethanol to remove the un-cured resin layer. The curing depth of the resin composite was then measured. Five specimens were used for each experiment. The distance between the light source and the resin surface was 3 mm.

4. Knoop hardness of the resin composite

Resin composite paste was injected into a brass mold, which had an inner diameter of 5 mm and a thickness of 1 or 2 mm. Visible light was irradiated for 60 seconds. During light irradiation, all specimens were fully covered with transparent plastic matrix strips. Knoop hardness of the irradiated side and that of the bottom side of the cured resin were measured with a Hardness Tester (HMV-2000, Shimadzu, Kyoto, Japan) equipped with a Knoop diamond. Each specimen's hardness was measured four times with a 10 g load for 30 seconds. Five specimens were used for each experiment. The distance between the exit window of the external light source and the resin surface was 3 mm.

① : Light-curing unit, ② : Light Sensor, ③ : Sample, ④ : Mold

Fig. 1 Experimental apparatus used to measure the transmittance of visible light through the resin composite. The Cure Master was used for light irradiation.

Statistical analyses

For each experimental group, the mean value and standard deviation (SD) for the transmitted amount of visible light, curing depth and Knoop hardness

were calculated for each resin composite. The results were analyzed by one-way analysis of variance (ANOVA) for the transmitted amount of visible light and curing depth or by two-way analysis of variance (ANOVA) for Knoop hardness, and then by Fisher's protected LSD post-hoc test. Statistical significance value was set at 0.01 level.

RESULTS

Refractive indices of the monomers, polymers, and colloidal silica

The refractive indices of the monomers, polymers, and colloidal silica are summarized in Table 1. The refractive index of the colloidal silica was 1.458. The monomer whose refractive index was closest to that of the silica was TEGDMA. The monomer's refractive index, by order of increasing rank was TEGDMA, UDMA, and BMPEPP. Differences in refractive index that existed between the silica and the monomer increased in this order.

In addition, the refractive index of the polymer became larger than its monomer during the hardening of the monomer, as shown in Fig. 2. As a result,

Table 1 Refractive indices of the base monomers, polymers, and silica

	Refractive index	
	monomer	polymer
Base monomer		
TEGDMA	1.460	1.508
TEGDMA/UDMA	1.474	1.510
UDMA	1.484	1.511
UDMA/BMPEPP	1.511	1.539
BMPEPP	1.540	1.565
Filler		
Colloidal silica	1.458

Fig. 2 Changes in the monomers' refractive indices during the hardening process.

differences in the refractive index between the polymer and the silica further became larger.

Effect of monomer type on the transmitted amount of visible light through the resin composite

Fig. 3 shows the typical transmittance curves of visible light through the resin composites as a function of the irradiation time by varying the monomer type. Thickness of the sample was 2 mm.

Immediately after irradiation by visible light, the transmittance of visible light dramatically increased. In addition, the transmittance's maximum value was obtained for each resin composite. By increasing the visible light's irradiation time, transmittance of the visible light gradually decreased.

The transmittance's maximum value for each resin composite differed depending on the type of base monomer used. Consequently, the resin composite based on TEGDMA, whose refractive index was closest to that of silica, exhibited a maximum transmittance value of 88%. Conversely, the resin composite based on BMPEPP, whose refractive index was the farthest from that of silica, exhibited a minimum transmittance value of 14%. The transmitted amounts of visible light through the resin composite are summarized in Table 2. Transmitted amount of visible light was obtained by dividing the transmitted area of visible light passing through the resin composite (obtained from the integration of the transmittance curve) by the area of the transmittance curve obtained in the absence of the resin composite.

Fig. 3 Typical transmittance curves of visible light passing through the resin composites as a function of the irradiation time.

Table 2 Transmitted amounts of visible light through the resin composites by varying the type of base monomer used

Type of monomer	Transmitted amount of visible light (%)
TEGDMA	81.6 (3.7) ^a
TEGDMA/UDMA	67.2 (5.1) ^b
UDMA	41.2 (6.6) ^c
UDMA/BMPEPP	21.9 (1.0) ^d
BMPEPP	12.8 (0.6) ^e

Means noted with different superscripts are significantly different at $p < 0.01$ level among the transmitted amounts of visible light

Curing depth and Knoop hardness of resin composite consisting of different types of monomer

Tables 3 and 4 show the curing depth and Knoop hardness of the resin composites by varying the type of base monomer used.

The curing depths of the resin composites ranged from 4.5 to 17.5 mm, as shown in Table 3. The depth was strongly dependent on the type of monomer used. Consequently, the resin composite based on TEGDMA, whose refractive index was closest to that of silica, exhibited a maximum curing depth of 17.5 mm. When refractive index difference between the monomer and the silica increased, the curing depth of the resin composite became shallower. In this connection, the resin composite based on BMPEPP, whose refractive index was farthest from that of silica, exhibited a minimum curing depth of

Table 3 Curing depths of the resin composites by varying the type of base monomer used

Type of monomer	Curing depth (mm)
TEGDMA	17.5 (0.4) ^a
TEGDMA/UDMA	14.7 (0.2) ^b
UDMA	9.6 (0.5) ^c
UDMA/BMPEPP	6.3 (0.2) ^d
BMPEPP	4.5 (0.1) ^e

Means noted with different superscripts are significantly different at $p < 0.01$ level among the curing depths

4.5 mm.

In addition, the Knoop hardness of the irradiated surface of the resin composites ranged from 19.5 to 21.9, as shown in Table 4. However, the Knoop hardness of the bottom surface for 1-mm thickness decreased by 7-31%, when compared with that of the irradiated surface. By increasing the thickness of the resin composite from 1 to 2 mm, the Knoop hardness of the bottom surface further decreased to 8-46%.

DISCUSSION

To increase polymerization conversion in the cavity floor of photo-cured resin composites, it is very important to understand the effects of two factors: refractive index difference that exists between the base resin and silica, as well as the transmittance of visible light through the resin composite. This is of importance since light scattering occurs at the resin-silica interface.

In this study, the effect of the transmitted amount of visible light through the resin composite on the curing depth and polymerization conversion of photo-cured resin composites was examined.

Immediately after visible light irradiation, the maximum value of the transmittance of visible light through the resin composite was obtained. As irradiation time increased, the transmittance's value gradually decreased. This effect was attributed to differences in the refractive index becoming larger during monomer polymerization. This was possible since the probability of light scattering at the resin-silica interface became higher as the differences in refractive index became larger.

To understand the types of parameters that control the curing depth and polymerization conversion, the transmitted amount of visible light through the resin composite was determined. The transmitted amount of visible light was strongly dependent on the magnitude of refractive index difference that existed between the resin and the silica. More specifically, it was dependent on the type of base monomer used. This is because the refractive index of a base monomer is strongly dependent on the type of atomic group in the monomer's chemical structure.

Table 4 Knoop hardness values of the resin composites by varying the type of base monomer used

Type of monomer	TEGDMA	TEGDMA/UDMA	UDMA	UDMA/BMPEPP	BMPEPP
Knoop hardness					
Top surface	19.5 (0.7) ^{a,b,c}	20.7 (1.7) ^{a,b,d}	21.6 (1.0) ^{a,d,e}	21.0 (2.4) ^{d,e}	21.9 (1.8) ^e
Bottom surface					
1 mm	18.2 (0.9) ^{a,b,c}	18.5 (3.7) ^{a,b,c}	18.6 (1.2) ^{a,b,c}	16.4 (2.0) ^{a,b,d}	15.2 (1.6) ^{a,d,e}
2 mm	17.9 (1.2) ^{b,c}	16.7 (2.6) ^c	15.1 (1.7) ^c	13.3 (2.5) ^c	11.9 (0.5) ^c

Means noted with different superscripts are significantly different at $p < 0.01$ level among the Knoop hardness values

Fig. 4 Effect of transmitted amount of visible light though the resin composite on the curing depth.

Fig. 4 shows the effect of the transmitted amount of visible light on the curing depth of the resin composites. The transmitted amount of visible light exhibited a correlation with the curing depth of the resin composite. The correlation coefficient was 0.999. In other words, the curing depth of the resin composite was strongly dependent on the transmitted amount of visible light. This was possible since visible light could reach a deeper depth when the refractive index of the monomer and its polymer were closer to that of silica. As a result, the resin composite based on BMPEPP, whose refractive index was farthest from that of silica, exhibited the shallowest curing depth. This occurred because the probability of light scattering at the BMPEPP-silica interface became greater during polymerization, since the refractive index of poly(BMPEPP) was greater than that of BMPEPP.

To further understand the polymerization conversion of the resin composite's cavity floor, the ratio of the Knoop hardness of the bottom surface of 2-mm thickness against that of the irradiated surface was calculated. Fig. 5 shows the effect of the transmitted amount of visible light through the resin composite on Knoop hardness ratio. Polymerization conversion of the bottom surface became higher when Knoop hardness ratio was closer to 1. The transmitted amount of visible light exhibited a correlation with Knoop hardness ratio. The correlation coefficient was 0.977. The greater the difference in refractive index between the monomer and the silica became, the lower the Knoop hardness ratio became. This result was possible because visible light, which had

Fig. 5 Effect of transmitted amount of visible light though the resin composite on the ratio of Knoop hardness of the cavity floor against the irradiated surface.

sufficient energy to polymerize the monomer, could not reach the bottom of the cavity floor due to light scattering at the interface. In particular, the resin composite based on BMPEPP, whose refractive index was farthest from that of silica, exhibited the largest decrease in the bottom surface's Knoop hardness. This was possible since the probability of light scattering at the resin-silica interface became higher as the difference in refractive index that existed between BMPEPP and silica increased during polymerization. Therefore, polymerization conversion was strongly dependent on the magnitude of refractive index difference that existed between the resin and the silica.

CONCLUSIONS

It can be concluded that the greater the amount of light passing through a resin composite is, the deeper the curing depth, and the higher the polymerization conversion of the resin composite will be. To improve the degree of polymerization conversion of the cavity floor, it is important to reduce the refractive index difference that exists between the base resin and the silica filler.

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