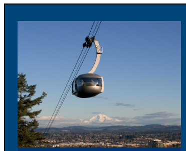

Monomer and Photoinitiator Type Affect Light Curing Reciprosity in Composites

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579

Introduction

Photocured dental composites are the most commonly placed restorative materials. Fundamental to the photochemical process is the ability of a photon to arrive at the photoinitiator in order to effect polymerization. The penetration of the photons depends upon the scattering, absorption, and index of refraction of the material through which it must pass. It can be assumed that the degree of cure (DC) at depth is directly related to the penetration of photons. Although this is simple in concept, there is currently no model that quantitatively describes how these factors affect the polymerization reaction. A model that takes these factors into consideration must, of course, be dynamic since the absorption, scattering, and index of refraction all change as the polymerization process proceeds. One method to begin looking at this is to determine whether the same number of sufficiently-energetic photons, incident over a short period of time compared to a longer period of time, effects the same DC with depth. If the DC is simply dependant upon the number of incident photons, then the DC would be the same for either time period, indicating complete reciprocity. Any deviation from reciprocity indicates that other factors must be affecting the DC (1). Inasmuch as the DC affects the mechanical properties of the material, the noted factors that affect the DC are ultimately related to the clinical performance of the composite. The results described in this project represent only a part of the overall goal to develop a model that quantitatively accounts for the factors mentioned above.

Specific Aims

The aim of this study was to determine whether the degree of conversion (DC) at any depth, based upon hardness, in several materials of the compositions 50, 70 and 90% BisGMA with 50, 30 and 10% TEGDMA, resp., 0.8% EDMAB, 0.4% CQ, and 64% silanated filler, varied as a function of exposing the sample to an equivalent radiant exposure over a short time period (10 s) compared to a longer time period (80 s). Reciprocity will be indicated for cases where the DC at depth, based upon Knoop hardness, is the same for an equivalent radiant exposure, irrespective of the duration of exposure.

Materials and Methods

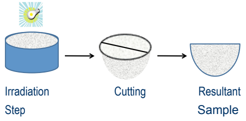
Materials with the compositions given in Table 1 were prepared by stirring the solids ethyl-4,8-dimethylaminobenzoate (EDMAB) and camphorquinone (CQ) in triethylene glycol dimethacrylate (TEGDMA) until completely dissolved. Bisphenol A–glycidyl methacrylate (BisGMA) was then added and the components thoroughly mixed. The mass percents corresponded to the mass of the component relative to the entire mass of the resin (without filler). The resin was then loaded to 64% (based upon total mass of filler and resin) with filler (0.4 µm spherical SiO_2/ZrO_2, refractive index 1.521).

Table 1. Mass percent composition of composite mixtures.

	Mass Percent		
	50:50	30:70	10:90
TEGDMA	49.4	30.3	9.4
BisGMA	49.4	68.5	89.4
CQ	0.4	0.4	0.4
EDMAB	0.8	0.8	0.8
Filler	64	64	64

The materials were mixed on a DAC-150 Speedmixer (Flacktek) to produce a homogeneous composite. The composite samples (N = 3) were packed into a cylindrical mold (8 mm deep x 19.2 mm diameter), covered with a piece of Mylar film, and secured in a fixed position relative to the irradiation source. The samples were irradiated with a DEMI light (10 mm tip; 573.2 mWcm^{-2}) for 10 s (no filter) and for 80 s (neutral density filter in place). In this way, each sample received the same radiant exposure of 5732 mJcm^{-2}. The radiant exposure was chosen so that approx 80% DC would occur for the top layer, but result in a gradient of DC with depth. This yielded samples that were hardened on top, but softened with depth to the point of being uncured at depths below 5-7 mm. Following irradiation, the bowl-shaped samples were removed from the mold, the uncured material removed by scraping, and then embedded in epoxy. Slices (~2 mm thick) were cut with a diamond blade (Struers Accutom cut-off saw) from the middle of the sample as illustrated in the scheme below.

Scheme 1.



Materials and Methods Continued

Hardness Measurements

The surface of the bowl-shaped slice, corresponding to the middle of the bulk sample, was polished with 1000 grit silicon carbide followed by 5 µm Al_2O_3 powder, and tested for hardness. Knoop hardness was measured in a 1 mm x 1 mm grid pattern across the entire sample with the use of a Struers Duramin instrument. A picture of one sample is shown in Figure 1.

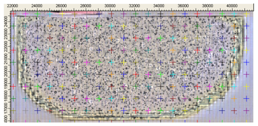
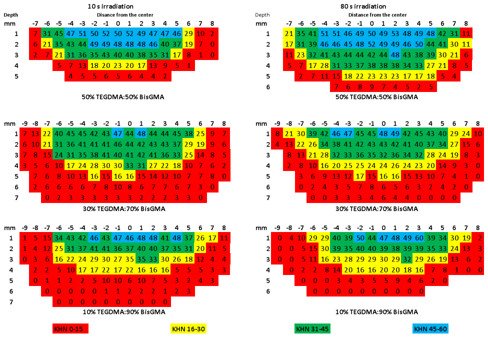


Figure 1. The cross-sectional area of one slice of a composite sample which has been sectioned into a 1 mm x 1 mm grid pattern. This video image was provided by P. Wang, Bruker Optics Inc.

Results

A map of the average (N = 3) Knoop hardness values (kg/mm^2) at each 1 x 1 mm intersection is shown in Figure 2 below for the three composite mixtures. The illustrations on the left correspond to irradiation times of 10 s while those on the right are for irradiation times of 80 s. The color coding corresponds to blue being the hardest, green next, yellow next, and red being the softest.



10 s irradiation

Disance from the center

Depth mm	-7	-6	-5	-4	-3	-2	-1	0	1	2	3	4	5	6	7	8
1	7	31	45	47	51	50	52	50	52	49	47	47	46	29	10	2
2	6	21	35	43	44	49	49	48	48	48	46	40	37	19	7	0
3	2	7	21	31	36	35	43	40	40	38	35	31	17	8	1	0
4			5	7	13	18	20	23	20	17	13	9	5	1		
5				4	5	5	6	5	6	4	4	2				

50% TEGDMA:50% BisGMA

80 s irradiation

Distance from the center

Depth mm	-7	-6	-5	-4	-3	-2	-1	0	1	2	3	4	5	6	7	8
1	21	35	41	51	51	46	49	50	49	53	48	49	48	42	31	11
2	17	31	39	46	46	45	48	52	49	49	46	50	44	41	30	11
3	11	23	32	41	43	44	44	42	44	48	43	38	39	30	21	6
4	5	7	17	28	31	33	37	38	38	38	34	33	27	21	8	5
5		2	7	11	15	18	22	23	23	23	17	17	18	5	4	
6					7	6	8	9	7	4	5	2	5			

50% TEGDMA:50% BisGMA

mm	-9	-8	-7	-6	-5	-4	-3	-2	-1	0	1	2	3	4	5	6	7	8
1	7	13	22	40	45	45	42	43	47	44	48	44	44	45	38	25	9	7
2	6	10	21	31	36	41	41	41	46	44	42	43	43	37	29	19	9	6
3	7	8	15	24	31	35	38	41	40	41	42	41	36	33	25	14	8	5
4	3	5	6	10	17	24	28	30	30	33	31	27	22	18	10	7	6	2
5		7	6	8	10	13	16	15	16	16	15	14	12	10	7	7	8	0
6		2	6	6	6	6	7	8	10	8	6	7	7	6	7	3	0	
7			0	2	3	3	3	3	3	3	2	2	2	3	3	0		

30% TEGDMA:70% BisGMA

mm	-9	-8	-7	-6	-5	-4	-3	-2	-1	0	1	2	3	4	5	6	7	8
1	8	21	30	39	42	46	47	45	45	48	49	42	45	43	40	29	24	10
2	4	13	22	26	34	38	41	42	43	43	42	41	40	37	34	27	15	6
3		8	13	21	28	32	33	36	35	32	36	34	32	28	24	19	8	3
4		2	8	10	16	20	25	25	24	24	26	24	23	20	14	9	3	0
5			3	6	9	13	12	17	15	16	16	15	13	10	7	4	1	0
6			0	2	4	3	5	7	8	6	5	6	3	2	4	2	0	
7				0	0	3	3	3	4	6	4	4	0	0	0	0		

30% TEGDMA:70% BisGMA

mm	-9	-8	-7	-6	-5	-4	-3	-2	-1	0	1	2	3	4	5	6	7	8
1	1	5	15	34	43	42	46	43	47	46	48	48	41	48	37	26	17	11
2	1	4	12	25	31	37	41	41	36	37	40	40	37	35	31	20	11	5
3	0	3	6	16	22	24	29	30	27	35	35	33	30	26	18	12	4	4
4		2	2	5	10	17	17	22	17	22	16	16	16	5	5	5	3	3
5		0	1	1	2	2	5	10	10	6	10	7	5	3	2	4	3	
6			0	0	0	0	0	1	1	2	2	2	1	2	3			
7				0	0	0	0	0	0	0	0	0	0					

10% TEGDMA:90% BisGMA

mm	-9	-8	-7	-6	-5	-4	-3	-2	-1	0	1	2	3	4	5	6	7	8
1	0	4	10	29	29	40	39	50	44	47	48	49	60	39	34	30	19	2
2	0	0	5	15	30	39	35	40	40	39	38	39	39	35	33	24	13	3
3	0	0	5	11	16	23	28	29	29	30	29	32	29	26	19	13	6	2
4		0	2	2	8	14	20	16	16	20	20	18	16	7	8	1	0	0
5			0	0	0	3	4	3	5	5	9	4	6	2	0			
6				0	0	0	0	0	0	0	0	0	0					

10% TEGDMA:90% BisGMA

🟥 KHN 0-15 🟨 KHN 16-30 🟩 KHN 31-45 🟦 KHN 45-60

Figure 2. KHN values measured as a function of the depth from the surface in mm and the distance from the center of the light source in mm for the three composites that contained 50% TEGDMA:50% BisGMA, 30% TEGDMA:70% BisGMA, 10% TEGDMA:90% BisGMA, and all containing 0.4% CQ, 0.8% EDMAB, and 64% spherical filler by mass.

The relationship between the hardness and degree of conversion (DC) was indicated by mapping the sample of 50% TEGDMA: 50% BisGMA (irradiated for 10 s) in the near IR region as shown in Figure 3. This figure shows that the quantity of unreacted monomer was least (blue region) in the hardest areas and greatest (red region) in the softest areas. The direct relationship between hardness and DC has been previously shown (2).

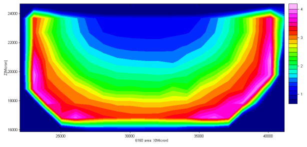
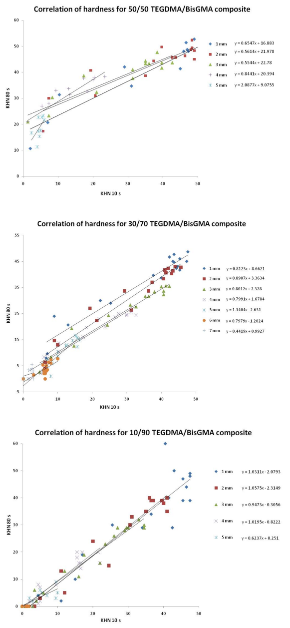


Figure 3. The area of the 6164 cm-1 peak, corresponding to the unreacted monomer, was monitored with depth from the surface and with distance from the center of the light source. Blue represents the smallest peak area while red the largest peak area. This figure was provided by P. Wang, Bruker Optics, Inc.

Results continued



The average hardness values (shown in Figure 2) at a specific depth for the 80 s irradiated sample were plotted against those at the same depth for the 10 s irradiated sample. The best fit line for all the data points at a given depth was then obtained using a linear regression analysis. The graphs on the left show the resultant plots for the three different composites along with the equation for the best fit line. If there were exact reciprocity, the slope of the lines would all be equal to 1. That is, the degree of conversion, based upon the hardness, would be identical at the same depth for each identical composite for the two different irradiation times. It is apparent that the greatest reciprocity occurs for the 10% TEGDMA:90% BisGMA sample (slope closest to 1) and least for the 50% TEGDMA:50% BisGMA sample.

Figure 4. The average hardness at a specific depth and distance away from the center of the light source, is plotted for an 80 s irradiation time vs a 10 s irradiation time. Each depth is indicated by a unique symbol shown to the right of the plot. The corresponding equation for each line was determined by a linear regression analysis; the slope represents the closeness of reciprocity.

Summary

Figures 2 and 3 show clearly that the degree of conversion (DC) is greatest near the center of the light source, and closest to the light source. The absorption and scattering of incident light resulted in lower DC as a function of the distance away from the light source, and the angle from the center of the light source. Overall, the 50:50 composite produced the greatest DC to a depth of 3 mm, and the 10:90 composite had the lowest DC. For the 50:50 composite there is greater DC at depth for the same radiant exposure applied over 80 s compared to that at 10 s. The DC at depth for the same radiant exposure is similar for the 30:70 and 10:90 composites regardless of the time over which the exposure occurred. The results shown in Figure 4 indicate nearly perfect reciprocity for the 10:90 composite, good reciprocity for the 30:70 composite, and poorest reciprocity for the 50:50 composite. This result is in agreement with previous studies (3). In addition to the expected different optical properties amongst these composites, viscosity differences also undoubtedly have a significant effect.

Conclusions

The DC for an identical radiant exposure is a function of the ratio of TEGDMA to BisGMA in the composite formulation. Composites that contain 70% BisGMA show similar curing with a short duration exposure as with a longer duration exposure. With 90% BisGMA, the composite cures equally well with a 10 s exposure as with an 80 s exposure for the same radiant exposure. With respect to clinical applications, for which the greatest DC at depth for the shortest time of light exposure is desired, composites that contain ≥70% BisGMA will produce the best results. However, these materials are, overall, softer and less mechanically robust than those based on formulations with 50% Bis-GMA.

References and Acknowledgements

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