Influence of composition on rate of polymerization contraction of light-curing resin composites

Erik Asmussen and Anne Peutzfeldt

Department of Dental Materials, School of Dentistry, Faculty of Health Sciences, University of Copenhagen, Copenhagen, Denmark

Asmussen E, Peutzfeldt A. Influence of composition on rate of polymerization contraction of light-curing resin composites. Acta Odontol Scand 2002;60:146–150. Oslo. ISSN 0001-6357.

A slow contraction may result in reduced gap formation when a restorative resin polymerizes in a dental cavity. It was the aim in the present work to investigate the rate of contraction in relation to composition of experimental light-curing resin composites. The monomer of the resin composites consisted of mixtures of BisGMA, TEGDMA, and in one series HEMA. The resins contained varying amounts of initiators, co-initiators, and inhibitor, and were made composite by adding a silanized glass filler to a content of 74% by weight of the composite paste. The polymerization contraction up to 120 sec was determined by means of the bonded-disk method. Within the ranges studied, the concentration of initiator and co-initiator in the monomer mixture had only an insignificant influence on rate of polymerization. In comparison to camphorquinone, the initiators 1-phenyl-1,2-propanedione and benzil reduced the rate of polymerization without affecting the final contraction. In comparison to N,N-dimethyl-*p*-aminobenzoic acid ethyl ester, N,N-cyanoethyl methylaniline was as effective, while N,N-diethanol-*p*-toluidine was less effective as co-initiator. A relatively high content of the inhibitor methoxyhydroquinone reduced the initial rate but not the final polymerization contraction. The rate of polymerization increased with the level of HEMA and TEGDMA in the monomer mixture. It was concluded that intrinsic slow cure may be obtained with certain compositions of resin composites without impairing the final extent of polymerization. ☐ *Co-initiator; initiator; inhibitor; photopolymerization; shrinkage*

Erik Asmussen, Department of Dental Materials, School of Dentistry, 20 Nörre Allé, DK-2200 Copenhagen N, Denmark. Tel: +45 3532 6580, fax: +45 3532 6505, e-mail: erik.asmussen@odont.ku.dk

Resin composites are normally cured by light and therefore much faster than so-called chemically cured composites. However, a slowly cured resin composite is preferable to a more rapidly cured one, because stress relief may reduce the polymerization contraction of resin restorations (1–3). The resin of a dental bonding agent, however, has to undergo fast polymerization so that the bond to the cavity walls is established before onset of contraction of the restorative resin.

A slow polymerization may be brought about by soft-start curing, where a reduced intensity of curing light is used during the first part of the polymerization period (1, 4). Another method is pulse-delay curing, where the polymerization is initiated by a short flash of light followed by a waiting period of one or several minutes before the final cure is performed (5, 6). In both cases, reduced gap formation has been observed, without mechanical properties being compromised.

The rate of polymerization may also be related to intrinsic factors (7). In chemically cured resin composites, such factors include the content of benzoyl peroxide, amine, and inhibitor (8). In light-curing resin composites, certain types of filler (7) and shades (1, 9) may give rise to intrinsic soft start. It is also conceivable that the content of initiator (diketone), co-initiator (tertiary amine), and inhibitor (phenol) influences the rate of polymerization. Mechanical properties tend to increase in resins with increasing concentrations of diketone (camphorquinone, CQ) and amine (10, 11), but the impact on rate of polymerization of the resins has not been determined. The type of diketone and amine may similarly be determinants for the rate of polymerization. Regarding the nature of the monomer, it is well documented that in mixtures of BisGMA (bisphenol-A glycidyl dimethacrylate) and TEGDMA (triethyleneglycol dimethacrylate) increasing amounts of TEGDMA will result in increased conversion (12). However, the rate of polymerization has not been measured in relation to the content of TEGDMA. HEMA (2-hydroxyethyl methacrylate) is a common component of bonding agents, but the rate of polymerization of resins containing HEMA has not been determined, and the same applies to resins containing DIAC (diacetyl) (13).

Thus, regarding a resin composite, desirable qualities would appear to be a relatively slow polymerization, but a high degree of final conversion. Shrinkage and conversion are closely related manifestations of the same process (14, 15). This means that a high value of final shrinkage is associated with a few remaining double bonds and hence with favorable mechanical properties (16, 17). The present work was conducted to investigate the possibilities of altering the rate of polymerization by varying the composition of the resin material. It was hypothesized that significant changes in rate could be obtained with only minor changes in the final contraction and thus in the final conversion.

Taylor&Francis healthsciences

© 2002 Taylor & Francis

Table 1. Rate of polymerization contraction C of resin composites in relation to composition of the initiator system. The resin originated from a monomer mixture with a content of BisGMA of 60 mol% and TEGDMA of 40 mol%. dC/dt[max] is the calculated maximum rate of contraction, C[3s] is the contraction after 3 s, C[10s] the contraction after 10 s, and C[120s] is the contraction after 120 s. Mean ± *s* (standard deviation)

Initiator w%	Co-initiator w%	Inhibitor w%	dC/dt[max] %/s	C[3s] %	C[10s] %	C[120s] %
CQ: 0.2	DABE: 0.3	0	0.55	^{f} 1.11 ± 0.10	^{f,g} 1.90 ± 0.11	^{d} 2.49 ± 0.12
CQ: 0.1	DABE: 0.3	0	0.49	^{e,f} 1.02 ± 0.02	^{f,g} 1.81 ± 0.08	^{d} 2.40 ± 0.07
CQ: 0.0	DABE: 0.3	0	0	^{a} 0	^{a} 0	^{a} 0
CQ: 0.2	DABE: 0.1	0	0.45	^{e,f} 0.95 ± 0.03	^{e,f} 1.73 ± 0.06	^{d} 2.39 ± 0.04
CQ: 0.2	DABE: 0.0	0	0.09	^{b} 0.07 ± 0.02	^{b} 0.37 ± 0.09	^{b} 1.80 ± 0.08
CQ: 0.2	CEMA: 0.3	0	0.49	^{e,f} 1.03 ± 0.14	^{f,g} 1.82 ± 0.05	^{d} 2.48 ± 0.07
CQ: 0.2	DEPT: 0.3	0	0.14	^{b} 0.11 ± 0.01	^{c} 0.91 ± 0.01	^{c} 2.11 ± 0.05
PPD: 0.2	DABE: 0.3	0	0.33	^{d} 0.62 ± 0.05	^{e} 1.65 ± 0.11	^{d} 2.48 ± 0.11
BZ: 0.2	DABE: 0.3	0	0.26	^{c} 0.45 ± 0.04	^{d} 1.40 ± 0.09	^{d} 2.38 ± 0.08
CQ: 0.2	DABE: 0.3	MHQ: 0.05	0.58	^{f} 1.13 ± 0.07	^{g} 1.95 ± 0.05	^{d} 2.45 ± 0.05
CQ: 0.2	DABE: 0.3	MHQ: 0.5	0.27	^{c} 0.48 ± 0.07	^{d} 1.49 ± 0.08	^{d} 2.45 ± 0.07

For each C[t], mean values with the same superscript letter do not differ from each other at $P = 0.05$.

Materials and methods

The rate of polymerization contraction was measured on a number of experimental resin composites. The monomers of the resin composite were BisGMA and TEGDMA, which were mixed in a molar ratio of either 60/40 or 40/60. In one series, the resins contained 10, 20, or 30 mol% HEMA. The compounds of the initiator system were camphorquinone (CQ), 1-phenyl-1,2-propanedione (PPD) or benzil (BZ). The co-initiators were N,N-dimethyl-*p*-aminobenzoic acid ethyl ester (DABE), N,N-cyanoethyl methylaniline (CEMA), or N,N-diethanol-*p*-toluidine (DEPT). The inhibitor was methoxyhydroquinone (MHQ). The initiators, co-initiators, and inhibitor were added and completely dissolved in the monomer mixtures in amounts that are accounted for in Tables 1 and 2. In one series, 10 mol% of DIAC served as initiator instead of CQ. The resins were made composite by adding a silanized glass filler to the monomer mixtures. The filler was added incrementally and a homogeneous paste was obtained by means of a plastic spatula. The final filler content was 74% by weight of the composite paste.

The bonded-disk method (9), as modified by Watts & Cash (18), was used as illustrated in Fig. 1. A brass ring of height 1.93 mm and inner diameter of 15 mm was glued to a microscope glass slide (thickness 1 mm) by means of a light-curing resin. In a dark room, a cylindrical teflon mold (h = 5.0 mm, d = 5.0 mm) was filled with resin composite. By means of a piston, the composite was then extruded onto the glass slide in the center of the brass ring. A cover glass slide (thickness 25 μm) was placed on top and by means of a parallelling device compressed to give a disk (h = 1.93 mm, d ≈ 7.7 mm). The assembly was positioned on a ring-shaped support, enabling irradiation from below the specimen. Irradiation was performed with Elipar Highlight (ESPE, Seefeld, Germany) in the standard mode for 20 sec with the exit window positioned 1 mm below the slide. The irradiance was measured by means of a radiometer to be 750 mW/mm^2. The core of a transducer (Model 7DCDT-050, Hewlett-Packard, Andover, Mass., USA) was lowered onto the surface of the cover glass, and an XY-recording voltmeter set at zero and at a paper speed of 1 mm/sec. The irradiation was initiated and the output from the transducer recorded for 120 sec. Three experiments were run for each resin composite. The output from the transducer was calibrated by means of a dial gauge placed on an adjustable table. The output was converted to microns and then to percent. The calibration

Table 2. Rate of polymerization contraction C of resin composites in relation to the composition of the monomer mixture. With the exception of one case,* the resin monomer contained 0.2% CQ, 0.3% DABE and 0% MHQ. dC/dt[max] is the calculated maximum rate of shrinkage, C[3s] is the contraction after 3 s, C[10s] the contraction after 10 s, and C[120s] is the contraction after 120 s. Mean ± *s* (standard deviation)

BisGMA Mol%	TEGDMA Mol%	Additive Mol%	dC/dt[max] %/s	C[3s] %	C[10s] %	C[120s] %
60	40	HEMA: 0%	0.55	^{a,b} 1.11 ± 0.10	^{a} 1.90 ± 0.11	^{a} 2.49 ± 0.12
54	32	HEMA: 10	0.72	^{b} 1.38 ± 0.18	^{b} 2.21 ± 0.09	^{b} 2.75 ± 0.07
48	32	HEMA: 20	0.73	^{b} 1.43 ± 0.18	^{c} 2.38 ± 0.07	^{c} 2.97 ± 0.07
42	28	HEMA: 30	0.78	^{b} 1.49 ± 0.21	^{d} 2.60 ± 0.05	^{d} 3.19 ± 0.13
40	60		0.75	^{b} 1.48 ± 0.06	^{e} 2.74 ± 0.05	^{e} 3.53 ± 0.04
57	33	DIAC: 10*	0.45	^{a} 0.94 ± 0.15	^{a} 1.83 ± 0.14	^{a} 2.51 ± 0.13

* Prepared without CQ.

For each C[t], mean values with the same superscript letter do not differ from each other at $P = 0.05$.

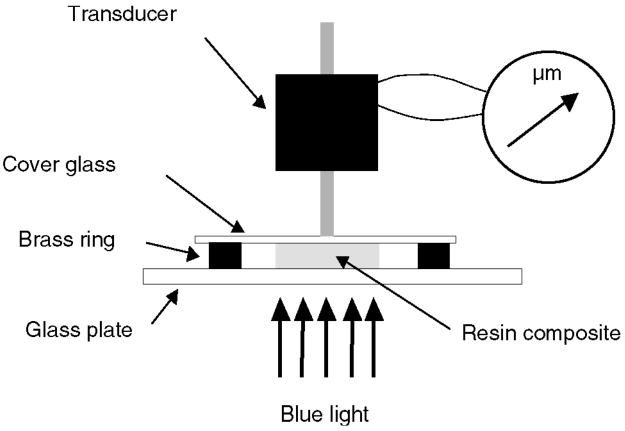

Fig. 1. Schematic representation of the method used for measuring the rate of polymerization of resin composite.

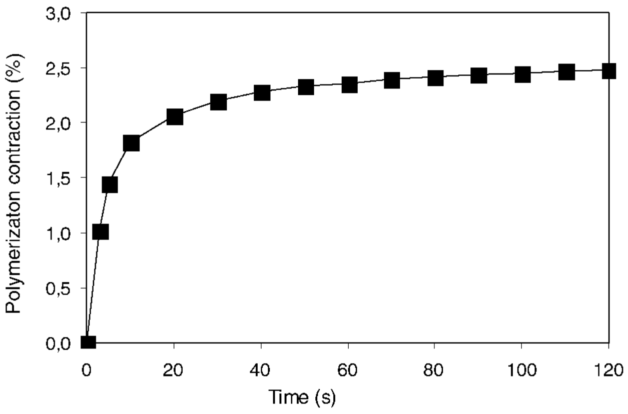

Fig. 2. Typical curve depicting the contraction as a function of time.

showed that 1 mm measured on the chart paper equaled 0.24 μm = 0.012%.

The shrinkage was determined at 3, 5, and 10 sec and thereafter for every 10 sec up to 120 sec.

Statistical analyses. The data were treated statistically by analysis of variance, regression analysis (19), and by Newman-Keuls' multiple range test (20).

Results

Fig. 2 shows a typical contraction curve. An almost straight line of initial contraction is followed by a slower rate. The curves obtained were fitted to a straight line $\ln C[t] = a + b/t$, in which expression C[t] is the contraction at time t. In all cases the coefficient of correlation was higher than 0.98, which is significant at $P < 0.0005$. Relationships of this shape fitted the measured values a little more accurately than the expression suggested by Watts & Cash (18). The first derivative dC/dt is the rate of polymerization. The maximum rate of polymerization dC/dt[max] was calculated by setting the second derivative $d^2C/dt^2 = 0$. The calculated maximum rate of contraction occurred 1.0–5.2 sec after the start of contraction, depending on composition.

Tables 1 and 2 give the contraction values after 3, 10, and 120 sec, designated as C[3s], C[10s], and C[120s]. Table 1 gives the results when the initiating system was varied and Table 2 the results when the composition of the monomeric part of the material was varied. Regression analysis showed a strong relationship between the calculated dC/dt[max] and C[3s] (r = 0.993).

Letting C[3s] and C[10s] be two measures of the rate of polymerization, Table 1 indicates that these rates varied between the experimental series with statistical significance. Regarding the initiators, no difference in rate of polymerization was observed between resin composites with 0.1 and 0.2% CQ, but polymerization did not occur when the CQ was left out. C[3s] and C[10s] were lower in the PPD and BZ series as compared to the CQ series, but no difference in C[120s] was observed between the three materials. Regarding the co-initiators, no statistically significant difference in rates of polymerization or in C[120s] was measured with the resin composites containing 0.3 and 0.1% of DABE. Without any co-initiator (DABE: 0%), a polymerization took place that was significantly slower and less complete. CEMA was as effective as DABE, whereas use of DEPT resulted in significant decreases in C[3s], C[10s], as well as C[120s]. MHQ at the higher concentration slowed down the initial rate of polymerization, but did not affect C[120s].

Table 2 indicates that although the differences in polymerization contraction were not statistically significant at 3 sec, C[10s] and also C[120s] increased with the content of HEMA and with the content of TEGDMA. Use of 10 mol% of DIAC instead of 0.2% CQ did not affect the results.

Discussion

It was demonstrated above that the rate of polymerization contraction of resin composites depends on a number of intrinsic variables. Since polymerization is initiated by a bimolecular reaction between a diketone and an amine (21), it is reasonable that both ketone and amine exert an influence. However, a reduction of the content of camphorquinone from 0.2 to 0.1% and a reduction of DABE from 0.3 to 0.1% had no significant influence, neither on the rate of polymerization nor on the contraction value at 120 sec. It would seem that the production of free radicals is not limited by the concentration of CQ or DABE in these ranges, but rather by the intensity of the light (1). Without CQ the resin composite did not polymerize at all. In contrast to this, the material polymerized to a certain degree without amine. Apparently the hydrogen abstraction necessary for polymerization may take place without amine, possibly by reactions between CQ and the BisGMA monomer, which contains an active hydrogen (21). When comparing the influence of the three initiators, the differences in molecular weight M should be taken into account. As $M_{CQ} = 166$, $M_{PPD} = 148$, and $M_{BZ} = 210$, and considering that C[3s] and C[10s] did not vary significantly in the range of 0.1 to 0.2% CQ, it follows that PPD and BZ reduce the rate of polymerization as compared to CQ without affecting the contraction at 120 sec. The reason for this may be found in differences between the initiators in absorption in the blue light range (Asmussen & Peutzfeldt, unpublished results). The finding that PPD and BZ reduced the rate of polymerization without compromising the contraction at 120 sec may make these initiators interesting from the point of view of gap formation. The slow initial cure may reduce the build up of stresses and therefore result in reduced gap formation (2).

When comparing the influence of the three co-initiators, the differences in molecular weight M must be taken into account. As $M_{DABE} = 193$ and $M_{CEMA} = 160$, 0.3% of CEMA corresponds to an equimolar content of DABE of 0.36%. Considering the insignificant influence of tripling the content of DABE from 0.1% to 0.3%, it may be safe to say that CEMA was as effective as DABE in the polymerization process. Since $M_{DEPT} = 192$, it follows that the use of DEPT reduced the rate of polymerization as well as C[120s], compared to the use of DABE. The lesser effectiveness of DEPT may be related to the reactivity of the α-hydrogen (21). This contrasts to chemically cured resins in which DEPT is a very effective co-initiator (12).

The monomers as purchased from the manufacturer contain an unknown level of inhibitor. An addition of 0.05% of MHQ had little effect on either the rate of contraction or on the contraction at 120 s, while 0.5% of MHQ had a significant effect on the rate of polymerization but not on the contraction at 120 s. In this respect, there is a profound difference between the light-curing resin composites of the present study and chemically cured composites. The rate of setting of chemically cured resins is strongly affected by the level of initiator, co-initiator and inhibitor (8). The explanation may be that with light-curing materials the production of radicals is so fast that only a minor amount of inhibitor has time to perform its inhibitory action before any differences in rate of polymerization can be observed.

The monomer composition was found to influence the rate of polymerization. The explanation may be related to changes in refractive index or to changes in monomer size, mobility, and functionality. Regarding the refractive index of the monomer, it may be assumed that the better it matches the refractive index of the filler particles, the less the scatter of penetrating light, and the higher the rate of polymerization will be. The refractive indices of BisGMA, TEGDMA and HEMA have been measured to be 1.55, 1.46, and 1.45, respectively (22). Thus, when the monomer composition was varied, as shown in Table 2, the index of refraction changed, and the possibility exists that this factor may have exerted an influence on the rates of polymerization given in Table 2. Regarding monomer size, mobility, and functionality, available information offers the alternative explanations discussed in the following.

Addition of the monomer HEMA resulted in an increased rate of polymerization. This may be explained by the small size and mobility of this monomer molecule. The relatively high value of C[120s] is due to the fact that HEMA is not only a small but also a monofunctional monomer. This feature leads to a high degree of conversion (23) and therefore to a high degree of contraction. The same applies to the influence of TEGDMA. Although bifunctional, this molecule is more mobile than BisGMA. As a consequence, a relatively fast and large polymerization contraction takes place when the content of TEGDMA is increased. Dentin bonding agents normally involve resins based on HEMA and often also on TEGDMA. It is essential that such resins polymerize fast in order that a bond be established before the main part of the restorative material polymerizes. In this manner, the contraction gaps may be reduced. The present study showed that the cure of such materials is indeed relatively fast, giving them an advantage as bonding agents from this perspective as well.

The addition of DIAC has previously been found to result in a reduced quantity of remaining double bonds (13). In that study, the mechanism leading to this reduction was attributed to either chain transfer or to the capability of DIAC to act as initiator. The present study shows that this second mode of action certainly may have played a role, since the resin composite showed fast and extensive polymerization.

As stated in the Introduction, contraction is intimately connected with the conversion of double bonds (14, 15, 23). When resin composites are cured, a high degree of conversion is normally aimed at. The corollary to a high degree of conversion is a high final contraction. In the present study, the measurements of contraction stopped at 2 min, a time at which the contraction was by no means at an end (1, 7, 14). In a pilot study, however, we have observed good correlation between 2 min contraction values and 1 h contraction values. The same may be inferred from other studies (1, 7, 14) although the cases of low early contraction occasionally showed a relatively high increase in contraction at later stages. However that may be, the contraction values C[120s] at 2 min may be taken as an indicator of final contraction, and hence final conversion. As stated in the Introduction, the desired mode of polymerization of a restorative resin is a slow initial contraction combined with a high final conversion. If the 2 min value is taken as a measure of final conversion, the results showed that such restorative resins may be based on initiator systems involving PPD or BZ, or have a high content of MHQ.

Returning to the hypothesis expressed in the Introduction, we found that the rate of polymerization could be reduced by changing the composition of the resin part of the composite material. Future research will show whether such materials will lead to reduced polymerization contraction of resin restorations.

References

1. Davidson-Kaban SS, Davidson CL, Feilzer AJ, de Gee AJ, Erdilek N. The effect of curing light variations on bulk curing and wall-to-wall quality of two types and various shades of resin composites. Dent Mater 1997;13:344–52.
2. Davidson CL, Feilzer AJ. Polymerization shrinkage and polymerization shrinkage stress in polymer-based restoratives. J Dent 1997;6:435–40.
3. Suh BI, Feng L, Wang Y, Cripe C, Cincione F, de Rijk W. The effect of the pulse-delay cure technique on residual strain in composites. Compendium 1999;2:4–12.
4. Uno S, Asmussen E. Marginal adaptation of a restorative resin polymerized at reduced rate. Scand J Dent Res 1991;99:440–4.
5. Kanca J, Suh BI. Reducing resin-based composite contraction stresses at the enamel cavosurface margins. Am J Dent 1999; 12:107–12.
6. Sahafi A, Peutzfeldt A, Asmussen E. Effect of pulse-delay curing on in vitro wall-to-wall contraction in dentin cavity preparations. Am J Dent 2001;14:295–6.
7. Watts DC, Hindi AA. Intrinsic 'soft-start' polymerization shrinkage-kinetics in an acrylate-based resin composite. Dent Mater 1999,15:39–45.
8. Asmussen E. Setting time of composite restorative resins vs. content of amine, peroxide, and inhibitor. Acta Odontol Scand 1981;39:291–4.
9. Walls AWG, McCabe JF, Murray JJ. The polymerization contraction of visible-light activated composite resins. J Dent 1988;16:177–81.
10. Peutzfeldt A, Asmussen E. Hardness of restorative resins: effect of champhorquinone, amine and inhibitor. Acta Odontol Scand 1989;47:229–31.
11. Asmussen E, Peutzfeldt A. Influence of selected components on crosslink density in polymer structures. Eur J Oral Sci 2001;109: 282–5.
12. Asmussen E. Factors affecting the quantity of remaining double bonds in restorative resin polymers. Scand J Dent Res 1982; 90:490–6.
13. Peutzfeldt A. Quantity of remaining double bonds of diacetyl-containing resin. J Dent Res 1994;73:511–5.
14. Silikas N, Eliades G, Watts DC. Light intensity effects on resin-composite degree of conversion and shrinkage strain. Dent Mater 2000;16:292–6.
15. Venhoven BA, de Gee AJ, Davidson CL. Polymerization contraction and conversion of light curing Bis-GMA based methacrylate resins. Biomater 1993;14:871–5.
16. Asmussen E. Restorative resins: hardness and strength vs. quantity of remaining double bonds. Scand J Dent Res 1982; 90:484–9.
17. Ferracane JL, Greener EH. The effect of resin formulation on the degree of conversion and mechanical properties of dental restorative resins. J Biomed Mater Res 1986;20:121–31.
18. Watts DC, Cash AJ. Determination of polymerization shrinkage kinetics in visible-light-cured materials: methods development. Dent Mater 1991;7:281–7.
19. Hald A. Statistical theory with engineering applications. New York: John Wiley & Sons; 1952.
20. Bruning JL, Kintz BL. Computational handbook of statistics. Glenview, IL: Scott, Foresman & Co.; 1977.
21. Ravve A. Principles of polymer chemistry. New York and London: Plenum Press; 1995.
22. Asmussen E, Uno S. Solubility parameters, fractional polarities, and bond strengths of some intermediary resins used in dentin bonding. J Dent Res 1993;72:558–65.
23. Rueggeberg FA, Tamareselvy K. Resin cure determination by polymerization shrinkage. Dent Mater 1995;11:265–8.

Received for publication 27 August 2001
Accepted 18 January 2002