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Volume contraction in photocured dental resins: The shrinkage-conversion relationship revisited

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Abstract Polymerization shrinkage and degree of conversion (DC) of resin composites are closely related manifestations of the same process. Ideal dental composite would show an optimal degree of conversion and minimal polymerization shrinkage. These seem to be antagonistic goals, as increased monomer conversion invariably leads to high polymerization shrinkage values.
Objectives: This paper aims at accurately determining the polymerization volume contraction of experimental neat resins and to link it to the number of actual vinyl double bonds converted in single ones instead of, as generally done, to the degree of conversion.
Methods: Different mixtures of Bis-GMA/TEGDMA (traditionally used monomers) were analyzed. Contraction of the polymers was determined by pycnometry and the use of a density column. DC was determined by the use of Raman spectrometry.
Results: An univocal relationship has been found between the volume contraction and the actual number of vinyl double bonds converted into single ones. A contraction value of 20.39 cm^3/mole (of converted $C=C$) was deduced from 27 measurements.
Significance: This relationship helps in finding solutions to the polymerization shrinkage problem. A reduction of the polymerization shrinkage due to the chemical reaction may obviously be expected from the addition of molecules allowing a decrease in the number of double bonds converted per unit volume of resin matrix, while maintaining the degree of conversion (of Bis-GMA and TEGDMA) and thus the mechanical properties. Further research will be directed at this objective.

Introduction

Dental resin composites comprise a blend of hard, inorganic particles bound together by a soft, resin

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matrix. During polymerization, the conversion of the monomer molecules of the matrix into a polymer network is accompanied by a closer packing of the molecules, which leads to bulk contraction [1-3].

To enhance the marginal integrity of composite resin restorations, bonding agents are used to withstand the polymerization contraction forces. The insertion of adhesive resin composites into cavity preparations leads to a competition between contraction forces and the strength of bonds to tooth structure [4-6]. This competition may lead to three different kinds of problems. Cohesive fractures due to the internal stresses can occur either in the tooth structure, or in the composite [7-9]. The resulting internal microcracks or the debonding at the filler particle/resin interface may accelerate damaging reactions such as wear [10]. A third possibility is the occurrence of adhesive fractures due to stress at the tooth-restoration interface that may lead to marginal gap formation, marginal discoloration, postoperative sensitivity, and secondary caries [5,6].

Viscous flow and polymerization shrinkage [5,6, 11-17] of the resin composites are both considered as significant determinants of gap formation. As a result of the time-dependent character of viscoelastic behavior, slower rates of polymerization reaction have been shown to be associated with lower contraction stress without compromising the final conversion [18,19].

The clinical consequences of polymerization shrinkage, and mainly imperfections in marginal adaptation and the appearance of recurrent caries, constitute the main reasons for premature replacement of resin composite restorations [11,20-23]. This explains why it is regarded as the main limitation of present-day resin composites and why its elimination or minimization is one of the most important research tasks in this field.

During the polymerization of methacrylate-based resins, the viscous liquid gradually transforms into a rigid material by radical polymerization involving the double bonds C=C of methacrylate groups. The extent of transformation of double to simple bonds (monomers in polymer) is called 'degree of conversion'. This polymerization involves a volume shrinkage which has three origins: a 'chemical' contraction (the most important), a 'thermal' contraction and a 'post-contraction'.

The chemical contraction is attributed to a change in inter-atomic spacing between molecules. Before polymerization, monomer molecules are about 4 Angströms apart and linked by secondary cohesion forces, the so-called van der Waals forces. During polymerization, the latter are replaced by single covalent bonds about 1,5 Angströms length [24,25].

Thermal contraction occurs during the cooling as the curing reaction is exothermic and overheats the resin, which contracts when returning to room temperature. This contraction is less important but it can create internal stresses.

During chemical reaction, the vitrification of the system induces a 'freezing' of the radicals in the cross-linked structure, stopping further chemical reaction. A so-called 'post-contraction' occurs up to about 24 h after polymerization [26].

Depending on the materials, the magnitude of the total volumetric 'free' curing contraction, mentioned in the literature, varies from more or less 5.3 vol % (pure Bis-GMA) [27] to 12.0 vol % (Bis-GMA/TEGDMA 20/80 w/w) for unfilled resins [3]. As polymerization shrinkage arises mainly from the chemical reaction itself, palliative solutions are to be searched for. This study focuses only on the chemical reaction and its related contraction in neat resins.

Shrinkage and conversion are closely related manifestations of the same process. In many studies, the rate of contraction is related to the degree of conversion. The general trend is that the volumetric shrinkage increases with an increasing degree of conversion [3,11,18,19, 28-30].

It is a common belief that, when resin composites are cured, a high degree of conversion is to be aimed for. Indeed, several studies have shown that, for a given monomer composition, a significant correlation is observed between the degree of conversion and nearly every physical and biological property of the polymer. In Bis-GMA based dental restorative resins, residual methacrylate groups appear clearly linked to the reduction of hardness [31-34], wear resistance [35], strength [31,34], color stability, fracture toughness and resistance to abrasive wear [35]. The degradative reactions are also responsible of formation and release of byproducts that could be sufficient to induce allergic reactions or may affect the compatibility of the resin with oral tissues [25,36].

The ideal composite would exhibit an optimal degree of conversion and minimal polymerization shrinkage. These seem to be antagonistic goals, as increased monomer conversion invariably leads to large polymerization shrinkage values. But both parameters are key ones for optimizing resin composite restoration.

However, instead to the degree of conversion (in %) the volume contraction has to be directly linked to the actual decrease of vinyl bond concentration (in mole/cm^3).

A linear correlation, between volume contraction and mole of converted double bonds, was first proposed in 1953 by Loshaeck [1] and recent literature [29] still refers to this early paper. In Loshaeck's study, it was determined that for every mole of C=C being converted in the C-C, there was an associated volume shrinkage of 23.0 cm^3/mole. In 1987, the results of a study conducted by Patel on a series of linear polymethacrylates [2] confirmed that the change in molar volume due to polymerization is reasonably constant at about 22.5 cm^3/mole. Moreover, this study, like others [29], uses polymerization shrinkage to determine the degree of conversion of a few bifunctional cured resins as used in dentistry. But, in the latter case, the correlation between volume shrinkage and degree of conversion has not been checked.

In the present study, the authors revisit and extend these results and attempt to determine more accurately the volume contraction of a series of cured dental resins and to link it to the number of actual vinyl double bonds converted using recent characterization techniques and the precision they offer.

Materials and methods

Preparation of the different resins:

The monomers most often used in the resinous matrix of present-day dental resin composites are Bis-GMA and TEGDMA, (the latter used as diluent). To determine the volume contraction associated with the number of double bonds converted, a range of Bis-GMA/ TEGDMA mixtures were analyzed. Eight different mixtures were prepared from Bis-GMA/TEGDMA consisting of 0, 20, 30, 40, 50, 60, 70 and 80% weight TEGDMA.

A photoinitiation system was added to each mixture in the proportion of 1%. This system consisted of a photosensitizer, camphorquinone (CQ) and an amine, the 3-(Methylphenylamino) propionitrile (A), in a proportion (CQ/A: 50/50).

Samples preparation

Samples were prepared as follows. A cylindrical brass mold, of 5 mm diameter and 5 mm height, was placed on a glass microscope slide and overfilled with the different mixtures of resins. Polymerization was initiated with a halogen light source (Translux Energy, Heraeus Kulzer, Germany) with an intensity of 900 mW/cm^2 using the 'conventional mode'. To assure complete polymerization the samples were irradiated on both sides (side in contact with air and through the cover glass) for 40 s.

Three samples per resin mixture were prepared, polymerized and analyzed.

The same samples of cured resin were used to determine the DC and the specific gravity.

Volume contraction

The polymerization shrinkage ($\Delta V/V_{\text{unpolymerized}}$) is obtained by comparing unpolymerized ($d_{\text{unpolymerized}}$) to polymerized ($d_{\text{polymerized}}$) specific masses by the following Eq. (1), where M is the weight of the sample.

$$\Delta V/V_{\text{unpolymerized}} = [M * (1/d_{\text{unpolymerized}} - 1/d_{\text{polymerized}})]/[M * 1/d_{\text{unpolymerized}}] \qquad (1)$$

After simplification, volume contraction percentage was thus calculated by the following Eq. (2):

$$\Delta V/V_{\text{unpolymerized}}(\%) = 100 * (d_{\text{polymerized}} - d_{\text{unpolymerized}})/d_{\text{polymerized}} \qquad (2)$$

The specific mass of 'pure' (liquid) uncured composite resin ($d_{\text{unpolymerized}}$) was measured by pycnometry. To determine the specific mass of the cured composite resin ($d_{\text{polymerized}}$) (solid), it turned out that the use of a density column (from Daventest Instruments) was more accurate that the use of a pycnometer. The pycnometer technique, using water as medium and the principle of Archimedes, needs to work at a low and strictly constant temperature to avoid any evaporation during measurements. In the density column technique, samples are immersed in a density gradient prepared by mixing potassium bromide and water to reach a density range between 1.00 and 1.41. The height at which samples stabilize is observed and compared with calibrated marker floats.

Number of double bonds converted

The degrees of conversion (i.e.: the percentage of vinyl functions converted to aliphatic functions) of the unpolymerized and polymerized resins were measured by a Raman spectrophotometer (Labram, Dilor Horiba-Jobin-Yvon, Lille, France). In their article Pianelli et al. [37] demonstrated that micro-Raman spectroscopy is by far easier and more adaptive than the FTIR technique usually used, to determine the degree of conversion (DC) of methacrylate-type dental composite resins.

Samples were excited at 632.8 nm by a He-Ne laser through a microscope objective (*100). The spectral resolution was 2 cm^{-1}. Raman spectra were obtained in the region 1600 cm^{-1}, with the following conditions: hole: 1000; irradiation time: 60 s.; number of accumulations: 5. This method allows the evaluation of the DC by comparing the vibration bands of the residual unpolymerized methacrylate C=C stretching mode at 1640 cm^{-1} to the aromatic C=C stretching mode at 1610 cm^{-1} used as internal standard. The unpolymerized resin enclosing the initiator/activator system is used as reference (DC=0).

The DC of the analyzed resins was calculated by the following Eq. (3):

$$DC(\%) = 100 * [1 - (R_{polymerized}/R_{unpolymerized})] \quad (3)$$

Where R=band height at 1640 cm^{-1} / band height at 1610 cm^{-1}.

The number of moles of C=C converted per gram was obtained with the following Eq. (4):

$$\text{Moles C}=\text{C poly/g} = DC * (\text{moles C}=\text{C init/g}) \quad (4)$$

Where the initial number of mole of C=C bonds per gram (moles C=C init/g) was obtained from the molar mass of the monomers and DC is the degree of conversion.

The molar conversion per cm^3 was finally obtained using the actual specific mass ($d_{polymerized}$) of the polymerized resin (5):

$$\text{Moles C}=\text{C poly/cm}^3 = d_{polymerized} * (\text{moles C}=\text{C poly/g}) \quad (5)$$

Results

Fig. 1 General trend of the values of the DC measured at 0 h and after 24 h. *Student's t-test* showed a significant difference ($p<0.05$) between the values of DC ($t=0$) and DC ($t\geq24$ h).

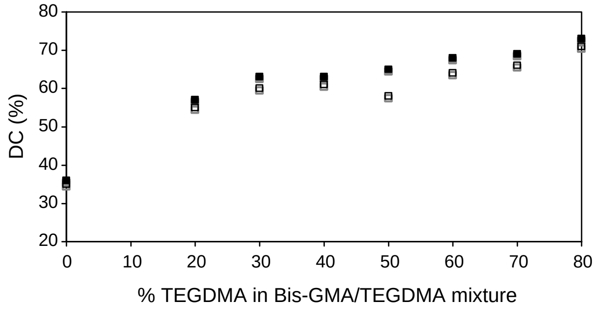

Figure 1 Comparison between DC measured at time=0 (□) and DC measured at time ≥24 h (■) for different percentages in TEGDMA in the investigated resin mixture. Values are average of three samples, except for B/T 20/80. (2 samples)

Table 1 shows all the data required to calculate the volume contraction with the specific masses of the uncured ($d_{unpolymerized}$) and the cured ($d_{polymerized}$) samples and to calculate the number of moles (M) of C=C polymerized per gram and per cm^3 with the initial number of mole of C=C bonds per gram and the conversion degree at 24 h after the polymerization.

The values of the contraction percentage have to be considered as 'free' volumetric shrinkage measurements (no residual forces).

Fig. 2 shows for each sample, the actual concentration of double bonds C=C converted into single ones (C-C) (in moles per cm^3) versus the corresponding volume shrinkage. Additional values, for Bis-GMA 100%, Bis-GMA/ TEGDMA 75/25; 50/50 and 25/75, were obtained beforehand from a pilot study. This graphic was thus obtained from 27 measurements. A linear correlation has been found between the volume contraction and the actual number of vinyl double bonds converted into single ones and a contraction of 20.39 cm^3 per mole of double bonds converted has been calculated.

Discussion

The extent of polymerization shrinkage depends, among other things, on the relative mobility, the molecular weight and functionality of the monomers. Comparing monomers of the same functionality (such as Bis-GMA and TEGDMA), polymerization shrinkage increases when initial molecular weight decreases [2,25]. Because of favorable stereochemistry, long-chain flexible TEGDMA exhibits a relatively high degree of conversion of the methacrylate double bonds. Due to the presence in the cross-linking section of a rigid and bulky bisphenol A moiety, aromatic monomer

Table 1 Unpolymerized ($d_{unpolymerized}$) and polymerized ($d_{polymerized}$) densities, volumetric contraction (%), initial number of mole (M) of C=C per gram (unpolymerized organic matrix), Degree of Conversion, number of mole (M) of C=C polymerized per gram and number of mole (M) of C=C polymerized per cm^3 for different weight percentage (w %) of monomers Bis-GMA and TEGDMA

Samples w/w	d unpolymerized	d polymerized (SD)	Contraction (%) (SD)	M.C=C init/g	DC (SD)	M.C=C poly/g (SD)	M.C=C poly/cm^3 (SD)
Bis-GMA 100	1.1735	1.2138 (0.0124)	3.31 (1.00)	0.00391	0.36 (0.02)	0.00142 (0.0001)	0.00172 (0.0001)
B/T 80/20	1.1526	(1.2226) (0.0067)	5.72 (0.52)	0.00452	0.57 (0.01)	0.00257 (0.00003)	0.00315 (0.00003)
B/T 70/30	1.1418	1.2276 (0.0094)	6.98 (0.71)	0.00483	0.63 (0.02)	0.00306 (0.00011)	0.00375 (0.00016)
B/T 60/40	1.1296	(1.2255) (0.0088)	7.82 (0.66)	0.00514	0.63 (0.03)	0.00325 (0.00015)	0.00399 (0.00021)
B/T 50/50	1.1205	(1.2322) (0.0048)	9.07 (0.36)	0.00545	0.65 (0.03)	0.00355 (0.00018)	0.00438 (0.00023)
B/T 40/60	1.1133	(1.2289) (0.0120)	9.39 (0.89)	0.00576	0.68 (0.08)	0.00390 (0.00045)	0.00480 (0.00060)
B/T 30/70	1.1043	(1.2273) (0.0170)	10.01 (1.25)	0.00607	0.69 (0.04)	0.00418 (0.00026)	0.00513 (0.00038)
B/T 20/80	1.0956	(1.2365) (0.0073)	11.40 (0.52)	0.00638	0.73 (0.01)	0.00465 (0.00006)	0.00575 (0.00010)

Three different samples were made for each (Bis-GMA/TEGDMA) blend (but B/T 20/80 only 2 samples due to fluorescence phenomenon). Each sample was observed in three different points on which DC values were averaged.

Bis-GMA is much more rigid [33]. Bis-GMA and TEGDMA, in their polymerized state, have a quite similar molecular weight. Since TEGDMA has a molecular weight, in its unpolymerized state, lower than Bis-GMA, many more covalent links are created during polymerization. In correspondence herewith, the degree of conversion and consequently the polymerization shrinkage increase with an increasing content of TEGDMA (Table 1) [31,38-40].

However, due to the molar mass difference between TEGDMA and Bis-GMA, the initial concentration of C=C moles is different for each ratio (Table 1). Thus, the degree of conversion does not allow a direct correlation with the contraction (Table 1). In this work, to take into account the molar mass difference, the shrinkage volume is related to the molar concentration of converted C=C (in mole/cm^3).

Conversion degree

To calculate this concentration, the DC has to be accurately measured. But as reported in a previous study [41], post-shrinkage occurs during 24 h after light curing and the DC values slightly change. As observed on the Fig. 1, a slight but significant difference is indeed observed between DC measured directly after the illumination of samples and DC measured 24 h after polymerization. The proposed explanation for this shrinkage is a physical phenomenon which consists of the decrease in the free volume trapped in samples during fast photopolymerization. This post-contraction creates a closer packing of the free radicals, which may then react and/or recombine. During this period, a decrease in free radical concentration and a slight but significant increase of the degree of conversion are observed [26].

In the mentioned study [26], volumetric changes were shown to stabilize after 24 h.

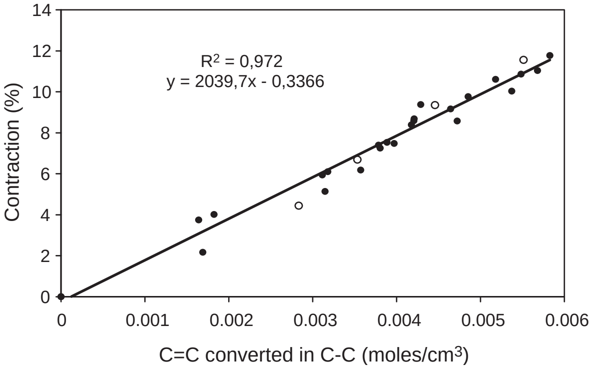

Figure 2 Evolution of the contraction related to the number of moles of C=C converted per cm^3 of sample. (○) Values are obtained from the pilot study and (●) values are obtained for each sample. (*)

As density column measurements need a few hours for equilibration, it was decided, in this study, to perform the calculations using both DC and specific masses measured after a stabilization period longer than 24 h.

Rate of contraction related to number of actual vinyl double bonds converted

As expected, contraction increases with an increasing percentage of TEGDMA (Table 1). But moreover, by observing the number of C=C in mole per cm^3 versus the volume contraction (Fig. 2) obtained from 27 measurements, an univocal relationship has been found. This proves that the contraction increases linearly with the number of double bonds converted and the slope of this straight line, which determines the contraction per mole of double bonds converted, was found to be 20.39 cm^3. This result differs from those calculated by Loshaek et al. [1] and Patel et al. [2] because they did not take in to account, in the calculation of this contraction, the incomplete DC obtained in glycol dimethacrylates. Moreover, for dental composites polymerization, which is stopped rapidly by the vitrification phenomenon [42], DC has to be included in the calculation because of its incompleteness. A plausible explanation for this difference is the assumption of Loshaek et al. and Patel et al. that the DC of polymethacrylate resins was always 100%.

Conclusion

Notwithstanding the efforts to develop new ('no-shrink') resins, the curing contraction, still remains, so far, inevitable and the practitioner has to 'live with' the problem of polymerization shrinkage and destructive shrinkage stress. Despite different clinical procedures to reduce their effects, there is nowadays no straightforward way of handling the adhesive restorative materials, which guarantees a leakproof restoration. As polymerization shrinkage arises mainly from the chemical reaction itself, palliative solutions are to be searched for. Only a proper understanding of what occurs during the chemical reaction will lead to finding solutions. The relationship between the number of C=C bonds converted in mole per cm^3 and the volume contraction helps in proposing solutions to the polymerization shrinkage problem. A reduction in the polymerization shrinkage due to the chemical reaction may obviously be expected from the addition of molecules permitting to decrease in the number of double bonds converted per unit volume of resin matrix, while maintaining the degree of conversion (of Bis-GMA and TEGDMA) and thus the mechanical properties. Such molecules must exhibit a volume as high as possible for a given number of vinyl bonds, which allows the molecules to be anchored in the network.

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