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Shrinkage behaviour of flowable resin-composites related to conversion and filler-fraction

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ABSTRACT

Objectives: To evaluate the shrinkage-strain, degree of conversion (DC) and percent filler of a range of flowable resin-composites.

Methods: Several commercially available flowable resin-composites were selected. The bonded-disk technique was used to measure shrinkage-strain kinetics. Measurements were obtained continuously for 60 min by irradiation for 40 s at 750 mW/cm² at two initial temperatures of 23 and 37 °C. Three repetitions ($n = 3$) were made at each temperature per material. The DC was measured by FTIR spectroscopy immediately post-cure. The percent filler was determined by combustion of specimens for 1 h at 400 °C.

Results: The final values of shrinkage-strain ranged from 2.61 to 6.25% at 23 °C and from 3.88 to 6.56% at 37 °C. Statistically significant differences ($p < 0.05$) were found in shrinkage-strain between the flowable resin-composites at both temperatures 23 and 37 °C. Significantly higher values were obtained at 37 °C ($p < 0.05$). A strong inverse correlation was found between the percent filler and the shrinkage-strain at 37 and 23 °C ($r^2 = 0.94$ and 0.87, respectively). No correlation was found between shrinkage-strain and DC ($p > 0.05$).

Conclusions: Flowable resin-composites vary widely in shrinkage-strain magnitude and the inverse relationship between filler percent and shrinkage-strain is explained by the corresponding decrease in volume fraction of monomers present to undergo polymerisation.

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1. Introduction

Restorative dentistry is experiencing a dynamic transition towards adhesive dentistry. A class of resin-composite systems, known as “flowable” composites, has become an integral part of the restorative process since they were first introduced in mid 1990’s. These restorative materials were developed in response to requests for easy handling properties.¹ They are characterized by either less filler loading or a greater proportion of diluent monomers in their composite formulation. They are designed to be less viscous, and so offer better adaptation to the internal cavity wall, easier insertion and greater elasticity than more highly viscous products.²

Flowability is regarded as a desirable handling property which allows the material to be injected through small gauge dispensers, thus simplifying the placement procedure and amplifying the possible range of clinical applications.³

Clinical applications of flowable materials have been critically reviewed by Bayne et al.,⁴ who examined their usefulness besides flow, after a preliminary screening of physical properties. The authors suggested that, since flowability seemed to be achieved mainly by lowering the filler concentration, the first generation flowable composites may shrink considerably more than current non-flowable composites. For the same reason, these resins can be expected to be less rigid than the conventional hybrids.

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The properties of resin-composites depend primarily on their material composition. Correlations between filler content and mechanical properties are established for modulus of elasticity; the higher the filler content, the higher the modulus and the greater the resistance to deformation. Conversely, the lower the filler content, the greater the expected polymerisation shrinkage and lower the ability to resist deformation.⁵

Dimensional stability of dental resin-composites is essential to the longevity and function of the restoration. Dental composites consisting of dimethacrylate resins filled with inorganic filler particles undergo volumetric shrinkage when cured.⁶ This shrinkage results in corresponding stresses which may cause mechanical failure at the composite/tooth interface, de-bonding, microleakage and secondary caries in addition to enamel fractures.^{7,8}

Significant differences in the polymerisation shrinkage exist among commercially available composite materials, depending on the resin formulation.⁹ The stress magnitude is dependent on C-factor, the ratio of bonded to free surfaces involved,^{10–12} on the material properties of the resin composite^{10,13,14} and on the amount of compliance of the substrate materials.^{15,16} Moreover, the kinetics of polymerization and network formation is dependent upon the wavelength, irradiation and duration of the initiating light, and especially upon the ambient and internal temperature levels produced during polymerization.¹⁷

Adequate polymerization is crucial in obtaining optimal physical properties and clinical performance of resin-composites.¹⁸ Ideally, a dental restorative resin might have all of its monomer converted to polymer during the polymerisation reaction. However, dimethacrylate monomers exhibit considerable residual C=C bonds in the final product, with degree of conversion ranging from 55 to 75% under conventional irradiation conditions.¹⁹ The final degree of conversion depends on the chemical structure of the methacrylate monomer and the polymerization conditions, such as temperature and light intensity.²⁰

However, the behaviour of flowable composites varies greatly, amongst the wide range of products now available, with a wide range of apparent viscosity.²¹

The aim of this study was to determine the shrinkage-strain of a range of commercially available flowable resin-composites in relation to the filler-fraction and the DC of these materials. The specific objectives were to measure: (i) shrinkage-strain at 23 and 37 °C, (ii) DC at 23 °C and (iii) filler percentage by weight.

The null hypotheses were (1) the shrinkage-strain values will not be dependent on the filler-fraction of the material and (2) there is no correlation between shrinkage-strain values and the DC of the flowable composite materials.

2. Materials and methods

Seven commercially available flowable resin-composites were selected for this study (Table 1).

The bonded-disk technique was used to measure polymerization shrinkage-strain kinetics. This apparatus was developed by Watts and Cash^{22,23} with further modification by these authors to allow resin specimens to be environmentally heated to maintain a steady temperature throughout each test cycle, so that resin cure kinetics at different temperature could be determined. A disk-shaped specimen (7 mm × 1.5 mm) was placed at the centre of a square cross-section circular brass ring acting as a spacer of internal diameter 16 mm and height 1.0 mm. This ring was adhesively bonded onto a rigid glass plate, 74 mm × 25 mm × 3 mm. The top edge of the ring and disc specimen were covered by a flexible 22 mm square cover-slip, thickness 0.1 mm (type 0, Chance-Propper Ltd., Warley, UK). The tip of a dental curing light was positioned underneath and in close proximity of the glass plate, so that light-cure could be achieved by irradiating from below, through the glass.

A LVDT (linear variable displacement transducer) measuring system was positioned centrally onto the cover slip. Following thermal and mechanical equilibration, measurement runs were made by irradiation for 40 s at 750 mW/cm² at either 23 or 37 °C. Measurements were for 60 min from photoinitiation (*n* = 3 per material at each temperature).

The DC of the investigated flowable composites was measured by FTIR spectroscopy. A small amount of each material was placed between two translucent polyethylene strips which were compressed hard between two plastic blocks to produce a very thin film (40–70 µm) of the material. Each material was then polymerised (*n* = 3), by irradiation at 23 °C. FTIR spectra of the thin films of uncured and cured material were recorded in transmission, on an FTIR spectrometer (Avatar 360, Nicolet Analytical Instruments, UK) operating under the following conditions: 2000–550 cm⁻¹ wavelength; 4 cm⁻¹ resolution; 16 scans co-addition. The DC was measured 10 min after curing and calculated using the ratios of two peaks (C=C stretch of 1638 cm⁻¹ analytical frequency and C=C stretch at 1608 cm⁻¹ reference frequency). The peak intensities as ratios of the uncured and cured material were calculated, and the DC was expressed in percentage relative to the uncured state.

The percent filler for each flowable composite was determined by combustion of the test specimens for 1 h at 400 °C. Before and after combustion, the weights of the specimens were measured with a precision balance (E400D, Ohaus, Pine Brook, USA, accuracy = 0.1 mg).

Table 1 – Flowable composites: codes and sources

Flowable composites	Code	Batch number	Manufacturer
Revolution Formula 2	RF	3-1190	Kerr, Avenue Orange, USA
X-Flow	XF	0404000035	Dentsply York, USA
Admira Flow	AF	440530	Voco, Cuxhaven, Germany
Filtek Flow	FF	3EP	3M ESPE, Seefeld, Germany
Tetric Flow	TF	F47540	Ivoclar Vivadent, Schaan, Liechtenstein
Grandio Flow	GF	361443	Voco, Cuxhaven, Germany
Point 4 Flowable	PF	305A23	Kerr, Avenue Orange, USA

Fig. 1 – Time-dependence of shrinkage-strain for Point 4 Flowable at 23 and 37 °C.

Fig. 2 – Time-dependence of shrinkage-strain for X-Flow at 23 and 37 °C.

All data were analyzed by one-way ANOVA SPSS (Version 11.5, SPSS Inc., USA) software package, with Student–Newman–Keuls post hoc test at the $\alpha = 0.05$ level. A paired t-test was also used to differentiate statistically between the shrinkage-strain data at 23 and 37 °C.

3. Results

Mean final values and standard deviations of polymerisation shrinkage-strain are presented in Table 2. These ranged from 2.61 to 6.25% at 23 °C and from 3.88 to 6.56 at 37 °C. Figs. 1 and 2 show the shrinkage-strain kinetics of Point 4 Flowable and X-Flow, respectively, at both temperatures. Statistically significant differences ($p < 0.05$), were found in final shrinkage-strain between the flowable composites at both temperatures. Higher shrinkage-strain values for all materials were obtained at 37 °C. The Student–Newman–Keuls post hoc test applied to each material showed that Point 4 Flowable, Grandio Flow and Tetric Flow had lower shrinkage-strains than the other flowable composites with statistically significant differences.

The filler percentages of the flowable composites determined by combustion ranged from 54.5 wt.% for Revolution Formula 2 to 71.3 wt.% for Point 4 Flowable (Table 2). The highest filler percent flowable composites resulted in the lowest shrinkage-strains. A correlation was found between the percent filler and the polymerisation shrinkage-strain for

both temperatures ($r^2 = 0.94$) and ($r^2 = 0.87$) for 37 and 23 °C, respectively (Fig. 3).

No correlation was found between shrinkage-strain and the DC of the flowable composites ($p > 0.05$). A statistically significant difference in DC at 23 °C was found between the composites ($p < 0.05$) with DC ranging from 67.68% for Point 4 Flowable to 60.49% for Filtek Flow (Fig. 4).

4. Discussion

A range of new flowable resin-composites of different composition was used in this study. Measurements of shrinkage-strain, at two temperatures, together with DC and filler percentage of these flowable composites were achieved using established methods.

The final shrinkage-strain values, ranging from 2.61 to 6.25% at 23 °C, are in broad agreement with previous results.^{3,4,24,25} Flowable composites exhibit generally higher shrinkage-strains than conventional composites,³ as expected from their lower filler loading. Point 4 Flowable demonstrated the lowest shrinkage-strain and Revolution Formula 2 showed the highest shrinkage value. This conforms with the idea that high filler loading reduces shrinkage-strain and can explain the range of values between the flowable resin-composites, together with the strong correlation between the shrinkage-strain and the filler content (Fig. 3). At high filler loadings the

Table 2 – Final mean percentage shrinkage-strains of flowable resin-composites after 60 min, irradiated at 23 and 37 °C

Flowable composites	Percent filler (wt.%) by manufacturers	Percent filler (wt.%) by combustion	Mean strain (%) at 23 °C (S.D.)	Mean strain (%) at 37 °C (S.D.)
RF	60.0	54.5 (0.97)	6.25 (0.53)	6.56 (0.29)
XF	60.0	60.6 (0.56)	5.92 (0.21)	6.10 (0.37)
AF	64.0	63.7 (0.78)	5.52 (0.15)	5.70 (0.06)
FF	68.0	65.7 (0.86)	4.62 (0.52)	4.93 (0.44)
TF	68.1	67.5 (0.32)	4.13 (0.13)	4.69 (0.27)
GF	80.2	70.8 (0.70)	3.57 (0.17)	3.88 (0.26)
PF	70.0	71.3 (0.57)	2.61 (0.65)	4.21 (0.42)

Percent filler of these resin-composites obtained by combustion and manufacturers.

Fig. 3 – Correlation between mean shrinkage-strain maxima after 60 min at 23 and 37 °C and percent filler for the flowable resin-composites.

plot tended to become curvilinear, which could by extrapolation express the possibility of zero shrinkage. Thus, the first hypothesis was rejected.

The higher shrinkage-strains of flowable resin-composites obviously relate to their resin content, and possibly also to the chemical nature of their resin and specific DC.²⁶ Flowables have a high proportion of monomers in the formulation of the composite paste, particularly a large amount of a diluent monomer, commonly TEGDMA, added to a bulkier and structurally rigid base monomer, such as Bis-GMA or UDMA to reduce the viscosity.²⁷ The number of polymerised double bonds increases with decreasing molecular weight of the monomers, such as TEGDMA. Therefore, the total shrinkage of the resin increases as TEGDMA percentage increases.^{28,29}

When the temperature was increased to 37 °C, the shrinkage-strain also increased. The effect of the increased temperature on shrinkage-strain values could be due to an increase in the network conversion of resin monomer. Due to the enhanced thermal mobility of the reacting network leading to an enhanced network of C–C bonds, the shrinkage-strain increases with temperature.^{23,30} When resin-composites are placed in dental cavities, the temperature will rise towards 37 °C at a rate normally governed by their thermal

diffusivity. Practically, it usually takes 1–2 min to place a resin composite in a dental cavity prior to irradiation. Hence, the materials may be irradiated clinically at temperatures anywhere between 23 and 37 °C. If the resin-composites were pre-refrigerated, the temperature could stay close to 23 °C.

In the present study, the percent filler content of flowable composite was investigated by combustion technique. This technique is based on elimination of the organic fraction of a resin-composite by heating at a constant temperature. Different temperatures have been previously used. Kim et al.³¹ ashed the composites at 600 °C during 30 min, while Chung and Greener³² used 700 °C to ash the materials. In this study, they were ashed for 60 min at 400 °C and the numbers obtained were similar to those provided by the manufacturers except for Grandio Flow and Revolution Formula 2. A reasonable explanation could be that the manufacturers' treat the filler–matrix interface according to their own original methods and used different ways of calculation of the percentage of fillers. Some manufacturers might calculate the percentage of fillers before the silanization process while others might include the percentage of silane coating in their calculations. For Grandio Flow, the nature of nanofillers might have contributed in them escaping during ashing with the organic fraction.

The DC values were obtained by a thin film transmission techniques. There are several methods to determine DC. Fourier transformation infrared spectroscopy (FTIR) has been proven to be a powerful technique and has been widely used as a reliable method.^{20,33,34} Even though there are several factors affecting the DC of resin-composites, the differences in the DC values observed here could be related to the differences in the resin matrix composition of these materials. DC increases when TEGDMA increases, up to a certain point. Flowable composite materials often have a greater proportion of TEGDMA which does not usually reach that critical TEGDMA concentration where primary cyclisation may be prevalent, due to high chain mobility, which may limit conversion. Generally, the higher the conversion in resin-composites, the higher the shrinkage.¹⁹ However, in the present work, no correlation was found between the DC and shrinkage-strain of flowable resin-composites. The second null hypothesis was rejected. It appears that the influence of filler loading on shrinkage-strain is the over-riding factor. Evidently, the correlation between DC and shrinkage-strain of flowable resin-composites is material-dependent and cannot be generalised to all flowable resin-composites. Moreover, shrinkage-strain and DC were tested, due to the nature of the experiments, using different sample thicknesses which may affect the correlation between shrinkage-strain and DC. The correlation of DC and shrinkage-strain might also be affected by particle size and shape and resultant elastic modulus.

A significant difference in shrinkage-strain between 37 and 23 °C was noticed with Point 4 Flowable compared with Filtek Flow. This could be attributed to the differences in composition of these materials. In addition to Bis-GMA and TEGDMA Filtek Flow contains a dimethacrylate polymer that modifies the rheology of the material and may influence the effect of temperature on the network conversion and thus the shrinkage-strain.

Fig. 4 – DC (%) at 23 °C for the flowable resin-composites.

5. Conclusion

The polymerisation shrinkage-strain of flowable composites should be taken into consideration in combination with their filler-fraction, which highly influences their shrinkage behaviour. Lower filler loading flowables, such as Revolution Formula 2 and X-Flow, are more likely to be highly fluid materials. Even though these materials exhibited substantial polymerisation shrinkage, they might be successfully used in micro-conservative occlusal cavities, as the consequences of polymerisation shrinkage would be low because of the limited volume of the material used.

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