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Polymerisation Shrinkage of Luting Agents for Crown and Bridge Cementation

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Abstract - *The volumetric contraction of a variety of luting agents, including Panavia 21, All-Bond C&B Cement, Superbond., Variolink and zinc phosphate cement, was assessed and compared using a minimal transducer. The contraction among the materials tested was determined from the post-gel linear displacement of a deflecting coverslip resting on 4 silicone rubber spacers between which a mixed material was centrally located. Finally, the rate and duration of shrinkage over a period of 60 minutes from the moment of rigid contraction for all materials were investigated, and the final shrinkage values among the materials tested were compared. The analysis of variance showed that there were highly significant differences (P< 0.001) between the materials and the mean of each group was significantly different from that of any of the other groups (Tukey's test). Superbond produced the highest values of the final polymerisation shrinkage, followed by All bond C&B, Variolink, Panavia 21 and zinc phosphate cement respectively. Also, there was a marked variation in the overall magnitude of shrinkage (from 1.34 % to 4.62 %) among the materials tested. The method used to measure the polymerisation shrinkage in the present study was shown to be a precise measure in that it produced consistent and reproducible results. It can also offer the ability to observe the development of polymerisation shrinkage against time, during the post-gelation phase, for a range of chemically-cured resin materials.*

KEY WORDS: Cementation, Shrinkage, Luting, Crown

INTRODUCTION

Traditionally, zinc phosphate cement has been the most popular cement for crown and bridge cementation, despite it well documentation disadvantages, particularly solubility and lack of adhesion. The advent of adhesive resin materials in modern dentistry can allow for crown and bridge procedures which are not possible with traditional cements, such as zinc phosphate, for example, when the crown is short or the prepared tooth is overtapered.

All available resin-based dental luting agents undergo some degree of polymerization contraction during setting, which varies from one material to another.

Reports have shown that adhesive and composite resin luting agents shrink considerably during setting and this may potentially contribute towards stress development (Davidson and Feilzer, 1997). A high shrinkage may imply a high stress, which is considered as a significant factor in destabilising the formation of adhesive bonds between a cast restoration and tooth structure (Verzijden et al., 1992). The effect of shrinkage on the interface between the resin and the substrate depends upon the balance between the force of adhesion and the force of contraction (Asmussen and Jorgensen, 1972).

The more the composite resin shrinks during polymerisation, the greater are the tensile stresses at the interface. Therefore, in clinical bridgework, the bond must develop rapidly, and be greater at all times than the tensile stresses that accompany polymerisation, in order to prevent disruption of the adhesion (Jensen and Chan, 1985). In addition, marginal leakage and early failure (Bowen et al., 1983; Davidson et al., 1984; Verziiden et al., 1992), or cracking of the enamel (Jorgensen et al., 1975), will also be prevented.

Many improvements have been made to improve the clinical performance of resins. Even so, it is apparent that problems related to polymerisation shrinkage still exist when adhesive resins are used for bonding a cast restoration to tooth structure (Davidson and Feilzer, 1997).

Recently, adhesive resin luting agents, such as Panavia 21, Superbond and All Bond C&B cement have been introduced for crown and bridge cementation.

Hence, the purpose of this present study was to determine the volumetric contraction of a variety of commercially available adhesive resin luting materials, in addition to zinc phosphate cement as a control, during the post-gelation phases.

MATERIALS AND METHODS

The materials used in this study are given in Table 1. The apparatus used to measure polymerisation contraction (Fig. 1) was a modification (Walls et al., 1988) of that described by Wilson (1978). The modified apparatus has the advantage in that it can measure the volumetric shrinkage from the start of rigid contraction, which is of clinical significance.

It consists of a Mikrokator stand and linear variable displacement transducer connected to a chart recorder. The dimensional change was measured using a minimal load

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Table 1. *Materials used for testing the shrinkage*

Material	*Composition*	*Bat. No*	*Mixing Time (sec)*	*Manufacturer's Working Time (s)*
All Bond C&B Cement	BIS-GMA self-cured Luting composite and Quartz filler	029045	15	165
Superbond	Monomer (liquid): MMA, 4-META Polymer (powder): PMMA Catalyst: TBB	41163	10	
Panavia 21	MDP monomer, Catalyst, Inorganic Fillers	60802	30	240
Variolink	Dimethacrylate, Fine Particle Glass filler	728484 Base 730346 Catalyst	10	> 200
Zinc phosphate Cement	Powder: zinc oxide + Magnesium oxide Liquid: phosphoric Acid	9509151 (powder) 9509180 (liquid)	90	150

There is no working time recommended for Superbond.
BIS-GMA: Bis-phenol glycidyl methacrylate; MMA: methyl-methacrylate; 4-META: methacryoxyethyle trimellitate anhydride; PMMA: polymethyle-methacrylate; TBB: tri-n-butyl borane; MDP: methacryloyloxydecyl dihydrogen phosphate.

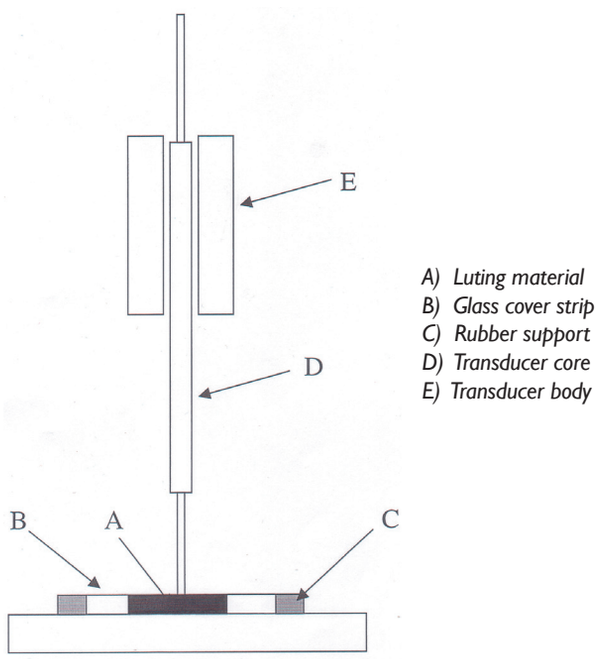


Figure 1. *The apparatus used to measure polymerisation contraction*

transducer (Sangamo Weston NDI, Bognor Regis, UK). The core of the transducer was suspended with fine monofilament polyamide so that it did not touch the walls of the transducer. A length of glass capillary tubing was attached to the pendent end of the transducer core. The position of the core was adjusted within the transducer to produce a linear output.

The set-up was then calibrated by raising and lowering the platform of the Mikrocator stand in increments of 10 µm over a range of 60 µm (as indicated by the Mikrocator gauge) and noting the corresponding value of output from the transducer as indicated on the pen recorder.

The test specimens were prepared by placing 4 sections of silicone rubber as spacers on the surface of a clean microscope slide. These rubbers were used to support the coverslip when it was placed over the mixed material.

Immediately before starting the mixing, the chart drive was switched on and left to run, and a level line was drawn on the chart in order to calculate an equal time elapsed between the end of mixing and the start of measurement on each occasion. All materials under test were mixed according to the manufacturer's instructions. Batch numbers of 9509151/9509180 (Powder/liquid), 730346/728484 (Catalyst/ base), 029045, 41163 and 60802 were recorded for zinc phosphate cement, Variolink, All Bond C&B Cement, Panavia 21 and Superbond respectively.

Each time before the start of measurement, an equal amount of a mixed material (1 ml) was syringed and placed centrally between the rubber spacers and covered with a glass coverslip which was then pressed gently into place, until it was in even contact with the spacers. For Panavia 21, Oxygard was placed on the periphery of the glass slide immediately before the application of the mixed cement to exclude air during setting. In order to simulate clinical crown and bridge situations, Variolink, which is a dual cure resin, was not light activated.

The specimen was placed upon the table of the mikrocator and the tip of the transducer core was positioned to touch the surface of the coverslip overlying the material under test. The location of the component was adjusted so that any movement of the coverslip, caused by dimensional change of the material under test, gave a response from the transducer within its linear response range.

Having placed the material in position and adjusted the pen on the chart recorder to zero, the chart drive was activated. The chart was allowed to run until the pen had become stable for a period of time indicating the completion of polymerisation. The material was removed from the coverslip and the percentage of shrinkage was calculated using a micrometer as follows:

$$\text{Percentage of shrinkage (\%)} = \frac{S \times 100}{R + S}$$

S = the amount of shrinkage
R = the residual thickness of the test material

This procedure was repeated on five occasions for each material. All experiments were carried out under the same conditions and performed at a room temperature of 22 °C.

The final overall shrinkage obtained were subjected to a one-way analysis of variance (ANOVA) and Tukey's pairwise comparisons testing using the Minitab Statistic Computing Package. The Tukey test was used to provide confidence intervals for all pairwise comparisons between mean values for all groups tested in this study. Test results at the level of P> 0.05 were regarded as non-significant.

RESULTS

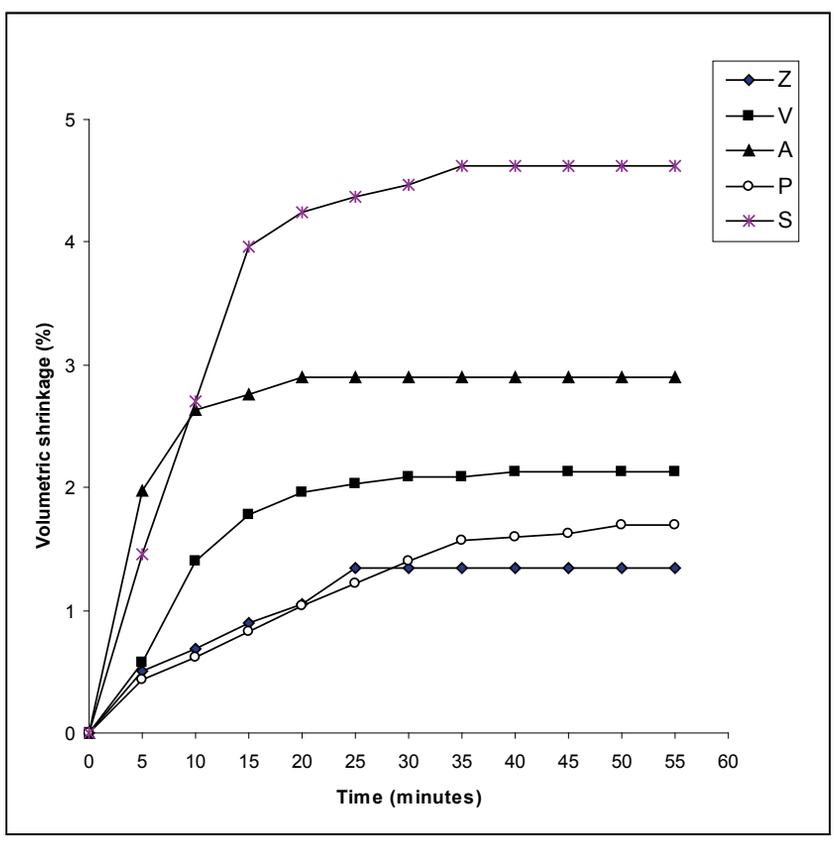
The mean and standard deviations of the final volumetric shrinkage values for all materials tested are given in Table 2. The rate and duration of shrinkage over a period of 60 minutes from the moment of rigid contraction for all materials tested are presented in Figure 2. The analysis of variance showed that there were highly significant differences (P< 0.001) between the materials (Table 2). Evaluation by the Tukey comparison test revealed that the mean of each group was significantly different from that of any of the other groups (Table 2.). There was a marked variation in the overall magnitude of shrinkage (from 1.34 % to 4.62 %) among the materials tested.

The zero time presented in Figure 2 is the time at which shrinkage was detectable as a consequence of movement of the coverslip. This time was different from one material to another. Representative shrinkage/time data presented in Figure 2 show that the rate of shrinkage during the first 5 and 15 minutes for All Bond C&B Cement and Superbond was markedly more rapid than that for the other materials. The rates of setting contraction during the first 25 minutes of the start of measurement of shrinkage were similar for zinc phosphate and Panavia 21. The Panavia 21 continued to shrink for a further 25 minutes while the zinc phosphate cement was dimensionally stable during this time. The shape of the shrinkage/time curve for Variolink is intermediate between All Bond C&B Cement and zinc phosphate in the first 25 minutes, before the latter is set and the contraction of Panavia 21 continues.

Table 2. *Final Shrinkage Values for all Materials Tested*

Material	*Mean (%)*	*SD*
Zinc phosphate cement	1.34	0.09
Panavia 21	1.69	0.06
Variolink	2.13	0.16
All Bond C&B Cement	2.90	0.06
Superbond	4.62	0.15

All mean values are significantly different from each other (P<001, ANOVA and Tukey test).



Z: Zinc phosphate cement;V:Variolink;A:All Bond C&B cement; P: Panavia 21; S: Superbond

Figure 2.

DISCUSSION

The curing contraction is usually determined linearly (Walls et al., 1988; Feilzer et al., 1989; Watts and Cash, 1991; de Gee et al., 1993). Due to the specimen geometry, however, volumetric contraction in the present study was determined from the "post-gel" linear displacement of a deflecting coverslip resting on 4 rubber spacers between which a mixed material was centrally located. The linear contraction in the current experiment was approximately equivalent to the volumetric shrinkage of the tested material because most of the shrinkage was confined to one dimension (e.g. high C factor). The coverslip will only move when the material can no longer provide viscous or plastic flow to compensate for the curing contraction. In other words, it could only monitor the "post gel" part of the curing contraction, when the material was sufficiently rigid to exert force (Davidson and Feilzer, 1997).

It should be noted that the times between the start of mixing and the commencement of the measurement of the shrinkage were different among the materials tested. These differences are due to factors include the mixing time and the rheological characteristics of the material tested, in additional to the movement of the upper coverslip before it is completely adapted to the rubber spacers.

The method used to measure the polymerisation shrinkage in the present study was shown to be a precise measure in that it produced consistent and reproducible results. It can also offer the ability to observe the development of polymerisation shrinkage against time, during the post-gelation phase, for a range of chemically-cured resin materials. A similar finding was also found by Walls and other workers (1988) when they used the same apparatus to monitor the polymerisation contraction of a range of visible-light activated composite resins.

Many parameters determine polymerisation shrinkage of the resins, including the molecular weight of the monomer, its amount and its degree of conversion, filler loading and the nature of the resin undergoing polymerisation (Walls et al., 1988). Thus, the shrinkages of a range of various luting resins are liable to be different due to the differences in their formulation and the degree of conversion. Although minimal shrinkage is desirable, it is difficult to define an acceptable level of shrinkage. Therefore, the results can only be used to compare the shrinkage behaviour of materials in order to predict which materials may be most suitable for clinical use, assuming that a lower shrinkage is preferable.

Although several adhesive resin luting agents, such as Panavia 21, Superbond and All Bond C&B Cement have been introduced for bonding cast restorations to abutment teeth, the quantitative data concerning the shrinkage characteristic of these adhesives are scarce. Zinc phosphate cement was included in the study because it has been used clinically for many years and shrinkage has not been reported as a significant problem for this material.

When the physical properties of Panavia 21 were compared with those of Panavia Ex, Kondo and Yamashita (1992) found that the former produces lower polymerisation contraction values (1.86%) than the latter (2.30%).

Generally, the values of the reported volumetric shrinkage of resin cements range between 3% and 8% (Schouboe et al., 1956) compared to those between 2% and 4% reported for composite resins (O'Brien, 1997). In the present study, the values of the final shrinkage for all materials tested are in the range 1.34% and 4.62%.

Although shrinkage stress takes place during both pre- and post-gel phases, it is clinically significant only after measurable stiffness develops (Sakaguchi et al., 1997). The shrinkage/time tests (see the Figure) showed that the rate and duration of the shrinkage, which occurs during setting, is different form one material to another. For example, All-Bond C&B Cement, zinc phosphate cement, Superbond, Variolink and Panavia 21 reached their final shrinkage, at the time 20, 25, 35, 40 and 50 minutes respectively. In addition, the initial slope of the shrinkage/time during the first 5 minutes was steeper for Superbond and All Bond C&B Cement than for any of the other materials tested. After 5 minutes, all materials exhibited similar behaviour, with the exception of Superbond for which shrinkage remained rapid for further 10 minutes before gradually reducing. Further observation noted that most of the shrinkage of the luting resins tested developed within the first 15 minutes of the post-gelation period, except for Panavia 21. The Figure also showed that zinc phosphate, Panavia 21, and to a lesser extent, Variolink demonstrated a relatively long duration of a gradual increasing and a low amount of shrinkage within the group of luting resins tested. All materials tested, however, showed significantly different shrinkage values.

The rapid initial polymerisation shrinkage and the highest final volumetric shrinkage produced by Superbond is most probably due to the nature of the setting reaction produced by methacrylate-based resins (see the average values of volumetric contraction of resin cements reported above by Schouboe et al. (1956) as opposed to dimethacrylate resin systems in the other resin-based materials). The absence of the filler content in the component of Superbond could be another factor. On the other hand, the filler type and loading, the initiating system and/or the catalyst systems and the degree of conversion of the monomers may be the reasons for the differences in the shrinkage among the materials tested.

In crown and bridgework, the configuration of the crown is an important factor regarding the contraction stress. According to Feilzer et al. (1989), contraction stress is more likely to accumulate with crown cementation that is highly restrained by the axial walls of the preparation (the C factor is high). This will result in the reduction of the flow capacity of the material (Davidson et al., 1984). Consequently, the setting stress may be detrimental to the integrity of the adhesive joint, and this can lead to restoration failure if the stress exceeds the adhesive or cohesive failure of the setting material (Verzijden et al., 1992).

In order to avoid such a problem, the luting agent should possess a high bond strength, low shrinkage and good flow capacity. The gradual absorption of a substantial amount of water would also help to lessen the stress, due to its contribution to the relaxation of stress developing in the final setting (Feilzer et al., 1988). Obviously, this can only be a benefit if the material has a bond strength adequate to resist the initial shrinkage stress. If marginal breakdown has occurred, the margin has the potential to leak irrespective of the hydroscopic expansion. Elastic modulus of the

shrinking material was also found to be a factor on which shrinkage stresses depend, because this property increases as the polymerisation reaction proceeds (Feilzer et al., 1990a). Furthermore, visco-elastic characteristics have also been shown to be associated with lower interfacial stress build-up during the setting shrinkage of the resin (Feilzer et al., 1990b). The thickness of the adhesive resin layer may have a significant effect in reducing the stress as well (Alster et al., 1995). This suggests that many factors in addition to the shrinkage property should be considered when selecting an adhesive material for crown and bridge cementation.

With the exception of All Bond C&B Cement and Superbond during the first 5 and 15 minutes respectively, the shrinkage of all materials occurred slowly. The slow development of shrinkage is of clinical significance. This is because it allows time for a proper bond to form between the lute and the tooth/ metal surfaces before the developing shrinkage stress is built up between the curing resin and its substrate. For this reason, the cast restoration may be able to resist the contraction force and subsequent tensile stress under the restriction condition during polymerisation.

Although Superbond produced the greatest rate and amount of polymerisation shrinkage (see Table 2), the reports in terms of its bond strength to various substrates have been promising. These reports have shown that Superbond is capable of providing satisfactory bond strength for the survival of the crowns and bridges, when bonded to Ni-Cr (Salonga et al., 1994) and Gold (Yoshida and Atsuta (1997). This is because most of the reported values of the bond strength reported for Superbond are above the minimum value (16.8 MPa) required for preventing the formation of gaps between the resin and its substrates (Munksgaard and Asmussen, 1985). These gaps are resulted from the stresses induced by the polymerisation shrinkage of the resin (Davidson et al., 1984).

Further reports have demonstrated that unfilled low-stiffness adhesives, such as Superbond, in thick layers, may have sufficient flexibility to compensate for the stress that would otherwise exceeds the bond strength (Kemp-Scholte and Davidson, 1990; Van Meerbeek et al., 1993).

On the other hand, Panavia 21 showed the slowest and the longest setting mechanism among the adhesives tested. This characteristic renders this adhesive the most suitable material for bridgework, because it would help to reduce clinical shrinkage and consequently contraction stress, particularly when the restoration is highly restricted. In such a situation, the behaviour of Variolink is an improvement upon Superbond and All-Bond C&B Cement, but it does not meet the same standard as Panavia 21or zinc phosphate, because its steady growth shrinkage curve is much higher.

Based on the results of the current study, the test materials can be divided into materials with high, medium and lower shrinkage. Panavia 21 and zinc phosphate cement gave the lowest shrinkage, whereas Variolink and All Bond C&B Cement gave intermediate shrinkage and highest shrinkage was produced by Superbond.

Clinical Significance

The findings of the present study have shown that Superbond produced the highest values of the final polymerisation shrinkage followed by All Bond C&B Cement, Variolink, Panavia and zinc phosphate cement respectively. However, one must be careful not to select materials for clinical bridgework solely on their contraction behaviour. This is because the significance of high or low polymerisation contraction is dependent on many factors that are of significance for the success of the clinical bridgework. For example, materials with higher filler loading might demonstrate lower contraction but these materials will also have a higher elastic modulus which can result in a higher contraction stress. Therefore, the criterion of the selection of the material for clinical bridgework requires the understanding of many characteristics.

CONCLUSION

- The method used provided a convenient way to measure the polymerisation shrinkage of a range of luting agents.
- The extent of the curing contraction during the polymerisation process is dependent on the characteristics of the individual material.
- The results demonstrated large variations in the final shrinkage values among the materials tested and all these values were significantly different from one another. Therefore, substantial differences in the clinical performance may be expected when any they are selected for crown cementation.
- The results demonstrated large variations in the final shrinkage values among the materials tested and all these values were significantly different from one another. Such variations should be considered, in addition to other properties, when selecting any of the materials tested for luting in crown and bridgework.
- In clinical bridgework, the potential for a significant increase in contraction stress, when Variolink or All Bond C&B Cement are used, may be less than for Superbond, but, not than for Panavia 21 or zinc phosphate cement.

MANUFACTURER'S DETAILS

- Zinc Phosphate cement - Dentsply De-Trey GmbH, Konstanz, Germany
- Panavia 21 - Kuraray Co. Osaka, Japan
- Variolink - Vivadent Ets. Schann, Liechtenstein
- All Bond Crown and Bridge - Bisco Inc., Itasca, Illinois, USA
- Superbond - Sun Medical Co. Kyoto, Japan

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