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Thermal expansion of composites

J. F. McCABE, R. W. WASSELL
Dental Materials Science Unit, Department of Restorative Dentistry, University of Newcastle upon Tyne, NE2 4BW, UK

Coefficient of thermal expansion (CTE) has been determined for selected composite materials using differential thermal analysis. Variables evaluated were: type of material, with particular emphasis on filler content; annealing; thermal history, with particular attention being payed to the effects of multiple heating and cooling cycles; ageing in wet or dry conditions. Filler content was a major factor involved in controlling CTE, although clearly other factors such as the type of filler, resin and degree of conversion are important. For an inlay material, annealing at 120 °C significantly reduced the value of coefficient of thermal expansion and this is most likely due to an increase in conversion of methacrylate groups. The findings of this study confirm those of previous studies regarding the reduction in CTE following an initial heating. This is most likely due to the relief of internal stress. New information reported here relates to the fact that stress release can occur slowly without heating and that rapid stress release can be achieved through water storage at mouth temperature. These results suggest that, clinically, internal stresses induced by polymerization will be dissipated rapidly. A further finding was that long-term water storage causes an increase in CTE, which may reflect changes at the resin–filler interface.

1. Introduction

Coefficient of thermal expansion (CTE) is recognized as being a clinically significant property for restorative dental materials. It is generally accepted that one of the main reasons for incorporating inert fillers into a resin when making composites is to lower the value of CTE to a level closer to that of the tooth substance. In this regard it has been shown [1] that CTE varies linearly with filler volume fraction and that composites with higher filler content are less susceptible to microleakage than products with low filler content [2]. Another factor which may affect the value of CTE is the degree of conversion of methacrylate groups, as this controls chain mobility. The introduction of commercially available composite inlay systems has resulted in the development of methods for subjecting composites to post-curing or annealing and since such treatments are known to increase the degree of conversion of methacrylate groups [3] it would be of interest to determine the effects of such treatments on CTE. Other work [4] suggests that CTE values should be sensitive to changes at the resin–filler interface. Information of this sort may prove valuable in relating microscopic changes in structure to clinical performance. It was the aim of this work therefore to measure values of CTE of a carefully selected range of composites and an unfilled resin and to determine the effect of thermal history, annealing and ageing in both wet and dry conditions upon this value. The hypotheses to be tested were as follows:

1. That increasing conversion by annealing can reduce the value of CTE.
2. That water absorption increases CTE by increasing chain mobility.
3. That CTE is independent of thermal history and therefore the same value of CTE would be determined for consecutive heating/cooling cycles.

2. Materials and methods

Four materials were used in the study. Three were composites and one was an unfilled resin. All four materials were based upon a BisGMA resin system. Details of the materials including filler content, which was determined by ashing, are given in Table I. Brilliant Dentin is used in the 'composite inlay' technique, during which the material is subjected to heat/light treatment (annealing). This material was therefore tested in both the pre- and post-annealing states.

Cylindrical test specimens were prepared in stainless steel moulds (6 mm × 4 mm diameter). The materials were packed into the mould and cured through a layer of Mylar matrix at each end for 1 min using

TABLE I Materials used

Product	Code	Supplier	Filler content (wt %)
Silux Plus	S	3M (UK)	55.7
Z100	Z	3M (UK)	79.4
Brilliant Dentin	B	Coltene (Switzerland)	73.2
Concise white sealant	C	3M (UK)	0

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a Visilux II curing unit (3M UK). After removal from the mould, each specimen was subjected to a further 1 min of exposure to activating radiation around the 'waist' area in order to ensure optimum polymerization.

Annealing of Brilliant Dentin was performed using a Coltene DI 500 oven (Coltene AG, Switzerland). This subjected the specimens to a temperature of 120 °C in the presence of intense white light for 7 min.

Specimens were stored dry at room temperature or wet at 37 °C. Some specimens were tested after 24 h storage while others were stored for 30 days (wet or dry) before testing. Five test specimens of each material were used to evaluate each of the test variables.

Determination of CTE was made using a thermal mechanical analyser (TMA, Stanton Redcroft, UK). The test specimen is placed in the instrument between an outer quartz jacket and an inner quartz rod. The rod is part of a balanced beam assembly which is used to minimize the load on the specimen during testing (1 g). The rod is connected to a displacement transducer which enables measurements of expansion to be made and recorded. The whole assembly is surrounded by a furnace capable of maintaining temperature at + / − 0.1 °C. Each specimen was subjected to five cycles of heating from 20 °C to 70 °C at 10 °C min^{-1}, followed by cooling to 20 °C again over a period of 10 min using a stream of compressed air. A separate value of CTE was calculated for each cycle. Five such specimens were tested for each material/age combination. The output of the TMA transducer was recorded as two traces on a chart recorder; one of temperature against time, the other of expansion against time. The maximum slope of each line was calculated and the CTE was computed as the ratio of the two slopes divided by the original specimen length as recorded using a micrometer.

The TMA equipment was calibrated using cylindrical samples of copper (99.99% pure) for which CTE is accurately known.

Data were analysed using ANOVA or Student's *t*-test as appropriate.

3. Results

In Figs 1–11 the value of CTE is plotted against the test cycle number. Most of the data points represent the mean of five determinations made on separate specimens. Occasionally, means were calculated from fewer (four or three) determinations due to unacceptable traces being produced on the instrument. The most common cause of this problem was the production of a spurious trace due to vibrations.

Fig. 1 gives the results obtained for the four test materials following 24 h dry storage. At the fifth test cycle the mean values obtained for all four materials are significantly different (ANOVA, SNK $p < 0.05$). At the first test cycle the CTE values for materials S and B are not significantly different.

Figs 2–5 give results for each material following 24 h storage in either wet (37 °C) or dry (room temp.) conditions. For S, Z and B the differences in mean values of CTE at the first cycle between wet and dry storage are significant (*t*-test, $p < 0.001$).

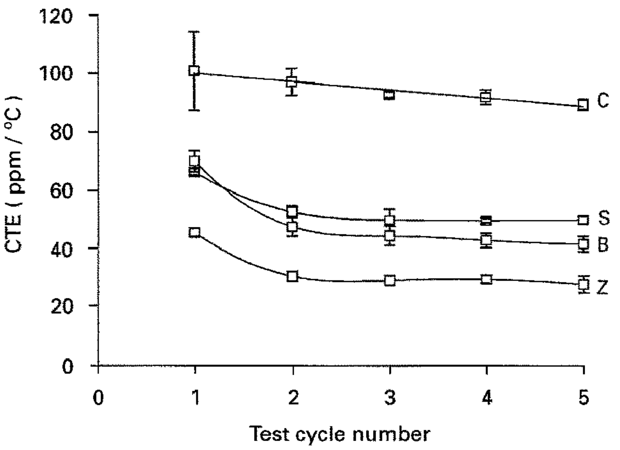

Figure 1 CTE of four materials following 24 h dry storage. Graph shows mean values. Error bars indicate standard deviations.

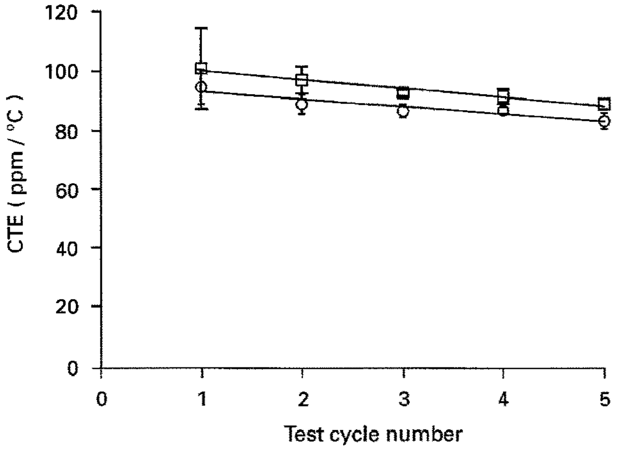

Figure 2 CTE of material C following 24 h wet (–○–) or dry (–□–) storage. Graph shows mean values. Error bars indicate standard deviations.

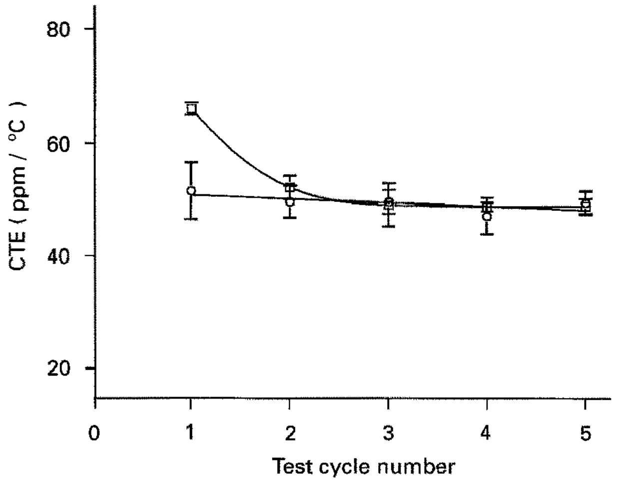

Figure 3 CTE of material S following 24 h wet (–○–) or dry (–□–) storage. Graph shows mean values. Error bars indicate standard deviations.

Fig. 6 shows the results for the annealed samples of material B following 24 h storage. There was a significant difference in the CTE values of wet and dry specimens at the first test cycle ($p < 0.001$) but not at cycles 2–5.

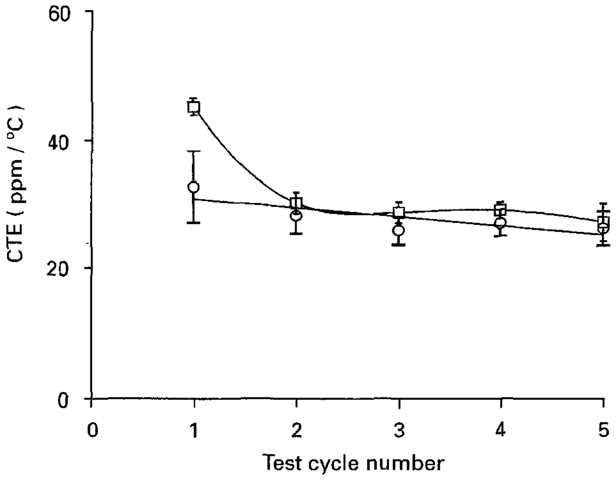

Figure 4 CTE of material Z following 24 h wet (–○–) or dry (–□–) storage. Graph shows mean values. Error bars indicate standard deviations.

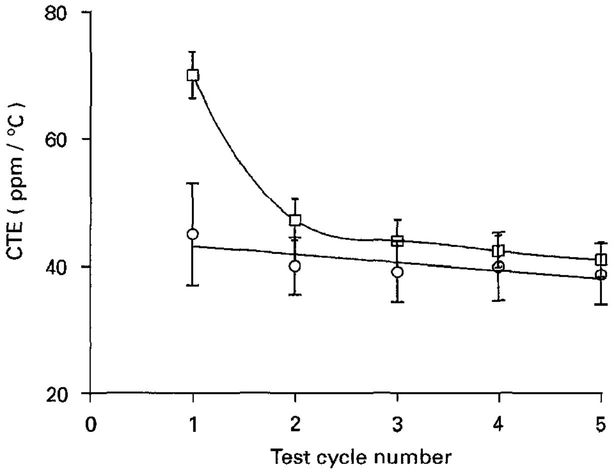

Figure 5 CTE of material B following 24 h wet (–○–) or dry (–□–) storage. Graph shows mean values. Error bars indicate standard deviations.

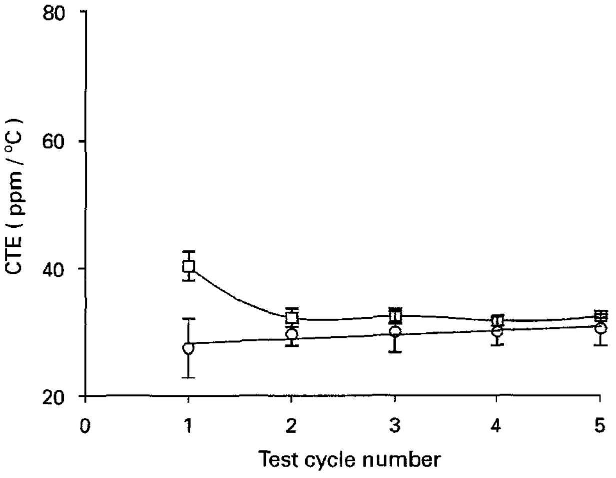

Figure 6 CTE of material B (annealed) following 24 h wet (–○–) or dry (–□–) storage. Graph shows mean values. Error bars indicate standard deviations.

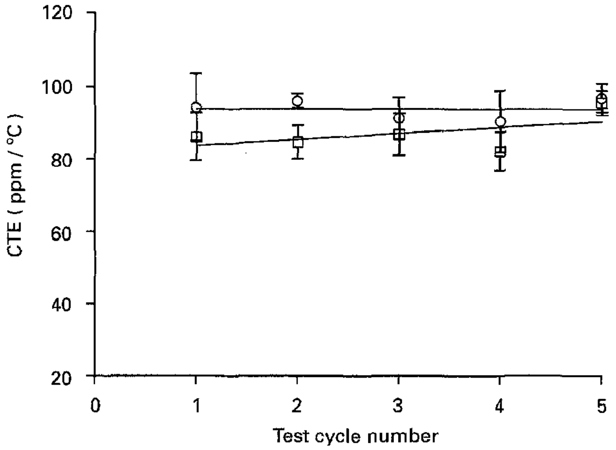

Figure 7 CTE of material C following 30 days wet (–○–) or dry (–□–) storage. Graph shows mean values. Error bars indicate standard deviations.

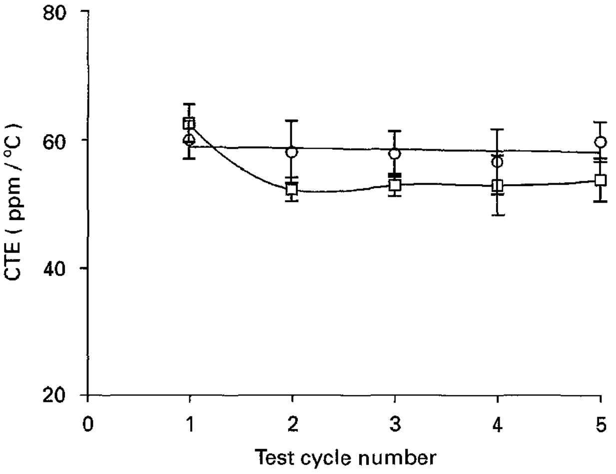

Figure 8 CTE of material S following 30 days wet (–○–) or dry (–□–) storage. Graph shows mean values. Error bars indicate standard deviations.

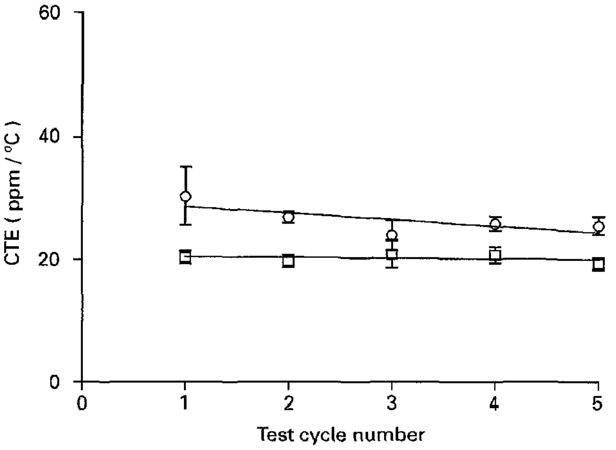

Figure 9 CTE of material Z following 30 days wet (–○–) or dry (–□–) storage. Graph shows mean values. Error bars indicate standard deviations.

Figs 7–11 show results for each material following 30 days storage under both wet (37 °C) and dry (room temp.) conditions. For most materials the value of CTE was slightly greater for specimens stored wet than for those stored dry. This was most noticeable for material B where the difference was around 12 ppm/°C and was significant ($p < 0.05$) at each test cycle.

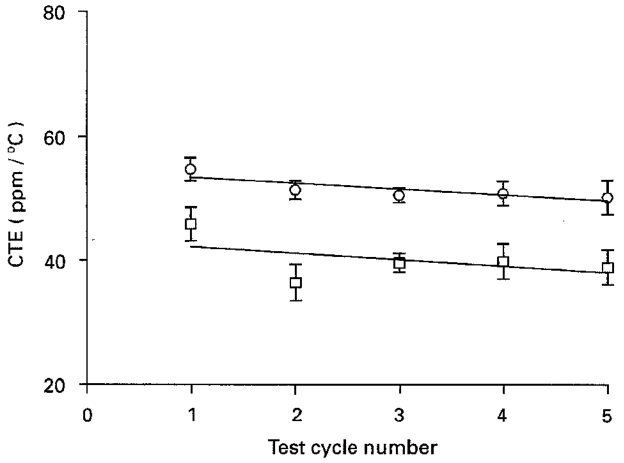

Figure 10 CTE of material B following 30 days wet (-○-) or dry (-□-) storage. Graph shows mean values. Error bars indicate standard deviations.

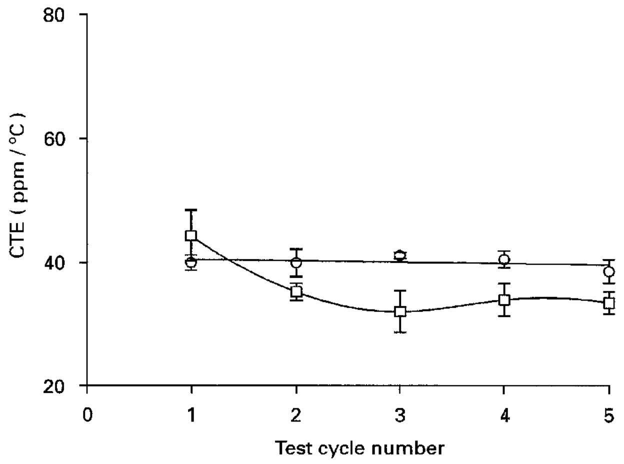

Figure 11 CTE of material B(annealed) following 30 days wet (-○-) or dry (-□-) storage. Graph shows mean values. Error bars indicate standard deviations.

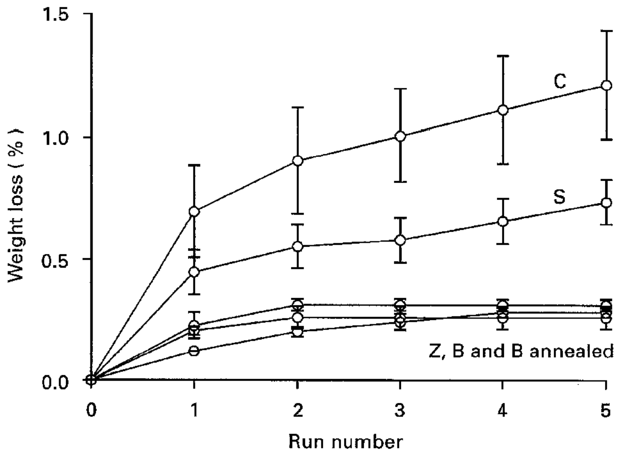

Figure 12 Weight loss for water saturated specimens during testing. Graph shows mean values. Error bars indicate standard error of mean. Statistical analysis (one way ANOVA and Tukey range test) indicated value for material C is significantly greater than for other materials.

Fig. 12 shows the weight loss measured for water-saturated specimens at each test cycle when subjected to five thermal expansion tests.

4. Discussion

The method of measuring CTE used in this study proved reproducible, as indicated by the relatively low values of standard deviation associated with the data points shown in the figures. Calculation of CTE was performed by determining the maximum slope of the displacement–time curve and dividing this by the slope of the temperature–time plot (the latter being the same in all cases). This method of calculation produces the maximum value of CTE over the temperature range of interest. A more conventional method of calculating CTE is to determine the total expansion associated with a known temperature rise and hence calculate an average value of CTE [5]. This method disguises the fact that CTE often varies with temperature and displacement – time plots are rarely linear over a wide temperature range. To completely characterize a material would require multiple experiments, each carried out over a relatively short temperature range. This approach has been used by other workers [6]. The method we have employed offers a means of avoiding such a time-consuming approach. The results generated appear to be sensitive to changes in material structure.

The initial ranking of materials as indicated in Fig. 1 is very much in line with what would be expected from the inorganic filler contents of the four materials (Table I), although other factors must also have an effect.

The importance of resin conversion is illustrated clearly by reference to Figs 5 and 6. The affect of annealing is to significantly increase the degree of conversion of methacrylate groups and this has clearly had a significant effect on CTE as indicated by the markedly lower values of CTE for the annealed specimens compared with control (un-annealed) specimens irrespective of the method of storage. This finding is important in two respects. Not only is the result of direct clinical significance, but also it suggests that measurement of CTE is a potentially useful method of indirectly evaluating conversion.

The relationship between CTE and test cycle is of scientific interest and potentially of clinical significance. Small changes in the value of CTE between the first and second heating cycles have been reported previously [1, 6, 7]. The changes reported in the present study (see Figs 3–5) are greater than those observed previously. This could be partly due to the fact that different materials are being considered but is more likely a function of the method of calculation of CTE as mentioned earlier. One explanation for this interesting observation is that the change is caused by stress release during the first heating cycle [6] and the present results would support this in view of the fact that the only other conceiveable mechanism involves further polymerization activated by heating to 70 °C. This mechanism appears to play a minimal part, as the same degree of change was not observed in the unfilled resin product (C). If further polymerization during testing were significant the latter product would show the most significant change. Stresses are likely to be concentrated at the resin–filler interface and at the specimen surface. These appear to be dissipated during the first heating cycle by a larger than expected expansion.

CTE has previously [1] been measured for a range of model composites in which the filler volume fraction was varied. Some composites were compounded with silanated fillers and in others silanation was not used. There was an inverse linear relationship between CTE and filler content but CTE was not affected by the use of silane treatment [1]. This result was surprising as other workers [4] had indicated that a composite containing unbonded fillers should behave like an unfilled resin. From this, it was concluded [1] that the shrinkage of resins in dental composites must result in hoop stresses in resin around each filler particle. This would account for the observation that silane treatment has no effect on CTE and for the stress release observed after the first heating. The levels of hoop stress developed during setting have been calculated [1] and their magnitude indicates that they could facilitate crack growth, crazing and debonding. In this previous work [1] model composites consisting of spherical glass fillers incorporated in a triethyleneglycoldimethacrylate (TEGDMA) resin were used. Specimens were tested immediately after manufacture. However, one factor not considered was the possibility that stress relief can occur through ageing or by water uptake.

Storage in water at 37 °C for 24 h appears to be capable of causing dissipation of stresses as illustrated in Figs 3, 4 and 5. Here we can see that the effect of wet storage has been to markedly change the shape of the CTE against test cycle plot, so that the initial decrease seen between the first and second cycles for dry specimens is no longer evident. This is a surprising result, in that during testing all test specimens lost a small amount of water. The results clearly demonstrate that this did not contribute in any noticeable way to a change in the value of CTE. The greatest weight loss during testing was noted for the unfilled resin (material C) while the smallest change was noted for materials Z, B and B (annealed), a result which may be expected from the relative filler contents of the materials. However, there is a less noticeable difference in both shape and separation between the CTE versus cycle plots for wet and dry specimens of material C (Fig. 7) than for S, Z, B, and B annealed (Figs 8–11). This suggests that differences in behaviour caused by water storage are more likely due to changes in stress distributions and the efficacy of resin–filler coupling than directly due to the influence of absorbed water on CTE.

It has been reported [8] that composites which had been stored in water for only 1 day appeared to expand and to exert a positive pressure against the cavity walls. The increase of pressure with time was correlated with increasing water absorption of the composite, but the initial pressure measured at only 1 day could, in part, be due to stress release.

A similar pattern of behaviour is seen for the annealed samples of B (Fig. 6), indicating that the annealing procedure does not dissipate the stress developed within the test specimens. It is possible that these stresses are in fact dissipated during heating, but are replaced by thermally induced stresses on cooling from the annealing temperature down to room temperature. This may be expected in view of the difference in coefficient of thermal expansion of resin and filler. Whatever the source of the internal stresses in these samples, it is clear that 24 h storage in water at 37 °C is able to cause stress relief. The behaviour of the 24 h dry sample (Fig. 6) is further evidence of the fact that the observed decreases in CTE between the first and second heating cycles is not caused by continued polymerization. In the case of annealed specimens, they have been subjected to heating to 120 °C in order to achieve optimum polymerization and it is unlikely that further heating to 70 °C would have any noticeable effect on conversion.

The effect of medium/long-term water storage varies according to the type of test material and on the storage conditions. Wet storage has the effect of dissipating the internal stresses in all materials, as indicated by the lack of any relationship between CTE and test cycle number (Figs 7–11). It is clear, however, that in materials S and B, stresses are able to survive 30 days of dry storage at room temperature. This result is of interest in helping to understand structure–property relationships of composites but probably has little clinical significance. In most cases, the values of CTE for specimens stored wet over 30 days are greater than those for specimens stored dry (neglecting the first heating cycle). This agrees with previous findings [5] which reported a small increase in CTE following 2 weeks water storage for a series of chemically activated anterior composites. A possible reason for this could be the plasticizing effect of water causing an increase in resin chain mobility. However, if this were a dominant factor we would expect the effect of water storage to be greatest for material C which has the greatest resin content (~100%). Reference to Figs 7–11 shows that this is not the case. For this product, although wet specimens generally have higher values of CTE than dry ones, the difference is only significant at the second heating cycle. For the same reason, vapour pressure effects related to absorbed water can probably be discounted as a possible explanation for the results.

The explanation for the change in CTE caused by water storage must be related to other structural parameters. One other factor which could contribute to a change in CTE on storage could be a change in the resin-filler interfacial bond [1]. The beneficial effects of filler can only be fully manifested when the two phases are linked together. Any destruction of this important link would cause the composite material to behave more like an unfilled resin. With regard to CTE, we would expect the value to increase as the interfacial bond breaks down and this could well be a significant factor in explaining the data given in Figs 8–11. There is evidence to suggest that a breakdown of the resin–filler coupling can occur, probably due to hydrolysis of Si–O bonds [9]. The proposed mechanism of debonding is that ageing and water absorption initially cause relief of the compressive hoop stresses in resin around filler particles. Secondly, absorbed water is responsible for resin–filler decoupling through hydrolysis of Si–O bonds at the interface.

These results suggest that measurements of CTE may offer a simple means of monitoring the efficacy of resin–filler coupling in dental composites. It appears that an in-depth study of the thermal expansion behaviour of dental composites can reveal information which is of scientific interest and clinical significance. The comparative values are likely to be of significance in determining relative stresses developed at the resin–tooth interface during *in vivo* thermal cycling. Changes in CTE can be used to monitor changes in conversion produced using different curing regimes and annealing. The relationship between CTE and thermal history (i.e. heating/cooling cycles) gives information on the levels of residual stress and stress relief. Finally, changes in CTE following water storage may offer a means of monitoring resin–filler coupling.

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