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Aspects of water sorption from the air, water and artificial saliva in resin composite restorative materials

L. Musanje, B.W. Darvell*

Dental Materials Science, Faculty of Dentistry, Prince Philip Dental Hospital, The University of Hong Kong, 34 Hospital Road, Hong Kong, People's Republic of China

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Abstract

Objectives. Primarily to establish whether artificial saliva (AS) at 37 °C is essential as a clinically relevant environment for testing filled, resin composite restorative materials. The effect of other storage conditions was also investigated for comparison and controls: desiccation, exposure to the laboratory atmosphere, high humidity cabinet, saturated water vapor, and deionized water.

Methods. Two visible light-cured products were used: Heliomolar Radiopaque (HR) and Tetric Ceram (TC) (Ivoclar, Schaan, Liechtenstein). Bar specimens ($26 \times 1.5 \times 1.0\ \text{mm}^3$) were cured at five overlapping spots for 60 s per spot and randomly distributed into groups of six. Trial 1: one group of each material was exposed first to atmospheric air at 24 °C, ~50% RH ($^{24}WV_{50}$), then to water vapor at 37 °C, ~97% RH ($^{37}WV_{97}$), and then immersed in deionized water at 37 °C (^{37}DW). Trial 2 used three groups of each material, one first exposed to $^{37}WV_{97}$ followed by ^{37}DW, the other two were immediately immersed in ^{37}DW or artificial saliva (^{37}AS). Trial 3: two groups of each material were vacuum desiccated at 37 °C, then exposed to 37 °C, ~100% RH ($^{37}WV_{100}$), then immersed in ^{37}DW or ^{37}AS. Trial 4: four groups of HR were treated similarly to Trial 3; one was left under desiccation, and another in $^{37}WV_{100}$ for the remaining period. Three-point bend tests for flexural strength (F), flexural modulus (E), and total energy to failure (W) were performed at the end of Trials 2–4.

Results. Environmental moisture absorption was substantial at $^{24}WV_{50}$(c. 0.2%), at least 40% of that in ^{37}DW (HR: c. 0.7%, TC: c. 0.5%). Saturation was achievable in $^{37}WV_{100}$. Mass loss on desiccation (HR: c. 0.4–0.5%, TC: c. 0.25%) was reversible in $^{37}WV_{100}$. There were some significant effects of exposure conditions on mechanical properties (e.g. F for HR: after desiccation, 85.7 ± 1.4 MPa; after $^{37}WV_{100}$, 73.2 ± 3.6 MPa; difference: $p < 0.0002$), but overall the results were unclear. After a rapid gain in mass, there was a gradual loss in both ^{37}DW and ^{37}AS for both materials, slightly more in ^{37}AS than ^{37}DW.

Significance. Water vapor absorption is substantial, hence attention must be paid to the laboratory working environment and conditions of storage and testing, i.e. temperature and RH must be stated to assist interpretation of data and comparisons between studies. Test conditions need to be standardized and with reference to normal oral conditions, immediate immersion in artificial saliva at 37 °C is the preferred treatment for these materials, whatever time of testing is chosen.

Keywords: Filled resin restorative materials; Water sorption; Strength; Modulus of elasticity; Degradation; Artificial saliva; Humidity

1. Introduction

The warm, wet nature of the mouth sets a clear demand for filled resin restorative materials (RCs), as well as all other dental restorative materials, to maintain reasonable stability in such an environment. However, it is well established that exposure of RCs to an aqueous environment lowers the values of their mechanical properties [1–4] and their resistance to wear [5,6]. These reductions have been attributed to the hydrolytic degradation of the polymer matrix [3] and of the filler [2], and to water-induced filler–matrix bond failure [7,8]. The main causes of replacement of filled resin restorations, i.e. insufficient wear resistance, marginal sealing, and (to a lesser extent) insufficient color stability [9,10] have also been associated with poor solvent stability [11]. Thus long-term survival of RCs under oral conditions is obviously of great concern. Previous studies of the behavior of RCs in a wet environment have mainly been conducted in water with a few in some other liquids, e.g. ethanol [12], food-simulating liquids [13,14], and sodium hydroxide [15,16], presumably with the intention of

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* Corresponding author. Tel.: +852-2859-0303; fax: +852-2548-9464.
E-mail address: b.w.darvell@hku.hk (B.W. Darvell).

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Table 1
Exposure conditions and durations (*d*) for the various trials conducted

Trial		^{37}VX	^{24}WV$_{50}$	^{37}WV$_{97}$	^{37}WV$_{100}$	^{37}DW	^{37}AS
1		–	45	66	–	410	–
2	a	–	–	63	–	389	–
	b	–	–	–	–	452	–
	c	–	–	–	–	–	452
3	a	139	–	–	62	106	–
	b	139	–	–	62	–	106
4	a	456	–	–	–	–	–
	b	83	–	–	373	–	–
	c	83	–	–	36	337	–
	d	83	–	–	36	–	337

Key: VX: vacuum desiccation over P_2O_5, ~76 mm Hg, WV: water vapor, AS: artificial saliva, prefix: temperature (°C), suffix: relative humidity (%).

mimicking the effects of saliva or temporary environmental challenges. To date, little is known about the behavior of RCs in artificial saliva as a simulation of real saliva. However, Söderholm et al. [17] have observed that RCs leached more ions on being exposed to artificial saliva than to water, casting doubt on the clinical relevance of the use of water as the storage medium and echoing previous concerns [18].

The main objective of the present study was to determine whether the use of an artificial saliva was essential as an approach to a clinically relevant environment for testing RCs. In addition, an attempt was made to elucidate some of the factors operating, with the aim of informing decisions about rational handling, storage and testing protocols. This was done by exposing specimens to various conditions of atmosphere and immersion, monitoring mass with time, and examining the mechanical properties of flexural strength, elastic modulus and total work to failure to ascertain whether these environments affected test results.

These experiments were in part motivated by the need to identify appropriate storage conditions and an appropriate time at which to conduct the testing of RC specimens to be reasonably assured of essentially complete post-irradiation reactions, and loss of volatiles and promptly soluble materials so that there would be minimal confounding of results from small variations in the timing of testing with respect to preparation and so on.

2. Materials and methods

Two visible light-cured RCs, Heliomolar Radiopaque (HR) (Batch A20633) and Tetric Ceram (TC) (Batch A07041) (both Shade A3, Ivoclar, Schaan, Liechtenstein) were used, representing microfilled and hybrid materials, respectively. The validated artificial saliva (AS) according to Leung and Darvell [19] was used (without CO_2), adjusted to pH 6 using NaOH from the initial pH ~4.3. Deionized water was obtained by reverse osmosis purification of tap water (Milli-RO 10 Plus, Millipore Corporation, Bedford MA, USA), followed by ultra-purification (Milli-Q, Millipore). Immersion media were changed every 5 d to counter the slight rise in pH that occurred due to leaching. Specimens were fabricated by extruding material from the supply syringe into the rectangular slot ($26 \times 1.5 \times 1.0$ mm^3) of a knife-edged split mold [20], covered with a mylar strip and formed under a load of 10 N for 3 min to allow full flow and relaxation. Specimens were then cured by placing the tip (8 mm diameter) of the curing light guide (Luxor 4000, ICI, Macclesfield, Cheshire, UK) in direct contact with the mylar strip and irradiating each specimen at five slightly overlapping spots, 60 s per spot, at an irradiance of 400 ± 5 mW/cm^2 (Demetron 100, Demetron Reseanch, Danbury, CT, USA). The mylar strip was removed and the mold disassembled, enabling free retrieval of the specimen. All specimens were visually inspected for defects and those (few) with visible flaws discarded. Any flash of material resulting from extrusion over the mold's knife edges was removed but the handling tab at each end, arising from the excess material, was spared. The specimens of each material were then randomly distributed into groups of six. Four separate trials were conducted.

Trial 1 consisted of one group of each material which was exposed, first, to atmospheric air at 24 °C and ~50% RH (^{24}WV$_{50}$), representing ordinary laboratory conditions, to a more or less stable mass, followed by exposure to water vapor at 37 °C and ~97% RH (^{37}WV$_{97}$), a typical humid cabinet atmosphere, again until an equilibrium mass was attained, and finally immersed in deionized water at 37 °C (^{37}DW), representing common storage conditions.

Trial 2 consisted of three groups, one of which was first exposed to ^{37}WV$_{97}$ to an equilibrium mass followed by immersion in ^{37}DW while the other two were separately immersed in ^{37}DW and artificial saliva at 37 °C (^{37}AS), as a better approximation to oral conditions than ^{37}DW, immediately after preparation, without prior desiccation.

Trial 3 consisted of two groups which were first desiccated at 37 °C over diphosphorus pentoxide under reduced pressure (~76 mm Hg) (^{37}VX), because of uncertainty over the as-supplied material conditions, then exposed to ^{37}WV$_{100}$ until an equilibrium mass was reached, and finally immersed separately in ^{37}DW and ^{37}AS.

Trial 4 was similar to Trial 3 except that it was run for a much longer period, but restricted to HR as this seemed to be more sensitive to changes. To reduce the premature loss of volatile reactants, which unwittingly may have influenced results in earlier trials, a more elaborate scheme was used. Soon after preparation, four groups of specimens were weighed and sealed in close-fitting soda glass miniature vials (minimum dead-volume, using a glass slug to fill remaining space). Specimens were then 'aged' for 7 d at 37 °C, then reweighed after cooling and removal from the vials. All groups were then exposed to ^{37}VX until equilibration. One group was then left under VX while the others were transferred to ^{37}WV$_{100}$. Again, after equilibration, one group was left in ^{37}WV$_{100}$ while the others were transferred to ^{37}DW or ^{37}AS. The timings of all trial stages are given in Table 1.

Relative humidity was determined with a dewpoint meter (model DP-989M, Protimeter, Bucks, England). Water sorption was monitored gravimetrically by weighing all six specimens as a group, to a precision of 0.01 mg, using a single-pan analytical balance (H542, Mettler Instrumente, Greifensee, Switzerland) at various intervals. The initial mass value (m_1) was obtained soon after preparation was completed. All specimens were equilibrated to room temperature, while remaining in their test exposure medium, for c. 60 min before weighing. Those specimens immersed in ^{37}DW or ^{37}AS were retrieved with tweezers, blotted with filter paper until free from visible moisture and waved in the air (^{24}WV$_{50}$) for c. 5 s before weighing. The new mass value (m_2) was recorded at c. 3 min from the time the first specimen of the group was removed from the corresponding liquid. Water sorption as a percentage mass change was then calculated from $100\{(m_2 - m_1)/m_1\}$.

Mechanical testing of the specimens in three-point bend (16 mm span) using a universal testing machine (1185, Instron, High Wycombe, UK) at 0.50 mm/min cross-head speed, was performed at the end of the exposure period for Trials 2–4 to determine flexural strength, flexural elastic modulus, and total work to failure to determine whether effects on mechanical properties were detectable. Testing was done in the specimens' corresponding exposure medium at 37 °C (expect those exposed to ^{37}VX where air at 37 °C was used, RH ~ 22%). Data acquisition was done in software (LabVIEW version 5.1, National Instruments, Austin TX, USA) on a personal computer, as was the programmed calculation of ultimate flexural strength (F), using the corrected formula [21,22], and flexural elastic modulus (E) as

$$F = \frac{3PL}{2bd^2}\left[1 + \frac{6D^2}{L^2} - \frac{4dD}{L^2}\right] \qquad (1)$$

$$E = \left(\frac{\Delta P}{\Delta y}\right)\frac{L^3}{4bd^3} \qquad (2)$$

where P is load to fracture; L the support span; D the maximum deflection of the beam; d and b the specimen depth and breadth, and $\Delta P/\Delta y$ the gradient of the (steepest) linear portion of the deflection curve [21]. Total energy to failure (W) was calculated as the area under the load-displacement curve. The two portions of the beam were retrieved after failure of the specimen; d and b were measured at the fracture using a screw micrometer (Mitutoyo No. 193-111, Tokyo, Japan). Load string stiffness was sufficiently high that cross-head displacement was an accurate enough proxy for beam deflection, simplifying the set-up; the maximum displacement error was calculated to be about + 1% of D, but the effect on the calculated value of E was much less because of the definition of $\Delta P/\Delta y$.

Graphical analysis was done using SigmaPlot (Version 6, SPSS, Chicago IL, USA) and the analysis of variance of mechanical property vs. conditions within materials with Genstat (Version 5, Release 4.1, Lawes Agricultural Trust, Rothamsted, UK).

3. Results

3.1. Trial 1

A steady increase in mass by ~ 0.21% (TC) and ~ 0.25% (HR) of the original mass occurred on standing in the laboratory environment (^{24}WV$_{50}$) (Fig. 1, open, light symbols); this was fairly stable from ~ 6–45 d (Fig. 1(a)). Exposure then to high humidity at 37 °C (^{37}WV$_{97}$) led to a large increase to a more or less stable value of 0.52% (TC) and 0.68% (HR) (Fig. 1(b)), but the immersion then in deionized water (^{37}DW) resulted in a prompt increase (TC: 0.60%, HR: 0.83%), i.e. within 1 d, followed by a continuous and marked decline which showed no sign of slowing down at 400 d (Fig. 1(c)), when the trial was terminated. The nature of these results prompted the further trials.

3.2. Trial 2

Exposure to ^{37}WV$_{97}$ gave a steady rise in mass to plateau values (TC: 0.48%, HR: 0.74%) (Fig. 1(b), grey symbols). Again, a prompt increase in mass was followed by a gradual but continuous loss on transfer to ^{37}DW, similar in pattern to the results for Trial 1 (Fig. 1(c)). In contrast, direct immersion in both ^{37}W and ^{37}AS gave a more rapid gain in mass, the curve turning over smoothly from the peak at about 7 d (TC: 0.5%, HR: ~ 0.9%) into a steady loss for both materials (Fig. 1(c), heavy symbols). Some slight differences between the results for ^{37}AS and ^{37}DW can be discerned, but no great systematic effect. The peak gain for HR was about 1.5 times that of TC in all environments.

3.3. Trials 3 and 4

These results are summarized in Figs. 2 and 3. A marked loss of mass occured on desiccation (VX) (Figs. 2(a) and 3(a)), with that of HR being somewhat greater than for TC. HR appeared to stabilize at around 100 d, but the evidence for TC was more equivocal, with the possibility of further loss, albeit slowly (Fig. 2(a)). On transfer to ^{37}WV$_{100}$, a greater increase in mass (compared with the data of Fig. 1(b)) for both materials to stable plateau values was observed (Figs 2(b) and 3(b)). Again, a gradual but continuous loss in mass occured on the subsequent immersion of the specimens in ^{37}DW and ^{37}AS (Figs. 2(c) and 3(c)). Mass loss was clearly greater in ^{37}AS than in ^{37}DW.

The results of the mechanical tests for Trials 2–4 are summarized in Table 2. For Trials 2 and 3, within

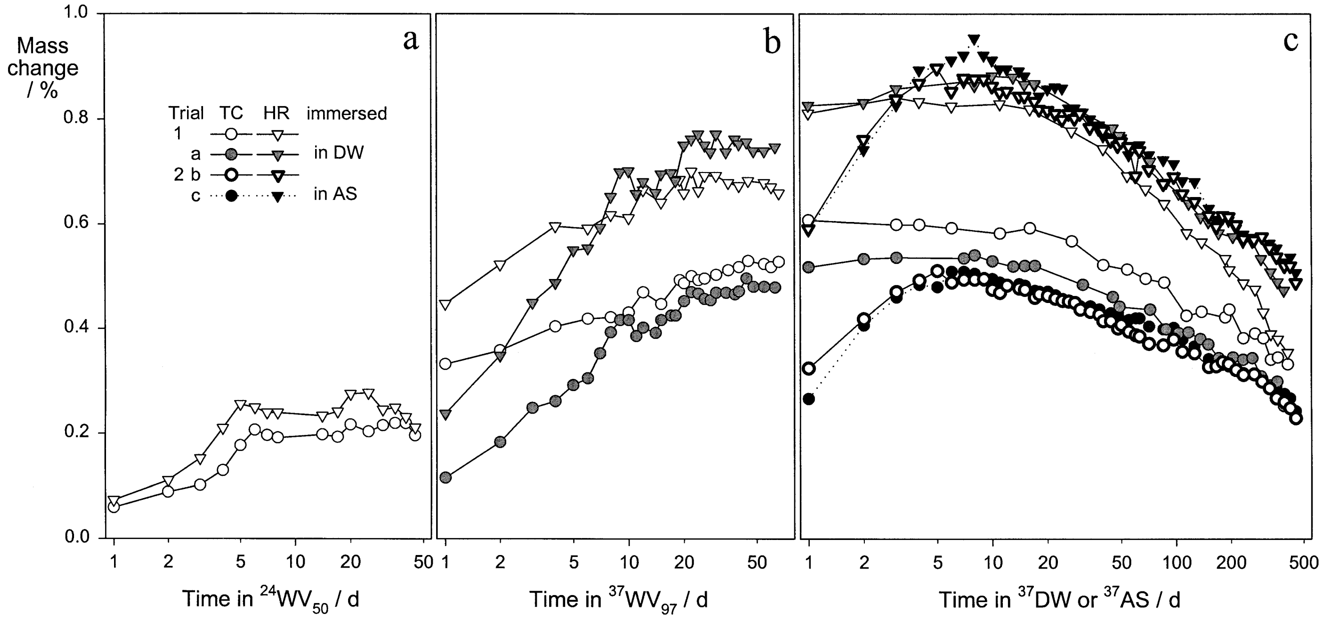

Fig. 1. Mass changes for Trials 1 and 2 for successive exposure of HR and TC to water vapor at 24 °C, 50% RH (^{24}WV$_{50}$); water vapor at 37 °C, 97% RH (^{37}WV$_{97}$), and deionized water (^{37}DW) or artificial saliva (^{37}AS) at 37 °C. Each panel (a, b, c) represents one stage, time (log scale) with zero set for the beginning of that stage; mass change scale common to all three.

materials, the effect of exposure medium on all three properties was not detectable. For Trial 4, HR saturated in water vapor (^{37}WV$_{100}$) gave significantly lower values of F ($p = 0.0001$) and E ($p = 0.0002$), and higher W ($p = 0.00002$), than desiccated (^{37}VX), while the comparison of ^{37}WV$_{100}$ with ^{37}DW gave significantly higher values of F ($p = 0.001$) and W ($p = 0.003$) (Table 2). No significant difference in mechanical properties of HR between artificial saliva and deionized water immersion was found.

4. Discussion

On exposure to the air, freshly prepared RCs would be expected to lose volatile compounds (in particular, low

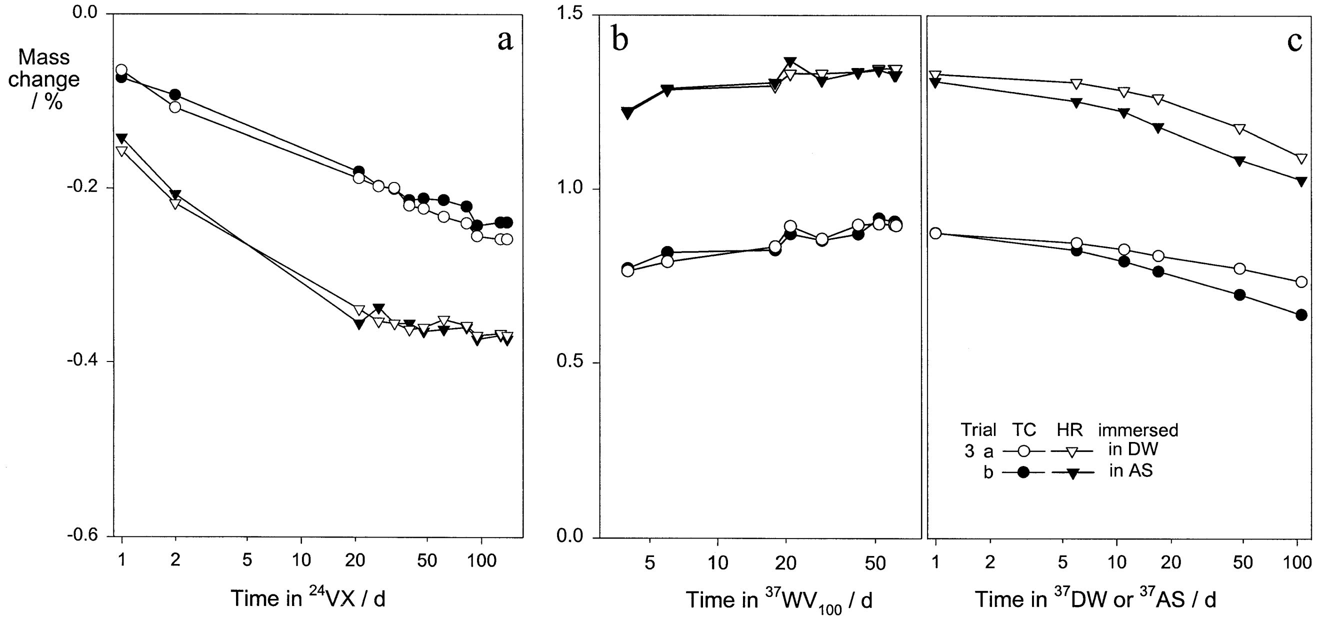

Fig. 2. Mass changes for Trial 3 for successive exposure of HR and TC to vacuum desiccation at 37 °C (^{37}VX), water vapor at 37 °C, 100% RH (^{37}WV$_{100}$), and deionized water (^{37}DW) or artificial saliva (^{37}AS) at 37 °C. Each panel (a, b, c) represents one stage, time (log scale) with zero set for the beginning of that stage; note: panel a represents mass loss, mass change scale for panels b and c reset to be with respect to mass at the beginning of WV stage.

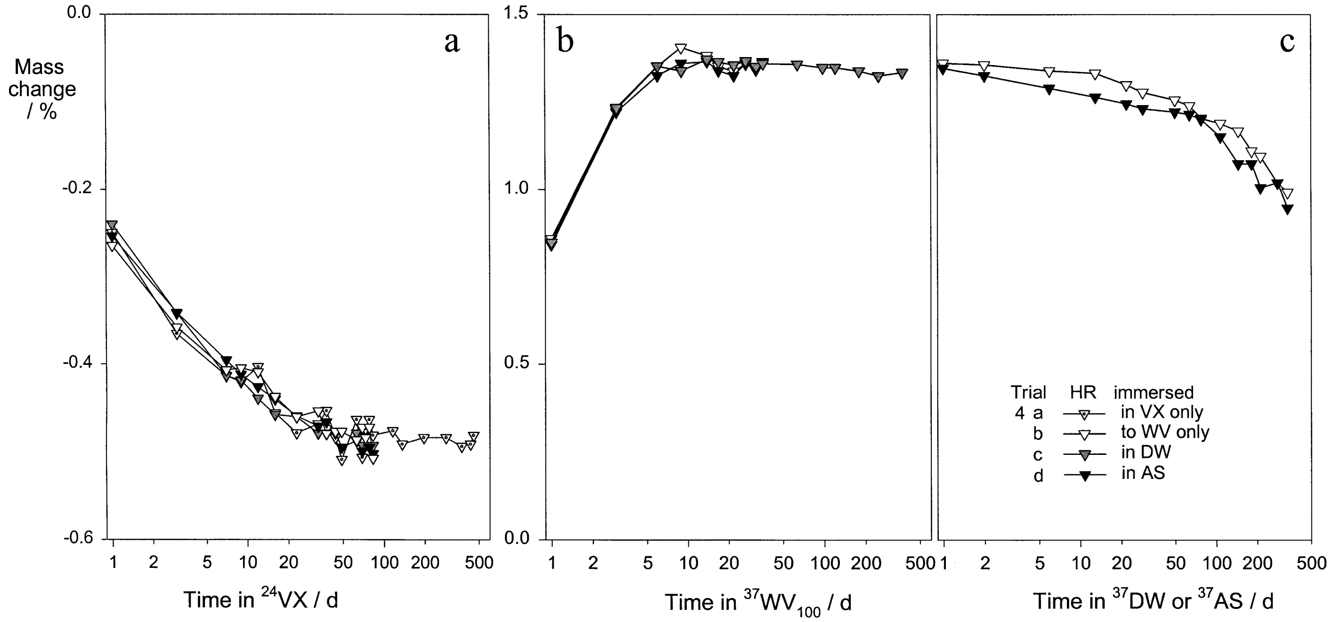

Fig. 3. Mass changes for Trial 4 for successive exposure of HR to vacuum desiccation at 37 °C (^{37}VX), water vapor at 37 °C, 100% RH (^{37}WV$_{100}$), and deionized water (^{37}DW) or artificial saliva (^{37}AS) at 37 °C. Each panel (a, b, c) represents one stage, time (log scale) with zero set for the beginning of that stage; note: panel a represents a mass loss, mass change scale for panels b and c reset to be with respect to mass at the beginning of WV stage.

molecular weight monomers). However, polar polymers in general absorb water from the surroundings depending on their hydrophilicity and the humidity of the environment, nylon being a familiar example. There appears to be no recognition in the dental literature of this, in particular in relation to RCs, whose general chemistry in this regard is broadly the same across products; all known work relates to absorption in aqueous media. Thus the present demonstration of appreciable absorption on exposure to the nominal 50% RH laboratory atmosphere has profound implications for the mechanical testing of these (and indeed other) materials (Fig. 1). 'Storage dry' is not

Table 2

A summary of mechanical properties of HR and TC after exposure to VX, WV, DW and AS for Trials 2–4. For key, see Table 1

A: Trial 2	TC			
Medium	^{37}WV$_{97}$–^{37}DW	^{37}DW	^{37}AS	
F (MPa)	91.33 (9.89)^{a}	101.58 (7.30)^{a}	101.35 (6.34)^{a}	
E (GPa)	6.64 (0.56)^{b}	7.11 (0.36)^{bc}	7.48 (0.53)^{c}	
W (mJ)	3.66 (1.03)^{d}	4.18 (0.64)^{d}	3.98 (0.53)^{d}	
B: Trial 2	HR			
Medium	^{37}WV$_{97}$–^{37}DW	^{37}DW	^{37}AS	
F (MPa)	65.18 (7.18)^{a}	66.55 (7.85)^{a}	70.09 (6.31)^{a}	
E (GPa)	3.91 (0.21)^{b}	4.26 (0.28)^{c}	4.47 (0.39)^{c}	
W (mJ)	2.33 (0.59)^{d}	2.05 (0.51)^{d}	2.18 (0.35)^{d}	
C: Trial 3	TC		HR	
Medium	^{37}DW	^{37}AS	^{37}DW	^{37}AS
F (MPa)	95.78 (13.98)^{a}	92.48 (12.60)^{a}	65.00 (7.79)^{b}	64.37 (3.75)^{b}
E (GPa)	6.60 (1.11)^{c}	5.71 (0.40)^{c}	3.46 (0.34)^{d}	3.53 (0.15)^{d}
W (mJ)	4.35 (1.48)^{e}	4.49 (1.28)^{e}	2.78 (0.75)^{f}	2.71 (0.33)^{f}
D: Trial 4	HR			
Medium	^{37}VX	^{37}WV$_{100}$	^{37}DW	^{37}AS
F (MPa)	85.74 (1.41)^{a}	73.20 (3.56)^{b}	64.04 (2.01)^{c}	69.97 (3.92)^{b}
E (GPa)	5.29 (0.41)^{d}	3.76 (0.31)^{e}	3.89 (0.25)^{e}	3.96 (0.17)^{e}
W (mJ)	2.311 (0.12)^{f}	3.30 (0.22)^{g}	2.41 (0.24)^{f}	2.82 (0.48)^{fg}

Values of the properties are given as (mean (standard deviation)). Common superscript letters indicates no significant difference at $p = 0.05$ (by row). *F*: flexural strength, *E*: flexural elastic modulus, *W*: total energy to failure.

a benign, zero-influence, stable condition (even disregarding post-irradiation reactions), appreciable variation in water content can be expected over a period of only a few days, and according to the prevailing relative humidity and temperature.

This problem of lack of specimen stability on preparation is exacerbated by the observation that both TC and HR lost mass on desiccation (Figs. 2(a) and 3(a)), which mass was recovered on immersion in both ^{37}AS and ^{37}DW as well as exposure to $^{37}WV_{100}$ (Figs. 1, 2(b) and 3(b)). This loss is therefore probably mostly of water, which was in turn probably present in the original material and thus a function of manufacturing conditions and history. Nevertheless, it raises the possibility that any measured water gain or loss will vary arbitrarily according to specimen preparation room conditions (the breath of the operator is a risk factor for such close work) as well as manufacturing variation, and therefore the state of a specimen for mechanical testing will be similarly uncertain. Indeed, it is evident from the present results that there is some variability in outcome that cannot simply be attributed to the measurement error (Fig. 1(a)). This might be one factor involved in the widely experienced difficulty of obtaining concordant results between laboratories in 'round-robin' testing for method validation in the context of standards specifications. Part of the motivation for the present work was just that kind of method control.

The water vapor exposures of Trials 1 and 2 were at a nominal 97% RH, the control of the environment being not very precise. Even so, the increase in mass on transfer to deionized water was plain, even if inconsistent (Fig. 1(b) and (c)). There was no such step increase for Trials 3 and 4 (Figs. 2 and 3(b) and (c)), where the saturated atmosphere was better controlled. Since by definition the condition of saturation involves identical chemical potential for water in the liquid and gaseous phases (i.e. unit activity), this is also the case for the water in the resins themselves when they are saturated, whether this is attained by immersion in pure water or in a water-saturated atmosphere at the same temperature.

Thus, in principle, the inherent water absorption characteristics of a material may be studied without the confounding effects of loss of soluble matter (cf. data for Trials 2 b,c; Fig. 1(c)). Further, as a matter of logical protocol, dissolution tests could be performed once specimens have been brought to a standardizable starting point, as in Trials 3 and 4. It is noted that the time for saturation is similar in the two circumstances ($\sim 5-10$ d), suggesting that the kinetics of absorption are (as expected) similar. Thus, exposure of RCs to saturated water vapor would seem to be a better approach for study of the state of the filler–matrix bond in the presence of water rather than immersion in water, as has been done in some previous studies [3,23].

The presence of volatile substances in such materials even when 'set' is a factor that compounds the problem of the determination of sensitivity to water vapor, as indeed it would affect any tests of mass change when materials are immersed. However, it cannot yet be said with any precision how much of a contribution there is from this source to the net mass change in Trials such as 2 b and c although it appears to be relatively small. Certainly, the extra precautions of Trial 4 did not change the outcome, although desiccation was contradictorily greater than in Trial 3. It is clear that a more detailed control of starting conditions is necessary, emphasizing the need for standardization in such work. Nevertheless, the practical importance of such trials is dubious in view of the probable variation in products as supplied: the water status of the resin precursors will be dependent on the exact history of ambient conditions. Thus, although desiccation (^{37}VX) had a considerable effect, the very long time-scale for stabilization makes it impractical as a routine step. More to the point, storage in a desiccator will not be unaccompanied by changes in properties (see Table 2), and storage 'dry' at 37 °C will be likely to exacerbate this. The critical point is that there appears to be no zero-effect storage condition that can be relied on to give an adequate control for any experiment involving such materials. It follows that reporting the details of preparation and storage, even temporarily, i.e. temperature, humidity, and time is of great importance for critical property studies. It may be that the value of data in many reports is diminished for the lack of such control.

Immersion in an aqueous medium is the normal and fairly prompt experience of nearly all applications of filled resins, and although the extent of contact may be limited by cavity walls or a luted device, saturated is the state in which the materials are expected to function [24]. Thus the mechanical properties that are dependent on absorption or dissolution processes will be expected to be time-dependent. It is clearly crucial to standardized testing that this is taken into account. However, and since dissolution processes appear to start promptly on immersion (Figs. 1(c)–3(c)), the selection of a suitable standard time is problematic, and all such decisions must be arbitrary unless careful monitoring of properties with time over a long period is entertained as routine. This is unlikely. Neither can it be argued safely that exposure to water vapor avoids such difficulties as it would remain to be proved that degradation was not occurring in water vapor. This, too, seems unlikely since such reactions would depend on water activity and, as has been shown, this is the same for $^{37}WV_{100}$ and ^{37}DW. The effects might be detectable as increased rate of loss of mass in ^{37}DW according to length of time in $^{37}DW_{100}$, or indeed, according to the relative humidity. The present data do not permit that analysis.

The use of a storage and test environment that is as close to service conditions as is practicable [25] is a logical requirement that requires no discussion unless it can be shown that some simpler system gives the same results. Convenience, cost and habit are insufficient justifications for the use of deionized water in preference to artificial saliva. The fact that there has been no general acceptance of a logical, justified or standardized such medium [26] cannot help. However, the question remains as to whether any such reasonable simulation has a demonstrable effect. It would appear from Figs. 2(c) and 3(c) that there is: ^{37}AS gave

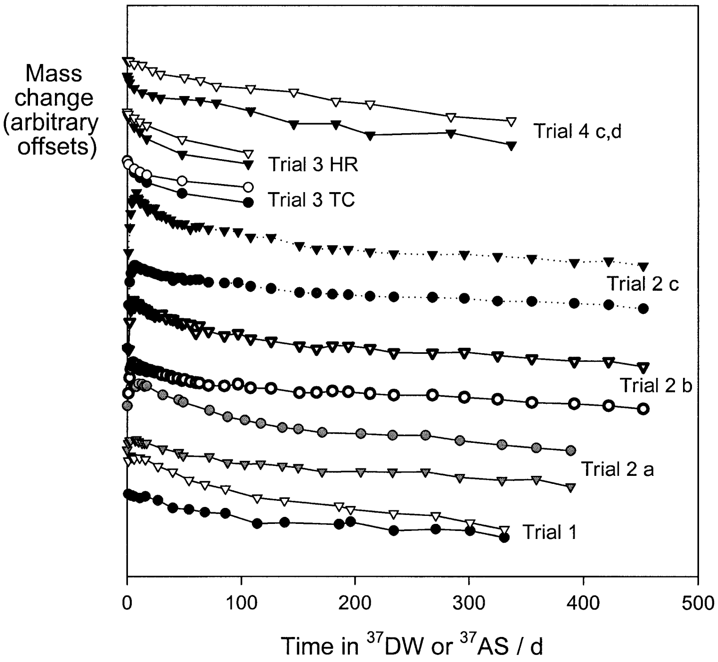

Fig. 4. Mass changes (with arbitrary offsets for clarity) for DW or AS stages of Trials 1–4 (i.e. data from Figs. 1(c), 2(c), and 3(c)) replotted on linear time scale to show common pattern of early exponential-like decay portion and more linear subsequent behavior.

a small but clear increase in the rate of loss of mass. There are two possible interpretations of this. Firstly, the activity of the water was diminished by the presence of the salts and therefore re-equilibration with respect to water content must occur, as on changing the humidity of the storage atmosphere. This is unlikely since the overall concentration of the solution is very low, but also the time-scale for the change is different: immersion in ^{37}DW after ^{37}WV$_{97}$ gave a marked step change in 1 d. By symmetry, a similar effect would be expected on reduction of water activity. If it is present in the data of Figs. 2(c) and 3(c), the magnitude of the effect is small. Secondly, 'corrosive' degradation of the filler occurs more readily in the presence of the ionic constituents of the artificial saliva. This latter seems the more likely, especially since there is an obvious and continuing loss of mass even in ^{37}DW which could not be accounted for on the basis of the activity of the water.

Söderholm et al. [17] analysed the immersion medium after RC exposure and demonstrated that more filler material was leached in AS than in DW, suggesting more filler degradation and thus also more property deterioration. However, such comparisons must be made with caution since the AS used then was different from that used here; a standardized AS for laboratory studies is clearly needed [26]. Even so, it can be argued that if such effects are seen in various such media, no special or spurious process is operating and the phenomenon can be assumed to be a general risk at best, i.e. affecting all products of this broad class.

What is perhaps of greater concern than the mere fact of probable degradation is that it seems not to be either superficial or short-lived: plotting the data of Figs. 1(c)–3(c) against linear time (Fig. 4) shows a period of about 30–100 d where the rate declines roughly exponentially (as might be expected anyway) but after that the loss of mass continues at a steady rate with no sign of halting up to ~450 d (the curvature of Fig. 3(c) is an artefact of the logarithmic time scale). This second stage would be consistent with progressive interfacial breakdown allowing deeper penetration at a rate rather lower than that of the diffusion of dissolved material, the breakdown is thus the rate-limiting process. Nevertheless, it is now apparent that since degradation occurs in ^{37}DW, which is often tacitly assumed to be entirely benign, it must also be occurring in water vapor and at a rate dependent on temperature and water activity (i.e. RH), since the absorbed water is chemically indistinguishable as to source. This would be worth further investigation. The implication is first that the effects of water sorption and degradation could not be disentangled by the use of a humid atmosphere as a storage environment, but also that such materials are not stable on storage while there is any water (vapor) present. In fact, the apparently exponential decline stage is evidence in support of the idea that degradation does occur in water vapor, since the products of this would be expected to be more diffusible and thus readily removed with just such a profile. Thus, and again, it cannot be assumed that any storage conditions are neutral and can therefore be treated as providing strict experimental controls.

Another process must be considered, i.e. loss in mass in the liquid media may be attributable to non-volatile organics. It has been reported that loss of nearly all unbound monomers and oligomers from cured, disk-shaped specimens of RCs (2.0 mm thick × 4.0 mm diameter) was complete within 24 h of immersion in water [27].

Since the present specimens were even thinner (1 mm thick) and with a higher surface area to volume ratio, loss of non-volatile organics might be expected to be complete in less than 1 d in both ^{37}DW and ^{37}AS, i.e. at the time of the earliest observation. However, the time-scale for water equilibration seems to be longer (of the order of 5–10 d), and since water is expected to be far more diffusible than any feasible organic compounds, loss in 24 h seems optimistic. A contribution to mass loss from this source therefore cannot be ruled out. Even so, this does not account for the long-term, steady loss of mass here ascribed to degradation. Furthermore, the very long time-scale for mass loss under vacuum desiccation (Figs. 2(a) and 3(a)) is suggestive of something other than water being lost in addition; there is apparently a very slight decline in mass for the long term exposure to ^{37}WV$_{100}$ which might be explicable as loss of low volatility organics (Fig. 3(b)). The rate of this latter change is nevertheless so low that it cannot interfere with the DW and AS immersion results.

The observation that water sorption by the microfilled resin material (HR) was higher than that of the hybrid-type material (TC) (by about 1.5 times) (Figs. 1 and 2) agrees with that of other workers [28,29]. It has been argued that this effect is simply related to filler volume fraction [28,29] since water sorption occurs predominantly in the resin [30–32]. However, this is insufficient to explain the difference between HR (46% inorganic filler by volume [33, U. Lendenmann, Ivoclar, pers. commun., 2001]) and TC (60% by volume [34]), as the ratio between the two by volume of the resin is then 54/40 = ~1.35. The discrepancy (if confirmed) may be attributed to water held at the filler–matrix interface [35], presumably due to imperfection in the bonding, HR having a proportionately larger interfacial surface area. Indeed, previous studies have shown that RCs absorb more water than estimated on the basis of polymer content [30–32].

Water sorption may alter the values of mechanical properties due to plasticizing and degradational effects—two distinctly different mechanisms. Absorbed water causes sorption expansion, increasing the effective free volume and the ease of movement of chain segments, thus reducing the elastic modulus of the material. Degradation, on the other hand, presumed to be due to leaching of the material's components, has been shown to occur both in water [2,7,36,37] and artificial saliva [17,20], with both organic [17] and inorganic [17,38] materials being lost. The latter has been attributed to hydrolytic degradation of the filler [8,38] and to reaction with the coupling agent, resulting in the failure of the filler–matrix bond [5]. Hence, anticipation of a reduction in the mechanical strength of RCs in a wet environment is not unreasonable since the behavior of composites in general is critically dependent on the matrix-core interfacial bond; indeed, previous studies have demonstrated that water storage lowers the strength of RCs [3,39].

The substantially lower values of F and E, and higher W, in WV$_{100}$ than in VX are clear evidence of the plasticizing effects of water (Table 2), at least for HR, while the significantly higher values of F and W in WV$_{100}$ than in ^{37}DW can only be attributed to leaching that occurs in ^{37}DW (Table 2). However, despite the apparently greater rate of leaching in ^{37}AS than ^{37}DW (Figs. 2(c) and 3(c)), no significant difference in mechanical properties of the material in the two media was found. To resolve this issue will require a larger scale trial with greater discriminatory power and sensitivity.

5. Conclusions

Resin composites are sensitive to atmospheric moisture and this has implications for handling and storage for any studies of properties. Saturation with water can be obtained in a 100% RH environment, but degradation (although not leaching) will occur even then. Exposure to ^{37}WV$_{100}$ may be preferable to ^{37}DW for studies on the effects of water on the properties of RCs while maintaining the materials' structural integrity by avoiding leaching immersion. Leaching appears to go at a greater rate in artificial saliva than in deionized water, although the effects on mechanical properties are not yet clear. On balance, immediate immersion in artificial saliva at 37 °C is the preferred treatment for these materials, whatever time of testing is chosen, on the basis of risk of effects. There is a clear need for, and a general consensus on, the standardization of laboratory tests with respect to environmental conditions. At the very least, temperature, relative humidity and duration should be reported to assist interpretation and comparison between studies.

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