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# Academy of Dental Materials guidance—Resin composites: Part II—Technique sensitivity (handling, polymerization, dimensional changes)

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## ABSTRACT

**Objective.** The objective of this work, commissioned by the Academy of Dental Materials, was to review and critically appraise test methods to characterize properties related to critical issues for dental resin composites, including technique sensitivity and handling, polymerization, and dimensional stability, in order to provide specific guidance to investigators planning studies of these properties.

**Methods.** The properties that relate to each of the main clinical issues identified were ranked in terms of their priority for testing, and the specific test methods within each property were ranked. An attempt was made to focus on the tests and methods likely to be the most useful, applicable, and supported by the literature, and where possible, those showing a correlation with clinical outcomes. Certain methods are only briefly mentioned to be all-inclusive. When a standard test method exists, whether from dentistry or another field, this test has been identified. Specific examples from the literature are included for each test method.

**Results.** The properties for evaluating resin composites were ranked in the priority of measurement as follows: (1) porosity, radiopacity, sensitivity to ambient light, degree of conversion, polymerization kinetics, depth of cure, polymerization shrinkage and rate, polymerization stress, and hygroscopic expansion; (2) stickiness, slump resistance, and viscosity; and (3) thermal expansion.

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*Significance.* The following guidance is meant to aid the researcher in choosing the most appropriate test methods when planning studies designed to assess certain key properties and characteristics of dental resin composites, specifically technique sensitivity and handling during placement, polymerization, and dimensional stability.

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## 1. Introduction

Much of the testing of dental resin composites is designed to ascertain various universal or standardized properties such as strength, hardness, and resistance to wear or deformation. Appropriate test methods for these important properties have recently been reviewed [1]. However, it is well recognized that obtaining the maximum level of these properties is dependent on the clinician and how well they manipulate the materials [2,3]. Therefore, characteristics that may affect the manipulation of the material, or the so called “technique sensitivity”, may have a profound impact on the ultimate properties obtained, and the clinical success of a resin composite restoration. Characteristics such as the stickiness and slump resistance, are very important for clinical handling, but are less amenable to being analyzed by typical standardized tests. Other properties, such as porosity and viscosity, are more likely to have standard tests, but can only be considered as imperfect surrogate measures for assessing the handling characteristic in question. Congruently, some handling characteristics, such as stickiness, can have an impact on other, more well-defined properties, such as porosity.

Extent of polymerization can be well characterized using methods such as Infrared or Raman spectroscopy. But the property itself is affected by a myriad of factors, some of which are inherent in the material (photoinitiator type and amount, resin monomer type), others of which are under the influence of the curing light (irradiance, beam profile, spectral output), and others yet that are under the control of the clinician (exposure time, exposure distance, light guide position) and therefore subject to technique sensitivity. Polymerization likewise results in dimensional changes that are readily measured with tests such as dilatometry, Archimedes principle, or the bonded disk, but the clinical results of such dimensional changes, which may include marginal leakage, interfacial gap formation and tooth fractures, are more difficult to accurately assess. While there might not be true “standard test methods” for properties related to technique sensitivity, there are specific recommended test methods for many of the pertinent properties. The purpose of this paper is to review various tests available for assessing properties associated with the placement technique sensitivity of resin composite, including handling, for characterizing the polymerization reaction of resin composites, and for assessing dimensional change during and after the curing process and its associated outcomes. These properties are summarized in Table 1, and are accompanied by a value representing their relative importance for measurement and study.

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## 2. Technique sensitivity: handling, placement

### 2.1. Stickiness

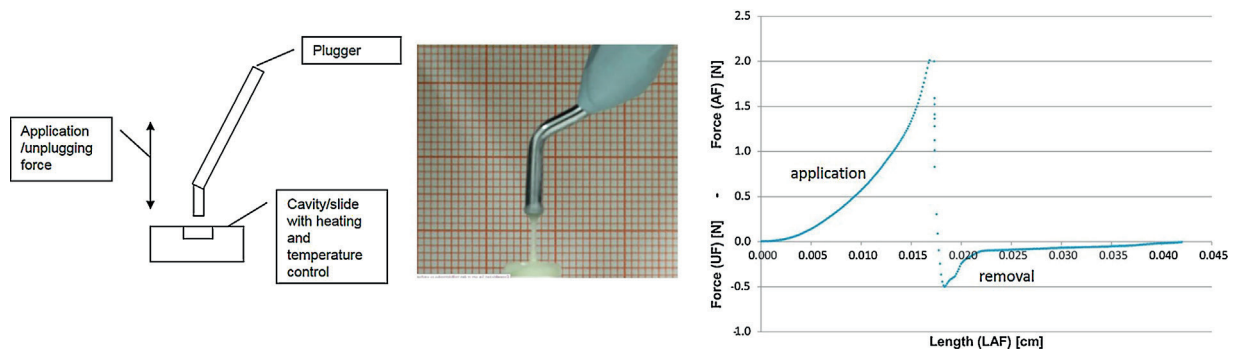
Stickiness refers to the propensity of a resin composite to be retained on an instrument while the material is being placed into the cavity preparation. There is an ideal, yet poorly defined level of stickiness whereby the resin composite will be retained in the cavity and not pulled out or deformed as the placement instrument is removed. A number of tests have been devised to assess stickiness, most of which follow a similar scheme. A set volume of composite is placed in a mold, and then a steel rod or instrument is inserted into the unset material at a constant rate or until a predetermined force or depth is reached; then the motion is reversed until the composite separates from the instrument (Fig. 1). Immediately upon separation, the composite is irradiated with a curing light to harden the material, leaving the surface in the shape of a peak. This peak of composite, sometimes called a “composite flag” can be measured for height and/or area and used as a measure of stickiness [2–5]. Depending on the instrumentation and measurement capability, the unplugging force and work (the force and work required for the composite to detach from the instrument in withdrawal direction) [2] can also be measured and calculated (Fig. 1). All of these methods have been found to be reliable measures of composite stickiness that allow for good differentiation among current materials. In addition, one study correlated the unplugging work and force of various resin composites to the subjective handling characteristics as assessed by dentists and found a good association between the two, indicating that these tests are a good proxy by which to evaluate resin composite stickiness [2]. Resin composite temperature, speed of the instrument/rod insertion and removal, and the surface area and roughness that the composite is in contact with have all been shown to be important factors influencing the results of these tests, and therefore should be well described whenever publishing results in this area.

### 2.2. Slump resistance

Slump resistance is the ability of a resin composite to maintain its shape after placement and prior to curing. This is important in a clinical situation when a clinician desires to sculpt the anatomy of a restoration in the unset paste prior to light curing, in part to reduce the amount of finishing required. This is particularly the case in class III or class V restorations, in large anterior restorations, e.g. a direct composite veneer or a class IV restoration, and when reconstructing the cuspal or crestal anatomy in posterior restorations (class I and II), especially

**Table 1 – Summary of available methods to assess technique sensitivity characteristics, polymerization and dimensional change properties of dental resin composites, ranked in the priority of the specific property/characteristics being tested, as well as of the specific test methods for evaluating that property.**

Clinical issue/ requirement	Properties	Property rank	Method	Test rank
Technique sensitivity: handling — placement	Stickiness	2	Unplugging force, unplugging work	1
			Measure length/area of withdrawn composite	2
	Slump resistance	2	Extrude and cure	1
			Imprint and cure (slump resistance index-SRI)	1
	Viscosity	2	Rheology (with Viscometer)	1
			Pressing under standard load and measure size	2
	Porosity	1	Section — assess under magnification	1
			3D micro-tomography	2
			Archimedes method, ASTM D3171-11	2
			X-ray	2
	Radiopacity	1	ISO 4049 (vs. aluminum step wedge) and ISO13116	1
	Sensitivity to ambient light	1	ISO 4049 (Xenon light box)	1
Polymerization	Degree of conversion	1	FTIR (Fourier transform infrared) spectroscopy	1
			Near IR	1
			FT-Raman	2
			DSC (differential scanning calorimetry)	2
			NMR	4
	Polymerization kinetics — rate	1	FT-IR, NIR, Raman	1
			DSC	1
			Shrinkage/dilatometry	2
			Optical — interferometry, fluorescent probes	2
			Elastic modulus — DMA, rheometer	3
			Acoustic	2
			DEA	2
	Depth of cure	1	ISO 4049 — scraping	2
			Microhardness vs. depth	1
			Chemical vs. depth (FTIR, NIR, Raman)	1
			Penetrometer	2
			Solvent dissolution	3
			Transition in translucency	3
Dimensional stability	Polymerization shrinkage	1	Bonded disk	1
			SSA = stress-strain analyser	1
			Linometer	2
			Dilatometer (e.g. Hg)	2
			Pyknometer	2
			Archimedes method — ISO (17304)	1
			Accuvol camera imaging	2
			Strain gage	2
			Digital image correlation	2
	Polymerization shrinkage rate/kinetics & gel point	1	e.g. from bonded disk or SSA	1
	Polymerization stress	1	via UTM = universal testing machine	1
			Bioman method	1
			Tensilometer (cantilever beam)	1
			SSA = stress-strain analyser	1
			Photoelastic method	2
			Thin ring	2
			Indentation crack analysis	3
	Hygro (swelling) expansion	1	Laser scanning of disk — stored for 3 months or more in water or other solvent.	1
			Calipers or dial gage	2
			Measuring microscope	2
	Thermal expansion	3	Displacement measured over a temperature range	2



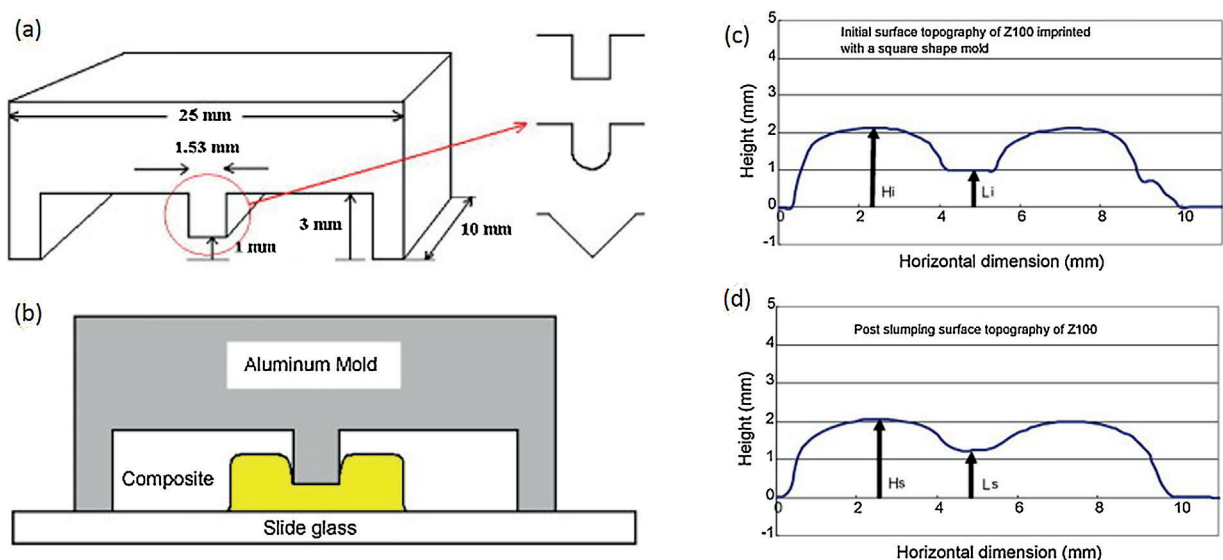
**Fig. 1 – Schematic diagram and photo showing experimental setup to measure forces during application and removal of plugger tip from unset composite to assess stickiness (courtesy of Dr. Martin Rosentritt). Graph shows force–time relationship during application and removal, with work being calculated as the area under the curve (force × distance) (adapted from Rosentritt et al. [2]).**

larger ones. Conversely, since slump resistance runs counter to adaptability, there may be situations in which the dentist might prefer that the composite readily flow and adapt, such as into pits and fissures. Because the viscosity of resin composites can vary widely, different tests are needed to assess differences in slump resistance for different classes of resin composites.

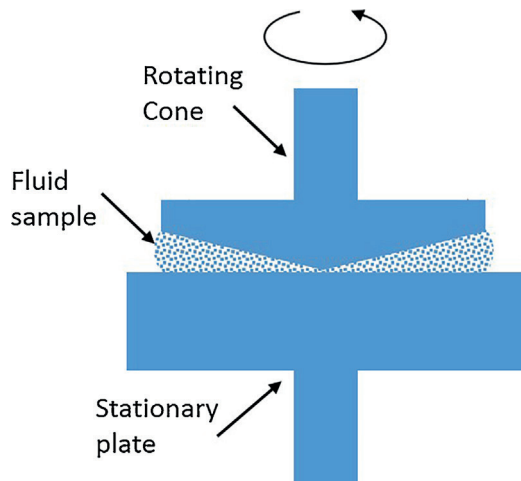
Two tests have been used to test slump resistance of more heavily filled resin composites. In one, a 3D laser scan is used to assess the dimensional change in pre-shaped resin composite at one-minute intervals [6]. Image registration and image matching are used to compare differences in the vertical axis from baseline to subsequent scans and is defined as slumping. The evaluation should be limited to clinically relevant periods, e.g. no more than 3–4 min. An advantage to this test is

that tooth-shaped samples can be used. Limitations of this technique are a vertical resolution of approximately  $10\ \mu\text{m}$ , an inability of the optical setup to measure surface inclinations greater than  $60^\circ$ , thereby making the specimen shape an important factor, and the necessity that the laser being used must emit light in a wavelength that will not initiate polymerization of the resin composite.

The other test (Fig. 2) for more viscous resin composites uses disc-shaped specimens in which a mold with a specific shape is pressed into the surface of the uncured composite [7]. One set of specimens is immediately light cured, while another set is allowed to slump for two minutes prior to light curing. White stone replicas are fabricated and specimen geometries are assessed with 3-D laser profilometry. Changes in the dimensions of the specimens before and after slump-



**Fig. 2 – Schematic showing the aluminum mold used to imprint on composite disks and the cutting profiles of the square, round and triangular shapes (a), the procedure to make an imprint on a composite disc with the aluminum mold (b), the shape of the imprint immediately after removal of the mold (c), and the shape of the imprint after two minutes (d). The slumping resistance index (SRI) was defined as  $H_s - L_s / H_i - L_i$  ( $H_i$ ,  $L_i$ : before slumping heights of the highest and lowest point from the base line, respectively;  $H_s$ ,  $L_s$ : after-slumping heights of the highest and lowest point from the base line, respectively) (adapted from Lee et al. [7]).**



**Fig. 3 – Schematic of the rotational cone and plate rheometer for measuring the viscosity of fluids.**

ing are used to calculate a Slump Resistance Index, which has shown a strong correlation with shear modulus and shear viscosity. This test method has very good resolution (approx.  $1\ \mu\text{m}$  with a high quality scanner). The results are independent of mold shape (triangular, circular, square), but are dependent on time and temperature.

Neither of the above two tests can be applied to flowable resin composites due to their lower viscosity, and therefore an alternative methodology has been developed to measure slump resistance of such materials. This method utilizes a custom-made loading device to extrude flowable resin composite from a syringe and needle of a specific size onto a glass slide [8]. The speed of extrusion is controlled by a stepper motor that moves the piston of the syringe down at a specific and precise rate. Once extrusion of the specified amount of material volume is complete, the resin composite is allowed to slump for 10 s before being light-cured. The outcome measure for this test is the aspect ratio (height/diameter) of the cured, slumped specimen. This test was found to reliably differentiate among flowable resin composites of varying slump resistance, and demonstrated a close correlation to complex viscosity as measured by dynamic oscillatory shear testing [8].

### 2.3. Viscosity

Closely related to slump resistance is viscosity, where viscosity is essentially defined as the resistance to flow for a material or fluid. The above citations note strong correlations between various rheologic (i.e. flow) properties of resin composite and slump resistance. Viscosity is a complex property and is most thoroughly assessed using a parallel plate or cone and plate rheometer to perform a rotational shear test at a specific rotation speed or over a range of frequencies (Fig. 3). The parallel plate arrangement is probably most ideal for filled and very viscous resin composites, because it is difficult to thin the viscous composite sufficiently to ensure that the tip of the cone is in contact with the plate for the latter method. A liquid holding cup with a cylinder rotating within it can also be used for assessing viscosity of very fluid materials, but is not suit-

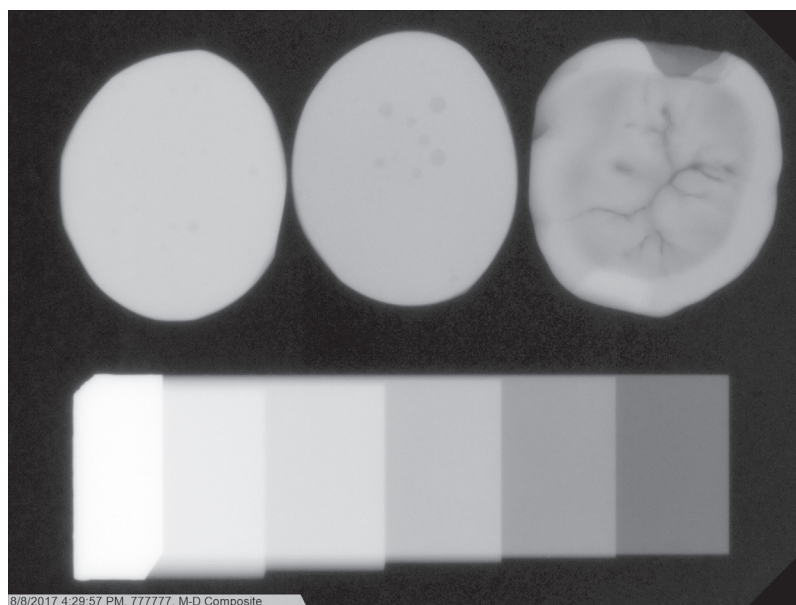
able for viscous composites. This basic design of the parallel plate system can also be employed using a dynamic oscillatory shear force to provide an assessment of complete rheologic properties, including storage shear modulus ( $G'$ ), loss shear modulus ( $G''$ ), loss tangent ( $\tan \delta$ ), and complex viscosity ( $\eta^*$ ) [9,10]. Frequency ( $\omega$ ) is an important variable in the measurement of viscosity using dynamic oscillatory shear tests. Due to the complex interactions of the particles during flow, the viscosity of filled systems is more difficult to measure than that of neat resins or lesser filled resin composites, although even unfilled resins can yield complex shear thinning or thickening behavior.

A much simpler and less expensive assessment of composite viscosity has been described [11]. It employs a methodology used in determining the consistency of elastomeric impression materials [12]. Samples of resin composite are prepared in a mold of predetermined dimensions, removed from the mold and weighed, placed between sheets of plastic and subjected to a constant predefined load for 1 min. At that time, the specimen is imaged, the circumference measured and the surface area computed to define the composite consistency. This test does not determine the actual viscosity of the resin composite, but rather provides a relative comparison of viscosity among various resin composites. A similar method has been used with composite specimens subjected to different heat treatments to reduce viscosity [13]. In this case, the thickness to volume ratio of flattened resin composites was measured after a specific volume of material was subjected to a specified load (4 kg) for a specific period of time (180 s), followed by light-curing. These methods may be more practical and easy to perform than experiments with more expensive rheological equipment, but they are typically less discriminating and provide less overall information.

### 2.4. Porosity

Porosity can exist in the form of voids at the surface or at interfaces between the resin composite and the tooth or another material, or they can be internal to the supplied material. Internal voids can be introduced during the manufacturing of the resin composite, but can also be formed during its clinical manipulation. When present at interfaces, porosity relates, at least indirectly, to the stickiness of the resin composite toward the cavity preparation. The stickier a composite is, the more likely it is to adhere to the placement instrument, poorly adapt to the preparation or previously placed resin composite increment, and form a void. Voids are significant in that they can degrade mechanical and esthetic properties of resin composite restorations [14]. Several assessments have been suggested for evaluating porosity. A simple, non-destructive and inexpensive test is to simply take a radiograph of a composite specimen and evaluate it for the presence of voids [15]. However, this is merely a 2-D representation of a 3-D specimen, therefore it is not possible to locate the voids within the bulk of the specimen, or to differentiate if there is more than one void superimposed on another. In addition, the void size that can be detected is limited by the resolution of the radiograph, making this test more valuable as a screening tool than a true measure of porosity.





**Fig. 4 – Digital dental X-ray showing two different dental composites (top-left and top-center) and a tooth slice (top right) in comparison to an aluminum step wedge, with thickness of 6, 5, 4, 3, 2, and 1 mm when going from left to right (courtesy of Dr. Wen Lien, United States Air Force Dental Evaluation & Consultation Service).**

Another relatively simple and inexpensive test for porosity is to fabricate resin composite specimens, and then section the specimens with a saw. The sections can be observed directly under magnification, or imaged and analyzed digitally, for example with image J software (free of charge from the National Institutes of Health, Bethesda, MD, and available at [imagej.nih.gov](http://imagej.nih.gov)). These sections are then amenable to a number of different assessments, including the number, diameter, area, and/or the location of voids [16]. The disadvantages to this method are that it is once again a 2-D representation of a 3-D phenomenon, and the outcomes will depend on the location and number of sections obtained from each specimen. Also, the assessment can be quite laborious and time consuming, depending on the number of specimens, sections and particular analysis used.

The use of a pycnometer can provide a determination of the overall density of a resin composite. When combined with a high-pressure mercury intrusion porosimeter, it is possible to estimate the pore size distribution as well [17]. This method requires more sophisticated and expensive testing equipment. Another relatively simple and easy method for measuring true density for dental composite is a helium pycnometer [18], though again this method does require special equipment.

A highly accurate, yet sophisticated assessment of porosity within resin composite can be obtained using 3-D X-ray micro-tomography [19]. Standardized samples are fabricated and subjected to high-resolution X-ray tomography (basically imaging a specimen with X-ray energy at a sequence of depths and then compiling the individual 2-D images), resulting in a 3-D rendering of the sample. The images must then undergo digital processing, such as low-pass filtering and edge contrast enhancement, followed by analysis with software to quantitate specimen porosity. This technique not only allows

computation of the percentage of porosity, but also permits visualization of the location of porosities within the sample.

## 2.5. Radiopacity

Radiographic examination is often the best, and sometimes the only way to adequately assess various aspects of the clinical quality of a restoration, including its integrity, the presence of secondary caries, voids, overhangs or open margins, as well as its contour and adaptation to the cavity wall and its contact with other teeth or restorations. To meet these goals, resin composite must have a certain level of radiopacity, the optimal level being debatable. The current ISO 4049 standard [20] calls for resin composite to be at least as radiopaque as an equal thickness of highly pure aluminum (Al) (Fig. 4). This has been shown to correspond to the same level of radiopacity as dentin [15,21,22]. However, the literature is equivocal as to whether this is the level of radiopacity that is most effective at distinguishing secondary caries from normal adjacent tooth structure or the restoration. One study indicated that a resin composite radiopacity close to dentin was most effective at diagnosing a simulated recurrent caries lesion [22]. Others have determined that the resin composite should have radiopacity equal to, or slightly greater than, that of enamel to accurately discern the tooth-restoration margin [15,21] and to accurately detect recurrent caries [23]. In addition, it has been suggested that specimens of enamel and dentin be included in the assessment along with the resin composite samples (see Fig. 4) to enhance clinical relevance [15,21,22]. One must also be aware that many resin dentin adhesives do not contain radiopacifying agents, and therefore may show up as a radiolucency between the resin composite and the tooth on a radiograph, depending upon its thickness.

The ISO 4049 test for radiopacity calls for the fabrication of 1 mm thick cylindrical resin composite specimens that are exposed to a standardized radiograph of specified voltage (kV) and target film distance along with an aluminum step wedge of at least 98% purity with a thickness range of 0.5–5.0 mm in 0.5 mm increments. The optical density (standard film radiograph) or grey scale (digital radiograph) of the step wedge is plotted for each thickness, which is used to convert the radiopacity of the specimen into a corresponding radiopacity of aluminum.

## 2.6. Sensitivity to ambient light

Most current resin composites are visible light cure (VLC), that is, the setting reaction is initiated when the resin composite is irradiated with energy in the visible wavelength region that is absorbed by a photoinitiator contained in the resin. While alternative photoinitiators are being used to some extent, camphorquinone (CQ) is most commonly incorporated into resin composites solely or in conjunction with another photoinitiator. Camphorquinone has a peak absorption around 470 nm, which is in the blue range of the visible light spectrum. Sources of light other than VLC units emit light in this range, such as the operatory room lights, dental operating lights, and sunlight, which can all initiate premature cure of VLC resin composite [24]. If the resin composite begins to harden prior to the dentist completing insertion and manipulation of the material, it can affect the handling characteristics, void formation and adaptation into the cavity preparation. ISO 4049 [20] specifies a value that a material must meet to be considered adequately resistant to ambient light. The current ISO dental standard [20] involves exposure of resin composite to an 8000 lux light source, which is less than other ISO standard testing methods with a 24,000 lux light source. Both methods may differ from the ambient light conditions that may be experienced in a dental operatory. Therefore, as with radiopacity, there is some question as to whether the ISO standard adequately assesses the effect of ambient light on initiating the cure of resin composite. The results of one study showed that the working time as determined when mimicking normal dental conditions was statistically the same as those obtained with the ISO test using 24,000 lux, while the current ISO standard of 8000 lux, being relatively low, significantly over estimated the “real world” working time of the resin composites [25].

The ISO 4049 test for ambient light sensitivity currently uses a xenon lamp, or alternate source with equivalent performance, with appropriate filters to simulate the light spectrum from a dental operating light. The light is placed in a dark room and an illuminance measuring device is used to determine the distance from the light source that provides 8000 lux illuminance. The measuring device is shielded with a black matt cover upon which a glass slide is placed. Approximately 30 mg of spherical-shaped resin composite is placed on the glass slide for 60 s, after which a second glass slide is placed on top of the resin composite and rotated. If no voids or inhomogeneities are discerned, the material is deemed to have passed the test.

## 3. Measurement of polymerization in resin-based dental materials

The extent of polymerization or degree of conversion (DC) is a critical determinant of the properties, potential performance and biocompatibility of polymer-based dental materials. The measurement of DC has typically focused on the photocuring of dental resins and resin composites with somewhat less attention applied to dental adhesives. The similar-sounding terminology of ‘degree of polymerization’ should be avoided in this context since this technically refers to the number of monomer units in a polymer chain and as such it is related to molecular weight rather than the fractional conversion of reactive groups during a polymerization process. Methacrylate functionality accounts for the large majority of reactive groups encountered in resin-based dental materials. Methacrylates can be introduced as monovinyl monomers, divinyl monomers, multifunctional monomers, reactive oligomers or macromers. It should be recognized that DC applies to changes relative to the overall, initial reactive group concentration rather than being directly associated with monomer consumption when crosslinkable monomers are involved. There are diverse examples of classes of monomers other than methacrylates under development for dental materials application such as (meth)acrylamide, thiol-ene, azide-alkyne and others [26,27].

Commercial resin composite restoratives and adhesives based on a cationic oxirane ring-opening polymerization process are in clinical use and have been widely studied. As with all alternative resin formulations, valid methods for conversion assessment must be developed [28–30]. In chain-growth copolymerizations, the conversion of each comonomer can differ [31–33] while in step-growth polymerization processes, such as thiol-ene reactions, conversion of the respective complementary functional groups can diverge due to potential homopolymerization of one of the components or off-stoichiometric ratios in the formulation, making the ability to independently measure conversion of each reactive group important. The situation quickly becomes even more complex with hybrid resin formulations that can include methacrylate conversion overlaid with a secondary reaction that may or may not be orthogonal in nature [34]. For resin composites, the reaction between the matrix phase and a coupling agent tethered to the filler surface should be considered since this also contributes to the overall reactive group concentration and the polymerization process [35,36].

There are a number of aspects of polymer network development and polymer property evolution that are obviously linked to DC. It may be important to know about the induction time that represents the lag between the onset of an initiation process and the actual start of polymerization. For example, this induction time can involve the rapid consumption of inhibitor and dissolved oxygen in a free radical-initiated polymerization or an extended inhibitor-based working time associated with a redox or dual-cure polymerization. The gel point conversion, which can be described as the point where a volume-spanning network structure is initially produced, is critical in polymerization stress studies. The maximum rate of polymerization and the conversion at which it occurs

are often used to discriminate between different resins, initiating systems or curing conditions. An understanding of the kinetics of the polymerization reaction is important for interpretation of separate measurements of polymer property development. Some polymer properties are known to advance in relatively linear fashion with respect to conversion, such as the case with refractive index change and polymerization shrinkage [37]; however, other properties develop in an exponential manner as conversion increases, which is the case for elastic modulus and polymerization stress [36,38]. Other aspects of polymerization, such as conversion-limiting vitrification, post-cure and sol/gel fractions, can only be studied in a meaningful manner if information about DC is available. Mechanical property measurements typically involve results averaged across bulk specimens. Since polymer properties are conversion dependent, it should also be recognized that conversion throughout a polymer sample is not necessarily uniform. A lack of homogeneity in terms of DC can introduce significant challenges in the characterization of materials as is evident in the depth of cure studies of photocured composite restoratives. DC is inevitably well below the 100% level for most dental polymers since achieving complete conversion under ambient curing conditions would result in a rubbery rather than glassy polymer. In the case of thermally assisted lab-processed composites, conversion can be driven to very high values and in heat-cured PMMA denture resins, near quantitative conversion is the expectation.

There are many techniques used to assess the DC of resin-based dental materials or at a minimum, to assure that an adequate level of cure has been achieved. Many of these techniques provide real-time data that allows dynamic monitoring of the polymerization process. Other approaches are static tests and can be relatively simple in nature. This section provides an overview of the available methods to characterize polymerization processes as primarily applied to dental resins and composite materials while highlighting their associated strengths and limitations.

### 3.1. Direct measurements of degree of conversion and reaction rate during polymerization

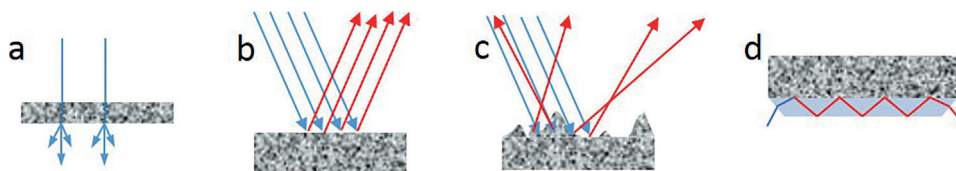
There are a variety of spectroscopic techniques that are appropriately applied to quantify the DC and potentially, the instantaneous rate of polymerization reactions. These include mid- and near-infrared spectroscopy in various forms, as well as Raman spectroscopy. These methods can directly provide the concentration of reactive groups associated with a polymerization process. Magic angle spinning  $^{13}\text{C}$  nuclear magnetic resonance (MAS-NMR) spectroscopy, while not widely used in the characterization of polymerization, also offers the capability to provide direct measurement of residual reactive group concentration [39–42]. The solid-state NMR analysis method does not readily permit dynamic conversion data; however other magnetic resonance imaging techniques do provide real-time data that has been used to monitor polymerization processes, but not coupled with DC [43,44]. Differential scanning calorimetry also can be used as it provides direct real-time conversion information based on the heat released as reactive groups engage in the polymerization.

#### 3.1.1. Mid-IR spectroscopy

The most commonly used analytical method for quantitative determination of DC is Fourier transform infrared (FTIR) spectroscopy. The mid-IR spectrum ( $\sim 4000\text{--}400\text{ cm}^{-1}$  that corresponds to  $2500\text{--}25,000\text{ nm}$ ) contains several fundamental absorbance bands associated with the carbon–carbon double bond in methacrylate monomers. Absorbance bands for alternative vinyl groups used in other polymerization strategies as well as alternate reactive groups including thiols, isocyanates, epoxides and others can also be identified in the mid-IR region. It is important to recognize that the molar absorptivity or the concentration-dependent intensity of different absorbance bands vary greatly. Depending on the resin composition, there may also be other overlapping absorptions that complicate or eliminate the choice of certain reactive group bands. The generally high absorbance level within the mid-IR spectral region effectively imposes specimen thickness constraints. Unfilled resins of about  $5\text{--}50\text{ }\mu\text{m}$  thickness can be used in direct transmission mid-IR analysis; however, this path length range can vary depending on the initial reactive group concentration and the specific molar absorptivity as related to the Beer–Lambert Law. Thicker films lead to signal saturation where peaks with absorbance-based optical density beyond 2.0, which corresponds to less than 1% light transmission, become nonlinear and should not be used for any quantitative assessment of conversion including use as an internal reference standard. In filled resin composite samples, the glass filler also absorbs strongly in the mid-IR and while the reactive group concentration is reduced as the filler loading increases, only very thin composite films can be analyzed in mid-IR in transmission mode. The restriction for thin film transmission means that reaction exotherm effects during curing are modest, however irradiative heating effects that may be associated with high output curing lights need to be considered since this can significantly alter reaction kinetics and the limiting conversion achieved in a photocuring process. As such, it is inadvisable to directly relate reaction kinetics or DC results obtained from a thin film specimen to thicker samples such as those used in mechanical property measurements. Another limitation of transmission mode mid-IR spectroscopy is the choice of substrates that can be used. Salt plates ( $\text{NaCl}$ ,  $\text{KBr}$ ,  $\text{CaF}_2$  and other materials) are typically used and specimens must be sandwiched between these substrates to avoid oxygen inhibition effects that are severe in thin-film situations. Use of sandwiched substrates with resins that form crosslinked polymers also requires a furnace or flame burnout treatment or aggressive solvent soaking to recover the salt plates for reuse.

Fortunately, there are several alternative approaches available for the collection of mid-IR spectra that avoid the transmission mode specimen restrictions [45] (Fig. 5). An attenuated total reflection (ATR) accessory can be fitted to a standard FTIR spectrophotometer or dedicated ATR-IR devices are available. The ATR approach uses a high refractive index substrate that gives multiple internal reflections of the IR signal at the specimen interface. The absorbance results from penetration of the signal approximately  $1\text{--}5\text{ }\mu\text{m}$  into the sample on each reflection. Therefore, this approach, which can accommodate a variety of specimen thicknesses, provides mid-IR spectral information exclusively from the surface





**Fig. 5 – Various modes for obtaining infrared spectra involving bulk characterization in transmission (a) or surface characterization based on either specular reflectance from smooth surfaces (b), diffuse reflectance from rough or ground samples (c) or attenuated total reflectance (d).**

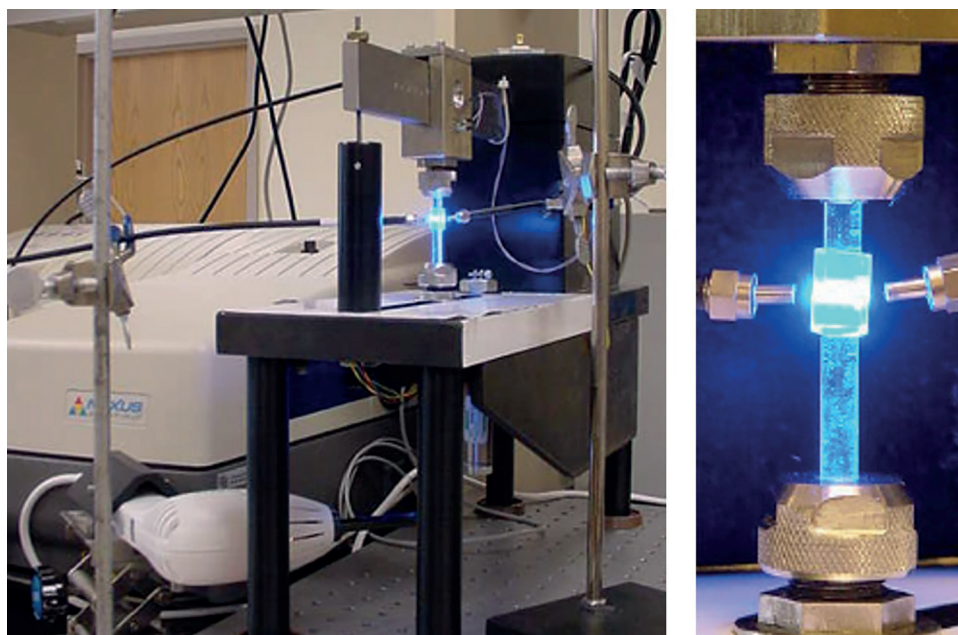
region. Specimens can be created in different thicknesses to allow comparison of the respective top and bottom surface conversion as a consequence of a given curing condition. This is typically employed in photocured resin composite materials where it offers an excellent method to obtain depth-dependent conversion information that is very relevant for studies applied to bulk fill materials. The actual path length of the ATR signal within the sample differs based on wavelength (longer wavelengths penetrate more deeply) and the penetration depth changes along with the increase in refractive index of the sample that accompanies polymerization. The change in bulk refractive index during photopolymerization of a resin composite material varies not only with conversion but also with filler content. Corrections for these factors are possible and required to get accurate conversion results. Other mid-IR sampling techniques can use ground materials that are diluted with an IR transmissive powder, such as KBr, to form a pellet that can then be analyzed in transmission mode. In similar fashion, a diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) accessory can be used to collect the scattered reflectance IR signal from abraded or otherwise powdered samples. These are static analyses not conducive to studies of reaction kinetics. A microscope attachment connected to an FTIR device can be used in either transmission or reflectance mode to obtain IR spectra useful for spatially resolved conversion measurements or to follow kinetics [46].

### 3.1.2. Near-infrared spectroscopy

The use of Fourier transform near-infrared (NIR) spectroscopy for conversion measurement in dental polymers has expanded significantly over the past decade [47]. As with the mid-IR analysis, the NIR spectrum, which spans from 4000 to 12,500  $\text{cm}^{-1}$  (2500–800 nm), provides a means to measure methacrylate and other reactive group concentrations directly. Since the NIR spectrum involves absorbances arising from overtone and combination bands rather than fundamental absorbances, the general absorptivity is considerably less than that in the mid-IR region. This means that thicker specimens that offer greater path lengths are best suited for NIR analysis in transmission mode while reflectance-based NIR measurements require special consideration. In general, appropriate specimen thickness can range from films of approximately 100  $\mu\text{m}$  up to sample geometries of 5–10 mm. This makes NIR spectroscopy convenient for averaged bulk conversion measurements within specimens created for mechanical testing, polymerization stress measurements or a wide variety of other testing protocols. Since the NIR spectrum empha-

sizes absorbances related to CH, OH and NH bonds, glass slides, which contribute a negligible SiOH surface layer, can be used as sample substrates. This also means that silica-based fillers, even at high loading levels, have a very limited effect on NIR signal transmission across thick composite samples. The NIR signal can also be transported very efficiently via fiber optic cables and this, along with a general insensitivity towards unpurged sampling environments, makes conversion measurement by NIR amenable to remote testing in conjunction with other dynamic testing procedures. NIR analysis has been coupled in real-time with simultaneous measurements of polymerization shrinkage, shrinkage stress (Fig. 6) and elastic modulus evolution as well as optical property changes and photoinitiator consumption. This capability to link polymer property evolution to the advancing DC rather than just to reaction time provides valuable information that helps distinguish differences among materials, especially when mechanistically distinct polymerizations are involved [47].

In any of the spectroscopic approaches where the FTIR signal cross-section and path length are uncertain, as occurs when separate monomer and polymer specimens are utilized, an internal reference peak is necessary to obtain valid conversion results. Selection of an appropriate internal reference standard is ideally based on a well-resolved peak in the vicinity of the reactive group absorbance that does not change during polymerization in terms of intensity, position, shape or baseline. All these constraints are rarely achieved so it should be acknowledged that a greater degree of uncertainty is introduced into the accuracy of the conversion calculations as greater compromises are made with the standard reference peak measurements. A common example is in the use of the ester carbonyl band as an internal reference since the reaction of the conjugated methacrylate C=C changes both the position and absorptivity of the carbonyl peak. Signal-to-noise issues that may limit the precision of the conversion measurement can be accommodated in static analyses through increased numbers of averaged spectral scans. Care also needs to be taken in the methods for constructing the baseline(s) used to measure peak areas, which are preferred to measurements based on peak heights [48]. In studies designed to look specifically at the reliability of varied baseline construction protocols, mixtures of active methacrylate monomers along with hydrogenated analogs of the same monomers in known proportions were used to determine the best fit [49,50]. Of course, different resins and alternative reactive groups as well as different internal reference peaks mean that the spec-



**Fig. 6 – Cantilever beam tensometer device for dynamic measurement of polymerization stress in coordination with real-time near-infrared spectroscopy for simultaneous monitoring of degree of conversion. The resin or composite specimen is placed in the gap between two silanized quartz rods with the lower rod serving as a light guide to convey the curing light. The NIR signal is directed to and from the specimen by fiber optic cables.**

tral acquisition parameters and the spectral analysis methods need to be revised with almost every new material evaluated. As mentioned, dynamic measurement of conversion by FTIR in real-time is frequently used to determine basic reaction kinetics. Depending on the spectrophotometer, full FTIR spectra can be acquired at millisecond rates, but sampling rates of 1–10 Hz are generally accessible and can reasonably be applied to even fast photopolymerizations. In dynamic evaluations of conversion where neither the specimen nor the FTIR beam are physically repositioned during the polymerization process, it may not be necessary to use an internal reference peak. This can be verified by a simple observation of a secondary peak that remains constant before and after polymerization. Variations in light scattering during polymerization [51] in both unfilled and filled materials can create artifacts in conversion measurements. In photopolymerizations, if the entire specimen is not exposed, the local conversion within the FTIR sampling area can display an obvious artifact with conversion that decreases from a maximum after the curing light is extinguished, which is due to monomer diffusion into the photocured region. This potential for monomer diffusion from an uncured region into a cured region should at least be considered when photocuring physically large samples, such as flexural strength specimens that require stepwise irradiation protocols.

### 3.1.3. Raman spectroscopy

Like FTIR approaches, Raman spectroscopy provides a means to directly measure reactive group concentrations during or following polymerization. Unlike IR, Raman analyses involve wavelength-dependent light scattering rather than light absorption. Raman relies on changes in wavelength of the

incident light as a result of its interaction with the rotational and vibrational energy levels in molecules, which includes vinyl groups and other reactive functionality in monomers. This distinction between Raman and IR means that certain functionality that provides a weak signal by one technique may give a strong response by the alternate testing mode. In certain cases, strong auto-fluorescence associated with samples can preclude Raman as a viable option. On the other hand, micro-Raman spectroscopy has been used very effectively to determine the quality of the polymerization within dental adhesive layers [52,53]. The use of confocal Raman depth profiling capabilities has been used to probe oxygen-inhibited surface layers [54] as well as a source of depth-dependent data on both polymer composition and conversion in dental adhesives. Accurate depth-dependent conversion data requires that optical variations at least be considered [55].

### 3.1.4. Differential scanning calorimetry

Rather than directly monitoring reactive group concentrations, differential scanning calorimetry (DSC) reports on enthalpic heat flow associated with chemical and physical transitions within materials. The specimen size is usually approximately 10 mg of material spread along the floor of a highly conductive, metallic sample pan. The exothermic polymerization process releases heat in direct proportion to the molar concentration of reactive groups undergoing conversion. The type of reactive group involved in the polymerization determines the specific molar heat coefficient and if this is known along with the initial molar concentration of reactive groups, then the heat flow at any time directly represents the reaction rate and the integrated time-dependent heat flow plot at any stage provides the advancing DC [56,57]. This is the

opposite situation compared with IR-based analyses where conversion is measured directly and reaction rate is calculated from the derivative of the conversion plot. Thermal polymerizations can be initiated with flexibly imposed heating programs where the externally applied heat is compensated by subtraction of the signal from an empty reference pan. Even quite volatile monomers such as methyl methacrylate can be analyzed in a sealed pan. Under isothermal conditions, photo-accessible DSC instrumentation allows the polymerization process to be photo-initiated in open sample pans typically with a nitrogen purge to avoid oxygen inhibition. Highly variable kinetic results are obtained if insufficient purge times are used. The heating effects due to light absorption, especially in filled and pigmented materials, cannot be compensated for with an empty reference pan so a pre-cured sample is often introduced on the reference side. The sample pans also create some uncertainty in the irradiant intensity used in a photopolymerization process since there is unavoidable reflection within the pan. In resin composite materials, it is also difficult to assign an appropriate initial reactive group concentration. At low reaction rates, such as when a reaction is approaching a vitrification-limited plateau, the sensitivity of DSC-based conversion measurements is challenged. At the other extreme, very fast polymerizations also pose difficulties for accurate DSC measurements. A modified device known as an optical pyrometer was developed specifically to accommodate photopolymerizations of very rapidly cured UV coatings [58]. For polymerizations associated with monomers other than conventional (meth)acrylates and epoxides, the heat of reaction may not be available, which requires that these values be determined through calculation or preliminary studies with model compounds that can achieve complete conversion. Individual contributions from mixed reactive groups in a polymerization cannot be differentiated unless used in staged reaction form. The DSC thermal analysis approach is relatively simple to conduct but as noted, careful consideration of complicating factors is required to obtain reliable polymerization data.

### 3.2. Indirect measurements polymerization and polymerization kinetics

There is a wide array of testing protocols, both static and dynamic, that do not directly track the conversion associated with a polymerization process but rather monitor some aspect of polymer property development that corresponds with polymer formation. In some cases, these tests have been calibrated with actual conversion measurements such that within a given material, DC can be estimated from the measured property; however, it is important to recognize that any type of indirect method to assess conversion requires recalibration even with a minor material formulation change or when the polymerization conditions are altered. As long as limitations are acknowledged, there can be considerable value in the comparative results obtained with these indirect methods used to monitor polymerization.

#### 3.2.1. Dilatometry

A variety of approaches related to dilatometry can provide a close approximation to a direct conversion measurement [59].

This is because there is a specific molar shrinkage coefficient that can be attributed to any type of reactive group involved in a polymerization. (Meth)acrylate and epoxy monomers are well characterized with respect to their polymerization shrinkage behavior and these shrinkage coefficients are available in the literature [60–62]. However, in some cases, these values may be unknown, which would require an experimental determination typically based on density change during a model reaction either taken to completion or coupled with a separate measure of conversion. The static determination of volume change with polymerization has been used with reasonable confidence to estimate the DC of a variety of polymerized dental resins and composites, where filler reduces the potential shrinkage based on its volume fraction. The application of dynamic dilatometry, or related methods as with the bonded disc or linometer techniques (see later section), to assess reaction rate are more complicated since any change in temperature during the polymerization process leads to thermal expansion or contraction that convolutes to the overall volume change. This leads to apparent reaction rates that are artificially suppressed early in conversion as heating effects including the reaction exotherm are increasing followed by artificially enhanced rates at moderate conversion as cooling begins. Even if careful measurement of temperature change is included with the shrinkage data, the compensation for the thermal effects on shrinkage is not straightforward since the coefficient of thermal expansion decreases as the polymerization proceeds. The latter stages of polymerization can also lead to diversions between shrinkage and conversion based on delayed shrinkage in glassy polymer networks [47,63]. There are potential issues associated with non-uniform shrinkage that result from different specimen geometries and bonded surface constraints that can skew the relationship between shrinkage rate and reaction rate.

#### 3.2.2. Optical property measurements associated with polymerization

As a liquid monomer is transformed to a rubbery or glassy polymer through polymerization, the optical properties of the material change. The refractive index of a monomer is determined by its chemical structure, molecular weight and polarizability [64]. Directly related to the increase in density monitored by dilatometry, the refractive index of the resin phase typically approaches or modestly exceeds that of the filler as polymerization progresses, which promotes enhanced translucency in the cured composite (Fig. 7). In similar fashion, interferometry can be used to follow the change in thickness and the refractive index transition as monomer is converted to polymer. These optical approaches can be linked directly to conversion through independent measurements [65] but they can also be used as a means to assess polymerization shrinkage rates as well as factors such as the extent of tooth deflection during restorative placement without any direct connection to conversion [66–68]. These optical techniques are quite sensitive to temperature variation, which means the test environment must be well controlled as the reaction exotherm or light-induced heating will affect any kinetic data. Fluorescent probes have also been used to examine changes in mobility restriction or polarity that accompany a polymer-



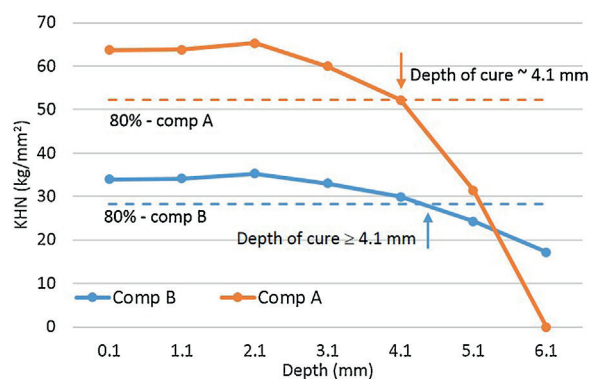


**Fig. 7 – Changes in shade and translucency of photocured composite (top) relative to the analogous uncured paste (bottom; both 1 mm thick) occur due to initiator consumption (CQ/amine here) and an improved refractive index match between resin and filler.**

ization process [69–72]. Probes have to be selected carefully to provide valid reporting within a given resin system.

### 3.2.3. Mechanical testing evaluations of polymerization — surface hardness

Knoop, Rockwell, Vickers, Brinell, Shore, etc. modes of hardness testing have been used mainly as a widely accessible means to determine that an adequate extent of polymerization has been achieved in a dental resin composite. Hardness testing involves the controlled insertion and removal of a probe that varies in dimension, shape and loading force depending on the test instrumentation employed and the material undergoing testing. Hardness tests do not provide dynamic data during polymerization; however, static measurements taken at various stages during a polymerization allow the progression of hardness to be assessed. Micro-hardness results are most often encountered in the dental literature although higher resolution studies are done using nanoindentation [73,74] and atomic force microscopy (AFM) [75]. Depending on the testing footprint and extent of penetration, the sampling sites should be selected to avoid edge effects and overlapping stress fields from adjacent indentations as well as running tests only on flat specimens that



**Fig. 8 – Hardness vs. depth profiles for two composites having very different surface hardness values, but nearly equivalent depth of cure. Depth of cure is depicted as the depth where the hardness just falls below 80% of the maximum hardness value, and is approximately 4.1 mm for both materials.**

are perpendicular to the probe and thick enough to eliminate effects from the substrate. The evolution of surface hardness is directly related to changes in polymer viscosity, shrinkage and modulus [76] and it increases exponentially relative to the DC [77]. Hardness measurements offer a convenient means to monitor extended post-cure potential of polymeric materials [78]. A depth of cure profile can be readily constructed by sequential sampling of hardness through the cross-section of a material (Fig. 8), with the potential to then connect the hardness data with localized measurements of conversion [79]. Micro-hardness mapping can be very appropriately applied to determine whether the lateral DC within a single material is equivalent across a given surface, and has been applied to study the potential for heterogeneous conversion of photocured resin composite irradiated with curing lights that may not provide a spatially homogeneous spectral output of intensity or wavelength [80]. The ability to compare the hardness of top and bottom surfaces for a given specimen thickness is an excellent method to determine an effective photocure depth for a particular material with a particular curing condition. A top versus bottom hardness (or alternatively, a comparison of the bottom hardness with the maximum hardness that may occur slightly below the irradiated surface) that is not statistically different over a certain thickness provides convincing proof that the entire sample is well polymerized. An assignment of a bottom surface hardness that is 80% the hardness measured at the top has also been used to indicate that a polymer-based specimen is adequately cured (Fig. 8), but this arbitrary value does not apply equally across different materials. For example, differences in resin phase modulus and shrinkage or in the filler types and volume levels used in resin composites will cause hardness to develop quite differently for different materials. In particular, surface hardness is quite sensitive to filler volume fraction and less sensitive to polymer modulus, so it may be inadvisable to directly compare hardness values between different materials. Hardness is also sensitive to the actual load applied in the test, and to the amount of time lapsed between curing and testing.



### 3.2.4. Elastic modulus development with polymerization

The transition of a fluid, low molecular weight monomer to a glassy polymer network structure typically involves a change of six or more orders of magnitude in the modulus of the material. In rapid polymerization reactions, these dramatic changes can occur within seconds. Modulus measurement can involve several different but related modes of modulus, which includes Young's modulus, which is the elastic or tensile modulus (obtained in extension), compressive modulus (that can differ considerably as compared with the tensile modulus), flexural modulus (obtained in three or four-point bending or in cantilever bending mode and includes both tensile and compressive components), and shear modulus (obtained by rotating plate or oscillating fiber devices). All these modes reflect the change in stiffness or elasticity of the material with polymerization. The testing is carried out with a range of instrumentation including universal mechanical testing device, dynamic mechanical analyzer (DMA) [38], rheometer (parallel plate or cone and plate typically but also torsional braid format), and ultrasonic or acoustic testing methods [81]. For real-time evaluations of modulus, these tests are conducted under isothermal conditions typically involving photopolymerization; however, many of these methods allow for controlled heating that can be used to statically define the rubbery modulus of a material, which is used in the calculation of polymer network crosslink density. Additional related testing protocols used to track polymer property development include dielectric analysis (DEA), which monitors ion permittivity and in some studies has been directly linked to polymer modulus [82,83]. DEA offers broad dynamic range with high sampling frequencies at the initial stages of polymerization where many other analytical methods cannot keep up with very rapid photocuring reactions.

### 3.2.5. Depth of cure

With the market-based move to bulk fill restoration placement, the importance in knowing the depth of cure of various photocured composite materials activated by exposure to a variety of dental curing lights has become a very active field within dental materials. The need to fill cavity preparations that may be four or more millimeters in depth with a single bulk restorative placement is an obvious challenge based on the significant light attenuation involved. The depth of cure methodology is defined by ISO standard 4049 and it involves scraping away the uncured/poorly cured material at the base of the specimen and then dividing the remaining cured depth by two to provide reasonable assurance of adequate cure to at least that point [20,84]. Other suggested measures for depth of cure involve direct conversion measurements by cross sectional profiling using a variety of mid-IR, NIR and Raman [85] spectroscopic techniques. As previously mentioned, top/bottom surface hardness of progressively thicker specimens or specimens overlaid with pre-cured material blocks have been used to assess an effective depth of cure. It should be noted that whenever interfaces are imposed, as with a glass slide or polymer film substrate as well as specimens that use adjoined pre-cured layers, the reflection at the interface will reduce the light transmission within the specimen. Penetrometer techniques that use a weighted probe that penetrates to a fixed point of resistance are widely used

with depth of cure obtained by difference. A recent approach proposes depth of cure determination with DEA or electron paramagnetic resonance (EPR) that can provide the depth at which the polymer transitions from a glassy to a rubbery state [86]. Another readily accessible method that can also distinguish between uncured, poorly cured and well cured polymer involves simply immersing depth of cure samples in an appropriate solvent and observing a zone of swelling as well as where complete dissolution occurs [87].

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## 4. Dimensional stability and marginal integrity

### 4.1. The clinical problem

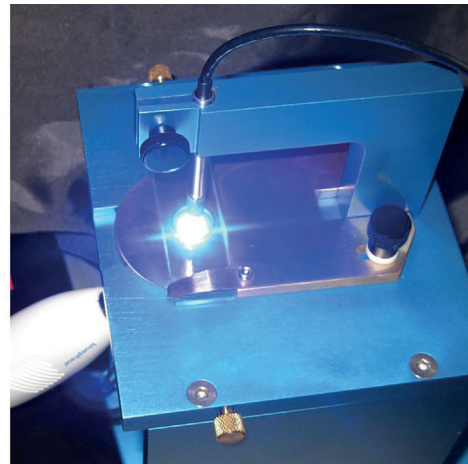
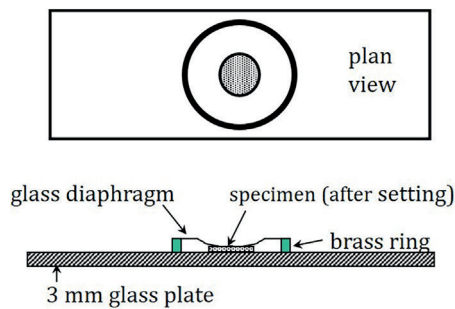
*Direct placement* means that dental restorative materials are placed during clinical treatment into a prepared cavity and undergo their setting reaction *in situ* under the conditions of temperature, moisture, etc. prevailing in the oral environment. Resin composite materials are supplied with a rather wide range of initial viscosities ranging from stiff pastes to flowable fluids, determined by the monomer mixture and especially by the volume fraction and size of dispersed particles. Dimensional stability and marginal integrity are initially influenced by the *adaptation* of the unset resin composite paste to the cavity walls and floor and by its *compatibility* with the adhesive-coated hard tissues. Micro-mechanical retention and/or molecular reactions that may be achieved at the interface will enhance subsequent marginal quality, other factors being equal.

Dimensional stability of resin composites in dental cavities can be challenged by both intrinsic and extrinsic factors. The latter include biomechanical fatigue loading and swelling due to liquid uptake in the oral environment. The loading aspect will be considered separately under the heading of *Durability and Stability*. The main *intrinsic* aspects arise from polymerization shrinkage phenomena, together with lesser thermal expansion/contraction effects.

Polymerization shrinkage is a complex phenomenon that originates at an intrinsic molecular level with matrix monomers that undergo addition polymerization mechanisms. The process of monomer addition, creating the 3D matrix network, also creates nano-scale free volume. This translates into bulk volumetric shrinkage of the resin composite mass, particularly when the material is unconstrained by its local environment. Accompanying the polymerization shrinkage is the time-dependent development of the solid material *modulus* (stiffness).

Whenever the material is subject to partial or total restraint – as in a dental cavity – the result is an interfacial shrinkage-stress. On the rather doubtful assumption of Hooke's law, to a first approximation the stress ( $\sigma_t$ ) at time  $t$  is the product of the instantaneous elastic modulus ( $E_t$ ) and the shrinkage ( $\epsilon_t$ ). However, the measured shrinkage-stress is not itself a material property but a synergistic effect of the test material and its host environment. There is much confusion on this point in the literature.

Though direct clinical evidence does not exist, post-operative effects with dental composites have most often



**Fig. 9 – Bonded disk device for measuring polymerization shrinkage. Cartoon and photograph of the method, in which a composite is cured through a thin cover slip supported by a rigid brass ring, causing the glass to deform a measureable amount, and thus quantitatively indicating the polymerization shrinkage of the composite.**

been suggested as a likely outcome from the shrinkage-stress. It is possible to be skeptical as to whether these are solely attributable to polymerization shrinkage. For ethical reasons it is not feasible to design randomised clinical trials to determine this. Nevertheless there is direct evidence for cuspal bending deformations in cavities restored with materials known to generate high shrinkage stresses. So there is a consensus that measurement of both shrinkage (strain) and shrinkage-stress can provide helpful information to guide material selection and future material development [88,89].

#### 4.2. Experimental design considerations for measuring shrinkage phenomena

It is desirable that *in vitro* laboratory investigations should mimic *in vivo* clinical realities, as far as possible. However, clinical restorations are custom made and of varying and irregular geometry. So, it is preferable to use standardized geometries for test specimens in the interests of both precision measurements and inter-laboratory comparisons. This is the universal approach within *International (ISO) Standards* for dental biomaterials. Moreover, such methods should ideally be capable of handling a range of viscosities, temperatures and irradiances. The finite-thickness light transmission properties of dental resin composites discussed in the earlier section means that at least one of the specimen dimensions should ideally be thin enough to permit approximately uniform irradiation throughout the specimen thickness. Hardness *versus* depth profiles suggest that for most resin composites, disk-shaped specimens of about 1 mm thickness usually satisfy these requirements, especially where they can be irradiated with complete light coverage that is perpendicular to the diametral surface.

##### 4.2.1. Shrinkage parameters

There are several aspects of shrinkage that can be measured for comparison with the clinical situation, as follows:

- The *direction* of shrinkage.
- The *magnitude* of shrinkage — normally the maximum value attained within a given time, expressed as a percentage (%).
- The *kinetics* of shrinkage. This can be plotted, *versus* time, either as shrinkage (%) or as the *rate* (time-derivative) of shrinkage with units %/s or % s<sup>-1</sup>.

It should be noted that there is a rather common linguistic confusion over the term 'rate'. Some scientists have referred to the 'rate' of shrinkage when they really mean the *magnitude* (%) of shrinkage.

#### 4.3. Specific polymerization shrinkage methods

##### 4.3.1. Bonded disk method

The bonded disk is a well-established method used for over two decades in both academia and industry [90–95] to measure the kinetics of shrinkage-strain development for disk-shaped specimens with a typical aspect ratio of 8:1 (Fig. 9). An 8 mm diameter disk specimen of composite paste is created upon a rigid 3 mm glass plate, to which it is effectively attached through the inherent stickiness of the matrix monomers. With very stiff pastes, the upper central portion of the plate may first be jet-blasted (air-abraded) to promote attachment. With flowable resin composites, or unfilled monomers, disk specimens can be created and contained within a soft wax ring. In all cases the specimen disk is centrally located within an outer peripheral brass ring of square cross-section (1 × 1 mm) and 15 mm internal diameter, bonded to the lower glass plate. Resting on the upper surface of the specimen disk, and similarly adherent, is a highly compliant glass diaphragm of 0.13 mm thickness. This cover-slip diaphragm is also supported by the brass ring. Hence, when the disk-fabrication procedure is carried out, the height of the specimen disk is determined by the 1.0 mm thickness of the brass ring. Most un-set pastes are completely plastic, but with some materials that might exhibit slight elastic 'memory', it may be advisable to allow a recovery period (e.g. 30 s) to allow a final equilibrium dimension to be attained, prior to irradiation and cure.

This specimen geometry has been carefully selected to ensure:

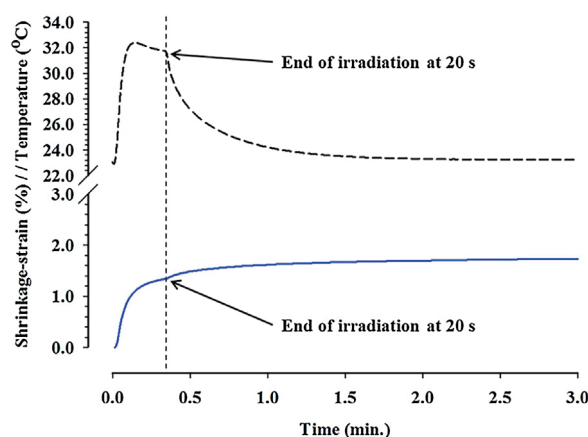
- A defined *configuration factor* — ratio of the area of bonded to unbonded (free) surfaces.
- Specimen diameter matching the light-beam diameter of visible light-curing units (LCUs).
- Specimen thin enough to ensure adequate light penetration and thus essentially equal monomer conversion on upper and lower surfaces, and hence throughout the thickness.
- Capability of control and variation of specimen temperature and curing irradiance ( $\text{mW}/\text{cm}^2$  absorbed from the light curing unit).
- An axial shrinkage direction governed by the configuration, rather than by the direction of light-irradiation.
- Essentially zero shrinkage in the radial direction and thus maximal shrinkage in the vertical (axial) direction. In consequence, axial shrinkage strain ( $\epsilon = \Delta L/L_0$ ) is essentially equal to volumetric shrinkage strain ( $\Delta V/V_0$ ) of the material, where  $L_0$ ,  $V_0$  are original specimen height and volume. This has been verified by several means. Nevertheless, caution should be exercised in direct comparisons between shrinkage results obtained by different methods, since the constraining boundary conditions may affect the results.

The bonded disk method is versatile in respect of the specimen viscosity. It may be applied to adhesives and biomaterials which are either light-cured or self-cured (after mixing), by either auto-cure or acid-base reaction. It is normally applied to the study of viscous pastes, but with some adaptations, as noted above, may be used successfully and reproducibly with low viscosity, unfilled resin monomers.

The glass plate and specimen assembly are mounted horizontally within a stable measurement frame that may incorporate a heating device to set the initial specimen temperature within the range  $20\text{--}80^\circ\text{C}$ , but normally  $20\text{--}37^\circ\text{C}$ . For light-activated products, cure is initiated from below by transillumination of the glass plate beneath the specimen by means of a LED-LCU (light curing unit), but preferably one with a uniform beam profile.

An upper arm rising above the platform carries a calibrated LVDT (linear variable differential transducer) and may have a precision height-adjustment facility incorporated. The LVDT displacement transducer, with sensitivity greater than  $0.1\text{ }\mu\text{m}$ , is positioned for axial measurements in contact with the center of the cover slip. The LVDT is connected via a signal-conditioning unit to a high resolution A/D converter and computer. The cover slip is pulled axially downwards as shrinkage takes place, and the displacement at the center of the cover slip is monitored by the LVDT transducer and displayed in real time on the computer screen. The axial displacement of the disk upper surface is sufficiently uniform to be representative, unless a LCU of uneven beam profile is used.

Normally the shrinkage kinetic is followed for 60 min, although the major change often occurs within 5 min and hence a period of 20 min may be sufficient in some circumstances. It is common to observe a *transient* effect of exothermic and radiant heating/expansion within the first few minutes after the start of irradiation. This is manifest as a 'blip', or change of gradient, in the kinetic plot (Fig. 10).



**Fig. 10 – Simultaneous exotherm and shrinkage data for a representative resin-composite plotted for the first 3 min. The temporary 'blip' in the shrinkage caused by thermal expansion is apparent.**

Any method that can determine continuous shrinkage data as a function of time can be converted into shrinkage rate ( $\text{s}^{-1}$ ) by numerical differentiation [95]. Key parameters are the maximum shrinkage-rate and the time-to-maximum.

#### 4.3.2. Linometer method

The linometer method is superficially similar to the bonded disk method in so far as it uses a disk specimen of similar dimensions, and measurements of  $\Delta L$  are made in the axial direction [96]. However, the shrinkage in the material is isotropic, not anisotropic if a grease film or other lubricant surface treatment of the rigid substrates is applied such that the disk is *non-bonded* to any support. Capacitance measurements are used to measure the isotropic changes in 1-D and these are then converted to volumetric strain (equivalent to three times the linear strain) by assuming isotropy.

#### 4.3.3. Strain-gage methods

Electrical resistance strain gages may be bonded to a substrate carrying a composite paste. When the material shrinks the dimensional change is registered via a change of resistance in the gage. It is usually necessary to correct for the heating effects arising from the reaction exotherm and the heating effect of the light, both of which can cause some transient expansion. The principal use of the method is to identify the onset of post-gel shrinkage in systems where this is distinguishable from total shrinkage [97].

#### 4.3.4. Archimedes method

The Archimedes method involves precision weighing of specimens supported in a fluid [98,99]. However the fluid should be non-aqueous, such as silicone oil, to avoid hygroscopic uptake. It is useful for long-period studies of slow-setting materials.

#### 4.3.5. Dilatometer methods

Dilatometric methods are long established [100] and can be applied to arbitrary specimen shapes. Normally, the specimen size is moderate such that the bulk specimen can be completely irradiated at one time. However the specimen must



be contained within a fluid medium that connects to a vertical capillary tube such that changes (reductions) in the fluid height can be related to volumetric changes of the specimen. Both water and mercury have been used as the fluid. Water may lead to inaccuracy if it is absorbed by the resin composite. Mercury is less favoured today because of health and safety concerns. Temperature control is difficult to achieve with these systems, although accurate measurements can be obtained, especially when temperature is monitored throughout the experiment and corrections are made based on these results.

#### 4.3.6. Pycnometer method

This uses the dilatometer principle with gas as the fluid medium [101]. It is capable of rapid and accurate measurements of the maximum (final) shrinkage value.

#### 4.3.7. Digital image correlation (DIC)

DIC is a specialist technique using digital methods to track and correlate displacements of virtual image elements for a specimen in a slotted cavity mold [102,103], providing both visual and quantitative data. Shrinkage of the material is displayed as a function of depth and location in the mold after irradiation has been applied at one end, corresponding clinically to irradiation on an occlusal surface.

### 4.4. Polymerization stress measurements

#### 4.4.1. Instrument design considerations

Design of suitable instrumentation for determination of polymerization stress requires a reproducible host environment for the test specimen where polymerization of the resin composite paste will cause mechanical stress transfer from the material to its immediate interfacial surroundings that can be registered by an associated load cell. The most common geometry involves placement of a specimen disk of high aspect ratio between two parallel flat-ended rods or between a single rod and a flat plate surface. At the completion of an experiment, the solid composite will be bonded to the contacting surfaces, requiring that the specimen assembly be capable of fairly rapid disassembly for the next measurement run prior to complete setup, or alternatively the use of disposable surfaces, such as glass rods.

In each measurement run the specimen assembly must permit irradiation at clinically relevant irradiance levels, so the assembly must be accessible by the LCU optic. With disk specimens, light access may be achieved preferably by irradiation transverse to the flat disk surface or, alternatively, by irradiation at the disk edge from one or more radial directions. Transverse irradiation is preferable and may be attained using either a transparent rod, of glass or glassy polymer, or by trans-illumination through a glass plate. This gives a more uniform irradiance across the material surface, assuming an even beam profile. Radial illumination may require a specimen disk of lower aspect ratio, such as 4:1, both to increase the rod/rod gap and to reduce the path for light transmission. The selected aspect ratio must be considered when interpreting the results.

A further experimental variable is the ambient temperature. It is challenging – but possible in some cases – to conduct

measurements at elevated temperatures, such as 37 °C [104]. However, the variation of shrinkage-stress with temperature for dental resin composites appears to be comparatively moderate, and evaluating temperature dependence is not a priority in this case. If the test material is studied at different temperatures, care must be taken to ensure thermal isolation to avoid temperature changes in the measuring load cell.

When polymerization stress occurs in a restored posterior tooth, cuspal deflection occurs. The magnitude depends upon the detailed cuspal geometry; for example, thin remaining cavity walls will be more compliant and thus deflect more [105]. It follows that compliance of the test assembly is an important variable and must be quantifiable. Several researchers have aimed for zero compliance in their measurements by using servo-hydraulic instrumentation with an appropriate feedback signal to maintain minimal change in the rod/rod separation. The limit of zero compliance is not actually attainable, as this would imply an infinitely stiff system. Other methods prefer to allow a defined compliance in a range comparable to that occurring in clinical situations with natural teeth. The more attachments or couplings that exist between the load cell and the specimen assembly, the more difficult it is to maintain a suitable compliance.

Measurements are normally made in an axial direction when using load cells. Another possibility arises with short cylindrical specimens fabricated in a thin-walled metal mold, to which a strain-gage is bonded to its outer surface [106]. In this way, the hoop stress created during the shrinkage of the resin composite, when it is bonded to the mold walls, can be measured via the strain gage.

Following the foregoing design considerations, two principal instrumental methods are utilized widely. They are considered to be of equal merit.

#### 4.4.2. Universal testing machine (UTM) method for shrinkage stress

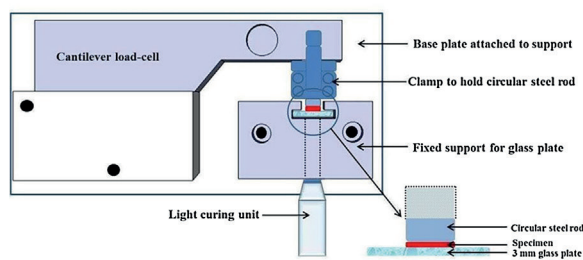
One method uses a tensile load cell mounted on a UTM [107,108]. The specimen is held between two flat-ended rods. These are either both steel rods, in which case radial irradiation must be used, or steel combined with transparent 'glass', which facilitates trans-illumination through the glass rod.

#### 4.4.3. Bioman method for shrinkage stress

The *Bioman* method uses a self-standing instrument assembly, designed at the University of Manchester, UK (Fig. 11). It has been widely used in both academia and industry for more than a decade [104,109–111]. The *Bioman* is based on a stiff steel cantilever incorporating an internal strain-gage load cell and carrying a 10 mm diameter flat-ended steel rod at the movable end of the cantilever. Beneath the rod, a thick glass plate is held in a rigid assembly, creating a gap. A resin composite paste specimen disk is created, normally of 10 mm diameter and 0.8 mm height. Sometimes a peripheral soft wax ring may be utilized to contain a flowable composite.

After thermal equilibration, the resin composite disk is irradiated from a LED-LCU by trans-illumination through the lower glass plate. Shrinkage is resisted in the axial (vertical) direction by the relatively rigid steel rod and cantilever arm. As stress is transferred to the upper steel rod, the cantilever bends very slightly and the load-cell signal (mV) is amplified, digitized





**Fig. 11 – Cartoon of the Bioman assembly device for measuring polymerization shrinkage stress (a) and photograph of the Bioman II apparatus, with a modified support for the glass plate (b).**

and transferred to the computer where it is displayed in real time. In the event of specimen detachment from rod or plate this is immediately apparent and the measurement run can be terminated. In many cases when using highly filled stiff resin composite pastes the steel rod-end and the central upper portion of the glass plate are air-abraded with aluminum oxide prior to use. Alternatively, the steel rod can be abraded with silicon carbide paper. In either case, it is common for the glass slide to then be treated with a silane coupling agent to promote attachment. It is also common to use a metal primer designed for prosthodontics for enhanced adhesion to the steel piston.

The cantilever assembly can be directly calibrated by dead-weight loading in the precise axial direction where measurements are normally taken. Stress data (MPa) can then be displayed as a continuous function of time (min), usually for a minimum of 30 min or 1 h. Measurements for longer periods, such as 24 h, are also feasible due to the stable instrument electronics. The shrinkage-stress rate [ $\text{MPa s}^{-1}$ ] can be obtained by numerical differentiation and plotted as a function of time.

The consequences of altering the specimen configuration factor, through variations in the specimen diameter and height have been explored experimentally [110]. Other common diameters are 5 mm, also with a height of 0.8 or 1.0 mm for a reduced configuration factor. In all cases it should be noted that the measured stress values are not only a function of the material formulation, but also of the system compliance and specimen dimensions. The specimen dimensions determine the volume (or, equivalently, the mass) of the test specimen. It is the amount (mass or volume) of the test specimen that determines the measured outcome. With bulk fill resin composites it may appear tempting to measure specimens of 4 mm height, but this is strongly contraindicated for several reasons that are implicit from the preceding discussion.

In addition to the Bioman method, another cantilever instrument has been reported [112–114]. This is termed a ‘tensometer’ method and was designed by the American Dental Association Health Foundation. It includes an adjustable compliance, and has an added benefit in that it can be coupled to a fiber optic near-IR source and detector to simultaneously collect monomer conversion data with shrinkage stress.

#### 4.4.4. Photoelastic method for shrinkage stress

The photoelastic method is an optical method that generates interference fringe images, representing stress, within a spe-

cial photoelastic material [115]. These images may be viewed qualitatively and also analyzed quantitatively. This approach, although accurate, is considered to be a secondary method on account of the limited availability of the photoelastic material. The data obtained relate mainly to the final stress level attained within the system, although time-dependent measurements may also be recorded.

#### 4.4.5. Indentation crack analysis for shrinkage stress

When a surface exhibits internal stress, arising from polymerization, cracks can grow from the corners of controlled surface indentations. This method is considered to be an indirect method of obtaining a single maximum stress value [116–118].

### 4.5. Hygroscopic expansion

Dimensional changes of resin composites, during and after curing, are critical for their long-term clinical success. These materials not only gradually release unbound monomer and initiator components, but also absorb water that leads to a volumetric hygroscopic expansion and is considered to partly compensate the negative effects associated with shrinkage. Water uptake potentially alters the polymer elastic modulus, which along with hygroscopic expansion in sufficient quantity could relax the internal stresses generated by constrained shrinkage. However, this is not so straightforward, as the expansion due to water may be uncontrolled and lead to alternative deleterious stresses. Also, the timescales for the two phenomena are very different. Shrinkage mainly occurs within seconds and at most minutes, while the absorption of water occurs over days and usually requires weeks to reach saturation. Despite hygroscopic expansion being a key property, assigned a value of 1 in Table 1, it has received limited interest in terms of research and there is no ISO test for it.

There is one technique developed and dedicated to the measurement of this property. It involves laser-scanning of a specimen disk. Specimen disks are measured by rotation through the beam of a laser micrometer at multiple time-intervals until a plateau is reached. The specimen is initially measured after light-curing is complete and subsequent measurements are done after specimens are stored in water or other media for a period of time, usually at 37 °C. The technique was first developed in 2003 [119] and has been modified more recently [120–123]. The main advantage of the technique

is that it is not affected by non-uniform expansion and therefore provides 3-D values for hygroscopic expansion. Although values at 1 week and 1 month can be useful it is recommended to monitor the expansion for up to 3 months to obtain more accurate data, or until a plateau has been reached.

Another technique for measuring hygroscopic expansion involves the use of an optical scanning system [124–126]. It employs teeth and provides accurate measurements, and thus it is more representative of a clinical situation. On the other hand, it is more time consuming, requires more expensive equipment and a highly trained skilled operator.

A simpler technique to measure expansion is based on the Archimedes principle. The initial volume of a material, V1, is calculated after the specimen is cured at room temperature by measuring its diameter and thickness with a mechanical caliper. After dark storage in water at 37°C, the final volume, V2, is calculated. The difference between the two is the hygroscopic expansion [127]. This method is very simple and inexpensive to use, but assumes uniform expansion of the specimen, and therefore is assigned a ranking of 2 (see Table 1).

#### 4.6. Thermal expansion

The link between dimensional stability and clinical success of resin composites has long been postulated. The primary concern for compromising dimensional stability is from shrinkage, which has been described extensively in the section above. A lesser factor that can also affect the dimensional stability of dental resin composites is thermal expansion. When exposed in the oral environment, resin composites are subjected to a range of temperatures from food and drink intake primarily. The restorative material, and the attached tooth structure, expand and contract, the magnitude being dependent on the coefficient of thermal expansion (CTE) of each material. The differential in these coefficients between the two materials lead to differences in movement and the generation of stress on the bonded interface between them. In like manner, the polymerization reaction of resin composites is exothermic, and during curing, there is an increase in temperature due to the reaction as well as the energy imported by the light curing unit, both of which lead to expansions.

Compared to other properties, thermal expansion has typically been considered to be of minor importance (a value of 3 in Table 1). However, with the high power output of some current light curing units (2000 mW/cm<sup>2</sup> and more), it is wise to be cautious and attempt to identify possible harmful effects related to this phenomenon. Also, a mismatch between the CTE of the material and the natural hard tissues creates interfacial stresses that may accelerate the degradation of that interface under certain *in vivo* conditions.

No standard, specifically for dental resin composites, exists. But thermal expansion is typically measured by displacement of the material over a temperature range. An early method involved strain gauges to measure the linear CTE applied over a range of temperatures [128]. Another method employs thermomechanical analysis (TMA) [129]. With this method the glass transition temperature of the resin composites can be measured and subsequently the linear CTE can be calculated at a range of temperature intervals. Both techniques can be fairly time consuming and require the use of

specialized instruments. Another method has been described recently where the CTE was calculated simultaneously with shrinkage [130], using the bonded-disk instrument described above, with some minor modifications that include the use of a thermocouple for temperature measurements. The measurements are fairly quick and the test represents a reasonable approximation of the clinical environment. The effect of the curing unit can be observed and by monitoring simultaneously three properties it provides a more comprehensive overview of the performance of the material.

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