COMMENTARY

The need to revise standards on dental restoratives

Padmanabhan Krishnan

There is a need to revise some of the existing specifications on polymers, adhesives, liners and composites as denture materials and restoratives. The requirement for equilibrium saturation conditioning of denture base polymers, restoratives, veneers and some crown and bridge materials in control media is spelt out here. The hygrothermal response of this class of materials demands stringent tests for their qualification as usable products.

Ceramic-filler polymeric resin hybrid composites, prepared with a careful selection of the resin, particle size distribution and chemistry, has recently found wide use in dentistry for direct posterior restorations due to its superior mechanical properties and long-term accommodative behaviour compared to other materials in any environment around the world. Of all the mechanical properties, wear, erosion, bio-corrosion and durability rule prime in qualifying the material for oral use. A wide variety of dental composites need to be analysed for their mechanical behaviour according to standards, as it is an important task to be borne in mind in the acceptance procedure of a material as a restorative or a base resin. Simulation of the environmental conditions like storage in distilled/de-ionized water and storage in artificial saliva prior to contact – wear testing in order to measure the weight loss of materials in abrasion, demands extreme caution and attention to the most minute detail before any correct and reliable result can be obtained. Water storage is considered important as a step before storage in saliva in the evaluation process, as it is less of a lubricant and hence more punishing on the material before it qualifies as a denture base or a restorative for intra oral use[1,2]. Further, water has the dual distinction of being both a lubricant and a non-lubricant, depending upon the material.

This commentary brings out the significance of saturation and equilibration of cured polymeric/glassy composites in the control media. In addition, it not only brings out the existing deficiencies in the American Dental Association (ADA) guidelines regarding the precise evaluation of fluid conditioned mechanical properties in general and wear loss of material in particular, but also suggests a procedural sketch based on ASTM and MIL guidelines that are a prerequisite before any further practice can be attempted.

Standards and the hygrothermal phenomenon

It is well established that polymers and their composites absorb fluids gradually and attain a steady state and/or get saturated in weight uptake in due course of time. This time period varies from polymer to polymer, for the prepared material to be tested for wear, strength and toughness (which is resistance to crack propagation) after conditioning. Though there are many standards in the practice of aqueous environment conditioning/ageing of plastics and polymer-based composites and established test procedures for estimation of water content, absorption and conditioning in real and accelerated environments like the MIL-HDBK-17B, ISO and ASTM[3–5], it is disturbing to see the standard specifications by ADA guidelines for denture base polymers, restoratives and prosthodontic materials (see Figure 1 for a schematic explanation in a denture composite). Though Figure 1 is schematic, it brings out the irreproducibility and transient nature of the ADA guidelines. Many publications exist that claim authenticity of data for qualification in the oral environment after storage in a control medium for just a fixed time of 24–72 h or one week[6–10]. Most of the specimens are in the process of picking up the solvent that diffuses into the polymer, if one continues to store them in these media. The specimens cannot be expected to attain equilibrium if the ADA guidelines as cited above are adhered to for all the materials, since the transport phenomena are unstable during uptake for most of them. Some investigators do quote the ISO 4049 stipulation of seven days immersion period for the evaluation of solubility of resin-based filling materials (!) in water[11] and an additional unspecified cure time at 37°C and 100% RH prior to mechanical testing corresponding to clinical situations as in American National Standard[11]. Recently, the ADA reaffirmed the guidelines for denture base polymers according to the ISO 1567:1999 standard[12]. However, it does not make the situation any better as the standard makes no specification about the equilibration saturation for the denture polymers like the established stan-

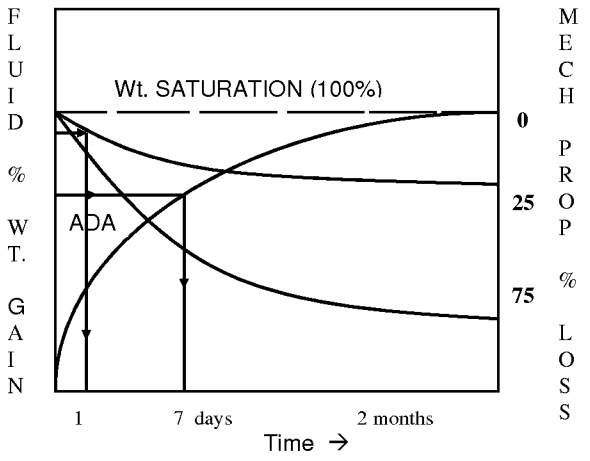

Figure 1. Fluid uptake, saturation and mechanical properties loss due to fluid immersion expressed in percentage for a polymeric denture material with ADA guidelines shown in arrows.

dards for plastics and reinforced plastics by the ASTM or MIL-HDBK. If the present standards practised by ADA are put to use, it does not help the discerning consumer/customer to distinguish the most durable product from the rest. Besides, the ADA could have chosen the moisture equilibrium standards by the ISO for plastics and reinforced plastics initially. However, they have not done so, the reasons for which are not known though the class of materials is broadly the same. This assumes importance as the ADA standards are widely followed in the dental world. Even the Indian Dental Association (IDA), follows ADA standards and hence there is a need to spell out the problem and seek remedies.

Standards and structures

It is worth mentioning here that considerable experience has been gained in the area of aerospace and other structural composites on the issue of equilibration and saturation way back in the eighties and nineties[13,14]. It was observed by many investigators that the tensile and the compressive strength values for moisture equilibrium-saturated glass/epoxy and carbon/epoxy specimens were only about 60% of the initial unsaturated values. Any attempt by prosthodontists to measure physical properties like weight (to calculate moisture uptake), wet T_g (the moisture saturated glass transition temperature that is lower than the dry T_g) and dimensional changes is bound to be futile as the results are irreproducible and transient and not even approximate in the oral environment, according to the current standard procedures for resins and restoratives. To explain further, the maximum operating temperature/maximum recommended test temperature (MRTT) of approximately 70°C in the oral environment should be at least 25°C lower than the lowest wet T_g recorded for any cured denture material, as wet T_g marks the transition from a practically integral and usable material to an unusable one, downward in the temperature scale. This aspect, well illustrated in the ASTM D5229M test method mainly for aircraft composites, if applied to denture materials, is bound to disqualify certain classes of polymeric materials that are being currently used. The ASTM 5229M clause on MRTT and wet T_g can bring about a few healthy revisions in the right direction in the qualification of polymeric materials for dental practice when applied to the denture materials.

Dental cavities are wet and equilibrated. The works of Kawai *et al.*[9] do not conform to the rationale of moisture conditioning up to saturation prior to wear testing. Prior to accepting the wear tests practised by dentists, it is preferable to conduct the standard pin-on-disc (POD) test to evaluate the wear parameters precisely. Here the human molar enamel of known properties is shaped into a pin with known surface roughness and the restorative material is shaped into a disc again with a known surface roughness. The pin is fixed vertically, sliding on the horizontally fixed disc and a known load is applied to the pin with the disc rotating at a known constant speed. Removal of materials from the pin and the disc (counterfaces) due to abrasion is measured after weighing the pin and the disc separately before and after the test. This test can be followed by some of the most approved dental wear-testing practices like those of Goldberg or Lambrechts as a requisite sequel before certifying the wear data for dental acceptance. Here again, the minimum weight restriction (>5 g per specimen) on the preconditioning requirements of polymer matrix composites by the ASTM STP 5229 for structural composites can be adapted to the precise needs of dental practice, as dental materials are mostly particulate-filled and not fibrous like structural materials. Although a filled denture may be less than one gram, the material taken for qualification test may measure the bulk properties more accurately by conforming to the minimum weight restriction. This leads to the topic of diffusion depth, minimum volume and thickness requirement for conditioning and stringent micro wear test methods that are required for certification purposes. More work has to be done on this aspect, which may resolve the issue of normalizing the conditioning requirements and results for two different wear test methods. This seems to be the crucial bridge that links a material's evaluation method like the POD with the dental wear tests and produce reliable, comparable and practical data and not lead one into a science of practising beliefs.

There are reports of round-robin testing with no clear understanding of this issue as the moisture absorption plots are not presented[6], probably due to a prescribed and agreed upon short time period of storage like 24 or 48 h. The very fact that the measured wear in micrograms (from POD) or micrometres (wear depth as in dental measurements) sometimes can be lower than the weight gain due to moisture saturation, demonstrates the importance of saturation equilibrium prior to testing among many others, particularly for wear tests done for shorter durations like annual wear[1].

In case of some lining materials with a steady state uptake of fluids without any apparent tendency to saturate in a few days or months like rigid polymers, any long-term evaluation is also bound to be difficult. This can be done only after a fluid storage test that demonstrates its steady state equilibrium condition and weight gain at a given time or the saturated value – if it happens. There are no logical prescriptions for water sorption tests of these important class of materials that can make or mar a restoration based on property and interfacial property changes arising from compatibility with the restorative or the lack of it in long-term ageing conditions.

It is comforting to see a handful of conducted studies on moisture saturation, clearly spelling out this problem with respect to glass ionomer cements, filled polymers and soft lining materials[15–18]. These studies have investigated the influence of water conditioning and saturation on many important mechanical properties like strength and toughness with respect to plasticity due to moisture absorption, though surprisingly wear has not been discussed. At this stage the reader is reminded that equilibration may not mean saturation but saturation means equilibration.

Since wear rate versus time for most of the restorative materials is logarithmic, and mostly nonlinear, wear evaluated corresponding to first few months of usage is more and critical for any further progress regarding precise evaluation for clinical acceptance, a simple initial shortcoming means a lot of mistakes and glorification of an otherwise potential failure of a material. Moisture saturation conditioning prior to testing may see a material like a heavily filled restorative (~90 wt%) barely qualifying a guideline and other restoratives based on Bis–GMA, UDMA and TEGDMA with 60 to 80 wt% inorganic fillers falling short by a week or two as they are still in the process of uptake when removed from conditioning. The typical saturation gain can be any-

where from 0.3 wt% to double digits. A typical acrylic denture may require a period of almost 15 to 30 days to become fully saturated with water. Wear by any of the prescribed methods for materials and mechanical scientists or dentists, annual or long-term, measured subsequent to this saturation conditioning is acceptable and reliable as it precisely influences many decisions that are involved in the classification and certification. Restorative materials, liners, adhesives, sealants, bonding agents, luting cements, impression materials, crown and bridge materials and glassy substances have their own absorption related properties. Surface preparation adds to the requirements, as it is important for mechanical evaluation. As the saliva runs in the mouth, conditioning up to saturation/equilibrium as suggested here, in stagnant and re-circulated control media makes sense. Studies might have been conducted on this front, but standardizing and prescribing them are more important.

Giving due credit to certain procedures that are listed within the corpus of ASTM standard test methods referred to here, certain tailor-made modifications as suggested can be carried out exclusively for prosthodontic polymeric materials by the ADA/ISO under the aegis of a technical committee. A complete re-look into the issue is warranted, as some of the past and foreseeable legal tangles associated with the acceptance of these materials and the patient protection rights of ADA can be resolved better now.

Geographical variations count. A thermal and humidity cycling procedure as in certain ASTM procedures like the D 5229M, can be set as a guideline for the qualification of dental materials. The author's own posterior Indian amalgam filling that lasted two years in 'above the 10°C environment' could not last the Maryland winter and the ensuing spring after a journey from Singapore. Though it was in an amalgam, one cannot rule out the possibility of the same happening to the polymer restorations in international travellers, who are also ethically and legally unprotected. That brings us to the aspect of interfacial staining and proper understanding of the interface. Falling out arising from mismatch in deformation, accommodative behaviour, leaching, digestion and erosion of long-term, aged polymeric dentures deterring their qualification as a dental restorative may be studied and more guidelines included in the ADA. The aspect of thermal spiking and shock appears to have been less understood by the ADA, though thermal cycling and spiking have been discussed in detail in the ASTM 5229M and MIL-HDBK standards. The influence of hygrothermal spiking on the interfacial bond strength between the tooth and the restorative is a major issue.

A distinction has to be made between the use of distilled water and de-ionized water as conditioning media in appropriate chambers since the presence of glassy ionomers, photo polymerization and residual monomers and reactivity can have drastic influences on their microstructure. The choice of de-ionized water is recommended for studies that involve ionomers and/or envisage tribochemical interactions to clearly distinguish the species evolved. A study by a machining group neither fulfils the requirement for moisture conditioning up to equilibration saturation nor is it demanding on the use of de-ionized water though tribochemical interaction (interactions that cause chemical transitions in the material due to wear, friction and lubrication) have been discussed in detail[10]. It is needless to say that the observed properties are only transient and not equilibrated and/or saturated.

The safety involved in the standardization of these materials is again dependent on the correct estimation of physical and chemical properties, wear, bulk fracture and the safe time period estimation in the oral environment which has been fixed by ADA as 18 months for composite restoratives. Further according to the ISO 7405 guidelines, the restoratives must demonstrate bio-compatibility which can be correctly evaluated only when the procedures are correct.

Though the author wanted to check only articles belonging to the last decade (1990 onwards), hoping to find more details on the subject of moisture conditioning, he was upset over the quantity of publications that are found wanting in the basic required details. A part of this commentary was submitted to the Singapore–MIT Alliance in a research project report earlier[19]. The author considers it worth mentioning that the aspect of fluid storage conditioning be taken up more seriously at an international level as it threatens the very 'veracity' that forms a part of the ADA principles of ethics and code of professional conduct. One can well imagine the implications on their health plan accountability involving the survival of these 'capsica' in the mouth, when the expiry dates are not the real ones!

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ACKNOWLEDGEMENT. I thank all the investigators with whom I had the opportunity to work and discuss this subject.

Padmanabhan Krishnan is in the Department of Mechanical Engineering, Sri Venkateswara College of Engineering, Pennalur, Sri Perumbudur 602 105, India. e-mail: paddy@svce.ac.in