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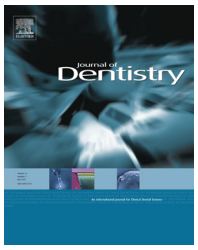

Post-irradiation hardness development, chemical softening, and thermal stability of bulk-fill and conventional resin-composites

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ABSTRACT

Objectives: To measure bottom/top hardness ratio of bulk-fill and conventional resin-composite materials, and to assess hardness changes after dry and ethanol storage. Filler content and kinetics of thermal decomposition were also tested using thermogravimetric analysis (TGA).

Methods: Six bulk-fill (SureFil SDR, Venus bulk fill, X-tra base, Filtek bulk fill flowable, Sonic fill, and Tetric EvoCeram bulk-fill) and eight conventional resin-composite materials (Grandioso flow, Venus Diamond flow, X-flow, Filtek Supreme Ultra Flowable, Grandioso, Venus Diamond, TPH Spectrum, and Filtek Z250) were tested ($n = 5$). Initial and 24 h (post-cure dry storage) top and bottom microhardness values were measured. Microhardness was re-measured after the samples were stored in 75% ethanol/water solution. Thermal decomposition and filler content were assessed by TGA. Results were analysed using one-way ANOVA and paired sample t-test ($\alpha = 0.05$).

Results: All materials showed significant increase of microhardness after 24 h of dry storage which ranged from 100.1% to 9.1%. Bottom/top microhardness ratio >0.9 was exhibited by all materials. All materials showed significant decrease of microhardness after 24 h of storage in 75% ethanol/water which ranged from 14.5% to 74.2%. The extent of post-irradiation hardness development was positively correlated to the extent of ethanol softening ($R^2 = 0.89$, $p < 0.001$). Initial thermal decomposition temperature assessed by TGA was variable and was correlated to ethanol softening.

Conclusions: Bulk-fill resin-composites exhibit comparable bottom/top hardness ratio to conventional materials at recommended manufacturer thickness. Hardness was affected to a variable extent by storage with variable inorganic filler content and initial thermal decomposition shown by TGA.

Clinical significance: The manufacturer recommended depth of cure of bulk-fill resin-composites can be reached based on the microhardness method. Characterization of the primary polymer network of a resin-composite material should be considered when evaluating its stability in the aqueous oral environment.

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1. Introduction

Light cured resin-composites are the most commonly used direct dental restorative materials nowadays.[1] One of the main limitations of the light-curing process is the limited depth of cure; generally, only increments up to 2 mm thick should be placed to ensure adequate light transmittance and full curing of a restoration. For filling a deep cavity, the incremental placement technique is time-consuming and may increase the risk of moisture contamination during the filling procedure. To overcome this problem, bulk-fill resin-composite materials that can be placed in either a single step or two-steps and cured in bulk have been introduced.[2]

Compromised depth of cure of a resin-composite material results in insufficient polymerization of deeper portions with subsequent degradation, poor physical properties and adverse biological reactions owing to leaching of the monomeric components of the uncured resin-composite.[3] Depth of cure studies using microhardness depth profiles and bottom to top hardness ratio, show adequate cure at depths up to 5 mm for some bulk-fill materials, usually linked with increased light transmittance of these bulk-fill materials.[4,5] On the other hand, some studies show significantly less depth of cure of some bulk-fill materials than that claimed by manufacturers.[6,7]

Surface hardness of resin-composite is an important property that indirectly reflects the mechanical performance and extent of polymerization of the material.[8] Researchers have extensively investigated composite's surface hardness and the effect of material composition and post-cure ageing on surface hardness.[9–14] Surface hardness is strongly influenced by the filler fraction of resin-composite[5,14,15] and for conventional resin-composites will develop over time after discontinuation of the curing light which is mainly attributed to post-irradiation polymerization.[16–18] An increase of hardness of 50–80% has been observed for some novel resin-composites including an ormocer, and a silorane based material.[19] Factors related to composition and characteristics of the material that may affect the extent of post-irradiation polymerization and hardness development are not fully understood. Also, the nature of the post-irradiation developed polymer network and its effect on the final material properties has not yet been assessed.

Cross-link density is a critical property in terms of hygroscopic and chemical stability of a polymeric material and its viscoelastic performance.[20,21] Increasing cross-link density results in reduced free volume and porosity of the polymer network with close proximity of the polymer chains. This provides limited space and pathways available for solvent molecules and residual monomers to diffuse in and out of the structure.[20] The highly functional dimethacrylate based polymer networks used in dental resin-composites are generally characterized by highly cross-linked structures; however, relative differences in the viscoelastic and hygroscopic behaviour attributed to slight variations in cross-link density are observed when chemically different dimethacrylate monomers and different light curing procedures are used.[22,23]

Methods to assess the degree of cross-link density include assessment of thermal stability in terms of the glass transition temperature measured by differential scanning calorimetry (DSC) and initial decomposition temperature measured by thermogravimetric analysis (TGA).[24] TGA is an extremely powerful thermal technique although it gives no direct chemical information. It has many applications in polymer science including assessment of composition, thermal stability and decomposition behaviour, and degree of moisture absorption.[25] Thermal stability measured in terms of the onset degradation temperature is enhanced as the degree of chemical cross-linking increases.[26–29] TGA analysis of dental resin-composites has been mainly used to assess the weight percent inorganic filler content.[14,30–32] Another indirect method to assess cross-link density is assessing the degree of softening when a material is stored in a solvent solution: higher degrees of softening usually indicate less cross-link density.[14,33] Ethanol solution is one of the most commonly used solvents and food simulating liquids and studying its effect on dental materials is highly relevant.[33] In a study of the chemical softening effect of ethanol and other food simulating solvents on dental composites, it was found that the greatest softening effect is obtained by pre-conditioning BisGMA-based resin-composite samples in a 75% ethanol/water solution.[34] Ethanol causes softening of the resin-composite surface by penetration into the polymer structure and replacement of the inter-chain secondary bonds and thereby pulling apart and dissolve linear polymer chains, oligomers, and residual monomers.[35] Regardless of the degree of conversion, the softening effect of ethanol is expected to be more pronounced with a linear or less cross-linked polymer structure since it is difficult for the solvent molecules to overcome primary valence cross-links.[24]

In view of the limited research in this area, the aims of this study were: (i) to assess initial and post-irradiation surface hardness, and bottom/top hardness ratio of selected bulk-fill and conventional resin-composite materials; (ii) to explore any correlation between initial hardness and the extent of post-irradiation hardness development; (iii) to assess the degree of softening after storage in a solvent solution; (iv) to assess the filler content, onset decomposition temperature, and thermal decomposition kinetics of the different resin-composites using TGA; and (v) to explore the correlation between thermal stability measured by TGA and the degree of chemical softening as two different techniques for assessing the degree of polymer cross-link density.

The first null hypothesis was that there would be no difference between bulk-fill and conventional resin-composite materials in terms of initial and post-irradiation surface hardness, bottom/top hardness ratio, the degree of chemical softening, and onset decomposition temperature. The second null hypotheses was that there would be no correlation between initial hardness and the extent of post-irradiation hardness development, and between thermal stability measured by TGA and the extent of chemical softening of the different materials.

2. Materials and methods

2.1. Study design

Bulk fill and conventional composite specimens were prepared using polytetrafluoroethylene (PTFE) moulds. All specimens

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