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ABSTRACT

Advances in digital impression technology and manufacturing processes have led to a dramatic paradigm shift in dentistry and to the widespread use of computer-aided design/computer-aided manufacturing (CAD/CAM) in the fabrication of indirect dental restorations. Research and development in materials suitable for CAD/CAM applications are currently the most active field in dental materials. Two classes of materials are used in the production of CAD/CAM restorations: glass-ceramics/ceramics and resin composites. While glass-ceramics/ceramics have overall superior mechanical and esthetic properties, resin-composite materials may offer significant advantages related to their machinability and intra-oral reparability. This review summarizes recent developments in resin-composite materials for CAD/CAM applications, focusing on both commercial and experimental materials.

KEY WORDS: mechanical properties, digital technology, high-pressure high-temperature polymerization, indirect restorations, prosthodontics, dental materials.

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Resin-composite Blocks for Dental CAD/CAM Applications

During the last decade, we have witnessed a dramatic increase in the use of computer-aided design and manufacturing (CAD/CAM) in dentistry, an increase triggered by spectacular advances in intra-oral imaging, in manufacturing technologies, and by environmental concerns related to the by-products of the classic manufacturing process of indirect dental restorations (Rekow, 2006; Beuer *et al.*, 2008; Miyazaki *et al.*, 2009; Miyazaki and Hotta, 2011; van Noort, 2012). Research into and production of materials suitable for CAD/CAM processing is one of the fastest-growing and -changing fields in dental materials.

Two main types of materials are currently available for esthetic CAD/CAM-processed indirect dental restorations: glass-ceramics/ceramics and resin-composites. To facilitate the review, a brief comparison of the general characteristics of the two types of materials may prove to be helpful. Ceramics are defined as crystalline, non-metallic materials, containing metallic and non-metallic elements bonded by ionic and/or covalent bonds, while glasses share the same definition but are amorphous (Smith, 1996). Glass-ceramics are composite-type materials in which the glassy phase acts as the matrix and the ceramic as the reinforcing filler (Höland, 1997; Höland and Beall, 2002). Resin composites consist of a polymeric matrix reinforced by fillers that could be inorganic (ceramics or glass-ceramics or glasses), organic, or composite (Ferracane, 2011).

The properties of materials being governed by their composition and structure, by the types of bonds that hold the “building blocks” together, it is not surprising that the flexural modulus (E_f) (an indirect measure of the strength of the bonds), flexural strength (σ_f), and hardness of glass-ceramics/ceramics are significantly higher ($E_f \geq 60$ GPa, $\sigma_f \geq 140$ MPa, Vickers hardness > 4 GPa) (Seghi *et al.*, 1995; Conrad *et al.*, 2007) than those of resin composites ($E_f = 9$ to 20 GPa, $\sigma_f \cong 100$ MPa, Vickers hardness = 0.4 GPa) (Quinn and Quinn, 2010; Ferracane, 2011; Nguyen *et al.*, 2012). Glass-ceramics/ceramics are strong, stiff, brittle materials, with low fracture toughness (K_{IC}) and high susceptibility to failure in the presence of flaws. The optical properties (translucency, fluorescence, opalescence, etc.) of glass-ceramics/ceramics are superior to those of resin-based materials (Lim *et al.*, 2010; Güth *et al.*, 2013). While glass-ceramics/ceramics (depending on their composition) might be adversely affected by the pH of the oral environment and/or of the diet, water sorption/desorption could lead to the degradation of the polymer matrix and/or of the coupling-agent-mediated polymer-filler bond (Nambu *et al.*, 1991).

In a direct comparison between properties, glass-ceramic/ceramic materials are superior to resin-composites. The attractiveness of the latter is based

Table. Selected Mechanical Properties of Commercial and Experimental Materials for CAD/CAM Applications*

Material	σ_f (in MPa)	E_f (in GPa)	K_{IC} (in MPa·m ^{1/2})
IPS e.max CAD	353.05 ± 37.52	69.36 ± 6.22	1.79 ± 0.29
Non-Aged Lava Ultimate	159.59 ± 20.14	14.21 ± 0.81	0.91 ± 0.15
Aged Lava Ultimate	116.21 ± 14.23	12.22 ± 0.72	0.99 ± 0.23
Non-Aged Enamic	139.68 ± 8.61	29.03 ± 2.98	0.88 ± 0.30
Aged Enamic	123.25 ± 8.16	27.11 ± 2.23	0.96 ± 0.15
Urethane with initiator (90°C 300 MPa for 4 hr)	174.1 ± 9.9	Not determined	1.38 ± 0.22
Urethane with initiator (190°C 300 MPa for 1 hr)	191.4 ± 11.2	Not determined	1.36 ± 0.28
Urethane no initiator (190°C 300 MPa for 1 hr)	184.8 ± 10.9	Not determined	1.23 ± 0.25
Paradigm	131.85 ± 36.38	Not determined	0.78 ± 0.21

*Data from Nguyen *et al.* (2012), Phan *et al.* (2014), and Thornton and Ruse (2014).

on ease of fabrication and the possibility of an easier and less visible intra-oral repair of minor defects induced by function. Thus, it is estimated that a set of CAD/CAM burs, which are relatively expensive (~\$20/bur), could be used to fabricate five to ten glass-ceramic/ceramic crowns or well over 100 resin-composite crowns. The intra-oral repair of glass-ceramic/ceramic crowns (the outer layer being almost exclusively feldspathic materials) involves preconditioning by acid-etching with the highly corrosive and toxic hydrofluoric acid (HF), followed by the placement of a resin-composite, with quite different mechanical and optical properties. Conversely, the intra-oral repair of resin-composite crowns could be accomplished by preconditioning by sand-blasting or bur-roughening, followed by the placement of a resin-composite with very similar mechanical and optical properties. Moreover, resin-composite materials may be less susceptible to chipping during the milling procedure (Tsitrou *et al.*, 2007).

This brief review focuses on the active area of resin-based materials for CAD/CAM applications. The first commercial resin-composite for CAD/CAM applications was Paradigm MZ100 (3M ESPE, St. Paul, MN, USA), obtained by the factory polymerization of their successful Z100 direct restorative resin-composite. The factory polymerization resulted in Paradigm having superior properties to those of Z100 [$\sigma_f \sim 130$ MPa and $K_{IC} \sim 0.8$ MPa·m^{1/2} (Nguyen *et al.*, 2012)], and some *in vitro* studies have reported good fatigue performance of the material (Magne and Knezevic, 2009; Tsitrou *et al.*, 2010; Kassem *et al.*, 2012). Paradigm MZ100 was replaced by Lava Ultimate (3M ESPE), most likely polymerized under different temperature and pressure conditions than Paradigm, with slightly improved mechanical properties [$\sigma_f \sim 155$ MPa and $K_{IC} \sim 0.9$ MPa·m^{1/2} (Thornton and Ruse, 2014)]. While the 3M ESPE materials are obtained by the classic incorporation of filler particles into a monomer mixture, in early 2013 VITA (VITA Zahnfabrik, Bad Säckingen, Germany) introduced Enamic, a resin-composite material obtained by the infiltration of a pre-sintered ceramic network by a monomer mixture. Through this process, a higher volume fraction filler was achieved (~70%) and, consequently, superior mechanical properties were obtained compared with those of Lava Ultimate (Coldea *et al.*, 2013a,b; Thornton and

Ruse, 2014). In a recent study, σ_f , E_f , and K_{IC} were determined for Lava Ultimate and Enamic under dry conditions and after 30 days' storage in water. As a control, the same properties were determined for IPS e.max CAD (Thornton and Ruse, 2014). The results (Table) have confirmed that the glass-ceramic material has higher σ_f , E_f , and K_{IC} than the resin-composites investigated and that the properties of the latter are influenced negatively by storage in water. The results have also shown that Enamic, the resin-infiltrated ceramic network, has properties superior to those of the "classic" resin composite and that the determined properties were less affected by storage in water.

In an attempt to significantly improve the properties of resin-composites for CAD/CAM applications, the group led by Michaël Sadoun conducted polymerization reactions of commercial and experimental direct restorative resin-composites under high pressure (HP, 300 MPa) and high temperature (HT, 180-200°C) (Nguyen *et al.*, 2012, 2013). The resulting HP/HT-polymerized resin-composite blocks exhibited dramatically improved flexural strength, Weibull modulus, hardness, and density in comparison with those of their photo-polymerized counterparts and, for most of the properties, with those of Paradigm. The flexural strength of the HP/HT-polymerized materials was over 200 MPa, significantly higher than that of any previously determined values for dental resin-composites and even better than that of some glass-ceramic materials. It is interesting to note that, in a study on the effect of HP/HT polymerization on the resin matrix alone, the changes observed in σ_f were significant but not as spectacular as the changes recorded in the case of HP/HT-polymerized composites (Table) (Phan *et al.*, 2014). This led to the hypothesis that, while HP/HT polymerization affects the polymer matrix, it most likely has a significant effect on the filler-matrix interaction as well, a hypothesis that needs to be tested. The unfilled urethane polymers obtained under HT/HP conditions had $\sigma_f \sim 190$ MPa and $K_{IC} \sim 1.35$ MPa·m^{1/2}, superior to those of the commercially available resin-composite blocks (Table). Further investigation into the structure of the HP/HT-polymerized matrices, using dynamic mechanical analysis (DMA), suggested that the polymers obtained had an increased crosslink density, and that the higher polymerization temperature or the lack of initiator was detrimental

to the viscoelastic properties determined (Béhin *et al.*, 2014). Atomic force microscopy (AFM) characterization revealed that polymerization under HP/HT led to noticeable changes in surface morphology, with either larger or higher density nodules, or smaller, oblong, less-well-defined and fewer nodules, depending on the other variables involved.

There are at least two more hypothesized major advantages of conducting the polymerization under HP/HT conditions: the possibility of avoiding the use of initiators and the decrease in monomer release. Both hypotheses have been tested, and the first was rejected while the second was accepted. Thus, it was shown that the presence of an initiator was beneficial and that the monomer release was dramatically reduced, often below the detection limit of the high-performance liquid chromatograph (HPLC) used (Phan *et al.*, 2014). However, differences in properties between polymers with and those without initiator were small enough (Table) to warrant further consideration of this issue. If the incorporation of initiators could be avoided, discoloration with aging due to the presence of initiators becomes moot.

In summary, HP/HT polymerization opened up an entire new area of research in dental resin-composites, and if the process is scaled up to an industrial level, it could lead to the introduction to the market of high-performance resin-composite blocks for CAD/CAM applications. It should be re-emphasized, however, that, being resin-composite materials, their expected properties will not surpass the properties of glass-ceramic/ceramic blocks, and that advantages and disadvantages of the available materials have to be considered on a case-by-case basis before decisions are made regarding patient treatment. Only long-term clinical trials will provide evidence of *in vivo* success. It is obvious that CAD/CAM technology is here to stay and that dental treatment has undergone a major shift in both materials and technology, a shift that is still in its infancy.

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