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The evolution of dental materials over the past century –  
silver and gold to tooth color and beyond.

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## Abstract

The field of dental materials has undergone more of a revolution than an evolution over the past 100 years. The development of new products, especially in the past half century, has occurred at a staggering pace, and their introduction to the market has been equally impressive. The movement has mostly come in the area of improved esthetics, marked by the gradual replacement of dental amalgam with dental composite and all-metal and porcelain-fused-to-metal indirect restorations with reinforced dental ceramics, and all made possible by the rapid improvements in dental adhesive materials. This article will cover the time course of dental materials development over the past century in which the Journal of Dental Research has been published. While there have been advances in nearly all materials used in the field, this manuscript will focus on several areas, including dental amalgam, dental composites and light curing, dental adhesives and dental cements, ceramics and new functional repair materials. A few short statements on future advances will be included at the end.

## Introduction

It would be hard to imagine a field in dentistry that has undergone a more explosive evolution than that of dental materials. The sheer breadth of new technologies, rate of development, and adoption are breathtaking. (Figure 1) The development of highly accurate impression materials enhanced the convenience of making precise and stable impressions for indirect restorations positively impacted the dental practitioner on a daily basis. Soon these materials may be replaced in most applications by amazing developments in optical scanning. Transformative changes in the treatment of edentulous spaces came with the successful use of commercially pure titanium (cpTi) for dental implants which osseointegrate with natural bone to provide stability. While there has been tremendous progress throughout the entire field of dental materials over the past century, this article will highlight pivotal advances in dental amalgams, dental composites and light curing, dental adhesives and cements, dental ceramics, and new functional repair materials, because these likely have had the greatest impact on the profession and the oral health of literally billions of dental patients. To highlight the research effort expended in the development and study of these five areas, one only needs to survey their appearance over the past few decades in publications in the Journal of Dental Research. (Figure) With these seminal discoveries in mind, the article will conclude with brief comments about the future of this exciting field.

## The Direct Restorative Revolution - Dental Amalgam

100 years ago dental amalgam was an established restorative material, fundamentally as modified by GV Black in the late 1800s. The alloy was basically  $\text{Ag}_3\text{Sn}$  ( $\gamma$ ) with some Cu and Zn, designed to minimize dimensional change while setting. (Greener, 1979) Irregular alloy particles were mixed with Hg and the plastic mass condensed into the cavity. The set material

contained two Ag-Hg phases,  $\sim\text{Ag}_2\text{Hg}_3$  ( $\gamma_1$ ) and  $\beta_1$  (with less Hg) and  $\sim\text{Sn}_8\text{Hg}$  ( $\gamma_2$ ), in addition to residual alloy particles. (Marshall and Marshall, 1992; Mahler, 1997). This material and procedure did not change significantly until the 1960s. Particle size varied from coarse to fine to speed setting for the clinician. Spherical particles were introduced to decrease the amount of mercury required. Traditional amalgam tended to corrode over time, particularly the  $\text{Sn}_8\text{Hg}$  phase, resulting in Sn- and Cl- containing corrosion products and causing discoloration clinically. (Holland and Asgar, 1974; Marshall and Marshall, 1980). Corrosion processes and oxidation of Zn were believed to help “seal” the margins of the restorations to mitigate secondary caries. Formation of the  $\text{Sn}_8\text{Hg}$  phase caused amalgam creep, resulting in observable deterioration of the margins. (Mahler and Van Eysden, 1969) Despite these problems amalgam restorations had high compressive strength and excellent clinical longevity.

In the 1960s the first major compositional change occurred with the introduction of more Cu in the starting alloy by adding additional particles composed of the Ag-Cu eutectic composition. (Innes and Youdelis, 1963) The additional Cu reacted preferentially with Sn, forming mostly  $\text{Cu}_6\text{Sn}_5$  instead of  $\text{Sn}_8\text{Hg}$ . (Vrijhoef and Driessens, 1973; Mahler et al., 1975) Most of the  $\text{Cu}_6\text{Sn}_5$  was incorporated with  $\gamma_1$  in a reaction zone surrounding the Ag-Cu particles, residing within a matrix that was largely  $\gamma_1$ . Replacement of  $\gamma_2$  by  $\text{Cu}_6\text{Sn}_5$  resulted in better oral corrosion resistance and improved mechanical properties, especially lower creep. These amalgams became known as high-Cu, Cu-rich or  $\gamma_2$ -free amalgams. The resulting restorations had less marginal degradation and improved clinical survival. (Letzel et al, 1997; Mahler, 1997) Further variations were explored, notably with the inclusion of the additional Cu in a single spherical particle of Ag-Sn-Cu with similar overall composition. (Mahler, 1997) The microstructure of the set

amalgam consisted of residual particles of Ag-Sn-Cu with  $\text{Cu}_6\text{Sn}_5$  particles more distinct in the reaction zone. The two most common commercial products were Dispersalloy (two particles) and Tytin (single particle). The spherical particle versions required less Hg for mixing (~ 43%) so the restorations contained less Hg. (Marshall and Marshall, 1992)

Over time amalgam restorations undergo several phase changes. (Marshall et al., 1992) When the Sn-Hg ( $\gamma_2$ ) phase in traditional amalgam corrodes, Sn- and Cl- containing products are formed and the small amount of Hg generated reacts with residual alloy particles to form more  $\gamma_1$ . The Cu-Sn phase corrodes less than the Sn-Hg phase, but some corrosion occurs, forming Cu-containing corrosion products. (Marshall et al., 1982). An additional phase change is the transition from  $\gamma_1$  to the more stable  $\beta_1$  in the matrix. (Marshall et al., 1992) This generates a small amount of Hg which may react further with residual alloy particles to form more  $\gamma_1$ .

To further reduce corrosion and stabilize the  $\gamma_1$  phase, Pd was added to the Ag-Cu eutectic particles. (Marshall et al., 1982) Resulting microstructures contained similar phase distributions with Pd incorporated in the reaction zones around the Ag-Cu-Pd particles. Corrosion resistance was improved, leading to a clinically n-improved amalgam. Another potential improvement utilized a polymeric bonding agent to improve the fracture resistance of amalgam restorations. (Staninec and Holt, 1988)

Further improvements were largely halted by the move to eliminate the use of amalgam because of its mercury content. Ultra-sensitive detection equipment revealed some Hg release from amalgams intraorally. Yet estimates of daily exposure were very low (Berglund, 1990) and

retrieved amalgam from clinical trials showed little Hg being lost during the lifetime of the restorations. (Marshall et al., 1989) Dental and scientific communities generally believe amalgam is safe and effective because little Hg ever escapes from restorations, but the demand for tooth-colored materials coupled with environmental concerns have led to a ban in some countries and a significant decline in use in others, and will eventually to a phase out in response to the Minamata convention of 2013. (ADA, 1991; Jones, 2008; Rekow et al., 2013).

### The Esthetic Dentistry Revolution - Dental Composites/Light curing

Dental composite materials have been transformational, producing esthetic restorations for all intraoral applications. Mixing polymerizable monomers with fine glass reinforcing inorganic filler particles produces an easily manipulated paste that is rapidly curable and provides outstanding esthetics. Based on the rule-of-mixtures, composite development has always sought to maximize filler volume fraction (i.e. up to ~80 wt% or 65 vol%) with good filler-matrix adhesion (Loebenstein and Kumpula, 1977) to enhance properties, (Chantler et al., 1999) without compromising handling.

The first dental composites were introduced in the 1950's as self-cure polymethyl methacrylate (PMMA) with quartz particles added for strengthening. To address the **clinical** issues of high shrinkage and poor abrasion resistance, Dr. Rafael Bowen, in the early 1960's, replaced the monomethacrylate (MMA) with dimethacrylate monomers, mainly Bis-GMA. (Bowen, 1963) These materials became popular for **clinical** use in the early 1970's. (Rupp, 1979) For decades, the Bis-GMA dimethacrylate molecule remained the main backbone for dental composites. Bis-GMA is extremely viscous and requires dilution with lower molecular weight dimethacrylates,

such as triethyleneglycol dimethacrylate (TEGDMA), which enhances overall curing and properties. (Ferracane and Greener, 1984) Dimethacrylate-based matrices produce highly cross-linked networks, good mechanical properties, relatively low water sorption and solubility, accommodation of high filler loading, good translucency, and reduced polymerization shrinkage, **all leading to better clinical performance compared to acrylics**. Yet, the polymerization shrinkage remains substantial, producing stress at the tooth-composite interface, and requiring the use of adhesives with high bond strengths. (Davidson et al., 1984; Feilzer et al., 1987) This led to intensive study into adhesives, as well as alternative placement methods for use by dental practitioners to mitigate curing stresses, and ultimately to new composites with lower shrinkage and shrinkage stress.

Early composites were two paste, self-cure systems with limited working time and high porosity due to air entrapment during mixing. Incorporating a UV photoinitiator produced a single paste system that polymerized only when exposed to UV light from a curing unit. (Cook, 1980) Health concerns over personnel exposure to UV and limited depth of cure stimulated the search for an alternative light curing system. In the late 1970's, the introduction of camphorquinone (CQ) with an amine accelerator produced a system with greater depth of cure (i.e. typically 2 mm) when exposed to visible blue light from a quartz tungsten halogen (QTH) source, the extent being dependent upon the composite's formulation. (Forsten, 1984) Alternative monomer systems, such as urethane dimethacrylate (UDMA), were introduced to partially or fully replace Bis-GMA. (Peutzfeldt, 1997)



A **clinical** problem with early composites was obtaining and maintaining a highly polished surface, because large filler particles (i.e. 10-50  $\mu\text{m}$ ) were exposed during finishing or intraoral wear **creating a “matte” finish**. This pushed composite design toward finer particle sizes. (Bayne et al., 1994) Initial efforts created the microfill composites, which actually employed nano-sized silica fillers (40-50 nm). These were highly polishable and remained smooth, but the high surface area of the particles limited filler concentration and lowered mechanical properties. (Lambrechts and Vanherle, 1983) In the early 1980's, hybrid composites arrived with a combination of larger fillers for strength and smaller particles to pack into the spaces between larger particles. These composites were strong, but early hybrids were still not very polishable and demonstrated limited clinical wear resistance. (Powers et al., 1983) Alternative grinding techniques produced smaller glass particles, leading to the “midifill” (largest particles of a few  $\mu\text{m}$ ) and “minifill” composites (largest particles less than 1  $\mu\text{m}$ ). Clinical wear decreased with reduced spacing between particles. (Bayne et al., 1992). These efforts ultimately led to the **highly clinically successful and popular** microhybrids (1990's) and nanohybrids (2000's).

A further advance (1990's) was possible with LED (light emitting diode) curing devices tuned to the 450-470 nm wavelength range required by CQ. (Mills et al., 1999) Early devices had relatively low power output, but redesigns ultimately replaced QTH lights. LED lights produced much less heat, required less energy, and were more amenable for battery powered options. With time, **more esthetic (less yellow)** photoinitiators were employed that absorbed closer to the UV range (around 400 nm). (Stansbury, 2000) These initiators require a light with an additional LED to match their absorbance, leading to the polywave lights. (Price et al., 2015)

Other formulations for dental composites have provided materials easier to manipulate and place, such as flowable composites, (Bayne et al., 1998) based initially on lower filler content and enabling placement from a small cannula syringe. Packable composites (Leinfelder et al., 1999) were viscous pastes that did not slump, were easier to shape, and tried to mimic amalgam handling. Recently (~2010) bulk-fill composites have been developed by enhancing translucency, allowing greater light penetration to cure 4-5 mm and potentially save clinical placement time. (Czasch and Ilie, 2013) These materials also boast lower shrinkage stress, which is critical when filling cavities with such large increments of material.

### The Adhesive Dentistry Revolution - Dental Bonding and Adhesive Cements

Well-adapted, bonded dental materials are believed to discourage or prevent salivary leakage and bacterial penetration. Optimism for successful adhesion in dentistry was spurred by early observations of adhesion in wet environments for things like mussels [Dove and Sheridan, 1986]. Perhaps the greatest advance in adhesion in dentistry occurred when acid etching was shown to enhance retention of an acrylic resin to enamel. [Buonocore, 1955].

A cascade of advancements followed the next 50 years. Investigators focused first on etching parameters: (1) acid types (mineral ( $H_3PO_4$ , HCl,  $H_2SO_4$ ), organic (citric, tartaric, maleic, EDTA, pyruvic); (2) acid concentration (10% to 85%); (3) etching times (10-120 seconds); (4) dissolution of the smear layer (Bowen, 1976); and (5) surface precipitates from etching. Surface reactions were studied: (6) enamel etching patterns (Type 1, 2, mixed) (Marshall et al., 1975), (7) dentin moisture effects (dry, moist, wet) (Tao and Pashley, 1989; Kanca, 1992); (8) etching extent (enamel-only, enamel and dentin, dentin only); (9) dentin depth (superficial, middle,

deep); and (10) dentin age (Tagami et al., 1993). Procedural variables were evaluated: (11) etchant application techniques (paint, dab, scrub); (12) number of system components (three-component (Pashley et al, 2011), two-component, one-component systems (Van Meerbeek et al., 2011)); (13) liquids versus gels; and (14) pre-treatments (bleaching (Shinohara et al., 2005; Toko and Hisamitsu, 1993), air-abrasion, fluoride, lasers; oxalate (Pashley et al., 1993), Gluma (Munksgaard and Asmussen, 1985), sealers; antibacterial treatments, cleansing agents. Hybrid layer contributions were revealed: (15) patterns of macro-and-micro resin tags (enamel: interprismatic and intraprismatic (Jorgensen and Shimokobe, 1975; Marshall GW et al., 1988); dentin: intertubular and hybrid layer with collagen (Nakabayashi, 1992)), (16) hybrid layer quality and variations (Van Meerbeek et al., 1992; 1993); (17) different enamel and dentin types (e.g., primary vs secondary teeth; hypoplasia, fluorosis (Opinya and Pamejier, 1986), imperfecta (Hiraishi et al., 2008), sclerotic dentin (Ritter et al., 2008), carious (Yoshiyama et al., 2002)); and (18) key monomers (HEMA (Ruyter, 1992), NPG-GMA (Alexieva, 1979; Jedrychowski et al., 1979), PMDM (Bowen RL, 1987)).

Very few in-depth clinical trials of variables exist or are long-term enough to detect differences between adhesives. Most only use Class-V adhesive preparation designs. In reality, most bonded restorations are placed within previous cavity preparations, which include gross mechanical retention and thus exclude determination of true adhesive properties. Thus, few correlations of laboratory results and clinical performance are observed (Bayne, 2012; Heintze et al., 2015). Successful bonding typically involves 20 MPa in macro-shear or 30-40 MPa in micro-tension. Bond strengths vary with time and storage solutions. Longevity is affected by fatigue, bond decomposition and extent of enamel versus dentin interface.

Enamel etching is best using  $H_3PO_4$  aqueous solutions on clean enamel with protection of selectively dissolved enamel rods. Dentin etching involves similar care, except agitation improves acid access to the dentin surface. Newer bonding strategies [Breschi et al., 2018] focus on preventing endogenous dentin enzymes (matrix metalloproteinases and cysteine cathepsins) from degrading the integrity of the hybrid layer's collagen necessary for the persistence of good bonding.

Adhesion involves more than just the interface to tooth structure. Adhesive joints require bonding teeth to other surfaces using other acids (e.g., HF) or air abrasion to create micro-relief on ceramics, composites and metals, and often employ coupling agents (e.g., silanes, 4-META).

Since the 1850s, cements have been used to attach cast restorations to tooth structure. Cement categories include traditional acid-base, polymeric-acid-base, and composite types. In 1870, cement choices were zinc phosphate (ZP) or zinc oxide eugenol (ZOE). ZOE released eugenol to produce obtundent quality, but had limited strength. Additives improved ZOE strength (EBA; Brauer and Stansbury, 1984), PMMA, hexyl vanillate (Brauer and Stansbury, 1984]), but ZP was preferred. Silicate cements (SC) were used as filling materials with the advantage of fluoride (F) release but underwent **clinical** disintegration relatively easily.

Cement retention relies on luting (mechanical interlocking) and/or chemical adhesion. Major cement advances occurred in the 1960s. Polyacrylic acid was substituted for phosphoric acid and was reacted with zinc oxide. (Smith, 1967) Glass ionomer (Wilson et al., 1977a) utilized

polyacrylic acid and replaced zinc oxide with fluoro-aluminosilicate glass, much like the powder component of SC. (Wilson et al., 1977b) GI was modified to produce several variants (metal-modified GI (Tjan and Morgan, 1989), resin-modified GI (Wilson, 1990a), compomers (Tay et al., 2001), giomers (Tay et al., 2001), and carbomers (Koenraads et al., 2009) intended as tooth-colored filling materials. Applications and compositions were quite varied including calcium phosphate (LeGeros, 1988) and calcium silicate versions (Duarte et al., 2018).

Cements formulated with a source of mobile F ions will release F over time (Forsten, 1977), with a large burst occurring in the first few hours followed by lower levels thereafter. F can be re-absorbed by those materials (recharging) if an external source with high F ion concentration is temporarily available, but levels again decay quickly (Forsten, 1996). Other cements release minor amounts of F ion due to additions of  $\text{CaF}_2$  as a mixing aid or  $\text{SnF}_2$  as an additive to counteract acid demineralization of the enamel. Clinical effects of this fluoride release remains unclear.

Dental cements have composite-like microstructures with continuous (or matrix) and dispersed (or filler) phases. Dispersed components invariably are stronger and control the properties of the final mixture, but increase pre-set viscosity. A great myth in dentistry is that cement film thicknesses should be  $\leq 25 \mu\text{m}$ . Lab sectioning of cemented crowns reveals true cement thicknesses varying from 50-250  $\mu\text{m}$ . The practical target for good fit is assumed to be  $\leq 100 \mu\text{m}$ , and is at least anecdotally supported by good clinical outcomes.

PC and GI cements, along with certain carboxylic and phosphoric acid containing resin cements, potentially chelate available  $\text{Ca}^+$  ions in tooth structure. While chemical adhesion is possible, the aqueous nature of these cements facilitates better adaptation to tooth structure and may contribute to improved micromechanical retention. Generally, it is more advantageous to use a CP cement for an all-ceramic restoration, while CP or GI work well with metal surfaces.

Target values for cement properties are defined in the latest ISO standards (ISO, 2018) but with little foundational support. Few clinical trials (Silvey and Myers, 1976; 1977) have ever been conducted, and fall far short of the 10-20 years needed to document problems (retention, resistance to dissolution, secondary caries) and define longevity. Without documentation only anecdotal reports are available. Luckily, absence of reports seems to infer that cement properties are sufficient for long term success.

### The Dental Ceramic Revolution

Up until about 1960 dental ceramic use was mainly limited to porcelain denture teeth. Land (1886) had produced ceramic crowns using a feldspathic ceramic, and Pincus (1920's) had explored ceramic for veneers. Neither became mainstream due to the low strength of the ceramics used. (Kelly et al., 1996)

Two developments in the 1960's profoundly changed the role of ceramic applications in dentistry. Both relied on the conclusion that the feldspathic ceramic developed by Land would only survive in the mouth if supported by a high strength substructure. One approach was to use a cast metal substructure onto which was fired a thin veneer of the ceramic, producing a porcelain-jacket crown (PJC). This became possible by adding leucite to the feldspathic glass to

match the coefficient of thermal expansion of the underlying metal substructure. (Weinstein et al., 1962). Another approach used a high-strength ceramic substructure by adding alumina to reinforce the feldspathic glass. (McClean and Hughes, 1965). For the first time dental practitioners could provide patients with highly aesthetic anterior and posterior restorations. These are still used today with only minor modifications to improve aesthetics and durability of the veneer, and in some cases reduce costs by using non-gold alloys for the substructure.

In contrast, the alumina-reinforced PJC for anterior crowns had a short clinical life because of the low strength of the core ceramic. One approach was to increase the alumina content of the core from the original (~40%), and a highly effective method was to partly pre-sinter pure alumina and then infiltrate the porous structure with a lanthanum glass. (Jung et al., 1999) The high strength core had high alumina content (~80%). The next evolution was to employ a 100% alumina core using a combination of digital processing and CAD-CAM technology. CAD-CAM soft machining produced a purposely over-sized core from a porous alumina block, which was then subjected to a high-temperature firing cycle to fully densify it and produce a final restoration of the correct size. When this system became available in the early 1990's (Russell et al., 1995), ceramic crowns and bridges for any location in the mouth became a possibility.

The first zirconia-based dental ceramics also became possible with the advent of digital processing (Kosmak et al. 1999). A porous block of yttria-stabilized zirconia (YTZ) was soft machined to the desired over-sized shape and densified by firing to a final correct size. (Suttor 2004) When veneering materials were added for aesthetics, their coefficient of thermal expansion needed to be somewhere between those of feldspathic veneering ceramics used for

alumina cores and leucite containing feldspars used for metals. (Kim et al. 2008) Zirconia ceramics are often used in posterior teeth without veneering, but this has met with limited initial success for anterior applications. (Denry and Kelly, 2014; Zhang and Lawn, 2018), even with newer formulations having enhanced translucency.

While all-ceramic restorations were being developed, an alternative concept was introduced called resin-bonded ceramic (Horn, 1983; Calamia, 1983). This process involved bonding thin, fragile ceramic veneers made from leucite-containing feldspathic ceramics to the tooth structure using a resin composite, thus relying on a combination of micromechanical bonding using phosphoric acid etched enamel and HF-etched ceramic. Ceramic veneers became a highly effective clinical modality to esthetically restore discolored teeth. With the advent of dentin bonding systems this concept was extended to resin-bonded crowns. Since no metal substructure was involved, the constraint of compatible thermal expansion coefficients was eliminated. New veneering ceramics optimized leucite content and strength. (Chen et al., 2011) However, for resin-bonded bridge and posterior crowns, something much stronger than a leucite-reinforced feldspar ceramic was required. This gap was filled by a lithium disilicate glass ceramic. (Dong et al., 1992) While not as strong as YTZ, lithium disilicate is more esthetic and sufficiently strong for anterior bridges and some low-load short-span posterior bridges. As with zirconia ceramics, efforts are being made to produce highly aesthetic lithium disilicate glass ceramics that do not require porcelain veneering (Harada et al., 2016). Monolithic resin bonded ceramic restorations that do not require veneers have the advantage of less clinical chipping and more simplified manufacturing.

The Evolution of Dental Materials for Tissue Repair – Functional Repair Materials



In the early 1900s, dental materials were designed only to replace tissue lost to disease or trauma. As understanding of disease processes such as dental caries occurred, approaches to restore function began to include repair of dental tissues as well. Use of fluoride to reverse early enamel caries was a significant milestone in dental research, establishing a basis for minimally invasive approaches to directly repair enamel, dentin and cementum.

Enamel remineralization is an accepted treatment (ten Cate, 2001, Featherstone, 2000) for early lesions, and several topically applied fluoride-delivery systems exist, including varnishes, rinsing solutions, drinking water, and toothpastes. Such remineralization is possible since enamel is mainly apatite mineral as a result of the almost complete removal of the guiding proteins during maturation. Bacterial metabolism of ingested carbohydrates within adherent biofilms results in a reduction in pH and partial loss of the surface of the enamel crystallites. When the pH returns to normal levels the crystallite size can be restored by remineralization in the presence of calcium and phosphate. Re-precipitation is enhanced by fluoride which can be incorporated in the apatite crystallite surfaces reducing susceptibility to future demineralization.

However, fluoride's ability to promote surface precipitation can block remineralization in deeper demineralized areas. Thus, significant recent research (ten Cate, 2012) has focused on casein-amorphous calcium phosphates (ACP) (Cochrane and Reynolds 2012) and chitosan-ACP (Zhang et al, 2014) to retard early surface precipitation while promoting subsurface remineralization. Other ion-releasing materials for promoting apatite formation include silicate-based bioglass. Because mature enamel is acellular, structure loss due to cavitation, attrition, or bruxism cannot be restored simply using fluoride treatments. Significant current research is aimed at

understanding how enamel is formed (Habelitz, 2015), and alternative future approaches may be directed to artificially build enamel (Yamagishi et al, 2005 Prajapati et al, 2018).

While dentin is also an apatitic structure, it is actually a reinforced hydrated composite with collagen. But its lower mineral content, smaller apatite crystallite size, and its higher carbonate content make it more susceptible to rapid demineralization by cariogenic acids compared to enamel. To restore its structure and mechanical properties, it is necessary to reintroduce mineral both within the collagen fibrils (intrafibrillar mineral) and between the collagen fibrils (extrafibrillar mineral) (Kinney et al., 2003; Bertassoni et al., 2009).

This requirement was often overlooked and approaches that successfully induced apatite mineral in enamel only produced superficial mineral for dentin. Gower and colleagues introduced the concept that proteins involved with biomineralization might be mimicked by charged polymers, such as polyaspartic acid, leading to the development of the polymer-induced liquid precursor (PILP) system (Olszta et al., 2003; 2007; Gower, 2008). PILP has been applied to many collagen-based matrices and provides *in vitro* remineralization of artificial caries lesions (Burwell et al., 2012). A related approach using polyacrylic acid was introduced by Tay and Pashley (2008; 2009).

There are many nucleation inhibitors, including phosphonates, osteopontin and others, that provide intrafibrillar mineralization in dentin and bone collagens by sequestering calcium and phosphate ions in nanodrops that eventually release the ions into collagen fibrils. Once in the fibrils, ACP forms and transforms to aligned apatite crystals similar to those in native dentin. This approach

provides 100% remineralization in the deeper half of 150  $\mu\text{m}$  deep artificial caries lesions after several weeks in solution, but only about 60% in the more demineralized outer portions (Burwell et al., 2012, Saeki et al., 2017). Efforts are ongoing to develop new cements that could be placed clinically to provide long term remineralization.

The efficacy of the PILP remineralization approach for dentin caries has not been proven clinically and a variety of additional barriers must be overcome **to provide new clinical treatments**. Compared to artificial lesions, natural caries is more complicated because it involves bacteria biofilms that change as the lesion progresses, and because collagen may be altered or partially degraded due to endogenous MMPs or cathepsins (Vidal et al., 2014; Mazzoni et al., 2015). Critical research continues on MMP inhibitors, as well as in gaining increased knowledge about the complexity of oral biofilms. Other active research areas to reduce caries involve cavity disinfectants and antimicrobials that can be added to composites and glass-ionomer restoratives (Imazato, 2009; Hirose et al., 2016; Farrugia and Calmilleri, 2015).

### Future discoveries

What is on the horizon for new dental restorative materials? Imagine a limitless bulk-fill composite that self-adheres to all tooth structure and has antibacterial properties. **Perhaps these materials will be hardened by alternative “instant” curing technologies, not relying upon light penetration through several mm, but by the delivery of other sources of activating energy.** Future materials will not only functionally restore without adverse biologic effects, but stimulate beneficial biological responses that encourage natural repair of **small defects in** the tooth. **In situ tissue engineered replacements of whole tooth structures and entire dental pulps are already being explored.** New research is underway to understand the complex interplay between

extracellular matrix properties, cell differentiation and angiogenesis. Materials with native antimicrobial characteristics could effectively deter the formation of deleterious microbial biofilms, not through indiscriminate killing, but via selective colonization and or antifouling strategies. These materials will accommodate beneficial “bioactive molecules” capable of being released in situ for an on-demand response to a potential problem. It is also likely that these new materials will contain sensor molecules or compounds that monitor events occurring at margins and surfaces to alert clinicians and patients to potential issues preventable by early intervention. And as the move continues toward more minimally invasive treatment strategies, repair of restorations will increase, possibly through infiltration techniques to effectively de-stain and/or reseal restoration margins. New ceramics will have high strength, rivaling zirconia, but be highly esthetic and translucent, completely circumventing the need for veneering. These materials will be fabricated chairside by additive manufacturing methods using a fully digital clinical workflow that will also incorporate computer controlled ion implantation techniques to esthetically color the final prosthesis. The further development of zirconia implants will provide more esthetic designs than titanium, while maintaining adequate strength and toughness and excellent biological tolerance.

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#### Conflict of Interest

The authors declare that they have no conflicts of interest to report related to this article and its contents.

## Author Contributions

All five authors contributed to conception, contributed to acquisition, analysis, and interpretation, drafted the manuscript, critically revised the manuscript, gave final approval, and agree to be accountable for all aspects of work ensuring integrity and accuracy.

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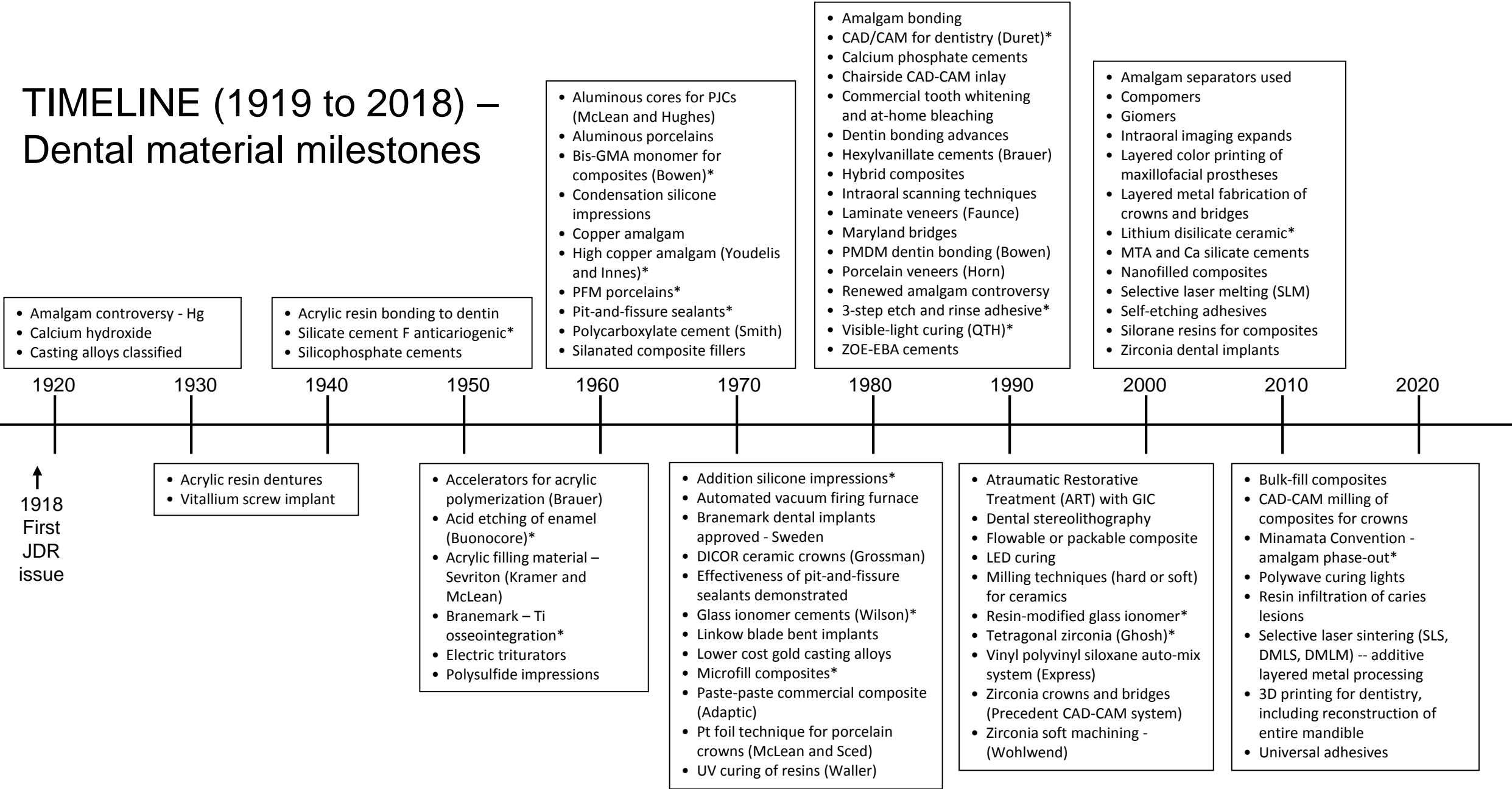
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## Figure Legends

Figure 1: Timeline of milestones in dental materials (1919-2018). Entries display in alphabetical order developments/discoveries that occurred during each decade, with specific efforts that had the highest clinical impact identified with an asterisk.

Figure 2: Publication milestones for dental materials in JDR (1918-2018). (Appearances of major topic words in Journal of Dental Research citation titles or abstracts in Pubmed from years 1945 through 2018. Search algorithms: J Dent Res AND amalgam; J Dent Res AND (ceramic or porcelain); J Dent Res AND (bond\* OR adhe\* OR luting) AND cement; J Dent Res AND composite; J Dent Res AND (Bioactive OR F-release OR reminer\*). Citations were not individually reviewed. All issues from 1919-1944 were manually searched.

# TIMELINE (1919 to 2018) – Dental material milestones



↑  
1918  
First  
JDR  
issue

- Amalgam controversy - Hg
- Calcium hydroxide
- Casting alloys classified

- Acrylic resin bonding to dentin
- Silicate cement F anticariogenic\*
- Silicophosphate cements

- Aluminous cores for PJC's (McLean and Hughes)
- Aluminous porcelains
- Bis-GMA monomer for composites (Bowen)\*
- Condensation silicone impressions
- Copper amalgam
- High copper amalgam (Youdelis and Innes)\*
- PFM porcelains\*
- Pit-and-fissure sealants\*
- Polycarboxylate cement (Smith)
- Silanated composite fillers

- Amalgam bonding
- CAD/CAM for dentistry (Duret)\*
- Calcium phosphate cements
- Chairside CAD-CAM inlay
- Commercial tooth whitening and at-home bleaching
- Dentin bonding advances
- Hexylvanillate cements (Brauer)
- Hybrid composites
- Intraoral scanning techniques
- Laminate veneers (Faunce)
- Maryland bridges
- PMDM dentin bonding (Bowen)
- Porcelain veneers (Horn)
- Renewed amalgam controversy
- 3-step etch and rinse adhesive\*
- Visible-light curing (QTH)\*
- ZOE-EBA cements

- Amalgam separators used
- Compomers
- Giomers
- Intraoral imaging expands
- Layered color printing of maxillofacial prostheses
- Layered metal fabrication of crowns and bridges
- Lithium disilicate ceramic\*
- MTA and Ca silicate cements
- Nanofilled composites
- Selective laser melting (SLM)
- Self-etching adhesives
- Silorane resins for composites
- Zirconia dental implants

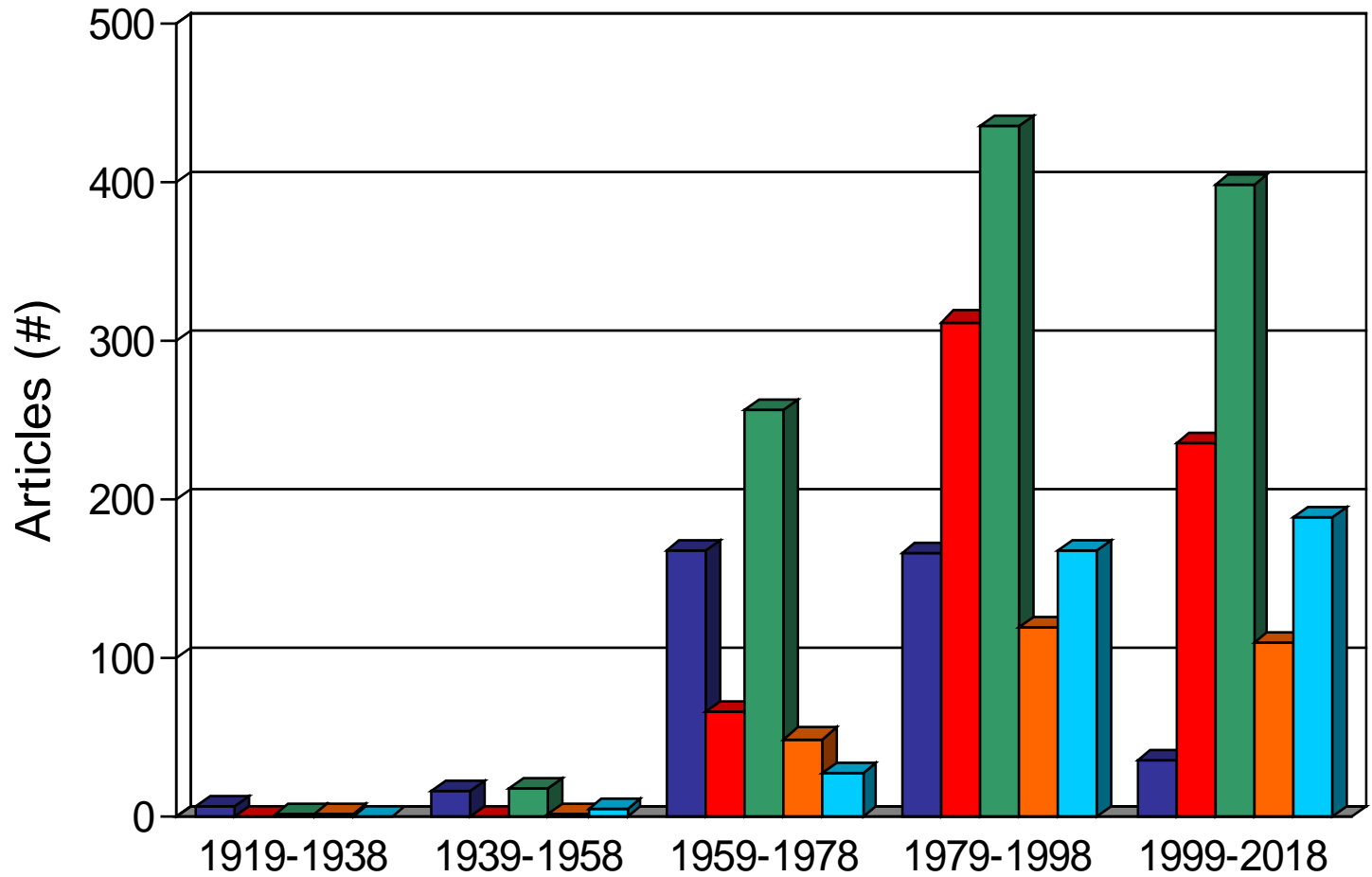
- Acrylic resin dentures
- Vitallium screw implant

- Accelerators for acrylic polymerization (Brauer)
- Acid etching of enamel (Buonocore)\*
- Acrylic filling material – Sevriton (Kramer and McLean)
- Branemark – Ti osseointegration\*
- Electric tritulators
- Polysulfide impressions

- Addition silicone impressions\*
- Automated vacuum firing furnace
- Branemark dental implants approved - Sweden
- DICOR ceramic crowns (Grossman)
- Effectiveness of pit-and-fissure sealants demonstrated
- Glass ionomer cements (Wilson)\*
- Linkow blade bent implants
- Lower cost gold casting alloys
- Microfill composites\*
- Paste-paste commercial composite (Adaptic)
- Pt foil technique for porcelain crowns (McLean and Sced)
- UV curing of resins (Waller)

- Atraumatic Restorative Treatment (ART) with GIC
- Dental stereolithography
- Flowable or packable composite
- LED curing
- Milling techniques (hard or soft) for ceramics
- Resin-modified glass ionomer\*
- Tetragonal zirconia (Ghosh)\*
- Vinyl polyvinyl siloxane auto-mix system (Express)
- Zirconia crowns and bridges (Precedent CAD-CAM system)
- Zirconia soft machining - (Wohlwend)

- Bulk-fill composites
- CAD-CAM milling of composites for crowns
- Minamata Convention - amalgam phase-out\*
- Polywave curing lights
- Resin infiltration of caries lesions
- Selective laser sintering (SLS, DMLS, DMLM) -- additive layered metal processing
- 3D printing for dentistry, including reconstruction of entire mandible
- Universal adhesives



Amalgam	6	16	168	166	35
Composite	0	0	66	312	236
Adhesive/Cement	1	18	256	435	399
Ceramic	1	2	49	119	110
Tissue Repair	0	5	27	168	189