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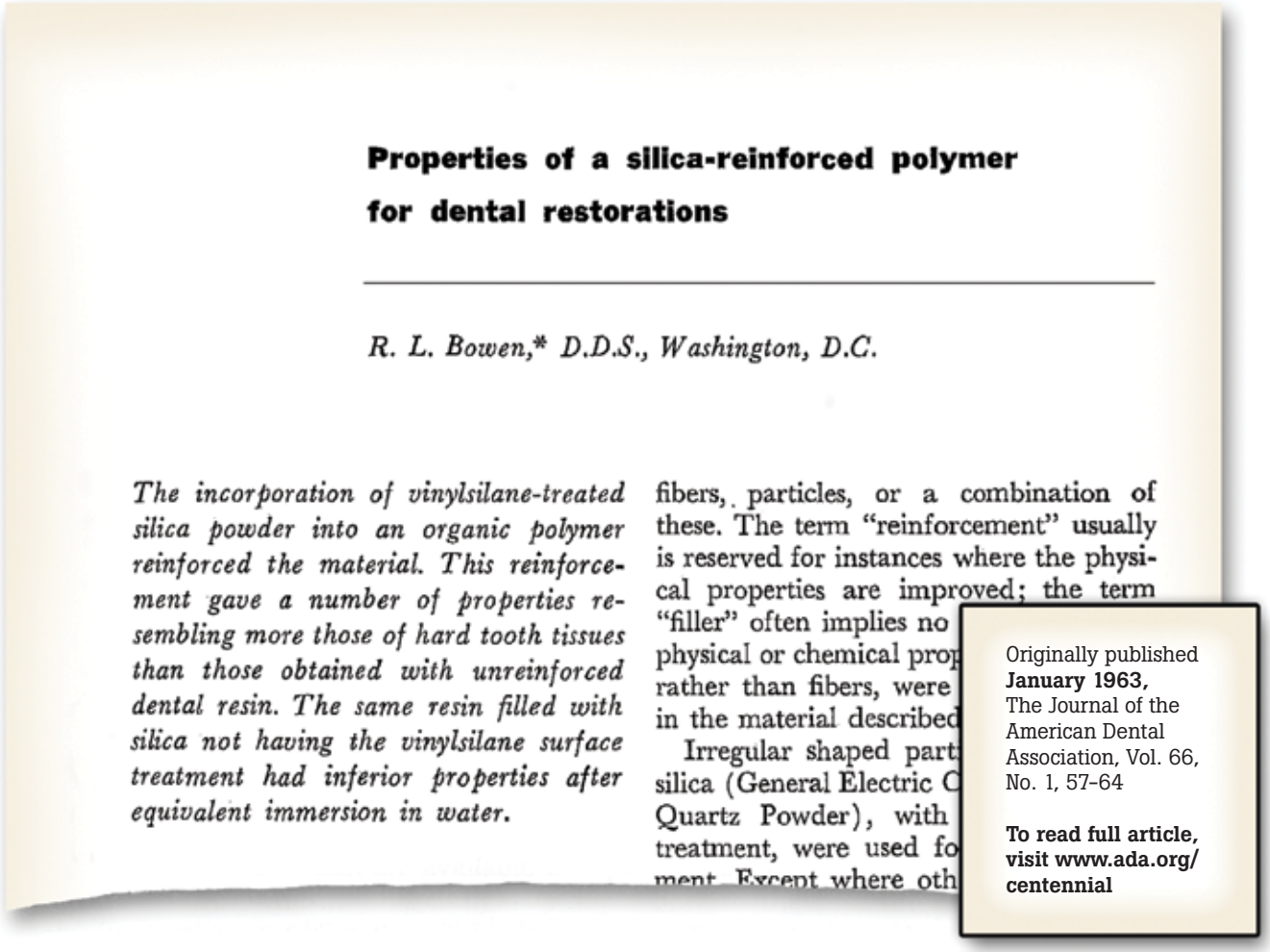
Spotlighting articles from past ADA Journals that have achieved landmark status thanks to their lasting impact on dental care and the dental profession



Properties of a silica-reinforced polymer for dental restorations

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The incorporation of vinylsilane-treated silica powder into an organic polymer reinforced the material. This reinforcement gave a number of properties resembling more those of hard tooth tissues than those obtained with unreinforced dental resin. The same resin filled with silica not having the vinylsilane surface treatment had inferior properties after equivalent immersion in water.

fibers, particles, or a combination of these. The term "reinforcement" usually is reserved for instances where the physical properties are improved; the term "filler" often implies no physical or chemical prop rather than fibers, were in the material described

Irregular shaped part silica (General Electric C Quartz Powder), with treatment, were used fo ment. Except where oth

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Beginnings of the dental composite revolution

Stephen C. Bayne, MS, PhD

The true age of dental composites was launched with this initial science into coupling agents. In the late 1950s and early 1960s, the word "composite" was still new to dentistry. Its predecessor, the adjective "reinforced," dominated the dental materials nomenclature instead. In this landmark article by Bowen, the term "composite" does not even appear. Dental materials science was just beginning to deal with the extreme challenges of chemically connecting internal interfaces of things to make ceramic-polymer composites. In materials science, the term "composite" means a physical mixture of any phases (metal-metal, metal-ceramic, ceramic-ceramic, ceramic-polymer, polymer-metal, polymer-polymer). Bulk properties of any composite depend on volume fraction and properties of each phase and the characteristics of the interfaces connecting those phases. Without strong internal interfaces, composites behave poorly.

That was the scientific backdrop for this early

experiment creating what everyone understands today as "dental composite." This 1963 publication by Dr. Rafael Bowen was a "proof of concept" that documented chemical treatment of silica particles so their surfaces could be intimately bonded into a mixture with polymer during curing and generate a strong restorative material. The magical coating material was tris(2-methoxyethoxy) vinyl silane. Ray Bowen borrowed this from those making glass-reinforced polyester laminates.[1] Materials that chemically bridge the interfaces of phases are called "coupling agents." There are very few types of these materials. Each depends on the chemistry of the ends of the coupling agent molecule being matched well to the phases on either side. Even today, coupling is a problem for many systems. Applying the coupling agent effectively is fickle. It works best in dilution, is often pH dependent, must avoid many side reactions and needs to form thin films. As demonstrated in his article, Dr. Bowen effectively coated silica, bonded it into bisphenol A-glycidyl methacrylate (bis-GMA) and produced a material with very encouraging early properties, as demonstrated in his plethora of laboratory tests. Contrary to the journal articles of today that tend to focus on only one or two property tests, Bowen tested setting times, shrinkage, solubility and disintegration, water sorption, coefficient of thermal expansion, color stability, visual opacity, compressive strength, tensile strength, modulus of elasticity, resistance to indentation and toxicity.

Dr. Rafael Bowen

Composites generally are complex structural designs. There are so many things that need to be managed to get good results. So often, the early trials with new components are exasperating. Table 1 is a chart of the components showing the fortuitous choices that Ray Bowen made for this particular experiment versus typical components for current composites. Figure 1 shows the position of the coupling agent in the composite. Dental composites start with a fluid monomer that forms a continuous phase and suspends reinforcing particles of silica that have been coated with a silane coupling agent. Bis-GMA is viscous and requires dilution with other monomers to create a usable mixture. Early composites were self-cured and prepared as two components to be mixed just before use. Often this mixture included inadvertent air incorporation that left pores as mechanical defects that were extremely deleterious to strength. Correctly choosing most of the components for this early experiment was quite remarkable. Since then, 50 years of continual refinement of the formula has taken place (1963-2013). This quite extraordinary revolu-

TABLE 1

Generic components in Bowen's* original and modern (circa 2010) resin-based composites.

COMPOSITE COMPONENTS	COMPOSITION OF REINFORCED RESIN-BASED COMPOSITE	
	1963 Original (Bowen*)	2010 Typical
Coupling Agent	Vinyl silane	Vinyl silane
Matrix: Acrylic Comonomers	80 percent bisphenol A-glycidyl methacrylate (bis-GMA), 10 percent methyl methacrylate, 10 percent triethylene glycol dimethacrylate (TEGDMA)	70 percent bis-GMA, 30 percent TEGDMA
Inhibitor	Hydroquinone	Butylated hydroxytoluene
Filler	55 volume percent quartz, < 150 micrometers	55 volume percent glass, < 0.5 μm
Initiator	Benzoyl peroxide	Camphoroquinone and others
Accelerator	N,N-Dimethyl-amino-p-toluidene	Visible light
External Interfacial Bonding	None	Etching-priming-bonding system

* Source: Original 1963 JADA article by Bowen.

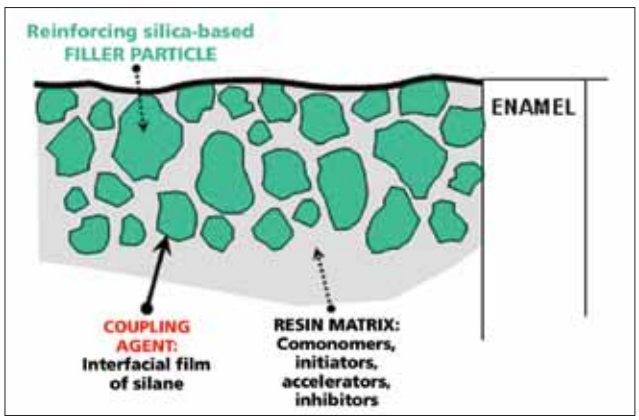

Figure 1. Schematic of dental composite and location of components.

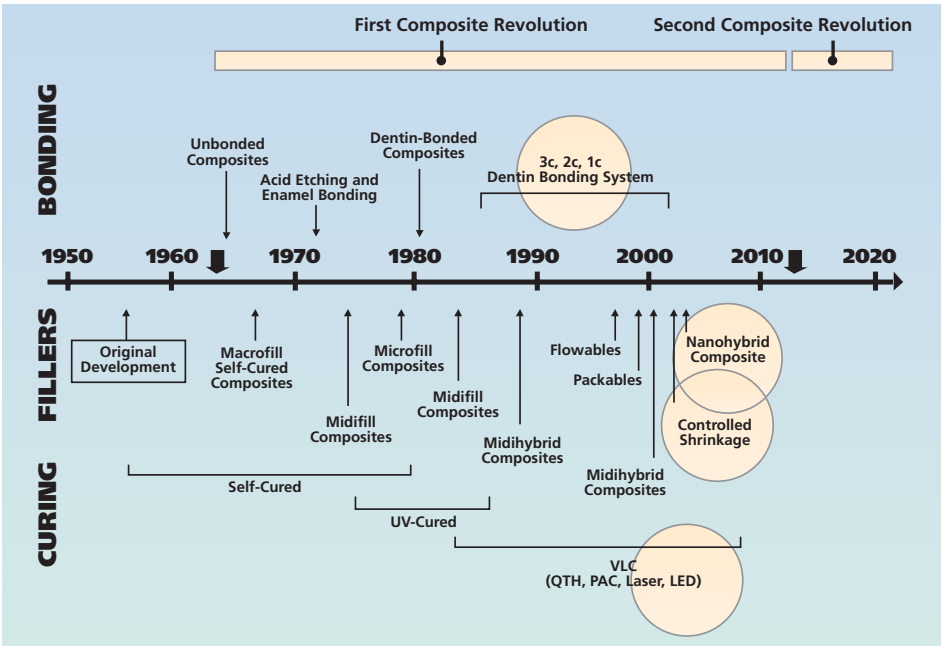

Figure 2. Schematic summary of the evolution of dental composite over more than 50 years. 3c: Three-component system (etch, prime, bond). 2c: Two-component system (etch, prime/bond or etch/prime, bond). 1c: One-component system (etch/prime/bond). LED: Light-emitting diode. PAC: Plasma arc light. QTH: Quartz-tungsten-halogen. UV: Ultraviolet. VLC: Visible light cured.

TABLE 2

Comparison of the mechanical properties of the original composite with those of a typical new material.

MECHANICAL PROPERTIES, ACCORDING TO YEAR	ULTIMATE COMPRESSIVE STRENGTH, IN MPa*	ULTIMATE TENSILE STRENGTH, IN MPa	ELASTIC MODULUS, IN GPa†
2010 Mean Composite Value (Range)‡	360 (189-463)	50 (32-64)	12 (5-25)
1963 Silica-Reinforced Bis-GMA§¶	157	27	11.0
1963 Control, Silicate Cement#	range, 157-186	5	21.4

* MPa: Megapascal.
† GPa: Gigapascal.
‡ Sources: Biomaterials Properties Database, University of Michigan.[2-4]
§ Bis-GMA: Bisphenol A-glycidyl methacrylate.
¶ Source: Original 1963 JADA article by Bowen. Glass particles from compressive strength specimens were collected by means of sieves ranging from no. 100 through no. 350. Glass particles from tensile strength and modulus specimens were collected by means of a no. 400 sieve.
# Source: Paffenbarger and Stanford.[5]

tion is schematically represented in Figure 2. Along this path virtually all of the original components have been investigated and most have been significantly changed. Table 2[2-5] reports the mechanical properties of the old to newer formulations. Compressive and tensile strengths have improved. The intermediate values of modulus of elasticity that represent less brittle materials have been preserved.

Discovery and invention usually depend on immersion within a rich environment of expanding knowledge. This was certainly true for dentistry from 1950 to 1970. In addition to dental materials research that was being conducted at several universities, the National Bureau of Standards (NBS) (later to become the American Dental Association Foundation Paffenbarger Research Center at the National Institute of Standards and Technology) was active in research. Dr. Bowen found a lifelong home at NBS starting in the 1950s. Dentistry was converting over to high-speed handpieces that allowed new types of cavity preparation designs for adhesive restorations. New dental chair designs transformed patient care procedures and facilitated four-handed dentistry.[6] By substantially reclining a patient, it was much easier to access intraoral spaces and to work in tandem with a dental assistant. Composite and bonding system placements were best managed by using four-handed dentistry. New areas of dental materials research were evolving such as animal testing for biocompatibility[7] and clinical research.[8] New dental companies were formed because of the chemistry involved in dental composites (for instance, 3M Dental[9] [now 3M ESPE, St. Paul, Minn.] commenced in 1964 with the market entrance of Addent dental composite restorative material). Old problems were being solved with new understandings of interfacial bonding challenges, such as matching porcelain to metal thermal expansion.[10,11] A huge number of experiments were revealing the success behind high-copper

dental amalgams.[12] It was an exciting time for restorative dentistry. Early work would soon be under way on both polycarboxylates[13] and glass ionomers.[14]

Original uses for composite restorative materials involved traditional retentive cavity preparation designs. However, just as this experiment featured coupling agents to produce intimate internal interfaces, new procedures called "bonding" were being devised to create intimate external interfaces of composites with enamel and dentin. Dental composite was part of a revolution in new restorative techniques. Acid-etching techniques had been introduced earlier.[15] New acrylic resin polymerization accelerators had been extensively explored.[16,17] Two major conferences had brought together the entire dental research community to discuss improved restorative materials and bonding to enamel.[18,19] Dental composite use was explored in anterior and posterior teeth (with products such as Adaptic [Johnson & Johnson, New Brunswick, N.J.] and Addent [3M Dental]). Bis-GMA was being evaluated for dental sealants.[20] Lightly reinforced composites subsequently were evaluated as preventive resin restorations.[21,22] Thus began a 30-year search to understand the wear behavior of these composite materials. This landmark publication by Bowen was really the tip of the iceberg that signaled rapidly expanding new science across a range of dental restorative materials.

General dental practice in 1950 was primarily focused on procedures involving dental amalgam, direct gold and cast gold restorations. Direct esthetic restorations involved silicate and polymethyl methacrylate fillings. Indirect esthetic restorations were primarily dental porcelain in areas of low or no stress. By 1980, sealants, composites, preventive resin restorations and glass ionomers were gaining huge momentum. Porcelain-fused-to-metal restorations were highly successful. Amalgams were being replaced in anterior tooth sites almost entirely by tooth-colored materials. The great debate in modern times over dental amalgam safety was just beginning, and the emotional misinformation of antiamalgamists began to capture headlines. There was new interest in potential alternatives to dental amalgam. Glass ionomers and composites were both touted as the materials of the future. Clinical trials of dental composite use in posterior tooth sites to replace amalgam restorations were already under way. There was an explosion of new composite filler types, filler combinations, new curing lights, new resin monomers and early bonding systems. The composite revolution was fully under way.

Where are we today? The first composite revolution is over. We are looking forward to a second composite revolution and an explosion of new ceramic materials and fabrication technologies as the mainstays for future restorative dentistry. In December 2012 in London, the Dental Materials Innovation Workshop took place, sponsored by Kings College and the International Association for Dental Research.[23] This planning may have represented the beginning of the end for dental amalgam, for conventional composites and for glass ionomers as we have known them. The conference was in response to a proposed treaty brokered by the United Nations Environmental Programme to produce a widely embraced world treaty to discontinue the use of all products based on mercury, including amalgam. In discussions of options for the future at the conference, the groundwork for potential new composite formulations was discussed. A new composite would include friendlier monomer systems and advanced nanofillers and focus on being crack tolerant. Coincidentally, the National Institute of Dental and Craniofacial Research, National Institutes of Health, posted a request in December 2012 for applications for entirely new dental composites that could be new amalgam replacements and last much longer. Dr. Ray Bowen, who has continually published for almost 60 years and contributed to most aspects of the first composite revolution (documented in more than 30 patents), continues to publish and seems certain to be involved in the second composite revolution as well. The length of this second composite revolution will depend on competition from readily available implant systems and tissue-engineered teeth but seems sure to continue through the next decade or more. ■

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