NATIONAL BUREAU OF STANDARDS REPORT

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Progress Report
on
ADHESIVE RESTORATIVE MATERIALS

NBS

U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

NATIONAL BUREAU OF STANDARDS

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ADHESIVE RESTORATIVE MATERIALS

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COMPOSITE RESTORATIVE MATERIALS

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COMPOSITE RESTORATIVE MATERIALS

I Historical Introduction

Although composite dental restorative materials are yet in their infancy, the roots of their development can be traced back through the scientific literature for many years. In 1843 a German chemist, Joseph Redtenbacher, reported a new acid to which he gave the name acrylic acid.[1] In the last part of the century, methacrylate esters and their polymers were discovered.[1] Probably before 1940, Schnebel had found that tertiary amines (such as Michler's ketone) would activate benzoyl peroxide to give self-hardening resins.[2] So far as can be determined, the first self-curing methyl methacrylate resin formulation for filling teeth was introduced in the United States in 1948.

There soon appeared on the market a number of direct filling resins, and many believed that these materials would be the answer to the shortcomings of the decades-old silicate cement. However, this idea was short-lived.[3] These resin restorations discolored,[4] tended to shrink away from the cavity walls,[5] allowed the exchange of oral fluids around their margins,[6] and were associated with pulpal inflammation[7-9] and a high incidence of recurrent decay.[10-11] Furthermore, discrimination between decalcified dentin and the unreinforced direct filling resin was difficult because they were both radiolucent. For these and other reasons, a great many practitioners returned to the use of silicate cements.[3]

The shortcomings as well as the merits of silicate cements are well known. After nearly a hundred years[12] of development and use, these esthetic materials with good thermal and anticariogenic properties still have distinct disadvantages.[3] Most obvious is the susceptibility to disintegration in a decay-like manner,[13-15] typically after about four years in the mouth.[3,14] Further description is given by Wilson elsewhere in this publication.

Because of the persistent need for a permanent, esthetic direct filling material, there were continued efforts to improve the methacrylate resins. An aluminum silicate filler (about 15%) was part of one methyl methacrylate monomer-polymer system.[16] The use of fillers with the proper index of refraction and a low thermal expansion, and the development of adhesion in the resin were advocated.[17] Indeed, when inert fillers were incorporated into poly(methyl methacrylate), there was a reduction in the coefficient of thermal expansion and in the water sorption in proportion to the concentration of fillers.[18] However, there was limited adhesive characteristics in these and certain other resins investigated.[19]

Epoxy resins,[20] developed early in the present century, had an annual production rate of about 20 million pounds by 1954. Certain formulations of these resins had intriguing properties including adhesive characteristics and the ability to harden at moderate temperatures with little shrinkage. These led numerous investigators to study epoxy resins as a binder for inorganic fillers.[19,21] Primarily with indirect techniques, composite restorations were prepared using powdered fused silica and porcelain, bonded together with minor quantities of (heat-cured) epoxy resins. The good esthetics and other favorable properties of these composites encouraged the further investigation of this approach to dental restorative materials.[21]

However, attempts to develop composite materials using epoxy resins with various hardening agents for use in direct techniques met with numerous difficulties. Although initially adhesive to hard tooth tissues, the strengths of bonds between epoxy resins and enamel or dentin after prolonged exposure to water were disappointing.[19,21,22]

II Early Composite Developments

The goal-directed research in which the composite dental restorative materials were developed was initiated at the National Bureau of Standards in 1956. After unsuccessful attempts to use various epoxy resins and hardening systems, a compromise between epoxy and methacrylate resins was concieved late in 1957.[23,24] The reaction sites (oxirane rings) of the epoxy molecule were replaced by methacrylate groups. This gave a hybrid molecule that polymerized through methacrylate groups.[25] It was suitable for use as a binder for reinforcing fillers because it was nonvolatile, had a relatively low polymerization shrinkage, and hardened rapidly under oral conditions when suitably formulated with an appropriate initiator system.

This dimethacrylate monomer (BIS-GMA) was synthesized by the reaction of bisphenol A and glycidyl methacrylate.[26] The same product is also produced by the reaction of the diglycidyl ether of bisphenol A and methacrylic acid.[25] Its structural formula[27] is shown in Figure 1.

Although BIS-GMA has been referred to as an epoxy resin, this is not the case; the original epoxy (oxirane) groups disappear during the synthesis and are, in effect, replaced by methacrylate groups. Unfortunately, this dimethacrylate monomer has also been called a polyester. The well-established term "polyester" should be restricted to the polycondensation products essentially of dicarboxylic acids with dihydroxy alcohols.[28]

Since the coefficients of thermal expansion of organic polymers are many times higher than that of the dental hard tooth tissues,[6,29] means for lowering this value were needed. Fillers[17] incorporated into the resin could do this.[18] Experimental composites prepared in 1953 utilized particles of fused silicon dioxide as a reinforcing filler because of the extremely low coefficient of thermal expansion of vitreous silica.[21] With the epoxy resin system, there was relatively good adhesion between the resin and the surfaces of these particles.

Later in the investigation, after the more-adhesive epoxy resins had been replaced by the less-adhesive dimethacrylate resins (BIS-GMA),[26] it became apparent that special means for attaining adhesive bonding between the resin matrix and the filler particle surfaces were required. At that time vinyl silane coupling agents appeared to be the most suitable means of improving this bonding.[30,31] The more reactive γ-methacryloxypropyl silane coupling agents[32,33] had not then become commercially available. A vinyl silane coupling agent applied to reinforcing filler gave composites that had about four times the tensile strength of composites utilizing the same filler without its being treated with the vinyl silane.[34] When the methacryloxypropyl silanes became available, their ability to promote adhesive bonding between the resin and glass was compared with that of vinyl silanes; the methacryloxypropyl silanes gave significantly stronger and hydrolytically more-stable bonding than did the vinyl silanes.[35-37]

Since the strength and durability of the composites depended on the quality of the bonding between the organic matrix and the reinforcing filler particles, it was of utmost importance that the best coupling agents be used in the optimal manner. The coupling agent most widely used was γ-methacryloxypropyltrimethoxy silane, also known as 3-(trimethoxysilyl)propyl methacrylate. This organofunctional silane was hydrolyzed and condensed on the surfaces of the filler particles. It made the particles water repellent, reducing the water sorption of the composites; it also formed chemical bonds at the surface of the particles, connecting the organic polymer and the inorganic filler,[38] converting inert fillers to reinforcing fillers.[39]

Although fused quartz or fused silica received a great deal of attention in experimental work,[14,21,23,24,26,34] many other filler materials were also investigated.[16,18,19,21,31-34] These included the synthetic mineral β-eucryptite and closely related materials,[35,40,41] microcrystalline glasses,[42] aluminosilicate glasses, barium-titanium glass, crystalline quartz and pyrogenic silica.[36] It has been widely held (although not universally accepted) that condensation between SiOH groups on the surfaces of these silica-containing fillers and SiOH groups of the hydrolyzed silane accounted for the bonding between the coupling agent of the filler and the filler particle itself. Copolymerization of the methacrylate groups of the silane with the methacrylate groups of the monomers comprising the organic continuous phase has been thought to complete the chemical linkage between the phases of the composites.[38]

The BIS-GMA monomer was too viscous to be readily mixed with these fillers without first being thinned with some suitable monomer having a lower viscosity. Among others, methyl methacrylate and ethylene and tetraethylene glycol dimethacrylate, have been used for this purpose.[23,24]

As with antecedent methacrylates,[16] stabilizers such as hydroquinone were first used to inhibit premature polymerization and give the necessary storage stability (shelf life) to the BIS-GMA formulations.[23,26] On polymerization, less discoloration occurred with the use of the monomethyl ether of hydroquinone. Later, hydroquinone was replaced by BHT (butylated hydroxytoluene; 2,6-di-tert-butyl-4-methylphenol), a stabilizer that appeared to contribute no discoloring effects.[43]

Other additives that contributed to color stability of the restorations were ultraviolet-absorbing compounds. While these may have contributed to the stability of the monomers during storage, their primary purpose was to reduce the amount of discoloration in the resin of the final composite material. Typical UV absorbers were 2-hydroxy-4-methoxy-benzophenone[43] and 2-(2′-hydroxy-5′methylphenyl)benzotriazole.

Since most of the experimental work on composite materials utilized an amine-peroxide initiating system, another important component has been the amine accelerator. The most commonly used of these was N,N-dimethyl-p-toluidine (DMPT). This compound interacted with peroxides to produce free radicals which brought about the polymerization of the methacrylate monomer groups and thus the hardening of the resin binder of the composite. Investigations of factors that produce discoloration in these materials led to the introduction of N,N-dimethyl-*sym*-*m*-xylidine (DMSX; also known as DMDA), which not only gave less discoloration but also was a more effective accelerator than DMPT when compared on an equimolar basis.[43]

In a composite material developed in Great Britain,[44] a long-chain mercaptan, together with an aliphatic peroxide, served as the hardening initiators.

Although other peroxides have been used,[44] benzoyl peroxide has been the one most used in composite restorative materials. It has been dispersed either in the reinforcing filler with the aid of a solvent that is removed by evaporation, or is dissolved in one of the monomeric liquids of the composite formulation.

Sulfinic acids or their derivatives were used in the initiator systems for experimental composite materials.[14]

III Some Properties of Experimental and Commercial Composites

Before proceeding with recent and current developments, perhaps it would be well to define "composite." For this discussion, the term "composite restorative material" refers to a man-made, three dimensional combination of at least two chemically different materials with a distinct interface separating the components;[39] properties are thus obtained for the restoration of the form and function of defective teeth which could not be achieved by any of the components acting alone. Thus, the use of the term "composite" distinguishes the combination of inorganic aggregates bonded together with organic polymers from unreinforced direct filling resins and from silicate cements.

It is primarily the high proportion of reinforcing filler in composite restorative materials that yields properties different from those of direct filling resins. Most of the physical properties of composite restorative materials have been improved by the incorporation of a maximum amount of reinforcing filler together with a minimum amount of a binder of cross-linking polymerizable organic resin.

The "first generation" of commercial dental composite materials used BIS-GMA resin binder, described previously, together with major portions of various particulate fillers and minor portions of various additives. Data that have been reported in the literature[45-60] and more recently obtained[61,62] show that composites have lower polymerization shrinkages and coefficients of thermal expansion, and higher compressive strengths and stiffnesses relative to unreinforced resins. Compared to silicate cements, the composites have lower solubilities and higher tensile strengths. More detailed data are given in Tables 1 and 2, including comparisons with dentin and enamel.[24,63,68] The quantitative information presented in the tables is incomplete since the methods and conditions of measurement are not described; however, these data will serve to illustrate the ranges of values and order of magnitude to be expected with these materials.

The smoothness of the finished surface is comparable with that of silicate cements[36,57,58] but inferior to that of unreinforced resins[52] and most of the other restorative materials. The abrasion resistance of composite materials is superior to direct filling resins.[36,47,48,51,56,58]

Similar to some other dental restorative materials, problems encountered in packaging and storage include volatility of some ingredients and premature gelation of resin components.[36]

IV Current Research

Current research has the goal of making improvements on this "first generation" of composite materials now available to the dental practitioner. For example, there is a degree of pulpal irritation caused by some of these materials,[69,70] and it has not yet been established which of the various ingredients contribute most to the inflammatory reactions of the dental pulp tissues. Other problems that have been encountered are incomplete color stability[62] and resistance to staining, difficulties encountered in finishing and polishing, and lack of x-ray opacity.

The recent investigations at the National Bureau of Standards have led to new dimethacrylate monomers, reinforcing fillers, accelerators, stabilizers, and adhesion-promoting coupling agents that will, hopefully, lead to an improved "second generation" of composite materials. For example, the BIS-GMA is not completely color stable and is too viscous for use without being thinned with a monomer of lower viscosity. Furthermore, it cannot be purified by distillation or by crystallization since it is inherently a mixture of non-volatile optical isomers. To overcome these problems, three dimethacrylate monomers were synthesized that can be prepared and purified separately by recrystallization.[27] These are the condensation products of 2-hydroxyethyl methacrylate with the acid chlorides of phthalic, isophthalic and terephthalic acids, respectively. Upon combining these three crystalline products, a ternary eutectic liquid mixture is formed that has a viscosity low enough to be used without the addition of any volatile ingredients. Preliminary tests show it to be non-toxic and non-irritating.[27]

Numerous other monomers[71-75] are currently being synthesized and evaluated for use in dental composite materials.

The research effort to improve polymerization accelerators[76] has led to the successful synthesis of aromatic amines having unusually high molecular weights[77] so as to minimize their solubilities in tissue fluids and thus their freedom to diffuse into the pulp or other tissues. The structure of these amines is based partly on the fact that the color stabilities of the composites have correlated better with the nature of the ring substituents than with the kind of nitrogen substituents in the amine accelerators.[76,77]

Color stability is also profoundly affected by the characteristics of the stabilizers that are used. Significant advances are being made in the synthesis and utilization of stabilizers that are non-toxic and that do not cause discoloration of composites.[43,76,77]

In the instance where there has been evidence of greater surface staining of composite restorations relative to the adjacent tooth enamel, it has not yet been determined to what extent this accretion of discolored material is due to inadequate hydrolytic stability of the adhesive bond between individual particles and the resin matrix, the chemical nature of the reinforcing filler materials, the chemical nature and degree of polymerization of the resin formulations, the roughness of the surface after the restoration is finished,[78] or some combination of these factors. These factors are currently being studied.

Until recently, these has been little or no effort to prepare special materials to serve as reinforcing fillers for dental composite materials, rather, materials already available were selected for this application. However, the unique demands on this kind of composite material warrant the development and use of the most suitable fillers as well as other ingredients.

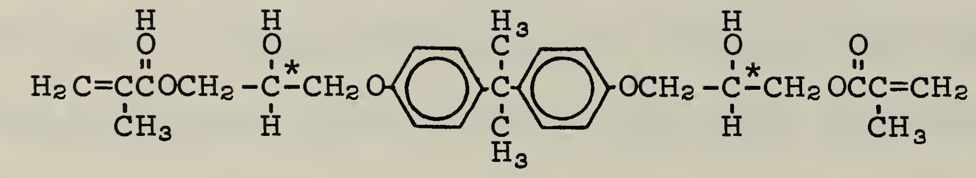
One experimental composite[79] contained a mixture of two reinforcing fillers: spherical particles of fused silica made up about two-thirds of the filler and smaller particles of an x-ray opaque glass made up about one-third of the filler. The smaller particles were composed of a special barium fluoride-containing glass that was developed for this purpose.[80] Radiopacity is desirable so that dentists can distinguish between the filling material and any carious dentin that underlies the filling.

The most recent investigations are involved with the preparation and evaluation of a single glass filler material containing silica and only enough barium to give the desired refractive index and x-ray opacity.[81] Preliminary indications are that it will be suitable for converting into spherical particles utilizing conventional techniques while retaining the appropriate refractive index, and will have a low coefficient of thermal expansion. Chemically, the glass is formulated to have, at least in theory, hydrolytic stability in its bonding with the silane coupling agents.

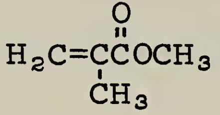
Since these composite materials are not intrinsically adhesive to the prepared tooth surface, special coupling agents have been developed which improve bonding between such composite filler materials and dentin and enamel. The chemical design of these special coupling agents was based on empirical observations of the types of groups that could displace water from the surfaces of powdered human enamel and dentin, thereby making the surface organophilic rather than hydrophilic.[82]

One of the coupling agents, NPG-GMA (the reaction product of N-phenylglycine and glycidyl methacrylate), has two functions in the same molecule. One function is that of a chelate group that can form multiple bonds with calcium in the tooth surface. The other function is that of a methacrylate group, which can copolymerize with the hardening organic matrix of the composite material.[83] A solution of the coupling agent placed on the prepared tooth surface with the excess solution being wiped away leaves an invisible film. Following this, the freshly mixed (but not yet hardened) composite material is placed on top of this treated surface and the subsequent polymerization apparently includes the methacrylate groups of the coupling agent. The coupling agent has presumably also formed ionic and coordinate bonds with the tooth surface. Laboratory data on tensile adhesion tests clearly demonstrate that the use of the coupling agent significantly improved the adhesion between composite materials and tooth surfaces.[83,84] Clinical evaluations are under way.[79]

There is a rapidly-expanding wealth of experience and information regarding composite dental materials, not only of the kind described here, but also of a wide diversity of materials and techniques.[85] Composite restorative materials, when they have been developed to their best potentialities, should eventually provide the dental profession and the public with greatly improved restorations for anterior teeth.



BIS-GMA



$$H_2C{=}\underset{CH_3}{C}\overset{\overset{O}{\|}}{C}OCH_3$$

MMA

FIG 1.—Structural formula of BIS-GMA. The asterisks indicate asymmetric carbon atoms that give rise to a number of steroisomers. Methyl methacrylate (MMA) is shown for comparison.[27]

TABLE 1

SOME PHYSICAL PROPERTIES OF ESTHETIC DIRECT-FILLING MATERIALS

	Hardening Time	Polymerization Shrinkage	Water Sorption	Solubility and Disintegration
	minutes	% (by volume)	% (by weight)	% (by weight)
Experimental Composites	4(14) 3-8(24,26) 5-7(34) 7-10(41) 5(61) 3.5-5(62)	2(23) 2.7-2.8(26)	0.9(26) 0.30-0.35(62)	0.00-0.08(23) 0.04(26) 0.15-0.22(61)
Commercial Composites	3-4(50) 1.5-4.5(52) 1-1.5(55) 2.5-5(59) 3-3.5(61)	1.2-1.5(52)	0.78-2.46(53) 1.60-3.68(56) 0.8-1.6(57) 1.12(62)	0.01-0.08(53) 0.12-0.16(62)
Silicate Cements	4-6(14) 4(34)	2(5) 3.3(26) 1.3(60)	--	0.4-1.1(14) 0.4-1.3(26)
Unreinforced Resin	6(14) 6(34) 3-3.5(50) 4(52) 2-4(59)	6-8(5) 6.2(26) 5.2(52) 5-6(60)	[1.0-1.5(5)]* [2.1(26)]†	[0.10(26)]† 0.1(60

* Volumetric expansion

† Self-curing denture base resins

TABLE 2

SOME PHYSICAL PROPERTIES OF ESTHETIC DIRECT-FILLING MATERIALS, DENTIN AND ENAMEL

	Tensile Strength	Compressive Strength	Modulus of Elasticity	Coefficient of Linear Thermal Expansion	Indentation Resistance and Recovery	
					Indentation	Recovery
	psi*	psi	psi x 10^6	ppm/°C	µm†	%
Experimental Composites	3,700-5,400(24) 4,000(26) 2,000-4,700(34) 5,400-7,100(41) 6,000-7,700(45) 3,700-6,000(61)	27,700(14) 23,000(23,26) 9,600-27,700(34) 12,000(41) 12,200-18,600(45) 23,600-31,200(61) 26,000-27,000(62)	1.4(14) 1.6(24) 1.2-1.7(34) 0.7-2.6(61)	26:35-45°C(14) 24:30-40°C(23) 22:30-40°C(26) 18,19,26:28-46°C(34) 19-39: 0-60°C(41) 30:24-58°C(61) 31.5-35.7:25-49°C(62)	55(26) 58-96(34) 50-70(61) 60-64(62)	77(26) 56-72(34) 69-74(61) 67-70(62)
Commercial composites‡	2,000-5,900(52) 1,800-8,500(57) 2,000-5,900(62)	17,400-29,000(52) 20,200-33,200(53) 15,900-35,000(57) 18,000-28,000(58) 26,800-33,700(62)	0.78-1.62(52) 0.75-1.25(53) 1.3-2.2(62)	27-41:24-88°C(52) 22-44:21-49°C(53) 27-35:25-45°C (56) 20-50: 0-60°C (57) 30-45:20-50°C (59) 31-41:30-55°C(62)	65-97(52) 50-90(62)	62-70(52) 48-72(62)
Silicate Cements	440-1,010(24) 930(34)	24,300-30,000(14) 24,600-31,000(34) 23,000(65) 25,600-32,100(66)	3.1(24) 2.4(65) 3.2-3.6(66)	7.6:20-50°C(67)	40(26)	83(26)
Unreinforced Resin	3,800-5,100(24) 3,300(52) 3,100(34)	12,100(14) 10,700(26) 11,000(65)	0.3(14) 0.26(24) 0.34(52) 0.27(65) 0.27(68)	100:35-35°C(14,34) 92:24-88°C(52)	125(34) 113(52) 95-115(68)	73(34) 74(52) 60-80(68)
Dentin	7,500(24)	43,100(63) 50,400(64) 31,500-44,200(65)	2.8(24) 2.8(26) 2.4-2.7(63) 2.2(64) 1.1-2.0(65)	8:20-50°C(67) 7:25-55°C(62)	46(26)	85(26)

TABLE 2 (continued)

	Tensile Strength	Compressive Strength	Modulus of Elasticity	Coefficient of Linear Thermal Expansion	Indentation Resistance and Recovery	
					Indentation	Recovery
	psi*	psi	psi x 10^6	ppm/°C	µm†	%
Enamel	1,500(24)	19,400-40,200(64) 13,700-41,800(65) 53,900-55,700(66)	1.8-8.2(64) 1.4-9.1(65) 11-12(66)	12:25-55°C(62)	33(26)	86(26)

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* To convert psi (pounds per square inch) to MN/m^2 (meganewtons per square meter) multiply by 6,895 x 10^{-6}

† Micrometers (microns)

‡ Not all products are represented in each range of values shown

V References

1. Luskin, L. S.: Milestones in the History of Acrylic Products, Or-Chem Topics, No. 23 Summer 1967, Philadelphia, Rohm & Haas Co.

2. Schnebel, Dentistische Reforme, 4 and 5/1942; Blumenthal, L.: Recent German Developments in the Field of Dental Resins, Fiat Final Report No. 1185, Field Information Agency, Technical, Office of Military Government for Germany (US), 27 May 1947.

3. Paffenbarger, G. C.: Dental Cements, Direct Filling Resins, Composite and Adhesive Restorative Materials: A Resume, (to be published by) Interscience Publishers in the Proceedings of the Engineering Foundation Research Conference on "Engineering in Medicine-Bioceramics," New England College, Henniker, New Hampshire, Aug 3-7, 1970.

4. Caul, H. J., and Schoonover, I. C.: Color Stability of Direct Filling Resins, JADA 47:448-452 Oct 1953.

5. Smith, D. L., and Schoonover, I. C.: Direct Filling Resins: Dimensional Changes Resulting from Polymerization Shrinkage and Water Sorption, *JADA* **46**: 540-544 May 1953.

6. Nelsen, R. J.; Wolcott, R. B., and Paffenbarger, G.C.: Fluid Exchange at the Margins of Dental Restorations, *JADA* **44**:288-295 March 1952.

7. Kramer, I.R.H., and McLean, J. W.: The Response of the Human Pulp to Self-Polymerizing Acrylic Restorations, *Brit Dent J* **92**:255-261, 281-287, 311-315 May-June 1952.

8. Grossman, L. I.: Pulp Reaction to the Insertion of Self-Curing Acrylic Resin Filling Materials, *JADA* **46**:265-269 March 1953.

9. Kramer, I.R.H.: The Relationship between Pain and Changes in the Dental Pulp Following the Insertion of Fillings, *Brit Dent J* **96**:9-13 Jan 1954.

10. Hedegard, B.: Cold-Polymerizing Resins as Restorative Materials, *Odontologisk Tidskrift* **65**:169-212 June 1957.

11. Hede̊gard, B.: Co-Report: Synthetic Plastics, *Internat Dent J* **8**:249-250 June 1958.

12. Fletcher, T.: British Patent No. 3028, 1878; Fletcher, T. Silicate of Lime and Alumina, *Brit D J Science* **22**:74, 1879.

13. Henschel, C. J.: Observations Concerning In Vivo Disintegration of Silicate Cement Restorations, *J Dent Res* **28**:528-529 Oct 1949.

14. Bowen, R. L.; Paffenbarger, G. C., and Mullineaux, A. L.: A Laboratory and Clinical Comparison of Silicate Cements and a Direct Filling Resin: A Progress Report, *J Pros Dent* **20**:426-437 Nov 1968.

15. Norman, R. D.; Swartz, M. L.; Phillips, R. W., and Virmani, R.: A Comparison of the Intraoral Disintegration of Three Dental Cements, *JADA* **78**:777-782 April 1969.

16, Knock, F. E., and Glenn, J. F.: Dental Material and Method, U. S. Patent No. 2,558,139 June 26, 1951.

17. Paffenbarger, G. C.; Nelsen, R. J., and Sweeney, W. T.: Direct and Indirect Filling Resins: A Review of Some Physical and Chemical Properties, JADA 47:516-524 Nov 1953.

18. Rose, E. E.; Lal, J.; Green, R., and Cornell, J.: Direct Resin Filling Materials: Coefficient of Thermal Expansion and Water Sorption of Polymethyl Methacrylate, J Dent Res 34:589-596 Aug 1955.

19. Rose, E. E.; Lal, J.; Williams, N. B., and Falcetti, J.P.: The Screening of Materials for Adhesion to Human Tooth Structure, J Dent Res 34:577-588 Aug 1955.

20. Lee, H., and Neville, K.: Handbood of Epoxy Resins New York, McGraw-Hill Book Co., 1967.

21. Bowen, R. L.: Use of Epoxy Resins in Restorative Materials, J Dent Res 35:360-369 June 1956.

22. Bowen, R. L., and Mullineaux, A. L.: Adhesive Restorative Materials, D Abstracts 14:80-82 Feb 1969.

23. Bowen, R. L.: Dental Filling Material Comprising Vinyl Silane Treated Fused Silica and a Binder Consisting of the Reaction Product of Bisphenol and Glycidyl Acrylate, U. S. Patent No. 3,066,112 Nov 1962.

24. Bowen, R. L., and Rodriguez, M. S.: Tensile Strength and Modulus of Elasticity of Tooth Structure and Several Restorative Materials, *JADA* **64**:378-387 March 1962.

25. Bowen, R. L.: A Method of Preparing a Monomer having Phenoxy and Methacrylate Groups Linked by Hydroxy Glyceryl Groups, U. S. Patent No. 3,179,623 April 1965.

26. Bowen, R. L.: Properties of a Silica-Reinforced Polymer for Dental Restorations, *JADA* **66**:57-64 Jan 1963.

27. Bowen, R. L.: Crystalline Dimethacrylate Monomers, *J Dent Res* **49**:810-815 July-Aug 1970.

28. Bjorksten, J.; Tovey, H.; Harker, B., and Henning, J.: *Polyesters and Their Applications*, New York, Reinhold Publishing Corp., 1956 p. 11.

29. *Guide to Dental Materials and Devices* (5th ed), American Dental Association, Chicago, 1970-71, pp 51, 98.

30. Vanderbilt, B. M., and Simko, J. P., Jr.: Silane Coupling Agents in Glass-Reinforced Plastics, *Modern Plastics* **38**:135-217 Dec 1960.

31. Vanderbilt, B. M., and Jaruzelski, J. J.: The Bonding of Fillers to Thermosetting Resins, *Ind and Eng Chem, Prod Res and Dev* **1**:188-194 Sept 1962.

32. Sterman, S., and Marsden, J. G.: Filler-Silane Interactions, *Modern Plastics* **41**:254-266, Oct 1963.

33. Sterman, S., and Marsden, J. G.: Silane Coupling Agents as Integral Blends in Resin-Filler Systems, *Modern Plastics* **40**:125-177 July 1963.

34. Bowen, R. L.: Effect of Particle Shape and Size Distribution in a Reinforced Polymer, *JADA* **69**:481-495 Oct 1964.

35. Bowen, R. L.: Development of an Adhesive Restorative Material, Adhesive Restorative Dental Materials - II, Public Health Service Publication No. 1494, Washington, D. C. 1966 p 225.

36. Bowen, R. L.: Unpublished data.

37. Holliday, L (ed): Composite Materials, New York, Elsevier Publishing Co., 1966 p 153.

38. Johannson, O. K.; Stark, F. O.; Vogel, G. E., and Fleischmann, R. M.: Evidence for Chemical Bonding Formation at Silane Coupling Agent Interfaces, J Composite Materials **1**:278-292 Jan 1967.

39. Broutman, L. J., and Krock, R. H. (eds.): Modern Composite Materials, Reading, Massachusetts, Addison-Wesley Publishing Co., 1967 pp 501, 7.

40. Hatch, R. A.: Phase Equilibrium in the System: $Li_2O \cdot Al_2O_3-SiO_2$, The American Minerologist **28**:471-496 Sept-Oct 1943.

41. Boyd, R. N., Colin, L., and Kaufman, E. G.: Dental Filling Composition of a Coefficient of Thermal Expansion Approximating that of Natural Tooth Enamel, U. S. Patent 3,503,128 March 31, 1970.

42. Smoke, E. J.: Ceramic Compositions Having Negative Linear Thermal Expansion, J Amer Ceramic Soc **34**:87-90 March 1951.

43. Bowen, R. L., and Argentar, H.: Diminishing Discoloration in Methacrylate Accelerator Systems, *JADA* **75**:918-923 Oct 1967.

44. McLean, J. W., and Short, I. G.: Composite Anterior Filling Materials, *Brit Dent J* **127**:9-18 July 1969.

45. Hirasawa, T.: Self-Curing Resins Containing Inorganic Fillers for Dental Restorations. II. Effect of Surface Treatment of Glass Fillers on Mechanical Properties, *Shika Zairyo Kenkyusho Hokoku* **2**:629-643, 644-655 March 1965.

46. Going, R. E., and Sawinski, V. J.: Microleakage of a New Restorative Material, *JADA* **73**:107-115 July 1966.

47. Buonocore, M. G.; Matsui, A., and Yamaki, M.: Abrasion of Restorative Materials, *N Y State Dent J* 32:395-400 Nov 1966.

48. Peterson, E. A.; Phillips, R. W., and Swartz, M. L.: A Comparison of the Physical Properties of Four Restorative Resins, *JADA* **73**:1324-1336 Dec 1966.

49. Bowen, R. L.: Adhesive Bonding of Various Materials to Hard Tooth Tissues VI. Forces Developing in Direct-Filling Materials During Hardening, JADA **74**:439-445 Feb 1967.

50. Matsui, A.; Buonocore, M., and Yamaki, M.: Heat of Polymerization of Certain New and Conventional Restorative Materials, J Dent Res 46:1106 Sept-Oct 1967.

51. Gotfredsen, C.: Addent® Investigations of a Plastic Filling Material, Tandlaegebladet **72**:407-429 May 1968.

52. Macchi, R. L., and Craig, R. G.: Physical and Mechanical Properties of Composite Restorative Materials, JADA **78**:328-334 Feb 1969.

53. Freeman, F. H.: Composite Restorative Materials, Presented before the Dental Materials Group, N Amer Div, IADR Mar 21, 1969, Houston, Texas.

54. Tani, Y., and Buonocore, M.: Marginal Leakage and Penetration of Basic Fuchsin Dye in Anterior Restorative Materials, JADA **78**:542-548 March 1969.

55. Lee, H. L.; Swartz, M. L., and Smith, F. F.: Epoxy Resins in Dentistry, presented at the ACS National Meeting, April 1969, Minneapolis, Minnesota (in press).

56. Gotfredsen, C.: Physical Properties of a Plastic Filling Material (Addent®), Acta Odontoligica Scandinavica 27:595-615 No 6, 1969

57. Lee, H. L.; Swartz, M. L., and Smith, F. F.: Physical Properties of Four Thermosetting Dental Restorative Resins, J Dent Res 48:526-535 July-Aug 1969.

58. Phillips, R. W.; Swartz, M. L., and Norman, R. D.: Materials for the Practicing Dentist, Saint Louis, C. V. Mosby Co, 1969 pp 182-191, 59.

59. Docking, A. R.: Modern Materials in Dental Practice, Australian Dent J 15:303-309 Aug 1970.

60. Schouboe, P. J.; Paffenbarger, G. C., and Sweeney, W. T.: Resin Cements and Posterior-Type Direct Filling Resins JADA 52:584-600 May 1956.

61. Barton, J. A., Jr.; Burns, C. L.; Chandler, H. H., and Bowen, R. L.: An Experimental, Intermediate-Restorative Composite Material (manuscript in preparation).

62. Barton, J. A., Jr., et al: Unpublished data.

63. Craig, R. G., and Peyton, F. A.: Elastic and Mechanical Properties of Human Dentin, J Dent Res **37**:710-718 Aug 1958.

64. Stanford, J. W.; Paffenbarger, G. C.; Kumpula, J. W., and Sweeney, W. T.: Determination of Some Compressive Properties of Human Enamel and Dentin, JADA **57**:487-495 Oct 1958.

65. Stanford, J. W.; Weigel, K. V.; Paffenbarger, G. C., and Sweeney, W. T.: Compressive Properties of Hard Tooth Tissues and Some Restorative Materials, JADA **60**:746-756 June 1960.

66. Craig, R. G.; Peyton, F. A., and Johnson, D. W.: Compressive Properties of Enamel, Dental Cements, and Gold, J Dent Res **40**:936-945 Oct 1961.

67. Souder, W., and Paffenbarger, G. C.: Physical Properties of Dental Materials, Washington, D. C. Government Printing Office, 1942 p 13.

68. Sweeney, W. T.; Sheehan, W. D., and Yost, E. L.: Mechanical Properties of Direct Filling Resins, JADA 49:513-521 Nov 1954.

69. Stanley, H. R.; Swerdlow, H., and Buonocore, M. G.: Pulp Reactions to Anterior Restorative Materials, JADA 75:132-141 July 1967.

70. Langeland, L. K.; Guttuso, J.; Jerome, D. R., and Langeland, K.: Histologic and Clinical Comparison of Addent with Silicate Cements and Cold-Curing Materials, JADA 72:373-385 Feb 1966.

71. French Patent No. 2,008,541 Jan 23, 1970.

72. Mihailov, M., and Boudevska H.: Synthesis and Polymerization of Polyestermethacrylates and Terephthallic and Furane-2,5-Dicarboxylic Acid, Compt Rend Acad Bulgare Sci 18:31-34 1965.

73. French Patent No. 2,010,896.

74. French Patent No. 2,010,905

75. Atsuta, M.: Hard Methacrylic Polymers, II. Copolymers of Methyl Methacrylate and 2,2-Di(4-Methacryloxyphenyl)Propane, J Biomed Mat Res (in press).

76. Bowen, R. L., and Argentar, H.: Amine Accelerators for Methacrylate Resin Systems, (accepted for publication in J Dent Res).

77. Bowen, R. L., and Argentar, H.: Tertiary Aromatic Amine Accelerators with Molecular Weights Above 400, (submitted to J Dent Res).

78. Chandler, H. H.; Bowen, R. L., and Paffenbarger, G. C.: A Method for Finishing Composite Restorative Materials, (approved for publication in JADA).

79. Chandler, H. H.; Bowen, R. L.; Paffenbarger, G. C., and Mullineaux, A. L.: Clinical Investigation of a Radiopaque Composite Material, JADA 81:935-940 Oct 1970.

80. Bowen, R. L., and Cleek, G. W.: X-ray-Opaque Reinforcing Fillers for Composite Materials, J Dent Res 48:79-82 Jan-Feb 1969.

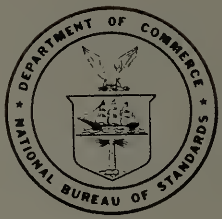
81. Bowen, R. L., and Cleek, G. W.: A New Series of X-ray-Opaque Reinforcing Fillers for Composite Materials, (submitted to J Dent Res).

82. Bowen, R. L.: Investigation of the Surfaces of Hard Tooth Tissues by a Surface Activity Test. Proceedings of the Workshop on Adhesive Restorative Dental Materials at Indiana University, Owen Litho Service, Spencer, Indiana-Publishers Sept 1961; Clearinghouse, U. S. Dept. Commerce, Springfield, Va. 22151, PB 173009, Phillips and Ryge, (ed.).

83. Bowen, R. L.: Surface-Active Comonomer and Method of Preparation, U. S. Patent No. 3,200,142 Aug 10, 1965.

84. Bowen, R. L.: Adhesive Bonding of Various Materials to Hard Tooth Tissues (Parts I-V), J Dent Res 44:690-695, 895-902, 903-905, 906-911, 1369-1373 July-Dec 1965.

85. Craig, G. G.: The Placement of Composite Resin Restorations, Australian Dent J 15:277-280 Aug 1970.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