NBSIR 85-3119

Properties and Interactions of Oral Structures and Restorative Materials

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
Center for Materials Science
Polymers Division
Dental and Medical Materials
Gaithersburg, MD 20899

Annual Report for Period
October 1, 1983 thru September 30, 1984

Issued March 1985

Interagency Agreement
Y01-DE-30001 (formerly Y01-DE-40015)

Prepared for
nal Institute of Dental Research
sda, MD 20205

NBSIR 85-3119

PROPERTIES AND INTERACTIONS OF ORAL STRUCTURES AND RESTORATIVE MATERIALS

J.A. Tesk, J.M. Antonucci, G.M. Brauer, J.E. McKinney
R.W. Penn, J.W. Stansbury, and W. Wu

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
Center for Materials Science
Polymers Division
Dental and Medical Materials
Gaithersburg, MD 20899

Annual Report for Period
October 1, 1983 thru September 30, 1984

Issued March 1985

Interagency Agreement
Y01-DE-30001 (formerly Y01-DE-40015)

Prepared for
National Institute of Dental Research
Bethesda, MD 20205

U.S. DEPARTMENT OF COMMERCE, Malcolm Baldrige, *Secretary*
NATIONAL BUREAU OF STANDARDS, Ernest Ambler, *Director*

TABLE OF CONTENTS

II. Wear Resistance and Related Physical Properties of Dental Composite Restorative Materials

ABSTRACT

Significant accomplishments during the FY84 are itemized as follows: (1) Synthesis of syringate esters and of polymerizable vanillates was achieved. Properties of cement composites were determined and found to hold potential as intermediate restorative materials. Formulations which adhered well to porcelains, composites, and metals were developed. (2) Preclinical evaluations of syringate and vanillate cements showed mild pulp reactions, negative Ames tests, high LD_{50} (oral values and only slight hemolysis). In general, biocompatibility was good. (3) Fluoride containing cements were found to be adequately strong. (4) New, polymerization expanding monomers were formulated in high yields. (5) High strength, low water absorption, fluorinated resin composites were achieved with reduced polymerization shrinkage. (6) Dimer and trimer acid cement formulations were discovered that expand on polymerization. (7) PETMP, a chain transfer agent was found effective in increasing the degree of cure of dual cured (light and chemical) composite resins. (8) Wear studies showed glass ionomer cements prone to catastrophic failure in the presence of lactic acid. (9) Preconditioning of dental composites in acids showed quartz and pure silica glass filled versions only slightly affected regarding wear. Radiopaque filled composites were more strongly attacked. (10) Experimenbts confirmed that composites swell in an inverse relationship relative to the filler content. (11) A sensitive, stable dialometer was constructed for measuring polymerization shrinkage. (12) More highly cured dental composites resisted clinical wear of a greater degree, except in one instance which revealed the importance of considering polymerization shrinkage and filler content. (13) Temperature dependent elastic properties of dental porcelains and nickel based alloys were determined. (14) The effectiveness of Weibul statistics in distinguishing between failure stresses of porcelain fused to metal systems was demonstrated. (15) The first mathematical descriptiuon of the effects of elemental composition on a castability value, C_v, as functions of alloy mold and casting tmeperatures was developed. (16) Preliminary studies of casting investment setting expansion using strain gauges showed internal expansion apparently much less than externally measured expansion.

PROPERTIES AND INTERACTIONS OF ORAL STRUCTURES AND RESTORATIVE MATERIALS

INTRODUCTION

The following pages contain reports on work involved with the development of basic generic science and engineering which is expected to be useful in the development or control of dental materials used for restorative or treatment purposes. Some of the developments involve investigations into new dental resin formulations (Part I) which might improve the performance of dental composites. Cements and adhesion to filler particles or tooth structure are also addressed in this part.

Part II deals with examination of the basic parameters affecting the wear and durability of materials with particular emphasis on dental composites. The resultant information is used to help guide developments in Part I.

Part III is concerned with dental casting alloys, and the strength of veneered dental systems, in particular, porcelain fused-to-metal. Factors affecting the castability of alloys and how to measure and define aspects of castability are addressed. Mathematical methods are employed to reveal effects of individual elements as well as other parameters. The strength of veneered systems is the characteristic receiving the most attention of porcelain-fused-to-metal. Special emphasis is being placed on measurement techniques and flaw analysis.

I. Synthesis and Evaluation of Dental Composites, Resins, Cements and Adhesion

A. High-Strength, Eugenol-Free Adhesive Cements and Restoratives.

Background

Non-eugenol containing cements based on vanillate esters, *o*-ethoxybenzoic acid (EBA) and zinc oxide, have been developed in this Laboratory [1,2]. These cements have the following advantages compared to the presently used Zinc Oxide-Eugenol (ZOE) or EBA cements: (1) they have excellent strength, (2) have much lower solubility than zinc oxide-eugenol cements, (3) do not inhibit free radical polymerization and can be used in conjunction with composite filling materials to which they adhere, (4) are compatible with acrylic monomers and can be formulated in conjunction with them, and (5) adhere strongly, even on prolonged water exposure, to nonprecious metals and composites. The cements exceed considerably the requirements of ANSI/ADA Specification No. 30 for Type II, III, and IV type restoratives.

Objective

The objective of this study is to continue to evaluate these cements for various dental applications and to further improve desirable properties. To achieve this objective the following tasks were planned for the period of this project: (1) synthesis and evaluation of divanillates and polymerizable vanillates such as methacryloylethyl vanillate and addition of these compounds to hexyl vanillate-ethoxybenzoic acid (HV-EBA) cements to improve mechanical properties; (2) quantitative measurements of the adhesive properties of HV-EBA cements; (3) development of intermediate restorative formulations (IRF) incorporating monomers and reinforcing fillers with cement ingredients and determination of their mechanical properties; (4) synthesis of cements using structurally related syringate esters and evaluation of their physical properties and (5) guidance and assistance for studies of (a) the biocompatibility, (b) pulp irritation and tissue response as well as for clinical studies using these cements to be conducted at such institutions as Indiana University, Baylor, Northwestern University, University of Tennessee and the University of South Carolina.

Progress Report

Phase I

(1a) Synthesis of vanillate monomers.

A series of divanillates and polymerizable vanillates such as methacryloylethyl vanillate and vanillyl methacrylates were synthesized. These compounds were incorporated successfully into dental cements and resulted in improved properties. A manuscript describing this investigation has been submitted to the Journal of Biomedical Materials Research.

(1b) Synthesis of Syringate esters.

These syntheses were essentially completed during the last reporting period. A paper describing this research was published in the February 1984 issue of the Journal of Dental Research (pp 137-140). A patent using cements containing syringate esters has been applied for by NBS.

(2) Formulations of new cements and intermediate restoratives.

This work is in progress and will be presented in FY85 report.

Phase II

(1) Evaluation of mechanical properties and bonding to metals, porcelains and composites.

(a) The evaluation of cements containing vanillate compounds with multifunctional groups or cements with syringate esters ingredients was completed.

(b) Additional properties of cement composites incorporating monomers and suitable polymerization accelerators in the liquid, and silanized glass and peroxide initiator in the powder were determined. These cement composite formulations, because of their high strength, low solubility and strong adhesion to various substrates, appear to be most useful as intermediate restoratives. A manuscript describing properties of the compositions investigated has been accepted for publication in the Journal of Dental Research.

(c) Incorporation of acids into vanillate or syringate cements.

Further improvement of these cements was obtained by kncorporating small concentrations of acid such as propionic acid into these formulations. Cements with better properties were obtained by coating 2% propionic acid on some of the zinc oxide powder rather than by adding acid to the liquid portion. Addition of the propionic acid coated powder improved working properties of the mixtures, decreased setting times to any desired time (thus permitting control of the cement cure) and allowed incorporation of higher concentrations of HV into chemically useful formulations. It also reduced brittleness of HV-EBA and ethylhexyl syringate (EHS-EBA) cements. Selected properties of these cements are given in Table 1. Dental luting agents of standard consistency with film thickness as low as 5 μm have been obtained. Maximum film thickness for ZOE cements is 25 μm in the ADA Specification. Adhesion of these cements to stainless steel and porcelain is excellent. Mean values for five measurements were as high as 19.2 MPa (2780 psi) for the stainless steel-cement and 14.6 MPa (2120 psi) for the porcelain-cement bond. On addition of plasticizing agents, e.g. zinc undecylate, flexible materials with potential usefulness as tissue packs were obtained. A talk describing these studies was presented before the International Association for Dental Research in March 1984.

(d) Improvement of cements by adding metal powders.

Metal powders such as stainless steel or titanium have been incorporated into typical HV-EBA-ZnO formulations. The results obtained so far do not indicate that addition of such metals will improve appreciably the mechanical properties of the cements.

(e) Measurement of the bond strength of the cements to various substrates.

ZOE cements and other temporary restoratives do not bond to composites or metals in an aqueous environment. The HV-EBA or HV-EHS-EBA cements as well as the "cement composites" adhered strongly to non-precious metals, composite resins and porcelain. They formed stronger bonds to these substrates than do ionomer cements. The joined specimens broke cohesively, often considerably above the tensile strength of the cement (Table 1). This high bond strength especially to stainless steel, may result from the extremely low film thickness of most formulations. Porcelain-to-porcelain or porcelain-to-composite specimens joined together with HV-EBA-ZnO cements had higher bond strength than joints prepared with commercial bonding agents. Pretreatment of the porcelain with a commercial porcelain-acrylic resin bonding agent or roughening the porcelain surface further increased bond strength. With proper pretreatment of enamel surfaces the adhesion of HV-EBA cements is similar to ionomer cements. The latter materials however, have a somewhat greater bond strength to dentin.

Table 1

Properties of Cements Containing ZnO Treated with Propionic Acid (PA)

Powder: 64% ZnO (untreated and treated) - 30% Al_2O_3 - 6% hydrogenated rosin. Liquid: 12.5% n-Hexyl Vanillate - 87.5% EBA

Untreated	Coated	P/L	Setting	Film	Strength		Solubility		Strength of Bond (MPa) to:		
%	w/2% PA	Ratio	Time	Thickness	Compressive	Tensile	Day	Week	Composite	Porcelain	St. Steel
		g/0.2 ml	min	µm	MPa	MPa	%	%	MPa	MPa	MPa
64.0	-	1.8	6.5	8	62.7±4.6	6.20±0.8	-.21	+.43	4.07±.29	14.66±2.5	16.4±3/6
58.7	5.3	1.8	5.5	10	-	-	-	-	-	-	-
56.0	8.0	1.3	5.5	8	41.9±3.2	5.95±.66	-0.27	+0.67	3.59±0.65	10.4±4.2	13.2±2.7
56.0	8.0	1.8	5.0	9	69.2±3.4	5.66±.45	-0.01	+0.65	2.85±0.70	8.77±1.7	19.2±5.2
56.0	8.0	2.0	4.5	-	-	-	-	-	-	-	-
48.0	16.0	1.8	3.5	-	-	-	-	-	-	-	-
42.7	21.3	1.3	4.5	-	-	-	-	-	-	-	-
42.7	21.3	1.8	3.0	-	-	-	-	-	-	-	-
32.0	32.0	1.8	2.5	-	-	-	-	-	-	-	-
-	64.0	1.8	2.25	-	-	-	-	-	-	-	-
56.0[1]	8.0[1]	1.3	7.0	6	49.3±4.1	4.6±1.6	-.32	-	3.55±.57	-	8.24±.73
56.0[2]	8.0[2]	1.5	8.0	5	56.8±8.4	5.2±1.5	-.06	-	3.25±.55	-	13.1±5.8
56.0[3]	8.0[3]	1.5	8.0	8	55.5±3.2	4.5±9.7	+2.6	-	4.10±.11	-	11.0±1.6
	Coated w/1% PA										
56.0	8.0	1.7	6.0	8	-	-	-	-	-	-	-
51.2	12.8	1.7	5.0	8	61.8±3.1	6.74±0.67	-.23	+.48	3.46±.66	8.65±3.8	10.1±3.4
42.7	21.3	1.8	3.5	-	-	-	-	-	-	-	-
-	64.0	1.8	2.5	-	-	-	-	-	-	-	-

---

[1] with 0.1% NaF
[2] with 0.2% ZrF_4
[3] with 5% stainless steel

Phase III

(1) Synthesis of materials for pre-clinical and clinical studies.

Vanillate and syringate esters synthesized in this laboratory have been made available to many researchers on request. Hexyl vanillate is now commerically available from two manufacturers of specialty chemicals.

(2) Pre-clinical studies of cements and IRM[1].

A number of studies on various aspects of the biocompatibility of these cements and their individual ingredients are being conducted at other institutions. These investigations are in various stages of completion.

(a) Pulp reactions to HV-EBA cements.

This investigation by Drs. Kafrawy and Phillips at Indiana University was reported at the 1984 IADR meeting (Abst. No. 2). It was concluded that the mild pulp reactions in monkeys were similar to those illicited by IRM.

(b) Mutagenicity.

Hexyl vanillate prepared in this laboratory gave a negative spot test by the procedure of Dr. Bruce Ames with Salmonella Strains TA97, TA98 and TA100. These tests were conducted by Drs. Miller, Washington, Zimmerman and Bowles of Baylor University. Results were reported at the 1984 IADR meeting (Abst. No. 1278).

A mutagenicity assay was conducted for o-ethoxybenzoic acid and also with 64% ZnO-30% Al_2O_3-6% hydrogenated rosin powder and compared with negative and positive blanks. Using Salmonella strains TA98 and TA-100 these compounds gave negative tests. The mutagenicity of HV by this

---

[1] A commercially available Intermediate Restorative Material.

more time-consuming procedure is nearing completion under the direction of Dr. C. Siew, Director of Toxicology, American Dental Association Health Foundation.

(c) Acute Oral LD_{50} for ZnO-Al_2O_3-hydrogenated rosin is >1.0 g/kg. These studies were conducted at the American Dental Association Laboratories.

(d) Hemolysis.

Both o-ethoxybenzoic acid and ZnO-Al_2O_3-hydrogenated rosin are slightly hemolytic (18.5 ± 2.5% and 19.9 ± 2.0 respectively, ADA Laboratories).

(e) Activation of complement by HV-EBA-ZnO cements.

Many foreign substances interact with the serum complement system and complement activation is important to immunopathological response to antigenic materials. With these thoughts in mind, work was undertaken by Drs. Keller, Hoyt and Boackle of the University of South Carolina to study the activation complement by HV-EBA-ZnO and other selected cements. These might interact with complement in the gingival sulcus and pulpal tissues of unlined cavity preparations. (1984 IADR, Abst. No. 428).

(3) As soon as results of the detailed Ames tests for hexyl vanillate become available, permission will be requested from the Human Research Ethics Committee of the National Bureau of Standards to place a limited number of HV-EBA-ZnO restorations in human patients.

Phase IV

(1) Continued bonding studies of cements to tooth structure.

Pretreatment of enamel with various acids increases the adhesion of this substrate to HV-EBA-ZnO cement. Some typical values of the bond strength are given in Table 2. Use of 37% phosphoric acid is quite effective. Such treatment is not biocompatible for dentin, but some adhesion of the cement is obtained by pretreatment of this substrate with either 1% sodium citrate or aq. polyacrylic acid (see also Phase II, 2e.)

New formulations to improve the materials compositions incorporating plasticizers, metal powders, or fluorides have been prepared and evaluated. See Phase II (2c, 2d) and Phase IV (3). Materials useful as tissue packs containing the suggested ingredients and Crisco[2] have been prepared and evaluated at Northwestern University. These materials have a low dimensional change.

(2) Evaluation of sealing properties.

The properties of the cements as endodontic sealers have been measured by Dr. Glick and Dr. Greener at Northwestern University. Sealing characteristics of these materials are better than those of a commercial endodontic sealer. The hexyl vanillate has some irritating action similar to eugenol, but the cement does not show a bacteriostatic zone of inhibition.

(3) Examine incorporation of fluoride into compositions. Study mechanical properties and fluoride release.

Incorporation of a leachable fluoride without lowering the physical properties should yield useful caries-reducing cements. HV-EBA-ZnO and EHS-HV-EBA-ZnO materials containing sodium fluoride, zirconium fluo-

---

[2] A vegetable oil product manufactured by Proctor and Gamble.

Table 2

EFFECT OF PRETREATMENT OF SUBSTRATE ON ADHESION TO HV-EBA CEMENTS

Powder: 64% ZnO - 30% Al_2O_3 = 6% hyd. rosin

Liquid: 12.5% n-Hexyl Vanillate - 87.5% EBA

Cement stored in water for 24 hours

Pretreatment of Substrate	Adhesion in MPa to Enamel	 Dentin
None	1.2 ± 0.4	0.5 ± 0.2
37% H_3PO_4	1.8 ± 0.3	-
37% H_3PO_4[3]	3.5 ± 1.9	-
1% Na Citrate	-	1.0 ± 0
0.1% Ferulic Acid	2.7 ± 0.7[4]	-
1.25% Ferulic Acid	3.5 ± 0.7	0
1.25% Ferulic Acid	2.7 ± 0.7[4]	2.3 ± 0.7[4]
5.0% Ferulic acid	0.2 ± 0.3[4]	-
Aq. Polyacrylic Acid[3]	1.8 ± 0.3	1.0 ± 0.2

---

[3] A cement-composite of the following composition was used:
Powder: 1 pt 64% ZnO - 30% Al_2O_3 - 6% hydr. rosin, 1 pt sil. glass
+ 1% Bz_2O_2
Liquid: 1 pt 12.5% n-Hexyl Vanillate - 87.5% EBA, 1 pt monomer + 1% DHEPT
+ 0.02% BHT

[4] Stored at 100% relative humidity

ride or disodium monofluorophosphate were prepared and their properties determined. Cement with 0.1 to 2.0% NaF in the powder had adequate tensile and compressive strength and adhered well to stainless steel and composite (for properties of selected compositions see Table 1). On storage HV-EHS-EBA-ZnO cements with above 0.5% NaF increased excessively the fluoride concentration in water. No unusual leaching was found for cement with 0.1 NaF or 0.2% ZrF_4. The dissolution of fluoride over long periods will be studied by means of the fluoride electrode. Cements with disodium monofluorophosphate were brittle.

Phase V

(1) Pre-clinical studies on biocompatilibity, toxicity of newer vanillate and syringate cements and IRM as appropriate.

Samples of some of these compositions have been prepared and distributed to interested parties. No results are available at this time.

B. Monomers Which Expand on Polymerization.

Objective

The objective of this portion of the study is to synthesize new spiro ortho-carbonate compounds which can be polymerized by free radical initiators to give expansion upon polymerization. The physical properties of the various homopolymers and selected copolymers will be evaluated and correlated to the overall degree of expansion observed. Enhanced adhesion is anticipated as a result of a zero or a positive expansion upon curing of resin. To take advantage of this, the study is focusing on highly substituted monomers which will yield expanding polymers with high glass transition (T_g) temperatures. Monomers will be synthesized to investigate the effect of ring size on the mechanism of ring opening polymerization.

Progress Report

Phase I.

Synthesis of suitable monomers that expand on polymerization.

Synthesis of the monomer, 3,3-dimethyl-9-methylene-1,5,7,11-tetraoxaspiro [5.5] undecane (Fig. 1) has been successfully accomplished. This novel compound was selected as a model compound to work out the synthetic difficulties encountered in preparing substituted, unsymmetrical spiro ortho-carbonates capable of free radical ring opening. The key step in the process involved development of a method to obtain six membered ring thiocarbonates (Compound 1, Fig. 1) which are fairly unstable intermediates and require a very mild synthetic reaction procedure. With this technique available, the new monomer was prepared in approximately 50% overall yield. Polymerization studies involving various initiators and conditions will be conducted to verify the ring opening mechanism and evaluate the degree of expansion.

While this monomer may have interesting applications of its own, especially with its low melting point of 34°C, this study was devised to prepare and evaluate monomers which are precursors of high T_g expanding polymers. Therefore, the new thiocarbonate synthesis was applied to a series of anthracene-based diols. The five membered ring anthracene-thionocarbonate adduct (Fig. 2A) was synthesized in good overall yield and the corresponding monomer (Fig. 2B) is currently being prepared. The six membered thionocarbonate (Fig. 3A) which arises from a 1,3-diol has been obtained, but only in poor yield. This particular compound appears to be extremely moisture-sensitive and its synthesis must be modified accordingly. A very small quantity of the desired monomer (Fig. 2B) has been

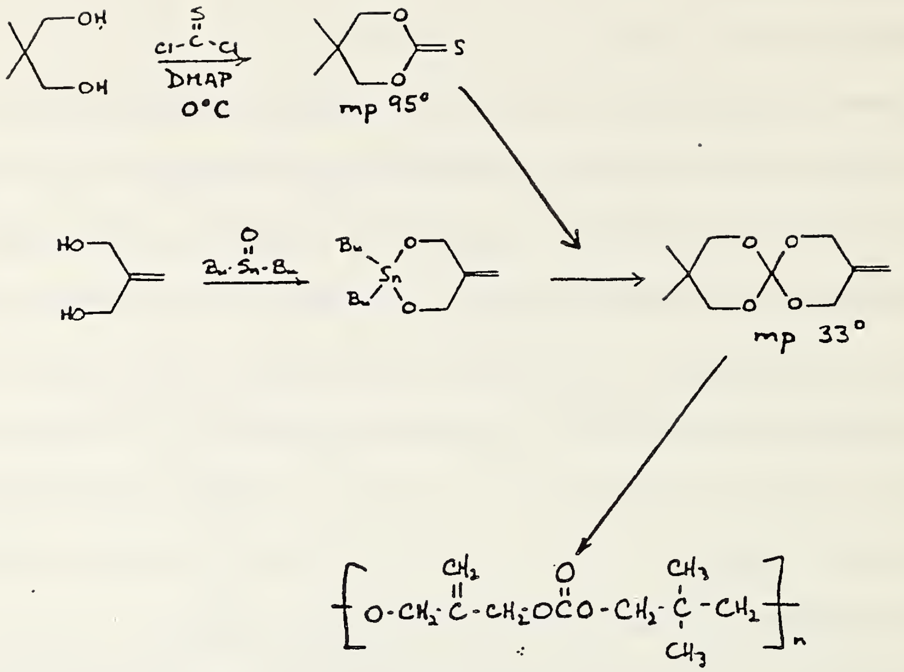
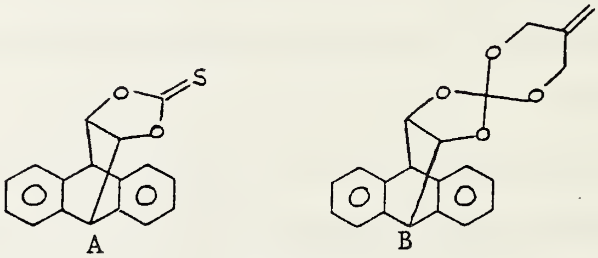


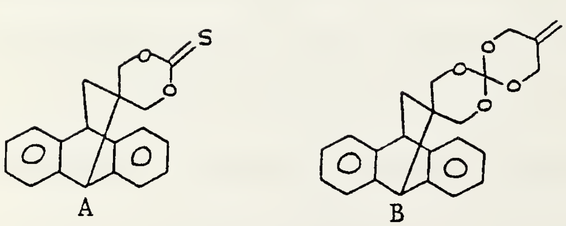
Fig. 1



A

B

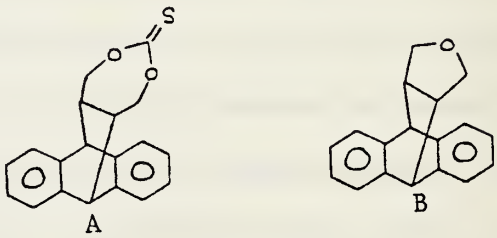
Fig. 2



A

B

Fig. 3



A

B

Fig. 4

prepared, but lack of the preceeding intermediate severely limited the scale of the reaction. From a single attempt at forming a seven membered thionocarbonate (Fig. 4A), the only isolated product was a cyclic ether (Fig. 4B) resulting from a ring contraction. The reaction will be rerun at a lower temperature in an attempt to stabilize the desired compound.

Phases II and III await completion of Phase I. These phases involve use of the monomers synthesized in Phase I to formulate composites and adhesives (Phase II) and evaluate properties (Phase III).

C. Changes in Esthetic Properties of Dental Resins on Aging.

Objective

The objective of this part of the study is to improve esthetic properties of dental resins and to establish causes and mechanisms of discoloration and aging.

Progress Report

Phase I

Determination of color changes in resin based dental materials.

Study the discoloration on aging in various environments due to exposure to different energy sources. Determine color changes of dental resins, plastic teeth and composites resulting from (1) irradiation of a 150K lux Xenon lamp under water or in air, (2) a standard RS light source used in the ADA specification tests, (3) exposure to elevated temperatures, in the dark in air and in water, and (4) exposure of specimens to the different environments for various periods of time.

Results during the previous period had shown that dental composites are more sensitive to color changes due to aging from exposure to radiation than denture base resins or plastic teeth. Thus, (1) conventional chemically cured, (2) chemical cured microfilled, (3) light cured, (4) light cured microfilled and (5) light cured and chemical cured composites were exposed to various conditions. The combined light cured and chemically cured material and some chemically cured brands showed perceptible color changes on 24 hr irradiation by the Xenon light source. Generally, longer irradiation did not increase the color changes. Masking of a portion of the specimen with foil improved the ability to differentiate color changes caused by exposure to the radiation. Light cured composites were more color stable than the chemically cured ones. Storage of the materials in the dark for a week at 60°C did not alter the color. The effect of shade (dark or light) of composite brands on color stability is being determined. An effort is being made to delineate the causes for the color changes on aging and to determine how to prevent them. For this reason analysis of the composition of the composites for the amine accelerator and any light stabilizer will be conducted.

D. Adhesion of Coatings and Restoratives to Dentin and Enamel.

Objective

The objective of this investigation is to synthesize compounds which will improve adhesion between dental tissues and restorative materials and to incorporate them into restorative compositions

Progress Report

Phase I.

Prepare and evaluate the adhesion of compositions based on allyl 2-cyanoacrylate containing cross-linking agents and hydrophobic components to improve hydrolytic stability.

The monomer was synthesized. On storage of extended time periods (several months) in a refrigerator, the monomer, even after addition of inhibitor, underwent polymerization. The depolymerization of this material to regenerate monomer of suitable purity is being pursued.

Phase II.

Synthesize and evaluate adhesive properties of oligomers of 2-isocyanatoethyl methacrylates to dental tissues.

This phase now appears to yield more important results. It is being initiated at this time, but will receive major attention during the following year.

Phase III.

If appropriate results are obtained, proceed to arrange pre-clinical and clinical studies as needed.

No studies have been conducted on this phase.

E. Improvement of Dental Composites, Sealant and Cement Materials

1. Dental Resins for Hydrophobic Composites

Objective

The goal of this research task is to enhance the durability of dental composite, sealant, cement and adhesive materials through the use of hydrophobic resins

Introduction

Previous research has indicated that the oral environmental resistance (OER) of resin-based dental restorative, sealant and adhesive materials is a significant factor in determining their performance and service life [3,4]. The sorption of relatively excessive amounts of water as well as other chemicals present in the oral cavity can promote plasticization of the organic matrix, and, ultimately, degradative attack not only of the polymeric binder but also of the interfacial bonding system and, in some cases, of the filler itself [5-8].

Two related approaches have been initiated in our laboratories as methods to enhance the OER of these materials. One involves the use of hydrophobic resin systems that have solubility parameters far removed from that prevalent in the oral environment. The other is aimed at increasing the degree of polymerization and the crosslink density of the resin systems by methods compatible with the clinical situation. The first approach involves the synthesis and formulation of resins that yield polymers containing significant amounts of fluorocarbon or siloxane segments to result in dental materials having the desired hydrophobicity and solubility parameters to resist the detrimental effects of the oral environment. The second approach, which also may encompass the first approach, involves the synthesis and formulation of multifunctional methacrylates, chain transfer agents and other types of network forming agents that can augment the degree of cure and crosslink density. Emphasis also is directed to monomers that should have minimal polymerization shrinkage. An ancillary part of this approach also involves the development of more efficient initiator systems for ambient polymerizations of dental resins.

Progress Report

Phase I

1. Synthesis of monomers, and
2. Formulation of resins, composites and cements.

a. Formulation and Evaluation of PFMA-Based Composites

We continued our study of resin-based composites formulated with the polyfluorinated prepolymer multifunctional methacrylate, PFMA.

The major achievement of this phase has been the successful development of a highly esthetic, mechanically strong, quartz filled fluorinated composite. Previous PFMA based composites formulated with a conventional barium oxide containing silanized glass were deficient in transluscency due to the mismatch of the refractive indices of the glass filler and fluorinated resin system. Fused quartz (refractive index = 1.4583) was optically compatible with the following fluoro-resin system: 68.84% PFMA, 29.50 DMDMA[5], 0.98 % PETMP[6], 0.40 DHPPT[7], and 0.28 DMAPE[8]. Using a powder/liquid formulation, P/L = 3, composites with excellent esthetics and having the following properties were obtained: setting time = 2.0 min., diametral tensile strength = 41 MPa, compressive strength = 232 MPa, water sorption = 0.17 mg/cm^2. The compressive strength value represents the highest achieved thus far with a PFMA formulation.

b. Synthesis of a Polyfluorinated Prepolymer Multifunctional Urethane Methacrylate (PFUMA)

The polyfluorinated oligomeric polyol, PFA, was converted to a multifunctional urethane type methacrylate using the difunctional monomer isocyanatoethyl methacrylate (IEM) as outlined below (Fig. 5):

---

[5] DMDMA - 1,10-decamethylene dimethacrylate
[6] PETMP - pentaerythritol tetra 3-mercaptopropionate)
[7] DHPPT - N,N-bis(2-hydroxypropyl)-p-toluidine
[8] DMAPE - p-N,N-dimethylaminophenethanol

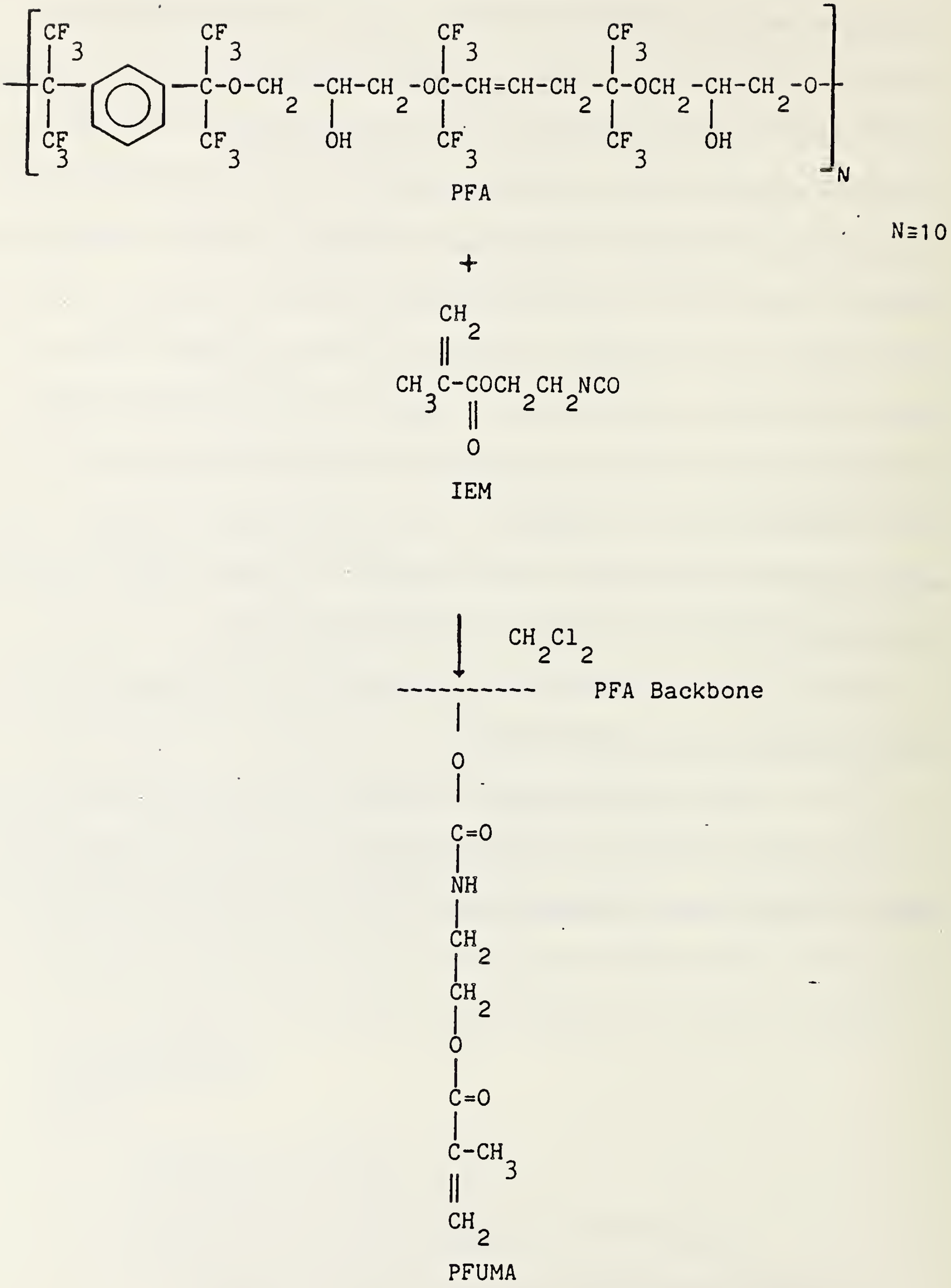


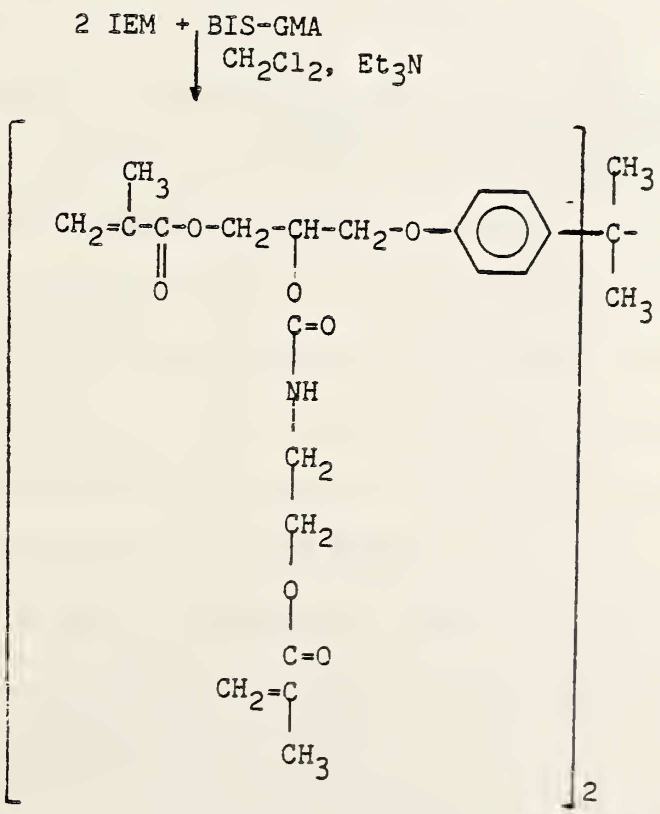
Figure 5

IEM via its -NCO group reacts with the -OH groups of PFA yielding a polyfluorinated prepolymer monomer, PFUMA, which contains pendant urethane and methacrylate groups. PFUMA is a pale yellow liquid of somewhat greater viscosity than PFMA. PFUMA also has a higher refractive index than PFMA (1.4347 vs 1.4197) which may make it more optically compatible with radiopaque glass fillers than PFMA. Structural confirmation by infrared and NMR analyses has been obtained. PFUMA is miscible with many conventional diluent monomers. Composites based on this unique fluorinated resin are currently being formulated for evaluation.

Dental Resins for Increased Degree of Polymerization and Crosslink Density.

c. Synthesis of a Diurethane tetramethacrylate (BIS-GMA/IEM).

The diadduct of BIS-GMA and IEM was prepared using in CH_2Cl_2 using triethyl amine (Et_3N) as a catalyst (Fig. 6):



BIS-GMA/IEM

Figure 6.

BIS-GMA/IEM is an almost colorless liquid somewhat less viscous than BIS-GMA despite its greater bulk (molecular weight = 822). Composites based on this tetrafunctional, bulky monomer are under study.

d. Synthesis of a Siloxane Tetramethacrylate

Again from BIS-GMA, a unique tetrafunctional vinyl monomer of great bulk was prepared using 3-methacryloxypropoxydimethylchlorosilane (MPDMCS) as shown in Fig. 7.

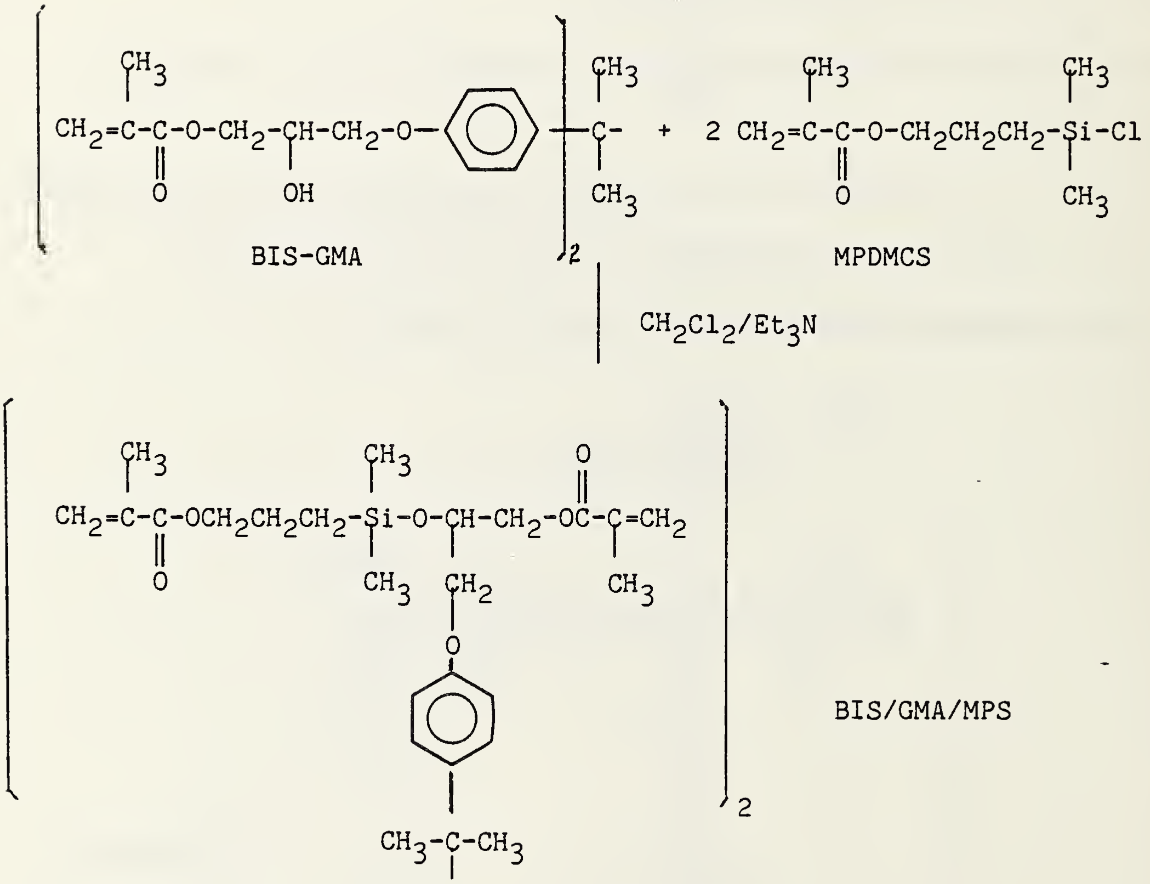


Figure 7.

BIS-GMA/MPS was isolated in excellent yield as a pale yellow liquid with a viscosity significantly less than that of BIS-GMA despite its much greater bulk (molecular weight = 880). Infrared analysis indicated that virtually all the OH absorption of BIS-GMA had disappeared. The resin polymerizes by the usual free radical methods. A preliminary investigation of composites prepared with this unique monomer alone revealed that an extremely high powder/liquid ratio of 6 was achievable using a conventional silanized barium oxide glass. That is, the filler content of these composites was 86% by weight; diametral tensile strength of visible light cured composites was 42 MPa. Other properties of this unique type of composite are under investigation.

e. Formulation and Evaluation of Composites Utilizing a Disiloxane Diluent Monomer (BIS-MPTMS).

This task is directed at assessing the effect of the disiloxane diluent monomer Bis-(methacryloxypropyl)tetramethyldisiloxane (BIS-MPTMS) on the properties of dental composites based on BIS-GMA and BIS-IPMA, 2,2-[p-(methacryloxyisopropoxy)phenyl] propane. Table 3 summarizes our results to date on the mechanical properites of such composites compared to typical BIS-GMA and BIS-IPMA composites (Formulations A-C). The salient point of these results is the maintenance of the good mechanical properites of the base resin even though significant amounts of the very flexible disiloxane diluent are used. The use of the less viscous, highly flexible BIS-MPTMS in place of TEGDMA also permits higher filler loadings with BIS-GMA. This unique diluent monomer is also compatible with urethane methacrylate monomers.

Table 3

MECHANICAL PROPERTIES OF COMPOSITES[9] USING BIS-MPTMS AS A DILUENT

Formulation	Resin Composition (in weight %)	P/L	Mechanical Strength in MPa	
			DTS	CS
A	BIS-GMA (70) TEGDMA (30)	4	50	239
B	BIS-IPMA (100%)	4	43	204
C	BIS-IPMA (100%)	5	47	253
D	BIS-GMA (80) BIS-MPTMS (20)	4	44	248
E	BIS-GMA (70) BIS-MPTMS (30)	4	48	232
F	BIS-IPMA (90) BIS-MPTMS (10)	4	42	209
G	BIS-IPMA (80) BIS-MPTMS (20)	4 4.5	45 44	210 188
H	BIS-IPMA (70) BIS-MPTMS (30)	4.5 5.0	40 42	200 227
I	BIS-IPMA (60) BIS-MPTMS (40)	5	45	210
J	BIS-IPMA (50) BIS-MPTMS (50)	6	44	201

---

[9] Composites were cured using visible light (Caulk Lite, L. D. Caulk, Milford, DE) for 70 s per side. The catalyst system consisted of 0.2% camphoroquinone and 0.7% ethyl 4-dimethylaminobenzoate. The glass filler was Corning Glass 7724 (3255 mesh) silanized with 0.5% 3-methacryloxypropyltrimethoxysilane as previously described.

f. The Effect of a Polythiol on the Degree of Polymerization of Dental Resin Based Materials.

Final properties of dental composites such as hardness, stength and wear are primarily related to the composition of the composite and to the conversion of double bonds in the resin.

As described in a recent study the decrease in hardness on composite surfaces caused by chemical softening can be diminished by about 40% when the curing temperature was 80°C instead of 37°C [9]. Also, the wear resistance was significantly improved due to higher degree of cure in the resin obtainable at the higher temperature.

Several studies [10,11] describe the determination of residual unsaturation in either commerical or experimental composites or unfilled resins. Ruyter [11] used multiple internal reflection to study the conversion of double bonds and reports remaining double bonds in commercial composites to vary between 25% and 48%. Others [12] used Fourier Transform Infrared Spectroscopy (FTIR) to evaluate the conversion of C=C double bonds in several unfilled BIS-GMA resin systems using a potassium bromide pellet sampling technique. Conversions between 52% and 74% were obtained; DTS (diametral tensile strength) and unreacted double bonds are apparently correlated for the system studied. The viscosity of the resin system has a significant effect on the degree of conversion; of diluents such as TEGDMA (triethylene glycol dimethacrylate) or MMA (methylmethacrylate) are used to increase the conversion of BIS-GMA.

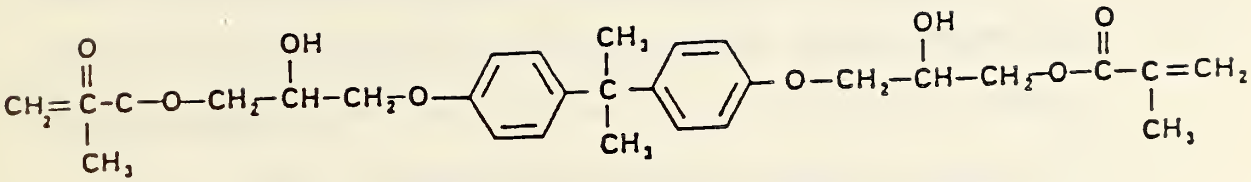
In another investigation [12] hardness and strength as a function of remaining C=C double bonds were shown to be well correlated.

Previous work [13] showed that adding modest amounts of pentaerythritol tetra (3-mercaptoproprionate), PETMP, to experimental resins yielded cured composites with enhanced esthetics and diametral tensile strength. This study was designed to assess quantitatively by FTIR infrared spectroscopic techniques the efficacy of PETMP as an agent for the reduction of the residual vinyl unsaturation present in cured dental resins materials. The objectives to be addresses are:

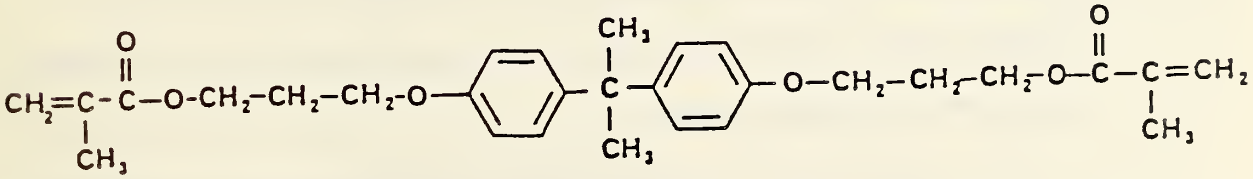
1. Measure the degree of conversion (DC) in composite films by FTIR.
2. Measure the diametral tensile strength (DTS) for some composites.
3. Investigate factors which influence DC.
4. Determine the effect of PETMP on DC and DTS.
5. Study the correlation between DTS and DC for several resin-based composites.

The details of this study were presented at the 1984 IADR meeting in Dallas and a manuscript has been prepared for publication [15]. The base resins used in this study with their chemical structures are shown in Figure 8. A summary of the salient points of the conclusions from this study are listed below:

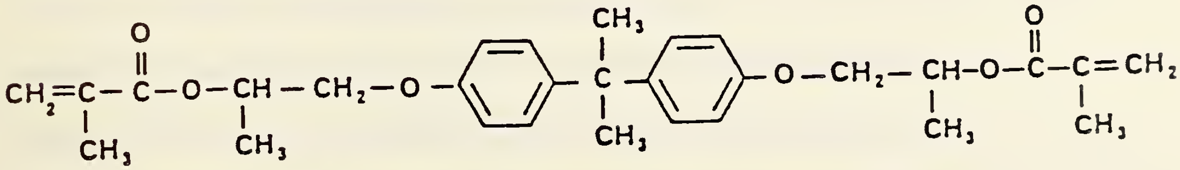
1. Addition of a multifunctional chain transfer agent, such as PETMP, in small amounts (1-5%) increased the conversion of C=C double bonds and the strength when used with resin formulations based on BIS-GMA, BIS-PMA or BIS-IPMA monomers.
2. The effectiveness of PETMP on the conversion is determined by structure and stiffness of the main resin component, e.g. PETMP



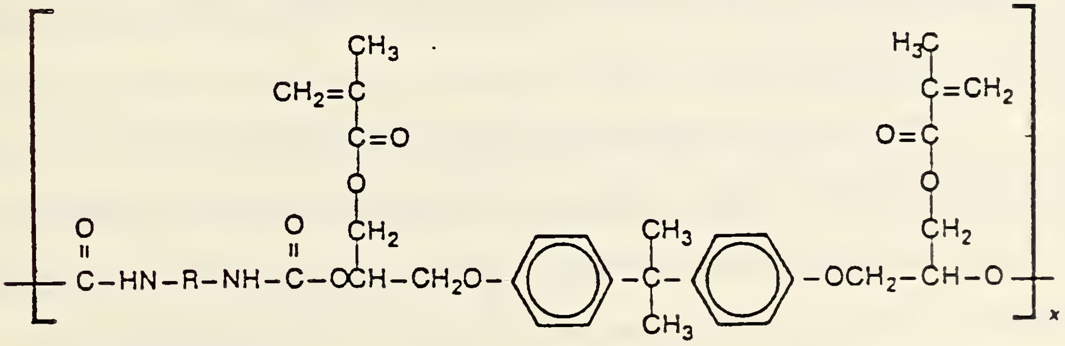
Bis GMA



Bis PMA



Isomer of Bis PMA



Generalized Chemical Structure of NCO Monomer
Mol. Wt. 1000

Where R is an Aliphatic Hydrocargon Group, Oligomeric Urethane
Methacrylate Also Contains Diluent Monomer
(e.g. Triethylene Glycol Dimethacrylate)

Figure 8.

used with the stiff prepolymer NCO monomer is ineffective, while when added to more flexible resins, as BIS-GMA plus diluent or BIS-PMA, an increase in the conversion of double bonds is noted.

3. The effect of PETMP on the DTS in composites follows a very similar pattern. Increase in stength through addition of PETMP is shown here to be influenced by (a) structure and stiffness of the main resin components, and (b) the number of C=C double bonds lost (new C-C- bonds formed).
4. A positive correlation exists between conversion of C=C double bonds and DTS (as reported by Ferracane and Asmussen). However, this correlation applies only within a given resin system.

g. New Initiator Systems for Resin-Based Dental Materials.

Previously we had shown that polythiols such as PETMP could function as polymerization accelerators for chemically cured dental resins. That is resins containing peroxides such as benzoyl peroxide or cumene hydroperoxide and PETMP were polymerizable under ambient conditions in clinically acceptable times [14].

We have also investigated the accelerative potential of PETMP on camphoroquinone (CQ). PETMP is not as effective as a photoreductant as are tertiary amines although it does act as reactive diluent as well. However, with dual cure, two part systems, PETMP is effective in increasing the degree of cure and diametral tensile stength [15]. The dual cure systems consist of a conventional silanzied glass powder coated with benzoyl peroxide and a liquid resin containing photoinitiators and slow activators (e.g. ascorbyl palmitate, ethyl-4-dimethylaminobenzoate, PETMP, etc.) for the peroxide. These systems yield composites with higher and more unifrom degrees of cure versus depth, minimal air inhibition and enhanced strength.

3. Halotopolymer Cements Based on Dimer and Trimer Acids.

Introduction

A novel, versatile class of dental cements, termed halatopolymer cements, was developed from the commerically available polycarboxylic acids, designated dimer (DA) and trimer (TA) acids [16,17]. The divalent metallic dimerates and trimerates matrices of these cements are halatopolymers, a term coined to denote their dual salt-like and polymer-like character. All of these cements have water repellent properties due to their large paraffin like core. Some of these cements, especially those based on the use of calcium bases, display energy-absorbing qualities under compressive stress. These cements do not inhibit the polymerization of resin based dental materials and in fact, can be formulated to yield hybrid composite cements. The calcium hydroxide based cement may promote secondary dentin formation. Further details on the properties of these cements are contained in the abstracts and microfilmed papers presented at IADR meeting in Dallas and the 10th Annual Meeting of the Society for Biomaterials in Washington, DC [16,17].

Objective

The aim of this particular phase of our general program to develop cements of improved durability was to evaluate new DA/$Ca(OH)_2$ cements having improved dimensional stability, low water solubility, enhanced mechanical strength and esthetics superior to ZOE cements but with comparable radiopacity. Strong, esthetic cements with various degrees of radiopacity were obtained using fillers such as radiopaque glass and certain titanium and zirconium compounds. Dilatometric measurements indicate that some of these cements display volumetric expansion on setting which suggests that these cements may result in reduced microleakage.

By proper selection of the base/filler component DA and TA cements with various degrees of translucency can be prepared. Some of these cements harmonize well with the appearance of enamel suggesting their potential for use as an esthetic intermediate restorative material. For example, translucent cements resulted from using calcium base powders (e.g. $Ca(OH)_2$) with fillers such as fumed alumina, pyrogenic silica, and various other vitreous fillers. With magnesium base powders (e.g. MgO) less translucent cements are formed and zinc base powders (e.g. ZnO) yield opaque cements. By proper selection of the filler components with refractive indices that match the cement matrix and which also contain radiopaque elements (e.g. Ba, Sr) it is possible to formulate translucent, radiopaque cements.

Phases II, III and IV

Due to the necessary concentration of efforts first on Phase I of this section, dealing with synthesis of monomers and development of formulations, progress has not developed to the stage of proceeding with Phases II, III and IV. These are listed here for clarity:

Phase II:

(1) Develop improved coupling agents for fillers (such as dual silanization.)

(2) Formulation of composite or cement systems with various fillers treated with coupling agents.

(3) Determination of physical, chemical or mechanical properties as appropriate. Develop new analytical techniques as required.

Phase III:

(1) Select systems for development toward systems with potentially clinical usefulness.

(2) Determine properties of near optimum systems.

Phase IV:

(1) Pre-clinical Testing

(2) Clinical Evaluation

II. Wear Resistance and Related Physical Properties of Dental Composite Restorative Materials.

Background

This part of the report includes the performance evaluations of dental composite restorative materials using both *in vivo* and *in vitro* wear testing, hardness measurements, diffusion studies, viscoelastic measurements, and volume dilatometry. From these evaluations, guidelines are obtained which facilitate the development of new or improved dental composite prototypes. Some examples will be given at the end of this section.

Damage to posterior occlusal restorations has been found to be both chemically and physically induced [18], therefore, the general wear test procedure that is followed is to precondition the *in vitro* wear specimens in organic food simulating liquids or oral environmental acids. These liquids or acids may damage the polymer matrix or inorganic reinforcing filler, respectively. Chemical damage from the preconditioning will decrease both the microhardness and wear resistance. The diffusion studies are done to assess the extent of penetration and degree of concentration of these liquids in the composites. Because diffusion and degree of cure are affected by the glass transition, dynamic mechanical (viscoelastic) measurements were initiated on dental polymers. From these measurements the glass transition temperature, T_g, and the dynamic shear modulus are obtained. The latter gives the rigidity below and above T_g. The FTIR measurements determine the degree of conversion of residual double bonds which may be used to define the degree of cure. From volume dilatometry the polymerization shrinkage is obtained, a quantity which is useful to assess the potential for marginal integrity or leakage. The clinical tests, involving the wear of restorations placed in partial dentures, were cconducted to check the relevance of the <u>in vitro</u> tests.

Finally, the information obtained from the investigations just described is being used to determine appropriate formulations for dental composite prototypes with improved durability.

This task is divided into the following sections:

A. Wear and Durability Assessment of Composite Restoratives

Phase I. Effect on wear and hardness from preconditioning in organic food simulating liquids.

Phase II. Effect of wear and hardness from preconditioning in oral environmental acics.

Phase III. Diffusion rates

Phase IV. Glass transition measurements

Phase V. FTIR measurements

Phase VI. Volume dilatometry

B. Formulation of New Dental Resins to Improve Durability

C. Clinical Studies

A. Wear and Durability Assessment of Composite Restoratives

<u>Objective</u>

The objective of this task is to identify the <u>in vivo</u> wear and degradation mechanisms of dental composite restorations. The results, when correlated with <u>in vivo</u> tests, facilitate the development of new dental composite materials.

Progress Report

Phase I.

Effect on wear and hardness from preconditioning in organic food simulating liquids.

Wear measurements employing a pin and disc technique [19] on specimens preconditioned for one week at 37°C in organic food simulating liquids were continued in this reporting period. As recommended by the FDA [20] the food simulating liquids have solubility parameters ranging from 1.5×10^{-4} (heptane) to $4.8 \times 10^{-4}\ J^{1/2}\ m^{-3/2}$ (water). According to solution theory, maximum miscibility occurs when the solubility parameters of the two component liquids are equal. Wear and hardness measurements were made on four commercial composites preconditioned in six food simulating liquids with solubility parameters encompassing the above range. These were Adaptic (chemically cured - conventional filler), Profile (chemically cured - strontium glass filled), Prisma Fil (visible light activated) and Silar (chemicaly cured, microfilled). The wear and hardness trends were consistent. The maximum decreases in wear resistance and hardness occurred from preconditioning in a 75% ethanol/25% water solution for which the solubility parameter is $3.15 \times 10^{-4}\ J^{1/2}\ m^{-3/2}$. The value for BIS-GMA, a common dental resin, is expected to approximate this value. This result implies that any low molecular weight food component with a solubility parameter proximate to this one will enhance the in vivo degradation of BIS-GMA based composites.

Additional hardness measurements were obtained for 12 more commerical composites [21] preconditioned in the same food simulating liquids. The specimens were performance rated in terms of an environmental index which involves the integral of the hardness ratio (after and before preconditioning) over the solubility parameter bounded over the food simulating range given above. All of the composites tested showed some influence on the hardness by these liquids.

In the course of continued studies, it was assumed that resistance to solvents and their diffusion into composites would be reduced if the degree of cure (DC) of the matrix were increased. In order to study the influence of the DC, cure temperatures were elvevated to several temperatures up to 80°C. A correlation was observed for which the hardness and wear resistance increased with cure temperature, or degree of cure. Although substantial elevation of the cure temperature of <u>in situ</u> placed restorations may not be practical, the need for increasing the DC is apparent and, presumably, can be accomplished by other means.

Phase II.

Effect on wear from preconditioning in oral environmental acids.

It has been found that silicon and combined metal ions are leached from pulverized dental composites when stored in initially pure water for extended periods. A considerable portion of our activity during this reporting period was devoted to determining the influence of preconditioning dental composite specimens in water and weak acids as found in the oral environment. Wear and hardness measurements were made on five commercial composites preconditioned for one week at 37°C in water and 0.02 N solutions of citric, acetic, and lactic acids. The composites were Adaptic (conventional), Adaptic Radiopaque (conventional with some barium silicate filler), Profile (strontium glass filler), Ful-fil (visible light activated) and Silar (microfilled). Except for the first and last, these composites employ radiopaque fillers. Preconditioning in air under the same conditions was done to obtain a control.

The wear and hardness measurements here were not always mutually consistent as with the organic liquid preconditioning however, some qualitative conclusions were reached. The quartz and pure silica glass filled composites (Adaptic and Silar), were the least susceptible to this kind of preconditioning. They seemed to be essentially unaffected by water and only a little by the acids. The radiopaques were, for the most part, more vulnerable and in two cases pure water produced more apparent damage than weak acids. This behavior indicates that in pure water the environment around the glass particles becomes alkaline from the sodium that is leached from the glass. This alkalinity attacks the silica portion of the glass. When acids are present the alkalinity is neutralized and the attack is, therefore, impeded [22]. Stress induced by wear accelerates the process [23].

This investigation has been recently extended to include some commerical ionomer cements, which harden primarily by ionic crosslinking reactions in contrast to the free radical network formation of resin based composites. These materials were studied because they appear to have some potential application for Class II restorations. The Commerical materials studied so far are Espe-Chelon, Ketac, and Ketac Fil, DeTrey-Chemfil II, and Fuji II. For the most part these involve acrylic acid copolymers and a calcium-alumina silicate glass. Ionic crosslinking is caused by calcium or aluminum ions reacting with ionized carboxyl groups. According to wear and hardness measurements, all of these materials reveal very little damage from preconditioning in water, but considerable damage is inflicted by preconditioning in lactic acid. The hardness and resistance of the chemically undamaged cements was sometimes larger than that for the composites listed in the previous paragraph. The ionomer cements, however, are very brittle, which sometimes causes cracking and subsequent catastropic failure during wear. Although this investigation is not complete, our tentative conclusion is that the extreme brittleness and susceptibility to lactic acid impose some serious limitations on the application of these materials to Class II restorations.

An experimental composite using a microporous glass with immiscible lithium aluminum silicate and barium silicate phases was prepared by the L. D. Caulk Company for wear testing. The objective was to determine whether, or not, wear and environmental resistance would be improved by the enhanced microscopic coupling at the polymer-glass interface obtained by etching out the lithium phase. Comparison between specimens with etched and unetched glasses showed that etching improved the wear resistance considerably. The results with respect to environmental resistance are inconclusive at this time. An additional inherent characteristic of this glass is that the thermal expansion of the lithium phase in crystalline form is negative. Thus with proper proportions of the ingredients the thermal expansion coefficient of the composite could be made approximate to that of enamel.

Phase III.

Diffusion, effect of fillers on the swelling ratio in composites.

Dental composites are known to degrade partially due to diffusion of foreign molecules which often cause swelling. It is well known that the equilibrium swelling ratio of the resin within a composite is less than that of the same materials in its neat form. The extent of the suppression in the resin swelling ratio has also been found to be dependent on the filler content. The basic reason for the above observations is that the resin at the filler-resin interfaces loses a certain amount of freedom for expansion.

A quantitative account for the above reasoning has been advanced for both the fiber and the particulate reinforced composites such as dental composites. Analytical solutions for both types of composites in theta solvents (those that do not change the polymer conformations) have been obtained. As to other solvents, the deviations in the swelling behavior from that of the theta solvents is predicted to be merely a function of n (1-2X): where n is the molecular weight between crosslinking points within the resins and x is the solvent resin interaction parameter. Numerical solutions for the non-theta solvents cases have also been obtained by solving a second order nonlinear differential equation.

The experimental data from our laboratory using dental composites with different filler contents confirm the above prediction. The results provide a quantitative insight into the effect of the bonding strength and the filler content on the oral environmental resistance of dental composites.

Phase IV.

Glass Transition Measurements.

Glass transition temperature, T_g, measurements were made on BIS-GMA resins using a Weisenberg Rheogoniometer. This is a rotary forced vibration device, which determines the complex shear modulus. From this T_g may be obtained by employing a temperature scan. Although the measurements were reliable at ambient conditions, some difficulties were encountered at elevated temperatures. Some of the problems inherant with chemically cured systems could be avoided by using a light cell attachment for visible light activated systems. This cell, however, is not commercially available and would have to be designed and constructed. The extent of renewed activity will depend upon the availability of the rheogoniometer and consideration of cost of cell construction vs benefits derived.

Phase V.

A composite dilatometer for measuring polymerization volume changes.

One of the factors considered to be important in the application of composite dental restorative materials as well as of certain adhesive materials is the degree of shrinkage which occurs during polymerization. In order to measure this shrinkage a simple mercury filled dilatometer system was assembled. The dilatometer itself is constructed from a spherical glass joint which is ground flat and covered by a flat quartz plate. The plate is held in place by the spring clamp normally used to assemble the joints. The stem of the joint is bent into a "U" tube and filled with mercury. The mercury is drawn up into the "U" tube by light vacuum and the sample is positioned by adherence to the inside of the quartz plate. When the vacuum is removed mercury flows down to fill the joint and surround the sample. Any trapped air leaks out between the plate and the ground surface of the joint. The high surface tension of mercury prevents it from leaking. Volume changes are monitored using a linear variable differential transformer whose core is attached to a poly(tetrafluoroethylene) slug which floats on the surface of the mercury in the "U" tube.

The system has a resolution of about 10^{-5} cc. This sufficient to measure alloy volume contraction/expansion of 2 to 5% with a standard deviation of 0.1%, using 150 mg samples. Primarily to test this instrument the shrinkages of three commerical composite materials were measured at 32.5°C. The results are shown in Table 4.

Table 4. Curing Shrinkage of Several Commerical Composites

Material	Shrinkage Percent	S.D.	No. of Samples
Espe-St	4.3	.13	3
Fulfil	3.5	.10	3
PrismaFil	3.8	.07	3

These are all light-activated materials for which one can introduce the sample and ensure that the dilatometer is at equilibrium before starting the polymerization which is initiated by directing visible light through the quartz plate. The problem of introducing chemically activated materials has been approached by standardizing the time after the start of mixing when the volume measurements are begun.

B. Formulation of New Dental Resins to Improve Durability (Also see Part I, section E; Improvement of Dental Composites, Sealant and Cement Materials.)

Objective

The objective of this task is to formulate and produce new dental resin prototypes for more durable composites.

Progress Report

Two guidelines to develop improved dental resins resulted from our wear research: (1) to increase the degree of cure of the resin and (2) to shift the solubility parameter of the polymer to values below the range of low molecular weight food ingredients.

The degree of cure was increased extraorally by elevating the cure temperature. Since this method is severely limited for in situ cured restorations, one alternative is to appropriately modify the chemical structure. The degree of cure of a resin by bulk free radical polymerization is limited by the glass transition of the developed polymer. Curing will be more complete if the difference between $T_{g\infty}$, the glass temperature of a completely cured system, and T_{gc}, the glass temperature at the in - situ temperature, is small. If this difference is too small, or negative, the cure will essentially go on to completion; however, the result will be a rubbery polymer which is unacceptable. Accordingly, a flexible resin chain yielding a polymer with a $T_{g\infty}$ of about 50-60°C is desired. That is, a resin system having a maximal degree of freedom, yet capable of maximal crossing and/or chain extension, resulting in a stiff, tough polymer is the ideal matrix.

With respect to the solubility parameter a flexible chain polymer may be expected to have a lower cohesive energy density than one with a rigid backbone. Accordingly, a polymer with a low solubility parameter value may be expected to have a low $T_{g\infty}$, unless it becomes highly crosslinked during the polymerization process. Thus it appears possible to satisfy both criteria with a low cohesive energy polymer of high crosslinked density.

In view of these guidelines the aforementioned (Section I) polyfluorinated and siloxane containing resin based composites are being developed and tested.

C. Clinical evaluations.

In collaboration with the American Dental Association Health Foundation Research Unit, clinical tests were designed to study the influence of degree of cure on wear resistance of composite restorations [18] This work provided a check on the validity of the assumptions used to design the *in vitro* tests discussed previously. Restorations were made from the following commerical composites: Adaptic (conventional), Profile (strontium glass filler), Prisma Fil (visible light activated) and Silar (microfilled). The restorations were placed extraorally on the occlusal surfaces of denture teeth in partial dentures and cured at 37 and 60 °C. After six months of *in vivo* wear the restorations were ranked for changes in anatomic form using SEM. With all specimens except Silar the enhanced polymerization improved the wear resistance. The adverse effect with Silar may be attributed to excessive polymerization shrinkage, since the polymer/filler ratio is larger in microfilled composites. This effect was not observed in the *in vitro* wear test. The distinction reveals the necessity of including complementary clinical tests in this kind of an evaluation program.

III. Dental Alloys and Ceramics

Background

In recent years, new dental alloy and ceramic systems have been introduced to dentistry at a rather regular rate. A need exists for a simple method to aid in characterizing the casting behavior of the new alloys. This can be useful in defining the operating conditions for employing an alloy in a dental laboratory, for assuring consistent behavior of alloys delivered to the market and in aiding the development of new alloys. For this purpose a polyester mesh screen has been developed in this laboratory for use as a casting monitor.

Among the needs for porcelain-fused-to-metal (PFM) systems, is a reliable, relevant method for characterizing the strengths of these and other porcelain veneered system(s) (PVS). As new PVS's appear and are developed, further improvements are likely to be hindered by lack of clear understanding of the flaws or properites leading to failure. For this purpose, work has been proceeding on development of a Bending Beam Composite (BBC), which can effectively and relatively rapidly develop quantitative information regarding failure stresses and flaw distributions.

In a related area stress compatibility of PVS's is a topic of concern and interest. An accepted method for characterizing this compatibility does not yet exist. If one is to be developed, an understanding of the roles of various material physical properties in developing stress induced failure needs to be delineated. Toward this end, work has been progressing on defining the stresses and strains developed in a bimaterial (porcelain veneered) split metal ring. Although it is questionable whether the analysis itself can define compatibility, useful information might be gathered which will lead to more comprehensive understanding and perhaps the development of simple, expedient, clinically relevant methods to evaluate compatibility.

The casting of dental alloys also affects the fit of the prosthesis. Previous studies [24 thru 30] have aptly demonstrated, the effects of investments on fit. Before improvements in investments can be effected, it is necessary to understand the physical processes taking place within the investment at the site of a pattern. For this purpose, strain gauges are being investigated as measurement devices to provide this information.

Finally, the introduction of new alloy systems requires that an agreed-upon, reliable method to evaluate soldered joints be developed. Such a method should involve the use of techniques employed in dental laboratories so that a reflection of the technique on the servicability of soldered joints may be obtained.

A. Porcelain-Alloy Compatibility (Thermo-mechanical Compatibility)

Objective

The objective of this part of the investigation is to explore the potential of using a porcelain veneered split substrate ring (usually metal) as a means for determining the thermal stress compatibility between the two (veneer and substrate). For this purpose, a finite element model (FEM) is being developed which will use the visco-elastic properites of porcelain, elastic properites of the substrate (metal), coefficients of thermal expansion and temperature gradients developed upon cooling in order to calculate stresses developed upon cooling. These parameters will be adjusted so that openings or closings of the gap will mimic those of experimental specimens. Origins of high stresses throughout the specimens then can be defined.

Progress Report

The phases of research are as follows:

Phase I

Determine the temperature dependence of elastic modulus for dental porcelains and alloys.

Two dental porcelains, one with essentially a completely glassy structure (Ceramco) and the other with a structure strongly crystalline in a glassy matrix were found to have essentially the same mechanical properties: Young's Modulus, ~68-69 GPa; shear modulus, ~28.5-29.5 GPa; and Poisson's ratio, 0.19. The Young's modulus decreased by about 1% for every 100°C increase in temperature up to 500°C. An estimate of the microcrack density, N, was calculated to be $N \approx 3.4 \times 10^4$ cm^{-3}. A manuscript "Elastic Constants of Two Dental Porcelains" has been prepared and accepted for publication in the Journal of Materials Science.

Determinations of elastic-moduli for three dental alloys were also made. The three alloys are representative of (1) a Be containing, multiphase alloy, (2) a non-Be containing, multiphase alloy and (3) a non-Be containing, large-grained alloy. The results are shown in Table V:

Table V

Alloy	Young's Modulus	Shear Modulus	Poisson's Ratio
1	171.7	65.1	0.32
2	191.7	75.6	0.27
3	143.6	57.8	0.24

As with the dental porcelains, the modulus decrement is about -1% for each 100°C increase in temperature. A manuscript "Elastic Constants of Three Representative Nonprecious Dental Alloys at Room and Elevated Temperature" has been submitted to the J. Biomedical Materials Research. This phase is completed.

FY 83 & 84.

Phase II

Finalize the ultimate computer program on the finite element model (FEM) of split ring stress. In progress FY84, expected to be completed in FY 85.

Phase III

Finalize material input parameters for split ring computer program and fine tuning for match with experimental results. Planned for FY85.

Phase IV

Devise simple analytical representation of split ring stress-strain caluclations if possible, (see #5).

Phase V

Examine results of FEM vs 2-dimensional theory developed by Scherer. FY86.

Phase VI

Modify expansion and other properties of porcelain and/or alloys to establish limits for clinical stress compatibility. To be explored in FY86.

Porcelain-Alloy Compatibiliby (Bond Strength)

This aspect of compatibility relates to the underlying strength of the material components in PVS's (porcelain veneered systems), including the strength of the bond itself. When initiated, this project was designed to measure PMBS (Porcelain Metal Bond Strength) however, as it progressed it became clear that what is important is the strength of the system as a whole and the subsequent developments related to this realization. A bending beam composite (BBC) has been developed for this purpose and its underlying features and method for stress computation have been described in previous reports. Progress, according to phases, is as follows:

Progress Report

Phase I

Determine the most appropriate method for representing BBC data. This has been done, with a two parameter Weibul Statistics plot. Essentially, this is a probability of failure, P_f, at a given stress level, σ_f, vs the stress level of failure, σ_f; i.e. P_f vs σ_f. This method shows statistically significant differences between systems which do not reveal such differences via application of normal distribution, two sided t test statistics. This was accomplished in FY84. For FY85 & 86, three parameter Weibul analysis will be explored.

Phase II

Determine three dimensional and two dimensional FEM of BBC. This phase was completed in FY83.

Phase III

Determine theoretical curve filling methods: exploration of 3-Parameter Weibul analysis. Will be pursued for FY85 & 86.

Phase IV

Photo elastic study of BBC...To be explored in FY85 & 86, if deemed necessary.

Phase V

Explore effects of alloy reuse, specimen reuse, annealing of porcelain, immersion in water (or saline solution) on system strength. To be initiated in FY85.

B. Castability (Filling a Mold With Cast Dental Alloy):

Objective:

The objective of this work is to investigate effects of processing variables on the castability value, C_V, for numerous dental alloys. (C_v is defined as the fraction or percentage of completely cast segments of a grid pattern). The variable, C_V, is evaluated as a function of mold and alloy casting temperatures. A transformed value of C_v, i.e. C_{vt} is employed for statistical curve fitting. A further objective is to define the effects of temperature on the effectiveness of alloying elements in producing complete castings. Ultimately, these data may be used for design of new alloys.

Another aspect of casting of dental alloys involves the factors affecting the fit (or accurate reproduction of a pattern) of dental castings. A new technique employing strain gauges is being used to investigate the internal setting expansion of dental investments.

Progress Report

Phase I

Statistical and functional representation of castability. This has been completed for (6) nickel based alloys and reported on in previous reports (FY82 & 83). One manuscript has been submitted for publication entitled "A Technique for Characterizing the Casting Behavior of Dental Alloys". Another manuscript, "Castability of Dental Alloys, Mold and Alloy Temperature Effects", is under preparation.

Phase II

Multivariant Analysis of Effects of Composition on Castability. The first determinations of this have been made, using data available from the six alloys mentioned in Phase 1. The following equation was found:

$$C_{v_t} = K_o + K_1 [Si] + K_2 [B] + K_3 [Cb \times Sn] + K_4 [Al \times Be] + K_5 [Mo \times Mn]$$

Where : K_i = function of mold and alloy temperature

[] = concentration of elements

This expression needs further refinement as it is not certain that the terms involving products of elemental compositions are sufficiently independent in each element, that is, some particular compositions appear to be too strongly correlated. Also, to be strictly correct, only one investment sould be used for obtaining the castability data. However, at this point, the technique has been demonstrated to be a viable method for analysis. A manuscript on this is being prepared for presentation as an invited paper at an International Precious Metals Institute Meeting in Israel, April, 1985.

Phase III

Extension of the method to other investments and mesh sizes. This is planned for FY85 & 86 and possibly beyond.

B. Castability (Fit of Dental Castings and Investment Expansion)

Objective

The objective of this work is to determine if a reliable method for obtaining the expansion of dental invetment, intrenally and at the locations of dental patterns, can be arrived at by using strain gauges.

The most common method for determining the setting expansion of a dental investment involves making external measurements on the surface of a mass of setting investment. This may not be representative of the effects occurring internally and the distortions that often occur in dental castings certainly indicate non-linear effects. The ability to determine internal effects should aid in developments of new investments/casting techniques aimed at eliminating non-linear effects.

Progress Report

Phase I

Preliminary studies showed that strain gauges do react to the setting of the dental investments. Results indicate that the internal expansion of dental investments is less than that measured externally, with external measurements showing ~1% and internal measurements ~0.1%. It is not yet clear what extent the plastic backing of the strain gauges is having on the results obtained. A paper on this topic was presented at the 1984 meeting of the IADR in Dallas, Texas.

C. Solderability

Objective

The original objective of this work was to examine whether bend or pure tensile testing was the most effective method for evaluating the strength of soldered joints. It may be stated now that it is not planned to continue this work beyond that reported on as the investigators do not believe that any particular difficulties exist with either bend or tensile testing of soldered joints; hence, there is not a considered need here for development.

Phase I

Develop solderability specimen pattern, theory and experiment. This was accomplished in a trial basis for FY84. Initially, cylindrical specimens ~2.5 mm in diameter, were soldered with a fixed size gap. These specimens were either pulled in tension or subjected to a four-point bend test. Either method was found to work satisfactorily, with the tension test, preferred due to its ability to reveal central area solder defects more easily from the raw data. At first, the bend test results were preferred; however, with proper application of Weibul statistics, each method should be equivalent.

The breaking strengths (σ_B) are tabulated below with standard deviations (s) and number of specimens (n).

	σ_B (MPa)	s	n
Tension	306	±156	(6)
Flexure	770	±289	(19)

We note that all of the specimens broke in a brittle manner with no evidence of yielding. We might possibly attribute the higher breaking stress observed in flexure to a non-uniform distribution of flux inclusions with more such material concentrated near the neutral axis.

Phases II, III, and IV

Phase II. Initiate tests (completed).

Phase III. Modification: no further effort is planned unless some feature of the testing, particularly germaine to dentistry, is discerned.

Phase IV. Evaluation of alloys and solders is not planned, this effort is being discontinued.

REFERENCES:

[1]. G. M. Brauer and J. W. Stansbury. Cement Containing Vanillate Esters, EBA and Zinc Oxide, J. Dent. Res. Prog. and Abstr. of Papers, 60th Gen. Sess, IADR, Abstr. 1377 (1982).

[2]. G. M. Brauer, J. W. Stansbury and H. Argentar, Development of High-Strength, Acrylic Resin-Compatible Adhesive Cements, J. Dent. Res. 62:366-370 (1983).

[3]. W. Wu and J. E. McKinney: Influence of Chemicals on Wear of Dental Composites, J. Dent. Res. 61: 1180-1183 (1982).

[4]. W. Wu and E. E. Debelius: Environmental Resistance of Dental Restorative Materials, J. Dent. Res. 63, 199, Abstr. No. 255, (1984).

[5]. K.-J. Soderholm: Degradation of Glass Filler in Experimental Composites, J. Dent. Res. 60, 1867-1875, (1981).

[6]. K.-J. Soderholm: Leaking of Fillers in Dental Composites, J. Dent. Res. 62, 126-130, (1983).

[7]. K.-J. Soderholm: Hydrolytic Degradation of Dental Composites, J. Dent. Res. 63, 1248-1254 (1984).

[8]. J. E. McKinney: Influence of Acids on Wear of Composite Restoratives, J. Dent. Res. 63, 199, Abst. 256 (1984).

[9]. J. E. McKinney and W. Wu: Effect of Cure on Hardness and Wear of Three Commerical Dental Composites, J. Dent. Res. 62, 285, Abst. 1047 (1983).

[10]. I. E. Ruyter and P. P. Gyorosi: An Infrared Spectroscopic Study of Sealants, Scand. J. Dent. Res. 84, 396-400 (1976).

[11]. I. E. Ruyter and S. A. Svendsen: Remaining Methacrylate Groups in Composite Restorative Materials, Acta, Odontol Scand. 36, 75-82, (1978).

[12]. J. L. Ferracane and E. H. Greener: Fourier Transform Infrared Analysis of Degree of Polymerization in Unfilled Resins - Methods Comparison. J. Dent. Res. 63, 1093-1095, (1984).

[13]. E. Asmussen: Restorative Resins: Hardness and Strength vs Quantity of Remaining Double Bonds, Scand. J. Dent. Res. 90,484-489 (1982).

[14]. J. M. Antonucci, J. W. Stansbury,D. J. Dudderar: Dental Resin and Initiator Systems Based on Polythiols, J. Dent. Res. 61, 270, Abst. 824 (1982).

[15] S. Venz and J. M. Antonucci: Effect of a Polythiol on the Degree of Polymerization of Resins, J. Dent. Res. 63, 199, Abst. 257 (1984).

[16] J. M. Antonucci, S. Venz, D. J. Dudderar, M. C. Pham and J. W. Stansbury: Non-Aqueous Polycarboxylate Cements Based on Dimer and Trimer Acids, J. Dent. Res. 63, 294, Abst. 394 (1984).

[17]. J. M. Antonucci, S. Venz, D. J. Dudderar, M. C. Pham and J. W. Stansbury: Energy-Absorbing, Hydrophobic Dental Cements Based on Dimer and trimer Acids, Second world Congress on Biomaterials, 10th Annual Meeting of the Society for Biomaterials, Transactions, VII, 137 (1984).

[18]. W. Wu, E. E. Toth, J. F. Moffa, and J. A. Ellison, Subsurface Damage of In Vivo Worn Dental Composite Restorations: J. Dent. Res., 63 675-680 (1984).

[19]. J. E. McKinney, Apparatus for Measuring Wear of Dental Restorative Materials, Wear 76, 337-347 (1982).

[20]. FDA Guidelines for Chemistry and Technology Requirements of Indirect Additive Petitions, March 1976.

[21]. W. Wu and E. E. Debelius, Environmental Resistance of Dental Restorative Composites, IADR-AADR Abstract 255, 62nd General Session, Dallas, TX, March 1984.

[22]. D. E. Clark; Carlo G. Pantano, Jr.; and Larry L. Hench, Corrosion of Glass, Magazines for Industry, Inc., 1979.

[23]. R. J. Charles, Static Fatigue of Glass, I., Appl. Phys. 29, 1549-1553.

[24]. W. G. DeRijk, M. L. Conner, K. A. Jennings, and W. Wu, In-Vivo Wear Resistance of Dental Composites with Enhanced Polymerization: IADR-AADR Abstract 951, 62nd General Session, Dallas, TX, March 1984.

[25]. R. W. Hinman, J. A. Tesk, E. E. Parry and G. T. Eden, Accepted for publication in the Journal of Prosthetic Dentistry.

[26]. G. T. Eden, O. M. Franklin, J. M. Powell, Y.Ohta, and G.Dickson, Fit of Porcelain Fused-to-Metal Crown and Bridge Castings, J. Dent. Res.,58(12), 2360-2368, (1979).

[27]. G. M. Hollenback, Science and Technique of the Cast REstoration, St. Louis, 1964, The C. M. Mosby Co.

[28]. R. W. Phillips, Skinner's Science of Dental Materials, Philadelphia, 1973, W. B. Sanders Co.

[29]. R. J. Schnell, et al. An Evaluation of Phsophate Bonded Investments Used with a High-Fusing Gold Alloy, J. Prosthetic Dentistry 13(21), 324-335, (1963).

[30]. K. Asgar, et al. Further Investigations into the Nature of Hygroscopic Expansion of Dental Casting Investments. J. Prosthetic Dentistry, 8(4), 673-684, (1958).

[31]. F. Marsaw, W. G. DeRijk, et al. Internal Vol;umetric Expansions of Casting Investments, J. Prosthetic Dentistry, 52(3), 361-366.

MANUSCRIPTS IN REVIEW OR ACCEPTED FOR PUBLICATION

Physical Metallurgy of Dental Casting Alloys, Part C, Cr-Co-Mo System; D, Ni-Cr System; E, Fe and Austenitic Stainless Steel; and F, Titanium Alloys. J. A. Tesk and R. M. Waterstrat, accepted for publication in Encyclopedia of Materials Science and Engineering, to be published in March 1985.

Fit of Multiple Unit Fixed Partial Denture Castings, R. W. Hinman, J. A. Tesk, E. E. Parry and G. T. Eden. Accepted for publication in Journal of Prosthetic Dentistry.

A Technique for Characterizing Casting Behavior of Dental Alloys, (Title changed from A Practical Method for Evaluating the Castability of Dental Alloys). R. W. Hinman, J. A.Tesk, R. P. Whitlock, E. E. Parry anbd J. S. Durkowski, submitted to J. Dental Research.

Elastic Constants of Two Dental Porcelains, H. R. Kase, E. D. Case and J. A. Tesk. Accepted for publication in J. Materials Science.

Elastic Constants of Three Representative Non-Precious Dental Alloys, H. R. Kase, J. A. Tesk, Submitted to J. Biomedical Materials Research.

Discoloration of Dental Cements and Composites in a Sulfide Solution, J. M. Antonucci, A. Sugawara, M. Ohashi, and G. C. Paffenbarger, Submitted to J. of Biomedical Materials Research.

Biocompatible Cementitious Compositions, G. M. Brauer and J. W. Stansbury, patent applied for.

Intermediate Restoratives from n-Hexyl Vanillate-EBA-ZnO-Glass Composites. G. M. Brauer and J. W. Stansbury. Accepted for publication in J. Dent. Res.

Divanillates and Polymerizable Vanillates and Ingredients as Ingredients of Dental Cements. J. W. Stansbury and G. M. Brauer, submitted for publication in J. Biomedical Materials Research.

Dental Applications (of Polymers) G. M. Brauer and J. M. Antonucci, Accepted for publication in Encyclopaedia of Polymer Science and Engineering

Chemical Softening and Wear of Composite Restoratives, J.E. McKinney and W. Wu, Submitted to J. Dent. Res.

Environmental Damage and Wear of Dental Composite Restorations. J. E. McKinney, Proc. Int. Symp. on Posterior Composites, St. Maarten, Netherlands Antilles, Jan. 1985, Submitted to WERB.

PAPERS PUBLISHED

Cements Containing Syringic Acid Esters-o-Ethoxybenzoic Acid and Zinc Oxide, G. M. Brauer and J. W. Stansbury, J. Dent. Res., 63, 137-140 (1984).

Accelerators and Acrylic Monomer Ingredients on the Properties of Bone Cement. G. M. Brauer and J. W. Stansbury, Proc. 1st Medical Plastics Conference, The Society of The Plastics Industry, Inc., New Brunswick, NJ, Oct. 1983.

Base Metal Alloys in Restorative Dentistry, R. W. Hinman and J. A. Tesk, in Advanced Restorative Dentistry, L. L. Baum and R. McCoy, editors, Chap. 17, p281-294, W. B. Saunders Company, Philadelphia, PA.

Low Surface Energy Dental Composites from a Polyfluorinated Prepolymer Multifunctional Methacrylate, J. M. Antonucci, S. Venz, J. W. Stansbury, D. J. Dudderar, Proce. 1st Medical Plastics Conference, The Society of the Plastics Industry, Inc., New Brunswick, NJ, Oct. 1983.

Subsurface Damage Layer of In Vivo Worn Dental Composite Restorations, W. Wu, E. E. Toth, J. F. Moffa and J. A. Ellison, J. Dent. Res., 63(5), May 1984.

Wear Mechanisms of Dental Composite Resins, W. Wu, Proc. of International Symposium on Posterior Composites, Chapel Hill, NC, Oct. 1982, ed. D. F. Taylor, 1984, p127-146.

INVITED TALKS

The Effect of Inhibitors, Accelerators, Cross-linking Agents and Monomers on the Properties of Acrylic Resins. G. M. Brauer, Howmedica, Groton, CT.

A Technique for Characterizing the Castability of Dental Alloys, J. A. Tesk, Northwestern University, Chicago, IL. February 1984.

The Promise of the Future in Dental Materials, J. A. Tesk, Johns Hopkins University, Baltimore, MD, January 1984

Characterization of Porcelain Fused-to-Metal Systems, J. A. Tesk, Tokyo Medical and Dental University, Tokyo, Japan, November 1983.

Low Surface Energy Dental Composites from a Polyfluorinated Prepolymer Multifunctional Methacrylate, First Annual Medical Plastics Conference of the Society of Plastic Industries, Inc., New Brunswick, NJ, Oct. 1983.

A Quantitative/Expedient Porcelain Fused-to-Metal Bond Test: Theoretical Basis and Experimental Basis, J. A. Tesk, Northwestern University, Chicago, IL, November 1983.

The Positive Impact of Investment in R&D for the Dental Industry at the University Level, the Government Level and the Corporate Level, J. A. Tesk, Dental Manufacturers of America, Hyannis, MA, July 1984.

Wear Mechanisms of Dental Composite Restoratives, J. E. McKinney, University of Maryland Dental School, Baltimore, MD, April 1984.

In Vitro and _In Vivo_ Wear Mechanisms of Dental Composites and Simulation of _In Vivo_ Wear, J. E. McKinney, University of Maryland Dental School, Baltimore, MD, April 1984.

PAPERS PRESENTED AT THE 1984 IADR/AADR MEETING IN DALLAS

A Performance Indicator for Partial Dentures, J. A. Tesk and W. DeRijk.

Environmental Resistance of Dental Restorative Composites, W. Wu and E. E. Debelius.

Bonding of Vanillate and Syringate Cements to Various Substrates, J. W. Stansbury and G. M. Brauer.

Influence of Acids on Wear of Composite Restoratives, J. E. McKinney.

Castability, C_v, of Nonprecious Alloys as a Function of Composition, H. R. Kase, S. Hirano, J. A. Tesk and T. P. Hoepfner.

Elastic Constants of Nonprecious Alloys at Room and Elevated Temperatures, H. R. Kase and J. A. Tesk.

Modification of Cements Containing Vanillate or Syringate Esters, G. M. Brauer and J. W. Stansbury.

Effect of a Polythiol on the Degree of Polymerization of Resins, S. Venz, and J. M. Antonucci.

Non-Aqueous Polycarboxylate Cements Based on Dimer and Trimer Acids, J. M. Antonucci, S. Venz, D. J. Dudderar, M. C. Pham and J. W. Stansbury.

Internal Setting Expansion of a Dental Casting Investment Measured with Strain Gauges, E. T. Meiser, W. G. deRijk, J. A. Tesk, R. W. Hinman, and R. Hesby.

ABSTRACTS SUBMITTED FOR 1985 IADR/AADR MEETING IN LAS VEGAS

Glass Transition Temperature of Dental Composite Resins, W. Wu and C. C. Yu.

An Improved Dilatometer for Measuring Polymerization Volume Changes, R. W. Penn.

Evaluation of Siloxane-Containing Dental Composites, J. S. Kuo, J. M. Antonucci and W. Wu.

Diametral Tensile Strength and Dental Composites, R. G. Craig, R. W. Penn and J. A. Tesk.

Esthetic, Non-Brittle Dental Cements Based on Dimer Acid, D. J. Dudderar.

Properties of Vanillate and Syringate Cements Containing Various Fluorides, J. W. Stansbury and G. M. Brauer.

Color Changes of Composites on Exposure to Various Energy Sources, G. M. Brauer and J. W. Stansbury.

Wear and Microhardness of Ionomer Cements, J. E. McKinney, J. M. Antonucci and N. W. Rupp.

Synthesis of a Polyfluorinated Prepolymer Multifunctional Urethane Methacrylate, J. M. Antonucci, J. W. Stansbury and S. Venz.

Biological Safety Evaluation of a Newly Developed High Strength, Acrylic Resin Compatible Adhesive Cement. C. Siew, S. Gruninger, R. Hsu, G. M. Brauer, J. A. Tesk.

U.S. DEPT. OF COMM. BIBLIOGRAPHIC DATA SHEET (See instructions)	1. PUBLICATION OR REPORT NO. NBSIR 85-3119	2. Performing Organ. Report No.	3. Publication Date March 1985

4. TITLE AND SUBTITLE

Properties and Interactions of Oral Structures and Restorative Materials

5. AUTHOR(S)

J. A. Tesk, J. M. Antonucci, G. M. Brauer, J. E. McKinney, R. W. Penn, J. W. Stansbury/ and W. Wu

6. PERFORMING ORGANIZATION (If joint or other than NBS, see instructions)

NATIONAL BUREAU OF STANDARDS
DEPARTMENT OF COMMERCE
WASHINGTON, D.C. 20234

7. Contract/Grant No.
2Y01-DE-30001

8. Type of Report & Period Covered

9. SPONSORING ORGANIZATION NAME AND COMPLETE ADDRESS (Street, City, State, ZIP)

National Institute of Dental Research, NIH, DHHS, Bethesda, MD 20205

ABSTRACT: Significant accomplishments during the FY84 are itemized as follows: (1) Synthesis of syringate esters and of polymerizable vanillates was achieved. Properties of cement composites were determined and found to hold potential as intermediate restorative materials. Formulations which adhered well to porcelains, composites, and metals were developed, (2) Preclinical evaluations of syringate and vanillate cements showed mild pulp reactions, negative Ames tests, high LD$_{50}$ (oral values and only slight hemolysis. In general, biocompatibility was good. (3) Fluoride containing cements were found to be adequately strong. (4) New, expanding polymerization expanding monomers were formulated in high yields. (5) High strength, low water absorption, fluorinated resin composites were achieved with reduced polymerization shrinkage. (6) Dimer and trimer acid cement formulations were discovered that expand on polymerization. (7) PETMP, a chain transfer agent was found effective in increasing the degree of cure of dual cured (light and chemical) composite resins. (8) Wear studies showed glass ionomer cements prone to catastrophic failure in the presence of lactic acid. (9) Preconditioning of dental composites in acids showed quartz and pure silica glass filled versions only slightly affected regarding wear. Radiopaque filled composites were more strongly attacked. (10) Experiments confirmed that composites swell in an inverse relationship relative to the filler content. (11) A sensitive, stable dialometer was constructed for measuring polymerization shrinkage. (12) More highly cured dental composites resisted clinical wear of a greater degree, except in one instance which revealed the importance of considering polymerization shrinkage and filler content. (13) Temperature dependent elastic properties of dental porcelains and nickel based alloys were determined. (14) The effectiveness of Weibul statistics in distinguishing between failure stresses of porcelain-fused to metal systems was demonstrated. (15) The first mathematical description of the effects of elemental composition on a castability value, Cv, as functions of alloy mold and casting temperatures was developed. (16) Preliminary studies of casting investment setting expansion using strain gauges showed internal expansion apparently much less than externally measured expansion.

12. KEY WORDS (Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)

Castability; dental alloys; dental casting alloys, dental cements; dental composites; dental materials; dental restoratives, wear; wear and degradation of composites.

3. AVAILABILITY

☒ Unlimited
☐ For Official Distribution. Do Not Release to NTIS
☐ Order From Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402.
☒ Order From National Technical Information Service (NTIS), Springfield, VA. 22161

14. NO. OF PRINTED PAGES
69

15. Price
$10.00