



A11107 390579

NBS

PUBLICATIONS

NBSIR 84-2843

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
Washington, DC 20234

Annual Report for Period
October 1, 1982 thru September 30, 1983

Issued May 1984

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

Certain commercial materials and equipment are identified in this report to specify the experimental procedure. In no instance does such identification imply recommendation or endorsement by the National Bureau of Standards or that the materials and equipment identified are necessarily the best available for the purpose.

Prepared for
National Institute of Dental Research
Bethesda, MD 20205

QC

100

.U56

84-2843

1984

c. 2

Circ

QC

100

456

84-2843

1984

C.2

NBSIR 84-2843

PROPERTIES AND INTERACTIONS OF ORAL STRUCTURES AND RESTORATIVE MATERIALS

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

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
Center for Materials Science
Polymers Division
Dental and Medical Materials
Washington, DC 20234

Annual Report for Period
October 1, 1982 thru September 30, 1983

Issued May 1984

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

Certain commercial materials and equipment are identified
in this report to specify the experimental procedure.
In no instance does such identification imply recommendation
or endorsement by the National Bureau of Standards or
that the materials and equipment identified are necessarily
the best available for the purpose.

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

	Page
ABSTRACT	1
INTRODUCTION	4
I. Synthesis and Evaluation of Dental Composites, Resins, Cements and Adhesion.	6
A. High-Strength, Eugenol-Free Adhesive Cements and Intermediate Restoratives.	6
Introduction	6
Phase I	7
(1) Synthesis of Vanillate Monomers	7
(2) Formulation of New Cements and Intermediate Restoratives	7
Phase II	10
(1) Evaluation of the Physical Properties of Various Cements	10
Phase III	10
(1) Synthesis of Materials for Pre-Clinical and Clinical Studies.	10
(2) Pre-Clinical Studies of Cements and IRM.	10
Phase IV	11
Phase V.	11
B. Monomers Which Expand on Polymerization.	11
Phase I.	12
Phase II	13
Phase III	13
Phase IV	13
C. Changes in Esthetic Properties of Dental Resins on Aging.	13
Phase I.	13

TABLE OF CONTENTS (continued)

Page

Phase II	14
D. Adhesion of Coatings and Restoratives to Dentin and Enamel	14
Phase I.	14
Phase II	14
Phase III.	14
E. Improvement of Dental Composite, Sealant and Cement Materials	14
Introduction	14
Phase I.	16
(1) Synthesis of Monomers	16
(2) Formulations of Hydrophobic Composites	16
Methodologies for the Assessment of Margin Leakage	18
The Reduction of Residual Vinyl Unsaturation in Dental Resin Materials by Polythiol Additives	18
Initiator Systems Based on Polythiols and Hydroperoxides	21
Non-Aqueous Polycarboxylate Cements	22
Phase II	23
Phase III.	25
II. Wear Resistance and Related Physical Properties of Dental Composite Restorative Materials	26
A. Wear and Hardness Measurements	27
Introduction.	27
1. Effect from Conditioning in Chemical Food Simulating Liquids	28

TABLE OF CONTENTS (continued)

- 2. Effect from Conditioning in Oral Environmental Acids 29
- 3. Influence of Degree of Cure. 29
- B. Solvent Diffusion Rates 30
 - Introduction 30
 - Progress Report 31
- C. Glass Transition Measurements 32
 - Introduction 32
 - Progress Report 33
 - Conclusions 33
- III. Dental Alloys and Ceramics 35
 - A. Porcelain-Alloy Compatibility 35
 - Phase I 35
 - Phase II 36
 - B. Alloy Castability 38
 - C. Solderability 43
- REFERENCES. 44
- ABSTRACTS SUBMITTED FOR 1984 IADR/AADR MEETING IN DALLAS. 48
- ABSTRACTS SUBMITTED FOR IADR AND AADR MEETINGS - 1983 49
- PUBLICATIONS - 1983 50
- INVITED TALKS 51
- MANUSCRIPTS IN REVIEW OR ACCEPTED FOR PUBLICATION 52

ABSTRACT

The past year has seen the attainment of a number of significant milestones. These include the following:

1. The development of high strength, eugenol-free cements has been accomplished. When blended with glass filler particles, these cements are expected to function well as intermediate restorative materials. In addition to high strength these cements are compatible with composite filling materials in that they adhere and do not inhibit polymerization of the composites. Also, these cements can be formulated with acrylic monomers and adhere strongly to many nonprecious alloys and glasses. Preliminary results indicate good biocompatibility.

2. Hydrophobic composite resin formulations have been developed that have lower water sorption than conventional BIS-GMA (Bis Phenol Glycidal Methacrylate). The altered solubility parameter of these resins is expected to improve in-mouth durability and the hydrophobic nature has been shown to reduce microleakage. The use of polyfluoromethacrylate in combination with pentaerythritol tetra-(3-mercaptopropionate) PETMP, produced resins with adequate strength and reduced residual double bonds; this is expected to lead to improved stability over time.

3. Studies on the effects of techniques for evaluating the aging of dental resins showed that exposure to a Xenon lamp produced greater changes than exposure to an RS lamp which in turn produced greater change than exposure under water to the Xenon lamp.
4. New, more stable, initiator systems such as cumene hydroperoxide and color stable polythiols such as PETMP were formulated together to produce more color and storage stable resin systems.
5. Flexible backbone dimer and trimer acids were shown to produce hydrophobic materials having high durability. These materials have potential for use as cavity liners, endodontic sealers and impression materials.
6. Wear and degradation studies showed further the importance of the environment-affected wear. A 75% ethyl alcohol - 25% water solution was found to significantly soften dental composites and produce reduced resistance to wear. Because this ethanol solution has the greatest effect compared to other percentages of alcohol, the solubility parameter of BIS-GMA is expected to be close to that for the 75% ethanol solution. Composite resins are being designed to have substantially different solubility parameters.
7. A simple equation was found to apply for describing the castability of each of six nickel based dental casting alloys.

Only two determinations of castability are necessary to completely describe castability as a function of mold and alloy temperature.

8. A unique four-point bend test specimen is used for porcelain-fused-to-metal strength determinations. A cumulative failure plot was found to be capable of distinguishing between different porcelain-alloy system fracture strengths. Weibull statistics are employed. Finite element analyses showed that some qualitative comparisons between apparent fracture modes are not valid for comparing failure of porcelain-nonprecious (high modulus) alloy systems with porcelain-low modulus alloys.

INTRODUCTION

The prime responsibility of the National Bureau of Standards (NBS) resides with measurements. Within the framework of development of new or improved measurement techniques and standards lies a vast realm of investigations into basic science and engineering necessary either for the advancement of metrology or requiring advanced metrology for further development. It is from these basics that has grown the program in dental and medical materials science at NBS.

The dental research program at NBS has developed into a long standing cooperative program between the American Dental Association Health Foundation Research Unit (ADA HFRU) as research associates, the National Institute of Dental Research (NIDR), and NBS. The funding and financial support has come from all three of these primary participants, as have personnel, with the bulk of the personnel residing with the ADA. Additional support has come from industry in the form of visitors who would either review the program as an informal method of technology transfer, or who would work on projects for a limited period to facilitate more rapid technology transfer. Significantly, industry has taken a more active role recently with the addition of the first industrial research associate to the program, this from Dentsply International. Other participants in the program have been research associates from various branches of the military and guest workers from numerous institutions throughout the world, making this one of the most comprehensive dental materials and equipment research programs in the world.

The objective of the research program is generally to provide the science and engineering base which will lead to improved dental materials and techniques for the practice of preventive and restorative dentistry.

As constituted, the NIDR-NBS supported program is divided into three major areas of research:

- I. Dental Composites, Resins, Cements and Adhesion: Synthesis and Evaluation
- II. Wear and Degradation Resistance and Related Physical Properties of Dental Composite Restorative Materials
- III. Dental alloys and Ceramics

The following pages provide only highlights of the progress made from October 1, 1982 to September 30, 1983. Detailed descriptions will be found in the publications by the authors, in their talks and abstracts and in future publications which have not yet reached the review stage. Readers who desire more detailed information are encouraged to contact the authors of the various sections and/or visit the NBS for comprehensive discussions.

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

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

Introduction

Recently 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) excellent strength, (2) 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, (5) adhere strongly, even on prolonged water exposure, to non-precious 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 are planned: (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) formulation of intermediate restorative formulations (IRF) incorporating monomers and reinforcing fillers with cement ingredients and determination of their mechanical properties; (4) synthesis of

cements using the structurally related syringate esters and evaluation of their physical properties; and (5) conduct pulp irritation and clinical studies in collaboration with Indiana University, United States Army Institute of Dental Research (USAIDR), United States Public Health Service (USPHS), University of Tennessee, University of South Carolina, and other institutions.

Phase I

(1a) Synthesis of divanillates and polymerizable vanillates as ingredients of dental cements.

To achieve higher strength and lower solubility compounds with multifunctional groups that react with metal oxides to give chain extended products have been synthesized. Divanillates such as decamethylene or hexamethylene divanillate were obtained from vanillic acid and the corresponding polymethylenediols. Methacryloyl ethyl vanillate (MEV) and vanyllyl methacrylates were prepared respectively from hydroxyethyl vanillate or vanyllyl alcohol and methacryloyl chloride.

A talk describing synthesis of these compounds and evaluation of the resulting cements has been given [3]. A manuscript has been prepared and is now under editorial review.

(1b) Synthesis of syringate esters

Two syringates, n-hexyl syringate and 2-ethyl hexyl syringate, have been synthesized. Cements containing these potentially caries-reducing compounds have been evaluated. A talk on this research has been presented. A manuscript has been submitted to J. Dental Research [4].

(2) Formulation of New Cements and Intermediate Restoratives (IRM)

(a) The usefulness of vanillate compounds with multifunctional groups that react with metal oxides to give chain extended products

as ingredients of dental cements has been studied [3]. Liquids containing divanillates or methacryloylethyl vanillate alone or in conjunction with n-hexyl vanillate and a chelating agent such as o-ethoxybenzoic acid (EBA) react with zinc oxide powders. The mixes harden rapidly. The resulting cements have lower solubility and have higher strength (compressive strength up to 74 MPa, tensile strength up to 11.2 MPa) compared to compositions based on zinc-oxide-eugenol (ZOE) or monovanillate-EBA-ZnO formulations. Any brittleness of these materials can be overcome by addition of an oligomeric methacryloylethyl vanillate to the liquid or silanized glass to the powder ingredient. Vanillyl methacrylate, when added to ingredients of dental composites inhibited polymerization.

(b) Cements prepared by mixing a syringate ester, n-hexyl vanillate and EBA with zinc oxide powder are rapid setting, water insoluble, possess high strength and adhere strongly to metal [4].

Because of the potentially caries-reducing syringate ingredient they should possess excellent biocompatibility. This should make them useful as insulating bases, pulp capping agents, root canal sealers, soft tissue packs or as intermediate restoratives.

(c) n-Hexyl vanillate-EBA-ZnO cements are compatible with acrylic monomers (dicyclopentenylloxyethyl methacrylate, cyclohexyl methacrylate). Such solutions mixed with powder, made up from silanized glass reinforcing agent and zinc oxide and containing suitable peroxide-amine initiator-accelerator systems, have good working properties and harden in a few minutes. Representative physical properties of the cements are given in Table 1. The cured materials have both compressive and tensile strengths one and a half to three times that of eugenol based intermediate restoratives. These cement-composites adhere strongly to

Table 1

Properties of Intermediate Restorative Materials

Powder: 1 part: 64% ZnO - 30% Al₂O₃ - 6% hydrogenated rosin
 1 part: silanized glass + 1% benzoyl peroxide
 Liquid: 1 part: 12.5% hexyl vanillate - 87.5% EBA
 1 part monomer + 1% N,N-dihydroxyethyl-p-toluidine + 0.02% BHT
 Powder/liquid ratio: 1.8g/0.2 mL

Percent of Monomer in Liquid	Setting Time min.	Strength, MPa*		Solubility %	Adhesion, MPa to Composite St. Steel	
		Compressive	Tensile			
Methyl methacrylate (MMA)	6	111.7 (20.6)	10.4 (0.7)	0.17	10.3±2.6	9.8±1.3
" " †	6	107.9 (5.2)	12.3 (0.3)	-	-	-
CM-657‡	8	104.3 (8.6)	13.2 (1.7)	0.24	7.0±2.2	11.7±1.0
65% dicyclopentenyl methacrylate + 35% MMA§	7	100.2 (10.3)	12.5 (2.1)	-	-	-
95% " " + 5% MMA	6.5	99.1 (17.3)	-	-	-	-
Isobornyl Methacrylate	8	105.3 (6.0)	15.2 (0.2)	-	-	-
Cyclohexyl Methacrylate	8.5	104.7 (8.6)	15.8 (2.0)	0.34	4.1±2.4	15.1±1.8
70% Cyclohexyl methacrylate + 30% MMA	8.5	106.7 (3.4)	13.2 (1.7)	0.53	7.3±1.6	15.6 ± 3.2
Commercial intermediate restorative (IRM)	7.5	62	5.2 (0.4)	1.11	0.1±0.1	1.1±0.2

* Average of 5 measurements ± standard deviation of 5 measurements

† Substituted 1% N,N-dimethylaminophenethanol for the 1% dihydroxyethyl-p-toluidine

‡ Dicyclopentenylmethoxyethyl methacrylate

§ Powder-liquid ratio 1.64/0.2 mL

composites, non-precious metals or porcelain (maximum 15.6 MPa). Rupture of the bond occurs as the result of cohesive failure. Incorporation of dimethacrylates into the liquid yields even stronger cements, but the cement liquid has poor storage stability. Because of their high strength and excellent adhesion, the cements, subject to their biocompatibility with dental tissues, show great promise as intermediate restorative resins and in the repair of fractured porcelain or porcelain to metal crown and bridges. A paper describing these studies was presented before the International Association for Dental Research in Sydney, Australia, August 1983. A manuscript has been prepared and is under editorial review prior to publication [5]. Three other talks discussing aspects of this investigation were given.

Phase II:

(1) Evaluation of the physical properties of various cements has been completed. See Phase I, part 2. A study of the bond strength of the cement to various substrates is nearing completion. Especially encouraging is the high bond strength of the cement to porcelain (maximum 6 MPa) which may lead to additional clinical uses of the cement.

Phase III:

(1) Vanillate and some syringate esters have been made available to over 25 preclinical investigators to pursue further studies. Two commercial organizations have synthesized larger quantities of hexyl vanillate.

(2) Pulp reactions to the cement have been completed [6] by Dr. Kafrawy at the University of Indiana. These reactions are similar to ZOE-based restoratives. When applied over exposed pulp the newly developed cements elicit milder reaction. A study of the effect of the cement

ingredients on the metabolism in dental pulp, which utilizes fresh bovine pulpal alkaline phosphatase acting on the artificial substrate p-nitrophenylphosphate has been completed by Dr. W. Bowles and co-workers at Baylor University.

Phase IV

(1) Studies of modification of dentin and enamel to improve bonding of vanillate-EBA-ZnO cement to tooth surface has been initiated. Moderate adhesion to acid-etched enamel (1.8 MPa) was obtained.

The following items are part of the sequential work plan of Phase IV and have not yet been initiated or completed:

(2) Evaluation of sealing properties (root canal sealer, etc.)

(3) Examine incorporation of fluoride into composition and study mechanical properties and fluoride release.

Phase V

(1) Preclinical studies on the tissue tolerance of syringate cements have been initiated.

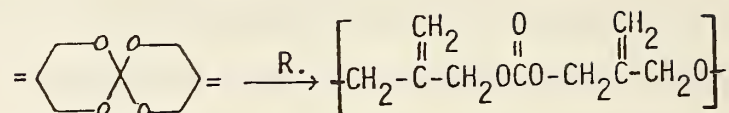
B. Monomers Which Expand on Polymerization

Objective

The objective of Part B of the study is to synthesize monomers which can be polymerized by free radical initiators to give expansion upon polymerization. The physical properties of the polymers and various copolymers obtained will be evaluated and correlated to the overall degree of expansion observed. Monomers will be synthesized to study the effect of ring size and substituent. The degree of expansion is directly related to the size of the rings in the spiro-ortho carbonate.

A simple, free radically cured, symmetrical spiro-ortho carbonate has previously been synthesized and the properties of the homopolymer

and several copolymers were evaluated.



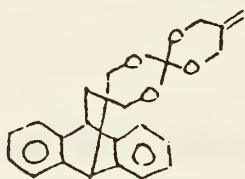
When a sufficient percentage of the spiro-ortho carbonate was included in a copolymer to yield zero polymerization shrinkage, the low glass transition temperature (T_g) of this component had an adverse effect on the physical properties of this material.

Progress Report

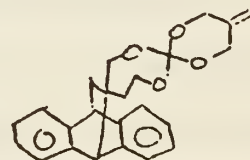
Phase I

The synthesis of several monomers that yield high T_g polymers is underway. Substantial quantities of the various intermediates necessary have been prepared and several attempts have been made to form the desired monomers. To date, the final step that forms the spiro group from the proposed reaction sequence has been unsuccessful in all cases. However, variations in this specific reaction have yet to be exhausted and alternative reaction pathways are under consideration.

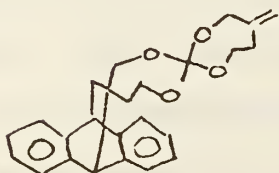
The monomers currently being synthesized include:



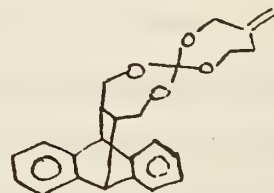
[5.5] Undecane



[6.5] Dodecane



[6.6] Tridecane I



[6.6] Tridecane II

This series of monomers, in addition to leading to high T_g polymers, will provide valuable information about the relative percentage of the double ring opening polymerization vs simple 1, 2, vinyl addition polymerization for various combinations of six and seven membered rings. The opening of two seven-membered rings is not only expected to be a more facile process, but should also result in a greater degree of polymerization expansion.

The following phases are part of the sequential work plan and have not yet been initiated or completed:

Phase II: Formulate composites and adhesive formulations with these monomers as ingredients.

Phase III: Evaluate the properties of such materials using standard specification tests.

Phase IV: Postulate optimal formulations and possible new monomers for dental applications.

C. Changes in Esthetic Properties of Dental Resins on Aging

Objective

The objective of Part C 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: Determine color changes of dental resins, plastic teeth and composites.

Evaluated exposure of plastic teeth and conventional, microfilled and photocured composites to Xenon (ISO Specification test, 150,000 lux intensity light source) and RS (ADA Specification test) light sources in air and under water. No change in color was observed for plastic teeth.

Some color change occurred when composites were exposed in air to the Xenon source. Placement of these specimens under water and exposure to this light source decreased the color change considerably. The magnitude of the discoloration decreased in the following order:

Specimens exposed to Xenon lamp in air > Specimens exposed to RS lamp in air > Specimens exposed to Xenon lamp under water.

Phase II: Analyze and establish the dependence of color change on different variables. This stage of work has not been completed to the point of reporting.

D. Adhesion of Coatings and Restoratives to Dentin and Enamel

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.

Phase II: Synthesize and evaluate adhesive properties of oligomers of 2-isocyanatoethyl methacrylate to dental tissues.

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

Due to the concentration of effort on parts A, B, C, and E, there was no progress achieved on this portion of the research other than that reported on in Phase IV, (1), of Part A.

E. Improvement of Dental Composite, Sealant and Cement Materials

1. Dental Resins for Hydrophobic Composites

Introduction

The solvent and/or chemical resistance of the polymeric matrices currently used in dental composites and sealants is expected to be a significant factor determining their service life in the oral cavity. The use of low surface energy resin binders based on highly fluorinated

methacrylates offers a reasonable method of altering the water sorption properties of dental composites and sealants and changing the solubility parameter of these materials to make them resistant to water and intra-oral derived chemicals that can lead to chemical softening and/or degradation. In addition, microleakage around margin gaps should be reduced because of the higher contact angles vs H₂O or saliva of the fluorinated copolymers compared to currently used organic binders.

Dental composites that were extremely hydrophobic but exhibited high polymerization shrinkage and relatively low diametral tensile and compressive strengths were formed from a fluid resin comprising 75 wt % 1,1,5-trihydrooctafluoropentyl methacrylate (OFPMA) and 25 wt % 2,2-bis-[p-β-methacryloxyethoxy)phenyl]propane (BIS-EMA), a non-hydroxylated homolog of BIS-GMA [7]. The deficiencies of these composites were mainly attributable to the high concentration of the comparatively small monomethacrylate, OFPMA, and the low concentration of the bulkier, crosslinking monomer, BIS-EMA (see Fig. 1).

This unique resin system, however, yields composites with many outstanding properties, e.g. high contact angles versus water, remarkably low water sorption and solubility, reduced marginal leakage, and resistance to plaque retention and surface staining [7- 10].

A major objective of this ongoing research is to develop alternate hydrophobic composite materials having, in addition to the excellent water-related properties of the OFPMA-based composites, improved physical and mechanical properties. To achieve these objectives new types of fluorine-containing resin systems were developed based on the use of a polyfluorinated prepolymer multifunctional methacrylate, PFMA, (Fig. 2), as the main monomeric component [11-13].

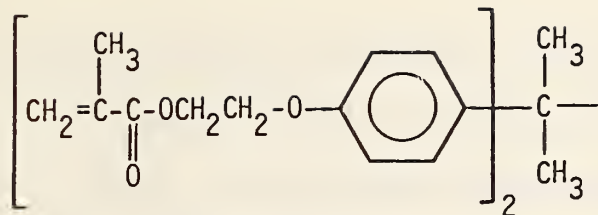
Phase I

(1) Synthesis of Monomers

and

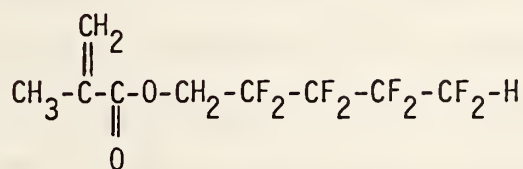
(2) Formulations of Hydrophobic Composites

Using experimental resins consisting of non-hydroxylated variants of BIS-GMA diluted with 1,10-decamethylene dimethacrylate (DMDMA) and minor amounts of the highly fluorinated monomethacrylate, pentadecafluorooctyl methacrylate (PDFOMA), it was possible to prepare dental composites having quite acceptable mechanical strength and average water sorption (0.41 mg/cm^2). Resins with significantly reduced water sorption (0.13 mg/cm^2) margin leakage were derived from experimental fluorine-containing resin systems based on the polyfluorinated oligomeric multifunctional methacrylate, PFMA, diluted with DMDMA or neopentylglycol



2,2-BIS[p-(β-methacryloxyethoxy)phenyl]propane

BIS-EMA

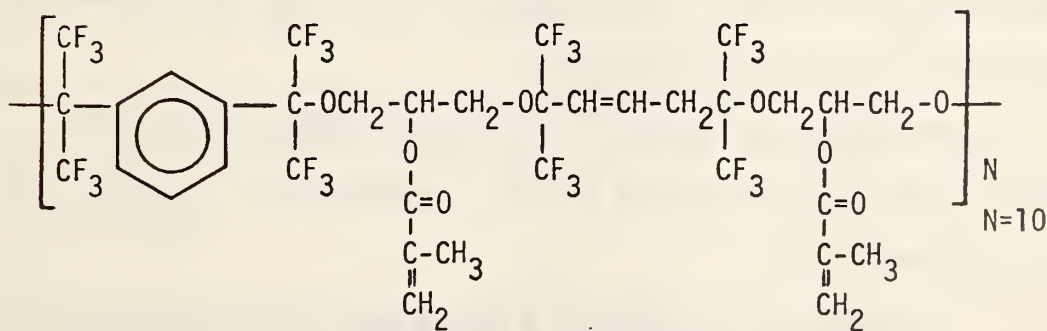


Percent F = 50.7, MW = 300

1,1,5-trihydrooctafluoropentyl
Methacrylate

OFPMA

Figure 1. Chemical structure of monomers used in formulation of Craig's hydrophobic dental resin system [7].



PFMA

MW of Repeating Unit = 1032

MW - 10,320

Percent F = 44.2

Figure 2. Chemical Structure of PFMA

dimethacrylate (NPDMA). By means of binary or ternary diluent systems consisting of one or two conventional dimethacrylate diluent monomers and a highly fluorinated monomethacrylate (e.g. octafluoropentyl methacrylate) it was possible to prepare fluoro-resins with extremely high contents of covalent fluorine (e.g. 42% by weight of resin). Composites based on these latter systems, which have adequate mechanical strength, will be evaluated for their water sorption and resistance to microleakage.

Two candidate diluent monomers designed to further improve the strength properties of PFMA composite were synthesized: the dimethacrylates of (a) 4,8-Bis(hydroxymethyl)tricyclo-[5.2.1.0^{2,6}] decane and (b) 2,2,4,4-tetramethylcyclobutandiol. Both of these monomers are compatible with PFMA.

Methodologies for the Assessment of Margin Leakage

During the course of this phase of our research project a comparative evaluation was made of the radioisotope (Ca^{45}) method and the newly developed silver nitrate method as techniques for assessing margin leakage (Wu, et al. [14]). The results of this study established the superiority of the latter methodology.

Two papers giving details of the preceding work were presented at the 1983 AADR meeting [15-16]. Manuscripts for publication are in preparation.

The Reduction of Residual Vinyl Unsaturation in Dental Resin Materials by Polythiol Additives

An important consideration for improved performance is the degree of cure of dental resins. Residual carbon-to-carbon double bonds in the polymerized resin component of dental composites and sealants are

potential sites for chemical degradative reactions (e.g. oxidation) which can lead to the discoloration and reduced service life of these dental materials. Using Fourier Transform Infrared Spectroscopy (FTIR) and previously described techniques, a comparative analysis of residual vinyl content in sealants and composites with and without PETMP was performed [17-21].

Extremely thin (50 μm) specimens of the sealant and composites were prepared between crossed glass slides and stored at 37°C in a 100% relative humidity chamber for specified times after polymerization.

The transmission infrared spectra of both the unpolymerized and the polymerized materials were obtained in the absorbance mode. The degree of polymerization (as the percent of reacted vinyl groups) was assessed by monitoring the change in the vinyl absorption band at 1637 cm^{-1} for each specimen [17-20].

Two experimental resin formulations, A and B (Table 2), having the indicated compositions were prepared. Polymeric films of each formulation were made by photopolymerization at 25°C using a visible light source (e.g. Caulk Lite, L. D. Caulk Co., Milford, DE) on specimens sandwiched between crossed glass slides. The time of irradiation was 5 minutes.

Table 2
Effect of PETMP on the Degree of
 Polymerization of Photocurable Sealant Resins

Components	Formulation A. (weight %)	Formulation B (weight %)
BIS-GMA	84.45	82.02
DHDM	14.90	14.48
N,N-dimethylamino-ethanol	0.45	0.00
Camphoroquinone	0.20	0.20
PETMP	0.00	3.30

The degree of polymerization, as determined by FTIR, was 52 and 63% for formulations A and B, respectively.

In addition, the effect of PETMP on the degree of polymerization of two commercial composites were investigated by the FTIR method. In the case of the photopolymerizable composite Durafil, (Kulzer and Co., GmbH, West Germany) the indicated amount of PETMP was added and blended by spatulation into a known weight of this single paste composite (Table 3). For the chemically activated two paste composite, Adaptic (Johnson and Johnson Dental Products, NJ, USA), PETMP was introduced by the addition and blending of a known amount of the polythiol into the accelerator (Universal) paste. As seen in Table 3 the use of relatively minor amounts of PETMP reduced the residual vinyl content or increased the degree of vinyl polymerization significantly. Polymerization was accomplished using the manufacturers' directions and the polymerized specimens were stored at 37°C and 100% relative humidity for the indicated storage times, t.

Table 3
Effect of PETMP on the Degree of Polymerization of Composites

Composite	Degree of Polymerization After Storage Time (t)		
	t=20 min	t=24 hrs	t=7 days
Durafil	37	43	43
Durafil + 4% PETMP	42	52	54
Adaptic	--	48	50
Adaptic + 0.5% PETMP	--	55	57

Initiator Systems Based on Polythiols and Hydroperoxides

As part of our overall program to improve dental composite and sealant materials, dental initiator systems based on hydroperoxides and polythiols are being investigated as methods to improve their storage and color stability. It has been known that two paste dental composite formulations based on benzoyl peroxide as the polymerization initiator possess relatively poor storage stability at ambient temperatures. At temperatures higher than those usually found in clinical usage (e.g. in transport, warehouses, military or similar field situations) the relatively unstable benzoyl peroxide will decompose prematurely at a still faster rate.

Another drawback of the usual paste/paste composites based on benzoyl peroxide is their use of a color-prone tertiary aromatic amine in the accelerator paste as the activator or promotor designed for the rapid decomposition of this peroxide into initiating radicals [21]. In view of these shortcomings, it would be desirable to have a dental initiator system of enhanced storage and color stability. The aim of this study was to design such a system based on the use of the more stable organic hydroperoxides, namely cumene hydroperoxide, and color-stable polythiols such as PETMP. The ancillary benefit of reduced vinyl unsaturation (see above) is another advantage of this type of initiator system. [22].

The accelerative effect of PETMP on the ambient decomposition of cumene hydroperoxide into initiating radicals was investigated by the formulations employing varying amounts of PETMP in the accelerator paste and 2% (weight percent) cumene hydroperoxide in the initiator paste. In addition, small amounts (5-20 ppm) of redox metals such as copper and iron, in their higher valence states (e.g. Cu^{+2} , Fe^{+3}), were added to some of the initiator pastes in form of organosoluble salts such as cupric and ferric

benzoylacetates. Typical formulations are illustrated in Table 4:

Table 4. Typical formulation of two paste systems investigated with PETMP additions

<u>Accelerator Paste</u>		<u>Initiator Paste</u>	
Components	Weight Percent	Components	Weight Percent
BIS-GMA	12.59	BIS-GMA	13.70
TEGDMA	5.39	TEGDMA	5.88
PETMP	2.00	CHP	0.40
BHT	0.02	BHT	0.02
Silanized Glass Filler (325 mesh)	80.00	Silanized Glass Filler (325 mesh)	80.00

On mixing equal parts of each paste in the usual fashion at room temperature a composite with the following properties was obtained: setting time (Gilmore Needle test) at 37°C and 100% relative humidity = 4 minutes, diametral tensile strength (5 specimens) = 43 MPa. In addition, these composite specimens have excellent esthetics and color stability. A paste/paste formulation similar to that shown above but with only 1% PETMP in the accelerator paste gave on mixing with the above initiator paste a composite of similar properties except the setting time was now 7.5 minutes. Formulations with intermediate amounts of PETMP (between 1 and 2%) gave setting times intermediate between 7.5 and 4 minutes. By the use of 10 ppm of cupric or ferric ions in the above initiator paste, composites having excellent esthetics and good strength (diametral tensile strength = 47 MPa) were obtained. The setting times obtained with the 2% and 1% PETMP accelerator pastes were now 2 and 4 minutes, respectively.

Non-Aqueous Polycarboxylate Cements

Introduction

Non-aqueous polycarboxylate cements based on dimer and trimer acids provide the potential for less soluble, non-brittle, cements which

incorporate calcium hydroxide, zinc oxide or other metal oxides and/or hydroxides. Conventional polycarboxylate cements are based on the acid-base of reaction of aqueous solutions of poly(alkenoic acids) such as poly(acrylic acid) and a basic inorganic powder (e.g. zinc oxide, ionomer glass). The polymeric matrices that form are ionically crosslinked by divalent and/or trivalent metal ions (i.e. Zn^{+2} , Ca^{+2} , Al^{+3}) and are characterized by their rigidity and hydrophilicity. Their most noteworthy property is probably their adhesiveness to tooth structure and base metals [23-24].

Objective

In an effort to develop a cement that is tough and ductile and less susceptible to the erosive effects of oral fluids, we have explored the feasibility of obtaining cements from dimer (DA) and trimer acids (TA) and various metal oxides and/or hydroxides (e.g. ZnO , CaO , $Ca(OH)_2$, MgO , etc.). DA and TA are moderately viscous liquid polyacids of high molecular weight possessing a unique chemical structure consisting of a bulky, flexible hydrophobic, hydrocarbon core which terminates in 2 and 3 hydrophilic carboxyl groups ($-CO_2H$), respectively. Because of the relatively low carboxyl content, large size and hydrophobic nature of these acids the corresponding cements should possess excellent biocompatibility.

Phase II

(1) Develop improved coupling agents for fillers (such as dual silanization). This part of Phase II has been postponed to pursue Parts 2 and 3, which follow.

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

Cements having clinically acceptable setting times, and good physical and mechanical properties were obtained from base powders containing calcium hydroxide, magnesium oxide and zinc oxide.

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

DA admixed with Ca(OH)_2 in a powder/liquid ratio of 1.5 gave a fast-setting cement (3 min.) with 24-hr compressive (CS) and diametral tensile strengths (DTS) of 25 and 4 MPa, respectively. The DA- Ca(OH)_2 cement had a low water solubility of only 1.5% after 24 hours at 37°C; the water after this period of storage was alkaline which should protect pulpal tissues from acid attack and stimulate secondary dentin formation. Under compressive stress (crosshead speed = 1 mm/min) specimens of this cement do not fracture but show significant deformations. A TA- Ca(OH)_2 cement behaved similarly. The addition of 17% tricalcium phosphate to a DA- Ca(OH)_2 formulation (P/L=2) gave a stronger material that hardened in 7 min and deformed only slightly under the usual compressive stress (CS=32, DTS=6 MPa). The absence of brittle failure is indicative of the non-friable nature of these cements. Thus far, the strongest DA- Ca(OH)_2 cement obtained consisted of a base powder comprising equal parts of $\text{Ca}_3(\text{PO}_4)_2$, Ca(OH)_2 and MgO (P/L=2); CS=41; DTS=6MPa. The energy-absorbing nature of all these Ca(OH)_2 cements makes them appealing for potential use as cavity liners, endodontic sealers, impression materials, etc. The strength and solubility characteristics of these Ca(OH)_2 cements is superior to those currently available.

DA and TA with micronized zinc oxide (P/L=7) yielded tough, extremely hydrophobic cements (solubility = 0.1%, setting time = 7.5 min) CS=50, DTS=7MPa) which may find use in temporary and intermediate restorative formulations. Because these cements do not inhibit the polymerization of composites they are amenable to the formulation of hybrid composite-cement materials. The setting mechanism of these novel polycarboxylate cements involves primarily chain extension through the formation of multi-divalent metal carboxylate linkages. The versatile nature of cementitious materials obtained from DA and TA with different base components suggests a wide range of potential dental applications.

In subsequent work we plan to explore the use of various reinforcing fillers with these cements, the effect of other acids as additives and their adhesion to various substrates.

The following phases have not yet reached the stages of reporting.

Phase III

- (1) Selection and development of systems having clinical potential.
- (2) Determination of 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

This part of the annual report involves the performance evaluation of dental composite restorative materials using in vitro wear testing, hardness measurements, and diffusion and glass transition studies. With the wear and hardness measurements the general procedure was to presoak the specimens in chemical food simulating or oral environmental liquids which may damage either the polymer matrix or inorganic filler. Sufficiently extensive damage will decrease both surface hardness and wear resistance. The diffusion studies are done to assess the rate and degree of penetration of these liquids into the polymer or composite. Since diffusion and degree of cure are apparently controlled by the glass transition process, dynamic mechanical measurements have been initiated on dental polymers. From these measurements the glass transition temperature and dynamic modulus are obtained, the latter of which is useful to assess the rigidity of these materials above and below the glass temperature.

This task is divided into the following parts:

- A. Wear and Hardness Measurements
 - 1. Effect from conditioning in chemical food simulating solvents
 - 2. Effect from conditioning in oral environmental acids
 - 3. Influence of degree of cure
- B. Solvent Diffusion Rates
- C. Glass Transition Studies

A. Wear and Hardness Measurements

Introduction

From past research (here and in other laboratories) we have determined that in vitro wear measurements on unconditioned dental composites are not appropriate to assess in vivo durability. Microdefect analyses, involving a silver staining technique [25] revealed surface damage on both stress bearing and non stress bearing regions of in vivo restorations. These results indicate that the chemical environment plays an important role in the degradation of composite restorations. We have found that in vitro wear resistance decreases after the composites are stored in certain food simulating or oral environmental liquids for a sufficient time.

Objective

The objective of this task is to identify in vivo wear and degradation mechanisms of dental composite restorative materials. The results are expected to facilitate the development of new dental composites as described in, for example, Task I of this report.

Progress Report

The wear measurements were made on a classical pin and disc apparatus [26] where the pin is stainless steel and the disc is the specimen. The apparatus is interfaced to a microcomputer and requires no attention during the entire wear run (usually 30 h). Measurements on each of the three rotors are taken at arbitrarily selected intervals (usually 1 h), at which 10 track depths are measured at equidistant positions around the track circumference. The average track depth (over 10 positions) is taken to be a reliable measure of the volume of material removed. Distilled water at 37°C flows over the specimen surfaces at all times.

Each polished composite disc specimen was soaked in one of the chemical liquids at 37°C for one week prior to wear testing. Knoop hardness measurements were made immediately before and after the soaking period. Two kinds of preconditioning chemical liquids were used: food simulating organic solvents, which are likely to swell or dissolve the matrix, and oral environmental acids which may attack the glass or coupling agent, thus weakening the interface.

1. Effect from Conditioning in Chemical Food Simulating Liquids

In this phase of the wear measurements the specimens were stored for one week in the food simulating liquids (designated by the FDA[27]) with solubility parameters ranging from 1.5×10^{-4} to $4.8 \times 10^{-4} \text{ J}^{1/2} \text{ m}^{-3/2}$ [28]. These liquids comprise heptane (1.51×10^{-4}) and aqueous solutions of 100, 75, 50, 29, and 0% (4.79×10^{-4}) ethanol. Four different commercial dental composites were evaluated: Adaptic, Profile, Prisma Fil, and Silar. These are a conventional, strontium glass filled, visible light activated, and microfilled composite, respectively.

Although the general wear behavior is too complicated for presentation here, it can be said that the largest increases in wear rates and decreases in hardness occurred for the specimens soaked in the 75% ethanol in water solution. The solubility parameter value for this mixture is $3.15 \times 10^{-4} \text{ J}^{1/2} \text{ m}^{-3/2}$. The value for BIS-GMA, which is commonly used as a dental resin is expected to approximate this value. This result implies that any liquid food ingredient for which the solubility parameter approximates the value above is likely to enhance in vivo degradation of BIS-GMA based composites.

2. Effect from Conditioning in Oral Environmental Acids

It has been suspected that some damage to dental composites may result from hydrolysis at the inorganic filler when exposed to acids commonly present in the oral environment. Degradation of this kind may apply in particular to some of the radiopaque composites for which their glasses, or radiopaque ingredients, are not as resistant to acid attack as, for example, quartz in conventional composites. Four commercial composites are being studied, namely, Adaptic, Adaptic Radiopaque, Profile, and Fulfil. The last three are radiopaque. Fulfil is both radiopaque and visible-light-activated. The acids employed are citric, pH= 2.62; lactic, pH=2.67, and acetic, pH=3.33. All solutions are 0.02 normal. The specimens are stored in these acids for one week at 37°C. Knoop hardness measurements are taken immediately before and after storing followed by the wear measurements.

Preliminary results indicate that for Adaptic (not radiopaque) the hardness is unaffected by the acid treatment, and the hardness of Adaptic Radiopaque is marginally decreased. Profile reveals a considerable decrease and even shows a slight decrease after storing in distilled water. The hardness of Fulfil is essentially unchanged by the acids. No significant changes were observed on any of the specimens stored in air at 37°C.

The wear analyses is not sufficiently complete to form general conclusions. One result which is evident, however, is that the wear of Profile is enhanced considerably when stored in either acids or distilled water over that when stored in air or heptane.

3. Influence of Degree of Cure

Recent investigations [29] indicated that the viscosity of the

monomer is the primary factor on limiting the degree of cure of polymeric resins. Since viscosity, in general, decreases with increasing temperature, the degree of cure may be increased by increasing the cure temperature. Increasing the degree of cure of a polymer will inhibit diffusion of solvents and also make the polymer more solvent resistant.

Specimens of Adaptic, Prisma Fil, and Silar were cured at various temperatures between 25 and 80°C. Specimens were stored for one week in water and 75% ethanol-25% water at 37°C. The 75% solution was chosen because it had the greatest effect on the wear of the BIS-GMA based composites. With the water soaked specimens there was essentially no improvement in hardness and wear resistance with increasing cure temperature. With the 75% ethanol considerable improvement in these properties with cure temperature was noted in all cases. The greatest improvement was noted for Silar, presumably because it is a microfil and has the largest matrix-filler ratio.

Although increasing the degree of cure by increasing the cure temperature may be taken to be impractical for in situ restorations, this study has given us insight on the relation between degree of cure and durability. More sophisticated methods, such as the changes in chemical formulation as mentioned in Section I, are being undertaken.

B. Solvent Diffusion Rates

Introduction

Based on the findings of our previous studies on clinical and laboratory dental composite specimens, the penetration of solvents and subsequent swelling of dental composites by the water mixtures of certain ingredients in the oral environments plays an important role in the in vivo wear process. Thus far no systematic data of the diffusion

process in dental composites is available.

Objective

1. Develop a precise measurement of both the diffusion coefficient and the degree of swelling of dental composites.
2. Elucidate the dependence of the diffusion process on the structure of composites in order to identify those structural parameters which will minimize both the rate and the degree of swelling.

Progress Report

The equipment for measuring the diffusion coefficient and swelling ratio has been completed. Isothermal diffusion processes can be monitored routinely, and the results are digitalized, stored and analyzed using a Bascom Turner Recorder.

Four commercial dental composites and seven experimental composites have been studied so far; the major findings will be presented as follows:

1. The diffusion process of water into the BIS-GMA base dental composites is of Fickian type; hereafter, the diffusion process of water in all other dental composites can be calculated according to the well established Fickian behaviors.
2. The water diffusion coefficient of the composites is not suppressed by the presence of fillers (in fact, it is slightly higher) in all but one of the composites studied so far. A weak filler matrix interface in the current dental composites is likely to be the cause of this anomaly.
3. The diffusion process of ethanol and the other substances with swelling power in dental resins is of non-Fickian type. In contrast to the Fickian behavior, detailed experimental data are required for almost each material.

4. The presence of fillers suppresses the degree of swelling considerably.

5. Enhancement of the degree of cure of the resin component in dental composites impedes the diffusion process.

6. The diffusion rate in the composites containing polythiols and fluorinated monomers is lower than that of the ordinary composites.

C. Glass Transition Measurements

Introduction

As stated earlier the ultimate degree of cure at a given cure temperature T_c is controlled by viscosity. The curing essentially stops when the viscosity reaches a critical value at which molecular diffusion ceases. At this point reactive groups cannot become proximate as required to crosslink. Eventually they are consumed in other ways, and the cure is terminated prematurely. Since viscosity is controlled by the glass transition temperature T_g , which may be taken to represent an isoviscous state, T_g measurements are expected to be indicators of the final limited degree of cure for the following reason. During an isothermal curing process T_g increases to a value which is expected to approximate the cure temperature T_c . At this point the molecular diffusion ceases and the reaction essentially terminates.

Objective

To make dynamic mechanical and Fourier Transform Infrared (FTIR) measurements appropriate to evaluate the glass transition and curing mechanisms of dental resins. In addition the forthcoming moduli values at temperatures above and below T_g are useful performance indicators.

Progress Report

Experimental activity on this project was initiated recently. The technique is mechanical spectroscopy using a Weissenberg Rheogonimeter to obtain the complex shear modulus $G^* = G' + iG''$ as a function of curing time and subsequently temperature. The frequency of forced torsional oscillation is 0.60 Hz. The specimens are torsional braids impregnated with the activated monomer. G^* is monitored during the isothermal curing process. At some time after the cure appears to stabilize a temperature scan is made. The temperature at which the ratio $G''/G' = \tan \delta$ reaches a maximum is taken to be the glass transition temperature of the specimen. If the cure is terminated, repetitive scans will give the same value of T_g .

Preliminary measurements have been made on a 70% BIS-GMA - 30% TEGDMA resin cured at 37°C. Measurements will be made at higher cure temperatures. Similar measurements will be made on other polymers under development.

Conclusions

The results summarized in this part of this report indicate certain directions to be taken in the design of new dental polymers. One approach as indicated by the wear and hardness data is to increase the degree of cure. In particular this produces a more insoluble polymer and reduces the diffusion of certain substances present in the oral environment. Since increasing the degree of cure by increasing the cure temperature may be considered to be impractical for in situ restorations, alternatives must be found.

One possibility to increase the degree of cure is to make use of flexible chain polymers with lower values of $T_{g\infty}$, which is the value of T_g for a complete cure. A smaller $T_{g\infty} - T_c$ is expected to produce a

larger degree of cure. The limitation on the smallness of $T_{g\infty}$ is the production of a rubbery polymer which would be impractical as a dental material.

Another possibility to make polymers resistant to swelling on oral solvents is to obtain one with a solubility parameter value out of range of those encountered in foods and the oral environment. For this reason fluorinated polymers are being investigated as described in Section I. These polymers are expected to have solubility parameters less than that of heptane ($1.51 \times 10^{-4} \text{ J}^{1/2} \text{ m}^{-3/2}$).

III. Dental Alloys and Ceramics

The evolution of dental casting alloys for fixed partial dentures and crowns (with and without ceramic or other veneers) has progressed steadily to nonprecious alloys and toward new noble and low noble alloy formulations. New alloys are sought which not only possess improved properties and handling characteristics but which are also more price-stable, supply stable and more readily controlled in processing. The predictability of performance becomes a major factor for development of new systems. Hence the development of more useful and reliable techniques for evaluation and identification of critical performance parameters is of key importance. The objective of the present investigation is directed toward development of standard test methodologies which will meet the needs of the dental industry/ profession in development and control of alloy and ceramic products, both as starting materials and in processing through to final systems as dental prostheses.

This project is divided into three major parts: A. Porcelain-Alloy Compatibility; B. Castability of Dental Alloys; and C. Solderability Evaluations.

A. Porcelain-Alloy Compatibility

Phase I

1. Work in this area has proceeded according to schedule. The temperature dependence of the elastic moduli, E , for two dental porcelains were determined and are shown in Table 5. These two porcelains are expected to represent extremes in structure, based on Raman Spectroscopy.

Table 5
Data for Vita- and Ceramco-Porcelain

E (GPa) of temperature, precise to $\leq 1.5\%$ at $P < .05$

	20°C	100°C	200°C	300°C
Ceramco	69.9	69.6	68.1	67.7
Vita	69.4	68.7	66.8	66.1

A paper on this was presented at the 1982 AADR meeting [30] and a manuscript is being prepared for publication.

2. The computer program for finite element modeling of porcelain veneered split metal rings has proceeded to the point of near final reconstruction. Methods are being developed for inputting data on physical and mechanical properties such that the data can be utilized by the program to simultaneously develop stress and temperature profiles. After the program is in the stage of running with properties of materials, analyses will be conducted to determine how precisely each property must be known; this will delineate which, if any, material properties need more precise determination.

Phase II

1. Porcelain-to-Metal Bond Strength

Data is acquired by means of a four point, bending beam composite. Fracture strengths are calculated using simple composite-beam theory. It has been found that a cumulative failure plot for fractures of all specimens from one system is effective in representing the data from each system (Fig. 3). A two parameter Weibull curve provides a reasonably good fit to the data. At present systems that could not be distinguished from each other on application of normal distribution (of test data) statistics are distinguishable from each other by use of Weibull

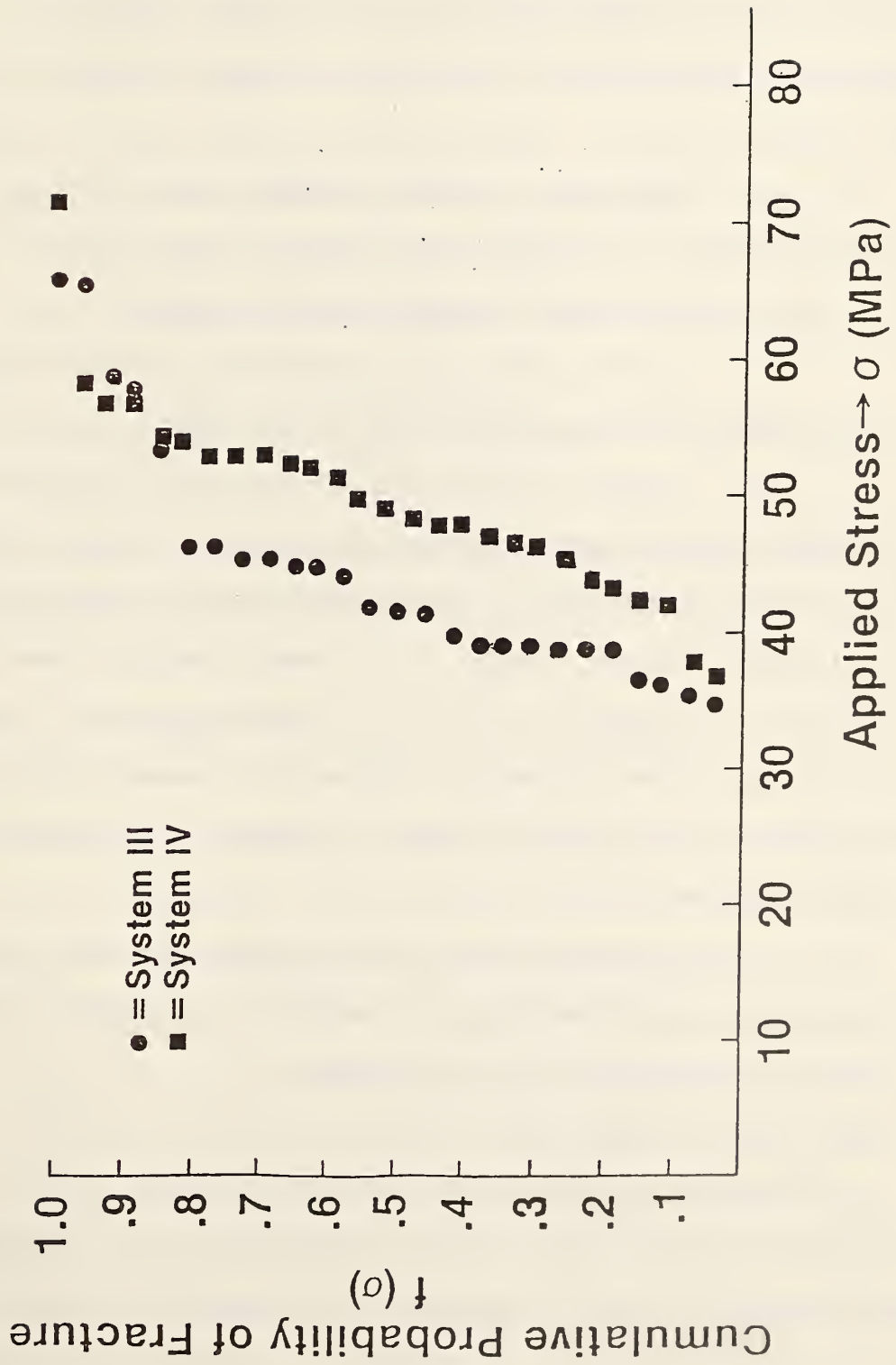


Figure 3 . Probability of failure at a given stress, $f(\sigma)$ vs stress

analysis, which recognizes the statistical nature of the failure of glassy materials.

2. Finite element analyses have been conducted for the bending beam composite: a three dimensional brick element program and a two dimensional plane stress program were constructed. Results of calculations show:

a. Beam theory provided reasonably good calculations of fracture stresses, (to within ~6% for elastic modulus ratios, $E_{\text{metal}}/E_{\text{porcelain}} \cong 2$, and better agreement for lower ratios.)

b. Fractures observed in experimental porcelain-alloy combinations agree with those expected from the calculated stress fields.

c. Stresses around cracks, in porcelain, that terminate at a horizontal porcelain-metal junction are expected to either produce lifting of the porcelain from nonprecious metal (high modulus) if the bond is \lesssim the porcelain fracture strength or to produce checked patterns if the alloy has a low modulus, $\sim E_{\text{porcelain}}$. This indicates that qualitative observations of bond failure are inadequate for comparing fracture from high modulus metal substrate systems vs fracture from low modulus metal substrate systems.

3. Other theoretical curve fitting methods are under consideration, for example, using higher Weibull parameters, to determine if additional information may be developed from the data.

B. Alloy Castability

A technique for determining a castability value, C_V , for a dental alloy has been described in previous reports [31]. C_V is determined as the percentage of cast alloy segments which comprise a rectangular grid. The castability value, C_V , is considered as indicative of the ability of

an alloy to fill a mold of this pattern under specific conditions of mold and alloy temperature among other variables.

Application of the aforementioned technique has been applied to six dental alloys, each of a unique composition. Mold and alloy temperatures were varied with other conditions held constant. According to the projected phases of development the following progress has been made:

- (1) Statistical and functional representation of castability:

Using the previously determined [31] transformation of

$$C_v \text{ to } C_{v_t} \left(C_{v_t} = \ln \frac{2/3 + \sqrt{C_v}}{2/3 + \sqrt{1-C_v}} \right), \text{ numerous functions were}$$

evaluated for their ability to represent C_{v_t} as a function of alloy casting temperature T_A and mold temperatures, T_m . The function

$$C_{v_t} = a + bT_A^{1/2}T_m^2, \text{ where } T_A = T_{\text{alloy}} - T_{\text{melting}},$$

was found to represent the castability of each alloy at the 99.95% confidence level; the constants a and b are characteristic for each alloy. Figs. 4 through 9 show the castability for several alloys and the constants a and b are given in Table 6. Because of the reasonably wide range of composition of the nickel based alloys investigated it is expected that equation 1 may be universally applicable to nickel based alloys. The usefulness of eq. 1 for alloy development and/or quality control (manufacturer and dental laboratory) may be noted by recognition that only two determinations of C_v (and hence C_{v_t}) are necessary to com-

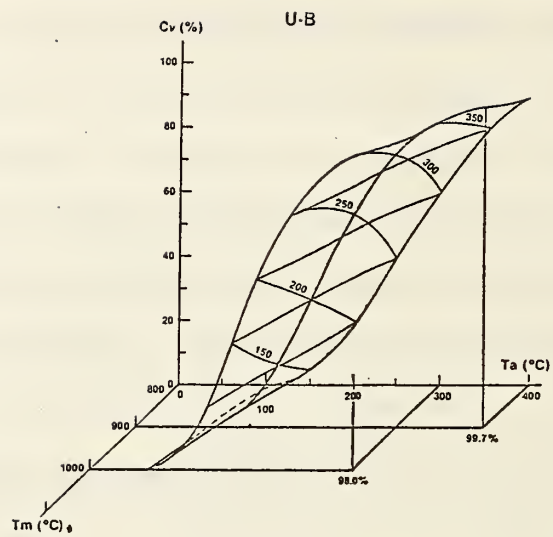


Figure 4. Regression curve surface obtained for U-B

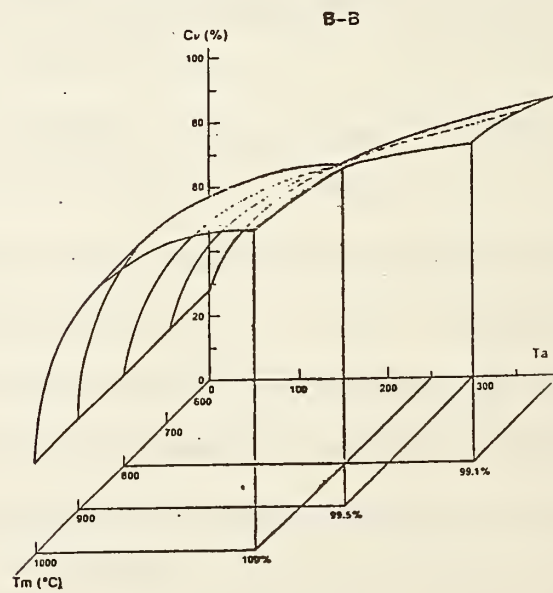


Figure 5. Regression curve surface obtained for B-B

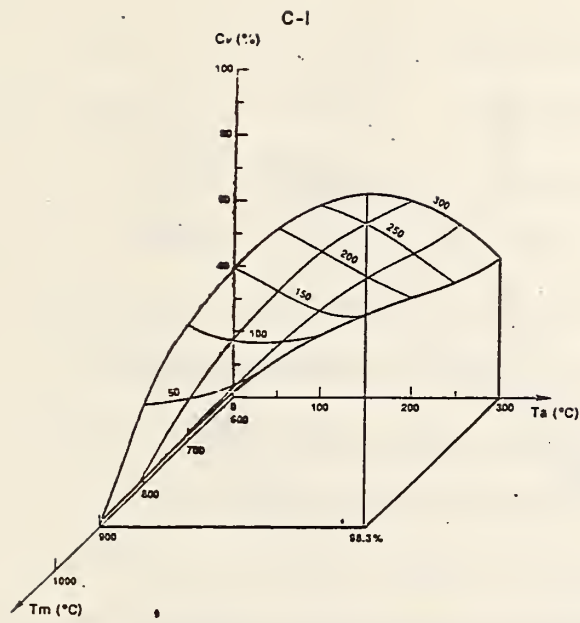


Figure 6. Regression curve surface obtained for C-1

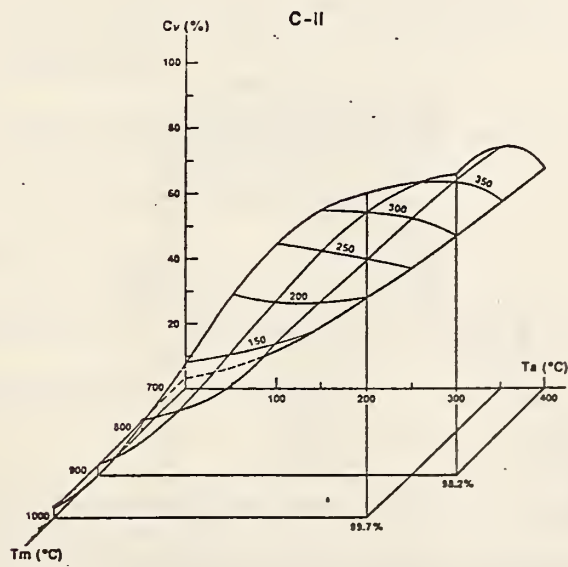


Figure 7. Regression curve surface obtained for C-11

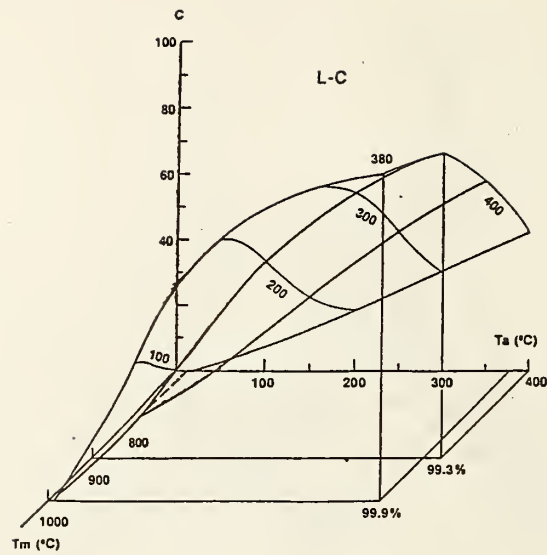


Figure 8. Regression curve surface obtained for L-C

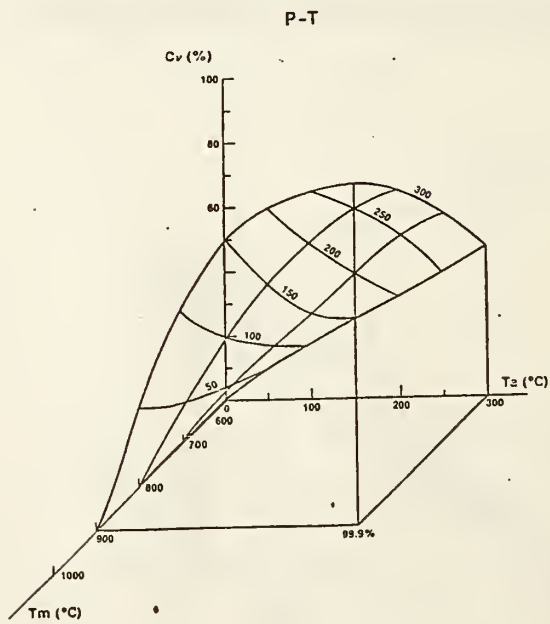


Figure 9. Regression curve surface obtained for P-T

pletely define C_v and C_{v_t} as functions of T_A and T_M (by evaluation of the constants a and b).

Further studies on newer alloy systems, such as palladium based alloys, are planned for the future. A manuscript on evaluation of C_v and C_{v_t} has cleared internal review and was submitted to J. Dent. Res.

(2) Multivariant analysis of effects of composition on castability.

Chemical analyses of each alloy are in progress. For any alloy, the castability, C_v , may be written as $C_v = A_0 + \sum_i b_i N_i$, where N is the weight percent of the i th element and A_0 and b_i are constants. A similar expression may be written for the transformed value of C_v , i.e. C_{v_t} . From this $\frac{\partial C_v}{\partial N_i} = b_i$. But $C_v = f(T_A, T_M)$; hence, $b_i = g(T_A, T_M)$ and the effect of each element on castability depends on T_A and T_M . The significance of the expected result is that by this approach, alloy design may be expedited via application of the temperature dependent effects of each element on castability.

Multivariant analysis for the nickel based alloys is expected to be completed by the end of FY84.

C. Solderability

Due to concentration of efforts on Parts A and B, no progress was made in this area for FY83.

Table 6
Values for the characteristic constants, a and b for different alloys

Alloy	a	b
Biobond	-0.09652	0.006484
Ceramalloy	-0.72939	0.010528
Ceramalloy II	-1.11902	0.011586
Litecast	-1.04606	0.009962
Pentillium	-0.81135	0.012137
Unibond	-1.15618	0.011071

References

1. Brauer, G. M.; Stansbury, J. W.; and Argentar, H.: Development of High-Strength, Acrylic Resin-Compatible Adhesive Cements, J. Dent. Res. 62, 366-370, 1983.
2. Brauer, G. M.; Argentar, H.; and Stansbury, J. W.: Cementious Dental Compositions Which do not Inhibit Polymerization, U. S. Patent 4,362,510, Dec. 7, 1982.
3. Stansbury, J. W.; and Brauer, G. M.: Divanillates and Polymerizable Vanillates as Ingredients of Dental Cements. Microfilm, Proc. Dent. Mat. Gp., AADR, Cincinnati, O. March 1983.
4. Brauer, G. M.; and Stansbury, J. W.: Cements Containing Esters of Syringic Acid, o-Ethoxybenzoic Acid and Zinc Oxide, Submitted to J. Dent. Res. for publication.
5. Brauer, G. M.; and Stansbury, J. W.: Intermediate Restoratives from n-Hexyl Vanillate-EBA-ZnO-Glass-Composites, Microfilm, Proc. Dent. Mat. Gp., IADR, Sydney, Australia, August 1983.
6. Kafrawy, A. H.: Private communication.
7. Douglas, W. H.; Craig, R. G.; and Chen, C. J.: A New Composite Restorative Based on a Hydrophobic Matrix, J. Dent. Res. 58, 1981-1986, (1979).
8. Craig, R. G.: Selected Properties of Dental Composites, J. Dent. Res. 58, 1544-50 (1979).
9. Douglas, W. H.; Chen, C. J.; and Craig, R. G.: Neutron Activation Analysis of Microleakage Around a Hydrophobic Composite Restorative, J. Dent. Res. 59, 1507-1510 (1980).

10. Douglas, W. H.; and Craig, R. G.: Resistance to Extrinsic Stains by Hydrophobic Composite Resin Systems, *J. Dent. Res.* 61, 41-43 (1982).
11. Antonucci, J. M.; Griffith, J.; Peckoo, R. J.; and Termini, D.: Synthesis of Polyfluorinated Polymethacrylates for Dental Applications, Abst. No. 599, *J. Dent. Res.* 58, Spec. Issue A (1979).
12. Antonucci, J. M.; New Monomers for Use in Dentistry, *Organic Coatings and Plastic Chemistry (ACS)* 42, 198-203 (1980).
13. Antonucci, J. M.: New Monomers for Use in Dentistry, *Biomedical and Dental Applications of Polymers*, Eds. Gebelein, C. G. and Koblitz, F. F., Plenum Press, NY, NY, 357-371 (1981).
14. Wu, W.; Cobb, E.; Dermann, K.; and Rupp, N. W.: Detecting Margin Leakage of Dental Composite Restorations, *J. Biomed. Mat. Res.* 17, 37-43 (1983).
15. Antonucci, J. M.; Benz, S.; Stansbury, J. W.; Dudderar, D. J.: Formulation and Evaluation of Fluorine-Containing Composite Resins, *J. Dent. Res.* 62, Abst. No. 1041, Annual Session AADR, March, 1983, Cincinnati, Ohio.
16. Venz, S.; Rupp, N. W.; and Antonucci, J. M.: Microleakage and Water Sorption of Hydrophilic and Hydrophobic Dental Composites, *J. Dent. Res.* 62, Abst. No. 766, Annual Session AADR, March, 1983, Cincinnati, Ohio.
17. Ruyter, I. E. and Gyorosi, P. P.: An Infrared Spectroscopic Study of Sealants, *Scand. J. Dent. Res.* 84, 396-400, 1976.
18. Ruyter, I. E.; and Svendsen, S. A.: Remaining Methacrylate Groups in Composite Restorative Materials, *Acta. Odontol. Scand.* 36, 75-82, 1978.

19. Stupp, S. I.; and Weertman, J.: Characterization of Monomer to Polymer Conversions in Dental Composites, IADR Prog. & Abstr. 58, No. 949, 1979.
20. Ferracane, J. L.; and Greener, E. H.: FTIR Analysis of Conversion in Unfilled BIS-GMA Resins: Methods Comparison, J. Dent. Res. 62, Abst. No. 1049, Annual Session, AADR, March, 1983, Cincinnati, Ohio.
21. Antonucci, J. M.; Grams, C. L.; and Termini, D. J.: New Initiator Systems for Dental Resins Based on Ascorbic Acid, J. Dent. Res. 58, 1887-1899, 1979.
22. Antonucci, J. M.; Stansbury, J. W. and Dudderar, D. J.: Dental Resin and Initiator Systems Based on Polythiols, J. Dent. Res. 61, Abst. 824, 60th General Session, IADR, March, 1982.
23. Smith, D. C.: A New Dental Cement, Brit. Dent. J. 125, 581-584 (1968).
24. Wilson, A. D.: Ionic Polymer Gels in Dentistry, Biomaterial and Dental Applications of Polymers, Eds. Gebelein, C. G. and Koblitz, F. F., Plenum Press, NY, NY, 419-426 (1981).
25. Wu, W.; and Cobb, E.: A Silver Staining Technique for Investigating Wear of Restorative Dental Composites, J. Biomed. Mat. Res. 15: 343-348, 1981.
26. McKinney, J. E.: Apparatus for Measureing Wear of Dental Restorative Materials, Wear 76: 337-347, 1982.
27. FDA Guidelines for Chemistry and Technology Requirements of Indirect Food Additive Petitions, March 1976.
28. Brandrup, J.; and Immergut, E. H., Eds.: Polymer Handbood, 2nd Edition, New York, John Wiley & Sons, 1975, Chapt. IV, pp 347-358.
29. Wu, W.; Post Curing of Dental Restorative Resin, Poly. Eng. & Sci., 23 (13), 704 (1983).

30. DeRijk, W. G.; Tesk, J. A.; Conner, M.; Jennings, K. A.; and Widera, G.E.O.: Porcelain to Metal Bond Strength Measurements as Determined by the Four Point Bending of a Composite Beam. J. Dent. Res. #62, Abst. 777, March 1983.
31. Cassel, J. M.; Tesk, J. A.; Brauer, G. M.; Antonucci, J. M.; Wu, W.; and McKinney, J. E.: Properties and Interactions of Oral Structures and Restorative Materials NBSIR 82-2623(NIH) 1982.

ABSTRACTS SUBMITTED FOR 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. Käse, S. Hirano, J. A. Tesk and T. P. Hoepfner.
- Elastic Constants of Nonprecious Alloys at Room and Elevated Temperatures, H. R. Käse, 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.

ABSTRACTS SUBMITTED FOR IADR AND AADR MEETINGS - 1983

Effect of Degree of Cure on Hardness and Wear of Three Commercial Dental Composites, J. E. McKinney and W. Wu.

Microleakage and Water Sorption of Hydrophilic and Hydrophobic Dental Composites, S. Venz, N. W. Rupp and J. M. Antonucci.

Effect of Elastic Modulus on Stresses in Ceramo-metal Systems, J. A. Tesk, R. W. Hinman, W. DeRijk, and H. R. Käse.

Divanillates and Polymerizable Vanillates as Ingredients of Dental Cements, J. W. Stansbury, G. M. Brauer and J. M. Antonucci.

Dental Cements Containing Hexyl Syringates, G. M. Brauer and J. W. Stansbury.

Factors Controlling the Degree of Polymerization in Dental Resins, W. Wu.

Formulation and Evaluation of Fluorine-Containing Composite Resins, J. M. Antonucci, S. Venz, G. M. Brauer, J. W. Stansbury and D. J. Dudderar.

Functional Representation of a Castability Value, C_v , for Dental Alloys, R. W. Hinman, J. A. Tesk, H. Argentar, and S. Hirano.

Castability of Dental Alloys, Repeated Casting, Mold and Alloy Temperature Effect, S. Hirano, J. A. Tesk, and R. W. Hinman.

Elastic Constants of Two Dental Porcelains, H. R. Käse, E. Case and J. A. Tesk.

Degree of Cure and Wear Resistance of Dental Composites, W. Wu.

Intermediate Restoratives from *n*-Hexyl Vanillate EBA-ZnO-Glass Composites, G. M. Brauer and J. W. Stansbury.

Stress Analysis of Bond Test Specimen, G. E. O. Widera, J. A. Tesk, W. G. de Rijk, and R. W. Hinman.

Porcelain to Metal Bond Strength Measurements as Determined by the Four Point Bending of a Composite Beam. W. G. de Rijk, J. A. Tesk, M. Conner, K. A. Jennings and G. E. O. Widera.

Publications - 1983

Extent of Polymerization of Dental Resins by Differential Scanning Calorimetry, J. M. Antonucci and E. E. Toth, J. Dent. Res. 62(2), 121-125 (1983).

Effects of Porcelain/Alloy Interfacial Diffusion Zones on Thermo-mechanical Strain, J. A. Tesk, R. W. Hinman, G. E. O. Widera, A. D. Holmes, and J. M. Cassel, J. Dent. Res, 62, #5, 585-589, May 1983.

Solders and Flexes, J. A. Tesk, 1st Rev., 2nd Ed., Dentists Desk Reference.

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

Initiation of Polymerization and Catalytic Aspects of Polymers, G. M. Brauer, and H. Argentar, ACS Symposium Series, #212, American Chemical Society, Washington, DC, 359-371, 1983.

The Effect of Inhibitors, Accelerators and Acrylic Monomers on the Properties of Bone Cement. G. M. Brauer, Proceedings of 1st Medical Plastics Conference, The Society of the Plastics Industry, New Brunswick, NJ 1983.

Detecting Margin Leakage of Dental Composite Restorations, W. Wu, E. Cobb, K. Dermann, N. W. Rupp, J. Biomed. Mat. Res. 17, 37-43 (1983).

Small Angle Neutron Scattering Studies of Plastic Deformation in Crystalline Polyethylene, G. D. Wignall, W. Wu, Polymer Preprint 24(2) 235-236 (1983).

Post-Curing of Dental Restorative Resin, W. Wu, B. M. Fanconi, Poly. Eng. and Sci, 23(13) 704-707 (1983).

Influence of Chemicals on Wear of Dental Composites, W. Wu and J. E. McKinney, J. Dent. Res. 61(10), 1180-1183 (1982).

A SANS Investigation into the Role of Melting and Recrystallization During Solid State Deformation of PE, G. D. Wignall and W. Wu, Polymer Communications.

Small Angle Neutron Scattering of Partially Segregated Polymer Blends, W. Wu, Polymer, 24, 43-46 (1983).

INVITED TALKS

"The Need for Beryllium in Base Metal Alloys", J. A. Tesk, American Association of Dental Schools, March 15, 1983, Cincinnati, Ohio.

"The World of Dental Materials", J. A. Tesk, (presented by N. W. Rupp), March 29, 1983, Johns Hopkins University, Baltimore, MD.

"New Cements Containing Vanillate and Syringate Esters" G. M. Brauer, L. D. Caulk Company, Milford DE, June 1983.

"Development of High-Strength Adhesive Cements, G. M. Brauer, Northwestern University School of Dentistry, Chicago, IL, June 1983.

"High-Strength Cements Containing Vanillate and Syringate Esters" G. M. Brauer, Australian Dental Standards Institute, Melbourne, Australia, July 1983.

"Small Angle X-Ray Scattering of Composites" Wen-li Wu, University of Hamburg, Hamburg, West Germany, October 1982.

"Small Angle Neutron Scattering of Partially Segregated Polyethylene Blends" Wen-li Wu, University of Hamburg, Hamburg, West Germany, October 1982.

"Small Angle Neutron Scattering of Partially Segregated Amorphous Polymeric Blends" Wen-li Wu, University of Mainz, West Germany, November 1982.

"Wear and Degradation of Dental Composites" Wen-li Wu, Free University of Berlin, West Germany, November 1982.

"Chemical Factors Affecting Wear Resistance of Dental Restorative Composite Resins", Wen-li Wu, Royal Dental College, Copenhagen, Denmark, December 1982.

"Random Phase Approximation to the Paraclustering Phenomena of Polymer Blends" Wen-li Wu, University of Hamburg, West Germany, December 1982.

"Surface Breakdown and Laboratory Wear Studies of Composites", Wen-li Wu, IADR Symposium, Sydney, Australia, August 1983.

MANUSCRIPTS IN REVIEW OR ACCEPTED FOR PUBLICATION

Physical Metallurgy of Dental Casting Alloys, Parts 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 Mid-1984.

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.

Base Metal Alloys in Restorative Dentistry, R. W. Hinman and J. A. Tesk, accepted for publication, Chapter 9 in Textbook - Advanced Restorative Dentistry, Edited by Baum and McCoy, to be published in 1984.

A Practical Method for Evaluating the Castability of Dental Alloys, R. W. Hinman, J. A. Tesk, R. P. Whitlock, E. E. Parry and J. S. Durkowski, Submitted for publication in J. Dental Research, April 1983.

Dental Resin and Initiator Systems Based on Polythiols, J. M. Antonucci, S. Venz, J. W. Stansbury, and D. J. Dudderar, in editorial review.

Hydrophobic Dental Composites from a Polyfluorinated Prepolymer Multifunctional Methacrylate, J. M. Antonucci, S. Venz, J. W. Stansbury and D. J. Dudderar, in editorial review.

Formulation and Evaluation of Dental Composites Derived from Resins Containing 1H,1H-Pentadecafluorooctyl Methacrylate, J. M. Antonucci, S. Venz and D. J. Dudderar.

A Synchrotron Study of the Deformation Mechanism of PET, W. Wu, H. G. Zachmann, and C. Rickiel, in press, Polymer Communications.

Small Angle Neutron Scattering of PE Blends, W. Wu, G. D. Wagnall, in editorial review.

Subsurface Damage Layer of In-Vivo Worn Dental Composite Restorations, Submitted to J. Dental Research.

A SANS Study of Polyethylene Terephthalate Blends, W. Wu, H. G. Zachmann, in editorial review.

U.S. DEPT. OF COMM. BIBLIOGRAPHIC DATA SHEET <i>(See instructions)</i>	1. PUBLICATION OR REPORT NO. NBSIR 84-2843	2. Performing Organ. Report No.	3. Publication Date May 1984
4. TITLE AND SUBTITLE Properties and Interactions of Oral Structures and Restorative Materials			
5. AUTHOR(S) J. A. Tesk, G. M. Brauer, J. M. Antonucci, W. Wu, J. E. McKinney, J. W. Stansbury			
6. PERFORMING ORGANIZATION <i>(If joint or other than NBS, see instructions)</i> NATIONAL BUREAU OF STANDARDS DEPARTMENT OF COMMERCE WASHINGTON, D.C. 20234		7. Contract/Grant No. Y01-DE-30001	8. Type of Report & Period Covered
9. SPONSORING ORGANIZATION NAME AND COMPLETE ADDRESS <i>(Street, City, State, ZIP)</i> National Institute of Dental Research National Institutes of Health Bethesda, MD 20205			
10. SUPPLEMENTARY NOTES <input type="checkbox"/> Document describes a computer program; SF-185, FIPS Software Summary, is attached.			
11. ABSTRACT <i>(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)</i> High strength, eugenol-free cements based on esters of vanillic acid show good biocompatibility in some tests, do not inhibit polymerization and have low solubility. Additional potential applications include pulp capping, endodontic sealing and intermediate restoratives. Hydrophobic resin formulations have lower water sorption than Bis Phenol Glycidal Methacrylate (BIS-GMA) and reduce microleakage. Flexible backbone dimer and trimer acids produce hydrophobic materials with potential for use as cavity liners, endodontic sealers and impression materials. A 75% ethanol-25% water solution softens composites more than other ratios; resins with solubility parameters more different from this solution than BIS-GMA are under development. The newer resins are fluoromethacrylates and urethaneacrylates. A cumulative failure plot, based on Wiebul statistics was shown capable of representing data obtained from a four point bending composite beam (porcelain-fused-to-metal). Castabilities of six nickel based alloys were shown to be represented by a simple, two term equation with constants characteristic of each alloy.			
12. KEY WORDS <i>(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)</i> Castability; degradation; dental alloys; dental casting alloys; dental cements; dental composites; dental materials; dental restoratives; porcelain-fused-to-metal; porcelain metal bond; wear; wear and degradation of composites.			
13. AVAILABILITY <input checked="" type="checkbox"/> Unlimited <input type="checkbox"/> For Official Distribution. Do Not Release to NTIS <input type="checkbox"/> Order From Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402. <input checked="" type="checkbox"/> Order From National Technical Information Service (NTIS), Springfield, VA. 22161		14. NO. OF PRINTED PAGES 58	15. Price \$10.00

