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Properties and Interactions of Oral Structures and Restorative Materials

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

CONTENTS

PART I - COMPOSITES, CEMENTS, AND ADHESION (Brauer, Stansbury, Antonucci, Venz, Iizuka, and Lee)

Section A through D - Brauer

Section E - Stansbury

PART III DENTAL ALLOYS, CERAMICS, AND METROLOGY
(Tesk, Penn, de Rijk and Asaoka)

ABSTRACT

The research program described herein is designed to achieve a number of objectives leading to improved dental restorative materials, techniques and applications of dental materials science for improved dental health care in general. Some of the research in dental composites is directed toward developing generic polymer science potentially useful for composite applications, e.g., durable resin matrices and stronger more durable coupling between fillers and resins. Improved reinforcement is sought by defining the type, and percentages of fillers which will result in improved performance of composites. Methods for reducing polymerization shrinkage and attendant stress and marginal leakage are also explored. Cements are investigated and basic formulations developed for lower solubility, higher biocompatibility, higher strength, greater toughness and adhesion to various substrates including enamel and dentin. Analysis techniques include IR spectroscopy, chromatography, x-ray analysis, mechanical testing, and dilatometry. Another major effort is directed at elucidating the fundamentals involved in wear and degradation of dental composites and restoratives. Wear and hardness measurement techniques are pursued as well as by identification of the origins and sources of flaws leading to failure. Weibull statistical analysis is expected to provide useful information for this task. In this regard an objective is to investigate improved correlations between clinical results of wear and failure of composites with laboratory test data via time-to-failure analysis. Metrology and analysis constitutes the underlying theme of investigations into porcelain-metal systems, casting of dental alloys and the expansion of dental casting investments.

> "The activity covered by this agreement consists of work which requires the definition of measurement methods, materials property data, and standards of basic scientific and engineering units and the application of primary standards to insure equity and comparability in U.S. commerce, international trade, and technical activities. As such it complies with OMB Circular A-76, revised under paragraph 5f (Activities classified as Government responsibilities or are intimately related to the public interest)."

FY 86 SIGNIFICANT ACCOMPLISHMENTS

- Cooperative studies with other institutions on the biocompatibility of Zinc Oxide Hexyl Vanillate Cements indicate that their biological performance is acceptable.

- An NBS - American Dental Association collobrative effort on evaluation of Syringate-Vanillate-EBA-ZNO cements indicates that this material is suitable for clinical evaluation.

- A radiopaque denture base formulation employing pentabromophenyl methacrylate as a polymerizable radiopaque agent was shown to be color stable.

- Adhesive formulations with the potential for use in dentin bonding and repair of manillofacial fractures were prepared and showed promise for continued research after early testing.

- Effects of film thickness and power/liquid ratios on retention of dental cements showed that composition of the brand was more influential than the type of cement.

- The use of expanding monomers in dental adhesives was found to result in increased bond strength. This is attributed to lower residual stress due to less shrinkage during curing.

- Silyl ether derivitives of Bis-GMA were found to import a variety of desirable properties to experimental dental composites.

- Amine salts and complexes were found to import improved color stability to resin based dental system.

- Resin-modified dimer-acid cements were shown capable of producing high tensile strength materials which may have utility as intermediate restoratives, bases, and liners.

- A modified glass-ionomer cement formulation was developed and shown to be stronger in tension with less susceptibility to hydration during setting.

- Dual silanization of composite fillers showed promise of yielding more durable composites. The use of a newly synthesized multifunctional silane coupling agent improved the hydrolytic stability of an experimental dental composite.

- Resin-toughened glass ionomer cement-composites were found to exhibit only slightly increased wear and without the brittle failures normally associated with conventional glass-ionomer cements.

- The effects of various elements on the castability of Ni-Cr alloys was determined as a function of alloy and mold temperatures. A synergistic effect between Si and Be was found.
- Continued experimentation on the internal setting expansion of dental phosphate-bonded investment showed internal setting strain of only .15%, between directions perpendicular to each other.
- Weibull statistical analysis has shown that some dental composite restoratives may be more prone to marginal failure than others.
- Confidence limits for Weibull statistical analyses were obtained by numerical methods.

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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 for the porcelain-fused-to-metal studies. Special emphasis is being placed on measurement techniques and flaw analysis.

I. COMPOSITES, CEMENTS AND ADHESION

A. High-strength Eugenol-free Adhesive Cements and Restorations

Overview

Cements are used in over 50 percent of all dental restorations. Zinc oxide-eugenol type cements, because of the excellent biocompatibility of the hardened material, are employed for such diverse applications as cementing media for crowns and bridges, sedative and insulating bases, temporary restorations, pulp capping agents, root canal sealers, soft tissue packs and as impression pastes.

Cements in current use are far from ideal. Their relatively low mechanical properties, high solubility and lack of resistance to wear and disintegration deters their more extensive use, especially for cementation for permanent protheses or for their use as intermediate restoratives.

Non-eugenol containing cements based on vanillate esters, o-ethoxybenzoeic acid (EBA) and zinc oxide, have been developed in this laboratory [1-7]. 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, porcelain and composites. The cements exceed greatly requirements of ANSI/ADA Specification No. 30 for Types II, III, and IV restoratives.

Objective

The initial objective of this study was to synthesize and evaluate these cements for various dental applications. To achieve this objective the following tasks were undertaken: (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 materials (IRM) incorporating monomers and reinforcing fillers with cement ingredients and determination of their mechanical properties; (4) synthesis of cements containing the potentially caries-reducing syringic esters and evaluation of properties of the resulting cements; (5) modification of the cements by addition of small concentrations of additives such as acids, metals or fluorides to improve their properties and (6) to furnish assistance and guidance to conduct investigations of the biocompatibility and toxicity of the cement and its ingredients and to collaborate in studies of the pulp irritation and in clinical studies at various dental research centers.

Accomplishments

Objectives 1 - 5 have been completed. Results of these studies have been summarized in References 1-16. They have lead to a number of cements and intermediate restoratives of potentially great usefulness for clinical dentistry.

Present objectives will be directed to (1) further improvements of the vanillate or syringate cements by addition of modifying agents, (2) increase the scope of the usefulness of these materials for clinical dentistry, (3) completion of studies of the biocompatibility of syringate cements and cement-composites containing acrylic monomers.

PROGRESS REPORT

Phase I. Further improvement of properties of vanillate and related cements

Because of the emphasis placed on other portions of research conducted under this interagency agreement, no studies were carried out on these phases (1a, 1b, 1c) during the year.

Phase II. New applications of these materials (1d and 1e)

No studies were conducted on these phases (1d and 1e) during the year due to emphasis on other portions of the research.

Phase III. Study of the Biocompatibility and Clinical Usefulness of Vanillate and Syringate Base Restoratives

(1) Biocompatibility

(a) Biological Performance of Zinc Hexyl Vanillate Cements. Studies conducted by J.C. Keller and co-workers of the Dental School, University of South Carolina of cements furnished by this laboratory were presented at the annual AADR meeting. They showed that the cellular and connective tissue reactions of the vanillate cement approximated those of zinc phosphate and ZOE cements. (Overall cell counts were lowest for the vanillate cement; however, the differences were not significant.) The investigators concluded that the vanillate cement had acceptable biological performance as compared to the clinically acceptable phosphate or ZOE cements.

(b) Biocompatibility of Syringate-Vanillate-EBA-ZnO cements. The biological safety evaluation of syringic acid ester cements has been conducted by Dr. Siew and co-workers at the American Dental Health Foundation. Oral LD_{50} for 2-ethylhexyl syringate (EHS) is approximately 5.3 g/kg, that is even lower than that of hexyl vanillate. Red blood cell hemolysis, cloning efficiencies and Ames mutagenicity tests with four bacterial strains of EHS or the cement extract were negative. Although these toxicity and mutagenicity tests are not exhaustive, the data indicate in both procaryotic and eucaryotic (mammalian) cell systems along with whole animal studies that this cement is neither toxic nor mutagenic. Thus, clinical testing of this cement is justified.

(c) Biological evaluation of vanillate-intermediate restoratives. Three formulations synthesized in this laboratory containing dicyclopentenyloxyethyl methacrylate or cyclohexyl methacrylate which have much better mechanical properties than commercial intermediate restoratives and bond well to composites, non-precious metal or porcelain are being evaluated for biological characteristics at the American Dental Association Health Foundation, the University of Texas at San Antonio and University of Tennessee Dental School.

(2) Assistance in Clinical Evaluation. A very limited clinical study of the cement has been initiated at the University of Louisiana School of Dentistry. No undesirable behavior has been reported after the four-month clinical observation period.

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B. Changes in Esthetic Properties of Dental Resins on Aging

Overview

Although the color stability of the presently employed dental resins is quite satisfactory, some discoloration of these materials can often be observed clinically. Under oral conditions, these restorations are exposed to the combined effects of light, moisture, stains and mechanical wear resulting in visibly detectable, and aesthetically undesirable color changes. Many of these changes are the results of photochemical reactions of ingredients of the composite caused by exposure of the restoration to various energy sources. Since clinical studies to determine color stability of restoratives are time-consuming, accelerated aging tests have been suggested to correlate laboratory findings and clinical performance. Most of these tests are based on short-term (24 hour) exposure of the materials to light sources or heat, often in an aqueous environment.

Objective

The objective of this study was to (1) investigate the color changes of a wide variety of dental resins resulting from the exposure to different radiation sources or to thermal exposure, under diverse environmental conditions for various periods of time, and (2) to try to correlate the experimental in vitro results with the composition of the materials as well as with their clinical performance. Results of this investigation should establish which ingredients of composites are responsible for color instability. Such data should assist in the development of more color stable resins.

Accomplishments

The results of the color stability of composites on exposure to irradiation by (1) a 150 Klux Xenon lamp, (2) a standard RS light source and (3) elevated temperature at 60 °C, in air or water and under different experimental conditions for various time periods were reported in last year's report.

PROGRESS REPORT

Phase I. Characterize minor components of the composites. Correlate aging behavior with presence of specific ingredients

Thermal exposure studies of the chemical or light cured, hybrid or microfilled, composites were extended for up to one year. Composites kept in the dark at 37 °C for one year showed no color changes. Materials stored in an oven at 60 °C did not discolor appreciably for at least six months except for the chemically cured Adaptic and Silar. More rapid and severe discoloration occurred in water with most specimens undergoing changes in the color ratings after one month. Color changes were observed by nearly all observers on viewing of all composites stored in water for six months. All materials gave perceptible or very perceptible color changes on 12 month storage in this medium.

The pastes of a number of brands were dissolved and subjected to high pressure liquid chromatography. Many ingredients present in the pastes could be identified from the chromatograms. A complete identification of all major and minor components in composite pastes will only be possible with a preparative chromatograph.

These studies were discontinued until such time when equipment becomes available to separate, for further identification, larger quantities of ingredients.

A manuscript summarizing these studies was prepared and is now under editorial review. It includes comparison of our laboratory data with clinical studies of color changes of two of the chemically cured composites. The data indicate that these two restoratives, which pass the ANSI/ADA or ISO specification tests, cause discoloration in clinical use after two to three years.

Phase II. If clinical experience with modern composites is favorable, then formulate new composites with improved color stability and aging characteristics.

No work on this phase is anticipated in the near future.

C. Development of Radiopaque Copolymeric Denture Resins

Overview

The ever increasing use of plastics, in dentistry makes it desirable and often even mandatory that such materials have adequate radiopacity to detect their presence in various environments [1]. Radiopacity is an important requirement for medical and dental implants or devices that may be ingested accidentally. The commonly available high molecular weight plastics are composed of elements of low atomic number. The low cross-sectional electron density of the polymer chain makes them radiolucent to x-ray imaging techniques. Attempts to render plastics radiopaque have taken the following approaches: (1) incorporation of radiopaque metals such a lead foil, gold or silver alloy, [2-4] (2) addition of heavy metal salts such as barium sulfate, barium fluoride, barium acrylate, or bismuth subnitrate as fillers, [5-8] or (3) incorporation of an element of relatively high atomic number into a silanized glass used as reinforcing filler of a composite resin, [9-12] (4) addition of halogenated saturated or unsaturated compounds such as tetrabromoethane or aliphatic bromoacrylates or methacrylates to the uncured resin. [13,14] All these modifications have certain disadvantages. Addition of metal or metal salts causes stress concentrations at the interface between the insert and the resin which will weaken the materials and may eventually result in fracture. It also lowers the mechanical properties (transverse-, impact-, compressive- and tensile strength). Translucency of such radiopaque plastics is usually lower than those containing no additives. Plastics with radiopaque glass ingredients are difficult to polish. Resins with halogenated aliphatic ingredients discolor with time and are unsuitable for many applications where esthetic characteristics are important. The state of the art of radiopaque plastics for dental applications has been reviewed.[1,2]

A desirable radiopaque plastic should have a homogeneous composition, with excellent mechanical, thermal and optical properties and high imaging characteristics so that its outline (including details) is readily visible in various environments on minimum exposure to x-ray radiation or ultrasonic waves. These properties should not deteriorate on aging in the surrounding environment.

Introduction

At present, plastics used for most dental appliances and materials including removable dentures and temporary crown and bridge materials are radiolucent. Radiopaque denture base materials combining adequate physical and esthetic properties with ease of processing similar to the well accepted radiolucent acrylic plastics are not available commercially.

Monomers with a high percentage of atoms of high molecular weight such as pentabromophenyl or triiodophenyl methacrylate are compatible with methyl methacrylate.[15] The pentabromophenyl methacrylate is commercially available and the triiodo derivative has been synthesized in this laboratory. The rate and kinetics of polymerization of monomer-polymer dough is not altered greatly by the addition of these halogenated compounds. Addition of 10 to 15 percent of the brominated monomer to methyl methacrylate results in radiopaque polymers. Such compositions are more homogeneous than filler containing compositions and have higher strengths than commercial bone cements with barium sulfate [15].

Objective

To develop a clinically useful radiopaque denture resin based on halogenated aromatic methacrylate copolymers.

PROGRESS REPORT

Phase I. Using commonly accepted testing procedures, study the curing characteristics, physical, chemical, esthetic and radiopaque properties of self-curing denture base materials prepared from copolymers of pentabromophenyl and triodophenyl methacrylate and methyl methacrylate copolymers.

> Compositions containing 10% and 15% pentabromophenyl methacrylate (PBPMA) or triiodophenyl methacrylate (TIPMA) in the liquid were mixed with commercial polymer powder. Resins with 15% halogenated monomers showed good radiopacity. Water sorption or water solubility of the cured resin was not changed on addition of halogenated monomer. The PBPMA containing resin passed the color

stability test whereas material with TiPMA gave a perceptible color change. Storage stability of liquids prepared with some batches of PBPMA did not pass the 60 °C storage stability test.

To overcome this problem, poly(methyl methacrylate) (90%) - pentabromophenyl methacrylate (10%) suspension copolymer powder has been synthesized in cooperation with Esschem. The radiopacity of mixtures containing this copolymer exhibited satisfactory radiopacity. Procedures to synthesize and characterize copolymers with a higher concentration of PBPMA are under active investigation.

Phase II. If properties of formulations studied in phase I pass all requirements of the ADA/ANSI, specification for denture base resins, have adequate working properties and good esthetic characteristics, then determine the biocompatibility of the added monomer and of the cured denture base copolymer resin.

Work on this phase may be initiated at a later date.

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D. Study of Adhesion and Adhesion Promoting Agents to Dentin

Overview

The main disadvantage of most dental restorative materials is the lack of adhesive bonding to tooth structures in the oral environment. These materials are kept in place solely by mechanical interlocking to the cavity preparation. A restorative that chemically bonds to tooth structure should inhibit the formation of secondary caries since it would prevent percolation of microorganisms and liquids by sealing the marginal areas of the restoration. With such a material, sealing of incipient carious lesions could be realized. An adhesive cement could lead to less invasive cavity preparations resulting in decreased loss of sound tooth substance.

Introduction

Many procedures to obtain permanent bonding to enamel or dentin have been suggested. Pretreatment of enamel with dilute acid enhances adhesion of restorative resins to enamel, but this is contraindicated for dentin. There are many constraints inherent in the long term bonding to dentin [1-4] and the present adhesives have found limited clinical use for this application. Surface grafting of monomers to mineralized tissues such as bone can be accomplished with persulfate [5] and to dentin with tri-n-butylborane oxide as initiator.[6,7] Zinc polyacrylates and glass ionomer cements adhere to enamel but only weakly to dentin. Excellent adhesion to dentin by acrylic resins is obtained with isobutyl 2-cyanoacrylate, but the bond strength decreases on water exposure.[8] A mixture of a phosphorus ester of BIS-GMA and diluent monomer polymerizable by peroxide, tertiary amine and sulfinic acid salt has been introduced commercially as a dentin-composite bonding agent.[9] Monomers with hydrophobic and hydrophilic moieties such as 4-methacryloxyethyl trimellitic anhydride (4-META) and the diadduct of hydroxyethyl methacrylate and pyromellitic anhydride (PMDM) bond dentin to acrylic resins.[10,11] Most effective are successive treatments of the dentin surface with ferric oxalate, a 5 to 10 percent acetone solution of a glycine derivative (adduct of N-phenyl or N-p-tolylglycine and glycidyl methacrylate) followed by a 5 percent solution of PMDM in acetone.[11] Another good bonding agent to dentin is the mixture of 2-hydroxyethyl methacrylate and glutaraldehyde.[12-14] Thus, investigations during the last five years have developed luting agents that adequately bond to dentin. Major disadvantages of the presently recommended dentin bonding systems are (1) the tooth surface must undergo a number of pretreatments which are time-consuming and may limit the clinical usefulness and cost effectiveness of the process, (2) strict adherence to the protocol such as removal of excessive monomer and water from the treated tooth surface in the drying cycles of the most efficient procedure [11] are mandatory to obtain optimum bonding, (3) the biocompatibility of the various regents and compounds used in many of these tooth treatment procedures has not been fully explored.

Objectives

Efforts, in this proposal, are directed to develop film-forming surfaces that could serve as adhesives or sealants and to synthesize compounds and formulations containing functional groups that are effective adhesion promoters to mineralized tissues. Specifically these studies will (1) determine the grafting efficiency of oligomers and polymers of isocyanatoethyl methacrylate having either functional isocyanate and methacrylate groups with the aim of obtaining a durable polymer coating on the dentin surface, (2) synthesize and evaluate the adhesive properties of methacrylate esters from a homocylic tetracarboxylic dianhydride which is closely related to the aromatic dianhydride, used to prepare PMDM, and (3) study the forces needed to fracture cemented surfaces and the relationship between retention of cemented crowns and the film thickness of the cement layer.

PROGRESS REPORT

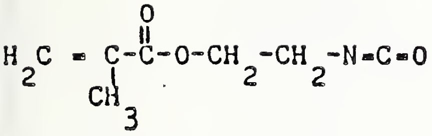
Phase I. Synthesize and evaluate adhesive properties of oligomers of 2-isocyanatoethyl methacrylate or other isocyanate containing monomers to dentin.

Phase Ia. Synthesize oligomers with pendant isocyanate groups.

2-Isocyanatoethyl methacrylate (IEM) and *m*-isopropenyl-β, β-dimethylbenzyl isocyanate (TMI) (Fig. 1) are difunctional monomers with reactive isocyanate (NCO) groups and a polymerizable vinyl double bond. Reactions with either function can be carried out independently of the other group.

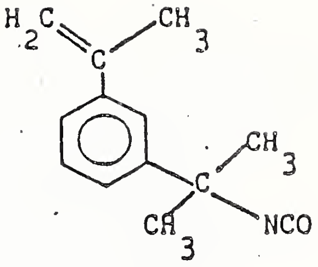
Oligomers (low molecular weight) polymers were synthesized using IEM, TMI, ethyl acrylate (EA), butyl methacrylate (BMA) or hydroxyethyl methacrylate (HEMA) as shown in Fig. 2. Liquid products resulted after evaporation of the solvent. Monomers used in the preparation of the respective oligomers, mole ratios of monomers used, and refractive indices, n_D, of the liquid products are given in the following table.

MONOMERS WITH ISOCYANATO GROUPS



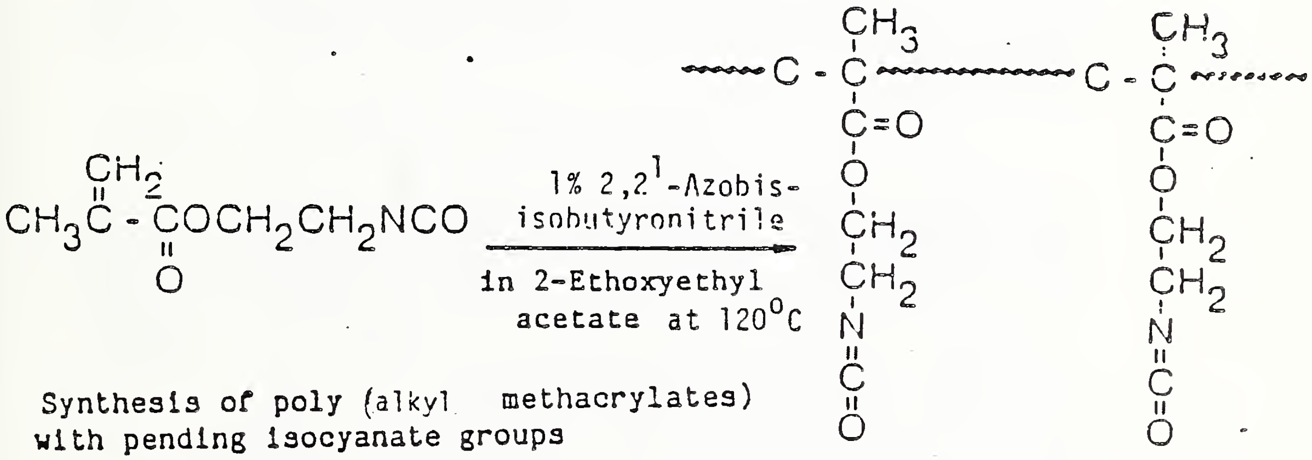
$H_2C=C(CH_3)-C(=O)-O-CH_2-CH_2-N=C=O$

2-Isocyanatoethyl methacrylate
IEM

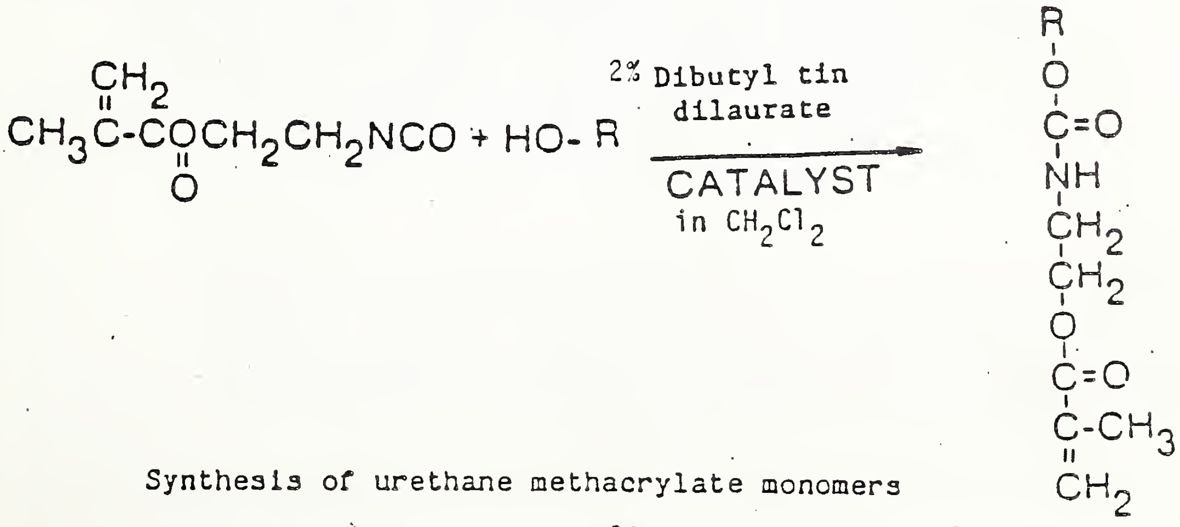


m-Isopropenyl-α,α-dimethylbenzyl Isocyana
m-TMI

FIGURE 1



Synthesis of poly (alkyl methacrylates) with pending isocyanate groups



Synthesis of urethane methacrylate monomers

FIGURE 2

MONOMER USED IN PREPARATION OLIGOMERS

Oligomer	Mole Ratio of Respective Monomer	n_D^{23} of Oligomer
IEM-EA	1:1.5	1.4719
IEM-BMA-EA	1:1.3:1.8	1.4593
TMI-EA	1:2	1.5065
TMI-BMA	1:1.4	1.5161
IEM-EA-TMI	1.3:1:1	1.5083
IEM-BMA-TMI	1.8:1.4:1	1.5055

Infra-red analysis of the oligomers confirmed the presence of the isocyanate groups. Idealized structures of TMI-BMA and IEM-BMA-TMI are given in Fig. 3. The urethane methacrylate of IEM or TMI with hydroxyethyl methacrylate were prepared at room temperature under the conditions outlined in Fig. 2.

Gel permeation chromatograms indicated that most of the TMI-BMA and IEM-BMA-TMI were a low molecular weight materials. Only a small fraction of the copolymers had an elution volume below 42, which for the polystyrene reference material would indicate a molecular weight of 1748. A trimer of IEM was also synthesizsed (MP = 77-78 °C, yield 69%).

Phase 1b. Prepare adhesive formulations and evaluate their properties.

Only formulations with isocyanate groups (not urethanes) in the side chain adhered to mineralized tissues whereas the urethanes or IEM trimer did not react directly with bone. Bone powder reacted at room temperature within three hours with IEM-EA or IEM-BMA-EA in the presence of dibutyltin dilaurate or triethyl amine. Dentin powder did not react with IEM-BMA-EA,in the presence of catalysts, but reacted at 42 °C with IEM-EA or IEM.

These experiments indicated that pretreatment of the mineralized tissue may improve bonding. The use of 5% to 25% aqueous glutaraldehyde solution suggested by Munksgaard and Asmussen [15-19] in combination with isocyanate containing formulations followed by application of a typical bonding agent based on BIS-GMA and triethylene glycol dimethacrylate greatly improved adhesion.

Shear and tensile strength of bone (conducted under another project) cemented with various adhesive compositions are given in Tables 1 and 2.

Shear strength of all isocyanate containing monomers and oligomers was very high. Maximum relative shear strength (54.1 kg load) was obtained with the IEM-BMA-TMI copolymer. The Gluma adhesive after ethylenediaminetetracactitic acid EDTA pretreatment of the bone also yielded a strong bond, but the ferric oxalate-NPG-PMDM procedure resulted in a weaker joint. Tensile adhesion after 24 hours storage in water was highest for the IEM (9.9 MPa) monomer. The TMI-BMA or IEM-BMA-TMI compositions had significantly higher bond strength than bone cemented with Gluma or butyl 2-cyanoacrylate. After 7-day therocycling between 5 °C and 55 °C the TMI-BMA oligomer adhesive had a tensile adhesive strength of 7.9 MPa. Thus, exposure to water and thermal shock produced no deterioration of the bond. For the other compositions the loss in bond strength is small compared to that experienced by butyl or other 2-cyanoacrylates.[8] All of the tensile strength specimens broke cohesively.

For dentin bonding, bovine dentin was cemented to a composite slurry placed into the recessed tip of a cylinder used in the static load testing procedure of Lee et al. [20] Generally, bond strength values after 24 hour storage of the joint in water were low. Results given in Table 3 show that cementation with IEM-BMA-TMI copolymer or IEM produced stronger joints than those obtained with GLuma or NPG-PMDM. (Table 1)

The bond strengths of pretreated human dentin joined to composite with various adhesives as measured by the more elaborate procedure suggested by Bowen is given in Table 4. These values were considerably higher than those obtained for bovine dentin using the procedure of Lee.

The lower bond strength of bovine dentin compared to human dentin may have been caused by the better bonding of the adhesive to the latter substrate. The higher bond strength values may result from the more thorough preparation of the flattened dentin surface and the better contact at the tooth-adhesive and the adhesive-composite interface in the technique employed for cementing human dentin to composite. A slight increase in adhesion occurred after purification of the oligomer by extraction with 85% hexane-15% ethyl acetate which removed residual monomer. Neither the difference in bond strength of dentin to NPG-PMDM, purified IEM-BMA-TMI or Gluma was statistically significant.

The suggested mechanism for the adhesion of aldehyde treated mineralized tissues to isocyanate monomers is shown in Fig. 4.

A survey of the available toxicity data for the monomer indicates that they may not be suitable for clinical applications. However, oligomers with TMI posses no residual isocyanate containing monomer. Molecular weights and concentration of isocyanate groups are adjustable. The oligomeric liquids have low volatility and should not diffuse readily into tissues, but their biocompatibility as adhesives to mineralized tissues will have to be established.

Conclusions

Monomers and low M.W. liquid copolymers containing pendant isocyanate groups form stronger, more permanent, water-resistant bonds to glutaraldehyde treated bone than other adhesives. The isocyanate group containing compositions should also be studied further as potential dental adhesives.

This work was presented at the IADR and American Chemical Society meetings.

Phase Ic. If studies conducted in Phase Ia and Ib are successful, initiate cooperative projects to study biocompatibility of these adhesive systems and their application in dental practice.

Although the adhesives prepared in phase Ib have not been completely characterized or optimum desirable properties have been determined, investigators at two universities (South Carolina, Missouri) have expressed an interest to conduct studies of the toxicological properties.

Phase II. Synthesize the dimethacrylate ester of 5-(2,5-dioxotetrahydrofuryl)-3-methyl-3-cyclohexene-1,2-dicarboxylic anhydride and determine its adhesion to dentin.

This dimethacrylate having a more non-polar homocyclic nucleus compared to the aromatic groups in 4-META or PMDM was synthesized at room temperature with hydroxyethyl methacrylate in CH_2Cl_2 and dimethylaminopyridine accelerator. The slightly yellow viscous product adhered well to ferric oxalate treated bone and composite. The bond strength appeared to be lower than that of the isocyanato containing oligomers (phase I). Thus, investigation with the oligomers described in phase I was emphasized during this period.

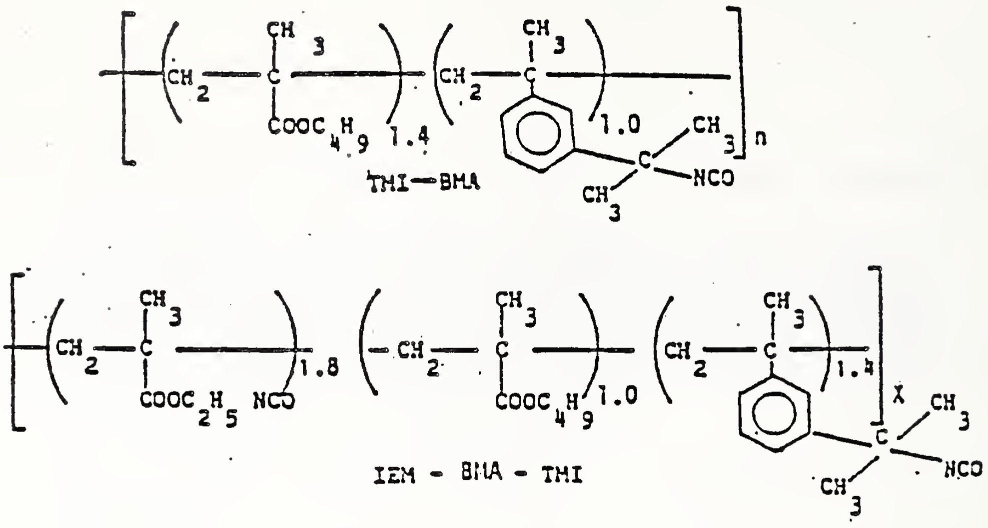
Phase III. Study the effects of film thickness on the retention of cements.

Film thickness (FT) and retention of zinc phosphate, polycarboxylate and ionomer cements as a function of powder-liquid (P/L) ratio was determined for both nonvented and vented crowns using the parallel plate specification test. FT increased with the P/L ratios especially at high cement consistencies. Cementation of vented crowns yielded thinnest FT usually followed by that obtained by the parallel plate method and the nonvented crown.

The effect of P/L ratio on FT or retention was more dependent on the composition of the brand than on the type of cement. For some polycarboxylate or ionomer cements retention decreased with increasing film thickness. Little retention of well-fitted crowns was found for zinc phosphate powder-water mixes as suggested previously.[21]

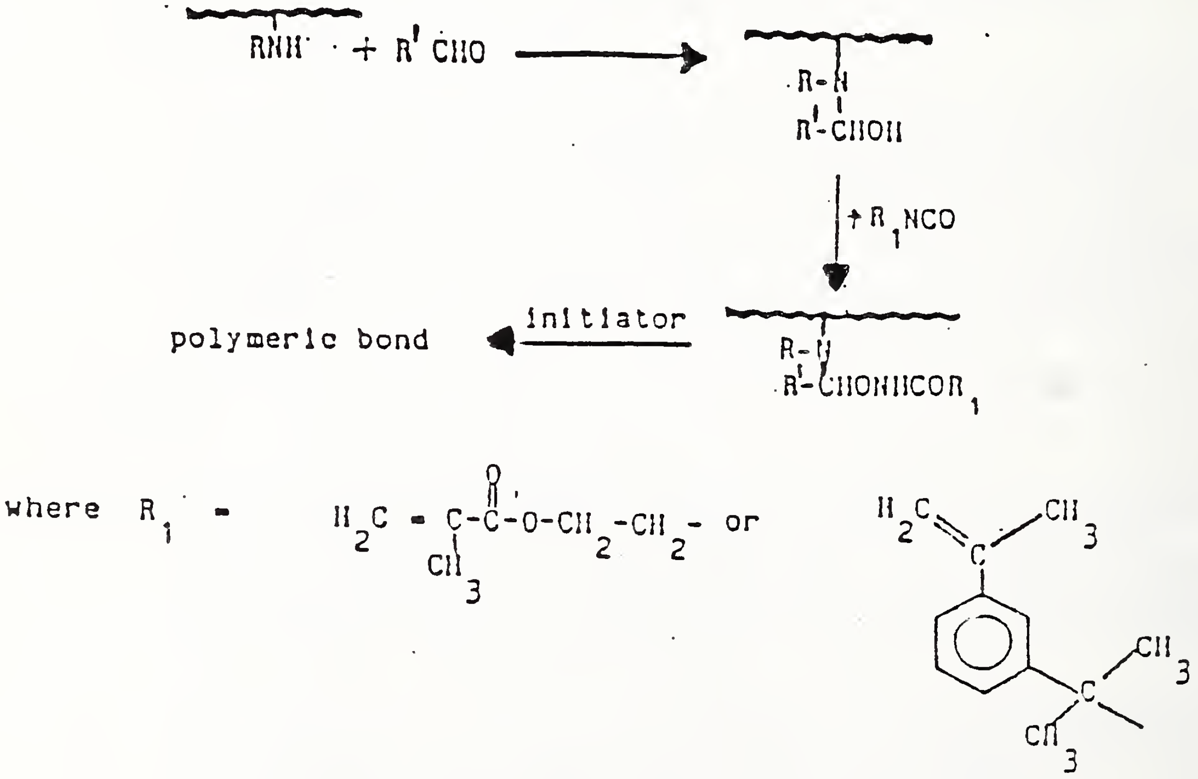
The P/L ratios suggested in the manufacturer's instructions did not always yield the maximum retention for either vented or unvented crowns. Venting of prepared crowns is indicated since this procedure usually increased their retention and was much less dependent on variations in P/L ratios.

IDEALIZED STRUCTURE OF COPOLYMERS STUDIED



F I G U R E 3

MECHANISM OF ADHESION OF COLLAGENOUS SURFACES
TO ISOCYANATE CONTAINING MONOMERS



F I G U R E 4

TABLE 1

RELATIVE SHEAR STRENGTH OF BONE CEMENTED WITH VARIOUS ADHESIVES

Adhesive	Breaking Load, kg[a]
IEM	42.1 ± 3.5
TMI	41.8 ± 6.1
TMI - BMA	40.7 ± 5.3
IEM - EA - TMI	41.0 ± 4.5
IEM - BMA - TMI	54.1 ± 9.4
Gluma	43.0 ± 13.3
FeOx - NPG - PMDM[b]	21.9 ± 4.0
Blank	6.0 ± 4.7

---

[a] Mean of 10 specimen (bonding area: 1 cm x 1 cm) after 24 hour storage in H_2O.

[b] Ferric oxalate-N-phenylglycine-dimethacryloxyethylpyromellitic acid

TABLE 2

TENSILE STRENGTH OF BONE CEMENTED WITH VARIOUS ADHESIVES

Adhesive	Bond Strength in MPa[a] after storage in H_2O for 24 h. at 23 °C	7 d. - thermocycled
IEM	9.89 ± 1.44	7.41 ± 1.17
TMI	9.03 ± 1.79	8.38 ± 2.25
TMI - BMA	7.94 ± 1.19	7.92 ± 2.21
IEM - BMA - TMI	8.60 ± 1.17	7.47 ± 2.15
Gluma[b]	7.14 ± 1.30	6.98 ± 0.93
Isobutyl cyanoacrylate	6.62 ± 1.73	4.52 ± 0.46[c]
Control	1.07 ± 0.61	2.75 ± 0.31

---

[a] Mean of 10 specimens or those not fractured within the bone.

[b] EDTA - glutaraldehyde - hydroxyethyl methacrylate

[c] one day

[d] 5 °C and 55 °C

TABLE 3

TENSILE STRENGTH OF BOVINE DENTIN BONDED TO COMPOSITE

Dentin was treated with 25% aq. glutaraldehyde prior to application of adhesive solution. Freshly mixed composite was then applied.

Adhesive	Bond Strength after 24 h in H_2O, MPa[a]
IEM	4.27 ± 2.22
TMI	2.53 ± 1.60
TMI - BMA	1.80 ± 1.63
IEM - BMA - TMI	4.51 ± 1.70
Gluma	1.83 ± 1.22
NPG - PMDM[b]	2.08 ± 1.42
Blank	0.25 ± 0.27

[a] Mean of six specimen

[b] Ferric oxalate - N-phenylglycine-dimethylacryloxyethyl pyromellitic acid.

TABLE 4

TENSILE STRENGTH OF HUMAN DENTIN BONDED TO COMPOSITE

Dentine was treated with 0.5M EDTA and 5% glutaraldehyde. A 5% solution of the adhesive in CH_2Cl_2 was applied, followed by application of bonding resin and composite.

Adhesive	Bond Strength after 14 hr in H_2O, MPa[a]
IEM	7.03 ± 1.51
TMI	7.47 ± 2.11
TMI-BMA	5.55 ± 1.96
IEM-BMA-TMI	6.53 ± 1.52
IEM-BMA-TMI[b]	7.68 ± 1.91
Gluma	7.47 ± 1.87
NPG-PMDM	8.61 ± 3.09
Blank	1.37 ± 1.02

[a] Mean of five specimen

[b] Purified by extracting twice with 85% hexane-15% ethyl acetate

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Manuscripts Under Review or Accepted for Publication

Iizuka, H., Brauer, G.M., Rupp, N., Ohashi, M. and Paffenbarger G. Forces fracturing cements at die interfaces and their dependence on film thickness. Submitted to Dent. Mat.

Brauer, G.M. Color changes of composites on exposure to various energy sources. Editorial Review.

Invited talks

Brauer, G.M. Adhesive Cements and Intermediate Restorations Containing Vanillate or Syringate Esters. G.M. Brauer, Lunch and Learning Session, IADR meeting in The Hague, 1986.

Contributed talks

Iizuka, H., Brauer, G.M., Rupp, N., Ohashi, M. and Paffenbarger, G. Film Thickness and Forces Fracturing Cements at Die Interfaces. AADR meeting 1986.

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Brauer, G.M. and Lee C. Adhesion of 2-Isocyanatoethyl methacrylate, m-isopropenyl-β,β-dimethylbenzyl isocyanate or their Copolymers to Bone. Mid-Atlantic Regional Meeting, American Chemical Society, Baltimore, MD, Sept. 1986.

E. Monomers which Polymerize with Expansion

Overview

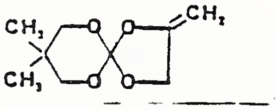
A great deal of attention in recent dental composite research has been focused on the problems of polymerization shrinkage and adhesion. To a large extent, the difficulties encountered in bonding composite to tooth structure can be attributed to the polymerization shrinkage.[1] Other deficiencies such as marginal gap formation, which may lead to hypersensitivity[2] and secondary caries[3], as well as micro-defects in the resin matrix, which may cause accelerated degradation, have also been linked to the problem of polymerization contraction.

Our effort in this area has centered on the formulation of spiro orthcarbonate monomers, which expand in volume during polymerization, with conventional monomers that contract. The resulting formulations should minimize polymerization shrinkage and many of the problems associated with it including limitations on the formation of strong, durable adhesive bonds to dentin and enamel.

PROGRESS REPORT

Phase I. Synthesis of spiro orthocarbonate monomers capable of free-radical polymerization with an expansion in volume.

Several new spiro orthocarbonate (SOC) monomers have been prepared with the basic idea of increased reactivity in mind. New methods were devised to allow the formation of fused five and six-membered rings as seen in monomers 1 and 2 which were recently synthesized.



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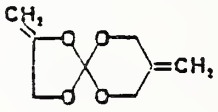
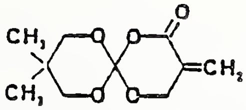


2

With an exocyclic double bond located on the five-membered ring, the monomer ring-opens by a different mechanism than that observed for six and seven-membered rings in which the double bond is not adjacent to one of the spiro-oxygens. These monomers are more reactive in free radical polymerization by virtue of steric factors as well as the different ring opening process. Monomer 2 was synthesized to directly compare the effect of double bond placement on the relative reactivities of the double bonds.

Another effort to achieve more energetic SOC monomers has resulted in the synthesis of the highly reactive compound 3. This monomer containing an acrylate-like double bond has been prepared, but not yet successfully isolated due to its reactivity.

Another SOC monomer 4 with a very bulky substituent on one of the rings has been synthesized.



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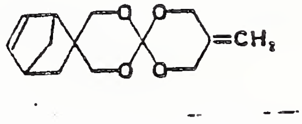

4

This monomer was designed to have a relatively high melting point and to provide a high modulus to copolymers in which it is incorporated. Further, the isobornyl group acts as a very efficient hydrophobic barrier around the moisture sensitive tetraoxaspiro linkage.

Phase II. Polymerize and characterize the monomers synthesized in Phase I.

The homopolymerization of several of the previously prepared SOC monomers has been achieved. The monomers (1 and 2) containing the unsaturated five-membered ring have been polymerized to fairly high molecular weight by di-*tert*-butyl peroxide (DTBP) at 120 °C. Polymers of 1 are powdery solids which are soluble in chloroform while polymers of 2 are slightly elastic, insoluble cross-linked solids. The more reactive monomer 3 underwent spontaneous thermal polymerization during an attempted vacuum distillation. Other SOC monomers have been polymerized to low molecular weight oligomers by either DTBP at 120 °C or BF_3-OEt_2 at 0 °C. These monomers do copolymerize with conventional acrylate-based monomers under a variety of free radical polymerization conditions.

Phase III. Formulate dental composites and adhesives based on monomers obtained from Phase I.

There appear to be two formulation techniques which take best advantage of the polymerization expansion of these SOC monomers. First, the liquid SOC's or those that melt just above room temperature, can be used to entirely replace the conventional diluent monomers used with BIS-GMA-based formulations. The favorable results obtained in this way can be rationalized by the fact that the conventional diluent monomers, such as TEGDMA, exhibit the greatest degree of polymerization shrinkage in these systems. Therefore, it is most practical to replace this type of monomer with a SOC monomer which can expand and still serve the function of a reactive diluent for the BIS-GMA.

A second useful formulation technique involves adding one of the higher melting, crystalline SOC monomers to a conventional dental resin mixture. Polymerization of the resulting reactive slurry at slightly elevated temperatures leads to the SOC melting, accompanied by a large volume increase, and then undergoing ring-opening copolymerization with an additional volume expansion.

Phase IV. Evaluate the physical properties of polymers derived from the formulations prepared in Phase III.

The SOC monomers can copolymerize with other monomers using visible light activation; however, slightly higher DTS results were consistently obtained from the chemically cured systems. Paralleling this was the finding that a dual cure (normal photo-curing accompanied by a slow chemical cure) system gave less polymerization shrinkage and higher mechanical strength than a photo-cure alone. This seems to indicate that the less reactive SOC's require a longer-lived source of free radicals to bring about efficient ring-opening of these monomers.

The following results were obtained when SOC monomers were substituted for TEGDMA in a BIS-GMA based dental composite resin formulation. Polymerization shrinkage was reduced by 31 percent compared to the control formulation. Enhancing the degree of conversion by using the dual cure technique resulted in less polymerization shrinkage for the SOC containing formulation while the control resin showed the expected increase in contraction with the greater degree of cure. The tensile adhesive strength of the experimental composite resin was approximately 250 percent greater than that of the control after the specimens of composite bonded-to-polished stainless specimens were stored 24 hours in 37 °C water.

Phase V. Biocompatibility testing of formulations selected on the basis of results from Phase IV.

Biocompatibility testing in the form of implantation toxicity studies have previously been conducted with a dimethylene substituted spiro orthocarbonate monomer[4]. The results indicated that the ring-opened polymer as well as a mixture of BIS-GMA and the spiro monomer illicit only mild inflamatory responses which are characteristic of a wide range of dental materials. No testing of the more reactive spiro monomers described here has yet been carried out. If the physical properties of formulations containing these new monomers demonstrate the expected advantages, then a new series of biocompatibility tests would be in order.

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F. Improvement of Dental Composites, Sealant Cement and Adhesive Materials

Overview

The quest for a durable, esthetic, adhesive and biocompatible material suitable for the restoration of lost tooth structure has long challenged dental materials researchers. A significant step toward the realization of this goal was the development of resin based dental composites which overcame many of the shortcomings of the silicate cements (purely inorganic composites) and unfilled resin restoratives (purely organic composites based on methyl methacrylate and its polymer). The synthesis of BIS-GMA (an offspring of the marriage of epoxy and acrylate chemistry) by Bowen, ushered in the modern era of resin based dental composite restorative materials and also other resin based dental materials [1,2]. The essential components of dental composites are: (1) a resin system comprising one or more vinyl monomers which on polymerization forms the matrix or continuous phase, (2) reinforcing fillers such as silanized glass, quartz, other ceramics, organic and hybrid organic-inorganic powders of various sizes and shapes which constitute the dispersed phase, (3) an interfacial phase for bonding the continuous and dispersed phases, derived from vinyl silanes, titanates, i.e., coupling agents, (4) a polymerization initiator system effective under ambient conditions, and (5) stabilizers for optimizing storage stability and also preserving the chemical stability of the hardened restoration. Unlike glass ionomer cements which bond to tooth structure, current resin based composites are non-adhesive in nature [3,4].

However, the acid-etch technique (Buonocore), in most situations, provides an effective micromechanical mechanism for bonding dental composites to enamel [5,6]. Bonding to dentin is a more challenging problem but recent developments appear to be yielding effective coupling agents for this substrate as well [7-16]. Efforts to enhance the durability and range of applications (e.g., posterior as well as anterior fillings) of dental composites include optimization of the types, sizes, shapes and volume of the dispersed phase, reductions in the solubility parameter, residual vinyl unsaturation and polymerization shrinkage of the resin phase, and the development of more effective interfacial bonding phases.

Dental sealants have similar compositions and chemistry but are unfilled or only lightly filled and usually contain a higher proportion of diluent monomer(s). Dental resins also are widely used in other applications (e.g., adhesives,core build-up and crown and bridge materials, laminating vaneers, etc.).

Dental cements, which also have a composite nature, find use in a wide variety of dental applications. In restorative dentistry they are employed as temporary, intermediate, and (in the case of glass ionomer cements) permanent filling materials. Their chemistry of hardening involves a series of acid-base reactions involving ion-exchanges that result in the development of a matrix into which are imbedded partially reacted basic filler particles [3]. An ion-exchange mechanism involving polyelectroylte cements (e.g., glass ionomer) and mineralized tissue also may explain their adhesion to tooth structure [4].

Two types of dental cements can be distinguished depending on their water content: (1) those that are aqueous based (e.g., zinc phosphate, polycarboxylate, glass ionomer) and in which water plays a role both in their setting and in the development of their molecular and micro structures, and (2) those that are relatively non-aqueous in nature, although catalytic amounts of water or other protic compounds (e.g., acetic acid) are needed to achieve clinically acceptable setting times (e.g., ZOE, EBA, HV-EBA, dimer acid, etc.)

This section is divided into four distinct parts:

I. Improvement of Dental Resin Systems for Composites and Sealants. (Synthesis, Formulation and Evaluation)
II. Improvement of Dental Cements. (Synthesis, Formulation and Evaluation)
III. Improvement of Interfacial Bonding Systems and Fillers for Composites and Cements. (Filler Portion of Project is New) (Synthesis, Formulation and Evaluation)
IV. Bonding of Low Surface Energy Resin Systems to Tooth Structure. (New Project) (Synthesis, Formulation and Evaluation)

I. Improvement of Dental Resin Systems for Composites and Sealants

Objective

The goal of this research task is to enhance the durability of dental composite, sealant, cement and adhesive materials through the use of low-shrinking, but highly thermosetting hydrophobic resins.

Background

Recent research has indicated that the oral environmental resistance (OER) of resin based dental materials is a significant factor in determining their in vivo performance and ultimate service life both in relatively stress-free as well as in stress-bearing applications [17-19]. The continual sorption of water and other intraoral substances can promote plasticization of the organic matrix, which can be viewed as the first line of defense of composites and related resin based dental materials against the constant assaults of the oral environment. Ultimately, this chemical softening process can lead to degradation reactions not only in the polymeric binder and critical interfacial phase but, in some cases, even in the filler phase as well [20-23]. 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 lower than that prevalent in the oral environment [24,25]. The other is aimed at increasing the degree of polymerization and the crosslink density of resin systems by methods compatible with the clinical situation [26-29]. The first approach involves the synthesis and formulation of resins that yield polymers containing significant amounts of fluorocarbon or siloxane segments to confer on dental materials the necessary hydrophobicity (by lowering solubility parameters) to resist the detrimental effects of the oral environment [24,25,30,31]. The second approach, which also may complement the first approach, involves the synthesis and formulation of multifunctional methacrylates, multifunctional chain transfer agents and other types of network forming agents that can augment the degree of cure and crosslink density [27-32]. Emphasis also is directed to monomers that should have minimal polymerization shrinkage[32]. An ancillary part of this approach also involves the development of more efficient, color stable initiator systems for ambient polymerizations of dental resins in a more uniform fashion [27].

PROGRESS REPORT

Phase I

(a) Synthesis of oligomeric multifunctional monomers of higher covalent fluorine content, lower viscosity and greater flexibility.

This part of Phase I will commence next year.

(b) Formulation and evaluation of PFMA (Fig 2) and PFUMA (Fig 1) based composites.

A visible light polymerizable composite formulation was prepared using the polyfluorinated prepolymer multifunctional urethane methacrylate, PFUMA, and a siloxane diluent monomer, BIS-MPTMS (Fig. 1). A fine (2-4 øm) fused, silanized quartz powder was used as the reinforcing filler and camphorquinone, CQ, and ethyl 4-dimethylaminobenzoate, 4EDMAB, were used as the photoinitiator system (Table 1). A second hydrophobic composite derived from the polyfluorinated prepolymer multifunctional methacrylate, PFMA, and the hydrocarbon dimethacrylate diluent, DMDMA (Fig. 2) was prepared using the same filler and photoinitiator system (Table 1). The wear properties of preconditioned specimens of these composites are described in Part II, section A, (Page 60) of the report.

Table 1

COMPOSITION OF HYDROPHOBIC, FLEXIBLE RESIN BASED COMPOSITES

Formulation	Component		Weight Percent
I	PFUMA		22.03
	BIS-MPTMS -	Resin	9.44
	CQ		0.05
	4-EDMAB		0.22
	Silanized Fused Quartz (2-4 øm)	Filler	68.26
II	PFMA		21.69
	DMDMA		9.04
	CQ		0.05
	4-EDMAB		0.20
	Silanized Fused Quartz (2-4 øm)		69.02

The task on new types of binary and tertiary diluent monomer system is deferred to a later date.

(c) Syntheses of highly fluorinated multifunctional methacrylates based on hexachlorocyclophosphazene. This part of the project is deferred until a later period, depending on the outcome of (a) and (b).

(d) Silyl ether derivatives of BIS-GMA

Previously, we reported the synthesis of a low viscosity, bulky tetramethacrylate derived from BIS-GMA and 3-methacryloxypropyldimethylchlorosilane (MAPDMCS) (Fig. 3). An alternate route to this disilyl ether derivative of BIS-GMA involves the use of 3-methacryloxypropyldimethylethoxysilane (MAPDMES) in place of MAPDMCS. Infrared and NMR analyses confirm the assigned structure.

Oligomeric silyl ether derivatives of BIS-GMA were prepared using the synthetic routes outlined (Figs. 4 and 5).

The tacky, viscous resin was characterized by IR and NMR analyses. Preliminary studies indicate that these silyl ether derivatives are compatible with themselves as well as a wide range of dental monomers and yield composites with acceptable mechanical properties (Table 2). The water sorption of these composites is expected to be lower than

BIS-GMA composites. The water uptake of the composite derived from formulation 2, Table 2 was only 0.22 mg/cm^2. A more detailed account of this study was presented at the 1986 AADR meeting.

Table 2

24 HOUR DIAMETRAL TENSILE STRENGTHS OF EXPERIMENTAL SILYL ETHER COMPOSITES

Composite	Resin Composition	Photo-Initiator	Powder Liquid Ratio	Diametral Tensile Strength in MPa, Standard Deviation (No. of Specimens)
1	BIS-GMA/$(MAPDMS)_2$	0.2 % CQ 0.7 % 4-EDMAB	6	42 ± 2 (5)
2	BIS-GMA/TMDSE 71% HMDMA 29%	0.15% CQ 0.8 % 4-EDMAB	4	35 ± 2 (5)
3	BIS-GMA/TMDSE 57.8% HMDMA 42.2%	0.15% CQ 0.8 % 4-EDMAB	5	42 ± 4 (5)
4	BIS-GMA 48.5% BIS-GMA/ $MAPDMS)_2$ 48.5% MAPDMES 3.0%	0.15% CQ 0.75% 4-EDMAB	5	43 ± 1 (6)

(e) Synthesis of hydrophobic urethane derivatives of BIS-GMA is deferred until next year.

(f) Additives to increase the degree of polymerization and crosslink density. Work in this area is deferred pending completion of related project (g).

(g) Improved initiator systems for dental resins. Visible light activated composites polymerize by a light induced reaction involving a photoxidant, e.g., camphorquinone (CQ) and a photoreductant, e.g., a tertiary amine. This study was undertaken to determine some of the factors that may influence the degree of cure (DC), depth of cure (DOC), and degree of discoloration (DOD) of resin based dental materials. The parameters that were evaluated for their effect on these properties were (1) concentration of CQ, (2) type and concentration of tertiary amine and (3) molar ratio of amine to CQ. For this study the same visible light source was used. DC was measured by FTIR methods. DOC composite specimens were prepared by 10s irradiation from one side of steel cylindrical molds. After the uncured portion was removed, the hardened portion was measured by a micrometer. DOD was determined visually after 24 hours exposure to a S275 sunlamp.

It was found that tertiary aromatic amines generally yield composites with higher DC's, DOC's and DOD's than tertiary aliphatic amines. For aromatic amines, the DOD depends on a number of factors, e.g., the amine concentration, the nature and position of substituents, and the duration of the exposure to the curing light. Increasing the concentration of CQ increases DC and DOC, while increasing amounts of tertiary amine have less effect on these properties.

In a related study, amine salts, derived from tertiary amines and certain acids (oxalic, pyruric, benzoylformic) and complexes, arising from the interaction of these amines and esters of the above acids as well as by their reaction with aliphatic or aromatic anhydrides, were assessed for their accelerative potential. In chemical cures using benzoyl peroxide the amine salts and complexes derived from tertiary aromatic amines were at least comparable in accelerative potential (determined by setting time, diametrial tensile strength) to their amine precursors and yielded composites with superior esthetics and color stabilities. Similarly these amine derivatives are effective, color-stable photoaccelerators for resin systems containing CQ and/or similar photooxidants. Thus, in addition to yielding resin based materials with high DC's and DOC, the amine salts and complexes provide cured materials of enhanced color stability. Significantly, some of these amine derivatives also can function as photoinitiators under appropriate irradiation (e.g., sunlight, UV).

Phase II. Prototype Composite for Clinical Evaluation

A chemically activated, power/liquid, PFMA composite formulation using a conventional fused quartz filler is being evaluated by Dr. Joseph Moffa of USADA.

Phase II Composites derived from Phase I, (b) e.g., PFUMA and PFMA with several types of diluent monomers have been evaluated for their mechanical properties (found to be at least adequate), water sorption (found to be extremely low) oral environment resistance (found to be highly resistant to the water end of the solubility parameter range, less so to the heptane-alcohol region), wear resistance (found to be less subject to environmental factors) and polymerization shrinkage (found to be low).

II. Improvement of Dental Cements

Overview

Although used in relatively small quantities, dental cements are essential in a number of dental applications as: (a) temporary, intermediate and, in some cases, more permanent restoratives; (b) cavity liners and bases, (c) luting agents to bond preformed restorations and orthodontic devices, (d) pulp capping agents and endodontic sealers and (e) impression pastes. This wide range of dental uses makes it virtually impossible for one type of cement to have all the necessary properties demanded in these diverse applications. Therefore, there is a need to develop "tailored" dental cements with a view toward maximizing the properties needed to fulfil their ultimate functions. One approach for improving the overall properties of dental cements involves developing hybrid cement-composites or resin-modified cements.

Objective

To enhance the durability of dental cements by improving their hydrolytic stability, especially under acidic oral conditions (e.g., in plaque coated areas), and by moderating their brittle nature while increasing their tensile and flexural strengths.

Introduction

A novel, versatile class of dental cements, non-aqueous polycarboxylate cements (termed haltopolymers), were developed from the commercially available C_{36} and C_{54} hydrocarbon polycarboxylic acids, designated dimer (DA) and trimer (TA) acids. The divalent metallic dimerates and trimerates matrices of these cements are haltopolymers, a term coined to denote their dual salt-like and polymer-like character. All of these cements have water repellent properties due to their chain structures consisting of large paraffin segments linked by a few hydrophilic carboxylate groups. Some of these cements, especially those derived from calcium bases, display energy-absorbing qualities under compressive stress. These cements do not inhibit the polymerization of resin based dental materials (as do engenol based cements) and, in fact, can be formulated to yield strong hybrid composite cements. The calcium hydroxide based cements have low solubilities and enhanced hydrolytic stability but still provide an alkaline environment which may promote secondary dentin formation, and thus have potential utility as cavity liners, endodontic sealers, etc. Further details on the properties of these cements are contained in the abstracts and microfilmed papers presented at IADR meetings in 1984 and 1985 and at the 10th Annual Meeting of the Society for Biomaterials in Washington, DC, 1984 [48-50]. An invited talk on the properties of hydrophobic, energy absorbing dimer acid cements was given at the Dental Materials Conference at St. Andrew's Scotland, UK, in 1985.

Glass ionomers are relatively high modulus cements which adhere to enamel and, to a lesser extent, to dentin. With minimal surface preparation, adhesive strength is higher to enamel than dentin (presumably because of the lower mineral content of the latter) but is relatively low in either case because of the low tensile strength inherent in this type of material. Glass ionomer cements also display a susceptibility to excessive hydration during the early stages of their setting reaction which results in an inferior cement. In addition, the hardened cement has a propensity to dehydration, brittle fracture and erosion under acidic conditions.

PROGRESS REPORT

Phase I

(a) A DA cement formulated with 1 part $Ca(OH)_2$ and 1 part $Ca_3(PO_4)_2$ in a powder-liquid ratio of 2 displayed a positive volume change on setting (24 h)of 2.04% ± 0.94%.

(b) Resin-modified dimer acid cements. Since dimer acid (DA) cements do not inhibit the free radical polymerization of vinyl monomers, resin-modified DA cements or hybrid cement-composites (HCC) with acceptable setting times (3-8m) can be formulated into high tensile strength materials that may have utility as intermediate restoratives, bases, liners, etc. Strong HCC's can be formulated containing various amounts of $Ca(OH)_2$ which may have potential as promotors of reparative dentin. HCC's can be formulated as paste/paste or powder/liquid chemically activated systems. Photochemically activated, single paste formulations also can be prepared. In table 3 are shown the formulation of two powder/liquid (P/L) HCC's with their 24h diametral tensile (DTS) and compressive strengths (CS). The glass used in these formulations was a conventional radiopaque glass (45um) silanized with 0.5% by weight of 3-methacryloxypropyltrimethoxysilane (A-174) and coated with 1% by weight of benzoyl peroxide. The DTS values represent a four-to fivefold increase over the unmodified DA/$Ca(OH)_2$ cement. CS values of HCC's also are significantly higher.

Table 3

24 H Mechanical Properties of Resin Modified (DA/$Ca(OH)_2$ Cement

Formulation	Components in Liquid/w%		Components in Powder/wt%		P/L	DTS(STD DEV)	CS(STD DEV)
I	DA	27.0	$Ca(OH)_2$	25.0	2.5	21.2 (1.4)	56.7 (5.4)
	EBPDMA	42.7					
	HMDMA	30.0	Silanized Glass (1%BP)	75.0			
	DHEPT	0.3					
II	DA	33.0			2.5	21.5 (0.6)	68.4 (6.4)
	BIS-GMA	48.1					
	HMDMA	18.7	Same as in I				
	DMAPE	0.2					

DA = Dimer Acid
EBPDMA = Exthoylated bisphenolA dimethacrylate
HMDMA = 1.6 hexamethylene dimethacrylate
DHEPT = N,N-bis(2-hydroxyethyl)p-toluidine
DMAPE = P-N,N-dimethylaminophenethanol
BP = Benzoyl peroxide

(a) Resin-Modified Glass Ionomer Cements (New). An approach towards ameliorating the aforementioned deficiencies of the glass ionomer cement is to incorporate into the formulation a water soluble or compatible vinyl resin capable of interpenetrating or blending with the cement during a dual cure process. Ideally an interpenetrating polymer network (1PN) develops by combining the ionic setting reaction of the glass ionomer with the vinyl addition polymerization of a compatible resin as shown in Fig. 6. The resulting resin-modified cement or hybrid cement-composite (HCC) is expected to have a "rubber toughened" and less permeable nature which should deter catastrophic failure and increase resistance to acidic penetrants. The tendency to undergo hydration/dehydration also should lessen.

Using a water hardening glass ionomer cement (Chemfil II), 2-hydroxyethyl methacrylate (HEMA), ascorbic acid (AA), hydrogen peroxide (HOOH) and a trace of a water soluble cupric salt ($CuSO_4$ $5H_2O$), a hybrid cement-composite (HCC) was formulated (Table 4). AA and $CuSO_4$ $.5H_2O$ were blended with the Chemfil II powder (a blend of powdered polyacid and ion-leachable calcium aluminum fluorosilicate). HEMA, an aqueous solution of HOOH, and a silane coupling agent (A-174) were added to distilled water to provide the liquid component of the HCC which contains about 30% less water than the unmodified Chemfil II cement.

Table 4

Compositon of Hybrid Cement Composite (HCC)

Composition of Powder	Weight Percent	Composition of Liquid	Weight Percent
Chemfill II powder*	99.28	HEMA	28.40
		A-174	0.60
Ascorbic Acid	0.70	HOOH	1.30
$CuSO_4$ $5H_2O$	0.02	H_2O	69.70

Maximum Powder/Liquid Ratio (wt/wt) =6 - 6.7
Detrey/Dentsply

On mixing the components, a workable paste results which appears less subject to hydration during setting than the unmodified glass ionomer. In addition, a significant improvement in diametrial tensile strength occurs along with a modest decrease in compressive strength (Table 5). The working and setting times of the HCC cement are somewhat longer than those of the unmodified cement but still clinically acceptable (working time about 2 m, set time about 4 m from start of mix at 23 °C).

Table 5

24 Hour Diametral Tensile (DTS) and Compressive Strengths (CS) of HCC

	Powder/Liquid Ratio	DTS, MPa,(STD DEV)	CS, MPa, (STD DEV)
HCC	6.7	25.1 (2.1)	138.9 (5.9)
HCC	6.0	24.3 (3.5)	130.3 (6.7)
Chemfil II	6.0	16.7 (1.9)	143.4 (10.1)

Other properties (transverse strength, adhesive strength, microleakage, etc.) of this type of HCC are being evaluated.

Phase I. Tasks (3) and (4) are deferred until later.

III. Development of Improved Interfacial Bonding Systems and Fillers for Composites and Cements

Overview (Filler)

On a weight basis the major component of dental composites is usually the reinforcing filler (e.g., 50-86%). For many properties of the composite the volume percent of the dispersed phase is a more significant parameter. The reinforcing filler performs many functions in a composite such as stiffening the lower modulus resin binder thereby increasing mechanical properties, enhancing dimensional stability, moderating the exotherm of polymerization and the mismatch between the thermal expansion of the organic matrix and tooth structure, reducing water sorption and polymerization shrinkage, and aiding in matching tooth appearance. By using glass or ceramic fillers that have refractive indices approximately those of the matrix they can be used to form translucent fillings that match the translucency of tooth structure. The selective inclusion of compounds with elements of high atomic number (e.g., barium, strontium, lanthanum, zinc, zirconium,titanium, etc.) in the preparation of glass fillers yields esthetic composites with a degree of radiopacity.

A variety of types, shapes and sizes of fillers have been used in dental composites, e.g., quartz, fused silica, borosilicate and aluminosilicate glasses, silicon nitride, calcium silicate, calcium phosphates, aluminum oxide, metals, etc. In addition, submicron fillers such as precipitated or pyrogenic silicas (0.14-0.007 øm) averaging 0.04 øm in size have been used in microfilled composites. The high surface area of this type of filler makes it difficult to achieve high filler loadings by weight in this type of composite, e.g., 50 weight percent is usually the maximum. To enhance their miscibility and dispersion in resin systems, small organic-rich, composite macrofillers are made from pulverized, prepolymerized composites derived from the silanized, microfine fillers and the same or similar monomer systems. Composites formulated with these prepolymerized composite fillers also are termed microfilled composites.

Compared to conventional composites with their larger filler sizes (0.7 to 100 øm, but usually 3-50øm), microfilled composites have a smoother, more easily polishable surface texture which may reduce the adherence of plaque and stains. On the other hand, they have lower moduli and tensile strength, exhibit more creep and have higher water uptake, thermal expansion and polymerization shrinkage than conventional or hybrid composites.

Hybrid composites, which incorporate major quantities of the smaller sized macrofillers along with small amounts of microfillers, achieve almost as smooth a surface texture as the microfilled composites without compromising (often actually improving) other properties. Some of the newer hybrid composites have a multimodal dispersed phase consisting of different types, shapes and sizes of fillers.

An innovative approach to enhance the interfacial bonding of the inorganic and organic phases of the composite is through the use of "semiporous" glass fillers obtained by selectively acid etching the more soluble phase of glass particles having two interconnected vitreous phases [52,53]. Properly done this results in a glass filler having superficial surface porosity into which the resin can flow and mechanically interlock on polymerization, thus complementing the usual bonding through silane coupling agents.

The search for dental composites of superior wear resistance for use in stress-bearing applications has spurred research into new types of stable fillers of sizes and shapes conductive to optimal packing efficiency. New techniques to significantly increase filler loadings have appeared in [54,55].

Overview (Interfacial Bonding Systems)

Although it is only a minor component of resin based dental restorative materials, an interfacial bonding agent exerts a profound effect on the durability of composites. The quality of the interfacial bonding phase existing between the polymeric matrix and the dispersed phase exerts a significant effect on the ultimate properties and the clinical performance of dental composites. Even composites prepared from the best of resin binders and reinforcing fillers will be deficient in durability if water and other contaminants penetrate and disrupt the interfacial bonding phase.

Bifunctional coupling agents such as organofunctional silanes, titanates, zirconates, etc., are used in composites to promote adhesion between mineral fillers and organic resin binders. Alkoxysilanes having terminal vinyl groups have been the most widely used type of coupling agent for dental composites. Initially, a vinyltrialkoxysilane was used but it was later found that 3-methacryloxypropyltrimethoxysilane was more effective.

Alkosysilanes can react with surface moisture, usually present at least as a monolayer on mineral surfaces, to generate silanol groups which can strongly hydrogen bond to hydroxylated surfaces. In addition, silanol groups can react chemically with surface hydroxyl groups of the filler via covalent bond formation. There is some direct (e.g., spectroscopic) evidence that suggests that these kinds of reactions do occur between silane coupling agents and many types of mineral fillers used to reinforce composites. Organofunctional silanes can be visualized as reacting by both hydrogen bonding and/or covalent attachment to mineral fillers by virtue of their silanol or derivative groups and by copolymerization with the resin system via their terminal vinyl groups. Indirect evidence for this interfacial bonding is provided by the observed enhancement in mechanical strength and resistance to water and other chemicals of silanized composites.

The effectiveness of coupling agents in a composite depends on a number of factors: (1) the nature of the resin binder and filler, (2) the structure and chemical reactivity of the coupling agent (3) the amount used and (4) the mode of application.

Objective

To develop filler and interfacial bonding systems of enhanced durability applicable to dental composites and cements (filler portion of project is new).

PROGRESS REPORT

Phase I. Development of Improved Interfacial Bonding Phases for Composites and Cements.

The objective of the first part of this study was to evaluate various types of silane agents and silanization techniques for their efficacy in dental composites.

Commercial silane agents evaluated included:
3-methacryloxypropyltrimethoxysilane (MAPS),
3-methacryloxypropyldimethylethoxysilane (MAPES)
3-methacryloxypropyldimethylchlorosilane (MAPCS),
3-mercaptopropyltrimethoxysilane (MPS),
3,N,N-dimethylaminopropyltrimethoxysilane (DMAPS)
3-N,N-dimethylaminophenyltriethoxysilane (DMAΣS)
and experimental multifunctional silane agent, BIS-GMA/(IPTES)$_2$ (see Fig. 7) which was synthesized for this study.

The results of this phase of this study indicate that methacryl based silanes performed best as interfacial bonding agents (assessed by diametral tensile strength and transverse strength measurements). MAPS yielded composites with the highest strength values; MPS had some modest coupling action compared to the control (composite with unsilanized glass). DMAPS, in addition to being a poor silane agent, is also a poor photoreductent for camphorquinone (CQ). DMAΣS, although a highly effective photoreductant for CQ, did not show any appreciable interfacial bonding qualities. The experimental silane agent, BIS-GMA/(IPTES)$_2$ yielded composites that had the most hydrolytically resistant interfacial bond as determined from DTS and TS measurements after 7 days thermal cycling (5 °C - 55 °C) experiments. TS measurements are more sensitive than DTS determinations in assessing the quality of the interactial bond.

Silanization techniques explored included (a) integral blending, (b) presilanization at different temperatures (80°, 110°, 140°C) and (c) dual silanization. Integral blending yielded composites with about the same diametral tensile strengths as presilanized derived composites. However, as measured by transverse strength techniques and after thermal cycling, presilanized composites gave higher TS and better retention of other mechanical properties. The use of a dual silanization technique combining presilanization and integral blending shows promise of yielding more durable composites. A more detailed description of this study was presented at the 1986 AADR meeting.

Phase II. To develop improved, more durable interfacial bonding systems and fillers for composites and cements. (Filler portion of project is new.)

In addition to our silanization studies using a conventional radiopaque glass, a preliminary silanization study of a softer, nonsiliceous filler was explored. Sodium calcium metaphosphate, $NaCa(PO_3)_3$, is a commercially available fibrous filler that is being used in a variety of composite applications. Composites were prepared using this filler as received and after treatment with a silane agent. No significant differences were noted in the diametral tensile strengths or transverse strength of the silanized and unsilanized specimens.

A potential non-silane coupling agent also was evaluated for calcium phosphate fillers. PMDM (the diadduct of HEMA and pyromelletic anhydride) was evaluated as a coupling agent for resin based calcium phosphates and metaphosphates composites. Preliminary results indicate that under the conditions used to apply PMDM to the mineral (room temperature, acetone) no significant coupling occurs between the methacrylate resin and tricalcium phosphate or calcium metaphosphate. Both chemical and visible light cured composites were used in the study.

IV. Bonding of Low Surface Energy Resin Systems to Tooth Structure (New Project)

Objective

To develop durable bonding systems for tooth structure compatible with a variety of resin based dental materials especially those of low surface energy.

Overview

Currently used resin based dental composites are not adhesive to tooth structure. However, the discovery of the acid etch technique made it possible to bond resin based dental materials to enamel by a micromechanical interlocking mechanism [5,6]. Surface microporosity is generated on enamel by a brief pretreatment with aqueous phosphoric acid or certain types of organic acids e.g., pyruvic, citric, etc. The usual acid etch technique is probably generally ineffective and contraindicated for use with dentin.

Adhesion to dentin has presented a more challenging problem. On a weight basis dentin consists of 69% hydroxyapatite, 18% organic matter (mainly collagen) and about 13% water. An adhesive bonding or coupling agent for this substrate would mean less invasive cavity preparations with decreased loss of sound tooth structure and a reduction in microleakage with its potential for secondary caries formation. Considerable effort has been devoted to the development of coupling agents that can mediate bonding between dental resins and apatitic substrates [7-16].

Surface-active comonomers that can bond to apatitic substrates by chelation of surface Ca^{+2} and/or other multivalent cations have been made by the reaction of N-substituted aryl glycines (for example, NPG, NTG) with glycidyl methacrylate (GMA). Other types of coupling agents are functional vinyl monomers that have groups capable of reacting with collagen by specific chemical reactions, e.g., esterification, urethane or schiff base formation. Another approach for chemically bonding to collagenous substrates involves graft polymerization techniques using free radical initiation [7-16].

Recently three types of adhesion-promoting systems have demonstrated rather strong adhesion to dentin. One system involves pretreatment of dentin with an aqueous solution of 2-hydroxyethyl methacrylate (HEMA) and glutaraldehyde [13,14]. The critical component of the second bonding system is the functional monomer 4-methacryloxyethyl trimellitic anhydride, 4-META [9,10]. The third bonding procedure utilizes a brief application of a cleanser, mordant aqueous solution of ferric or aluminum oxalate, a surface active comonomer such as NPG-GMA or NTG-GMA and PMDM, the diadduct of HEMA and pyromellitic anhydride [8,15,16]. The latter two bonding systems display significant adhesion to enamel as well as dentin.

PROGRESS REPORT

Phase I. In collaboration with Dr. Rafael Bowen of the American Dental Association Health Foundation, Paffenbarger Research Center (APAHFPRC) we are synthesizing a series of carboxylated monomers, one of which should act in a manner analogous to PMDM and 4-META [8-10,15]. These coupling agents should exhibit improved compatibility with dentin because they have amide groups in their structure as well as carboxyl groups (CO_2H).

> A surface-active monomer analogous to PMDM, was prepared from $3,3^1,4,4^1$-benzophenonetetracarboxylic diahydride (BTDA) and t-butylaminoethyl methacrylate (TBAEM). The reaction was carried out in methylene chloride by adding dropwise a solution of TBAEM in this solvent to a stirred solution of BTDA at room temperature. Two moles of TBAEM were used to one of BTDA to yield after removal of the solvent the diadduct as a viscous yellow liquid. Purification by trituration with cyclohexane yields a purer product which slowly solidifies on standing. This monomer is polymerizable

by exposure to UV irradiation. IR analysis supports the structure of this coupling agent as having difunctional amidoethyl methacrylate with free CO_2H groups. The benzophenone unit in the structure confers on this monomer photoactivity.

Phase II. A third type of bonding agent based on some of our early work and that of Asmussen will be synthesized from 2-hydroxyhexanedial and methacryloxyl chloride and evaluated as an adhesion promoting comonomer for dentin later in the project [11,13,14]. Research on the synthesis of fluorinated coupling agents also has been deferred pending availability of starting materials. A new project utilizing the potential bonding capabilities of the newly developed resin modified glass ionomer cements or hybrid cement-composites (HCC) has been initiated in collaboration with members of ADAHPRC.

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McKinney, J.E., Antonucci, J.M., and Rupp N.W. Wear and microhardness of a metal-filled glass-ionomer cement.

Kuo, J.S., Antonucci, J.M. and Wu, W. Evaluation of sioxane-containing dental composites.

Dudderar, D.J. and Antonucci, J.M. Esthetic, non-brittle dental cements based on dimer acid.

Manuscripts Under Review by WERB

Antonucci, J.M., Stansbury, J.W., Dudderar, D.J. and Venz, S. Dental resin and initiator systems based on polythiols.

Venz, S. and Antonucci, J.M. Effect of a polythiol on the degree of polymerization of resins.

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Venz, S., Rupp, N.W. and Antonucci, J.W. Microleakage and water sorption of hydrophilic and hydrophobic dental composites.

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Antonucci, J.M. New trends in dental composites, Dentsply Intl., York, PA (July 1986).

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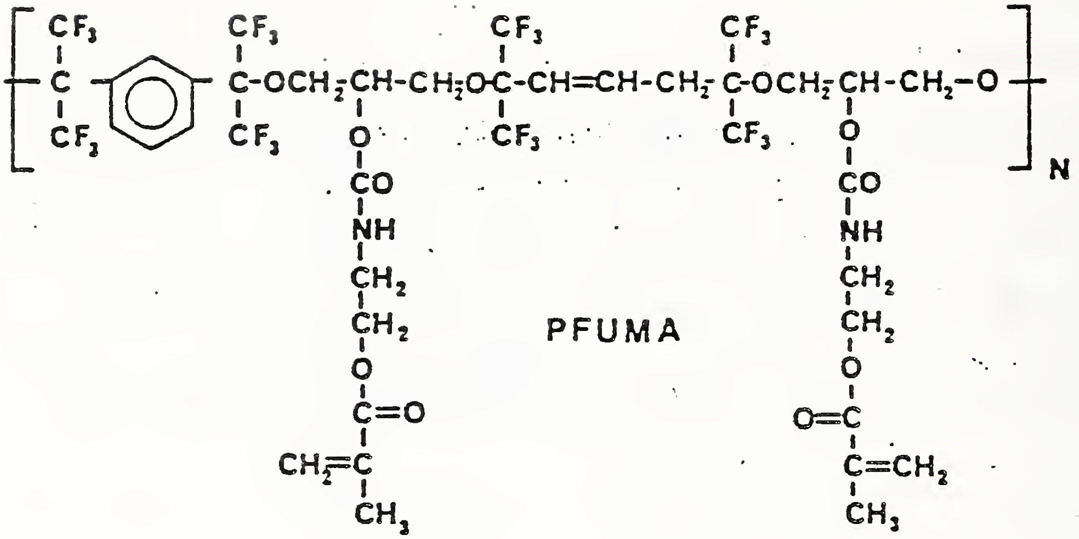
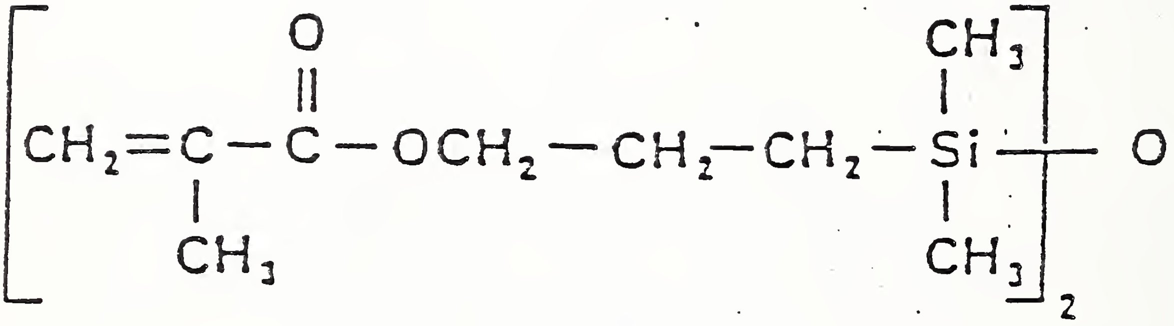
Figure 1



PFUMA

MW = 12,060

%F = 37.8

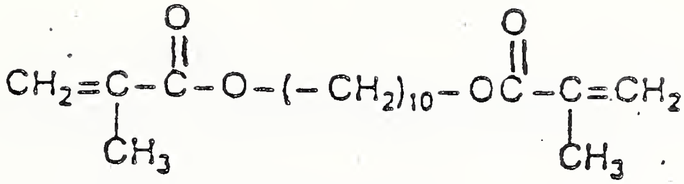


$$\left[CH_2{=}C(CH_3)-C(=O)-OCH_2-CH_2-CH_2-Si(CH_3)_2\right]_2O$$

(BIS-MPTMS)

Structural formulas for (a) PFUMA and (b) BIS-MPTMS

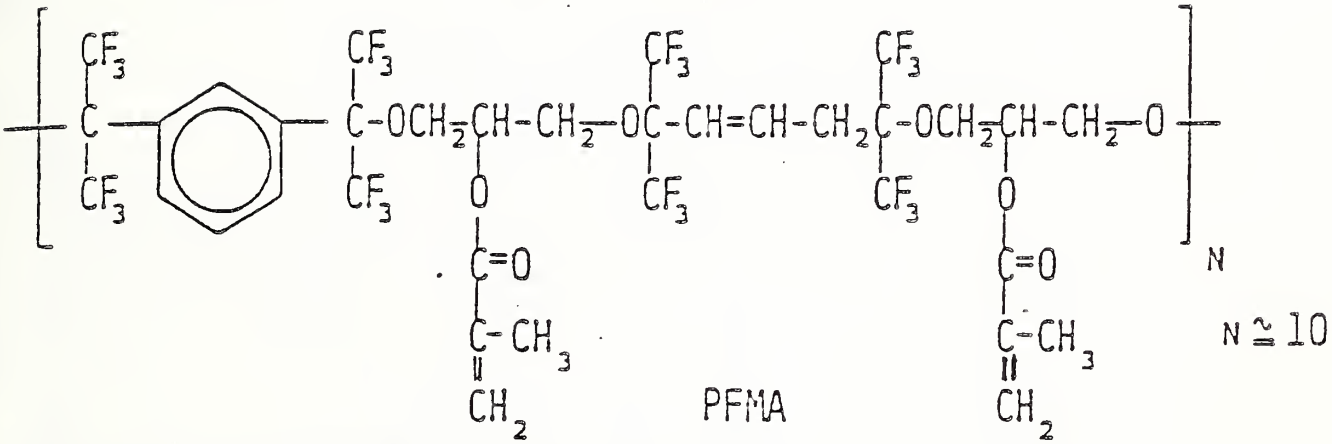
Figure 2



$CH_2=C(CH_3)-C(=O)-O-(-CH_2)_{10}-OC(=O)-C(CH_3)=CH_2$

DMDMA

1, 10-Decamethylene Dimethacrylate MW= 310



PFMA

MW of Repeating Unit = 1032
MW = 10,320 Percent F = 44.2

Figure 3

SYNTHESIS OF BIS(METHACRYLOXYPROPYLDIMETHYLSILYL)
ETHER OF BIS-GMA

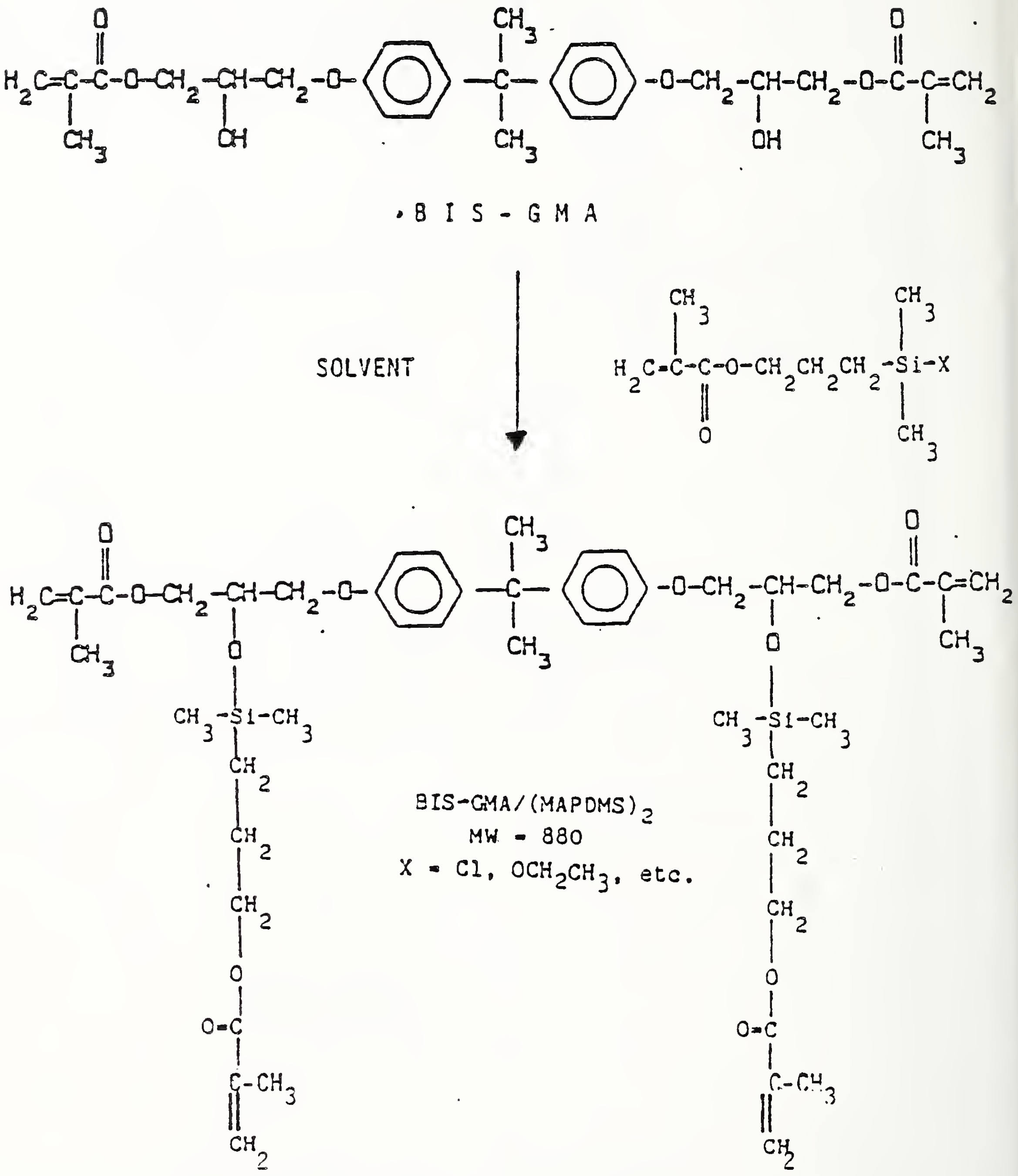
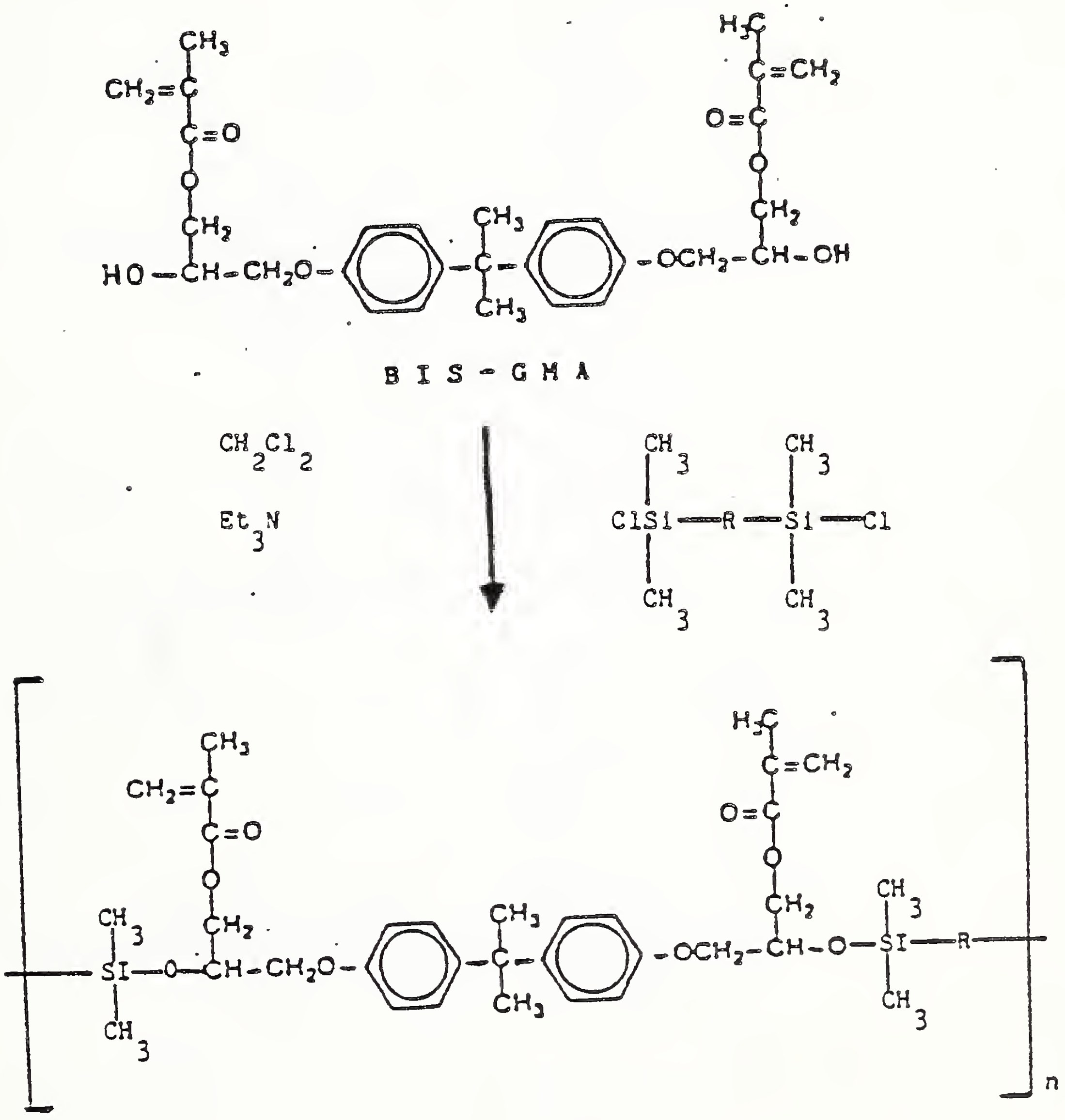


Figure 4

SYNTHESIS OF OLIGOMERIC SILYL ETHERS OF BIS-GMA

METHOD A



R = CH_2CH_2, $(CH_2)_6$ etc.

Figure 5

SYNTHESIS OF OLIGOMERIC SILYL ETHERS OF BIS-GMA

METHOD B

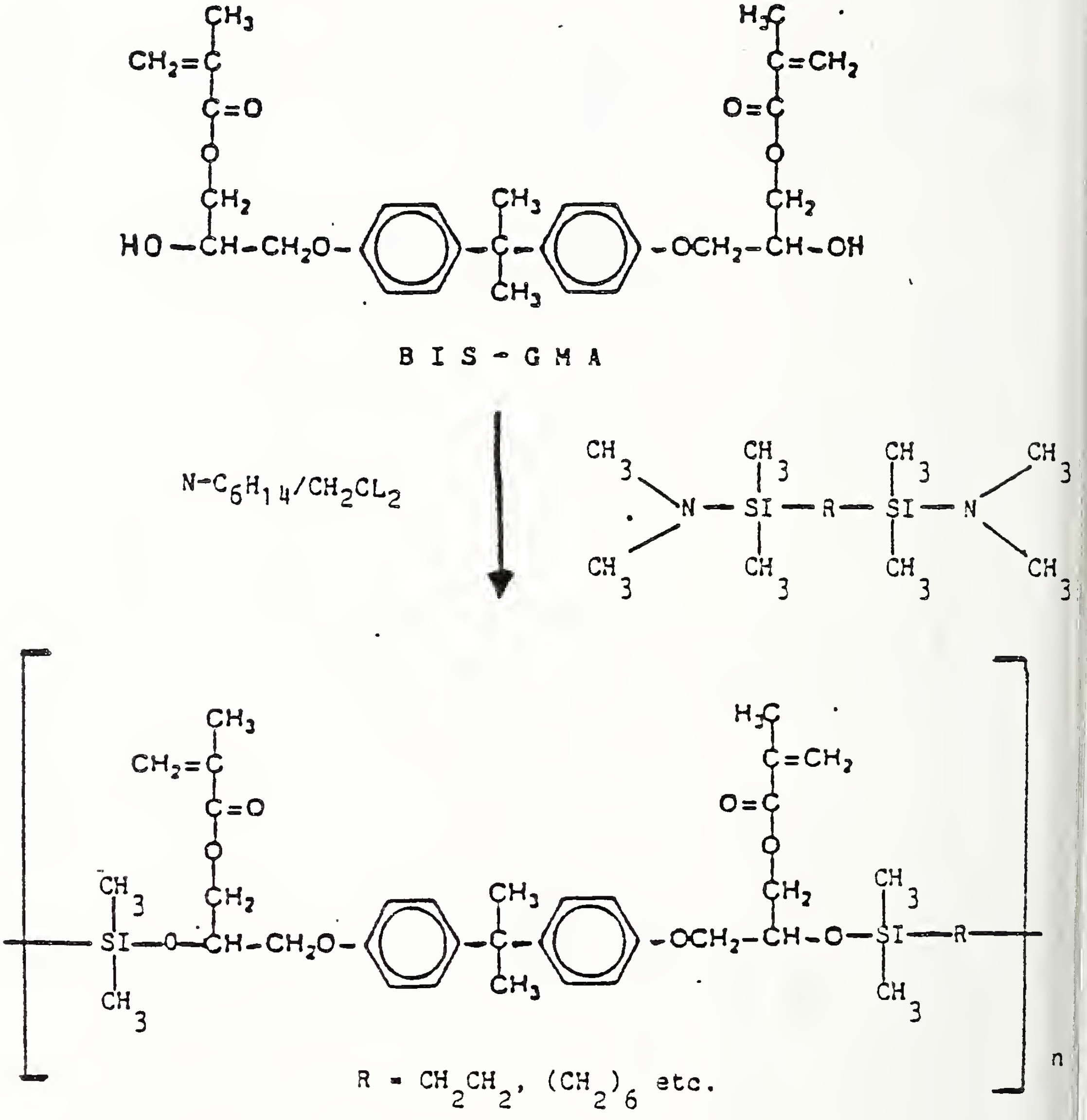
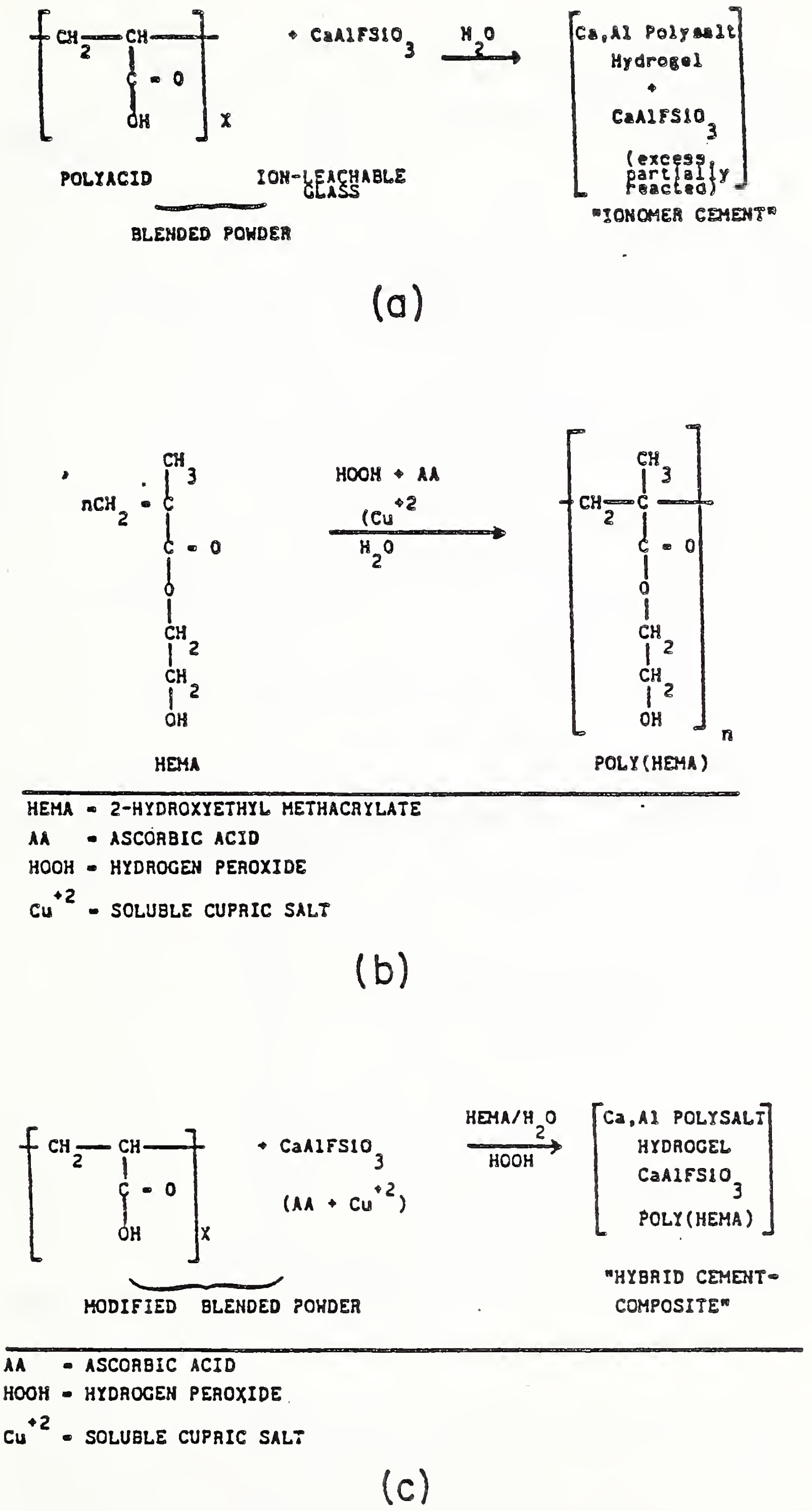


Figure 6

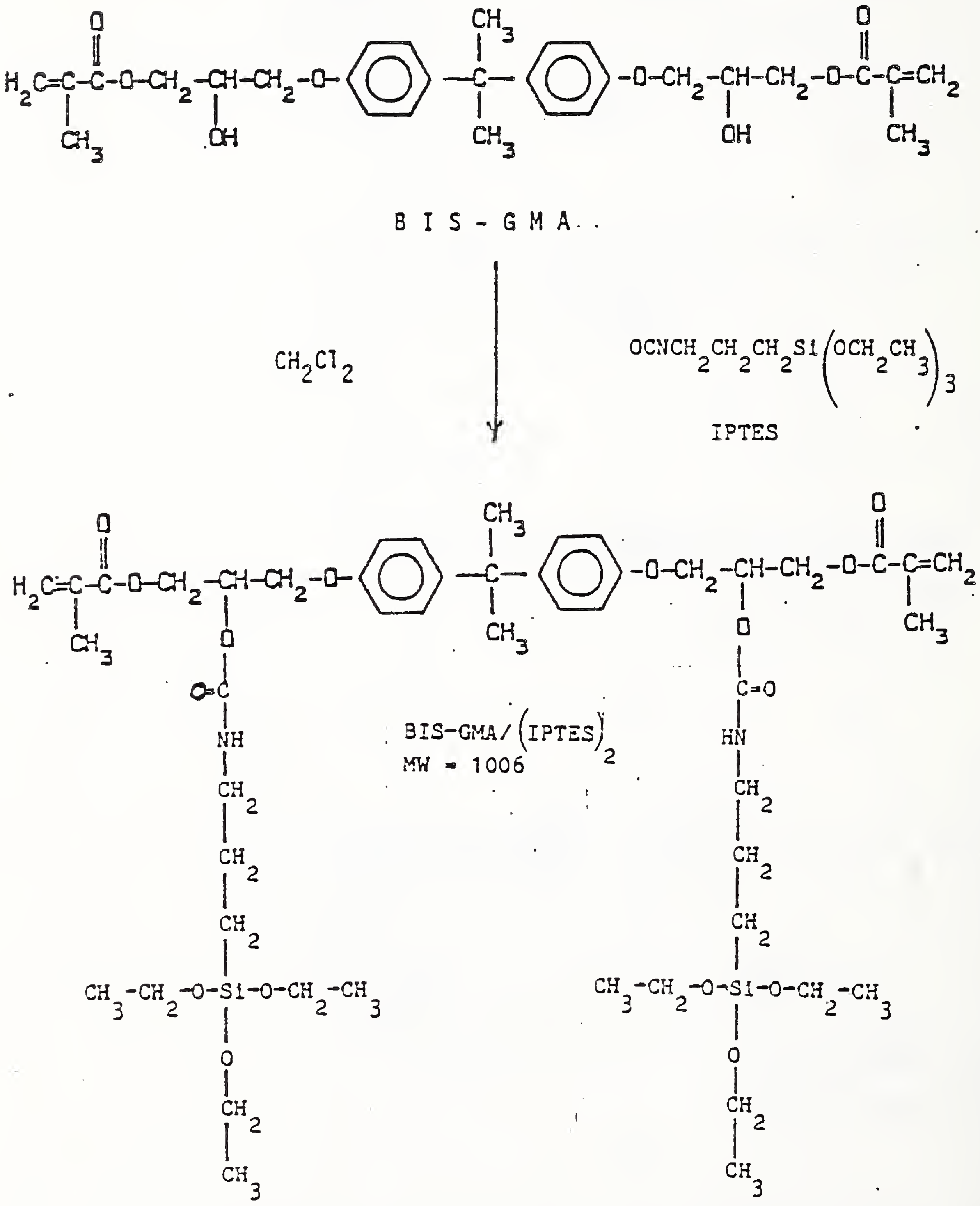


Polymerization mechanisms for (a) conventional water hardenable glass ionomer cement, (b) aqueous free radical polymerization of water soluble monomer, and (c) hybrid cement composite (HCC).

Figure 7

SYNTHESIS OF A MULTIFUNCTIONAL SILANE AGENT

(DIADDUCT OF BIS-GMA AND 3-ISOCYANATOPROPYLTRIETHOXYSILANE)



II. WEAR RESISTANCE AND DURABILITY ASSESSMENT OF DENTAL COMPOSITE RESTORATIVE MATERIALS

Overview

This part of the annual report includes descriptions and results of experimental procedures used by the NBS Dental and Medical Materials Group to evaluate the performance of dental composite restorative materials. The methods employ both in vivo and in vitro wear testing, microhardness, viscoelastic measurements, and microdefect analyses. The objectives are to use appropriate techniques to define and delineate fundamental wear mechanisms applicable to the in vivo wear of these materials. The results from these studies are expected to facilitate the development of improved prototype composite restoratives here and at other laboratories.

This task is divided into the following sections:

A. Wear and Durability Assessments of Composite Restoratives

Phase I. Recent commercial composites which appear promising for posterior occlusal application.

Phase II. Experimental composites with flexible polymers.

Phase III. Glass-ionomer cements: conventional, metal-filled, and modified experimental.

Phase IV. Susceptibility of commercial dental composites to topical fluoride gels (new task).

Phase V. Experimental studies on experimental composites employing apatite fillers (not active this period).

B. Glass-Transition Temperature (T_g) of Matrix Polymers

C. Wear Instrumentation (new task).

Phase I. Methodology for improved wear apparatus.

D. Clinical Examinations Employing Removable Partial Dentures

A. Wear and Durability Assessments of Composite Restoratives

Background

Clinical data and microdefect analyses on in vivo worn restoration biopsies revealed that both mechanical wear and the intraoral environment play an important role in the degradation of composite restorations. For this reason we believe that a relevant wear test should, in some way, include the influence of the intraoral environment. Accordingly, the wear test specimens were preconditioned in appropriate liquids prior to testing. Since dental composites comprise two major components, polymer matrix and inorganic reinforcing filler, appropriate fluids were selected to evaluate the corresponding degradation mechanisms separately.

Our earlier work involved microhardness and wear tests, along with certain other tests, on commercial composite specimens in order to delineate their degradation mechanisms. In order to study potential problems with the matrix, the composite specimens were preconditioned (for usually one week) in selected organic solvents for which the solubility parameter was varied over the range applicable to liquid-food ingredients. When the solubility parameter of the solvent approximated that of the matrix resin, softening was observed by microhardness tests, which usually corresponded to enhanced wear [1][1]. The influence of preconditioning diminished during the course of wear as the wear track depth into the specimen increased.

One serious limitation with dental polymers is that the curing process terminates at a low degree of conversion at the <u>in situ</u> temperature (37 °C). With the free-radical activated processes the increase of viscosity during polymerization inhibits molecular diffusion which, in turn, prevents the proximation of reactive species, which, in the meantime, are used up by oxidation. We have found that increasing the degree of cure decreased the extent of softening and improved the wear resistance of the specimens which would otherwise be damaged from preconditioning [2]. The degree of cure was enhanced by simply elevating the cure temperature.

Since a sufficient elevation in temperature would be impracticable for <u>in situ</u> placed restorations, a more difficult and sophisticated approach involving changes in chemical structure is one of our current activities as explained later in this chapter and Part I, Section F. It has to be remembered; however, that increasing the degree of cure may commensurately increase the polymerization shrinkage, which may lead to a greater loss of marginal integratity in application.

The inorganic reinforcing filler was evaluated by preconditioning commercial dental composite specimens in weak intraoral acids which have damage potential to the filler and the interface. Composites employing modified glasses with alkaline earth elements to obtain radiopacity were more sensitive than the pure silica reinforced composites. It was determined that stress corrosion plays an important role in the degradation of composite restorations as evident from the leaching experiments of Soderholm [3,4] and the wear and hardness measurements made at NBS [5].

Since glass-ionomer cements have good bonding properties to dental tissue [6], it was decided to include the evaluation of their wear behavior in our studies. The cure process of the glass-ionomer cements does not seem to be as viscosity limited as with the resin-based composites.

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[1] Figures in brackets designate references included at the end of this chapter.

Accordingly, higher degrees of cure can be reached at the in situ temperature with the former.

With the three commercial glass-ionomer materials studied, the wear resistance of the water-preconditioned specimens was good except that the incidence of catastrophic failure from brittle fracture during wear was frequent [7]. Specimens preconditioned in dilute lactic acid revealed considerable chemical dissolution as apparent from electron micrographs and accelerated wear. More recent work [8] on a commercial silver-filled glass-ionomer cement showed that although the wear resistance improved considerably, the susceptibility to brittle fracture and chemical dissolution in lactic acid were still serious problems. These problems stress the need for appropriate modifications in the composition and structure of this class of materials for enhanced durability as will be discussed later in this chapter.

PROGRESS REPORT

Phase I. Recent commercial composites which appear promising for posterior occlusal application.

No experimental activity work in Phase I was undertaken during this reporting period. Our past work on commercial composites provided a sufficient basis to initiate research on NBS experimental composites. During this reporting period; however, a manuscript concerned with the wear of selected commercial composites preconditioned in relevant organic solvents was completed and published in the Journal of Dental Research [1]. At a later time we will very likely conduct some evaluations of selected commercial posterior composites.

Phase II. Experimental Composites with Flexible Polymers

The specific objective of this task was to obtain a multifunctional polymer matrix with a high degree of cure (at in situ temperature), a low solubility parameter, and low polymerization shrinkage. The first experimental composite used in this study was a hydrophobic, flexible resin comprising 70 wt % poly(fluorourethane methacrylate) (PFUMA) and a siloxane diluent bis(methacryloxypropyl) tetramethyldisiloxane (BIS-MPTMS). These were mixed with a silanized fused-quartz filler. (For further details of structure and composition, see Part I, Section F of this report and Reference [9].) The polymerization shrinkage was reduced by using a prepolymer of PFUMA having about 20 repeat units corresponding to a molecular weight of about 12,000.

The results for the PFUMA/BIS-MPTMS system are shown on Fig. 1, which includes the Knoop Hardness Ratio, p_f/p_i; the early wear, s_5; and the steady state wear, m_s. p_i is the initial hardness before preconditioning in the selected media, and p_f, after. s_5 is the wear at five hours, and m_5 is the asymptotic steady-state wear rate. The preconditioning media were water and pure ethanol. From the hardness ratio data, it is apparent that considerable matrix softening results from the penetration of ethanol. On the other hand, both wear quantities are essentially unaffected. This result is attributed to the high degree of crosslinking which, in this case, permits some diffusion, but very limited dissolution from organic solvents.

The results of this work were presented before the IADR Conference at the Hague [10] and a manuscript was presented to the Dental Materials Group (DMG) microfilm series.

Although the wear of the PFUMA/BIS-MPTMS system appears to be unaffected by ethanol preconditioning, the absolute hardness (not shown in Fig. 1) is less and the wear much larger than that observed for the more conventional resin-based composites. For this reason we have initiated a study involving a composite with a resin of a higher flourine content and greater flexibility. The system currently under study is a 70/30 mixture of poly(fluoromethacrylate) (PFMA) and 10-decamethylene dimethacrylate (DMDMA) diluent. (See Part I, Section F and Reference [9].)

Phase III. Glass-ionomer cements: conventional, metal-filled, and modified experimental.

The experimental work on the commercial glass-ionomer cements, including several conventional ones and one metal filled, was completed during the last reporting period. This year a manuscript concerned with the wear of the conventional glass-ionomer cements was prepared and was submitted to the Journal of Dental Research. The work on the metal-filled system was presented before the AADR Conference and a manuscript was submitted to the DMG microfilm series. [8] A similar manuscript has been approved by the Washington Editorial Review Board (WERB) for archival publication.

The conclusions are that these materials need modifications to produce properties necessary for posterior application. The work on some experimental modified glass-ionomer cements, referred to here as hybrid cement-composites was initiated during this period.

The so called hybrid cement-composites (HCC) formulated at NBS are designed to overcome the deficiencies of glass-ionomer cements, namely, susceptibility to brittle fracture and dissolution in intraoral acids. The experimental system (HCC) contained a water-soluble monomer, 2-hydroxyethyl methacrylate (HEMA) in the liquid (to be mixed with the powder) with appropriate catalysts added to a conventional glass-ionomer cement powder (See Part I, Section F) After mixing, the two reactions (polymerization of HEMA and glass-ionomer cement) occur simultaneously producing a "rubber toughened" glass-ionomer cement-composite which is more flexible than the conventional glass-ionomer cements. The experimental results on the HCC specimens showed that the wear rate was slightly larger than that for the conventional glass-ionomer cement, but brittle failures were absent. In addition, unlike the conventional glass-ionomer cements, the hardness was unchanged, and the wear was not enhanced from preconditioning in organic solvents and weak intraoral acids.

The results of this work were presented before the IADR Conference at the Hague [10] and a manuscript was submitted to the DMG microfilm series.

Phase IV. Susceptibility of Commercial Dental Composites to Topical Fluoride Gels.

Another specific source of damage is from the application of topical fluoride gels, which may eventually reach composite restorations even though not applied to them directly. In this connection collaborative efforts were started with the University of Maryland (UMd) Dental School at Baltimore to determine the effects of various topical fluorides on wear of composite resins. Using the NBS pin-on-disc wear apparatus, no significant differences in wear of a silicon dioxide microfil were noted following treatment with 10 six-minute imersions in either water, 1.23% acidulated phosphate fluoride (APF) gel (12,200 ppm) or 0.5% APF gel (5,000 ppm). A composite resin with barium boroaluminum silicate filler is currently being tested.

Since the modified-glass fillers using alkaline earth elements to achieve radiopacity are more subject to chemical dissolutions in weak acids, some sensitivity to the APF Gels with the barium boroaluminum silicate filler is anticipated. Corresponding clinical tests are being conducted at the (UMd) Dental School.

Phase V. Experimental Studies on Experimental Composites Employing Apatite Reinforcing Fillers

This phase has not been initiated as yet. As stated earlier radiopaque composite fillers employing alkaline-earth modified glasses are subject to stress from the intra-oral environment during wear. The conjecture is that corresponding apatites, e.g., barium will satisfactorily satisfy the radiopacity requirements and be essentially insensitive to stress corrosion.

B. Glass Transition Temperature (T_g) of Matrix Polymers

There was no experimental activity on this project during this period. For details on Background, Objective, and Progress Report, see Reference [9]. A manuscript including the results of T_g measurements as a function of cure time on pure BIS-GMA and 70/30 (wt/wt) BIS-GMA/TEGDMA was prepared and submitted to WERB during this reporting period.

C. Wear Instrumentation (New Task)

Background

The wear measurements mentioned throughout this chapter were made using a pin on disc apparatus described in Reference [11]. The original version was designed and assembled at the University of Indiana [12]. A second version was constructed at the National Bureau of Standards and essentially completed in 1976. This version was automatic, being programmed on a tape, but did not involve a central processing unit (CPU). The mechanical portion of the apparatus (involving unique components manufactured at NBS) was reinterfaced, and a programmable instrumentation controller with a CPU was incorporated [11]. This modification resulted in a more convenient, flexible, and reliable system, which has been used up to the present time. The next version is now being considered, for which the salient features are described below.

Phase I. Methodology for improved wear apparatus

As a consequence of increased demand and modified methodology in dental wear measurements, a new pin on disc wear apparatus is being designed, and some of the commercially available components have been purchased in FY 1986. The new version calls for independent stepping motors as drives for the rotating specimen discs and other mechanical controls. These motors are fully programmable with respect to angle, rate, and function, e.g., constant speed, sine function, ramps, or steps. They also eliminate the need for the positioning scanners used in the present version. If funding permits, instrumentation will be provided to measure friction during the course of wear in this connection. Torque monitoring devices are now commercially available. An important feature to be incorporated is the facility to conduct submerged wear tests in selected media (in the present version, fresh distilled water at 37 °C flows over the specimen surface continuously). An effort will be made to use generic commercial components and modular devices as much as possible to facilitate repair and replacement of defective components.

Recently, some of the components of the present version were damaged by a transient in the electrical supply. Since there is some redundancy incorporated in the apparatus, and some repairs were successful, reprogramming permitted us to continue our wear studies; however, at some loss in performance and convenience. It now may become necessary to incorporate some of the new equipment into the old version. This will, of course, slow down the development and construction of the new apparatus in order to continue wear studies currently in progress and planned.

D. Clinical Examinations Employing Removable Partial Dentures

Background

In vitro data obtained by McKinney and Wu [2], as well as the results by Wu and Fanconi [13] have shown that post curing of dental composite resins increases the degree of conversion, and enhances the wear resistance of the composite resins.

In order to evaluate the clinical significance of the effects of post cure of composite resins a clinical study was initiated in cooperation with the American Dental Association using partial denture teeth as a vehicle for evaluation. The design of this study has been reported to the AADR including the preliminary results after six months of in vivo wear [14].

Accomplishments

Phase I. The retrieval of all denture teeth with composite resin restorations and replacement of these teeth with new denture teeth and establishing proper masticatory and esthetic function of the prostheses. The entire clinical aspect of this study has been completed.

Phase II.

(a) Photograph under low power magnification (20X or 1:1 on film) the retrieved restorations; in order to have a record of discoloration.

(b) Clinically evaluate the restorations with a dental explorer and visually for degree of wear.

Both aspects of Phase II have been completed and results have been reported at the IADR, The Hague, The Netherlands June 26-28, 1986. A summary of the data is shown in the following table. Data are given for four dental composite resins: the number of pairs refers to the number of sample pairs for the entire patient population (each sample was paired with a control). The score represents the difference in wear between sample and control, averaged over the entire set. The percent restorations represents the fraction of all restorations (experimental and control) that showed signs of clinical wear.

TABLE 1

Composite	# Pairs	Clinical Difference in wear, Score (Percent)	Percentage of Restorations Showing Wear
I	29	+4 (+5)	29
II	32	-6 (-6)	27
III	30	-1 (-1)	22
IV	29	+5 (+6)	16

Phase IV (Still to be completed)

(a) Evaluate whether technology developed by the NBS Materials Science Division for measuring galling of metals can be applied to the surfaces of denture teeth. If so, then

(b) Obtain quantitative data about the volume of material lost for each composite restoration and obtain a measure of the surface roughness by means of computer aided profilometry.

Phase V (Still to be completed)

Evaluate and record surface appearance with SEM.

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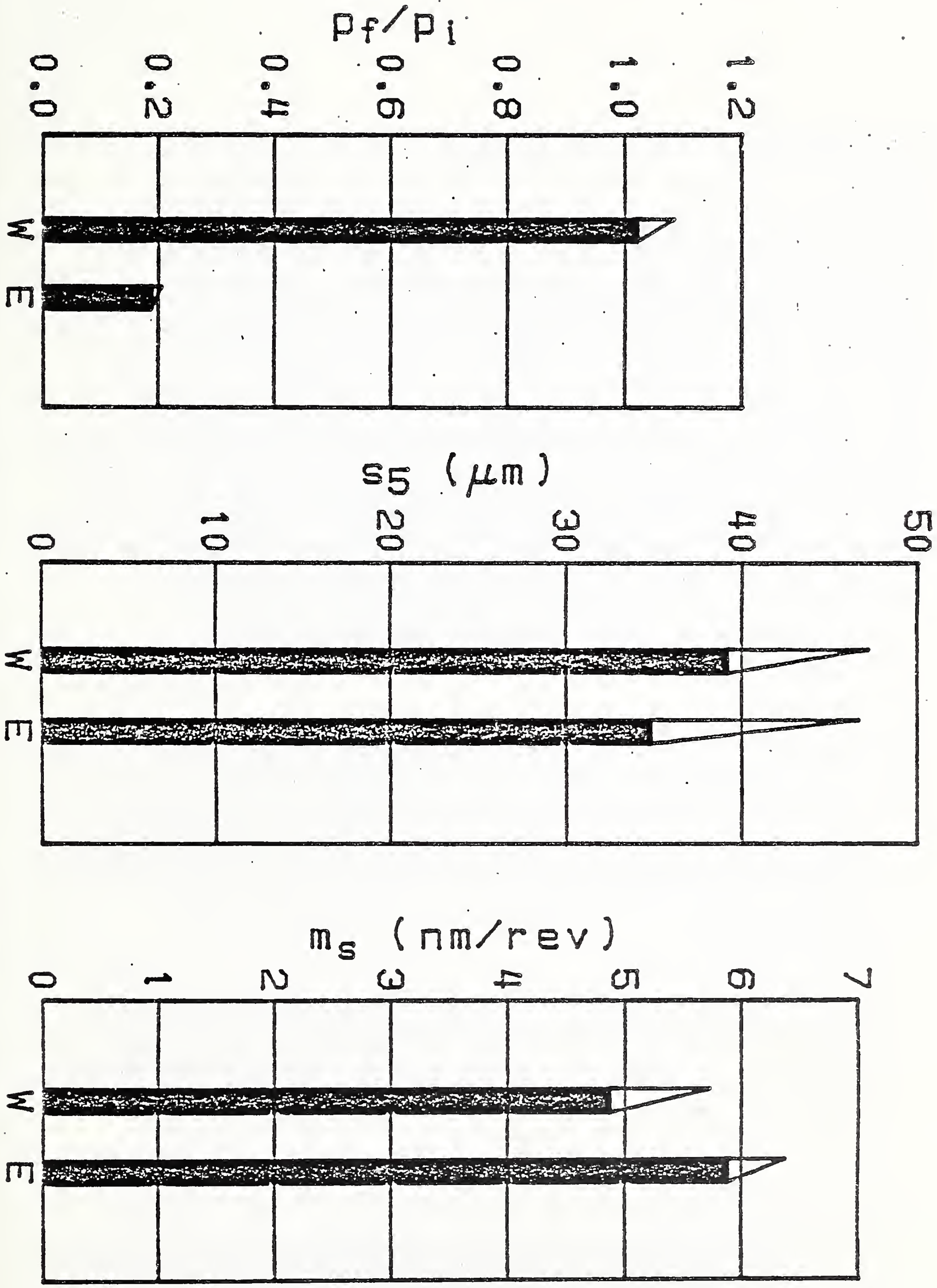

Figure 1: Hardness ratio, P_f/P_i, early wear, S_5, and steady-state wear rate, m_s, for the PFUMA/BIS-MPTMS experimental composite. W, water preconditioned; E, ethanol preconditioned

III. DENTAL ALLOYS, CERAMICS AND METROLOGY

Overview

The past decade has witnessed widely fluctuating costs for dental restorative casting alloys. These have led to a large increase in the types of dental alloys marketed as replacements for gold alloys. Porcelain-veneered cast fixed partial dentures and drowns comprise a significant fraction of these protheses fabricated. Because the newly introduced alloys can vary considerably in their fabrication characteristics and clinical performance, more reliable methods than now exist are desirable for evaluating their properties, both independently and as systems with porcelain. The development of such techniques will be of aid to the manufacturer and dental consumer in understanding and controlling the factors which determine satisfactory clinical performance. Of these, those considered to be of prime importance are that porcelain-alloy thermal-stress compatibility, the porcelain-to-metal system strength, alloy castability and the attendant capability of producing good fitting castings, and alloy solderability. Work has focussed on these subjects with the objective of defining and confirming measurement techniques which will be of aid in new product development, product control and evaluation.

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

PROGRESS REPORT

Overview

Residual stress from the porcelain firing cycle is considered to be a major factor leading to failure of porcelain fused-to-metal restorations. This study is undertaken to clarify the parameters which are most important in developing residual stress. These can include the thermoplastic properties of the porcelain, thermal conductivities, temperature dependent elastic moduli, glass transition temperatures (porcelain) and coefficients of thermal expansion.

Accomplishments

The objective of this part of the investigation was to explore the potential of using the gap of a porcelain veneered split-metal ring as a means for determing the thermal stress compatibility between porcelain and metal. It is hoped that ultimately tables of material properties which correlate with gap change and calculated stress can be constructed. At the very minimum, results of this investigation should help to identify the major sources for the build-up of residual stress.

Phase I. Complete development of the required Finite Element Model (FEM) and Program

A two dimensional FEM has been constructed which consists of 50 layers of material. The FEM program is first being used to study the effects of material parameters for porcelain alone, cooled at various rates. The model simulates the development of a temperature distribution during cooling, examines the effects of cooling rate on this temperature distribution, incorporates cooling rate dependence for the glass transition temperature, Tg, a temperature dependent coefficient of thermal expansion below Tg and a constant (but a manipuble variable) coefficient of thermal expansion above Tg, and a temperature dependent elastic modulus for the porcelain. The results are now being analyzed. One result shows that less than a 1% difference exists between calculations which incorporate a temperature dependent elastic modulus versus a constant value for elastic modulus.

Phase II.

At present, analyses are in progress on the sensitivity of calculated stress (at the surface and center of the porcelain slab) to material parameters such as coefficient of thermal conductivity, temperature dependent shear viscosity, cooling rate dependence of Tg and coefficients of thermal expansion. Following completion of analysis of the stress for the multilayered porcelain slab, the program will be modified to analyze a multimaterial problem consisting of porcelain on metal. Results will be compared with previously obtained results for the change in gap of porcelain veneered split-metal rings [1].

Phase III

Finalization of material input parameters has been delayed due to the complexity which was involved in developing the 50 layer FEM of porcelain (see Phase I).

Phase IV

Devise simple analytical representation of stress-strain in porcelain metal systems, if possible, for a split ring. This will follow Phases I-III.

Phase V

Compare results of FEM vs theory developed by Scherer. [2]

B. Porcelain-Alloy Compatibility

PROGRESS REPORT

Overview

A bending beam composite specimen was designed to produce quantitative measurements of the tensile strength of dental porcelain fused-to-metal systems. This system permits the production of test specimens with materials and equipment present in most commercial dental laboratories, providing an expedient evaluation method for PFM systems.

Multiple fracture data can be obtained from a single sample, making some form of ordered statistics a necessary part of the data evaluation.

Accomplishments

Phase II

Determine three dimensional and two dimensional Finite Element Model (FEM) of Bending Beam Composite (BBC). This has been completed. However, on the basis of new work in progress on stress in porcelain-metal systems (see Part A, Thermo-mechanical Stress), this work will continued toward a new FEM which includes the variables of temperature dependent material properties etc., as discussed in Part A.

Phase III

The fracture data for the PFM systems have been evaluated assuming a two parameter Weibull distribution. The data have been evaluated both by curve fitting (CV), by using the most likely estimate (MLE) and the best linear unbiased estimate (BLU). The Weibull parameters and the scale parameters have been determined. The test results are presented in Table I.

A confidence limit for the values has been calculated from the tables by Thoman et al [3]. The values are listed in Table 2. Other than System II, the agreement between the values obtained by the two methods is satisfactory.

The agreement between experimental and theoretical values is shown in Figures 9-10. The m = 9 value indicates that the distribution of the failure stresses is definitely not normal; but follows the Weibull distribution for a brittle material. (Rice and Ruff have shown, a Weibul parameter of m=3.6 produces a probability distribution similar to the normal distribution.)

The same algorithms have been tried on composite resin bonding data by Thompson et al [4] and it was found that again a non-normal distribution (m=1), i.e., the exponential distribution described the data.

It would seem that the algorithms developed for the evaluation of PFM systems may find wider application than just this one instance.

The above section pertains to Phase III as stated in NBSIR 86-3320 [4]. For future work a continuation is seen, particular in the resolution of the discrepancy between the parameters obtained by curve fitting and those obtained by maximum likelihood estimates.

Phase IV

Algorithms that show agreement in the Weibull parameters obtained by different methods such as curve fittings and point estimates.

Phase V

Determine the conditions for and the confidence limits associated with complete and censored data sets.

Phave VI

Develop an algorithm to incorporate the sample shape factor into the point estimate routine of the computer.

C. Castability (Filling of a Mold with Cast Dental Alloy)

PROGRESS REPORT

Overview

Because of the many dental alloys appearing on the market there has existed the need for an uncomplicated and expedient method of evaluating casting behavior and for determining the most favorable conditions for their performance. Such a method can be useful in the selection of new materials, in dental laboratory and manufacturing process control and in the design of new alloys.

Numerous methods have been proposed in the past for determining various aspects of the casting of dental alloys. A number of procedures have been proposed. These have been discussed in NBSIR 86-3320 [6].

A primary effort at NBS has been the development of a method for evaluating the ability to cast an alloy to fill a mold under prescribed casting conditions. For this purpose a method employed a polyester-grid mesh pattern has been chosen to embrace the following requirements.

(1) The procedure should provide a measurement of the capability of an alloy to fill a mold.

(2) The method should make use of equipment, facilities, and materials generally available to the dental industry.

(3) The experimental conditions found in dental prosthetic laboratories should be duplicated.

(4) The pattern and mold should be easily produced.

(5) The manner of evaluating the casting should be objective and accomplished without the need for sophisticated measuring instruments.

(6) The method should be sensitive to materials, temperature, techniques, or other variables affecting castability. Hinman et al [7] have reported on a method which meets these requirements.

Accomplishments

Phase I

A manuscript, "Castability of Dental Alloys, Mold and Alloy Temperature Effects" has been submitted to the Journal of Dental Materials for publication.

Phase II. Analysis of Effects of Composition on Castability.

This work has been refined, with the addition of data from the casting of alloys under controlled-variables conditions.

The alloy compositions were designed to avoid statistically correlated affects of compositional changes (for example, simple doubling of the amounts of two elements from one alloy to another) so that chemically relevant effects could be observed. The following equation has been used.

$$C_{vt} = k_o \frac{N_i}{C_R} + k_1 (M_o) + k_2 (S_i) + k_3 (N_b)$$

$$+ k_5 (AL) + k_6 (B_e) + k_7 (B_e \times S_i)$$

where the terms within the parenthesis are the elemental compositions in weight percent and each K reflects the effectiveness of each element.

C_{vt} is the transformed castability value [4]. Because C_{vt} is a function of alloy casting temperature T_A and mold temperature T_M, each K is also a function of those same variables. The K's are shown on Figs. 1-8. These figures show the relative importance of each element at various temperatures.

From the figures it is obvious that B and Be have the largest effects on increasing C_v (through C_{vt}). The effect of higher mold temperature on K_4 for B is to slightly decrease C_{vt}, while alloy casting temperatures have virtually no effect on K_4. For Be, higher mold temperatures result in greatly higher values of K_6 while casting temperatures have only a small effect.

The exact reasons for the behavior of K_4 and K_6 with temperature are, of course, not known, but it is possible to infer something about reactions between the alloys and investments, and the oxidation of the melts. For example, an increase of an alloy's chemical reaction with the investment will cause wetability to increase and the castability value might correspondingly be increased due to this. On the other hand, an increase in the amount of oxide film on the advancing front of the cast melt surface should make it more difficult for the melt to flow easily as the oxide film could be expected to resist the moving of the alloy; this should tend to cause a decrease in the castability value. With these thoughts in mind, one may hypothesize about why increasing mold temperature results in a decreasing value of K_4 for B and in an increasing value of K_6 for Be. Higher mold temperatures might tend to cause more oxidation of B on the melt surface while Be might interact more with the investment. It should be kept in mind that in the case of increasing mold temperature, only the advancing liquid alloy in close contact with the mold will drop quickly in temperature as the alloy moves through the mold. The temperature and the fluidity of the melt which follows should not be as drastically changed.

When the casting temperature of the alloy increases, the temperature of a the advancing melt correspondingly increases. An increasing casting temperature affects not only the chemical reactions, but also the fluidity of the melts. It is, therefore, difficult to conjecture more about the complex relations between the K_i's and casting temperature. How much the fluidity changes and how much oxidation or interaction with the mold occurs with increasing casting temperature is not known. K_i must reflect the net balance in these and other factors perhaps not even considered. Similar types of inferences can be made regarding the effects of aluminum (K_5), NB, (K_3), and all of the other elements on the castability value.

One interesting feature is the apparently synergistic effect seen between Si and Be; this is the largest effect of all as may be seen through the value of K_7. Note, however, that for 0.1 wt % each of Be and Si, the large K_7 is multiplied by only 0.01 in equation 3, if Be and Si present are each increased by a factor of 5 to 0.5 wt %, K_7 is multiplied by 0.25, a net increase of 25. Hence, C_{vt} and C_v can be highly sensitive to change in the combination of these elements. This result suggests that the product of these elements is an important factor in control of the quality of alloys having both these elements.

The results of this study were obtained by assuming linear effects on C_{vt} with changes in composition. Because C_{vt} and C_v are almost linearly related throughout most of the range of C_v ($0.1 \leq C_v \leq 0.9$), this is equivalent to assuming ideal solution behavior. Examination of binary phase diagrams such as Ni-B and Ni-Al shows this condition is not likely to extend very far for some elements which cause precipitation at low concentrations. This should be kept in mind if the data are used to predict changes in C_{vt} with changes in composition. It is the simplest and most wieldy assumption; however, and facilitates the calculations, the results of which provide some insight into casting temperature, mold temperature, and investment effects. Another point that should be kept in mind is that these results were all obtained with one particular phosphate bonded investment. As will be shown in a paper in preparation, the constants in equation 1 can be affected by the investment. This may be expected in the light of the previous discussion. For example, if an alloy with B is used in an investment (or with a pattern coat) that discourages interaction between the investment and the alloy, the castability value might increase. Other factors, of course, such as particle size distribution and permeability of the investment could be expected to affect C_{vt}. A previous paper (4) has shown that batches of the same investment can affect the values of C_{vt} through changes in the intercept, a, of equation 1, but that the temperature coefficient, b, is not affected.

With the aforementioned points in mind, equation 3 may be useful for computer aided design of Ni-Cr alloys. The calculated changes in the castability value as a function of mold and alloy temperature can be balanced against practical factors such as temperature limitations and/or hot tearing as well as grain size, corrosion resistance, surface finish, strength and so forth. In using equation 3 for design of new alloys a method for estimating T_s must be used. One such equation has been developed and is under further review at this time.

The most important aspect of this work is considered to lie in the demonstration of the method for using data acquired with the mesh monitor to gain further insight into the complex effects occurring during casting and to show how the results can be used. For design of new alloys these methods may be applied to other alloy systems.

D. Castability (Accuracy of Fit of Dental Castings)

PROGRESS REPORT

Overview

In light of the results obtained by Eden et al [8], Marsaw [9] , and Meiser [10] the need for a better understanding of the role of the setting expansion of a dental casting investment in the production of a cast prosthesis that fits becomes more and more prominent.

Previous measurements here indicate that the expansion during the setting at the site of the wax pattern is significantly less than the expansion observed by the change of the external dimensions of the setting investment.

Accomplishments

The results obtained by Meiser et al. have proven to be reproducible by R. Engler et al. A design change has been incorporated in the experiment to reduce variability in the experiment, in order to reduce fluctuations in the measurements during the pour of the investment.

The standard deviation of the resulting data has been significantly reduced by the design modification while confirming the results obtained by Meiser. (The results have been presented at the General Session at the AADR and the DMG microfilm.)

Experiments have been continued with the use of multidirectional strain gauges. These gauges are comprised of four individual gauges in a Wheatstone Bridge configuration spatially oriented such that the electrical signal represents the differential strain between the X and Z direction. The multidirectional gauge was placed such that the x direction was radially placed in the casting ring with the z direction parallel to the cylindrical axis.

It was found that the difference between the axes, x, and z was -0.02% (± 0.08) a value undistinguishable from 0 (with our experimental detection limit of approximately 0.01%) or the scatter in the data.

A manuscript describing these results has been submitted to the Journal of Prosthetic Dentistry.

Phase I

(a) The design of cellulose acetate wings attached to the strain gauge substrate has met all the objectives set forth in the workplan. The zero drift during the investing process is now small compared to the overall setting expansion (0.15%).

(b) The differential setting expansion in three dimensions has been evaluated. The casting ring is cylindrically symmetric; hence, x and y directions are identical (the z direction is the cylindrical axis). Therefore, measurements in only the x and z directions are needed. It was found that with a Kaowool Liner no difference is observed between the x and z directions.

E. Metrology and Clinical Performance

PROGRESS REPORT

Overview

This part of the program involves an investigation of the application of the disciplines of fracture mechanics and the statistical theory of fracture to the study of dental materials. The tecniques to be used are applicable to any materials which are subject to failure by a brittle crack growth mechanism.

The use of such techniques can be expected to eliminate or at least reduce the effects of experimental artifacts on test results due to differences of specimen size, geometry of loading, etc. The first part of the program can be described as a study of the strength of composite restorative materials.

Objective

The objective of this project was to apply the concept of fracture statistics: "that fracture initiates at a worst inherent flaw when it is subjected to its critical stress", to obtain information about the underlying flaw distribution. Four studies have been undertaken: (1) Specimen size effects in the diametral tensile test (DTT), (2) The effects of loading geometry of rectangular beams, (3) The effect of exposure of DTT specimens to food simulating fluids, and (4) An investigation of the precision of parameter estimation for the Weibull distribution.

Accomplishments

Phase I. The effects of specimen size on the diametral tensile strength of composite restoratives.

Using Weibull's concept of the statistical nature of the failure of brittle materials (11,12) we have investigated the specimen size effect in the diametral tensile test for one experimental composite. Both standard size (6 mm dia x 3 mm) and small (3 mm dia x 2 mm) specimens were tested. The results for the small specimens are plotted as a cumulative distribution function in Figure 11 where they are fitted by the Weibull distribution function with the parameters shown. The results for the standard sized specimens are plotted in Figure 12 along with distributions calculated from that of Figure 1 by means of the weakest link formula:

$$1 - F = (1 - F_o)^n$$

where n is the multiple of the number of flaws in the small specimens which is thought to be contained in the standard specimens and Fo is the distribution function for the small specimens.

The agreement of the data with the curve for n = 2 is quite remarkable. Although the large specimens have four times the surface area and six times the volume they apparently contain only twice as many effective flaws as the small specimens.

Attempts to reproduce this result with another material have failed. The smaller specimens actually showed lower strength than the standard specimens. This might be explained by differences in the manner of specimen preparation. A more rapid heat flow from the smaller specimens which probably occurred during polymerization would cause them to polymerize at lower temperature and thus to attain a lower degree of cure. In the first experiment (reported above) the small specimens were cured in poly (tetra flouroethylene) molds while in the latter experiments molds for both sizes were of metal. The PTFE, having a lower thermal conductivity, may have retarded the heat flow allowing the small specimens to attain a larger part of the strength that might be expected due to the specimen size effect. These results dramatically show the effect of experimental procedures/conditions on the test results obtained.

Phase II. The strength distribution of beams of rectangular cross section.

Another experiment that should be capable of distinguishing between surface flaws and volume flaws involves the bending of beams of rectangular (non-square) cross section in each of two orientations one with the bending axis perpendicular to the height (h) the other with the bending axis perpendicular to the width (w). One must first integrate Weibull's risk of rupture equation over the non-uniform stress distribution assumed for the bent beam (12). In the integral for flaws distributed throughout the volume of the material, h and w appear symmetrically and one should observe no difference in characteristic stress for the two orientations. However for flaws distributed on the surface of the specimen the height of the beam is weighted as $1/m+1$ where m is the Weibull exponent or modulus and one should observe a different characteristic stress for the two orientations.

Specimens were prepared from Visiofil (Espe), a conventional composite restorative, (1 mm x 4 mm x 25 mm) and broken in four point bending. The ratio of the characteristic stresses observed was 1.108 ± .05. That predicted by Weibull theory is 1.107. When the experiment was repeated using Visiodispers (Espe), a microfilled material, the ratio obtained was 0.90 ± .04, a result that cannot be explained by Weibull theory.

One can speculate that this result might be due to the nature of the fracture produced when removing mold flash from the specimens. If in the microfilled Visiodispers specimens these fractures produced flaws which reduced the flexural strength while with the conventionally filled Visiofil they did not these results can be explained. This argument can be reinforced by observing that the more serious flashes were found along both edges of one side of each specimen. Thus with the beam in the vertical orientation one of these flashes is always on the tensioned face of the specimen while with the beam in the horizontal orientation there are either both or neither of the flashed edges on the tensioned face. From this one would expect a much wider distribution of strengths for the horizontal specimens than for the vertical. This was observed for the Visiodispers specimens but not for the Visiofil specimens. The result does indicate that some composite formulations are more sensitive to flash or finishing of restorations. This sensitivity could be important in the design of restorative materials which will have greater marginal integrity.

Phase III. Investigation of the effect of food simulating fluids on the strength distribution in composite restorative materials.

One hundred twenty-six diametral tensile test (DTT) specimens were prepared from Adaptic (Johnson & Johnson). One third of these were stored in de-ionized water, one third in 70% ethanol and one third in n-heptane. After two weeks they were tested. The distributions of failure stresses were in all cases found to be irregular. When plotted on Weibull coordinates they were concave upward. This is thought to indicate that the underlying distribution of flaws is composed of two distinct populations such as, perhaps surface flaws and volume flaws. If the two distributions are represented as:

$$F_1 = 1 - \exp-(s/s_1)^{m1}$$
$$F_2 = 1 - \exp-(s/s_2)^{m2}$$

then, assuming statistical independence of the two populations, the combined distribution, F, will be related to them as:

$$1 - F = (1 - F_1)(1 - F_2).$$

The experimental data was fitted to F by a non-linear least squares technique to determine the constants s1, m1, s2, and m2. The derived distributions are shown in Figure 13. It would appear that compared to the water treatment, the alcohol treatment weakened only that population of flaws with the higher characteristic stress, while treatment with heptane weakened both populations about equally. The results demonstrate the importance of environment on the strength of dental composites.

Phase IV. An investigation of the precision of parameter estimation for the Weibull distribution.

Since the distributions encountered in fracture studies are frequently not normal another more versatile function is commonly used. This function has come to be known as the Weibull distribution:

$$F = 1 - \exp -(s/s_o - s_u/s_o)^m$$

F is the cumulative distribution function of the fracture stress s; m is the modulus or shape parameter; s_o is the scale or position parameter; and s_u is the cut off parameter. This function can represent distributions which are skewed to the left or to the right. It can be easily inverted. It can be easily differentiated to obtain the probability density function (f). It can be readily multiplied by another similar function. It can be raised to a power. All of these operations are very difficult with the normal distribution.

To estimate the parameters of a distribution from a particular sample taken from that distribution the preferred technique is known as the method of maximum likelyhood. This technique determines estimates of the parameters m, s_o, and s_u that will maximize the likelyhood function which is the probability of obtaining that particular sample or set of independent selections from the distribution. This technique is preferred because it enables one to include censored data where it is known only that a particular test result is greater or less than some value but with the exact result unknown.

For the present study we can set $s_o = 1$ and $s_u = 0$ and sample from the resulting distribution. This is done by generating random values for F from the uniform distribution and solving for the corresponding s. Samples were taken of size N = 5, 10, 20, 40, and 80 from distributions with exponents m = 2, 4, 8, and 16. Fifty such samples were taken for each of the twenty combinations of N and m. Estimates of m and s_o, $\langle m \rangle$ and $\langle s_o \rangle$ were then determined by the maximum likelyhood technique for each of the twenty sets. The estimates were found to be distributed non-normally around the values of m and $s_o = 1$. The distributions of $\langle m \rangle$ and $\langle s_o \rangle$ were found to be well described by three parameter Weibull functions. From these functions the tenth and ninetieth percentile points were determined. These are plotted in Figures 14 and 15 for $\langle m \rangle$ and $\langle s_o \rangle$ respectively for the values of m and the sample sizes used. From Figure 14 it is seen that the distribution of $\langle m \rangle/m$ is nearly independent of the value of m while in Figure 15 the distribution of $\langle s_o \rangle/s_o$ depends strongly on the value of m for the distribution from which the samples were taken. These curves and similar ones for other percentiles can be used for the testing of hypotheses and assigning confidence intervals for Weibull parameters.

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Manuscripts Under Review or Accepted for Publication

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Tesk, J.A., Widera, G.E.O., Hinman, R.W. and de Rijk, W.G. A porcelain-metal composite specimen in determining system strength. Cleared WERB review, to be submitted to Dental Materials Journal with companion paper (see next paper).

de Rijk, W.G., Tesk, J.A. and Conner, M. A quantative and expedient test for the tensile strength of porcelain-to-metal systems - Part II. Experimental procedures and results.

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

Tesk, J.A., Okuno O., and Penn R. Mesh Monitor Casting of Ni-Cr Alloys Element Effects. Editorial Review

Okuno, O., Tesk, J., and Penn R. Mesh Monitor Casting of Dental Alloys: Investment Effects. Editorial Review

Engler, R.A., de Rijk, W.G., Tesk, J.A. and Morris, D. Multidimensional internal setting expansion of a phosphate-bonded casting investment measured with strain gauges. Submitted to J. Prosth. Dentistry.

Tesk, J.A. Review of Paper - Casting Metals, by Kamal Asgar. Proceedings of the International State-of-the-art conference on restorative materials at NIH. In press.

de Rijk, W.G., Brown, W.E. and Chow, L.C. The clinical evaluation of ahydroxyapatite forming paste in the treatment of dental hypersensitivity. Biomedical Engineering. Current Concepts VI, S. Saha. ed. Pergamon Press (in press).

Bundy, K.J., and Penn, R.W. Improvement of metal/bone cement interfacial strength. Submitted to J. Biomed. Mater. Res.

Invited Talks

Tesk, J.A. The dental space program, or; you said a mouthful. Johns Hopkins University, March 1976.

Tesk, J.A. The use of a mesh cating monitor for control of dental laboratory processes. Washington Section of the National Associatioin of Dental Laboratories. March 1986.

Tesk, J.A. Review of paper by Kamal Asgar. Casting metals, presented at International State-of-the-art conference on restorative materials at NIH, Sept. 1986.

Tesk, J.A. The use of a mesh casting monitor for evaluation and control of dental laboratory casting processes. Richmond Dental Laboratory Group, Richmond, VA, Sept. 1986.

de Rijk, W. Dental adhesion, bonding or luting. Gordon Research Conference on the science of adhesion, Aug. 1986.

Contributed Talks

de Rijk, W.G. and Tesk, J.A. The distribution of failure stresses in porcelain to metal systems, IADR/AADR meeting, March 1986.

Liao, R., Grolman, K., Thompson, V.P. and de Rijk, W.G. Adhesive Resins: Tensile Bond to Metal and Resin Thickness Effects, IADR/AADR meeting, March 1986.

Thompson, V.P. and de Rijk, W. Statistical Distributions of Tensile Adhesive Bond Strengths, IADR/AADR meeting, March 1986.

Engler, R.A., de Rijk, W.G., Tesk, J.A. and Morris, D. Internal Setting Expansion of a Phosphate Bonded Casting Investment Measured by Strain Gauges, IADR/AADR meeting, March 1986.

Okuno, O. and Tesk, J.A. Mesh Monitor Casting of Dental Alloys: Investment Effects, IADR/AADR meeting, March 1986.

Tesk, J.A., Okuno, O., and Penn, R. Mesh Monitor Casting of Ni-Cr Alloys: Element Effects.

Siew, C., Gruninger, S.E., Brauer, G.M. and Tesk, J.A. Biological Safety Evaluation of Syringic Acid Ester Cement, IADR/AADR meeting, March 1986.

Natarajan, R., Widera, G.E.O., Min, B.J., and Tesk, J.A. Residual Stress Distribution in Metal Ceramic Crowns, IADR/AADR meeting, March 1986.

Penn,R.W. and Tesk, J.A. Fracture Statistics of the Diametral Tensile Test, IADR/AADR meeting, March 1986.

Widera, G.E.O., Natarajan, R., Parthasarathi, T., and Tesk, J.A. Stress in Cement Bonded Ceramic Crown Systems, IADR/AADR meeting, March 1986.

de Rijk, W.G., Jennings, K.A. and Menis, D.L. A Comparison of Chemical Durability Test Solutions for Dental Porcelains, Society of Bioengineering Conference, Oct. 1985.

Captions for Figs.

Fig. 1 to 8

The effect of casting temperature and mold temperature on the conefficience, k_1, for the equation describing C_{vt}, (page 67)

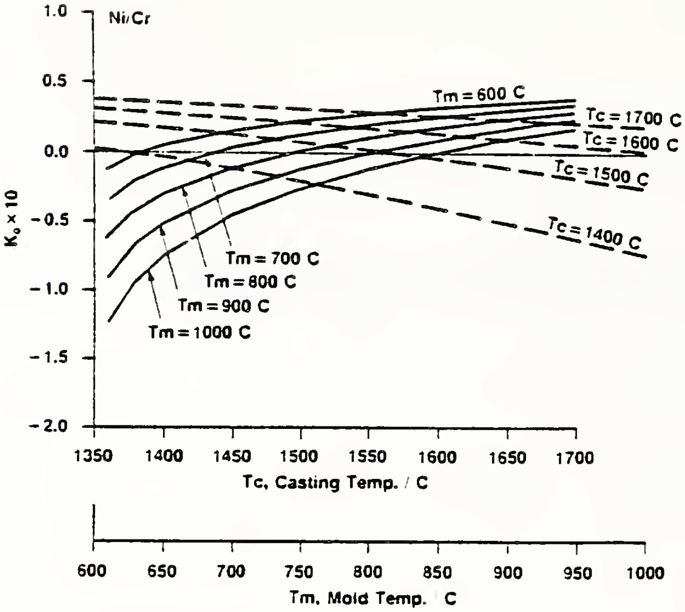


FIGURE 1

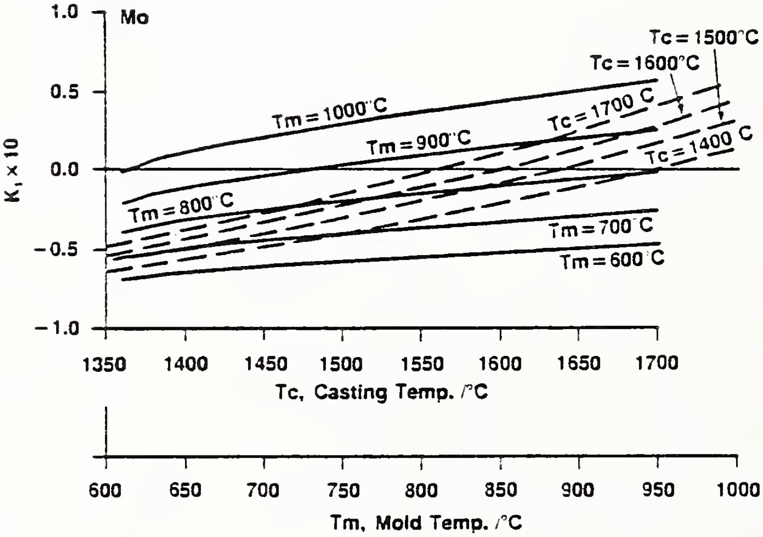


FIGURE 2

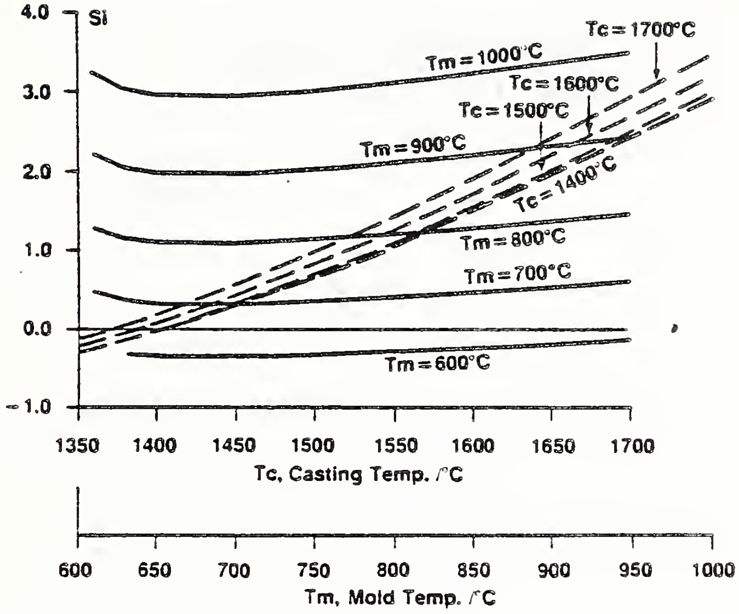


FIGURE 3

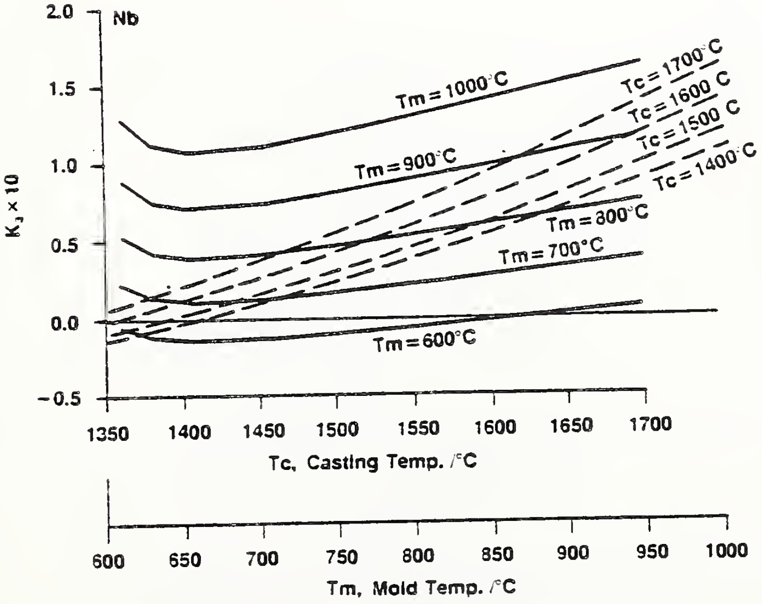


FIGURE 4

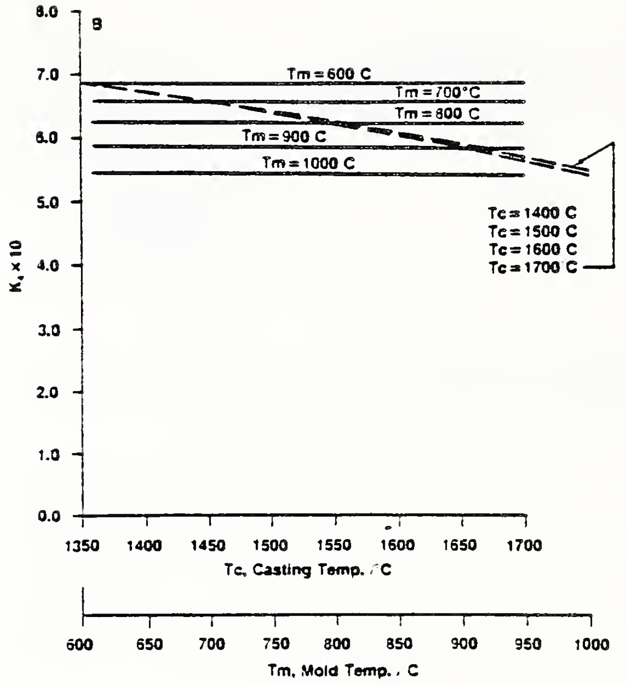


FIGURE 5

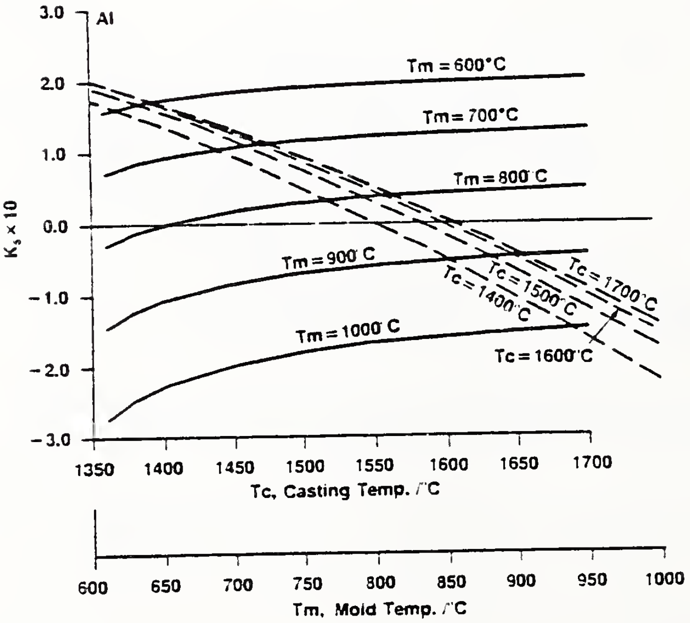


FIGURE 6

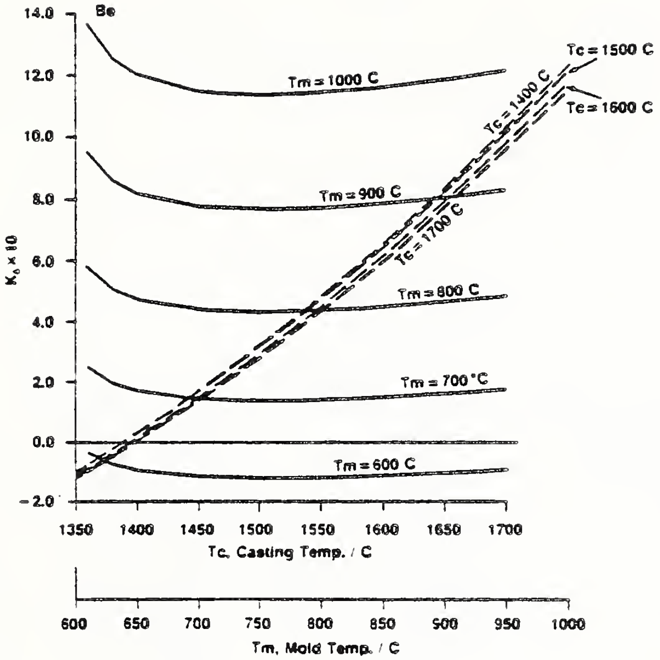


FIGURE 7

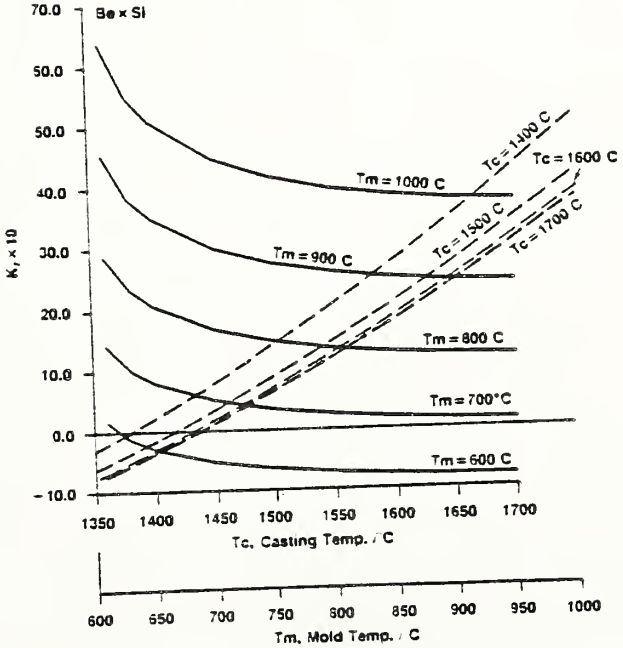


FIGURE 8

Table I

Results

Porcelain Metal System	m(MLE) biased	m(MLE) unbiased	m(CF)
I	3.2	4.2	5.1
II	5.0	7.2	10.0
III	6.7	9.2	9.0
IV	3.5	5.2	5.0
V	2.2	3.2	3.9

Table II

Results

PM System	m(MLE) unbiased	m(BLU)	n	Confidence Interval (at α = 0.1)*
I	4.2	4.8	46	1.19
II	7.2	7.2	27	1.28
III	9.2	9.8	26	1.28
IV	5.2	5.1	22	1.32
V	3.2	3.2	17	1.40

*From tables of Thoman, et al.

$$P\left[\frac{m(BLU)}{m} < L\right] = 1-\alpha$$

FIGURES 9 and 10

The cumulative failure probability as a function of applied stress. Experimental data (●) and theoretical calculation (——) assuming a Weibull distribution.

FIGURE 9

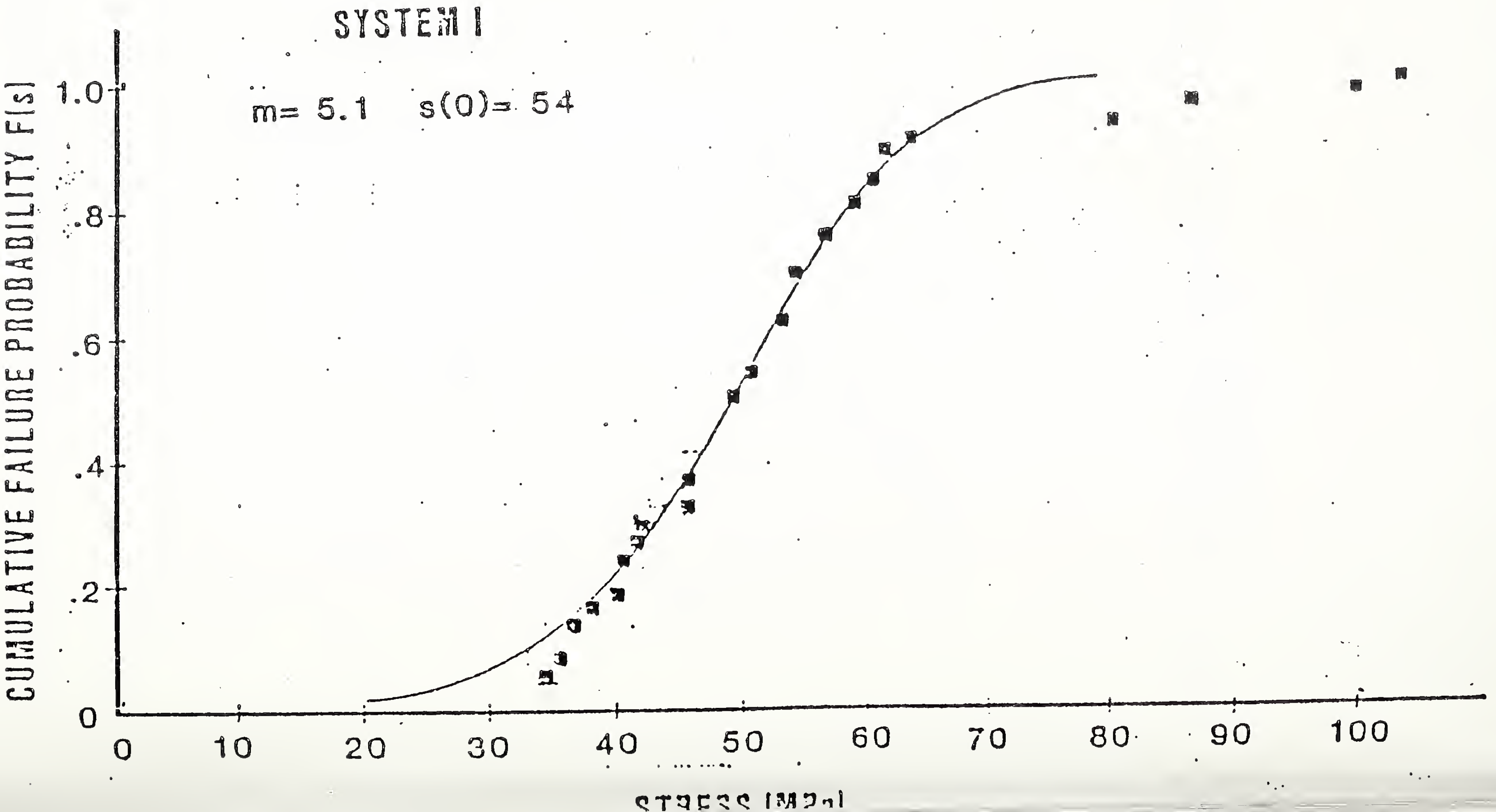
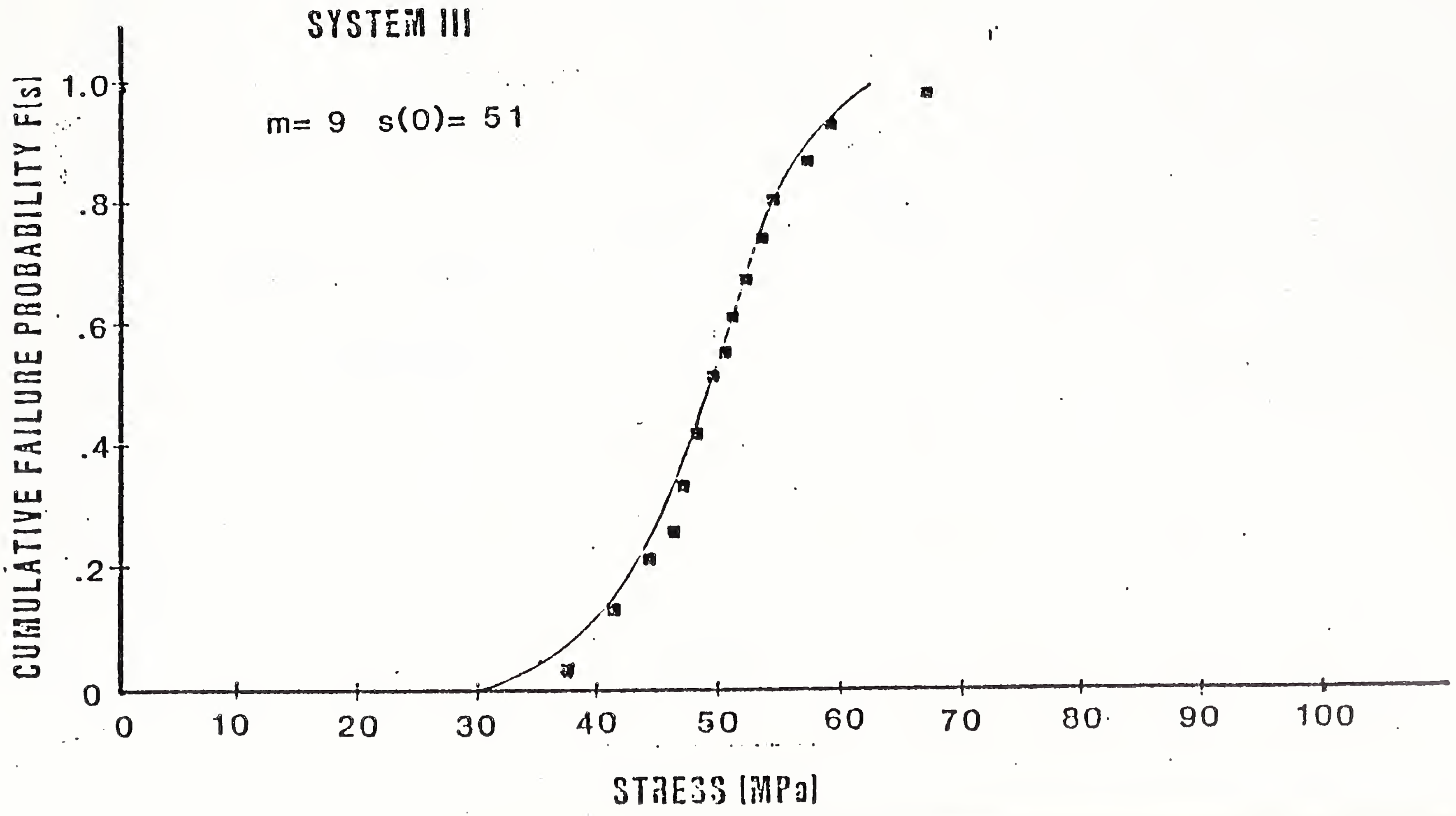

SYSTEM I
m= 5.1   s(0)= 54
CUMULATIVE FAILURE PROBABILITY F(s)
1.0
.8
.6
.4
.2
0
0
10
20
30
40
50
60
70
80
90
100
STRESS (MPa)

FIGURE 10


SYSTEM III
m= 9 s(O)= 51
CUMULATIVE FAILURE PROBABILITY F(s)
1.0
.8
.6
.4
.2
0
0
10
20
30
40
50
60
70
80
90
100
STRESS [MPa]

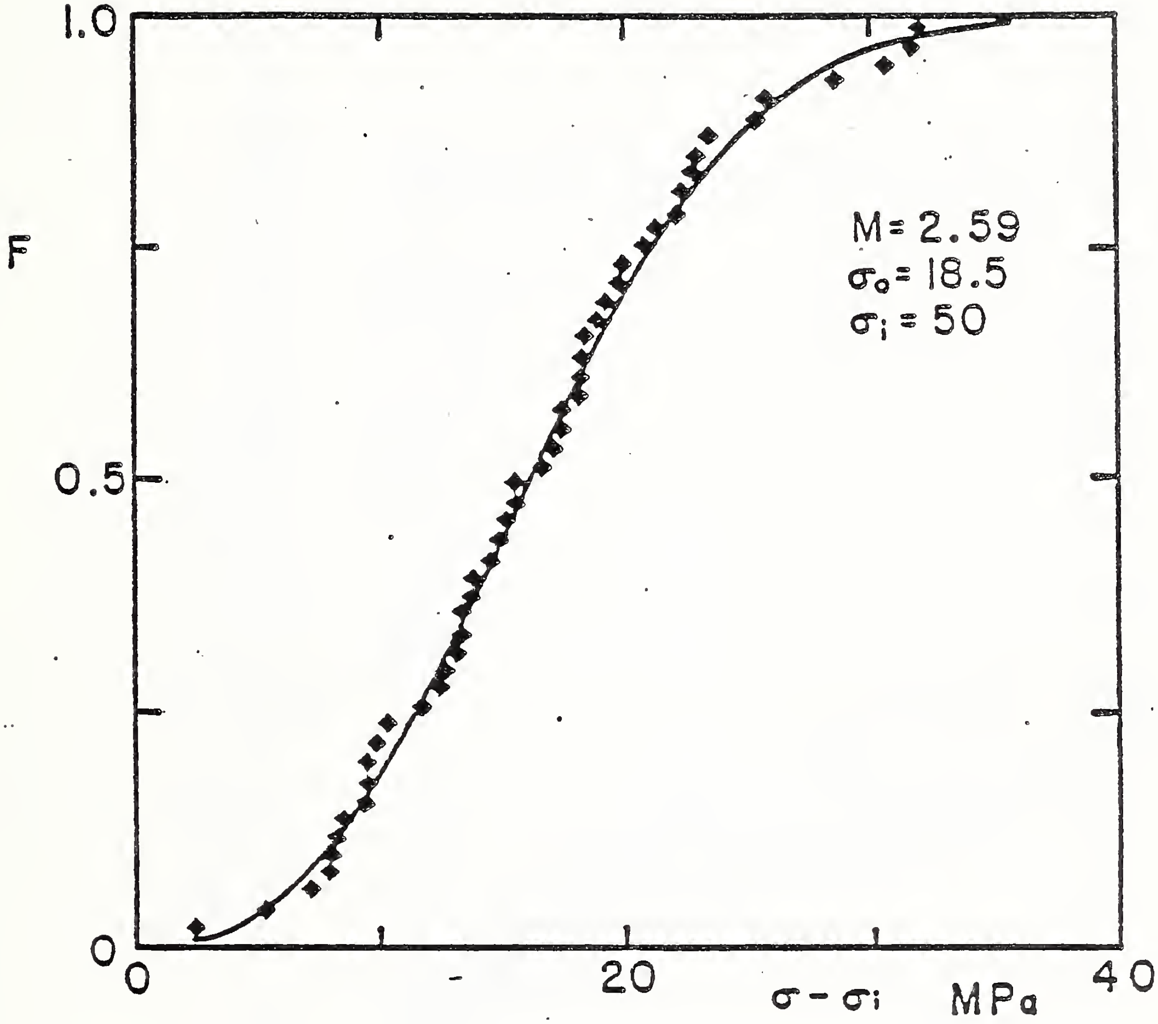


Figure 11. Distribution of diametral tensile strength for 2 mm x 3 mm diameter specimens. The curve is for the Weibull distribution with parameters shown.

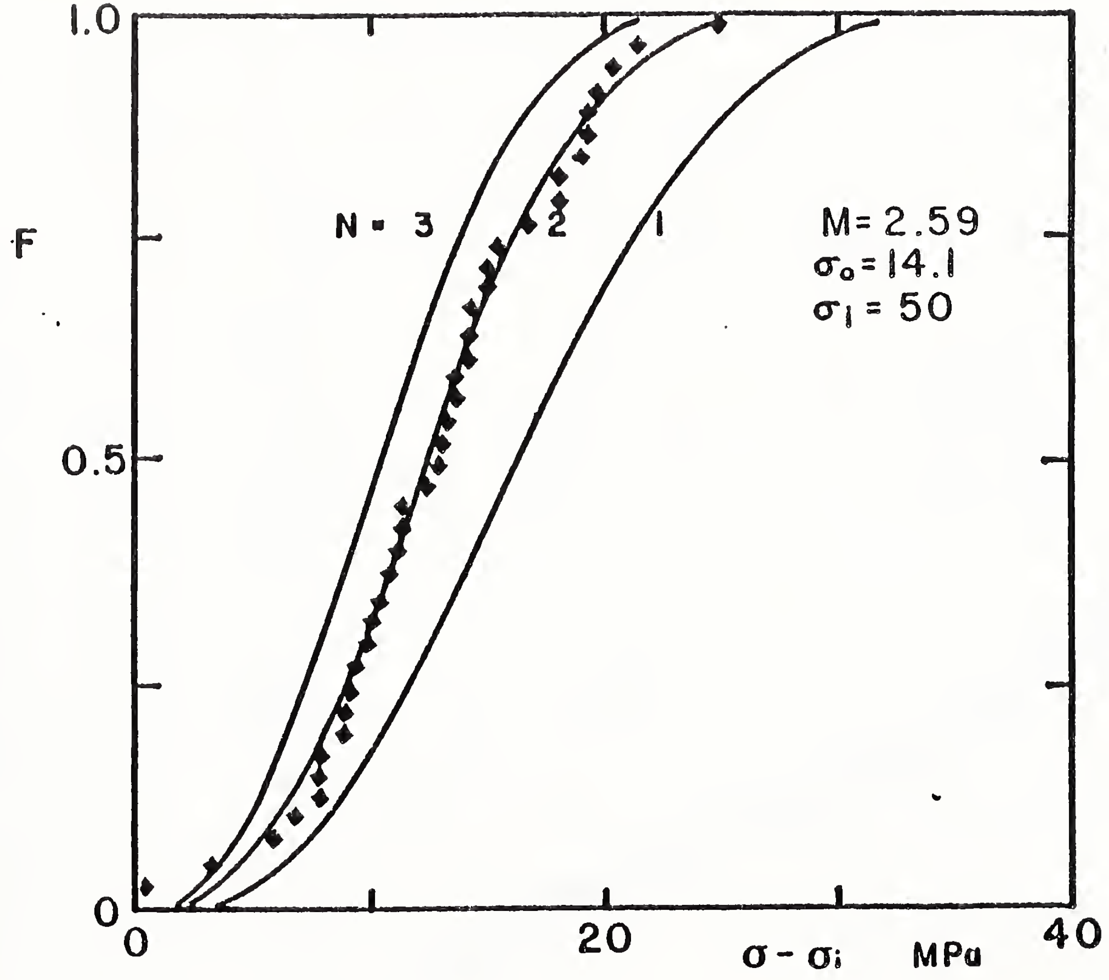


FIGURE 12 Experimental distribution of Diametral Tensile Strength for standard size specimens with curves calculated from the distribution for small specimens

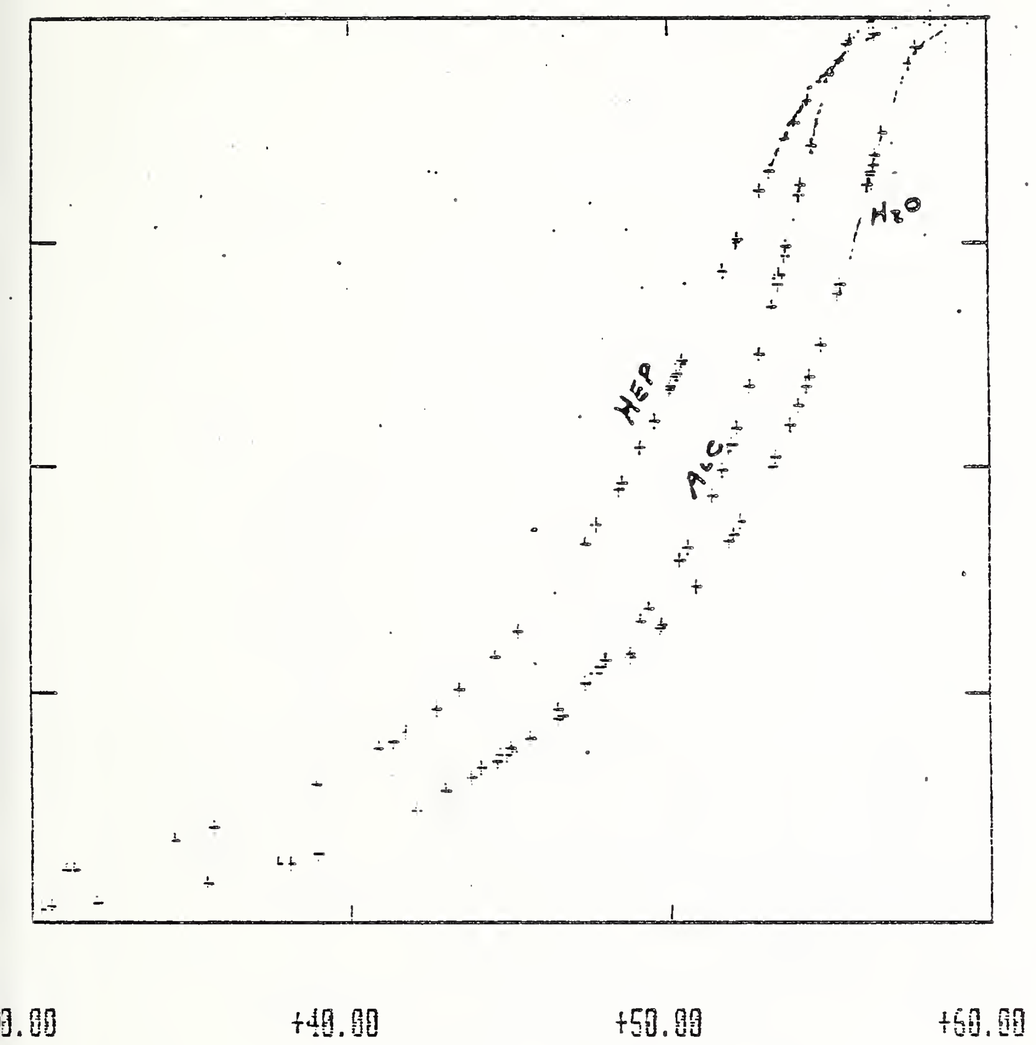


FIGURE13 Distributions of Diametral Tensile Strength fitted to compound Weibull distribution for Adaptic specimens after soaking in Heptane, Ethanol, and water for two weeks

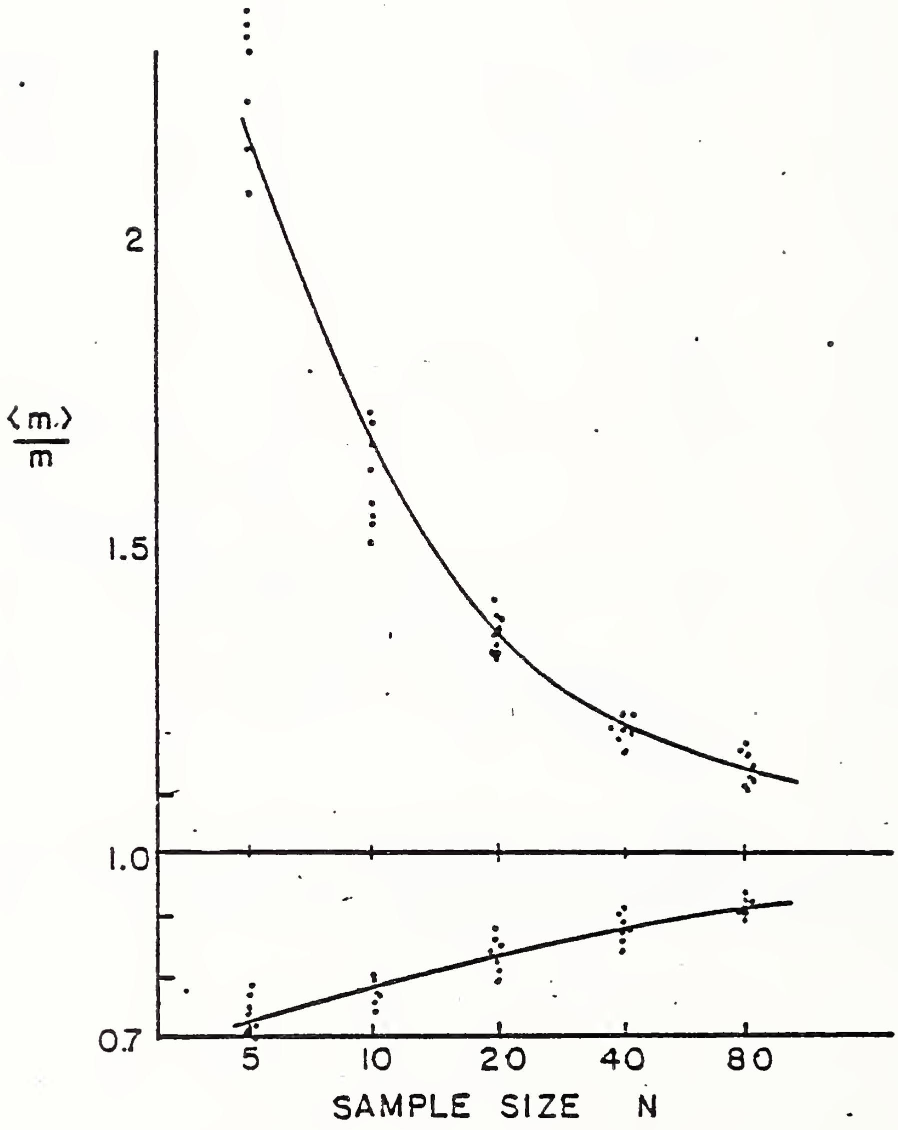


FIGURE 14 10th an 90th Percentile points for estimates <m> for samples of size N taken from a Weibull distribution with exponent m.

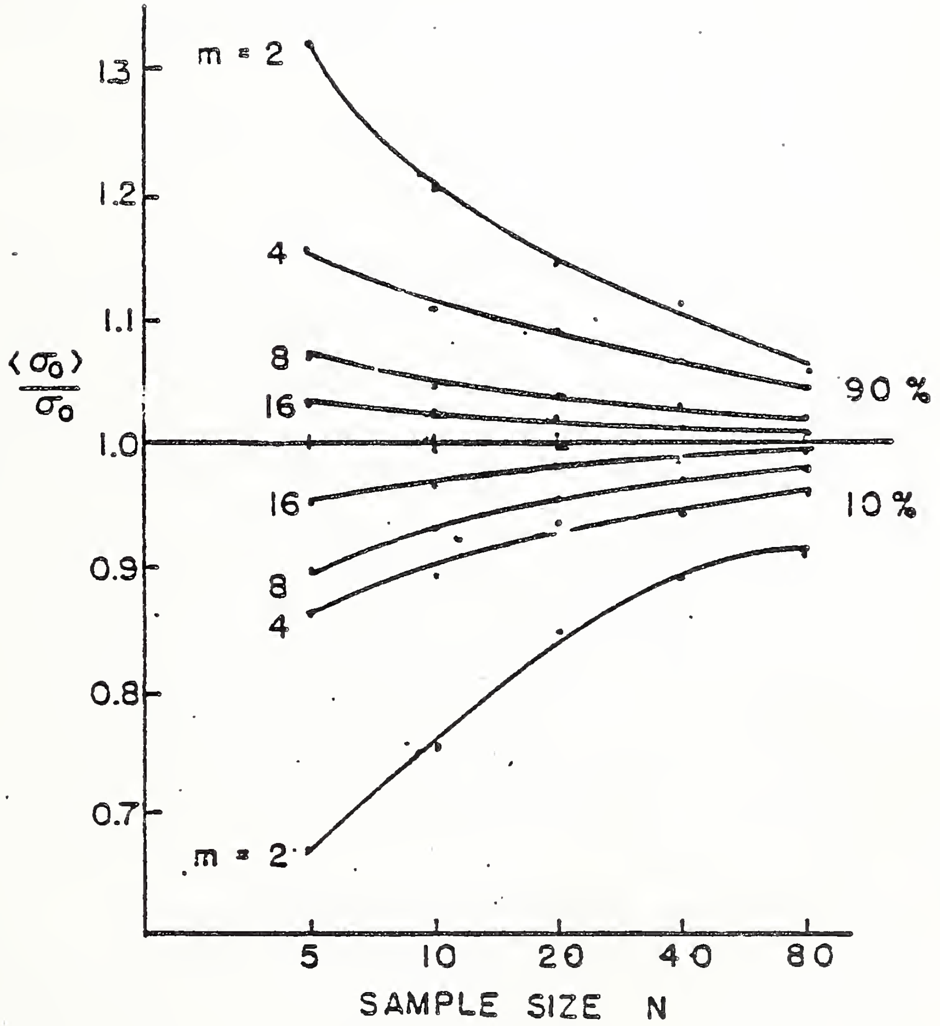


FIGURE 15 10th and 90th Percentile points for estimates $<\sigma_0>$ for samples of size N taken from Weibull distributions with exponent m and position parameter σ_0.

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10. SUPPLEMENTARY NOTES

☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

1 The research program described herein is designed to achieve a number of objectives leading to improved dental restorative materials, techniques and applications of dental materials science for improved dental health care in general. Some of the research in dental composites is directed toward developing generic polymer science potentially useful for composite applications, e.g., durable resin matrices and stronger more durable coupling between fillers and resins. Improved reinforcement is sought by defining the type, and percentages of fillers which will result in improved performance of composites. Methods for reducing polymerization shrinkage and attendant stress and marginal leakage are also explored. Cements are investigated and basic formulations developed for lower solubility, higher biocompatibility, higher strength, greater toughness and adhesion to various substrates including enamel and dentin. Analysis techniques include IR spectroscopy, chromatography, x-ray analysis, mechanical testing, and dilatometry. Another major effort is directed at elucidating the fundamentals involved in wear and degradation of dental composites and restoratives. Wear and hardness measurement techniques are pursued as well as by identification of the origins and sources of flaws leading to failure. Weibull statistical analysis is expected to provide useful information for this task. In this regard an objective is to investigate improved correlations between clinical results of wear and failure of composites with laboratory test data via time-to-failure analysis. Metrology and analysis constitutes the underlying theme of investigations into porcelain-metal systems, casting of dental alloys and the expansion of dental casting investments.

13. AVAILABILITY

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